The Syntheses and Molecular Structure of a Branched Oligosilyl Anion with a Record of Nine Silicon Atoms and of the First Branched Oligosilyl Dianion

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$(Me_3Si)_3Si(Me_2Si)_2(Me_3Si)_2SiLi$ (**1**) and $LiSi(Me_3Si)_2(Me_2Si)_2Si(Me_3Si)_2Li$ (**2**) were synthesized by the reaction of $(Me_3Si)_3Si(Me_2Si)_2Si(Me_3Si)_3$ in THF with one or two mol-equivalents, respectively, of MeLi. Both **1** and **2** were characterized spectroscopically and by trapping reactions, and **1** also by X-ray crystallography.

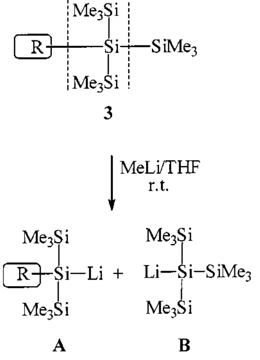
Introduction

Silyl anions are potentially important reagents in synthesis[1] and they are probably involved in the formation and degradation of polysilanes.[2] However, the number and variety of synthetically useful silyl anions and the information on their structures is very limited,[1] especially in comparison to carbanions; e.g., $CH_3(CH_2)_nCH_2Li$ reagents are widely used in synthesis, while the analogous $Me_3Si(SiMe_2)_nSiMe_2Li$ are unknown, except for $Me_3SiSiMe_2Li$.[3] Of contemporary interest is the branched "hypersilyl" anion, $(Me_3Si)_3Si^-$, first prepared in situ[4] and later isolated as stable THF[5a,5b] or DME[5c] complexes of the lithium salt, e.g., $(Me_3Si)_3SiLi{\cdot}3THF$. The large steric requirements,[6] the interesting electronic properties[7] and the solubility of its derivatives in organic solvents has made the $(Me_3Si)_3Si$ group a popular ligand in main-group[8] and in transition-metal chemistry.[9] Recently, several new branched polysilyl anions have been synthesized by us[10a] (and were used to prepare novel stable silenes[10b]), as well as by other groups.[11] However, these anions have a relatively small number of silicon atoms, and in anions which were structurally characterized the maximum number of silicon atoms is only four.[10a,11a]

We report here[12] the synthesis and the full structural characterization of a new branched polysilyl anion $(Me_3Si)_3SiMe_2SiMe_2Si(Me_3Si)_2SiLi{\cdot}3THF$ (**1**) holding two records for silyl anions: (a) It has nine silicon atoms – the highest known; and (b) it has a chain of 5 silicon atoms (including the anionic center) – the longest known. We also report on the synthesis of the first known branched oligosilyl dianion, the corresponding nTHF$\cdot LiSi(Me_3Si)_2Me_2SiMe_2Si(Me_3Si)_2SiLi\cdot n$THF (**2**).

Results and Discussion

Recently we found[10a] that the products obtained from the reaction of branched polysilanes **3** with methyllithium (Scheme 1) depend on the substituent R as follows: when R has one or two silicon atoms (series 1) CH_3Li attacks preferentially at the sterically less-hindered Si atom, yielding the silyllithium **A** (bond A is cleaved). However, when R is a branched polysilane fragment (series 2) only $(Me_3Si)_3SiLi$ (**B**) was obtained (bond B is cleaved).



Series 1: R = $SiMe_2tBu$, $SiMe_2SiMe_3$; $SiMe_2SiMe_2tBu$.

Series 2: R = $SiMe(SiMe_3)_2$; $Si(SiMe_3)_3$; $SiMe_2Si(SiMe_3)_3$; $SiMeHSi(SiMe_3)_3$.

Scheme 1

To gain a better understanding of the reaction in Scheme 1 we also studied the cleavage of the doubly branched polysilane **4**.[13] Reaction of **4** with one equivalent of MeLi leads to cleavage of bond A [i.e., **4** behaves as a member of series 1, even though it possesses a $(Me_3Si)_3Si$ fragment], producing the novel branched polysilyl anion **1** (Scheme 2). The structure of **1** was first assigned by isolating the expected trapping products $(Me_3Si)_3SiMe_2SiMe_2Si(Me_3Si)_2SiR$ (R = tBuMe$_2$Si, PhMe$_2$Si, CH_3OCH_2) when treated with tBuMe$_2$SiCl, PhMe$_2$SiCl and CH_3OCH_2Cl, respectively (see Experimental Section). These compounds were characterized by their ^1H, ^{13}C and ^{29}Si NMR spectra

