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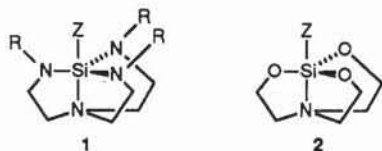
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Summary: Trigonal-bipyramidal azasilatranes of the type $\text{ZSi}(\text{NHCH}_2\text{CH}_2)_3\text{N}$ ($\text{Z} = \text{H, Me, OEt}$) solvolyze in MeOH to give $\text{N}(\text{CH}_2\text{CH}_2\text{NH}_2)_3$ (tren) and $\text{ZSi}(\text{OMe})_3$. Whereas intermediates in this reaction are not detected, $\text{ZSi}[\text{N}(\text{SiR}_3)\text{CH}_2\text{CH}_2]_3\text{N}$ species afford detectable intermediates of the type $\text{ZSi}[\text{N}(\text{SiR}_3)\text{CH}_2\text{CH}_2]_n(\text{NHCH}_2\text{CH}_2)_{3-n}\text{N}$ ($n = 1, 2$) before complete conversion to tren and $\text{ZSi}(\text{OMe})_3$ occurs. In cases where steric encumbrances weaken the $\text{Si}-\text{N}_{\text{ax}}$ bond in these molecules, monocyclic intermediates are detected. In contrast, methanolysis of $\text{HSi}[\text{N}(\text{BMe}_2)\text{CH}_2\text{CH}_2]_3\text{N}$ gives $\text{N}(\text{CH}_2\text{CH}_2\text{NHBMe}_2)_3$ (and $\text{HSi}(\text{OMe})_3$), which in the presence of CD_3OD gives $(\text{CD}_3\text{O})_n\text{Si}(\text{OMe})_{4-n}$ and the novel adduct $\text{N}[\text{CH}_2\text{CH}_2\text{NHD}-\text{B}(\text{OCD}_3)\text{Me}_2]_3$. The possible steric and electronic influences of the equatorial substituents on the solvolysis pathways are discussed.

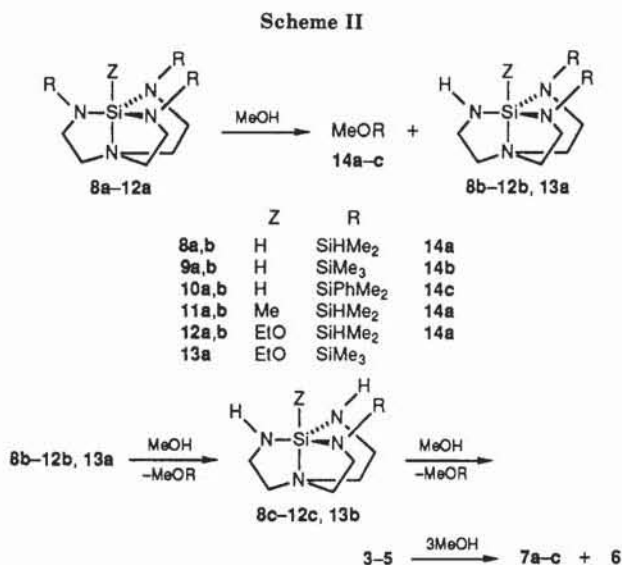
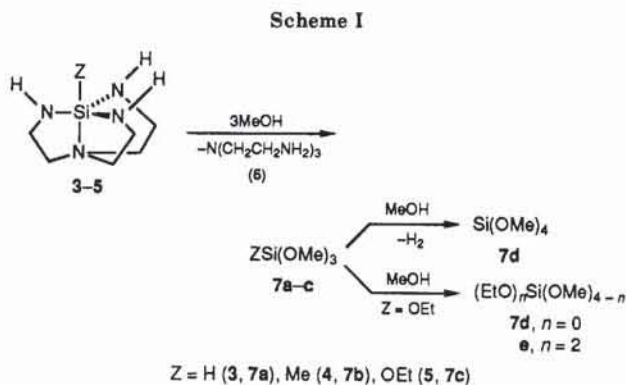
In recent publications we have shown that azasilatranes of type 1, where $\text{R} = \text{H}$, undergo stepwise substitution of the NH hydrogens with a variety of electrophilic groups (e.g., R_3Si ,^{2,3} PPh_2)⁴ as well as protonation of one of the NH sites.⁵ During the course of those investigations we



