Radicals

Nonsolvated, Aggregated 1,1-Dilithiosilane and the Derived Silyl Radicals**

Dmitry Bravo-Zhivotovskii, Ilya Ruderfer, Semyon Melamed, Mark Botoshansky, Boris Tumanskii, and Yitzhak Apeloig**

Dedicated to Professor Josef Michl on the occasion of his 65th birthday

The chemistry of the potentially synthetically versatile geminal 1,1-dilithiosilyl compounds [R_2SiLi_2] is still in its infancy, in contrast to the chemistry of monosilyllithium compounds [R_3SiLi], which have been studied intensively.[1] Several [R_2SiLi_2] compounds have been reported,[2,3] although only a few of them have been isolated and characterized by X-ray crystallography (all in solvated form).[2e,f,3c] The aggregation behavior and the structures of dilithiosilanes in weakly solvating media are unknown. Only limited structural information is also available for geminal

[*] Dr. D. Bravo-Zhivotovskii, I. Ruderfer, S. Melamed, Dr. M. Botoshansky, Dr. B. Tumanskii, Prof. Y. Apeloig
Department of Chemistry and
the Lise Meitner-Minerva Center for Computational Quantum Chemistry
Technion-Israel Institute of Technology
Haifa 32000 (Israel)
Fax: (+972) 4829-4601
E-mail: chrbrzh@tx.technion.ac.il
chrapel@tx.technion.ac.il

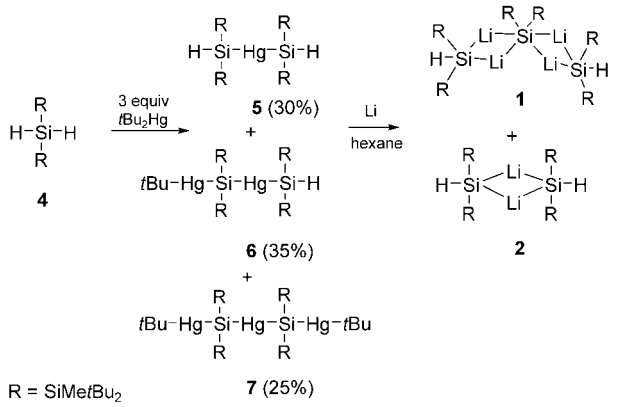
[**] This research was supported by the Israel Science Foundation, administered by the Israel Academy of Sciences and Humanities, the Fund for the Promotion of Research at the Technion, and the Minerva Foundation in Munich. B.T, M.B., and D.B.-Z. are grateful to the Ministry of Immigrant Absorption, State of Israel, for a Kamea scholarship.

Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.

 DOI: 10.1002/ange.200461765

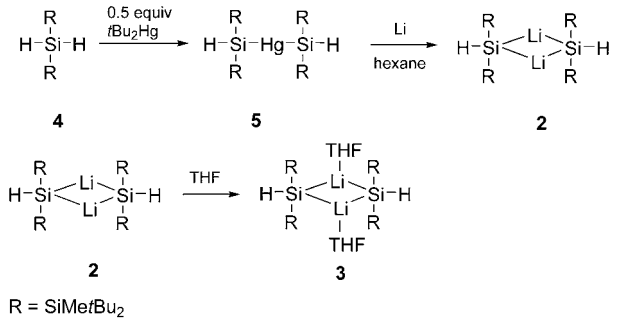
organodilithium compounds $[R_2CLi_2]$,[4] although they have already found interesting synthetic applications.[5] Such structural information is important because the chemistry of organolithium and silyllithium reagents is solvent dependent.[6,7]

Herein we report the preparation and the X-ray molecular structure analysis of the first unsolvated aggregates of the *gem*-dilithiosilane $[(R_2SiLi_2)(R_2HSiLi)_2]$ ($R = SiMe_2tBu$; **1**, Scheme 1), the hydridosilyllithium $[(R_2HSiLi)_2]$ ($R =$



Scheme 1. Synthesis of the aggregated *gem*-dilithiosilane **1**.

$SiMe_2tBu$; **2**, Scheme 2),[8] and the THF solvate of **2** (**3**, Scheme 2).[8] Compound **1** is also the first known example of a hexacoordinated silicon atom with an $\{R_2SiLi_4\}$ core. We also report the photochemical generation and characterization by EPR spectroscopy of a novel family of silyl radicals,[9] in which the silyl radical center is part of a silyllithium aggregate, and that photolysis of **1** yields a triplet-state silyl biradical.[10]



Scheme 2. Synthesis of the aggregated hydridosilyllithium **2** and its THF solvate **3**.

