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Synthesis of an Azadisilacyclopropane and Two Cyclodisilazanes from 1,1,2,2-Tetrachloro-1,2-dimesityldisilane

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1,1,2,2-Tetrachloro-1,2-dimesityldisilane (1) was synthesized from 2.1 equiv of MesLi·Et$_2$O and Si$_2$Cl$_6$. Reaction of 1 with two MesNHLi at −78 °C in THF afforded *trans*-2-chloro-1,2,3,4-tetramesitylcyclodisilazane (**4a**), 21%, *cis*-2-chloro-1,2,3,4-tetramesitylcyclodisilazane (**4b**), 4%, and *trans*-2,3-bis(mesitylamino)-1,2,3-trimesitylazadisilacyclopropane (**5**), 26%. When 1 equiv of MesNHLi was used, **1**, **4a**, and **4b** were the major species present. Use of 4 equiv of MesNHLi led mainly to the formation of **5** (80%). The molecular structure of **5**·2C$_6$H$_6$ was determined by X-ray crystallographic analysis. Compound **5**·2C$_6$H$_6$ crystallized in the monoclinic space group $C2/c$ with cell parameters $a = 21.887(6)$ Å, $b = 12.364(3)$ Å, $c = 18.878(5)$ Å, $\beta = 101.44(2)°$, $V = 5007(2)$ Å^3, $Z = 4$, d(calcd) = 1.131 g/cm^3, and $R = 4.98\%$.

Introduction

The cyclosilazane family of ring compounds, with alternating silicon and nitrogen atoms, have long been known.[1–3] These are prepared most simply by the reaction of amines with dihalosilanes but are also obtainable by many other routes.[1] Recently, along with the growing interest in small-ring organosilicon compounds,[4] several new classes of Si–N rings have been synthesized. These include a diazasilacyclopropane,[5] a 1,2-diaza-3,4-disilacyclobutane,[6] and several azadisilacyclopropanes,[7] the last obtained by the reaction of disilene with covalent azides. The short Si–Si bond distances in the Si$_2$N ring, and in the related Si$_2$O cycles,[8] have spurred theoretical interest leading to several theoretical treatments of chemical bonding in these molecules.[9]

In this paper we report the reaction of *N*-lithio-2,4,6-trimethylaniline with 1,1,2,2-tetrachloro-1,2-dimesityldisilane, leading unexpectedly to cyclic products: two cyclodisilazane isomers and an azadisilacyclopropane.

Experimental Section

General Considerations. All manipulations were performed using standard Schlenk techniques under an atmosphere of nitrogen or argon. All liquids were transferred using a syringe or cannula. Toluene, THF, diethyl ether, *n*-hexane, and benzene were distilled from sodium benzophenone ketyl under nitrogen. Si$_2$Cl$_6$ was distilled from anhydrous K$_2$CO$_3$ under reduced pressure prior to use. MesNH$_2$ was distilled under reduced pressure from NaOH prior to use. Infrared spectra were recorded on a Mattson Polaris FTIR using NaCl plates. ^{29}Si NMR spectra were obtained on a Bruker WP-270 spectrometer using INEPT pulse sequences and were referenced to external tetramethylsilane. ^{13}C NMR spectra were recorded on a Varian Gemini 300-MHz spectrometer. ^{1}H NMR spectra were recorded on a Bruker WP-200 spectrometer and were referenced to the residual solvent proton resonances which were calibrated against tetramethylsilane. High resolution mass spectra were recorded on a Kratos MS-80 spectrometer. Reported melting points are uncorrected. *n*-BuLi was titrated before use. MesLi·Et$_2$O was prepared as described in the literature, except the 200-mL benzene wash was replaced with 2 × 50 mL hexane washes.[10]

