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Influence of Steric Hindrance on Cyclodisilazane Formation from Tetrachlorodisilanes

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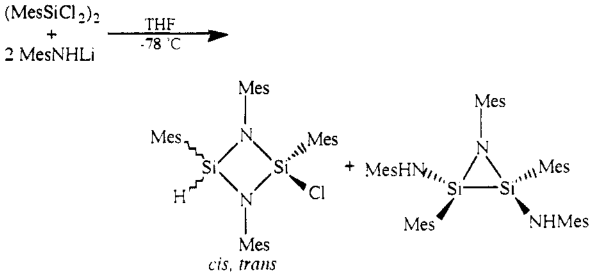
The reaction of Mes*NHLi (Mes* = 2,4,6-tri-*tert*-butylphenyl) with $(MesSiCl_2)_2$ (Mes = 2,4,6-trimethylphenyl) in THF led to the formation of 1,1,2-trichloro-2-((2,4,6-tri-*tert*-butylphenyl)-amino)-1,2-dimesityldisilane (**1**). The action of 2 equiv of MesNHLi on $(t\text{-}BuSiCl_2)_2$ in THF resulted in the formation of a 2:1 to 4:1 *cis/trans* mixture of 2-(mesitylamino)-1,3-dimesityl-2,4-di-*tert*-butylcyclodisilazane (**2a**, **2b**). A 3:1 mixture of **2a** and **2b** was subsequently chlorinated with *N*-chlorosuccinimide in benzene yielding a 3:1 *cis/trans* mixture of 2-chloro-4-(mesitylamino)-1,3-dimesityl-2,4-di-*tert*-butylcyclodisilazane (**3a**, **3b**). The molecular structures of **2a** and **3a** $0.5C_6H_{14}$ were determined by X-ray crystallographic analysis. Compounds **2a** and **2b** cocrystallized as a 85:15 mixture in the triclinic space group $P\bar{1}$ with cell parameters a = 8.609(2) Å, b = 10.084(2) Å, c = 20.333(5) Å, α = 101.75(2)° β = 92.42(2)°, γ = 92.418(16)°, V = 1724.3(6) Å^3, Z = 2, d(calcd) = 1.102 g/cm^3, and R = 5.51%. Compound **3a**·$0.5C_6H_{14}$ crystallized in the tetragonal space group $P\bar{4}2_1c$ with cell parameters a = 17.2385(7) Å, c = 28.568(6) Å, V = 8489.5(18) Å^3, Z = 8, d(calcd) = 1.017 g/cm^3, and R = 6.08%.

Introduction

The interest in the Si–N bond has led to many important developments in cyclosilazane chemistry. In order to study a variety of strained cyclodisilazanes, a number of synthetic methods have been developed.[1] Several studies have shown that substitution chemistry can be accomplished on the ring framework or ligands without degradation of the cyclodisilazane.[2] Others have demonstrated that cyclodisilazanes can be opened under the appropriate conditions.[3] Structural analysis of cyclodisilazanes has revealed that these rings are almost always planar with nearly planar nitrogen centers.[4]

Though the area of Si–N chemistry is very active, little work has been done with amine reagents and polychlorodisilanes. Under the proper conditions, it has been observed that amines are capable of cleaving Si–Si bonds in polychlorodisilanes.[5] The reaction of a sterically congested 1,2-dichlorodisilane with alkali metal amides, MNHR, can result in the formation of ring compounds with or without the Si–Si bond intact.[6]

We have recently reported the synthesis of various Si–N rings from the reaction of MesNHLi (Mes = 2,4,6-trimethylphenyl) with the tetrachlorodisilane $(MesSiCl_2)_2$ (eq 1).[7] In this paper we report the products of the related reactions of MesNHLi with $(t\text{-}BuSiCl_2)_2$ and Mes*NHLi (Mes* = 2,4,6-tri-*tert*-butylphenyl) with $(MesSiCl_2)_2$. These more hindered reagents react to give quite different products, showing the marked effect of steric bulk on the reaction pathway.



(1)

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, hexanes, and benzene were distilled from sodium benzophenone ketyl under nitrogen. $MesNH_2$ 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. ^1H 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 in hexanes was titrated before use. $(MesSiCl_2)_2$,[7] Mes*NH_2,[8] and $(t\text{-}BuSiCl_2)_2$[9] were

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prepared as described in the literature. *N*-Chlorosuccinimide (NCS) was washed with ethyl alcohol and dried under vacuum prior to use.