Silyllithium aggregate $[(R_3SiLi)_n]$ can be synthesized by lithiation, in hexane, of the corresponding silylmercury compounds $[Hg(SiR_3)_2]$,[11] which, in turn, are prepared by reaction of hydridosilanes with $[Hg(tBu)_2]$.[12] By analogy, silyldimercury compounds of the type -Hg-SiR_2-Hg- may serve as precursors to *gem*-dilithium compounds. Treatment of dihydridosilane **4** with three equivalents of $[Hg(tBu)_2]$ leads to a product mixture containing (based on ^{29}Si NMR spectroscopy) the silylmercury compounds **5**, **6**, and **7** (Scheme 1). Lithiation of this mixture in hexane yields the novel unsolvated aggregate **1** as the major (60%) product and the silyllithium dimer **2** as the minor product (25%). Compound **1** was isolated as green crystals suitable for X-ray crystallography upon crystallization from hexane.[13,14]

Treatment of **4** with only half an equivalent of $[Hg(tBu)_2]$ leads exclusively to **5** (Scheme 2). Lithiation of **5** in hexane resulted in the formation of the hydridosilyllithium dimer **2**, which was crystallized from hexane as colorless crystals.[13,15] Dissolving **2** in THF leads to **3**, which was also isolated by crystallization from hexane. The molecular structure of **3**[13,16] is similar to that of the recently reported compound $[(R_2HSiLi)_2(thf)_2]$ ($R = SiMe_2tBu$).[8]

ORTEP drawings of the molecular structures of **1** and **2** are shown in Figures 1 and 2, respectively. Compound **1** is the

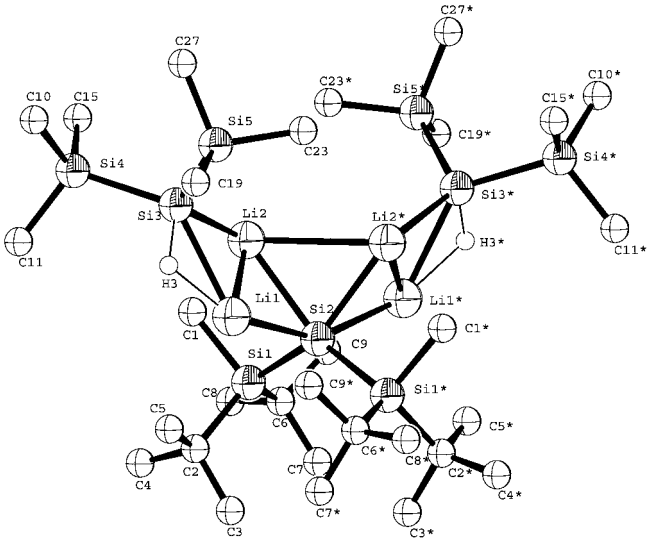


Figure 1. ORTEP diagram of the aggregated *gem*-dilithiosilane **1**. Hydrogen atoms, except for Si–H, and some of the carbon atoms have been omitted for clarity. Selected bond lengths [pm] and bond and dihedral angles [°]: Si2-Li1 264.1(10), Si2-Li2 261.3(8), Si3-Li2 267.1(9), Si3-Li1 268.2(9), Li1-Li2 264.7(13), Li2-Li2* 315.9(16), Li1-H3 190.0(5), Si3-H3 147.0(5), C1-Li2 257.9(10), Si1-C1 192.3(5), Si2-Si1 235.79(15), Si2-Si1* 235.79(15), Si3-Si4 239.33(17); Si1-Si2-Si1* 125.74(10), Si1-Si2-Li2 84.04(19), Si1*-Si2-Li2 146.14(19), Li1-Si2-Li1* 151.2(4), Li2-Si2-Li1-Si3 11.7, H3-Si3-Li1-Li2 159.6, Li1-Li2-Li*2-Li1* 114.2.

