Hydride and Fluoride Transfer Reactions Accompanying Nucleophilic Substitution at Pentacoordinate Silicon

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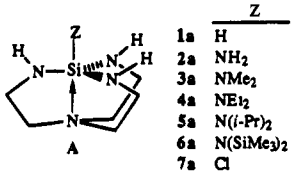
Abstract: The syntheses of aminoazasilatranes of the type $R_2NSi(R'NCH_2CH_2)_3N$ (R′ = H, R = H (**2a**), CH_3 (**3a**), CH_2CH_3 (**4a**), $Si(CH_3)_3$ (**6a**), R′ = CH_3, R = H (**2b**), CH_3 (**3b**), CH_2CH_3 (**4b**), $Si(CH_3)_3$ (**6b**) via nucleophilic substitution reactions of $ClSi(R'NCH_2CH_2)_3N$ (R′ = H (**7a**), R′ = CH_3 (**7b**), respectively) with amide anions are reported. Reactivities of **7a** and **7b** toward other nucleophilic reagents such as alkyllithiums and Group 1 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** predominated along with some nucleophilic substitution products and hydride transfer product $HSi(HNCH_2CH_2)_3N$, **1a**. With **7b**, however, equatorial nitrogen lithiation is precluded and its reaction with nucleophiles can produce substantial amounts of nucleophilic substitution product as well as hydride transfer product $HSi(CH_3NCH_2CH_2)_3N$, **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**), $FSi(CH_3NCH_2CH_2)_3N$ (**14b**), and $C_6F_5Si(CH_3NCH_2CH_2)_2(o\text{-}C_6F_4CH_3NCH_2CH_2)N$ (**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 $p\pi-d\pi$ interaction between a pentacoordinate silicon and a nitrogen. However, the axial moiety in analogue **6b** freely rotates around the apical Si−N bond due to steric interactions with nearby methyl groups on the cage.

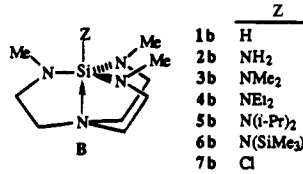
Introduction

As part of our exploration of the chemistry of atranes,[1] we became interested in synthesizing candidates for the MOCVD of metallic and nonmetallic nitrides. In the case of silicon nitride, such volatile precursors are represented by **1a**−**6a** of



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

A



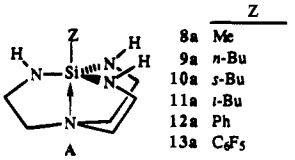
	Z
1b	H
2b	NH_2
3b	NMe_2
4b	NEt_2
5b	N(*i*-Pr)$_2$
6b	$N(SiMe_3)_2$
7b	Cl

B

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 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.

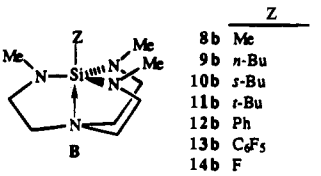
Although **1a**[3] and **1b**[4] have been reported, we here describe improved syntheses for these azasilatranes and the results of our attempts to make the new compounds **2a,b**−**6a,b**. It may be noted here that our earlier attempts to make **3a** and **3b** by the transamination of $Si(NMe_2)_4$ with $(H_2NCH_2CH_2)_3N$ and $(HMeNCH_2CH_2)_3N$, respectively, failed,[4,5] although the former reaction was reported in a patent[6a] 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 hybride 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 might occur giving **8a,b**−**12a,b**, and to what extent such reactions might be accompanied by hydride transfer to give **1a** and **1b**. As we will demonstrate,



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

A



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

B

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.

We also observe that 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** as we briefly described in a recent communication.[6b]

[⊗] Abstract published in *Advance ACS Abstracts*, December 1, 1994.

(1) Verkade, J. G. *Acc. Chem. Res.* **1993**, *26*, 483.

(2) For ease in associating compounds with structure types **A** and **B**, we place a lower case letter corresponding to the structure type with the compound number.

(3) Lukevics, E.; Zelchan, G. I.; Solomennikova, I. I.; Liepinsh, E. E.; Yankovska, I. S.; Mazheika, I. B. *J. Gen. Chem. USSR (Engl. Transl.)* **1977**, *47*, 98.

(4) Gudat, G.; Verkade, J. G. *Organometallics* **1989**, *8*, 2772.

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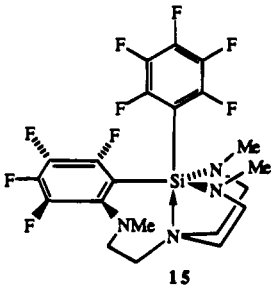
Additional features of these compounds including the NMR spectral behavior of **13b** and **15** as a function of temperature and details of the X-ray crystal and molecular structure studies of **14b** and **15** are also described.



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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. *tert*-Butyllithium, *sec*-butyllithium, lithium dimethylamide, lithium diethylamide, lithium bis(trimethylsilyl)-amide, phenyllithium, and methyllithium were purchased from Aldrich and were used as received. *n*-Butyllithium 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 × 10^{-3} Torr from $LiAlH_4$ upon 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 diisopropylamide was prepared by adding *n*-butyllithium in hexane to excess $(i\text{-}Pr)_2NH$ followed by evaporation of the solvent and unreacted amine.[9] Perfluorophenyllithium was prepared *in situ* by mixing equivalent amounts of pentafluorobromobenzene and *n*-butyllithium 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. ^7Li (116.568 MHz) NMR spectra were referenced[11] to LiOD (4 M solution) in D_2O as an external standard. ^2H (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, AZ. 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 × 10^{-3} mmHg in 90.0% yield (based on tren) (lit.,[4] 72−84% yield): mp 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 ($NHCH_2CH_2CH_2$), 36.52 ($NHCH_2CH_2$); ^{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 reluxed 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 × 10^{-3} mmHg afforded 15.5 g of **1b** 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, NCH_3), 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 (CH_3N); ^{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. 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 temperature. 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 °C 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): ^1H NMR (C_6D_6) 2.55 (dt, 6 H, $HNCH_2CH_2$, $^3J_{HCNH}$ = 2.4 Hz, $^3J_{HCCH}$ = 5.7 Hz), 1.90 (t, 6 H, $HNCH_2CH_2$), 1.41 (b, 3 H, NH); ^1H NMR ($CDCl_3$), 3.07 (t, 6 H, $HNCH_2CH_2$), 2.81 (t, 6 H, $HNCH_2CH_2$), 1.55 (b, 3 H, NH); ^{13}C NMR (C_6D_6) 51.92 ($HNCH_2CH_2$), 37.16 ($HNCH_2CH_2$); ^{29}Si NMR (C_6D_6) −82.18. Although the first two ^1H 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 and ^{29}Si NMR 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.

1-Chloro-*N*,*N*,*N*-trimethylazasilatrane, 7b. Although this compound was prepared earlier in our laboratories,[5] a modified approach

(7) Shriver, D. F.; Drezdon, M. A. *The Manipulation of Air-Sensitive Compounds*; Wiley-Interscience: New York, 1986.