1,1,2,2-Tetrachloro-1,2-dimesityldisilane (1). To a toluene suspension (90 mL) of MesLi·Et$_2$O (10.9 g, 54.6 mmol) was added Si$_2$Cl$_6$ (7.00 g, 26.0 mmol) via syringe, and the mixture was refluxed for 16 h. The solution was filtered under a nitrogen blanket, and the toluene was removed under reduced pressure. The crude residue was recrystallized from 20/2 mL of hexanes–diethyl ether at −20 °C to give 1 in an isolated yield of 5.11 g (45%, 11.7 mmol). Analytical data for 1: ^{1}H NMR (δ, in C$_6$D$_6$) 6.49 (s, 4 H), 2.53 (s, 12 H), 1.91 (s, 6 H); INEPT ^{29}Si NMR (δ, in C$_6$D$_6$, 53.67 MHz vs external TMS) 4.66; ^{13}C NMR (δ, in C$_6$D$_6$, 75 MHz) 21.0 (*p*-CH$_3$), 25.2 (*o*-CH$_3$), 126.5 (C–Si), 130.4 (C–H), 142.4 (*C*-*p*-CH$_3$), 144.9 (*C*-*o*-CH$_3$); exact mass for C$_{18}$H$_{22}$^{35}Cl$_3$^{36}ClSi$_2$ calculated *m*/*e* 435.9985, found 435.9981; mp 100–2 °C.

***cis*-2-Chloro-1,2,3,4-tetramesitylcyclodisilazane (4a).** MesNH$_2$ (0.88 g, 6.50 mmol) was dissolved in THF (20 mL), and the solution was cooled to −78 °C in a dry ice/2-propanol bath. *n*-BuLi (5.1 mL, 1.27 M) was added via syringe to the MesNH$_2$ solution. The resulting white suspension of MesNHLi was stirred for 45 min and rapidly cannulated into a THF (20 mL) solution of 1 (1.42 g, 3.25 mmol) also at −78 °C. The precipitate rapidly disappeared, and the solution became yellow. The reaction mixture was stirred for 1 h at −78 °C and slowly warmed to room

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Table I. Summary of Crystal Data Collection for 5

empirical formula	$C_{45}H_{57}N_3Si_2 \cdot 2(C_6H_6)$
fw	852.3
cryst syst	monoclinic
space group	$C2/c$
b, Å	21.887(6)
b, Å	12.364(3)
c, Å	18.878(5)
β, deg	101.42(2)
V, Å^3	5007(2)
Z	4
d(calcd), g/cm^3	1.131
cryst size, mm	0.6 × 0.5 × 0.4
color; habit	colorless block
abs coeff, mm^{-1}	0.105
F(000)	1840
T, °C	−160(2)
2θ range, deg	4.0–50.0
scan type	Wyckoff
scan speed, deg/min	variable, 2.00–20.00
scan range (ω), deg	0.80
index ranges	$-26 \leq h \leq 1, 0 \leq k \leq 14, -22 \leq l \leq 22$
no. of reflns collected	5016
no. of indep reflns	4411 (R_{int} = 1.65%)
final R indices (obs data), %	$R = 4.98$, $R_w = 6.87$
goodness of fit	1.95
largest and mean Δ/σ	0.001, 0.000
data-to-param ratio	12.3:1
largest diff peak/hole, e Å^{-3}	0.43/−0.45

temperature. After 12 h of stirring, the solution was colorless. The THF was removed under reduced pressure, the residue was redissolved in diethyl ether (30 mL), and the solution was filtered under a nitrogen atmosphere. The diethyl ether was removed under reduced pressure, the residue was dissolved in 30 mL of hot n-hexane, and the solution was cooled to −20 °C to give **4a** in an isolated yield of 0.40 g (21%, 0.67 mmol). Analytical data for **4a**: ^1H NMR (δ, in C_6D_6) 6.93 (s, 1 H), 6.69 (s, 4 H), 6.56 (s, 2 H), 6.50 (s, 2 H), 2.45 (s, 18 H), 2.31 (s, 6 H), 2.07 (s, 6 H), 1.95 (s, 3 H), 1.93 (s, 3 H); INEPT ^{29}Si NMR (δ, in C_6D_6, 53.67 MHz vs external TMS) −25.21, −26.50 ($^1J_{Si-H}$: −241.7 Hz); exact mass for $C_{36}H_{47}ClN_2Si_2$ calculated m/e 596.2810, found 596.2789; mp 160 °C (dec); IR (cm^{-1}, Nujol) 2159.5 (Si–H).

