Synthetic Approaches to Cyclodisilazanes and Branched Silazanes

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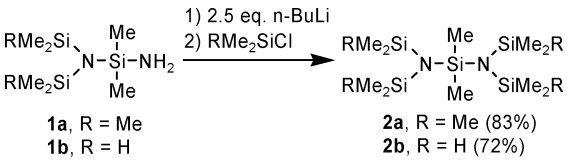
The syntheses of cyclosilazanes and branched silazanes from silylamines are described. The silylamines are deprotonated with 2 equiv of n-BuLi and then undergo a rearrangement to give 1,3-dilithium silylamides. After reaction with 1 equiv of a chlorosilane, the monolithiated compound can either react with another equivalent of chlorosilane to give a branched silazane or undergo an intramolecular cyclization to give a cyclodisilazane. The cyclization reaction is quite general and can be used to synthesize a number of new silyl-substituted cyclodisilazanes in good to excellent yields.

Interest in silicon-containing dendrimers has increased markedly since the early 1990s. Many dendritic varieties of the well-known linear silicon polymers have been synthesized, including dendritic silanes, carbosilanes, siloxanes, carbosiloxanes, and carbosilazanes.[1,2] Noteworthy omissions in this category are dendritic *silazanes*, with symmetrical N−Si−N connectivity along the branches. The lack of mention of these materials in the literature is due to their relative sensitivity and the synthetic challenges these materials represent. In this paper we describe the syntheses of small branched silazanes that may serve as starting materials for silazane dendrimer growth. Furthermore, our investigations into the mechanisms of these syntheses have revealed a new and general method for the synthesis of silyl-substituted cyclodisilazanes.

In the course of our exploratory investigations into the syntheses of branched silazanes, we attempted the monosubstitution of silylamine compound **1a**, $[(Me_3Si)_2N]SiMe_2NH_2$, by deprotonation with 1 equiv of n-BuLi at 0 °C followed by addition of Me_3SiCl at −78 °C. To our surprise, GC−MS analysis of the reaction mixture revealed not only the presence of the expected product but also a significant amount of the symmetrical disubstituted branched product **2a**. In an effort to increase the amount of **2a** formed, we repeated this reaction with 2.5 equiv of n-BuLi in the deprotonation step. This indeed resulted in the isolation of analytically pure **2a** as a white solid in 83% yield (eq 1). The structure of compound **2a** was confirmed by GC−MS, multinuclear NMR spectroscopy, and elemental analysis.

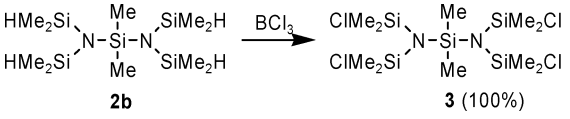
We were surprised by the relative ease with which **2a** was formed primarily because of the known difficulty in synthesizing **2a** by more conventional means. The synthesis of **2a** has been reported only twice (in older patents), either by a lengthy high pressure/temperature reaction between lithium bis(trimethylsilylamide) and



(1)

dichlorodimethylsilane[3] or by a low-yielding reaction between potassium bis(trimethylsilylamide) and dichlorodimethylsilane.[4] It should also be noted that these two patents list different melting points for **2a** (Fink, 79−81 °C; Wannagat, 68−72 °C), while our observed melting point for **2a** (90 °C) matched neither of the values.

Extension of this methodology to synthesize the dimethylsilyl-substituted derivative proved to be straightforward. Accordingly, silylamino compound **1b** was treated with excess n-BuLi followed by HMe_2SiCl. We were pleased to see that this resulted in the isolation of previously unknown **2b** in 72% yield after distillation (eq 1). Compound **2b** is a stable, clear, colorless liquid and may be handled freely in air. Si-H moieties may undergo a number of chemical transformations, but we attempted chlorination of **2b**, as we felt that this would provide the most flexibility in terms of subsequent functionalization. This conversion was not as trivial as might be expected, and many of the standard well-known conditions for this reaction proved to be unsuccessful. Finally however, the utilization of BCl_3 as reported by Neilson[5] resulted in the conversion of **2b** to the novel Cl-terminated dendritic core compound **3** as a white moisture-sensitive solid in quantitative yield (eq 2). Compound **3** is an ideal precursor for further dendritic silazane growth, due to its symmetry and reactivity at the exterior.



(2)

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(1) Son, D. Y. In *The Chemistry of Organic Silicon Compounds*; Rappoport, Z., Apeloig, Y., Eds.; John Wiley & Sons: New York, 2001; Vol. 3, p 745.

(2) Frey, H.; Schlenk, C. *Top. Curr. Chem.* **2000**, *210*, 69.

(3) Fink, W. U.S. Pat. 3,253,008, 1966.

(4) Wannagat, U.; Niederpruem, H.; Carduck, F. J. Ger. Pat. 1158972, 1963.

(5) Neilson, R. H. *Inorg. Chem.* **1980**, *19*, 755.

10.1021/om049579q CCC: $27.50
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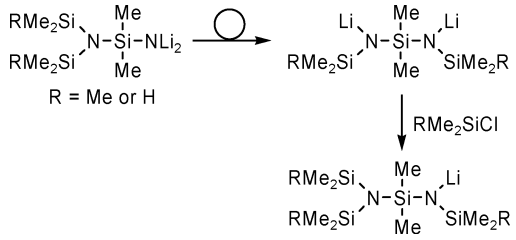
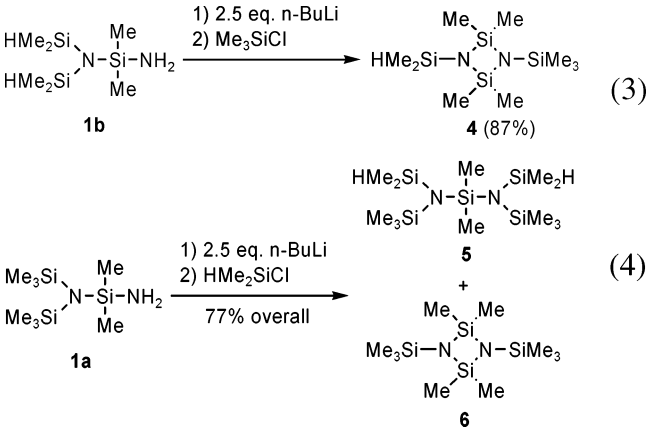
Scheme 1. Rearrangement and Reaction of Dilithiated Silylamide