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(9) (a) Amonoo-Neizer, E. H.; Shaw, R. A.; Skovlin, D. O.; Smith, B. C. *Inorg. Synth.* **1966**, *8*, 19. (b) Bush, R. P.; Lloyd, N. C.; Dearce, C. A. *J. Chem. Soc. (A)* **1969**, *253*, 808. (c) Lappert, M. F.; Power, P. P.; Sanger, A. R.; Srivastava, R. C. *Metal and Metalloid Amides*; Ellis Horwood Ltd.: Hemel, Hempstead, UK, 1980.

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(11) (a) Harris, R. K.; Mann, B. E. *NMR and the Periodic Table*; Academic Press: New York, 1978. (b) Jameson, C. J. in *Multinuclear NMR*; Mason, J., Ed., Plenum Press: New York, 1987.

providing purer product is given here. *N*-Chlorosuccinmide (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 × 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 byproduct succinimide, which was removed by sublimation at 46 °C/15 × 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 succinimide:[5] mp 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.,[5] −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.

1-Aminoazasilatrane, 2a. 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 ^{1}H NMR spectrum. By subliming this material at 35 °C/15 × 10^{-3} mmHg, a colorless crystalline form of the product was collected in 92% yield: mp 40−41 °C; ^{1}H 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, $SiHNCH_2CH_2$), 0.83 (br, 3 H, NH), 0.08 (br, 2 H, NH_2); ^{1}H NMR ($CDCl_3$) 2.98 (t, 6 H, $HNCH_2CH_2$, $^3J_{HCCH}$ = 5.7 Hz), 2.64 (t, 6 H, $HNCH_2CH_2N$), 0.95 (very br, s, 3 H, NH); ^{1}H NMR (CD_3CN), 2.87 (t, 6 H, $NHCH_2CH_2$, $^3J_{HCCH}$ = 5.9 Hz), 2.56 (t, 6 H, $NHCH_2CH_2$), 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.

1-Amino-*N*,*N*′,*N*″-trimethylazasilatrane, 2b. 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 ^{1}H 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 × 15 mL portions of pentane. Evaporation of the pentane under vacuum afforded a crystalline solid which upon sublimation at 60 °C and 10 × 10^{-3} mmHg afforded **2b** in 87% yield: mp 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.

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 × 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 × 10^{-3} mmHg: mp 74−75 °C; ^{1}H NMR (C_6D_6) 2.75 (s, 6 H, $(CH_3)_2$), 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, $N(CH_3)_2$), 0.81 (s, 3 H, NH); ^{13}C NMR (C_6D_6) 50.57 ($HNCH_2CH_2N$), 37.67 ($HNCH_2CH_2N$) 41.00 ($(CH_3)_2$); ^{13}C NMR ($CDCl_3$): 50.53 ($HNCH_2CH_2$), 37.13 ($HNCH_2CH_2N$), 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. Calcd for $C_8H_{21}N_5Si$: 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 × 15 mL portions of benzene. A ^{1}H NMR spectrum of the solution revealed the formation of **3b** and **1b** 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 **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, $N(CH_3)_2$), 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. 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 ^{1}H 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 × 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 semisolid in 19% yield: ^{1}H NMR (C_6D_6) 3.07 (q, 4 H, NCH_2CH_3, $^3J_{HCCH}$ = 6.9 Hz), 2.77 (t, 6 H, $HNCH_2CH_2$, $^3J_{HCCH}$ = 5.7 Hz), 2.12 (t, 6 H, $HNCH_2CH_2$), 1.18 (t, 6 H, NCH_2CH_3, $^3J_{HCCH}$ = 6.9 Hz); ^{1}H NMR ($CDCl_3$) 2.96 (t, 6 H, $HNCH_2CH_2$, $^3J_{HCCH}$ = 6.0 Hz), 2.75 (q, 4 H, NCH_2CH_3, $^3J_{HCCH}$ = 6.9 Hz), 2.59 (t, 6 H, $HNCH_2CH_2$), 0.93 (t, 6 H, NCH_2CH_3); ^{13}C NMR ($CDCl_3$) 50.37 ($HNCH_2CH_2N$), 41.75 (NCH_2CH_3), 37.09 ($HNCH_2CH_2$), 16.55 (NCH_2CH_3); ^{29}Si NMR ($CDCl_3$) −75.51; 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^+ − $HNCH_2CH_2$).

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, NCH_2CH_3, $^3J_{HCCH}$ = 7.8 Hz), 2.56 (s, 9 H, CH_3), 2.54 (t, 6 H, $CH_3NCH_2CH_2$, $^3J_{HCCH}$ = 5.7 Hz), 2.40 (t, 6 H, $CH_3NCH_2CH_2$), 1.17 (t, 6 H, NCH_2CH_3); ^{13}C (C_6D_6) 52.13 ($MeNCH_2CH_2$), 51.08 ($MeNCH_2CH_2$), 40.05 (NCH_2CH_3), 36.28 (NCH_3), 15.23 (NCH_2CH_3); ^{29}Si NMR (C_6D_6) −37.92.

Attempted Synthesis of 1-(Diisopropylamino)azasilatrane, 5a. Into an NMR tube was placed a solution of 4 mg (0.04 mmol) of Li-*i*-Pr_2 in 0.4 mL of THF-d_8: ^{1}H NMR 3.02 (h, 2 H, $NHC(CH_3)_2$, $^3J_{HCCH}$ = 6.3 Hz), 0.98 (d, 12 H, CH_3); ^{13}C NMR 52.21 ($NCH(CH_3)_2$), 27.77 ($NCHC(CH_3)_2$). 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: ^{1}H NMR (THF-d_8) for $HN(CH(CH_3)_2)_2$, 2.86 (h, 2 H, $^3J_{HCCH}$ = 6.3 Hz, $CH(CH_3)_2$), 0.98 (d, 12 H, CH_3); ^{13}C NMR (THF-d_8), 45.85 ($CH(CH_3)_2$), 23.86 (CH_3).

