

Influence Of Lithium Coordinating Additives On The Structure Of Phenyl dimethylsilyllithium

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Dedicated to Prof. Christoph Janiak on the Occasion of his 60th Birthday.

The synthesis and structural investigation of two dimethylphenylsilyllithium adducts with coordinating nitrogen donors quinuclidine and 1,3,5-tri-tert-butylhexahydro-1,3,5-triazine (*tbtac*) are presented. The structures show a comparatively long Si–Li distance and one amongst the shortest in monomeric silyllithiums reported so far, respectively. The structural investigations shed light on the influence of the donating additive for the lithium center on the structure of silyllithium compounds.

Introduction

Dimethylphenyllithiosilane and other simple organosilylanions are known for many years and get frequently used in organic synthesis for silylation reactions, as precursors for silyl cuprates or silyl-Grignard reagents, to name a few.^[1] However, considering the strong structure-reactivity relationship of homologous alkyl lithiums^[2], the structural investigations of simple lithiosilanes are comparably scarce.^[3]

Recent work by COATES et al. and SHELDON et al. has shown the synthetic potential of dimethylphenyllithiosilane and other silanides in defluoro-silylation reactions of industrially relevant fluoroolefins and other fluorocarbons.^[4] In their investigations, the coordination sphere around the lithium center turned out to be a crucial factor for the reactivity of such type of compounds. The simple thf adduct of dimethylphenyllithiosilane showed a different reactivity than its adducts with nitrogen donors such as bis(2-dimethylaminoethyl)methylamine (*pmdta*) or *N,N,N',N'*-tetramethylethane-1,2-diamine (*tmeda*). DAESCHLEIN et al. reported structural investigations for (–)-sparteine adducts of

dimethylphenylsilyllithium in the solid state and in solution.^[5,6] However, as (–)-sparteine is a comparably large ligand, steric effects are assumed to be responsible for observations concerning the structural features of these adducts such as bond length and -angles. Another work by DAESCHLEIN et al. showed the crystal structure of the *pmdta* adduct of phenyl dimethylsilyllithium and a bending of the silicon-bound phenyl group^[7], which is observed for a multitude of anionic silicon species in the literature, even for heavier alkali metals.^[8] The influence of cation complexing donors was further illustrated by LEICH et al. and SCHUHNECHT et al.^[8,9] They reported on the hydrogenolysis of a series of alkali metal silanides Ph₃SiM (M=Li–Cs). Interestingly, only adducts with the nitrogen donor bases tris-[2-(dimethylamino)-ethyl]-amine (*Me₆TREN*) for potassium and 1,4,7,10-tetramethyl-1,4,7,10-tetraaminocyclododecane (*Me₄TACD*) for Li–Cs showed a reactivity against H₂, whereas other adducts with *pmdta*, crown ethers or simple thf solvates of silyl potassium did not show any reactivity in the investigated reactions.^[9] According observations were reported by LERNER et al. as they found a correlation between the ²⁹Si-NMR shift of *t*Bu₂PhSiM (M = alkali metal) and the donor abilities of the used solvent, which influences the aggregation behavior of such compounds.^[10] This clearly illustrates the importance of choosing the correct donor base for cation complexation in alkali metal silanides. Therefore, in this work we report the synthesis and structural investigation of two different dimethylphenyllithiosilane adducts with nitrogen donor bases for the lithium center, focusing on the influence on the structure by the different donor abilities of the nitrogen additive.

Results and Discussion

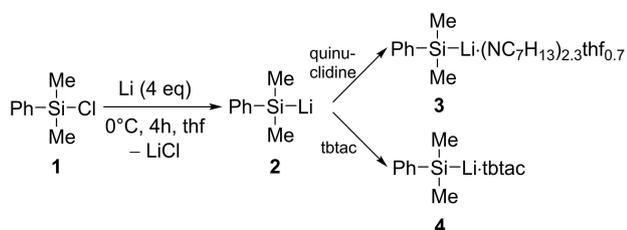
In order to elucidate the influence of the coordination sphere around the lithium center, we synthesized two dimethylphenyl-lithiosilanes under application of different nitrogen donors for the cation. Lithiosilanes **3** and **4** are easily accessible by reduction of commercially available dimethylphenylchlorosilane **1** with lithium metal in thf^[11] and subsequent replacement of solvating thf molecules in **2** by the appropriate nitrogen donor bases (Scheme 1).

