formation for methylsilylene and dimethylsilylene. For CH_3SiH the calculated value at 298 K is 49.2 kcal/mol. Reactions 4–7 predict heats of formation of 32.8, 32.6, 33.1, and 32.0 kcal/mol, respectively, for dimethylsilylene. The agreement among these four reactions is encouraging, particularly since all but reaction 6 make use of the calculated value for methylsilylene. It is estimated that the average of these four values (32.6 kcal/mol) is accurate to 3–4 kcal/mol. The implications of these results are discussed in light of recent experimental results in the accompanying papers by Ring, O'Neal, and co-workers[12] and Walsh.[13]

Acknowledgment. This work was supported in part by grants from the National Science Foundation (CHE86-40771) and the Air Force Office of Scientific Research (87-0049). The computer time made available by the North Dakota State University Computer Center is gratefully acknowledged.

Registry No. SiH_2, 13825-90-6; CH_3SiH, 55544-30-4; $(CH_3)_2Si$, 6376-86-9; SiH_4, 7803-62-5; CH_3SiH_3, 992-94-9; $(CH_3)_2SiH_2$, 1111-74-6.

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(13) Walsh, R. *Organometallics*, third of four papers in this issue.

Stoichiometric and Catalytic Ring Opening of Hexaalkylcyclodisilazanes by Organoalkali Reagents

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The action of organoalkali reagents (RLi, RLi/Me_3CONa, RLi/Me_3COK) on cyclo-$(Me_2SiNMe)_2$ and cyclo-$(Me_2SiNPr^i)_2$ results in ring opening to give alkali-metal amides of the type $RMe_2SiNMeSiMe_2NMeM$ (M = Li, Na, K) which react with chlorosilanes, $R'Me_2SiCl$, to give the expected linear trisilazanes. Relatively unhindered lithium amides also open the cyclo-$(Me_2SiNMe)_2$ ring. The use of a catalytic amount of RLi or RLi/Me_3CONa (but not of RLi/Me_3COK) results in ring-opening polymerization of cyclo-$(Me_2SiNMe)_2$ but not of the more hindered cyclo-$(Me_2SiNPr^i)_2$.

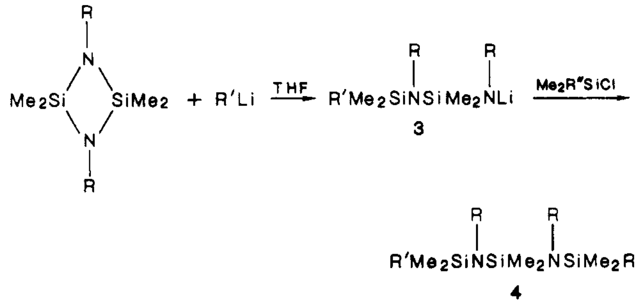
Introduction

Stoichiometric and catalytic ring opening of cyclotrisiloxanes by the action of strong nucleophilic reagents (OH^-, OR^-, $OSiMe_3^-$, RLi, etc.) is well-known,[1] and the catalytic processes are useful in the preparation of linear polysiloxanes. Applied to cyclopolysilazanes, cyclo-$(R^1R^2SiNR^3)_n$, such processes might be expected to result in formation of linear polysilazanes. However, none have been reported thus far.[2] Our interest in polysilazanes as precursors for silicon nitride and silicon carbonitride[3] led us to investigate the possibility of organoalkali reagent catalyzed ring-opening polymerization of cyclic polysilazanes.

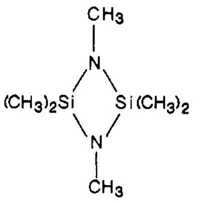
Results and Discussion

In the cyclopolysiloxane series, cyclo-$(R_2SiO)_n$, the four-membered ring is known only when R is an extremely bulky organic group,[4] and for the R = CH_3 series the cyclotrisiloxane is the smallest ring known. Hexamethylcyclotrisiloxane has enhanced reactivity, compared with the larger cyclics, and is readily cleaved by strong nucleophiles.[1] In the cyclopolysilazane series the four-membered cyclodisilazane ring system is very stable, and many examples of Si_2N_2 rings have been reported.[5]

Scheme I



Before investigating the possibility of the catalytic ring-opening polymerization of cyclodisilazanes, we have studied the stoichiometric opening of the cyclodisilazane ring by organoalkali reagents. The cyclodisilazanes chosen for study were 1 and 2. Both compounds are stable, distillable liquids. Hexamethylcyclodisilazane was found



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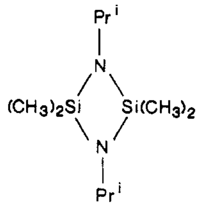

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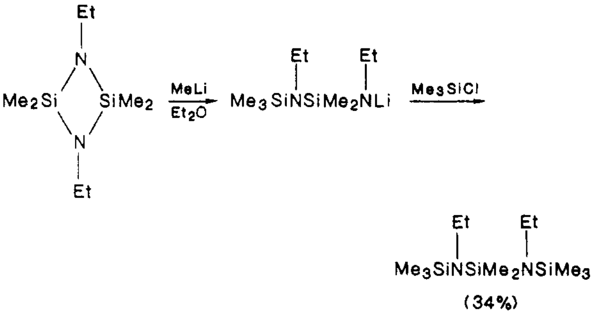
Table I. Stoichiometric Ring Opening of cyclo-($Me_2SiNMe)_2$ and (cyclo-$Me_2SiNPr^i)_2$ by Organoalkali Reagents

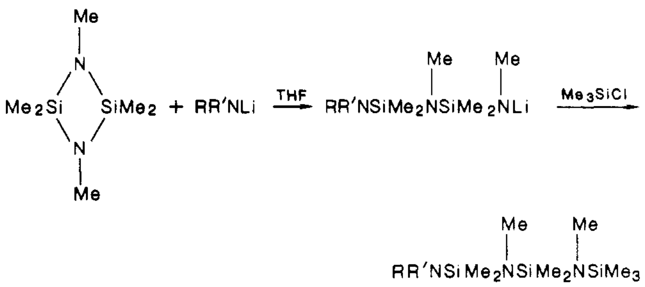
RLi	chlorosilane quench	product (% yield)
	I. Reactions of cyclo-$(Me_2SiNMe)_2$	
MeLi	Me_3SiCl	$Me_3SiNMeSiMe_2NMeSiMe_3$ (70)
MeLi	Me_2HSiCl	$Me_3SiNMeSiMe_2NMeSiMe_2H$ (83)
MeLi	Me_2SiCl_2	$Me_3SiNMeSiMe_2NMeSiMe_2Cl$ (57)
n-BuLi	Me_3SiCl	*n*-$BuMe_2SiNMeSiMe_2NMeSiMe_3$ (81)
n-BuLi	Me_2HSiCl	*n*-$BuMe_2SiNMeSiMe_2NMeSiMe_2H$ (86)
t-BuLi	Me_3SiCl	*t*-$BuMe_2SiNMeSiMe_2NMeSiMe_3$ (87)
t-BuLi	Me_2HSiCl	*t*-$BuMe_2SiNMeSiMe_2NMeSiMe_2H$ (80)
MeLi/ Me_3CONa	Me_3SiCl	$Me_3SiNMeSiMe_2NMeSiMe_3$ (70)
MeLi/ Me_3CONa	$Me_2ViSiCl$	$Me_3SiNMeSiMe_2NMeSiMeVi$ (60)
MeLi/Me_3COK	Me_3SiCl	$Me_3SiNMeSiMe_2NMeSiMe_3$ (60)
	II. Reactions of cyclo-$(Me_2SiNPr^i)_2$	
MeLi	Me_2HSiCl	$Me_3SiNPr^iSiMe_2NPr^iSiMe_2H$ (64)
n-BuLi	Me_2HSiCl	*n*-$BuMe_2SiNPr^iSiMe_2NPr^iSiMe_2H$ (67)

in a gas-phase electron diffraction study to contain a planar Si_2N_2 ring, with an SiNSi angle of 98° and an Si–N bond distance of 1.74 Å,[6] very similar to SiNSi bond angles and Si–N bond lengths of solid cyclodisilazanes as determined by X-ray diffraction.[7] It has been noted[5c] that the cyclodisilazane ring is quite strained compared with the six-membered cyclotrisilazane and the eight-membered cyclotetrasilazane rings. In view of this, one might expect that attack at a silicon atom of these cyclodisilazanes by a strongly nucleophilic organoalkali reagent will result in opening of the strained Si_2N_2 ring.

