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Synthesis of (Dialkylamino)disilanes

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The only reported preparation of a hexakis(dialkylamino)disilane, namely, $(Me_2N)_3SiSi(NMe_2)_3$ (**1**) (Wiberg, E.; et al. *Inorg. Nucl. Chem. Lett.* **1965**, *1*, 33) was stated to proceed quantitatively. In our hands, this preparation repeatedly gave a mixture of only ~40% **1** and ~60% of the new compound $(Me_2N)_3SiSi(NMe_2)_2Cl$ (**2**). Compound **1** was made in 84% yield, however, by treating the aforementioned mixture with $LiNMe_2$ in THF, and **2** can be prepared in 91% yield from Si_2Cl_6 and excess $HNMe_2$ using ether as the solvent. Also reported here are syntheses for the new compounds $(Me_2N)_3SiSi(NMe_2)_2OMe$, $(Et_2N)_3SiSi(NEt_2)_3$, and $(Me_2N)_3SiOSi(NMe_2)_3$. The possible role of steric hindrance in the complete substitution of Cl groups in Si_2Cl_6 by NR_2 moieties is discussed. Crystallographic parameters for **1** are as follows: monoclinic space group $P2_1/c$, $a = 9.563$ (1) Å, $b = 13.765$ (1) Å, $c = 8.515$ (9) Å, $\alpha = 90.0°$, $\beta = 115.313$ (8)°, $\gamma = 90.0°$, and $Z = 2$. The structural metrics give some indication of steric compression of the substituents around the waist of the molecule.

Introduction

In contrast to the well-known class of compounds $Si(N<)_4$, reports of the corresponding disilanes $(>N)_3SiSi(N<)_3$ are restricted to a paper on the synthesis of $(OCN)_3SiSi(NCO)_3$[1] and a communication regarding the quantitative formation of $(Me_2N)_3SiSi(NMe_2)_3$[2] (**1**) via reaction 1. Although the latter

$$Si_2Cl_6 + 12HNMe_2 \rightarrow \underset{\mathbf{1}}{(Me_2N)_3SiSi(NMe_2)_3} + 6[H_2NMe_2]Cl \qquad (1)$$

preparation has been cited in reviews[3,4] and a compilation,[5] we have not been able to repeat it under the conditions given,[2] namely, by allowing a mixture of Si_2Cl_6 and excess $HNMe_2$ mixed at liquid nitrogen temperature to warm slowly to room temperature, followed by extractive workup and sublimation. In our hands, the reported procedure[2] consistently gave a mixture of ~40% **1** and ~60% of the heretofore unreported $(Me_2N)_3SiSi(NMe_2)_2Cl$ (**2**), which converts to **1** in 84% yield upon further treatment with $LiNMe_2$. We also demonstrate that the chloro derivative **2** can be made in 91% yield when reaction 1 is carried out in diethyl ether at room temperature.

Also reported here are preparations of the new compounds $(Me_2N)_3SiSi(NMe_2)_2OMe$ (**3**), $(Et_2N)_3SiSi(NEt_2)_3$ (**4**), and $(Me_2N)_3SiOSi(NMe_2)_3$ (**5**). Some steric crowding in **1** is reflected in the structural metrics determined for this compound by X-ray crystallography. Steric factors affecting the synthesis of hexakis(dialkylamino)disilanes are discussed.

Experimental Section

All reactions were carried out with the strict exclusion of moisture using conventional vacuum lines and Schlenk techniques.[6] Solvents such as tetrahydrofuran (THF), toluene, benzene, and ether were dried by standard methods and distilled before use. $LiNMe_2$, $LiNEt_2$, and $HNMe_2$ were purchased from Aldrich Chemical Co. and used as received unless stated otherwise. Si_2OCl_6 was purchased from Hüls Petrarch Systems and was used without further purification. ^1H NMR spectra were recorded on a Nicolet NT-300 300-MHz spectrometer using the proton impurity of the solvent as an internal reference. ^{13}C NMR and ^{29}Si NMR experiments were carried out on a Varian VXR-300 300-MHz instrument. Mass spectra were obtained on a Finnigan 4000 (70 eV, EI) or a Kratos MS-50 (70 eV, EI, HRMS) instrument. Melting points were measured with a Thomas Hoover capillary apparatus and are uncorrected. Elemental analyses were performed by Desert Analytics, Tucson, AZ.

