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Communications

Novel Aggregation Motif of *gem*-Dilithiosilanes: Coaggregation of Two R_2SiLi_2 Molecules with Two RLi Molecules

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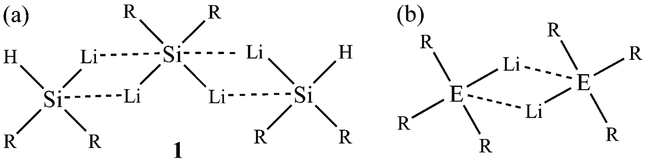
Summary: Three novel nonsolvated gem-dilithiosilanes, R_2SiLi_2, were prepared by reacting in hexane lithium metal with silyl mercury precursors. X-ray structure analysis showed for two of them an unprecedented coaggregation of two R_2SiLi_2 molecules with two R′Li molecules, exhibiting novel structural motifs: the Li_6 core in these coaggregates is strongly distorted from the classic Li_6 core of $(RLi)_6$, and each R_2Si group bridges simultaneously two Li triangles of the Li_6 core.

In nonsolvated aggregates of alkyllithium[1] and silyllithium[2] ($(R_3ELi)_n$, E = C, Si) the lithium atoms form a core with the R_3E groups bridging several lithium atoms.[1,2] For example, in $(t\text{-BuLi})_4$ the lithium atoms form a tetrahedral core,[3] and in $(Me_3SiLi)_6$ they form an octahedral core[4] with each of the four *t*-Bu groups and each of the six Me_3Si groups, respectively, bridging a triangle of lithium atoms.

In contrast to the wealth of structural information of alkyl- and silyllithiums, very limited structural information is available for nonsolvated *geminal di*lithium aggregates of the general type R_2ELi_2 (both for E = C[5] and for E = Si[6,7]). In particular, the few R_2SiLi_2 compounds characterized by X-ray crystallography are *solvated* monomers.[6e,f,7c] Recently, we reported the molecular structure of the first nonsolvated *gem*-dilithiosilane, **1**, and its X-ray structure exhibited one molecule of R_2SiLi_2 coaggregated with two molecules of R_2SiHLi: i.e., $R_2SiLi_2{\cdot}2R_2SiHLi$ (R = $t\text{-Bu}_2MeSi$)[8] (Chart 1a). In **1** each Si−Li bond is coaggregated with another Si−Li bond, similarly to R_3ELi (E = C, Si) dimers (Chart 1b).[1,2] Thus, within the Si−Li core **1** does not exhibit novel structural features which are not found in $(R_3ELi)_n$.

Chart 1



1

R = $t\text{-Bu}_2MeSi$

E = C, Si

We report the synthesis of three novel nonsolvated *gem*-dilithiosilanes and concentrate on the unique molecular structure of two of them, in which two R_2SiLi_2 molecules are coaggregated with two R′Li molecules: i.e., $(R_2SiLi_2)_2{\cdot}2R'Li$ (**2**, R = $i\text{-Pr}_3Si$, R′ = *t*-Bu; **3**, R = $t\text{-Bu}_2MeSi$, R′ = $t\text{-BuMe}_2Si$). Furthermore, **2** and **3** exhibit novel structural motifs which are significantly different from those in **1** and in $(RLi)_n$ aggregates. In contrast to **1**, which is composed of *three* molecules, i.e., $R_2SiLi_2{\cdot}2R'Li$ (Chart 1a),[8] **2** and **3** are composed of *four* molecules. In addition, **2** and **3** have six lithium atoms and *only four* bridging groups (two R_2Si and two R′ groups), in contrast to $(RLi)_6$,[1,2] which has six lithium atoms and *six* R groups, each *bridging one lithium triangle*. The smaller number of bridging groups in **2** and **3** dictates an unusual arrangement of the Li_6 core which is strongly distorted from the classic octahedral core found in $(RLi)_6$, as well as an unprecedented bridging mode by the silyl substituents where each R_2Si group in **2** and **3** *bridges simultaneously two Li triangles* of the Li_6 core.