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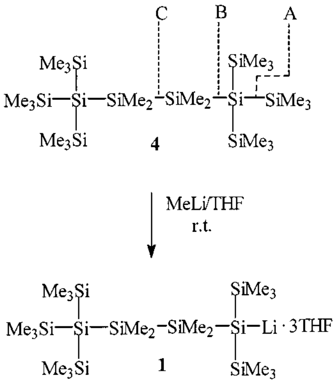
and finally by X-ray crystallography. To the best of our knowledge, **1** is *the isolated silyl anion with the highest number of silicon atoms* (i.e., nine) *and with the longest polysilicon chain* (5 silicon atoms), of any other known silyl anion.



Scheme 2

Our results contrast with those of Pannell et al.[13] who reported that the reaction of **4** with CH_3Li followed by reaction with CH_3I yields $(Me_3Si)_4Si$, implying the presence of $(Me_3Si)_3SiMe_2SiLi$ and thus cleavage of bond C in **4**. Preliminary experiments aimed at the resolving this discrepancy, which we have carried out, suggest that Pannell's observation may result from the presence of impurities in the precursor which was used. Thus, when **4** was purified by crystallization (according to Pannell's procedure[13]) reaction with CH_3Li followed by addition of water led exclusively to $(Me_3Si)_4Si$ (as observed by Pannell et al.[13] who, however, used CH_3I). No traces of $(Me_3Si)_3SiSiMe_2H$ (expected if bond C in **4** is cleaved) were detected. On the other hand, **4** (which was carefully purified by liquid chromatography) produced only **1**.[14] HPLC chromatography of **4** purified by crystallization, showed 10% of two additional compounds, yet unidentified. We therefore speculate that these impurities catalyze the production of $(Me_3Si)_4Si$ which was observed by Pannell et al.[13]

The structure of **1**·3THF, as determined by X-ray crystallography, is shown in Figure 1. Except for $(Me_3Si)_3SiLi$[5] and the closely related tBuMe$_2$Si(Me$_3$Si)$_2$SiLi·3THF[10a] this is the only other reported X-ray structure of a solvated[15] branched silyllithium compound.

Table 1 summarizes the most important structural parameters of the four known solvated[15] branched silyl lithium compounds: **1**·3THF, $(Me_3Si)_3SiLi$·3THF (**5**·3THF), tBuMe$_2$Si(Me$_3$Si)$_2$SiLi·3THF (**6**·3THF)[10a] and $(Me_3SiMe_2Si)_3SiLi$·3THF (**7**·3THF) – recently synthesized by our group.[16] In general the four structures are quite similar, but some differences can be noted;[17] r(Si–Li) in **1**·3THF (2.657 Å) is similar to that in **5**·3THF (2.644 Å),[5a] and in **6**·3THF (2.684 Å)[10a] but it is 0.11 Å shorter than in **7**·3THF (2.767 Å). We refrain from interpreting these differences because quantum-mechanical calculations show that the force-constant for the Si–Li bond stretching is very small,[16] so that even small effects (including crystal packing forces), can cause significant changes in r(Si–Li). The Si–Si bonds around the anionic center [Si(5)] are slightly longer in **1**·3THF, **6**·3THF and **7**·3THF than in **5**·3THF, (average bond lengths: 2.355 Å, 2.347 Å, 2.361 Å and 2.334 Å, respectively), probably reflecting repulsions between the bulky branched silicon chains. The average Si–Si–Si angles around Si(5) are similar in all compounds. Comparison with the neutral silane **4**[13] reveals distortions in the polysilicon backbone of **1**·3THF; the Si(2)–Si(3) and Si(4)–Si(5) bonds in **1**·3THF are slightly elongated, while r[Si(3)–Si(4)] is slightly shortened relative to **4**. The Si(3)–Si(4)–Si(5) angle in **1**·3THF is contracted to 109.9° (117.1° in **4**), while the Si(2)–Si(3)–Si(4) angles in **1**·3THF and **4** are similar.