In our case we chose quinuclidine and 1,3,5-tri-tert-butylhexahydro-1,3,5-triazine (*tbtac*) as suitable additives, as they are differing in their donor abilities. Lithiosilane **3** crystallizes from *n*-pentane at –80 °C as orange plates in space

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Scheme 1. Synthesis of lithiosilanes **3** and **4** via reduction of dimethylphenylchlorosilane with lithium metal.

group $P2_1/n$ (Figure 1). The asymmetric unit of **3** in the solid state contains one monomeric lithiosilane, in which the lithium center is coordinated by two quinuclidine molecules, one thf and the anionic silicon center. The thf donor competes with a third quinuclidine donor for the same coordination side on the lithium center, whereas the nitrogen is located at the position of the oxygen. The occupancy ratio is 70:30 in favour of the thf donor. More detailed information is included in the Supporting Material. The Si–Li bond length is comparably long with 2.710(3) Å in contrast to already known silyl lithiums ranging from 2.65 Å to 2.675(5) Å.^[5,12] This may result from the strong coordination of the quinuclidine as well as thf donors towards the lithium center, therefore decreasing the electrostatic interaction between silicon and lithium, resulting in an elongated bond. The lithium–nitrogen distance of 2.111(4) Å

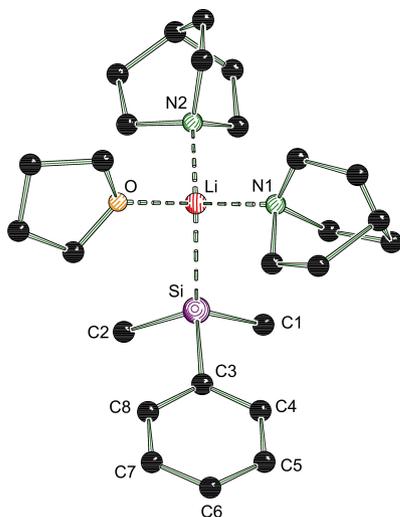


Figure 1. Molecular structure of lithiosilane **3** in the solid state. All hydrogen atoms and disorders are omitted for clarity. The thf donor shows an occupational disorder as it competes with a third quinuclidine donor, whereas the nitrogen is located at the same position as the thf oxygen. The occupancy ratio is 70:30 in favour of the thf. The third quinuclidine is omitted for clarity. Selected bond length [Å] and angles [°]: Si–Li 2.710(3), Si–C1 1.926(2), Si–C2 1.921(2), Si–C3 1.919(2), N1–Li 2.111(4), N2–Li 2.084(4), O–Li 2.013(4), C1–Si–C2 99.73(13), C1–Si–C3 101.90(9), C2–Si–C3 100.24(10), Li–Si–C3 111.47(9), Si–C3–C4–C5 175.46(16).

and 2.084(4) Å is comparable to other silyl lithiums containing nitrogen donors ranging from 2.098 Å to 2.166 Å.^[6,7]

Analogous conditions led to lithiosilane **4**, which crystallizes from diethyl ether at -80°C as colorless blocks in space group $P2_12_12_1$. Similar to **3**, the asymmetric unit of **4** contains a monomeric lithiosilane, in which the lithium center is coordinated by the anionic silicon center and three nitrogen donors of the tbtac. The lithium cation is located beneath the triazine ring which leads to unfavorable angles for a coordination by the triazine nitrogen centers. Hence, the interaction between the donor and the lithium center is weakened. The silicon–lithium contact is significantly shortened to 2.569(3) Å and is to the best of our knowledge amongst the shortest reported bond distances in monomeric triorganosilyllithium compounds to date being 2.588(4) Å^[13] and 2.598(5) Å^[14], respectively.

The extremely short Si–Li distance in **4** results from the opposite effect than the long distance in **3**. Due to the unfavourable coordination angles of the triazine ring, the lithium cation is electronically less saturated, which leads to an increased electrostatic interaction between silicon and lithium (Figure 2).

In both structures a bending of the phenyl rings can be observed as previously reported for other lithiosilanes.^[5,7] The bending can occur due to Pauli-repulsion between the lone pair at the anionic silicon center and the highest occupied molecular orbital of the phenyl ring. In order to decrease this repulsive interaction, the arene is slightly bent and beyond that the frontier orbital of the phenyl ring is deformed, leading to an unsymmetrical distribution of the very same. Another possible explanation could be a stabilizing bonding interaction between the C_{ipso} and the backwards lobe of the “lone pair” at silicon. In order to increase this stabilizing interaction, the arene is bent. A