1-(Diisopropylamino)-*N*,*N*′,*N*″-trimethylazasilatrane, 5b. Compound **7b** (24 mg, 0.10 mmol) was mixed with 12 mg (0.11 mmol) of Li(*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 **5b** and **1a** formed in a ratio of about 1:2. ^{1}H 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 ($NCH(CH_3)_2$), 14.52 ($NCH(CH_3)_2$); ^{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 ^{1}H NMR spectrum. THF was removed under vacuum and the residue was extracted with 4 × 10 mL of benzene. Evaporation of the volatiles under vacuum and slow distillation at 60°/10 × 10^{-3} mmHg afforded the colorless liquid product in 50% yield: ^{1}H NMR (C_6D_6) 2.81 (t, 2 H, $SiNCH_2CH_2$, $^3J_{HCCH}$ = 5.4 Hz), 2.69 (m, 4 H, $HNCH_2CH_2$), 2.15 (m, 4 H, $HNCH_2CH_2$), 1.97 (t, 2 H, $SiNCH_2CH_2$, $^3J_{HCCH}$ = 5.4 Hz), 0.82 (b, 3 H, HN); 0.31 (s, 9 H, $Si(CH_3)_3$), 0.28 (s, 9 H, $Si(CH_3)_3$); ^{13}C NMR (C_6D_6 at 20 °C) 56.17 (1C, $HNCH_2CH_2N$), 53.59 (2C, $NHCH_2CH_2N$), 42.33 (1C, $HNCH_2CH_2$), 38.46 (2C, $HNCH_2CH_2$), 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, $HNCH_2CH_2N$), 54.50 (2C, $HNCH_2CH_2N$), 42.95 (1C, $HNCH_2CH_2N$), 38.99 (2C, $HNCH_2CH_2$), 2.79 (3C, $Si(CH_3)_3$), 2.55 (3C, $Si(CH_3)_3$); ^{29}Si NMR (C_6D_6) −65.29 (SiN_5), 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, $M^+ - CH_2CHNCH_2$), 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*″-trimethylazasilatrane, 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 × 10^{-3} mmHg: ^{1}H NMR (C_6D_6) 2.71 (s, 9 H, NCH_3), 2.65 (t, 6 H, $CH_3NCH_2CH_2$, $^3J_{HCCH}$ = 5.8 Hz), 2.18 (t, 6 H, $CH_3NCH_2CH_2$), 0.25 (s, 18 H, $Si(CH_3)_3$); ^{1}H ($CDCl_3$ at 20°), 2.81 (t, 6 H, $CH_3NCH_2CH_2$, $^3J_{HCCH}$ = 5.8 Hz), 2.64 (t, 6 H, $CH_3NCH_2CH_2$), 2.50 (s, 9 H, NCH_3), 0.14 (s, 18 H, $Si(CH_3)_3$); ^{1}H ($CDCl_3$ at −55°), 2.78 (t, 6 H, $CH_3NCH_2CH_2$), 2.49 (s, 9 H, NCH_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 ($Si(CH_3)_3$); ^{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 (SiN_4), 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 × 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 × 10^{-3} mmHg to give a 26% yield of **8a**. The spectroscopic data are consistent with the literature values.[4]

Attempted Synthesis of 1,*N*,*N*′,*N*″-tetramethylazasilatrane, 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 ^{1}H 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 × 10^{-3} mmHg.

Method B. The aforementioned procedure was repeated in the presence of 2 mol equiv of TMEDA (tetramethylethylenediamine) and the solution was refluxed for 24 h. The ^{1}H NMR spectrum revealed only **7b** 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 0.5 h. The solvent was evaporated under vacuum and the residue was extracted with 3 × 20 mL portions of pentane. Removal of pentane under vacuum and sublimation of the solid residue at 56 °C/11 × 10^{-3} mmHg gave 0.032 g of **9a** in 14% yield: ^{1}H NMR (C_6D_6) 2.74 (dt, 6 H, $HNCH_2CH_2N$, $^3J_{HNCH}$ = 2.7 Hz, $^3J_{HCCH}$ = 5.85 Hz), 2.15 (t, 6 H, $HNCH_2CH_2$), 1.49 (b, 6 H $-CH_2CH_2CH_2$), 1.02 (t, 3 H, CH_3); ^{13}C (C_6D_6) 50.54 ($HNCH_2CH_2N$), 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, $M^+ - Bu$), 57.0 (16.11, Bu^+), 149 (22.5), 116.1 (87.2); HMRS 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 0.5 h. The toluene was removed under vacuum and the residue was extracted with 4 × 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, $CH_2CH_2CH_3$), 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-*sec*-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 × 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, $^3J_{HCCH}$ = 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 carbons).

Attempted Synthesis of 1-*sec*-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 **10b**: ^{1}H NMR (C_6D_6) 2.46 (t, 6 H, $^3J_{HCCH}$ = 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-*tert*-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, HNCH_2CH$_2$), 2.09 (t, 6 H, HNCH$_2$CH_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$_3$)$_3$).

Attempted Synthesis of 1-*tert*-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 exclusive **1b** and isobutene: ^{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-Phenylazasilatrane, 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 of 0.24 M PhLi in ether/cyclohexane 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 solvents, a muddy solid resulted which contained some **12a** as shown by the ^{1}H and ^{13}C NMR resonances of the cage moiety: ^{1}H NMR (C_6D_6) 2.74 (dt, 6 H, HNCH_2CH, $^3J_{HNCH}$ = 2.4 Hz, $^3J_{HCCH}$ = 5.7 Hz), 2.15 (t, 6 H, HNCH$_2$CH_2); ^{13}C NMR (C_6D_6) 51.12 (HNCH$_2$CH$_2$N), 37.16 (HN*C*H$_2$CH$_2$); 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** of 5 mL of toluene was added 0.70 mL of a 1.5 M (1.1 mmol) solution of PhLi in ether/cyclohexane. The reaction mixture was refluxed for 0.5 h. After filtration and removal of the solvent under vacuum, **12b** was sublimed in 96% yield: mp 60−62 °C; ^{1}H 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$_2$CH_2); ^{13}C NMR (C_6D_6) 136.60, 129.00, 127.81, 127.44 (C_6H_5), 50.51 (CH$_3$NCH$_2$*C*H$_2$N), 50.45, (CH$_3$N*C*H$_2$CH$_2$), 38.08 (CH$_3$N); ^{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 (0.080 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 minutes later a ^{1}H NMR spectrum of the solution showed exclusive conversion of **7b** to **12b**.

1-(Perfluorophenyl)azasilatrane, 13a. Although the full preparation and characterization of this compound was reported earlier by us,[6b] the attempt to synthesize it by a different route is described here (see also Discussion). 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. Although the preparation and characterization of this compound was described earlier by us,[6b] the additional data which follow are important to the Discussion: ^{29}Si NMR (C_6D_6) (temperature) −69.94 (50 °C), −70.94 (20 °C), −71.76 (10 °C); LRMS (70 ev, EI) *m/z* (relative intensity, proposed ion), 380.0 (100.0, M$^+$), 336.0 (56.0, M$^+$ − CH$_6$N), 324.2 (25.3), 295.3 (18.8), 281.3 (12.1), 213 (8.3, M$^+$ − C_6F_5).

1-Fluoro-*N,N',N''*-trimethylazasilatrane, 14b, and the Tetrafluorobenzyne Insertion Product 15. Although the preparation and characterization of these compounds from the same reaction was reported by us earlier,[6b] additional characterization data important to the Discussion are presented here.

(12) Machazashvili, A. A.; Shklover, V. E.; Struchkov, Y. T. *J. Organomet. Chem.* **1988**, *349*, 23.

Additional characterization for **14b**: LRMS (70 ev, EI) *m/z* = (relative intensity, proposed ion) 232.2 (100, M$^+$), 188.1 (86.1, M$^+$ − CH$_3$NCH$_2$CH$_2$); HRMS for M$^+$ ($C_9H_{21}FN_4Si$) calcd 232.15195, found 232.15201.

Additional characterization for **15**: ^{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, $^5J_{CF}$ = 7.0 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, $^5J_{FC}$ = 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).