There has been one previous report of the cleavage of a cyclodisilazane by an organolithium reagent (eq 1).[8] In our study of such ring-opening reactions we found such reactions of **1** and **2** to be fairly general in terms of the alkyllithium reagent that may be used (MeLi, *n*-BuLi, *t*-BuLi) and to proceed in high yield when carried out in THF solution (Table I and Scheme I). In all reactions, the cyclodisilazane was added to a two- to fourfold excess of the respective organolithium reagent solution which had been cooled to a suitably low temperature (to minimize reaction of RLi with the solvent). The final reaction temperature depended on the lithium reagent used. Reactions with the reactive *n*- and *tert*-butyllithium could be carried out at 0 °C, but reactions with the less reactive methyllithium sometimes were carried out at room temperature or by heating briefly at reflux. The final quench with a chlorosilane was carried out at room temperature or at reflux. In contrast to the facile ring opening of cyclo-$(Me_2SiO)_3$ by organolithium reagents and other strong nucleophiles,[1] cyclo-$(Me_2SiNMe)_3$ did not react with *n*-butyllithium in THF.



(1)



If cyclodisilazane ring opening is to be a useful oligomerization/polymerization procedure, the propagation steps involving further cyclodisilazane cleavage by lithium amide **3** and by higher oligomers and then polymers, i.e., by $R'[Me_2SiN(R)SiMe_2N(R)]_nLi$ in the case of cyclo-$(Me_2SiNMe)_2$, must occur at a reasonable rate. Such ring-opening reactions were examined first in stoichiometric reactions (Scheme II). They were found to proceed in good yield (R, R′ = Me, 70%; R = Me, R′ = Me_3Si, 83%) when the lithium amide was not too hindered and when the reaction mixture was heated at reflux. More hindered lithium amides such as $Pr^i{}_2NLi$ and $(Me_3Si)_2NLi$ did not react with hexamethylcyclodisilazane. More to the point, a reaction of the initially formed methyllithium ring-opening product $Me_3SiNMeSiMe_2NMeLi$ with a second molar equivalent of hexamethylcyclodisilazane, i.e., the first propagation step, gave the expected $Me_3SiNMeSiMe_2NMeSiMe_2NMeSiMe_2NMeLi$ and addition of Me_3SiCl to the reaction mixture resulted in formation of $Me_3SiNMeSiMe_2NMeSiMe_3$ (4% yield) and $Me_3Si(NMeSiMe_2)_3NMeSiMe_3$ (25% yield), as well as higher, nonvolatile oligomers. Thus we could expect such polymerization to occur, at least with cyclo-$(Me_2SiNMe)_2$.

The initial ring-opening products, the lithium amides **3**, appeared to be stable in solution, even in refluxing THF, at least for limited periods of time. A potential decomposition process of the type described by Fink[9] (eq 2) was not observed. Apparently higher temperatures are required for such a cycloreversion process.

$$(Me_3Si)_2NSiMe_2N(SiMe_3)Li \xrightarrow[\text{reflux 8 h}]{\text{xylene}} LiN(SiMe_3)_2 + \text{cyclo-}(Me_2SiNSiMe_3)_2 \quad (2)$$

Lithium amide intermediates of type **3** could be observed by ^{29}Si NMR spectroscopy. A solution of $Me_3SiNMeSiMe_2NMeLi$ in which most of the THF had been removed by trap-to-trap distillation in vacuo and replaced by C_6D_6 showed the ^{29}Si resonance (DEPT technique[10]) for the Me_3SiN silicon atom at δ_{Si} 2.53 and the $NSiMe_2NLi$ resonance at δ_{Si} −7.74. By comparison, the Me_3SiCl quench product of this lithium amide, $Me_3SiNMeSiMe_2NMeSiMe_3$, showed two ^{29}Si resonances at δ_{Si} 5.35 (Me_3Si) and −0.26 ($SiMe_2$). (Hexamethylcyclodisilazane in C_6D_6 shows a single ^{29}Si resonance at 8.01 ppm.) The ^{29}Si NMR spectra of this lithium amide and of *n*-$BuMe_2SiNMeSiMe_2NMeLi$ [δ_{Si} 3.96 (*n*-$BuMe_2SiN$) and −9.61 ($NSiMe_2N$)] were devoid of other resonances,

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(9) Fink, W. *Chem. Ber.* **1963**, *96*, 1071.

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Scheme III

Initiation

$\mathrm{RLi + cyclo\text{-}(Me_2SiNMe)_2 \rightarrow RMe_2SiNMeSiMe_2NMeLi}$

Propagation

$\mathrm{RMe_2SiNMeSiMe_2NMeLi + cyclo\text{-}(Me_2SiNMe)_2 \rightarrow RMe_2SiNMe(SiMe_2NMe)_3Li}$

$$\downarrow \mathrm{cyclo\text{-}(Me_2SiNMe)_2}$$

$\mathrm{RMe_2SiNMe(SiMe_2NMe)_5Li}$

$$\downarrow \text{etc.}$$

$\mathrm{RMe_2SiNMe(SiMe_2NMe)_{\mathit{n}}Li}$ ("living polymer")

Termination

$\mathrm{RMe_2SiNMe(SiMe_2NMe)_{\mathit{n}}Li + Me_2R'SiCl \rightarrow RMe_2SiNMe(SiMe_2NMe)_{\mathit{n}}SiMe_2R'}$

an indication that a clean ring opening had taken place.

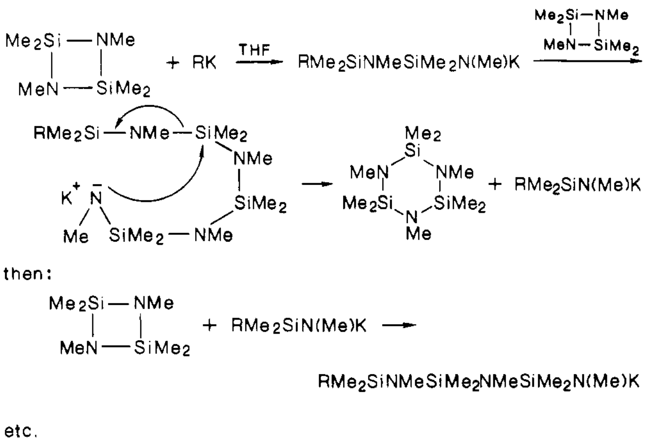
Organosodium and -potassium reagents in general are more reactive than organolithium reagents, so it was of interest to study the action of organosodium and -potassium nucleophiles on hexamethylcyclodisilazane. The sodium reagents chosen were of the Lochmann base type,[11] $\mathrm{RLi/Me_3CONa}$ (R = *n*-Bu, Me). These react readily with hexamethylcyclodisilazane to give $\mathrm{RMe_2SiNMeSiMe_2NMeNa}$ below room temperature. Subsequent reaction of these sodium amide intermediates with a chlorosilane gave good yields of linear trisilazanes.

Organopotassium reagents of the $\mathrm{MeLi/Me_3COK}$ type[11] also reacted with hexamethylcyclodisilazane under mild conditions (−15 °C). Addition of $\mathrm{Me_3SiCl}$ to such a reaction mixture gave $\mathrm{Me_3SiNMeSiMe_2NMeSiMe_3}$ in 60% yield, in addition to some nonvolatile material.

Since stoichiometric ring opening of cyclo-$\mathrm{(Me_2SiNMe)_2}$ by RLi, RNa, and RK could be readily effected and since such cyclodisilazane ring opening also occurred with $\mathrm{Me_2NLi}$ and $\mathrm{Me_3Si(Me)NLi}$, we undertook a study of organoalkali-catalyzed ring-opening polymerization of **1** and **2**. The expected chemistry is shown in Scheme III. If, as anticipated, the rate of initiation is much greater than the rates of the propagation steps, then the molecular weight of the product will be determined by the monomer/initiator molar ratio (in the absence of side reactions).

Catalytic ring opening polymerization of hexamethylcyclodisilazane by *n*-butyl- and methyllithium and *n*-butyl- and methylsodium did indeed occur. The required reaction temperatures reflected the reactivity of these organoalkali reagents in the stoichiometric reactions. Thus, the RLi-initiated reactions were started at 0 °C, and then the reaction mixtures were heated at reflux (in THF) until no more cyclo-$\mathrm{(Me_2SiNMe)_2}$ could be detected by GLC. In the case of the RNa-initiated polymerizations, the cyclodisilazane was added to the $\mathrm{RLi/Me_3CONa}$ reagent at −78 °C and subsequently the reaction mixture was warmed to −15 °C and finally to room temperature. The products in general were white waxy solids. Their molecular weights, determined by cryoscopy in benzene, were in the 1000–3000 range and in most cases were not too far off from the theoretical molecular weight calculated from the monomer/catalyst molar ratio. However, cryoscopic molecular weights in that range are only approximate and no useful quantitative data are in hand. However, it is clear that ring-opening polymerization of hexamethylcyclodisilazane has been effected. Polymers of type $\mathrm{RMe_2SiNMe(SiMe_2NMe)_{\mathit{n}}SiMe_2R'}$ with n = about 11–35 have been prepared.