first known unsolvated *gem*-dilithiosilane. Its structure is best described as a co-aggregate of the *gem*-dilithiosilane $[(R_3Si)_2SiLi_2]$ with two molecules of the hydridosilyllithium $[(R_3Si)_2HSiLi]$. The central silicon atom (Si2) in **1** is six-coordinate and is bonded to four Li atoms, with Si2–Li bond lengths of 264 and 261 pm. These can be compared to the slightly shorter Si–Li bond lengths of 258 and 260 pm in $[\{(Me_3Si)_3SiLi\}_2]$.[11c] The two spiro four-membered $\{Si_2Li_2\}$ rings, which are slightly nonplanar (with a Si–Li–Si–Li dihedral angle within each ring of 11.7°), form an angle of 70.6° (Figure 1). The four Li atoms are arranged in a transoid open chain with a Li1-Li2-Li2*-Li1* dihedral angle of 114° and bond lengths Li1–Li2 (and Li2*–Li1*) = 265 pm and Li2–Li2* = 316 pm. The Li1···Li1* distance is 511 pm. This

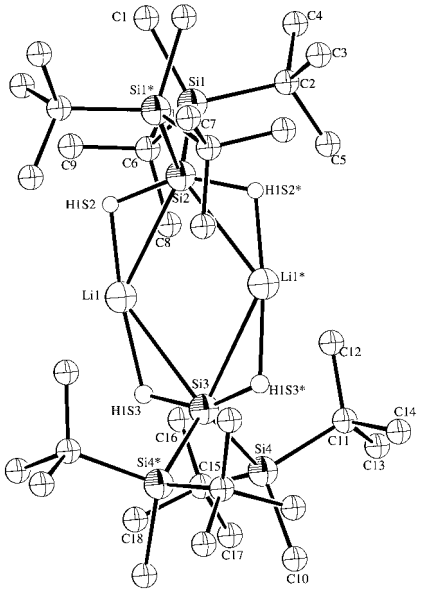


Figure 2. ORTEP diagram of the unsolvated hydridosilyllithium dimer **2**. Hydrogen atoms, except for Si–H, have been omitted for clarity. Selected bond lengths [pm] and bond and dihedral angles [°]: Si2-Li1 269.8(7), Si2-Li1* 269.8(7), Si3-Li1 276.7(7), Si3-Li1* 276.7(7), Li1-Li1* 300.3(16), Si2-H1S2 151.0(6), Si3-H1S3 145.0(5), Li1-H1S3 196.0(5), Li1-H1S2 184.0(5), Si1-Si2 238.35(10), Si1-C1 189.6(4), Si1-C6 192.5(4); Si1*-Si2-Si1 111.13(7), Si1*–Si2-Li1 124.23(18), Si1-Si2-Li1 112.15(17), Li1-Si2-Li1* 67.6(3), Si1*-Si2-H1S2 100(2), Si1-Si2-H1S2 98(2), Li1-Si3-Li1-*Si2 0.0, H1S2-Li1-Si2-Li1* 164.7, H1S3-Li1-Si3-Li1* 160.7.

open-chain arrangement is unique, as silyllithium and alkyllithium aggregates usually adopt polycyclic-type arrangements of the lithium atoms.[11d,17] The Si···Si distance within each of the spiro four-membered rings in **1** is 457 pm, similar to that in dimer **2** and much longer than a normal covalent Si–Si bond (235 pm). The Si–Li bond lengths in **1** (261–267 pm) are somewhat shorter than those in **2** (270 and 277 pm), while the Li1···Li2 distance in **1** (265 pm) is significantly shorter than that in **2** (300 pm).

Dimer **2** exhibits the usual structure of aggregated silyllithium compounds carrying bulky substituents.[11a–c] The four-membered ring in **2** is planar and the bond lengths within the $\{Si_2Li_2\}$ ring are in the range found for other silyllithium dimers.[11a–c]

In both **1** and **2** the Si–H bonds participate in agostic-type interactions with lithium atoms to form two {SiHLi} rings. Similar agostic interactions have been reported for $[(R_2HSi\text{-}Li)_2(thf)_2]$ ($R = SiMe_2tBu$).[8] The two Li atoms (Li2 and Li2*) in **1** that do not interact with the Si–H hydrogen atoms interact instead with the hydrogen atoms of the methyl groups of the tBu_2MeSi substituents (C1 and C1* in Figure 1), thereby forcing a rotation of the tBu_2MeSi groups on Si2 to an unfavorable, sterically hindered conformation in which the *t*Bu groups are oriented towards each other. This orientation causes an increase in the Si1–Si2–Si1* bond angle to 125°. The Si4–Si3–Si5 bond angle of 119.8° in the $[(R_3Si)_2HSiLi]$ fragments of **1** (Figure 1) and the Si1–Si2–Si1* bond angle of 111.5° in **2** (Figure 2) are significantly smaller.

