Organometallics **1997,** *16,* 1265−1269

A New Method for the Synthesis of Branched Polysilane Anions

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Received August 26, 1996⊗

Lithiation by MeLi of three families of branched polysilanes $(Me_3Si)_3Si{-}X$ {(**1**) X = $SiMe_2H$, *t*-$BuMe_2Si$, $SiMe_2SiMe_3$, *t*-$BuSiMe_2SiMe_2$; (**2**) X = $SiMe(SiMe_3)_2$, $Si(SiMe_3)_3$, $SiMe_2Si(SiMe_3)_3$, $SiMeHSi(SiMe_3)_3$; (**3**) X = $Si(SiMe_3)_2Cl$, $Si[Si(SiMe_3)_3]MeCl$, $Si[Si(SiMe_3)_3]HCl$} yields, depending on X, one of the following: (a) novel branched polysilyllithium compounds; (b) the known $(Me_3Si)_3SiLi$; (c) various mixtures. The cleavage of family **1** can be understood in terms of steric effects, i.e., assuming that MeLi attacks preferentially the sterically less hindered Si atom leading to the formation of new polysilyllithium compounds, e.g., *t*-$BuMe_2Si(Me_3Si)_2SiLi{\cdot}3THF$ and *t*-$BuMe_2SiSiMe_2(Me_3Si)_2SiLi{\cdot}3THF$, which were isolated in a crystalline form. The X-ray structure of the former is presented. In contrast to **1** the lithiation of the branched polysilanes **2** leads exclusively (mostly with $(Me_3Si)_3SiSiMe(SiMe_3)_2$**)** to the known $(Me_3Si)_3SiLi$. Lithiation of **3** leads to a number of novel polysilyllithium compounds. We tentatively propose that the lithiation of **3** proceeds by a two step reaction in which a disilene is formed as an intermediate, and this is followed by fast addition of a second molecule of MeLi to produce the final silyllithium product.

Introduction

Many of the recent achievements in silicon chemistry are connected to the branched "hypersilyl" anion, $(Me_3Si)_3Si^-$,[1] first prepared *in situ* by Gilman and Smith[2] and later isolated as a stable DME[3a] or THF[3b] complex of its lithium salt, e.g., $(Me_3Si)_3SiLi{\cdot}3THF$. For example, $(Me_3Si)_3SiLi$ was used in the synthesis of the first stable silene $(Me_3Si)_2Si{=}CR(OSiMe_3)$,[4] iminoborane $(Me_3Si)_3SiB{=}NCR_3$,[5] and formylsilane $(Me_3Si)_3SiC({=}O)H$.[6] Furthermore, the large steric requirements of compounds containing the $(Me_3Si)_3Si$ group and their good solubility in organic solvents make this "hypersilyl" substituent a popular ligand in main-group[7] and in transition metal-chemistry.[8] Recently there was also considerable interest in the electronic[9a] and steric[9b,10] properties of the "hypersilyl" group. In view of the above and the recent interest in polysilane dendrimers[11] we have embarked on a program to prepare more highly branched polysilanes, which can be used to stabilize a variety of organosilicon reactive intermediates, e.g. silenes, disilenes, silylenes, and silicenium ions. *We report here a new synthetic method that allows us to prepare a variety of novel branched polysilane anions.*

Our strategy is based on the facile cleavage of branched polysilanes by alkyl lithium reagents to give silyl anions (e.g., reaction 1 for X = Me_3Si, Me, *t*-Bu, Ph).[12]

$$(Me_3Si)_3SiX \ + \ MeLi \longrightarrow X(Me_3Si)_2SiLi \ + \ Me_4Si \qquad (1)$$

Results and Discussion

We have studied the outcome of reaction 1 for three families of branched polysilanes of the general type $(Me_3Si)_3SiX$, shown in Chart 1, where X was varied as follows: In family **1**, X has either one or two silicon atoms. In **2**, X is a branched polysilane fragment

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⊗ Abstract published in *Advance ACS Abstracts*, February 1, 1997.

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S0276-7333(96)00733-9 CCC: $14.00

Chart 1

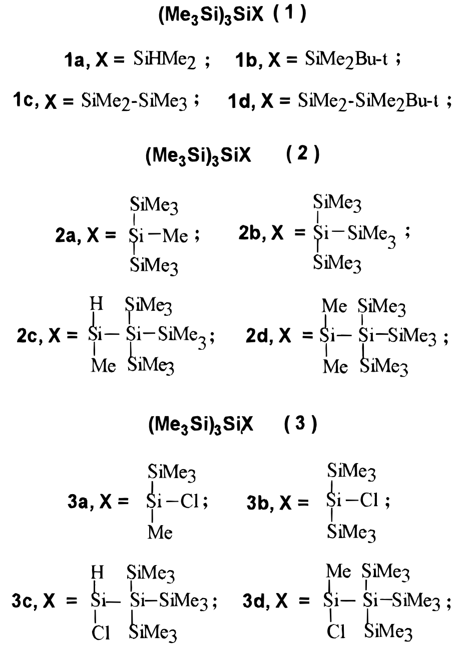


Table 1. Relative Yields (%) of Products in the Lithiation of Branched Polysilanes $(Me_3Si)_3SiX$ of Types 1 and 2 (Eq 2)