observed, as had others in a smaller number of examples,⁶ that azasilatranes appeared to be more sensitive to hydrolysis than the analogous silatranes 2. It was therefore of interest to determine whether the substituents Z and R in 1 were influential in the course and rate of solvolysis. Here we show that room-temperature methanolysis of 1 cleaves the tricyclic system via $\text{Si}-\text{N}_{\text{eq}}$ bond cleavage. Such cleavage generally follows stepwise solvolysis of the R groups when R is a silyl moiety, but not when $\text{R} = \text{BMe}_2$. In the case where $\text{R} = \text{SiMe}_3$ and $\text{Z} = \text{Me}$, $\text{Si}-\text{N}_{\text{eq}}$ cleavage is followed by formation of detectable quantities of two eight-membered-ring intermediates.

Results and Discussion

Equatorial Hydrogen Azasilatranes. Azasilatranes 3-5 reacted with methanol at room temperature to give tren (6) and the $\text{XSi}(\text{OMe})_3$ derivatives 7a-c (Scheme I). Silanes 7a and 7c were found to react further with methanol to give 7d and a mixture of 7c-e, respectively, as the final silicon-containing products. Consumption of more than 99% of the starting material was found to require less



than 2 h for 3, about 6 h for 4, and 12 h for 5 (50% CD_3OD in CDCl_3 at room temperature). Monitoring these reactions by ^1H and ^{29}Si NMR spectroscopy revealed the absence of detectable quantities of intermediates containing silicon and tetraamine. Because the tricyclic structure of 3-5 gains considerable stability from a strong $\text{N}_{\text{ax}} \rightarrow \text{Si}$ interaction⁷ and the entropic chelating effect, it is reasonable to assume that solvolysis occurs by a stepwise ring-opening process. Thus, the first $\text{N}_{\text{eq}}-\text{Si}$ cleavage by MeOH is suggested to be the rate-determining step. Since no NMR spectroscopic evidence for methoxyazasilatrane (1, $\text{R} = \text{H}$, $\text{Z} = \text{OMe}$)⁸ could be detected throughout the reactions of 3 or 5 with MeOH, the formation of 7d from 3 probably occurs via oxidative methanolysis⁹ of 7a rather than by substitution of the hydrogen in 3. Similarly, the formation of 7c-e from 5 is attributable to exchange of the alkoxy groups of 7c (Scheme I).

Equatorial Silyl Azasilatranes. Azasilatranes 8a-12a and 13a (Scheme II) possess organosilyl substituents on

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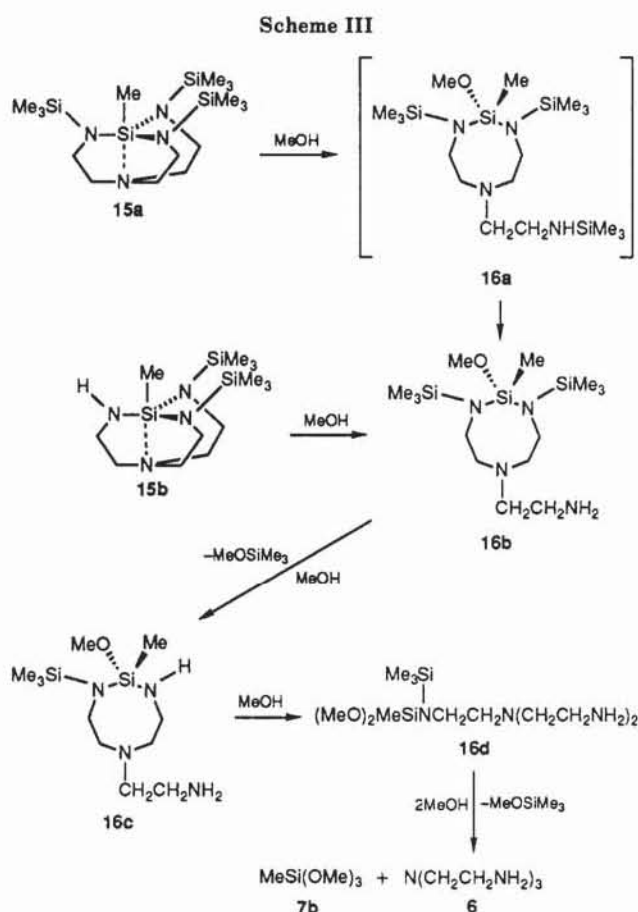
Table I. Selected ^1H and ^{29}Si NMR Data for N-Silylated Azasilatranes of Formula $\text{ZSi}(\text{NRCH}_2\text{CH}_2)_n(\text{NHCH}_2\text{CH}_2)_{3-n}\text{N}^a$