The ^{29}Si NMR chemical shift of the central, hexacoordinated Si2 atom in **1** is $\delta = -251$ ppm; this signal is shifted to lower field by 41 ppm relative to that of the central silicon atom of the THF solvate $[(iPr_3Si)_2SiLi_2(thf)_4]$ ($\delta = -292$ ppm).[3] However, it is strongly shifted to higher field compared to that of Si3 of **1** ($\delta = -182$ ppm) and the anionic silicon atoms in **2** ($\delta = -171$ and -176 ppm) and **3** ($\delta = -189$ ppm), which exhibit normal chemical shift values for silyl anions.[8,11c]

UV irradiation ($\lambda = 300$ nm) of **1**, **2**, or **3** in hexane leads to the observation by EPR spectroscopy of several novel silyl radicals as well as a biradical, all with unprecedented structures. Irradiation of a solution of **3** in hexane at 220 K yields a septet EPR signal (Figure 3 a), which results from the splitting of the main line by two equivalent ^7Li nuclei ($I = 3/2$)

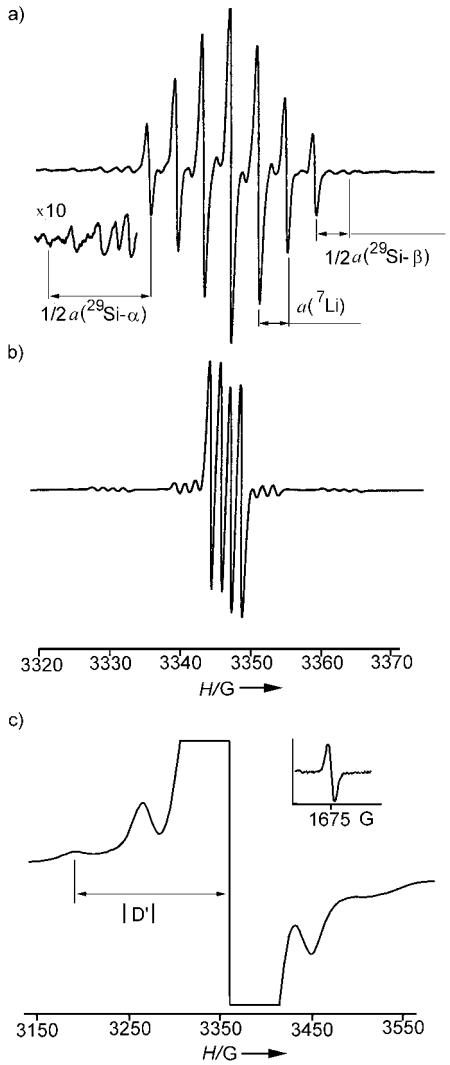
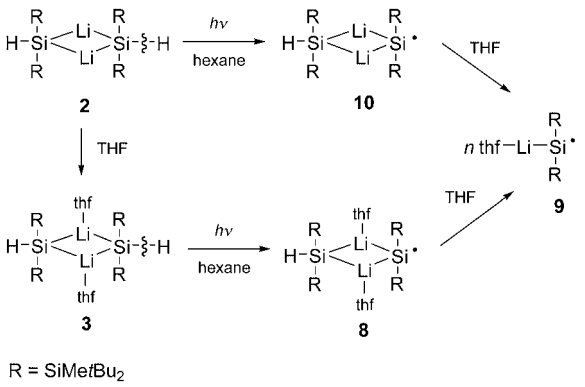


Figure 3. a) The EPR spectrum of silyl radical **8** observed during UV irradiation of **3** in hexane at 220 K. b) The EPR spectrum of silyl radical **9** observed after addition of THF to a solution of **8** or **10** in hexane. The EPR spectrum of **9** has the following parameters: $g = 2.0067$, $a(\alpha\text{-}^{29}Si) = 33.25$ G, $a(\beta\text{-}^{29}Si) = 9.5$ G, $a(^7Li) = 1.5$ G. c) The EPR spectrum observed during UV irradiation of **1** in frozen hexane at 150 K. It is a superposition of the spectra of biradical **13** and of an unassigned silyl radical. The insert shows the forbidden $\Delta M_s = 2$ resonance.

with a hyperfine coupling (hfc) constant $a(2\,^{7}\mathrm{Li})$, of 4.17 G. The *g*-factor of the signal is 2.0073 and the hfc constants with the ^{29}Si atoms are $a(\alpha\text{-}^{29}\mathrm{Si}) = 30.0$ G and $a(2\beta\text{-}^{29}\mathrm{Si}) = 9.0$ G. The hyperfine structure of the EPR signal and the aggregated structure of the precursor **3** allow us to confidently assign this signal to radical **8** (Scheme 3), which is the first known example of a silyl radical that is part of a silyllithium aggregate skeleton.



