Synthesis and Interconversions of Azagermatranes

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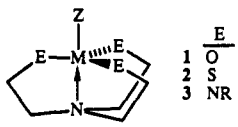
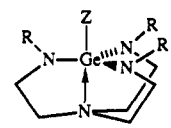
The syntheses of the first examples of the title compounds, namely, $ZGe(NRCH_2CH_2)_3N$ (**4**, R = H, Z = Me; **5**, R = Me, Z = Me; **6**, R = H, Z = *t*-Bu; **7**, R = Me, Z = *t*-Bu; **8**, R = Me, Z = NMe_2) are reported. Syntheses of the new compounds $MeGe(NMe_2)_3$ and *t*-$BuGe(NMe_2)_3$ and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

Introduction

Atranes (**1**) have been extensively studied for a variety of M atoms and Z substituents and have been known for a long time,

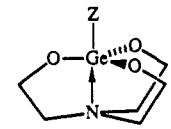


	E
1	O
2	S
3	NR



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

particularly for the group 14 elements.[1] By contrast, group 14 thiatranes (**2**) are much less well-known.[2] Azatranes (**3**) were also quite rare (except for a few examples for M = Si[3]) until our interest in such compounds was aroused by their potential as MOCVD agents for metal and non-metal nitrides. Thus we have recently expanded this class of compounds to include a broad variety azasilatranes (Z = R, OR, NR_2)[4] and the first examples of azatitanatranes (Z = NR_2),[5] azavanadatranes (Z = O, NR),[6,7] azamolybdatranes (Z = N),[6] azastannatranes (Z = R, NR_2),[6,7] azaboratranes (Z = nothing),[8] azaalumatranes (Z = nothing),[8] and azaphosphatrane cations (Z = H^+).[9] Herein we report the first azagermatranes, **4–8**. We also demonstrate that the alkylazagermatranes can be transformed to other azagermatranes and to germatranes. Thus **5** and **7** are labile with respect to replacement of their tetraamino cage moiety by a $(HNCH_2CH_2)_3N$ fragment in the presence of $(H_2NCH_2CH_2)_3N$, giving **4** and **6**, respectively. The azagermatranes **4–7** react with $(HOCH_2CH_2)_3N$ to yield the corresponding germatranes **9** and **10**. Also reported here are convenient preparations for the new compounds $RGe(NMe_2)_3$ (R = Me, *t*-Bu) and an improved synthesis for $Ge(NMe_2)_4$.



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

Experimental Section

All reactions were carried out with the strict exclusion of moisture by using standard inert-atmosphere and Schlenk techniques. Solvents such as tetrahydrofuran (THF), benzene, and Et_2O were dried by standard methods and distilled before use. Commercially available (Gelest, Inc.) $MeGeCl_3$, *t*-$BuGeCl_3$, and $GeCl_4$ were used without further purification. $LiNMe_2$ was purchased from Aldrich and used directly. "tren" ($(H_2NCH_2CH_2)_3N$) was distilled at 85 °C and 15 × 10^{-3} Torr from $LiAlH_4$ before use. Me_3tren ($(MeHNCH_2CH_2)_3N$) was prepared from the purified tren by using a standard procedure.[10] Triethanolamine (TEA) was distilled under vacuum at 97 °C and 14 × 10^{-3} Torr and stored over type 4A molecular sieves.

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

Tris(dimethylamino)methylgermane, $MeGe(NMe_2)_3$. To a 20-mL suspension of 1.08 g of $LiNMe_2$ (21.2 mmol) in ether cooled to −50 °C was added dropwise 1.27 g of $MeGeCl_3$ (6.54 mmol) via a nitrogen-flushed syringe. A white precipitate formed instantly. The mixture was allowed to warm to room temperature and was stirred for an additional 2 h. After filtration, the solid residue was washed with 3 × 5 mL of ether. The ether was removed under vacuum, giving a cloudy liquid which was distilled at 40 °C and 1.0 Torr, affording 1.10 g of colorless product in 77% yield. $MeGe(NMe_2)_3$ decomposes in air, instantly forming a white solid which is soluble in water. Liquid density: 1.03 g/mL. ^1H NMR (C_6D_6): δ 2.60 (s, 18 H, NMe_2), 0.21 (s, 3 H, GeMe). ^{13}C NMR (C_6D_6): δ 39.92 (NMe_2), −8.49 (GeMe). MS (70 eV, EI for ^{74}Ge): *m/z* (relative intensity, proposed ion) 221.2 (10.1, M^+), 222.2 (31.1, M^+ +

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1), 206.2 (1.5, $M^+ - Me$), 177.1 (100.0, $M^+ - NMe_2$), 162.2 (2.1, $M^+ - NMe_2 - Me$), 133.1 (2.4, $M^+ - 2NMe_2$), 118.1 (9.7, $M^+ - 2NMe_2 - Me$).