	Z	R	n	$\delta(^{29}\text{Si})$, ppm		$\delta(^1\text{H})_Z$, ppm	$^1J_{\text{HSi}}$, Hz	ref
				ZSiN_4	NSiR_3			
3	H		0	-83.2		3.82	177	1
8a	H	SiHMe_2	3	-78.0	-8.8	4.50	184	
8b	H	SiHMe_2	2	-79.7	-8.6	4.20	182	
8c	H	SiHMe_2	1	-81.1	-8.6	4.01	181	
9a	H	SiMe_3	3	-70.1	3.2	4.62	197	2
9b	H	SiMe_3	2	-79.4	3.9	4.34	184	
9c	H	SiMe_3	1	-81.4	4.4	4.12	178	
10a	H	SiPhMe_2	3	-78.3	-1.9	4.76	198	2
10b	H	SiPhMe_2	2	-80.1	<i>b</i>	4.54	187	
10c	H	SiPhMe_2	1	-81.6	<i>b</i>	4.22	180	
4	Me		0	-68.3		-0.54		1
11a	Me	SiHMe_2	3	-29.2	-9.3	0.24		
11b	Me	SiHMe_2	2	-43.4	-9.0	0.00		
11c	Me	SiHMe_2	1	-60.8	-8.3	-0.23		
5	EtO		0	-82.9				1
12a	EtO	SiHMe_2	3	-58.7	-9.0	3.80 (q), 1.12 (t)		2
12b	EtO	SiHMe_2	2	-75.7	-7.6	<i>b</i>		
12c	EtO	SiHMe_2	1	-80.9	-7.6	<i>b</i>		
13b	EtO	SiMe_3	2	-65.5	3.4	3.45 (q), 0.98 (t)		2
13c	EtO	SiMe_3	1	-79.4	2.5	3.45 (q), 0.98 (t)		2

^a Room temperature in CDCl_3 . ^b No unequivocal assignment possible.

all three and on two N_{eq} sites, respectively. With the steric encumbrance at the pentacoordinate silicon engendered by N_{eq} substitution, it may be anticipated that the four-coordinate silicon atoms of the N_{eq} substituents will be favored for nucleophilic attack by methanol. This hypothesis is substantiated by the observed course of the methanolysis of these equatorially substituted azasilatranes. Thus, upon treatment of CDCl_3 solutions of **8a–12a** and **13a** with ca. one-third the stoichiometric amount of MeOH for complete methanolysis, ^1H and ^{29}Si NMR spectroscopic monitoring of the reaction revealed the presence of a mixture of products identified as partially N_{eq} -silylated azasilatranes **8b,c–12b,c** and **13b**² and the methoxytriorganosilanes **14a–c** (Scheme II). Only traces of tren (**6**) and **7a–c** were observed at this stage of the solvolysis, thus strongly suggesting cleavage of the exocyclic Si– N_{eq} bonds as the predominating reaction. The formulation of the methanolysis intermediates **8b,c–12b,c** as azasilatranes was ascertained independently by synthesizing mixtures of the identical products via partial silylation of **3–5**. Further substantiation of these tricyclic structures came from the ^1H and ^{29}Si NMR data in Table I. The high-field ^{29}Si shifts in this table attest to retention of the pentacoordinate geometry of the central silicon.^{2,6,10} Complete methanolysis to give tren (**6**) and the silanes **7a–e** and **14a–c** was observed by ^1H and ^{29}Si NMR spectroscopy following the addition of excess methanol.