Hexakis(dimethylamino)disilane (1). To a dry thick-walled glass reaction tube equipped with a stirring bar was added 1.76 g (6.54 mmol) of Si_2Cl_6 via a nitrogen-flushed syringe. The tube was then cooled to −186 °C in liquid N_2, and 5.1 g (110 mmol, 40% molar excess) of precooled anhydrous $HNMe_2$ was then added to the tube via a 10-mL precooled syringe. The tube was then flame sealed and allowed to warm to room temperature slowly by decanting the liquid N_2 from the dewar and allowing the tube to remain in the dewar. After the tube warmed to room temperature, a white thick pasty material was formed which was shaken from time to time during a 3-h period. After the tube was cooled in a freezer at −15 °C, the tube was quickly opened in the hood and connected to a bubbler to monitor the evaporation of the excess $NHMe_2$. The white solid residue was extracted with 4 × 18 mL of diethyl ether. Vacuum evaporation of the ether afforded 1.89 g of a crystalline solid. ^1H NMR spectroscopy revealed the solid to be a mixture of 38% $Si_2(NMe_2)_6$ (**1**) and 62% $Si_2(NMe_2)_5Cl$ (**2**). Full characterization of these compounds is described later. The mixture sublimes easily at 60 °C at 10×10^{-3} Torr and dissolves well in C_6H_6, ether, THF, and hexane. Attempted separation of the compounds by recrystallization from hexane was not successful because of their similar solubilities. The mixture was then dissolved in 25 mL of THF. The solution was added to 2.0 g of $LiNMe_2$ (39 mmol), and the mixture was refluxed for 42 h. After filtration and removal of solvent under vacuum, the solid residue was sublimed at 60 °C at 10×10^{-3} Torr giving 1.70 g of **1** (5.32 mmol, overall yield 84%) as colorless crystals (mp 217–19 °C with sublimation), which slowly decomposed in air to a white powder: ^1H NMR (300 MHz, C_6D_6) δ 2.53 (s, 36 H); ^1H NMR (300 MHz, $CDCl_3$) δ 2.40 (s, 36 H); ^{13}C NMR (300 MHz, C_6D_6) δ 37.12; ^{29}Si NMR (300 MHz, C_6D_6) δ −24.98; MS (EI, 70 eV, for ^{28}Si) m/z (relative intensity) 320.3 (6.7, M^+), 277.3 (1.4, $M^+ - NMe_2$), 232.2 (0.90 $M^+ - 2NMe_2$), 160.2 (100, $M^+/2$), 116.1 (2.8, $M^+ - Si(NMe_2)_4$). HRMS m/z for $C_{12}H_{36}N_6Si_2$ (M^+): calcd, 320.254 00; found, 320.254 16. Anal. Calcd for $C_{12}H_{36}N_6Si_2$: C, 44.95; H, 11.32; N, 26.21. Found: C, 44.67; H, 11.42; N, 26.40.

Pentakis(dimethylamino)chlorodisilane (2). Method A. A solution of 1.66 g of Si_2Cl_6 (6.17 mmol) in 25 mL of THF was placed in a 50-mL three-necked flask. A 50-mL graduated addition funnel containing several small pieces of freshly cut sodium was attached to the flask. About 15 mL of $HNMe_2$ was added to the addition funnel directly from a cylinder precooled in a freezer, and the contents of the funnel were gently swirled for 5 min. Cooling the flask with liquid N_2 and stoppering the funnel allowed 8 mL (~130 mmol) of $HNMe_2$ to slowly vaporize into the flask

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[1] Hoefler, F.; Peter, W. *Z. Naturforsch. B, Anorg. Chem., Org. Chem.* **1975**, *30B*, 282.

[2] Wiberg, E.; Stecher, O.; Neumaier, A. *Inorg. Nucl. Chem. Lett.* **1965**, *1*, 33.

[3] Lappert, M. F.; Power, P. P.; Sanger, A. R.; Srivastava, R. C. *Metal and Metalloid Amides: Syntheses, Structures, Physical and Chemical Properties*; Wiley and Sons: New York, 1980.

[4] Hengge, E. *Top. Curr. Chem.* **1974**, *51*, 35.

[5] Fluck, E. *Si, Gmelin Handbook of Inorganic Chemistry*; Verlag Chemie: Weinheim, Germany, 1989; Vol. 4B, p 255.

[6] Shriver, D. F.; Drezdon, M. A. *The Manipulation of Air Sensitive Compounds*; Wiley and Sons: New York, 1986.

