Azasilatrane Methanolysis Pathways: Stereoelectronic Influences

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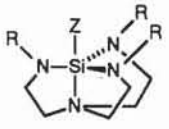
Summary: Trigonal-bipyramidal azasilatranes of the type $ZSi(NHCH_2CH_2)_3N$ (Z = H, Me, OEt) solvolyze in MeOH to give $N(CH_2CH_2NH_2)_3$ (tren) and $ZSi(OMe)_3$. Whereas intermediates in this reaction are not detected, $ZSi[N(SiR_3)CH_2CH_2]_3N$ species afford detectable intermediates of the type $ZSi[N(SiR_3)CH_2CH_2]_n(NHCH_2CH_2)_{3-n}N$ (n = 1, 2) before complete conversion to tren and $ZSi(OMe)_3$ occurs. In cases where steric encumbrances weaken the Si–N_{ax} bond in these molecules, monocyclic intermediates are detected. In contrast, methanolysis of $HSi[N(BMe_2)CH_2CH_2]_3N$ gives $N(CH_2CH_2NHBMe_2)_3$ (and $HSi(OMe)_3$), which in the presence of CD_3OD gives $(CD_3O)_n Si(OMe)_{4-n}$ and the novel adduct $N[CH_2CH_2NHD{\cdot}B(OCD_3)Me_2]_3$. 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 R = 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



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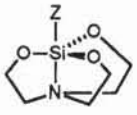

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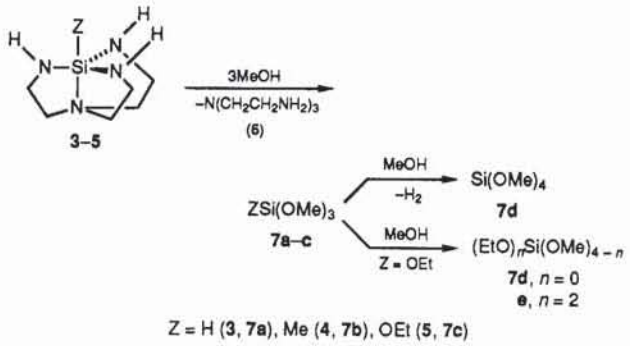
observed, as had others in a smaller number of examples,[6] that azasilatranes appeared to be more sensitive to hydrolysis than the analogous silatranes **2**. It was therefore of interest to determine whether the substituents Z and R in **1** were influential in the course and rate of solvolysis. Here we show that room-temperature methanolysis of **1** cleaves the tricyclic system via Si–N_{eq} bond cleavage. Such cleavage generally follows stepwise solvolysis of the R groups when R is a silyl moiety, but not when R = BMe_2. In the case where R = $SiMe_3$ and Z = Me, Si–N_{eq} cleavage is followed by formation of detectable quantities of two eight-membered-ring intermediates.

Results and Discussion

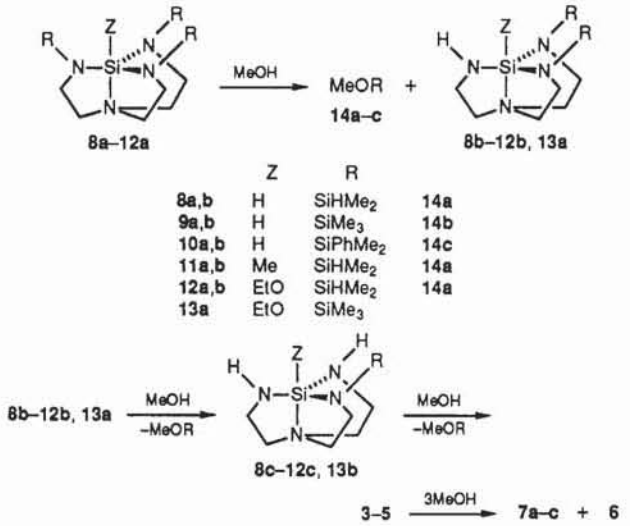
Equatorial Hydrogen Azasilatranes. Azasilatranes **3–5** reacted with methanol at room temperature to give tren (**6**) and the $XSi(OMe)_3$ derivatives **7a–c** (Scheme I). Silanes **7a** and **7c** were found to react further with methanol to give **7d** and a mixture of **7c–e**, respectively, as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

Scheme I



Z = H (**3**, **7a**), Me (**4**, **7b**), OEt (**5**, **7c**)

Scheme II



	Z	R	
8a,b	H	$SiHMe_2$	**14a**
9a,b	H	$SiMe_3$	**14b**
10a,b	H	$SiPhMe_2$	**14c**
11a,b	Me	$SiHMe_2$	**14a**
12a,b	EtO	$SiHMe_2$	**14a**
13a	EtO	$SiMe_3$	

