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Deaggregation of Trimethylsilylmethyllithium

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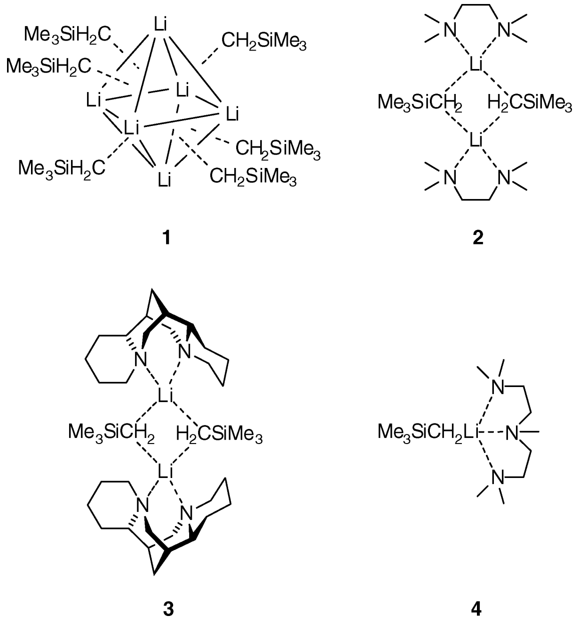
Polyamine donor bases such as *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TMEDA), (–)-sparteine and *N*,*N*,*N*′,*N*′′,*N*′′-pentamethyldiethylentriamine (PMDETA) have been employed to deaggregate parent trimethylsilylmethyllithium (**1**). The crystal structures of the dimers $[(TMEDA){\cdot}LiCH_2SiMe_3]_2$ (**2**) and $[\{(–)\text{-sparteine}\}{\cdot}LiCH_2SiMe_3]_2$ (**3**) were determined and reveal a four-membered ring as the central structural motif. The two lithium atoms are each coordinated by the chelating ligands and the carbanions. The Li–C contacts show alternating bond lengths. The monomer $[(PMDETA){\cdot}LiCH_2SiMe_3]$ (**4**) has the shortest Li–C contact of the aggregates discussed, and the Me_3Si group points toward the central nitrogen atom of the PMDETA ligand, even if this alignment seems unfavourable for steric reasons. The bond lengths and angles of compounds **2**–**4** are discussed in relation to the orientation of the lone pair at the carbanion.

Donor free organolithium compounds would hardly ever give separate monomers in solution or in the solid state but would rather form oligomeric aggregates instead.[1] Hence, the identification of their molecular structures is vital to deduce structure–reactivity relationships.[2]

Basic lithium organic reagents such as *n*BuLi[3] and *i*PrLi[4] form hexameric aggregates without coordinating donor bases, while *t*BuLi[3] and MeLi[5] form tetramers. The monomeric compounds are supposed to be the most reactive species, which makes the Lewis donor base essential in the deaggregation process.[6] This increases the reaction potential of the lithiated compounds dramatically, because, for example, toluene ($pK_s = 37.0$) cannot be metallated with *n*BuLi directly without the addition of *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TMEDA).[7] Likewise, ferrocene can only be monolithiated by *n*BuLi, while the addition of TMEDA yields the 1,1′-dimetallated ferrocenyllithium.[8] Furthermore, the regioselective 1,1′,3,3′-ferrocenyltetraanion can only be obtained with a more basic mixture of butylsodium, butylmagnesium and diisopropylamine.[9]

To date only the donor free molecular structure of trimethylsilylmethyllithium $[LiCH_2SiMe_3]_6$ (**1**) has been reported.[10] Because of the excellent storage features of crystalline trimethylsilylmethyllithium, it is perfectly applicable in silyl transfer reactions.[11]

Herein, we report on the deaggregation of the hexameric trimethylsilylmethyllithium (**1**) with the nitrogen donor cbases TMEDA, (–)-sparteine and *N*,*N*,*N*′,*N*′′,*N*′′-pentamethyldiethylenetriamine (PMDETA) (Figure 1) and on the resulting molecular structures $[(TMEDA){\cdot}LiCH_2SiMe_3]_2$ (**2**), $[\{(–)\text{-sparteine}\}{\cdot}LiCH_2SiMe_3]_2$ (**3**) and $[(PMDETA){\cdot}LiCH_2SiMe_3]$ (**4**). Compounds **2**–**4** show an increasing sensitivity towards moisture and oxygen relative to **1**. The crystals thus had to be handled under protective atmosphere at temperatures below –20 °C by applying special cryo application techniques.[12]



1 **2** **3** **4**

Figure 1. Coordination motifs of trimethylsilylmethyllithium.