***tert*-Butyltris(dimethylamino)germane, *t*-BuGe(NMe$_2$)$_3$.** In 15 mL of ether was dissolved 2.56 g (10.8 mmol) of $BuGeCl_3$. This solution was added dropwise to 25 mL of an ether suspension of 1.72 g (33.7 mmol) of $LiNMe_2$ cooled to −50 °C. The reaction mixture was allowed to warm to room temperature and was stirred for another 3 h. After filtration and removal of ether under vacuum, 2.83 g of crude product was obtained. Distillation at 80–82 °C and 10 Torr afforded 2.27 g of a crystalline product in 80% yield. Mp: 43–44 °C. Liquid density: 1.01 g/mL. ^{1}H NMR (C_6D_6): δ 2.64 (s, 18 H, NMe_2), 1.16 (s, 9 H, CMe_3). ^{1}H NMR ($CDCl_3$): δ 2.59 (s, 18 H, NMe_2), 1.13 (s, 9 H, CMe_3). ^{13}C NMR ($CDCl_3$): 41.06 (NMe_2), 29.25 (CMe_3), 0.55 (CGe). MS (70 eV, EI for ^{74}Ge): *m*/*z* (relative intensity, proposed ion) 263.1 (1.1, M^+), 219.1 (8.2, $M^+ - NMe_2$), 206.1 (47.1, $M^+ - t$-Bu), 162.0 (19.9, $M^+ - NMe_2 - t$-Bu), 118.0 (100.0, $M^+ - 2NMe_2 - t$-Bu). HRMS for $C_{10}H_{27}N_3{}^{74}Ge$ (M^+): calcd 263.142 40, found 263.141 85.

Tetrakis(dimethylamino)germane, Ge(NMe$_2$)$_4$. The synthesis of this compound via the reaction of $GeBr_4$ with excess $HNMe_2$[11] or by reacting $GeCl_4$ with excess $HNMe_2$ in a sealed ampule was reported earlier.[11] An alternate route we devised was to add dropwise a solution of 2.59 g (12.1 mmol) of $GeCl_4$ to a mixture of 2.66 g (52.2 mmol) of $LiNMe_2$ cooled in 40 mL of ether to −50 °C. After stirring of the solution for an additional 2 h at room temperature, filtration, and vacuum evaporation of the ether, 2.91 g of crude product was obtained. Distillation at 50 °C and 0.2 Torr (lit. 82–83 °C at 12 Torr[11]) gave 2.34 g of pure colorless product. Yield: 79%. ^{1}H NMR (C_6D_6): δ 2.64 (s, 24 H). ^{13}C NMR (C_6D_6): δ 40.24.

Methylazagermatrane 4. A mixture of 0.397 g (1.81 mmol) of $MeGe(NMe_2)_3$ and 0.250 g (1.71 mmol) of tren reacted after about 1 min, as evidenced by solidification of the mixture and the release of $HNMe_2$. By sublimation at 5 × 10^{-3} Torr and 75 °C, 0.31 g of colorless crystalline product was collected in 78% yield. Mp: 74–75 °C. ^{1}H NMR (C_6D_6): δ 2.77 (t, 6 H, $HNCH_2$, $^3J_{HH}$ = 5.7 Hz), 2.22 (t, 6 H, $N(CH_2)_3$), 0.54 (b s, 3 H, NH), 0.08 (s, 3 H, MeGe). ^{13}C NMR (C_6D_6): δ 52.55 ($NHCH_2$), 38.59 ($N(CH_2)_3$), 1.37 (MeGe). MS (70 eV, EI for ^{74}Ge): *m*/*z* (relative intensity, proposed ion) 232.1 (9.8, M^+), 217.1 (100.0, $M^+ - Me$), 188.0 (80.9, $M^+ - NH_2CHCH_2$). HRMS (70 eV, EI) for $C_7H_{18}N_4{}^{74}Ge$ (M^+): calcd 232.075 05, found 232.074 41.