X	rel yields path A[b]	rel yields path B[b]
polysilanes **1**		
$HSiMe_2$ (**1a**)	<2	>98
$SiMe_2Bu$-*t* (**1b**)	>99	<1
$SiMe_2SiMe_3$ (**1c**)	70	30
$SiMe_2SiMe_2Bu$-*t* (**1d**)	98	2
polysilanes **2**		
$SiMe(SiMe_3)_2$ (**2a**)	40	60
$Si(SiMe_3)_3$ (**2b**)[a]	<2	>98
$SiMeHSi(SiMe_3)_3$ (**2c**)	<2	>98
$SiMe_2Si(SiMe_3)_3$ (**2d**)	<2	>98

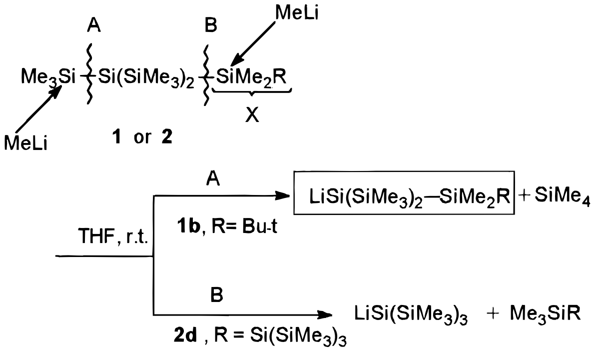
[a] From: Gilman, H.; Harrell, R. L., Jr. *J. Organomet. Chem.* **1967**, *9*, 67. [b] See eq 2.

containing up to six silicon atoms. In **3**, X is a branched *chloro*-substituted polysilane with up to 5 silicon atoms.

The required $(Me_3Si)_3SiX$ polysilanes (**1**–**3**) were prepared by coupling reactions of $(Me_3Si)_3SiLi{\cdot}3THF$ with the appropriate chlorosilanes. For example, **1b**,**d** were prepared by the coupling of $(Me_3Si)_3SiLi{\cdot}3THF$ in toluene at −78 °C with *t*-$BuSiMe_2Cl$ or *t*-$BuMe_2SiSiMe_2Cl$, respectively. $[(Me_3Si)_3Si]_2SiHCl$, **3c**, the first known silane with two "hypersilyl" substituents bonded to the same silicon atom, was prepared in 68% yield by the very slow addition at −78 °C of $HSiCl_3$ to a toluene solution of a 2-fold molar excess of $(Me_3Si)_3SiLi{\cdot}3THF$. **2c**,**d** and **3d** were synthesized from **3c** by standard methylation and chlorination reactions. The details of these syntheses are given in the Experimental Section.

Lithiation with MeLi of polysilanes belonging to family **1** gave the results shown in Table 1. The relative yields of the silyllithium products were determined by GC/MS analysis of the product mixtures obtained by quenching of the reaction mixtures with the following: (a) water, leading to the hydrolysis products $HSi(SiMe_3)_2SiR_3$ and $HSi(SiMe_3)_3$; (b) $ClCH_2OCH_3$, leading to the corresponding methyl ethers $CH_3OCH_2Si(SiMe_3)_2SiR_3$ and $CH_3OCH_2Si(SiMe_3)_3$.

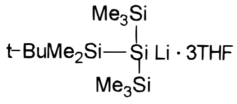
The results in Table 1 indicate that the polysilanes **1** are cleaved by two major pathways (eq 2). The desired



(2)

novel silyllithium reagents are formed via path A in eq 2, while cleavage of the Si−X bond (path B) leads to the undesired formation of $(Me_3Si)_3SiLi$ (and of the corresponding Me_3SiR silane).

The cleavage of polysilanes of family **1** can be understood in terms of steric effects, i.e., assuming that MeLi attacks preferentially at the sterically less hindered Si atom. Thus, with **1a** when R = H (eq 2) attack occurs exclusively at the less hindered $SiHMe_2$ group (path B) and $(Me_3Si)_3SiLi$ is the only silyllithium product which is observed. With **1b**, where R is the larger *t*-Bu group, attack occurs exclusively at the terminal Me_3Si group and cleavage occurs along path A to give the novel polysilyl lithium reagent **4**. Path A predominates the cleavage reaction also with **1d** where a *t*-Bu group is in the β-position, i.e. **1**, with R = *t*-$BuMe_2Si$, leading to the novel **5** (Table 1). When the *t*-Bu group in **1b** is substituted by the smaller $SiMe_3$ group[10] (**1c**), path B competes to ca. 30%. The new silyllithium reagents obtained *via* reaction 2, **4** and **5**, were both isolated in excellent yields.