***trans*-2-Chloro-1,2,3,4-tetramesitylcyclodisilazane (4b).** After isolation of **4a**, the mother liquor was stripped, the residue was redissolved in 10 mL of n-hexane, and the solution was cooled to −20 °C. This procedure yielded 0.08 g (4%, 0.13 mmol) of **4b**. Analytical data for **4b**: ^1H NMR (δ, in C_6D_6) 6.91 (s, 1 H), 6.69 (s, 4 H), 6.57 (s, 2 H), 6.54 (s, 2 H), 2.52 (broad, 12 H), 2.44 (s, 6 H), 2.36 (s, 6 H), 2.08 (s, 6 H), 1.97 (s, 6 H); INEPT ^{29}Si NMR (δ, in C_6D_6, 53.67 MHz vs external TMS) −25.70, −27.27 ($^1J_{Si-H}$: −242.6 Hz); exact mass for $C_{36}H_{47}ClN_2Si_2$ calculated m/e 596.2810, found 596.2808; mp 232 °C (dec); IR (cm^{-1}, Nujol) 2157.6 (Si–H).

***trans*-2,3-Bis(mesitylamino)-1,2,3-trimesitylazadisilacyclopropane (5).** The insoluble portion from the diethyl ether wash was stirred with benzene (20 mL) and filtered. The benzene was removed under reduced pressure, leaving **5** as the only product in an isolated yield of 0.59 g (26%, 0.84 mmol). Analytical data for **5**: ^1H NMR (δ, in C_6D_6) 6.82 (s, 4 H), 6.60 (s, 4 H), 6.39 (s, 2 H), 3.27 (s, 6 H), 3.06 (s, 2 H), 2.18 (s, 12 H), 2.13 (s, 6 H), 2.12 (s, 3 H), 2.01 (s, 6 H), 1.98 (s, 12 H); INEPT ^{29}Si NMR (δ, in C_6D_6, 53.67 MHz vs external TMS) −42.23; HRMS (EI, 70 eV, M^+ − MesN) calculated m/e 562.3199, found 562.3151; mp 228 °C (dec); IR (cm^{-1}, Nujol) 3351.8 (N–H).

Direct synthesis of 5. The same reaction conditions were used as in the synthesis of **4a**, except that 4 equiv of MesNHLi (5.78 mmol) was reacted with **1** (0.63 g, 1.44 mmol). The ^1H NMR spectrum of the crude reaction mixture indicated that ~80% of **5** was present. After the reaction was complete, the THF was removed under reduced pressure, and the residue was treated with 20 mL of diethyl ether. Some **5** was also dissolved and lost in this washing. The solution was filtered, and the residue was taken up in 20 mL of benzene. Removal of the benzene under vacuum yielded 0.44 g (43%, 0.62 mmol).

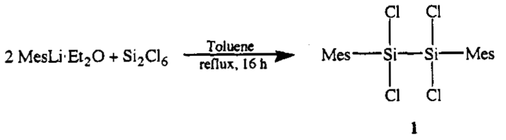
NMR Experiments. The crude products that were used in the ^1H NMR experiments were synthesized using the standard reaction conditions, unless otherwise stated. Lithium chloride was removed from the product mixtures prior to making the NMR samples.

X-ray Structure Determination. X-ray crystallographic analysis was performed with the use of a Siemens P3f diffractometer equipped with a graphite crystal monochromator and a Mo X-ray tube. Orientation matrix and unit cell parameters were determined by the least squares fitting of 25 centered reflections (27° < 2θ < 29°). Intensities of 3 check reflections were monitored every 97 reflections throughout the data collection. Structure solution and refinement were performed using Siemens SHELXTL PLUS (VMS). Details on crystal and intensity data collection are given in Table I.