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$_2$$C_6H_5$ in 20 mL of toluene and the mixture was refluxed for 0.5 h. After filtration and removal of the solvent, the residue was extracted with 3 × 15 mL portions of pentane. Evaporating the pentane under vacuum gave **26** as a liquid in 84% yield: ^{1}H NMR (C_6D_6) 7.45 (d, 2 H, $^2J_{HH}$ = 7.2 Hz, *m*-H), 7.23 (t, 2 H, $^2J_{HH}$ = 7.8 Hz, *o*-H), 7.09 (t, 1 H, *p*-H), 2.51 (t, 6 H, $^3J_{HCCH}$ = 5.4 Hz, CH$_3$NCH_2CH$_2$), 2.46 (s, 9 H, NCH$_3$), 2.28 (t, 6 H, CH$_3$NCH$_2$CH_2), 2.14 (s, 2 H, C$H_2$$C_6H_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.

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 × 15 mL of pentane. Removal of pentane under vacuum afforded solid **29a** in 85% yield. ^{1}H 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$_2$CH_2); ^{1}H 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$_2$CH_2); ^{13}C NMR ($CDCl_3$) 57.70 (OCH$_3$), 50.51 (HNCH$_2$*C*H$_2$), 37.02 (HN*C*H$_2$CH$_2$); ^{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 **29b**. 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 × 10 mL of pentane. Removal of pentane under vacuum followed by sublimation at 55 °C/15 × 10^{-3} mmHg gave the crystalline product in 85.3% yield: ^{1}H NMR (C_6D_6) 3.76 (s, 3 H, OCH$_3$), 2.95 (s, 9 H, NCH$_3$), 2.67 (t, 6 H, CH$_3$NCH_2CH$_2$, $^3J_{HCCH}$ = 5.7 Hz), 2.05 (t, 6 H, CH$_3$NCH$_2$CH_2); ^{13}C NMR (C_6D_6) 51.35 (OCH$_3$), 48.25 (CH$_3$NCH$_2$*C*H$_2$), 47.80 (CH$_3$N*C*H$_2$CH$_2$), 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$_3$H$_6$, 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$_4$Si) 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 × 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, 2 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, 3 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 ^1H 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 × 10 mL of pentane. After evaporation under vacuum, the clear liquid product was obtained in 80% yield: ^1H 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-*tert*-Butoxy-*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 × 10 mL portions of pentane. After evaporation under vacuum, the product remained as a liquid in 86% yield: ^1H 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 flame-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 flame-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 for $Si(NMe_2)_3NEt_2$ (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 flame-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 flame-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.

Table 1. 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 × 0.35 × 0.09	0.22 × 0.16 × 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	Cu Kα (λ = 1.54178 Å)	Cu Kα (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
scan type	$\omega-2\theta$	$2\theta-\theta$
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_{int} (%)	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 Å^{-3})	0.225 e Å^{-3}	0.24 e Å^{-3}
largest hole (e Å^{-3})	−0.220 e Å^{-3}	−0.21 e Å^{-3}
R (%)^b	3.48	3.21
R_w (%)^c		4.66
R^2_w(%)^d	9.26	
GOF^e	1.130	2.10

^{a} $P = (\mathrm{Max}(F_o^2, 0) + 2*F_c^2)/3$. ^{b} $R = \sum||F_o| - |F_c||/\sum|F_o|$. ^{c} $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w(F_o)^2]^{1/2}$. ^{d} $R_w^2 = [\sum[W(F_o^2 - F_c^2)^2]/\sum[W(F_o^2)^2]]^{0.5}$. ^{e} GOF $= [\sum s(|F_o| - |F_c|)^2/(n_{obs} - n_{var})]^{1/2}$.

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 flame-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 1.

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 semiempirical 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

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

atom	x	y	z	U_{eq}[a]
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)

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

Table 3. Selected Bond Distances (Å) and Angles (deg) for **14b**[a]

	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.

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.

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 2 and 3 for **14b**, and Tables 4 and 5 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

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

atom	x	y	z	U_{eq}[a]
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)
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)

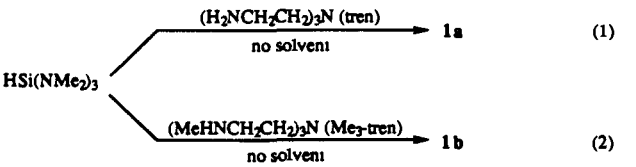
[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table 5. Selected Bond Distances (Å) and Angles (deg) for the Insertion Product **15**[a]

	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.

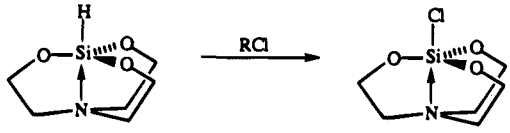
more than 15 years ago,[3] the 51−55 °C melting point of this compound (and presumably its purity) was considerably lower



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-chlorosilatrane (**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



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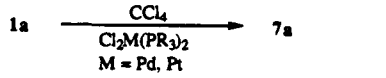
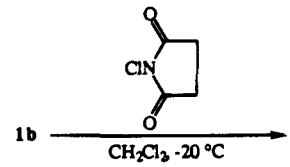


(4)

of **7a**.[4] However, the isolated yield in this reaction was only 30% and substantial insoluble byproduct 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* 10 min) the product yield is doubled (60−70%), it is NMR spectroscopically pure and it is colorless.

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]

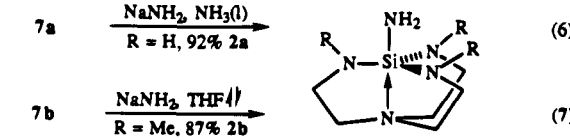
Attempts to carry out reaction 4 with **1b** to prepare **7b** resulted in less than 5% yield of the desired product and large quantities of an intractable red solid at room temperature after only 3 h. Using no catalyst in reaction 4 at room temperature eventually causes **1b** to be consumed, but the 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 reaction 5 which was developed in our laboratories by a previous co-



(5)

worker.[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 byproduct 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 Attempts to Synthesize 5a. The 1-amino compounds **2a** and **2b** are formed in high yields according to reactions 6 and 7. Both compounds



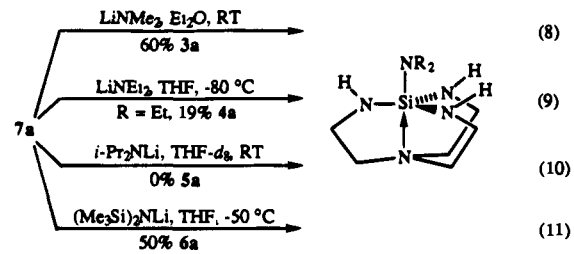
(6) (7)

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 h. 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)



(8) (9) (10) (11)

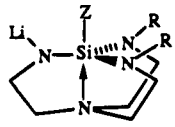
(13) SHELXTL-Plus, Siemens Analytical X-ray Instruments, Inc., Madison, WI.

(14) Sheldrick, G. *J. Appl. Crystallogr.* manuscript in preparation.

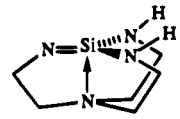
(15) (a) Voronkov, M. G.; Baryshok, V. P.; Petukhov, L. P.; Rakhlin, V. I.; Mirskov, R. G.; Pestunovich, V. A. *J. Organomet. Chem.* **1988**, *358*, 39. (b) Frye, C. L.; Vincent, G. A.; Finzel, W. A. *J. Am. Chem. Soc.* **1971**, *93*, 6805. (c) Voronkov, M. G.; Petukhov, L. P.; Vakulskaya, T. I.; Baryshok, V. P.; Tandura, S. N.; Pestunovich, V. A. *Izv. Akad. Nank SSSR, Ser. Khim.* **1979**, 1665.