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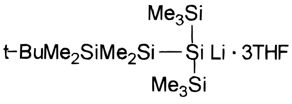

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Attempts to use the same strategy to produce more highly branched polysilyl anions were disappointing. In contrast to **1** the lithiation of the branched polysilanes **2** leads exclusively (or mostly with **2a**) to cleavage along the *undesired* path B (Table 1). Steric effects alone cannot account for the observed cleavage patterns of **2**. Thus, although the *t*-Bu and the $(Me_3Si)_3Si$ groups have similar steric sizes,[10] cleavage of $(Me_3Si)_3SiSiMe_2Si(SiMe_3)_3$ (**2d**) occurs exclusively along path B (yielding $(Me_3Si)_3SiLi$), while the cleavage of *t*-$BuMe_2SiSi(SiMe_3)_3$ (**1b**) occurs exclusevely along path A (eq 2). Apparently, the undesired cleavage of the internal Si−Si bond (path B) is facilitated by the branched polysilyl substituent present in **2b**−**d,** indicating that the electronic effect of these branched polysilyl groups is more important than their steric bulk in dictating the cleavage of **2**.

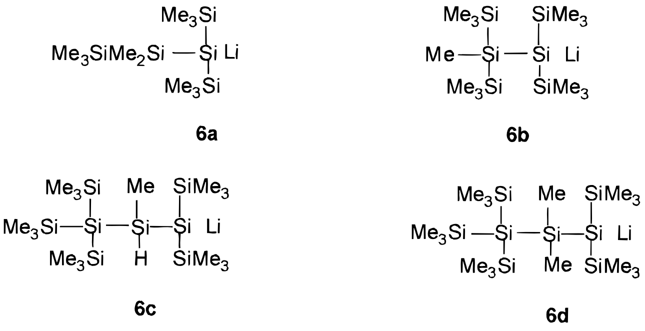
The cleavage reaction takes an entirely different course with the highly branched *chloro*-substituted polysilanes of type **3** (Table 2). Lithiation of **3** with 2 mol of MeLi (PhLi was also used in the case of **3c**) leads to the formation (in 50−60% yield) of the corresponding novel branched silyl anions, previously unknown, as

Table 2. Relative Yields (%) of Products in the Lithiation with Methyllithium of Branched Chloropolysilanes $(Me_3Si)_3SiSiR^1R^2Cl$ of Type 3 (Eq 3)

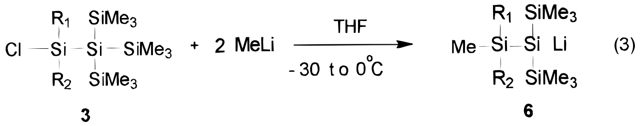
			rel yields	
compd	R_1[a]	R_2[a]	$R_1R_2MeSiSi(SiMe_3)_2Li$[b]	$R_1R_2MeSiSi(SiMe_3)_3$
3a	$SiMe_3$	Me	83	17
3b	$SiMe_3$	$SiMe_3$	59	41
3c	$Si(SiMe_3)_3$	H	62[c]	38[c]
3d	$Si(SiMe_3)_3$	Me	57	43

[a] See eq 3. [b] Identified as the corresponding $R_1R_2MeSiSi(SiMe_3)_2H$ or $R_1R_2MeSiSi(SiMe_3)_2CH_2OCH_3$ after quenching with water or with CH_3OCH_2Cl, respectively. [c] Similar results were obtained in the reaction with phenyllithium.

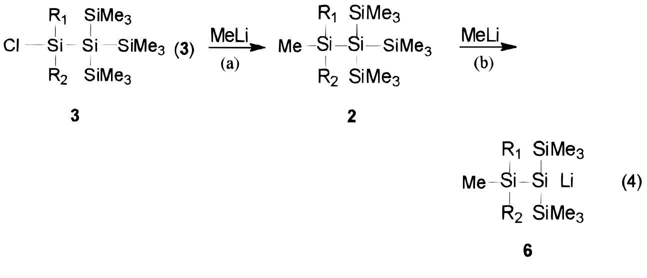
Chart 2



shown in eq 3. The other observed product is $MeR_1R_2SiSi(SiMe_3)_3$, resulting from substitution of chlorine by a methyl group (from MeLi). Using this reaction, four new silyllithium reagents, **6** (Chart 2), were prepared and identified by their hydrolysis products and the ethers produced in their reaction with CH_3OCH_2Cl (i.e., $MeR_1R_2SiSi(SiMe_3)_2CH_2OCH_3$; see Experimental Section).



We first assumed that reaction 3 proceeds *via* the two-step mechanism shown in eq 4 involving the following: (a) substitution of Cl by Me; (b) lithiation.



However, the significant differences in the cleavage selectivity between polysilanes of type **3** and of type **2** shows that this cannot be the case. For example, according to the above mechanism cleavage of **3c** or **3d** should have produced $(Me_3Si)_3SiLi$, the cleavage product of **2c** or **2d** (Table 1), in contrast to observation (Table 2). The cleavage reactions of compounds of families **3** and **2** are contrasted in Scheme 1.

We tentatively propose that the cleavage of **3** proceeds by an elimination−addition mechanism (either concerted or stepwise) *via a disilene intermediate*, as shown schematically in eq 5. Studies designed to support this interesting mechanism are in progress.

