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# Synthesis, Characterization, and Reactivity of $[LiC(SiMe_2H)_3]\cdot 2THF$: Formation of 1,1,3,3-Tetramethyl-2,2,4,4-tetrakis(dimethylsilyl)-1,3-disilacyclobutane, $[Me_2SiC(SiMe_2H)_2]_2$

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*Summary: Reaction of* $[HC(SiMe_2H)_3]$ *with* $[(CH_3)_2CH]_2NLi$ *in tetrahydrofuran afforded* $[LiC(SiMe_2H)_3]\cdot 2THF$ *(**1**) in excellent yield. Reactions of **1** with* $Me_3SiCl$*,* $MeSiHCl_2$*,* $HSiCl_3$ *and* $MeSiCl_3$ *at −78 °C gave* $[Me_3SiC(SiMe_2H)_3]$ *(**2**),* $[(HMeClSi)C(SiMe_2H)_3]$ *(**3**),* $[(HCl_2Si)C(SiMe_2H)_3]$ *(**4**), and* $[(MeCl_2Si)C(SiMe_2H)_3]$ *(**5**), respectively. At room temperature, reaction between **1** and* $SiCl_4$ *in toluene resulted in multiple products, including a new highly substituted 1,3-disilacyclobutane* $[Me_2SiC(SiMe_2H)_2]_2$ *(**6**). **6** was isolated in moderate yield from reaction of **1** with 2 equiv of* $SiCl_4$*.*

## Introduction

Bulky silicon-substituted alkyllithium compounds of the type $[LiC(SiMe_2R)_3]$ (R = Me,[1] Ph,[2] $CHMe_2$,[3] $NMe_2$,[4] $C_6H_4Me$-o,[5] and OMe[6]) and $[LiC(SiMe_3)_2(SiMe_2R')]$ (R′ = Ph,[7] OMe,[8] and SMe[9]) have been used to synthesize highly sterically hindered compounds of a range of elements, many of which possess unique structures and display novel reactivity.[10] In particular, compounds derived from $[LiC(SiMe_3)_3]$ have been widely studied.[10,11] The solvent-free species $[LiC(SiMe_3)_3]$ can be isolated as a dimer with a $Li\{\mu\text{-}C(SiMe_3)_3\}_2Li$ core and additional agostic Me−Li interactions,[12] while the solvated species form dialkyllithiate complexes $[Li(THF)_4][Li\{C(SiMe_3)_3\}_2]$ (THF = tetrahydrofuran)[13] or $[Li(TMEDA)_2][Li\{C(SiMe_3)_3\}_2]$ (TMEDA = *N*,*N*,*N*′,*N*′-tetramethylethylenediamine).[14] The solvated species $[LiC(SiMe_2Ph)_3]\cdot THF$ is monomeric and contains phenyl−metal interactions, in which the Li atom interacts with the *ipso* carbon of a phenyl group.[2,10a] The lithium derivative of the related ligand $C(SiMe_2NMe_2)_3$, which has neutral donor groups available for further coordination, crystallizes as a linear polymeric species $\{(Me_2NMe_2Si)_3CLi\}_n$, in which Li atoms are attached to two $NMe_2$ groups from one $(Me_2NMe_2Si)_3C$ ligand and to one $NMe_2$ group from another.[4] The remarkable range of structures adopted by alkali metal compounds containing bulky silicon-substituted ligands led us to examine the synthesis of $[LiC(SiMe_2H)_3]\cdot 2THF$ (**1**). Herein, we describe its characterization and results of a preliminary study of its reaction chemistry, including the formation of a highly substituted 1,3-disilacyclobutane, $[Me_2SiC(SiMe_2H)_2]_2$ (**6**).