Scheme IV



The oligomeric/polymeric products obtained must be linear species of the type shown in Scheme III. For instance, the ^{1}H NMR spectrum (in $\mathrm{CDCl_3}$) of the wax obtained by the action of 5 mol % *n*-$\mathrm{BuLi/Me_3CONa}$ on cyclo-$\mathrm{(Me_2SiNMe)_2}$ ($\mathrm{Me_3SiCl}$ quench) showed only two resonances at δ 0.12 ($\mathrm{SiCH_3}$) and 2.40 ($\mathrm{NCH_3}$). The *n*-$\mathrm{C_4H_9}$ resonances were observed only when the spectrum intensity was increased by several orders of magnitude. The ^{29}Si NMR spectrum in $\mathrm{CDCl_3}$ of the wax showed a single resonance at δ_{Si} −2.27. In contrast, the ^{29}Si NMR spectrum (in $\mathrm{CDCl_3}$) of the product obtained by the action of 10 mol % $\mathrm{MeLi/Me_3CONa}$ on cyclo-$\mathrm{(Me_2SiNMe)_2}$ ($\mathrm{Me_3SiCl}$ quench), which was of lower molecular weight (1425–1500), showed the resonances due to the terminal $\mathrm{Me_3Si}$ groups (5.17 ppm), the $\mathrm{Me_2Si}$ next to the $\mathrm{Me_3Si}$ groups (−1.53 ppm), and the $\mathrm{Me_2Si}$ groups further inward (−2.25 ppm). These values should be compared with the ^{29}Si NMR spectrum of $\mathrm{Me_3SiNMeSiMe_2NMeSiMe_2NMeSiMe_2NMeSiMe_3}$ which was isolated as a pure compound and, in $\mathrm{CDCl_3}$ solution, showed ^{29}Si resonances at δ_{Si} 4.97, −1.46, and −2.63).

It would appear that in the case of RK initiation of the ring-opening polymerization of hexamethylcyclodisilazane the propagation process (Scheme III) is complicated by "back-biting" of the reactive potassium amide chain terminus, a process which results in extrusion of cyclo-$\mathrm{(Me_2SiNMe)_3}$ as shown in Scheme IV in its simplest form. Presumably, only the potassium amide chain end (vs lithium or sodium amide) is reactive enough to effect such nucleophilic chain scission.

The chemistry of the organoalkali-initiated ring-opening polymerization of hexamethylcyclodisilazane does not appear to be a general process. The $\mathrm{R_2NLi}$ stoichiometric ring opening of cyclo-$\mathrm{(Me_2SiNMe)_2}$ is, as mentioned above, subject to steric hindrance. Thus, it was not surprising that attempted ring-opening polymerization of cyclo-$\mathrm{(Me_2SiNPr^i)_2}$ by 5 mol % *n*-BuLi in THF at room temperature, then at reflux, was unsuccessful. Obviously, the initially formed $\mathrm{R'SiMe_2NPr^iSiMe_2N(Pr^i)Li}$ intermediate is too hindered, so initiation is not followed by the propagation steps. Although this was not investigated, one would expect that bulky substituents on silicon also would prevent ring-opening polymerization of cyclodisilazanes by RLi.

Linear organosilicon polymers do not give ceramic residues in high yield when they are pyrolyzed if they do not contain functional substituents whose thermally induced reactions lead to extensive cross-linking during the initial stages of pyrolysis. Linear polysilazanes of the type prepared in this study do not contain such substituents, and thus it was not surprising that, as the TGA trace in Figure

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[11] Lochmann, L.; Pospisil, J.; Lim, D. *Tetrahedron Lett.* **1966**, 257.

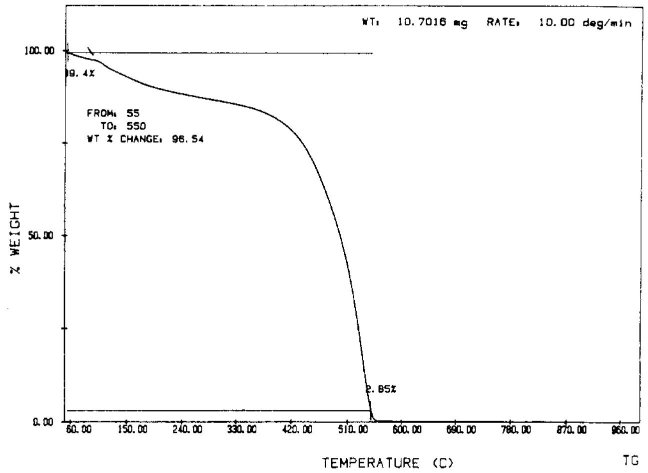

Figure 1. Pyrolysis of a Me(SiMe$_2$NMe)$_x$SiMe$_3$ polymer: TGA trace (under argon at 10 °C/min).

1 shows, there is no ceramic residue when they are pyrolyzed. Thus, as expected, linear polysilazanes with an R$_2$SiNR′ repeat unit are not useful preceramic polymers. Trapping of the volatile pyrolysis products of a Me$_3$Si-[NMeSiMe$_2$]$_x$NMeSiMe$_3$ polymer showed them to consist of cyclo-(Me$_2$SiNMe)$_2$ and cyclo-(Me$_2$SiNMe)$_3$, with the former predominating. The formation of these small cyclics can be rationalized either in terms (a) of a radical chain scission/back-biting process or (b) of a decomposition to give an unsaturated Me$_2$Si=NMe intermediate which then undergoes cycloaddition. It may be that the cyclic trimer is formed by process a and the cyclic dimer by process b.

Experimental Section

General Comments. All reactions were performed under a nitrogen atmosphere by using standard Schlenk techniques or a nitrogen-filled Vacuum Atmospheres drybox. All solvents were distilled under nitrogen from the appropriate drying agents. Chlorosilanes were purchased from Petrarch Systems, Inc. or Silar, and distilled from magnesium chips before use. Methyl- and *tert*-butyllithium were purchased from Aldrich. Organolithium reagents were titrated for RLi content by the Gilman double titration method. Unsolvated potassium *tert*-butoxide (Aldrich) and sodium *tert*-butoxide (Alfa) were used as received.

Gas chromatographic (GLC) analyses were performed on a Hewlett-Packard 5890A gas chromatograph equipped with a 6 ft, 0.25 in. column packed with 10% SE-30 silicone rubber gum on Chromosorb P. The internal standard method was used in yield determinations with a temperature program of 6 °C/min from 100 to 275 °C. Internal standards used were octane (C$_8$), nonane (C$_9$), and decane (C$_{10}$). Preparative GLC (Gow Mac 550 thermal conductivity detector gas chromatograph, 6 ft, 0.25 in. 10% SE-30 on Chromosorb P column) was used to collect samples for analysis and spectroscopy.

Proton NMR spectra were obtained either with a JEOL FX-90Q, a Bruker WM-250, or a Varian XL-300 NMR spectrometer using CDCl$_3$/CHCl$_3$ as a reference at 7.24 ppm downfield from tetramethylsilane. ^{29}Si NMR spectra (fully proton decoupled) were obtained by using a Varian XL-300 operating at 59.59 MHz in CDCl$_3$ or C$_6$D$_6$ with 0.05 M Cr(acac)$_3$ as a relaxation reagent. Tetramethylsilane (at 0.00 ppm) was used as an external standard. As indicated in the experiments below, some ^{29}Si NMR spectra were obtained by using a DEPT pulse sequence.[10]

Molecular weights were determined by cryoscopy in benzene at M.I.T. or by vapor pressure osmometry by Galbraith Laboratories, Knoxville, TN. Elemental analyses were performed by the Scandinavian Microanalytical Laboratory, Herlev, Denmark.

For the polymers, the "theoretical" analytical values are those calculated on the basis of the experimental molecular weights. Since the latter were only approximate, the agreement between calculated and found analytical values was not always good.