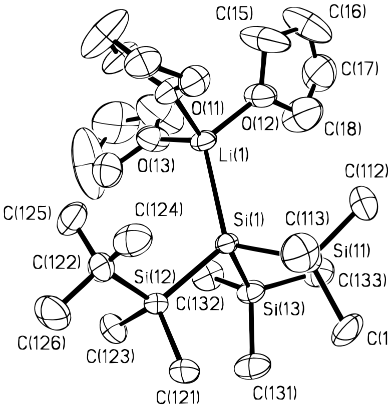
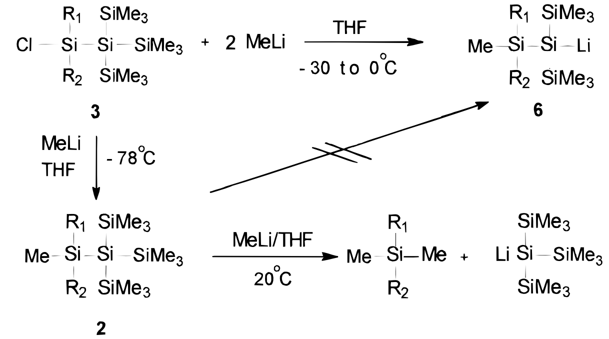
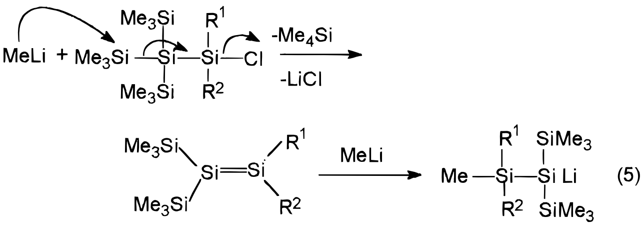


Figure 1. Molecular structure of **4** (one of the two independent molecules shown). Hydrogen atoms have been omitted for clarity. Probability ellipsoids at the 50% level are shown.

Scheme 1





The reaction of branched chloropolysilanes with MeLi (reaction 3) opens new possibilities to synthesize a variety of novel highly branched polysilyl anions. Additional experimental studies as well as *ab initio* calculations are in progress in order to provide a better understanding of the cleavage mechanisms of branched polysilanes.

Structural Data for 4. **4** is a crystalline compound, and its X-ray structure could be determinated.[13] The unit cell (see Supporting Information) contains four molecules, but **4** is essentially monomeric in the crystaline form, as evidenced by the fact that the shortest intramolecular atomic distances within the unit cell are larger than 4.0 Å. Two of the four molecules are independent, but as they have essentially identical

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[13] Crystallographic data for **4**: MW = 342.00; crystal system monoclinic, space group $P2_1$; $a = 11.062(2)$ Å, $b = 16.3331(3)$ Å, $c = 18.906(4)$ Å; $\beta = 99.49(3)$; $V = 3370.8(11)$ Å^3; $d_{calcd} = 1.011$ g cm^{-3} for $Z = 4$ at 293(2) K; $R = 0.0623$, $R_w = 0.1516$. Details of data collection and refinement are given in the Supporting Information.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for 4

molecule 1		molecule 2	
Si(1)−Li(1)	2.684(9)	Si(2)−Li(2)	2.669(9)
Si(1)−Si(11)	2.353(2)	Si(2)−Si(21)	2.343(2)
Si(1)−Si(12)	2.346(2)	Si(2)−Si(22)	2.338(2)
Si(1)−Si(13)	2.341(2)	Si(2)−Si(23)	2.340(2)
Si(11)−C(111)	1.870(6)	Si(21)−C(211)	1.876(6)
Si(11)−C(112)	1.879(7)	Si(21)−C(212)	1.914(7)
Si(11)−C(113)	1.890(7)	Si(21)−C(213)	1.900(7)
Si(12)−C(121)	1.883(6)	Si(22)−C(221)	1.876(8)
Si(12)−C(123)	1.885(6)	Si(22)−C(222)	1.884(8)
Si(12)−C(122)	1.921(6)	Si(22)−C(223)	1.869(9)
Si(13)−C(131)	1.889(7)	Si(23)−C(231)	1.875(8)
Si(13)−C(132)	1.888(7)	Si(23)−C(232)	1.875(7)
Si(13)−C(133)	1.895(8)	Si(23)−C(233)	1.896(8)
C(122)−C(124)	1.518(10)	C(212)−C(214)	1.535(10)
C(122)−C(125)	1.516(9)	C(212)−C(215)	1.507(11)
C(122)−C(126)	1.537(9)	C(212)−C(216)	1.531(10)
O(11)−Li(1)	1.953(9)	O(21)−Li(2)	1.974(11)
O(12)−Li(1)	1.955(11)	O(22)−Li(2)	1.950(11)
O(13)−Li(1)	1.975(11)	O(23)−Li(2)	1.985(10)
Si(12)−Si(1)−Si(11)	105.37(8)	Si(22)−Si(2)−Si(23)	99.98(9)
Si(13)−Si(1)−Si(11)	99.42(8)	Si(22)−Si(2)−Si(21)	106.22(9)
Si(13)−Si(1)−Si(12)	100.00(8)	Si(23)−Si(2)−Si(21)	99.56(8)
Si(11)−Si(1)−Li(1)	117.8(2)	Si(21)−Si(2)−Li(2)	118.9(2)
Si(12)−Si(1)−Li(1)	120.7(2)	Si(22)−Si(2)−Li(2)	117.1(2)
Si(13)−Si(1)−Li(1)	110.1(2)	Si(23)−Si(2)−Li(2)	112.1(2)

geometric parameters, we discuss below only the geometry of one of these molecules.