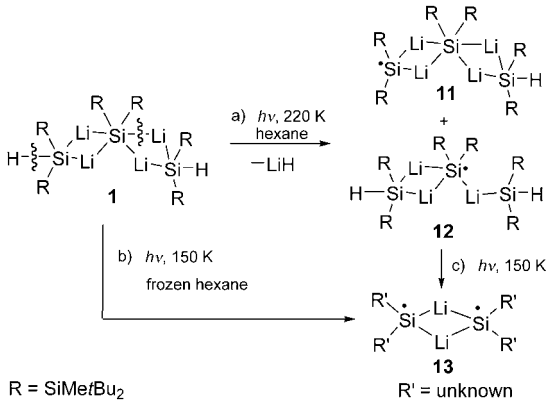
Scheme 3. Generation of radicals **8** and **10** centered on a silicon atom that is part of a silyllithium aggregate skeleton. The cleavage of the silyllithium aggregate in **8** and **10** by THF leads to formation of **9**.

Addition of THF to a solution of radical **8** in hexane gives a new, stable, silicon-centered radical with a quartet EPR signal (Figure 3b). This signal was assigned to the monomeric, lithium-substituted silyl radical **9**,[18] thus indicating that addition of THF cleaves the $\{Si_2Li_2\}$ skeleton of **8** (Scheme 3).

Irradiation of the unsolvated dimer **2** leads to a more complex EPR spectrum,[19] which is a superposition of two multiplet signals: one signal is a septet with $a(2\,^{7}\mathrm{Li}) = 6.6$ G, and the second is a multiplet resulting from the interaction of the unpaired electron with two nonequivalent lithium atoms ($a(^{7}\mathrm{Li}) = 6.0$ G and $a(^{7}\mathrm{Li}) = 7.9$ G).[19] Addition of THF to this solution also results in the formation of radical **9**. Therefore, we assume that the observed septet signals can be assigned to radical **10**, which is the unsolvated form of radical **8** (Scheme 3). The radical with two different $a(^{7}\mathrm{Li})$ splittings has not yet been fully identified.

The photochemistry of **1** leads to even more intriguing novel radicals. Thus, irradiation of a solution of **1** in hexane at 220 K leads to a complex EPR spectrum[19] that is a superposition of several EPR signals.[19] One of these signals has a septet pattern, similar to **10** but with $a(2\,^{7}\mathrm{Li}) = 6.6$ G, and we assigned it to radical **11** (Scheme 4, path a). The second of the observed signals belongs to a novel silyl radical with a splitting pattern resulting from interaction of the unpaired electron with *three* nonequivalent lithium atoms with hfc constants of 4.4, 7.1, and 15.3 G, as confirmed by a computer simulation of the EPR spectrum (using the SimFonia software).[19] This analysis indicates that the electron spin is centered on the central Si atom of **1** and we tentatively assign these signals to the radical **12** shown in Scheme 4.

UV irradiation of a frozen hexane solution (150 K) of **1** (Scheme 4, path b) or of the frozen solution obtained after



Scheme 4. Generation of silyl biradical **13**.

irradiation of **1** at 220 K (Scheme 4, path c) results in a characteristic EPR signal of a triplet biradical[10] with four sidebands from $\Delta M_s = 1$ transitions and a signal at half-field (1675 G) resulting from the forbidden $\Delta M_s = 2$ transition (Figure 3c). The zero-field splitting parameter $|D'|$ of 172 G indicates a substantial interaction between the two radical centers of the biradical. The distance between the two spin centers, calculated on the basis of $|D'|$, is 435 pm.[20] This distance is similar to that between Si(2) and Si(3) in **1** and **2** (457 pm). We therefore assumed that the unpaired electrons of the biradical are centered on the silicon atoms of a $\{(R'_2Si)_2Li_2\}$ fragment with a geometry similar to that in **1** and **2**, and we can assign the biradical structure **13** shown in Scheme 4. The typical, broadened EPR lines of biradicals means that we cannot extract more information, such as the hfc constant, and, as a result, the nature of the substituents R′ in **13** is not known.