1,1,2-Trichloro-2-((2,4,6-tri-*tert*-butylphenyl)amino)-1,2-dimesityldisilane (1). Mes*NH$_2$ (0.72 g, 2.77 mmol) was dissolved in THF (20 mL), and the solution was cooled to −78 °C in a dry ice/2-propanol bath. *n*-BuLi (2.2 mL, 1.27 M) was added via syringe to the Mes*NH$_2$ solution and stirred for 45 min. The resulting Mes*NHLi solution was rapidly cannulated into a THF solution (20 mL) of (MesSiCl$_2$)$_2$ (1.21 g, 2.77 mmol) also at −78 °C. The resulting reaction mixture was maintained at −78 °C for 30 min and slowly warmed to room temperature where it was then refluxed for 7 h. The solvent was removed under reduced pressure and the resulting colorless residue was redissolved in hexanes (10 mL). This solution was filtered under nitrogen, reduced in volume to *ca.* 5 mL, and cooled to −20 °C to give 1 in an isolated yield of 0.25 g (13%, 0.37 mmol) as a colorless and moisture sensitive solid. A consistent melting point could not be obtained due to an apparent lack of thermal stability. Analytical data for 1: ^{1}H NMR (δ, in C$_6$D$_6$) 7.32 (s, 2 H), 6.56 (s, 2 H), 6.51 (s, 2 H), 4.68 (s, 1 H), 2.68 (s, 6 H), 2.21 (s, 6 H), 1.95 (s, 3 H), 1.90 (s, 3 H), 1.46 (s, 18 H), 1.29 (s, 9 H); INEPT ^{29}Si NMR (δ, in C$_6$D$_6$, 53.67 MHz vs external TMS) −17.25, 5.95; exact mass for C$_{36}$H$_{52}$NSi$_2$Cl$_3$ calculated *m/e* 659.2704, found 659.2681; IR (cm^{-1}, Nujol) 3374.5 (N–H).

2-(Mesitylamino)-1,3-dimesityl-2,4-di-*tert*-butylcyclodisilazane (*cis*-2a, *trans*-2b). MesNH$_2$ (0.44 g, 3.28 mmol) was dissolved in THF (20 mL), and the solution was cooled to −78 °C in a dry ice/2-propanol bath. *n*-BuLi (2.6 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 solution (20 mL) of (*t*-BuSiCl$_2$)$_2$ also at −78 °C. No immediate change was observed, and the suspension was stirred for 1 h at −78 °C and slowly warmed to room temperature. After 12 h of stirring, a clear colorless solution resulted. The solvent was removed under reduced pressure, the resulting residue was redissolved in Et$_2$O (30 mL), and the solution was filtered under a nitrogen atmosphere. Et$_2$O was removed under reduced pressure. The resulting residue was redissolved in hexanes (5 mL), and the solution was cooled to −20 °C to yield a 2:1 mixture of **2a** and **2b** in an isolated yield of 0.33 g (35%, 0.57 mmol). Analytical data for **2a**: ^{1}H NMR (δ, in C$_6$D$_6$) 6.86 (s, 4 H), 6.61 (s, 2 H), 5.57 (s, 1 H), 3.31 (s, 1 H), 2.84 (s, 6 H), 2.65 (s, 6 H), 2.17 (s, 6 H), 2.00 (s, 3 H), 1.84 (s, 6 H), 1.15 (s, 9 H), 1.00 (s, 9 H); INEPT ^{29}Si NMR (δ, in C$_6$D$_6$, 53.67 MHz vs external TMS) −22.56, −12.60 ($^1J_{\text{Si-H}}$: −224.6 Hz); IR (cm^{-1}, Nujol) 2112.9 (Si–H), 3379.7 (N–H). Analytical data for **2b**: ^{1}H NMR (δ, in C$_6$D$_6$) 6.86 (s, 4 H), 6.62 (s, 2 H), 5.56 (s, 1 H), 3.18 (s, 1 H), 2.75 (s, 6 H), 2.68 (s, 6 H), 2.17 (s, 6 H), 2.04 (s, 6 H), 2.00 (s, 3 H), 1.06 (s, 9 H), 0.84 (s, 9 H); INEPT ^{29}Si NMR (δ, in C$_6$D$_6$, 53.67 MHz vs external TMS) −25.51, −18.68 ($^1J_{\text{Si-H}}$: −215.2 Hz); IR (cm^{-1}, Nujol) 2080.4 (Si–H), 3379.7 (N–H). Anal. Calcd for C$_{35}$H$_{53}$N$_3$Si$_2$ (**2a, 2b**) (*m/e* 571.3778): C, 73.50; H, 9.34; N, 7.35. Found (*m/e* 571.3783): C, 72.75; H, 9.50; N, 7.26.

2-Chloro-4-(mesitylamino)-2,4-di-*tert*-butyl-1,3-dimesitylcyclodisilazane (*cis*-3a, *trans*-3b). A 2:1 mixture of **2a** and **2b** (0.50 g, 0.88 mmol) and NCS (0.18 g, 1.32 mmol) was dissolved in benzene (40 mL), and the solution was refluxed for 10 h. The benzene was removed under reduced pressure. The resulting residue was dissolved in hexanes (20 mL) and the solution was gravity filtered through filter paper. The clear solution was reduced in volume to *ca.* 5 mL and cooled to −20 °C to give a 2:1 mixture of **3a** and **3b** in an isolated yield of 0.21 g (40%, 0.35 mmol). Analytical data for **3a**: ^{1}H NMR (δ, in C$_6$D$_6$) 6.85 (s, 4 H), 6.60 (s, 2 H), 3.42 (s, 1 H) 3.00 (s, 6 H), 2.65 (s, 6 H), 2.15 (s, 6 H), 1.99 (s, 3 H), 1.86 (s, 6 H), 1.22 (s, 9 H), 1.11 (s, 9 H); INEPT ^{29}Si NMR (δ, in C$_6$D$_6$, 53.67 MHz vs external TMS) −23.94, −13.16; exact mass for C$_{35}$H$_{52}$N$_3$Si$_2$Cl calculated *m/e* 605.3388, found 605.3388; IR (cm^{-1}, Nujol) 3379.8 (N–H). Analytical data for **3b**: ^{1}H NMR (δ, in C$_6$D$_6$) 6.84 (s, 4 H), 6.60 (s, 2 H), 3.14 (s, 1 H), 2.89 (s, 6 H), 2.72 (s, 6 H), 2.15 (s, 6 H), 1.99 (s, 3 H), 1.93 (s, 6 H), 1.16 (s, 9 H), 1.05 (s, 9 H); INEPT ^{29}Si NMR (δ, in C$_6$D$_6$, 53.67 MHz vs external TMS) −22.72, −15.13; IR (cm^{-1}, Nujol) 3379.8 (N–H). No extraneous lines were found in the ^{1}H NMR spectrum of the **3a,b** mixture, indicating that the purity of the sample was >95%.