Whereas rupture of all of the Si–N bonds in the methyl azasilatranes **15a,b** was observed in excess methanol, partial methanolysis experiments revealed the stepwise nature of the reaction (Scheme III). Treatment of **15a** or **15b** with 2 equiv of MeOH gave the three new products **16b–d** in addition to **7b**, **14b**, and traces of tren (**6**). Interestingly, **15b** was not detected in the partial methanolysis of **15a**. Assignments of the structures of **16b–d** were made on the basis of ^1H and ^{29}Si NMR data and on GC/MS data obtained from the reaction mixture. Selective enrichment of intermediate **16c** was achieved by modifying the reaction conditions, thus allowing the isolation of a product mixture containing only **16c** (88%), tren (8%), and **4** (4%). The last compound was not present in the original reaction mixture and may have formed

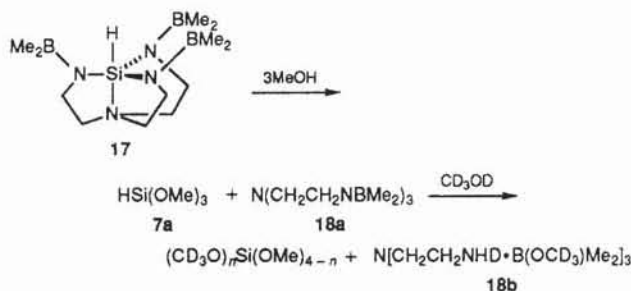


because of the relatively vigorous workup conditions employed in the modified reaction (see Experimental Section). Confirmation of the structure of **16c** was obtained by high-resolution MS and one-dimensional (^1H , ^{13}C , ^{29}Si) and two-dimensional (^1H – ^1H , ^1H – ^{13}C COSY) NMR spectroscopies. With excess methanol and longer reaction times, **15a** and **15b** gave **7b**, **14b**, and tren (**6**).

The formation of **16b–d** can be rationalized if the reactivities of both the endo- and exocyclic Si– N_{eq} links are assumed to be similar, leading to nonregiospecific bond cleavage. Because **15b** is not detected in the methanolysis

(10) Kupce, E.; Liepin'sh, E. E.; Lapsina, A.; Zelchan, G. I.; Lukevics, E. E. *J. Organomet. Chem.* 1987, 333, 1.

Scheme IV



of 15a, it is reasonable to suppose that the initial reaction of 15a with MeOH involves cleavage of the endocyclic Si-N_{eq} bond, giving 16a, which is not detected because of its rapid conversion to detectable 16b (Scheme III). Subsequent methanolyses cleave another Me₃Si-N bond, then a ring Si-N link, and finally the remaining Si-N bonds in acyclic 16d. All of the intermediates 16b-d display ²⁹Si chemical shifts that reflect the presence of tetracoordinate silicon rather than a pentacoordinate geometry induced by coordination of the C₃N tertiary nitrogen.

In contrast to 8a-10a, 12a, and 13a, which display ²⁹Si shifts typical of a pentacoordinate geometry for the central silicon (Table I), the ²⁹Si shifts of 11a, 15a, and 15b are below this range (-29.2, -25.7, and -36.2 ppm, respectively³), in accord with a more tetrahedral silicon.¹¹ As we have recently shown, 15a is sufficiently sterically congested to markedly weaken and lengthen the Si-N_{ax} bond and this is probably also the case in 11a.³ The resultant destabilization of the chelated tricyclic structure in 15a would be expected to render the central silicon at least electronically and perhaps sterically more susceptible to nucleophilic attack, giving rise to the initial ring-opening reaction observed (Scheme III) rather than an initial exocyclic Me₃Si-N_{eq} cleavage. Steric congestion of the type described here for 15a and 15b is expected to be less than in 8a-10a, 12a, and 13. The Me₂SiH groups in 11a, being sterically more accessible to nucleophilic attack and also more electrophilic than the Me₃Si groups in 15a, apparently allow 11a to methanolyze by initial attack at the exocyclic Me₂SiH group.

Equatorial Boryl Azasilatrane. In contrast to equatorial silyl substituents, the boryl groups in 17 form B-N_{eq} bonds sufficiently robust to survive methanolysis (Scheme IV). Reaction of 17 with 3 equiv of MeOH instantaneously produced 7a and the new borylamine 18a, which was characterized by ¹H, ¹³C, and ¹¹B NMR and mass spectroscopies. Further reaction of CD₃OD with 7a and 18a resulted in solvolysis of the B-N bonds in 18a, to give a product whose NMR data are consistent with the tren adduct 18b in Scheme IV.¹² With less than 3 equiv of MeOH, no evidence for intermediates was detected.