(16) Gudat, D.; Verkade, J. G. *J. Am. Chem. Soc.* **1989**, *111*, 8520.

increasingly dominates in reactions 9 and 10. If an intermediate



	Z	R
18	Cl	H
19	CH_3	$SiMe_3$



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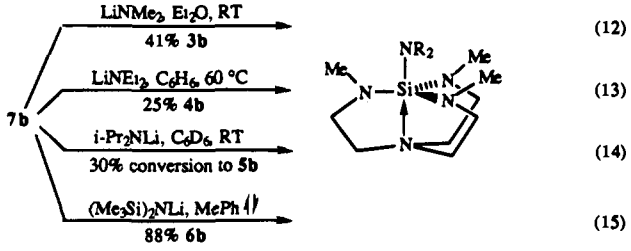
such as **18** is formed, concomitant liberation of the corresponding amine HNR_2 is expected. Indeed, the only species observed in solution is *i*-Pr_2NH in reaction 10. Some support for **18** is gained from our previous isolation of stable **19**.[16] Also formed in reactions 8–10 is a precipitate which may be a polymeric form of **20** created *via* concerted LiCl elimination from **18** to form unstable **20**, or by nucleophilic attack of the anion of **18** on **7a**. Although silaimines are known, the Si=NR 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=$NSi(t\text{-}Bu)_3$).[17] In any case, it is clear that deprotonation of **7a** becomes more competitive with nucleophilic chloride displacement from this molecule by these amides whose basicities lie in the order $^-N(SiMe_3)_2 < ^-NMe_2 < ^-NEt_2 \leq ^-N\text{-}i\text{-}Pr_2$.[18] Interestingly, when reaction 9 was carried out at room temperature, ^1H NMR spectroscopic monitoring revealed quantitative $HNEt_2$ formation and no **4a**, in analogy to reaction 10 wherein HN-*i*-Pr_2 was quantitatively observed to form. 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



(12)

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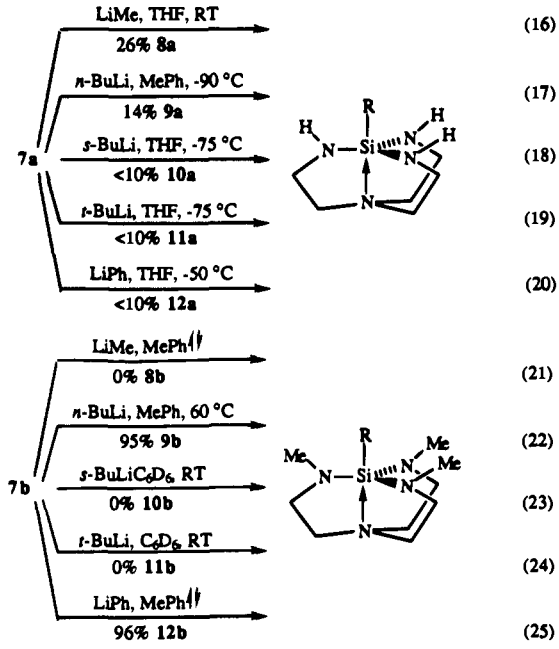
(14)

(15)

in **7b**, deprotonation/lithiation cannot be the cause of the poor yields of **3b**, **4b**, and **5b**. These results and the seemingly oddly high yield of **6b** will be addressed in a later section.

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^- > 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 presumably the smaller Me^- in reaction 21 gives only unreacted starting material even after 24 h of refluxing the



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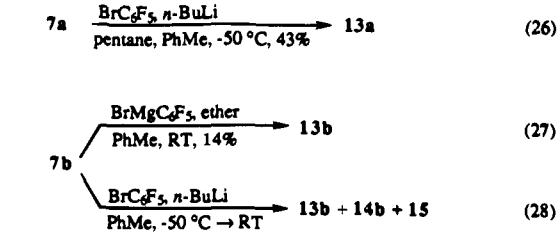
reaction mixture in the presence of $Me_2NCH_2CH_2NMe_2$ (TMEDA) as a lithium complexing agent. Reaction 21 starkly contrasts reaction 16 in which a 26% yield of its analogue **8a** was isolated despite competitive deprotonation/lithiation. We tentatively attribute this result to insufficient ionization 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



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(28)

$BrMgC_6F_5$ in ether at room temperature provided an almost quantitative conversion of the Grignard reagent to HC_6F_5, presumably from metalation 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 that contained about 90% pure **14b**. Repeated sublimation of this fraction at 35 °C/15 × 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.

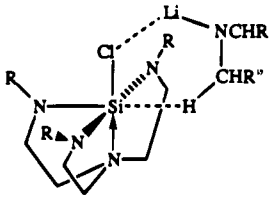
Hydride Transfer Reactions. Except for the transformation of **7b** to **6b** by $LiN(SiMe_3)_2$ in 88% yield in reaction 15, the analogous reactions 12–14 produced mediocre yields of the corresponding amides **3b**–**5b**. By monitoring reactions 12–14 with ^1H NMR spectroscopy, it was observed that the ratios of the amidated to hydrogenated product (**1b**) were ap-

(17) Wiberg, N.; Schurz, K.; Reber, G.; Müller, G. *J. Chem. Soc. Chem. Commun.* **1986**, 591.

(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 10 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 in cyclohexylamine 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.

proximately 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 increases in size. Four lines of evidence make



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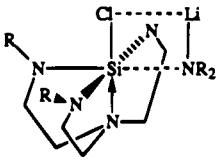
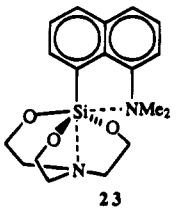


22

this suggestion plausible. (1) Imines such as $Me_2HCN{=}CMe_2$ produced in reaction 14 are known.[20] (2) The addition of the Li^+ complexing agent TMEDA to these reaction substantially suppresses the rates of hydride transfer and nucleophilic substitution, presumably because formation of the six and four-centered intermediates **21** and **22**, respectively, is inhibited. (3) Reaction 15 gives a high yield of amide substitution product **6b** owing to the lack of a proton on a carbon α 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,[21] **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 interaction.[22]



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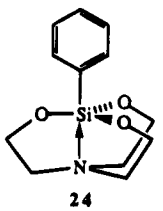
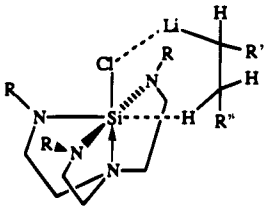


24

The transannular 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 three diastereomers, namely, **25a** (R′ = Et, R″ = H), **25b** (R′ = H, R″ = Et) and **25c** (R′ =



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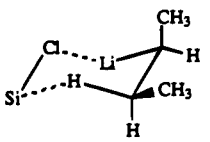
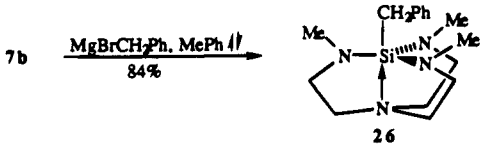


R″ = Me). In the presence of the more sterically hindered **7b**, *s*-BuLi apparently favors the formation of **25a** (R = Me) at the expense of **25c** (R = Me). Stereoisomer **25b** (R = Me) would be disfavored by steric interactions of the R″ = Et and R = Me groups. The 1.5:1 *Z* to *E* ratio of 2-butenes in reaction 23 also becomes understandable if the six-membered ring in **25c** adopts a conformation approximating the one shown above. Such a conformation for **25c** (R = Me) dominates if the methyl group on the carbon β 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 α 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.