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via the side arm of the addition funnel. Formation of a colorless precipitate was observed immediately. The mixture was allowed to warm to room temperature and stirred for an additional 1 h while the excess $HNMe_2$ evaporated. The solid precipitate which formed was filtered off and washed with 3 × 15 mL of C_6H_6. The solvents were removed in vacuum, and the solid product was sublimed at 65 °C and 10×10^{-3} Torr to give 1.76 g of crystalline product **2** in 91% yield. See method B for characterization.

Method B. Anhydrous precooled $HNMe_2$ (13.2 g, 293 mmol) was added to a 50-mL precooled Schlenk flask. Hexachlorodisilane (7.85 g, 29.2 mmol) was then dissolved in 50 mL of toluene in a 100-mL flask. The flasks were connected with a nitrogen-flushed Tygon tube, and $HNMe_2$ was slowly transferred to the 100-mL flask by placing it in ~−100 °C ethanol liquid nitrogen cooled cold bath.

After transfer of the $HNMe_2$ was complete, the mixture was allowed to warm to room temperature and was stirred for another 2 h. After filtration, all the volatiles were removed in vacuum leaving 8.05 g of a muddy solid. ^1H NMR spectroscopy indicated that the solid was a mixture of ~55% $Cl(Me_2N)_2SiSi(NMe_2)_3$ (**2**) and ~45% $Cl(Me_2N)_2SiSi(NMe_2)Cl$ (**3**): ^1H NMR (300 MHz, C_6D_6) δ 2.50 (s); ^1H NMR (300 MHz, $CDCl_3$) δ 2.53 (s); ^{13}C NMR (300 MHz, $CDCl_3$) δ 36.76. Both compounds sublime readily at 5×10^{-3} Torr and 60 °C and dissolve well in common organic solvents. The mixture of products was then stirred with 0.804 g of $LiNMe_2$ (15.7 mmol) in 30 mL of C_6H_6 for $^1/_2$ h. After filtration, the solid residue was washed with 3 × 5 mL of C_6H_6. Removal of benzene from the solution in vacuum afforded 7.8 g of **2**: Yield 86% overall; mp 157–159 °C; ^1H NMR (300 MHz, C_6D_6) δ 2.55 (s, 12 H, $Si(NMe_2)_2Cl$), 2.51 (s, 18 H, $Si(NMe_2)_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 2.50 (s, 12 H, $Si(NMe_2)_2Cl$), 2.44 (s, 18 H, $Si(NMe_2)_3$); ^{13}C NMR (300 MHz, C_6D_6) δ 37.07 ($SiN(CH_3)_3$), 37.28 ($SiNMe_2)_2Cl$); ^{29}Si NMR (300 MHz, C_6D_6) δ −26.63 ($SiNMe_2)_3$), −14.54 ($SiNMe_2)_2Cl$); MS (EI, 70 eV for ^{28}Si and ^{35}Cl) *m/z* (relative intensity) 311.2 (1.25, M^+), 276.2 (0.3, $M^+ - Cl$), 267.1 (3.1, $M^+ - NMe_2$), 107.0 (1.55, $M^+ - Si(NMe_2)_4$], 116.1 (3.5, $M^+ - Si(NMe_2)_3Cl$). HRMS (EI, 70 eV) *m/z* for $C_{10}H_{30}N_5Si_2Cl$ (M^+): calcd, 311.172 83; found, 311.172 16. Anal. Calcd for $C_{10}H_{30}N_5ClSi_2$: C, 38.49; H, 9.69; Cl, 11.37. Found: C, 37.75, H, 9.68; Cl, 10.59.

Pentakis(dimethylamino)methoxydisilane (**3**). In the drybox a mixture of 0.52 g (1.7 mmol) of **2** and 0.18 g (3.3 mmol, 94% excess) of NaOMe was placed in a 50-mL flask equipped with a side arm. The mixture was dissolved in 30 mL of THF, and the solution was refluxed for 36 h. THF was removed under vacuum, and the solid residue was extracted with 4 × 15 mL of C_6H_6. After filtration, the benzene was removed in vacuo. The solid residue was subjected to sublimation at 0.2 Torr at room temperature. After a small amount of liquid was collected and discarded during the first half hour, a crystalline product was obtained by sublimation at 2×10^{-2} Torr and 45 °C: Yield 42%; mp 143–145 °C; ^1H NMR (300 MHz, C_6D_6) δ 2.59 (s, 12 H, $Si(N\mathit{Me}_2)_2OMe$), 3.44 (s, 3 H, OMe), 2.56 (s, 18 H, $Si(NMe_2)_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 2.45 (s, 12 H, $Si(N\mathit{Me}_2)_2OMe$), 3.35 (s, 3 H, OMe), 2.41 (s, 18 H, $Si(NMe_2)_3$); ^{13}C NMR (300 MHz, C_6H_6) δ 49.41 (OMe), 37.20 ($Si(NMe_2)_3$), 37.33 ($Si(N\mathit{Me}_2)_2OMe$); ^{29}Si NMR (300 MHz, C_6D_6) δ −27.49 ($Si(NMe_2)_2OMe$), −24.00 ($Si(NMe_2)_3$); MS (EI, 70 eV for ^{28}Si) *m/z* (relative intensity) 307.3 (13.4, M^+), 263.2 (32.5, $M^+ - NMe_2$), 219.2 (7.5, $M^+ - 2NMe_2$), 160.1 (100.0, $M^+ - Si(NMe_2)_2OMe$), 147.1 (7.5, $M^+ - Si(NMe_2)_3$). HRMS (EI, 70 eV) *m/z* for $C_{11}H_{33}N_5OSi_2$ (M^+): calcd, 307.222 37; found, 307.222 83.

