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Synthesis, characterization and novel reactions of azasilatranes and azagermatranes

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Synthesis, characterization and novel reactions of azasilatranes and azagermatranes

by

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DEDICATION

To My Father and Mother

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GENERAL INTRODUCTION

Dissertation organization

This dissertation consists of four papers. The first two papers represent research as it was published, the third paper has been submitted and the fourth one will be submitted soon for journal publication. Literature citations, tables and figures pertain only to the paper in which they are included. Preceding the first paper is a brief general introduction. References cited in the general introduction are listed at the end of that chapter. Following the last paper is a general summary and acknowledgments.

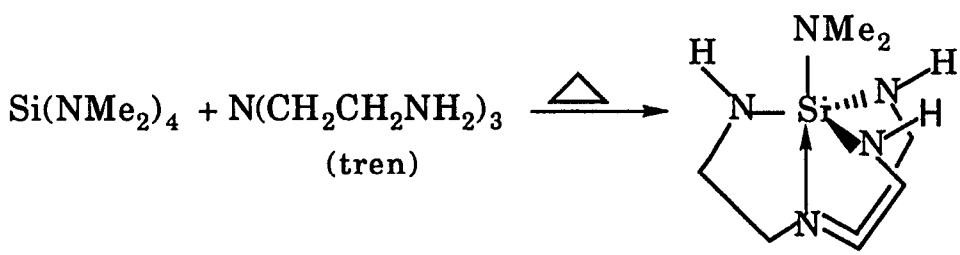
Introduction

The initial goal of this research was to develop a series of pentacoordinate silicon compounds, i.e., aminoazasilatranes $R_2NSi(R'NCH_2CH_2)_3N$ (R, R' = H, alkyls etc.), exclusively coordinated by nitrogens as candidates for potential single-source MOCVD precursors for silicon nitride films. There is a large variety of applications of silicon nitride in industry, owing to its great hardness, wear resistance, chemical stability and high mechanical strength at temperatures up to 1300 °C. There have been several well-investigated and well-established methods to prepare bulk silicon nitride powder or ceramics[1]. The manufacture of silicon nitride fibers or films, however, proceeds preferentially by the pyrolysis of organic silazanes etc. as precursors, because of the high melting point of silicon nitride[2]. The search for ideal precusors is still ongoing, because pyrolysis products of carbon-containing precursors are

generally contaminated with elemental silicon and carbon and silicon carbide which is virtually inseparable from silicon nitride[3]. The high molar ratio of nitrogen to silicon in aminoazasilatranes and no direct bonding between silicon and carbon in these proposed precursors, may favor the formation of pure silicon nitride upon pyrolysis.

A knowledge of the chemistry of a variety of azatranes has recently expanded substantially mainly owing to the endeavors of our group in synthesizing them as potential volatile precursors for other non-metallic nitrides and metal nitrides[4]. A broad range of azatranes is now known, including azatitanatranes[5], azaboratranes[6], azaaluminatranes[7], azagalla-tranes[8], azastannatranes[9], azaphosphatrane cations[10]. In particular, a group of new alkyl and alkoxy azasilatranes has been readily synthesized by heating a mixture of tris(dimethylamino)silanes and tris(2-aminoethyl)amine (tren) or its tris-N-substituted derivatives in the presence of acidic catalysts[11].

To our surprise, no report of aminoazasilatranes with amino substituents at the apical position of azasilatranes was ound in the primary literature. This does not indicate the lack of an interest in this type of compound however, since as early as in 1971, Le Grow claimed the synthesis



of aminoazasilatrane according to the above reaction in a patent[12]. However, no characterization or yield was reported and no structural discussion was included. In our laboratory, repeated attempts to duplicate this synthesis produced only nonvolatile oligomeric materials[13, 11]. Another approach we tried, based on the well-known amide-catalyzed reaction of silanes with amines[14], was to mix dialkylamines such as $HN(CH_2CH_3)_2$ with hydroazasilatranes in the presence of $LiNEt_2$ as a catalyst but this also failed. Only the starting material was recovered quantitively.

As we shall see in papers 3 and 4, nucleophilically substituting the chloride in chlorazasilatranes $ClSi(R'NCH_2CH_2)_3N$ (R' = H (**2**), CH_3 (**4**)) with various amide anions afforded some of the desired aminoazasilatranes. These new compounds indeed show high volatility, which makes them attractive candidates to be evaluated as silicon nitride precursors. In the course of the synthesis of aminoazasilatranes, an interesting hydride transfer mechanism, depending substantially on the steroelectronic properties of the nucleophiles as well as on the equatorial NR' functionalities, was observed. This process was also observed when various alkyl lithiums or phenyl lithium served as nucleophilic reagents, but not with metal alkoxides. The results of the comparison of the reactivity between chloroazasilatranes and the acyclic tetracoordinate analog $ClSi[N(CH_3)_2]_3$ toward nucleophiles is in agreement with the well-established fact that the reactivity of extracoodinated silicon species is much higher than that of their tetravalent analogs[15]. In the reaction of **4** with C_6F_5Li, a novel fluoride transfer reaction is observed, resulting in the isolation of three new compounds, i.e., the fluoride transfer

product $FSi(CH_3NCH_2CH_2)_3N$, a substitution product $C_6F_5Si(CH_3NCH_2CH_2)_3N$, and the tetrafluorobenzyne insertion product $C_6F_5Si(CH_3NCH_2CH_2)_2(C_6F_4CH_3NCH_2CH_2)N$. The insertion product has been fully characterized by ^1H, ^{13}C, ^{29}Si, DQF COSY, ^1H-^{13}C HETCOR and VT^{19}F NMR spectroscopy as well as an X-ray crystallographic analysis. The transannular Si-N bond (2.246 Å) is strong despite the presence of a seven-membered ring in the insertion product.

In the course of preparing hexa(dimethylamino)disilane according to a literature report[16] as a starting material for an unsuccessful attempt to synthesize a "head to head" dimer containing two azasilatranes, a new compound that proved to be pentakis(dimethylamino)chlorodisilane was discovered. It is readily synthesized by mixing excess of $HNMe_2$ with Si_2Cl_6 in ether. This compound proved to be a precursor for generating bis(dimethylamino)silylene under relatively mild conditions.

Despite the extensive documentation of germatranes[17] and thiogermatranes[18], no azagermatranes were reported in the literature. As the first examples of such compounds, azagermatranes are readily accessible via conventional transamination reactions. The underlying driving force of the interesting interconversion between azagermatranes and less sterically hindered tripodal ligands to give the less sterically hindered atranes was elucidated with the aid of X-ray structure determinations of two azagermatranes.

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PAPER 1. SYNTHESIS OF DIALKYLAMINO DISILANES

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ABSTRACT

The only reported preparation of a hexakis-dialkylamino disilane, namely, $(Me_2N)_3SiSi(NMe_2)_3$, **1** (E. Wiberg et al., *Inorg. Nucl. Chem. Letters* **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: monoclinic space group $P2_1/c$, a = 9.563 (1) Å, b = 13.765 (1) Å, c = 8.515 (9) Å, α = 90.0°, β = 115.313 (8)°, γ = 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

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

latter 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 work-up 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 diethylether 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 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 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, Arizona.

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 hr period. After cooling the tube 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 $HNMe_2$. The white solid residue was extracted with 4 x 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 x 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 0.20 g of $LiNMe_2$ (3.9 mmol) and the mixture was refluxed for 2 h. After filtration and removal of solvent under vacuum, the solid residue was sublimed at 60 °C at 10 x 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 (75.429 MHz, C_6D_6) δ 37.12; ^{29}Si NMR (59.585 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 320.25400, found 320.25416; 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. By cooling the flask with liquid N_2 and stoppering the funnel, 8 mL (~ 130 mmol) of $HNMe_2$ was slowly vaporized into the flask 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 hour while the excess $HNMe_2$ evaporated. The solid precipitate which formed was filtered and washed with 3 x 15 mL of C_6H_6. The solvents were removed in vacuum and the solid product was sublimed at 65 °C and 10 x 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), (300 MHz, $CDCl_3$) δ 2.53 (s), ^{13}C NMR (75.429 MHz, $CDCl_3$) δ 36.76). Both compounds sublime readily at 5 x 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 x 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 (75.429 MHz, C_6D_6) δ 37.07 ($SiN(CH_3)_3$) 37.28 ($Si(NMe_2)_2Cl$); ^{29}Si NMR (59.585 MHz, C_6D_6) δ -26.63 ($Si(NMe_2)_3$) -14.54 ($Si(NMe_2)_2Cl$); 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 311.17283, found 311.17216; 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 dry box 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 x 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 crude product was obtained by sublimation at 2 x 10^{-2} torr and 45 °C. Yield, 42%; mp, 143-145 °C; ^{1}H NMR (300 MHz, C_6D_6) δ 2.59 (s, 12 H, Si(N*Me*$_2$)$_2$OMe), 3.44 (s, 3 H, OMe), 2.56 (s, 18 H, Si(NMe$_2$)$_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.45 (s, 12 H, Si(N*Me*$_2$)$_2$OMe), 3.35 (s, 3 H, OMe), 2.41 (s, 18 H, Si(NMe$_2$)$_3$); ^{13}C NMR (75.429 MHz, C_6H_6) δ 49.41 (OMe), 37.20 (Si(NMe$_2$)$_3$), 37.33 (Si(N*Me*$_2$)$_2$OMe); ^{29}Si NMR (59.585 MHz, C_6D_6) δ -27.49 (Si(NMe$_2$)$_2$OMe), -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$_2$)$_2$OMe), 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 307.22237, found 307.22283.

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 x 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 atmosphere. The solid residue was extracted with 4 x 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 (75.429 MHz, C_6D_6) δ 38.54 (NCH_2), 14.50 (Me); ^{29}Si NMR (59.585 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 a 25 mL of a THF solution containing 0.81 g (16 mmol, 20% excess) of $LiNMe_2$ at -20 °C. After stirring 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 x 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 x 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 (75.429 MHz, C_6D_6) δ 37.54; ^{29}Si NMR (59.585 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 336.24892, found 336.24817.

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 190° for 1/2 h caused browning of the colorless compound. ^1H, ^{13}C and ^{29}Si NMR spectroscopy revealed peaks for $SiCl(NMe_2)_3$, which were compared favorably with those of an authentic sample of $SiCl(NMe_2)_3$. (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 based on 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]

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
crystal size, mm	0.50 x 0.40 x 0.30
$\mu(MoK_\alpha)$, cm^{-1}	1.7
data collec instrument	Enraf-Nonius CAD4
radiation	MoK_α (λ = 0.71073 Å)
orientation reflections: range (2θ), deg	25, 17.6 < θ < 32.1
t, °C.	25(1)
scan method	θ - 2θ
data collcn range, 2θ, deg	4.0-50.0
no. data collcd	3824
no. unique data	2385
tot. no. of data with $F^2_o > 2.5\sigma(F^2_o)$:	945

Table I. Continued.

no. of parameters refined	91
Trans. 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] $R = \Sigma||F_o|-|F_c||/\Sigma|F_o|$

[b] $R_w = [\Sigma w(|F_o|-|F_c|)^2/\Sigma w|F_o|^2]^{1/2}$; $w = 1/\sigma^2(|F_o|)$

[c] Quality-of-fit = $[\Sigma w(|F_o|-|F_c|)^2(N_{obs}-N\text{parameters})]^{1/2}$

Table II. Table of Positional 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)
C31	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]Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: (4/3) * [a^2*B(1,1) + b^2*B(2,2) + c^2*B(3,3) + ab(cos gamma)*B(1,2) + ac(cos beta)*B(1,3) + bc(cos alpha)*B(2,3)]

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 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.

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

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 co-sublime easily, but the mixture is readily converted in good yield (86%) to **2** upon treatment with $LiNMe_2$ in benzene at room temperature. Conversion of the mixture of **1** and **2**

$$Si_2Cl_6 + 10HNMe_2 \xrightarrow{\text{toluene}} \underset{\sim 45\%}{Cl(Me_2N_2)SiSi(NMe_2)_2Cl} + \underset{\sim 55\%}{2} \qquad (3)$$

to **1** in reaction 1 was accomplished by reaction 4. An 84% yield of **1** was realized after sublimation.

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

Compound **2** is 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]

$$\mathbf{2} + xsNaOMe \xrightarrow[\text{reflux}]{\text{THF}} \underset{\mathbf{3}}{(Me_2N)_3SiSi(NMe_2)OMe} \qquad (5)$$

The new hexakisdiethylamino 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

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

$$Si_2Cl_6 + xsHNEt_2 \xrightarrow[\text{reflux}]{Et_2O} \mathbf{4} \qquad (7)$$

condition of refluxing ether. This result contrasts the nucleophilic Si-Si bond cleavage that has been reported to occur[11] (reaction 8). Related

$$Si_2Cl_6 + 7HNEt_2 \longrightarrow Cl_2Si(NEt_2)_2 + ClHSi(NEt_2)_2 + 3[H_2NEt_2]Cl \qquad (8)$$

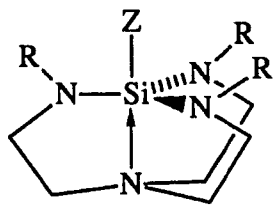
disproportionations of a variety of disilanes to mono and polysilanes have also been reported to be induced by tertiary amines.[12]

The new disiloxane **5** is apparently formed as a mixture with the mono chloro 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**.

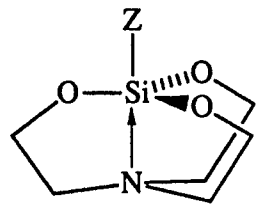
$$O(SiCl_3)_2 \xrightarrow[THF,\ rt]{xsLiNMe_2} \underset{\sim 70\%}{(Me_2N)_3SiOSi(NMe_2)_2Cl} + \underset{\sim 30\%}{O[Si(NMe_2)_3]_2} \xrightarrow[THF,\ reflux]{LiNMe_2} \underset{5}{5} \qquad (9)$$

Reactivities. Although **1** slowly hydrolyzes in air,[2] we have found it to be thermally stable at 230 °C for 48 hours in a sealed tube. In contrast, **2** disproportionates at 190 °C to form $Si(NMe_2)_3Cl$ as an identifiable product plus a oligomeric material perhaps arising from the silylene $:Si(NMe_2)_2$ which was mass spectrally detected as the cation $:Si(NMe_2)_2^+$ (*m/z* 116, 3.5%) under EI conditions. Interestingly, the cation: $Si(NMe_2)Cl^+$ (*m/z* = 107, 1.55%) was also detected in the mass spectrum of **2**.

In an earlier publication we reported the synthesis of azasilatranes **6** via

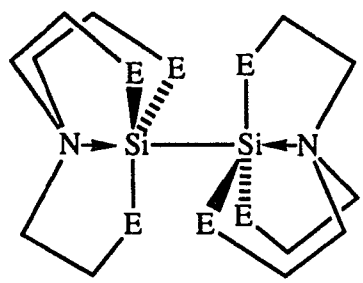


Z	R
H	Me
OEt	Me
H	$SiMe_3$
OEt	H



6 7

condensation of $ZSi(NMe_2)_3$ with the corresponding tetramine.[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 $(H_2NCH_2CH_2)_3N$ (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

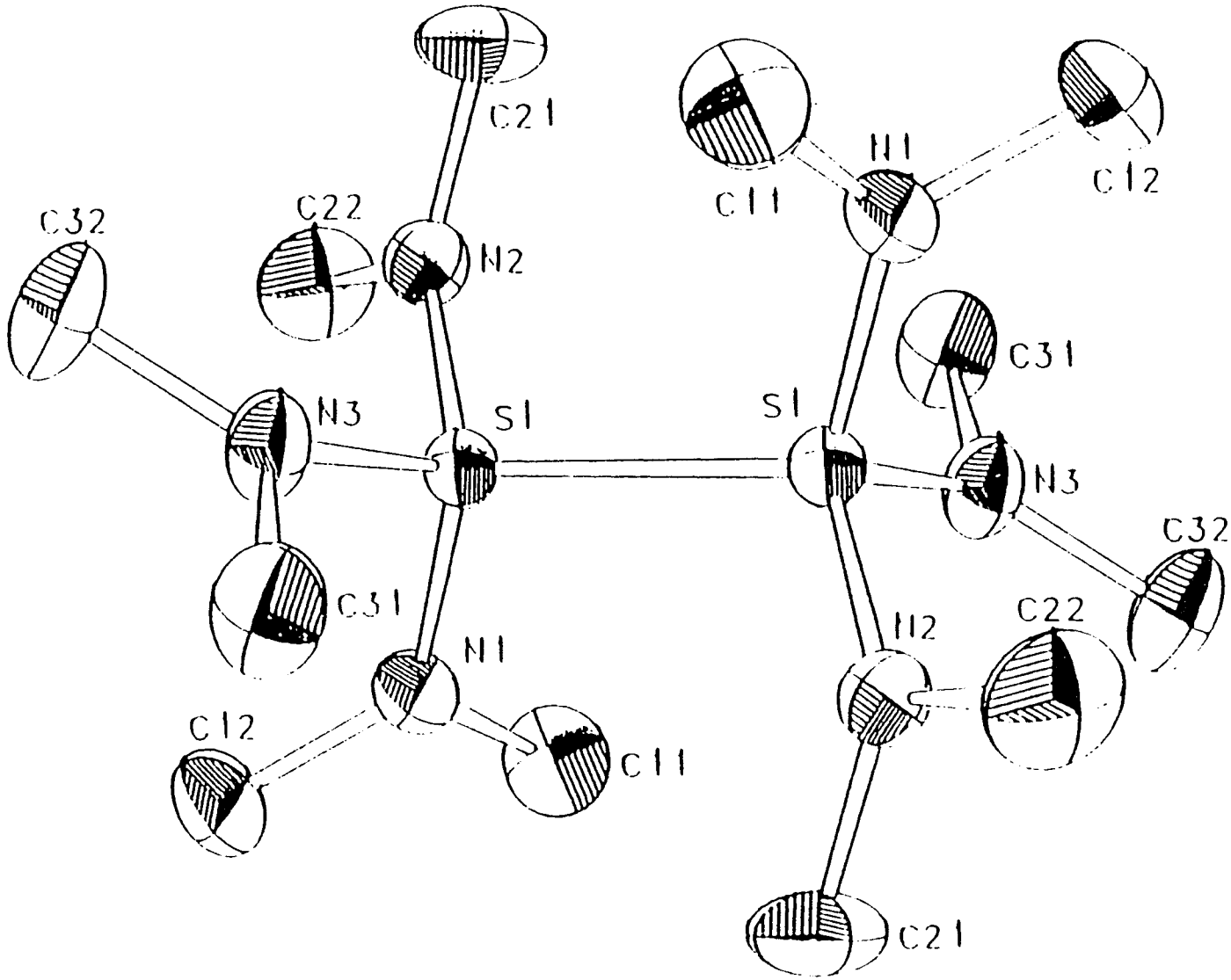
8

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 Si_2Me_6 (2.34 (10) Å), slightly longer than in $Me_3SiSiPh_3$ (2.355 (1) Å), and shorter than 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 amino silane 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



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

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 two-fold. First, an upfield shift is seen from $Si(NMe_2)_4$ (-28.13 ppm) to $Si(OMe)_4$ (-79.2 ppm[18]) and secondly, shielding is also observed from disilane **1** (-24.98 ppm) to disiloxane **5** (-51.47 ppm).

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However, the origin of the sample was not given. We thank one of the referees for bringing this paper to our attention.

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SUPPLEMENTARY MATERIAL

Table I. Anisotropc Displacement Coefficient ($Å^2$) for **1**

Name	U(1,1)	U(2,2)	U(3,3)	U(1,2)	U(1,3)	U(2,3)
SI	0.0381(6)	0.0488(8)	0.0424(6)	-0.001(1)	0.0162(4)	0.002(1)
N1	0.051(3)	0.053(3)	0.063(3)	0.008(2)	0.019(2)	0.010(3)
N2	0.051(2)	0.068(4)	0.058(2)	0.003(2)	0.030(2)	0.005(3)
N3	0.051(3)	0.073(4)	0.055(2)	-0.018(3)	0.021(2)	-0.015(3)
C21	0.115(5)	0.079(5)	0.086(4)	0.024(4)	0.056(3)	0.039(4)
C11	0.092(5)	0.054(4)	0.099(5)	0.002(4)	0.032(4)	-0.015(4)
C31	0.087(4)	0.124(6)	0.051(3)	-0.030(5)	0.033(3)	-0.028(4)
C22	0.101(4)	0.103(6)	0.108(4)	0.018(4)	0.079(2)	-0.002(4)
C32	0.074(4)	0.088(5)	0.108(5)	-0.039(4)	0.046(3)	-0.025(5)
C12	0.056(5)	0.096(6)	0.112(6)	0.011(4)	0.002(4)	0.039(5)

This form of the anisotropic displacement parameter is:
$\exp[-2\pi^2\{h^2a^2U(1,1)+k^2b^2U(2,2)+l^2c^2U(3,3)+2hkabu(1,2)+2hlacU(1,3)$
$+2klbcU(2,3)\}]$, where a,b and c are reciproocal lattice constants

Table II. Postional Parameters and Their Estimated Standard Deviations (Å) for 1

Atom	x	y	z	B(Å²)
H111	0.6369	0.2509	0.1262	8*
H112	0.6875	0.2646	-0.0223	8*
H113	0.5287	0.3041	-0.0423	8*
H121	0.8602	0.3161	0.3284	10*
H122	0.8942	0.4265	0.3308	10*
H123	0.9332	0.3575	0.2108	10*
H211	0.5063	0.6233	-0.2508	9*
H212	0.5649	0.5816	-0.3812	9*
H213	0.6688	0.6517	-0.2352	9*
H221	0.8308	0.4200	-0.0938	9*
H222	0.8527	0.5096	-0.1910	9*
H223	0.7307	0.4312	-0.2918	9*
H311	0.6166	0.5643	0.3362	8*
H312	0.7081	0.6611	0.3783	8*
H313	0.7947	0.5636	0.4443	8*
H321	0.8691	0.6288	0.0852	8*
H322	0.9531	0.6291	0.2859	8*
H323	0.8373	0.7113	0.1888	8*

Starred atoms were refined isotropically

Table III. Bond Distances in Angstroms for 1

Atom 1	Atom 2	Distance	Atom 1	Atom 2	Distance
SI	SI	2.369(1)	N1	C12	1.462(4)
SI	N1	1.708(2)	N2	C21	1.485(4)
SI	N2	1.720(2)	N2	C22	1.462(4)
SI	N3	1.720(2)	N3	C31	1.499(4)
N1	C11	1.485(4)	N3	C32	1.460(4)

Estimated standard deviation in the least significant figure are given in parentheses

Table IV. Intromolecular Bond Angles for 1 in degrees.

Atom 1	Atom 2	Atom 3	Angle	Atom 1	Atom 2	Atom 3	Angle
SI	SI	N1	110.35(9)	C11	N1	C12	111.7(2)
SI	SI	N2	109.87(9)	SI	N2	C21	122.2(2)
SI	SI	N3	110.44(9)	SI	N2	C22	123.7(2)
N1	SI	N2	108.8(1)	C21	N2	C22	113.1(3)
N1	SI	N3	108.5(1)	SI	N3	C31	121.1(2)
N2	SI	N3	108.8(1)	SI	N3	C32	125.4(2)
SI	N1	C11	122.5(2)	C31	N3	C32	112.6(3)
SI	N1	C12	124.9(2)				

*Numbers in parentheses are estimated standard deviation in the least significant digits.

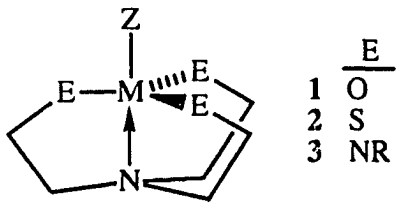
PAPER 2. SYNTHESIS AND INTERCONVERSIONS OF AZAGERMATRANES

ABSTRACT

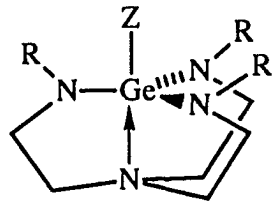
The syntheses of the first examples of the title compounds, namely, $ZGe(NRCH_2CH_2)_3N$ (**4**, R = H, Z = Me; **5**, R = Me, Z = Me; **6**, R = H, Z = *t*-Bu; **7**, R = Me, Z = *t*-Bu; **8**, R = Me, Z = NMe_2) are reported. Syntheses of the new compounds $MeGe(NMe_2)_3$ and *t*-$BuGe(NMe_2)_3$ and an improved synthesis of $Ge(NMe_2)_4$ are also recorded. The azagermatranes **5** and **7** are transformed to **4** and **6**, respectively, in the presence of $(H_2NCH_2CH_2)_3N$. This reaction was not found to be reversible, however. Azagermatranes **4** or **5** and **6** or **7** in the presence of $(HOCH_2CH_2)_3N$ easily react to give $MeGe(OCH_2CH_2)_3N$ and *t*-$BuGe(OCH_2CH_2)_3N$, respectively. Because of steric factors, one or more of compounds **6**, **7** or **8** may display weakened or even an absence of transannular Ge<-N bonding.

INTRODUCTION

Atranes (**1**) have been extensively studied for a variety of M atoms and Z substituents, and have been known for a long time, particularly for the Group 14 elements.[1] By contrast, Group 14 thiatranes (**2**) are much less well known.[2] Azatranes (**3**) were also quite rare (except for a few examples for M =



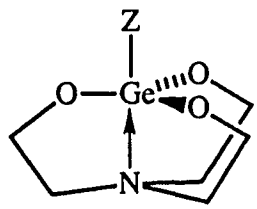
	E
1	O
2	S
3	NR



	Z	R
4	Me	H
5	Me	Me
6	*t*-Bu	H
7	*t*-Bu	Me
8	NMe_2	Me

Si[3]) until our interest in such compounds was aroused by their potential as MOCVD agents for metal and non-metal nitrides. Thus we have recently expanded this class of compounds to include a broad variety azasilatranes (Z = R, OR, NR_2),[4] and the first examples of azatitanatranes (Z = NR_2),[5] azavanadatranes (Z = O, NR),[6,7] azamolybdatranes (Z = N),[6] azastannatranes (Z = R, NR_2),[6,8] azaboratranes (Z = nothing),[7] aza-alumatranes (Z = nothing),[7] and azaphosphatrane cations (Z = H^+).[9] Herein we report the first azagermatranes, **4-8**. We also demonstrate that the alkyl azagermatranes can be transformed to other azagermatranes and to germatranes. Thus **5** and **7** are labile with respect to replacement of their tetra-amino cage moiety by a $(HNCH_2CH_2)_3N$ fragment in the presence of $(H_2NCH_2CH_2)_3N$, giving **4** and **6**, respectively. The azagermatranes **4-7** react with $(HOCH_2CH_2)_3N$ to yield the corresponding germatranes **9** and **10**. Also reported here are

convenient preparations for the new compounds $RGe(NMe_2)_3$ (R = Me, *t*-Bu) and an improved synthesis for $Ge(NMe_2)_4$.



9, Z = Me
10, Z = *t*-Bu

EXPERIMENTAL SECTION

All reactions were carried out with the strict exclusion of moisture by using standard inert-atmosphere and Schlenk techniques. Solvents such as tetrahydrofuran (THF), benzene and Et_2O were dried by standard methods and distilled before use. Commercially available (Gelest, Inc.) $MeGeCl_3$, *t*-$BuGeCl_3$ and $GeCl_4$ were used without further purification. $LiNMe_2$ was purchased from Aldrich and used directly. "Tren" $(H_2NCH_2CH_2)_3N$ was distilled at 85 °C at 15 x 10^{-3} torr from $LiAlH_4$ before use. Me_3-tren ($(MeHNCH_2CH_2)_3N$) was prepared from the purified tren by using a standard procedure.[10] Triethanolamine (TEA) was distilled under vacuum at 97 °C and 14 x 10^{-3} torr and stored over type 4Å molecular sieves.

^1H NMR and ^{13}C NMR spectra were recorded on a Nicolet-300 300 MHz spectrometer or on a Varian VXR-300 300 MHz instrument using the solvent peaks as an internal reference. Low and high resolution mass spectra were obtained on a Finnigan 4000 instrument (70 eV, EI) and a Kratos MS-5 spectrometer (70 eV, EI), respectively. Melting points were measured with a Thomas Hoover capillary apparatus and are not corrected. Elemental analysis were performed by Desert Analytics, Tucson, Arizona.

Tris(dimethylamino)methylgermane, $MeGe(NMe_2)_3$. To a 20 mL suspension of 1.08 g of $LiNMe_2$ (21.2 mmol) in ether cooled to -50 °C, was added dropwise 1.27 g of $MeGeCl_3$ (6.54 mmol) via a nitrogen-flushed syringe. A white precipitate formed instantly. The mixture was allowed to warm to

room temperature and was stirred for an additional 2h. After filtration, the solid residue was washed with 3 x 5 mL of ether. The ether was removed under vacuum, giving a cloudy liquid which was distilled at 40 °C and 1.0 torr, affording 1.10 g of colorless product in 77% yield. $MeGe(NMe_2)_3$ decomposes in air, instantly forming a white solid which is soluble in water. Liquid density, 1.03 g/mL; ^1H NMR (C_6D_6): 2.60 (s, 18 H, NMe_2), 0.21 (s, 3 H, GeMe); ^{13}C NMR (C_6D_6): 39.92 (NMe_2), -8.49 (GeMe); MS (70 eV, EI for ^{74}Ge): *m/z* (relative intensity, proposed ion) 221.2 (10.1, M^+), 222.2 (31.1, M^++1), 206.2 (1.5, M^+-Me), 177.1 (100.0, M^+-NMe_2), 162.2 (2.1, M^+-NMe_2-Me), 133.1 (2.4, M^+-$2NMe_2$), 118.1 (9.7, M^+-$2NMe_2$-Me).

***t*-Butyltris(dimethylamino)germane, *t*-BuGe(NMe$_2$)$_3$.** In 15 mL of ether was dissolved 2.56 g (10.8 mmol) of $BuGeCl_3$. This solution was added dropwise to 25 mL of an ether suspension of 1.72 g (33.7 mmol) of $LiNMe_2$ cooled to -50 °C. The reaction mixture was allowed to warm to room temperature and was stirred for another 3 h. After filtration and removal of ether under vacuum, 2.83 g of crude product was obtained. Distillation at 80-82 °C at 10 torr afforded 2.27 g of a crystalline product in 80% yield. Mp, 43-44 °C; liquid density 1.01 g/mL; ^1H NMR (C_6D_6): 2.64 (s, 18 H, NMe_2), 1.16 (s, 9 H, CMe_3); ^1H NMR ($CDCl_3$): 2.59 (s, 18 H, NMe_2) 1.13 (s, 9 H, CMe_3); ^{13}C NMR ($CDCl_3$): 41.06 (NMe_2), 29.25 (CMe_3), 0.55 (CGe); MS (70 eV, EI for ^{74}Ge): *m/z* (relative intensity, proposed ion) 263.1 (1.1, M^+), 219.1 (8.2, M^+-NMe_2), 206.1 (47.1, M^+-*t*-Bu), 162.0 (19.9, M^+-NMe_2-*t*-Bu), 118.0 (100.0, M^+-$2NMe_2$-*t*-Bu); HRMS for $C_{10}H_{27}N_3{}^{74}Ge$ (M^+): calcd 263.14240, found 263.14185.

Tetrakis(dimethylamino)germane, $Ge(NMe_2)_4$. The synthesis of this compound via the reaction of $GeBr_4$ with excess $HNMe_2$[11] or by reacting $GeCl_4$ with excess $HNMe_2$ in a sealed ampoule was reported earlier.[11] An alternate route we devised was to add dropwise to a mixture of 2.66 g (52.2 mmol) of $LiNMe_2$ cooled in 40 mL of ether to -50 °C, a solution of 2.59 g (12.1 mmol) of $GeCl_4$. After stirring the solution for an additional 2 h at room temperature, filtration and vacuum evaporation of the ether, 2.91 g of crude product was obtained. Distillation at 50 °C at 0.2 torr (lit. 82-83 °C at 12 torr[11]) gave 2.34 g of pure colorless product. Yield, 79%; ^1H NMR (C_6D_6): d 2.64 (s, 24 H); ^{13}C NMR (C_6D_6): d 40.24.

Methylazagermatrane 4. A mixture of 0.397 g (1.81 mmol) of $MeGe(NMe_2)_3$ and 0.250 g (1.71 mmol) of tren reacted after about 1 minute as evidenced by solidification of the mixture and the release of $HNMe_2$. By sublimation at 5 x 10^{-3} torr at 75 °C, 0.31 g of colorless crystalline product was collected in 78% yield. Mp, 74-75 °C; ^1H NMR (C_6D_6): 2.77 (t, 6 H, $HNCH_2$, $^3J_{HH}$ = 5.7 Hz), 2.22 (t, 6 H, $N(CH_2)_3$), 0.54 (bd s, 3 H, NH), 0.08 (s, 3 H, MeGe); ^{13}C NMR (C_6D_6): 52.55 ($HNCH_2$), 38.59 ($N(CH_2)_3$), 1.37 (MeGe); MS (70 eV, EI for ^{74}Ge): *m/z* (relative intensity, proposed ion) 232.1 (9.8, M^+), 217.1 (100.0, M^+-Me), 188.0 (80.9, M^+-NH_2CHCH_2); HRMS (70 eV, EI) for $C_7H_{18}N_4{}^{74}Ge$ (M^+): calcd 232.07505, found 232.07441.

Methylazagermatrane 5. A mixture of $MeGe(NMe_2)_3$ (0.619 g, 2.82 mmol), Me_3-tren (0.420 g, 2.24 mmol) and a catalytic amount of $(NH_4)_2SO_4$

was heated at 125 °C with stirring. After 3 h, release of $HNMe_2$ ceased and a yellowish liquid resulted which distilled very slowly at 60 °C at 5 x 10^{-2} torr giving 0.48 g of colorless liquid product in 63% yield. ^1H NMR (C_6D_6): 2.71 (s, 9 H, NMe), 2.66 (t, 6 H, MeNCH_2, $^3J_{HH}$ = 5.7 Hz), 2.24 (t, 6 H, $N(CH_2)_3$, 0.56 (s, 3 H, MeGe); ^{13}C NMR (C_6D_6): 49.64 (NMe), 49.47 (MeNCH_2) 39.14 ($N(CH_2)_3$), -0.28 (MeGe); MS (70 eV, EI for ^{74}Ge): *m/z* (relative intensity, proposed ion) 274.2 (13.1, M^+), 259.1 (25.4, M^+-Me), 215.1 (10.8, M^+-$CH_2CHNMeH$), 200.1 (2.8, M^+-Me-$CH_2CHNMeH$); HRMS (70 eV, EI) for $C_{10}H_{24}N_4{}^{74}Ge$ (M^+): calcd 274.12200, found 274.12163.

***t*-Butylazagermatrane 6.** A mixture of 0.909 g (3.47 mmol) of *t*-BuGe(NMe_2)$_3$ and 0.456 g (3.12 mmol) of tren was heated at 120 °C for 2 h. Because a ^1H NMR spectrum of a sample of the mixture in C_6D_6 revealed no evidence of reaction, a catalytic amount of $(NH_4)_2SO_4$ was added. After stirring the mixture at 120 °C for another 2 h, the mixture stopped evolving $HNMe_2$ and upon cooling it to room temperature, it solidified. The colorless crystalline product was collected in 54% yield by sublimation at 55 °C at 14 x 10^{-3} torr. Mp, 75-76°; ^1H NMR (C_6D_6): 2.74 (t, 6 H, HNCH_2, $^3J_{HH}$ = 5.4 Hz), 2.20 (t, 6 H, $N(CH_2)_3$), 1.10 (s, 9 H, *t*-BuGe), 0.62 (bd s, 3 H, NH); ^{13}C NMR (C_6D_6): 53.40 ($HNCH_2$), 39.00 ($N(CH_2)_3$) 28.51 (Me), 26.53 (GeC); MS (70 eV, EI for ^{74}Ge): *m/z* (relative intensity, proposed ions) 274.2 (0.7, M^+), 217.1 (100.0, M^+-Bu); HRMS for $C_{10}H_{25}{}^{74}GeN_4$ (M^++H): calcd 275.12982, found 275.12984; HRMS (70 eV, EI) for $C_6H_{15}{}^{74}GeN_4$ (M^+-*t*-Bu): calcd 213.05397, found

213.05375; Anal. calcd for $C_6H_{15}GeN_4$: C, 44.01; H, 8.86; N, 20.52. Found: C, 43.83; H, 9.15; N, 20.54.

***t*-Butylazagermatrane 7.** A mixture of 0.400 g (1.53 mmol) of *t*-Bu(NMe_2)$_3$, Me_3-tren (0.24 g, 1.28 mmol) and a catalytic amount of $(NH_4)_2SO_4$ as a catalyst was stirred at 120 °C until escape of dimethylamine ceased (2.5 h). The crude liquid was distilled very slowly at 50 °C at 20 x 10^{-3} torr, affording 0.29 g of product in 61% yield. ^{1}H NMR (C_6D_6): 2.64 (s, 9 H, NMe), 2.53 (t, 6 H, MeNC*H*$_2$, $^3J_{HH}$ = 5.0 Hz), 2.33 (t, 6 H, N(CH_2)$_3$), 1.39 (s, 9 H, CMe_3); ^{13}C NMR (C_6D_6): 53.52 (NMe) 50.18 (MeN*C*H$_2$), 38.11 (N(CH_2)$_3$), 31.05 (*Me*$_3$C), 27.20 (*C*Me$_3$); MS (70 eV, EI for ^{74}Ge): *m/z* (relative intensity, proposed ion) 316.2 (0.05, M$^+$) 259.1 (100.0, M$^+$-*t*-Bu), 202.0 (6.2, M$^+$-$CH_2CHNHCH_3$); HRMS (70 eV, EI) for $C_{12}H_{27}N_4$ ^{74}Ge (M$^+$): calcd 301.14547, found 301.14521.

Dimethylamino-azagermatrane 8. In a Schlenk tube, 0.645 g (2.60 mmol) of Ge(NMe_2)$_4$ was mixed with 0.443 g (2.36 mmol) of Me_3-tren and a catalytic amount of $(NH_4)_2SO_4$. The mixture was heated at 120 °C with stirring until no more $HNMe_2$ was evolved (3 h). The crude product was purified by slow distillation at 45 °C at 25 x 10^{-3} torr giving 0.15 g of pure liquid product in (19% yield). ^{1}H NMR (C_6D_6): 2.97 (s, 6 H, NMe_2), 2.73 (s, 9 H, GeNMe), 2.66 (t, 6 H, MeNC*H*$_2$, $^3J_{HH}$ = 5.7 Hz), 2.12 (t, 6 H, N(CH_2)$_3$; ^{13}C NMR (C_6D_6): 50.40 (NMe) 50.30 (MeN*C*H$_2$), 41.34 (GeN*Me*$_2$), 39.05 (N(CH_2)$_3$); MS (70 eV, EI for ^{74}Ge) *m/z* relative intensity, proposed ion): 303.2 (6.4; M$^+$),

259.1 (100.0, M^+-NMe_2), 246.2 (0.6, M^+-$NMeHCHCH_2$) 202.1 (14.2, M^+-NMe_2-$NMeHCHCH_2$); HRMS for $C_{11}H_{27}N_5$ ^{74}Ge (M^+): calcd 303.14854, found 303.14823.

Reaction of 5 with tren: To a solution of 20 mg (0.073 mmol) of **5** in 0.45 mL of C_6D_6 in an NMR tube, was added 11 mg (0.075 mmol) of tren. The ^1H NMR spectrum recorded 1/2 h later revealed that ~50% of **5** had converted to **4**. Eight h later, the reaction was complete, as evidenced by the ^1H and ^{13}C NMR spectra which revealed the presence of free Me_3-tren, and **4** as the only germanium-containing product.

Reaction of 7 with tren. To a solution of 30 mg (0.095 mmol) of **7** in 0.5 mL of C_6D_6 in an NMR tube was added 15 mg (0.096 mmol) of tren. The product, *t*-butylazagermatrane **6** was detected instantly by ^1H NMR spectroscopy. After 12 h, the reaction was complete as evidenced by ^1H and ^{13}C NMR spectroscopy which revealed only the presence of *t*-butylazagermatrane **6** and free Me_3-tren.

Reactions of 4-7 with TEA. These NMR tube experiments were carried out in C_6D_6 (0.5 mL) at ambient temperature using approximately equimolar amounts (~0.07-0.1 mmol) of each of the title compounds and TEA. Monitoring the reactions by ^1H NMR spectroscopy showed that the reaction was over for **4** and **5** by the time the spectra were run. In the case of **6** the reaction took about 14 h whereas for **7** it was complete by the time the

spectrum was run. The purity of the reaction products in all of these mixtures was also verified by ^{13}C NMR spectroscopy.

Reaction of $MeGe(NMe_2)_3$ and *t*-$BuGe(NMe_2)_3$ with TEA. These NMR tube experiments were carried out as described in the proceding paragraph except ca. equimolar amounts of the title compounds (~0.02-0.04 mmol) and TEA were used. In the case of $MeGe(NMe_2)_3$, the reaction to form the corresponding germatrane was over immediately whereas with *t*-$BuGe(NMe_2)_3$ only 60% conversion was evident by ^1H NMR spectroscopy even after 44 h at reflux temperature.

DISCUSSION

Syntheses. An effective route to two new *tris*-dimethylamino germanes synthesized in this work is shown in reactions 1 and 2. The *tetrakis* analogue

$$RGeCl_3 + 3LiNMe_2 \xrightarrow{Et_2O} RGe(NMe_2)_3 + 3LiCl \quad (1)$$

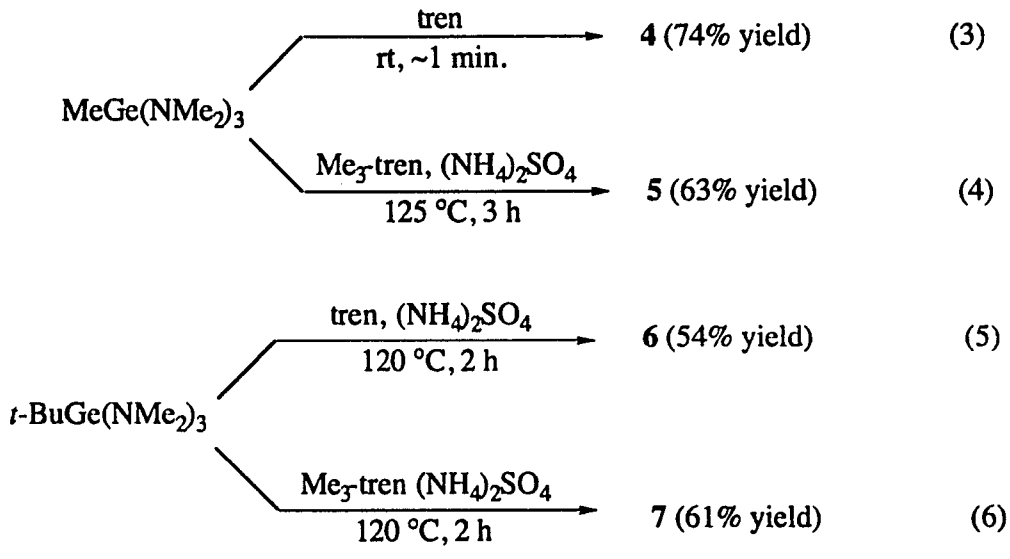
R = Me, 77% yield
R = *t*-Bu, 80% yield

$$GeCl_4 + 4LiNMe_2 \xrightarrow{Et_2O} Ge(NMe_2)_4 + 4LiCl \quad (2)$$

79% yield

$Ge(NMe_2)_4$ was reported to form in ~79% yield in the reaction of $GeBr_4$ with excess $HNMe_2$ in cyclohexane.[11] Using $GeCl_4$, however, this procedure led to incomplete conversion and only by heating the products with excess $HNMe_2$ to 110 °C in a sealed ampoule was $Ge(NMe_2)_4$ formed, and that in mediocre yield (58%).[11] Because of the generally greater availability and considerably lower price of $GeCl_4$ compared with $GeBr_4$, the preparation under mild conditions described here (reaction 2) appears to be the method of choice.