An ORTEP picture of the X-ray structure of **4**[13] is presented in Figure 1, and the most important bond distance and bond angles are given in Table 3. The molecular structure of **4** resembles closely that of the analogous $(Me_3Si)_3SiLi{\cdot}3THF$.[14a] The Si−Li distance in **4** of 2.680 Å is quite similar to that in $(Me_3Si)_3SiLi{\cdot}3THF$ (2.669 Å). The Si−Si−Si angles at the negatively charged silicon are quite acute (102°) as in other known silyllithium compounds.[3a,14] The Si−Si bond lengths have a narrow range, 2.338−2.353 Å, longer by 0.01 Å than in $(Me_3Si)_3SiLi{\cdot}3THF$.[14a] The only significant structural consequence of replacing a methyl in the $(Me_3Si)_3Si$ group by the bulkier *t*-Bu group is the significantly elongated β-Si(12)−C(122) bond (1.92 Å) vs ca. 1.87−1.89 Å for the two other β-Si−Me bonds (i.e., Si(12)−C(121) and Si(12)−C(123)) or the α-Si−Me bonds.

Experimental Section

Standard Schlenk techniques were used for all syntheses and all sample manipulations. NMR spectra were recorded at room temperature in $CDCl_3$ or C_6D_6 solutions using a Bruker EM-200 or Bruker-400 instrument. Mass spectroscopy (MS) data were obtained with a Finnigan MAT TSQ 45 triple-stage quadrupole mass spectrometer. Elemental analyses were performed by the Microanalytical Laboratory of the University of Essen (Essen, Germany).

Preparation of 1 and 3a,b. The corresponding chlorosilane [HMe_2SiCl, *t*-$BuMe_2SiCl$, Me_3SiMe_2SiCl, *t*-$BuMe_2SiMe_2SiCl$] or dichlorodisilanes [$Cl_2MeSiMe_2Si$, $Cl_2Si(SiMe_3)_2$] (15 mmol) in 50 mL of toluene was added to a solution of 10 mmol of $(Me_3Si)_3SiLi$ 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 >95%.

$(Me_3Si)_3SiSiHMe_2$ (1a). ^1H NMR ($CDCl_3$, δ): 0.16 (27H, s, $(Me_3Si)_3Si$); 0.25, 0.23 (6H, d, Me_2Si); 4.10 (1H, q, SiH). MS(EI): *m/e* 305 ($M^+ - H$), 291 ($M^+ - Me$), 232 ($M^+ - H - Me_3Si$). Anal. Calcd for $C_{11}H_{34}Si_5$: C, 43.06; H, 11.17. Found: C, 43.58; H, 10.90.

$(Me_3Si)_3SiSiMe_2Bu$-*t* (1b). ^1H NMR ($CDCl_3$): δ 0.14 (6H, s, Me_2Si), 0.21 (27H, s, Me_3Si), 0.92 (9H, s, *t*-Bu). ^{13}C NMR ($CDCl_3$): δ −0.9 (*t*-$BuSiMe_2$), 3.5 (Me_3Si), 18.8 ($Me_3\textit{C}Si$), 28.3 ($\textit{Me}_3C$); ^{29}Si NMR. ($CDCl_3$): δ −136.4 ($Si\textit{Si}Si$), −9.6 (Me_3Si), 4.8 (*t*-BuSi). MS(EI): *m/e* 347 ($M^+ - Me$), 305 ($M^+ -$ *t*-Bu). Anal. Calcd for $C_{15}H_{42}Si_5$: C, 49.64; H, 11.67. Found: C, 48.98; H, 11.20.

$(Me_3Si)_3SiSiMe_2SiMe_3$ (1c). MS(EI): *m/e* 378 (M^+), 363 ($M^+ - ME$), 305 ($M^+ - Me_3Si$). ^1H NMR ($CDCl_3$): δ 0.10 (6H, s, Me_3Si), 0.20 (27H, s, Me_3Si), 0.22 (6H, s, $SiSiMe_2Si$). Anal. Calcd for $C_{14}H_{42}Si_6$: C, 44.37; H, 11.71. Found: C, 44.78; H, 11.50.

$(Me_3Si)_3SiMe_2SiSiMe_2Bu$-*t* (1d). ^1H NMR ($CDCl_3$): δ 0.08 (6H, s, Me_2Si), 0.20 (27H, s, Me_3Si), 0.32 (6H, s, $SiSiMe_2Si$), 0.92 (9H, s, *t*-Bu). ^{29}Si NMR (C_6D_6): δ −128.0 (quaternary silicon), −36.4 ($Si\textit{Si}Me_2Si$), −9.5 (Me_3Si), −6.3 (*t*-BuSi). MS(EI): *m/e* 420 (M^+), 405 ($M^+ - Me$), 363 ($M^+ -$ *t*-Bu). Anal. Calcd for $C_{17}H_{34}Si_5$: C, 44.37; H, 11.71. Found: C, 43.88; H, 11.96.