Hexakis(diethylamino)disilane (4). Method A. To 40 mL of a diethyl ether solution of 1.07 g of $LiNEt_2$ (13.5 mmol) was added dropwise 0.34 g (1.30 mmol) of Si_2Cl_6 at −20 °C. The solution was allowed to warm to room temperature and was refluxed for 2 h. After filtration and removal of the solvent in vacuum, the solid residue was extracted with 3 × 10 mL of C_6H_6. After the C_6H_6 was evaporated, 0.54 g of the liquid product was obtained in 85% yield. (See method B for characterization.)

Method B. Hexachlorodisilane (1.02 g, 3.80 mmol) was dissolved in 45 mL of diethyl ether, and the solution was cooled to ~−100 °C with a liquid N_2/ethanol slush bath. Anhydrous $HNEt_2$ (8.48 g, 116 mmol) was added to the solution. The mixture was allowed to warm to room temperature, it was stirred for 1 h, and then it was refluxed for another 2 h. The ether and excess $HNEt_2$ were removed by distillation at 1 atm. The solid residue was extracted with 4 × 10 mL of C_6H_6. After removal of the C_6H_6 under vacuum, 1.42 g of liquid product was collected: Yield 77%; ^1H NMR (300 MHz, C_6D_6) δ 1.07 (t, 36 H, Me), 3.04 (q, 24 H, CH_2); ^{13}C NMR (300 MHz, C_6D_6) δ 38.54 (NCH_2), 14.50 (Me); ^{29}Si NMR (300 MHz, C_6D_6) δ −23.24; MS (EI, 70 eV for ^{28}Si) *m/z* (relative intensity) 488.3 (0.04, M^+), 416.4 (13.0, $M^+ - NEt_2$), 344.2 (4.0, $M^+ - 2NEt_2$), 244.2 (11.4, $M^+/2$), 172.2 (22.0, $M^+ - 4N(Et_2)$).

Hexakis(dimethylamino)disiloxane (5). Hexachlorodisiloxane (0.631 g, 2.21 mmol) was added dropwise to 25 mL of a THF solution containing 0.81 g (16 mmol, 20% excess) of $LiNMe_2$ at −20 °C. After being stirred for 1 h at room temperature, the solution contained ~30% of product **5** and ~70% of the apparent intermediate $(Me_2N)_3SiOSi(NMe_2)_2Cl$ (^1H NMR (300 MHz, C_6D_6) δ 2.59 (s, 18 H $(Me_2N)_3Si$), 2.53 (s, 12 H, $(Me_2N)_2SiCl$)). The solution was refluxed for 2 h causing the ^1H NMR peaks for the presumed $(Me_2N)_3SiOSi(NMe_2)_2Cl$ to disappear. The THF was removed under vacuum, and the solid residue was extracted with 4 × 10 mL of benzene. Removal of the benzene under vacuum afforded 0.71 g of product in 96% yield. Further purification was achieved by sublimation at 85 °C and 5×10^{-3} Torr: Mp 108–110 °C; ^1H NMR (300 MHz, C_6D_6) δ 2.57 (s, 36 H, $Si(NMe_2)_3$); ^{13}C NMR (300 MHz, C_6D_6) δ 37.54; ^{29}Si NMR (300 MHz, C_6D_6) δ −51.47; MS (70 eV, EI for ^{28}Si) *m/z* (relative intensity) 336.3 (56.1, M^+), 291.2 (50.6, $M^+ - HNMe_2$), 246.1 (94.7, $M^+ - 2HNMe_2$). HRMS (70 eV, EI) *m/z* for $C_{12}H_{36}OSi_2$ (M^+): calcd, 336.248 92; found, 336.248 17.