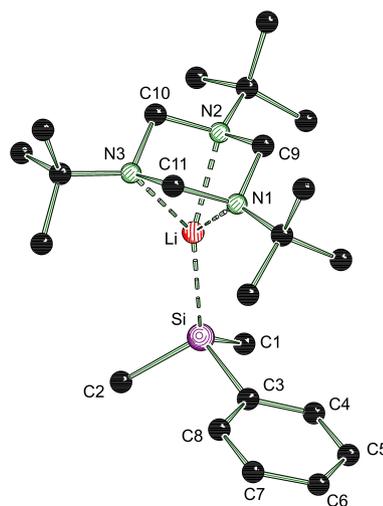


Figure 2. Molecular structure of lithiosilane **4** in the solid state. All hydrogen atoms are omitted for clarity. Selected bond length [Å] and angles [°]: Si–Li 2.569(3), Si–C1 1.9181(18), Si–C2 1.9197(18), Si–C3 1.9171(15), N1–Li 2.135(3), N2–Li 2.133(3), N3–Li 2.162(3), C1–Si–C2 101.08(11), C1–Si–C3 101.60(8), C2–Si–C3 102.64(7), Li–Si–C3 107.32(8), N1–Li–N2 67.31(10), N2–Li–N3 66.10(9), N3–Li–N1 66.39(9), Si–C3–C4–C5 175.56(12).

suitable indicator for this bending is the torsional angle φ between $\text{Si}-\text{C}_i-\text{C}_o-\text{C}_m$. Both analyzed lithiosilanes **3** and **4** exhibit torsional angles for the phenyl group significantly smaller than 180° (Figure 3). Interestingly, in both structures the phenyl ring is bent to roughly the same extent. This inevitably leads to the assumption that the choice of donor base does not necessarily influence the bending of phenyl groups in lithiosilanes. The most important crystallographic and structure refinement data for lithiosilanes **3** and **4** are summarized in Table 1 (More detailed information is given in the Supporting Information).

NMR spectroscopy of **3** and **4** gained deeper insight into the formed structures in solution (Figure 4). The ^{29}Si -NMR shift for **3** is -27.9 ppm and -26.0 ppm for **4**, respectively and is in accordance with similar systems reported in the literature so far.^[5] Interestingly, the quinuclidine/thf adduct **3** shows a broadened singlet at room temperature, whereas the tbtac-coordinated lithiosilane **4** shows a quartet caused by Si–Li coupling. The observed coupling pattern clearly indicates a strong Si–Li interaction in **4** even in solution, thus supporting the short Si–Li contact observed in the solid state of $2.569(3)$ Å. The broad singlet for **3** is in well accordance with the long Si–Li distance of $2.710(3)$ Å in the solid state and the presence of strong donor bases, revealing weaker interactions between silicon and lithium even in solution.

In summary, the structural data from x-ray analyses and NMR spectroscopy reveal a dependency between the structure of organo-silyllithiums and the applied additive for cation complexation. A strong donor base for complexation of the cation leads to an elongated Si–Li distance, whereas a less strong donor leads to a shortened distance with **4** representing one of the shortest reported Si–Li distance in organosilyllithiums so far. Further work needs to elucidate how the coordination sphere not only influences the structure, but also the reactivity of organosilyllithiums.

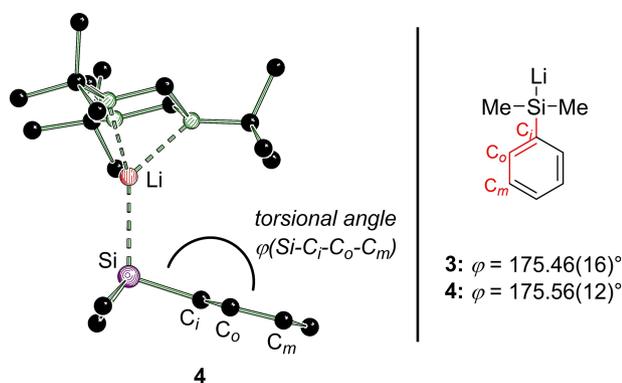


Figure 3. Side-view of the bent phenyl group in lithiosilane **4** in the solid state (left) and torsional angles of **3** and **4** (right).

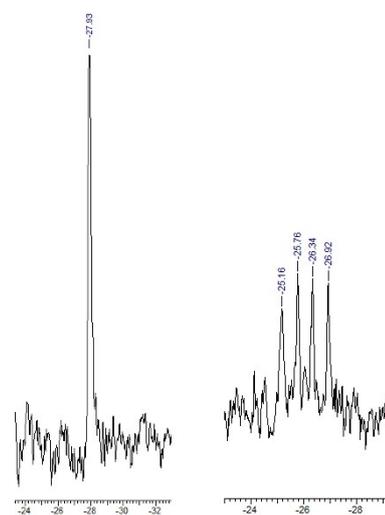


Figure 4. Section of the ^{29}Si -NMR spectrum of lithiosilane **3** (left) and **4** (right) at 24°C in toluene- d_8 .