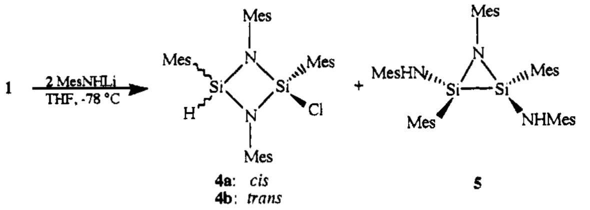
Suitable crystals of **5** were grown from a concentrated benzene solution at room temperature. A colorless block shaped crystal of **5**, cut to the approximate dimensions of 0.6 mm × 0.5 mm × 0.4 mm under an argon blanket, was mounted on a thin glass thread with Paratone-N. The structure was solved by direct methods. In the final cycles of refinement, all non-hydrogens were assumed to vibrate anisotropically, and the hydrogen atoms were assumed to vibrate isotropically.

Results and Discussion

Synthesis and Characterization. 1,1,2,2-Tetrachloro-1,2-dimesityldisilane (**1**) was synthesized from 2.1 equiv of MesLi·Et_2O and Si_2Cl_6 in refluxing toluene. In a typical



(1)

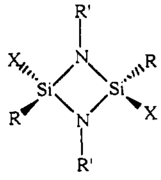


(2)

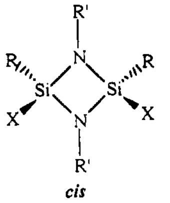
experiment, **1** was isolated in a 45% yield. ^1H, ^{29}Si, and ^{13}C NMR spectra were consistent with the assigned structure. This solid is mildly moisture sensitive but can be handled in air for short periods of time without decomposition. The reaction of **1** with 2 equiv of MesNHLi in THF at −78 °C was quite rapid and led to the formation of a product mixture from which the *cis*-cyclodisilazane **4a**, *trans*-cyclodisilazane **4b**, and the azadisilacyclopropane **5** were isolated in 21%, 4%, and 26% yields, respectively. These three compounds are colorless and moisture stable solids. A ^{29}Si NMR spectrum of the remaining crude material revealed that **1**, **4a**, **4b**, **5**, along with several other unidentifiable silicon-containing compounds were present.

Significant solubility differences between **4a**, **4b**, **5**, and the remaining material allowed for clean separation of the various species. The isolation of **4a** from the reaction mixture was accomplished by recrystallization from a hot n-hexane solution which was cooled to −20 °C. After **4a** was isolated, **4b** could be recovered from the remaining crude material in an analogous manner, but with less solvent. The ^1H NMR spectra of **4a** and **4b** showed deshielded silyl hydrides with resonances of 6.93 and 6.91 ppm, respectively. Both compounds have equivalent mesityl rings on nitrogen and nonequivalent mesityl rings on silicon. IR analyses of **4a** and **4b** confirmed the presence of the silyl hydrides with stretching frequencies of 2160 and 2158 cm^{-1}. These data along with the high resolution mass spectra are consistent with the cyclodisilazane structures **4a** and **4b**.

The assignment of **4a** as the *cis* and **4b** as the *trans* structure was based on the ^{29}Si NMR spectra of the two compounds. The ^{29}Si NMR spectrum of **4a** revealed resonances at −25.21 and −26.50 ppm with a $^{1}J_{Si-H}$ of −241.7 Hz, and the spectrum of **4b** had resonances at −25.70 and −27.27 ppm with a $^{1}J_{Si-H}$ of −242.6 Hz. Klingebiel and co-workers have shown earlier that the ^{29}Si resonances in *cis*-cyclodisilazanes fall at lower field than those for the *trans* isomers.[11] Since both silicon atoms in **4a** are shifted downfield relative to the corresponding silicon atoms in **4b**, **4a** is assigned as the *cis* isomer, which has the mesityl groups on the same face of the Si_2N_2 ring.