Pyrolysis of 2. Into a 5-mm NMR tube equipped with a septum was introduced 20 mg of $Si_2(NMe_2)_5Cl$ (**2**). Heating the compound at about 190 °C for $^1/_2$ h caused browning of the colorless compound. ^1H, ^{13}C, and ^{29}Si NMR spectroscopy revealed peaks for $Si(NMe_2)_4$, which were shown to be consistent with that of commercially available $Si(NMe_2)_4$ (C_6D_6: 2.42, 37.10, −28.13 ppm, respectively).

Reaction of 1 with $(H_2NCH_2CH_2)_3N$ (tren). Compound **1** (0.35 g, 1.1 mmol) was mixed with 0.32 g of tren (2.2 mmol) in a 5-mL flask. A particle of $(NH_4)_2SO_4$ was added as a catalyst, and the mixture was heated at 130 °C. Compound **1**, which sublimed onto the walls of the flask, was scraped back to the bottom of the flask several times. The reaction mixture, which was monitored over a period of 2 h by ^1H NMR spectroscopy, contained only the reactants. In a second attempt, 0.71 g (2.2 mmol) of **1** and 0.63 g (4.4 mmol) of tren plus one drop of Me_3SiCl as a catalyst were mixed in a small thick-walled glass reaction tube. After flame sealing, the tube was heated and stirred at 225 °C for 48 h. At the end of this time ^1H NMR spectroscopy revealed only the presence of tren and **1**.

Reaction of 1 with $(HOCH_2CH_2)_3N$ (TEA). To compound **1** (0.233 g, 0.73 mmol) was added 0.23 g (1.5 mmol) of TEA. The mixture was then dissolved in 10 mL of toluene, and the solution was refluxed for 24 h. Only the starting materials tren and **1** could be detected by ^1H NMR spectroscopy at the end of this period, however. In the absence of solvent, 1.76 g (5.51 mmol) of **1** was mixed with 0.813 g (5.46 mmol) of tren and a catalytic amount of $(NH_4)_2SO_4$. Heating the mixture at 145 °C caused **1** to be sublimed onto the walls of the flask thus necessitating scraping the material back to the bottom of the flask several times during the 3-h period of reaction time. Although the reaction mixture turned brownish, it contained only the starting materials, as confirmed by ^1H NMR spectroscopy.

Crystal Structure of 1. A clear crystal grown by refrigerating a pentane solution of **1** was sealed in a Lindemann capillary which was mounted on the diffractometer. Pertinent data collection and reduction information are listed in Table I. Lorentz and polarization corrections were applied. A correction based on a decay in the standard reflections of 3.9% was applied to the data. An absorption correction based on a series of ψ-scans was also applied.

Axial photographs indicated that the lattice was monoclinic. The space group $P2_1/c$ was chosen on the basis of the systematic absences, and the crystal structure was solved by direct methods.[7] The structure refined well enough that at least one hydrogen of every methyl group could be found in a difference Fourier map. These peaks were used to generate ideal hydrogen positions with C–H distances set equal to 0.95 Å and with isotropic thermal parameters fixed at a factor of 1.3 times the corresponding carbon. All refinement calculations were performed on a Digital Equipment Corp. Micro VAX II computer using the CAD4-SDP programs.[8]

Results and Discussion

Syntheses. The report in 1965[2] of the preparation of $(Me_2N)_3SiSi(NMe_2)_3$ (**1**) involved slow warming of a mixture

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(7) SHELXS-86. Sheldrick, G. M. Institut für Anorganische Chemie der Universität, Göttingen, FRG, 1986.

(8) *Enraf-Nonius Structure Determination Package*; Enraf-Nonius: Delft, Holland. Neutral-atom scattering factors and anomalous scattering corrections were taken from: *International Tables for X-ray Crystallography*; The Kynoch Press: Birmingham, England, 1974; Vol. IV.