$[(TMEDA){\cdot}LiCH_2SiMe_3]_2$ (**2**) crystallises in the monoclinic space group $P2_1/n$ (Figure 2).[13] The asymmetric unit contains the whole dimer. The central structural motif is

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a (Li_2C_2) four-membered ring with alternating Li–C bond lengths. They vary from 218.3(4) to 231.7(4) pm (Table 1). The short Li–C bonds coincide with the orientation of the lone pairs at the methanide anions, which were deduced from the determined hydrogen atom positions. Thus, there are two different Li–C contacts evident, of which the shorter one has more covalent character while the longer contact implies a greater ionic contribution. The Li–C bonds in $[LiCH_2SiMe_3]_6$ (**1**) (214.9 to 229.4 pm) are slightly shorter than those of **2**.

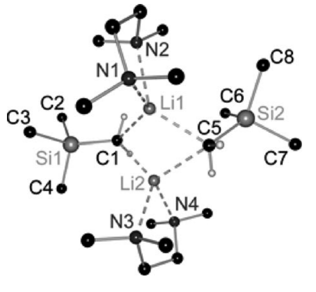

Figure 2. Molecular structure of $[(TMEDA){\cdot}LiCH_2SiMe_3]_2$ (**2**) (constrained hydrogen atoms omitted for clarity).

Table 1. Selected bond lengths [pm] and angles [°] in **2**–**4**.

	2	**3**[a]	**4**
Li1–C1	231.7(4)	214.7(3)	211.3(2)
Li1–C5	225.3(4)	266.1(3) (C1′)	–
Li2–C1	218.3(4)	–	–
Li2–C5	230.6(4)	–	–
Li1–N1	228.0(4)	209.4(3)	214.5(2)
Li1–N2	231.9(4)	214.0(3)	218.9(2)
Li2–N3	218.8(4)	–	216.9(2)
Li2–N4	223.2(4)	–	–
Si1–C1	182.3(2)	181.7(2)	179.7(1)
Si1–C2	189.1(2)	189.1(1)	188.7(1)
Si1–C3	188.0(2)	187.9(2)	188.2(1)
Si1–C4	188.1(2)	187.7(2)	189.7(1)
Si2–C5	181.9(2)	–	–
Si2–C6	188.1(3)	–	–
Si2–C7	188.8(3)	–	–
Si2–C8	188.2(2)	–	–
Li1–C1–Li2	67.9(2)	85.3(2) (Li1′)	–
Li2–C5–Li1	66.9(1)	–	–
C1–Li1–C5	105.0(2)	93.4(2) (C1′)	–
C1–Li2–C5	107.7(2)	–	–

[a] Averaged over both halves of the dimer.

With regard to the Si–C_α bonds in **2** [181.9(2) and 182.3(2) pm], they are significantly shorter than the standard Si–C single bond (187 pm)[14]. According to a charge density investigation,[15] this results mainly from a strong electrostatic attraction between two highly charged atoms (negatively charged carbanion and positively charged silicon atom) and to a minor extent from negative hyperconjugation.[16] Nevertheless, this conjugation explains the longer Si–C_α bonds in **1** (182.2 to 185.2 pm). The lone pairs in **2** are better orientated towards the *anti* C_β-methyl groups (dihedral angle about 162°). Thus, both Si–$C_{\beta,\mathrm{anti}}$ bonds are elongated [189.1(2) and 188.8(3) pm vs. 188.1(2) pm on average].

The sum of the bond angles in the central (Li_2C_2) four-membered ring adds up to 347.4°, which shows the envelope conformation of the ring with a folding angle of 44.6° along the transannular C1···C5 distance. This leaves one side of the dimer more open (closest C···C distances of the donor molecules approximately 450 vs. 745 pm at the other side) (Figure 4).

The Li–N distances lie between 218.8(4) and 231.9(4) pm; they are in the range of those of $[(TMEDA){\cdot}Li\mathit{n}Bu]_2$[17] {220.9(12) to 222.3(10) pm} and $[(TMEDA){\cdot}(Li\mathit{n}Bu)_4]_\infty$[18] {213.1(8) pm}.