Table 1. Summary of Crystal Data Collection for 2a,b and 3a

	2a,b	3a
empirical formula	C$_{35}$H$_{53}$N$_3$Si$_2$	C$_{35}$H$_{52}$ClN$_3$Si$_2$·0.5C$_6$H$_{14}$
fw	572.0	649.7
cryst syst	triclinic	tetragonal
space group	$P\bar{1}$	$P\bar{4}2_1c$
a, Å	8.609(2)	17.2385(7)
b, Å	10.084(2)	
c, Å	20.333(5)	28.568(6)
α, deg	101.75(2)	
β, deg	92.42(2)	
γ, deg	92.418(16)	
V, Å^3	1724.3(6)	8489.5(18)
Z	2	8
d(calcd), g/cm^3	1.102	1.017
cryst size, mm	0.2 × 0.3 × 0.5	0.2 × 0.3 × 0.5
color; habit	colorless prism	colorless block
abs coeff, mm^{-1}	1.110	1.532
F(000)	624	2824.68
T, °C	−160(2)	−160(2)
2θ range, deg	4.0–114.0	4.0–114.0
scan type	Wyckoff	2θ–θ
scan speed, deg/min	variable, 2.00–20.00	variable, 4.00–30.00
scan range (ω), deg	0.60	0.76 plus Kα separation
index ranges	$-9 \le h \le 0$ $-10 \le k \le 10$ $-22 \le l \le 22$	$-13 \le h \le 13$ $-1 \le k \le 18$ $-31 \le l \le 31$
no. of reflns collected	5011	12811
no. of indep reflns	4641 (R_{int} = 2.44%)	5736 (R_{int} = 4.80%)
R, R_w, %	5.51, 7.63	6.08, 7.43
goodness of fit	1.97	2.38
largest and mean Δ/σ	0.021, 0.001	0.001, 0.000
data-to-param ratio	10.4	11.6:1
largest diff peak/hole, e Å^{-3}	0.42/−0.44	0.71/−0.96

X-ray Structure Determinations for 2a, 2b, and 3a. X-ray crystallographic analyses were performed with the use of a Siemens P3f diffractometer for **2a** and **2b** and a Siemens P4 diffractometer for **3a** equipped with a graphite crystal monochromator and a Cu X-ray tube. Orientation matrices and unit cell parameters were determined by the least squares fitting of 25 centered reflections (45° < 2θ < 50°) for **2a** and **2b** and 40 centered reflections (20° < 2θ < 55°) for **3a**. Intensities of three check reflections were monitored every 50 reflections throughout the data collection. Structure solutions and refinements were performed using Siemens SHELXTL PLUS (VMS) for **2a** and **2b** and Siemens SHELXTL PLUS (SGI) for **3a**. Details on crystal and intensity data collection are given in Table 1.

Suitable crystals of **2a** and **2b** were grown from a concentrated hexanes solution while crystals of **3a** were grown from concentrated *n*-hexane at −20 °C. A colorless prism shaped crystal of **2a** and **2b** and a colorless block shaped crystal of **3a**, cut to the approximate dimensions of 0.2 mm × 0.3 mm × 0.5 mm under an argon blanket, were mounted on a thin glass thread with Paratone-N. The structures were 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. Atomic coordinates and equivalent isotropic displacement coefficients for **2a** and **2b** are given in Table 4 and for **3a** in Table 5.

Results and Discussion

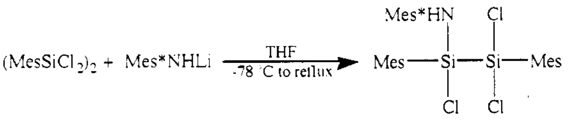
Synthesis and Characterization. The reaction of Mes*NHLi with (MesSiCl$_2$)$_2$ in THF produced 1 as the principal product of conversion (eq 2). This reaction required some refluxing as the addition of the amino group

Table 2. Selected Bond Distances (pm) for Compounds 2a and 3a

2a		3a	
Si(2)–C(15)	188.0(5)	Si(2)–C(23)	190.3(6)
Si(1)–N(2)	175.4(3)	Si(1)–N(2)	174.0(5)
Si(2)–N(2)	174.5(3)	Si(2)–N(2)	175.7(5)
Si(1)–N(1)	175.3(3)	Si(1)–N(1)	172.4(5)
Si(2)–N(1)	175.0(3)	Si(2)–N(1)	175.4(5)
Si(1)–N(5)	171.6(3)	Si(2)–N(3)	171.1(5)
Si(1)–C(1)	188.9(4)	Si(1)–C(1)	189.4(6)
		Si(1)–Cl(1)	208.8(2)