2 was synthesized by reaction in hexane of the trimercury silyl compound **4**[9] with lithium powder (Scheme 1). During the reaction **2** precipitated as pale yellow crystals in 10% yield.[10] X-ray crystallography revealed that **2** is the first known coaggregate of a silyllithium and an alkyllithium. **2** crystallizes

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[8] (a) Bravo-Zhivotovskii, D.; Ruderfer, I.; Melamed, S.; Botoshansky, M.; Tumanskii, B.; Apeloig, Y. *Angew. Chem., Int. Ed.* **2005**, *44*, 739. (b) In THF **1** transforms to a unique dianionic silyllithium cluster: Bravo-Zhivotovskii, D.; Ruderfer, I.; Melamed, S.; Botoshansky, M.; Schmidt, A.; Apeloig, Y. *Angew. Chem. Int. Ed.*, in press.

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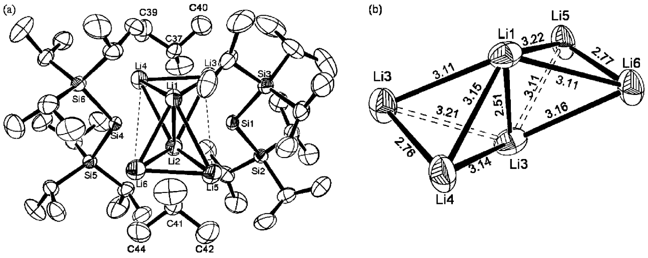
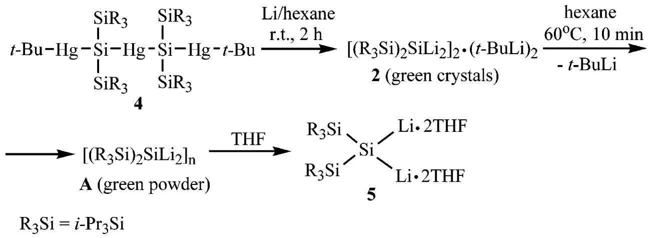


Figure 1. (a) ORTEP diagram (50% probability) of the molecular structure of $[(i\text{-}Pr_3Si)_2SiLi_2]_2{\cdot}2t\text{-}BuLi$ (**2**). The hydrogen atoms are omitted for clarity. Dashed lines are given for clarity and do not necessarily indicate a chemical bond. (b) The Li_6 core of **2**; indicated values are bond distances in Å. Selected bond lengths (Å) and bond angles and dihedral angles (deg) for **2**: Si1−Si2, 2.3524(13); Si1−Si3, 2.3507(13); Si1−Li1, 2.570(6); Si1−Li2, 2.565(6); Si1−Li3, 2.663(7); Si1−Li5, 2.710(6); C37−Li3, 2.127(7); C37−Li4, 2.1427; Li1−Li2, 2.515(8); Li1−Li3, 3.107(9); Li1−Li4, 3.146(10); Li1−Li5, 3.21; Li3−Li5, 5.09; Li3−Li4, 2.76; Li5−Li6, 2.77; Li6−Li4, 5.06; Si3−Si1−Si2, 11.29(5); Li1−Si1−Li2, 58.65(19); Li3−Si1−Li5, 142.9(2); Li1−Si1−Li3, 72.8(2); Si1−Li1−Li2, 60.6(2); Li3−C37−Li4, 80.6(3); C37−Li3−Li4, 49.5(2); Li3−Li1−Li6, 136.1(3); Li1−Li2−Li4, 66.6(3); Li3−Si1−Li1−Li2, 83.4(3); Li3−Si1−Li1−Li4, 28.2(2); Li4−Li1−Li2−Li3, 57.1(2); Si3−Si1−Li3−C37, 122.0(10); Li3−Li5−Li6−Li4, 7.2; Li1−Li2−L3−Li6, 0.1; Li1−Li2−L4−Li5, 0.1. Full structural details are given in the Supporting Information.