The conditions for the syntheses of **4-7** (reactions 3-6) reflect the steric properties of the reactants. Thus whereas tren reacts in minutes in reaction 3 to give **4** at room temperature, the formation of **5-7** requires heating for 2 to 3 hours above 100 °C in the presence of a catalyst. NMR tube reactions in C_6D_6 of the two reactants in reactions 3-6 (without catalyst) revealed formation of **4** within minutes at room temperature, partial conversion to **5** after 10 h at reflux temperature, and no detectable **6** or **7** after 10 h at reflux

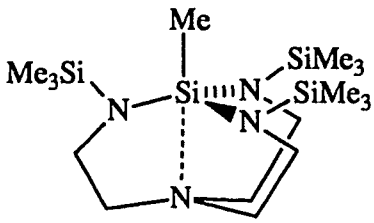


temperature. Interestingly, reaction 7 for the preparation of **8** (albeit in low yield) gives only a polymeric material when tren is used instead of Me_3-tren. This contrasting behavior between the two tetramines has also been noted

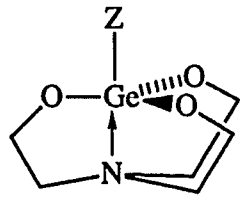
$$Ge(NMe_2)_4 + (MeHNCH_2CH_2)_3N \xrightarrow[(NH_4)_2SO_4]{120\ ^\circ C,\ 3\ h} \underset{(19\%\ yield)}{\mathbf{8}} \qquad (7)$$

with other $M(NMe_2)_x$ species in our laboratories (e.g., M = B,[8] Al,[8] Ti[5] and Si[12]). It may be that these atoms activate the second hydrogen on the primary amine nitrogens to further substitution, thus leading to oligomers.

Because sterically unhindered azasilatranes[4] and azastannatranes[7] possess transannular bonds, it is expected that the same is true for **4** and **5**. In view of the quasi-azasilatrane structure of **11** estabished by X-ray means, however,[4a] it is possible that one or more of compounds **6-8** could exhibit an



11



	Z
12	*t*-Bu
13	Et
14	α-naphthyl
15	ICH_2
16	(-)-1-menthoxy

analogous structure. Unfortunately, a comparison of the ^1H and ^{13}C NMR data for these compounds with their acyclic precursors provides no meaningful trends that might suggest the presence or absence of a transannular bond in **4-8**. Until suitable crystals of **4** or **6** for X-ray analysis can be grown (**5**, **7** and **8** are liquids) this question remains unanswered.

Azagermatrane interconversions. Although germanium compounds are well known to undergo monodentate ligand exchange in thermodynamically controlled equilibrium reactions,[13] reactions 8 and 9 demonstrate that a

$$\mathbf{5} + \underset{\text{tren}}{(H_2NCH_2CH_2)_3N} \longrightarrow \mathbf{4} + (MeHNCH_2CH_2)_3N \qquad (8)$$

$$\mathbf{7} + (H_2NCH_2CH_2)_3N \longrightarrow \mathbf{6} + (MeHNCH_2CH_2)_3N \qquad (9)$$

tetradentate amino ligand can be quantitatively replaced by another. Interestingly this reaction is not reversible to any detectable extent, suggesting that steric factors probably dominate in the replacement of the more sterically hindered $(MeNCH_2CH_2)_3N$ moiety by the $(HNCH_2CH_2)_3N$ fragment. Such a replacement may also permit a stronger transannular

interaction. It is worth noting that reaction 9 was carried out at room temperature in C_6D_6 and was ~50% complete in 0.5 h, whereas reaction 5 produced no detectable product at 120° for two hours unless a catalyst was present. (That a solvent effect is not operative here was shown by the absence of a detectable amount of **6** when reaction 5 was carried out for 10 h in refluxing C_6D_6.) This result is contrary to expectation since reaction 5 is entropically and thermodynamically favored, and the reactant *t*-$BuGe(NMe_2)_3$ is less sterically encumbered than **7** in reaction 9. We are presently unable to explain this result satisfactorily. It is possible that if there is significant (albeit strained) transannular bonding in **7**, the hybridizational promotion energy from a tetrahedral to a trigonal bipyramidal Ge geometry required in reaction 5 (which could be virtually absent in reaction 9) favors the azagermatrane interconversion in reaction 9. Reactions 10 and 11, carried out as NMR tube experiments, are quantitative at room temperature. For **4**, **5** and **7** the reaction was over in

$$\mathbf{4}\text{ or }\mathbf{5} + \underset{\text{TEA}}{(HOCH_2CH_2)_3N} \xrightarrow{C_6D_6} \mathbf{9} + \text{tren or } Me_3\text{-tren} \qquad (10)$$

$$\mathbf{6}\text{ or }\mathbf{7} + (HOCH_2CH_2)_3N \xrightarrow{C_6D_6} \mathbf{10} + \text{tren or } Me_3\text{-tren} \qquad (11)$$

minutes whereas for **6** it took ~14 h. The reason for slowness of **6** to react may be due to steric inhibition. Although this factor is expected to be larger in the case of **7**, it may be sufficiently large that the transannular bond is weakened or broken in this compound, thus rendering the Ge center more electrophilic.

The replacement of three Ge-N linkages by three stronger Ge-O bonds favors these reactions, as does the reduction in the steric requirements of the $(OCH_2CH_2)_3N$ group. The structures for **12**, **13** and **14** determined by X-ray means reveal the presence of Ge<-N transannular bonds (2.238 (6), 2.24 and 2.24 Å, respectively.[14] This distance appears to be slightly shorter in **15** (2.19 (3) Å[15]) and **16** (2.150 (7) Å[16]). These data strongly suggest that **9** and **10** also contain transannular bonds, whose strengths are probably enhanced by the three electronegative alkoxy oxygens over the three less electronegative amido nitrogens present in azagermatranes. The reaction of **8** with TEA gave a complicated mixture, undoubtedly owing to competitive departure of the Me_2N substituent with that of the MeN nitrogens in the $(MeNCH_2CH_2)_3N$ moiety during nucleophilic displacement by the triol.

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(12) Here $Si(NMe_2)_4$, whether heated with or without a catalyst in the presence of tren or Me_3-tren, does not give the corresponding dimethylamino-azasilatrane,[4a] although $Me_2NSi(HNCH_2CH_2)_3N$ has been claimed to be formed in this manner in a patent (LeGrow, G. E. U.S. Patent 3,576,026, 1971).

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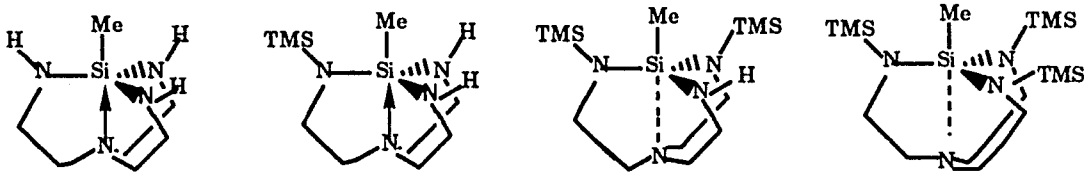
SUPPLEMENTARY MATERIAL

X-ray Structure Determinations of Two Azagermatranes

Since our paper on azagermatranes was submitted, we remained interested in an attempt to account for the interconversion of azagermatranes using additional experiments. One possible choice was the measurement of ^{73}Ge NMR chemical shifts of the azagermatranes **4-8** to compare the relative strength of the transannular bonds. This was suggested by the effectiveness of the ^{29}Si NMR spectroscopic method to probe the relative strength of various azasilatranes[1]. For example, increasing steric congestion around the silicon of azasilatrane by stepwise trimethylsilylation of the equatorial HN functionalities as shown below leads to downfield ^{29}Si chemcial shifts which indicate



4a -68.3 ppm

4b -56.7ppm

4c -36.2ppm

4d -25.7ppm

weakening of transannular Si<-N bond[2]. Indeed, an X-ray diffraction analysis showed that **4d** possesses the longest transannular bond (2.87 Å) ever found in an azasilatrane, consistent with the most downfield chemical shift.

We decided to extend this approach to the study of azagermatranes with ^{73}Ge NMR spectrosocpy. Also we were encouraged by the reports of ^{73}Ge shifts for germatranes.[3]

However, we have not been able to observe any ^{73}Ge resonance for the *t*-butylazagermatranes **6** or methylazagermatrane **4**. To our surprise, the resonances of *t*-butylgermatranes **12** and methylgermatrane **10** were not seen either, which were prepared by adding one equivalent of triethanolamine (TEA) to **6** and **4**, respectively. The failure to observe ^{73}Ge signals may stem from the unfavorable ^{73}Ge NMR properties, i.e., low natural abundance (7.8%) and low detection sensitivity, the high nuclear spin (I = 9/2) and hence a quadrupole moment[4]. Similar phenomena have been reported. For instance, Comparison of a ^{73}Ge NMR resonance for $GeCl_4$·BPY (-313.7ppm) with that of $GeCl_4$ (30.9ppm) revealed the formation of a hexa-coordinated Ge species. However, no ^{73}Ge resonance was observed for analogs $GeBr_4$·BPY and GeI_4·BPY[5]. In light of the fact that germatranes whose ^{73}Ge shifts have been recorded almost have alkoxys groups at the apical postion, the electric field gradient around the germanium atoms in **4**, **6**, **9** and **10** may be too large to observe any ^{73}Ge NMR peaks. Nevertheless, the ^{73}Ge chemical shifts we recorded for $Ge(NMe_2)_4$ (48.6ppm) and $GeCl_4$ (29.7 ppm) compared favorably with the literature values.[4a, 6]

A second approach to elucidating transannular bonding in these systems is the X-ray crystal structure analysis of azagermatranes. The molecular structures of both **4** and **6** have been determined. Their crystals were grown readily by sublimation at 30 and 50 °C at $15x10^{-3}$ mmHg for **4** and **6**,

respectively. These crystals were extremely moisture sensitive and decomposed in air instantly, thus, they were mounted in 0.5 mm glass capillaries in a nitrogen-filled glove box and flame-sealed. The diffraction intensity data for **4** and **6** were collected on a RIGAKU AFC6R diffractometer with graphite monochromated Mo Kα radiation and a 12 KW rotating anode generator.

For **4**, cell constant and an orientation matrix for data collection, obtained from a least-squares refinement using the setting angles of 21 carefully centered reflections in the range of $25.18<2\emptyset<29.63^{\circ}$ corresponded to a monoclinic cell. Based on the systematic absences of h0l:l≠2n; 0k0:k≠2n and the successful solution and refinement of the structure, the space group was determined to be $P2_1/c$.

For **6**, the similar operation using the setting angles of 12 carefully centered reflections in the range of $30.95<2\emptyset<38.32^{\circ}$ corresponded to a rhombohedral (hexagonal axes) cell with dimensions a = 10.370(4) Å, c = 21.416(2) Å. Based on the systematic absences of hkl:-h+k+l≠3n, packing considerations, a statistical analysis of intensity distribution and the sucessful solution and refinement of the structure, the space group was determined to be R3(h).

For both **4** and **6**, the intensities of three representative reflections which were measured after every 150 reflections remained constant within the errors of measurement throughout data collection, thus no decay correction was applied. On the other hand, Lorentz and polarization corrections were applied. An empirical absorption correction, based on azimuthal scans of

several reflections, was also applied which resulted in transmission factors ranging from 0.88 to 1.00 for **4** and from 0.84 to 1 for **6**, respectively.

The crystal data and the experimental conditions for data collection, solution and structure refinement are listed in Table **1**. The structures of **4** and **6** were solved by direct methods and were refined by a full-matrix least-squares method using the TEXSAN(VAX) crystallographic software package[8]. All non-hydrogen atoms were refined with anisotropic thermal parameters. All the hydrogens in **4** and **6** were placed and refined. Neutral atom scattering factors were taken from Cromer and Waber.[9] The bond distances, bond angles and postional parameters for **4** are listed in Tables II, III, and IV, respectively. The corresponding data for **6** are given in Tables V, VI, VII, and VIII, respectively.

As illustrated in Figures 1 and 2, the germanium atoms in both **4** and **6** possess a somewhat distorted trigonal bipyramidal coordination sphere similar to that in germatranes [10], azasilatranes[11] or azastannatranes[12]. The transannular bond distances, 2.395(1) Å in **4** and 2.361(6) Å in **6** are considerably longer than those in ethylgermatrane[10] (2.24 Å), *t*-butylgermatrane[10] (2.238(6) Å) and in phenylazasilatrane (2.132(4) Å)[11]. However, these values are close to that in phenylazastannatrane[12] (2.415 Å). This clearly demonstrates that the transannular Ge<-N bond exists in both **4** and **6** but is weaker than those in germatranes. This is consistent with the fact that nitrogen has lower electronegativity than oxygen. Based on the reasonable prediction that the transannular bonds in more sterically hindered N, N', N'''-trimethylazagermatranes are even weaker, it is easily understandable

that the strengthening of transannular bond contributes to the interconversion of sterically hindered azagermatranes in the presence of less sterically hindered tripodal ligands to give the less sterically hindered atrane systems.

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Table I. Crystallographic Data for **4** and **6**

	4	**6**
empirical formula	$GeN_4C_7H_{18}$	$GeN_4C_{10}H_{21}$
fw	241.92	269.89
color; habit	colorless, monoclinic	colorless, monoclinic
crystal size (mm)	0.40x 0.40 x 0.35	.400x .60 x 0.20
crystal system	monoclinic	rhombohedral
space group	$P2_1/c$(#14)	R3(h) (#148)
a (Å)	8.650(2) Å	10.370(4) Å
b (Å)	8.3244(9) Å	10.370(4) Å
c (Å)	13.845(2) Å	21.416(2) Å
a (deg)	90.0°	90.0°
b (deg)	95.40(1)°	90.0°
g (deg)	90.0°	120.0°
volume $(Å)^3$	992.5(2)	1994(1)
Z	4	6
d_{calcd} (g/cm^3)	1.619	1.349
abs coeff (cm^{-1})	30.05	22.52
F(000)	524	846
diffractometer	Rigaku AFC6R	Rigaku AFC6R
radiation	MoKa (0.71069 Å)	MoKa (0.71069 Å)
temperature (K)	296	296
monochromator	graphite crystal	graphite crystal

Table I. Continued.

2ø scan range	6.76 to 50.1	6.0 to 60.1
scan type	ω-2θ	ω-2θ
scan speed (deg/min)	16.0(in omega)	16.0(in omega) (2 rescans)
$2\theta_{max}$	50.1	60.1
collected reflcns	4229	2761
independent reflecns	1899	1303
R_{int} (%)	5.1	5.8
observed reflcns, n_{obs}	922 ($I \geq 3.00\sigma(I)$)	872 ($I > 3.00\sigma(I)$)
p-factor	0.03	0.03
Least-square Weights	$4F_o^2/\sigma^2(F_o^2)$	$4F_o^2/\sigma^2(F_o^2)$
no. of variable, n_{var}	109	46
solution	direct methods	direct methods
largest and mean D/s	0.001, 0.000	0.001, 0.000
data-to-parameter ratio	8.46	18.96
largest peak ($e \cdot A^{-3}$)	0.58	0.56
largest hole ($e \cdot A^{-3}$)	-0.47	-0.55
R (%)[a]	4.7	4.2
R_w (%)[b]	7.0	5.1
GOF[c]	3.23	1.57

$R^a = \Sigma||F_o|-|F_c||/\Sigma|F_o|$

$R_w{}^b = [\Sigma w(|F_o|-|F_c|)^2/\Sigma w|F_o|^2]^{1/2}$; $w = 1/\sigma^2(|F_o|)$

$GOF^c = [\Sigma w(|F_o|-|F_c|)^2(N_{obs}-N\text{parameters})]^{1/2}$

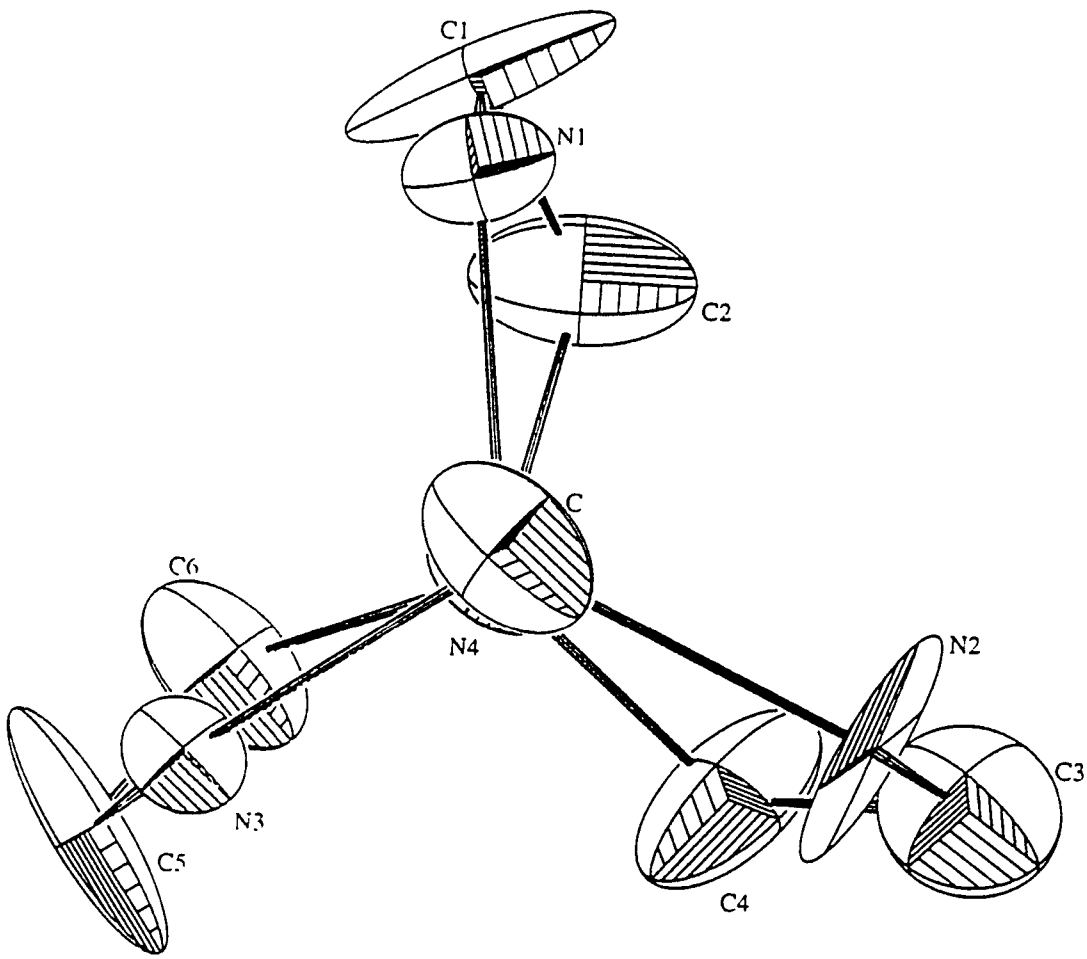


Figure 1. The Molecular structure of $MeGe(HNCH_2CH_2)_3N$ 4 (a) topview showing the propeller-like conformation of the molecule and eclipse of the axial atoms.

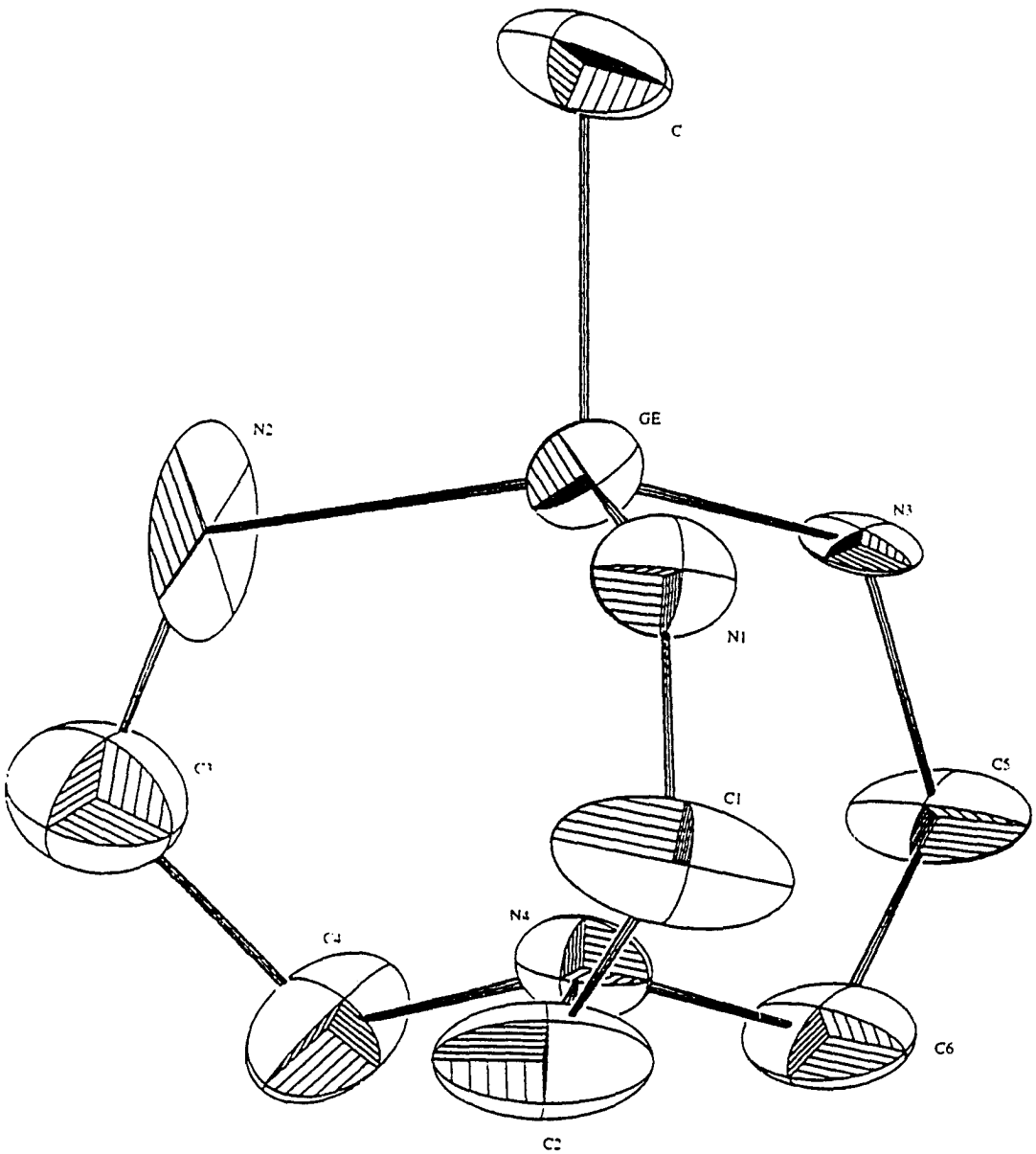


Figure 1. Continued (b) sideview showing the TBP geometry around germanium of **4**.

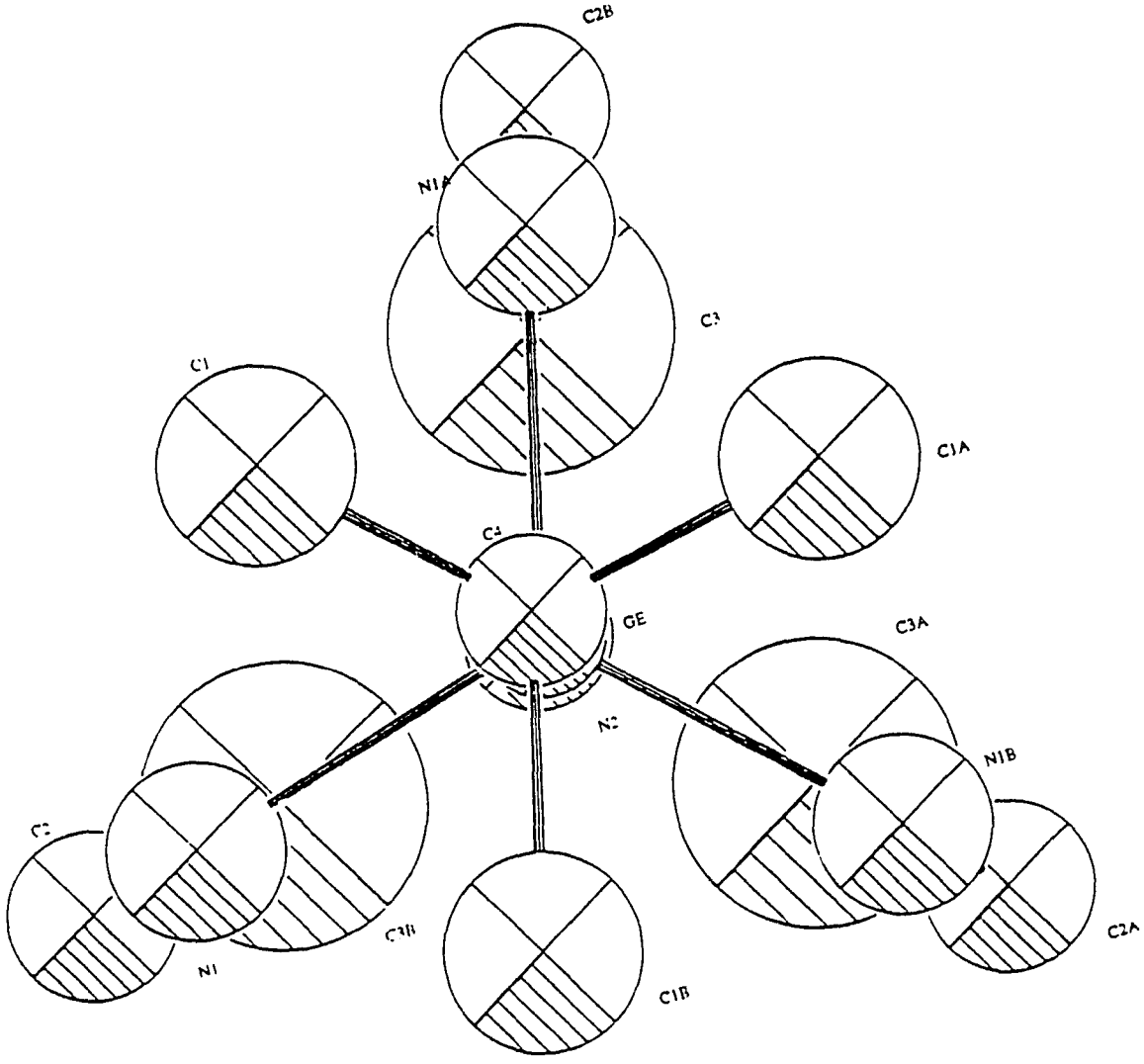


Figure 2. The Molecular structure of *t*-BuGe($HNCH_2CH_2$)$_3$N **6**, (a) topview showing the propeller-like conformation of the molecule and eclipse of the axial atoms

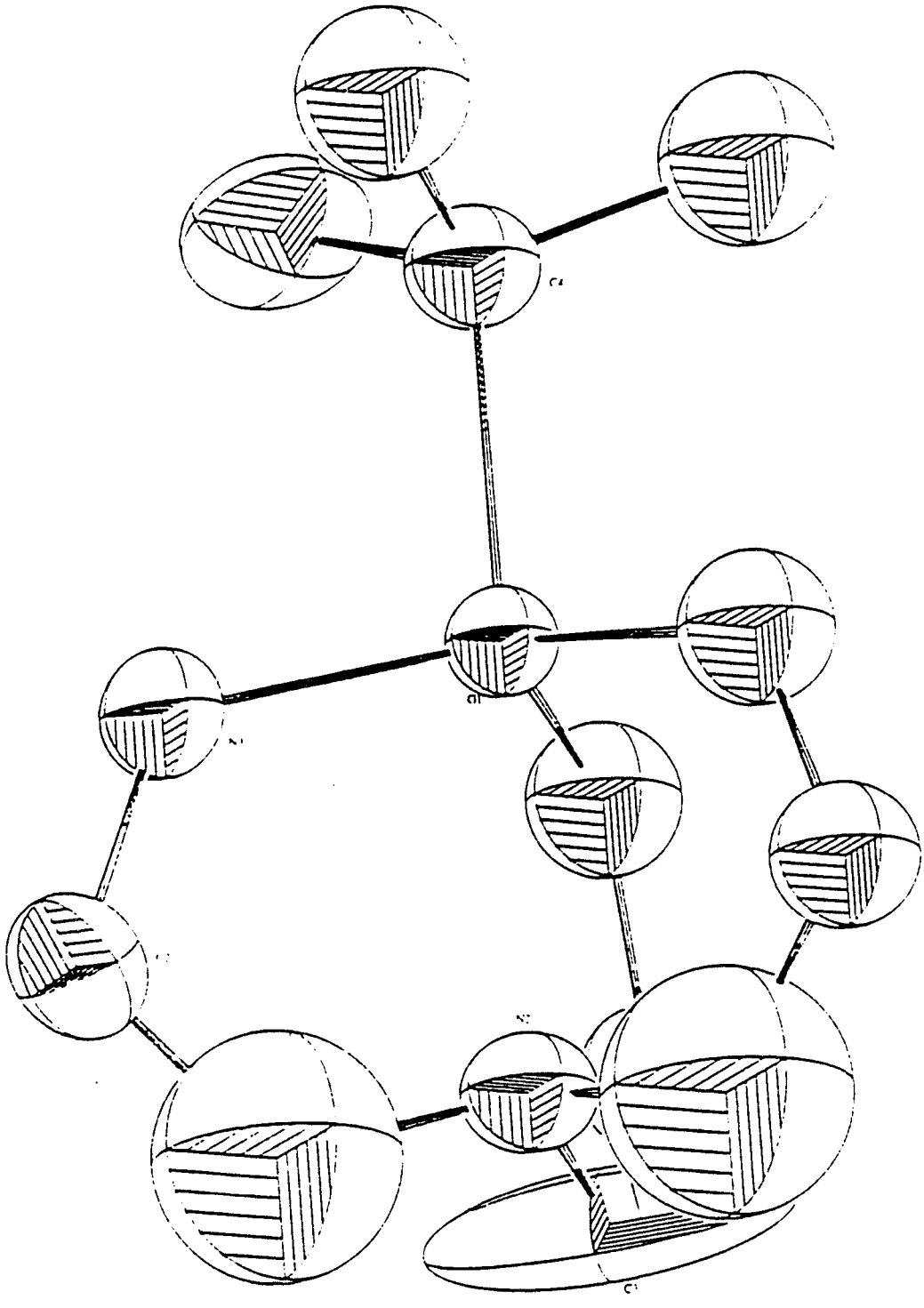


Figure 2. Continued b) sideview showing the TBP geometry around germanium

Table II. Intromolecular Bond Distances (Å) and Bond Angles (degs) for **4**

		distances	
Ge-N(1)	1.873(7)	N(4)-C(2)	1.49 (1)
Ge-N(2)	1.96 (1)	N(4)-C(4)	1.55 (1)
Ge-N(3)	1.790(9)	N(4)-C(6)	1.37 (2)
Ge-C	1.98 (1)	C(1)-C(2)	1.45 (2)
N(1)-C(1)	1.43 (1)	C(3)-C(4)	1.57 (2)
N(2)-C(3)	1.41 (2)	C(5)-C(6)	1.43 (2)
N(3)-C(5)	1.44 (2)		
		angles	
N(1)-Ge-N(2)	117.5 (6)	C(2)-N(4)-C(4)	112 (1)
N(1)-Ge-N(3)	114.1(4)	C(2)-N(4)-C(6)	118 (1)
N(1)-Ge-C	102.1 (4)	C(4)-N(4)-C(6)	113 (1)
N(2)-Ge-N(3)	116.8 (5)	N(1)-C(1)-C(2)	116.9(8)
N(2)-Ge-C	99.2 (8)	N(4)-C(2)-C(1)	110.1 (1)
N(3)-Ge-C	103.3 (6)	N(2)-C(3)-C(4)	114(1)
Ge-N(1)-C(1)	120.6(6)	N(4)-C(4)-C(3)	112(1)
Ge-N(2)-C(3)	122(1)	N(3)-C(5)-C(6)	113(1)
Ge-N(3)-C(5)	125.0(9)	N(4)-C(6)-C(5)	113(1)

[a]Estimated standard deviation in the least significnat figure are given in parentheses

Table III. Postional Parameters and Thermal parameters ($Å^2$) for **4**

atom	x	y	z	B(eq)
Ge	0.4416(1)	0.2524(2)	0.40545(6)	2.37(4)
N(1)	0.4379(9)	0.246(2)	0.5404(5)	3.2(3)
N(2)	0.377(2)	0.453(2)	0.339(1)	8(1)
N(3)	0.382(1)	0.069(1)	0.3455(6)	2.0(4)
N(4)	0.1689(8)	0.241(1)	0.4194(5)	2.6(3)
C	0.667(1)	0.262(2)	0.3913(8)	4.3(5)
C(1)	0.294(1)	0.245(3)	0.5829(7)	6.6(7)
C(2)	0.156(1)	0.295(2)	0.5213(8)	5.1(7)
C(3)	0.221(2)	0.502(2)	0.328(1)	5(1)
C(4)	0.101(2)	0.366(2)	0.344(1)	5.4(7)
C(5)	0.224(2)	0.010(2)	0.333(1)	6(1)
C(6)	0.125(1)	0.087(2)	0.396(1)	4.1(6)
H(1)	0.5328	0.2436	0.5810	3.8
H(2)	0.4536	0.5188	0.3135	9.1
H(3)	0.4601	0.0055	0.3203	2.4
H(4)	0.7162	0.1704	0.4216	5.2
H(5)	0.6827	0.2623	0.3244	5.2
H(6)	0.7091	0.3566	0.4212	5.2
H(7)	0.2763	0.1388	0.6041	7.9
H(8)	0.3040	0.3153	0.6373	7.9
H(9)	0.1479	0.4086	0.5227	6.1
H(10)	0.0668	0.2482	0.5446	6.1
H(11)	0.2080	0.5858	0.3729	6.3
H(12)	0.1988	0.5421	0.2636	6.3
H(13)	0.0737	0.3131	0.2843	6.4
H(14)	0.0116	0.4130	0.3670	6.4
H(15)	0.1842	0.0286	0.2673	6.9
H(16)	0.2254	-0.1020	0.3454	6.9
H(17)	0.1256	0.0256	0.4536	4.9
H(18)	0.0223	0.0891	0.3640	4.9

$B(eq)=8\pi 2/3 \sum i \sum j Uij ai^*.aj^*(ai, aj)$

Table IV Anisotropc Displacement Coefficient ($Å^2$) for 4

atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ge	.0344(3)	.0344	.0337(2)	0.0172	0	0
N(1)	0.042(2)	0.108(3)	0.046(2)	0.038(2)	-0.003(2)	-0.008(2)
N(2)	0.052(2)	0.052	0.037(3)	0.026	0	0
C(1)	0.099(4)	.079(4)	0.051(3)	0.034(3)	0.013(3)	0.021(3)
C(3)	0.052	0.072(3)	0.057(3)	0.034(2)	-0.011(2)	-0.004(2)
C(4)	0.38(1)	0.24(1)	0.044(3)	0.27(1)	0.012(6)	-0.007(5)
C(5)	0.050(2)	0.050	0.039(4)	0.025	0	0

Table V. Intromolecular Bond Distances in **6** (Å)

GE	N1	1.834(3)	N2	N2	06
GE	N1	1.834(3)	N2	N2	06
GE	N1	1.834(3)	N2	C3	1.379(6)
GE	N2	2.361(6)	N2	C3	1.430(6)
GE	N2	2.361(6)	N2	C3	1.388(6)
GE	N2	2.361(6)	C1	C4	1.466(6)
GE	C4	1.991(7)	C1	C4	1.596(6)
GE	C4	1.991(7)	C1	C4	1.527(6)
GE	C4	1.991(7)	C2	C3	1.388(8)
N1	C2	1.431(5)	C4	C4	0.14
N1	H2	0.95	C4	C4	0.14

Estimated standard deviation in the least significant figure are given in parentheses

Table VI. Intromolecular Bond Angles in **6**

N1	GE	N1	115.88(7	N2	GE	N2	1.370(3)
N1	GE	N1	115.88(7	N2	GE	C4	177.610(8)
N1	GE	N2	77.8(1)	N2	GE	C4	176.952(8)
N1	GE	N2	78.9(1)	N2	GE	C4	178.280(8)
N1	GE	N2	77.6(1)	N2	GE	C4	178.280(8)
N1	GE	C4	102.0(1)	N2	GE	C4	177.610(8)
N1	GE	C4	103.8(1)	N2	GE	C4	176.952(8)
N1	GE	C4	99.8(1)	C4	GE	C4	4.01(1)
N1	GE	N1	115.89(7	C4	GE	C4	4.01(1)
N1	GE	N2	77.6(1)	C4	GE	C4	4.01(1)
N1	GE	N2	77.8(1)	GE	N1	C2	123.3(3)
N1	GE	N2	78.9(1)	GE	N2	N2	89.315(2)
N1	GE	C4	99.8(1)	GE	N2	N2	89.315(2)
N1	GE	C4	102.0(1)	GE	N2	C3	105.1(3)
N1	GE	C4	103.8(1)	GE	N2	C3	103.3(3)
N1	GE	N2	78.9(1)	GE	N2	C3	104.8(3)
N1	GE	N2	77.6(1)	N2	N2	N2	60.00
N1	GE	N2	77.8(1)	N2	N2	C3	97.5(5)
N1	GE	C4	103.8(1)	N2	N2	C3	25.4(4)
N1	GE	C4	99.8(1)	N2	N2	C3	137.7(5)
N1	GE	C4	102.0(1)	N2	N2	C3	153.6(5)
N2	GE	N2	1.370(3)	N2	N2	C3	40.8(5)
N2	GE	N2	1.370(3)	N2	N2	C3	80.1(5)
N2	GE	C4	176.952(8)	C3	N2	C3	113.3(3)
N2	GE	C4	178.280(8)	C3	N2	C3	116.0(3)
N2	GE	C4	177.610(8)	C3	N2	C3	112.8(2)

Estimated standard deviation in the least significant figure are given in parentheses

Table VII. Postional parameters and Thermal Parameters (Å) for **6**

atom	x	y	z	B(eq)
H(1)	0.2574	0.0639	0.2587	6.2
H(2)	0.2070	0.1824	0.1734	7.7
H(3)	0.1137	0.1491	0.1128	7.7
H(4)	0.0846	0.2262	0.1687	7.7
H(5)	0.2843	-0.0037	0.3598	5.6
H(6)	0.3285	0.1630	0.3596	5.6
H(7)	-0.1237	0.0597	0.4262	16.1
H(8)	0.0432	0.1818	0.4260	16.1
Ge	0	0	0.27494(3)	2.70(2)
N(1)	0.1920(4)	0.0483(5)	0.2926(2)	5.1(2)
N(2)	0.0022	0.0036	0.3852(3)	3.7(1)
C(1)	0.1114(7)	0.1544(6)	0.1571(2)	6.4(2)
C(2)	0.2485(5)	0.0639(5)	0.3547(2)	4.6(2)
C(3)	-0.036(1)	0.109(1)	0.4014(3)	13.4(5)
C(4)	0.0018	0.0085	0.1820(3)	3.7(2)

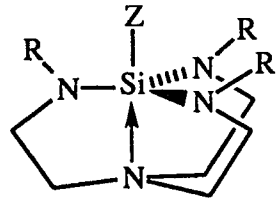
Table VIII. Anisotropic Displacement Coefficient (Å) for **6**

atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ge	0.0293(5)	.0332 (6)	.0275(5)	-0.005	0.0025(3)	-0.000(1)
N(1)	0.037(4)	0.054(5)	0.029(3)	0.00(1)	-0.000(3)	0.004(8)
N(2)	0.15(2)	0.051(8)	0.10(1)	0.02(1)	0.07(1)	0.067(8)
N(3)	0.004(4)	.036(5)	0.034(5)	0.001(4)	-0.007(4)	-0.005(4)
N(4)	0.025(3)	0.041(4)	0.034(4)	-0.000(8)	0.003(3)	-0.015(6)
C	0.029(5)	0.066(8)	0.070(7)	0.01(1)	0.009(5)	-0.03(1)
C(1)	0.047(6)	0.17(2)	0.032(5)	0.04(2)	0.013(5)	0.06(1)
C(2)	0.039(6)	0.12(2)	0.038(6)	-0.002(8)	0.013(5)	-0.008(7)
C(3)	0.05(2)	0.08(1)	0.07(1)	0.00(1)	-0.001(1)	-0.01(1)
C(4)	0.039(8)	0.08(1)	0.08(1)	-0.017(8)	-0.027(8)	0.04(1)
C(5)	0.021(1)	0.051(8)	0.15(1)	-0.022(9)	0.02(1)	-0.07(1)
C(6)	0.022(6)	0.061(9)	0.07(1)	-0.013(6)	-0.004(6)	-0.029(7)

PAPER 3. INTERESTING HYDRIDE AND FLUORIDE TRANSFER REACTIONS DURING NUCLEOPHILIC SUBSTITUTION AT SILICON

ABSTRACT

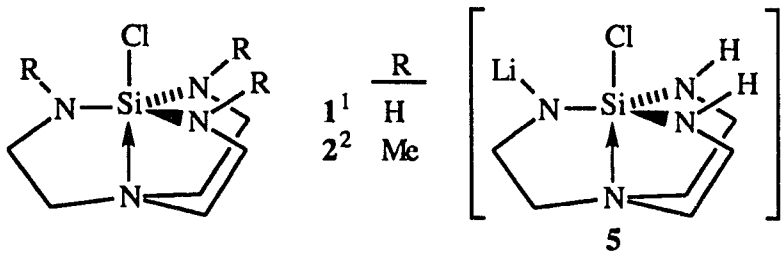
While **1** (Z = Cl, R = H) and **2** (Z = Cl, R = Me) undergo nucleophilic substitution of Cl by a variety of R^- and $^-NR_2$, **2** is particularly prone to



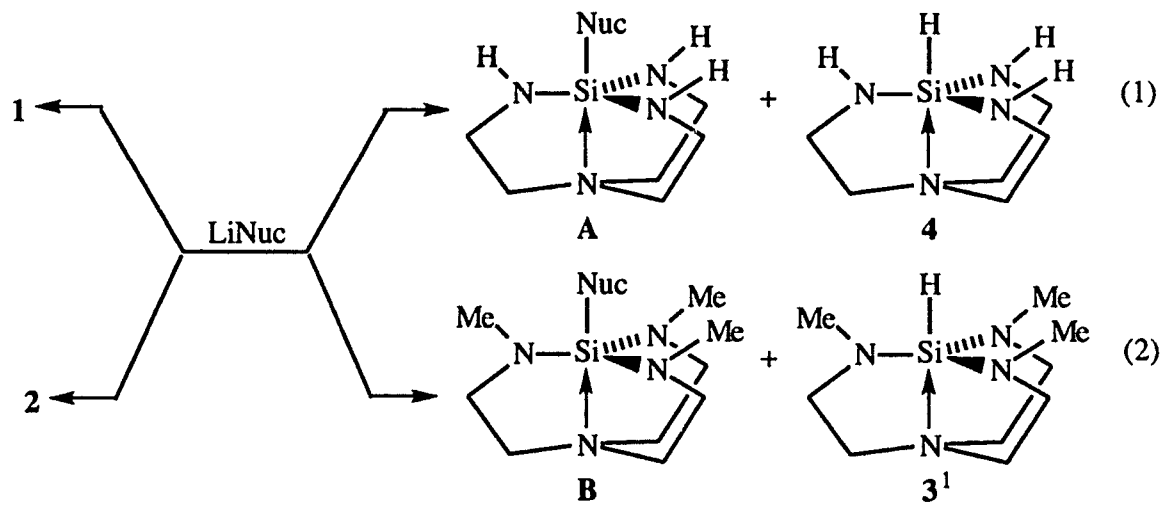
hydride transfer from these nucleophiles to form **3** (Z = H, R = Me), particularly when the alkyl groups are large. Interestingly, **2** undergoes nucleophilic substitution under milder conditions than $ClSi(NMe_2)_3$. The reaction of **1** with LiC_6F_5 gives the expected product **4** (Z = C_6F_5, R = H) but with **2**, three products are formed, namely, **5** (Z = C_6F_5, R = Me), the fluoride transfer product **8** (Z = F, R = Me) and the tetrafluorobenzyne insertion product of **5** (**9**) in which expansion of one of the rings of **5** has occurred via the benzyne moiety insertion reaction into an equatorial Si-N bond. The structures of **8** and **9** determined by X-ray crystallography are reported.