## Experimental Section

**General Information.** All reactions were carried out under a nitrogen atmosphere. Solvents were dried and distilled twice over sodium and benzophenone prior to use. Benzene-$d_6$ was distilled and stored under nitrogen atmosphere over 4 Å molecular sieves. $HC(SiMe_2H)_3$ was prepared via modification of a literature method.[15] Lithium diisopropylamide (LDA),

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SiCl$_4$, MeSiCl$_3$, MeSiHCl$_2$, and Me$_3$SiCl were purchased from Aldrich. NMR spectra were recorded on a Varian Gemini 200 or a Varian VXR-400 spectrometer. $^1$H and $^{13}$C chemical shifts were measured relative to residual solvent signal. $^{29}$Si chemical shifts were measured relative to an internal tetramethylsilane (TMS) standard. $^7$Li chemical shifts were measured with 1.0 M LiCl in D$_2$O as internal reference. Solid-state NMR experiments were performed on a Varian Unity Plus 300 MHz WB spectrometer using a 7 mm magic angle NMR probe with a spinning rate of 5000 Hz at room temperature. Delay times of 10−30 s were used for all experiments. The $^{13}$C cross-polarization magic angle spinning [CP-MAS using the TOSS sequence (total sideband suppression)] and magic angle spinning (MAS) experiments (75.4 MHz) used a pulse width of 4 ms. Chemical shifts are reported relative to external hexamethylbenzene (132.1 ppm). $^{29}$Si NMR spectra were obtained using CP-MAS (with TOSS) and MAS experiments (59.5 MHz) with a pulse width of 4.5 ms and referenced relative to external talc (−90 ppm). $^7$Li NMR data were also collected using CP-MAS (with TOSS) and MAS experiments (116.5 MHz) with a pulse width of 3.8 ms and were referenced relative to external LiCl (0 ppm). Mass spectral data were obtained on a Hewlett-Packard 5890 series II gas chromatograph with a Hewlett-Packard 5972 series mass selective detector at an ionizing potential of 70 eV or a Kratos Analytical Concept IH mass spectrometer at an ionizing potential of 15 eV. Infrared spectra were obtained on a Mattson Galaxy Series FTIR 5000 spectrophotometer. Microanalyses were performed by E + R Microanalytical Laboratory, Inc., Corona, NY.

**Preparation of [LiC(SiMe$_2$H)$_3$]·2THF (1).** Tris(dimethylsilyl)methane[15] (11.7 g, 61.0 mmol) was dissolved in THF (25 mL). Lithium diisopropylamide (6.57 g, 61.0 mmol) in THF (125 mL) was added dropwise with stirring. The orange-red solution was stirred at ambient temperature for 6 h, after which time GLC/MS analysis of an aliquot quenched with chlorotrimethylsilane showed complete conversion. The THF was removed in vacuo. The resulting solid was washed three times with pentane (3 × 5 mL) at −20 °C and dried under vacuum, to give the product as an off-white powder (20.3 g, 97%). Anal. Calcd for C$_{15}$H$_{37}$Si$_3$O$_2$Li: C, 52.89; H, 10.95. Found: C, 52.53; H, 10.97. $^1$H NMR (C$_6$D$_6$, 200 MHz): $\delta$ 0.56 (d, 18H, Si*Me*$_2$H), 1.23 (m, 8H, C$_4$H$_8$O), 3.37 (m, 8H, C$_4$H$_8$O), 4.91 (m, 3H, SiMe$_2$*H*). $^{13}$C{$^1$H} NMR (C$_6$D$_6$, 50 MHz): $\delta$ −2.10 (quat. C), 3.93 (SiMe$_2$ H), 25.09 (C$_4$H$_8$O), 68.43, (C$_4$H$_8$O). TOSS CP-MAS $^{13}$C{$^1$H} NMR: $\delta$ −0.87 (quat. C), 5.11 (SiMe$_2$ H), 27.05 (C$_4$H$_8$O), 70.17 (C$_4$H$_8$O). $^{29}$Si{$^1$H} NMR (C$_6$D$_6$, 79.4 MHz): $\delta$ −22.15 (SiMe$_2$H). TOSS CP-MAS $^{29}$Si{$^1$H} NMR: $\delta$ −21.67 (SiMe$_2$H). $^7$Li{$^1$H} NMR (C$_6$D$_6$, 155 MHz): $\delta$ 0.51 (br s). CP-MAS $^7$Li{$^1$H} NMR: $\delta$ 1.10 ([Li{C(SiMe$_2$H)$_3$}$_2$]), 1.62 ([Li(THF)$_4$]$^+$).