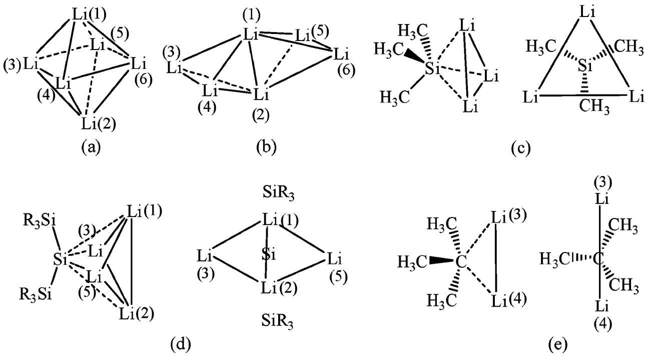
Scheme 1



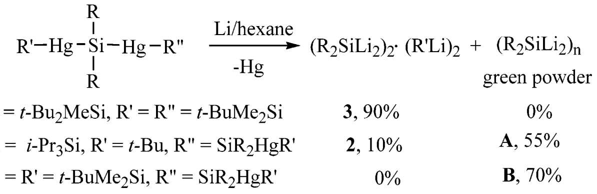
as an aggregate of four molecules: two *gem*-dilithiosilane $(i\text{-}Pr_3Si)_2SiLi_2$ molecules and two *t*-BuLi molecules, all obtained from lithiation of a single molecule, **4** (Figure 1).[11] An attempt to dissolve **2** in hexane at 60 °C resulted in its rapid decomposition to *t*-BuLi and a green powder (**A**)[10] insoluble in hydrocarbons. When THF is added to **A**, the ^1H and ^{29}Si NMR spectra (in d_8-toluene) are identical with those of the known THF-solvated dilithiosilane **5**.[7c] We therefore conclude that **A** is a polyaggregated *gem*-dilithiosilane, $[(i\text{-}Pr_3Si)_2SiLi_2]_n$, which in THF yields **5** (Scheme 1).

The molecular structure of **2** is presented in Figure 1a and its unique Li_6 core in Figure 1b. To appreciate the unique structure of the Li_6 core of **2** (Chart 2b), it is convenient to compare it with the regular[4] Li_6 core of $(Me_3SiLi)_6$ (**6**) (Chart 2a). First, in **2** r(Li1−Li2) = 2.51 Å, while in **6** r(Li1−Li2) is longer than 5 Å. Second, the Li3−Li5 and Li4−Li6 distances in **2** are very long at 5.1 Å, relative to 3.2 Å in **6**. Thus in **2**, in contrast to **6**, there is a Li1−Li2 chemical bond and there are no Li3−Li5 and Li4−Li6 bonds. Thus, the core Li_4 square in **6** is distorted in **2** to an elongated rectangle, and the octahedron's top and bottom lithium atoms are much closer to each other in **2** than in **6**. The Li_6 core of **2** may be described as composed of two distorted tetrahedra (Li1−Li2−Li3−Li4 and Li1−Li2−Li5−Li6) sharing a common Li1−Li2 edge.

Chart 2



Scheme 2



7,	R = *t*-Bu_2MeSi, R' = R'' = *t*-BuMe$_2$Si	**3**, 90%	0%
4,	R = *i*-Pr_3Si, R' = *t*-Bu, R'' = SiR$_2$HgR'	**2**, 10%	**A**, 55%
8,	R = R' = *t*-BuMe$_2$Si, R'' = SiR$_2$HgR'	0%	**B**, 70%