Preparation of Starting Materials. (a) Dimethylbis(methylamino)silane. A 1-L, three-necked flask equipped with a septum, an overhead mechanical stirrer, and a cold condenser (dry ice/acetone) was flame-dried under nitrogen and charged with 85.1 g (0.66 mol) of Me$_2$SiCl$_2$ and 400 mL of diethyl ether and cooled to 0 °C. Gaseous methylamine (Matheson) was bubbled into the solution through a 6-in. stainless-steel needle during the course of 3 h. The reaction mixture was allowed to warm to room temperature overnight. The precipitated [MeNH$_3$]Cl was filtered under nitrogen and washed with two 50-mL portions of ether. The combined organic phase was distilled to remove the Et$_2$O. The residue was distilled (1-ft. Vigreux column) to give 48.8 g (63%) of Me$_2$Si(NHMe)$_2$: bp 109 °C (lit.[12] bp 57–58 °C at 132 mmHg); ^{1}H NMR (90 MHz, CDCl$_3$) δ −0.07 (s, 6 H, Me$_2$Si), 0.44 (br s, 2 H, NH), 2.41 (s, 6 H, NMe).

(b) Dimethylbis(isopropylamino)silane. A similar reaction in which 26.2 g (0.2 mol) of Me$_2$SiCl$_2$ was added to 52.7 g (0.89 mol) of isopropylamine (Aldrich, distilled from CaO) in 400 mL of Et$_2$O gave 28.9 g (82%) of Me$_2$Si(NHPr^i)$_2$: bp 44 °C (10 mmHg) [lit.[13] bp 47–48 °C (11 mmHg)]; ^{1}H NMR (90 MHz, CDCl$_3$) δ −0.02 (s, 6 H, Me$_2$Si), 1.02 (d, J = 6.7 Hz, 12 H, Me$_2$C), 3.20 (br m, 2 H, NC*H*).

(c) Hexamethylcyclodisilazane. A 1-L, three-necked flask equipped with a mechanical stirrer, a condenser topped with a gas inlet tube (connecting to an oil bubbler in a Schlenk line), and a septum was flame-dried and charged with 24.73 g (0.21 mol) of Me$_2$Si(NHMe)$_2$ and 62 mL of hexane. By means of a 250-mL addition funnel 277 mL of 1.51 M "halide-free" methyllithium (0.42 mol) was added at 0 °C, dropwise over 2 h. After the mixture had been stirred at 0 °C for 2 h, 26.9 g (0.21 mol) of Me$_2$SiCl$_2$ was added dropwise at 0 °C. The reaction mixture was stirred and heated at reflux for 24 h. Filtration (or centrifugation) removed the LiCl. Removal of the solvent by trap-to-trap distillation (room temperature, 70 mmHg) was followed by distillation of the product, 23.8 g (65%) of cyclo-(Me$_2$SiNMe)$_2$: bp 50 °C (50 mmHg) or 60–62 °C (70 mmHg) (lit.[12] bp 52–52.5 °C at 51 mmHg); ^{1}H NMR (90 MHz, CDCl$_3$) δ 0.12 (s, 12 H, SiMe$_2$), 2.42 (s, 6 H, MeN); ^{13}C NMR (67.9 MHz, C$_6$D$_6$) δ_C 0.44 (q, J = 177.0 Hz, Me$_2$Si), 26.87 (q, J = 134.9 Hz, MeN); ^{29}Si NMR (59.59 MHz, C$_6$D$_6$, DEPT) δ_{Si} 8.06; IR (thin film) 2955 (m), 2900 (s), 2810 (s), 1435 (vw), 1250 (vs), 1190 (vs), 860 (vs), 840 (sh), 785 (vs), 675 (vw) cm^{-1}.

(d) *N,N′*-Diisopropyltetramethylcyclodisilazane. The reaction flask was charged with 15.06 g (0.086 mol) of Me$_2$Si(NHPr^i)$_2$ and 250 mL of Et$_2$O. *n*-Butyllithium (65 mL of 2.68 M in hexane, 0.173 mol) was added. After the resulting solution had been heated at reflux for 30 min, 11.2 g (0.087 mol) of Me$_2$SiCl$_2$ was added. The reaction mixture was stirred and heated at reflux for 3 h and then was centrifuged to separate the LiCl. The organic layer, after removal of the Et$_2$O was distilled (1-ft Vigreux column) to give 16.3 g (82%) of cyclo-(Me$_2$SiNPr^i)$_2$: bp 48.5 °C (2.5 mmHg); ^{1}H NMR (90 MHz, CDCl$_3$) δ 0.19 (s, 12 H, Me$_2$Si), 1.01 (d, J = 6.3 Hz, 12 H, Me$_2$C), 3.19 (sept, J = 6.3 Hz, 2 H, NCH), which agrees with the literature.[15]

Reaction of cyclo-(Me$_2$SiNMe)$_2$ with Methyllithium. (a) Trimethylchlorosilane Quench. A 50-mL, three-necked, round-bottomed flask equipped with a condenser topped with a gas inlet/outlet tube connected to an oil bubbler in a Schlenk line, a stir-bar, a glass stopper, and a septum (henceforth, the "standard reaction apparatus") was flame-dried and charged with 30 mL of THF and 13.0 mL of 1.51 M methyllithium (LiBr complex) (19.6 mmol) in diethyl ether. This solution was heated to reflux, and 0.873 g (5.0 mmol) of cyclo-(Me$_2$SiNMe)$_2$ was added dropwise by syringe during the course of 20 min. The resulting solution was heated at reflux for 25 min, and then 5.36 g (49.3 mmol) of Me$_3$SiCl was added. The reaction mixture was stirred and heated at reflux for 30 min. At this point, a GLC yield determination was carried out. The solvent then was removed by trap-to-trap distillation (room temperature under vacuum). The residue was extracted with 20 mL of hexane, and the extracts

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were filtered to remove LiCl. Distillation of the hexane left an oily residue from which the product was isolated by GLC (this is the "standard workup"). The GLC analysis (C_8 internal standard) showed the presence of one major product, identified as $Me_3SiNMeSiMe_2NMeSiMe_3$, in 70% yield. Anal. Calcd for $C_{10}H_{30}N_2Si_3$: C, 45.74; H, 11.51; N, 10.69. Found: C, 45.50; H, 11.33; N, 10.87. ^1H NMR (90 MHz, $CDCl_3$): δ 0.05 (s, 18 H, Me_3Si), 0.07 (s, 6 H, Me_2Si), 2.40 (s, 6 H, MeN).

(b) Dimethylchlorosilane Quench. The same procedure, with the exception that Me_2SiHCl was the chlorosilane used, gave $Me_3SiNMeSiMe_2NMeSiMe_2H$ in 83% yield. Anal. Calcd for $C_9H_{28}N_2Si_3$: C, 43.48; H, 11.35; N, 11.27. Found: C, 43.57; H, 11.39; N, 11.30. ^1H NMR (90 MHz, $CDCl_3$): δ 0.06 (s, 9 H, Me_3Si), 0.07 (s, 6 H, NMe_2SiN), 0.09 (d, *J* = 3.4 Hz, 6 H, *Me_2*SiH), 2.39, 2.41 (both s, 6 H, MeN), 4.42 (sept, *J* = 3.4 Hz, MeSi*H*).

(c) Dimethyldichlorosilane Quench. The same procedure was used except that Me_2SiCl_2 (an excess) was the chlorosilane added at the end. The product $Me_3SiNMeSiMe_2NMeSiMe_2Cl$ was obtained in 57% yield. Anal. Calcd for $C_9H_{27}N_2ClSi_3$: C, 38.19; H, 9.62; N, 9.90. Found: C, 38.54; H, 9.63; N, 9.92. ^1H NMR (250 MHz, $CDCl_3$) δ 0.069 (s, 9 H, $SiMe_3$), 0.15 (s, 6 H, $SiMe_2$), 0.46 (s, 6 H, $SiMe_2Cl$), 2.42 (s, 3 H, NMe), 2.49 (s, 3 H, NMe).

Reaction of this compound with an excess of CH_3NH_2 in hexane at −78 °C gave $Me_3SiNMeSiMe_2NMeSiMe_2NHMe$ in 79% yield. Anal. Calcd for $C_{10}H_{31}N_3Si_3$: C, 43.26; H, 11.26; N, 15.13. Found: C, 43.43; H, 11.17; N, 15.11. ^1H NMR (250 MHz, $CDCl_3$): δ 0.052 (s, 6 H, $SiMe_2$), 0.056 (s, 9 H, $SiMe_3$), 0.100 (s, 6 H, $SiMe_2$), 2.41 (s, 9 H, NCH_3).