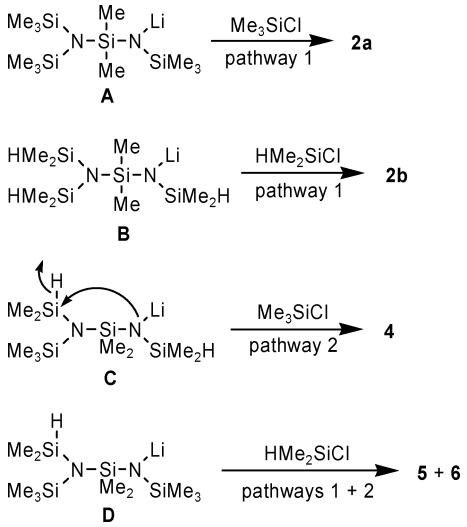


Initially, we believed the mechanisms of the reactions to form **2a** and **2b** were straightforward. Addition of n-BuLi to **1a** or **1b** results in a dilithiated species, which then reacts with 2 equiv of chlorosilane to give the fully substituted silylamine compound. However, further investigations revealed that such a mechanism was unsatisfactory. For example, reaction of **1b** with n-BuLi and Me_3SiCl under the conditions described above did not result in the expected unsymmetrically substituted silazane, but rather the new silyl-substituted cyclodisilazane **4** in 87% yield (eq 3). "Reversing" the reactants, i.e., reacting compound **1a** with n-BuLi and HMe_2SiCl, gave branched silazane **5** and also the unexpected symmetrical cyclodisilazane **6** in an approximately 1:1 ratio in 77% overall yield (eq 4). In this case the presence of compound **4** in the product mixture was not detected.

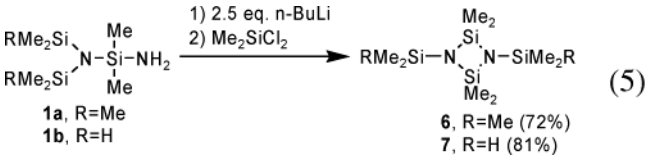


As an explanation for these results, we believe the initially formed dilithiated species undergoes a rearrangement to form a 1,3-dilithium silylamide, which then undergoes a monosubstitution reaction with a chlorosilane (Scheme 1). The resulting lithium silylamide (**A**−**D**) can then undergo one of two possible competing reaction pathways (Scheme 2): (1) a second substitution with chlorosilane to give the fully substituted product (e.g., **2a**, **2b**, and **5**) or (2) intramolecular reaction to give the cyclodisilazane and lithium hydride (e.g., **4**).[6] In the case of intermediate **A**, reaction with Me_3SiCl is clearly the only possible reaction pathway. As a result, compound **2a** is formed in high yield. For intermediates **B**−**D** however, either reaction pathway is possible, with the preferred reaction pathway being markedly sensitive to the size of the chlorosilane and the size of the silicon substituents already present in the molecule. In the case of intermediate **B**, both

Scheme 2. Possible Reactions of Monolithiated Silylamide



reaction pathways are possible. However, the small sizes of the dimethylsilyl groups (and HMe_2SiCl) result in the second substitution being preferred, giving **2b**. With intermediate **C**, the larger sizes of both the existing and incoming trimethylsilyl groups decrease the rate of the second substitution to the point that intramolecular cyclization becomes the preferred reaction to give **4**. Finally, in the case of **D**, the size of the two trimethylsilyl groups in the molecule slows the second substitution to the point where the two competing rates are approximately the same, resulting in both **5** and **6** being formed in roughly equal amounts. This particular sensitivity of lithiated silylamine compounds toward silyl substituent sizes is unusual, but similar behavior has been observed previously in other silylamine systems.[6−10] In additional experiments, we felt we could increase the likelihood of intramolecular cyclization by treating the rearranged dilithium silylamide with a dichlorosilane[11] rather than a chlorohydrosilane. This indeed turned out to be the case, as reactions of dilithiated **1a** and **1b** with dichlorodimethylsilane gave the corresponding cyclodisilazanes **6** and **7** in 72% and 81% yields, respectively (eq 5).



With this working mechanism in hand, we realized that we could now synthesize a variety of silyl-substituted cyclodisilazanes using these methods. Cyclodisilazanes[12−14] are well-known precursors to linear

(6) Wiseman, G. H.; Wheeler, D. R.; Seyferth, D. *Organometallics* **1986**, *5*, 146.

(7) Junge, K.; Popowski, E.; Michalik, M. *Z. Anorg. Allg. Chem.* **1999**, *625*, 1532.

(8) Schneider, J.; Popowski, E.; Junge, K.; Reinke, H. *Z. Anorg. Allg. Chem.* **2001**, *627*, 2680.

(9) Schneider, J.; Popowski, E.; Peulecke, N. *Z. Naturforsch.* **2000**, *55b*, 924.

(10) Kosse, P.; Popowski, E. *Z. Anorg. Allg. Chem.* **1993**, *619*, 613.

(11) Fink, W. *Helv. Chim. Acta* **1964**, *47*, 498.

(12) Fink, W. *Angew. Chem., Int. Ed. Engl.* **1966**, *5*, 760.

(13) Zhinkin, D. Y.; Varezhkin, Y. M.; Morgunova, M. M. *Russ. Chem. Rev.* **1980**, *49*, 1149.

silazane polymers,[15,16] and a general synthesis to these compounds would be useful. As demonstrated above, reactions of dilithiated **1b** with chlorotrialkylsilanes give cyclodisilazanes (with loss of LiH), as do reactions of dilithiated **1a** and **1b** with dichlorosilanes (with loss of LiCl). It should be apparent that the choice of starting silylamine and dichlorosilane determines the substituents on the final cyclodisilazane. We examined a variety of silylamines and chlorosilanes for this intramolecular cyclization reaction. Representative examples are shown in Table 1.