$[\{(-)\text{-Sparteine}\}{\cdot}LiCH_2SiMe_3]_2$ (**3**) crystallises in the chiral orthorhombic space group *F*222 (Figure 3). The absolute structure was successfully determined from the diffraction experiment [Flack parameter:[19] 0.05(8)]. The asymmetric unit contains two independent halves of the dimer. The bond lengths and angles in both dimers are almost identical, therefore averaged values will be discussed. The central structural motif is a nearly planar (Li_2C_2) parallelogram (mean deviation: 13.2 pm) with a much smaller folding angle along the C1···C5 axis (17°) than that in **2**. The parallelogram consists of two remarkably different Li–C bonds (215 and 266 pm; Table 1), one of which is even shorter than that in **2** (218 pm). This contact again is influenced by the lone pair. The second bond is about 34 pm longer than the longest Li–C contact discussed in this report, and one is inclined to regard this as only a weak electrostatic dimerisation of two $LiCH_2SiMe_3{\cdot}(-)$-sparteine units.

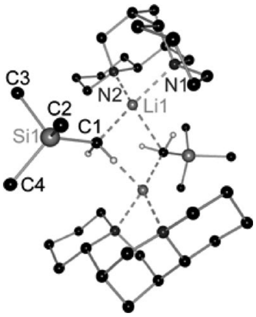

Figure 3. Molecular structure of $[\{(-)\text{-sparteine}\}{\cdot}LiCH_2SiMe_3]_2$ (**3**) (constrained hydrogen atoms omitted for clarity).

Interestingly, the Si–C bonds form a perfect line Si–C···C–Si, while in **2**, the silyl groups are bent away to opposite sides of the (Li_2C_2) ring. In **3**, this is prevented by the sterically demanding (–)-sparteine ligands. They even force the $SiMe_3$ groups to be ecliptically orientated. The Si–C_α bonds are further shortened (181.6 pm) because of electrostatic interactions and negative hyperconjugation.

The two (–)-sparteine ligands of one dimer are related by a crystallographic C_2 axis. The space-filling models of **3** show one hemisphere of the metal core to be more shielded than the other (Figure 4, right side). Therefore, an electrophilic attack at the carbanion is only possible from one side.[20] Thus, we are currently investigating the stereoselective transfer of the silyl groups to an electrophile.

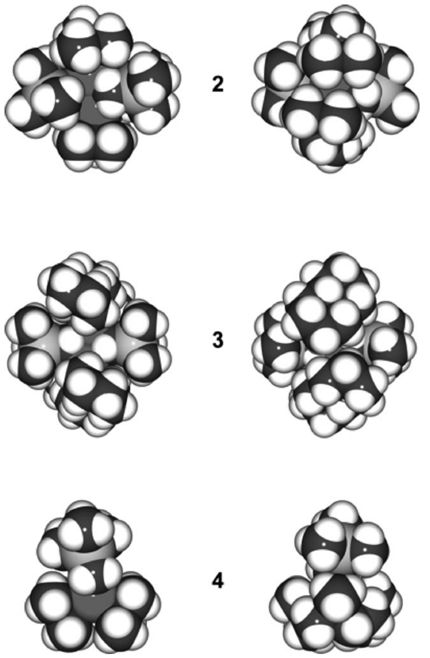

Figure 4. Space-filling models of the molecular structures **2**–**4** in the solid state, which depict the open lithium face (left column) and the sterically crowded opposite side (right column).[21]

In comparison with the molecular structure of [{(–)-sparteine}·Li*n*Bu]$_2$[22] (**5**), similarities in the aggregation grade and ligand arrangement can be found. Nevertheless, the bigger Me$_3$Si group has a distinctly different effect on the dimerisation in the crystal relative to the *n*Pr substituent. The central four-membered ring in **5** does not have the shape of a parallelogram but rather of a slightly bent rhombus. The mean Li–C bond [226.9(5) pm] is longer than the directed Li–C contact in **3**, but significantly shorter than the electrostatic interaction. This is caused by the lone pairs, which point to the midpoint of the Li···Li vector. Furthermore, the Li–N bonds in **5** [217.2(4) to 224.3(5) pm] are surprisingly longer than those in **3** [209.4(3) to 214.0(3) pm], even if the carbanion is much smaller in **5**. This can be explained by the shorter mean Li–C bonds in **5** (226.9 pm) relative to those in **3** (240.4 pm). Obviously, the lithium atoms compensate for their positive charge in **5** through the C$_\alpha$ atoms and not through the contacts to the donor molecules. At a first glance it is surprising that (–)-sparteine forms a dimer with trimethylsilylmethyllithium and a monomer with the putatively smaller *t*BuLi.[23] In this case, it is important to note that the Si–C bond is much longer than the C–C bond. Additionally, there is also a CH$_2$ spacer between the SiMe$_3$ group and the Li$_2$C$_2$ four-membered ring, so that the dimerisation cannot be prevented because of steric reasons.