Experimental Section

General Considerations

All reactions were performed in flame dried glass ware under an inert atmosphere of argon. Solvents were dried over sodium and distilled prior to use. Unless otherwise stated, commercially purchased chemicals were used without further purification. Chlorodimethylphenylsilane was distilled and stored over 4 \AA molecular sieves at 4°C . NMR spectra were recorded on a Bruker Avance III HD spectrometer at 24°C . ^1H and ^{13}C chemical shifts (δ) were referenced to the solvent residual peak [$\text{C}_6\text{D}_5\text{H}$: $\delta(^1\text{H}) = 7.16$ ppm, $\text{C}_7\text{D}_7\text{H}$: $\delta(^1\text{H}) = 2.08$ ppm] and the solvent peak [C_6D_6 : $\delta(^{13}\text{C}) = 128.4$ ppm, C_7D_8 : $\delta(^{13}\text{C}) = 20.4$ ppm], respectively. ^{29}Si NMR were calibrated using tetramethylsilane [$\delta(^{29}\text{Si}) = 0.0$ ppm] as external standard and the spectra were recorded using the INEPT pulse sequence. Spin-spin coupling constants (J) are reported in Hertz (Hz). Coupling patterns in the ^1H NMR spectra are abbreviated as following: *s* (singlet), *br s* (broadened singlet), *d* (doublet), *t* (triplet), *q* (quartet), *m* (multiplet), *dq* (doublet of quartets), *dspt* (doublet of septets).

X-RAY structure determination

Single crystal X-ray data were collected on a Bruker D8 Venture four-circle diffractometer from Bruker AXS GmbH, equipped with a Photon II CPAD detector. The measurements were carried out at 100 K using $\text{MoK}\alpha$ radiation ($\lambda = 0.71703\text{ \AA}$). Radiation source: $1\mu\text{S}$ Mo microfocus source by Incoatex GmbH, equipped with HELIOS mirror optics and a single-hole collimator from Bruker AXS GmbH. Air and moisture sensitive crystals were mounted using the X-TEMP² system^[15] in combination with a SMZ1270 stereo microscope from Nikon Metrology GmbH. The crystals were mounted on MicroMounts, MicroLoops or MicroGrippers from MiTeGen in perfluoropolyalkylethers. APEX3 in connection with SAINT (integration) and SADABS (adsorption correction) from Bruker AXS GmbH were used for the data collection. The molecular structures were solved with SHELXT^[16] and refined using SHELXL.^[17] The final processing of structures was carried out with OLEX².^[18] All non-hydrogen atoms were refined anisotropically and all carbon-bound hydrogen atoms

Table 1. Most important crystal and structure refinement data for **3** and **4**.

	3	4
Empirical formula	C _{26,9} H _{46,5} LiN _{2,3} O _{0,7} OSi	C ₂₃ H ₄₄ LiN ₃ Si
Formula weight	448.39	397.64
Crystal system	monoclinic	orthorhombic
Space group	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ 2 ₁ 2 ₁
<i>a</i> /Å	9.9152(5)	10.129(3)
<i>b</i> /Å	17.1270(9)	15.619(3)
<i>c</i> /Å	15.7470(9)	16.021(5)
α /°	90	90
β /°	97.581(2)	90
γ /°	90	90
Volume/Å ³	2650.7(2)	2534.5(11)
<i>Z</i>	4	4
$\rho_{\text{calc}}/\text{g cm}^{-3}$	1.124	1.042
μ/mm^{-1}	0.108	0.105
<i>F</i> (000)	986.0	880.0
2 Θ range/°	4.596 to 52.792	3.642 to 75.726
<i>R</i> _{int}	0.0697	0.0597
Goodness-of-fit on <i>F</i> ²	1.038	1.041
<i>R</i> [<i>I</i> ≥ 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0592, <i>wR</i> ₂ = 0.1527	<i>R</i> ₁ = 0.0515, <i>wR</i> ₂ = 0.1475
<i>wR</i> (all data)	<i>R</i> ₁ = 0.0727, <i>wR</i> ₂ = 0.1646	<i>R</i> ₁ = 0.0562, <i>wR</i> ₂ = 0.1516
$\Delta\rho$ (min, max)/eÅ ⁻³	0.44/−0.40	1.18/−0.17

were placed in geometrically calculated positions according to a riding model.