The ^{29}Si NMR chemical shift of the anionic center Si(5) in **1** is at $\delta = -181.5$, strongly shielded, as expected, compared to the corresponding silane **4** ($\delta = -119.6$). This shift is similar to that observed on going from $(Me_3Si)_4Si$ ($\delta = -135.5$) to $(Me_3Si)_3SiLi$·3THF ($\delta = -189.0$). A comparison

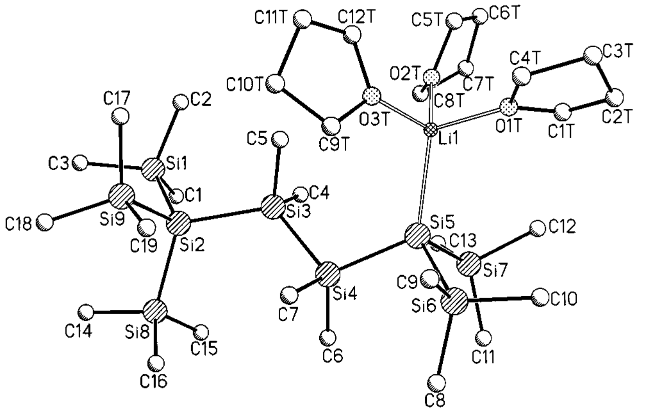


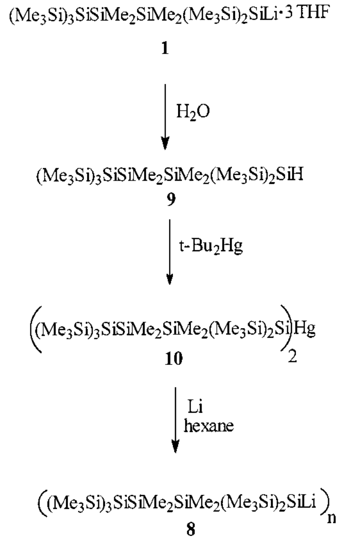
Figure 1. Molecular structure of **1**; hydrogen atoms have been omitted for clarity; selected bond lengths (Å) and bond angles (°): Si(1)–Si(2) 2.361(1), Si(2)–Si(9) 2.355(2), Si(2)–Si(8) 2.348(1), Si(2)–Si(3) 2.378(1), Si(3)–Si(4) 2.355(1), Si(4)–Si(5) 2.363(1), Si(7)–Si(5) 2.352(1), Si(6)–Si(5) 2.348(1), Si(5)–Li, 2.657(6); Si(1)–Si(2)–Si(9) 105.9(1), Si(1)–Si(2)–Si(8) 107.3(1), Si(2)–Si(3)–Si(4) 118.2(1), Si(3)–Si(4)–Si(5) 109.9(1), Si(4)–Si(5)–Si(6) 101.0(1), Si(4)–Si(5)–Si(7) 104.2(1), Si(6)–Si(5)–Si(7) 100.2(1)

Table 1. Selected bond lengths [Å] and bond angles [°] for solvated branched silyllithium compounds and silanes

Compound	r(Si–Li)	r(Si–Si)[a]		α(Si–Si–Si)[b]	
		individual	average	individual	average
1·3THF	2.657(6)	2.352, 2.348, 2.363	2.355	100.2, 101.0, 104.2	101.7
5·3THF[5a]	2.644(12)	2.330[c]	2.330	102.4[c]	102.4
5·3THF[5b]	2.669(13)	2.330, 2.328, 2.336	2.331	103.1, 101.7, 103.1	102.6
5·1.5DME[5c]	2.630(5)	2.338, 2.347, 2.340	2.342	104.7, 104.0, 103.1	103.9
6·3THF[10a]	2.684(9)	2.353, 2.346, 2.341	2.347	105.4, 99.4, 100.0	101.6
7·3THF[16]	2.767(11)	2.361[c]	2.361	100.1[c]	100.1
$(Me_3Si)_4Si$[5a]		2.346[c]	2.346[c]	109.5[c]	109.5[c]
4[13]		2.361, 2.355, 2.345, 2.375	2.359	107.0, 109.0, 115.3	110.3

[a] Between the central silicon atom (the anionic center) and an α-silicon atom. – [b] Around the central silicon atom (the anionic center). – [c] All values are identical by symmetry.