**Preparation of (Me$_3$Si)C(SiMe$_2$H)$_3$ (2).** [LiC(SiMe$_2$H)$_3$]·2THF (0.10 g, 0.29 mmol) was dissolved in THF (5 mL). Trimethylchlorosilane (37 $\mu$L, 0.29 mmol) was introduced via microsyringe. The reaction mixture was stirred at ambient temperature for 30 min. The solvent was removed in vacuo, and the resulting solid was extracted with pentane (20 mL). After filtration, the solvent was removed in vacuo to leave the product as an off-white solid (0.074 g, 98%), identified by comparison of $^1$H NMR data with literature values[16] and mass spectral data (EI, 70 eV): *m/z* 261 [M − H]$^+$.

**Preparation of (HMeClSi)C(SiMe$_2$H)$_3$ (3).** [LiC(SiMe$_2$H)$_3$]·2THF (4.07 g, 11.7 mmol) was dissolved in THF (75 mL). The solution was cooled to −78 °C and then a THF (25 mL) solution of methyldichlorosilane (1.22 mL, 11.7 mmol) was added dropwise. The reaction mixture was stirred for 3 h at −78 °C and then allowed to warm to room temperature. The solvent was removed in vacuo, and the resulting brown solid was extracted with pentane (10 mL). After filtration, the solvent was removed in vacuo to leave the product as a yellow solid (2.87 g, 91%). Anal. Calcd for C$_8$H$_{25}$Si$_4$Cl: C, 35.74; H, 9.30. Found: C, 35.85; H, 9.37. $^1$H NMR (C$_6$ D$_6$, 200 MHz): $\delta$ 0.26 (d, 18H, Si*Me*$_2$H), 0.51 (d, 3H, Si*Me*ClH), 4.31 (sept, 3H, SiMe$_2$*H*), 5.11 (q, 1H, SiMeCl*H*). $^{13}$C{$^1$H} NMR (C$_6$D$_6$, 50 MHz): $\delta$ −1.70 (SiMe$_2$H), −1.53 (SiMeHCl), 2.91 (quat. C). $^{29}$Si{$^1$H} NMR (C$_6$D$_6$, 79.4 MHz): $\delta$ −15.6 (SiMe$_2$H), 8.0 (SiMeHCl); MS (EI, 70 eV) *m/z* 267 [M − H]$^+$. Mp: 130−133 °C.

**Reaction of [LiC(SiMe$_2$H)$_3$]·2THF with MeSiHCl$_2$ in Benzene-*d*$_6$.** Methyldichlorosilane (10 $\mu$L, 0.096 mmol) was introduced via a microsyringe into a benzene-*d*$_6$ (1 mL) solution of [LiC(SiMe$_2$H)$_3$]·2THF (37.7 mg, 0.11 mmol) in an NMR tube. The tube was shaken vigorously, and the $^1$H NMR spectrum, obtained after standing for 2.5 h at ambient temperature, revealed exclusive formation of **3** along with excess [LiC(SiMe$_2$H)$_3$]·2THF.