trans



cis

The isolation of **5** was accomplished by first washing the crude reaction mixture with diethyl ether and then washing the extract that was insoluble in diethyl ether with benzene. Evaporation of the benzene produced **5** in pure form. The ^{1}H NMR of **5** shows resonances for three sets of mesityl groups, as well as an N–H proton resonance at 3.06 ppm. The presence of the N–H group was confirmed by observation of a band at 3352 cm^{-1} in the infrared spectrum, characteristic for N–H stretching. The ^{29}Si resonance was observed at −42.2 ppm, as compared with −52 ± 2 ppm for the other known azadisilacyclopropanes.[7] This difference may possibly result from the greater σ acceptor ability of the exocyclic amino groups present in **5**. A ^{29}Si NMR spectrum of the remaining crude material did not show any other resonances in this region, indicating that only one isomer was present. This conclusion is consistent with the ^{1}H NMR spectrum of the reaction mixture.

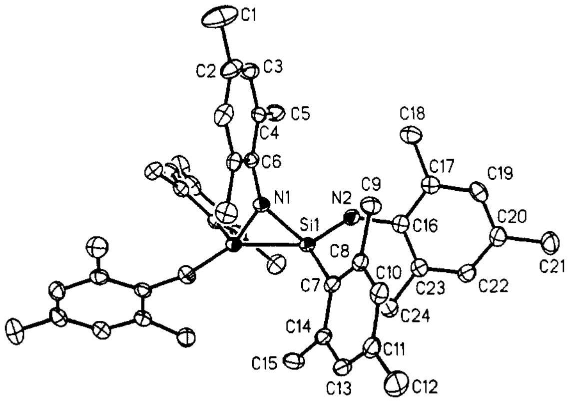


Figure 1. Thermal ellipsoid diagram of **5** showing 50% probability thermal ellipsoids. Hydrogen atoms are omitted for clarity.

Table II. Selected Bond Distances (pm) and Angles (deg) for Compound 5

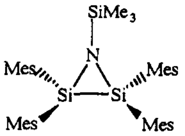
	Distances		
Si(1)–Si(1A)	228.8(1)	Si(1)–C(7)	188.3(3)
Si(1)–N(1)	174.8(2)	N(1)–C(6)	143.0(4)
Si(1)–N(2)	172.5(2)	N(2)–C(16)	142.6(3)
	Angles		
N(1)–Si(1)–N(2)	111.6(1)	Si(1)–N(1)–C(6)	140.4(1)
N(2)–Si(1)–C(7)	110.7(1)	N(2)–Si(1)–Si(1A)	123.5(1)
Si(1)–N(2)–C(16)	131.7(2)	Si(1A)–Si(1)–C(7)	125.2(1)
Si(1A)–Si(1)–N(1)	50.4(1)	N(1)–Si(1)–C(7)	117.5(1)
Si(1)–N(1)–Si(1A)	79.2(1)		

Table III. Atomic Coordinates (×10^5) and Equivalent Isotropic Displacement Coefficients (pm^2) for 5