$(Me_3Si)_3SiSiClMeSiMe_3$ (3a). ^1H NMR ($CDCl_3$): δ 0.19 (9H, s, $Me_3SiSiCl$), 0.24 (27H, s, $(Me_3Si)_3Si$), 0.66 (6H, s, Me_2SiCl). ^{29}Si NMR (C_6D_6): δ −124.0 ($(Me_3Si)_3\textit{Si}$), −66.5 (SiCl), −13.1 ($ClSi\textit{Si}$), −9.5 ($(Me_3\textit{Si})_3Si$). MS(EI): *m/e* 383 ($M^+ - Me$), 363 ($M^+ - Cl$), 325 ($M^+ - Me_3Si$). Anal. Calcd for $C_{11}ClH_{34}Si_5$: C, 43.06; H, 11.17. Found: C, 43.58; H, 10.90.

$(Me_3Si)_3SiSiCl(SiMe_3)_2$ (3b) was purified by column chromotography on silica gel with hexane as eluent. ^1H NMR ($CDCl_3$): δ 0.19 (18H, s, $Si(SiMe_3)_2$), 0.27 (27H, s, $Si(SiMe_3)_3$). ^{29}Si NMR (C_6D_6): δ −135.5 ($Si\textit{Si}Si$), −121.2 (SiCl), −10.0 ($(Me_3\textit{Si})_3Si-$), −9.0 ($(\textit{Si}Me_3)_2SiCl$). MS(EI): *m/e* 441 ($M^+ - Me$), 421 ($M^+ - Cl$), 363 ($M^+ - Me_3Si$). Anal. Calcd for $C_{15}ClH_{45}Si_7$: C, 39.38; H, 9.91. Found: C, 39.87; H, 10.50.

$(Me_3Si)_3SiSiMe(SiMe_3)_2$ (2a). An equimolar amount of MeLi in ether was added to a solution of **3b** in THF at −30 °C and then stirred for 10 h at room temperature. After aqueous workup the product was isolated by column chromatography on silica gel with hexane as eluent. ^1H NMR ($CDCl_3$): δ 0.17 (18H, s, $(Me_3Si)_2Si$), 0.22 (27H, s, $(Me_3Si)_3Si$). ^{29}Si NMR (C_6D_6): δ −129.2 (quaternary silicon), −78.9 ($(Me_3Si)_2\textit{Si}$), −11.0 ($(Me_3\textit{Si})_2Si$), −9.0 ($(Me_3\textit{Si})_3Si$). MS(EI): *m/e* 436 (M^+), 421 ($M^+ - Me$), 363 ($M^+ - Me_3Si$), 348 ($M^+ - MeSiMe_3$). Anal. Calcd for $C_{16}H_{48}Si_6$: C, 43.96; H, 11.07. Found: C, 43.75; H, 10.64.

$(Me_3Si)_3SiSi(SiMe_3)_3$ (2b) was prepared according to the following: Gilman, H.; Harrell, R. L., Jr. *J. Organomet. Chem.* **1967**, *9*, 67.

$[(Me_3Si)_3Si]_2SiHCl$ (3c). A 5 mmol amount of $HSiCl_3$ in 150 mL of hexane cooled to −30 °C was very slowly added (by vacuum transfer) to a solution of 10 mmol of $(Me_3Si)_3SiLi{\cdot}3THF$ in 100 mL of toluene, cooled to −78 °C. The reaction mixture was stirred overnight at −78 °C and then for 12 h at room temperature. After evaporation of the solvent and sublimation of the solid residue (110 °C/1 mmHg), 1.73 g (63%) of **3c** was obtained. ^1H NMR ($CDCl_3$): δ 0.26 (54H, s, Me_3Si), 5.40 (1H, s, SiH). MS(EI): *m/e* 557 ($M^+ - H$). Anal. Calcd for $C_{18}ClH_{55}Si_9$: C, 38.62; H, 9.90. Found: C, 39.16; H, 10.14.

$[(Me_3Si)_3Si]_2SiHMe$ (2c). The equivalent amount of MeLi in ether was added at room temperature to an ether solution of **3c**, and it was stirred for 10 h. The product was isolated by column chromatography on silica gel with hexane as eluent. ^1H NMR ($CDCl_3$): δ 0.23 (54H, s, Me_3Si), 0.39, 0.42 (3H, d, MeSi), 3.92 (1H, m, HSi). MS(EI): *m/e* 523 ($M^+ - Me$), 464

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($M^+ - HSiMe_3$), 450 ($M^+ - MeSiMe_3$). Anal. Calcd for $C_{19}H_{58}Si_9$: C, 42.31; H, 10.84. Found: C, 41.95; H, 10.35.