Reaction of cyclo-($Me_2SiNMe)_2$ with *n*-Butyllithium. (a) Trimethylchlorosilane Quench. The standard reaction apparatus was charged with 30 mL of THF and cooled to 0 °C, and then 9.0 mL of 2.58 M *n*-butyllithium (23.2 mmol) in hexane was added. Subsequently, 1.28 g (7.33 mmol) of cyclo-$(Me_2SiNMe)_2$ was added. The reaction mixture was stirred at 0 °C for 30 min, and then 4.29 g (39.5 mmol) of Me_3SiCl was added by syringe. The resulting reaction mixture, from which LiCl had precipitated, was warmed to room temperature. The standard workup followed. The product *n*-$BuMe_2SiNMeSiMe_2NMeSiMe_3$ was obtained in 81% yield. Anal. Calcd for $C_{13}H_{36}N_2Si_3$: C, 51.24; H, 11.91; N, 9.19. Found: C, 51.30; H, 11.90; N, 9.38. ^1H NMR (90 MHz, $CDCl_3$): δ 0.04 (s, 6 H, *n*-Bu*Me_2*Si), 0.06 (s, 9 H, Me_3SiN), 0.08 (s, 6 H, $NSiMe_2N$), 0.68–1.42 (complex m, 9 H, *n*-Bu), 2.40 (s, 6 H, MeN).

(b) Dimethylchlorosilane Quench. The same procedure was used, but Me_2SiHCl was added to the end rather than Me_3SiCl. The product *n*-$BuMe_2SiNMeSiMe_2NMeSiMe_2H$ was obtained in 86% yield. Anal. Calcd for $C_{12}H_{34}N_2Si_3$: C, 49.76; H, 11.48; N, 9.67. Found: C, 49.73; H, 11.84; N, 9.44. ^1H NMR (90 MHz, $CDCl_3$): δ 0.04 (s, 6 H, *n*-Bu*Me_2*Si), 0.07 (s, 6 H, $NSiMe_2N$), 0.10 (d, *J* = 2.9 Hz, 6 H, Si*Me_2*H), 0.68–1.42 (complex m, 9 H, *n*-Bu), 2.39, 2.40 (both s, 6 H, MeN), 4.43 (complex m, 1 H, Me_2Si*H*).

Reaction of cyclo-$(Me_2SiNMe)_2$ with *tert*-Butyllithium. (a) Trimethylchlorosilane Quench. The standard reaction apparatus was charged with 30 mL of THF and cooled to −78 °C (dry ice/Me_2CO), and 10.0 mL of a 2.10 M solution of *tert*-butyllithium (21.0 mmol) in pentane was added. By syringe, 1.32 g (7.56 mmol) of cyclo-$(Me_2SiNMe)_2$ was added. The mixture was stirred at −78 °C for 30 min, and then the −78 °C bath was replaced with an ice bath. After the mixture had been stirred at 0 °C for 30 min, 4.29 g (39.5 mmol) of Me_3SiCl was added. The reaction mixture was warmed to room temperature. The standard workup showed that the expected product *t*-$BuMe_2SiNMeSiMe_2NMeSiMe_3$ had been formed in 87% yield. Anal. Calcd for $C_{13}H_{36}N_2Si_3$: C, 51.24; H, 11.91; N, 9.19. Found: C, 51.31; H, 11.91; N, 9.09. ^1H NMR (90 MHz, $CDCl_3$): δ 0.05 (s, 15 H, t-Bu*Me_2*Si and Me_3Si), 0.10 (s, 6 H, $NSiMe_2N$), 0.86 (s, 9 H, *t*-Bu), 2.41, 2.44 (both s, 6 H, MeN).

(b) Dimethylchlorosilane Quench. The same procedure, except that Me_2SiHCl was used instead of Me_3SiCl, gave *t*-$BuMe_2SiNMeSiMe_2NMeSiMe_2H$ in 80% yield. Anal. Calcd for $C_{12}H_{34}N_2Si_3$: C, 49.76; H, 11.48; N, 9.67. Found: C, 49.60; H, 11.83; N, 9.41. ^1H NMR (90 MHz, $CDCl_3$): δ 0.10 (d, *J* = 3.2 Hz, 6 H, *Me_2*SiH), 0.10 (s, 6 H, *t*-Bu*Me_2*Si), 0.19 (s, 6 H, $NSiMe_2N$), 0.91 (s, 9 H, *t*-Bu), 2.32, 2.41 (both s, 6 H, MeN), 4.67 (sept, *J* = 3.2 Hz, 1 H, Me_2Si*H*).

Reaction of cyclo-$(Me_2SiNMe)_2$ with Lithium Dimethylamide. The standard reaction apparatus was charged with 20 mL of THF and cooled to −78 °C (dry ice/Me_2CO). Dimethylamine (3 mL liquid, 2.04 g, 0.045 mol) at −78 °C was cannulated into the reaction flask. By syringe, 3.70 mL of a 2.32 M solution of *n*-BuLi (8.60 mmol) in hexane was added to this solution. The resulting Me_2NLi solution was warmed to room temperature and then was heated to reflux, and 0.923 g (5.29 mmol) of cyclo-$(Me_2SiNMe)_2$ was added by syringe, dropwise during the course of 20 min. The reaction mixture was cooled to room temperature, and 1.03 g (9.47 mmol) of Me_3SiCl was added. The standard workup followed. The product $Me_2NSiMe_2NMeSiMe_2NMeSiMe_3$ was obtained in 70% yield. Anal. Calcd for $C_{11}H_{33}N_3Si_3$: C, 45.30; H, 11.40; N, 14.41. Found: C, 45.02; H, 11.60; N, 14.36. ^1H NMR (250 MHz, $CDCl_3$): δ 0.17 (s, 12 H, $NSiMe_2N$), 0.20 (s, 9 H, Me_3Si), 2.40, 2.42 (both s, 6 H, SiNMeSi), 2.44 (s, 6 H, Me_2N).

Reaction of cyclo-$(Me_2SiNMe)_2$ with Lithium *N*-Methyl(trimethylsilyl)amide. The standard reaction apparatus was charged with 20 mL of THF and 0.786 g (7.61 mmol) of $Me_3SiNHMe$ and cooled to −78 °C. By syringe, 3.28 mL of a 2.32 M solution of *n*-BuLi in hexane (5.15 mmol) was added. After the mixture had been stirred for 10 min at −78 °C, it was warmed to room temperature and then heated to reflux. Hexamethylcyclodisilazane (0.9 g, 5.15 mmol) was added dropwise by syringe. After the mixture had been stirred for 30 min at reflux, 1.03 g (9.47 mmol) of Me_3SiCl was added. The standard workup followed. The product $Me_3SiNMeSiMe_2NMeSiMe_2NMeSiMe_3$ was obtained in 83% yield. Anal. Calcd for $C_{13}H_{39}N_3Si_4$: C, 44.63; H, 11.24; N, 12.01. Found: C, 44.84; H, 11.18; N, 12.13. ^1H NMR (90 MHz, C_6D_6): δ 0.19 (s, 18 H, Me_3Si), 0.25 (s, 12 H, $NSiMe_2N$), 2.44 (s, 9 H, MeN).

Reaction of cyclo-$(Me_2SiNMe)_2$ with $Me_3SiNMeSiMe_2NMeLi$. The standard reaction apparatus was charged with 25 mL of THF and cooled to 0 °C. By syringe, 3.0 mL of a 1.35 M solution of methyllithium (4.05 mmol) in Et_2O was added. Subsequently, 0.711 g (4.08 mmol) of cyclo-$(Me_2SiNMe)_2$ was added to the MeLi solution, dropwise over 10 min. The resulting solution was stirred for 20 min at 0 °C and then for 30 min at reflux. Another portion (0.60 g, 3.44 mmol) of cyclo-$(Me_2SiNMe)_2$ then was added. After this solution had been heated for 30 min at reflux, it was cooled to room temperature and 3.0 mL (23.7 mmol) of Me_3SiCl was added. After 30 min at room temperature the standard workup was done. GLC analysis (C_9 internal standard) showed the presence of two volatile products: $Me_3SiNMeSiMe_2NMeSiMe_3$ (14%), identified by its ^1H NMR spectrum (see above), and the pentasilazane, $Me_3SiNMeSiMe_2NMeSiMe_2NMeSiMe_2NMeSiMe_3$ (25%). The latter was isolated by GLC and characterized. Anal. Calcd for $C_{16}H_{48}N_4Si_5$: C, 43.98; H, 11.07; N, 12.82. Found: C, 43.84; H, 11.00; N, 13.08. ^1H NMR (250 MHz, $CDCl_3$): δ 0.05 (s, 18 H, Me_3Si), 0.07 (s, 18 H, Me_2Si), 2.4 (s, 12 H, MeN). ^{29}Si NMR (59.59 MHz, $CDCl_3$): δ_{Si} −2.63 (s, 1 Si, $SiMe_2$ central), −1.46 (s, 2 Si, $SiMe_2$ first from end), 4.97 (s, 2 Si, Me_3Si).