It may be noted that all of the rates of these reactions are significantly inhibited in the presence of TMEDA. 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 ^1H NMR spectroscopy after refluxing a toluene solution of **9b** for 2 h. Consistent with the desirability of a proton on the carbon β to the lithium in the LiR reagent is the lack of **1b** as a product in reaction 29 and the high yield of **26**.



(29)

26

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** may be present, which weakens the LiO−Si bond while simultaneously opening a sixth coordination site on 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**.

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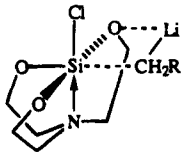
(21) Pawlenko, S. in *Houben-Weyl*, Bd XIII/5; George Thieme Verlag: Stuttgart, 1980, s. 227f.

(22) Carré, F.; Cerveau, G.; Chuit, C.; Corriu, R. J. P.; Nayyar, N. K.; Reyé, C. *Organometallics* **1990**, *9*, 1989.

(23) Cerveau, G.; Cuit, C.; Corriu, R. J. P.; Nayyar, N. K.; Reyé, C. *J. Organomet. Chem.* **1990**, *389*, 159.



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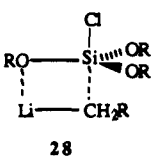

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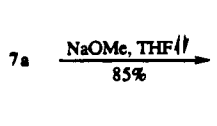
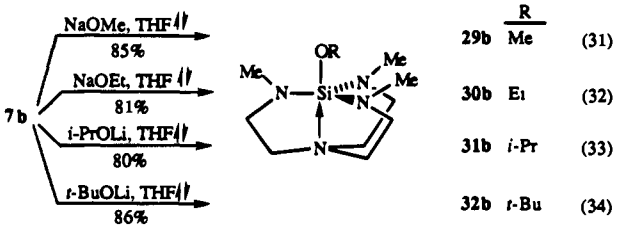
We have not observed hydride transfer products in reactions 30–34. This result is attributable to the great strength of the

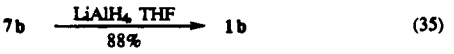


(30)



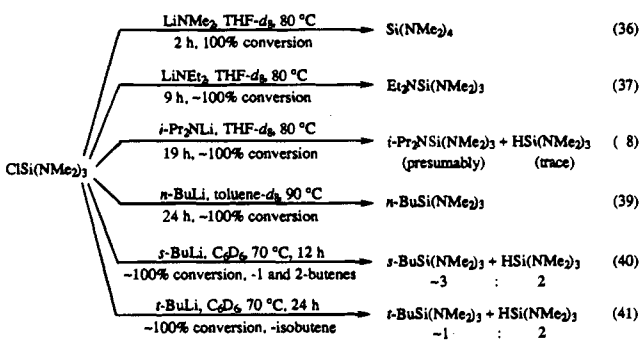
(31)–(34)

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 30–32, reactions 33 and 34 would appear to be ideally set up for producing **1b** accompanied by the elimination of acetone. The fact that these products are not observed supports the dominant role of Si–O bond formation. As is perhaps expected, hydride transfer readily occurs from $LiAlH_4$ in reaction 35. Not surprisingly, **7a** in the presence of $LiAlH_4$ evolved hydrogen owing to the formation of aluminum bonds to the equatorial nitrogens.



(35)

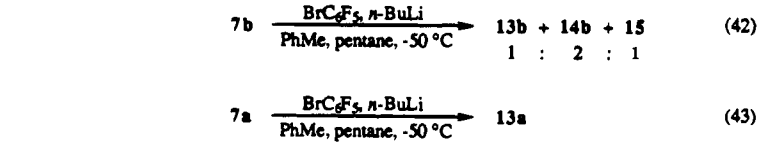
Compared with **7a** and **7b**, the acyclic four-coordinate analogue $ClSi(NMe_2)_3$ reacts more sluggishly with $LiNR_2$ and LiR, requiring higher temperatures and longer times (reactions 36–41). This observation corroborates earlier work indicating



(36)–(41)

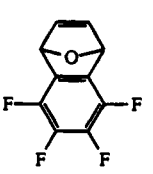
the lower reactivity of four-coordinate silicon species compared with five-coordinate analogues.[24a–c] It should be mentioned here that halosilanes have been observed to undergo reduction as well as alkylation in the presence of *t*-BuLi[24d] and sterically hindered Grignard reagents.[24e]

A Fluoride Transfer Reaction. Because of the substantial strength of the Si–F bond (565 kJ/mol[25]) the reactions of LiC_6F_5 with **7a** and **7b** were carried out. Indeed the dominant product in reaction 42 is the fluoride transfer species **14b**. By contrast, reaction 43 gives only the perfluorophenylated product **13a**.



(42)–(43)

Reaction 42 also produces the tetrafluorobenzyne insertion product **15**, which is rather surprising 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 ^{1}H, ^{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



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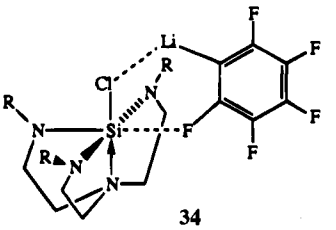
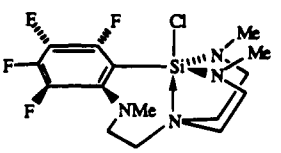


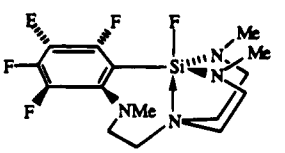
34

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 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 was observed. Even when



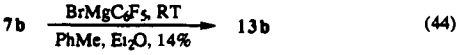
35b



36b

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 $BrMgC_6F_5$ is stable up to 80 °C,[26] it is not



(44)

surprising that the tetrafluorobenzyne insertion 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. It is conceivable that 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 decomposition reaction 45. We did observe such a reaction as a minor pathway in the EI mass spectrum of **13b**. However, no evidence for decomposition was observed in a toluene solution of **13b** from room temperature to 100 °C.