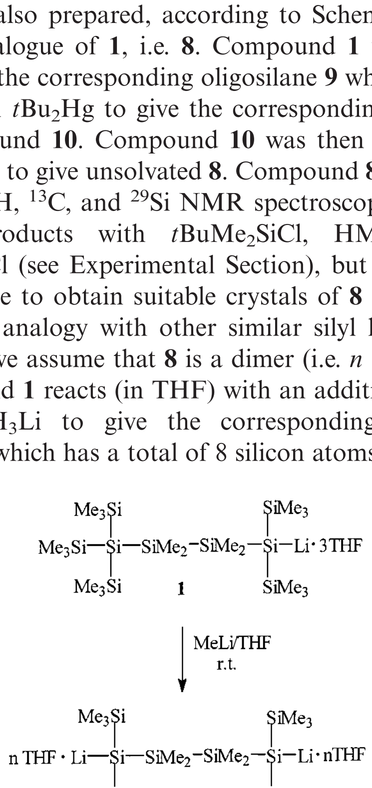
with other silyl anions shows that the ^{29}Si chemical shift of the anionic center in **1** is shifted slightly downfield compared to that in $(Me_3Si)_3SiLi·3THF$ (δ = –189.0) and slightly upfield compared with that in **7**·3THF (δ = –176.8). These changes probably reflect a combination of steric and electronic effects. Interestingly, in **1** the chemical shifts of Si(4) (δ = –22.2) and of the more remote Si(3) (δ = –33.5) are shifted in opposite directions (by 7 ppm downfield and by 4 ppm upfield, respectively) relative to their positions in **4** (δ = –29.5). The chemical shift of Si(2) in **1** (δ = –129.9) is shifted upfield by 10.3 ppm relative to **4** (δ = –119.6).



Scheme 3

We have also prepared, according to Scheme 3, the unsolvated analogue of **1**, i.e. **8**. Compound **1** was first hydrolyzed to the corresponding oligosilane **9** which was then reacted with *t*Bu_2Hg to give the corresponding disilylmercury compound **10**. Compound **10** was then reacted with Li in hexane to give unsolvated **8**. Compound **8** was characterized by ^{1}H, ^{13}C, and ^{29}Si NMR spectroscopy and by its reaction products with *t*$BuMe_2SiCl$, HMe_2SiCl and CH_3OCH_2Cl (see Experimental Section), but we have not yet been able to obtain suitable crystals of **8** for an X-ray analysis. In analogy with other similar silyl lithium compounds[1,2] we assume that **8** is a dimer (i.e. $n = 2$).

Compound **1** reacts (in THF) with an additional equivalent of CH_3Li to give the corresponding dianion **2** (Scheme 4) which has a total of 8 silicon atoms and a chain of 4 silicon atoms. The proposed structure of **2** is supported by ^{1}H, ^{13}C and ^{29}Si NMR spectroscopy and by the isolation of the expected trapping products: $R(Me_3Si)_2SiMe_2SiMe_2SiSi(SiMe_3)_2R$ (R = $SiMe_2$*t*Bu, $SiMe_2H$, CH_2OCH_3) in the reactions with *t*$BuMe_2SiCl$, $ClSiMe_2H$ and $ClCH_2OCH_3$, respectively (see Experimental Section). Recently we have also isolated the unsolvated **2**.[16] Attempts to crystallize **2** in order to determine its molecular structure by X-ray crystallography are in progress. Several linear α,ω-dilithium oligosilanes were reported previously.[11b,18] However, **2** is the first isolated and spectroscopically characterized branched silyldilithium compound.



Scheme 4

Conclusion

We have synthesized, isolated and determined using X-ray crystallography the molecular structure of a new branched polysilyllithium compound $(Me_3Si)_3SiMe_2SiMe_2Si(Me_3Si)_2SiLi·3THF$ (**1**) holding two records for silyl anions: (a) it has nine silicon atoms – the highest known; and (b) it has a chain of 5 silicon atoms (including the anionic center) – the longest known. We have also synthesized the first branched oligosilyldilithium compound, the corresponding *n*$THF·LiSi(Me_3Si)_2Me_2SiMe_2Si(Me_3Si)_2SiLi·$*n*THF (**2**). Compounds **1** and **2** are expected to have a variety of synthetic applications; e.g., most recently Lambert et al. have applied **1** (prepared according to our procedure[12]) for synthesizing a nanometer-scale dendritic polysilane.

We are continuing our efforts to synthesize even longer branched polysilyl anions and to study their properties and their potential applications.

Experimental Section

General Remarks: Standard Schlenk techniques were used for all syntheses and all sample manipulations. – NMR spectra were recorded at room temperature in C_6D_6 solution using a Bruker EM-200 or Bruker-400 instruments. – Mass spectroscopy (MS) data were obtained with a Finnigan MAT TSQ 45 triplestage quadrupole mass spectrometer.