Another major difference in the structures of **2** and **6** is the position of the silyl (and alkyl) groups. In **6** each Me_3Si group is centrally located above a triangular face of the Li_6 octahedron (Chart 2c), while in **2** each $(i\text{-}Pr_3Si)_2Si$ group *bridges simultaneously two triangle faces* formed by four lithium atoms (Chart 2d). There are two sets of Si−Li bond distances in **2**: four short distances in the range of 2.565−2.570 Å (of Si1 and Si4 with Li1 and Li2) and four somewhat longer distances in the range of 2.663−2.710 Å (Si1−Li3 (Li5) and Si4−Li4 (Li6)). The environment of the *t*-Bu groups in **2** is also unusual: each *t*-Bu group is bridging *only two* lithium atoms (Chart 2e).[12] In contrast, in $(t\text{-}BuLi)_4$ the *t*-Bu groups bridge *three* lithium atoms[3] (similarly to the Me_3Si group in Chart 2c). In **2** there are four nearly equal C−Li distances in the range of 2.125−2.142 Å (C37−Li3 (Li4) and C41−Li5 (Li6)). There are several short CH−Li distances in **2** (2.318−2.340 Å), which may indicate the presence of agostic CH−Li interactions (e.g., between hydrogens bonded to C39, C40, C42, C44 and Li4, Li3, Li5, Li6, respectively).

To prepare other *gem*-dilithiosilanes, we synthesized two new silyl mercury precursors: **7** carrying the bulky *t*-Bu_2MeSi substituents and **8** carrying the smaller *t*-BuMe$_2$Si substituents. The lithiation products (using lithium metal powder in hexane) of **7**, **8**, and **4** are given in Scheme 2. **8** yields exclusively a green powder (**B**) identified as oligomeric $[(t\text{-}BuMe_2Si)_2SiLi_2]_n$.[13] On the other hand, **7** yields 90% of $[(t\text{-}Bu_2MeSi)_2SiLi_2]_2{\bullet}$(*t*-

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[10] A mixture of 4 g (3 mmol) of **4** and 0.3 g (43 mmol) of dispersed lithium metal in hexane (30 mL) was stirred at room temperature for 2 h. During this period the solution changed in color from green-yellow to green-red and 0.3 g (10%) of pale yellow crystals of **2** precipitated. Attempts to obtain more crystals of **2** from the mother liquid failed. Instead, a green powder identified as $[(i\text{-}Pr_3Si)_2SiLi_2]_n$ (**A**) was obtained in 55% yield. The NMR of **2** was not measured, since the compound was obtained in a small quantity and it decomposes rapidly when dissolved in hydrocarbons.

[11] Crystal data of **2** (293 K): $C_{44}H_{102}Li_6Si_6$; fw 841.44; triclinic; space group $P\bar{1}$, $a = 11.267(2)$ Å, $b = 11.591(2)$ Å, $c = 24.066(4)$ Å, $\alpha = 96.00(2)°$, $\beta = 94.02(2)°$, $\gamma = 112.80(2)°$, $V = 2860.4(9)$ Å^3, $Z = 2$, $D_{calcd} = 0.977$ mg/m^3, R1 = 0.0659 ($I > 2\sigma(I)$), wR2 = 0.1737 (all data), GOF = 1.041.

[12] A similar aggregation motif of *t*-BuLi was reported in $(t\text{-}BuLi)_2{\cdot}2OEt_2$[3] and in two coaggregates of *t*-BuLi with organolithium: (a) Williard, P. G.; Sun, C. *J. Am. Chem. Soc.* **1997**, *119*, 11693. (b) Hardman, N. J.; Twamley, B.; Stender, M.; Baldwin, R.; Hino, S.; Schiemenz, B.; Kauzlarich, S. M.; Power, P. P. *J. Organomet. Chem.* **2002**, *643*, 461.

[13] For experimental details see the Supporting Information. Solid-state MAS NMR data of **B** (δ in ppm): ^7Li, 3.1, ^{13}C, 3.5−4.5 (*t*-Bu*Me*$_2$Si), 30.2−29.07 (*t-Bu*Me$_2$Si); ^{29}Si, 12.8, 11.8 (*t*-BuMe$_2$*Si*), −252.6, −256.5 (*Si*Li$_2$). The green powders **A** and **B** were reacted with a variety of substrates. These reactions will be reported elsewhere.