As can be seen from Table 1, the cyclization reaction is indeed quite general and works well in the presence of various functional groups. The cyclodisilazanes, most of which are new compounds, are formed in good to excellent yields. Reactions with trichlorosilanes result in the formation of cyclodisilazanes with chloro substitution on the ring (entries 6, 7, and 11). Phenyl substitution on the original silylamine does not hinder the rearrangement, and the expected product is observed (entry 12). All compounds were characterized using multinuclear NMR spectroscopy and elemental analysis.

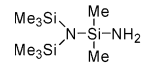
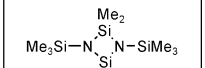
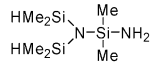
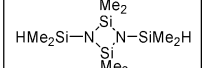
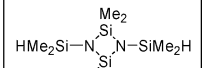
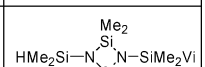
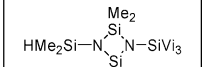
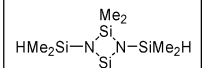
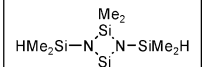
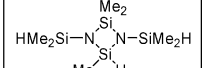
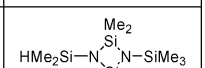
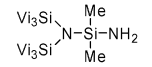
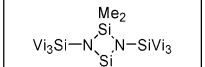
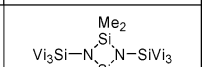
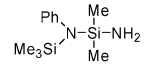
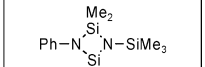
In conclusion, we describe a general method for the synthesis of silyl-substituted cyclodisilazanes that occurs via a rearrangement. In the cases where cyclization does not occur, small branched silazanes are formed, which may be useful as cores for silazane dendrimer growth.

Experimental Section

General Comments. All reactions were performed under an atmosphere of dry argon. Tetrahydrofuran (THF) and ethyl ether were distilled from Na/benzophenone under a N_2 atmosphere prior to use. NH_3 gas was dried by passing through KOH pellets. The following compounds were synthesized according to the literature: 2-(aminodimethylsilyl)-1,1,1,3,3,3-hexamethyldisilazane (**1a**),[17] 2-(aminodimethylsilyl)-1,1,3,3-tetramethyldisilazane (**1b**),[17] and 1-chloro-1,1,3,3,3-pentamethyl-2-phenyldisilazane.[18] ^{1}H (400 MHz), ^{13}C (100.6 MHz), and ^{29}Si (79.4 MHz) NMR spectra were recorded from samples dissolved in $CDCl_3$, d_6-DMSO, or C_6D_6. Elemental analyses were obtained from Galbraith Laboratory, Knoxville, TN, or with a CE Elantech Flash 1112 CHN elemental analyzer. Melting points were obtained using a TA Instruments DSC 2010 calorimeter.

Synthesis of 2-(Aminodimethylsilyl)-1,1,1,3,3,3-hexavinyldisilazane (1c). A 250 mL round-bottomed single-neck flask equipped with septum, Ar gas inlet, and a magnetic stir bar was charged with 1,1,1,3,3,3-hexavinyldisilazane (11.7 g, 0.05 mol) and 50 mL of THF. The flask was placed in an ice/water bath, and n-BuLi (20 mL, 0.05 mol, 2.5 M solution in hexane) was added slowly with stirring. After completion of addition, the mixture was stirred for an additional 30 min. Then it was transferred via cannula to a solution of dichlorodimethylsilane (6.6 mL, 0.055 mol) in 50 mL of THF under −78 °C. After stirring cold for an additional 15 min, the mixture was allowed to warm to room temperature and left overnight. The volatiles were removed under vacuum, and the residue was suspended in 100 mL of hexane. The white precipitation was filtrated off under Ar and washed with two 25 mL portions of hexane. The hexane was evaporated, leaving 2-(chlorodimethylsilyl)-1,1,1,3,3,3-hexavinyldisilazane as a colorless liquid (14.5 g, 89.0% yield). No further purification is needed for the next step. ^{1}H NMR (C_6D_6): δ 0.72 [s, 6H, −Si(CH_3)$_2$−], 5.98 [dd, ^3J = 20.4 Hz, ^2J = 3.6 Hz, 1H, CH=C*H*H], 6.10 [dd, ^2J = 3.6 Hz, ^3J = 14.8 Hz, 1H, CH=CH*H*], 6.48 [dd,

Table 1. Cyclodisilazane Products[a]

	starting silylamine	chloro-silane	product (yield)[b]
1	 **1a**	Me_2SiCl_2	 **6** (72%)
2	 **1b**	Me_2SiCl_2	 **7** (81%)
3	**1b**	$MeViSiCl_2$	 **8** (76%)
4	**1b**	$MeVi_2SiCl$	 **9** (81%)
5	**1b**	Vi_3SiCl	 **10** (78%)
6	**1b**	$HSiCl_3$	 **11** (68%)
7	**1b**	$MeSiCl_3$	 **12** (64%)
8	**1b**	$MeHSiCl_2$	 **13** (71%)
9	**1b**	Me_3SiCl	 **4** (87%)
10	 **1c**	Me_2SiCl_2	 **14** (75%)
11	**1c**	$MeSiCl_3$	 **15** (69%)
12	 **1d**	Me_2SiCl_2	 **16** (81%)

[a] Vi = −CH=CH$_2$. [b] Purified yields.

(14) Varezhkin, Y. M.; Zhinkin, D. Y.; Morgunova, M. M. *Russ. Chem. Rev.* **1981**, *50*, 1158.
(15) Bouquey, M.; Brochon, C.; Bruzaud, S.; Mingotaud, A.-F.; Schappacher, M.; Soum, A. *J. Organomet. Chem.* **1996**, *521*, 21.
(16) Seyferth, D.; Schwark, J. M.; Stewart, R. M. *Organometallics* **1989**, *8*, 1980.
(17) Mignani, G.; Seyferth, D. *Synth. React. Inorg. Met. Chem.* **1993**, *23*, 113.
(18) Fink, W. U.S. Pat. 3,565,934, 1971.