$(Me_3Si)_3SiMe_2SiMe_2Si(Me_3Si)_2SiLi·3THF$ (1): Compound **4**[13] (7.0 g, 11.3 mmol) in dry THF (30 mL) was placed in a Schlenk flask under vacuum, and 9 mL of a 1.4 M solution of CH_3Li in diethyl ether was added in 10 portions over 72 h (conversion was followed by NMR spectroscopy). The THF solvent was removed and **1** was crystallized from hexane to give 6.5 g of colorless crystals of **1**·3THF (75% yield), suitable for X-ray analysis. – ^{1}H NMR (C_6D_6): δ = 0.42 [s, 27 H, $Si(SiMe_3)_3$], 0.55 [s, 18 H, $SiLi(SiMe_3)_2$], 0.60 (s, 6 H, $SiMe_2$), 0.73 (s, 6 H, $SiMe_2$), 1.37 (m, 12 H, CH_2 of THF), 3.50 (m, 12 H, OCH_2 of THF). – ^{13}C NMR (C_6D_6): δ = 3.7 [$Si(SiMe_3)_3$], 1.6 ($SiMe_2$), 6.9 ($SiMe_2$), 7.5 [$SiLi(SiMe_3)_2$], 25.3 (CH_2 of THF), 68.5 (OCH_2 of THF). – ^{29}Si NMR (C_6D_6): δ = –181.5 [*Si*$Li(SiMe_3)_2$], –129.9 [*Si*$(SiMe_3)_3$], –33.5 ($SiMe_2$), –22.2 ($SiMe_2$), –9.4 [Si(*Si*$Me_3)_3$], –5.0 [SiLi(*Si*$Me_3)_2$].

***n*$THF·LiSi(Me_3Si)_2Me_2SiMe_2Si(Me_3Si)_2SiLi·$*n*THF (2):** Compound **1** (6.5 g, 8.5 mmol) in dry THF (30 mL) was placed in a Schlenk flask under vacuum, and 9 mL of a 1.4 M solution of CH_3Li in ether was added in 10 portions over 72 h (conversion was followed by NMR spectroscopy). Removal of the solvent gave 4.7 g of **2**·*n*THF (60% yield). – ^{1}H NMR (C_6D_6): δ = 0.49 [s, 36 H, $SiLi(SiMe_3)_2$], 0.64 (s, 12 H, $SiMe_2$), 1.37 (m, 12 H, CH_2 of THF), 3.50 (m, 12 H, OCH_2 of THF). – ^{29}Si NMR (C_6D_6): δ = –187.6 [$\mathit{Si}Li(SiMe_3)_2$], –25.6 ($SiMe_2$), –4.3 [$SiLi(\mathit{Si}Me_3)_2$].

Trapping Reactions. – General Procedure: The trapping reagent (15 mmol) in 50 mL of toluene was added to a solution of **1** (10 mmol) or **2** (5 mmol) in 40 mL of toluene cooled to –78 °C. All operations were carried out under vacuum using Schlenk techniques. The reaction mixture was stirred at room temperature for 10 h. The pure products were isolated after filtration of the reaction mixture and evaporation of the solvent, in yields which generally exceeded 90%.

Reaction of 1 with $PhMe_2SiCl$. – $(Me_3Si)_3SiMe_2SiMe_2Si(Me_3Si)_2SiSiMe_2Ph$: ^{1}H NMR ($C_6D_6$): δ = 0.31 [s, 27 H, $Si(SiMe_3)_3$], 0.33 [s, 18 H, $Si(Si\mathit{Me}_3)_2SiMe_2Ph$], 0.40 [s, 6 H, $Si(SiMe_3)_2Si\mathit{Me}_2Ph$], 0.50 (s, 6 H, $SiMe_2$), 0.59 (s, 6 H, $SiMe_2$), 7.19 [m, 3 H, $Si(SiMe_3)_2SiMe_2\mathit{Ph}$], 7.56 [m, 2 H, $Si(SiMe_3)_2SiMe_2\mathit{Ph}$]. – ^{13}C NMR ($C_6D_6$): δ = 1.4 ($SiMe_2$), 1.7 ($SiMe_2$), 2.4 [$Si(SiMe_3)_2Si\mathit{Me}_2Ph$], 3.8 [$Si(SiMe_3)_3$], 3.9 [$Si(Si\mathit{Me}_3)_2SiMe_2Ph$], 127.9, 129.6, 133.3, 134.7 [$Si(SiMe_3)_2SiMe_2\mathit{Ph}$]. – ^{29}Si NMR ($C_6D_6$): δ = –127.3 [$\mathit{Si}(SiMe_3)_3$], –125.8 [$\mathit{Si}(SiMe_3)_2SiMe_2Ph$], –29.0 ($SiMe_2$), –28.8 ($SiMe_2$), –9.4 [$Si(\mathit{Si}Me_3)_3$], –9.0 [$Si(\mathit{Si}Me_3)_2SiMe_2Ph$], –2.1 [$Si(SiMe_3)_2\mathit{Si}Me_2Ph$]. – MS (CI); *m/z*: 674 [M^+ + 2], 657 [M^+ – Me], 595 [M^+ – Ph].