In conclusion, we have prepared and structurally characterized the first nonsolvated, aggregated *gem*-dilithiosilanes. These aggregated silyllithium compounds were found to be photolytic precursors for the generation of previously unknown intriguing silyl radicals, as well as of a silyl biradical, in which the spins are centered on silicon atoms that are part of silyllithium aggregates. We are continuing to study the photochemistry and other reactions of the intriguing novel silyllithium compounds **1** and **2**.

Experimental Section

Standard Schlenk techniques were used for all syntheses and sample manipulations.

1: $[Hg(t\mathrm{Bu})_2]$ (27.4 g, 87 mmol) was added under argon to **4** (10.0 g, 29.0 mmol) in three equal portions while heating the mixture to 120 °C. A new portion of $[Hg(t\mathrm{Bu})_2]$ was added only after evolution of isobutene from the reaction mixture had ceased (approximately every 4 h). After evaporation of the volatile compounds, hexane (100 mL) and Li powder (7.0 g, 1.0 mol) were added and the mixture was stirred at room temperature for 6 h. The mixture was then decanted from the lithium powder. Crystallization from hexane gave 6.1 g (5.8 mmol) of **1** as green crystals (60% yield based on **4**). ^{7}Li NMR (194.3 MHz, C_6D_6, 25 °C, LiCl in methanol): $\delta = 5.4$, 4.2 ppm; ^{29}Si NMR (99.4 MHz, C_6D_6, 25 °C, TMS): $\delta = 27.4$, 23.8, 22.1 ($Si(t\mathrm{Bu})_2\mathrm{Me}$), −182 ($SiHSi_2Li_2$), −251 ppm ($Si_2SiLi_4$).

2: $[Hg(t\mathrm{Bu})_2]$ (2.3 g, 7 mmol) was added under argon to **4** (5 g, 14 mmol), and the mixture was then heated to 120 °C for approx-

imately 4 h. The heating was terminated after evolution of isobutene from the reaction mixture had ceased. After evaporation of the volatile compounds, hexane (50 mL) and Li powder (7.0 g, 1.0 mol) were added and the mixture was stirred at 60 °C for 1 h. The mixture was then decanted from the lithium powder. Crystallization from hexane gave 3.6 g (5.1 mmol) of **2** as colorless crystals (70% yield based on **4**). ^{7}Li NMR (194.3 MHz, hexane with C_6D_6 capillary, 25 °C, LiCl in methanol): $\delta = 4.4$ ppm; ^{29}Si NMR (99.4 MHz, hexane with C_6D_6 capillary, 25 °C, TMS): $\delta = 22.6$, 21.6 ((tBu$_2$Me*Si*)$_2$SiHLi), −170.8, −176.5 ppm ((tBu$_2$MeSi)$_2$*Si*HLi).

3: Compound **2** (1 g, 1.4 mmol) was dissolved in THF (10 mL). Removal of the THF and recrystallization from hexane gave 0.9 g (1.1 mmol) of **3** as colorless crystals. ^{1}H NMR (500 MHz, C_6D_6, 25 °C, TMS): $\delta = 3.52$ (8H, thf), 1.42 (8H, thf), 1.14 (36H, $(CH_3)_3C$), 0.44 ppm (6H CH_3Si) ppm; the Si-H proton was not identified; ^{7}Li NMR (194.3 MHz, C_6D_6, 25 °C, LiCl in methanol): $\delta = 2.1$ ppm; ^{13}C NMR (125 MHz, C_6D_6, 25 °C, TMS): $\delta = 68.7$ and 25.3 (thf), 30.7 ((CH_3)$_3$C), 20.7 ((CH_3)$_3$*C*), −2.5 ppm (CH_3Si); ^{29}Si NMR (99.4 MHz, C_6D_6, 25 °C, TMS): $\delta = 21.1$ ((tBu$_2$Me*Si*)$_2$SiHLi), −188.8 ppm ((tBu$_2$-MeSi)$_2$*Si*Li).