Methylazagermatrane 5. A mixture of $MeGe(NMe_2)_3$ (0.619 g, 2.82 mmol), Me_3tren (0.420 g, 2.24 mmol), and a catalytic amount of $(NH_4)_2SO_4$ was heated at 125 °C with stirring. After 3 h, release of $HNMe_2$ ceased and a yellowish liquid resulted which distilled very slowly at 60 °C and 5 × 10^{-2} Torr, giving 0.48 g of colorless liquid product in 63% yield. ^{1}H NMR (C_6D_6): δ 2.71 (s, 9 H, NMe), 2.66 (t, 6 H, $MeNCH_2$, $^3J_{HH}$ = 5.7 Hz), 2.24 (t, 6 H, $N(CH_2)_3$), 0.56 (s, 3 H, MeGe). ^{13}C NMR (C_6D_6): δ 49.64 (NMe), 49.47 ($MeNCH_2$), 39.14 ($N(CH_2)_3$), −0.28 (MeGe). MS (70 eV, EI for ^{74}Ge): *m*/*z* (relative intensity, proposed ion) 274.2 (13.1, M^+), 259.1 (25.4, $M^+ - Me$), 215.1 (10.8, $M^+ - CH_2CHNMeH$), 200.1 (2.8, $M^+ - Me - CH_2CHNMeH$). HRMS (70 eV, EI) for $C_{10}H_{24}N_4{}^{74}Ge$ (M^+): calcd 274.122 00, found 274.121 63.

***tert*-Butylazagermatrane 6.** A mixture of 0.909 g (3.47 mmol) of *t*-$BuGe(NMe_2)_3$ and 0.456 g (3.12 mmol) of tren was heated at 120 °C for 2 h. Because a ^{1}H NMR spectrum of a sample of the mixture in C_6D_6 revealed no evidence of reaction, a catalytic amount of $(NH_4)_2SO_4$ was added. After the mixture was stirred at 120 °C for another 2 h, evolution of $HNMe_2$ ceased, and when it was cooled to room temperature, the remaining mixture solidified. The colorless crystalline product was collected in 54% yield by sublimation at 55 °C and 14 × 10^{-3} Torr. Mp: 75–76 °C. ^{1}H NMR (C_6D_6): δ 2.74 (t, 6 H, $HNCH_2$, $^3J_{HH}$ = 5.4 Hz), 2.20 (t, 6 H, $N(CH_2)_3$), 1.10 (s, 9 H, *t*-BuGe), 0.62 (b s, 3 H, NH). ^{13}C NMR (C_6D_6): δ 53.40 ($HNCH_2$), 39.00 ($N(CH_2)_3$), 28.51 (Me), 26.53 (GeC). MS (70 eV, EI for ^{74}Ge): *m*/*z* (relative intensity, proposed ions) 274.2 (0.7, M^+), 217.1 (100.0, $M^+ - t$-Bu). HRMS for $C_{10}H_{25}{}^{74}GeN_4$ ($M^+ + H$): calcd 275.129 82, found 275.129 84. HRMS (70 eV, EI) for $C_6H_{15}{}^{74}GeN_4$ ($M^+ - t$-Bu): calcd 213.053 97, found 213.053 75. Anal. Calcd for $C_6H_{15}GeN_4$: C, 44.01; H, 8.86; N, 20.52. Found: C, 43.83; H, 9.15; N, 20.54.

***tert*-Butylazagermatrane 7.** A mixture of 0.400 g (1.53 mmol) of *t*-$Bu(NMe_2)_3$, Me_3tren (0.24 g, 1.28 mmol), and a catalytic amount of $(NH_4)_2SO_4$ as a catalyst was stirred at 120 °C until escape of dimethylamine ceased (2.5 h). The crude liquid was distilled very slowly at 50 °C and 20 × 10^{-3} Torr, affording 0.29 g of product in 61% yield.