The high sensitivity of the Si-N_{eq} bonds in 17 compared with that of its B-N_{eq} links can be attributed at least in part to the formally double-bond character of the B=N_{eq} link. Donation of N_{eq} lone-pair density to the boron would also be expected to weaken the N_{eq}-Si bond. The multiple character of the B=N_{eq} bond is substantiated by our observation of two sets of diastereotopic methyl groups in

the ¹H NMR spectra of 17 and also in 18a.

Conclusions. The solvolysis of azasilatranes by methanol does not occur by initial displacement of the monodentate axial substituent but rather by attack on the tricyclic structure. Scission of the cage structure can be preceded by solvolytic displacement of exocyclic (silyl) substituents. In some cases monocyclic intermediates can be observed in the stepwise opening of the tricyclic structure. The rate and pathway of methanolysis appear to be strongly dependent on the strength of the exocyclic substituent bond and on the steric crowding these groups experience with the exocyclic axial group. Substantial steric crowding of this sort leads to weakening of the Si-N_{ax} interaction.

Experimental Section

All reactions were carried out with strict exclusion of moisture under an atmosphere of dry argon. Solvents were dried by standard methods and distilled before use. Commercially available bromodimethylborane (Aldrich) was used without purification. Azasilatranes 3-5, 8a-12a, and 13a were prepared as described elsewhere.^{2,3}

NMR spectra were recorded on Nicolet NT 300 (¹H, ¹³C) and Bruker WM200 (¹H, ²⁹Si) instruments with internal lock. TMS (¹H, ¹³C, ²⁹Si) and BF₃·OEt (¹¹B) were used as external standards. ²⁹Si NMR data of H-Si or Me-Si azasilatranes and their decomposition products were obtained with use of the DEPT technique.¹³ The remaining spectra were recorded under inverse gated decoupling conditions. Assignments of CH₂ and CH₃ resonances were made from DEPT-¹³C spectra. Assignment of the NCH₂ protons of 16c was established from ¹H-¹H and ¹H-¹³C 2D (COSY) NMR spectra. High-resolution mass spectra were recorded on a Kratos MS-50 spectrometer with electron impact ionization (70 eV). GC/MS and normal-resolution MS measurements were made on a Finnigan 4000 GC/MS instrument using both EI (70 eV) and CI techniques.

Hydro-N,N',N''-tris(dimethylboryl)azasilatrane (17). To a stirred solution of 771 mg (4.50 mmol) of 3 in 7 mL of benzene was added via syringe 3 mL of triethylamine, followed by 1.83 g (15.2 mmol) of bromodimethylborane. The solution became hot, and a colorless precipitate began to form immediately. Another 5 mL of benzene was added, and the solution was stirred for 2.5 h. The precipitate was removed by filtration and washed twice with 5-mL portions of benzene. The combined filtrates were evaporated to dryness. Fractional sublimation of the residue (0.1 Torr with a bath temperature of 35-45 °C) produced a small amount of colorless solid, which was discarded. Increasing the bath temperature to 100-130 °C produced 760 mg (58% yield) of pure 17 as colorless crystals: mp 125-126 °C; ²⁹Si NMR (CDCl₃) δ -55.1 (d, ¹J_{SiH} = 237 Hz); ¹¹B NMR (CDCl₃) δ 51.1; ¹³C NMR (CDCl₃) δ 57.91, 42.00 (NCH₂), 7.0 (br, BCH₃); ¹H NMR (CDCl₃) δ 5.34 (s, 1 H, ¹J_{SiH} = 236 Hz, SiH), 2.98 (m, 6 H, NCH₂), 2.49 (m, 6 H, NCH₂), 0.49 (s, 9 H, BCH₃), 0.34 (s, 9 H, BCH₃); HRMS (EI, 70 eV) *m/e* (relative intensity) calcd for C₁₂H₃₀(¹¹B)₃N₄Si (M⁺ - H) 291.25188 found 291.25466 (100), calcd for C₁₁H₂₈(¹¹B)₃N₄Si (M⁺ - CH₃) 277.23623, found 277.23675 (55).