Table 3. Selected Bond Angles (deg) for Compounds 2a and 3a

2a		3a	
N(1)–Si(2)–N(2)	86.4(1)	N(1)–Si(2)–N(2)	85.8(2)
Si(1)–N(1)–Si(2)	93.4(1)	Si(1)–N(1)–Si(2)	93.8(2)
N(1)–Si(1)–N(2)	86.0(1)	N(1)–Si(1)–N(2)	87.2(2)
Si(1)–N(2)–Si(2)	93.5(1)	Si(1)–N(2)–Si(2)	93.1(2)
C(1)–Si(1)–N(5)	109.8(1)	Cl(1)–Si(1)–N(2)	115.9(2)
N(5)–Si(1)–N(1)	117.2(1)	C(1)–Si(1)–N(2)	117.1(2)
N(5)–Si(1)–N(2)	109.6(1)	N(1)–Si(2)–C(23)	113.9(2)
Si(1)–N(5)–C(6)	134.0(2)	N(2)–Si(2)–N(3)	109.2(2)
Si(1)–N(1)–C(19)	133.5(2)	Si(2)–N(1)–C(5)	132.7(4)
Si(1)–N(2)–C(28)	133.8(2)	Si(1)–N(2)–C(14)	131.4(4)
C(1)–Si(1)–N(1)	114.9(1)	Si(2)–N(3)–C(27)	134.8(4)
C(1)–Si(1)–N(2)	117.7(1)	Cl(1)–Si(1)–C(1)	101.0(2)
C(15)–Si(2)–N(1)	119.7(2)	Cl(1)–Si(1)–N(1)	112.1(2)
C(1)–Si(2)–N(2)	118.6(2)	C(1)–Si(1)–N(1)	124.3(3)
Si(2)–N(1)–C(19)	128.9(2)	N(2)–Si(2)–C(23)	119.3(2)
Si(2)–N(2)–C(28)	127.7(2)	N(1)–Si(2)–N(3)	118.1(2)
		C(23)–Si(2)–N(3)	109.2(2)
		Si(1)–N(1)–C(5)	130.9(4)
		Si(2)–N(2)–C(14)	132.5(4)

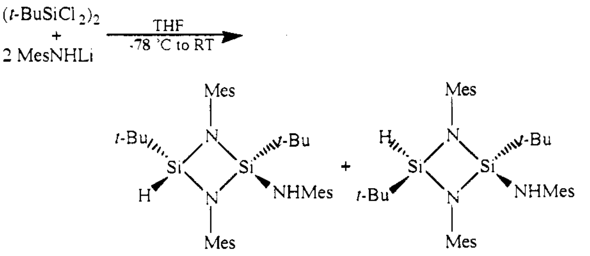


1

(2)

was slow. The conversion of 1 was greater than 50%, as determined by ^{1}H NMR of the crude reaction mixture after filtration. The isolated yield was low due to the high solubility of 1. The ^{1}H NMR spectrum of 1 showed an N–H resonance at 4.68 ppm. In the IR spectrum, a band was observed in the N–H stretching region at 3374 cm^{-1}, confirming the presence of an amine proton. The ^{29}Si NMR spectrum of 1 showed signals at −17.2 ppm, due the amino-substituted silicon, and 6.0 ppm. The latter resonance is slightly downfield of that for $(MesSiCl_2)_2$, at 4.8 ppm. Attempts to attach additional Mes*NH– groups onto the disilane were unsuccessful. Mes*NHLi did not react with $(t\text{-}BuSiCl_2)_2$, even after refluxing.

The reaction of $(t\text{-}BuSiCl_2)_2$ with 2 equiv of MesNHLi in THF (eq 3) was relatively slow as compared to the $(MesSiCl_2)_2$ reaction. The presence of yet unreacted lithium amide was observed until the temperature of the reaction flask neared 0 °C. In the $(MesSiCl_2)_2$ case, the amide was completely consumed at −78 °C. From the reaction mixture, a mixture of **2a** and **2b** was isolated in 35% yield. ^{1}H and ^{29}Si NMR spectra of the crude reaction mixtures showed that approximately 10% of the mixture was unreacted $(t\text{-}BuSiCl_2)_2$, 32% was **2a**, 13% was **2b**, and 15% was a mixture of remaining products. The remaining 30% of the mixture was tentatively assigned as the aminodisilane analogous to 1. There are signals in the ^{29}Si NMR spectrum of the residue at −18.8 and +21.1 ppm which probably correspond to an aminodisilane analogous to 1, as the t-BuCl$_2$Si resonance in such an analogue would be expected to shift slightly downfield of that for $(t\text{-}BuSiCl_2)_2$ at 19.0 ppm. Typically, the *cis*:*trans* ratios varied from 2:1 to 4:1. Multiple recrystallizations increased the relative amount of **2a** to 6:1 but lowered the overall yield. Compounds **2a** and **2b** are colorless and moisture stable solids. Attempts to use Et$_2$O or hexane as a reaction solvent did not lead to the formation of **2a** and **2b**. Use of 3 equiv of MesNHLi resulted in a more complicated product mixture which could not separated.