Reaction of cyclo-$(Me_2SiNPr^i)_2$ with Methyllithium. The standard reaction apparatus was charged with 25 mL of THF and 2.50 mL of a 1.66 M solution of MeLi in Et_2O (4.15 mmol). This solution was heated to reflux, and 0.430 g (1.87 mmol) of cyclo-$(Me_2SiNPr^i)_2$ was added. After the mixture had been stirred and heated at reflux for 30 min, 0.85 g (9.0 mmol) of Me_2SiHCl was added. The standard workup followed. The product $Me_3SiNPr^iSiMe_2NPr^iSiMe_2H$ was obtained in 64% yield. Anal. Calcd for $C_{13}H_{36}N_2Si_3$: C, 51.26; H, 11.91; N, 9.20. Found: C, 51.37; H, 11.90; N, 9.32. ^1H NMR (250 MHz, $CDCl_3$): δ 0.14 (s, 9 H, Me_3Si), 0.17 (d, *J* = 3.6 Hz, 6 H, *Me_2*SiH), 0.19 (s, 6 H, $NSiMe_2N$), 1.15 (d, *J* = 6.7 Hz, 6 H, *Me_2*CH), 1.17 (d, *J* = 6.7 Hz, 6 H, *Me_2*CH), 3.46 (sept, *J* = 6.7 Hz, 2 H, Me_2C*H*), 4.53 (sept, *J* = 3.7 Hz, Me_2SiH).

Reaction of cyclo-$(Me_2SiNPr^i)_2$ with *n*-Butyllithium. Using the same procedure, the reaction of 0.865 g (3.76 mmol) of cyclo-$(Me_2SiNPr^i)_2$ in 25 mL of THF with 4.20 mmol of *n*-BuLi in hexane was carried out at room temperature. Addition of 0.87 g (9.20 mmol) of Me_2SiHCl and the standard workup followed. The product *n*-$BuMe_2SiNPr^iSiMe_2NPr^iSiMe_2H$ was obtained in 67% yield. Anal. Calcd for $C_{16}H_{42}N_2Si_3$: C, 55.42; H, 12.21; N, 8.08. Found: C, 55.34; H, 12.14; N, 8.20. ^1H NMR (250 MHz, $CDCl_3$): δ 0.13 (s, 6 H, *n*-Bu*Me_2*Si), 0.17 (d, *J* = 3.6 Hz, 6 H, *Me*$_2$SiH), 0.20 (s, 6 H, NSi*Me*$_2$N), 0.60–1.42 (complex m, 9 H, *n*-*Bu*), 1.15, 1.17 (both d, *J* = 6.7 Hz, 12 H, *Me*$_2$CH), 3.47 (sept, *J* = 6.7 Hz, 12 H, Me$_2$C*H*), 4.53 (sept, *J* = 3.6 Hz, 1 H, Me$_2$Si*H*).

A trimethylchlorosilane quench of such a cyclo-(Me$_2$SiNPr^i)$_2$/*n*-BuLi reaction mixture gave *n*-BuMe$_2$SiNPr^{i}SiMe$_2$NPr^{i}SiMe$_3$ in 60% yield. Anal. Calcd for $C_{17}H_{44}N_2Si_3$: C, 56.59; H, 12.29; N, 7.76. Found: C, 56.50; H, 12.28; N, 7.84. ^{1}H NMR (250 MHz, CDCl$_3$): δ 0.14 (s, 6 H, *n*-Bu*Me*$_2$Si), 0.15 (s, 9 H, Me$_3$Si), 0.21 (s, 6 H, NSiMe$_2$N), 0.60–1.42 (complex m, 9 H, *n*-Bu), 1.17 (d, *J* = 6.0 Hz, 12 H, *Me*$_2$CH), 3.52, 3.57 (both sept, *J* = 6.0 Hz, 2 H, Me$_2$C*H*).

Attempted Reaction of cyclo-(Me$_2$SiNMe)$_2$ with Lithium Bis(trimethylsilyl)amide. The standard reaction apparatus was charged with 20 mL of THF and 2.50 mL of (Me$_3$Si)$_2$NH (1.93 g, 0.012 mol) and cooled to −78 °C in a dry ice/acetone bath. By syringe, 4.50 mL of a 2.66 M solution of *n*-butyllithium (12.0 mmol) in hexane was added over 5 min. The dry ice/acetone bath was removed after 15 min, and the reaction mixture was warmed to room temperature and then heated to reflux. By syringe, cyclo-(Me$_2$SiNMe)$_2$ (0.961 g, 5.51 mmol) was added dropwise over 30 min. After an additional 16 h at reflux, the reaction mixture was cooled to room temperature and trimethylchlorosilane (1.58 mL, 1.36 g, 12.50 mmol) was added. A white precipitate formed. The GLC analysis (internal standard C$_9$) of the reaction mixture showed the presence of unreacted (Me$_2$SiNMe)$_2$ in 100% yield, which was identified by comparison of its ^{1}H NMR spectrum with that of an authentic sample.

Reaction of cyclo-(Me$_2$SiNMe)$_2$ with *n*-Butyllithium/Sodium *tert*-Butoxide. (a) Trimethylchlorosilane Quench. The standard apparatus, equipped also with a low-temperature thermometer, was charged with 0.905 g (9.42 mmol) of *t*-BuONa and 40 mL of THF and, after cooling to −78 °C, 3.66 mL of a 2.57 M solution of *n*-BuLi in hexane (9.42 mmol). After 5 min, 0.816 g (4.68 mmol) of cyclo-(Me$_2$SiNMe)$_2$ was added. The mixture was warmed to −15 °C, at which point the cyclodisilazane dissolved. After 10 min trimethylchlorosilane (2.14 g, 19.7 mmol) was added, and the reaction mixture was stirred at room temperature for 30 min. Standard workup showed the presence of *n*-BuMe$_2$SiNMeSiMe$_2$NMeSiMe$_3$ in 87% yield. The product had proton NMR and IR spectra identical with those of an authentic sample (see above).

(b) Vinyldimethylchlorosilane Quench. Essentially the same procedure as in (a) was used, except that only 10% of the cyclo-(Me$_2$SiNMe)$_2$ was added at −78 °C and the rest at −15 °C. Also, ViMe$_2$SiCl was used in place of Me$_3$SiCl. The product *n*-BuMe$_2$SiNMeSiMe$_2$NMeSiMe$_2$Vi was obtained in 68% yield. Anal. Calcd for $C_{14}H_{36}N_2Si_3$: C, 53.09; H, 11.46; N, 8.84. Found: C, 52.92; H, 11.46; N, 9.23. ^{1}H NMR (250 MHz, CDCl$_3$): δ 0.04 (s, 6 H, *n*-Bu*Me*$_2$Si), 0.08 (s, 6 H, NSiMe$_2$N), 0.13 (s, 6 H, Si*Me*$_2$Vi), 0.54 (t, 2 H, *n*-PrC*H*$_2$Si), 0.86 (t, 3 H, CH$_3$ of *n*-Bu), 1.27 (br m, 6 H, internal CH$_2$CH$_2$ of *n*-Bu), 2.4 (s, 6 H, MeN), 5.6–6.3 (complex m, 3 H, CH$_2$=CH).

Reaction of cyclo-(Me$_2$SiNMe)$_2$ with Methyllithium/Sodium *tert*-Butoxide. (a) Trimethylchlorosilane Quench. The same procedure was used as in (b) immediately above, except that methyllithium in Et$_2$O was used in place of *n*-BuLi and Me$_3$SiCl was the chlorosilane added. The product Me$_3$SiNMeSiMe$_2$NMeSiMe$_3$, a known compound (see above), was obtained in 70% yield. Its ^{1}H NMR spectrum was identical with that reported above.

(b) Vinyldimethylchlorosilane Quench. The same procedure as that described immediately above was used, except that ViMe$_2$SiCl was the chlorosilane used. The product Me$_3$SiNMeSiMe$_2$NMeSiMe$_2$Vi was obtained in 60% yield. Anal. Calcd for $C_{11}H_{30}N_2Si_3$: C, 48.10; H, 11.00; N, 10.20. Found: C, 48.09; H, 11.17; N, 10.55. ^{1}H NMR (250 MHz, CDCl$_3$): δ 0.05 (s, 9 H, Me$_3$Si), 0.08 (s, 6 H, NSiMe$_2$N), 0.13 (s, 6 H, Si*Me*$_2$Vi), 2.4 (s, 6 H, MeN), 5.6–6.3 (complex m, 3 H, CH$_2$=CH).