[(PMDETA)·LiCH$_2$SiMe$_3$] (**4**) crystallises in the orthorhombic space group *Pbca* (Figure 5). The asymmetric unit contains one monomer. The lithium atom is coordinated by three nitrogen atoms of the donor base and the deprotonated C$_\alpha$ atom C1. This results in the shortest Li–C bond [211.3(2) pm] of all the aggregates discussed (Table 1). The lone pair density of the carbanion is associated only with one lithium atom and is not shared between the additional positive charges. This leads to a distorted tetrahedral coordination sphere for the carbon atom and a Li–C$_\alpha$–Si angle of 126.42(8)°.

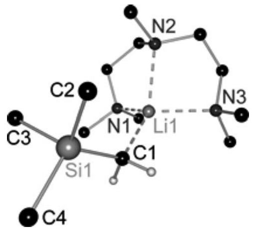

Figure 5. Molecular structure of [(PMDETA)·LiCH$_2$SiMe$_3$] (**4**) (constrained hydrogen atoms omitted for clarity).

The Si–C$_\alpha$ distance is 179.7(1) pm and is shorter than in compounds **1**–**3**. The negative hyperconjugation is almost fully established because of a dihedral angle of 173.2(2)°, which is not far from the ideal value 180°. Simultaneously, the longest Si–C$_{anti}$ bond [189.7(2) pm] is in **4**. It is interesting that the Me$_3$Si group points toward the central nitrogen atom of the PMDETA ligand, even if this alignment seems unfavourable for steric reasons. But two molecules in the unit cell are arranged in a way such that the lithium atom of one monomer points to the carbanion of the other (nonbonding distance: 462 pm). This constellation can be interpreted as some kind of weak interaction.

The complete deaggregation to the monomer increases its reactivity relative to that of the dimeric aggregates because of improved accessibility to the carbanion and the lithium atom.[24] This was only possible with the tridentate PMDETA ligand.

In summary, the reaction potential of commercially available trimethylsilylmethyllithium could be increased with the use of nitrogen donor ligands. This expands the application potential of this basic lithium organic reagent dramatically.

Experimental Section

2–4: The nitrogen donor bases TMEDA (for **2**), (–)-sparteine (for **3**) or PMDETA (for **4**) (1.5 equiv.) were added to trimethylsilylmethyllithium in hexane at room temperature under a protective atmosphere. Crystallisation was carried out in the freezer. Yields of crystalline product: 5.10 mmol, 48% (**2**), 0.26 mmol, 8% (**3**), 2.87 mmol, 27% (**4**).

2: ^{1}H NMR (500 MHz, $C_6D_5CD_3$, 25 °C): δ = –1.86 (s, 2 H, C*H*$_2$Li), 0.36 [s, 9 H, Si(C*H*$_3$)$_3$], 1.95 (s, 4 H, C*H*$_2$N), 2.00 [s, 12 H, N(C*H*$_3$)$_2$] ppm. ^{13}C NMR (126 MHz, C_6D_6): δ = –5.70 (*C*H$_2$Li), 6.04 [Si(*C*H$_3$)$_3$], 45.90 [N(*C*H$_3$)$_2$], 56.58 (*C*H$_2$N) ppm. ^{7}Li (194 MHz, $C_6D_5CD_3$): δ = 2.02 (s) ppm. ^{29}Si NMR (99 MHz, C_6D_6): δ = –2.58 (s) ppm. $C_{20}H_{54}Li_2N_4Si_2$ (420.7): calcd. C 57.10, H 12.94, N 13.32; found C 54.89, H 13.08, N 14.09.[25]

3: ^{1}H NMR (500 MHz, C_6D_6, 25 °C): δ = –1.28 (s, 2 H, C*H*$_2$Li), 0.57 [s, 9 H, Si(C*H*$_3$)$_3$], 0.75–2.64 [m, 26 H, (–)-sparteine] ppm. ^{13}C NMR (126 MHz, C_6D_6): δ = –4.78 (*C*H$_2$Li), 6.62 [Si(*C*H$_3$)$_3$], 18.10, 24.02, 24.77, 25.22, 26.50, 28.20, 30.14, 34.06, 34.94, 45.82, 54.19, 57.46, 59.36, 60.86, 66.44 ppm. ^{7}Li (194 MHz, C_6D_6): δ = 3.10 (s) ppm. ^{29}Si NMR (99 MHz, C_6D_6): δ = –2.50 (s) ppm. $C_{19}H_{37}LiN_2Si$ (328.5): calcd. C 69.46, H 11.35, N 8.53; found C 68.22, H 11.41, N 8.54.