**Preparation of (HCl$_2$Si)C(SiMe$_2$H)$_3$ (4).** [LiC(SiMe$_2$H)$_3$]·2THF (1.50 g, 4.40 mmol) was dissolved in THF (5 mL). The solution was cooled to −78 °C and then a THF (5 mL) solution of trichlorosilane (596 mg, 4.40 mmol) was added dropwise. The reaction mixture was stirred for 1 h at −78 °C and then allowed to warm to room temperature. The solvent was removed in vacuo, and the resulting residue was extracted with pentane (10 mL). After filtration, the solvent was removed in vacuo to leave a yellowish-orange residue. The residue was dissolved in a minimum of pentane and placed in the freezer. The product was recrystallized from pentane and isolated as a white solid (0.251 g, 20%). Anal. Calcd for C$_7$H$_{22}$Si$_4$Cl$_2$: C, 29.04; H, 7.66. Found: C, 28.85; H, 7.46. $^1$H NMR (C$_6$D$_6$, 200 MHz): $\delta$ 0.25 (d, 18H, Si*Me*$_2$H), 4.31 (sept, 3H, SiMe$_2$*H*), 5.64 (s, 1H, SiCl$_2$*H*). $^{13}$C{$^1$H} NMR (C$_6$D$_6$, 50 MHz): $\delta$ 1.86 (Si*Me*$_2$H), 5.93 (quat. C). $^{29}$Si{$^1$H} NMR (C$_6$D$_6$, 79.4 MHz): $\delta$ −15.4 (*Si*Me$_2$H), 4.8 (*Si*Cl$_2$H); MS (EI, 70 eV) *m/z* 273 [M − Me]$^+$. Mp: 147−49 °C.

**Preparation of (MeCl$_2$Si)C(SiMe$_2$H)$_3$ (5).** [LiC(SiMe$_2$H)$_3$]·2THF (0.50 g, 1.47 mmol) was dissolved in THF (10 mL). The solution was cooled to −78 °C and then a THF (4 mL) solution of methyltrichlorosilane (172 $\mu$L, 1.47 mmol) was added dropwise. The reaction mixture was stirred for 1 h at −78 °C and then allowed to warm to room temperature. The solvent was removed in vacuo, and the resulting yellow solid was extracted with pentane (40 mL). After filtration, the solvent was removed in vacuo to leave the product as a light yellow solid (0.399 g, 96%). Anal. Calcd for C$_8$H$_{24}$Si$_4$Cl$_2$: C, 31.67; H, 7.91. Found: C, 31.74; H, 8.03. $^1$H NMR (C$_6$D$_6$, 200 MHz): $\delta$ 0.31 (d, 18H, Si*Me*$_2$H), 0.71 (s, 3H, Si*Me*Cl$_2$), 4.27 (sept, 3H, SiMe$_2$*H*). $^{13}$C{$^1$H} NMR (C$_6$D$_6$, 50 MHz): $\delta$ −1.25 (quat. C), 1.10 (SiMe$_2$H), 10.1 (SiMeCl$_2$). $^{29}$Si{$^1$H} NMR (C$_6$D$_6$, 79.4 MHz): $\delta$ −15.3 (SiMe$_2$H), 26.2 (SiMeCl$_2$). MS (EI, 70 eV) *m/z*: 301 [M − H]$^+$. Mp: 183−185 °C.

**Reaction of [LiC(SiMe$_2$H)$_3$]·2THF with 1 equiv of SiCl$_4$ in Toluene.** Tetrachlorosilane (14 $\mu$L, 0.12 mmol) was introduced via a microsyringe into a toluene (2 mL) solution of [LiC(SiMe$_2$H)$_3$]·2THF (33.4 mg, 0.098 mmol) and stirred at ambient temperature for 15 min. After introducing pentane (10 mL), the mixture was filtered and analyzed by GLC-MS. The product distribution was Cl$_2$HSiC(SiMe$_2$H)$_3$ (**4**) (26%), HC(SiMe$_2$H)$_3$ (28%), and [Me$_2$SiC(SiMe$_2$H)$_2$]$_2$ (**6**) (38%). In addition, (HMe$_2$Si)$_3$CSiMe$_2$CH(SiMe$_2$H)$_2$ (8%) was tentatively identified based on the following data: *m/z* 378 [M]$^+$, 363 [M − Me]$^+$, 247 [M − CH(SiMe$_2$H)$_2$]$^+$, 189 [M − Me$_2$SiCH(SiMe$_2$H)$_2$]$^+$.