Syntheses

Synthesis of tbtac: The synthesis of tbtac was carried out according to a modified instruction of KHOMA et al.^[19] To an aqueous solution of formaldehyde (30 wt% in H₂O, 6.72 ml, 82.9 mmol, 1 eq.) was added *t*-butylamine (6.06 g, 82.9 mmol, 1 eq.) at 0 °C. The reaction was kept stirring for 24 hours at 0 °C. Subsequently the aqueous solution was extracted three times with Et₂O, the combined organic phases were dried over Na₂SO₄ and concentrated *in vacuo*. Kugelrohr distillation (115 °C, 2 · 10⁻¹ mbar) gave tbtac as a colorless liquid (5 g, 20 mmol, 24%). ¹H-NMR (400 MHz, C₆D₆) δ = 1.14 [s, 27H; NC(CH₃)₃], 3.77 [s, 6H, NCH₂N], ppm. {¹H}¹³C-NMR (101 MHz, C₆D₆) δ = 28.2 [s, 9C, NC(CH₃)₃], 53.5 [s, 3C; NC(CH₃)₃], 64.6 (s, 3C, NCH₂N) ppm.

Preparation of lithiosilane 3: To a suspension of lithium metal (56.0 mg, 8.07 mmol, 7 eq.) in thf (4 ml) was added chlorodimethylphenylsilane (0.21 g, 1.23 mmol, 1 eq.). The reaction was stirred for 4 h at 0 °C before the thf was removed *in vacuo* and the residue was dissolved in *n*-pentane. The supernatant was decanted and transferred into a fresh SCHLENK tube. Subsequently, quinuclidine (0.78 g, 7.02 mmol, 6 eq.) was added at room temperature and the resulting solution was stored at −80 °C for crystallization. Lithiosilane **3** was obtained as orange plates. The supernatant was decanted and the crystals were washed three times with cold (−78 °C) *n*-pentane and subsequently dried *in vacuo*. The dried crystals were dissolved in dry toluene-*d*₈ and submitted for NMR measurements. Due to solubility issues of **3** in toluene, the NMR spectra were recorded at room temperature. However, as the concentration of **3** in solution is still low at room temperature, the signals from ¹H and ¹³C NMR are not assigned at this point. For more detailed information and full spectra see the SI. {¹H}²⁹Si NMR (80 MHz, toluene-*d*₈) δ = −27.9 (br s, 1Si; Si) ppm.

Preparation of lithiosilane 4: To a suspension of lithium metal (62.0 mg, 8.93 mmol, 7.64 eq.) in thf (4 ml) chlorodimethylphenylsilane (0.20 g, 1.17 mmol, 1 eq.) was added and the solution was stirred for 4 h at 0 °C. After complete reduction, the thf was removed *in vacuo* and the residue was dissolved in Et₂O. The supernatant was decanted and transferred into a fresh SCHLENK tube. After addition of tbtac (0.33 g, 1.29 mmol, 1.1 eq.) the solution was stored at −80 °C for crystallization. Lithiosilane **4** was obtained as colorless crystals. The supernatant was decanted and the crystals were washed three times with cold (−78 °C) *n*-pentane and subsequently dried *in vacuo* to yield **4** (0.27 g, 0.68 mmol, 58%). The crystals were dissolved in dry toluene-*d*₈ and submitted for NMR measurements. ¹H NMR (600 MHz, toluene-*d*₈) δ = 0.80 (s, 6H, SiCH₃), 1.12 [s, 27H, NC(CH₃)₃], 3.73 (s, 6H, NCH₂N), 7.11–7.20 (m, 2H, CH_{ar}), 7.30–7.33 (t, 1H, *J* = 7.43 Hz), 7.41–7.43 (m, 1H, CH_{ar}), 7.87 (d, *J* = 6.69 Hz, 1H, CH_{ar}) ppm, {¹H}¹³C NMR (151 MHz, toluene-*d*₈) δ = 7.34 (2C, SiCH₃) 27.8 [9C, NC(CH₃)₃], 53.1 [3C, NC(CH₃)₃], 64.15 (3C, NCH₂N), 123.6 (1C, C_{para}), 126.9 (2C, C_{meta}), 134.1 (2C, C_{ortho}), 162.8 (1C, C_{ipso}) ppm, {¹H}²⁹Si NMR (119 MHz, toluene-*d*₈) δ = −26.0 (q, 1Si; Si) ppm.

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Keywords: lithiosilane · silanides · lithium · silicon · reductions

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