[(Me$_3$Si)$_3$Si]$_2$SiHClMe (3d). A mixture of 0.7 g (1.3 mmol) of **2c** and 0.3 g (1.5 mmol) of PCl_5 in 20 mL of CCl_4 was stirred at 80 °C for 10 h. After solvent evaporation and sublimation (110 °C/1 mmHg), 0.5 g (0.9 mmol, 70%) of **3d** was isolated. ^1H NMR ($CDCl_3$): δ 0.27 (54H, s, Me_3Si), 0.89 (3H, s, MeSi). MS(EI): *m*/*e* 557 ($M^+ - Me$), 537 ($M^+ - Cl$), 499 ($M^+ - Me_3Si$). Anal. Calcd for $C_{19}ClH_{57}Si_9$: C, 39.77; H, 10.01. Found: C, 38.98; H, 10.40.

[(Me$_3$Si)$_3$Si]$_2$SiMe$_2$ (2d). An equimolar amount of MeLi in ether was added to a solution of **3d** in THF at −30 °C and then stirred for 10 h at room temperature. After aqueous workup the product was isolated by column chromatography on silica gel with hexane as eluent. ^1H NMR ($CDCl_3$): δ 0.23 (54H, s, Me_3Si), 0.30 (6H, s, Me_2Si). MS(EI): *m*/*e* 537 ($M^+ - Me$), 464 ($M^+ - MeSiMe_3$), 305 ($M^+ - Si(SiMe_3)_3$). Anal. Calcd for $C_{20}H_{60}Si_9$: C, 42.40; H, 10.93. Found: C, 43.11; H, 10.81.

***t*-BuMe$_2$Si(SiMe$_3$)$_2$SiLi·3THF (4) and *t*-BuMe$_2$SiSiMe$_2$(Me$_3$Si)$_2$SiLi·3THF (5)** were prepared by lithiation of silanes **1b**,**d**, respectively. Crystallization from hexane at room temperature resulted in the formation of colorless crystals.

***t*-BuMe$_2$Si(SiMe$_3$)$_2$SiLi·3THF (4).** ^1H NMR (C_6D_6): δ 0.45 (6H, s, Me_2Si), 1.05 (18H, s, $(Me_3Si)_2$), 1.19 (9H, s, *t*-Bu). ^{13}C NMR (C_6D_6): δ 1.9 (Me_2Si), 7.6 (Me_3Si), 18.7 (Me_3C-), 25.6 (Me_3C-). ^{29}Si NMR (C_6D_6): δ −0.192.8 (*t*-BuSi*Si*Si), −5.2 (Me_3Si), 9.4 (*t*-BuSi).

***t*-BuMe$_2$SiSiMe$_2$(Me$_3$Si)$_2$SiLi·3THF (5).** ^1H NMR (C_6D_6): δ 0.21 (6H, s, $SiSiMe_2Si$), 0.51 (18H, s, $Si(SiMe_3)_2$), 0.68 (6H, s, *t*-BuSi*Me$_2$*), 1.15 (9H, s, *t*-Bu). ^{13}C NMR (C_6D_6): δ −7.34 (*t*-BuSi*Me$_2$*), 3.31 (SiSi*Me$_2$*Si), 7.39 ($SiMe_3$), 19.21 (Me_3C), 25.37 (*Me$_3$*C). ^{29}Si NMR (C_6D_6): δ −178.1 (SiLi), −36.4 (SiSiSi), −9.5 (Me_3Si), −6.3 (*t*-BuSi).

Lithiation of 3 was carried out (using Schlenk techniques) by slow addition (2−3 h) of 2 equiv of MeLi in ether to a THF solution of **3** at −30 °C. The yellow-orange reaction mixture was kept at 0 °C for 10 h. An excess of $ClCH_2OCH_3$ was added to the reaction mixture, and the corresponding ethers $CH_3OCH_2Si(SiMe_3)_2X$ were isolated by column chromatography on silica gel with hexane as eluent.

CH$_3$OCH$_2$Si(SiMe$_3$)$_2$SiMe$_2$SiMe$_3$ (obtained from **6a**). ^1H NMR ($CDCl_3$): δ 0.14 (9H, s, Me_3Si), 0.16 (18H, s, $(SiMe_3)_2Si$), 0.34 (6H, s, Me_2Si), 3.23 (3H, s, $O-CH_3$), 3.41 (2H, s, $-CH_2O-$). MS (EI): *m*/*e* 335 ($M^+ - Me$), 277 ($M^+ - Me_3Si$), 247 ($M^+ - Me_3SiOMe$).

CH$_3$OCH$_2$Si(SiMe$_3$)$_2$Si(SiMe$_3$)$_2$Me (obtained from **6b**). ^1H NMR ($CDCl_3$): δ 0.14 (18H, s, (*Me$_3$*Si)$_2$Si−CH$_2$OCH$_3$), 0.16 (18H, s, (*Me$_3$*Si)$_2$SiMe), 0.17 (3H, s, MeSi), 3.20 (3H, s, $-OCH_3$), 3.41 (2H, s, $SiCH_2O$). HRMS: calcd for $C_{15}H_{44}OSi_6$ ($M^+ - Me$) *m*/*e* 393.1794, found 393.1796. MS (EI): 335 ($M^+ - Me_3Si$), 304 ($M^+ - Me_3SiOMe$).