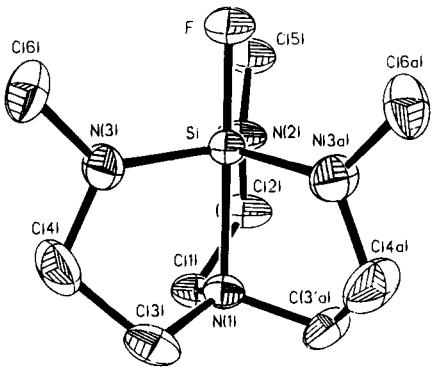
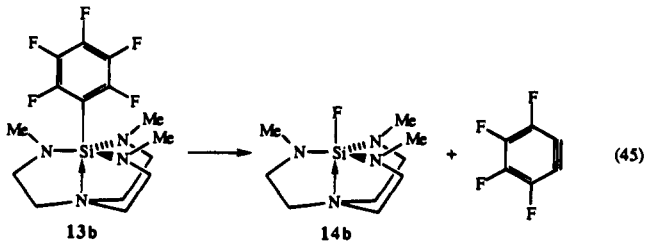
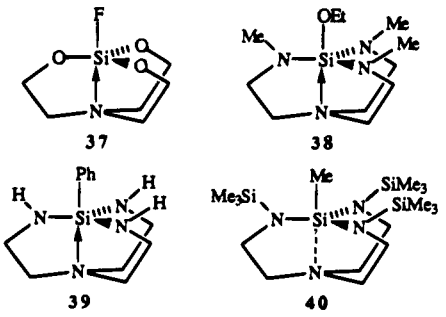


Figure 1. ORTEP drawing of **14b**. Ellispoids are drawn at the 50% probability level.



Molecular Structures of 14b and 15. It is interesting that the N→Si transannular bond length of 2.034 (2) Å in **14b** (Figure 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]),[26] which may be expected from 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]).

Despite the expansion of one of the five-membered rings in **13b** by tetrafluorobenzyne insertion, the N→Si transannular bond is preserved in **15** (Figure 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 it is shorter than that observed in **40** (2.775 (7) Å[16]) in which this interaction is stretched by steric

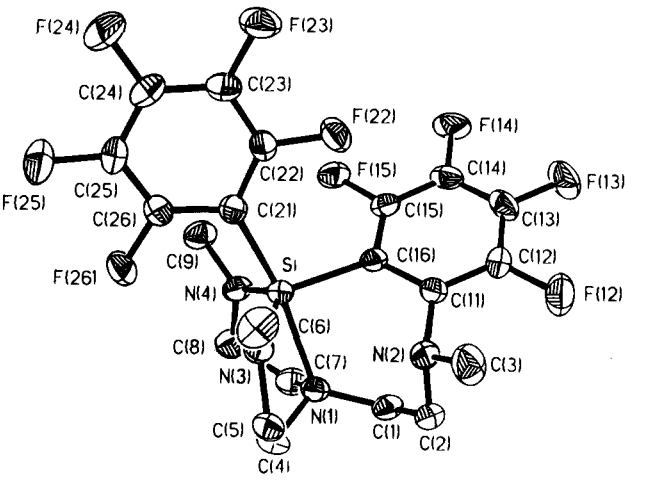
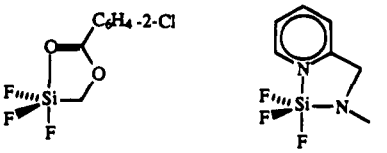


Figure 2. ORTEP drawing of **15**. Ellispoids are drawn at the 50% probability level.



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]).

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 Figure 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 azasila-

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(31) Schomburg, D.; Krebs, R. *Inorg. Chem.* **1984**, *23*, 1378.

(32) Schomburg, D. *J. Organomet. Chem.* **1981**, *221*, 137.

(33) Bondi, A. *J. Phys. Chem.* **1964**, *68*, 441. It should be recognized, however, that at least three lower values down to 2.69 Å have been proposed for this distance (Klaebe, G. *J. Organomet. Chem.* **1985**, *293*, 147).

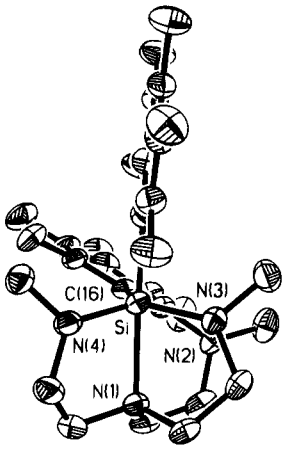


Figure 3. ORTEP drawing of **15** showing the conformation of the axial C_6F_5 ring relative to the C_6F_4 moiety in the seven-membered ring.

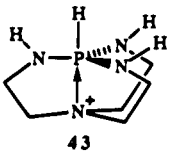
Table 6. Solution ^{29}Si Chemical Shifts of Azasilatranes[a]

compound	Z	δ ^{29}Si (ppm)	compound	Z	δ ^{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	**4a**	NEt_2[b]	−75.5
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).

tranes, and they generally move to lower field on stretching the transannular bond.[4] From Table 6 it is seen that electronegative apical Z groups such as halide and OR result in δ ^{29}Si values in the −80 to −100 ppm range for azasilatranes of both types **A** and **B**. δ ^{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 δ ^{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 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



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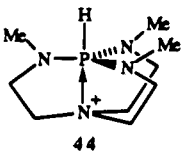
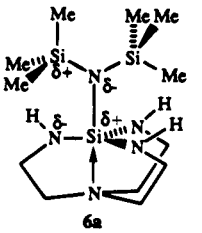


44

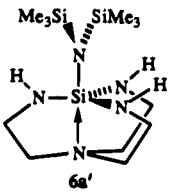
can be used to account for the greater shielding (by 19 ppm) of the ^{29}Si nucleus in **1a** over **1b**. It is remarkable that the solution δ ^{29}Si value for the tetrafluorobenzyne insertion product **15** (−70.6 ppm) is almost identical with that of its precursor **13b** (−69.9 ppm). This result 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 δ ^{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 Section). 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 6 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 σ bond behavior of the $(Me_3Si)_2N$ group owing to π 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



6a



6a′

accounts for the appearance of the ^1H NMR 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 (Figure 4). In addition there are two complicated but 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 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

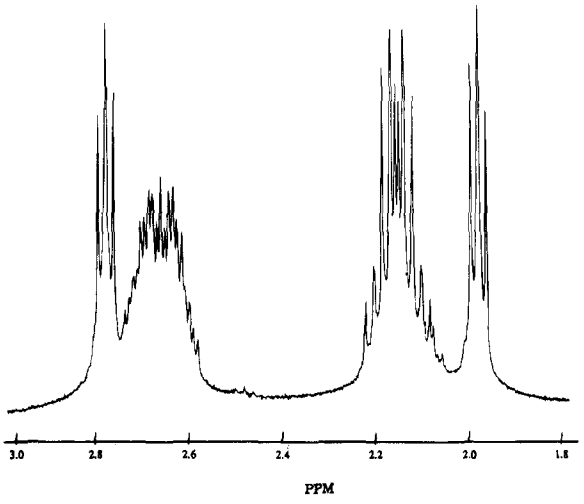


Figure 4. ^{1}H NMR spectrum of the cage moiety of **6a**.

two sets of silyl methyl groups into an eclipsed conformation. A second stabilizing force favoring **6a** over **6a′** is the head-to-tail arrangement of the bond dipoles as shown in **6a**. A third advantage of the structure shown for **6a** is that unlike **6a′**, the unhybridized *p*-orbial 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* or σ^*) on the central silicon. The robustness of the π bonding in **6a** is revealed in its EI mass spectrum in which the base peak still retains this substituent, in contrast to (dialkylamino)-azasilatranes 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 ^{1}H 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, each of the *o*- and *m*-fluorines of the axial C_6F_5 substituent of **15** appear as two resonances each (see Experimental Section). The *o*-fluorine chemical shifts are more separated (2.2 ppm) than the *m*-fluorines (1.0 ppm) owing to the greater difference in local environment of the *o*-fluorines in the frozen out structure which is expected to be similar to that found in the solid state (Figure 2). The coalescence temperature (Figure 5) of the *o*-fluorines (36 °C) and the *m*-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, but 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) 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 protons on C(9) with F(26) and F(15) in **15** (Figure 2). The CH_3 singlet seems best assigned to the protons on C(6) which are relatively distant from fluorine atoms in this structure. 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

