Silyllithium Compounds

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$[\{(t\text{Bu}_2\text{Me})_2\text{Si}\}_3\text{Li}_4]^{2-}$: An Aggregated Dianion of a 1,1-Dilithiosilane with a Unique Structural Motif[**]

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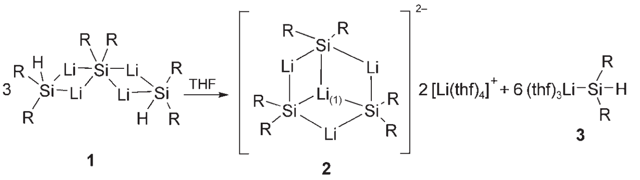
In memory of Vadim A. Pestunovich

The chemistry of geminal dilithio reagents of the general type R_2ELi_2 (E = C,[1] Si,[2,3] Ge[4]) is a rapidly developing field. However, the structures of these compounds and their aggregation preferences are still largely unknown. Thus, only a few R_2SiLi_2 compounds have been characterized by X-ray crystallography, all as solvated unaggregated structures.[2e,f,3c] Recently, we reported the structure of unsolvated **1** [see Eq. (1)], which has a unique R_2SiLi_4 core fragment, formed by co-aggregation of one molecule of R_2SiLi_2 with two molecules of R_2SiHLi.[5] Also for solvated geminal dilithio organic compounds R_2CLi_2[1a] only limited structural information is available, although they have important synthetic applications.[1b,6] A solvated dimeric aggregate of a 1,1-dilithiogermane was reported.[4] Gaining structural information on R_2ELi_2 reagents is important because of their synthetic applications[6] and because the chemistry of organolithium and silyllithium reagents is solvent-dependent.[7,8]

Herein we report isolation, X-ray structure analysis, and NMR spectroscopic studies of silyllithium aggregate **2** [Eq. (1), R = tBu$_2$MeSi], which contains the first known aggregated silyllithium dianion $[(R_2Si)_3Li_4]^{2-}$. The formation of an aggregated anionic metallic core is common for clusters of Group 13 elements, e.g., $(RIc)_n{}^{m-}$ (Ic = Al, Ga, In)[9] and for transition metal complexes,[10] but such aggregates were not yet observed for RLi compounds.



(1)

When **1** is dissolved in THF two compounds are produced [Eq. (1)]: solvated silyllithium **3**[5] and **2** in 6:1 molar ratio. The formation of aggregate **2** in THF is unexpected, because in most previous cases studied addition of THF led to solvated lithiosilanes[11] or dilithiosilanes.[3c] Evaporation of THF solvent and addition of hexane allowed the separation of hexane-insoluble **2** from hexane-soluble **3**. Crystallization of crude **2** from toluene yielded red crystals suitable for X-ray crystallography.[12] An ORTEP plot of the anion of **2** is shown in Figure 1.

Compound **2** is a new aggregated solvated form of the known dilithiosilane R_2SiLi_2[3d–h] (R = tBu$_2$MeSi) containing three R_2SiLi_2 molecules and eight THF molecules (Figure 1). Its structure consists of $[(R_2Si)_3Li_4]^{2-}$ cluster dianions with a starlike tetralithium core, and with two lithium cations each solvated by four THF molecules. The distance between the solvated lithium cations and the closest silicon atom of around 9 Å indicates that **2** has an ionic structure. The structure of **2** is reminiscent of known ate complexes of the type $(Li^+)_2$-$[R'_3M]^{2-}$, where M = Cu.[13] In **2**, M is the central Li atom (Li1) and R′ is R_2LiSi.