^3J = 20.4 Hz, ^3J = 14.8 Hz, 1H, C*H*=CH2]. A 100 mL round-bottomed three-neck flask equipped with septum, gas inlet and outlet, and a magnetic stir bar was charged with 2-(chlorodimethylsilyl)-1,1,1,3,3,3-hexavinyldisilazane (3.26 g, 10 mmol) and 50 mL of hexane. The solution was cooled with a xylene/dry ice bath, and ammonia gas was bubbled into the solution for 2 h. Then the mixture was slowly warmed to room temperature with stirring while a flow of Ar was passed through. The precipitated ammonium chloride was filtered off and washed thoroughly with hexane. The solvent was distilled off, and pure **1c** was isolated by distillation under reduced pressure through a short Vigreux column as a clear colorless solid (2.63 g, 85% yield, bp 82 °C/0.5 mmHg, mp 63.8 °C). ^{1}H NMR (C_6D_6): δ 0.45 [s, 6H, −Si(CH_3)$_2$−], 0.91 [b, 2H, −Si(CH$_3$)$_2$NH_2], 5.95 [dd, ^3J = 20.3 Hz, ^2J = 3.8 Hz, 1H, CH=C*H*H], 6.10 [dd, ^2J = 3.8 Hz, ^3J = 14.6 Hz, 1H, CH=CH*H*], 6.49 [dd, ^3J = 20.3 Hz, ^3J = 14.6 Hz, 1H, C*H*=CH2]. ^{13}C NMR (C_6D_6): δ 5.47 [−Si(*C*H$_3$)$_2$−], 133.80 [*C*H=CH$_2$], 139.61 [CH=*C*H$_2$]. ^{29}Si NMR (C_6D_6): δ −24.44 [−*Si*(vinyl)$_3$], −3.43 [−*Si*(CH$_3$)$_2$]. IR film (cm^{-1}): 3407 and 3486 (w, NH$_2$). Anal. Calcd for $C_{14}H_{26}N_2Si_3$: C, 54.84; H, 8.55. Found: C, 54.50; H, 8.49.

Synthesis of 1-Amino-1,1,3,3,3-pentamethyl-2-phenyldisilazane (1d). A 250 mL round-bottomed three-neck flask equipped with septum, gas inlet and outlet, and a magnetic stir bar was charged with 1-chloro-1,1,3,3,3-pentamethyl-2-phenyldisilazane (12.9 g, 50 mmol) and 100 mL of hexane. The solution was cooled in an ice/water bath, and ammonia gas was bubbled into the solution for 2 h. Then the mixture was slowly warmed to room temperature with stirring while a current of Ar was passed through. The precipitated ammonium chloride was filtered off and washed thoroughly with hexane. Removal of the solvent under vacuum left a colorless solid, which was purified by distillation under reduced pressure, giving **1d** as a clear colorless liquid (9.6 g, 80% yield, bp 65 °C/0.3 mmHg). ^{1}H NMR (C_6D_6): δ 0.18 [s, 6H, −Si(CH_3)$_2$−], 0.27 [s, 9H, −Si(CH_3)$_3$], 0.49 [b, 2H, NH_2], 7.00−7.29 [m, 5H, Ar-*H*]. ^{13}C NMR (C_6D_6): δ 2.26 [−Si(*C*H$_3$)$_2$−], 2.60 [−Si(*C*H$_3$)$_3$], 124.07, 128.97, 130.48, and 148.23 [*C*$_6$H$_5$]. ^{29}Si NMR (C_6D_6): δ −5.42 [−*Si*(CH$_3$)$_2$], 4.03 [−*Si*(CH$_3$)$_3$]. IR film (cm^{-1}): 3409 and 3489 (w, NH$_2$). Anal. Calcd for $C_{11}H_{22}N_2Si_2$: C, 55.40; H, 9.30. Found: C, 55.70; H, 9.33.

Synthesis of 1,1,1,3,3,5,5,5-Octamethyl-2,4-bis(trimethylsilyl)trisilazane (2a). A 100 mL round-bottomed single-neck flask equipped with septum, Ar gas inlet, and a magnetic stir bar was charged with **1a** (4.68 g, 20 mmol) and 20 mL of THF. The flask was placed in an ice/water bath, and n-BuLi (20 mL, 50 mmol, 2.5 M solution in hexane) was added slowly with stirring. After completion of addition, the mixture was stirred for an additional 3 h at room temperature. Then it was cooled under a dry ice/acetone bath, and chlorotrimethylsilane (6.35 mL, 50 mmol) was added dropwise during 30 min. After stirring cold for an additional 15 min, the mixture was allowed to warm to room temperature and left overnight. The volatiles were removed under vacuum, and the residue was suspended in 50 mL of hexane. The white precipitate was filtered off and washed thoroughly with hexane. The hexane was evaporated, leaving **2a** as a colorless solid (6.3 g, 83.3% yield, mp 90.3 °C, lit.[3] mp 79−81 °C). ^{1}H NMR ($CDCl_3$): δ 0.21 [s, 36H, −Si(CH_3)$_3$], 0.31 [s, 6H, −Si(CH_3)$_2$−]. ^{13}C NMR ($CDCl_3$): δ 5.61 [−Si(*C*H$_3$)$_3$], 8.89 [−Si(*C*H$_3$)$_2$−]. ^{29}Si NMR ($CDCl_3$): δ −5.88 [−*Si*(CH$_3$)$_2$], 1.50 [−*Si*(CH$_3$)$_3$]. Anal. Calcd for $C_{14}H_{42}N_2Si_5$: C, 44.38; H, 11.17. Found: C, 44.48; H, 11.24.