atom	*x*	*y*	*z*	*U*(eq),[a] Å^2
Si(1)	45 623(3)	5 070(5)	20 820(4)	180(2)
N(1)	50 000	−5 823(22)	25 000	183(9)
N(2)	45 488(9)	5 368(17)	11 653(10)	227(7)
C(1)	50 000	−52 320(34)	25 000	575(21)
C(2)	50 000	−40 057(30)	25 000	307(13)
C(3)	52 955(11)	−34 293(21)	20 398(15)	270(8)
C(4)	53 088(11)	−23 076(20)	20 314(13)	200(8)
C(5)	56 580(12)	−17 333(22)	15 309(14)	279(9)
C(6)	50 000	−17 391(27)	25 000	170(10)
C(7)	37 544(11)	6 942(20)	22 670(13)	205(8)
C(8)	32 900(11)	−739(21)	20 090(13)	212(8)
C(9)	34 085(12)	−10 299(20)	15 587(15)	254(8)
C(10)	26 988(12)	346(23)	21 703(14)	265(8)
C(11)	25 478(12)	88 878(23)	25 785(14)	283(9)
C(12)	18 969(13)	99 957(30)	27 251(18)	447(11)
C(13)	30 123(12)	16 283(22)	28 475(14)	272(8)
C(14)	36 079(12)	15 444(20)	27 044(13)	230(8)
C(15)	40 848(13)	23 734(22)	30 469(16)	315(9)
C(16)	40 756(11)	8 517(20)	5 675(13)	217(8)
C(17)	38 856(12)	1 193(21)	−47(14)	235(8)
C(18)	41 985(13)	−9 663(22)	−89(15)	322(9)
C(19)	34 121(12)	4 151(23)	−5 759(14)	277(8)
C(20)	31 180(12)	14 159(23)	−6 008(14)	272(8)
C(21)	26 094(14)	17 200(28)	−12 265(15)	406(10)
C(22)	33 289(12)	21 340(22)	−417(14)	265(8)
C(23)	38 090(12)	18 809(21)	5 368(13)	239(8)
C(24)	40 474(13)	27 401(21)	10 912(15)	306(9)
C(1S)	18 955(17)	1 628(28)	53 178(18)	486(12)
C(2S)	13 998(17)	−306(33)	56 496(18)	559(13)
C(3S)	8 305(17)	4 233(28)	53 900(18)	501(12)
C(4S)	7 366(18)	10 731(27)	47 834(20)	512(13)
C(5S)	12 271(19)	12 556(30)	44 364(21)	594(15)
C(6S)	18 063(18)	8 139(30)	47 151(20)	558(14)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Crystal Structure Determination of $5\cdot 2C_6H_6$. Crystals of $5\cdot 2C_6H_6$ suitable for X-ray analysis were grown from benzene at room temperature. These crystals quickly lose solvent and become a white powder, so they were covered immediately with Paratone-N. X-ray crystallographic study showed that **5** is the *trans* isomer (Figure 1). Table II contains selected bond distances and angles for **5**. In **5**, a crystallographic center of symmetry results in the equivalence of the two silicon atoms and their substituents. The structure of one other azadisilacyclopropane, **6**, has been determined and is found to be very similar to that of **5**.[7] In both compounds, the ring nitrogen is planar; the Si–C–N(2) framework is nearly planar, as the sum of the bond angles N(2)–Si(1)–C(7), Si(1A)–Si(1)–C(7), and Si(1A)–Si(1)–N(2) is 359.4°; and the Si–Si bond distance is abnormally short, near 223 pm. This distance is more similar to a typical Si–Si double bond (215 pm) than to