COMMUNICATION

In the course of exploring the axial nucleophilic substitution chemistry of azasilatranes **1** and **2** (reactions 1 and 2) we were surprised to encounter



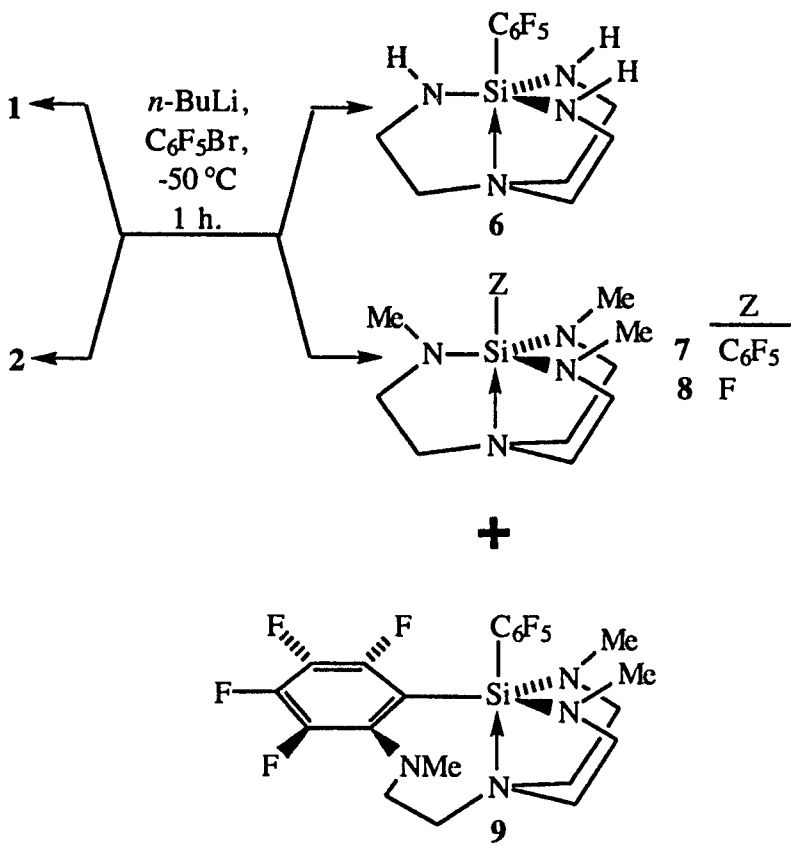
the formation of the hydride substitution product of **2**, namely, **3** (reaction 2)



using nucleophilic reagents such as $LiNR_2$ (R = Me, Et, *i*-Pr) and LiR (*n*-Bu, *s*-Bu, *t*-Bu, Ph). By contrast, the same nucleophiles gave exclusively the

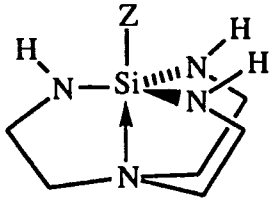
expected product **A** (Nuc = NMe_2) or a mixture of **A**, HNR_2 and a polymeric form of metallated intermediate **5** (Nuc = NEt_2 and $LiN(i\text{-}Pr)_2$) when **1** is the substrate. As we also describe herein, the amount of **3** formed in reaction 2 ranges from *ca.* 15-60% depending on the $LiNR_2$ reagent used. In the case of the LiR reagents, low conversion of **1** to **A** is observed, with the major product being polymeric **5**. Only in the case of *s*-BuLi and *t*-BuLi were small amounts of **4** seen (**A**:**4** ≈ 5:1). With **2**, however, **3** is observed to form with all LiR in *ca.* 5-100% conversion, depending on the R group.

Whereas **1** gives only the expected substitution product **6** in reaction 3, **2**

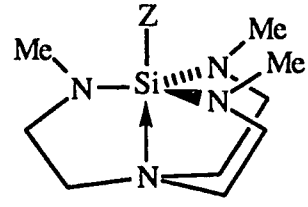


remarkably gives rise to the three products **7**, **8** (a fluoride transfer product) and **9** in a ratio of approximately 1:2:1, respectively, of which **8** and **9** have been structured by X-ray means. Evidence is presented for the formation of **8** and **9** via a benzyne intermediate.

The reaction of equimolar quantities of **1** with $LiNMe_2$ in Et_2O at room temperature gives exclusively **10**. Under the same conditions, **2** gives a



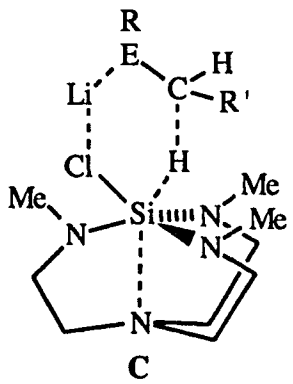
	Z
10	NMe_2
12	NEt_2
15	*n*-Bu
17	*s*-Bu
18	*t*-Bu
20	C_6H_5



	Z
11	NMe_2
13	NEt_2
14	$N(i\text{-}Pr)_2$
16	*n*-Bu
19	CH_2Ph
21	Ph

mixture of **11** and **3** in a 5:1 ratio. In the presence of $LiNEt_2$ at room temperature, **1** in THF gave ^1H NMR spectra consistent with the immediate and exclusive formation of $HNEt_2$ plus an intractable precipitate presumably arising from a polymeric form of intermediate **5**, whereas at -80 °C, NMR evidence for low conversion to **12** was observed. On the other hand, **2** with $LiNEt_2$ gave a 4:1 ratio of **13** and the hydride transfer product **3**. Similarly, $LiN(i\text{-}Pr)_2$ with **1** gave only **4** and $HN(i\text{-}Pr)_2$ at room temperature while with **2**, **14** and **3** were synthesized in a *ca.* 1:2 ratio. It appears that **1** becomes increasingly prone to deprotonation at the expense of axial substitution as the nucleophile becomes more basic and sterically encumbered in the order $^-NMe_2 < ^-NEt_2 < ^-N(i\text{-}Pr)_2$. In contrast, **2** becomes increasingly likely to undergo axial hydride transfer with the nucleophile at the expense of normal

nucleophilic substitution. It is reasonable to suppose that hydride transfer is sterically favored by the equatorial methyl groups in **2** as depicted in the postulated intermediate **C**, in which the transannular Si-N bond is probably weakened relative to that in **2**.[3] In substantiation of such a pathway, ^{1}H and



C

	E
C	N
D	CH

^{13}C NMR spectra compared favorably with that of the expected imine elimination product $Me_2HCN{=}CMe_2$ were observed in the reaction of **2** with $LiN(i\text{-}Pr)_2$. Moreover, the addition of the Li^+ complexing agent $Me_2N\text{-}CH_2CH_2NMe_2$ (TMEDA) greatly inhibited nucleophilic substitution and hydride transfer presumably owing to interference with four- and six-center intermediate formation, respectively.

Interestingly, an acyclic near-analogue of **2**, namely, $ClSi(NMe_2)_3$[4] requires more vigorous conditions (80 °C, 2 to 19 h) for substitution or hydride transfer to occur. Thus $LiNMe_2$ and $LiNEt_2$ in NMR tube experiments convert $ClSi(NMe_2)_3$ almost quantitatively in 2 and 10 h, respectively, at 80° to $(Me_2N)_4Si$ and $Et_2NSi(NMe_2)_3$, while $LiN(i\text{-}Pr)_2$ gives rise to a barely detectable amount of $HSi(NMe_2)_3$ over a period of 19 h at 80°. These results

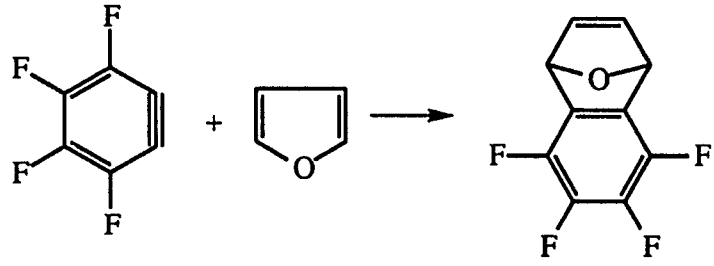
are in accord with earlier reports that four-coordinate silicon compounds do not undergo nucleophilic substitution as easily as pentacoordinate species.[5]

n-Butyl lithium reacts with **1** at -90° in 0.5 h to give exclusively the substitution product **15** in low conversion, whereas **2** with *n*-BuLi gives a *ca.* 20:1 ratio of **16** to the hydride transfer product **3** at 7°. Azasilatrane **1** with *s*-BuLi and *t*-BuLi is partially converted to **17** and **18**, respectively, along with barely detectable ^{1}H NMR peaks for **4** in 1 h at -75°. However, both of these reagents cause the quantitative conversion of **2** to the hydride transfer product **3** plus a 4:1 ratio of 1- and 2-butenes (Z:E ≈ 3:2) from the former reagent and *iso*-butene from the latter.

As in the postulated intermediate **C** for amide nucleophiles, **D** is sterically favored for carbanionic nucleophiles. Structure **D** is also consistent with the observed formation of a higher proportion of 1-butene compared with 2-butenes, since R = Et, R' = H in this structure would be sterically favored over R = Me, R' = Me. It was also observed that introduction of TMEDA strongly inhibits both alkylation and hydridation of **2**. That a hydrogenated carbon alpha to the lithiated carbon is involved in these reactions was confirmed by reacting **2** with $BrMgCH_2Ph$. Here as expected, the exclusive process is substitution giving **18**.

When $ClSi(NMe_2)_3$ is reacted with *n*-BuLi, *s*-BuLi or *t*-BuLi, a higher temperature is required for reaction (80 °C) as well as longer times (typically ca. 23 h). Interestingly the amounts of $HSi(NMe_2)_3$ formed in these reactions (0, ~ 40 and ~ 70%, respectively) is low compared with **2**.

The alpha carbon bearing the hydrogen for hydride transfer can also be present in an aromatic ring. Whereas **1** in the presence of LiPh at -50° for 30 min gives **20**[6] in low conversion plus polymeric **4**, **2** reacts with LiPh at -45° or at room temperature in 2 h to give *ca.* 90% substitution product **21** and about 5% **3**. Using LiC_6F_5, **1** produces **6** at -50° in 1 h as the exclusive product while the same reaction with **2** gives a 1:2:1 mixture of **7**, the fluoride transfer product **8** and the novel expanded ring product **9**. As seen in Figures 1 and 2, both **8**[7] and **9**[8] feature transannular bonds (2.034 (2) and 2.246 (3) Å, respectively) in the solid state. This bond in **9** is longer owing to the presence of the seven-membered ring. That the tetrafluorophenylene group in **9** probably arises from the attack of benzyne (liberated as **8** is formed) on **7**, was shown by the generation of **9** in the reaction of **7** with a mixture of C_6F_5Br and *n*-BuLi warmed from -50° to room temperature (80% conversion) and by the trapping of tetrafluorobenzyne as the known Diels-Alder adduct **22**[9] in this reaction at -50°. It is interesting in this regard that **21** does not form a product analogous to **9** under the same reaction conditions.



22 (5)

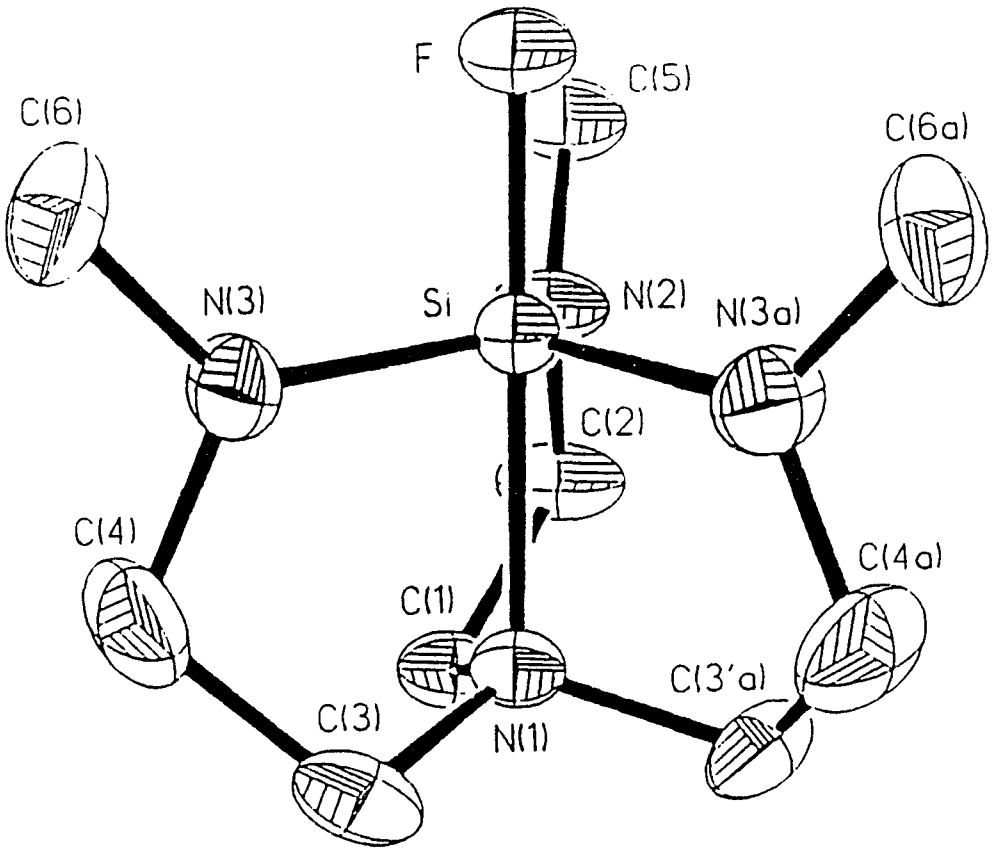


Figure 1. ORTEP drawing of **8**. Ellipoids are at the 50% level.

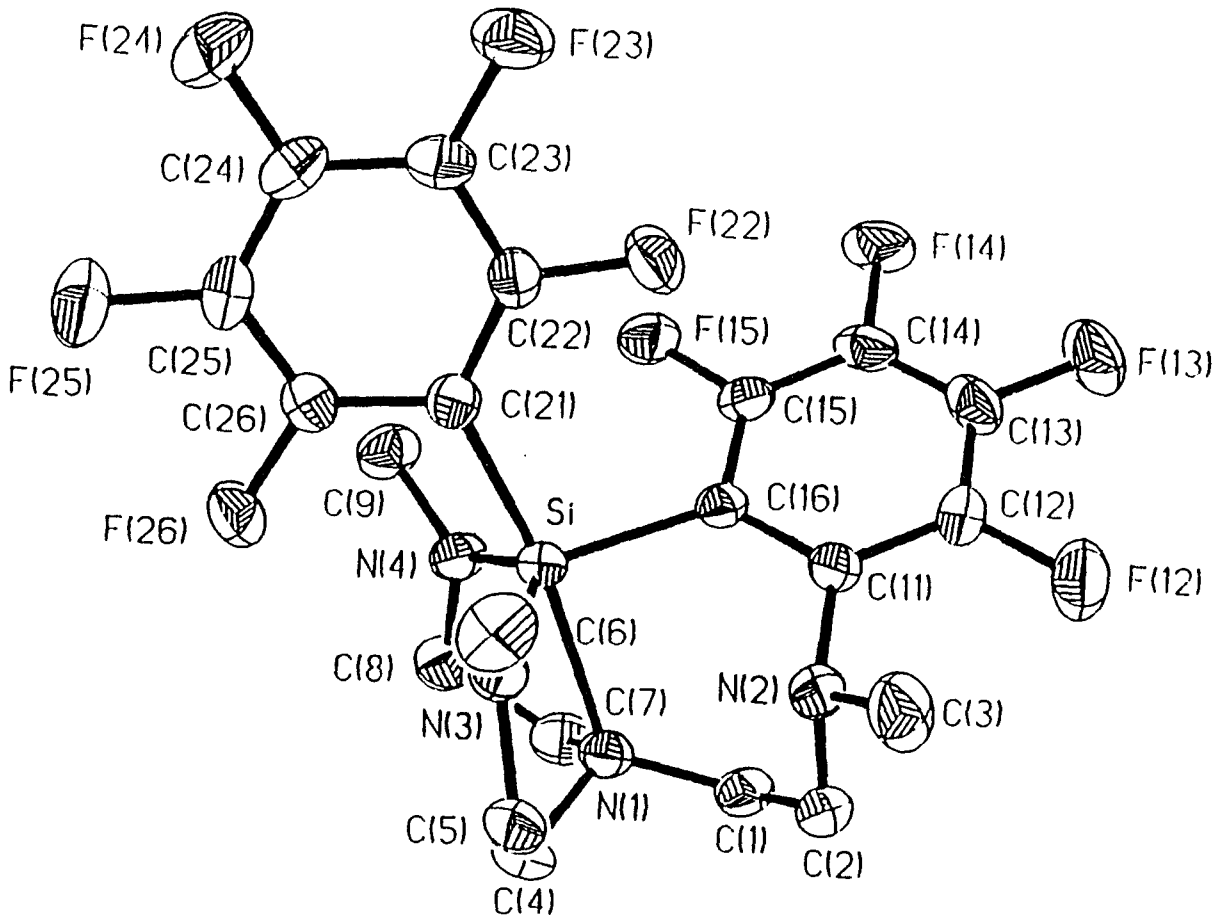


Figure 2 . ORTEP drawing of **9**. Ellipoids are at the 50% level.

ACKNOWLEDGMENTS.

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(7) Crystal data for **8**: monoclinic, space group $P2_{1/m}$, a = 7.352 (1), b = 12.361 (2),and c = 7.512 (1) Å, b = 119.30 (1)°, V = 595.3 (2) $Å^3$, Z = 2, D_c = 1.716 g/cm^3; 1659 reflections measured, 805 observed ($I \geq 2$ s (1)); R = 0.0348, R_w = 0.0926. The structure was solved by direct methods.

(8) Crystal data for **9**: Triclinic, space group $P\bar{1}$, a = 8.586 (2), b = 10.215 (2), and c = 13.745 (3) Å, a = 95.62 (2), b = 102.25 (2), g = 107.74 (2)°, V = 1104.8 (4) $Å^3$, Z = 2, D_c = 1.589 g/cm^3; 3210 reflections measured, 2679 observed ($F \geq 4.0$ s (F)); R = 0.0321, R_w = 0.0466. The structure was solved by direct methods.

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SUPPLEMENTARY MATERIAL 1

PREPARATIONS OF 2, 6-19, 21

Compound 2. Chlorosuccinimide (2.47 g, 19.2 mmol) dissolved in 50 mL of CH_2Cl_2 was slowly added to a solution of **3** (4.03 g, 18.8 mmol) in 25 mL of CH_2Cl_2 at -50 °C. The solution was allowed to warm to -10 °C and stirred for 20 min. All the volatiles were removed under vacuum while the solution was kept at -10 °C. The solid was extracted with 4 x 30 mL portions of toluene. Evaporation of the toluene under vacuum afforded 2.62 g of white crystalline product, contaminated by a trace amount of by-product succinimide, which was removed by sublimation at 46 °C/15 x 10^{-3} mmHg for ~ 72 h. The solid was once again extracted with toluene and 2.34 g of pure crystalline **2** was obtained in 52% yield by removing the solvent under vacuum. ^{1}H NMR (C_6D_6) 3.08 (s, 9 H, NCH_3), 2.61 (t, 6 H, $^3J_{HCCH}$ = 6.0 Hz, $CH_3NCH_2CH_2$), 2.01 (t, 6 H, $CH_3NCH_2CH_2$); ^{1}H NMR ($CDCl_3$), 2.96 (t, 6 H, $^3J_{HCCH}$ = 6.0 Hz, $CH_3NCH_2CH_2$), 2.77 (t, 6 H, $CH_3NCH_2CH_2$), 2.75 (s, 9 H, NCH_3); ^{13}C NMR (C_6D_6) 47.68 ($CH_3NCH_2CH_2$), 46.77 ($CH_3NCH_2CH_2$), 39.25 (CH_3); ^{29}Si NMR (C_6D_6) -87.22. LRMS (70 ev, EI) *m/z* (relative intensity, proposed ion) 248.1 (31.2, M^+), 213.2 (100, M^+ - Cl), 204.1 (59.2, M^+ - NMe_2). HRMS for M^+ ($C_9H_{21}SiN_4Cl$) calcd: 248.12240, found: 248.12229.

Compound 6. C_6F_5Br (0.13 g, 0.52 mmol) was dissolved in 18 mL of pentane and the solution was cooled to -50 °C. *n*-BuLi (0.26 mL, 0.52 mmol) in hexane was added and the mixture was stirred for 30 min. A precooled (-50 °C) toluene solution (15 mL) containig 0.084 g (0.41 mmol) of **1** was added

dropwise. After stirring at -50 °C for 1 h, the mixture was allowed to warm slowly to room temperature and then filtered. Removal of the solvents under vacuum followed by sublimation afforded 0.076 g of crystalline product in 43% yield (0.22 mmol). M.p. 102-104°. ^{1}H NMR (C_6D_6) 2.66 (t, 6 H, $^{3}J_{HCCH}$ = 5.9 Hz, SiNC*H*$_2$CH$_2$), 2.01 (t, 6 H, SiHNCH$_2$C*H*$_2$), 0.91 (b, 3 H, NH); ^{13}C NMR (C_6D_6) 50.76 (HNCH$_2$*C*H$_2$N), 36.79 (HN*C*H$_2$CH$_2$); ^{29}Si NMR (C_6D_6) -84.51; ^{19}F NMR (C_6D_6) -125.71 (dd, 2 F, *o*-F, $^{3}J_{FF}$ = 27.4 Hz, $^{4}J_{FF}$ = 9.0 Hz) -157.3 (t, 1 F, *p*-F, $^{3}J_{FF}$ = 21.45 Hz), -162.26 (m, 2 F, *m*-F). MS (70 ev, EI) *m/z* (relative intensity, proposed ion) 338.1 (3.4, M$^+$), 171.1 (3.5, M$^+$ - C_6F_5), 240.0 (33.2), 225.0 (17.3), 200.0 (16.6), 168.0 (83.3).

Compound 7. To 0.64 g (2.6 mmol) of compound **2** in 25 mL of toluene was added 2.8 mmol of MgBrC_6F_5 as a mixture prepared by mixing 0.70 g of C_6BrF_5 with 0.70 g of Mg in 10 mL of ether at room temperature. The reaction mixture was stirred for 1/2 h. After filtration, all the volatiles were removed under vacuum over a period of 5 h. By sublimation at 50°/5 x 10^{-3} mmHg, 0.14 g of a crystalline solid, identified as pure product **7** was obtained in 14% yield. M.p., 105-106 °C. ^{1}H NMR (C_6D_6) 2.53 (t, 6 H, $^{3}J_{HCCH}$ = 5.9 Hz, CH$_3$NC*H*$_2$CH$_2$), 2.36 (s, 9 H, NMe), 1.96 (t, 6 H, CH$_3$NCH$_2$C*H*$_2$); ^{13}C NMR (C_6D_6) 50.18 (CH$_3$NCH$_2$*C*H$_2$), 48.47 (CH$_3$N*C*H$_2$CH$_2$), 38.20 (CH$_3$N); ^{29}Si NMR (C_6D_6) (temperature) -69.94 (50 °C), -70.94 (20 °C), -71.76 (10 °C); ^{19}F NMR (C_6D_6) -126.46 (dd, 2 F, *o*-F, $^{3}J_{FF}$ = 24.55 Hz, $^{4}J_{FF}$ = 9.3 Hz), -156.32 (t, 1 F, *p*-F, $^{3}J_{FF}$ = 19.75 Hz), -162.96 (m, 2 F, *m*-F). LRMS (70 ev, EI) *m/z* (relative intensity, proposed ion), 380.0 (100.0, M$^+$), 336.0 (56.0, M$^+$ - CH_6N), 324.2 (25.3),

295.3 (18.8), 281.3 (12.1), 213 (8.3, $M^+ - C_6F_5$); HRMS for M^+ ($C_{15}H_{21}N_4F_5Si$): calcd, 380.14557, found, 380.14740.

Compounds 8 and 9: To 25 mL of a pentane solution of C_6F_5Br (0.433 g, 1.79 mmol) at -50 °C was added 0.9 mL of a 2.01 M (1.89 mmol) hexane solution of *n*-BuLi. After stirring at -50 °C for 3 h, 0.42 g (1.7 mmol) of **2** in 8 mL of toluene was slowly added. The mixture was stirred at ~ -50 °C for an additional 0.5 h and then allowed to warm to room temperature. The mixture turned brownish red upon warming up. After filtration and washing with 3 x 15 mL portions of toluene a ^1H NMR spectrum of the filtrate revealed three major products **7**, **8** and **9** in a ratio of approximately 1:2:1. After removal of the solvent under vacuum, **8** sublimed first at 35 °C/15 x 10^{-3} mmHg with about 90% purity. Repeated sublimation gave 0.12 g of pure **8** in 28% yield. M.p., 120-122 °C. The residual mixture was then sublimed at 55 °C to remove **7** together with unseparated **8** and a small amount of **9**. After removal of **7** and **8** was complete (as shown by the ^1H NMR spectra of the sublimed solid) 0.189 g (21% yield) of **9** was readily sublimed at 110°/15 x 10^{-3} mmHg as a white crystalline solid. M.p., 168-169 °C. Compound **9** dissolved well in THF, toluene but did not dissolve in water. Crystals of **8** and **9** suitable for X-ray studies were grown by sublimation at 60 °C in an unevacuated tube sealed under nitrogen and at 5 x 10^{-2} mmHg, respectively.

Characterization for **8**: ^1H NMR (C_6D_6) 2.97 (s, 9 H, NMe), 2.60 (dt, 6 H, $CH_3NCH_2CH_2$, $^3J_{HCCH}$ = 6.0 Hz, $^4J_{FSiCH}$ = 1.2 Hz), 2.03 (t, 6 H, $CH_3NCH_2CH_2$); ^{13}C NMR (C_6D_6) 48.32 (s, $MeNCH_2CH_2$), 47.05 (d,

$MeNCH_2CH_2N$, $^3J_{CF}$ = 1.5 Hz), 37.28 (d, $^3J_{CF}$ = 8.0 Hz, CH_3N); ^{19}F NMR (C_6D_6) -136.19; ^{29}Si NMR (C_6D_6) -99.69 (d, $^1J_{FSi}$ = 191.76 Hz). LRMS (70 ev, EI) *m/z* = (relative intensity, proposed ion) 232.2 (100, M^+), 188.1 (86.1, M^+ - $CH_3NCH_2CH_2$); HRMS for M^+ ($C_9H_{21}FN_4Si$). Calcd: 232.15195, found: 232.15201. Anal. calcd for $C_9H_{21}FN_4Si$: C, 46.55, H, 9.05, N, 24.14; found: C, 46.74; H, 9.17; N, 24.37.

Characterization for **9**: ^1H NMR (toluene-D_8) 2.60 (d, 3 H, $CH_2NC\mathit{H}_3C_6F_4Si$, $^5J_{FCH}$ = 1.05 Hz), 2.56 (b, 3 H, $NCH_2CH_2NC\mathit{H}_3Si$), 2.14 (s, 3 H, $NCH_2CH_2NC\mathit{H}_3Si$), 2.78 (m, 1 H), 2.60 (m, 1 H), 2.59 (m, 1 H), 2.57 (m, 1 H), 2.44 (m, 1 H), 2.10 (m, 1H), 2.08 (m, 1 H), 1.79 (m, H), 1.73 (m, 2 H), 1.70 (m, 1 H), 1.51 (dt, 1 H); ^{13}C NMR (C_6D_6) 57.58, 55.87, 51.87, 51.32, 48.46, 48.33, 42.36 (d, $^3J_{FC}$ = 7.54 Hz), 39.26 (m), 38.52; ^{29}Si NMR (C_6D_6, 20 °C) -70.30; ^{29}Si NMR (solid state) -62.6. ^{19}F NMR (282.186 Hz, toluene-D_8, 20 °C) -126.35 (b, 1 F), -128.38 (b, 1 F), -129.83 (dd, 1 F, $^3J_{FF}$ = 27.7Hz, $^4J_{FF}$ = 12.4 Hz), -146.01 (t, 1 F, $^3J_{FF}$ = 15.2 Hz), -154.63 (t, 1 F, $^3J_{FF}$ = 21.2 Hz), -155.18 (t, 1 F, $^3J_{FF}$ = 18.3 Hz), -158.48 (t, 1 F, $^3J_{FF}$ = 24.6 Hz), -161.98 (b, 2 F); LRMS (70 ev, EI) *m/z* (relative intensity, proposed ion) 528.1 (34.1, M^+), 484.1 (95.1, M^+ - C_2H_6N), 292 (45), 361.1 (152, M^+ - C_6F_5), 206.1 (100.0), 144.2 (89.2), 99.1 (85.2), 69.0 (40); HRMS for M^+ ($C_{21}H_{21}F_9N_4Si$) calcd: 428.13918, found: 528.14039. Anal for $C_{21}H_{21}F_9N_4Si$, calcd: C, 47.73; H, 3.98; N, 10.60; found: C, 48.19; H, 3.87; N, 10.87.

Compound 10. Compound **1** (0.25 g, 1.2 mmol) was mixed with 0.07 g (1.3 mmol) of $LiNMe_2$ in a dry box and then 25 mL of diethyl ether was added.

The suspension was stirred at room temperature for 48 h. After filtration, the ether was removed under vacuum and then the solid residue was extracted with 3 x 10 mL portions of benzene. Evaporation of the benzene resulted in a crystalline product which was purified by sublimation at 75 °C and 6 x 10^{-3} mmHg (0.155 g, 60% yield). M.p. 74-75°. ^{1}H NMR (C_6D_6) 2.75 (s, 6 H, NMe_2), 2.74 (dt, 6 H, $HNCH_2CH_2$, $^3J_{HNCH}$ = 3.0, $^3J_{HCCH}$ = 5.7 Hz), 2.08 (t, 6 H, $HNCH_2CH_2N$), 0.76 (b, 3 H, NH); ^{1}H NMR ($CDCl_3$) 2.93 (dt, 6 H, $HNCH_2CH_2$, $^3J_{HNCH}$ = 2.7 Hz, J_{HCCH} = 5.7 Hz), 2.57 (t, 6 H, $HNCH_2CH_2$), 2.35 s, 6 H, NMe_2), 0.81 (s, 3 H, NH); ^{13}C NMR (C_6D_6) 50.57 ($HNCH_2CH_2N$), 37.67 ($HNCH_2CH_2N$) 41.00 (NMe_2); ^{13}C NMR ($CDCl_3$): 50.53 ($HNCH_2CH_2$), 37.13 ($HNCH_2CH_2N$), 40.51 (NMe_2); ^{29}Si NMR (C_6D_6) -72.58; ^{29}Si NMR ($CDCl_3$) -75.26. LRMS (70 ev, EI) *m/z* (relative intensity, proposed ion) 215.2 (13.5, M^+), 171.1 (100, M^+ - NMe_2), 128.1 (3.4, M^+ - NMe_2 - $NH_2CH_2CH_2$); HRMS for M^+ ($C_8H_{21}N_5Si$) calcd: 215.15662, found: 215.15664. Anal. for $C_8H_{21}N_5Si$: calcd: C, 44.61; H, 9.83; N, 32.52. Found: C, 44.76; H, 10.19; N, 32.59.

Compound 11. To a mixture of 1.02 g (4.11 mmol) of **2** and 0.23 g (4.4 mmol) of $LiNMe_2$ was added 50 mL of diethyl ether. The solution was stirred at room temperature for 72 h. After removal of ether under vacuum, the residue was extracted with 3 x 15 mL portions of benzene. A ^{1}H NMR spectrum of the solution revealed the formation of **11** and **3** in a ratio of approximately 5:1. A crystalline mixture (0.87 g) was obtained after evaporating the volatiles. Separation was achieved by subliming the lighter **3** at 30 °C for 2 d, followed by subliming **11** at 60 °C or above. Repeated slow sublimation afforded 0.43 g of pure **11** in 41% yield. ^{1}H NMR (C_6D_6) 2.82 (s, 6

H, NMe_2), 2.64 (s, 9 H, NCH_3), 2.61 (t, 6 H, $Si(CH_3)NCH_2CH_2$, $^3J_{HCCH}$ = 5.7 Hz), 2.21 (t, 6 H, $Si(CH_3)NCH_2CH_2$); ^{13}C NMR (C_6D_6) 51.16 ($SiNCH_2CH_2$), 50.99 ($SiNCH_2CH_2$), 40.22 ($N(CH_3)_2$), 37.71 ($SiNCH_3$); ^{29}Si NMR (C_6D_6) -51.39. LRMS (70 ev, EI) *m/z* (relative intensity, proposed ion) 257.2 (2.4, M^+), 213.2 (100.0, M^+ - NMe_2), 199.1 (1.7), 170.1 (4.9), 156.1 (12.8), 129.1 (4.5), 113.1 (11.3); HRMS for M^+ ($C_{11}H_{27}N_5Si$) calcd: 257.20358, Found: 257.20387.

Compound 12.

Method A: A solution of **1** (8 mg, 0.04 mmol) in 0.5 mL of THF-D_8 was prepared. ^1H NMR data for **1** (THF-D_8) 2.99 (t, 6 H, $^3J_{HCCH}$ = 5.85 Hz, $HNCH_2CH_2$), 2.75 (t, 6 H, $HNCH_2CH_2$), 1.29 (b, 3 H, NH); ^{13}C NMR data for **1** (THF-D_8), 52.08 ($HNCH_2CH_2$), 37.95 ($HNCH_2CH_2$). $LiNEt_2$ (3 mg, 0.04 mmol) was dissolved separately in 0.4 mL of THF-D_8. ^1H NMR data for $LiNEt_2$ (THF-D_8), 2.83 (q, 4 H, $^3J_{HCCH}$ = 7.2 Hz, CH_2), 1.04 (t, 6 H, CH_3); ^{13}C NMR data for $LiNEt_2$ (THF-D_8), 50.36 (br, CH_2), 18.56 (CH_3). The ^1H, ^{13}C NMR spectra of the combined THF-D_8 solutions revealed the instant and almost quantitative formation of HEt_2N. ^1H NMR of $HNEt_2$ (THF-D_8), 2.55 (q, 4 H, CH_2), 1.02 (t, 6 H, CH_3, $^3J_{HCCH}$= 7.2 Hz); ^{13}C NMR: 44.80 (CH_2), 15.82 (CH_3).

Method B: To a solution of 0.10 g (0.5 mmol) of **1** in 25 mL of THF at ~-80 °C was very slowly added 20 mL of a THF solution of 50 mg (0.60 mmol) of $LiNEt_2$ until all the starting material was consumed as monitored by ^1H NMR spectroscopy. The mixture was stirred at -80 °C for 1 h. Removal of THF under vacuum followed by extraction of the residue with 4 x 5 mL portions of benzene gave a yellowish solution. Evaporation of the solvent

under vacuum afforded the crude product **12** as a semi-solid (0.045 g, 19% yield). ^{1}H NMR (C_6D_6) 3.07 (q, 4 H, NC*H*$_2$CH$_3$, $^3J_{HCCH}$ = 6.9 Hz), 2.77 (t, 6 H, HNC*H*$_2$CH$_2$, $^3J_{HCCH}$ = 6.0 Hz), 2.12 (t, 6 H, HNCH$_2$C*H*$_2$), 1.18 (t, 6 H, NCH$_2$C*H*$_3$, $^3J_{HCCH}$ = 6.9 Hz); ^{1}H NMR ($CDCl_3$) 2.96 (t, 6 H, HNC*H*$_2$CH$_2$, $^3J_{HCCH}$= 6.0 Hz), 2.75 (q, 4 H, NC*H*$_2$CH$_3$, $^3J_{HCCH}$ = 6.9 Hz), 2.59 (t, 6 H, HNCH$_2$C*H*$_2$), 0.93 (t, 6 H, NCH$_2$C*H*$_3$); ^{13}C NMR ($CDCl_3$) 50.37 (HNCH$_2$CH$_2$N), 41.75 (NCH$_2$CH$_3$), 37.09 (HNCH$_2$CH$_2$), 16.55 (NCH$_2$CH$_3$). MS (70 ev, EI) *m/z* (relative intensity, proposed ion) 243.4 (4.7 M$^+$), 171.1 (100, M$^+$ - NEt$_2$), 200.2 (3.3, M$^+$ - HNCH$_2$CH$_2$).

Compound 13. Compound **2** (0.42 g, 1.7 mmol) was mixed with 0.15 g (1.8 mmol) of LiNEt$_2$ in 45 mL of benzene. The solution was heated at 65 °C for 24 h. A ^{1}H NMR spectrum of the solution showed the absence of the starting material and the formation of compounds **13** and **3** in a ratio of about 4:1. After filtration and removal of the solvent under vacuum, 0.34 g of crystalline solid was obtained. Repeated sublimations at 30 °C for 1 day to remove the lighter **3** followed by further sublimation at 70 °C afforded 0.12 g of pure **13** (25%). ^{1}H NMR (C_6D_6) 3.14 (q, 4 H, NC*H*$_2$CH$_3$, $^3J_{HCCH}$ = 7.8 Hz), 2.56 (s, 9 H, CH$_3$), 2.54 (t, 6 H, CH$_3$NC*H*$_2$CH$_2$, $^3J_{HCCH}$ = 5.7 Hz), 2.40 (t, 6 H, CH$_3$NCH$_2$C*H*$_2$), 1.17 (t, 6 H, NCH$_2$C*H*$_3$); ^{13}C (C_6D_6) 52.13 (MeNCH$_2$CH$_2$), 51.08 (MeNCH$_2$CH$_2$), 40.05 (NCH$_2$CH$_3$), 36.28 (NCH$_3$), 15.23 (NCH$_2$CH$_3$); ^{29}Si NMR (C_6D_6) -37.92.

Compound 14. Compound **2** (24 mg, 0.10 mmol) was mixed with 12 mg (0.11 mmol) of LiN(*i*-Pr)$_2$ in an NMR tube and 0.5 mL of C_6D_6 was added after

the tube was cooled in ice water. The tube was then sealed and allowed to warm slowly to room temperature. ^{1}H and ^{13}C NMR spectra showed that **14** and **3** formed in a ratio of about 1:2. ^{1}H NMR (C_6D_6) for **14**: 2.47 (s, br, 9 H, NCH_3) 2.40 (s, br, 6 H, $CH_3NC\mathit{H}_2CH_2$), 2.24 (s, br, 6 H, $CH_3NCH_2C\mathit{H}_2$), 1.04 (d, 12 H, $(CH_3)_2CN$); ^{13}C NMR (C_6D_6) 51.13 ($CH_3NCH_2\mathit{C}H_2$), 50.45 ($CH_3N\mathit{C}H_2CH_2$), 35.68 ($\mathit{C}H_3NCH_2CH_2$), 34.38 ($NCH(CH_3)_2$), 14.52 ($NCH(\mathit{C}H_3)_2$).

Compound 15. To 0.205 g (0.993 mmol) of **1** in 50 mL of toluene was added dropwise 10 mL of a 0.201 M *n*-BuLi solution (2.01 mmol) in toluene at -90 °C. The solution was allowed to warm to room temperature and stirred for 1/2 h. The solvent was evaporated under vacuum and the residue was extracted with 3 x 20 mL portions of pentane. Removal of pentane under vacuum and sublimation of the solid residue at 56 °C/11 x 10^{-3} mmHg gave 0.032 g of **15** in 14% yield. ^{1}H NMR (C_6D_6) 2.74 (dt, 6 H, $HNC\mathit{H}_2CH_2N$, $^{3}J_{HNCH}$ = 2.7 Hz, $^{3}J_{HCCH}$ = 5.85 Hz), 2.15 (t, 6 H, $HNCH_2C\mathit{H}_2$), 1.49 (b, 6 H -$CH_2CH_2CH_2$), 1.02 (t, 3 H, CH_3); ^{13}C (C_6D_6) 50.54 ($HNCH_2\mathit{C}H_2N$), 37.15 ($HNCH_2CH_2$), 29.59, 28.06, 20.74, 14.47 ($CH_2CH_2CH_2CH_3$); ^{29}Si NMR (C_6D_6) -65.34. LRMS (70 ev, EI) *m/z* (relative intensity, proposed ion) 228.1 (0.43, M^+), 171.1 (100.0, M^+ - *n*-Bu), 57.0 (16.11, Bu^+), 149 (22.5), 116.1 (87.2); HRMS for M^+ - Bu ($C_6H_{15}N_4Si$) Calcd: 171.10660, found: 171.10661.

Compound 16. To 0.5 mL of a C_6D_6 solution of 20 mg (0.080 mmol) of **2** cooled to 7 °C was added 1.04 mL of 2.01 M *n*-BuLi solution in hexane (0.080 mmol). The ^{1}H NMR spectrum taken after 10 min revealed that the reaction was complete and that ~ 5% fo **3**, ~ 95% of **16** and ~ 5% of 1-butene had formed.

The ^1H NMR chemical shifts of 1-butene compared favorably with those from commercially available 1-butene.

Characterization of **16**: ^1H NMR (C_6D_6) 2.61 (s, 9 H, NCH_3), 2.57 (t, 6 H, $CH_3NCH_2CH_2$, $^3J_{HCCH}$ = 5.7 Hz), 2.27 (t, 6 H, $CH_3NCH_2CH_2$), 1.6 (m, 6 H, $CH_2CH_2CH_2$), 0.97 (t, 3 H, $^3J_{HCCH}$ = 2.6 Hz); ^{13}C (C_6D_6) 50.43 ($CH_3NCH_2CH_2$), 49.28 ($CH_3NCH_2CH_2$), 39.08 (NCH_3), 28.24, 27.92, 16.95, 14.40 ($CH_2CH_2CH_2CH_3$); ^{29}Si NMR (C_6D_6) -40.85. LRMS (70 ev, EI) *m/z* (relative intensity, proposed ion) 270.2 (0.5, M^+), 213.2 (100.0, M^+ - *n*-Bu), 156.1 (20.1); HRMS for M^+ - *n*-Bu ($C_9H_{21}N_4Si$) calcd: 213.15350, found: 213.15378.

Compound 17: To 25 mL of a toluene solution of 0.12 g (0.58 mmol) of **1** at -75° was slowly added 3.5 mL of 0.2 M solution of *sec*-BuLi (0.7 mmol, 20% excess). The solution was stirred for 15 min and a ^1H NMR spectrum of an aliquot showed low conversion of **1** into **17** and **4**, as well as a substantial amount of **1**. The ratio of **17**:**4**:**1** was estimated to be about 5:1:5 according to ^1H NMR integration. Addition of another 3.5 mL of the *sec*-BuLi (0.7 mmol) caused the starting material to disappear but it also destroyed a considerable portion of the products. Removal of toluene under vacuum and extraction with pentane (3 x 15 mL portions) followed by evaporating the volatiles gave a semisolid residue containing a small amount of substitution product **17** (yield < 10%). ^1H NMR (C_6D_6) 2.76 (t, 6 H, $^3J_{HCCH}$ = 5.9 Hz, $HNCH_2CH_2$), 2.07 (t, 6 H, $HNCH_2CH_2$); ^{13}C NMR (C_6D_6) 50.56 ($HNCH_2CH_2$), 37.27 ($HNCH_2CH_2$), 27.51, 24.18, 14.31, 14.21 (*s*-butyl).

Compound 18. Following the procedure for **17**, it was found that **18** and **4** formed in a ratio of approximately 5:1 during the reaction. Addition of excess of *t*-BuLi in order to consume all the starting material, also led to a low conversion to product. A small amount of compound **18** was identified by ^{1}H NMR in the reaction residue after removing the volatiles. ^{1}H NMR (C_6D_6) 2.76 (dt, $^{3}J_{HCNH}$ = 2.7 Hz, $^{3}J_{HCCH}$ = 5.9 Hz, HNC*H*$_2$CH$_2$), 2.09 (t, 6 H, HNCH$_2$C*H*$_2$), 1.02 (s, 9 H, (CH$_3$)$_3$C); ^{13}C NMR (C_6D_6) 50.57 (HNCH$_2$*C*H$_2$), 37.65 (HN*C*H$_2$CH$_2$), 24.20 (C(*C*H$_3$)$_3$), 10.72 (*C*(CH$_3$)$_3$).