Synthesis of 1,1,3,3,5,5-Hexamethyl-2,4-bis(dimethylsilyl)trisilazane (2b). In the same manner described above, compound **2b** was prepared from **1b** (4.12 g, 20 mmol), n-BuLi (20 mL, 50 mmol, 2.5 M solution in hexane), and chlorodimethylsilane (5.55 mL, 50 mmol). Pure **2b** was isolated by distillation under reduced pressure through a short Vigreux column as a clear colorless liquid (4.62 g, 72% yield, bp 74 °C/0.05 mmHg). ^{1}H NMR ($CDCl_3$): δ 0.19 [d, ^3J = 3.4 Hz, 24H, −Si(CH_3)$_2$H], 0.23 [s, 6H, −Si(CH_3)$_2$−], 4.55 [h, ^3J = 3.4 Hz, 2H, Si*H*]. ^{13}C NMR ($CDCl_3$): δ 0.79 [−Si(*C*H$_3$)$_2$H], 4.88 [−Si(*C*H$_3$)$_2$−]. ^{29}Si NMR ($CDCl_3$): δ −13.08 [−*Si*(CH$_3$)$_2$H], −5.55 [−*Si*(CH$_3$)$_2$−]. IR film (cm^{-1}): 2122 (s, Si-H). Anal. Calcd for $C_{10}H_{34}N_2Si_5$: C, 37.20; H, 10.62. Found: C, 37.40; H, 10.32.

Synthesis of 1,5-Dichloro-1,1,3,3,5,5-hexamethyl-2,4-bis(chlorodimethylsilyl)trisilazane (3). A 50 mL Schlenk flask equipped with septum, Ar gas inlet, and a magnetic stir bar was charged with **2b** (1.61 g, 5 mmol) and 10 mL of CH_2Cl_2. The flask was placed in a dry ice/acetone bath, and BCl_3 (10 mL, 10 mmol, 1 M solution in CH_2Cl_2) was added slowly with stirring. After completion of addition, the mixture was slowly warmed to room temperature and was stirred for an additional 3 h. The volatiles were removed under vacuum and were killed with 2-propanol at −78 °C, leaving **3** as a colorless solid (2.30 g, 100% yield). ^{1}H NMR ($CDCl_3$): δ 0.65 [s, 6H, −Si(CH_3)$_2$−], 0.72 [s, 24H, −Si(CH_3)$_2$Cl]. ^{13}C NMR ($CDCl_3$): δ 8.10 [−Si(*C*H$_3$)$_2$−], 8.44 [−Si(*C*H$_3$)$_2$Cl]. ^{29}Si NMR ($CDCl_3$): δ 0.68 [−*Si*(CH$_3$)$_2$−], 14.25 [−*Si*(CH$_3$)$_2$Cl]. Anal. Calcd for $C_{10}H_{30}Cl_4N_2Si_5$: C, 26.08; H, 6.57. Found: C, 25.85; H, 6.50.

Synthesis of 1-(Dimethylsilyl)-2,2,4,4-tetramethyl-3-(trimethylsilyl)cyclodisilazane (4). In the same manner described above, compound **4** was prepared from **1b** (4.12 g, 20 mmol), n-BuLi (20 mL, 50 mmol, 2.5 M solution in hexane), and chlorotrimethylsilane (6.35 mL, 50 mmol). Pure **4** was isolated by distillation under reduced pressure through a short Vigreux column as a clear colorless liquid (4.80 g, 87% yield, bp 42−43 °C/0.25 mmHg, lit.[19] no data). ^{1}H NMR ($CDCl_3$): δ −0.02 [s, 9H, Si(CH_3)$_3$], 0.06 [d, ^3J = 3.0 Hz, 6H, Si(CH_3)$_2$H], 0.22 [s, 12H, Si(CH_3)$_2$], 4.38 [h, ^3J = 3.0 Hz, 1H, Si*H*]. ^{13}C NMR ($CDCl_3$): δ 0.39 [−Si(*C*H$_3$)$_2$H], 1.94 [−Si(*C*H$_3$)$_3$], 4.65 [−Si(*C*H$_3$)$_2$−]. ^{29}Si NMR ($CDCl_3$): δ −19.72 [−*Si*(CH$_3$)$_2$H], −4.02 [−*Si*(CH$_3$)$_3$], 4.47 [−*Si*(CH$_3$)$_2$−]. IR film (cm^{-1}): 2102 (s, Si-H). Anal. Calcd for $C_9H_{28}N_2Si_4$: C, 39.07; H, 10.20. Found: C, 39.24; H, 10.20.

Synthesis of 1,1,1,3,3,5,5-Heptamethyl-2-(dimethylsilyl)-4-(trimethylsilyl)trisilazane (5) and 1,3-Bis(trimethylsilyl)-2,2,4,4-tetramethylcyclodisilazane (6). In the same manner described above, compounds **5** and **6** were prepared from 2-(aminodimethylsilyl)-1,1,1,3,3,3-hexamethyldisilazane (4.68 g, 20 mmol), n-BuLi (20 mL, 50 mmol, 2.5 M solution in hexane), and chlorodimethylsilane (5.55 mL, 50 mmol). Pure **6** was isolated by distillation under reduced pressure through a short Vigreux column as a colorless solid (2.40 g, 41% yield, bp 65 °C/3 mmHg, mp 41.8 °C, lit.[20] mp 42−44 °C). ^{1}H NMR ($CDCl_3$): δ 0.03 [s, 18H, −Si(CH_3)$_3$], 0.21 [s, 12H, −Si(CH_3)$_2$−]. ^{13}C NMR ($CDCl_3$): δ 1.97 [−Si(*C*H$_3$)$_3$], 4.95 [−Si(*C*H$_3$)$_2$−]. ^{29}Si NMR ($CDCl_3$): δ −4.25 [−*Si*(CH$_3$)$_3$], −3.54 [−*Si*(CH$_3$)$_2$−]. Compound **6** can also be prepared from 2-(aminodimethylsilyl)-1,1,1,3,3,3-hexamethyldisilazane (1.17 g, 5 mmol), n-BuLi (5 mL, 12.5 mmol, 2.5 M solution in hexane), and dichlorodimethylsilane (1.52 mL, 12.5 mmol) in 72% yield. Pure **5** was also isolated by distillation under reduced pressure through a short Vigreux column as a clear colorless liquid (2.49 g, 36% yield, bp 79 °C/0.025 mmHg). ^{1}H NMR ($CDCl_3$): δ 0.17 [s, 18H, −Si(CH_3)$_3$], 0.21 [d, ^3J = 3.6 Hz, 12H, −Si(CH_3)$_2$H], 0.26 [s, 6H, −Si(CH_3)$_2$−], 4.62 [h, ^3J = 3.6 Hz, 2H, Si*H*]. ^{13}C NMR ($CDCl_3$): δ 1.58 [−Si(*C*H$_3$)$_2$H], 3.93 [−Si(*C*H3)$_3$], 6.90 [−Si(*C*H$_3$)$_2$−]. ^{29}Si NMR ($CDCl_3$): δ −13.57 [−*Si*(CH$_3$)$_2$H], −5.99 [−*Si*(CH$_3$)$_2$−], 2.58 [−*Si*(CH$_3$)$_3$]. IR film (cm^{-1}): 2136 (s, Si-H). Anal. Calcd for $C_{12}H_{38}N_2Si_5$: C, 41.08; H, 10.92. Found: C, 41.46; H, 10.91.