Table I. Crystal Data for **1**

formula	$Si_2N_6C_{12}H_{36}$
fw	320.63
space group	$P2_1/c$
a, Å	9.563 (1)
b, Å	13.765 (1)
c, Å	8.5151 (9)
α, deg	90.0
β, deg	115.313 (8)
γ, deg	90.0
V, Å^3	1013 (3)
Z	2
d_{calc}, g/cm^3	1.05
cryst size, mm	0.50 × 0.40 × 0.30
μ(Mo Kα), cm^{-1}	1.7
data collecn instrument	Enraf-Nonius CAD4
radiation (λ, Å)	Mo Kα (0.710 73)
orientation reflcns: no.; range (2θ), deg	25; $17.6 < \theta < 32.1$
t, °C.	25 (1)
scan method	θ–2θ
data collcn range, 2θ, deg	4.0–50.0
no. of data collcd	3824
no. of unique data	2385
tot. no. of data with $F_0^2 > 2.5\sigma(F_0^2)$	945
no. of params refined	91
transm factors: max, min (ψ-scans)	0.999, 0.908
R^a	0.038
$R_w{}^b$	0.053
quality-of-fit indicator^c	1.35
largest shift/esd, final cycle	0.05
largest peak, e/Å^3	0.23 (2)

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$; $w = 1/\sigma^2(|F_o|)$. [c] Quality-of-fit $= [\sum w(|F_o| - |F_c|)^2(N_{obsvns} - N_{params})]^{1/2}$.

of Si_2Cl_6 and excess $HNMe_2$ from liquid N_2 temperature to room temperature in a sealed tube (reaction 1) followed by ether extraction and sublimation of the residue after evaporation. The only characterization of compound **1** mentioned was the measurement of its molecular weight in benzene, although no numerical results were given.[9] Repeated attempts to duplicate this preparation (including up to a 20:1 ratio of amine to Si_2Cl_6) resulted in ~40% **1** and ~60% of the new compound **2** (reaction 2). Compounds **1** and **2** show similar solubilities and easily cosublime. Moreover, in view of their similar molecular weights (320 and 311, respectively) it is not surprising that the molecular weight measurement of the sublimate reported in 1965[2] was concluded to be consistent with a quantitative yield of **1**. When the sealed tube reaction was run with a 12:1 ratio of $HNMe_2$ to Si_2Cl_6, a ^1H NMR singlet at 2.50 ppm was also observed which we tentatively attribute to the presence of some $Cl(Me_2N)_2SiSi(NMe_2)_2Cl$. This species (which disappears upon adding $LiNMe_2$) is also a main product in reaction 3, which is carried out at room temperature. Both compounds cosublime easily, but the mixture is readily converted in good yield (86%) to **2** upon treatment with $LiNMe_2$ in benzene at room temperature.

$$\mathrm{Si_2Cl_6 + xs\ HNMe_2 \rightarrow \underset{\mathbf{1}}{Si_2(NMe_2)_6} + \underset{\mathbf{2}}{(Me_2N)_3SiSi(NMe_2)_2Cl} + [H_2NMe_2]Cl} \qquad (2)$$

$$\mathrm{Si_2Cl_6 + 10HNMe_2 \xrightarrow{toluene} \underset{\sim 45\%}{Cl(Me_2N)_2SiSi(NMe_2)_2Cl} + \underset{\sim 55\%}{\mathbf{2}}} \qquad (3)$$

Conversion of the mixture of **1** and **2** to **1** in reaction 1 was accomplished by reaction 4. An 84% yield of **1** was realized after sublimation.

$$\mathbf{1} + \mathbf{2} + \mathrm{LiNMe_2} \xrightarrow[\text{reflux}]{\text{THF}} \mathbf{1} + \mathrm{LiCl} \qquad (4)$$

Compound **2** is easily converted to the corresponding methoxy derivative **3** via reaction 5. The sublimed crystalline product was realized in 42% yield. The low yield may be due to side reactions involving Si–Si breakage in the presence of nucleophiles.[10]

$$\mathbf{2} + \mathrm{xs\ NaOMe} \xrightarrow[\text{reflux}]{\text{THF}} \underset{\mathbf{3}}{\mathrm{(Me_2N)_3SiSi(NMe_2)_2OMe}} \qquad (5)$$

The new hexakis(diethylamino)disilane (**4**) is formed in 85% yield in reaction 6 and in 77% yield in reaction 7. We find it somewhat surprising that this sterically hindered compound is formed in good yield under the mild condition of refluxing ether. This result contrasts the nucleophilic Si–Si bond cleavage that has been reported to occur[11] (reaction 8). Related disproportionations of a variety of disilanes to mono- and polysilanes have also been reported to be induced by tertiary amines.[12]

$$\mathrm{Si_2Cl_6 + 6LiNEt_2} \xrightarrow[\text{reflux}]{\mathrm{Et_2O}} \underset{\mathbf{4}}{\mathrm{(Et_2N)_3SiSi(NEt_2)_3}} \qquad (6)$$

$$\mathrm{Si_2Cl_6 + xs\ HNEt_2} \xrightarrow[\text{reflux}]{\mathrm{Et_2O}} \mathbf{4} \qquad (7)$$

$$\mathrm{Si_2Cl_6 + 7HNEt_2 \rightarrow Cl_2Si(NEt_2)_2 + ClHSi(NEt_2)_2 + 3[H_2NEt_2]Cl} \qquad (8)$$