Compound 19. Compound **2** (0.20 g, 0.82 mmol) was mixed with 0.14 g (0.90 mmol) of MgBrCH$_2$C$_6$H$_5$ in 20 mL of toluene and the mixture was refluxed for 0.5 h. After filtration and removal of the solvent, 0.21 g of liquid **19** was collected in 84% yield. ^{1}H NMR (C_6D_6) 7.45 (d, 2 H, $^{2}J_{HH}$ = 7.2 Hz, *m*-H), 7.23 (t, 2 H, $^{2}J_{HH}$ = 7.8 Hz, *o*-H), 7.09 (t, 1 H, *p*-H), 2.51 (t, 6 H, $^{3}J_{HCCH}$ = 5.4 Hz, CH$_3$NC*H*$_2$CH$_2$), 2.46 (s, 9 H, NCH$_3$), 2.28 (t, 6 H, CH$_3$NCH$_2$C*H*$_2$), 2.14 (s, 2 H, C*H*$_2$C$_6$H$_5$); ^{13}C NMR (C_6D_6) 143.06, 130.17, 128.15, 123.95 (C_6H_5), 50.73 (CH$_3$NCH$_2$*C*H$_2$N), 49.72 (CH$_3$N*C*H$_2$CH$_2$N), 36.63 (NCH$_3$), 24.47 (Ph*C*H$_2$); ^{29}Si NMR (C_6D_6) -37.7.

Compound 21.

Method A: To 0.23 g (0.93 mmol) of **2** in 5 mL of toluene was added 0.70 mL of 1.5 M (1.1 mmol) of an ether/cyclohexane solution of PhLi and the solution was refluxed for 0.5 h. After filtration followed by removal of the solvent under vacuum, 0.26 g (0.90 mmol) of crystalline **21** was sublimed. M.p. 60-62 °C. ^{1}H NMR (C_6D_6) 8.06 (dd, 2 H, *o*-H, $^{3}J_{HH}$ = 7.8 Hz, $^{5}J_{HH}$ = 1.2

Hz), 7.38 (t, 2 H, *m*-H), 7.27 (t, 1 H, *p*-H), 2.64 (t, 6 H, NCH_2CH_2, $^3J_{HCCH}$ = 5.7 Hz), 2.54 (s, 9 H, NCH_3), 2.26 (t, 6 H, NCH_2CH_2); ^{13}C NMR (C_6D_6) 136.60, 129.00, 127.81, 127.44 (C_6H_5), 50.51 ($CH_3NCH_2CH_2N$), 50.45, ($CH_3NCH_2CH_2$), 38.08 (CH_3N); ^{29}Si (C_6D_6) -44.41. LRMS (70 ev, EI) *m/z* (relative intensity, proposed ion) 290.2 (30.1, M^+), 213.2 (100.0, M^+ - Ph), 246 (37.1), 234.1 (50.2), 191 (33.8); HRMS for M^+ ($C_{15}H_{26}N_4Si$) calcd: 290.19268; found: 290.191868. Anal, calcd for $C_{15}H_{26}N_4Si$: C, 62.21; H, 8.97; N, 19.31; found: C, 61.99, H, 9.20, N, 19.38.

Method B: To 0.5 mL of a C_6D_6 solution of 20 mg (0.08 mmol) of **2** was slowly added 0.06 mL of a 1.5 M PhLi solution (0.09 mmol) in ether/cyclohexane at 10 °C. ^1H and ^{13}C NMR spectra of the solution showed the formation of **21** and **3** in a molar ratio of approximately 90:5 plus a small amount of biphenyl, whose ^1H and ^{13}C NMR peaks compared favorably with a commercially available sample. Its identity was further verified by LRMS (*m/z*: 154).

SUPPLEMENTAL MATERIAL 2

X-RAY DATA FOR 1-FLUORO-N,N',N''-TRIMETHYLAZASILATRANE, 8

A colorless crystal of the title compound was attached to a glass fiber for a data collection at -50±1 °C on the P4RA diffractometer. The cell constants for data collection were determined from a list of reflections found by a rotation photograph. Pertinent data collection and reduction information is given in Table I. Atomic coordinates and equivalent isotropic displacement parameters are listed in Table II. Bond distances and angles are listed in Tables III and IV , respectively.

Lorentz and polarization correction were applied. A correction based on a nonlinear decay in the standard reflections was applied to the data. A semi-empirical absorption correction[1] was applied by using a set of azimuthal scans.

The centric space group $P2_1/m$ was determined by intensity statistics and systematic absences. the structure was solved by direct methods.[1] All non-hydrogen atoms were placed directly from the E-map. All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atom positions were generated with ideal geometries and were refined as riding, isotropic atoms.

The structure is found as a C_3 molecule that is disordered across a crystallographic mirror. The $P2_1/m$, space group requires that the contents of the asymmetric unit have mirror symmetry with another, therefore both left- and right-handed ' twists' of the molecule are found on the same site. The

only non-hydrogen atoms that are affected are C1 and C3. All other atoms are sufficiently modeled with one atom. C1 is refined as a half-atom: the other half is produced by symmetry. C3 and its disordered component, C3' are refined as half atoms on general sites. The necessity for splitting these sites also requires dual, riding-atom assignments for the hydrogens on C4.

The Si-F bond distance is 1.643(2) Å . The Si-N1 introatomic length is 2.034(2) Å. The N-Si-N angle average to 119.8°. The molecular drawings showing the disordering of the carbons adjacent to the axial nitrogen are illustrated in Figure 1.

X-ray data collection and structure solution were carried out at the Iowa State Molecular Structure Laboratory. Refinement calculations were performed on a Digital Equipment Corp. VAXStation 3100 computer using the SHELXTL-Plus [1] and SHELXL-93 programs.[2]

References

1. SHELXTL-plus, Siemens Analytical X-ray Instruments, Inc. Madison, Wi.

2. SHELXL-93, *J. Appl. Cryst.* **1993**, in preparation.

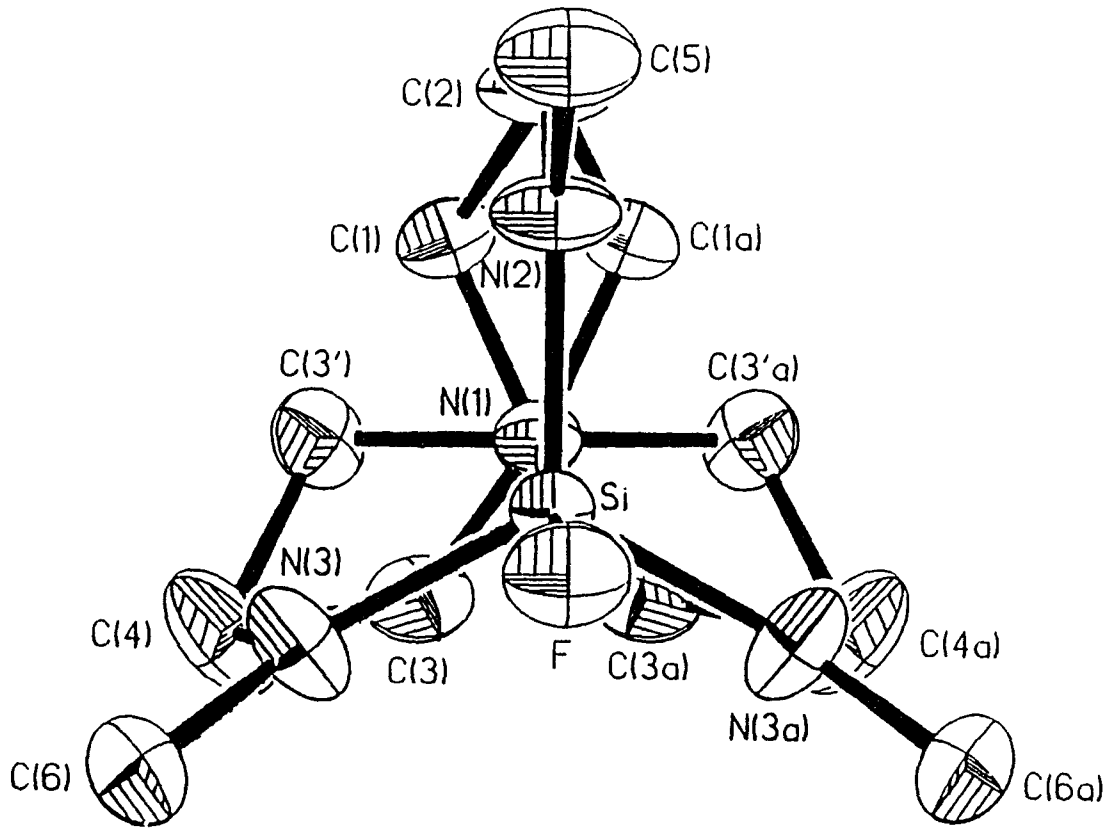


Figure 1. Molecular Structure of $FSi(CH_3NCH_2CH_2)_3N$ **8** (a) Showing the disordering of the carbons attached to the axial nitrogen.

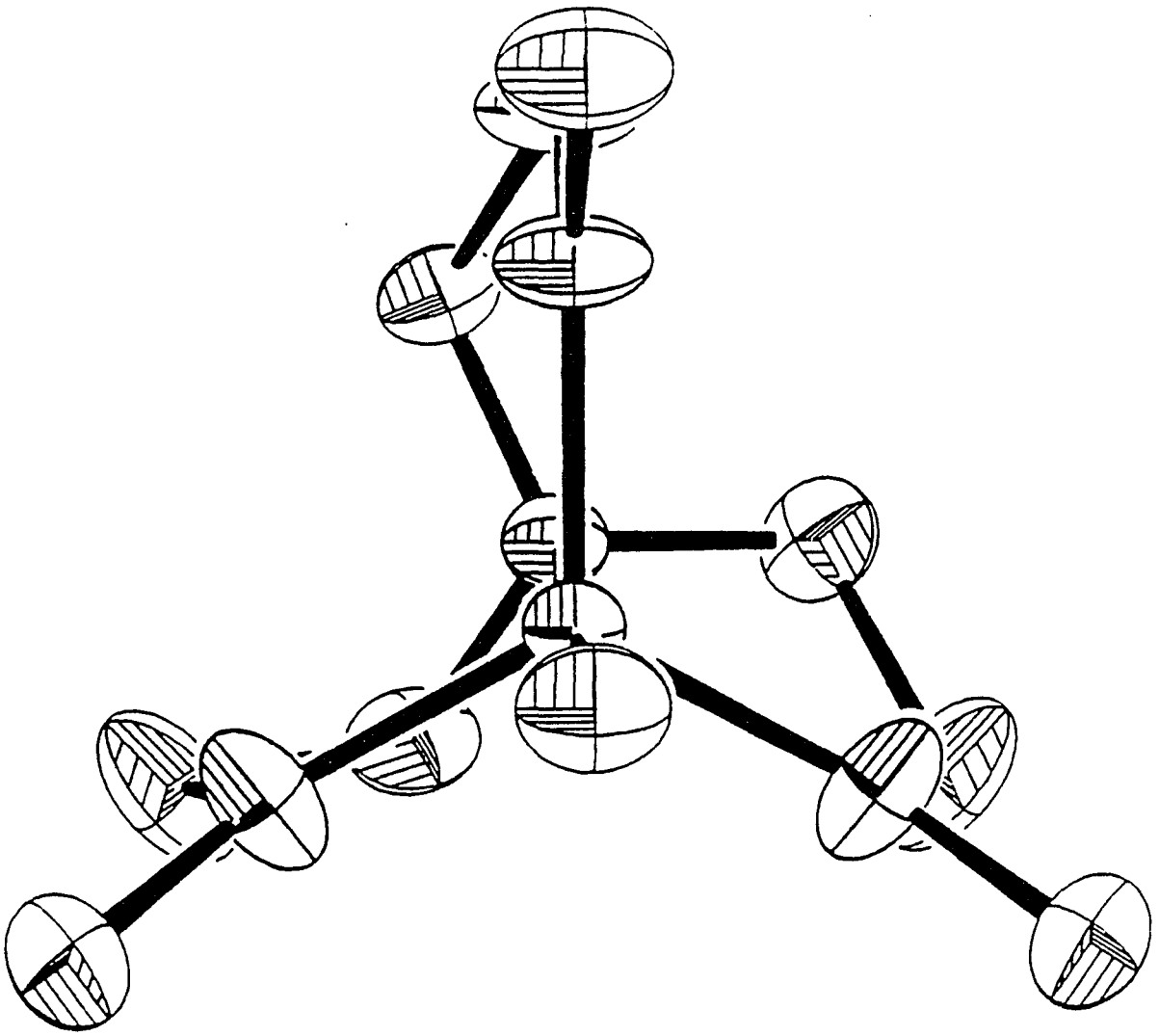


Figure 1. Continued (b) showing the twist of the NCH_2CH_2N bridges around the C_3 axis after selection of one of the disordered carbons on each bridge.

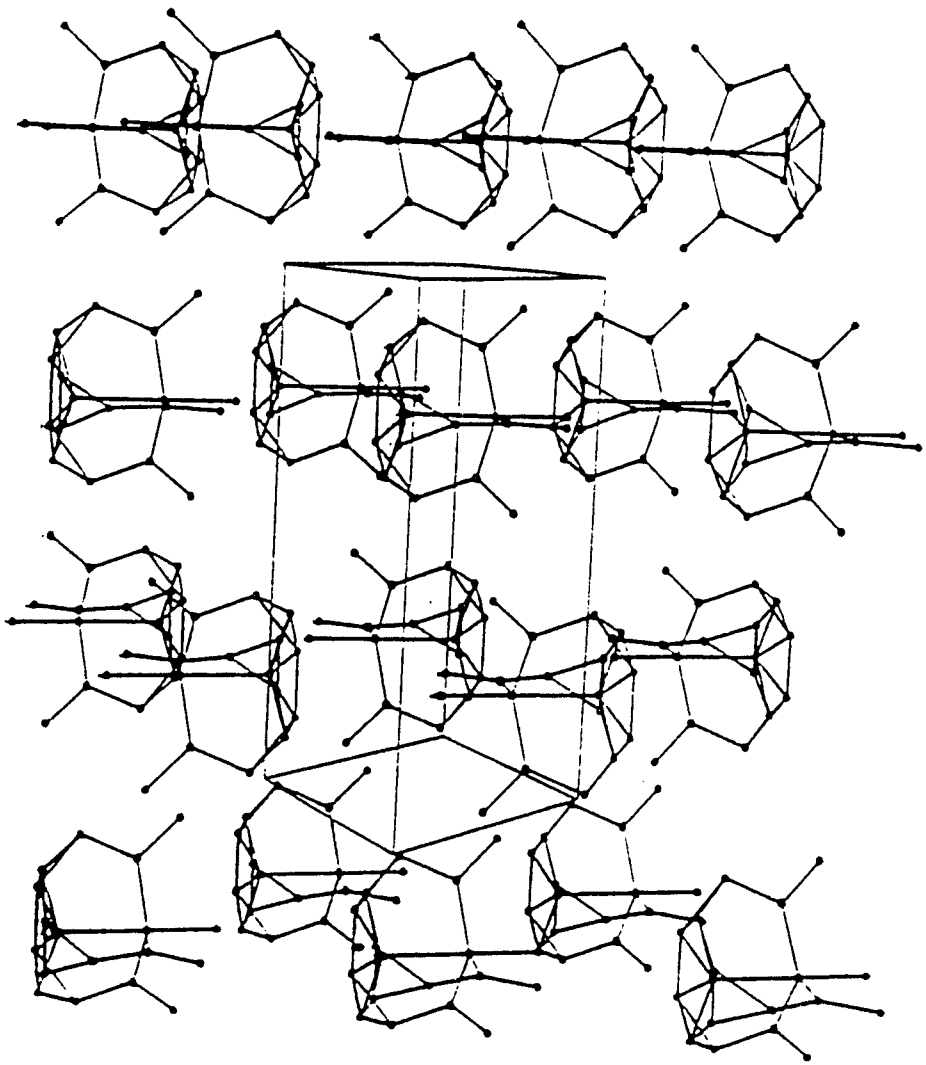


Figure 2. Unit Cell Drawing for the Structure of 8

Table I. Crystallographic Data fo 8

Empirical Formula	$C_{14}H_{36}FN_4Si$
Color; Habit	Colorless, plate
Crystal Size (mm)	0.50 x 0.35 x 0.09
Crystal System	Monoclinic
Space Group	$P2_1/m$
Unit Cell Dimensions	a = 7.352(1) Å
	b = 12.361(2) Å
	c = 7.512(1) Å
	α = 90.0 °
	β = 119.30(1) °
	γ = 90.0 °
Volume	595.3(2) $Å^3$
Z	2
Formula Weight	307.56
Density(calc.)	1.716 Mg/m^3
Absorption Coefficient	1.828 mm^{-1}
F(000)	342
Diffractometer Used	Siemens P4RA
Radiation	CuKα (λ =1.54178Å)

Table I. Continued.

Temperature (K)	223(2)
Monochromator	graphite
θ Range	6.76 to 56.80°
Scan Type	$\omega - 2\theta$
Standard Reflections	3 measured every 97 reflections
Index Ranges	$-7 \leq h \leq 7$, $-13 \leq k \leq 0$ $-8 \leq l \leq 8$
Reflections Collected	1659
Independent Reflections	841 (Rint = 0.0340)
Observed Reflections	805 ($I \geq 2\sigma(I)$)
Refinement Method	Full-matrix least-squares on F^2
Extinction Correction	0.0124(14)
Hydrogen Atoms	Riding model fixed isotropic U
Parameters Refined	102
Final R Indices [$I \geq 2\sigma(I)$]	R1 = 0.0348, wR =0.0926
R Indices (all data)	R1 = 0.0361, wR = 0.0935
GooF, Observed and All Data	1.130, 1.113
Largest and Mean Δ/σ	0.001, 0.000
Largest Difference Peak	0.225e/Å^{-3}
Largest Difference Hole	-0.220e/Å^{-3}

Table II. Atomic Coordinates ($x10^4$) and Equivalent Isotropic Displacement Coefficients ($Å^2x10^3$) for 8

Atom	x	y	z	U(eq)
Si	5200(1)	2500	739(1)	23(1)
F	2696(2)	2500	-929(2)	36(1)
N(1)	8302(4)	2500	2788(3)	28(1)
N(2)	6026(4)	2500	-1060(3)	34(1)
N(3)	5167(3)	1297(2)	1896(3)	42(1)
C(1)	9378(6)	2014(4)	1773(6)	33(1)
C(2)	8219(5)	2500	-446(4)	43(1)
C(3)	8556(7)	1885(4)	4568(6)	41(1)
C(3')	8911(7)	1335(4)	3312(7)	41(1)
C(4)	7078(4)	862(2)	3544(4)	57(1)
C(5)	4734(5)	2500	-3242(4)	42(1)
C(6)	3426(4)	599(2)	1371(4)	48(1)

Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor

Table III. Bond Distances (Å) for **8**

Si-F	1.643(2)	C(1)-C(1)#1	1.200(9)
Si-N(3)#1	1.728(2)	C(1)-C(2)	1.573(5)
Si-N(3)	1.728(2)	C(1)-C(3')	1.596(6)
Si-N(2)	1.732(2)	C(2)-C(1)#1	1.573(5)
Si-N(1)	2.034(2)	C(3)-C(3')	1.290(7)
N(1)-C(3)#1	1.469(5)	C(3)-C(3)#1	1.520(10)
N(1)-C(3)	1.469(5)	C(3)-C(4)	1.598(6)
N(1)-C(1)'	1.468(4)	C(3')-C(4)	1.555(5)
N(1)-C(1)	1.468(4)		
N(1)-C(3')#1	1.502(5)		
N(1)-C(3')	1.502(5)		
N(2)-C(5)	1.437(4)		
N(2)-C(2)	1.444(4)		
N(3)-C(6)	1.430(3)		
N(3)-C(4)	1.447(3)		

[a] Symmetry transformations used to generate equivalent atoms: #1 x, -y+1/2,z

Table IV. Bond Angles in degrees for 8

C(3)-N(1)-C(3')	51.4(3)	N(1)-C(1)-C(2)	104.1(3)
C(1)#1-N(1)-C(3')	111.1(3)	C(1)#1-C(1)-C(3')	121.8(2)
C(1)-N(1)-C(3')	65.0(3)	N(1)-C(1)-C(3')	58.6(2)
C(3')#1-N(1)-C(3')	146.9(4)	C(2)-C(1)-C(3')	140.5(3)
C(3)#1-N(1)-Si	106.5(2)	F-Si-N(3)#1	95.58(7)
C(3)-N(1)-Si	106.5(2)	F-Si-N(3)	95.58(7)
C(1)#1-N(1)-Si	107.3(2)	N(3)#1-Si-N(3)	118.70(14)
C(1)-N(1)-Si	107.3(2)	F-Si-N(2)	95.47(10)
C(3')#1-N(1)-Si	106.2(2)	N(3)#1-Si-N(2)	119.27(7)
C(3')-N(1)-Si	106.2(2)	N(3)-Si-N(2)	119.27(7)
C(5)-N(2)-C(2)	112.1(2)	F-Si-N(1)	179.64(9)
C(5)-N(2)-Si	127.0(2)	N(3)#1-Si-N(1)	84.60(7)
C(2)-N(2)-Si	121.0(2)	N(3)-Si-N(1)	84.60(7)
C(6)-N(3)-C(4)	112.0(2)	N(2)-Si-N(1)	84.17(10)
C(6)-N(3)-Si	127.7(2)	C(3)#1-N(1)-C(3)	62.3(4)
C(4)-N(3)-Si	120.2(2)	C(3)#1-N(1)-C(1)#1	113.6(3)
C(1)#1-C(1)-N(1)	65.9(2)	C(3)-N(1)-C(1)#1	145.4(3)
C(1)#1-C(1)-C(2)	67.6(2)	C(3)#1-N(1)-C(1)	145.4(3)

Table IV. Continued

N(2)-C(2)-C(1)#1	106.2(2)	C(3)-N(1)-C(1)	113.6(3)
N(2)-C(2)-C(1)	106.2(2)	C(1)#1-N(1)-C(1)	48.3(4)
C(1)#1-C(2)-C(1)	44.8(3)	C(3)#1-N(1)-C(3')#1	51.4(3)
C(3')-C(3)-N(1)	65.6(3)	C(3)-N(1)-C(3')#1	111.6(3)
C(3')-C(3)-C(3)#1	121.8(3)	C(1)#1-N(1)-C(3')#1	65.0(3)
N(1)-C(3)-C(3)#1	58.8(2)	C(1)-N(1)-C(3')#1	111.1(3)
C(3')-C(3)-C(4)	64.1(3)	C(3)#1-N(1)-C(3')	111.6(3)
N(1)-C(3)-C(4)	102.6(3)		
C(3)#1-C(3)-C(4)	142.3(2)		
C(3)-C(3')-N(1)	62.9(3)		
C(3)-C(3')-C(4)	67.6(3)		
N(1)-C(3')-C(4)	103.0(3)		
C(3)-C(3')-C(1)	116.4(4)		
N(1)-C(3')-C(1)	56.5(2)		
C(4)-C(3')-C(1)	141.6(3)		
N(3)-C(4)-C(3')	107.3(2)		
N(3)-C(4)-C(3)	105.4(2)		
C(3')-C(4)-C(3)	48.3(2)		

Estimated standard deviation in the least significant figure are given in parentheses

Table V. Hydrogen Coordinates and Isotropic Displacement Parameters ($Å^2 x 10^3$) for 8

Atom	U11	U22	U33	U23	U13	U12
Si	23(1)	25(1)	22(1)	0	12(1)	0
F	24(1)	48(1)	33(1)	0	12(1)	0
N(1)	27(1)	34(1)	20(1)	0	10(1)	0
N(2)	23(1)	60(2)	18(1)	0	10(1)	0
N(3)	35(1)	39(1)	47(1)	15(1)	17(1)	-5(1)
C(1)	25(2)	45(2)	28(2)	-3(2)	11(2)	4(2)
C(2)	28(2)	78(3)	24(2)	0	15(1)	0
C(3)	42(3)	57(3)	22(2)	7(2)	13(2)	11(2)
C(3')	34(2)	40(3)	44(3)	15(2)	16(2)	12(2)
C(4)	52(2)	52(2)	61(2)	32(1)	23(1)	3(1)
C(5)	36(2)	64(2)	23(2)	0	12(1)	0
C(6)	55(2)	35(1)	68(2)	-3(1)	41(1)	-10(1)

SUPPLEMENTAL MATERIAL 3

X-RAY DATA FOR THE INSERTION PRODUCT 9

A crystal of compound **9** was attached to the tip of a glass fiber and mounted on the Siemens P4RA diffractometer for a data collection at 223± 1K. The cell constants for data collection were determined from reflections found from a rotation photograph. Pertinent data collection and reduction information is given in Table I. Atomic coordinates and equivalent isotropic displacement parameters are listed in Table II. Bond distances and angles are listed in Tables III and IV , respectively.

Lorentz and polarization correction were applied. A nonlinear correction based on the decay in the standard reflections was applied to the data. A series of azimuthal reflections was collected for this specimen. A semi-empirical absorption correction based on the azimuthal scans was applied to the data.

The centrosymmetric space group $P\bar{1}$ was chosen based on the lack of symmemtric absences and intensity statistics . However, no suitable solution was derived from direct methods[1]. A correct direct methods solution was found in the noncentrosymmetric space group P1 which has enantiomers related by a center of inversion. The position of all atom found in one enantiomer were shifted relative to the inversion center to yield the $P\bar{1}$ molecular structure.

All non-hydrogen atoms were refined with anisotropic thermal parameters. Methylene hydrogen atoms refined as riding atoms with C-H distances of 0.96 Å with individual isotropic thermal parameters. Methyl

hydrogen atoms were refined initially as rigid bodies to give the best torsion angle. During the final set of least-squares these were not refined positionally, but refined with individual group isotropic thermal parameters.

The most interesting feature of this structure is the perfluorobenzyne group which is found inserted into a Si-N bound. The benzyne Si-N moiety is planar.

X-ray data collection and structure solution were done at the Iowa State Molecular Structure Laboratory. Refinement calculations were performed on a Digital Equipment MicroVAX 3100 computer using the SHELXTL-Plus [1].

Reference

1. SHELXTL-plus, Siemens Analytical X-ray Instruments, Inc., Madison, WI.

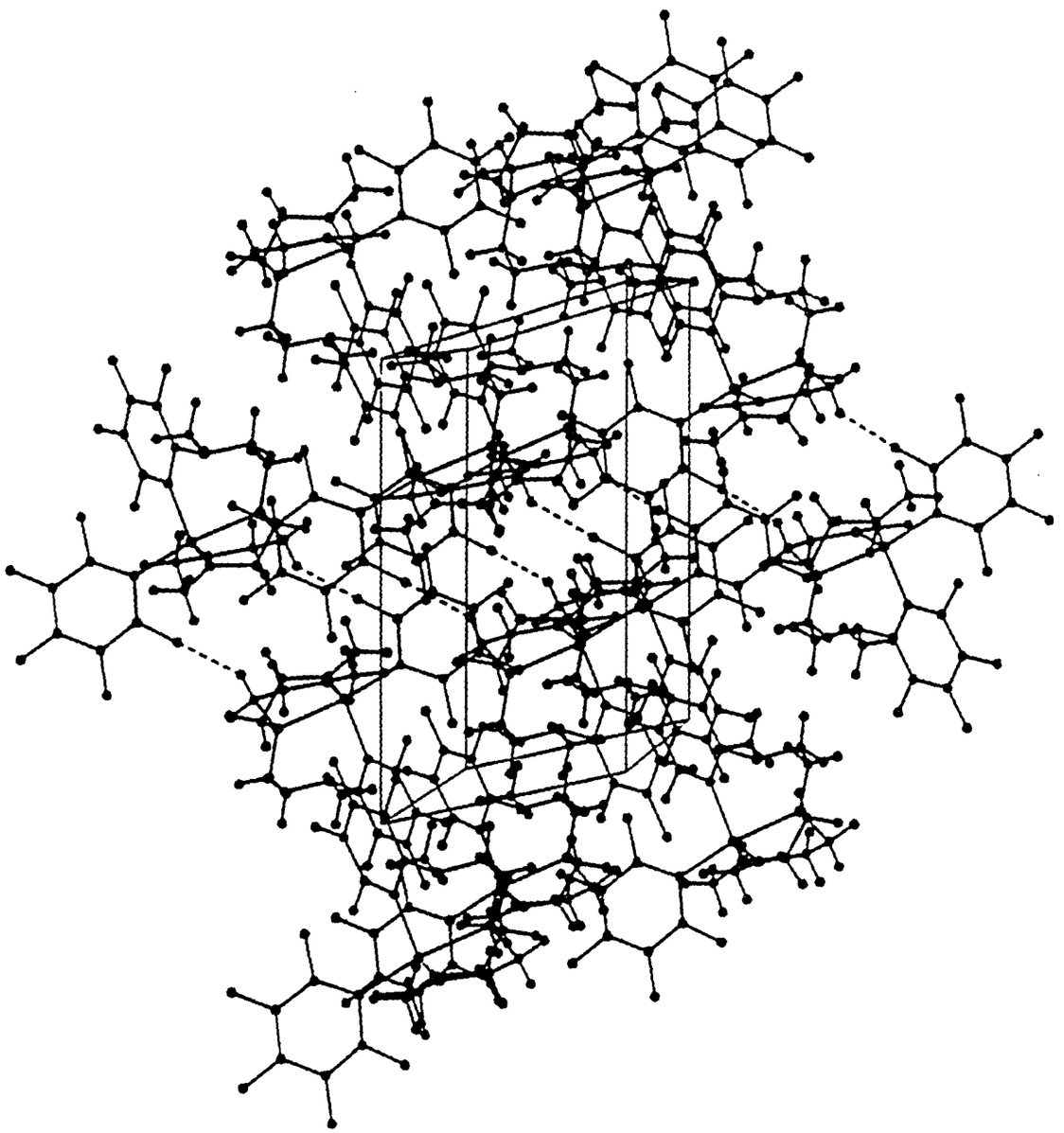


Figure 1. Unit Cell Drawing for the Structure of **9**

Table I. Crystallographic Data for the Insertion Product 9

Empirical Formula	$C_{21}H_{21}F_9N_4Si$
Color; Habit	Colorless, plate
Crystal Size (mm)	0.22 x 0.16 X 0.09
Crystal System	Triclinic
Space Group	$P\bar{1}$
Unit Cell Dimensions	a = 8.586(2) Å
	b = 10.215(2) Å
	c = 13.745(3) Å
	α = 95.62(2)°
	β = 102.25(2)°
	γ = 107.74(2)°
Volume	1104.8(4) $Å^3$
Z	2
Formula Weight	528.5
Density(calc.)	1.589 Mg/m^3
Absorption Coefficient	1.819 mm^{-1}
F(000)	540

Table I. Continued

Diffractometer Used	Siemens P4RA
Radiation	CuKα (λ = 1.54178 Å)
Temperature (K)	223
Monochromator	Highly-oriented graphite crystal
2θ Range	4.0 to 115.0°
Scan Type	$2\theta - \theta$
Scan Speed	Variable; 6.01 to 23.44°/min. in ω
Scan Range (ω)	1.00° plus Kα-separation
Background Measurement	Stationary crystal and stationary counter at beginning and end of scan, each for 25.0% of total scan time
Standard Reflections	3 measured every 97 reflections
Index Ranges	$-9 \leq h \leq 0$, $-10 \leq k \leq 11$ $-14 \leq l \leq 14$
Reflections Collected	3210
Independent Reflections	2969 (R_{int} = 0.85%)
Observed Reflections	2679 ($F \geq 4.0\sigma$ (F))
Absorption Correction	Semi-empirical
Min./Max. Transmission	0.7282 / 0.9435

Table I. Continued

System Used	Siemens SHELXTL-Plus (VMS)
Solution	Direct Methods
Refinement Method	Full-Matrix Least-Squares
Quantity Minimized	$\Sigma\ w(F_o - F_c)^2$
Absolute Structure	N/A
Extinction Correction	$\chi = 0.0083(10)$, where $F^* = F_c\ [1+0.002\chi F^2/\sin(2\theta)]^{-1/4}$
Hydrogen Atoms	Riding model, fixed isotropic U
Weighting Scheme	$w^{-1} = \sigma^2\ (F) + 0.0003F^2$
Parameters Refined	332
Final R Indices (obs. data)	R = 3.21 %, wR = 4.66 %
R Indices (all data)	R = 3.50 %, wR = 4.71 %
Goodness-of-Fit	2.10
Largest and Mean Δ/σ	0.001, 0.000
Data-to-Parameter Ratio	8.1:1
Largest Difference Peak	0.24 e/Å^{-3}
Largest Difference Hole	-0.21 e/Å^{-3}

Table II. Atomic Coordinates ($x10^4$) and Equivalent Isotropic Displacement Coefficients ($Å^2x10^3$)

Atom	x	y	z	U_{eq}
Si	-2249(1)	1597(1)	-2775(1)	27(1)
N(1)	-4692(2)	206(2)	-2555(1)	31(1)
C(1)	-5050(3)	258(3)	-1543(2)	39(1)
C(2)	-5006(3)	1643(3)	-1026(2)	42(1)
N(2)	-3454(2)	2780(2)	-967(1)	34(1)
C(3)	-3466(4)	4124(3)	-497(2)	49(1)
C(4)	-5939(3)	564(3)	-3306(2)	39(1)
C(5)	-5311(3)	2108(3)	-3293(2)	37(1)
N(3)	-3506(2)	2567(2)	-3209(1)	32(1)
C(6)	-2887(3)	4088(3)	-3138(2)	48(1)
C(7)	-4729(3)	-1231(2)	-2880(2)	40(1)
C(8)	-3823(3)	-1205(3)	-3704(2)	42(1)
N(4)	-2312(2)	31(2)	-3424(1)	33(1)
C(9)	-986(3)	-229(3)	-3838(2)	42(1)
C(11)	-1966(3)	2433(2)	-620(2)	30(1)
C(12)	-1201(3)	2600(3)	407(2)	36(1)
F(12)	-1865(2)	3075(2)	1124(1)	56(1)

Table II. Continued.

C(13)	226(3)	2255(3)	740(2)	40(1)
F(13)	965(2)	2453(2)	1738(1)	59(1)
C(14)	867(3)	1680(3)	50(2)	37(1)
F(14)	2269(2)	1338(2)	364(1)	53(1)
C(15)	73(3)	1455(2)	-965(2)	31(1)
F(15)	789(2)	880(1)	-1611(1)	42(1)
C(16)	-1323(3)	1836(2)	-1340(2)	27(1)
C(21)	-273(3)	2807(2)	-3183(2)	30(1)
C(22)	1249(3)	3740(2)	-2584(2)	32(1)
F(22)	1610(2)	3873(1)	-1565(1)	48(1)
C(23)	2494(3)	4610(2)	-2944(2)	34(1)
F(23)	3934(2)	5493(2)	-2299(1)	50(1)
C(24)	2276(3)	4573(2)	-3961(2)	37(1)
F(24)	3479(2)	5399(2)	-4324(1)	58(1)
C(25)	790(3)	3675(2)	-4604(2)	36(1)
F(25)	532(2)	3623(2)	-5618(1)	54(1)
C(26)	-420(3)	2845(2)	-4212(2)	34(1)
F(26)	-1856(2)	2021(2)	-4907(1)	47(1)

Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor

Table III. Bond Distances (Å) for the Insertion Product **9**

Si-N(1)	2.246 (2)	Si-N(3)	1.731 (2)
Si-N(4)	1.734 (2)	Si-C(16)	1.924 (2)
Si-C(21)	1.996 (2)	N(1)-C(1)	1.487 (3)
N(1)-C(4)	1.480 (3)	N(1)-C(7)	1.481 (3)
C(1)-C(2)	1.505 (4)	C(2)-N(2)	1.458 (3)
N(2)-C(3)	1.463 (4)	N(2)-C(11)	1.427 (3)
C(4)-C(5)	1.500 (4)	C(5)-N(3)	1.452 (3)
N(3)-C(6)	1.467 (3)	C(7)-C(8)	1.503 (4)
C(8)-N(4)	1.456 (3)	N(4)-C(9)	1.456 (4)
C(11)-C(12)	1.394 (3)	C(11)-C(16)	1.406 (4)
C(12)-F(12)	1.358 (3)	C(12)-C(13)	1.376 (4)
C(13)-F(13)	1.350 (3)	C(13)-C(14)	1.363 (4)
C(14)-F(14)	1.350 (3)	C(14)-C(15)	1.379 (3)
C(15)-F(15)	1.364 (3)	C(15)-C(16)	1.384 (3)
C(21)-C(22)	1.388 (3)	C(21)-C(26)	1.397 (3)
C(22)-F(22)	1.352 (3)	C(22)-C(23)	1.382 (3)
C(23)-F(23)	1.352 (2)	C(23)-C(24)	1.365 (4)

Table III. Continued.

C(24)-F(24)	1.341 (3)	C(24)-C(25)	1.379 (3)
C(25)-F(25)	1.357 (3)	C(25)-C(26)	1.372 (3)
C(26)-F(26)	1.361 (2)		

[a]Estimated standard deviation in the least significant figure are given in parentheses

Table IV. Bond Angles in degrees for **9**

N(1)-Si-N(3)	82.1(1)	N(1)-Si-N(4)	81.2(1)
N(3)-Si-N(4)	125.0(1)	N(1)-Si-C(16)	87.7(1)
N(3)-Si-C(16)	118.3(1)	N(4)-Si-C(16)	112.9(1)
N(1)-Si-C(21)	171.4(1)	N(3)-Si-C(21)	92.7(1)
N(4)-Si-C(21)	96.4(1)	C(16)-Si-C(21)	100.8(1)
Si-N(1)-C(1)	121.0(1)	Si-N(1)-C(4)	101.1(1)
C(1)-N(1)-C(4)	112.3(2)	Si-N(1)-C(7)	104.8(2)
C(1)-N(1)-C(7)	107.0(2)	C(4)-N(1)-C(7)	110.2(2)
N(1)-C(1)-C(2)	117.2(2)	C(1)-C(2)-N(2)	113.3(2)
C(2)-N(2)-C(3)	112.4(2)	C(2)-N(2)-C(11)	113.0(2)
C(3)-N(2)-C(11)	116.8(2)	N(1)-C(4)-C(5)	108.8(2)
C(4)-C(5)-N(3)	109.2(2)	Si-N(3)-C(5)	122.5(2)
Si-N(3)-C(6)	124.3(2)	C(5)-N(3)-C(6)	108.8(2)
N(1)-C(7)-C(8)	108.2(2)	C(7)-C(8)-N(4)	108.2(2)
Si-N(4)-C(8)	122.6(2)	Si-N(4)-C(9)	127.0(1)
C(8)-N(4)-C(9)	110.3(2)	N(2)-C(11)-C(12)	121.8(2)
N(2)-C(11)-C(16)	118.3(2)	C(12)-C(11)-C(16)	119.8(2)
C(11)-C(12)-F(12)	121.3(2)	C(11)-C(12)-C(13)	121.7(2)
F(12)-C(12)-C(13)	117.0(2)	C(12)-C(13)-F(13)	120.6(2)

Table IV. Continued

C(12)-C(13)-C(14)	119.2(2)	F(13)-C(13)-C(14)	120.2(2)
C(13)-C(14)-F(14)	119.9(2)	C(13)-C(14)-C(15)	119.4(2)
F(14)-C(14)-C(15)	120.7(2)	C(14)-C(15)-F(15)	116.1(2)
C(14)-C(15)-C(16)	123.6(2)	F(15)-C(15)-C(16)	120.2(2)
Si-C(16)-C(11)	123.1(2)	Si-C(16)-C(15)	120.6(2)
C(11)-C(16)-C(15)	116.2(2)	Si-C(21)-C(22)	129.4(2)
Si-C(21)-C(26)	118.3(1)	C(22)-C(21)-C(26)	112.1(2)
C(21)-C(22)-F(22)	120.8(2)	C(21)-C(22)-C(23)	124.9(2)
F(22)-C(22)-C(23)	114.3(2)	C(22)-C(23)-F(23)	120.6(2)
C(22)-C(23)-C(24)	119.8(2)	F(23)-C(23)-C(24)	119.6(2)
C(23)-C(24)-F(24)	120.7(2)	C(23)-C(24)-C(25)	118.6(2)
F(24)-C(24)-C(25)	120.8(2)	C(24)-C(25)-F(25)	119.9(2)
C(24)-C(25)-C(26)	119.6(2)	F(25)-C(25)-C(26)	120.5(2)
C(21)-C(26)-C(25)	125.1(2)	C(21)-C(26)-F(26)	119.9(2)
C(25)-C(26)-F(26)	115.0(2)		

[a]Estimated standard deviation in the least significant figure are given in parentheses

Table V. Anisotropic Displacement Coeffiicients ($Å^2x10^3$) for **9**

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Si	22(1)	31(1)	26(1)	9(1)	6(1)	4(1)
N(1)	24(1)	34(1)	32(1)	8(1)	5(1)	7(1)
C(1)	26(1)	49(1)	40(1)	6(1)	12(1)	13(1)
C(2)	28(1)	67(2)	34(1)	17(1)	11(1)	11(1)
N(2)	30(1)	43(1)	32(1)	18(1)	9(1)	4(1)
C(3)	57(2)	56(2)	39(1)	32(1)	6(1)	-3(1)
C(4)	22(1)	50(2)	39(1)	10(1)	0(1)	6(1)
C(5)	31(1)	49(1)	34(1)	21(1)	3(1)	8(1)
N(3)	31(1)	34(1)	32(1)	14(1)	8(1)	8(1)
C(6)	55(2)	39(1)	58(2)	21(1)	24(1)	16(1)
C(7)	31(1)	32(1)	50(2)	5(1)	8(1)	7(1)
C(8)	37(1)	33(1)	48(2)	5(1)	9(1)	-4(1)
N(4)	26(1)	33(1)	38(1)	8(1)	11(1)	1(1)
C(9)	37(1)	42(1)	50(2)	16(1)	16(1)	0(1)
C(11)	24(1)	34(1)	28(1)	7(1)	5(1)	6(1)
C(12)	38(1)	45(1)	26(1)	13(1)	12(1)	5(1)
F(12)	68(1)	74(1)	34(1)	35(1)	15(1)	8(1)
C(13)	37(1)	47(1)	27(1)	6(1)	-2(1)	14(1)

Table V. Continued

F(13)	59(1)	78(1)	31(1)	20(1)	-5(1)	15(1)
C(14)	22(1)	46(1)	42(1)	10(1)	3(1)	20(1)
F(14)	29(1)	77(1)	56(1)	23(1)	3(1)	29(1)
C(15)	23(1)	35(1)	37(1)	9(1)	11(1)	11(1)
F(15)	29(1)	59(1)	46(1)	22(1)	11(1)	12(1)
C(16)	21(1)	31(1)	28(1)	5(1)	7(1)	8(1)
C(21)	30(1)	31(1)	29(1)	11(1)	8(1)	2(1)
C(22)	34(1)	35(1)	25(1)	10(1)	7(1)	5(1)
F(22)	46(1)	48(1)	28(1)	-8(1)	1(1)	4(1)
C(23)	27(1)	28(1)	43(1)	5(1)	6(1)	6(1)
F(23)	35(1)	45(1)	55(1)	-3(1)	3(1)	12(1)
C(24)	38(1)	33(1)	46(2)	11(1)	23(1)	15(1)
F(24)	55(1)	56(1)	62(1)	3(1)	29(1)	23(1)
C(25)	49(2)	37(1)	27(1)	18(1)	16(1)	10(1)
F(25)	72(1)	56(1)	36(1)	17(1)	22(1)	16(1)
C(26)	33(1)	35(1)	29(1)	9(1)	4(1)	1(1)
F(26)	42(1)	53(1)	28(1)	0(1)	0(1)	1(1)

The anisotropic displacement factor exponent takes the form:
$-2\pi^2(h^2a^{*2}U_{11}+ ...+2hka^*b^*U_{12})$

Table VI. H-atom Coordinates ($x10^4$) and Isotropic Displacement Coefficients ($Å^2x10^3$) for **9**

Atom	x	y	z	U_{eq}
H(1A)	-4178	26	-1107	35(6)
H(1B)	-6110	-446	-1582	47(7)
H(2A)	-5136	1612	-351	48(7)
H(2B)	-5945	1848	-1416	52(8)
H(3A)	-2371	4810	-406	67(5)
H(3B)	-3745	4091	142	67(5)
H(3C)	-4295	4370	-959	67(5)
H(4A)	-6925	399	-3049	54(8)
H(4B)	-6245	-19	-3956	67(9)
H(5A)	-5541	2663	-2771	29(6)
H(5B)	-5890	2248	-3932	42(7)
H(6A)	-1679	4474	-3010	86(6)
H(6B)	-3243	4456	-2587	86(6)
H(6C)	-3406	4331	-3752	86(6)
H(7A)	-5888	-1779	-3195	41(7)
H(7B)	-4316	-1673	-2345	50(8)
H(8A)	-4529	-1253	-4359	43(7)

Table VI. Continued.