Synthesis of 1,3-Bis(dimethylsilyl)-2,2,4,4-tetramethylcyclodisilazane (7). In the same manner described above, compound **7** was prepared from **1b** (1.65 g, 8 mmol), n-BuLi (8 mL, 20 mmol, 2.5 M solution in hexane), and dichlorodimethylsilane (2.42 mL, 20 mmol). Pure **7** was isolated by

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distillation under reduced pressure through a short Vigreux column as a clear colorless liquid (1.71 g, 81% yield, bp 45 °C/5 mmHg, lit.[21] bp 53 °C/12 mmHg). ^{1}H NMR (C_6D_6): δ 0.06 [d, ^3J = 3.1 Hz, 12H, −Si(CH_3)$_2$H], 0.23 [s, 6H, −Si(CH_3)$_2$], 4.37 [h, ^3J = 3.1 Hz, 2H, Si(CH$_3$)$_2$*H*]. ^{13}C NMR (C_6D_6): δ 0.34 [−Si(*C*H$_3$)$_2$H], 4.33 [−Si(*C*H$_3$)$_2$]. ^{29}Si NMR (C_6D_6): −18.03 [−*Si*(CH$_3$)$_2$H], 5.02 [−*Si*(CH$_3$)$_2$−]. IR film (cm^{-1}): 2102 (s, Si-H).

Synthesis of 1,3-Bis(dimethylsilyl)-2,2,4-trimethyl-4-vinylcyclodisilazane (8). In the same manner described above, compound **8** was prepared from **1b** (2.06 g, 10 mmol), n-BuLi (10 mL, 25 mmol, 2.5 M solution in hexane), and dichloromethylvinylsilane (3.25 mL, 25 mmol). Pure **8** was isolated by distillation under reduced pressure through a short Vigreux column as a clear colorless liquid (2.09 g, 76% yield, bp 31−32 °C/0.05 mmHg). ^{1}H NMR (C_6D_6): δ 0.25 [d, ^3J = 3.1 Hz, 12H, −Si(CH_3)$_2$H], 0.42 [s, 3H, −Si(CH_3)(CH$_3$)−], 0.44 [s, 3H −Si(CH$_3$)(CH_3)−], 0.50 [s, 3H, −SiCH_3], 4.88 [h, ^3J = 3.1 Hz, 2H, Si*H*], 5.94 [dd, ^3J = 20.1 Hz, ^2J = 3.8 Hz, 1H, CH=C*H*H], 6.03 [dd, ^2J = 3.8 Hz, ^3J = 14.7 Hz, 1H, CH=CH*H*], 6.26 [dd, ^3J = 20.1 Hz, ^3J = 14.7 Hz, 1H, C*H*=CH2]. ^{13}C NMR ($CDCl_3$): δ 1.00 [−Si(*C*H$_3$)$_2$H], 2.10 [−Si(*C*H$_3$)], 4.87 [−Si-(*C*H$_3$)$_2$], 134.04 [*C*H=CH$_2$], 140.37 [CH=*C*H$_2$]. ^{29}Si NMR (C_6D_6): δ −18.56 [−*Si*(CH$_3$)$_2$H], −7.84 [−*Si*(CH$_3$)], −7.01 [−*Si*(CH$_3$)$_2$−]. IR film (cm^{-1}): 2103 (s, Si-H). Anal. Calcd for $C_9H_{26}N_2Si_4$: C, 39.36; H, 9.54. Found: C, 38.91; H, 9.63.

Synthesis of 1-(Dimethylsilyl)-3-(dimethylvinylsilyl)-2,2,4,4-tetramethylcyclodisilazane (9). In the same manner described above, compound **9** was prepared from **1b** (2.93 g, 14 mmol), n-BuLi (14 mL, 35 mmol, 2.5 M solution in hexane), and chlorodimethylvinylsilane (4.90 mL, 35 mmol). Pure **9** was isolated by distillation under reduced pressure through a short Vigreux column as a clear colorless liquid (3.26 g, 81% yield, bp 32 °C/0.005 mmHg). ^{1}H NMR (C_6D_6): δ 0.05 [d, ^3J = 3.7 Hz, 6H, −Si(CH_3)$_2$H], 0.06 [s, 6H, −Si(CH_3)$_2$vinyl−], 0.22 [s, 3H, −Si(CH_3)$_2$], 4.38 [h, ^3J = 3.1 Hz, 1H, Si*H*], 5.61 [dd, ^3J = 20.2 Hz, ^2J = 3.7 Hz, 1H, CH=C*H*H], 5.84 [dd, ^2J = 3.7 Hz, ^3J = 14.8 Hz, 1H, CH=CH*H*], 6.07 [dd, ^3J = 20.2 Hz, ^3J = 14.8 Hz, 1H, C*H*=CH$_2$]. ^{13}C NMR ($CDCl_3$): δ 0.18 [−Si(*C*H$_3$)$_2$H], 0.38 [−Si(*C*H$_3$)$_2$CH=CH$_2$], 4.87 [−Si(*C*H$_3$)$_2$], 130.39 [CH=*C*H$_2$], 140.71 [*C*H=CH$_2$]. ^{29}Si NMR (C_6D_6): δ −19.67 [−*Si*(CH$_3$)$_2$H], −12.92 [−*Si*(CH$_3$)$_2$CH=CH$_2$], 5.10 [−*Si*(CH$_3$)$_2$−]. IR film (cm^{-1}): 2102 (s, Si-H). Anal. Calcd for $C_{10}H_{28}N_2Si_4$: C, 41.60; H, 9.78. Found: C, 41.88; H, 9.86.