The new disiloxane **5** is apparently formed as a mixture with the monochloro derivative shown in the first step of reaction 9. However, treatment with $LiNMe_2$ in the second step affords a crude yield of 96% of sublimable **5**.

$$\mathrm{O(SiCl_3)_2} \xrightarrow[\text{THF, rt}]{\mathrm{xs\ LiNMe_2}} \underset{\sim 70\%}{\mathrm{(Me_2N)_3SiOSi(NMe_2)_2Cl}} + \underset{\mathbf{5}}{\underset{\sim 30\%}{\mathrm{O[Si(NMe_2)_3]_2}}} \xrightarrow[\text{THF, reflux}]{\mathrm{LiNMe_2}} \mathbf{5} \qquad (9)$$

Reactivities. Although **1** slowly hydrolyzes in air,[2] we have found it to be thermally stable at approximately 230 °C for 48 h in a sealed tube. In contrast, **2** disproportionates at ca. 190 °C to form $Si(NMe_2)_4$ as an identifiable product plus a polymeric material perhaps arising from the silylene $:Si(NMe_2)Cl$, which was mass spectrally detected as the cation $:Si(NMe_2)Cl^+$ (m/z 107, 1.55%) under EI conditions. The cation $:Si(NMe_2)_2{}^+$ (m/z = 116, 3.5%) was also detected in the mass spectrum of **2** as well as in that of **1**.

In an earlier publication we reported the synthesis of azasilatranes **6** via condensation of $ZSi(NMe_2)_3$ with the corresponding tetraamine.[13] Silatranes of type **7** with a wide variety of Z groups can similarly be easily synthesized from $ZSi(NMe_2)_3$ and $(HOCH_2CH_2)_3N$ (TEA).[14] Attempts to react **1** with

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(9) In a later paper (Hengge, E.; Pletka, H. D.; Höfler, F. *Monatsh. Chem.* **1970**, *101*, 325) a $\delta(^1H)$ value of **1** in CCl_4 of 2.56 ppm was reported which compares favorably with our value of 2.53 ppm in C_6D_6. In this reference an interpretation of the IR spectrum of this compound was also put forth. However, the origin of the sample was not given. We thank one of the reviewers for bringing this paper to our attention.

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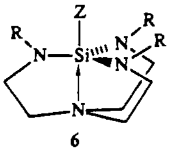
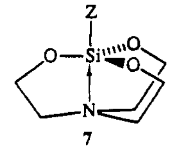


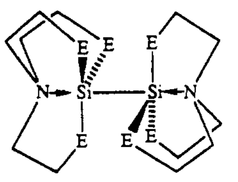
6

Z	R
H	Me
OEt	Me
H	SiMe$_3$
OEt	H



7

$(H_2NCH_2CH_2)_3N$ (tren) or $(HOCH_2CH_2)_3N$ to form disilatranes **8** under a variety of conditions failed, leaving starting materials as the only detectable species present.



E = O, NH

8

Structure of 1. The ORTEP drawing of **1** is shown in Figure 1, and its positional coordinates are collected in Table II. The Si–Si bond distance of 2.369 (1) Å in **1** is within experimental error of that of Si_2Me_6 (2.34 (10) Å), slightly longer than that in $Me_3SiSiPh_3$ (2.355 (1) Å), and shorter than that in Si_2Ph_6 (2.519 (4) Å) and in $Si_2(t\text{-}Bu)_6$ (2.697 Å).[15] The bond distance in **1** is close to that in Si_2H_6 (2.331 (3) Å[15]), indicating little if any of the steric congestion that is likely to be present in $Si_2(t\text{-}Bu)_6$. The average Si–N distance in **1** (1.716 (2) Å) is within experimental error of that in H_3SiNMe_2 (1.715 (4) Å) and $ClSi(NMe_2)_3$ (1.715 (2) Å).[16] Interestingly, the average N–C bond distance for the distal methyl groups (1.461 (4) Å) is shorter than for the proximal methyls (1.490 (4) Å). Since the former distance lies within the range (1.446–1.468 Å) for $HNMe_2$, $ClSi(NMe_2)_3$, and other (dialkylamino)silanes,[15] the proximal methyl groups may be responding to steric congestion around the "waist" of the molecule.