H(8B)	-3460	-2006	-3730	45(7)
H(9A)	37	562	-3621	50(4)
H(9B)	-1354	-409	-4563	50(4)
H(9C)	-779	-1032	-3606	50(4)

PAPER 4. NON-STRAIGHTFORWARD SUBSTITUTION REACTIONS AT PENTACOORDINATE SILICON: INTERESTING HYDRIDE AND FLUORIDE TRANSFER REACTIONS

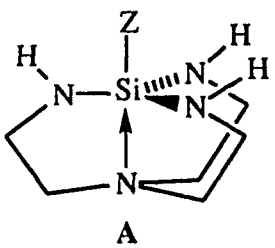
ABSTRACT

The syntheses of aminoazasilatranes of the type $R_2NSi(R'NCH_2CH_2)_3N$ (R' = H, R = H (**2a**), CH_3 (**3a**), CH_2CH_3 (**4a**), $Si(CH_3)_3$ (**6a**), R' = CH_3, R = H (**2b**), CH_3 (**3b**), CH_2CH_3 (**4b**), $Si(CH_3)_3$ (**6b**) via nucleophilic substitution reactions of $ClSi(R'NCH_2CH_2)_3$ (R' = H (**7a**), R' = CH_3 (**7b**), respectively) with amide anions are reported. Reactivities of **7a** and **7b** toward other nucleophilic reagents such as alkyl lithiums and group I metal alkoxides are also described. It is found that the equatorial NR' functionalities significantly influence the reaction pathways. With strong bases, lithiation of the equatorial NH hydrogens of **7a** was observed to be the main pathway along with some nucleophilic substitution products and hydride transfer product **1a**. With **7b**, however, equatorial nitrogen lithiation is precluded and its reactions with nucleophiles can produce substantial amounts of nucleophilic substitution product as well as hydride transfer product **1b**. The relative ratios of these products depend substantially on stereoelectronic factors, the nature of the nucleophilic reagents and the reaction conditions. In the case of the reaction of **7b** with BrC_6F_5/*n*-BuLi, three products, namely, $C_6F_5Si(CH_3NCH_2CH_2)_3N$ (**13b**), $FSi(CH_2NCH_2CH_2)_3N$ (**14b**) and $C_6F_5Si(CH_3NCH_2CH_2)_2(C_6F_4CH_3NCH_2CH_2)N$ (**15**) formed in an approximate ratio of 1:2:1. The formation of **15** is attributed to perfluorobenzyne insertion into a Si-N_{eq} bond of (**13b**). Interestingly, the plane defined by the axial NSi_2 moiety in **6a** is found to be fixed at the apical position of the silicon, providing an interesting example of pπ-dπ interaction between a pentacoordinate silicon

and a nitrogen. However, the counterpart axial moiety in **6b** freely rotates around the apical Si-N bond due to steric interactions with nearby methyl groups on the cage. Compounds **14b** and **15** have been characterized by single crystal X-ray diffraction studies. The relatively short transannular distance between Si and N of 2.246 (2) Å in **15** indicates the preservation of donor-acceptor Si←N in the presence of the seven-membered ring. The crystal data are as follows: **14b**, monoclinic, $P2_{1/m}$, a = 7.352 (1) Å, b = 12.361 (2) Å, c = 7.512 (1) Å, β = 119.30 (1)°, Z = 2; **15**, triclinic, $P\bar{1}$, a = 8.586 (2) Å, b = 10.215 (2) Å, c = 13.745 (3) Å, 2 = 95.62 (2)°, β = 102.25 (2)°, γ = 107.74 (2)°, and Z = 2.

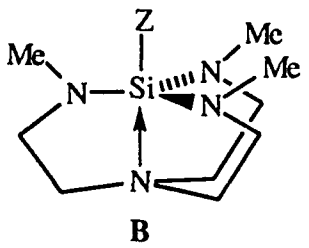
INTRODUCTION

As part of our exploration of the chemistry of atranes,[1] we became interested synthesizing candidates for the MOCVD of metallic and non-metallic nitrides. In the case of silicon nitride, such compounds are represented by **1a-6a** of structure type **A** and **1b-6b** of structure type **B**.[2] The preferred Z substituents in such precursors are H, NH_2 or NR_2 in order to



A

	Z
1a	H
2a	NH_2
3a	NMe_2
4a	NEt_2
5a	$N(i\text{-}Pr)_2$
6a	$N(SiMe_3)_2$
7a	Cl



B

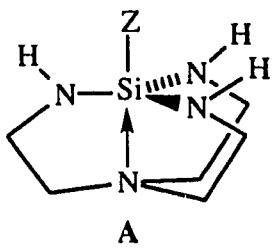
	Z
1b	H
2b	NH_2
3b	NMe_2
4b	NEt_2
5b	$N(i\text{-}Pr)_2$
6b	$N(SiMe_3)_2$
7b	Cl

minimize silicon carbide impurity formation. Also potentially militating against silicon carbide formation is the immediate proximity to silicon of five nitrogens, four of them in the chelating portion of these molecules.

Although **1a**[3] and **1b**[4] have been reported, we here describe improved syntheses for these azasilatranes and the results of our attempts to make the new compounds **2a,b-6a,b**. It may be noted here that our earlier attempts to make **3a** and **3b** by the transamination of $Si(NMe_2)_4$ with $(H_2NCH_2CH_2)_3N$ and $(HMeNCH_2CH_2)_3N$, respectively, failed,[4,5] although the former reaction was reported in a patent[6] to give **3a**. We therefore turned our attention to the possibility of nucleophilically substituting the chloride in the known

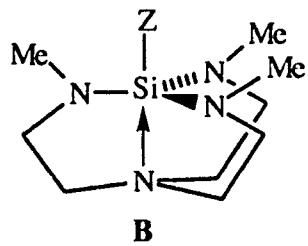
compound **7a**[4] and the new derivative **7b** (whose synthesis we report here) in order to achieve the target compounds **2a,b-6a,b**. We shall see that the reaction of **7a** and **7b** with $LiNR_2$, in addition to direct nucleophilic substitution, also gives **1a** and **1b** in small to substantial amounts in an interesting hydride transfer process that depends on R and on the structure type (**A** or **B**).

During our investigation of some of the scope of the above-mentioned hydride transfer reactions, we also reacted **7a** and **7b** with lithium alkyls and aryls in order to determine to what degree substitution reactions would occur giving **8a,b-12a,b**, and to what extent such reactions might be accompanied by



A

	Z
8a	Me
9a	*n*-Bu
10a	*s*-Bu
11a	*t*-Bu
12a	Ph
13a	C_6F_5



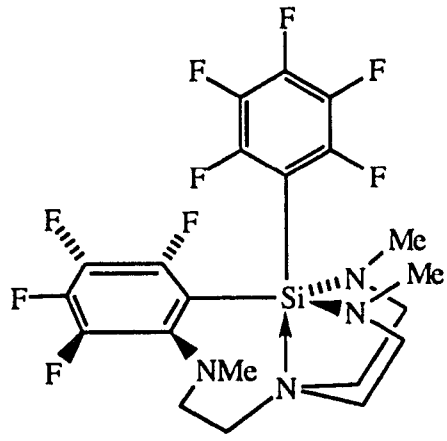
B

	Z
8b	Me
9b	*n*-Bu
10b	*s*-Bu
11b	*t*-Bu
12b	Ph
13b	C_6F_5
14b	F

hydride transfer to give **1a** and **1b**. We demonstrate that the hydride transfer product can be the dominating and even the exclusive product. We also show that $ClSi(NMe_2)_3$ is less susceptible to such hydride transfer reactions, undergoing such transformations only at higher temperatures over prolonged reaction times.

The reaction of **7b** with LiC_6F_5 gives not only the expected species **13b**, but also the fluoride transfer product **14b** and the novel tetrafluorobenzyne

insertion product **15**. The structures of both **14b** and **15** have been determined by X-ray diffraction methods.



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EXPERIMENTAL SECTION

All reactions were carried out under the strict exclusion of moisture using vacuum line and Schlenk techniques.[7] Solvents such as toluene, tetrahydrofuran (THF) and diethyl ether were distilled from sodium benzophenone ketyl prior to use. *t*-Butyl lithium, *sec*-butyl lithium, lithium dimethyl amide, lithium diethyl amide, lithium bis(trimethylsilyl) amide, phenyl lithium and methyl lithium were purchased from Aldrich and were used as received. *n*-Butyl lithium was obtained from Alfa Products as a 2.01 M solution in hexane and was used without purification. Tris(dimethylamino)silane was obtained from Hüls America, Inc. and was used as received. Tren ($(H_2NCH_2CH_2)_3N$) was distilled at ~85 °C/15 x 10^{-3} Torr from $LiAlH_4$ after receipt as a research sample from the W. R. Grace Co. Me_3-tren ($(MeNHCH_2CH_2)_3N$) was prepared from tren using a literature procedure.[8] Carbon tetrachloride was distilled from P_4O_{10} before use. Lithium di(isopropyl)amide was prepared by adding *n*-butyl lithium in hexane to excess $(i\text{-}Pr)_2NH$ followed by evaporation of the solvent and unreacted amine.[9] Perfluorophenyl lithium was prepared *in situ* by mixing equivalent amounts of pentafluorobromobenzene and *n*-butyl lithium in pentane at -50 °C.[10]

NMR spectra were recorded on a Nicolet NT 300 (^1H) or a Varian VXR 300 machine (^1H, ^{13}C, ^{29}Si, ^{19}F) with a deuterated solvent as an internal lock. ^1H NMR (299.949 MHz) spectra were referenced to the chemical shift of the residual proton signal of the deuterated solvent (7.15 ppm for benzene-d_6) or TMS as the internal reference. ^{13}C (75.429 MHz) spectra were referenced to

solvent signals (128.0 ppm for C_6D_6 and 77.0 ppm for $CDCl_3$). ^{29}Si (59.585 MHz) NMR spectra were referenced to TMS in C_6D_6 (20% by volume) as an external standard and recorded in the presence of ~5% by weight (with respect to the sample) of $Cr(acac)_3$ as a relaxation agent. The recording temperature was 20 °C except where specified. ^{19}F (282.186 MHz) NMR spectra were referenced to perfluorobenzene (-163.00 ppm relative to $CFCl_3$[11]) in C_6D_6 (15% by volume) as an external standard. ^{7}Li (116.568 MHz) NMR spectra were referenced[11] to LiOD (4 M solution) in D_2O as an external standard. ^{2}H (46.043 MHz) NMR spectra were recorded with C_6D_6 as the internal reference.[11] Variable temperature (VT) NMR spectra were measured in toluene-d_8 from -70 to +95 °C on a Varian VXR 300 spectrometer with an accuracy of ±1 °C. Coalescence temperatures were determined by recording a series of spectra taken at incremental temperatures (1 °C for the final ones). Frequency differences $\Delta\nu_{AB}$ of ^{19}F NMR spectra were measured at 10 temperatures in the low temperature region and were extrapolated to the corresponding T_c.

Mass spectra were obtained on a Finnigan 4000 instrument (low resolution, 70 eV, EI) and a Kratos MS-50 instrument (high resolution, 70 ev, EI). The masses are reported for the most abundant isotope present. Elemental analyses were performed by Desert Analytics, Tucson, Arizona. Melting points were measured with a Thomas-Hoover capillary apparatus and are uncorrected.

1-Hydroazasilatrane, 1a. Although this compound was prepared earlier,[3,4] an improved method is given here. To a solution of 1.87 g (12.8 mmol) of tren

in 10 mL of toluene was added 2.30 g (14.3 mmol) of $HSi(NMe_2)_3$. The clear solution was warmed at 100 °C for 3 h and then was refluxed until $HNMe_2$ evolution ceased (*ca.* 3 h). After slow removal of the solvent under vacuum, clear crystals (1.98 g) of product **1a** were collected by sublimation at 50 °C/20 x 10^{-3} mmHg in 90.0% yield (based on tren) (lit.[4], 72-84% yield). M.p. 78-80 °C (lit.[4], 77-79 °C). ^1H NMR (C_6D_6) 4.64 (s, 1 H, SiH), 2.71 (dt, 6 H, $NHCH_2CH_2$, $^3J_{HCNH}$ = 2.5 Hz, $^3J_{HCCH}$ = 5.7 Hz), 2.13 (t, 6 H, $NHCH_2CH_2$), 0.95 (br, 3 H, NH). ^{13}C NMR (C_6D_6) 50.89 ($HNCH_2CH_2CH_2$), 36.52 ($HNCH_2CH_2$); ^{29}Si NMR (C_6D_6) -80.98. ^1H, ^{13}C and ^{29}Si NMR spectra in $CDCl_3$ were the same as those reported earlier.[4,11]

1-Hydro-N, N', N''-trimethylazasilatrane, 1b. Although this compound was synthesized earlier in our laboratories,[4] a preparation giving a substantially higher yield is provided here. A solution of $HSi(NMe_2)_3$ (13.6 g, 84.3 mmol) and 14.6 g (76.0 mmol) of $(HMeNCH_2CH_2)_3N$ in 140 mL of toluene was warmed at 100 °C for 3 h and then refluxed until no more $HNMe_2$ was evolved (*ca.* 7 h). Slow removal of the solvent in vacuo gave a clear crystalline product. Further purification by sublimation at 60 °C/30 x 10^{-3} mmHg afforded 15.5 g of **3** in 93% yield (based on Me_3-tren), (lit.[4], 54%). ^1H NMR (C_6D_6) 4.33 (s, 1 H, SiH), 2.85 (s, 9 H, NMe), 2.60 (t, 6 H, $SiN(CH_3)CH_2CH_2$, $^3J_{HCCH}$ = 5.7 Hz), 2.12 (t, 6 H, $SiN(CH_3)CH_2CH_2$); ^{13}C NMR (C_6D_6): 48.56 ($MeNCH_2CH_2$), 45.86 ($MeNCH_2CH_2N$), 36.62 (MeN); ^{29}Si NMR (C_6D_6): -62.37. Anal. calcd for $C_9H_{22}N_4Si$: C, 50.42; H, 10.34; N, 26.13; Si, 13.10; Found: C, 48.44; H, 9.78; N, 28.67; Si, 13.63.

1-Chloroazasilatrane, 7a. Although this compound was prepared earlier in our laboratories,[4] a synthesis with an improved yield and requiring no purification is given here, as well as two new routes to **7a.**

Method A: Compound **1a** (2.05 g, 11.9 mmol) was introduced into an addition funnel equipped with a side arm whose connections to the funnel were near the top and bottom. Between these connections was a medium size frit, and a stopcock was attached near the top of the funnel. The funnel was attached via a 20/24 joint to a 100 mL round bottom flask containing a stirring bar. To the funnel was added 40 mL of CCl_4 and then the funnel was stoppered. The extract that drained from the funnel was stirred at room tempertuare. After *ca.* 5 h, the apparatus was inverted to move the suspension through the side arm of the funnel to the opposite side of the funnel. The apparatus was set upright to filter and collect the suspension that had formed in the flask. After the extract had drained back into the flask through the filter, stirring was resumed for approximately another 5 h. This separation/reaction cycle was repeated (*ca.* ten times) until the solution in the flask remained clear after stirring for 5 h, indicating completion of the reaction. After evaporating excess carbon tetrachloride and chloroform under vacuum, the solid residue was extracted with benzene by converting the (cleaned) apparatus into a soxhlet extractor. The benzene solution was refluxed at ~35° under vacuum to avoid coloration (decomposition) of product at higher temperature. Removal of C_6H_6 under vacuum afforded a pure white powder in yields ranging from 60-70% (lit,[4] 30% yield).

^{1}H NMR (C_6D_6) 2.55 (dt, 6 H, HNC*H*$_2$CH$_2$, $^3J_{HCNH}$ = 2.4 Hz, $^3J_{HCCH}$ = 5.7 Hz), 1.90 (t, 6 H, HNCH$_2$C*H*$_2$), 1.41 (b, 3 H, NH); ^{1}H NMR ($CDCl_3$), 3.07 (t, 6 H, HNC*H*$_2$CH$_2$), 2.81 (t, 6 H, HNCH$_2$C*H*$_2$), 1.55 (b, 3 H, NH); ^{13}C NMR (C_6D_6) 51.92 (HNCH$_2$CH$_2$), 37.16 (HNCH$_2$CH$_2$); ^{29}Si NMR (C_6D_6) -82.18. Although the first two ^{1}H NMR chemical shifts in $CDCl_3$ are ~0.3 ppm to lower field than the values we reported earlier in the same solvent,[4] our ^{13}C NMR and ^{29}Si data in this solvent were consistent with those given earlier.[4] This compound decomposed in the presence of H_2O, MeOH and EtOH giving tren. However, it is stable in air over a period of ~5 h.

Method B. Compound **1a** (0.46 g, 2.6 mmol) was mixed with 0.64 g (2.7 mmol) of C_2Cl_6 in 15 mL of toluene. The solution was refluxed for 24 h, and then filtered. The solid residue was washed with 4 x 20 mL of C_6H_6 giving 0.25 g (~46% yield) of brownish crude product after drying at 5 x 10^{-3} mmHg at room temperature overnight. Despite the discoloration, the ^{1}H NMR spectrum indicated only the presence of **7a**.

Method C. Compound **1a** (0.361 g, 2.10 mmol) was mixed with 0.581 g (2.10 mmol) of $ClCPh_3$ in 20 mL of toluene. The solution was refluxed for 12 h resulting in the formation of a yellowish solid. The toluene was removed under vacuum and the solid was extracted with pentane to remove $HCPh_3$. The solid residue was then washed with 40 mL of C_6H_6 giving a 42% yield of brownish crude product. The ^{1}H NMR spectrum indicated contamination by of the product $HCPh_3$.

1-Chloro-N, N, N-trimethylazasilatrane, 7b. Although this compound was prepared earlier in these laboratories,[5] a modified approach and one additional route are given here.

Method A: N-chlorosuccinimide (2.47 g, 19.2 mmol) dissolved in 50 mL of CH_2Cl_2 was slowly added to a solution of **1b** (4.03 g, 18.8 mmol) in 25 mL of CH_2Cl_2 at -50 °C. The solution was allowed to warm to -10 °C and was stirred for 20 min. All the volatiles were removed under vacuum while the solution was kept at -10 °C. The solid was then extracted with 4 x 30 mL portions of toluene. Evaporation of the toluene under vacuum afforded 2.62 g of white crystalline product, contaminated by a trace amount of the by-product succinimide, which was removed by sublimation at 46 °C/15 x 10^{-3} mmHg for ~ 72 h. The solid was once again extracted with toluene and 2.34 g of pure colorless crystalline **7b** was obtained in 52% yield by removing the solvent under vacuum. The yield of this reaction was somewhat erratic, ranging from 50-87%. The previous yield of 60% obtained in our laboratories was crude **7b** contaminated by succinmide.[5] M.p. 174-175 °C. ^{1}H NMR (C_6D_6) 3.08 (s, 9 H, NCH_3), 2.61 (t, 6 H, $^3J_{HCCH}$ = 5.7 Hz, $CH_3NCH_2CH_2$), 2.01 (t, 6 H, $CH_3NCH_2CH_2$); ^{1}H NMR ($CDCl_3$), 2.96 (t, 6 H, $^3J_{HCCH}$ = 5.7 Hz, $CH_3NCH_2CH_2$), 2.77 (t, 6 H, $CH_3NCH_2CH_2$), 2.75 (s, 9 H, NCH_3); ^{13}C NMR (C_6D_6) 47.68 ($CH_3NCH_2CH_2$), 46.77 ($CH_3NCH_2CH_2$), 39.25 (CH_3); ^{29}Si NMR (C_6D_6) -87.22 (lit.,[18] -85.6, CCl_2D_2). LRMS (70 ev, EI) *m/z* (relative intensity, proposed ion) 248.1 (31.2, M^+), 213.2 (100, M^+ - Cl), 204.1 (59.2, M^+ - NMe_2). HRMS for M^+ ($C_9H_{21}SiN_4Cl$) calcd: 248.12240, found: 248.12229.

Method B: A mixture of 0.278 g (1.30 mmol) of **1b** and 0.0308 g (1.30 mmol) of C_2Cl_6 was dissolved in 20 mL of toluene. No product was observed by ^1H NMR after evaporating a portion of the yellowish brown solution that formed after 10 h at 65 °C. After refluxing the solution for 13 h, a clear solution with a dark precipitate resulted. The mixture was filtered and the solid residue was washed with 3 x 10 mL portions of benzene. The combined solutions were dried under vacuum at 10 x 10^{-3} mmHg for 5 h and 0.130 g of a brownish red product was obtained in ~40% yield. Despite the coloration, the ^1H and ^{13}C NMR spectra revealed only resonances consistent with product.

1-Amino-azasilatrane, 2a.

Method A: Compound **7a** (0.99 g, 4.8 mmol) was mixed with 0.21 g (5.1 mmol) of $NaNH_2$ (95% purity, Aldrich) in a dry box. About 80 mL of liquid ammonia from a blue NH_3/Na solution was condensed into the liquid-N_2-cooled flask. The reaction mixture was stirred at ~ -35 °C for 3 h after which it was allowed to warm up slowly to evaporate the ammonia. The slightly yellowish solid residue that remained was pure product according to its ^1H NMR spectrum. By subliming this material at 35°/15 x 10^{-3} mmHg, a colorless crystalline form of the product was collected in 92% yield. M.p. 40-41 °C; ^1H NMR (C_6D_6) 2.74 (dt, 6 H, SiHNCH_2CH$_2$, $^3J_{HCCH}$ = 5.70 Hz, $^3J_{HNCH}$ = 2.4), 2.10 (t, 6 H, SiHNCH$_2$CH_2), 0.83 (br, 3 H, NH), 0.08 (br, 2 H, NH_2); ^1H NMR ($CDCl_3$) 2.98 (t, 6 H, HNCH_2CH$_2$, $^3J_{HCCH}$ = 5.7 Hz), 2.64 (t, 6 H, HNCH$_2$CH_2N), 0.95 (very br, s, 3 H, NH); ^1H NMR (CD_3CN), 2.87 (t, 6 H, NHCH_2CH$_2$, $^3J_{HCCH}$ = 5.9 Hz), 2.56 (t, 6 H, NHCH$_2$CH_2), 0.38 (br, 3 H, NH);

^{13}C NMR (C_6D_6) 50.50 ($HNCH_2CH_2$), 37.53 ($HNCH_2CH_2$); ^{13}C NMR ($CDCl_3$) 50.18 ($HNCH_2CH_2$), 36.82 ($HNCH_2CH_2$); ^{29}Si NMR (C_6D_6) -74.54. MS (EI, 70 ev) *m/z* (relative intensity, proposed ion) 187.0 (57.5, M^+), 171 (40.9, M^+-NH_2), 159.1 (100.0, M^+-CH_2N), 145.1 (73.3, M^+-CH_2CH_2NH), 101 (24.3, M^+-$2CH_2CH_2NH$); HRMS for M^+ ($C_6H_{17}N_5Si$) calcd. 187.12532, found 187.12534; M^+-CH_2N ($C_5H_{15}N_4Si$) calcd. 159.10578, found 159.10619. Anal. calcd for $C_6H_{17}N_5Si$: C, 38.46; H, 9.25; N, 36.36; found: C, 37.75; H, 9.28; N, 36.62.

Method B: About 40 mL of NH_3 distilled from a blue liquid-NH_3/Na solution was condensed into a 50 mL flask (with a side arm) containing 0.36 g (1.7 mmol) of **7a**. Sodium (40 mg, 1.7 mmol) was then added and the characteristic blue color appeared instantly. The blue solution was stirred at -35 °C for 3 h and then was allowed to warm to room temperature with slow evaporation of NH_3. The residue was extracted with 3 x 15 mL portions of benzene and then all the volatiles were removed under vacuum. ^1H NMR of 0.25 g of the crude product so obtained revealed that it contained **2a** and tren in a ratio of about 3:2 and some unreacted **7a**. No attempt was made to separate the mixture.

1-Amino-N,N',N''-trimethylazasilatrane, 2b.

Method A: In a drybox, **7b** (0.13 g, 0.52 mmol) was mixed with 0.030 g (0.75 mmol) of $NaNH_2$. To this mixture was added 20 mL of THF and the solution was refluxed for 60 h. Only about half of the starting material was converted into the substitution product according to the ^1H NMR spectrum of the reaction mixture. After refluxing for another 80 h, the solvent was removed under vacuum and the solid residue was extracted with 4 x 15 mL

portions of pentane. Evaporation of the pentane under vacuum afforded a crystalline solid which upon sublimation at 60 °C and 10 x 10^{-3} mmHg afforded **2b** in 87% yield. M.p. 116-117 °C. ^{1}H NMR (C_6D_6) 2.90 (s, 9 H, CH_3), 2.70 (t, 6 H, $^3J_{HCCH}$ = 5.7 Hz, $CH_3NCH_2CH_2$), 2.15 (t, 6 H, $CH_3NCH_2CH_2$); ^{13}C NMR (C_6D_6) 48.08 ($CH_3NCH_2CH_2$), 47.35 ($CH_3NCH_2CH_2$), 38.97 (CH_3); ^{29}Si (C_6D_6) -85.08. LRMS (70 ev, EI) 229.2 (93%, M^+), 213.2 (100.0%, M^+-NH_2); HRMS for M^+ ($C_9H_{23}SiN_5$), calcd: 229.17206, found: 229.17227.

Method B: To a mixture of 0.13 g (0.52 mmol) of **7b** and 0.060 g (1.5 mmol) of $NaNH_2$ was condensed *ca.* 25 mL of sodium-dried liquid NH_3. The reaction mixture was stirred at -30 °C for 2 1/2 h. After slowly evaporating all the ammonia, only unreacted **7b** remained according to the ^{1}H NMR spectrum of residue. The starting material was transferred into a thick-walled glass tube together with freshly cut sodium (18 mg, 0.78 mmol, 50% excess). About 3 mL of dry ammonia was condensed into the tube which was flame sealed while the contents were cooled at -80 °C. The tube was then placed in a large metal can in the hood where it was kept at room temperature for 26 d and then warmed at 65 °C for 4 d. The tube was cooled in liquid nitrogen, opened, and the solid residue extracted with 3 x 10 mL portions of pentane after evaporating NH_3. Removal of pentane under vacuum afforded 0.075 g of a crystalline product whose ^{1}H NMR spectrum revealed an approximate ratio of 5:1 of **2b** to **7b**.

1-Dimethylamino-azasilatrane, 3a. Compound **7a** (0.25 g, 1.2 mmol) was mixed with 0.070 g (1.3 mmol) of $LiNMe_2$ in a dry box and then 25 mL of diethyl ether was added. The suspension was stirred at room temperature

for 48 h. After filtration, the ether was removed under vacuum and then the solid residue was extracted with 3 x 10 mL portions of benzene. Evaporation of the benzene resulted in a 60% yield of crystalline product which was purified by sublimation at 75 °C and 6 x 10^{-3} mmHg. M.p. 74-75°. ^{1}H NMR (C_6D_6) 2.75 (s, 6 H, $(CH_3)_2$), 2.74 (dt, 6 H, HNC*H*$_2$CH$_2$, $^3J_{HNCH}$ = 3.0, $^3J_{HCCH}$ = 5.7 Hz), 2.08 (t, 6 H, HNCH$_2$C*H*$_2$N), 0.76 (b, 3 H, NH); ^{1}H NMR ($CDCl_3$) 2.93 (dt, 6 H, HNC*H*$_2$CH$_2$, $^3J_{HNCH}$ = 2.7 Hz, J_{HCCH} = 5.7 Hz), 2.57 (t, 6 H, HNCH$_2$C*H*$_2$), 2.35 (s, 6 H, NMe_2), 0.81 (s, 3 H, NH); ^{13}C NMR (C_6D_6) 50.57 (HNCH$_2$*C*H$_2$N), 37.67 (HN*C*H$_2$CH$_2$N) 41.00 ($(CH_3)_2$); ^{13}C NMR ($CDCl_3$): 50.53 (HNCH$_2$*C*H$_2$), 37.13 (HN*C*H$_2$CH$_2$N), 40.51 ($(CH_3)_2$); ^{29}Si NMR (C_6D_6) -72.58; ^{29}Si NMR ($CDCl_3$) -75.26. LRMS (70 ev, EI) *m/z* (relative intensity, proposed ion) 215.2 (13.5, M^+), 171.1 (100, M^+ - NMe_2), 128.1 (3.4, M^+ - NMe_2 - $NH_2CH_2CH_2$); HRMS for M^+ ($C_8H_{21}N_5Si$) calcd: 215.15662, found: 215.15664. Anal. for $C_8H_{21}N_5Si$: calcd: C, 44.61; H, 9.83; N, 32.52. Found: C, 44.76; H, 10.19; N, 32.59.

1-Dimethylamino-N,N',N''-trimethylazasilatrane, 3b. To a mixture of 1.02 g (4.11 mmol) of **7b** and 0.23 g (4.4 mmol) of $LiNMe_2$ was added 50 mL of diethyl ether. The solution was stirred at room temperature for 72 h. After removal of ether under vacuum, the residue was extracted with 3 x 15 mL portions of benzene. A ^{1}H NMR spectrum of the solution revealed the formation of **3b** and **1b** in a ratio of approximate 5:1. A crystalline mixture (0.87 g) was obtained after evaporating the volatiles. Separation was achieved by subliming the lighter **1b** at 30 °C for 2 d, followed by subliming **3b** at 60 °C or above. Repeated slow sublimation afforded 0.43 g of pure **3b** in 41% yield. ^{1}H

NMR (C_6D_6) 2.82 (s, 6 H, NMe_2), 2.64 (s, 9 H, NCH_3), 2.61 (t, 6 H, ($CH_3NCH_2CH_2$, $^3J_{HCCH}$ = 5.7 Hz), 2.21 (t, 6 H, $CH_3NCH_2CH_2$); ^{13}C NMR (C_6D_6) 51.16 ($CH_3NCH_2CH_2$), 50.99 ($CH_3NCH_2CH_2$), 40.22 ($N(CH_3)_2$), 37.71 ($SiNCH_3$); ^{29}Si NMR (C_6D_6) -51.39. LRMS (70 ev, EI) *m/z* (relative intensity, proposed ion) 257.2 (2.4, M^+), 213.2 (100.0, M^+ - NMe_2), 199.1 (1.7), 170.1 (4.9), 156.1 (12.8), 129.1 (4.5), 113.1 (11.3); HRMS for M^+ ($C_{11}H_{27}N_5Si$) calcd: 257.20358, Found: 257.20387.

1-Diethylamino-azasilatrane, 4a.

Method A: A solution of **7a** (8 mg, 0.04 mmol) in 0.5 mL of THF-d_8 was prepared. ^1H NMR data for **7a** (THF-d_8) 2.99 (dt, 6 H, $^3J_{HCCH}$ = 5.9 Hz, $^3J_{HNCH}$ = 2.4 Hz, $HNCH_2CH_2$), 2.75 (t, 6 H, $HNCH_2CH_2$), 1.29 (b, 3 H, NH); ^{13}C NMR data for **7a** (THF-d_8), 52.08 ($HNCH_2CH_2$), 37.95 ($HNCH_2CH_2$). $LiNEt_2$ (3 mg, 0.04 mmol) was dissolved separately in 0.4 mL of THF-d_8. ^1H NMR data for $LiNEt_2$ (THF-d_8), 2.83 (q, 4 H, $^3J_{HCCH}$ = 7.2 Hz, CH_2), 1.04 (t, 6 H, CH_3); ^{13}C NMR data for $LiNEt_2$ (THF-d_8), 50.36 (br, CH_2), 18.56 (CH_3). The ^1H and ^{13}C NMR spectra of the combined THF-d_8 solutions revealed the instantaneous and almost quantitative formation of HEt_2N plus a precipitate. ^1H NMR of $HNEt_2$ (THF-d_8), 2.55 (q, 4 H, CH_2), 1.02 (t, 6 H, CH_3, $^3J_{HCCH}$= 7.2 Hz); ^{13}C NMR: 44.80 (CH_2), 15.82 (CH_3).

Method B: To a solution of 0.10 g (0.5 mmol) of **7a** in 25 mL of THF at -80 °C was slowly added 20 mL of a THF solution of 67 mg (0.80 mmol) of $LiNEt_2$ until all the starting material was consumed as monitored by ^1H NMR spectroscopy. The mixture was stirred at -80 °C (*ca.* 1 h). Removal of THF under vacuum followed by extraction of the residue with 4 x 5 mL portions of

benzene gave a yellowish extract. Evaporation of the solvent from the extract under vacuum afforded the crude product **4a** as a semi-solid in 19% yield. ^{1}H NMR (C_6D_6) 3.07 (q, 4 H, NC*H*$_2$CH$_3$, $^3J_{HCCH}$ = 6.9 Hz), 2.77 (t, 6 H, HNC*H*$_2$CH$_2$, $^3J_{HCCH}$ = 5.7 Hz), 2.12 (t, 6 H, HNCH$_2$C*H*$_2$), 1.18 (t, 6 H, NCH$_2$C*H*$_3$, $^3J_{HCCH}$ = 6.9 Hz); ^{1}H NMR ($CDCl_3$) 2.96 (t, 6 H, HNC*H*$_2$CH$_2$, $^3J_{HCCH}$= 6.0 Hz), 2.75 (q, 4 H, NC*H*$_2$CH$_3$, $^3J_{HCCH}$ = 6.9 Hz), 2.59 (t, 6 H, HNCH$_2$C*H*$_2$), 0.93 (t, 6 H, NCH$_2$C*H*$_3$); ^{13}C NMR ($CDCl_3$) 50.37 (HNCH$_2$CH$_2$N), 41.75 (N*C*H$_2$CH$_3$), 37.09 (HN*C*H$_2$CH$_2$), 16.55 (NCH$_2$*C*H$_3$). MS (70 ev, EI) *m/z* (relative intensity, proposed ion) 243.4 (4.7 M$^+$), 171.1 (100, M$^+$ - NEt$_2$), 200.2 (3.3, M$^+$ - HNCH$_2$CH$_2$).

1-Diethylamino-N,N',N''-trimethylazasilatrane, 4b. Compound **7b** (0.42 g, 1.7 mmol) was mixed with 0.15 g (1.8 mmol) of LiNEt$_2$ in 45 mL of benzene. The solution was heated at 65 °C for 24 h. A ^{1}H NMR spectrum of the solution showed the absence of the starting material and the formation of compounds **4b** and **1b** in a ratio of about 4:1. After filtration and removal of the solvent under vacuum, 0.34 g of crystalline solid was obtained. Repeated sublimations at 30 °C for 1 day to remove the lighter **1b** followed by further sublimation at 70 °C afforded 0.12 g of pure **4b** in 25% yield. ^{1}H NMR (C_6D_6) 3.14 (q, 4 H, NC*H*$_2$CH$_3$, $^3J_{HCCH}$ = 7.8 Hz), 2.56 (s, 9 H, CH$_3$), 2.54 (t, 6 H, CH$_3$NC*H*$_2$CH$_2$, $^3J_{HCCH}$ = 5.7 Hz), 2.40 (t, 6 H, CH$_3$NCH$_2$C*H*$_2$), 1.17 (t, 6 H, NCH$_2$C*H*$_3$); ^{13}C (C_6D_6) 52.13 (MeNCH$_2$CH$_2$), 51.08 (MeN*C*H$_2$CH$_2$), 40.05 (N*C*H$_2$CH$_3$), 36.28 (NCH$_3$), 15.23 (NCH$_2$CH$_3$); ^{29}Si NMR (C_6D_6) -37.92.

Attempted synthesis of 1-di-isopropylamino-azasilatrane, 5a. Into an NMR tube was placed a solution of 4 mg (0.04 mmol) of LiN-*i*-Pr_2 in 0.4 mL of THF-d_8. ^1H NMR 3.02 (h, 2 H, N*H*C$(CH_3)_2$, $^3J_{HCCH}$ = 6.3 Hz), 0.98 (d, 12 H, CH_3); ^{13}C NMR 52.21 (N*C*H$(CH_3)_2$), 27.77 (NCHC(*C*$H_3)_2$). When 0.4 mL of a THF-d_8 solution of 8 mg (0.04 mmol) of **7a** was added at room temperature, immediate virtually quantitative conversion to HN$(CH(CH_3)_2)_2$ was observed. ^1H NMR (THF-d_8) for HN$(CH(CH_3)_2)$, 2.86 (h, 2 H, $^3J_{HCCH}$ = 6.3 Hz, C*H*$(CH_3)_2$), 0.98 (d, 12 H, CH_3); ^{13}C NMR (THF-d_8), 45.85 (*C*H$(CH_3)_2$), 23.86 (CH_3).

1-Di-isopropylamino-N,N',N''-trimethyl-azasilatrane, 5b. Compound **7b** (24 mg, 0.10 mmol) was mixed with 12 mg (0.11 mmol) of LiN(*i*-$Pr)_2$ in an NMR tube and 0.5 mL of C_6D_6 was added after the tube was cooled in ice water. The tube was then sealed and allowed to warm slowly to room temperature. ^1H and ^{13}C NMR spectra showed that **5b** and **1a** formed in a ratio of about 1:2. ^1H NMR (C_6D_6) for **5b**: 2.47 (s, br, 9 H, NCH_3) 2.40 (s, br, 6 H, $CH_3NCH_2CH_2$), 2.24 (s, br, 6 H, $CH_3NCH_2CH_2$), 1.04 (d, 12 H, $(CH_3)_2CNH$); ^{13}C NMR (C_6D_6) 51.13 ($CH_3NCH_2CH_2$), 50.45 ($CH_3NCH_2CH_2$), 35.68 ($CH_3NCH_2CH_2$), 34.38 (N*C*H$(CH_3)_2$), 14.52 (NCH(*C*$H_3)_2$); ^{29}Si NMR (C_6D_6) -30.59.

1-Bis(trimethylsilyl)amino-azasilatrane, 6a. To 25 mL of a THF solution of 0.50 g (2.4 mmol) of **7a** was slowly added 20 mL of a THF solution of 0.48 g (2.7 mmol) of lithium bis(trimethylsilyl)amide at -50 °C. The solution was stirred and was allowed to warm to room temperature. After 1 h, **7a** was totally consumed according to the ^1H NMR spectrum. THF was removed under

vacuum and the residue was extracted with 4 x 10 mL of benzene. Evaporation of the volatiles under vacuum and slow distillation at 60°/10 x 10^{-3} mmHg afforded the colorless liquid product in 50% yield. ^{1}H NMR (C_6D_6) 2.81 (t, 2 H, SiNCH_2CH$_2$, $^{3}J_{HCCH}$ = 5.4 Hz), 2.69 (m, 4 H, HNCH_2CH$_2$), 2.15 (m, 4 H, HNCH$_2$CH_2), 1.97 (t, 2 H, SiNCH$_2$CH_2, $^{3}J_{HCCH}$ = 5.4 Hz), 0.82 (b, 3 H, HN); 0.31 (s, 9 H, SiMe$_3$), 0.28 (s, 9 H, SiMe$_3$). ^{13}C NMR (C_6D_6 at 20 °C) 56.17 (1C, HNCH$_2$*C*H$_2$N), 53.59 (2C, NHCH$_2$*C*H$_2$N), 42.33 (1C, HN*C*H$_2$CH$_2$), 38.46 (2C, HNCH$_2$CH$_2$), 2.92 (3C, Si(CH$_3$)$_3$), 2.82 (3C, Si(CH$_3$)$_3$); ^{13}C NMR (toluene-d_8, at 111 °C), 56.94 (1C, HNCH$_2$*C*H$_2$N), 54.50 (2C, HNCH$_2$*C*H$_2$N), 42.95 (1C, HNCH$_2$CH$_2$N), 38.99 (2C, HNCH$_2$CH$_2$), 2.79 (3C, Si(CH$_3$)$_3$), 2.55 (3C, Si(CH$_3$)$_3$); ^{29}Si NMR (C_6D_6) -65.29 (SiN$_4$), 2.06 (Si(CH$_3$)$_3$), -2.24 (Si(CH$_3$)$_3$). MS (70 ev, EI) *m/z* (relative intensity, proposed ion) 331.2 (13.8, M$^+$), 286.1 (3.8, M$^+$-CH$_2$CHNCH$_2$), 316.2 (37.9, M$^+$-Me), 301.2 (63.2, M$^+$-2Me), 171.1 (3.4, M$^+$-N(Si(Me$_3$)$_2$); HRMS for M$^+$ ($C_{12}H_{33}N_5Si_3$) calcd: 331.20438, found: 331.20398.

1-Bis-(trimethylsilyl)amino-N,N',N''-trimethyl-azasilatrane, 6b. Compound **7b** (0.28 g, 1.1 mmol) was mixed with 0.19 g (1.1 mmol) of LiN(SiMe$_3$)$_2$ in 25 mL of toluene and the mixture was refluxed for 24 h. After filtration and removal of solvent under vacuum, the clear liquid product was obtained in 88% yield by distillation at 65 °C/12 x 10^{-3} mmHg. ^{1}H NMR (C_6D_6) 2.71 (s, 9 H, 3NCH$_3$), 2.65 (t, 6 H, CH$_3$NCH_2CH$_2$, $^{3}J_{HCCH}$ = 5.8 Hz), 2.18 (t, 6 H, CH$_3$NCH$_2$CH_2), 0.25 (s, 18 H, Si(CH$_3$)$_3$); ^{1}H (CDCl$_3$ at 20°), 2.81 (t, 6 H, CH$_3$NCH_2CH$_2$, $^{3}J_{HCCH}$ = 5.8 Hz), 2.64 (t, 6 H, CH$_3$NCH$_2$CH_2), 2.50 (s, 9 H, 3NCH$_3$), 0.14 (s, 18 H, Si(CH$_3$)$_3$); ^{1}H (CDCl$_3$ at -55°), 2.78 (t, 6 H, CH$_3$NCH$_2$CH_2), 2.49 (s, 9 H, N(CH$_3$)$_3$), 0.10 (s, 18 H, Si(CH$_3$)$_3$); ^{13}C NMR

(C_6D_6) 48.06 ($CH_3NCH_2CH_2$), 47.12 ($CH_3NCH_2CH_2$), 38.27 (NCH_3), 5.76 ($Si(CH_3)_3$); ^{13}C NMR ($CDCl_3$ at 20 °C), 47.68 ($CH_3NCH_2CH_2$), 47.58 ($CH_3NCH_2CH_2$), 38.02 (CH_3N), 5.55 ($SiMe_3$); ^{13}C NMR ($CDCl_3$ at -41 °C), 47.41 ($CH_3NCH_2CH_2$), 46.99 ($CH_3NCH_2CH_2$), 37.82 (CH_3N), 5.39 ($Si(CH_3)_3$); ^{29}Si NMR (C_6D_6) -71.17 ($SiNCH_3$), 1.82 ($SiMe_3$); ^{29}Si NMR ($CDCl_3$) -69.59 ($SiNCH_3$), 2.5 ($Si(CH_3)_3$). LRMS (70 ev, EI) (relative intensity, proposed ion), 373.3 (20.3, M^+), 358.2 (34.9, M^+-CH_3), 329.2 (18.5), 275.1 (100.0), 246.1 (41), 218.1 (62.2), 213.2 (31.2, M^+-$N(TMS)_2$); HRMS for M^+ ($C_{15}N_5H_{39}Si_3$) calcd: 373.25133, found: 373.25106.

1-Methylazasilatrane, 8a. To 50 mL of a THF solution of 0.20 g (0.91 mmol) of **7a** was slowly added 0.76 mL of a 1.4 M MeLi solution at -50 °C. The solution was allowed to warm to room temperature and was stirred for an additional 1 h. THF was removed under vacuum and the residue was extracted with 3 x 15 mL portions of pentane. The removal of pentane under vacuum gave solid **8a** (0.023 g) which was purified by sublimation at 60 °C/10 x 10^{-3} mmHg to give a 26% yield of **8a**. The spectroscopic data are consistent with the literature values.[4]

Attempted synthesis of 1-methyl-N,N',N''-trimethylazasilatrane, 8b.

Method A: To 15 mL toluene solution of **7b** (0.12 g, 0.48 mmol) was added 0.5 mL of 1.5 M LiMe (0.75 mmol, 56% excess) solution in diethyl ether. The solution was refluxed for 24 h. A ^1H NMR spectrum of the reaction mixture showed the presence of **7b** only. Another 0.5 mL of LiMe was added and the solution was further refluxed for 24 h. After filtration and removal of toluene

under vacuum, only **7b** (~0.05 g) was recovered by sublimation at 85 °C/5.1 x 10^{-3} mmHg.