Synthesis of 1-(Dimethylsilyl)-3-(trivinylsilyl)-2,2,4,4-tetramethylcyclodisilazane (10). In the same manner described above, compound **10** was prepared from **1b** (1.03 g, 5 mmol), n-BuLi (5 mL, 13 mmol, 2.5 M solution in hexane), and chlorotrivinylsilane (1.94 mL, 13 mmol). Pure **10** was isolated by distillation under reduced pressure through a short Vigreux column as a clear colorless liquid (1.22 g, 78% yield, bp 51 °C/0.025 mmHg). ^{1}H NMR (C_6D_6): δ 0.26 [d, ^3J = 3.1 Hz, 6H, −Si(CH_3)$_2$H], 0.45 [s, 6H, −Si(CH_3)$_2$], 4.84 [h, ^3J = 3.1 Hz, 1H, Si*H*], 5.93 [dd, ^3J = 20.1 Hz, ^2J = 3.7 Hz, 1H, CH=C*H*H], 6.09 [dd, ^2J = 3.7 Hz, ^3J = 14.7 Hz, 1H, CH=CH*H*], 6.30 [dd, ^3J = 20.1 Hz, ^3J = 14.7 Hz, 1H, C*H*=CH2]. ^{13}C NMR (C_6D_6): δ 1.06 [−Si(*C*H$_3$)$_2$H], 5.50 [−Si(*C*H$_3$)$_2$], 134.26 [CH=*C*H$_2$], 137.41 [*C*H=CH$_2$]. ^{29}Si NMR (C_6D_6): δ −29.60 [−*Si*(CH=CH$_2$)$_3$], −19.17 [−*Si*(CH$_3$)$_2$H], 6.61 [−*Si*(CH$_3$)$_2$−]. IR film (cm^{-1}): 2101 (s, Si-H). Anal. Calcd for $C_{12}H_{28}N_2Si_4$: C, 46.09; H, 9.03. Found: C, 46.20; H, 8.97.

Synthesis of 1,3-Bis(dimethylsilyl)-2-chloro-4,4-dimethylcyclodisilazane (11). In the same manner described above, compound **11** was prepared from **1b** (2.06 g, 10 mmol), n-BuLi (10 mL, 25 mmol, 2.5 M solution in hexane), and trichlorosilane (2.52 mL, 25 mmol). Pure **11** was isolated by distillation under reduced pressure through a short Vigreux column as a clear colorless liquid (2.0 g, 67.7% yield, bp 24 °C/0.05 mmHg). ^{1}H NMR (C_6D_6): δ 0.25 [d, ^3J = 3.2 Hz, 12H, −Si(CH_3)$_2$H], 0.30 and 0.35 [s, 6H, −Si(CH_3)$_2$], 4.81 [h, ^3J = 3.2 Hz, 2H, Si(CH$_3$)$_2$*H*], 6.04 [s, 1H, SiCl*H*]. ^{13}C NMR (C_6D_6): δ 0.24 and 0.29 [−Si(*C*H$_3$)$_2$H], 3.67 and 4.60 [−Si(*C*H$_3$)$_2$]. ^{29}Si NMR (C_6D_6): −16.10 [−*Si*(CH$_3$)$_2$H], 11.70 [−*Si*(CH$_3$)$_2$−]. IR film (cm^{-1}): 2188 (s, ClSi-H), 2114 (s, Si-H). Anal. Calcd for $C_6H_{21}ClN_2Si_4$: C, 26.78; H, 7.87. Found: C, 27.18; H, 8.18.

Synthesis of 1,3-Bis(dimethylsilyl)-2-chloro-2,4,4-trimethylcyclodisilazane (12). In the same manner described above, compound **12** was prepared from **1b** (1.03 g, 5 mmol), n-BuLi (5 mL, 13 mmol, 2.5 M solution in hexane), and methyltrichlorosilane (1.47 mL, 13 mmol). Pure **12** was isolated by distillation under reduced pressure through a short Vigreux column as a clear colorless liquid (0.9 g, 64% yield, bp 26 °C/0.15 mmHg). ^{1}H NMR (C_6D_6): δ 0.26 [d, ^3J = 3.1 Hz, 12H, −Si(CH_3)$_2$H], 0.32 and 0.39 [s, 6H, −Si(CH_3)$_2$], 0.67 [s, 3H, SiClCH_3], 4.82 [h, ^3J = 3.1 Hz, 2H, Si(CH$_3$)$_2$*H*]. ^{13}C NMR (C_6D_6): δ 0.50 [−Si(*C*H$_3$)$_2$H], 3.80 and 4.10 [−Si(*C*H$_3$)$_2$], 6.67 [SiCl*C*H$_3$]. ^{29}Si NMR (C_6D_6): −17.00 [−*Si*(CH$_3$)$_2$H], −11.53 [*Si*ClCH$_3$], 7.82 [−*Si*(CH$_3$)$_2$−]. IR film (cm^{-1}): 2110 (s, Si-H). Anal. Calcd for $C_7H_{23}ClN_2Si_4$: C, 29.70; H, 8.19. Found: C, 29.84; H, 7.87.