Reaction of cyclo-(Me$_2$SiNMe)$_2$ with Methyllithium/Potassium *tert*-Butoxide. The standard apparatus was charged with 1.04 g (9.27 mmol) of *t*-BuOK and 30 mL of THF. To this solution, cooled to −78 °C, was added 17.0 mL of a 0.545 M solution of MeLi in Et$_2$O (9.27 mmol). After 5 min, one-tenth of a solution of 1.645 g (9.43 mmol) of cyclo-(Me$_2$SiNMe)$_2$ was added by syringe. The mixture then was warmed to −15 °C, and the rest of the cyclodisilazane solution was added. The resulting mixture was warmed to room temperature, and now 1.20 g (11.1 mmol) of Me$_3$SiCl was added. After 30 min, the standard workup gave 3.26 g of a clear, very viscous oily solid. This was diluted with THF and trap-to-trap distilled to give 2.1 g of a clear, yellowish liquid. GLC analysis showed Me$_3$SiNMeSiMe$_2$NMeSiMe$_3$ (see above) to be present in 60% yield.

Ring-Opening Polymerization of cyclo-(Me$_2$SiNMe)$_2$. (1) With Organolithium Reagents. The general procedure was as follows.

The standard reaction apparatus was charged with the solvent and cooled (either to 0 °C or −78 °C), and then the (Me$_2$SiNMe)$_2$ was added by syringe. Subsequently, the organolithium reagent solution was added, and the reaction mixture was stirred at room temperature and then at the reflux temperature for some hours. The chlorosilane, generally an excess, then was added to "kill" the living polymer (LiCl precipitated), and the mixture was stirred at room temperature for 30–60 min. Volatiles were removed at reduced pressure, leaving a white solid which then was extracted with 15–20 mL of hexane. The extracts were centrifuged to remove LiCl, and the supernatant solution was distilled (trap-to-trap in vacuo), leaving, generally, a white, waxy solid. The latter was soluble in organic solvents such as hexane, benzene, chloroform, carbon tetrachloride, and THF.

(a) 10% MeLi in THF. Hexamethylcyclodisilazane (1.546 g, 8.9 mmol) and 0.66 mL of 1.35 M (0.89 mmol) of MeLi in diethyl ether were allowed to react in 25 mL of THF (2.5 h at reflux). Trimethylchlorosilane (0.26 g, 2.4 mmol) was added. Workup gave 1.148 g (75% yield) of a white, waxy solid. Anal. Calcd: C, 42.33; H, 10.66; N, 14.81. Found: C, 40.65; H, 9.85; N, 14.02. ^{1}H NMR (250 MHz, CDCl$_3$): δ 0.11 (s, 2.2 H, SiMe), 2.39 (s, 1 H, NMe). ^{29}Si NMR (59.59 MHz, DEPT, CDCl$_3$): δ_{Si} −2.18 (s, SiMe$_2$), −1.4 (s, Me$_3$SiNMe*Si*Me$_2$–), 5.2 (s, SiMe$_3$). Mol wt (cryoscopy): 1140 (calcd from monomer/RLi ratio 1735).

(b) 5% Methyllithium in THF. (Me$_2$SiNMe)$_2$ (1.743 g, 9.99 mmol) and 0.39 mL of 1.30 M MeLi (0.51 mmol) in Et$_2$O were allowed to react in 25 mL of THF (mixed at −78 °C and at reflux for 4 h); 1.72 g (15.8 mmol) of Me$_3$SiCl was added. Workup gave a white, waxy solid (1.65 g, 94% yield). Mol wt (cryoscopy): 3000–3200 (calcd from monomer/RLi ratio 3400).

(c) 5% *n*-Butyllithium in THF. (Me$_2$SiNMe)$_2$ (0.468 g, 2.68 mmol) and 53 mL of 2.52 M (0.13 mmol) of *n*-BuLi in hexane were allowed to react in 25 mL of THF, initially at −78 °C and then, after slow warming, at reflux for 1 h. Dimethylchlorosilane (20 mg, 0.18 mmol) was added. Workup gave 0.414 g (89%) of a white, waxy solid. Anal. Calcd: C, 41.80; H, 10.00; N, 14.82. Found: C, 40.78; H, 9.39; N, 14.59. ^{1}H NMR (300 MHz, C$_6$D$_6$): δ 0.36 (s, 2 H, SiMe), 2.56 (s, 1 H, NMe). ^{13}C NMR (67.9 MHz, C$_6$D$_6$): δ_C 1.94 (q, *J* = 118.3 Hz, SiMe), 30.25 (q, *J* = 136.0 Hz, NCH$_3$). ^{29}Si NMR (59.59 MHz, DEPT, C$_6$D$_6$): δ_{Si} −1.82. Mol wt (VPO): 1500.

(d) 10% *n*-Butyllithium in Hexane. (Me$_2$SiNMe)$_2$ (1.831 g, 10.5 mmol) and 0.45 mL of 2.42 M (1.1 mmol) of *n*-BuLi in hexane were allowed to react in 30 mL of hexane (initially at 0 °C and then at reflux for 1 h). Trimethylchlorosilane (23.7 mmol) was added. Workup gave 1.67 g (91%) of a white, waxy solid. ^{1}H NMR (250 MHz, CDCl$_3$): δ 0.12 (s, 6.2 H, SiMe), 0.4–1.25 (complex m, 1 H, C$_4$H$_9$), 2.39 (s, 2.8 H, NMe). Mol wt (cryoscopy): 1020 (calcd 1680).

(2) With the RLi/Me$_3$CONa Reagent. The standard reaction apparatus was charged with the sodium *tert*-butoxide and the THF, and the solution was cooled to −78 °C. Subsequently, an equimolar quantity of the organolithium reagent was added, and the mixture was stirred at −78 °C for a few minutes. One-tenth of the total amount of the (Me$_2$SiNMe)$_2$ to be added then was introduced by syringe. The dry ice/acetone bath was removed, and the rest of the cyclodisilazane was added at −15 °C over a period of 10 min. The reaction mixture was allowed to warm to room temperature, and then an excess of a chlorosilane was added. After 30 min of stirring the volatiles were removed at reduced pressure. The residue was extracted with hexane. Centrifugation and removal of hexane at reduced pressure generally left a white waxy solid.

(a) 10% MeLi/Me$_3$CONa. (Me$_2$SiNMe)$_2$ (2.036 g, 11.67 mmol), 0.11 g (1.14 mmol) of Me$_3$CONa, and 2.1 mL of 1.35 M (1.14 mmol) of MeLi in Et$_2$O were allowed to react in 25 mL of

THF, initially at −78 °C and then at room temperature. Trimethylchlorosilane (2.37 mmol) was added. Workup gave 1.737 g (85%) of a white, waxy solid. Anal. Calcd: C, 41.96; H, 10.56; N, 15.29; Si, 32.19. Found: C, 40.95; H, 9.38; N, 13.89; Si, 33.18. ^{1}H NMR (250 MHz, $CDCl_3$): δ 0.12 (s, 2.15 H, SiMe), 2.39 (s, 1 H, NMe). ^{29}Si NMR (59.59 MHz, DEPT, $CDCl_3$): δ_{Si} −2.25 (s, inner $SiMe_2$), −1.53 (s, $Me_3SiNMe\mathit{Si}Me_2$–), 5.17 (s, $SiMe_3$). Mol wt (cryscopy): 1425–1500 (calcd 1780). Ceramic yield (by TGA, to 950 °C at 10 °C/min under argon): 0%.

In another such experiment, the living polymer was quenched with $Me_2(CH_2{=}CH)SiCl$ to give a polymer with a $SiMe_2CH{=}CH_2$ end group as a white, waxy solid in 97% yield, mol wt 1960.

(b) 10% *n*-BuLi/Me_3CONa. $(Me_2SiNMe)_2$ (0.90 g, 5.2 mmol), 0.05 g (0.52 mmol) of Me_3CONa, and 0.20 mL of 2.57 M (0.52 mmol) of *n*-BuLi in hexane were allowed to react in 30 mL of THF, initially at −78 °C and then at room temperature. Trimethylchlorosilane (0.13 g, 0.12 mmol) was added. Workup gave 0.833 g (93%e of a white, waxy solid. Anal. Calcd: C, 42.94; H, 10.65; N, 14.95. Found: C, 41.91; H, 10.03; N, 14.03. ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.13 (s, 2 H, SiMe), 2.40 (s, 1 H, NMe). ^{1}H NMR (400 MHz, C_6D_6): δ 0.35 (s, 2 H, SiMe), 2.56 (s, 1 H, NMe). ^{29}Si NMR (59.59 MHz, DEPT, $CDCl_3$): δ_{Si} −2.25; in C_6D_6, δ_{Si} −1.79. Mol wt (cryoscopy): 1580 (calcd 1730).