Although the angles around the silicons in **1** are close to tetrahedral, the Si–Si–N angles (average 110.22 (9)°) are somewhat larger, and the N–Si–N angles somewhat smaller (average 108.7 (1)°). These data also suggest that there is rather close packing of the methyl groups in this molecule, particularly around its waist. The sum of the bond angles around the nitrogens (average 359.2°) indicates a near trigonal planarity geometry around these atoms, as is consistently observed in aminosilane compounds.[16,17]

NMR Spectra. Although the assignments of the ^1H and ^{13}C NMR spectral shifts were quite straightforward, the ^{29}Si chemical shift assignments deserve comment since they did not always follow the usual electronegativity argument. The association of the −26.63 and −14.54 ppm shifts in **2** with the $(Me_2N)_3Si$ and $Si(NMe_2)_2Cl$ moieties, respectively, was made in the present work on the basis of shifts to lower field observed for ^{29}Si by others[18] on substituting a chlorine for a less electronegative bromine in $SiBr_4$ (−92.7 ppm) to give $SiClBr_3$ (−69.8 ppm) and for an iodine in SiI_4 (−346.2 ppm) to give $SiClI_3$ (−245.9 ppm). On the other hand, the upfield ^{29}Si chemical shift in **3** is assigned to the $Si(NMe_2)_2OMe$ fragment (−27.49 ppm), and the downfield one, to the $(Me_2N)_3Si$ group (−24.00 ppm). The reasons for this are 2-fold. First, an upfield shift is seen from $Si(NMe_2)_4$ (−28.13 ppm) to $Si(OMe)_4$ (−79.2 ppm[18]), and second, shielding is also observed from disilane **1** (−24.98 ppm) to disiloxane **5** (−51.47 ppm).

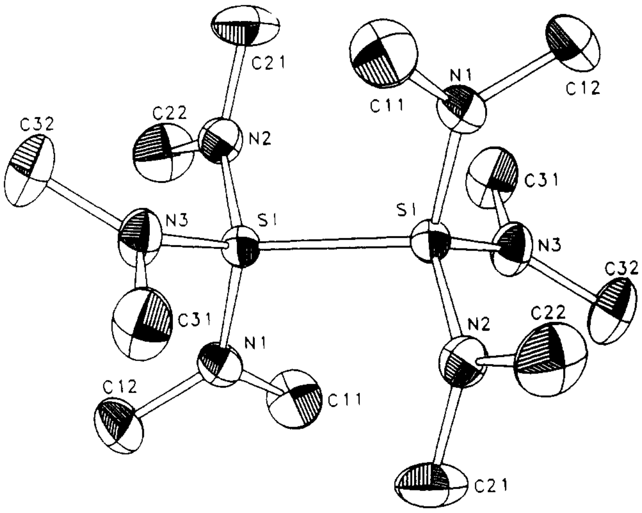


Figure 1. ORTEP drawing of **1** with ellipsoids drawn at the 50% probability level.

Table II. Positional and *B* Parameters and Their Estimated Standard Deviations for **1**[a]

atom	*x*	*y*	*z*	*B*, Å^2
Si	0.6340 (2)	0.4972 (1)	0.0359 (2)	3.43 (3)
N1	0.7084 (6)	0.3862 (4)	0.1203 (6)	4.5 (1)
N2	0.6636 (5)	0.5169 (4)	−0.1471 (6)	4.5 (1)
N3	0.7314 (5)	0.5848 (4)	0.1872 (6)	4.8 (1)
C21	0.5947 (9)	0.6010 (6)	−0.2641 (9)	7.0 (2)
C11	0.6336 (9)	0.2936 (5)	0.037 (1)	6.7 (2)
C(31)	0.7111 (9)	0.5944 (7)	0.3516 (8)	6.8 (2)
C22	0.7793 (8)	0.4552 (6)	−0.185 (1)	7.3 (2)
C32	0.8587 (8)	0.6440 (6)	0.189 (1)	6.9 (2)
C12	0.8625 (6)	0.3701 (6)	0.260 (1)	7.9 (3)

[a] *B* values for anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as $(4/3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$.

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Supplementary Material Available: Tables of general displacement parameters, hydrogen positional parameters, and bond distances and angles for **1** (3 pages). Ordering information is given on any current masthead page.

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(18) Watkinson, P. J.; Mackay, K. M. *J. Organomet. Chem.* **1984**, *275*, 39. Downfield shifts are also recorded in this article as *x* increases to 4 in $SiCl_xBr_{4-x}$ and $SiCl_xI_{4-x}$.