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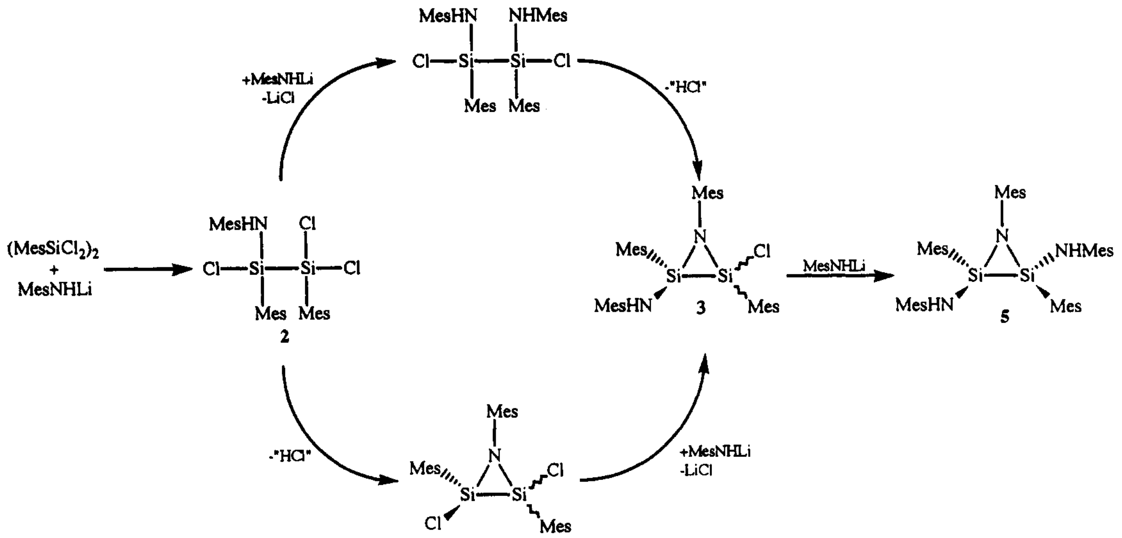
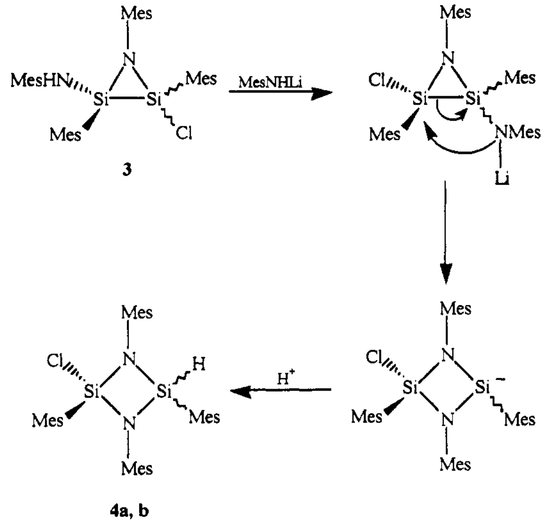
[11] Bartholmei, S.; Klingebiel, U.; Sheldrick, G. M.; Stalke, D. *Z. Anorg. Allg. Chem.* **1988**, *556*, 129.

Scheme I



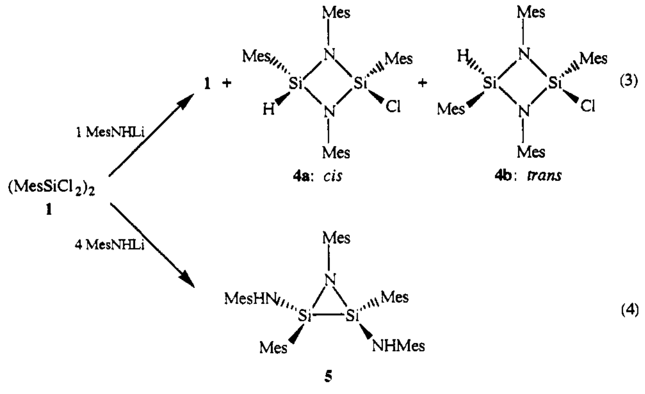
Scheme II



a typical Si–Si single bond (235 pm).[12] The major structural difference in the Si_2N frameworks of **5** and **6** is that the Si–N distance in **5** (174.8 pm) is somewhat shorter than that in **6** (average 177.2 pm). As a result, the internal bond angles are somewhat different, 50.4(1) and 79.2(1)° in **5**, as compared to 51.0(2) and 78.0(2)° in **6**. Again, this difference can perhaps be explained by the presence of the σ acceptor, MesHN– in **5**, which causes a slight ring contraction due to the higher ionic character in the Si–N bonds.