**Preparation of [Me$_2$SiC(SiMe$_2$H)$_2$]$_2$ (6).** [LiC(SiMe$_2$H)$_3$]·2THF (0.63 g, 1.85 mmol) was dissolved in toluene (30 mL). Tetrachlorosilane (425 $\mu$L, 3.70 mmol) in toluene (30 mL) was introduced all at once with vigorous stirring. The mixture was stirred for 15 min, during which time a precipitate formed. The solvent was removed in vacuo, and the resulting solid was extracted with pentane (50 mL). After filtration, the solution

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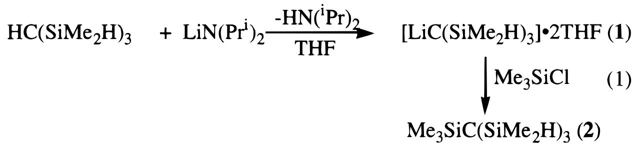
(16) A previous preparation of **2** involved reduction of [Me$_3$SiC(SiMe$_2$Cl)$_3$] with LiAlH$_4$. Eaborn, C.; Lickiss, P. D. *J. Organomet. Chem.* **1985**, *294*, 305.

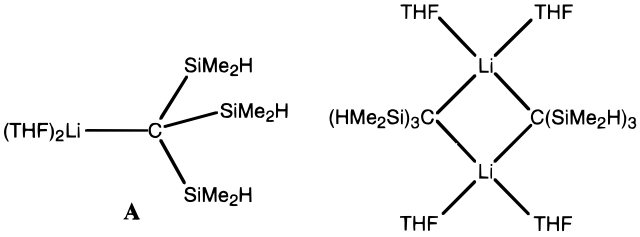
was concentrated under vacuum and then cooled to −78 °C. The product was obtained as an off-white solid, which was isolated via filtration and dried under vacuum (0.18 g, 52%). Anal. Calcd for $C_{14}H_{40}Si_6$: C, 44.64; H, 10.62. Found: C, 44.43; H, 10.49. $^1H$ NMR ($C_6D_6$, 200 MHz): $\delta$ 0.18 (d, 24H, Si*Me*$_2$H), 0.56 (s, 12H, Si*Me*$_2$), 4.68 (sept, 4H, SiMe$_2$*H*). $^{13}C\{^1H\}$ NMR ($C_6D_6$, 50 MHz): $\delta$ 0.55 (quat. C), 1.61 ($SiMe_2H$), 4.00 ($SiMe_2$). $^{29}Si\{^1H\}$ NMR ($C_6D_6$, 79.4 MHz): $\delta$ −14.3 ($SiMe_2H$), 7.2 ($SiMe_2$). MS (EI, 15 eV) *m*/*z*: 376 $[M]^+$. IR ($CCl_4$): $\nu$(Si−H) 2116 $cm^{-1}$.

## Results and Discussion

The reaction of $HC(SiMe_2H)_3$[15] with 1 equiv of lithium diisopropylamide (LDA) in THF resulted in quantitative formation of $[LiC(SiMe_2H)_3]$•2THF (**1**) (eq 1). When the reaction was monitored by GLC-MS analysis of aliquots quenched with $Me_3SiCl$, the sole product observed after 6 h was $Me_3SiC(SiMe_2H)_3$ (**2**)[16] (eq 1). **1** was isolated as an air- and moisture-sensitive, off-white solid in 97% yield. It is sparingly soluble in pentane but quite soluble in toluene and tetrahydrofuran. **1** can be stored as a powder under $N_2$ at ambient temperature for months without decomposition. It is remarkably stable in THF at room temperature (∼25 °C). For example, the concentration of a THF solution of **1** changed from 0.097 to 0.095 M after 29 h; such stability is comparable to that reported for $[LiC(SiMe_3)_3]$ in THF.[1b] The formulation of $[LiC(SiMe_2H)_3]$•2THF (**1**) was confirmed by microanalysis and NMR data. Its $^1H$ NMR spectrum contains a doublet at $\delta$ 0.56 ppm ($SiMe_2$), two multiplets at 1.23 and 3.37 ppm (THF), and a septet at 4.91 ppm (SiH) in 18:8:8:3 ratio. The solid-state CP MAS $^7Li$ NMR spectrum of **1** shows that it exists as the dialkyllithiate species, $[Li(THF)_4][Li\{C(SiMe_2H)_3\}_2]$, analogous to related organolithium compounds $[Li(THF)_4][Li\{C(SiMe_3)_3\}_2]$ and $[Li(TMEDA)_2][Li\{C(SiMe_3)_3\}_2]$.[13,14b] Two types of lithium environments are observed in the spectrum, as two singlets at $\delta$ 1.10 and 1.62 ppm for ($[Li\{C(SiMe_2H)_3\}_2]$) and ($[Li(THF)_4]^+$), respectively.[17] The solution ($C_6D_6$) $^7Li$ NMR spectrum of **1** showed only one kind of lithium, observed as a broad singlet at $\delta$ 0.51 ppm.[18] The solid-state structure is apparently not maintained in solution. **A** and **B** represent two probable structures for **1** in solution (Chart 1). Presumably, structure **B** would be sterically crowded[19] and is less likely than structure **A**. Crystalline $[(Me_2PhSi)_3CLi]$•THF has a structure analogous to **A** with one THF molecule and a phenyl−lithium interaction.[2] Since the $(HMe_2Si)_3C$ group would be less bulky than the $(PhMe_2Si)_3C$ group, it is possible that a second molecule of THF could be coordinated.