Reaction of 1 with $\mathit{t}BuMe_2SiCl$. – $(Me_3Si)_3SiMe_2SiMe_2Si(Me_3Si)_2SiSiMe_2\mathit{t}Bu$: ^{1}H NMR ($C_6D_6$): δ = 0.28 [s, 6 H, $Si(SiMe_3)_2Si\mathit{Me}_2\mathit{t}Bu$], 0.34 [s,27 H, $Si(SiMe_3)_3$], 0.37 [s, 18 H, $Si(Si\mathit{Me}_3)_2SiMe_2\mathit{t}Bu$], 0.57 (s, 6 H, $SiMe_2$), 0.60 (s, 6 H, $SiMe_2$), 1.02 [m, 3 H, $Si(SiMe_3)_2SiMe_2\mathit{t}Bu$]. – ^{13}C NMR ($C_6D_6$): δ = 0.2 [$Si(SiMe_3)_2Si\mathit{Me}_2\mathit{t}Bu$], 2.0 ($SiMe_2$), 2.7 ($SiMe_2$), 3.9 [$Si(SiMe_3)_3$], 5.0 [$Si(Si\mathit{Me}_3)_2SiMe_2\mathit{t}Bu$], 19.1 [$Si(SiMe_3)_2SiMe_2C\mathit{CH}_3$], 28.6 [$Si(SiMe_3)_2SiMe_2CCH_3$]. – ^{29}Si NMR ($C_6D_6$): δ = –127.7 [$\mathit{Si}(SiMe_3)_3$], –126.6 [$\mathit{Si}(SiMe_3)_2SiMe_2\mathit{t}Bu$], –29.3 ($SiMe_2$), –27.0 ($SiMe_2$), –9.4 [$Si(\mathit{Si}Me_3)_3$], –9.0 [$Si(\mathit{Si}Me_3)_2SiMe_2\mathit{t}Bu$], 5.7 [$Si(SiMe_3)_2\mathit{Si}Me_2\mathit{t}Bu$]. – MS (CI); *m/z*: 652 [M^+ + 2], 637 [M^+ + 2 – Me], 595 [M^+ + 2 – *t*Bu].

Reaction of 1 with H_2O. – $(Me_3Si)_3SiMe_2SiMe_2Si(Me_3Si)_2SiH$ (9): ^{1}H NMR (C_6D_6): δ = 0.28 [s, 18 H, $Si(Si\mathit{Me}_3)_2H$], 0.32 [s, 27 H, $Si(SiMe_3)_3$], 0.45 (s, 6 H, $SiMe_2$), 0.46 (s, 6 H, $SiMe_2$), 2.7 [s, 1 H, $Si(SiMe_3)_2\mathit{H}$]. – MS (EI); *m/z*: 449 [M^+ – $HSi(SiMe_3)$], 375 [M^+ – $HSi(SiMe_3)_2$].