Methanolysis of Azasilatranes 3-5, 8a-12a, and 13a (General Procedure). Typically, 100-300 mg of azasilatrane was dissolved in 2.5 mL of CDCl₃ in a 10-mm NMR tube. Approximately one-third of the amount of MeOH necessary for complete alcoholysis was added via syringe, and the reaction was monitored by ¹H and ²⁹Si NMR spectroscopy, until the spectra showed no further change. Excess MeOH was then added, and the reaction was monitored until complete solvolysis was achieved. The identities of the silanes formed (7a-e and 14a-c) were confirmed by comparison of their ²⁹Si NMR data with literature values.¹⁴ Partially substituted azasilatranes were identified in the reaction mixture by comparison of their ²⁹Si and ¹H NMR data (Table I) with those of independently synthesized samples (see below).

(11) For 1,3-dioxo-6-aza-2-silacyclooctanes, the formation of a transannular Si-N interaction is accompanied by upfield ²⁹Si NMR shifts that are similar to those for the corresponding silatranes (Kupce, E.; Liepin'sh, E. E.; Lukevics, E. E. *J. Organomet. Chem.* 1983, 248, 131).

(12) Compare Me₂BOMe-NMe₃: δ(¹¹B) = 32.9 (Nöth, H.; Vahrenkamp, H. *Chem. Ber.* 1966, 99, 1049).

(13) Blinka, T. A.; Helmer, B. J.; West, R. *Adv. Organomet. Chem.* 1984, 23, 193.

(14) Marsmann, H. In *NMR-Basic Principles and Progress*; Diehl, P., Fluck, E., Kosfeld, R., Eds.; Springer-Verlag: Berlin, 1981; Vol. 17, p 65ff.

The assignment of the constitution of the intermediates **16b–d** was supported by the following data.

5-(2-Aminoethyl)-1-methoxy-1-methyl-2,8-bis(trimethylsilyl)-2,5,8-triaza-1-silacyclooctane (16b): ^{29}Si NMR (CDCl_3) δ 4.1 (SiMe_3), –19.5 (SiMe); GC/MS (CI, NH_3) 363 (100%, MH^+) 331 (63%, $\text{MH}^+ - \text{MeOH}$); ^1H NMR (CDCl_3) 3.27 (OCH_3), 0.14 (SiCH_3), 0.10 ($\text{Si}(\text{CH}_3)_3$).

5-(2-Aminoethyl)-1-methoxy-1-methyl-2-(trimethylsilyl)-2,5,8-triaza-1-silacyclooctane (16c). The presence and constitution of **16c** were further substantiated by spectroscopic characterization of an enriched sample obtained under optimized reaction conditions. Thus, undried methanol (64 mg, 2.0 mmol) was added via syringe to a solution of 314 mg (0.950 mmoles) of **13b** in 3 mL of CHCl_3 . The solution was refluxed for 15 min. After the solution was cooled to room temperature, volatiles were removed in vacuo. The residue was distilled in a Kugelrohr distillation apparatus, yielding 217 mg of a yellow oil (bp 85–90 °C/0.1 Torr), which was identified by its NMR and GC/MS data as a mixture of **16c** (ca. 88%), **4** (ca. 4%), and **tren** (6, ca. 8%). No further purification of the product was attempted: ^{29}Si NMR (CDCl_3) δ 2.90 (SiMe_3), –21.70 (SiMe); ^{13}C NMR (CDCl_3) δ 61.21, 58.51, 56.66, 48.13, 42.17, 39.04 (NCH_2), 49.43 (OCH_3), 0.97 ($\text{Si}(\text{CH}_3)_3$), –2.62 (SiCH_3); ^1H NMR (CDCl_3) δ 3.28 (s, 3 H, OCH_3), 2.99 (m), 2.88 (m), 2.77 (m), 2.74 (m), 2.73 (m), 2.68 (m), 2.59 (m), 2.55 (m), 2.45 (m), 2.36 (m), 2.28 (m), 2.27 (m, NCH_2), 1.09 (br, NH), 0.79 (br t, NH), 0.01 (s, 3 H, SiCH_3), –0.02 (s, 9 H, $\text{Si}(\text{CH}_3)_3$); GC/MS (CI, isobutane) m/e (relative intensity) 291 (100, MH^+), 275 (12), 260 (33), 259 (44, $\text{MH}^+ - \text{MeOH}$), 231 (18); HRMS (EI, 70 eV) m/e calcd for $\text{C}_{10}\text{H}_{27}\text{N}_4\text{OSi}_2$ ($\text{M}^+ - \text{CH}_3$) 275.17234, found 275.17207.