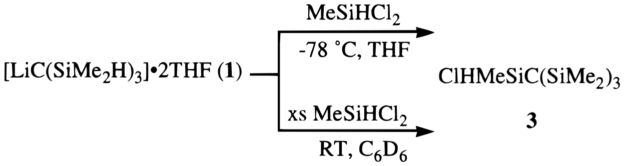


### Chart 1

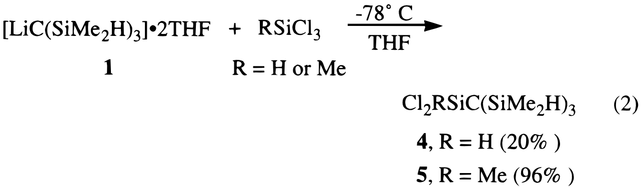


**A** **B**

### Scheme 1



Treatment of a THF solution of $[LiC(SiMe_2H)_3]$•2THF (**1**) at −78 °C with 1 equiv of methyldichlorosilane resulted in quantitative formation of $(HMeClSi)C(SiMe_2H)_3$ (**3**), isolated as an air-stable, yellow solid in excellent yield (Scheme 1). The reaction also proceeds in benzene-$d_6$ at room temperature to yield **3** as the only product. Substitution of both chlorine atoms did not occur when an excess of **1** was employed in the reaction (Scheme 1), indicative of a large steric hindrance by the $(HMe_2Si)_3C$ group to substitution at silicon. Analogous results were reported by Eaborn for reactions between $[LiC(SiMe_3)_3]$ and halosilanes.[20] The reactions between **1** and 1 equiv of $HSiCl_3$ or $MeSiCl_3$ in THF at −78 °C produced air- and moisture-stable solids, $Cl_2HSiC(SiMe_2H)_3$ (**4**) and $(Cl_2MeSi)C(SiMe_2H)_3$ (**5**), respectively (eq 2). At room temperature, the reaction of **1** with $SiCl_4$ (1 equiv) in toluene yielded a new highly substituted 1,3-disilacyclobutane $[Me_2SiC(SiMe_2H)_2]$ (**6**)[21] as the major product, along with **4**, $HC(SiMe_2H)_3$, and a compound tentatively assigned as $(HMe_2Si)_3CSiMe_2CH(SiMe_2H)_2$ (see Experimental Section) (eq 3).



Presumably, hydrogen−halogen exchange[22] between **1** and $SiCl_4$ is the first step in the formation of **6** (Scheme 2). Hydrogen−halogen exchange followed by LiCl elimination would generate the silene $(HMe_2Si)_2$-

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[17] The signal for the $[Li(THF)_4]^+$ cation was assigned at $\delta$ 1.7 ppm in the CP MAS $^7Li$ NMR spectrum of $[Li(THF)_4][Li\{C(SiMe_3)_3\}_2]$.[14b] The solid-state structure of **1** was confirmed by an X-ray diffraction study. Although the crystal structure confirms that **1** exists as a dialkyllithiate, the anion is severely disordered and the residual *R* value for the structure was high.