Reaction of 1 with $ClCH_2OCH_3$. – $(Me_3Si)_3SiMe_2SiMe_2Si(Me_3Si)_2SiCH_2OCH_3$: ^{1}H NMR ($C_6D_6$): δ = 0.32 [s, 18 H, $Si(Si\mathit{Me}_3)_2CH_2OCH_3$], 0.33 [s, 27 H, $Si(SiMe_3)_3$], 0.51 (s, 6 H, $SiMe_2$), 0.54 (s, 6 H, $SiMe_2$), 3.13 [s, 3 H, $Si(SiMe_3)_2CH_2O\mathit{CH}_3$], 3.48 [s, 2 H, $Si(SiMe_3)_2\mathit{CH}_2OCH_3$]. – ^{13}C NMR ($C_6D_6$): δ = –0.4 ($SiMe_2$), 0.9 ($SiMe_2$), 1.8 [$Si(Si\mathit{Me}_3)_2CH_2OCH_3$], 3.6 [$Si(SiMe_3)_3$], 62.9 [$Si(SiMe_3)_2\mathit{CH}_2OCH_3$], 63.1 [$Si(SiMe_3)_2CH_2O\mathit{CH}_3$]. – ^{29}Si NMR ($C_6D_6$): δ = –128.3 [$\mathit{Si}(SiMe_3)_3$], –76.2 [$\mathit{Si}(SiMe_3)_2CH_2OCH_3$], –32.8 ($SiMe_2$), –31.0 ($SiMe_2$), –11.7 [$Si(\mathit{Si}Me_3)_2CH_2OCH_3$], –9.5 [$Si(\mathit{Si}Me_3)_3$]. – MS (EI); *m/z*: 567 [M^+ – Me], 637 [M^+ – $Si SiMe_3)_3$].

Reaction of 2 with $PhMe_2SiCl$. – $PhMe_2SiSi(Me_3Si)_2Me_2SiMe_2Si(Me_3Si)_2SiSiMe_2Ph$: ^{1}H NMR ($C_6D_6$): δ = 0.29 [s, 36 H, $Si(Si\mathit{Me}_3)_2SiMe_2Ph$], 0.38 [s, 12 H, $Si(SiMe_3)_2Si\mathit{Me}_2Ph)$], 0.57 (s, 12 H, $SiMe_2$), 7.57 [m, 5 H, $Si(SiMe_3)_2SiMe_2\mathit{Ph}$]. – ^{13}C NMR ($C_6D_6$): δ = 1.5 ($SiMe_2$), 2.5 [$Si(SiMe_3)_2Si\mathit{Me}_2Ph$], 4.0 [$Si(Si\mathit{Me}_3)_2SiMe_2Ph$], 129.6, 134.7, 141.5 [$Si(SiMe_3)_2SiMe_2\mathit{Ph}$]. – ^{29}Si NMR ($C_6D_6$): δ = –126.2 [$\mathit{Si}(SiMe_3)_2SiMe_2Ph$], –28.6 ($SiMe_2$), –12.1 [$Si(SiMe_3)_2\mathit{Si}Me_2Ph$], –9.0 [$Si(\mathit{Si}Me_3)_2SiMe_2Ph$]. – MS (CI); *m/z*: 703 [M^+ – 2Me], 657 [M^+ – Ph].

Reaction of 2 with $\mathit{t}BuMe_2SiCl$. – $\mathit{t}BuMe_2SiSi(Me_3Si)_2Me_2SiMe_2Si(Me_3Si)_2SiSiMe_2\mathit{t}Bu$: ^{1}H NMR ($C_6D_6$): δ = 0.27 [s, 12 H, $Si(SiMe_3)_2Si\mathit{Me}_2\mathit{t}Bu$], 0.31 [s, 36 H, $Si(SiMe_3)_2$], 0.63 (s, 12 H, $SiMe_2$), 1.03 [s, 18 H, $Si(SiMe_3)_2SiMe_2\mathit{t}Bu$].

Reaction of 2 with H_2O. – $HSi(Me_3Si)_2Me_2SiMe_2Si(Me_3Si)_2SiH$: ^{1}H NMR ($C_6D_6$): δ = 0.28 [s, 36 H, $Si(SiMe_3)_2$], 0.44 (s, 12 H, $SiMe_2$), 2.70 [s, 1 H, $Si(SiMe_3)_2H$].