CH$_3$OCH$_2$Si(SiMe$_3$)$_2$SiHMeSi(SiMe$_3$)$_3$ (obtained from **6c**). ^1H NMR ($CDCl_3$): δ 0.17, 0.19 (18H, d, $(Me_3Si)_2Si$), 0.21 (27H, s, $(Me_3Si)_3Si$), 0.28, 0.31 (3H, d, MeSi), 3.23 (3H, s, OCH_3), 3.40, 3.42 (2H, d, $SiCH_2O$), 3.77 (1H, m, SiH). ^{29}Si NMR (C_6D_6): δ −129.2 (quaternary silicon), −77.0 ($SiCH_2$), −68.6 (SiH), −10.4, 11.0 (d, (Me$_3$*Si*)$_2$Si), −9.0 (Me$_3$*Si*)$_3$Si. MS(CI): *m*/*e* 510 (M^+), 495 ($M^+ - Me$), 437 ($M^+ - Me_3Si$), 406 ($M^+ - Me_3SiOMe$). HRMS: calcd for $C_{18}H_{54}OSi_8$, *m*/*z* 510.2372; found, *m*/*z* 706.3349.

CH$_3$OCH$_2$Si(SiMe$_3$)$_2$SiMe$_2$Si(SiMe$_3$)$_3$ (obtained from **6d**). ^1H NMR ($CDCl_3$): δ 0.18 (18H, s, $(Me_3Si)_2Si$), 0.22 (27H, s, $(Me_3Si)_3Si$), 0.38 (6H, s, Me_2Si), 3.21 (3H, s, OCH_3), 3.41 (2H, s, $SiCH_2$). HRMS: calcd for $C_{19}H_{56}OSi_8$ ($M^+ - Me$) *m*/*z* 509.2230, found *m*/*z* 509.2280. MS (EI): 451 ($M^+ - Me_3Si$), 420 ($M^+ - Me_3SiOMe$).

X-ray Structure Analysis of 4. A prismatic colorless crystal of **4** was coated with Nujol and mounted in a thin-walled glass capillary. The data were collected on a Siemens P4 diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.710 69 Å). Final unit-cell parameters for the complex were obtained by least-squares analysis of setting angles for 30 reflections, $22 < 2\theta < 27°$. The intensities of two standard reflections were measured every 98 reflections during the data collection. The data were corrected for decay as well as for Lorenz and polarization effects. Pertinent crystallographic and experimental parameters for compound **4** are summarized in Table 4. After location of all silicon atoms by direct methods the full structure was derived by conventional electron density methods and was refined by full-matrix least-squares methods based on F^2, minimizing the function $\Sigma[w(F_o^2 - F_c^2)^2]$. Hydrogen atoms were refined at ideal positions with groupwise relaxed C−H distances and isotropic displacement parameters. Non-hydrogen atoms were refined with anisotropic thermal parameters. Finally, a correction for secondary extinction was applied. All calculations were performed with the programs SHELXS86 and SHELXL93 using the internal scattering factors. Selected bond lengths and angles are listed in Table 3. A view of the molecular structure of **4** is shown in Figure 1. Final positional and equivalent isotropic thermal parameters are given in the Supporting Information.

Table 4. Crystal Data and Structure Refinement for 4

formula	$C_{24}H_{57}O_3LiSi_4$
fw	512.70
temp, K	293(2)
cryst size, mm	0.8 × 0.6 × 0.4
cryst system	monoclinic
space group	$P2_1$
a, Å	11.069(2)
b, Å	16.331(3)
c, Å	18.906(4)
β, deg	99.49(3)
V, Å^3	3370.8(11)
Z	4
ρ_{calc}	1.011
μ(Mo Kα), cm^{-1}	1.96
F(000)	1136
scan type	ω
scan range, deg	1
scan rate, deg/min	8−29
data collcd	$+h,+k,\pm l$
$2\theta_{max}$, deg	54.00
cryst decay, %	3.5
tot. reflcns	7963
obsd reflcns (N_o)	7143
refnd params (N_p)	644
$R1$ ($I > 2\sigma(I)$)[a]	0.0623
w$R2$ (all data)[a]	0.1516
gof	1.002
abs struct param	0.1(2)
extinction coeff	0.0004(4)
resid density, e/A	−0.228 to 0.255

[a] $wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$ with $w^{-1} = \sigma^2(F_o^2) + (0.0603P)^2$ and $P = 0.33333\max(0,F_o^2) + 0.66667F_c^2$. $R1 = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$. Gof $= \{\Sigma[w(F_o^2 - F_c^2)^2]/(N_o - N_p)\}^{1/2}$.

Acknowledgment. This research was partially supported by the Israel Science Foundation administrated by the Israel Academy of Science, by the German Federal Ministry of Science, Research, Technology, and Education (BMBF), and the Minerva Foundation and by the Technion VPR Fund for the Promotion of Research. D.B.-Z. is grateful to the Ministry of Immigrant Absorption, State of Israel, for a Gilhadi scholarship.

Supporting Information Available: A table giving atomic coordinates and equivalent isotropic displacement parameters for **4** and a figure of the unit cell of **4** (4 pages). Ordering information is given on any current masthead page.

OM960733L