Method B: The aforementioned procedure was repeated in the presence of 2 molar equivalents of TMEDA (tetramethylethylenediamine) and the solution was refluxed for 24 h. The ^{1}H NMR spectrum revealed **7b** only along with TMEDA.

1-*n*-Butylazasilatrane, 9a. To 0.205 g (0.993 mmol) of **7a** in 50 mL of toluene was added dropwise 10 mL of a 0.201 M *n*-BuLi solution (2.01 mmol) in toluene at -90 °C. The solution was allowed to warm to room temperature and was stirred for 1/2 h. The solvent was evaporated under vacuum and the residue was extracted with 3 x 20 mL portions of pentane. Removal of pentane under vacuum and sublimation of the solid residue at 56 °C/11 x 10^{-3} mmHg gave 0.032 g of **9a** in 14% yield. ^{1}H NMR (C_6D_6) 2.74 (dt, 6 H, HNC*H*$_2$CH$_2$N, $^3J_{HNCH}$ = 2.7 Hz, $^3J_{HCCH}$ = 5.85 Hz), 2.15 (t, 6 H, HNCH$_2$C*H*$_2$), 1.49 (b, 6 H -C*H*$_2$C*H*$_2$C*H*$_2$), 1.02 (t, 3 H, CH$_3$); ^{13}C (C_6D_6) 50.54 (HNCH$_2$*C*H$_2$N), 37.15 (HN*C*H$_2$CH$_2$), 29.59, 28.06, 20.74, 14.47 (*C*H$_2$*C*H$_2$*C*H$_2$*C*H$_3$); ^{29}Si NMR (C_6D_6) -65.34. LRMS (70 ev, EI) *m/z* (relative intensity, proposed ion) 228.1 (0.43, M$^+$), 171.1 (100.0, M$^+$ - Bu), 57.0 (16.11, Bu$^+$), 149 (22.5), 116.1 (87.2); HRMS for M$^+$ - Bu ($C_6H_{15}N_4Si$) Calcd: 171.10660, found: 171.10661.

1-*n*-Butyl-N,N',N''-trimethylazasilatrane, 9b.

Method A: To 0.5 mL of a C_6D_6 solution of 20 mg (0.080 mmol) of **7b** cooled to 7 °C was added 0.04 mL of 2.01 M *n*-BuLi solution in hexane (0.080 mmol). The ^{1}H NMR spectrum taken after 10 min revealed that the reaction

was complete and that ~ 5% of **1b**, ~ 95% of **9b** and ~ 5% of 1-butene had formed. The ^{1}H NMR chemical shifts of 1-butene compared favorably with those from commercially available 1-butene.

Method B: Compound **7b** (0.14 g, 0.56 mmol) was dissolved in 20 mL of toluene and 0.3 mL of a 2.01 M *n*-BuLi solution (0.6 mmol) was added. The solution was stirred and heated at 60 °C for 1/2 h. The toluene was removed under vacuum and the residue was extracted with 4 x 15 mL portions of pentane. Removal of pentane in vacuum afforded crystalline **9b** in 95% yield.

Characterization of **9b**: ^{1}H NMR (C_6D_6) 2.61 (s, 9 H, NCH_3), 2.57 (t, 6 H, $CH_3NCH_2CH_2$, $^3J_{HCCH}$ = 5.7 Hz), 2.27 (t, 6 H, $CH_3NCH_2CH_2$), 1.6 (m, 6 H, $CH_2CH_2CH_2$), 0.97 (t, 3 H, $^3J_{HCCH}$ = 2.6 Hz); ^{13}C (C_6D_6) 50.43 ($CH_3NCH_2CH_2$), 49.28 ($CH_3NCH_2CH_2$), 39.08 (NCH_3), 28.24, 27.92, 16.95, 14.40 ($CH_2CH_2CH_2CH_3$); ^{29}Si NMR (C_6D_6) -40.85. LRMS (70 ev, EI) *m/z* (relative intensity, proposed ion) 270.2 (0.5, M^+), 213.2 (100.0, M^+ - Bu), 156.1 (20.1); HRMS for M^+ - Bu ($C_9H_{21}N_4Si$) calcd: 213.15350, found: 213.15378.

1-*s*-Butylazasilatrane, 10a. To 25 mL of a toluene solution containing 0.12 g (0.58 mmol) of **7a** at -75° was slowly added 3.5 mL of a 0.2 M solution of *s*-BuLi (0.7 mmol, 20% excess). The solution was stirred for 15 min and a ^{1}H NMR spectrum of an aliquot showed a low conversion of **7a** into **10a** as well as a small amount of **1a**. The ratio of **10a**:**1a**:**7a** was estimated to be about 5:1:5 according to ^{1}H NMR integration. Addition of another 3.5 mL of the *s*-BuLi (0.7 mmol) caused the starting material to disappear but it also destroyed a considerable portion of the products. Removal of toluene under vacuum and

extraction with pentane (3 x 15 mL portions) followed by evaporation of the volatiles gave a semisolid residue containing a small amount of compound whose ^{1}H and ^{13}C NMR spectra were consistent with the substitution product **10a** based on the favorable comparison of these spectra with those of **9a** (estimated conversion to **10a** < 10%). ^{1}H NMR (C_6D_6) 2.76 (t, 6 H, $^{3}J_{HCCH}$ = 5.9 Hz, $HNCH_2CH_2$), 2.07 (t, 6 H, $HNCH_2CH_2$); ^{13}C NMR (C_6D_6) 50.56 ($HNCH_2CH_2$), 37.27 ($HNCH_2CH_2$).

Attempted synthesis of 1-*s*-butyl-N,N',N''-trimethylazasilatrane, 10b.

Method A: Compound **7b** (21 mg, 0.085 mmol) was dissolved in 0.5 mL of C_6D_6 and 0.065 mL of 1.3 M *s*-BuLi (0.085 mmol) was added at room temperature. The solution turned slightly cloudy and the ^{1}H NMR spectrum 10 min later revealed the exclusive formation of **1b**, 1-butene (~80%) and (Z, E-2-butene (~20%) in a ratio of 3:2 of Z to E.

Method B: To 0.5 mL of C_6D_6 solution containing 20 mg of **7b** (0.080 mmol) was added 20 mg of TMEDA (0.17 mmol) followed by 0.06 mL 1.3 M *s*-BuLi solution. The ^{1}H NMR spectra taken 1 h, 2 h, 1 d later showed only a small amount of **1b** and unreacted **7b**. Addition of 0.15 mL 1.3 M *s*-BuLi solution led to formation of an additional species, whose ^{1}H and ^{13}C NMR spectra were consistent with those of the presumed **10b**. ^{1}H NMR (C_6D_6) 2.46 (t, 6 H, $^{3}J_{HCCH}$ = 5.7 Hz, $SiNCH_2CH_2$), 2.34 (t, 6 H, $SiNCH_2CH_2$), 2.39 (s, 9 H, NCH_3); ^{13}C NMR (C_6D_6) 51.09 ($SiNCH_2CH_2$), 50.16 ($SiNCH_2CH_2$).

1-*t*-Butylazasilatrane, 11a. Following the procedure for **10a** except using *t*-BuLi, it was found that **11a** and **1a** formed in a ratio of approximately 5:1.

Addition of excess *t*-BuLi in order to consume all the starting material, still led to only a low conversion to product. A small amount of compound **11a** was identified by ^{1}H NMR in the reaction residue after removing the volatiles. ^{1}H NMR (C_6D_6) 2.76 (dt, $^3J_{HCNH}$ = 2.7 Hz, $^3J_{HCCH}$ = 5.7 Hz, HNC*H*$_2$CH$_2$), 2.09 (t, 6 H, HNCH$_2$C*H*$_2$), 1.02 (s, 9 H, (CH$_3$)$_3$C); ^{13}C NMR (C_6D_6) 50.57 (HNCH$_2$CH$_2$), 37.65 (HNCH$_2$CH$_2$), 24.20 (C(*C*H$_3$)$_3$), 10.72 (*C*(CH$_3$)$_3$).

Attempted synthesis of 1-*t*-butyl-N,N',N''-trimethylazasilatrane, 11b. A series of ambient temperature ^{1}H NMR spectra of **7b** (20 mg, 0.080 mmol) in 0.5 mL of C_6D_6 with 0.05 mL of *t*-BuLi solution in pentane (1.7 M, 0.085 mmol) taken over a period of 24 h showed that **7b** slowly reacted with *t*-BuLi, giving exclusively **1b** and *iso*-butene. ^{1}H NMR (C_6D_6) 1.59 (s, CH$_3$). In the presence of TMEDA, the conversion of **7b** into **1b** did not occur at a measurable rate at room temperature, and required heating to 65 °C for completion in 3 h.

1-Phenyl-azasilatrane, 12a. This compound was reported earlier[3] by a superior route and its crystal structure has been determined.[12] The following route is described insofar as it reflects the chemistry of **7a**. To 0.13 g (0.62 mmol) of **7a** in 50 mL of toluene was slowly added 3.8 mL 0.24 M PhLi at ~10 °C. The solution was allowed to warm up to room temperature. A ^{1}H NMR spectrum of an aliquot showed low conversion of **7a** into **12a** as well as a substantial amount of **7a**. Addition of excess PhLi in order to consume all the starting material, also led to a low conversion to product. After filtration and removal of solvent, a muddy solid resulted which contained some of the product. ^{1}H NMR (C_6D_6) 2.74 (dt, 6 H, HNC*H*$_2$CH, $^3J_{HNCH}$ = 2.4 Hz, $^3J_{HCCH}$

= 5.7 Hz), 2.15 (t, 6 H, $HNCH_2CH_2$); ^{13}C NMR (C_6D_6) 51.12 ($HNCH_2CH_2N$), 37.16 ($HNCH_2CH_2$). LRMS (70 ev, EI) *m/z* (relative intensity, proposed ion) 248.3 (0.1, M^+), 171.16 (100.0, M^+-Ph).

1-Phenyl-N,N',N''-trimethylazasilatrane, 12b.

Method A: To 0.23 g (0.93 mmol) of **7b** in 5 mL of toluene was added 0.70 mL of a 1.5 M (1.1 mmol) ether/cyclohexane solution of PhLi. The reaction mixture was refluxed for 0.5 h. After filtration followed by removal of the solvent under vacuum, **12b** was sublimed in 96% yield. M.p. 60-62 °C. ^1H NMR (C_6D_6) 8.06 (dd, 2 H, *o*-H, $^3J_{HH}$ = 7.8 Hz, $^5J_{HH}$ = 1.2 Hz), 7.38 (t, 2 H, *m*-H), 7.27 (t, 1 H, *p*-H), 2.64 (t, 6 H, NCH_2CH_2, $^3J_{HCCH}$ = 5.7 Hz), 2.54 (s, 9 H, NCH_3), 2.26 (t, 6 H, NCH_2CH_2); ^{13}C NMR (C_6D_6) 136.60, 129.00, 127.81, 127.44 (C_6H_5), 50.51 ($CH_3NCH_2CH_2N$), 50.45, ($CH_3NCH_2CH_2$), 38.08 (CH_3N); ^{29}Si (C_6D_6) -44.41. LRMS (70 ev, EI) *m/z* (relative intensity, proposed ion) 290.2 (30.1, M^+), 213.2 (100.0, M^+ - Ph), 246 (37.1), 234.1 (50.2), 191 (33.8); HRMS for M^+ ($C_{15}H_{26}N_4Si$) calcd: 290.19268; found: 290.191868. Anal, calcd for $C_{15}H_{26}N_4Si$: C, 62.21; H, 8.97; N, 19.31; found: C, 61.99, H, 9.20, N, 19.38.

Method B: To 0.5 mL of a C_6D_6 solution of 20 mg (0.08 mmol) of **7b** was slowly added 0.06 mL (0.09 mmol) of a 1.5 M PhLi solution (ether/cyclohexane) cooled to 10 °C. ^1H and ^{13}C NMR spectra of the solution showed the formation of **12b** and **1b** in a molar ratio of approximately 90:5 plus a small amount of biphenyl, whose ^1H and ^{13}C NMR peaks compared favorably with a commercially available sample. Its identity was further verified by LRMS (*m/z*: 154) by subliming it at room temperature/15 x 10^{-3}

mmHg from the residue left after evaporation of a scaled-up reaction mixture.

Method C: To 0.5 mL of a C_6D_6 solution of 20 mg (0.080 mmol) of **7b** in an NMR tube was quickly added 0.15 mL of a 1.5 M (2.3 mmol) PhLi solution (ether/cyclohexane) at room temperature. The mixture was shaken vigorously. Ten min later a ^1H NMR spectrum of the solution showed exclusive conversion of **7b** to **12b**.

1-Perfluorophenylazasilatrane, 13a.

Method A: C_6BrF_5 (0.13 g, 0.52 mmol) was dissolved in 18 mL of pentane and the solution was cooled to -50 °C. *n*-BuLi (0.26 mL, 0.52 mmol) in hexane was added and the mixture was stirred for 30 min. A precooled (-50 °C) toluene solution (15 mL) containig 0.084 g (0.41 mmol) of **7a** was added dropwise. After stirring at -50 °C for 1 h, the mixture was allowed to warm slowly to room temperature and then filtered. Removal of the solvents under vacuum followed by sublimation afforded crystalline product in 43% yield. M.p. 102-104°. ^1H NMR (C_6D_6) 2.66 (t, 6 H, $^3J_{HCCH}$ = 5.7 Hz, $SiNC\mathit{H}_2CH_2$), 2.01 (t, 6 H, $SiHNCH_2C\mathit{H}_2$), 0.91 (b, 3 H, NH); ^{13}C NMR (C_6D_6) 50.76 ($HNCH_2\mathit{C}H_2N$), 36.79 ($HNCH_2CH_2$). The complicated pattern of the C_6F_5 carbons caused by fluorine couplings provided barely detectable resonances. ^{29}Si NMR (C_6D_6) -84.51; ^{19}F NMR (C_6D_6) -125.71 (dd, 2 F, *o*-F, $^3J_{FF}$ = 27.4 Hz, $^4J_{FF}$ = 9.0 Hz) -157.3 (t, 1 F, *p*-F, $^3J_{FF}$ = 21.5 Hz), -162.26 (m, 2 F, *m*-F). MS (70 ev, EI) *m/z* (relative intensity, proposed ion) 338.1 (3.4, M^+), 171.1 (3.5, M^+ - C_6F_5), 240.0 (33.2), 225.0 (17.3), 200.0 (16.6), 168.0 (83.3).

Method B: To 0.5 mL of a toluene solution of 10 mg (0.048 mmol) of **7a** was added 0.1 mL of 0.5 M (0.05 mmol) of $MgBrC_6F_5$[10] solution in ether at room temperature. The reaction was immediately monitored by ^{19}F NMR spectroscopy and C_6F_5H was observed to have formed nearly quantitatively, along with a trace amount of **13a**. ^{19}F NMR: -138.23 (t), -153.68 (t), -161.183 (t). These spectral data were consistent with those of intentionally hydrolyzed $MgBrC_6F_5$.

1-Perfluorophenyl-N,N',N''-trimethylazasilatrane, 13b. To 0.64 g (2.6 mmol) of compound **7b** in 25 mL of toluene was added 2.8 mmol of $MgBrC_6F_5$ as a mixture prepared by mixing 0.70 g of C_6BrF_5 with 0.070 g of Mg in 10 mL of ether at room temperature. The reaction mixture was stirred for 1/2 h. After filtration, all the volatiles were removed under vacuum over a period of 5 h. By sublimation at 50°/5 x 10^{-3} mmHg, a crystalline solid, identified as pure product **13b** was obtained in 14% yield. M.p., 105-106 °C. ^1H NMR (C_6D_6) 2.53 (t, 6 H, $^3J_{HCCH}$ = 5.7 Hz, $CH_3NCH_2CH_2$), 2.36 (s, 9 H, NCH_3), 1.96 (t, 6 H, $CH_3NCH_2CH_2$); ^{13}C NMR (C_6D_6) 50.18 ($CH_3NCH_2CH_2$), 48.47 ($CH_3NCH_2CH_2$), 38.20 (CH_3N); ^{29}Si NMR (C_6D_6) (temperature) -69.94 (50 °C), -70.94 (20 °C), -71.76 (10 °C); ^{19}F NMR (C_6D_6) -126.46 (dd, 2 F, *o*-F, $^3J_{FF}$ = 24.6 Hz, $^4J_{FF}$ = 9.3 Hz), -156.32 (t, 1 F, *p*-F, $^3J_{FF}$ = 19.8 Hz), -162.96 (m, 2 F, *m*-F). LRMS (70 ev, EI) *m/z* (relative intensity, proposed ion), 380.0 (100.0, M^+), 336.0 (56.0, M^+ - CH_6N), 324.2 (25.3), 295.3 (18.8), 281.3 (12.1), 213 (8.3, M^+ - C_6F_5); HRMS for M^+ ($C_{15}H_{21}N_4F_5Si$): calcd, 380.14557, found, 380.14740.

1-Fluoro-N,N',N''-trimethylazasilatrane, 14b, and the tetrafluorobenzyne insertion product 15. To 25 mL of a pentane solution of C_6F_5Br (0.433 g, 1.79 mmol) at -50 °C was added 0.9 mL of a 2.01 M (1.89 mmol) hexane solution of *n*-BuLi. After stirring at -50 °C for 3 h, 0.42 g (1.7 mmol) of **7b** in 8 mL of toluene was slowly added. The mixture was stirred at ~ -50 °C for an additional 0.5 h and then allowed to warm to room temperature whereupon the mixture turned brownish red. After filtration and washing with 3 x 15 mL portions of toluene a ^1H NMR spectrum of the filtrate revealed three major products **13b**, **14b** and **15** in a ratio of approximately 1:2:1. After removal of the solvent under vacuum, **14b** sublimed first at 35 °C/15 x 10^{-3} mmHg in about 90% purity. Repeated sublimation under these conditions gave pure **14b** in 28% yield. M.p., 120-122 °C. The residual mixture was then sublimed at 55 °C to remove **13b** together with unseparated **14b** and a small amount of **15**. After removal of **13b** and **14b** was complete (as shown by the ^1H NMR spectra of the sublimed solid) a 21% yield of **15** was readily sublimed at 110°/15 x 10^{-3} mmHg as a white crystalline solid. M.p., 168-169 °C. Compound **15** dissolved well in THF and toluene but did not dissolve in water. Crystals of **14b** and **15** suitable for X-ray studies were grown by sublimation at 60 °C in an unevacuated tube sealed under nitrogen and at 5 x 10^{-2} mmHg, respectively.

Characterization for **14b**: ^1H NMR (C_6D_6) 2.97 (s, 9 H, NCH_3), 2.60 (dt, 6 H, $CH_3NCH_2CH_2$, $^3J_{HCCH}$ = 5.7 Hz, $^4J_{FSiCH}$ = 1.2 Hz), 2.03 (t, 6 H, $CH_3NCH_2CH_2$); ^{13}C NMR (C_6D_6) 48.32 (s, $CH_3NCH_2CH_2$), 47.05 (d, $CH_3NCH_2CH_2N$, $^3J_{CF}$ = 1.5 Hz), 37.28 (d, $^3J_{CF}$ = 8.0 Hz, CH_3N); ^{19}F NMR

(C_6D_6) -136.19; ^{29}Si NMR (C_6D_6) -99.69 (d, $^1J_{FSi}$ = 191.8 Hz). LRMS (70 ev, EI) *m/z* = (relative intensity, proposed ion) 232.2 (100, M^+), 188.1 (86.1, M^+ - $CH_3NCH_2CH_2$); HRMS for M^+ ($C_9H_{21}FN_4Si$). Calcd: 232.15195, found: 232.15201. Anal. calcd for $C_9H_{21}FN_4Si$: C, 46.55, H, 9.05, N, 24.14; found: C, 46.74; H, 9.17; N, 24.37.

Characterization for **15**: ^1H NMR (toluene-D_8) 2.60 (d, 3 H, $CH_2NCH_3C_6F_4Si$, $^5J_{FCH}$ = 1.05 Hz), 2.56 (b, 3 H, $NCH_2CH_2NCH_3Si$), 2.14 (s, 3 H, $NCH_2CH_2NCH_3Si$), 2.78 (m, 1 H), 2.60 (m, 1 H), 2.59 (m, 1 H), 2.57 (m, 1 H), 2.44 (m, 1 H), 2.10 (m, 1H), 2.08 (m, 1 H), 1.79 (m, H), 1.73 (m, 2 H), 1.70(m, 1 H), 1.51(dt, 1 H); ^{13}C NMR (C_6D_6) 57.58, 55.87, 51.87, 51.32, 48.46, 48.33, 42.36 (d, $^3J_{FC}$ = 7.5 Hz), 39.26 (m), 38.52; ^{13}C NMR (toluene-d_8) 151.87 (m), 150.42 (m), 149.59 (m), 148.75 (m), 147.46 (m), 146.25 (m), 142.68 (m), 140.60 (m), 139.12 (m), 135.6 (m), 133.71 (m), 57.69, 56.9, 51.00, 51.44, 49.59, 48.46, 42.30 (d, $^3J_{CF}$ = 7.5 Hz), 39.24 (m), 138.52 (s); ^{13}C NMR (toluene-d_8, 100 °C), 57.12, 56.04, 52.14, 51.60, 50.16, 48.94, 42.35 (d, $^3J_{FC}$ = 7.5 Hz), 38.83 (m), 38.27; ^{29}Si NMR (toluene-d_8) (temperature, °C) -66.06 (80), -68.47 (50), -70.30 (20), -72.55 (10), -73.24 (-20), -74.39 (-30), -74.91 (-40), -76.40 (-50), -77.87 (-60), -77.88 (-67.5); ^{29}Si NMR (solid state, 20 °C) -62.6. ^{19}F NMR (C_6D_6) -128.38 (b, 1 F), -129.83 (dd, $^3J_{FF}$ = 27.7 Hz, 1 F, $^4J_{FF}$ = 12.4 Hz), -146.01 (t, 1 F, $^3J_{FF}$ = 15.2 Hz), -154.63 (t, 1 F, $^3J_{FF}$ = 21.2 Hz), -155.18 (t, 1 F, $^3J_{FF}$ = 18.3 Hz), -158.48 (t, 1 F, $^3J_{FF}$ = 24.6), -161.98 (b, 2 F). ^{19}F NMR (toluene-d_8, -70 °C) -126.81 (d, 1 F, $^3J_{FF}$ = 27.4), -129.03 (d, 1 F, 24.3 Hz), -130.00 (dd, $^3J_{FF}$ = 27.4 Hz, $^4J_{FF}$ = 9.0 Hz, 1 F), -146.00 (t, 1 F, J = 22.9 Hz), -158.44 (t, 1 F, $^3J_{FF}$ = 21.2 Hz), -155.07 (t, 1 F, $^3J_{FF}$ = 19.9 Hz), -154.26 (t, 1 F, $^3J_{FF}$ = 21.2 Hz), -161.13 (m, 1 F), -162.06 (m, 1 F); LRMS (70

ev, EI) *m/z* (relative intensity, proposed ion), 528.1 (34.1, M^+), 484.1 (95.1, M^+-C_2H_6N), 292.1 (45), 361.1 (15.2, M^+-C_6F_5), 206.1 (100.0), 144.2 (89.2), 99.1 (85.2), 69.0 (40). HRMS for M^+ ($C_{21}H_{21}F_9N_4Si$) calcd: 528.13918, found 528.14039. Anal. for $C_{21}H_{21}F_9N_4Si$, calcd: C, 47.73; H, 3.98; N, 10.60; found, C, 48.19; H, 3.87; N, 10.87.

1-Benzyl-N,N',N''-trimethylazasilatrane 26. Compound **7b** (0.20 g, 0.82 mmol) was mixed with 0.14 g (0.90 mmol) of $MgBrCH_2C_6H_5$ in 20 mL of toluene and the mixture was refluxed for 0.5 h. After filtration and removal of the solvent, the residue was extracted with 3 x 15 mL portions of pentane. Evaporating the pentane under vacuum gave as a liquid in 84% yield. ^1H NMR (C_6D_6) 7.45 (d, 2 H, $^2J_{HH}$ = 7.2 Hz, *m*-H), 7.23 (t, 2 H, $^2J_{HH}$ = 7.8 Hz, *o*-H), 7.09 (t, 1 H, *p*-H), 2.51 (t, 6 H, $^3J_{HCCH}$ = 5.4 Hz, $CH_3NCH_2CH_2$), 2.46 (s, 9 H, NCH_3), 2.28 (t, 6 H, $CH_3NCH_2CH_2$), 2.14 (s, 2 H, $CH_2C_6H_5$); ^{13}C NMR (C_6D_6) 143.06, 130.17, 128.15, 123.95 (C_6H_5), 50.73 ($CH_3NCH_2CH_2N$), 49.72 ($CH_3NCH_2CH_2N$), 36.63 (NCH_3), 24.47 ($PhCH_2$); ^{29}Si NMR (C_6D_6) -37.7.

1-Methoxyazasilatrane 29a. $NaOCH_3$ (0.15 g, 2.8 mmol) was mixed with 0.10 g (0.48 mmol) of **7a** in 35 mL of THF and the solution was refluxed for 84 h. THF was removed by distillation at atmospheric pressure and the residue was extracted with 3 x 15 mL of pentane. Removal of pentane under vacuum afforded presumably pure solid **28** in 85% yield. ^1H NMR (C_6D_6) 3.14 (s, 3 H, OCH_3), 2.75 (t, 6 H, $HNCH_2CH_2$, $^3J_{HCCH}$ = 5.7 Hz), 2.06 (t, 6 H, $HNCH_2CH_2$); ^1H NMR ($CDCl_3$) 3.30 (s, 3 H, OCH_3), 2.99 (t, 6 H, $HNCH_2CH_2$, $^3J_{HCCH}$ = 5.7 Hz), 2.63 (t, 6 H, $HNCH_2CH_2$); ^{13}C NMR ($CDCl_3$) 57.70 (OCH_3), 50.51

($HNCH_2\mathit{C}H_2$), 37.02 ($HN\mathit{C}H_2CH_2$); ^{29}Si NMR ($CDCl_3$) -82.49. HRMS for M^+ ($C_7H_{18}N_4OSi$) calcd: 202.12499, found: 202.12507.

1-Methoxy-N,N',N''-trimethylazasilatrane 29b. Compound **7b** (0.13 g, 0.52 mmol) was mixed with 0.12 g (2.0 mmol) of $NaOCH_3$ in 5 mL of THF. After the addition of 20 mL of toluene, the solution was refluxed for ~14 h, but only about 30% of the starting material **7b** was converted into **29**. Refluxing for another 58 h caused the reaction to reach completion. The solvents were removed under vacuum and the solid residue was extracted with 4 x 10 mL of pentane. Removal of pentane under vacuum followed by sublimation at 55 °C/15 x 10^{-3} mmHg gave the crystalline product in 85.3% yield. ^1H NMR (C_6D_6) 3.76 (s, 3 H, OCH_3), 2.95 (s, 9 H, NCH_3), 2.67 (t, 6 H, $CH_3NC\mathit{H}_2CH_2$, $^3J_{HCCH}$ = 5.7 Hz), 2.05 (t, 6 H, $CH_3NCH_2C\mathit{H}_2$); ^{13}C NMR (C_6D_6) 51.35 (OCH_3), 48.25 ($CH_3NCH_2\mathit{C}H_2$), 47.80 ($CH_3N\mathit{C}H_2CH_2$), 38.72 (NCH_3); ^{29}Si (C_6D_6) -88.55. LRMS (70 ev, EI), *m/z* (proposed ion, relative intensity) 244.2 (M^+, 45.1), 213.2 (M^+-OCH_3, 47.0), 200.1 (M^+-$N(CH_3)_2$, 96.7), 188.1 (M^+-NC_3H_6, 100.0), 159.1 (M^+-$C_4H_9N_2$, 45.31), 145.1 (59.3), 131.1 (38.5); HRMS for M^+ ($C_{10}H_{24}ON_4Si$) calcd: 244.17194, found: 244.17180.

1-Ethoxy-N,N',N''-trimethylazasilatrane 30b. This compound was synthesized earlier by another route.[4] Compound **7b** (0.20 g, 0.80 mmol) was mixed with 15 g (2.2 mmol) of NaOEt in 15 mL of THF and 20 mL of toluene. The solution was refluxed for 136 h. The solvents were removed under vacuum and the solid residue was extracted with 4 x 8 mL portions of benzene. Removal of the benzene under vacuum afforded crude product in

81% yield. ^{1}H NMR (C_6D_6) 4.04 (q, 4 H, OCH_2CH_3, $^3J_{HCCH}$ = 6.9 Hz), 2.94 (s, 9 H, NCH_3), 2.66 (t, 6 H, $CH_3NCH_2CH_2$, $^3J_{HCCH}$ = 5.7 Hz), 2.05 (t, 6 H, $CH_3NCH_2CH_2$), 1.42 (t, 6 H, OCH_2CH_3); ^{13}C NMR (C_6D_6), 57.19 (OCH_2CH_3), 48.43 ($CH_3NCH_2CH_2$), 48.01 ($CH_3NCH_2CH_2$), 38.85 (NCH_3), 18.87 (OCH_2CH_3); ^{29}Si NMR (C_6D_6) -88.29 (lit.[4] -87.7 in CCl_3D).

1-Isopropoxy-N,N',N''-trimethylazasilatrane 31b. To a mixture of **7b** (0.18 g, 0.72 mmol) and $LiOCH(CH_3)_2$ (0.12 g, 1.8 mmol) was added 15 mL of THF. The solution was refluxed for 26 h whereupon the ^{1}H NMR spectrum of the reaction mixture indicated the absence of acetone or **7b**. THF was removed under vacuum and the residue was extracted with 4 x 10 mL of pentane. After evaporation under vacuum, the clear liquid product was obtained in 80% yield. ^{1}H NMR (C_6D_6) 4.57 (h, 1 H, $-CH(CH_3)_2$, $^3J_{HCCH}$ = 6.0 Hz), 2.83 (s, 9 H, NCH_3), 2.56 (t, 6 H, $CH_3NCH_2CH_2$, $^3J_{HCCH}$ = 5.7 Hz), 2.10 (t, 6 H, $CH_3NCH_2CH_2$), 1.47 (d, 6 H, $OCH(CH_3)_2$); ^{13}C NMR (C_6D_6) 64.53 ($CH(CH_3)_3$), 49.87 ($CH_3NCH_2CH_2$), 49.60 ($CH_3NCH_2CH_2$), 38.60 ($CH_3NCH_2CH_2$), 26.35 ($CH(CH_3)_2$); ^{29}Si NMR (C_6D_6) -74.28.

1-Tertiarybutoxy-N,N',N''-trimethylazasilatrane 32b. Compound **7b** (0.11 g, 0.44 mmol) was added to $LiOC(CH_3)_3$ (0.036 g, 0.45 mmol) in 12 mL of THF and the mixture was refluxed for 44 h. THF was removed under vacuum and the residue was extracted with 3 x 10 mL portions of pentane. After evaporation under vacuum, the product remained as a liquid in 86% yield. ^{1}H NMR (C_6D_6) 2.72 (s, 9 H, NCH_3), 2.58 (t, 6 H, $CH_3NCH_2CH_2$, $^3J_{HCCH}$ = 5.7 Hz), 2.22 (t, 6 H, $CH_3NCH_2CH_2$), 1.51 (s, 9 H, $C(CH_3)_3$); ^{13}C NMR (C_6D_6) 70.95

($OC(CH_3)_3$), 50.77 ($CH_3NCH_2CH_2$), 50.73 ($CH_3NCH_2CH_2$), 37.84 (NCH_3), 32.32 ($C(CH_3)_3$); ^{29}Si NMR (C_6D_6) -68.5.

Reaction of $ClSi(NMe_2)_3$ with $LiNMe_2$. $LiNMe_2$ (10 mg, 0.2 mmol) was dissolved in 0.5 mL of THF-D_8 in a septum-sealed NMR tube. ^1H NMR (THF-D_8) 2.66; ^{13}C NMR (THF-D_8) 47.67. According to the ^1H and ^{13}C NMR spectra, no reaction occurred at room temperature after the addition of 40 mg (0.2 mmol) of $ClSi(NMe_2)_3$. After the solution was warmed at 80 °C for 2 h almost quantitative conversion to $Si(NMe_2)_4$ was observed. ^1H NMR (THF-D_8) for $Si(NMe_2)_4$: 2.45 (s, 24 H); ^{13}C NMR (THF-D_8): 38.34.

Reaction of $ClSi(NMe_2)_3$ with $LiNEt_2$. $LiNEt_2$ (10 mg, 0.13 mmol) was dissolved in 0.5 mL of THF-D_8 in a septum-sealed NMR tube. ^1H NMR (THF-D_8): 2.83 (2, 4 H, CH_2, $^3J_{HCCH}$ = 7.2 Hz), 1.04 (t, 6 H, CH_3); ^{13}C NMR (THF-D_8): 50.36 (CH_2), 18.56 (CH_3). After $ClSi(NMe_2)_3$ (25 mg, 0.13 mmol) was added, no reaction was observed. After heating at 80 °C for 2 h, ~40% of the $ClSi(NMe_2)_3$ was converted into $Si(NMe_2)_3NEt_2$. The reaction was complete after another 7 h at 80 °C. ^1H NMR to $Si(NMe_2)_3NEt_2$ (THF-D_8) 2.82 (q, 4 H, CH_2, $^3J_{HCCH}$ = 6.9 Hz), 2.46 (s, 18 H, $N(CH_3)_2$), 1.00 (t, 6 H, CH_2CH_3); ^{13}C NMR 39.80 (NCH_2CH_3), 38.54 ($N(CH_3)_2$), 15.18 (CH_2CH_3).

Reaction of $ClSi(NMe_2)_3$ with *i*-Pr_2NLi. *i*-Pr_2NLi (15 mg, 0.14 mmol) was dissolved in 0.5 mL of THF-d_8. ^1H NMR (THF-d_8): 3.02 (h, 2 H, $CH(CH_3)_2$, $^3J_{HCCH}$ = 6.3 Hz), 0.98 (d, 6 H, $CH(CH_3)_2$); ^{13}C NMR (THF-d_8) 52.21 ($NCH(CH_3)_2$), 27.77 ($NCH(CH_3)_2$). When $ClSi(NMe_2)_3$ (30 mg, 0.15 mmol) was added, no reaction was observed. After heating at 80 °C for ~20 h, all the

starting material was consumed according to the ^{13}C NMR spectrum which was quite complicated. However, peaks consistent with the formation of a small amount of $HSi(NMe_2)_3$ were detected. ^{13}C NMR (THF-d_8) for $HSi(NMe_2)_3$: 36.97. This value compared favorably with that of a commercially available sample.

Reaction of $ClSi(NMe_2)_3$ with *n*-BuLi. $ClSi(NMe_2)_3$ (40 mg, 0.2 mmol) was added to 0.5 mL of a toluene-d_8 solution of *n*-BuLi (0.25 mmol) in a septum-sealed NMR tube. The ^1H NMR spectrum showed that no reaction occurred at room temperature and so the solution was heated at 90 °C for ~24 h whereupon the conversion into the substitution product was complete. ^1H NMR ($C_6D_5CD_3$) for *n*-$BuSi(NMe_2)_3$: 2.48 (18 H, $N(CH_3)_2$), 1.36 (b, 6 H, $(CH_2)_3$), 0.93 (3 H, CH_3); ^{13}C NMR: 38.00 ($N(CH_3)_2$), 27.49, 26.89, 14.29, 11.53 (*n*-Bu).

Reaction of $ClSi(NMe_2)_3$ with *s*-BuLi. $ClSi(NMe_2)_3$ (40 mg, 0.2 mmol) was added to 0.5 mL of a toluene-d_8 solution of *s*-BuLi (0.22 mmol) in a septum-sealed NMR tube. A small amount of $HSi(NMe_2)_3$ formed after 1 h at room temperature according to the ^1H NMR spectrum. Because no further reaction was observed at room temperature, the mixture was heated at 90 °C for ~24 h, after which the ^1H NMR spectrum displayed peaks consistent with the formation of *s*-$BuSi(NMe_2)_3$ and $HSi(NMe_2)_3$ in an approximate ratio of 3:2. ^1H NMR data ($CD_3C_6D_5$) for *s*-$BuLi(NMe_2)_3$: 2.49 (18 H, $N(CH_3)_2$), 1.3, 0.95. ^{13}C NMR ($CD_3C_6D_5$): 38.22, 27.30, 25.03, 13.77, 13.45.

Reaction of $ClSi(NMe_2)_3$ with *t*-BuLi. $ClSi(NMe_2)_3$ (40 mg, 0.2 mmol) was added to 0.5 mL of a toluene-d_8 solution of *t*-BuLi (0.23 mmol) in a septum-

sealed NMR tube. No reaction was observed for 1 h at room temperature according to its ^1H NMR spectrum. The solution was heated at 90 °C for ~24 h at which time the ^1H NMR spectrum revealed that *t*-$BuSi(NMe_2)_3$ and $HSi(NMe_2)_3$ formed in a ratio estimated to be 1:2. ^1H NMR for *t*-$BuSi(NMe_2)_3$: 2.49 (18 H, $N(CH_3)_2$), 1.2 (9 H, $C(CH_3)_3$); ^{13}C NMR: 38.23, 26.99, 17.9.

Single-crystal X-ray structural determination of 14b and 15. Colorless crystals of **14b** and **15**, grown by slow sublimation, were attached to a glass fiber and mounted on the Siemens P4RA diffractometer for data collection at -50 ± 1 °C. The cell constants for the data collection were determined from a list of reflections found by a rotation photograph. Crystal data and experimental conditions for data collection, solution and structure refinement are listed in Table I.

Lorentz and polarization corrections were applied for both compounds as was a nonlinear correction based on the decay in the standard reflections. A series of azimuthal reflections was collected for **14b** and **15**, and a semi-empirical absorption correction based on the azimuthal scans was applied to the data for both compounds.

For **14b**, the centric space group $P2_{1/m}$ was determined from intensity statistics and systematic absences. The structure was solved by direct methods using the SHELXTL-Plus[13] and SHELXTL-93[14] programs. All non-hydrogen atoms were located directly from the E-map. All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atom positions were generated with ideal geometries and were refined as riding, isotropic atoms.

The C_3 structure of **14b** is disordered across a crystallographic mirror. The $P2_{1/m}$ space group requires that the contents of the asymmetric unit have mirror symmetry with another unit. Thus both left and right handed "twists" of the molecule are found on the same site. The only non-hydrogen atoms that are affected are C1 and C3. All other atoms are sufficiently modeled with one atom. C1 is refined as a half-atom; the other half is produced by symmetry. C3 and its disordered component, C_3', are refined as half-atoms on general sites. The necessity of splitting these sites also requires dual, riding-atom assignments for the hydrogens on C4.

For **15**, the centrosymmetric space group $P\bar{1}$ was chosen based on the lack of systematic absences and the intensity statistics. However, no suitable solution was derived from direct methods. A correct direct-method solution was found in the noncentrosymmetric space group P1 which has enantiomers related by a center of inversion. The positions of all atoms found in one enantiomer were shifted relative to the inversion center to yield the $P\bar{1}$ molecular structure. Again, all non-hydrogen atoms were refined with anisotropic thermal parameters. Methylene hydrogen atoms were refined as riding atoms with C-H distances of 0.96 Å and with individual isotropic thermal parameters. Methyl hydrogen atoms were refined initially as rigid bodies to find the best torsion angles. During the final set of least-squares procedures, these were not refined positionally, but were refined with individual group isotropic thermal parameters.

Table I. Crystallographic Data for **14b** and **15**.

	14b	**15**
empirical formula	$C_{14}H_{36}FN_4Si$	$C_{21}H_{21}F_9N_4Si$
fw	307.56	528.5
color; habit	colorless, plate	colorless, plate
crystal size (mm)	0.50 x 0.35 x 0.09	0.22 x 0.16 x 0.09
crystal system	monoclinic	triclinic
space group	$P2_1/m$	$P\bar{1}$
a (Å)	7.352(1) Å	8.586(2) Å
b (Å)	12.361(2) Å	10.215(2) Å
c (Å)	7.512(1) Å	13.745(3) Å
α (deg)	90.0°	95.62(2)°
β (deg)	119.30(1)°	102.25(2)°
γ (deg)	90.0°	107.74(2)°
volume (Å)	595.3(2)	1104.8(4)
Z	2	2
d_{calcd} (g/cm^3)	1.716	1.589
abs coeff (cm^{-1})	1.828	1.819
F(000)	595.34	540
diffractometer	Siemens P4RA	Siemens P4RA
radiation	CuKα (λ = 1.54178 Å)	CuKα (λ = 1.54178 Å)
temperature (K)	223(2)	223
monochromator	graphite crystal	graphite crystal
2θ scan range	6.76 to 56.80	4.0 to 115.0

Table I. Continued.

scan type	ω-2θ	2θ-θ
scan speed (deg/min)	8.08-23.44	6.01-23.44
scan range (ω)	1.0° plus α_1, α_2 separation	1.00° plus Kα-separation
collected reflcns	1659	3210
independent reflecns	841	2969
R_{init} (%)	3.40	0.85
observed reflcns, n_{obs}	805 ($I \geq 2\sigma(I)$)	2679 ($F \geq 4.0\sigma(F)$)
hydrogen atoms	Riding model fixed isotropic U	Riding model, fixed isotropic U
weighting scheme, w^{-1}	$[\sigma^2(F_o^2)+(0.04*p)^2+0.37*p]$[a]	$\sigma^2(F) + 0.0003F^2$
no. of variable, n_{var}	102	332
goodness-of-fit	1.130, 1.113	2.10
largest and mean Δ/σ	0.001, 0.000	0.001, 0.000
data-to-parameter ratio	7.9:1	8.1:1
largest peak ($e \bullet A^{-3}$)	0.225	0.24
largest hole ($e \bullet A^{-3}$)	-0.220	-0.21
R (%)[b]	3.48	3.21
R_w (%)[c]		4.66
R^2_w(%)[d]	9.26	
GOF[e]	1.130	2.10

[a] $P = (\text{Max}(F_o^2, O)+2*F_c^2)/3$. [b] $R = \Sigma||F_o|-|F_c||/\Sigma|F_o|$. [c] $R_w = [\Sigma w(|F_o|-|F_c|)^2/\Sigma w(F_o)^2]^{1/2}$. [d] $R_w^2 = [\Sigma[W(F_o^2-F_c^2)^2]/\Sigma[W(F_o^2)^2]]^{0.5}$. [e] $GOF = [\Sigma s(|F_o|-|F_c|)^2/(n_{obs}-n_{var})]^{1/2}$.

Table II. Atomic Coordinates (x 10^4) and Equivalent Isotropic Displacement Parameters ($Å^2$ x 10^3) for **14b**.

Atom	x	y	z	U(eq)
Si	5200 (1)	2500	739 (1)	23 (1)
F	2696 (2)	2500	-929 (2)	36 (1)
N (1)	8302 (4)	2500	2788 (3)	28 (1)
N (2)	6026 (4)	2500	-1060 (3)	34 (1)
N (3)	5167 (3)	1297 (2)	1896 (3)	42 (1)
C (1)	9378 (6)	2014 (4)	1773 (6)	33 (1)
C (2)	8219 (5)	2500	-446 (4)	43 (1)
C (3)	8556 (7)	1885 (4)	4568 (6)	41 (1)
C (3'a)	8911 (7)	1335 (4)	3312 (7)	41 (1)
C (4)	7078 (4)	862 (2)	3544 (4)	57 (1)
C (5)	4734 (5)	2500	-3242 (4)	42 (1)
C (6)	3426 (4)	599 (2)	1371 (4)	48 (1)

Equivalent isotropic U defined as one third of the trace of the orthogonalized Uij tensor.

Table III. Selected Bond Distances (Å) and Angles (deg) for **14b**.

		distances	
Si-F	1.643 (2)	Si-N(1)	2.034 (2)
Si-N(3)	1.728 (2)	F-Si-N(3a)	95.58 (7)
Si-N(2)	1.732 (2)	F-Si-N(3)	95.58 (7)
Si-N(3a)	1.728 (2)	F-Si-N(2)	95.47 (10)
		angles	
F-Si-N(1)	179.64 (9)	Si-N(3a)-C(6a)	127.7 (2)
Si-N(3)-C(6)	127.7 (2)	Si-N(3a)-C(4a)	120.7 (2)
Si-N(3)-C(4)	120.2 (2)	C(3)-N(1)-C(3a)	111.1 (3)
Si-N(2)-C(5)	127.0 (2)	C(3a)-N(1)-C(1)	111.1 (3)
Si-N(2)-C(2)	121.0 (2)	C(1)-N(1)-C(3)	113.6 (3)

[a]Numbers in parentheses are estimated standard deviations in the least significant digits.