Synthesis of 8. – 1. Synthesis of the Precursor $[(Me_3Si)_3SiMe_2SiMe_2Si(Me_3Si)_2Si]_2Hg$ (10): $(\mathit{t}Bu)_2Hg$ (0.99 g, 3.15 mmol) and **9** (6.5 mmol) (see above) were heated under argon to 120 °C. The reaction mixture was stirred for 4 h, during which time 5.25 mmol of 2-methylpropane was formed. Evaporation of the volatile compounds and crystallization of the reaction mixture from pentane gave **10** (3.40 g, 85% yield). – ^{1}H NMR (C_6D_6): δ = 0.44 [s, 18 H, $Si(SiMe_3)_2$], 0.54 [s, 27 H, $Si(SiMe_3)_3$], 0.63 (s, 6 H, $SiMe_2$), 0.64 (s, 6 H, $SiMe_2$). – ^{13}C NMR (C_6D_6): δ = 3.6 [$Si(SiMe_3)_3$], 5.5 [$Si(SiMe_3)_2$], 25.8 ($SiMe_2$), 67.8 ($SiMe_2$). – ^{29}Si NMR (C_6D_6): δ = –128.9 [$\mathit{Si}(SiMe_3)_3$], –53.1 [$\mathit{Si}(SiMe_3)_2$], –33.0 ($SiMe_2$), –19.2 ($SiMe_2$), –9.4 [$Si(\mathit{Si}Me_3)_3$], –2.7 [$Si(\mathit{Si}Me_3)_2$].

2. Synthesis of $(Me_3Si)_3SiMe_2SiMe_2Si(Me_3Si)_2SiLi$ (8): A hexane solution of **10** (3.4 g, 2.67 mmol) was sonicated with an excess of Li. After Hg precipitation the solvent was separated from the metallic residue. Evaporation of hexane gave **8** (2.5 g, 85% yield). – ^{1}H NMR (C_6D_6): δ = 0.42 [s, 27 H, $Si(SiMe_3)_3$], 0.55 [s, 18 H, $SiLi(SiMe_3)_2$], 0.60 (s, 6 H, $SiMe_2$), 0.73 (s, 6 H, $SiMe_2$). – ^{13}C NMR (C_6D_6): δ = 1.4 ($SiMe_2$), 3.8 [$Si(SiMe_3)_3$], 6.5 ($SiMe_2$), 7.6 [$SiLi(SiMe_3)_2$]. – ^{29}Si NMR (C_6D_6): δ = –181.5 [$\mathit{Si}Li(SiMe_3)_2$], –129.9 [$\mathit{Si}(SiMe_3)_3$], –33.0 ($SiMe_2$), –22.6 ($SiMe_2$), –9.4 [$Si(\mathit{Si}Me_3)_3$], –5.0 [$SiLi(\mathit{Si}Me_3)_2$].

X-ray Crystallographic Study: Crystal data of **1**·3THF: $C_{19}H_{57}LiSi_9\cdot 3C_4H_8O$, crystal dimensions 0.37 × 0.29 × 0.24 mm, measured on a Nicolet R3 diffractometer with Mo-K_α radiation at T = 128 K. Cell dimensions: a = 19.071(3), b = 15.113(2), c = 17.379(3) Å, V = 5009(1) Å^3, orthorhombic crystal system, Z = 4, $d_{calcd.}$ = 1.010 g·cm^{-3}, μ = 0.263 mm^{-1}, space group $Pca2_1$, data collection of 10872 intensities ($2\Theta_{max}$ = 50°), 8347 independent (R_{merg} = 0.0190), 7531 observed [$F_o > 4\sigma(F)$], structure solution with direct methods (Siemens-SHELXS) and refinement on F^2 (Siemens-SHELXTL 5.03) (397 parameters). The hydrogen atom positions were calculated and refined as rigid groups with the 1.2-fold (1.5 for methyl groups) U_{iso} values of the corresponding C atoms. The absolute structure was confirmed by refinement of the x parameter resulting in –0.27(13). $R1$ = 0.0460, $wR2$ (all data) = 0.1255, $w^{-1} = \sigma^2(F_o^2) + (0.0839\,P)^2 + 2.0556\,P$, where $P = [(\max F_o^2) + (2F_c^2)]/3$, GoF ($F^2$) = 1.04, maximum residual electron density 0.780 eÅ^{-3}. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-1994140. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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[16] D. Bravo-Zhivotovskii, Y. Apeloig et al., to be published.

[17] In the structural discussion we use the structure of **5**$\cdot$3THF reported by Sheldrick et al.,[5a] who reported the structures of both pure **5**$\cdot$3THF and of **5**$\cdot$3THF cocrystallized with $Si(SiMe_3)_4$. The structural data of Power et al.[5b] is very similar to that reported by Sheldrick for **5**$\cdot$3THF cocrystalized with $Si(SiMe_3)_4$ [5a] but the presence or absence of $Si(SiMe_3)_4$ was not mentioned.[5b] We therefore assumed that the most reliable data for pure **5**$\cdot$3THF is that reported in ref.[5a]

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