A similar reaction in which $Me_2(CH_2{=}CH)SiCl$ was used in place of Me_3SiCl gave a white, waxy solid, molecular weight around 1550.

(c) 5% *n*-BuLi/Me_3CONa. The same procedure as above was used except that 5% *n*-BuLi/Me_3CONa (0.25 mmol/4.9 mmol of $(Me_2SiNMe)_2$) was used. A white, tacky solid (0.875 g, 100%) was obtained. Anal. Calcd: C, 42.18; H, 10.53; N, 15.47. Found: C, 42.31; H, 9.89; N, 15.12. ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.12 (s, 2 H, SiMe), 2.40 (s, 1 H, NMe). ^{1}H NMR (400 MHz, C_6D_6): δ 0.36 (s, 2 H, SiMe), 2.56 (s, 1 H, NMe). ^{29}Si NMR (59.59 MHz, $CDCl_3$): δ_{Si} −2.27; in C_6D_6 δ_{Si} −1.79.

Reaction of cyclo-$(Me_2SiNMe)_2$ with 20% *n*-Butyllithium/Potassium *tert*-Butoxide in THF. Trimethylchlorosilane Quench. The standard reaction apparatus was charged with potassium *tert*-butoxide (0.054 g, 0.50 mmol) in the drybox, connected to a nitrogen line, and cooled to −78 °C in a dry ice/acetone bath. By syringe, 15 mL of THF was added and then 0.21 mL of a 2.40 M solution of *n*-butyllithium (0.50 mmol) in hexane was added. After 5 min, cyclo-$(Me_2SiNMe)_2$ (0.428 g, 2.45 mmol) was added all at once. The cyclodisilazane was frozen in the reaction mixture. The bath was removed and the reaction mixture warmed until the cyclodisilazane dissolved. The −78 °C bath was replaced and the reaction mixture cooled again to −78 °C. A GLC analysis of the reaction mixture showed no remaining cyclodisilazane, so trimethylchlorosilane (0.13 g, 1.20 mmol) was added and the bath was removed. The reaction mixture was warmed to room temperature and a white precipitate formed. The standard workup was done. A GLC analysis (internal standard C_9) of the reaction mixture showed the presence of one major product, $(Me_2SiNMe)_3$ (0.40 g, 1.5 mmol, 94% based on the conversion of 3 equiv of the cyclodisilazane to 2 equiv of the cyclotrisilazane), which was identified by comparison of its ^{1}H NMR spectrum and melting point (34 °C; lit.[12] 33–34 °C) with those of an authentic sample.

Reaction of cyclo-$(Me_2SiNMe)_2$ with 10% KH in THF. The standard reaction apparatus was charged with 30 mL of THF and 0.02 g of KH (0.05 mmol). By syringe cyclo-$(Me_2SiNMe)_2$ (0.892 g, 5.11 mmol) was added over 20 min. After an additional 1 h at room temperature, the KH was still present as an insoluble solid in the reaction mixture which settled rapidly when the reaction mixture was not stirred. A GLC analysis of the supernatant solution showed that cyclo-$(Me_2SiNMe)_2$ had completely reacted and a new product was present. Methyl iodide (1.0 mL, 2.28 g, 16.2 mmol) was added. No precipitate formed. A standard workup of the reaction mixture was performed to remove the unreacted KH. The GLC analysis (internal standard C_{10}) of the reaction mixture showed the presence of one major product, cyclo-$(Me_2SiNMe)_3$ (0.895 g, 3.42 mmol, 89% based on the conversion of 3 equiv of the cyclodisilazane to 2 equiv of the cyclotrisilazane), which was GC collected and identified by comparison of its ^{1}H NMR spectrum and melting point (34 °C; lit.[12] 33–34 °C) with those of an authentic sample. Another lower boiling minor product was also present by GLC analysis, but in a quantity too small to collect and identify.

Attempted Polymerization of cyclo-$(Me_2SiNPr^i)_2$ with 5% Methyllithium in THF. Trimethylchlorosilane Quench. The standard reaction apparatus was charged with 20 mL of THF and 0.972 g of cyclo-$(Me_2SiNPr^i)_2$ (4.22 mmol), and the reaction mixture was heated to reflux. By syringe, 0.13 mL of a 1.59 M solution of methyllithium (0.21 mmol) in Et_2O was added. After an additional 18 h at reflux, trimethylchlorosilane (0.030 mL, 0.026 g, 0.21 mmol) was added. A white precipitate formed. The standard workup of the reaction mixture was performed. The GLC analysis (internal standard C_9) of the reaction mixture showed the presence of one major product, unreacted cyclo-$(Me_2SiNPr^i)_2$ (0.885 g, 3.84 mmol, 91%), which was identified by comparison of its ^{1}H NMR spectrum with that of an authentic sample.

The same result was observed when *n*-butyllithium was used in place of methyllithium.

Pyrolysis of a $Me(SiMe_2NMe)_xSiMe_3$ Polymer. A 4.604-g sample of the polymer (mol wt 1425–1500) was divided between two silica boats and pyrolyzed in a stream of nitrogen in a Lindberg tube furnace equipped with a controller (30–300 °C at 10 °C/min; 30 min at 300 °C; 300–700 °C at 10 °C/min). The exit end of the pyrolysis tube led to two traps that were immersed in liquid nitrogen. Upon completion of the pyrolysis the tubes were found to contain white solids. These were dissolved in diethyl ether. Evaporation of most of the ether at reduced pressure left a concentrated solution of the volatile pyrolysis products. This solution was examined by GLC. Two products were present. These were collected, and yields were determined (*n*-nonane internal standard): cyclo-$(Me_2SiNMe)_2$ (38% yield) and $(Me_2SiNMe)_3$ (12% yield). They were identified by comparison of their IR and ^{1}H NMR spectra with those of authentic samples.[12]

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Registry No. 1, 1073-92-3; 2, 98689-74-8; 3 (R = Me, R' = Me), 121270-00-6; 4 (R = Me, R' = Me, R′ = Me), 920-75-2; 4 (R = Me, R' = Me, R′ = H), 121269-92-9; 4 (R = Me, R' = Me, R′ = Cl), 121269-93-0; 4 (R = Me, R' = Me, R′ = NHMe, 121269-94-1; 4 (R = Me, R' = *n*-Bu, R′ = Me), 121269-95-2; 4 (R = Me, R' = *n*-Bu, R′ = H), 121269-96-3; 4 (R = Me, R' = *t*-Bu, R′ = Me), 121269-97-4; 4 (R = Me, R' = *t*-Bu, R′ = H), 121269-98-5; 4 (R = Me, R' = NMe_2, R′ = Me, 121269-99-6; 4 (R = Pr-*i*, R' = Me, R′ = H), 121270-01-7; 4 (R = Pr-*i*, R' = *n*-Bu, R′ = H), 121270-02-8; 4 (R = Pr-*i* R' = *n*-Bu, R′ = Me), 121270-03-9; Me_2SiCl_2, 75-78-5; $Me_2Si(NHMe)_2$, 10519-99-0; $Me_2Si(NHPr^i)_2$, 6026-42-2; Me_3SiCl, 75-77-4; Me_2SiHCl, 1066-35-9; Me_2NLi, 3585-33-9; $Me_3SiNMeSiMe_2NMeSiMe_2NMeSiMe_3$, 30725-39-4; $Me_3SiNMeSiMe_2NMeSiMe_2NMeSiMe_2NMeSiMe_3$, 30746-48-6; *n*-$BuMe_2SiNMeSiMe_2NMeSiMe_2Li$, 121270-04-0; $Me_3SiNMeSiMe_2NMeSiMe_2Li$, 121270-05-1; $Me_3SiNMe(SiMe_2NMe)_nSiMe_3$, 121270-06-2; *n*-$BuMe_2SiNMe(SiMe_2NMe)_nSiMe_2H$, 121270-07-3; *n*-$BuMe_2SiNMe(SiMe_2NMe)_nSiMe_3$, 121270-08-4; $Me_3SiNMe(SiMe_2NMe)_nSiMe_2CH{=}CH_2$, 121270-09-5; *n*-$BuMe_2SiNMe(SiMe_2NMe)_nSiMe_2CH{=}CH_2$, 121270-10-8; $(Me_2SiNMe)_3$, 1080-38-2; methylamine, 74-89-5; isopropylamine, 75-31-0; methyllithium, 917-54-4; *n*-butyllithium, 109-72-8; *tert*-butyllithium, 594-19-4; lithium *N*-methyl(trimethylsilyl)amine, 10568-44-2; lithium bis(trimethylsilyl)amine, 4039-32-1; sodium *tert*-butoxide, 865-48-5; vinyldimethylchlorosilane, 1719-58-0.