Table IV. Atomic Coordinates (x 10^4) and Equivalent Isotropic Displacement Coefficients ($Å^2$ x 10^3) for **15**.

Atom	x	y	z	Ueq
Si	-2249 (1)	1597 (1)	-2775 (1)	27 (1)
N(1)	-4692 (2)	206 (2)	-2555 (1)	31 (1)
C(1)	-5050 (3)	258 (3)	-1543 (2)	39 (1)
C(2)	-5006 (3)	1643 (3)	-1026 (2)	42 (1)
N(2)	-3454 (2)	2780 (2)	-967 (1)	34 (1)
C(3)	-3466 (4)	4124 (3)	-497 (2)	49 (1)
C(4)	-5939 (3)	564 (3)	-3306 (2)	39 (1)
C(5)	-5311 (3)	2108 (3)	-3293 (2)	37 (1)
N(3)	-3506 (2)	2567 (2)	-3209 (1)	32 (1)
C(6)	-2887 (3)	4088 (3)	-3138 (2)	48 (1)
C(7)	-4729 (3)	-1231 (2)	-2880 (2)	40 (1)
C(8)	-3823 (3)	-1205 (3)	-3704 (2)	42 (1)
N(4)	-2312 (2)	31 (2)	-3424 (1)	33 (1)
C(9)	-986 (3)	-229 (3)	-3838 (2)	42 (1)
C (11)	-1966 (3)	2433 (2)	-620 (2)	30 (1)
C(12)	-1201 (3)	2600 (3)	407 (2)	36 (1)
F(12)	-1865 (2)	3075 (2)	1124 (1)	56 (1)
C(13)	266 (3)	2255 (3)	740 (2)	40 (1)
F(13)	965 (2)	2453 (2)	1738 (1)	59 (1)
C(14)	867 (3)	1680 (3)	50 (2)	37 (1)
F(14)	2269 (2)	1338 (2)	364 (1)	53 (1)

Table IV. Continued

C(15)	73 (3)	1455 (2)	-965 (2)	31 (1)
F(15)	789 (2)	880 (1)	-1611 (1)	42 (1)
C(16)	-1323 (3)	1836 (2)	-1340 (2)	27 (1)
C(21)	-273 (3)	2807 (2)	-3183 (2)	30 (1)
C(22)	1249 (3)	3740 (2)	-2584 (2)	32 (1)
F(22)	1610 (2)	3873 (1)	-1565 (1)	48 (1)
C(23)	2494 (3)	4610 (2)	-2944 (2)	34 (1)
F(23)	3934 (2)	5493 (2)	-2299 (1)	50 (1)
C(24)	2276 (3)	4573 (2)	-3961 (2)	37 (1)
F(24)	3479 (2)	5399 (2)	-4324 (1)	58 (1)
C(25)	790 (3)	3675 (2)	-4604 (2)	36 (1)
F(25)	532 (2)	3623 (2)	-5618 (1)	54 (1)
C(26)	-420 (3)	2845 (2)	-4212 (2)	34 (1)
F(26)	-1856 (2)	2021 (2)	-4907 (1)	47 (1)

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

Table V. Selected Bond Distances (Å) and Angles (deg) for the Insertion Product **15**.

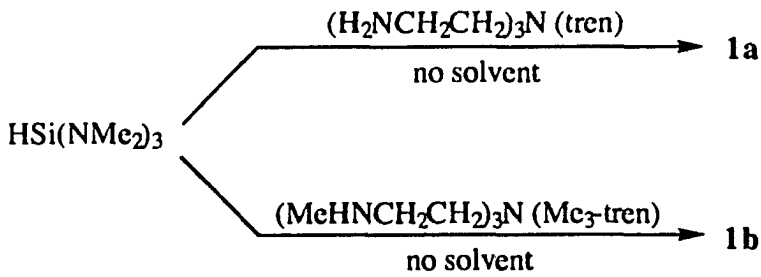
		distances	
Si-N(1)	2.246 (2)	Si-C(16)	1.924 (2)
Si-N(3)	1.731 (2)	C(21)-Si-N(1)	171.4 (1)
Si-N(4)	1.734 (2)	C(16)-Si-N(1)	87.7 (1)
Si-C(21)	1.996 (2)	N(4)-Si-N(1)	81.2 (1)
		angles	
Si-C(21)	1.996 (2)	C(8)-N(4)-Si	122.6 (2)
Si-C(16)	1.924 (2)	C(9)-N(4)-C(8)	110.3 (2)
N(3)-Si-N(1)	82.1 (1)	C(5)-N(3)-C(6)	108.8 (2)
C(8)-N(4)-Si	122.6 (2)	C(6)-N(3)-Si	124.3 (2)
C(11)-N(2)-C(2)	113.0 (2)	Si-N(3)-C(5)	122.5 (2)
C(3)-N(2)-C(2)	112.4 (2)	Si-C(16)-C(11)	123.11 (2)
C(11)-N(2)-C(3)	116.8 (2)	C(1)-N(1)-C(4)	112.3 (2)
C(9)-N(4)-Si	127.0 (1)	C(1)-N(1)-C(7)	107.0 (2)
		C(7)-N(1)-C(4)	110.2 (2)

[a]Numbers in parentheses are estimated standard deviations in the least significant digits.

All the X-ray data collections and the structure solutions were carried out at the Iowa State Molecular Structure Laboratory. All calculations were performed on a digital Equipment Corp. Micro VAXII computer. Positional parameters and selected bond distances and angles are listed in Tables II and III for **14b**, and Tables IV and V for **15**, respectively.

RESULTS AND DISCUSSION

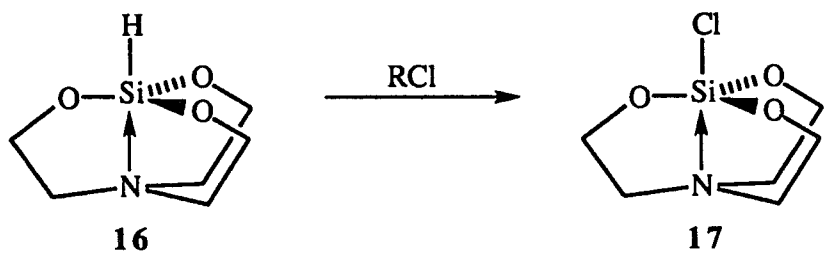
Synthesis of 1a and 1b. Although the synthesis of **1a** via reaction 1 had been reported to proceed in quantitative yield more than 15 years ago,[3] the 51-55 °C melting point of this compound (and presumably its purity) was considerably



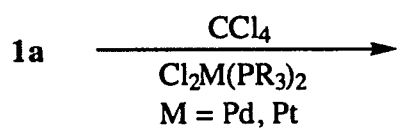
lower than that of the product we had obtained (77-79 °C) in the same reaction carried out in the presence of a catalytic amount of Me_3SiCl or $(NH_4)_2SO_4$.[4] It was our belief that the yield we reported for the latter reaction (72-84%) and for reaction 2 (54%) could be further improved by the use of a solvent to avoid the polymer formation which was observed to dominate when these reactions were carried out over long periods of time. A further impetus for improvement of these yields was the fact that **1a** and **1b** are the precursors for starting materials **7a** and **7b**, respectively, used in the present study. Indeed we discovered that the use of refluxing toluene raised our earlier yields of **1a** and **1b** to 90 and 93%, respectively, and the melting point of **1a** obtained by this method (78-80 °C) was comparable with the previously reported value.[4] Because no catalysts were used in the present syntheses, the reactions took

longer than those we described earlier. On the other hand, polymerization was minimized.

Synthesis of 7a and 7b. Because reactions of $ClSi(NMe_2)_3$ with tren or Me_3-tren gave polymeric mixtures,[4] an alternate route was required. By analogy to the synthesis of 1-chloro-silatrane **17** via the oxidation of 1-hydrosilatrane **16** with halogenated hydrocarbons (reaction 3),[15] we had earlier reported reaction 4 in the presence of metal catalysts for the preparation of **7a**.[4] However, the isolated yield in this reaction was only 30% and substantial



16 **17** (3)

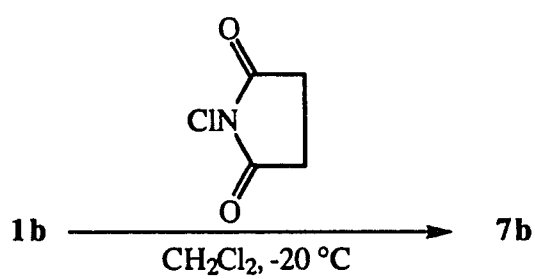


1a **7a** (4)

insoluble by-product formation was also observed. Heating the reaction mixture only resulted in darkening owing presumably to decomposition. Here we report that although reaction 4 takes longer without catalyst (several days *versus* ten minutes) the product yield is doubled (60-70%) and it is NMR spectroscopically pure and it is white.

Efforts to speed up the synthesis of **7a** by using other chlorinating agents such as N-chlorosuccinimide,[5] Ph_3CCl and Cl_3CCCl_3 (which were previously used in reaction 3)[15] proved to be unsuccessful in that the separation of **7a** from the corresponding reduction product was tedious owing to similar solubilities. Chlorinating agents commonly used in organic chemistry such as MeO_2SCl and Cl_2SO gave intractable solids in the presence of **1a**. Although the transformation in reaction 3 had been reported to occur in 80% yield in the presence of Me_3SiCl and quinoline,[15a] this approach is unsuccessful for converting **1a** to **7a** owing to trimethylsilylation of the equatorial nitrogens as had been reported by us earlier.[4,16]

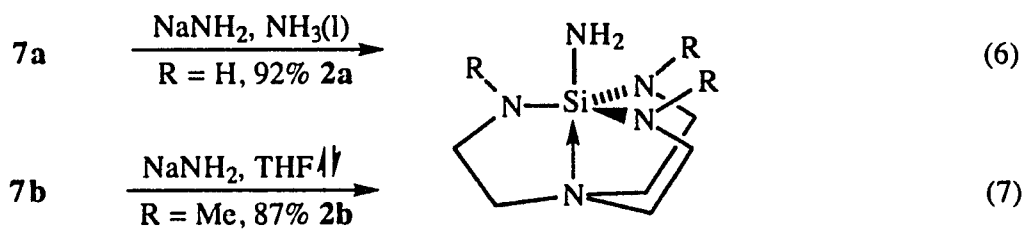
Attempts to carry out reaction 4 with **1b** to prepare **7b** resulted in the formation less than 5% yield of the desired product and large quantities of an intractable red solid at room temperature after only 3 h. Using no catalyst in reaction 4 at room temperature eventually causes **1b** to be consumed, but the yield of desired product is negligible. At room temperature or at 65 °C in toluene, the reaction mixture of **1b** with Cl_3CCCl_3 was observed to turn dark brown over 10 h, but no detectable product was formed. When this reaction was carried out in refluxing toluene, impure (brown) **7b** was realized in 40% yield. The most successful approach to colorless crystalline **7b** appears to be



(5)

reaction 5 which was developed in our laboratories by a previous coworker.[5] Side reactions leading to intractable products are minimized by keeping the reaction mixture at -10 °C or below even during solvent evaporation. Trace amounts of succinimide by-product left in the product after toluene extraction of the residue remaining after evaporation of the reaction mixture, were removed by sublimation, affording yields of crystalline **7b** ranging from 50-87% in this somewhat erratic reaction.

Syntheses of 2a-4a, 6a and 2b-6b and the attempts to synthesize 5a. The 1-amino compounds **2a** and **3b** are formed in high yields according to reactions



(6)

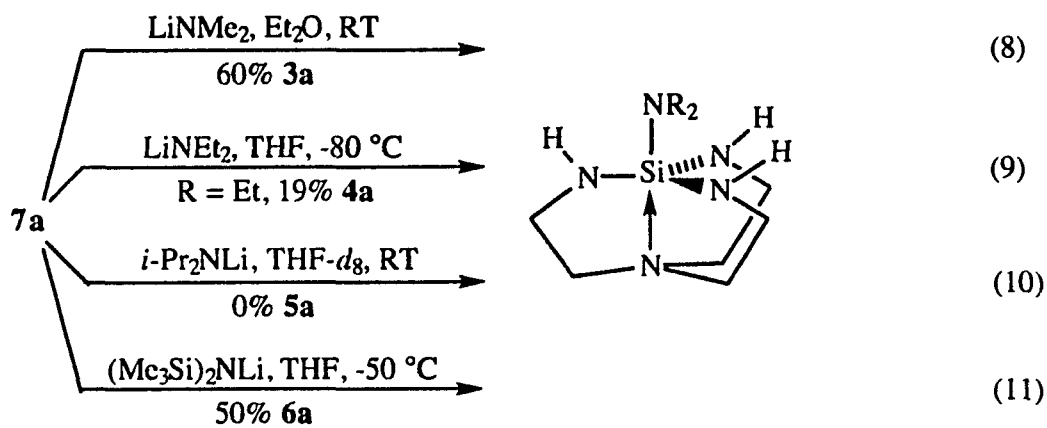
(7)

6 and 7. Both compounds are sublimable for further purification purposes. It is important to use only a stoichiometric amount of $NaNH_2$ in reaction 6, since excess of this reagent leads to darkening the reaction mixture and considerable lowering of the yield. Substituting ether or THF as a solvent for liquid NH_3 in this reaction was unsuccessful, probably owing to the poor solubility of the $NaNH_2$. $LiNH_2$ in liquid NH_3 or THF also failed to react with **7a** and the use of a blue solution of Na in liquid NH_3 was only partially successful in that $(H_2NCH_2CH_2)_3N$, a reduction product, was formed along with **2a** in an approximate ratio of 2:3.

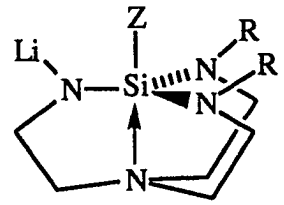
Compound **2a** is a solid at room temperature, but it is a volatile liquid at 42 °C. Thus purification can be achieved by sublimation or distillation. At 200 °C it decomposes with the release of NH_3. It is soluble in common organic solvents and it is stable to solvolysis by EtOH in C_6D_6 at room temperature over a period of 2 h.

In contrast to **7a**, **7b** is relatively unreactive to $NaNH_2$ in liquid NH_3 and starting material was recovered quantitatively after 2.5 hours. This may be due to the poor solubility of **7b** in liquid ammonia. Although conversion of **7b** to **2b** does occur with Na in liquid NH_3 over a period of 30 days, the reduction product **1b** is also formed (ratio of **2b**:**1b** = 5:1) and no $(HMeNCH_2CH_2)_3N$ is observed. Reaction 7 takes about six days.

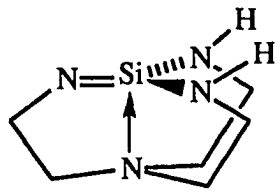
Whereas reaction 8 proceeds in reasonable yield, a side reaction involving lithiation of an equatorial NH proton(s) increasingly dominates in



reactions 9 and 10. If an intermediate such as **18** is formed, concomitant liberation of the corresponding amine HNR_2 is expected. Indeed, the only



	Z	R
18	Cl	H
19	CH_3	$SiMe_3$



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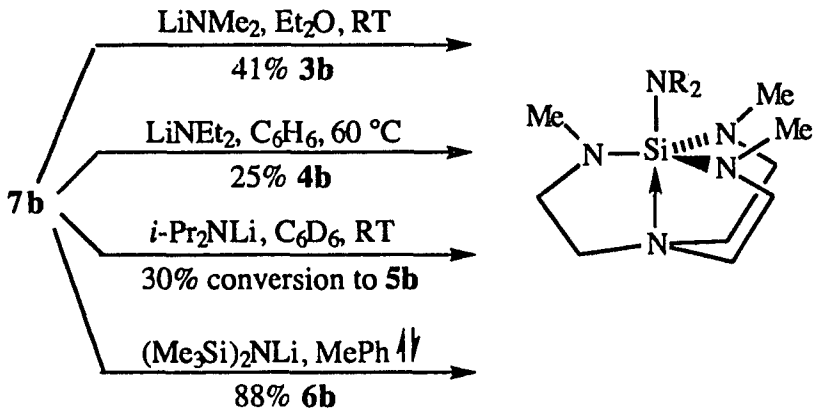
species observed in solution is *i*-Pr_2NH in reaction 10. Some support for **18** is gained from our previous isolation of stable **19**.[16] Also formed in reactions 8-10 is a precipitate which may be a polymeric form of **20** created *via* concerted LiCl elimination to form unstable **18**, or by nucleophilic attack of the anion of **18** on **7a**. Although sila-imines are known, the Si=N-R skeleton tends to be close to linear (177.8°(2) in *t*-Bu_2Si=N-*t*-Bu and 161.51°(5) in THF•Me_2Si=NSi(*t*-Bu)$_3$).[17] In any case, it is clear that deprotonation of **7a** becomes more competitive with nucleophilic chloride displacement from this molecule caused by these amides whose basicities lie in the order $^-N(SiMe_3)_2$ < $^-NMe_2$ < $^-NEt_2$ ≤ $^-$N-*i*-Pr_2.[18] Interestingly, when reaction 9 was run at room temperature, ^1H NMR spectroscopic monitoring revealed almost quantitative $HNEt_2$ formation and no **4a**, in analogy to reaction 10 wherein HN-*i*-Pr_2 was quantitatively observed to formed. It would also appear that a nucleophilicity order based on steric factors is not of overriding importance here since the yields of **3a** and **6a** are comparable.

Compounds **3b-6b** were made according to reactions 12-15, respectively. In view of the lack of equatorial NH protons in **7b**, deprotonation/lithiation cannot be the cause of the poor yields of **3b** and **4b**, nor can it be origin of the mediocre conversion of **7b** to **5b**. These results and the seemingly oddly high yield of **6b** will be addressed in a later section.



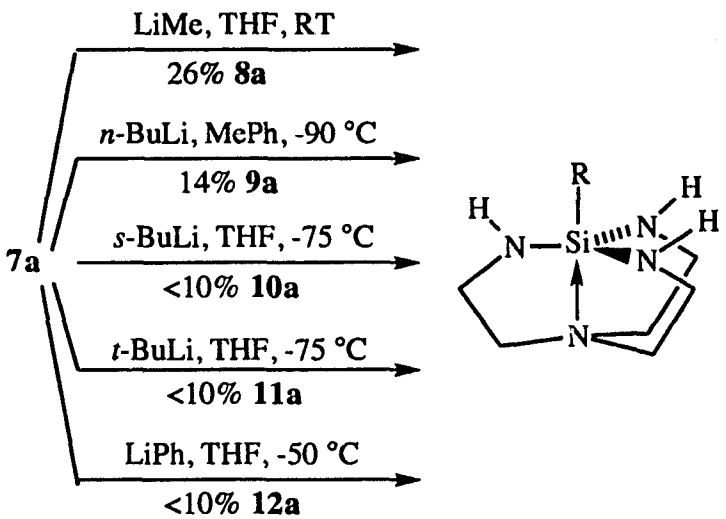
(12)

(13)

(14)

(15)

Synthesis of 8a, 9a,b and 12a,b and attempted synthesis of 8b, 10a,b and 11a,b. Reactions 16-20 summarize our efforts to synthesize **8a-12a** and reactions 20-24 do the same for **8b-12b**. The basicity order[19] *t*-Bu$^-$ > *s*-Bu$^-$ > *n*-Bu$^-$ > Me$^-$ >



(16)

(17)

(18)

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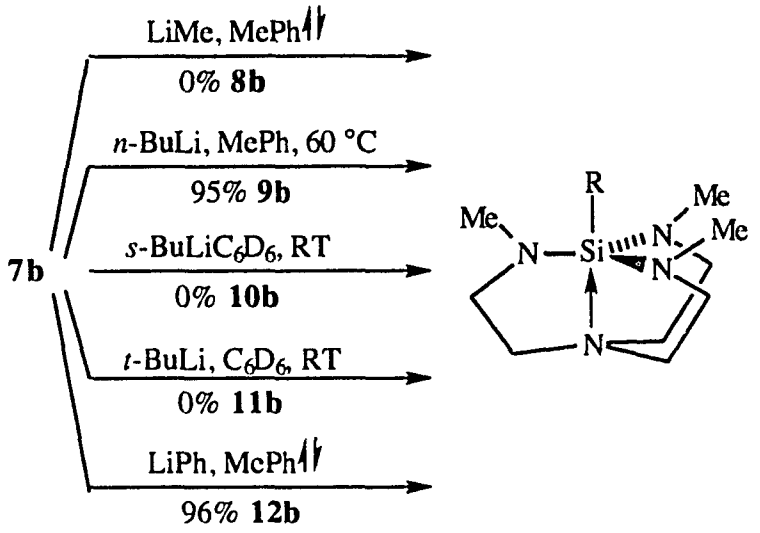


(21)

(22)

(23)

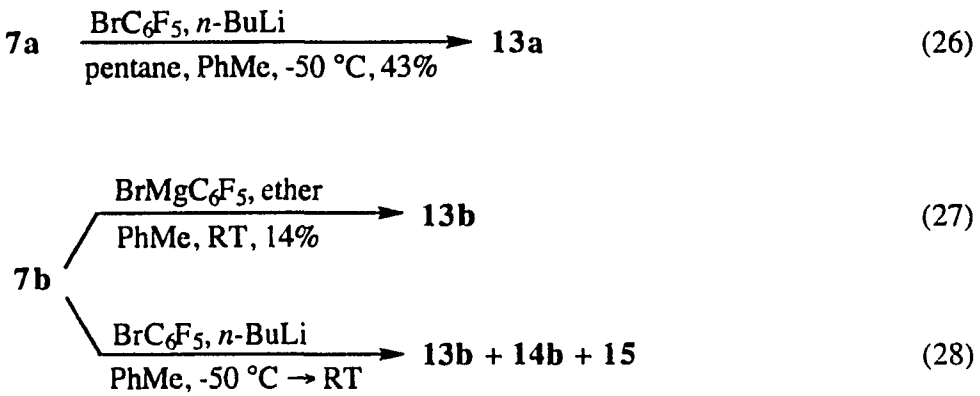
(24)

(25)

Ph^- partially accounts for the general decrease in yield from **8a-11a**.

It is remarkable that reaction 22 leads to a 95% yield of **9b** while the presumably the smaller Me^- in reaction 21 gives only unreacted starting material even after 24 hours of refluxing the reaction mixture in the presence of $Me_2NCH_2CH_2NMe_2$ (TMEDA) as a lithium complexing agent. Reaction 21 starkly contrasts reaction 16 in which a 26% yield of its analogue **8a** was isolated despite competitive deprotonation/lithiation. We tentatively attribute this result to insufficient ionization of the oligomeric LiMe in toluene compared with THF. It should be noted that **8b** is a known compound, and was made by reacting $MeSi(NMe_2)_3$ with $(HMeNCH_2CH_2)_3N$.[4] The apparently anomalous lack of formation of **10b** and **11b** in reactions 22 and 23 are addressed in a later section.

Synthesis of 13a, 13b, 14b and 15. These compounds were synthesized according to reaction 26-28. Whereas reaction 26 gives a 43% yield of product,

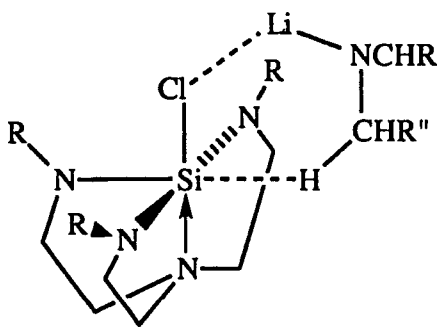


a similar reaction carried out with $BrMgC_6F_5$ in ether at room temperature provided an almost quantitative converison of the Grignard reagent to HC_6F_5, presumably from metallation of the NH hydrogens of **7a**. From the analogous reaction with **7b** (reaction 27) a low yield of pure **13b** was obtained after sublimation of the residue left after solvent removal from the reaction mixture.

After removal of solvent from the mixture remaining upon completion of reaction 28, sublimation gave first a mixture which contained aobut 90% pure **14b**. Repeated sublimation of this fraction at 35 °C/15 x 10^{-3} mmHg gave pure **14b** in 28% yield. Sublimation of the remaining reaction residue at 55 °C removed **13b** together with unseparated **14b** plus a small amount of **15**. After **13b** and **14b** were removed (as shown by ^1H NMR spectroscopy) **15** was sublimed at 110 °C in 21% yield.

Hydride transfer reactions. Except for the transformation of **7b** to **6b** by $LiN(SiMe_3)_2$ in reaction 15, the analogous reactions 12-14 produce mediocre yields of the corresponding amides **3b-5b**. By monitoring reactions 12-14 with

^{1}H NMR spectroscopy, it was observed that the ratios of the amidated to hydrogenated product (**1b**) were approximately 5:1, 4:1 and 1:2, respectively. In fact, **1b** was also isolated and unambiguously identified from reactions 12 and 13. Since reaction 14 was carried out in the deuterated solvent C_6D_6, the only plausible source of hydrogen in **1b** formed in reactions 12-14 is the amide reagent. It is suggested that the formation of **1b** in these reactions comes about via a hydride transfer pathway involving intermediate **21** (or a structurally distorted conformer thereof) which would be increasingly favored over nucleophilic attack by the nitrogen (e.g., **22**) as the amide group



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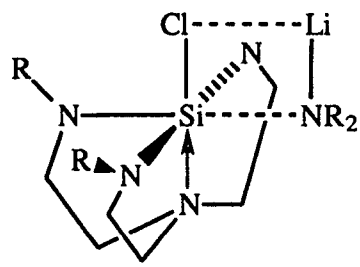
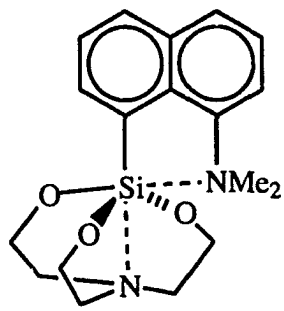


22

increases in size. Four lines of evidence make this suggestion plausible. 1) The ^{13}C NMR chemical shifts of one byproduct are compared favorably with those of the expected imine elimination product $Me_2HCN{=}CMe_2$[20] in reaction 14. 2) The addition of the Li^+ complexing agent TMEDA to these reactions substantially suppressed the rates of hydride transfer and nucleophilic substitution, presumably because formation of the six and four-centered intermediates **21** and **22**, respectively, would be inhibited. 3) Reaction 15 gives

a high yield of amide substitution product **6b** owing to the lack of a proton on the carbon alpha to the amide nitrogen, thus requiring a sterically less favored seven-membered ring if an intermediate analogous to **21** is indeed required. 4) Whereas the Si-H bond in four-coordinate silanes is well known to react with amines in amide-catalyzed reactions to form Si-NR_2 bonds,[20] **1a** and **1b** do not undergo such reactions,[4] presumably because the amide concentration and hence the concentration of intermediate **21** is very low. Silanes are sterically more favored than silatrane systems to undergo direct nucleophilic attack, with no necessity to expose an electrophilic site by ring formation as in **21**. That such a site can indeed arise in a silatrane species was shown in the structure determination of **23** wherein the Me_2N-Si distance of 2.95 Å in the rather distorted structure indicates a weak N-Si



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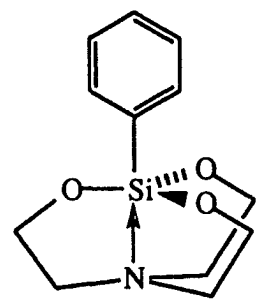
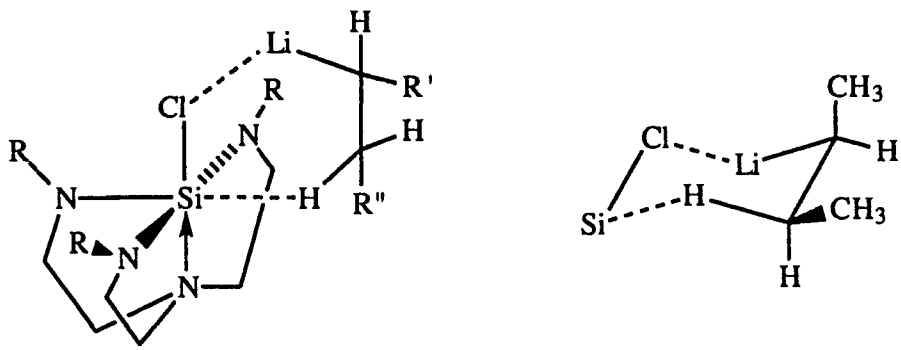


24

interaction.[22] The trans-annular Si←N interaction is also weak since its distance of 2.42 Å is considerably longer than in **24** (2.19 Å).[12]

In reactions 18 and 19 consumption of the starting material **7a** was incomplete. A ratio of about 1:5 hydride transfer product **1a** to substitution product (**10a** and **11a**) was observed in each case, however. Thus hydride

transfer product **1a** is not observed with the less sterically hindered LiR reactants LiMe and *n*-BuLi (reactions 16 and 17, respectively). With the more sterically hindered substrate **7b**, however, hydride transfer product **1b** (along with 1-butene) is already observed with *n*-BuLi (reaction 22) and the ratio of **1b** to substitution product rises from approximately 1:20 in this reaction to 1:0 with the more sterically hindered *s*-BuLi and *t*-BuLi in reactions 23 and 24, respectively. It is interesting to compare the ratios of the three olefins produced from *s*-BuLi in reactions 18 (1-butene:Z-2-butene:E-2-butene ≈ 1:1:1) and 23 (10:1.5:1, respectively). These data are consistent with an intermediate of type **25** which in the case of *s*-BuLi can form two diastereomers, namely, **25a** (R' = Et, R" = H), and **25b** (R' = R" = Me). In the presence of the more sterically hindered **7b**, *s*-BuLi apparently favors the

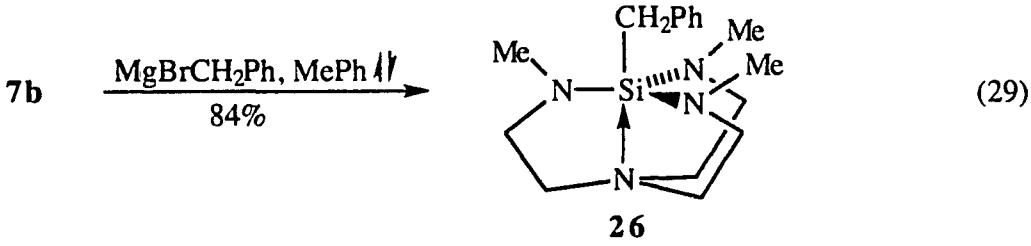


25

formation of **25a** (R = Me) at the expense of **25b**(R = Me) because of steric interactions interactions of the R" = Me and R = Me groups. The 1.5:1 Z to E ratio of 2-butenes in reaction 23 also becomes understandable if the six-membered ring in **25b** adopts a conformation approximating the one shown

above. Such a conformation for **25b** (R = Me) dominates if the methyl group on the carbon beta to the lithium were induced to be equatorial (owing to steric interactions with a methyl group on the silatrane cage if it were axial) and if the methyl on the carbon alpha to the lithium were axial (because of a more favored interaction of the hydrogen on this methyl group with the axial lone pair on chlorine). Dreiding models show that a ca. 90° Cl–Si---H angle distorts the six-membered ring to favor the cis relationship of the methyl group as shown rather than a trans diequatorial structure. As hydride transfer and Li–C cleavage progresses, Z-2-butene would be expected to form.

Although no hydride transfer product **1a** stemming from an aromatic hydrogen in LiPh was detected in reaction 20, a small amount of **1b** (~5%) is observed in reaction 25 when it is carried out at room temperature or at -45 °C. This observation suggests that benzyne is eliminated from an intermediate of type **25** (R = Me). Also detected in this reaction is a very small amount of biphenyl which could arise from the attack of phenyl anion on benzyne to form biphenyl anion, followed by proton abstraction from the solvent toluene to form $LiCH_2Ph$. Consistent with the desirability of a proton on the carbon beta to the lithium in the LiR reagent is the lack of **1b** as a product in reaction 29 and the high yield of **26**. It may be noted that all of the rates of these reactions are significantly inhibited in the presence of TMEDA.

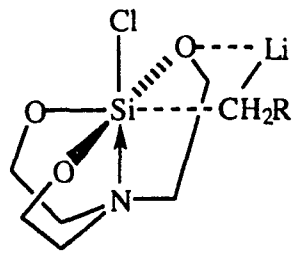


(29)

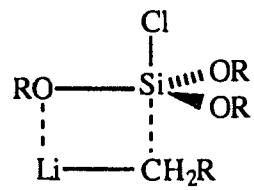
26

That conversion of a nucleophilic substitution product to a hydride substitution product is not occurring in these reactions is supported by the lack of detection of **1b** by ^{1}H NMR spectroscopy after refluxing a toluene solution of **9b** for 2 hours.

In contrast to the reactions of **7a** and **7b** with LiR, the analogue **17** reacts with *n*-BuLi to cleave an Si-O bond rather than the Si-Cl linkage, as is the case with tetracoordinate silicon species.[23] In view of the preceding discussion, it is reasonable to suggest that since oxygen is more electronegative than chlorine, an intermediate of type **27** which weakens the LiO-Si bond while simultaneously opening a sixth coordination site on



27

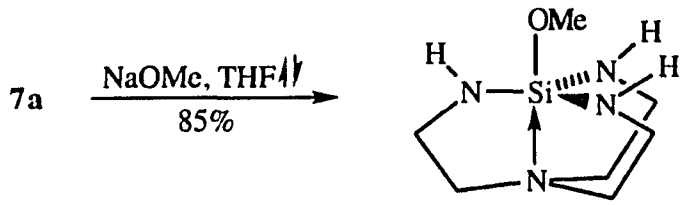


28

silicon for nucleophilic attack of $^-CH_2R$. In similar reactions with tetracoordinate $ClSi(OR)_3$ compounds, any such weakening of the LiO-Si bond

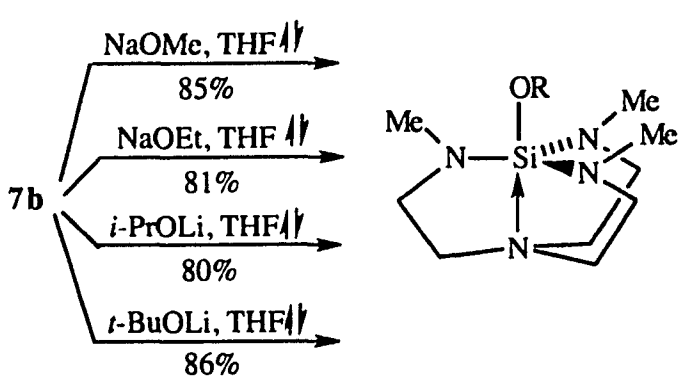
would be dominated by weakening of the Si–Cl link of the linear 3-center 4-electron MO system in **28**.

We have not observed hydride transfer products in reactions 30-34. This



(30)

29a



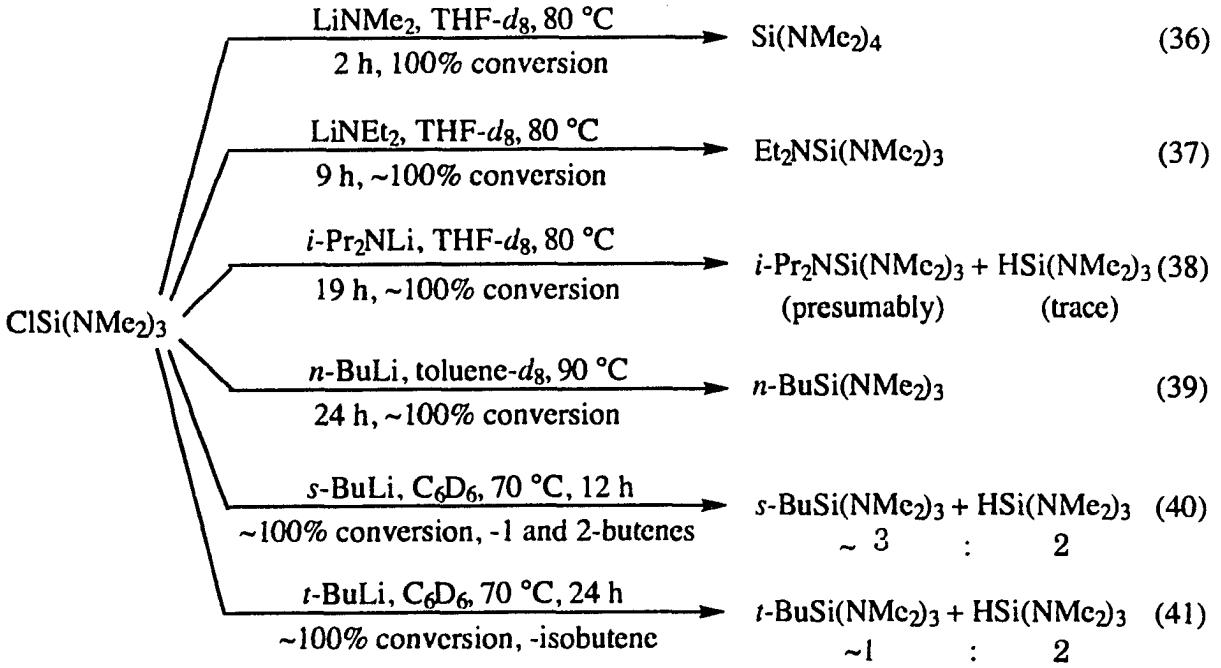
	R	
29b	Me	(31)
30b	Et	(32)
31b	*i*-Pr	(33)
32b	*t*-Bu	(34)

result is attributable to the great strength of the Si-O bond and the minimal steric requirement of the oxygen in $^{-}$OR. While the poorer complexing ability of sodium with the chlorine substituent might be blamed for the lack of hydride transfer product in reactions 27-29, reactions 33 and 34 would appear to be ideally set up for producing **1b** with accompanying elimination of acetone. The fact that these products are not observed supports the dominant role of Si–O bond formation. As perhaps expected, hydride transfer readily occurs from $LiAlH_4$ in reaction 35. Not surprisingly, **7a** in the presence of

$$\mathbf{7b} \xrightarrow[88\%]{LiAlH_4,\ THF} \mathbf{1b} \qquad (35)$$

$LiAlH_4$ evolved hydrogen owing to the formation of aluminum bonds to the equatorial nitrogens.

Compared with **7a** and **7b**, the acyclic four-coordinate analogue $ClSi(NMe_2)_3$ reacts more sluggishly with $LiNR_2$ and LiR, requiring higher temperatures and longer times (reactions 36-41). This observation



corroborates earlier work indicating the lower reactivity of four-coordinate silicon species compared with five-coordinate analogues.[24]

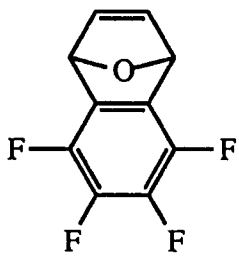
A fluoride transfer reaction. Our observation of a small amount of hydride transfer product **1b** when reaction 25 was carried out at low temperature

prompted us to repeat the reaction with LiC_6F_5, since the Si–F bond strength exceeds that of the SiH bond by ~214 kJ/mol.[25] Indeed the dominant product in reaction 42 is the fluoride transfer species **14b**. By contrast, reaction 43

$$\mathbf{7b} \xrightarrow[\text{PhMe, pentane, -50 °C}]{BrC_6F_5,\ n\text{-BuLi}} \underset{1\ :\ 2\ :\ 1}{\mathbf{13b} + \mathbf{14b} + \mathbf{15}} \qquad (42)$$

$$\mathbf{7a} \xrightarrow[\text{PhMe, pentane, -50 °C}]{BrC_6F_5,\ n\text{-BuLi}} \mathbf{13a} \qquad (43)$$

gives only the perfluorophenylated product **13a**. Reaction 42 also produces the tetrafluorobenzyne insertion product **15**, which is rather suprising because such a reaction might have been expected to occur more readily with sterically less hindered **14b**. It is also not obvious why no tetrafluorobenzyne insertion product is detected in reaction 43. That **15** can arise from benzyne insertion into **13b** was shown by reacting isolated **13b** with a solution in which tetrafluorobenzyne was generated. When reaction 42 was carried out in the presence of furan, the Diels-Alder adduct **33**[26] was detected by ^1H, ^{13}C and ^{19}F NMR spectroscopies in addition to **13b**, **14b** and **15**. However, the percentage of **15** decreased somewhat. It is inconclusive whether any of the tetrafluorobenzyne moiety in **33** emanated from the fluoride transfer intermediate **34** rather than from warming the *n*-BuLi/BrC_6F_5 solution. Further support for an intermediate of the type **34** to account for the formation of **14b** comes from our failed attempts to fluorinate **7b** by exchange with LiF in refluxing THF. Thus it seems unlikely that **14b** arises from the



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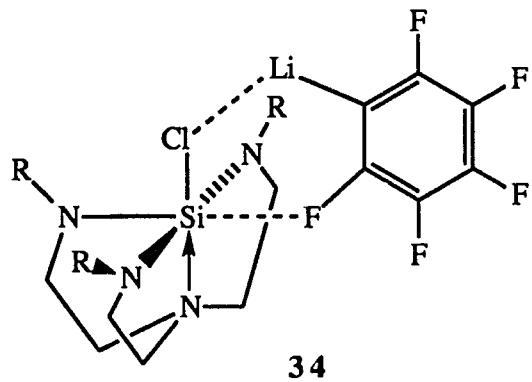
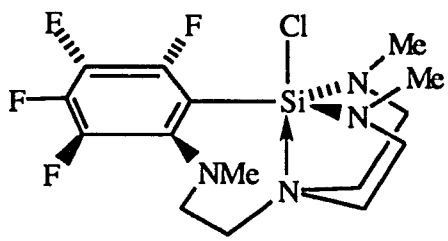


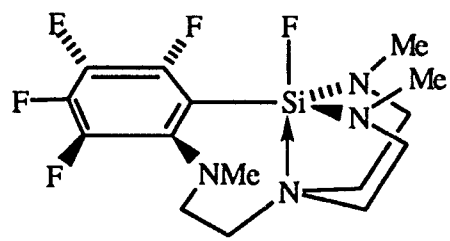
34

interaction of liberated LiF with unreacted starting material in reaction 42.

Tetrafluorobenzyne insertion could conceivably occur directly on **7b** giving **35b**, followed by nucleophilic substitution to form **13b**. If this were the case, however, then the formation of some **36b** might be expected, but none



35b



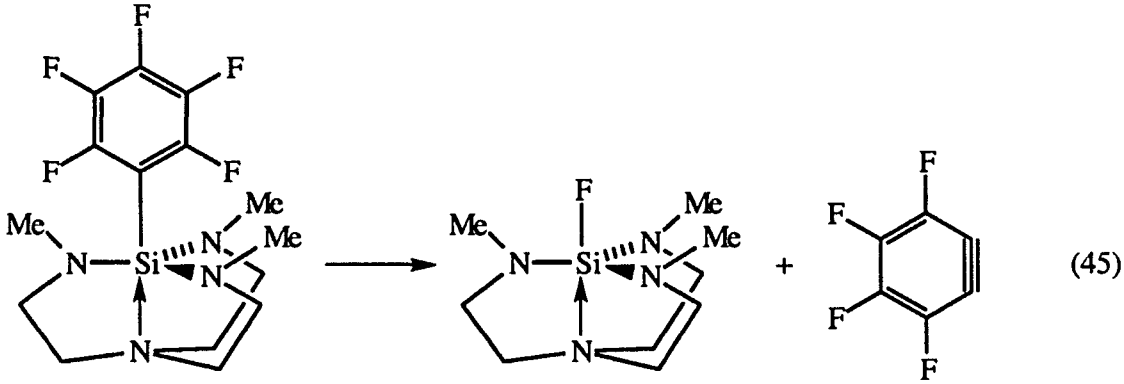
36b

was detected. Even when excess **7b** was used in reaction 42, no **35b** was detected.