2a: *cis* 2b: *trans*

(3)

Table 4. Atomic Coordinates (×10^5) and Equivalent Isotropic Displacement Coefficients (pm^2) for 2a and 2b

atom	x	y	z	U(eq)[a]	occ
Si(1)	28358(9)	974(9)	74488(4)	324(3)	
C(1)	15548(37)	10028(36)	69247(17)	448(12)	
C(2)	−1671(40)	7649(41)	70779(20)	574(15)	
C(3)	17122(44)	4869(46)	61663(18)	636(16)	
C(4)	19738(44)	25357(39)	71001(21)	629(16)	
N(5)	47579(29)	5117(27)	73580(12)	394(10)	
C(6)	55629(33)	11111(31)	68842(14)	328(10)	
C(7)	57709(34)	3753(31)	62332(15)	347(10)	
C(8)	65470(36)	10076(34)	57850(16)	417(12)	
C(9)	71591(37)	23242(35)	59631(17)	437(12)	
C(10)	70097(39)	30119(34)	66180(17)	444(12)	
C(11)	62270(37)	24468(32)	70821(16)	389(11)	
C(12)	52545(42)	−10980(32)	60182(17)	469(12)	
C(13)	79866(48)	29809(45)	64620(21)	690(17)	
C(14)	61178(47)	32299(38)	77949(18)	594(15)	
Si(2)	21772(13)	−14480(11)	82575(5)	351(4)	0.846(4)
C(15)	3538(57)	−20726(46)	86004(22)	479(11)	0.846(4)
C(16)	5421(69)	−14917(63)	93661(28)	758(17)	0.846(4)
C(17)	−11513(55)	−16011(51)	83499(26)	676(14)	0.846(4)
C(18)	3354(85)	−36147(68)	84612(36)	843(22)	0.846(4)
Si(2A)	11712(104)	−12100(73)	80899(38)	546(26)	0.154(4)
C(15A)	9887(279)	−24211(236)	86610(109)	384(54)	0.154(4)
C(16A)	26715(352)	−32161(314)	86401(166)	847(94)	0.154(4)
C(17A)	−253(305)	−36265(256)	82464(134)	413(63)	0.154(4)
C(18A)	8592(203)	−20847(196)	93442(86)	212(42)	0.154(4)
N(1)	23077(29)	−16233(25)	73876(12)	373(9)	
C(19)	26128(37)	−28269(32)	68892(15)	379(11)	
C(20)	13009(39)	−34154(35)	64194(16)	436(12)	
C(21)	15809(44)	−45331(35)	59236(17)	485(13)	
C(22)	29802(46)	−51256(33)	58752(17)	471(13)	
C(23)	41463(42)	−45831(33)	63554(17)	451(12)	
C(24)	39447(38)	−34618(32)	68622(16)	397(11)	
C(25)	−2996(42)	−28584(43)	64352(20)	644(16)	
C(26)	32516(54)	−63238(38)	53240(20)	668(16)	
C(27)	52749(40)	−29518(35)	73646(18)	493(13)	
N(2)	24883(30)	2917(26)	83064(12)	393(9)	
C(28)	29410(41)	13229(33)	88952(15)	438(12)	
C(29)	43953(42)	13237(36)	92329(16)	467(13)	
C(30)	47638(50)	23141(40)	98150(18)	585(15)	
C(31)	37724(59)	32958(41)	100765(19)	645(17)	
C(32)	23502(55)	32904(38)	97336(20)	625(16)	
C(33)	18948(46)	23193(36)	91524(17)	499(13)	
C(34)	56010(45)	3218(40)	90091(18)	591(15)	
C(35)	41858(66)	43214(46)	107195(21)	873(20)	
C(36)	3011(48)	23605(42)	88398(21)	664(16)	

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

The ^{1}H NMR spectrum for **2a** and **2b** showed the silyl hydride signals at 5.57 and 5.56 ppm and amine proton

Table 5. Atomic Coordinates (×10^5) and Equivalent Isotropic Displacement Coefficients (pm^2) for 3a