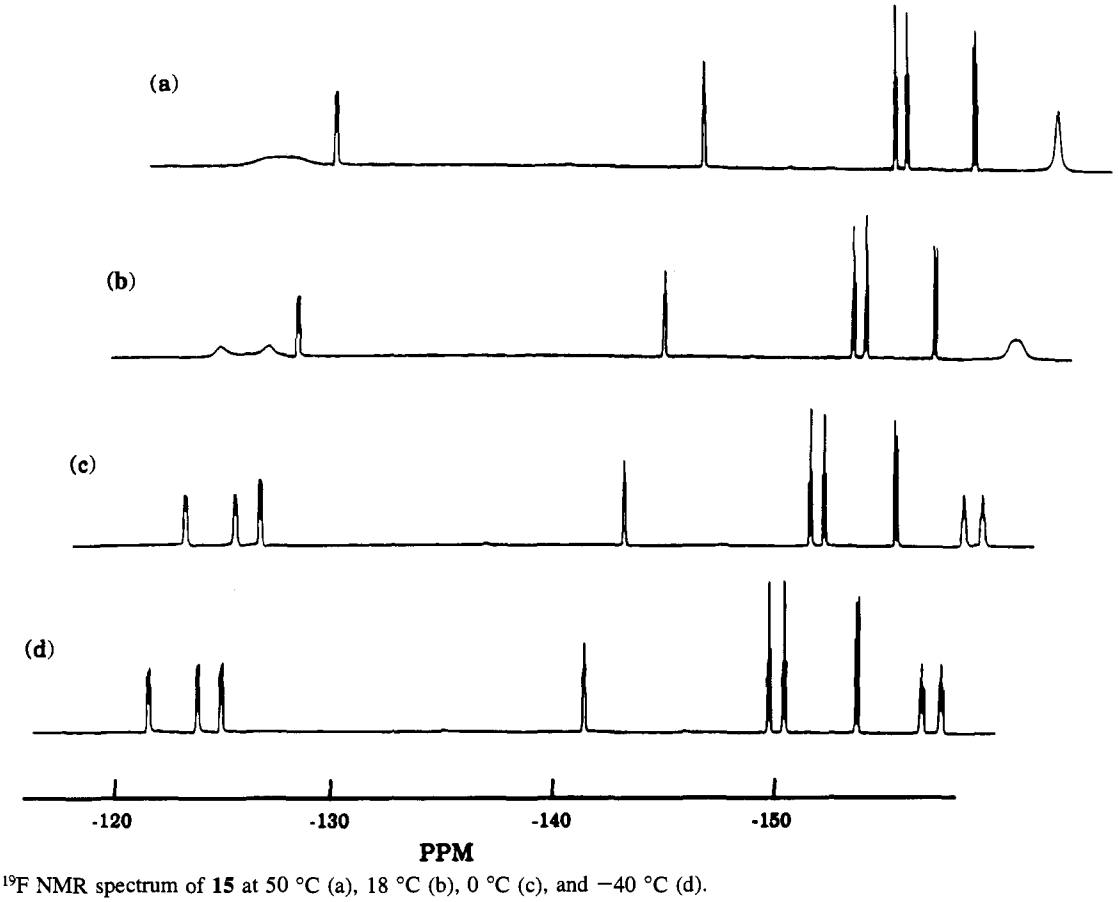


Figure 5. ^{19}F NMR spectrum of **15** at 50 °C (a), 18 °C (b), 0 °C (c), and −40 °C (d).

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 2D NMR spectroscopy along with a knowledge of the structure of **15**, we were able to correlate the ^{1}H with the ^{13}C chemical shift 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 7). 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 7. A second pair 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 7). 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 δ^{13}C values for **14b** 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 δ^{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 π 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.

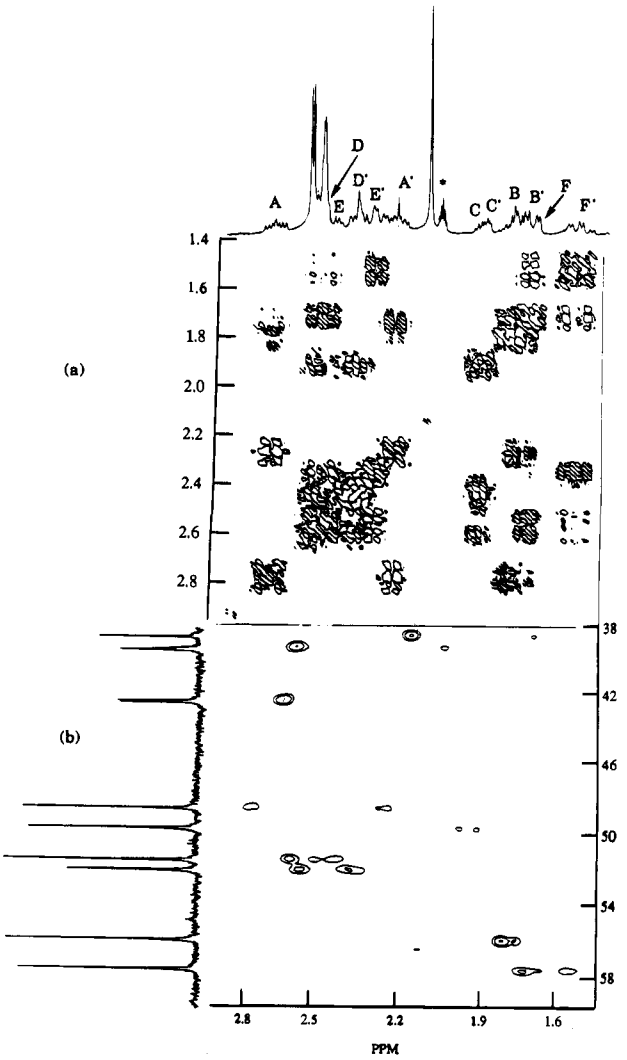


Figure 6. The 300 MHz ^{1}H–^{1}H DQF COSY 2D NMR spectrum of **15** (a). Pairs of ^{1}H multiplets associated with the same carbon are labeled A, A′ or B, B′, etc. The asterisk marks residual methyl protons in the $CD_3C_6D_5$ solvent. The 300 MHz ^{1}H–^{13}C HETCOR 2D NMR spectrum of **15** (b).

Table 7. Correlations of ^{1}H with ^{13}C NMR Chemical Shifts in **15**

δ ^{13}C (ppm)	δ ^{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), 2.44 (D′)	C(4)
51.87	2.49 (E), 2.37 (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.

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Supplementary Material Available: Tables of crystal data, bond distances, bond angles, positional and anisotropic thermal parameters least-squares planes (39 pages); calculated and observed structure factors (11 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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