By using $BrMgC_6F_5$ in reaction 44, only **13b** was observed to form. Since

$$\mathbf{7b} \xrightarrow[\text{PhMe, } Et_2O,\ 14\%]{BrMgC_6F_5,\ RT} \mathbf{13b} \qquad (44)$$

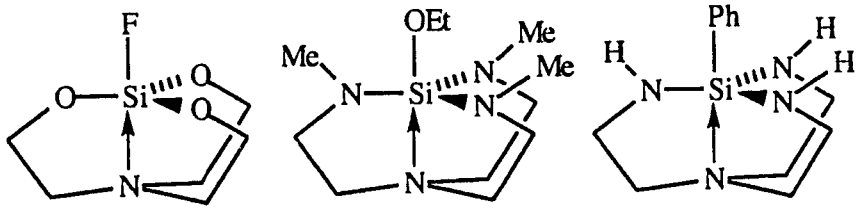
$BrMgC_6F_5$ is stable up to 80 °C,[26] it is not surprising that the tetrafluorobenzyne product **15** is not seen in this reaction until it is heated above this temperature. Somewhat surprising, however, is the lack of fluoride transfer product. Perhaps the BrMg analogue of intermediate **34** is disfavored because the Mg-Cl bond is 58 kJ/mol weaker than the Li-Cl link,[25] and because the bromine atom places greater steric demands on such an intermediate. Another possible source of tetrafluorobenzyne and **14b** is the



13b **14b** (45)

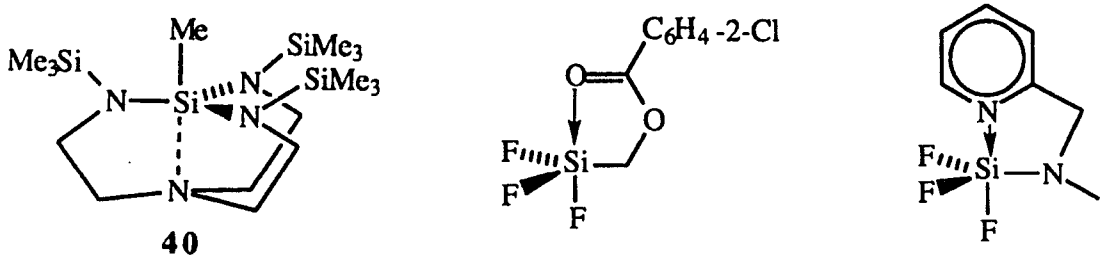
decomposition reaction 45. We did observe such a reaction as a minor pathway in the EI mass spectrum of **13b**. However, a toluene solution of **13b** is stable from room temperature to 100 °C.

Molecular structures of 14b and 15. It is interesting that the N→Si transannular bond length of 2.034 (2) Å in **14b** (Fig. 1) is shorter than that reported for **37** (2.042 (1) Å[27]). On the other hand this link in **14b** is longer than the 2.023 Å reported for **17**.[28] The Si-F bond in **14b** (1.643 (2) Å) is somewhat longer than that in **37** (1.622 (1) Å[27]), which may be expected from



37 38 39

the greater donation of electron density from the transannular nitrogen in **14b**, as is suggested by its shorter N→Si transannular bond. The Si-F bond length in **14b** is comparable with the axial Si-F lengths in **41** (1.62 Å[29]), **42** (1.621 (5) Å[30]), SiF_5^- (1.646 Å[31]) and $PhSiF_4^-$ (1.669 (3) Å[32]).



40 41 42

Despite the expansion of one of the five-membered rings in **13b** by tetrafluorobenzyne insertion, the N→Si transannular bond is preserved in **15** (Fig. 2). The length of this bond in azasilatranes such as **14b** (2.034 (2) Å, **38** (2.135 (2) Å[3]) and **39** (2.132 (4) Å[12]) is augmented by the introduction of the seven-membered ring in **15**, but is is shorter than that observed in **40** (2.775 (7) Å[16]) in which this interaction is stretched by steric interactions among the methyl groups. Even in the latter compound, however, the transannular interaction length is shorter than the sum of the van der Waals radii (3.65 Å[33]).

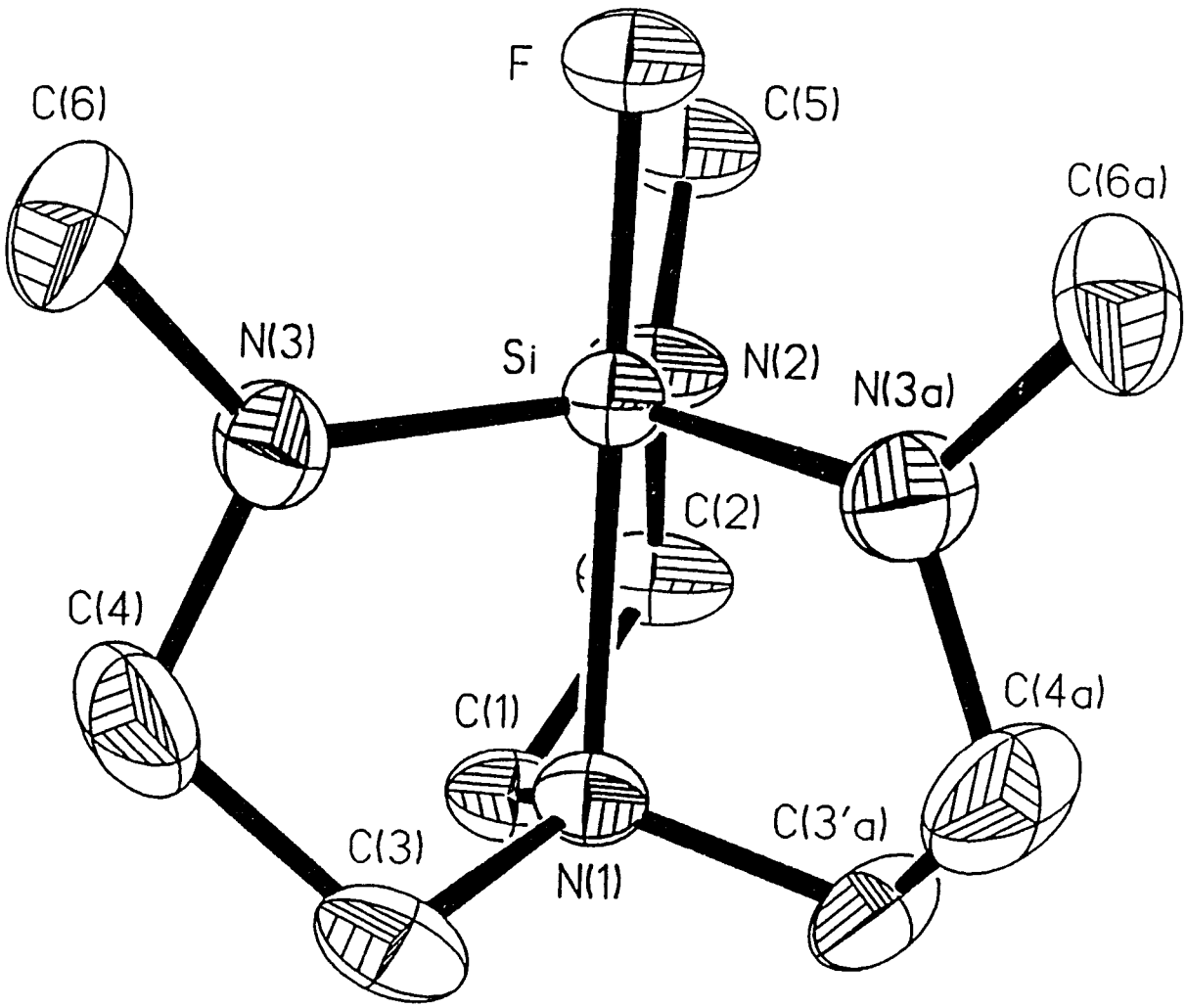


Fig. 1. ORTEP drawing of **14b**. Ellipsoids are drawn at the 50% probability level.

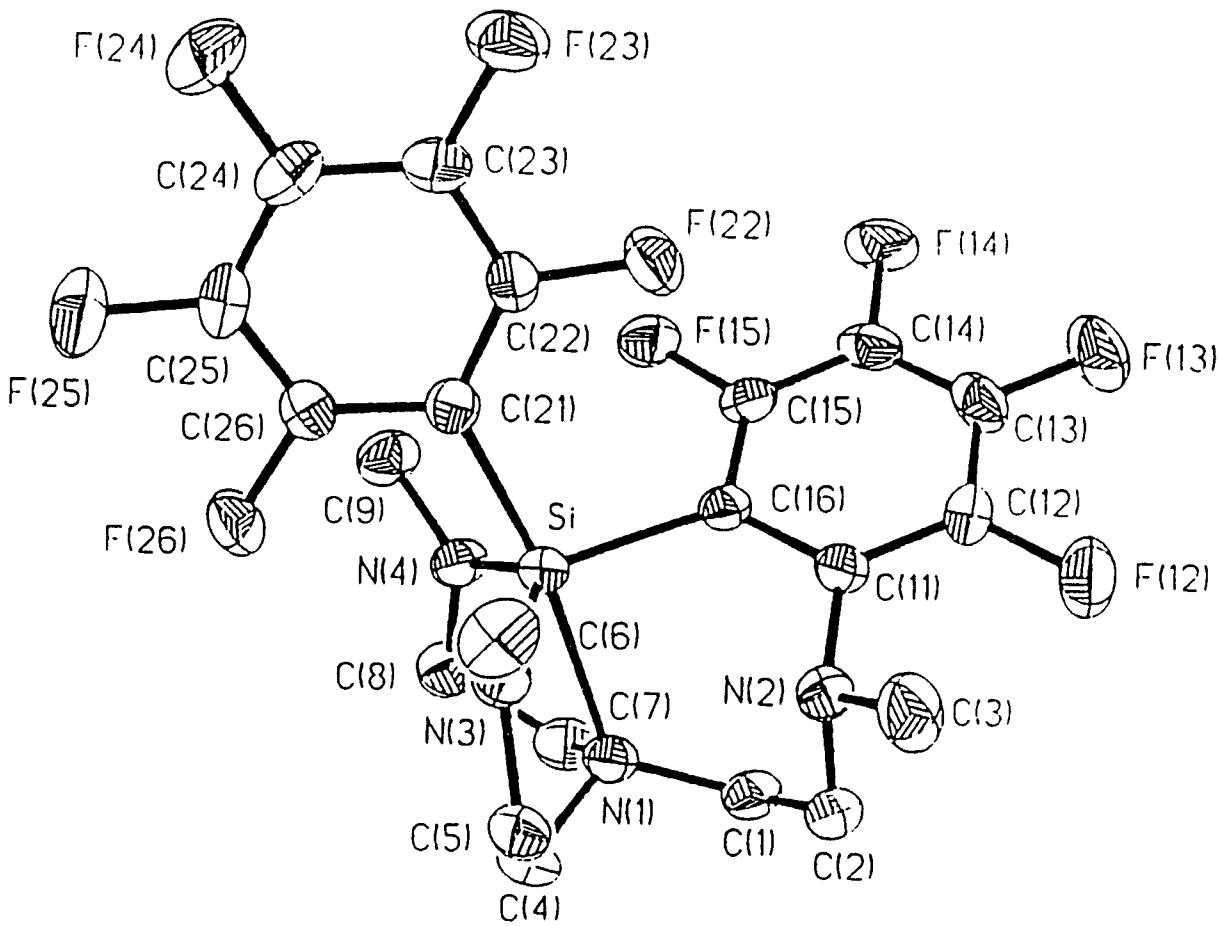


Fig. 2. ORTEP drawing of **15**. Ellipsoids are drawn at the 50% probability level.

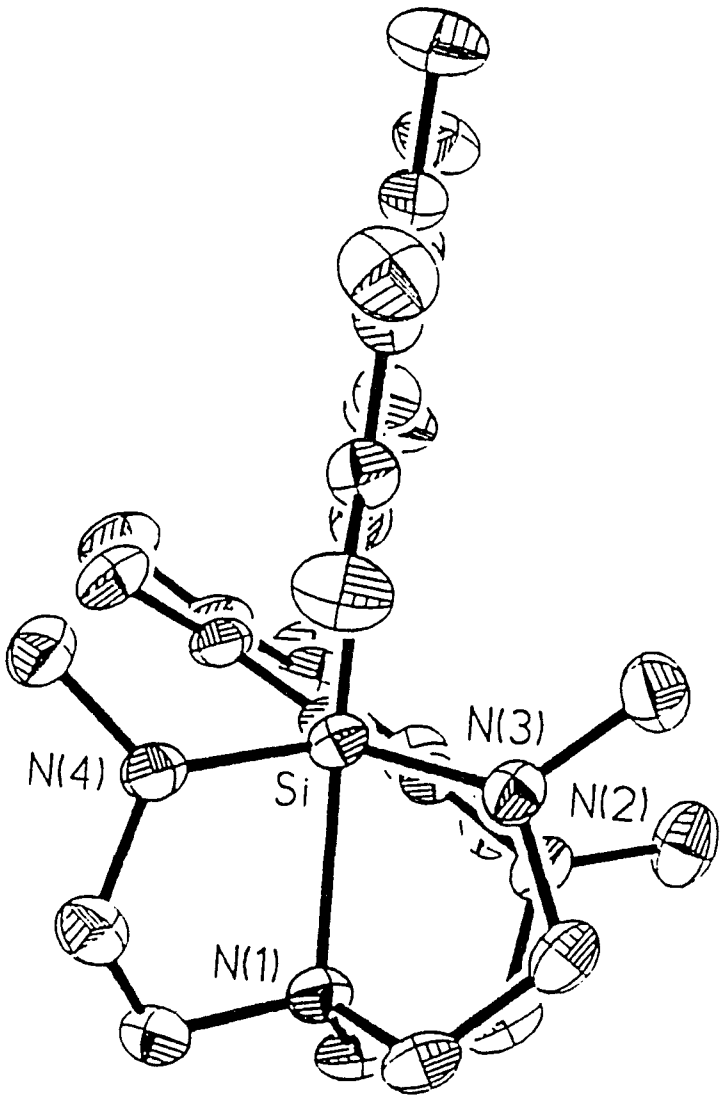


Fig. 3. ORTEP drawing of **15** showing the conformation of the axial C_6F_5 ring relative to the C_6F_4 moiety in the seven-membered ring.

The steric hindrance introduced by the tetrafluorobenzyne group results in a noticeable reduction in the linearity of the axial framework observed in symmetrical atranes to 171.4° for the N_{ax}-Si-C(21) bond angle in **15**. In spite of the distortion of the axis and the stretched transannular interaction in **15** in the solid state, the transannulated structure apparently remains intact in solution. This is indicated by the upfield ^{29}Si NMR chemical shift observed in solution (-70.6 ppm) which is actually somewhat higher than that observed in the solid state (-62.8 ppm) suggesting the possibility of an even stronger transannular interaction in the solution state.

From the view of **15** shown in Fig. 3 it is seen that the plane of the axial C_6F_5 group almost bisects the angle formed by the two five-membered rings of the atrane cage and minimizes steric interactions of F(26) and the methyl groups containing C(6) and C(9) (Figure 2). This C_6F_5 conformation also minimizes steric hindrance between F(22) and F(15). The average of the sum of the angles around N(3) and N(4) in **15** is 355.6 and 359.9°, respectively, which is comparable with the value of 359.9° for the equatorial nitrogens in **14b**. By contrast, the sum of the angles around N(2) in **15** is 342.2° for this more pyramidal nitrogen. The larger sum of the C-N-C angles around the axial nitrogen N(1) in **14b** (335.8°) compared with the same nitrogen in **15** (329.5°) is somewhat surprising in view of the longer transannular bond in **15**.

Nmr spectral features. ^{29}Si NMR chemical shifts are a reflection of the degree of transannular interaction in azasilatranes, and they generally move to lower field on stretching the transannular bond.[4] From Table VI it is seen

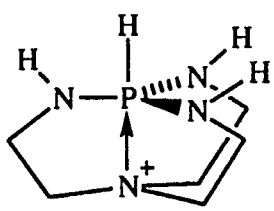
Table VI. Solution ^{29}Si Chemical Shifts of Azasilatranes.[a]

compound	Z	$\delta^{29}Si$ (ppm)	compound	Z	$\delta^{29}Si$ (ppm)
14b	F	-99.7	**2a**	NH_2	-74.5
7a	Cl	-82.2	**2b**	NH_2	-85.1
7b	Cl	-87.2	**3a**	NMe_2	-72.6
29a	OMe	-82.5	**3b**	NMe_2	-51.4
29b	OMe	-88.6	**26**	$CH_2C_6H_5$	-37.7
30a	OEt	-82.9[b]	**4b**	NEt_2	-37.9
30b	OEt	-88.3	**5b**	*i*-Pr_2N	-30.6
31b	*i*-PrO	-74.3	**6a**	$N(SiMe_3)_2$	-65.3
32b	*t*-BuO	-68.5	**6b**	$N(SiMe_3)_2$	-71.2
12a	Ph	-77.2[c]	**1a**	H	-81.0
13a	C_6F_5	-84.2	**1b**	H	-62.4
12b	Ph	-44.4	**8a**	Me	-68.3
13b	C_6F_5	-69.9	**8b**	Me	-70.8[d]
15	C_6F_5	-70.6	**9a**	*n*-Bu	-65.3
			9b	*n*-Bu	-40.9

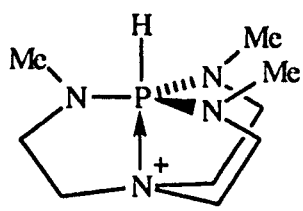
[a]All chemical shifts are recorded in C_6D_6 except where indicated. [b]In $CDCl_3$ (Ref. 4). [c]In $CDCl_3$ (Ref. 35). [d]In $CDCl_3$ (Ref. 36).

that electronegative apical Z groups such as halide and OR result in $\delta^{29}Si$ values in the -80 to -100 ppm range for azasilatranes of both types **A** and **B**. $\delta^{29}Si$ for **31b** falls about 15 ppm below its lower homologues **29b** and **30b**, and **32b** falls about 20 ppm lower, possibly owing to steric hindrance which stretches the transannular bond. Such steric congestion could also be operative in the 33 ppm shift to lower field from **12a** to **12b** and the 14 ppm shift in the same direction from **13a** to **13b**, although both $\delta^{29}Si$ values for these compounds are at higher field relative to their phenyl-substituted analogues **12a** and **12b**, respectively, owing to the more electronegative nature of the C_6F_5 group which strengthens the transannular interaction.

It is interesting that relatively small electronegative Z groups such as Cl, OMe, NH_2 and CH_3 cause upfield shifts from compounds of type **A** to their **B** analogues. This phenomenon may be associated with increased steric congestion in **B**-type compounds which stretches the Z–Si bond, thereby augmenting the (δ-)Z-Si(δ+) bond polarity and hence strengthening the transannular N→Si interaction. The exception to this observation is Z = H for which $\delta^{29}Si$ seems anomalously upfield (by 19 ppm) for the **A**-type compound **1a** compared with **1b**. A similar phenomenon was observed in our laboratories for cations **43** (-42.9 ppm) and **44** (-10.1 ppm) in which the shift



43



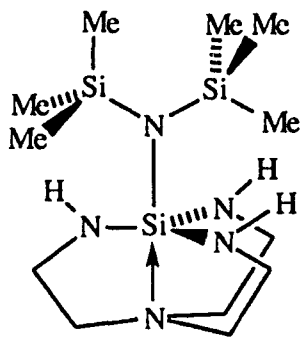
44

difference was even larger.[34] This was attributed to smaller orbital charge imbalance terms in the paramagnetic shielding equation leading to pronounced shielding and greater orbital charge balance for **43** compared with **44**. The same argument can be used to account for the greater shielding (by 19 ppm) of the ^{29}Si nucleus in **1a** over **1b**. It is remarkable that the solution $\delta^{29}Si$ value for the tetrafluorobenzyne insertion product **15** (-70.6 ppm) is almost identical with that of its precursor **13b** (-69.9 ppm). This result is taken to suggest that the length and strength of the transannular bond in these two compounds is very similar in the solution state. However, it must be noted that the solid state ^{29}Si NMR chemical shift for **15** (-62.8 ppm) indicates considerably weaker transannular bonding in the solid state. It is interesting that $\delta^{29}Si$ in solution progresses quite monotonically with increasing temperature from -77.9 ppm at -67.5 °C to -66.1 ppm at 80.0 °C (see Experimental). This result also supports our hypothesis that the N→Si transannular bond is strengthened by solvent forces.

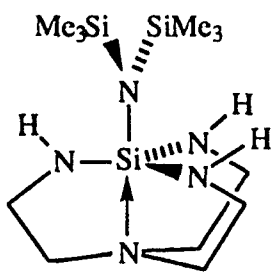
It is also observed from the data in Table VI that R groups larger than H or Z groups of type NR_2 produce increasingly downfield shifts from **A**-type compounds to their **B**-type counterparts, again reflecting the greater weakening of the transannular bond owing to steric congestion. This is also seen in the 7 ppm shift to lower field from **4b** to **5b**. While the downfield shift from **4a** to **6a** is expected on steric grounds, the upfield shift from **4b** (or **5b**) to **6b** is not. The reason for this is not presently obvious. It may be associated with a dominance of an electronegative sigma bond behavior of the $(Me_3Si)_2N$ group owing to pi delocalization of the nitrogen lone pair into the silicon

orbitals of the Me_3Si groups which is accentuated by sterically induced stretching of the $(Me_3Si)_2N$–Si bond.

The strength of the $(Me_3Si)_2N$–Si axial link in sterically less congested **6a** is apparently sufficient to prevent rotation of this bond at room temperature according to its ^1H and ^{13}C NMR spectra, whereas free rotation of this bond at this temperature is observed for **6b**. Thus **6a** displays two sets of ^1H and two sets of ^{13}C peaks for the $SiNCH_2$, $N(CH_2)_3$ and $N(SiMe_3)_2$ protons and carbons, respectively. Also observed are two ^{29}Si resonances for the $N(SiMe_3)_2$ silicons. These data are consistent with the Si_2NSiN_3 configuration shown below for **6a** in which the Me_3Si environments are different. This configuration also accounts for the appearance of the ^1H NMR



6a



6a'

spectrum of the cage CH_2 protons, which consists of two virtual triplets representing the AA'XX' spectra of the CH_2CH_2 protons of the unique bridge. In addition there are two complicated by symmetrical multiplets of twice the intensity representing the ABXY patterns of the protons in the two remaining identical CH_2CH_2 bridges. If configuration **6a'** were to be favored

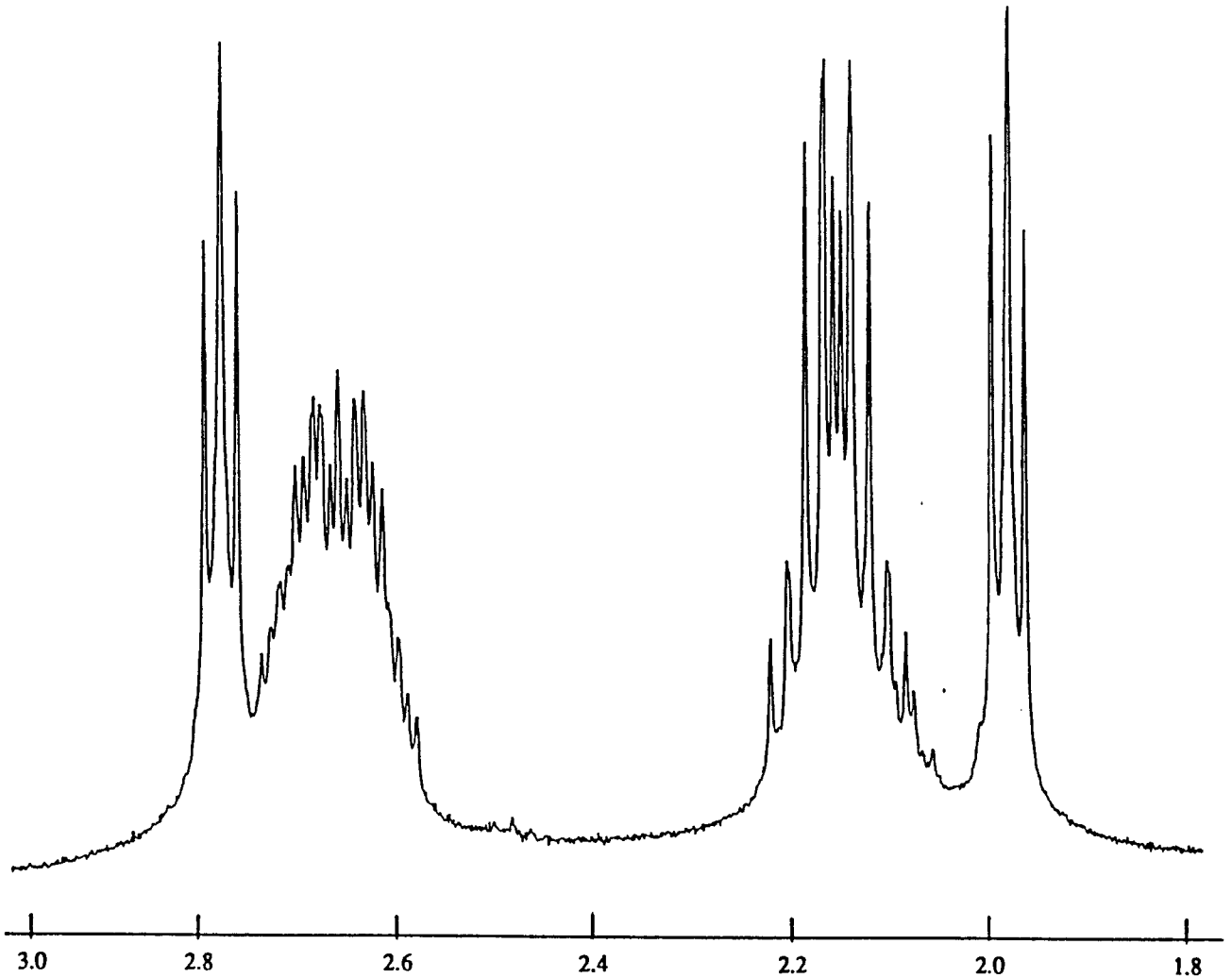


Fig. 4. ^{1}H NMR spectrum for the methylene groups of **6a**.

for this framework, the Me_3Si environments would be identical. An advantage of the former structure shown for **6a** is that, according to Dreiding models, a staggered conformation for the Me groups is permitted by the staggering of the three of the methyls with the hydrogens on the equatorial methyls. These models also show that structure **6a'** would tend to force the two sets of silyl methyl groups to be eclipsed. A second advantage of the structure shown for **6a** is that unlike **6a'**, the unhybridized *p*-orbital lone pair on the axial nitrogen is staggered with respect to the equatorial Si–N bonds, and may therefore delocalize lone pair density more effectively into empty orbitals (*d* and or σ*) of the central silicon. The robustness of the pi bonding in **6a** is revealed in its EI mass spectrum in which the base peak still retains this substituent, in contrast to dialkylaminoazasilatranes in this study for which the base peak contains only a cage fragment. Further evidence for the rigidity toward rotation of the axial substituent of **6a** is our failure to observe coalescence of the ^{13}C NMR peaks even at 110 °C in toluene-d_8. By contrast, free rotation was observed in the ^1H and ^{13}C NMR spectra of **6b** down to -40 °C in toluene-d_8. Interestingly, **6b** also displays an EI MS base peak containing an axial substituent. Efforts to obtain crystals of X-ray quality of **6a**, which is a liquid at room temperature, have thus far not been successful.

At -70 °C, the *ortho* and *meta*-fluorines of the axial C_6F_5 substituent of **15** appear as two resonances each (see Experimental Section). The *ortho*-fluorine chemical shifts are more separated (2.2 ppm) to than the *meta*-fluorines (1.0 ppm) owing to the greater difference in local environment of the *ortho*-fluorines in the frozen out structure which is expected to be similar to

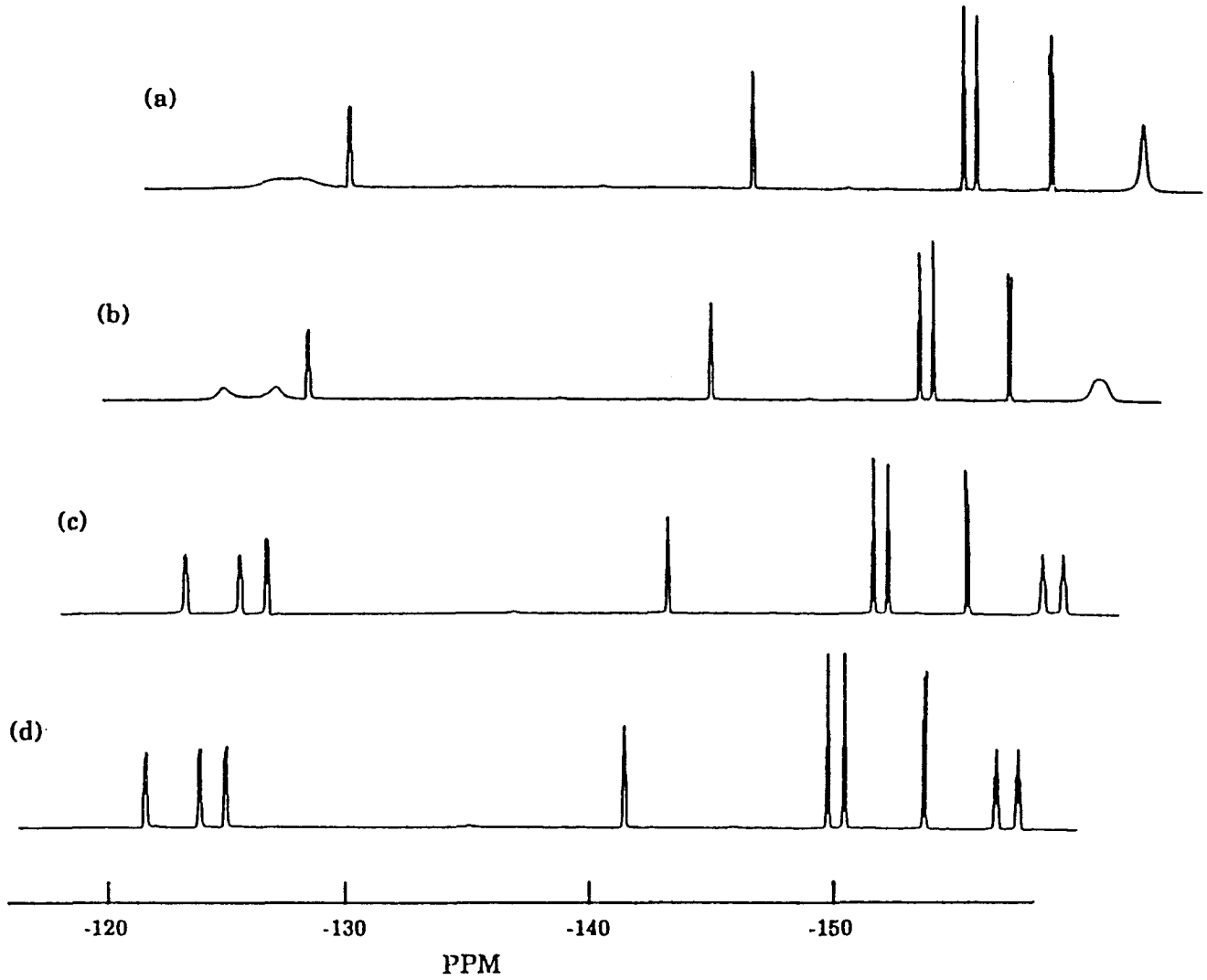


Fig. 5. ^{19}F NMR spectrum of **15** at 50 °C(a), 18 °C(b), 0 °C(c) and -40 °C(d).

that found in the solid state (Figure 2). The coalescence temperature (Figure 5) of the *ortho*-fluorines (36 °C) and the *meta*-fluorines (18 °C) indicate ΔG_{TC}^{*} values of 57.3 and 56.4 kJ/mol,[37] respectively, for the C–Si bond rotation barrier.

The ^{1}H NMR spectrum of **15** is complicated by the diastereotopicity of the hydrogens imposed by the unsymmetrical rigidity of the framework. Not only do all three methyl groups display different chemical shifts, one of them is a doublet (J_{FH} = 1.1 Hz) one is an unresolved multiplet and one is a singlet (see Experimental Section). The former multiplicity may be due to a five-bond F–H coupling involving F(12) and the protons on C(3) (2.840Å) in Figure 2. However, the proximity of these atoms to one another may favor through-space coupling.[38] The broad CH_3 multiplet probably arises from the interaction of proton on C(9) with F(26) and F(15) in **15** (3.039 and 3.044 Å, respectively) (Figure 2). The CH_3 singlet seems best assigned to the protons C(6) which is relatively distant from fluorine atoms in this structure(3.493 Å). The proton-decoupled ^{13}C NMR spectrum of this compound in the methyl region parallels the ^{1}H NMR spectrum in that there is a singlet, a doublet and a multiplet, the latter two resonances undergoing splitting by the nearby fluorines. There are also six singlets in the methylene carbon region, confirming their diastereotopicity in this rigid structure. We have shown that the cage moiety of **15** does not racemize up to 95 °C in toluene-d_8. Using ^{1}H DQF COSY 2DNMR spectroscopy along with a knowledge of the structure of **15**, we were able to correlate the ^{1}H with the ^{13}C chemical shift

Table VII. Correlations of ^{1}H with ^{13}C NMR Chemical Shifts in **15**.

$\delta^{13}C$ (ppm)	$\delta^{1}H$ ppm	carbon atom[a]
	methyl groups	
38.51 (s)	2.14 (s)	C(6)
39.19 (m)	2.56 (m)	C(9)
42.26 (d)	2.60 (d)	C(3)
	methylene groups	
48.34	2.78 (A), 2.25 (A')	C(8)
49.46	2.10 (C), 2.08 (C')	C(5)
51.32	2.60 (D), 2.57 (D')	C(4)
51.87	2.59 (E), 2.44(E')	C(2)
55.87	1.79 (B), 1.73 (B')	C(7)
57.57	1.70 (F), 1.51 (F')	C(1)

[a]The carbon atom numbering scheme is that shown in Figure 2.

assignments. The two-bond ^{13}C-^{1}H couplings which manifest themselves in the correlation diagram in Figure 6 allow pairs of carbons to be identified for each CH_2CH_2 bridge in the cage portion of **15** (Table VII). The following reasonability argument then allows us to correlate each CH_3 chemical shift with a pair of ethylene carbon shifts. The similarity of the CH_3 and the CH_2CH_2 shifts of **13b**, the precursor of **15**, to one set of the analogous resonances in **15** suggests the correlation shown in Table VII. A second pair

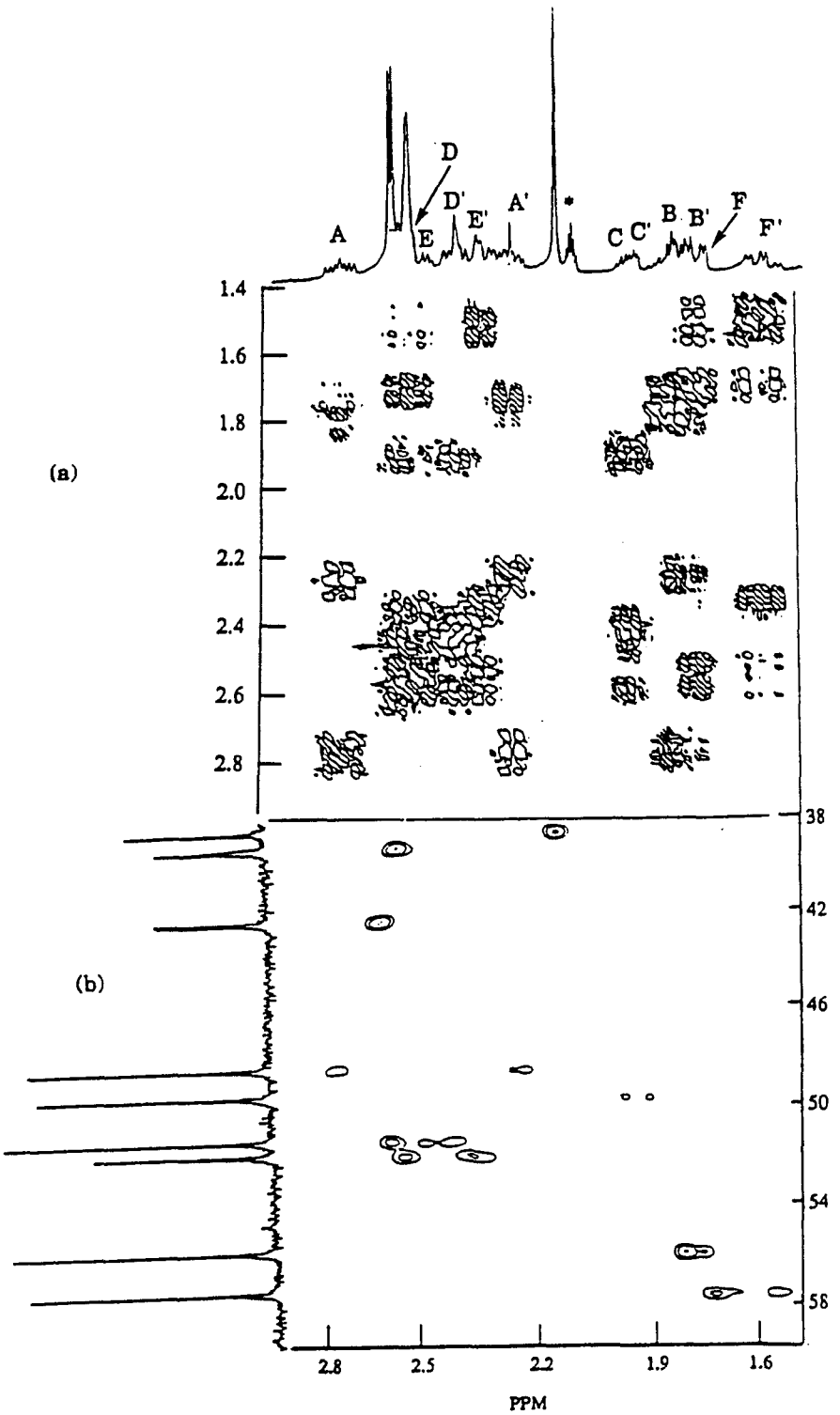


Fig. 6. The 300 MHz ^{1}H-^{1}H DQF COSY 2D NMR spectrum of **15** (a). Pairs of ^{1}H multiplets associated with the same carbon are labeled A, A' or B, B', etc. The asterisk marks residual protons in the $C_6D_5CD_3$ solvent. . The 300 MHz ^{1}H-^{13}C HETCOR 2D NMR spectrum of **15** (b).

of CH_2CH_2 chemical shifts is somewhat different from those in the precursor compound **13b**, and they are associated with the remaining five-membered ring. The substituent methyl group of this ring possesses a carbon whose ^{13}C resonance appears as a multiplet owing to its proximity to F(26) and F(15) in Figure 2 (Table VII). The values of the remaining pair of CH_2CH_2 shifts are relatively different from those in **13b** and are assigned to the CH_2CH_2 portion of the seven-membered ring of **15** which is then correlated with the methyl substituent whose ^{13}C resonance appears as a doublet because of its proximity to F(12).

The ^{19}F chemical shift and $^1J_{SiF}$ value for **14b** (-136.4 ppm) lies somewhat downfield of that reported for **37** (-142.8 ppm[39]) and $^1J_{SiF}$ for **14b** (191.1 Hz) is larger than for **37** (131.2 Hz[39]). The higher ^{29}Si-^{19}F coupling value for **14b** could be taken to suggest the presence of a weaker transannular bond since that would allow the Si–F bond to acquire more *s* character. It should be noted, however, that the shorter transannular bond distance in **14b** contradicts this conclusion. The higher coupling in **14b** is not likely to stem from a greater positive charge on the silicon since the equatorial nitrogens are less electronegative than the equatorial oxygens in **37**. Although the CH_2 $\delta^{13}C$ values are only ca. 1 ppm apart, their assignment is based on the three-bond H_2CNSiF and H_3CNSiF couplings (1.5 and 8.0 Hz, respectively) observed in contrast to the lack of fluorine coupling to the carbon of the $N(CH_2)_3$ moiety. These couplings were assigned using the J-modulated spin-echo (APT) technique.[40] The $\delta^{19}F$ values for **13a** and **13b** are quite similar (see Experimental Section) indicating that any stereoelectronic changes induced

by the change in equatorial substituents and the cage are greatly attenuated at the fluorines.

Mass spectra measured under EI conditions reflect the expected order of Si–Z bond energies, namely, Si–F > Si–O > Si–N > Si–C.[41] Thus Z = F, Cl and OR display molecular ion peaks and in fact this is the base peak for Z = F (**14b**). When Z = NR_2, the molecular ion peak is barely detectable except for Z = $N(SiMe_3)_2$ (**6a**, **6b**) wherein the Si–$N(SiMe_3)_2$ bond may be strengthened by *pi* delocalization (see earlier discussion). When Z = alkyl, the cage moiety cation generally provides the base peak. As expected CI mass spectra consistently display parent ion peaks.

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(18) a) The pK_a values for $HNEt_2$ (11.090) and HN-*i*-Pr_2 (11.13) are within experimental error, while the value for $HNMe_2$ is 10.992 (Peerin, D. D. *Dissociation Constants of Organic bases in Aqueous Solution, Supplement*; Butterworths: London, 1972). b) Since the pK_a of HN-*i*-Pr_2

(35.7) is ten orders of magnitude greater than the value of 25.8 measured for $HN(SiMe_3)_2$ in tetrahydrofuran using lithiated silylamines (Fraser, R. R.; Mansour, T. S.; Savard, S. *J. Org. Chem.* **1985**, *50*, 3232) it is reasonable to pose the overall order shown.

(19) pK_a values measured for carbanions give rise to the order $Ph^- < Me^- < t\text{-}Bu^-$ (43, 48, ~53, respectively; March, J. *Advanced Organic Chemistry*, John Wiley & Sons: New York, 1992). It is plausible to suggest that since the pK_a of the secondary carbanion Me_2CH^- in experiments was 51, and since *n*-Bu^- is more basic than CH_3^- (Dessy, R. E.; Kitching, W.; Psarras, T.; Salinger, R.; Chen, A.; Chiers, T. *J. Am. Chem. Soc.* **1966**, *88*, 46) the order given is reasonable.

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GENERAL SUMMARY

This thesis demonstrates that aminoazasilatranes are accessible via nucleophilic substitution reactions of chloroazasilatranes and various amide anions. The high volatility and exclusive coordination of silicon with five nitrogens in these compounds make them attractive candidates for evaluation as single-source silicon nitride precursors using MOCVD techniques. We also demonstrated interesting reactivities of various azasilatranes and several somewhat unexpected pathways in organosilicon chemistry, i.e.: a benzyne insertion reaction into a Si-N bond of an azasilatrane and hydride and fluoride transfer reactions in competition with nucleophilic substitution reactions at silicon of chloroazasilatranes.

Also observed in this work is a correlation of the ^{29}Si chemical shifts of various azasilatranes with the strength of the transannualr Si<-N bonds, which depends on the overall stereoelectronic environment around the central silicon and the apical group. A small size and high electonegativity of the apical functionalities is usually acompanied by upfield ^{29}Si shifts for the central silicon. This trend is more pronounced in the N,N',N''-trimethylazasilatranes than in the unsubstituted counterpart. ^{1}H, ^{13}C, ^{29}Si, ^{19}F, DQF COSY and ^{1}H-^{13}C HETCOR 2DNMR experiments together with X-ray studies establish the structure of the insertion product as the first example of an azatrane with an expanded arm. A strong transannular bond (2.246 Å) is maintained even in the presence of the seven-membered ring. It

also displays an appropriate geometry for the successful observation of 'through-space' ^{1}H-^{19}F and ^{13}C-^{19}F couplings.

This thesis also reports that azagermatranes can be easily synthesized by transamination reactions between tren or its derivatives and tris-(dimethylamino)germanes. The facile conversion of *t*-butyl-N,N',N''-trimethylazagermatrane in the presence of less sterically hindered tren into *t*-butylazagermatrane compared with the more demanding reaction conditions for the direct transamination between tren and *t*-BuGe(NMe_2)$_3$ suggests that the transmetalation pathway involving the complex exchange of multidentate ligand involves less activation energy than the transamination pathway. The longer transannular Ge<-N bond distances found here in azagermatranes than those in germatranes is consistent with the lower electronegativity of nitrogen than that of oxygen.

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