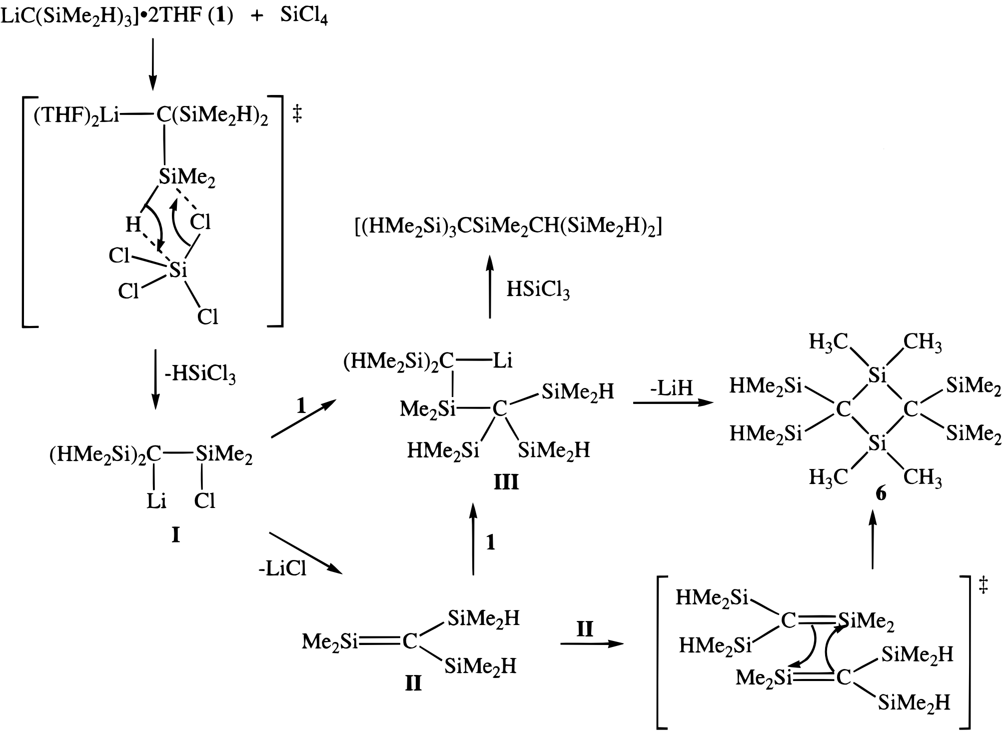
[18] $^1H$ NMR spectra of $[LiC(SiMe_2H)_3]$•2THF (**1**) recorded before and after the $^7Li$ NMR experiment in $C_6D_6$ showed no detectable decomposition.

[19] The C···C distance of $[LiC(SiMe_2H)_3]$•2THF (**1**) would have to be considerably longer than that of the solvent-free dimer $[LiC(SiMe_3)_3]$ to reduce steric crowding in structure **B**. The solvent-free dimer $[LiC(SiMe_3)_3]_2$ has a C···C distance (3.946(5) Å)[12] similar to that of the zinc alkyl $[ZnC(SiMe_3)_3]$ (3.964(4) Å),[7] which contains sufficiently interlocked alkyl groups to block attack of the Zn−C bond by many electrophilic or nucleophilic reagents.

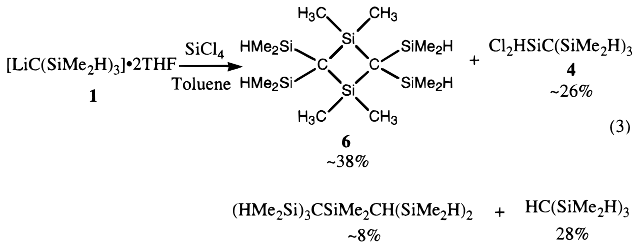
[20] Dua, S. S.; Eaborn, C.; Happer, D. A. R.; Hopper, S. P.; Safa, K. D.; Walton, D. R. M. *J. Organomet. Chem.* **1979**, 75.