atom	*x*	*y*	*z*	*U*(eq)^a	occ
Cl(1)	103186(9)	17637(9)	26542(6)	384(5)	
Si(1)	94676(9)	24169(9)	23147(6)	271(5)	
Si(2)	85187(9)	18831(9)	17156(5)	227(5)	
C(1)	96663(36)	34175(37)	25611(20)	324(21)	
C(2)	96207(43)	33992(41)	31007(22)	488(26)	
C(3)	90849(41)	40303(35)	23697(23)	418(24)	
C(4)	104934(40)	36312(39)	23928(27)	500(27)	
N(1)	85748(27)	19668(25)	23265(15)	239(15)	
C(5)	81615(33)	15859(32)	27061(18)	253(19)	
C(6)	83072(35)	8054(33)	28178(18)	244(20)	
C(7)	78836(37)	4445(36)	31611(20)	346(22)	
C(8)	73125(40)	8249(37)	34149(21)	377(23)	
C(9)	71853(36)	16063(35)	33157(21)	336(22)	
C(10)	75922(34)	19951(31)	29680(19)	264(20)	
C(11)	89341(38)	3318(37)	25856(24)	383(23)	
C(12)	68442(47)	4159(40)	37936(26)	578(29)	
C(13)	74114(37)	28356(33)	28971(21)	328(21)	
N(2)	94359(27)	23280(26)	17082(16)	265(15)	
C(14)	100397(34)	23607(34)	13598(19)	250(19)	
C(15)	105599(33)	17386(34)	12917(19)	271(20)	
C(16)	111294(33)	17840(36)	9433(19)	268(20)	
C(17)	112115(34)	24175(36)	6603(19)	280(20)	
C(18)	106866(35)	30195(36)	7219(20)	314(21)	
C(19)	101024(34)	30150(33)	10585(19)	255(20)	
C(20)	105396(37)	10031(34)	15756(21)	347(21)	
C(21)	118433(38)	24625(43)	3070(21)	437(24)	
C(22)	95735(38)	37117(34)	11048(22)	367(23)	
C(23)	76571(34)	24098(33)	14465(18)	266(19)	
C(24)	68996(37)	20072(36)	15865(24)	420(24)	
C(25)	77337(41)	24290(39)	9037(20)	421(24)	
C(26)	76062(36)	32537(33)	16263(21)	341(21)	
N(3)	85904(28)	9769(28)	14748(17)	315(18)	
C(27)	81188(37)	5243(32)	11695(20)	279(20)	
C(28)	74701(37)	1031(34)	13367(20)	293(20)	
C(29)	70268(37)	−3108(37)	10240(22)	365(23)	
C(30)	72025(38)	−3655(35)	5538(20)	312(21)	
C(31)	78558(38)	215(36)	3904(20)	310(22)	
C(32)	83196(36)	4586(32)	6906(20)	309(21)	
C(33)	72720(39)	1011(41)	18530(20)	406(23)	
C(34)	66909(45)	−8140(43)	2147(26)	547(28)	
C(35)	90406(39)	8510(38)	5043(21)	391(23)	
C(1S)	55413(125)	12221(124)	5145(71)	1000	0.502(6)
C(2S)	52634(134)	19444(123)	3258(72)	1000	0.502(6)
C(3S)	48247(135)	24830(131)	6214(71)	1000	0.502(6)
C(4S)	45477(134)	30933(131)	4814(74)	1000	0.502(6)
C(5S)	40820(139)	36750(125)	7430(72)	1000	0.502(6)
C(6S)	46013(127)	41724(117)	9576(72)	1000	0.502(6)

^{a} Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

signals at 3.31 and 3.18 ppm, respectively. IR analysis shows only one broad N–H stretch at 3380 cm^{-1}, while separate Si–H stretches for **2a** and **2b** are seen at 2113 and 2080 cm^{-1}. ^{29}Si NMR spectra of **2a** have signals at −22.6 and −12.6 ppm ($^1J_{\text{Si-H}}$: −225 Hz) while in **2b** they are at −25.5 and −18.7 ppm ($^1J_{\text{Si-H}}$: −215 Hz). These data are consistent with the general rule that ^{29}Si resonances for *trans*-cyclodisilazanes are shifted upfield of the *cis* isomers.[10]

A comparison of the cyclodisilazanes formed in eqs 1 and 3 clearly shows the effects of steric bulk. In both cases, the *cis* isomer is formed predominantly, with the *trans* isomer having greater solubility in hexane. The type of cyclodisilazane, amino- versus chloro-substituted, that is formed is related directly to the degree of hindrance as well as whether or not ring formation can occur. A curious difference between the two sets of cyclodisilazanes is that silyl hydride resonances in the (SiN)$_2$ rings in eq 1 are seen at 6.93 and 6.91 ppm, shifted downfield of **2a** and **2b**.

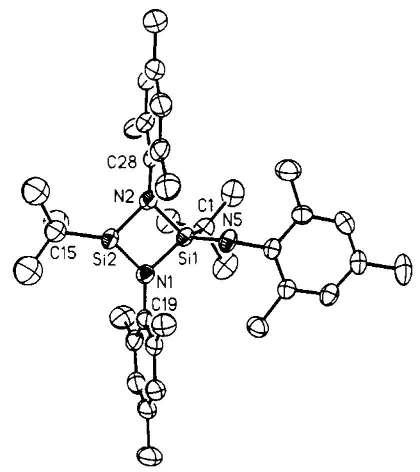


Figure 1. Thermal ellipsoid diagram of **2a** showing 50% probability thermal ellipsoids. Hydrogen atoms are omitted for clarity.

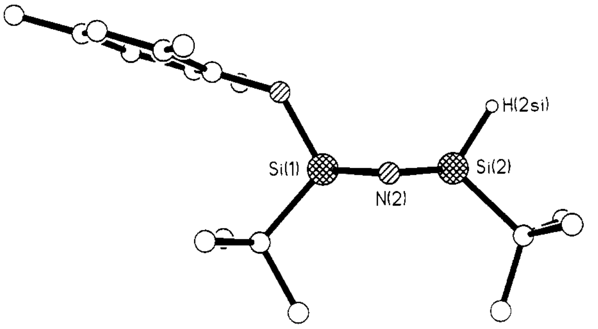
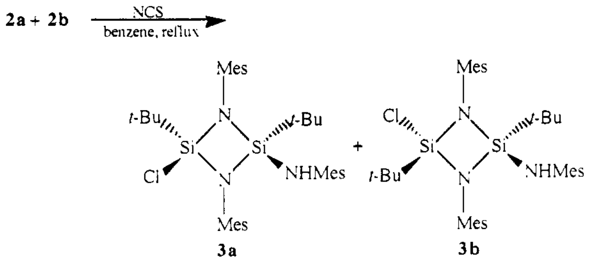


Figure 2. Edge-on view of a ball and stick representation of **2a**. Hydrogen atoms and the ring nitrogen mesityl rings have been omitted for clarity.