Synthesis of 1,3-Bis(dimethylsilyl)-2,4,4-trimethylcyclodisilazane (13). In the same manner described above, compound **13** was prepared from **1b** (2.06 g, 10 mmol), n-BuLi (10 mL, 25 mmol, 2.5 M solution in hexane), and dichloromethylsilane (2.60 mL, 25 mmol). Pure **13** was isolated by distillation under reduced pressure through a short Vigreux column as a clear colorless liquid (1.76 g, 71% yield, bp 26 °C/0.05 mmHg, lit.[19] no data). ^{1}H NMR (C_6D_6): δ 0.24 [d, ^3J = 3.1 Hz, 12H, −Si(CH_3)$_2$H], 0.39 and 0.41 [s, 6H, −Si(CH_3)$_2$], 0.45 [d, ^3J = 1.9 Hz, 3H, SiHCH_3], 4.86 [h, ^3J = 3.1 Hz, 2H, Si(CH$_3$)$_2$*H*], 5.64 [q, ^3J = 1.9 Hz, 2H, SiCH$_3$*H*]. ^{13}C NMR (C_6D_6): δ 0.70 [−Si(*C*H$_3$)$_2$H], 0.78 [−Si*C*H$_3$H], 4.53 and 5.42 [−Si-(*C*H$_3$)$_2$]. ^{29}Si NMR (C_6D_6): −18.05 [−*Si*(CH$_3$)$_2$H], −10.92 [*Si*-HCH$_3$], 9.40 [−*Si*(CH$_3$)$_2$−]. IR film (cm^{-1}): 2109 (s, Si-H). Anal. Calcd for $C_7H_{24}N_2Si_4$: C, 33.82; H, 9.73. Found: C, 34.23; H, 9.61.

Synthesis of 1,3-Bis(trivinylsilyl)-2,2,4,4-tetramethylcyclodisilazane (14). In the same manner described above, compound **14** was prepared from **1c** (1.02 g, 3.3 mmol), n-BuLi (3.3 mL, 8.3 mmol, 2.5 M solution in hexane), and dichlorodimethylsilane (1.0 mL, 8.3 mmol). Pure **14** was isolated by distillation under reduced pressure through a short Vigreux column as a colorless liquid (0.74 g, 30.7% yield, bp 56−7 °C/0.005 mmHg). ^{1}H NMR (C_6D_6): 0.51 [s, 12H, −Si(CH_3)$_2$], 5.98 [dd, ^3J = 20.2 Hz, ^2J = 4.1 Hz, 6H, CH=C*H*H], 6.13 [dd, ^2J = 4.1 Hz, ^3J = 14.7 Hz, 6H, CH=CH*H*], 6.37 [dd, ^3J = 20.2 Hz, ^3J = 14.7 Hz, 6H, C*H*=CH$_2$]. ^{13}C NMR (C_6D_6): 6.13 [−Si-(*C*H$_3$)$_2$−], 134.40 [*C*H=CH$_2$], 137.49 [*C*H=CH$_2$]. ^{29}Si NMR (C_6D_6): δ −29.53 [−*Si*(vinyl)$_3$], 7.51 [−*Si*(CH$_3$)$_2$−]. Anal. Calcd for $C_{16}H_{30}N_2Si_4$: C, 52.97; H, 8.34. Found: C, 52.93; H, 8.50.

Synthesis of 1,3-Bis(trivinylsilyl)-2-chloro-2,4,4-trimethylcyclodisilazane (15). In the same manner described above, compound **15** was prepared from **1c** (1.02 g, 3.3 mmol), n-BuLi (3.3 mL, 8.3 mmol, 2.5 M solution in hexane), and trichloromethylsilane (0.97 mL, 8.3 mmol). Pure **15** was isolated by distillation under reduced pressure through a short Vigreux column as a clear colorless liquid (0.87 g, 69% yield, bp 87 °C/0.025 mmHg). ^{1}H NMR (C_6D_6): δ 0.43 and 0.50 [s, 6H, −Si(CH_3)$_2$], 0.77 [s, 3H, SiClCH_3], 6.00 [dd, ^3J = 20.2 Hz, ^2J = 4.0 Hz, 1H, CH=C*H*H], 6.13 [dd, ^2J = 4.0 Hz, ^3J = 14.8 Hz, 1H, CH=CH*H*], 6.33 [dd, ^3J = 20.2 Hz, ^3J = 14.8 Hz, 1H, C*H*=CH$_2$]. ^{13}C NMR (C_6D_6): δ 5.10 and 5.24 [−Si(*C*H$_3$)$_2$], 7.63 [SiCl*C*H$_3$], 135.10 [CH=*C*H$_2$], 136.23 [*C*H=CH$_2$]. ^{29}Si NMR (C_6D_6): −28.67 [−*Si*(vinyl)$_3$], −10.44 [*Si*ClCH$_3$], 9.22 [−*Si*(CH$_3$)$_2$−]. Anal. Calcd for $C_{15}H_{27}ClN_2Si_4$: C, 47.02; H, 7.10. Found: C, 46.46; H, 7.02.

Synthesis of 1-(Trimethylsilyl)-2,2,4,4-tetramethyl-3-phenylcyclodisilazane (16). A 50 mL round-bottomed single-neck flask equipped with septum, Ar gas inlet, and a magnetic stir bar was charged with **1d** (1.19 g, 5 mmol) and 10 mL of

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THF. The flask was placed in an ice/water bath, and n-BuLi (5 mL, 12.5 mmol, 2.5 M solution in hexane) was added slowly with stirring. After completion of addition, the mixture was stirred for an additional 3 h at room temperature. Then it was cooled under a dry ice/acetone bath, and dichlorodimethylsilane (1.52 mL, 12.5 mmol) was added dropwise during 30 min. After stirring cold for an additional 15 min, the mixture was allowed to warm to room temperature and left overnight. The volatiles were removed under vacuum, and the residue was suspended in 20 mL of hexane. The white precipitation was filtered off and washed thoroughly with hexane. The hexane was evaporated, leaving **16** as a colorless solid (1.2 g, 81% yield, bp 76 °C/0.01 mmHg, mp 90.5 °C, lit.[21] mp 95 °C). ^{1}H NMR (C_6D_6): δ 0.19 [s, 9H, $-Si(CH_3)_3$], 0.47 [s, 12H, $-Si(CH_3)_2-$], 6.69−7.25 [m, 5H, Ar-*H*]. ^{13}C NMR (C_6D_6): δ 2.75 [$-Si(CH_3)_2-$], 3.55 [$-Si(CH_3)_3$], 118.30, 118.64, 129.97, and 147.17 [C_6H_5]. ^{29}Si NMR (C_6D_6): δ −2.07 [$-Si(CH_3)_2$], 5.20 [$-Si(CH_3)_3$].

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