$BuMe_2SiLi)_2$ (**3**), which similarly to **2** is a coaggregate composed of four molecules: two molecules of the *gem*-dilithiosilane $(t\text{-}Bu_2MeSi)_2SiLi_2$ and two $t\text{-}BuMe_2SiLi$ molecules (Scheme 2). **3** crystallizes from hexane, and its structure was determined by X-ray crystallography. The X-ray analysis, despite the low resolution ($R = 0.12$), clearly shows that **3**, similarly to **2**, has novel structural features.[14]

The data in Scheme 2 point to an interesting substituent effect controlling the degree of aggregation of the dilithiosilane product. Bulky substituents sterically hinder polyaggregation, and with R = $t\text{-}Bu_2MeSiLi$ only the coaggregate **3** is obtained. Furthermore, **3** is stable at room temperature also in hexane solution, as indicated by the similarity of its NMR spectra in the solid state and in hexane solution.[14] In contrast, with the smaller R = $t\text{-}BuMe_2SiLi$ and $i\text{-}Pr_3Si$ substituents polyaggregation predominates.

The ^{29}Si chemical shift of the formally dianionic silicon in **3**, δ −217 ppm, is significantly shifted downfield compared with that in **1**, $(t\text{-}Bu_2MeSi)_2SiLi_2 \cdot 2(t\text{-}Bu_2MeSi)_2SiHLi$ (δ −251 ppm[8]). The ^{7}Li chemical shift in **3** (δ 2.4 ppm) is shifted upfield compared with that in **1**, δ 5.4 ppm.[15] In contrast to **3**, in $[(t\text{-}BuMe_2Si)_2SiLi_2]_n$ (**B**), δ(^{29}Si) values of the formally dianionic silicon (−253 and −256 ppm) and δ(^{7}Li) (4.2 ppm) are similar to those observed for **1**.

In summary, we synthesized three novel nonsolvated *gem*-dilithiosilanes and determined that two of them, **2** and **3**, have a unique coaggregate molecular structure, $(R_2SiLi_2)_2 \cdot 2R'Li$ (R′ = t-Bu, $t\text{-}BuMe_2Si$).[16] The structure of these coaggregates is unusual with respect to both the shape of the Li_6 core and the bridging mode of the silyl and alkyl groups. We continue our studies of this intriguing new family of dilithiosilane aggregates.

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Supporting Information Available: CIF files of the structures of compounds **2** and **3** and text and figures giving details on the syntheses and NMR spectra of compounds **7**, **8**, **3**, and **B**. This material is available free of charge via the Internet at http://pubs.acs.org.

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[14] See the Supporting Information for more details. NMR of **3** (in hexane with a DMSO-d_6 capillary as external standard, δ in ppm): ^{1}H, 1.2 (18H, *t-Bu*Me_2Si), 1.1 (72H, *t-Bu*$_2$MeSi), 0.3 (12H, t-Bu*Me*$_2$Si), 0.5 (24H, t-Bu$_2$*Me*Si); ^{7}Li, 2.4, 1.9; ^{13}C, 2.5, 1.3 (t-Bu*Me*$_2$Si and t-Bu$_2$*Me*Si), 31.9, 29.9 (*t-Bu*Me$_2$Si and *t-Bu*$_2$MeSi); ^{29}Si, −17.4 (t-BuMe$_2$*Si*), 26.5, 26.3 (t-Bu$_2$Me*Si*), −217.7 (*Si*Li$_2$). Solid-state MAS NMR (δ in ppm): ^{7}Li, 2.4, 2.0, −0.3; ^{13}C, 2.5, 1.3 (t-Bu*Me*$_2$Si and t-Bu$_2$*Me*Si), 31.9, 29.9 (*t-Bu*Me$_2$Si and *t-Bu*$_2$MeSi); ^{29}Si, −16.0 (t-BuMe$_2$*Si*), 28.1 (t-Bu$_2$Me*Si*), −217.2 (*Si*Li$_2$).

[15] The reasons for these differences in the NMR chemical shifts of **3** and **1** are not yet understood and are under current study.

[16] Due to the extreme air and moisture sensitivity of **2**, **3**, **A**, and **B**, determination of their elemental analysis and melting point is not practical and therefore was not carried out.