The mixture of **2a** and **2b** was chlorinated with excess NCS in refluxing benzene producing **3a** and **3b** (eq 4). It



(4)

was determined that the NCS must be washed with EtOH and dried under vacuum, otherwise no chlorination occurred. CCl$_4$ was also found to be a suitable solvent, but offers no advantage over benzene. The reaction was quantitative, confirmed by ^{1}H NMR, and the ratios of **2a**:**2b** and **3a**:**3b** were identical. The stereoisomeric structure of **3a** was confirmed by X-ray crystallography. The IR spectrum of the isomer mixture showed a broad band at 3380 cm^{-1} due to the N–H group. The ^{1}H NMR spectrum of **3a** and **3b** showed the N–H signals at 3.42, deshielded by the chloride, and 3.14 ppm, respectively. ^{29}Si NMR revealed that **3a** and **3b** do not follow the usual trend of downfield shifts for *cis*-cyclodisilazanes versus *trans*-cyclodisilazanes. In this case, **3a** had ^{29}Si signals at −23.9 and −13.2 ppm while **3b** had signals at −22.7 and −15.1 ppm.

Crystal Structures and Comparisons of 2a, 2b, and 3a. The Si$_2$N$_2$ frameworks of **2a** (Figure 1) and **3a** (Figure

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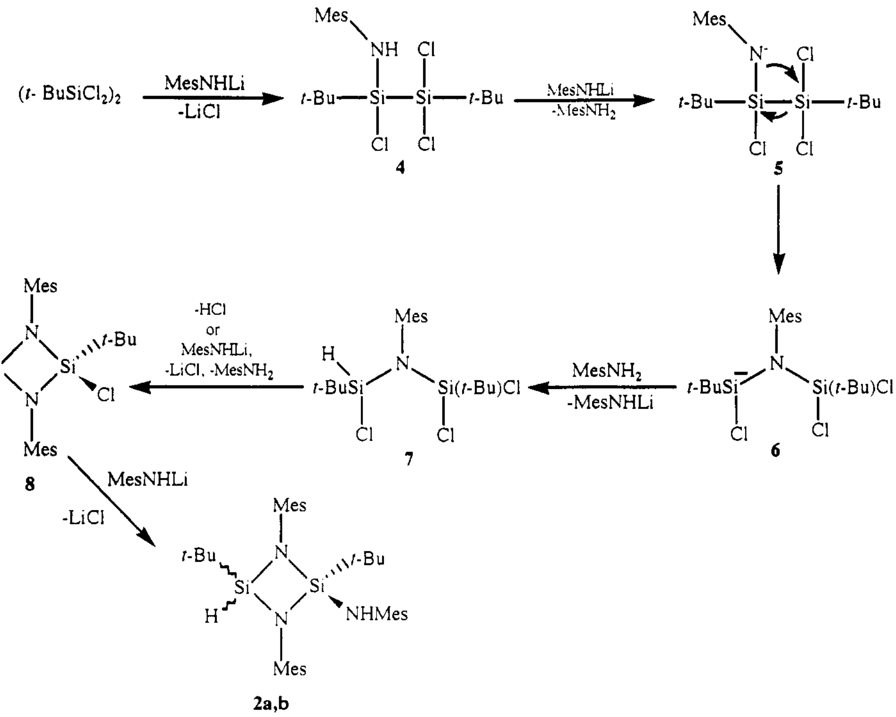
[10] Bartholmei, S.; Klingebiel, U.; Sheldrick, G. M.; Stalke, D. *Z. Anorg. Allg. Chem.* **1988**, *556*, 129.

Scheme 1



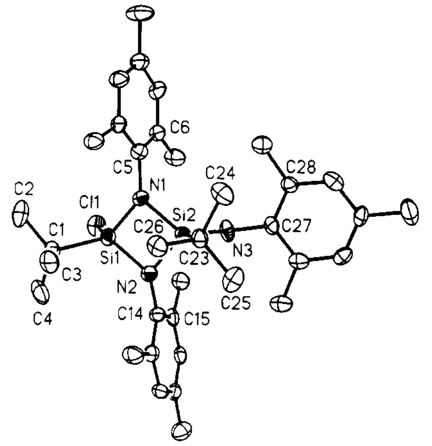


Figure 3. Thermal ellipsoid diagram of **3a** showing 50% probability thermal ellipsoids. Hydrogen atoms are omitted for clarity.

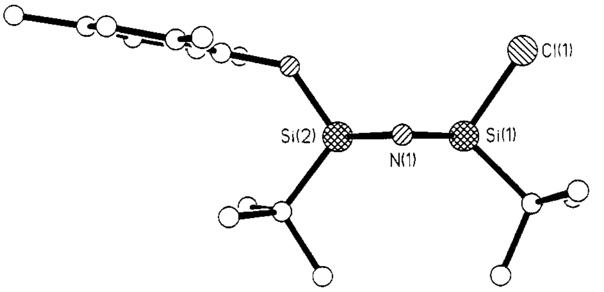


Figure 4. Edge-on view of a ball and stick representation of **3a**. Hydrogen atoms and the ring nitrogen mesityl rings have been omitted for clarity.