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 $N_{ax} \rightarrow Si$ interaction[7] and the entropic chelating effect, it is reasonable to assume that solvolysis occurs by a stepwise ring-opening process. Thus, the first N_{eq}–Si cleavage by MeOH is suggested to be the rate-determining step. Since no NMR spectroscopic evidence for methoxyazasilatrane (**1**, R = H, Z = OMe)[8] could be detected throughout the reactions of **3** or **5** with MeOH, the formation of **7d** from **3** probably occurs via oxidative methanolysis[9] 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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(2) Gudat, D.; Verkade, J. G. *Organometallics* **1989**, *8*, 2772.
(3) Gudat, D.; Daniels, L. M.; Verkade, J. G. *J. Am. Chem. Soc.* **1989**, *111*, 8520.
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(6) Lukevics, E.; Zelchan, G. I.; Solomennikova, I. I.; Liepin'sh, E. E.; Yankovska, I. S.; Mazheika, I. B. *J. Gen. Chem. USSR (Engl. Transl.)* **1977**, *47*, 98.
(7) Voronkov, M. G.; Dyakov, V. M.; Kirpichenko, S. V. *J. Organomet. Chem.* **1982**, *233*, 1 and references cited therein.
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(9) Pawlenko, S. In *Houben-Weyl Methoden der Organischen Chemie*; Thieme: Stuttgart, FRG, 1980; Vol. 13, Part 5.

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Table I. Selected ^1H and ^{29}Si NMR Data for N-Silylated Azasilatranes of Formula $ZSi(NRCH_2CH_2)_n(NHCH_2CH_2)_{3-n}N$[a]

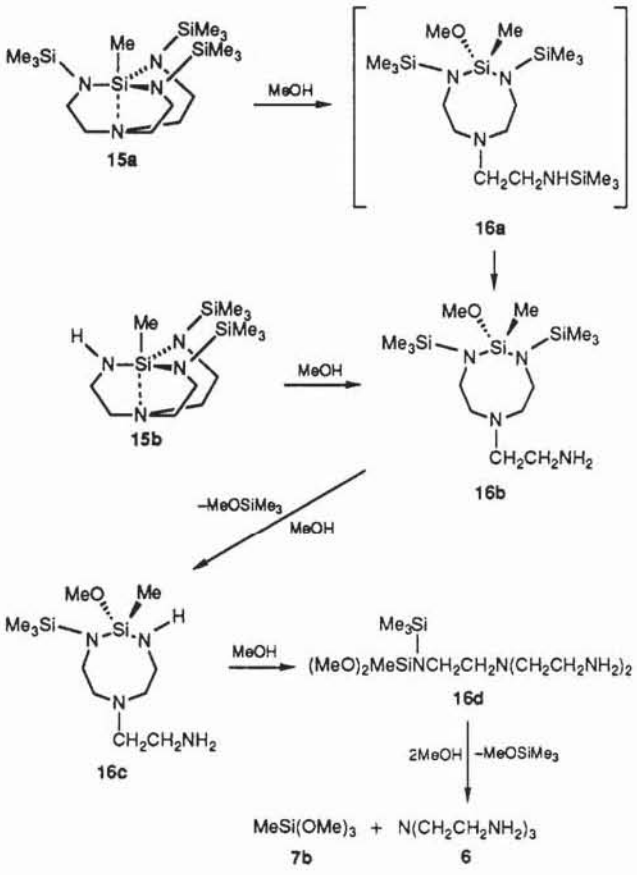
	Z	R	n	δ(29Si), ppm ZSiN4	δ(29Si), ppm NSiR3	δ(1H)Z, ppm	1JHSi, Hz	ref
3	H		0	−83.2		3.82	177	1
8a	H	$SiHMe_2$	3	−78.0	−8.8	4.50	184	
8b	H	$SiHMe_2$	2	−79.7	−8.6	4.20	182	
8c	H	$SiHMe_2$	1	−81.1	−8.6	4.01	181	
9a	H	$SiMe_3$	3	−70.1	3.2	4.62	197	2
9b	H	$SiMe_3$	2	−79.4	3.9	4.34	184	
9c	H	$SiMe_3$	1	−81.4	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	b	4.54	187	
10c	H	$SiPhMe_2$	1	−81.6	b	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	b		
12c	EtO	$SiHMe_2$	1	−80.9	−7.6	b		
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

Scheme III

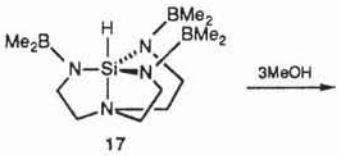


because of the relatively vigorous workup conditions employed in the modified reaction (see Experimental Section). Confirmation of the structure of **16c** was obtained by high-resolution MS and one-dimensional (^1H, ^{13}C, ^{29}Si) and two-dimensional (^1H–^1H, ^1H–^{13}C COSY) NMR spectroscopies. 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



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$$HSi(OMe)_3 \ (\mathbf{7a}) + N(CH_2CH_2NBMe_2)_3 \ (\mathbf{18a}) \xrightarrow{CD_3OD} (CD_3O)_nSi(OMe)_{4-n} + N[CH_2CH_2NHD\cdot B(OCD_3)Me_2]_3 \ (\mathbf{18b})$$

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 Me_3Si–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 ^{29}Si chemical shifts that reflect the presence of tetracoordinate silicon rather than a pentacoordinate geometry induced by coordination of the C_3N tertiary nitrogen.