4: ^{1}H NMR (300 MHz, $C_6D_5CD_3$, 25 °C): δ = –1.57 (s, 2 H, CH_2Li), 0.48 [s, 9 H, $Si(CH_3)_3$], 1.74 (s, 8 H, CH_2N), 1.94 [s, 12 H, $N(CH_3)_2$], 2.05 (s, 3 H, NCH_3) ppm. ^{7}Li (117 MHz, C_6D_6): δ = –1.76 (s) ppm. ^{13}C NMR (300 MHz, $C_6D_5CD_3$): δ = –5.60 (CH_2Li), 6.42 [$Si(CH_3)_3$], 45.06 (NCH_3), 46.17 [$N(CH_3)_2$], 57.26 (CH_2N) ppm. $C_{13}H_{34}LiN_3Si$ (267.5): calcd. C 58.38, H 12.81, N 15.71; found C 54.47, H 12.10, N 14.09.

Supporting Information (see footnote on the first page of this article): Crystallographic data for compounds **2**–**4** are presented.

Acknowledgments

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[13] Single-crystal structural analysis of **2**–**4**: The data sets were collected on a Bruker Smart Apex II with a D8 goniometer (**2**, **3**) or a Bruker TXS rotating anode with INCOATEC Mo-mirror optics, Apex II detector and D8 goniometer (**4**) from oil–coated, shock-cooled crystals[12] (Mo-K_α λ = 71.073 pm). The integration was performed with SAINT V7.34A [V7.46A (**3**)], which was followed by an empirical absorption correction with SADABS-2004/1 [SADABS-2007/5(**3**)]. The structures were solved by direct methods and refined with SHELXL against F^2.[26] **2**: $C_{20}H_{54}Li_2N_4Si_2$, M = 420.74 g mol^{-1}, crystal size 0.5 × 0.4 × 0.2 mm, monoclinic, $P2_1/c$, a = 1063.3(2) pm, b = 1365.8(3) pm, c = 2140.2(5) pm, β = 104.335(3)°, V = 3.0113(10) nm^3; Z = 4, $\rho_{calcd.}$ = 0.928 Mg m^{-3}, μ = 0.128 mm^{-1}, T = 200(2) K, $2\theta_{max}$ = 50.00°, 26836 reflections measured, 5212 independent reflections, R_{int} = 0.0296, $R1$ = 0.0489 [$I > 2\sigma(I)$], $wR2$ = 0.1328 (all data), 0.313/–0.170 e Å^{-3} residual densities. **3**: $C_{41}H_{81}Li_2N_4Si_2$, M = 700.16 g mol^{-1}, crystal size 0.4 × 0.33 × 0.2 mm, orthorhombic, $F222$, Flack parameter 0.05(8), a = 2129.28(13) pm, b = 2563.81(15) pm, c = 3295.5(3) pm, V = 17.99(1) nm^3; Z = 16, $\rho_{calcd.}$ = 1.034 Mg m^{-3}, μ = 0.109 mm^{-1}, T = 100(2) K, $2\theta_{max}$ = 52.04°, 46200 reflections measured, 8877 independent reflections, R_{int} = 0.0258, $R1$ = 0.0346 [$I > 2\sigma(I)$], $wR2$ = 0.0905 (all data), 0.851/–0.249 e Å^{-3} residual densities. **4**: $C_{13}H_{34}LiN_3Si$, M = 267.46 g mol^{-1}, crystal size 0.8 × 0.6 × 0.6 mm, orthorhombic, $Pbca$, a = 1170.6(3) pm, b = 1674.2(4) pm, c = 1904.5(4) pm, V = 3.7323(14) nm^3; Z = 8, $\rho_{calcd.}$ = 0.952 Mg m^{-3}, μ = 0.116 mm^{-1}, T = 200(2) K, $2\theta_{max}$ = 53.52°, 53911 reflections measured, 3968 independent reflections, R_{int} = 0.0226, $R1$ = 0.0385 [$I > 2\sigma(I)$], $wR2$ = 0.1116 (all data), 0.187/–0.269 e Å^{-3} residual densities. CCDC-687124 (**2**), -687125 (**3**), -687126 (**4**) 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.

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