The structure of **2** is very unusual. It has a nearly planar central Si_3Li_3 hexagon and a central lithium atom (Li1) which is located 0.4 Å above the hexagon plane[14] (the sum of the Si1-Li1-Si4, Si1-Li1-Si7, and Si4-Li1-Si7 bond angles is 355.2°, and that of the Li4-Li1-Li3, Li4-Li1-Li2, and Li2-Li1-Li3 bond angles is 348.3°). Li1 is somewhat closer to one of the lithium atoms (Li4) than to the other two (Li2 and Li3). Two of the three Li–Li bonds are in the regular Li–Li bond-length range[15] (2.53 and 2.62 Å) while the third is unusually short (2.18 Å). The Si–Li bond lengths in **2** vary quite significantly (2.42–2.76 Å) but are all in the range of other known Si–Li bond lengths.[11]

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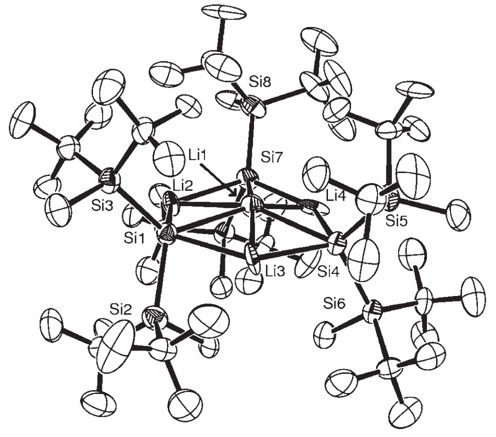

Figure 1. ORTEP plot of the anion of **2**. Hydrogen atoms are omitted for clarity. Selected distances [Å] and angles [°]: Li1-Li3 2.53(2), Li1-Li2 2.62(2), Li1-Li4 2.18(3), Si1-Li3 2.556(16), Si1-Li2 2.613(17), Si1-Li1 2.76(2), Si4-Li4 2.497(16), Si4-Li3 2.610(18), Si4-Li1 2.69(2), Si7-Li4 2.422(17), Si7-Li2 2.675(16), Si7-Li1 2.687(19), Si1-Si2 2.333(5), Si1-Si3 2.350(5); Si2-Si1-Si3 114.89(18), Li3-Si1-Li2 112.6(6), Li3-Si1-Li1 56.6(6), Li2-Si1-Li1 58.3(6), Li4-Si4-Li3 105.1(7), Li4-Si4-Li1 49.6(7), Li3-Si4-Li1 56.9(6), Li4-Si7-Li2 106.2(7), Li4-Si7-Li1 50.2(8), Li2-Si7-Li1 58.5(6), Li4-Li1-Li3 118.7(10), Li4-Li1-Li2 116.1(10), Li2-Li1-Li3 113.5(9), Si1-Li1-Si4 117.4(6), Si1-Li1-Si7 118.7(8), Si4-Li1-Si7 119.1(8), Li3-Li1-Si4 60.0(5), Si4-Li1-Li4 60.6(6); Si1-Li3-Li4-Si7 0.7(5), Si1-Li3-Si4-Li4 −5.7(14), Si1-Li2-Si7-Li4 15.0(12), Li2-Si7-Li4-Si4 −11.9(16), Li2-Si1-Li3-Si4 10.4(15).

Compound **2** was also studied by solid-state and solution NMR spectroscopy. In the solid state the ^{29}Si MAS-NMR chemical shifts of the dianionic Si atoms (Si1, Si4, Si7) appear at −239 and −243 ppm, while in THF solution the signal is shifted slightly to higher field (−254 ppm). These chemical shifts are similar to those of the unsolvated neutral aggregate **1** ($\delta = -251$ ppm) and are shifted downfield by 30–40 ppm relative to that of the central silicon atom in solvated $[(i\mathrm{Pr}_3\mathrm{Si})_2\mathrm{SiLi}_2(\mathrm{thf})_4]$ ($\delta = -282$ ppm).[3c] However, they are strongly shifted to higher field in comparison to those of $[(\mathrm{Me}_3\mathrm{Si})_3\mathrm{SiLi}]_2$ ($\delta = -189$ ppm).[16]