3) have many similar features along with a few key differences. Some of the similarities between **2a** and **3a** are as follows: internal angles of the ring are 359.3° for **2a** and 359.6° for **3a**, Si–N bond distances in the ring are 175.0 pm (average) in **2a** and 174.4 pm (average) in **3a**, the Si–Si distance is 254.0(2) pm in **3a** and 255.0(2) pm in **2a**, and the exocyclic Si–N bond distances (**2a**: 171.6(3) pm, **3a**: 171.1(5) pm) are shorter than the Si–N distances found in the rings. These bond distance (Table 2) and angles (Table 3) are typical for other structurally characterized cyclodisilazanes.[4]

In **2a**, the ring nitrogens are slightly more pyramidal, as the sum of the angles around each nitrogen average 355.4°, than in **3a** where the average sum is 357.2°. The Si(1)–N(1)–Si(2) and Si(1)–N(2)–Si(2) planes in **2a** form a 9.1° angle with respect to each other, while in **3a** this angle is only 1.3°. The bend in **2a** is an unusual feature, as we have been able to find only one other example of a bent cyclodisilazane,[11] with a 12.2° angle between the equivalent planes. The bend in **2a** could be due to repulsion of the *tert*-butyl groups, while in **3a** the chlorine–mesitylamino group repulsion offsets this interaction.

The X-ray structural study of 85% **2a**–15% **2b** gave a reliable structure for **2a** but not for **2b**. In order to solve the structure for **2b**, Si(1), N(1), and N(2) were assumed to be fixed in the same positions as in **2a** and this led to unreliable values for bond lengths and angles, so they are not reported. These results do confirm, however, that **2b** is the *trans* isomer.

Possible Reaction Pathway. In our previous results, we reported that the reaction of MesNHLi with $(MesSiCl_2)_2$ gave a mixture of three- and four-membered ring compounds (eq 1). The change in the silicon substituent from mesityl to *tert*-butyl appears to prevent the formation of any Si_2N three-membered rings, as no ^{29}Si signals could be observed upfield of −35 ppm in a crude reaction mixture sample.[7,12] In order to explain these observations, we suggest an alternate reaction pathway (Scheme 1), replac-

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[11] Kosse, P.; Popowski, E. *Z. Anorg. Allg. Chem.* **1992**, *613*, 137.

[12] Gillette, G. R.; West, R. *J. Organomet. Chem.* **1990**, *394*, 45.

[13] It has been shown that partially substituted chlorosilanes can be cleaved by amines. The formation of an amino-substituted silyl anion intermediate such as **6** has precedent, as similar anions have been synthesized and shown to be quite stable. See: Tamao, K.; Kawachi, A.; Ito, Y. *J. Am. Chem. Soc.* **1992**, *114*, 3989.

[14] Kliebisch, U.; Klingebiel, U.; Vater, N. *Chem. Ber.* **1985**, *118*, 4561.

ing our earlier proposal. It should be recognized that several conceivable pathways could lead to the final products **2a** and **2b** and that this is only one possible route.

The first step is the formation of aminodisilane **4** which has been observed in crude product mixtures. This is a slow step, since unreacted $(t\text{-BuSiCl}_2)_2$ was present after reaction. Deprotonation of **4** would yield anion **5**, which could react by intramolecular displacement on the neighboring silicon, breaking the Si–Si bond to give **6**.[13] Reprotonation of the anion could then take place from the mesitylamine generated during the deprotonation step, yielding **7**. Intramolecular HCl elimination,[14] or deprotonation followed by ring closure,[15] would lead to cyclodisilazane **8**. The final step is then substitution of the last chlorine atom by MesNH^- to give **2a,b**.

We hypothesize that a second substitution of MesNH on **4** is very slow, allowing time for the deprotonation and Si–Si bond-breaking reactions to occur. For the less hindered $(\text{MesSiCl}_2)_2$ employed in our earlier study, a second substitution to give $[\text{Mes(MesNH)SiCl}]_2$ may compete with deprotonation and Si–Si cleavage, leading ultimately to the three-membered ring product.

Summary

The net overall reaction for the formation of the cyclodisilazanes can be summarized as

$$3\text{MesNHLi} + (t\text{-BuSiCl}_2)_2 \rightarrow \mathbf{2a} + \mathbf{2b} + 3\text{LiCl} + \text{HCl}$$

This explanation is consistent with our earlier results with less hindered molecules. Use of the smaller mesityl group on silicon allows for a second substitution reaction to compete with deprotonation. When increased substitution occurs, three-membered ring formation is the net result. With *tert*-butyl groups on silicon, a second substitution reaction does not compete favorably with the anionic rearrangement and four-membered ring formation results exclusively. Further work is needed in order to further understand the observed stereochemistry, how Si–Si bond cleavage occurs, and how ring closure takes place.

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Supplementary Material Available: Tables of crystal data, positional parameters, bond distances and angles, and anisotropic thermal parameters for **2a**(**2b**) and for $\mathbf{3a}\cdot 0.5\text{C}_6\text{H}_{14}$ and figures showing NMR spectra (20 pages). Ordering information is given on any current masthead page.

OM930777J

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(15) Gade, L. H.; Becker, C.; Lauher, J. W. *Inorg. Chem.* **1993**, *32*, 2308.