***N,N*-Bis(2-aminoethyl)-*N'*-(trimethylsilyl)-*N'*-(dimethoxymethyl)silyl)ethylenediamine (16d):** ^{29}Si NMR (CDCl_3) δ 2.84 (SiMe_3), –26.2 (SiMe); GC/MS (CI, NH_3) m/e (relative intensity) 323 (100, MH^+); ^{13}C NMR (CDCl_3) δ 57.57, 57.48, 41.49, 39.55 (NCH_2), 49.20 (OCH_3), 0.90 ($\text{Si}(\text{CH}_3)_3$), –5.35 (SiCH_3); ^1H

NMR (CDCl_3) δ 3.16 (OCH_3), –0.19 ($\text{Si}(\text{CH}_3)_3$), –0.23 (SiCH_3).

Methanolysis of 17. MeOH (48 mg, 1.5 mmol) was added via syringe to a solution of 145 mg (0.500 mmol) of **17** in 2.5 mL of CDCl_3 . Formation of **7a** and a second product was established by ^1H and ^{29}Si NMR spectroscopy. The constitution of the second product was determined to be **18a** by its NMR (^1H , ^{11}B , ^{13}C , ^{29}Si) and MS data. In a separate experiment, the mixture of **7a** and **18a** obtained by the procedure described was treated with excess CD_3OD . The products formed in this reaction were assigned as $(\text{CH}_3\text{O})_n\text{Si}(\text{OCD}_3)_{4-n}$ ($n = 3, 4$)¹⁴ and $\text{N}[\text{CH}_2\text{CH}_2\text{NHD} \cdot \text{B}(\text{OC}_2\text{D}_5)(\text{CH}_3)_2]_3$ (**18b**) via NMR spectroscopy.

Tris[2-((dimethylboryl)amino)ethyl]amine (18a): ^{11}B NMR (CDCl_3) δ 45.7; ^{13}C NMR (CDCl_3) δ 56.8, 40.7 (NCH_2), 6.6 (br), 2.4 (br, BCH_3); ^1H NMR (CDCl_3) δ 4.2 (br, 3 H, NH), 2.98 (m, 6 H, NCH_2), 2.42 (t, 6 H, NCH_2), 0.20 (br, 9 H, BCH_3), 0.16 (br, 9 H, BCH_3); MS (CI, NH_3) m/e (relative intensity) 323 (100, MH^+).

Tris[(methoxy- d_3)dimethylborane-(2-(deuterioamino)-ethyl)amine (18b): ^{11}B NMR (CDCl_3) δ 26.6; ^{13}C NMR (CDCl_3) δ 54.2, 37.9 (NCH_2), 5.0 (br, BCH_3); ^1H NMR (CDCl_3) δ 3.5 (br, 3 H, NH), 2.63 (m, 6 H, NCH_2), 2.42 (m, 6 H, NCH_2), –0.12 (s, 18 H, BCH_3), 3.47 (s, wk, BOCH_3 due to $\text{OCH}_3/\text{OCD}_3$ scrambling).

Synthesis of Mixtures of Partially Silylated Azasilatranes 8a–c and 12a–c. Typically, 1 mmol of the azasilatranes **3–5** was dissolved in 5 mL of benzene, to which was then added 2.5 mL of triethylamine followed by 1.5–2 mmol of chlorotriorganosilane via syringe. The mixture was then stirred for 1 h, after which the precipitate that formed was removed by filtration. After the volatiles were removed in vacuo, the residue was dissolved in CDCl_3 , and the products were characterized by ^1H and ^{29}Si NMR spectroscopy (see Table I).

Acknowledgment. J.G.V. thanks the Air Force Office for Scientific Research for a grant. We also thank the W.R. Grace Co. for research samples of **tren**.