[21] For highly substituted 1,3-disilacyclobutanes, see for example: (a) Wiberg, N.; Vasisht, S.-K. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 93. (b) Seyferth, D.; Lefferts, J. L. *J. Organomet. Chem.* **1976**, *116*, 257. (c) Fritz, G.; Chang, J. W.; Braunagel, N. *Z. Anorg. Allg. Chem.* **1975**, *416*, 211. (d) Damrauer, R. *Organometal. Chem. Rev. A* **1972**, *8*, 67.

**Scheme 2**



C═SiMe$_2$ (**II**) and HSiCl$_3$. Silenes are known to undergo dimerization in solution to give 1,3-disilacyclobutanes.[9a,23]



(3)

For example, Me$_2$Si═C(SiMe$_3$)$_2$ is very unstable with regard to dimerization at −100 °C.[23b] Therefore, (HMe$_2$Si)$_2$C═SiMe$_2$ (**II**) could undergo head-to-tail dimerization to produce **6**. Alternatively, LiC(SiMe$_2$H)$_2$(SiMe$_2$Cl) (**I**), generated via hydrogen−halogen exchange, could react with a second equivalent of **1** to produce **III**, which could eliminate LiH to give **6** (Scheme 2). **III** could also be formed by reaction between **1** and the silene **II** since additions of organometallic reagents across the silicon−carbon double bonds of silenes occur with regiochemistry expected of a Si$^{\delta+}$═C$^{\delta-}$-polarized double bond.[24] [(HMe$_2$Si)$_3$CSiMe$_2$CH(SiMe$_2$H)$_2$] can be formed via abstraction of hydrogen from HSiCl$_3$ by **III**. Since reaction between [LiC(SiMe$_2$H)$_3$]·2THF] (**1**) and HSiCl$_3$ is facile (vide supra), the relative rates of hydrogen−halogen exchange and nucleophilic reaction between **1** and HSiCl$_3$ should mainly determine the yield of **6**. The formation of **6** was observed in the reaction of **1** with SiCl$_4$ (in toluene) but not with the less electrophilic MeHSiCl$_2$ (in benzene-$d_6$). This suggests that the transition state for hydrogen−halogen exchange is dominated by electrophilic attack at the hydrogen atom of a Si−H bond of **1**. A similar transition state in which Si−H bond breaking precedes nucleophilic attack at silicon has been suggested for reaction of silanes with halocarbons[22a−c] or halogens.[22d,e]

Compound **6** was isolated as an air-stable, off-white solid in 52% yield from the reaction between **1** and 2 equiv of SiCl$_4$. Both mass spectrometry and microanalysis data are consistent with the proposed formulation. The NMR ($^1$H, $^{13}$C, and $^{29}$Si) spectra in benzene-$d_6$ showed the expected signals, including two signals in the $^{29}$Si NMR spectrum at $\delta$ 7.20 ppm, for bridging silicon atoms, and at $\delta$ −14.3 ppm, due to terminal silicon atoms. We are continuing our studies of the structure and reactions of [LiC(SiMe$_2$H)$_3$]·2THF (**1**). In addition, we are continuing our studies of the formation and reactivity of [Me$_2$SiC(SiMe$_2$H)$_2$]$_2$ (**6**). We are particularly interested in the potential of the reaction as a route to other highly substituted 1,3-disilacyclobutanes. We will report our findings in future publications.

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(23) See for example: (a) Boudjouk, P.; Sommer, L. H. *J. Chem. Soc., Chem. Commun.* **1973**, 54. (b) Wiberg, N.; Kopf, H. *J. Organomet. Chem.* **1986**, *315*, 9. (c) Wiberg, N.; Link, M. *Chem. Ber.* **1995**, *128*, 1241. (d) Wiberg, N.; Joo, K.-S.; Polborn, K. *J. Organomet. Chem.* **1996**, *524*, 147.

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