The solid-state ^{7}Li MAS-NMR spectrum of **2** shows two signals: a narrow signal at 0.1 ppm, assigned to the THF-solvated Li$^+$ cations and a broad signal at 7 ppm corresponding to the four core lithium atoms of **2**.[17] This is the most downfield $\delta(^7\mathrm{Li})$ value reported, except for $[(\mathrm{Li}(\mathrm{dme}_2)]_2$-$[1,2,4,5\text{-}(\mathrm{Me}_3\mathrm{Si})_4\mathrm{C}_6\mathrm{H}_2]$, for which $\delta(^7\mathrm{Li}) = 10.7$ ppm was explained by the strong deshielding effect on the lithium atom of paratropic ring currents resulting from the presence of an 8π antiaromatic system.[18]

The ^{7}Li chemical shifts of solvated silyllithium compounds are around 0.5 ppm,[19] while those of aggregated silyllithium[19] and organolithium[20] compounds are around 3 ppm. Compound **1**, a coaggregate of mono- and dilithium silyl units, has $\delta(^7\mathrm{Li})$ values of 4.2 and 5.4 ppm.[5] The observed $\delta(^7\mathrm{Li})$ value of 7 ppm in **2** is further downfield and consistent with **2** being an aggregate of dilithiosilane.

In THF solution we observed a broad peak from 4.0 ppm to −0.5 ppm and a peak at 6.3 ppm.[17] The significantly lower intensity of the latter indicates that in solution most of **2** dissociates into other silyllithium derivatives.

Compound **2** reacts with water and with MeCl to form in high yields the corresponding disubstitution products $\mathrm{R_2SiH_2}$ and $\mathrm{R_2SiMe_2}$, respectively. Thus, **2** reacts as a 1,1-dilithiosilane.

In conclusion, we have prepared and structurally characterized the first aggregated silyllithium dianion, $[(\mathrm{R_2Si})_3\mathrm{Li}_4]^{2-}$, which reacts as a 1,1-dilithiosilane. We are continuing to study the chemistry of **2** and other related dimetal organosilicon compounds.

Experimental Section

Standard Schlenk techniques were used for all syntheses and sample manipulations. **2**: **1** (2.5 g, 2.3 mmol) in THF (20 mL) was gently warmed to 40–60 °C until it had completely dissolved (storage of **1** in THF at room temperature for several days led to substantial decomposition). Immediately afterwards the THF was evaporated. The resulting solid product was washed with hexane (3 × 20 mL) to remove **3**. Crystallization of the crude solid from toluene gave 0.9 g (0.5 mmol, 65 % yield based on **1**) of red crystals of **2**. Solid-state ^{29}Si MAS-NMR (25 °C, TMS): $\delta = 27.7$, 24.8, 23.2 (Si(tBu)$_2$Me), −238.6, −243.2 ppm ($\mathrm{Si}_2\mathit{Si}\mathrm{Li}_4$); solid-state ^{7}Li MAS-NMR (25 °C, LiCl): $\delta = 7$ (br), 0.1 ppm. Solution ^{29}Si NMR (99.4 MHz, THF with [D$_6$]DMSO capillary, 25 °C, TMS): $\delta = 28.5$ (br; Si(tBu)$_2$Me), −254 ppm (br; $\mathrm{Si}_2\mathit{Si}\mathrm{Li}_4$). Solution ^{7}Li NMR (73.6 MHz, THF with DMSO capillary, 25 °C, LiCl in MeOH) $\delta = 6.3$ (br, low-intensity peak), broad peak from 4 to −0.5 ppm.[17]

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[12] Crystallographic data for **2**: $C_{86}H_{170}Li_6Si_9O_8$, $M_r = 1626.67$, monoclinic, space group *Cc*, $a = 18.831(4)$, $b = 24.571(5)$, $c = 24.113(5)$ Å, $\beta = 96.34(2)°$, $V = 11\,089(4)$ Å^3, $Z = 4$, Nonius Kappa CCD, $Mo_{K\alpha}$ radiation (0.71073 Å), 220 K, $2\theta_{max} = 50°$, $R = 0.0673$ ($I > 2\sigma I$), $wR2 = 0.1109$ ($I > 2\sigma I$), $R_w = 0.2312$ (all data), GOF = 0.838. CCDC 283189 contains 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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[17] For ^{7}Li MAS-NMR and ^{7}Li NMR spectra of **2**, see Supporting Information.

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