Possible Reaction Pathway. In order to try to understand how this product mixture came about, a number of variations of the reaction conditions were examined. The addition rates of MesNHLi were varied from 30 s to 30 min without any substantial change in the yield of **4a**. The reaction was also carried out at several different temperatures. At −100 °C, the addition of amide was done over several minutes, and complete disappearance of the MesNHLi suspension required several more minutes. At −45 °C, the amide was completely dissolved and the addition was done over several minutes. In both of the cases, these reaction mixtures were worked up by the standard procedure described in the Experimental Section. The yields were identical (within experimental error) to those obtained at −78 °C. When the reaction was carried out at 0 °C, however, a more complicated product mixture was produced from which pure compounds could not be isolated, although the presence of **4a**, **4b**, and **5** in the mixture was confirmed by ^{1}H NMR. These results indicate that neither the rate of addition, nor the reaction temperature, nor the state of the MesNHLi (soluble or in suspension) affects the reaction pathway below −45 °C. At higher temperatures, however, side reactions also occur.

Under our standard reaction conditions and rapid addition of the amide, the relative amount of MesNHLi determines which products are formed. Using 1 equiv of amide resulted in an approximate 6:3:1 mixture of **1**:**4a**:**4b**, accounting for ~90% of the products, along with ~10% unknown material, as determined by ^{1}H NMR of the reaction mixture. Since **1** was present in a substantial amount, the reactive intermediates on the way to **4a** and **4b** must be more reactive than **1**. The reaction of 4 equiv of amide with **1** led to the formation of **5** in greater than 80% conversion by ^{1}H NMR, with an isolated yield of 43%. The reaction did not produce any cyclodisilazane. These experiments indicate that the formation of **5** is more rapid than the formation of **4a** or **4b**, but only when there is sufficient amide present. It is important to mention that in all ^{1}H NMR spectra of crude reaction mixtures which contain **4a** and **4b** the ratio of these isomers is consistently 3:1.



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(12) Sheldrick, W. S. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappaport, Z., Eds.; Wiley: Chichester, England, 1989; Chapter 2, pp 227–303.

A possible pathway is proposed (Scheme I) to account for the formation of **5**. The first step is the formation of an aminodisilane (**2**). At this stage, either a second amino group can add to give a bis(amino)disilane, which can then ring close via a HCl elimination to yield **3**, or **2** could lose HCl to form an azadisilacyclopropane, which can react with another equivalent of MesNHLi to give **3**. The HCl elimination can arise from either a deprotonation followed by LiCl elimination or an intramolecular condensation to evolve HCl, which can eventually react with MesNHLi. Once **3** has been formed, it is trapped by reaction with another equivalent of MesNHLi to produce **5**. The reason why only the *trans* isomer of **5** is formed is not presently understood.

The pathway leading to the cyclodisilazanes **4a** and **4b** is also not clearly understood. One possibility is deprotonation of the N–H bond of **3** followed by ring closure on the neighboring silicon atom with cleavage of the Si–Si bond (Scheme II). This closure would result in a silyl anion, which upon reprotonation would produce **4a** and **4b**. There are a few precedents for the cleavage of Si–Si single bonds by amine or amide reagents.[13] Further study will be required, however, to understand this transformation and how it relates to the stereochemistry of the final products.

Conclusions

$(MesSiCl_2)_2$ was successfully used in the syntheses of three- and four-membered Si–N ring systems. The reaction of MesNHLi with $(MesSiCl_2)_2$ proceeds rapidly even at −78 °C. Cyclodisilazanes **4a** and **4b** are formed as a 3:1 mixture of *cis* and *trans* isomers, while the azadisilacyclopropane **5** is formed as a *trans* isomer exclusively. The crystal structure of **5** revealed a short Si–Si bond length. Product formation has been shown to be directly related to the amount of amide used. Small amounts of amide favored the formation of the four-membered rings, while larger amounts favored the three-membered ring.

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Supplementary Material Available: Tables of crystal data, positional parameters, bond distances and angles, and anisotropic thermal parameters (9 pages). Ordering information is given on any current masthead page.

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[13] (a) Weidenbruch, M.; Pan, Y.; Peters, K.; von Schnering, H. G. *Chem. Ber.* **1989**, *122*, 885. (b) Hengge, E. *Top. Curr. Chem.* **1974**, *51*, 1.