Received: August 23, 2004
Published online: December 21, 2004

Keywords: aggregation · EPR spectroscopy · lithium · radicals · silicon

[1] a) P. Lickiss, C. Smith, *Coord. Chem. Rev.* **1995**, *145*, 75 – 124; b) K. Tomao, A. Kawachi, *Adv. Organomet. Chem.* **1995**, *38*, 1 – 58; c) J. Belzner, U. Dehnert, in *The Chemistry of Organic Silicon Compounds*, *Vol. 2* (Eds.: Z. Rappoport, Y. Apeloig), Wiley, Chichester, **1998**, pp. 779 – 825; d) A. Sekiguchi, V. Y. Lee, M. Nanjo, *Coord. Chem. Rev.* **2000**, *210*, 11 – 45.

[2] a) J.-H. Hong, P. Boudjouk, S. Castellino, *Organometallics* **1994**, *13*, 3387 – 3389; b) U. Bankwitz, H. Sohn, D. R. Powell, R. West, *J. Organomet. Chem.* **1995**, *499*, C7 – C9; c) S.-B. Choi, P. Boudjouk, *Tetrahedron Lett.* **2000**, *41*, 6685 – 6688; d) H. Sohn, *J. Organomet. Chem.* **2004**, *689*, 134 – 138; e) R. West, H. Sohn, U. Bankwitz, J. Calabrese, Y. Apeloig, T. Mueller, *J. Am. Chem. Soc.* **1995**, *117*, 11608 – 11609; f) S.-B. Choi, P. Boudjouk, P. Wei, *J. Am. Chem. Soc.* **1998**, *120*, 5814 – 5815. Several disodium and dipotassium silole derivatives are also known: g) W.-C. Joo, J.-H. Hong, S.-B. Choi, H.-E. Son, C. H. Kim, *J. Organomet. Chem.* **1990**, *391*, 27 – 36; h) W. P. Freeman, T. D. Tilley, G. P. A. Yap, A. L. Rheingold, *Angew. Chem.* **1996**, *108*, 960 – 962; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 882 – 884; i) Y. Liu, T. C. Stringfellow, D. Ballweg, I. A. Guzei, R. West, *J. Am. Chem. Soc.* **2002**, *124*, 49 – 57.

[3] a) S. K. Mehrotra, H. Kawa, J. R. Baran, Jr., M. M. Ludvig, R. J. Lagow, *J. Am. Chem. Soc.* **1990**, *112*, 9003 – 9004; b) N. Tokitoh, K. Hatano, T. Sadahiro, R. Okazaki, *Chem. Lett.* **1999**, *28*, 931 – 932; c) A. Sekiguchi, M. Ichinohe, S. Yamaguchi, *J. Am. Chem. Soc.* **1999**, *121*, 10231 – 10232.

[4] Several molecular structures of 1,1-dilithioalkanes with oxygen, nitrogen, or aromatic substituents have been reported. These aggregates are formed by the strong interaction of Li with the substituents, rather than interactions between Li and the central carbon atoms of neighboring molecules. For a review see: C. Strohmann, D. Schildbach, in *The Chemistry of Organolithium Compounds* (Eds.: Z. Rappoport, I. Marek), Wiley, Chichester, **2004**, pp. 941 – 996.

[5] I. Marek, J. F. Normant, *Chem. Rev.* **1996**, *96*, 3241 – 3268.

[6] M. Schlosser, in *Organometallics in Synthesis: a Manual* (Ed.: M. Schlosser), Wiley, Chichester, **2002**, pp. 5 – 352.

[7] G. Korogodsky, M. Bendikov, D. Bravo-Zhivotovskii, Y. Apeloig, *Organometallics* **2002**, *21*, 3157 – 3161; D. Bravo-Zhivotovskii, G. Korogodsky, Y. Apeloig, *J. Organomet. Chem.* **2003**, *686*, 58 – 65; R. Balasubramanian, J. Oliver, *J. Organomet. Chem.* **1980**, *197*, C7 – C11.

[8] The preparation and X-ray analysis of another THF-solvated hydridosilyllithium $[(R_2HSiLi)_2(thf)_2]$ (R = SiMe$_2t$Bu) was reported recently: T. Iwamoto, J. Okita, C. Kabuto, M. Kira, *J. Am. Chem. Soc.* **2002**, *124*, 11604 – 11605.

[9] For reviews on silyl radicals see: C. Chatgilialoglu, *Chem. Rev.* **1995**, *95*, 1229 – 1251; C. Chatgilialoglu, C. Schiesser, in *The Chemistry of Organic Silicon Compounds*, *Vol. 3* (Eds.: Z. Rappoport, Y. Apeloig), Wiley, Chichester, **2001**, pp. 341 – 390.