In contrast to **8a–10a**, **12a**, and **13a**, which display ^{29}Si shifts typical of a pentacoordinate geometry for the central silicon (Table I), the ^{29}Si shifts of **11a**, **15a**, and **15b** are below this range (−29.2, −25.7, and −36.2 ppm, respectively[3]), 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 Me_3Si–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 Me_2SiH groups in **11a**, being sterically more accessible to nucleophilic attack and also more electrophilic than the Me_3Si groups in **15a**, apparently allow **11a** to methanolyze by initial attack at the exocyclic Me_2SiH 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, ^{13}C, and ^{11}B NMR and mass spectroscopies. Further reaction of CD_3OD 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, ^{13}C) and Bruker WM200 (^{11}B, ^{29}Si) instruments with internal lock. TMS (^1H, ^{13}C, ^{29}Si) and BF_3-OEt (^{11}B) were used as external standards. ^{29}Si 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 CH_2 and CH_3 resonances were made from DEPT-^{13}C spectra. Assignment of the NCH_2 protons of **16c** was established from ^1H–^1H and ^1H–^{13}C 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; ^{29}Si NMR ($CDCl_3$) δ −55.1 (d, $^1J_{SiH}$ = 237 Hz); ^{11}B NMR ($CDCl_3$) δ 51.1; ^{13}C NMR ($CDCl_3$) δ 57.91, 42.00 (NCH_2), 7.0 (br, BCH_3); ^1H NMR ($CDCl_3$) δ 5.34 (s, 1 H, $^1J_{SiH}$ = 236 Hz, SiH), 2.98 (m, 6 H, NCH_2), 2.49 (m, 6 H, NCH_2), 0.49 (s, 9 H, BCH_3), 0.34 (s, 9 H, BCH_3); HRMS (EI, 70 eV) *m/e* (relative intensity) calcd for $C_{12}H_{30}(^{11}B)_3N_4Si$ (M^+ − H) 291.251 88 found 291.254 66 (100), calcd for $C_{11}H_{28}(^{11}B)_3N_4Si$ (M^+ − CH_3) 277.236 23, found 277.236 75 (55).

Methanolysis of Azasilatranes 3–5, 8a–12a, and 13a (General Procedure). Typically, 100–300 mg of azasiltrane was dissolved in 2.5 mL of $CDCl_3$ 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 ^{29}Si 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 ^{29}Si NMR data with literature values.[14] Partially substituted azasiltranes were identified in the reaction mixture by comparison of their ^{29}Si and ^1H NMR data (Table I) with those of independently synthesized samples (see below).

(11) For 1,3-dioxa-6-aza-2-silacyclooctanes, the formation of a transannular Si–N interaction is accompanied by upfield ^{29}Si 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 $Me_2BOMe\cdot NMe_3$: $\delta(^{11}B)$ = 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.

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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%, MH^+ − MeOH); ^{1}H NMR ($CDCl_3$) 3.27 (OCH_3), 0.14 ($SiCH_3$), 0.10 ($Si(CH_3)_3$).

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 ($Si(CH_3)_3$), −2.62 ($SiCH_3$); ^{1}H 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, $Si(CH_3)_3$); GC/MS (CI, isobutane) m/e (relative intensity) 291 (100, MH^+), 275 (12), 260 (33), 259 (44, MH^+ − MeOH), 231 (18); HRMS (EI, 70 eV) m/e calcd for $C_{10}H_{27}N_4OSi_2$ ($M^+ - CH_3$) 275.172 34, found 275.172 07.

***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 ($Si(CH_3)_3$), −5.35 ($SiCH_3$); ^{1}H NMR ($CDCl_3$) δ 3.16 (OCH_3), −0.19 ($Si(CH_3)_3$), −0.23 ($SiCH_3$)$_3$).

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 ^{1}H and ^{29}Si NMR spectroscopy. The constitution of the second product was determined to be **18a** by its NMR (^{1}H, ^{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 $(CH_3O)_nSi(OCD_3)_{4-n}$ (n = 3, 4)[14] and $N[CH_2CH_2NHD{\cdot}B(OCD_3)(CH_3)_2]_3$ (**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); ^{1}H 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); ^{1}H 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 OCH_3/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 ^{1}H and ^{29}Si NMR spectroscopy (see Table I).

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