[10] The first triplet silyl biradical was reported only recently: I. Toulokhonova, T. Stringfellow, S. Ivanov, A. Masunov, R. West, *J. Am. Chem. Soc.* **2003**, *125*, 5767 – 5773.

[11] a) M. Yuzefovich, M. Bendikov, D. Bravo-Zhivotovskii, D. Bläser, R. Boese, Y. Apeloig, *Angew. Chem.* **2001**, *113*, 3106 – 3109; *Angew. Chem. Int. Ed.* **2001**, *40*, 3016 – 3020; b) M. Naio, A. Sekiguchi, H. Sakurai, *Bull. Chem. Soc. Jpn.* **1999**, *72*, 1387 – 1393; c) K. Klinkhammer, *Chem. Eur. J.* **1997**, *3*, 1418 – 1431; d) A. Sekiguchi, M. Nanjo, C. Kabuto, H. Sakurai, *Organometallics* **1995**, *14*, 2630 – 2632; e) H. Gilman, F. K. Cartledge, *J. Organomet. Chem.* **1965**, *3*, 255 – 257; f) N. Vyazankin, G. Razuvaev, E. Gladyshev, S. Korneva, *J. Organomet. Chem.* **1967**, *7*, 353 – 357.

[12] G. Razuvaev, N. Vyazankin, *Pure Appl. Chem.* **1969**, *41*, 353 – 374.

[13] CCDC-247482 (**1**), -247483 (**2**), and -247484 (**3**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk)..

[14] Crystallographic data for **1**: $C_{27}H_{64}Li_2Si_{4.5}$, $M_r = 529.07$, monoclinic, space group $C2/c$, $a = 27.500(5)$, $b = 12.626(3)$, $c = 23.480(5)$ Å, $\alpha = 90$, $\beta = 118.86(2)$, $\gamma = 90°$, $V = 7140(3)$ Å^3, $Z = 8$, Nonius Kappa CCD diffractometer, Mo K_α radiation (0.71073 Å), 220 K, $2\theta_{max} = 50.04°$, $R = 0.0625$ ($I > 2\sigma I$), $wR2 = 0.0954$ ($I > 2\sigma I$), $R_w = 0.2137$ (all data), GOF = 0.759.

[15] Crystallographic data for **2**: $C_{36}H_{86}Li_2Si_6$, $M_r = 701.47$, monoclinic, space group $C2/c$, $a = 23.8790(11)$, $b = 14.1750(6)$, $c = 15.3980(11)$ Å, $\alpha = 90.0000(14)$, $\beta = 114.9070(19)$, $\gamma = 90.0000(15)°$, $V = 4727.2(4)$ Å^3, $Z = 4$, Nonius Kappa CCD diffractometer, Mo K_α radiation (0.71073 Å), 220 K, $2\theta_{max} = 50.2°$, $R = 0.0565$ ($I > 2\sigma I$), $wR2 = 0.1221$ ($I > 2\sigma I$), $R_w = 0.1562$(all data), GOF = 0.8. As shown in Figure 2, the Si–H hydrogen atoms are disordered and occupy two sites, each with a refined occupancy ratio of 50:50.

[16] The X-ray molecular structure of **3** will be reported elsewhere.

[17] W. Ilsley, T. F. Schaaf, M. Glick, J. P. Oliver, *J. Am. Chem. Soc.* **1980**, *102*, 3769 – 3773.

[18] An analogous Li-substituted silyl radical with R$_3$Si=*i*Pr$_3$Si was previously observed in the photolysis of the corresponding silylmercury compound: D. Bravo-Zhivotovskii, M. Yuzefovich, N. Sigal, K. Klinkhammer, B. Tumanskii, A. Shames, Y. Apeloig, *Angew. Chem.* **2002**, *114*, 671 – 673; *Angew. Chem. Int. Ed.* **2002**, *41*, 649 – 651.

[19] The Supporting Information consists of the EPR spectra observed during irradiation of **1** and **2** and the simulated (using the SimFonia software) EPR spectra of silyl radicals substituted by two or three Li atoms.

[20] Assuming that the spin–spin dipole interaction $|D'|$ is approximately given by the equation $|D'| = (3/2 g^2 b^2 r^{-3})$, where g is the EPR g-factor, b is the Bohr magneton, and r is the average distance between the two unpaired electrons; see: J. Wertz, J. Bolton, *Electron Spin Resonance*, McGraw-Hill, New York, **1972**, chap. 10.