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^{1}H NMR (C_6D_6): δ 2.64 (s, 9 H, NMe), 2.53 (t, 6 H, $MeNCH_2$, $^3J_{HH}$ = 5.0 Hz), 2.33 (t, 6 H, $N(CH_2)_3$), 1.39 (s, 9 H, CMe_3). ^{13}C NMR (C_6D_6): δ 53.52 (NMe), 50.18 ($MeNCH_2$), 38.11 ($N(CH_2)_3$), 31.05 (Me_3C), 27.20 (CMe_3). MS (70 eV, EI for ^{74}Ge): *m*/*z* (relative intensity, proposed ion) 316.2 (0.05, M^+), 259.1 (100.0, $M^+ - t$-Bu), 202.0 (6.2, $M^+ - CH_2CHNHCH_3$). HRMS (70 eV, EI) for $C_{12}H_{27}N_4{}^{74}Ge$ (M^+): calcd 301.145 47, found 301.145 21.

(Dimethylamino)azagermatrane 8. In a Schlenk tube, 0.645 g (2.60 mmol) of $Ge(NMe_2)_4$ was mixed with 0.443 g (2.36 mmol) of Me_3tren and a catalytic amount of $(NH_4)_2SO_4$. The mixture was heated at 120 °C with stirring until no more $HNMe_2$ was evolved (3 h). The crude product was purified by slow distillation at 45 °C and 25 × 10^{-3} Torr, giving 0.15 g of pure liquid product in 19% yield. ^{1}H NMR (C_6D_6): δ 2.97 (s, 6 H, NMe_2), 2.73 (s, 9 H, GeNMe), 2.66 (t, 6 H, $MeNCH_2$), $^3J_{HH}$ = 5.7 Hz), 2.12 (t, 6 H, $N(CH_2)_3$). ^{13}C NMR (C_6D_6): δ 50.40 (NMe), 50.30 ($MeNCH_2$), 41.34 ($GeNMe_2$), 39.05 ($N(CH_2)_3$). MS (70 eV, EI for ^{74}Ge): *m*/*z* (relative intensity, proposed ion): 303.2 (6.4, M^+), 259.1 (100.0, $M^+ - NMe_2$), 246.2 (0.6, $M^+ - NMeHCHCH_2$), 202.1 (14.2, $M^+ - NMe_2 - NMeHCHCH_2$). HRMS for $C_{11}H_{27}N_5{}^{74}Ge$ (M^+): calcd 303.148 54, found 303.148 23.

Reaction of 5 with tren. To a solution of 20 mg (0.073 mmol) of **5** in 0.45 mL of C_6D_6 in an NMR tube was added 11 mg (0.075 mmol) of tren. The ^{1}H NMR spectrum recorded $^1/_2$ h later revealed that ~50% of **5** had converted to **4**. Eight hours later, the reaction was complete, as evidenced by the ^{1}H and ^{13}C NMR spectra, which revealed the presence of free Me_3tren and of **4** as the only germanium-containing product.

Reaction of 7 with tren. To a solution of 30 mg (0.095 mmol) of **7** in 0.5 mL of C_6D_6 in an NMR tube was added 15 mg (0.096 mmol) of tren. The product, *tert*-butylazagermatrane **6** was detected instantly by ^{1}H NMR spectroscopy. After 12 h, the reaction was complete, as evidenced by ^{1}H and ^{13}C NMR spectroscopy, which revealed only the presence of *tert*-butylazagermatrane **6** and free Me_3tren.

Reactions of 4–7 with TEA. These NMR tube experiments were carried out in C_6D_6 (0.5 mL) at ambient temperature using approximately equimolar amounts (~0.07–0.1 mmol) of each of the title compounds and TEA. Monitoring the reactions by ^{1}H NMR spectroscopy showed that the reaction was complete for **4** and **5** by the time the spectra were run. In the case of **6** the reaction required about 14 h whereas for **7** it was complete by the time the spectrum was run. The purity of the reaction products in all of these mixtures was also verified by ^{13}C NMR spectroscopy.

Reaction of MeGe(NMe$_2$)$_3$ and *t*-BuGe(NMe$_2$)$_3$ with TEA. These NMR tube experiments were carried out as described in the preceding paragraph except approximately equimolar amounts of the title compounds (~0.02–0.04 mmol) and TEA were used. In the case of $MeGe(NMe_2)_3$, the reaction to form the corresponding germatrane was over immediately whereas, with *t*-$BuGe(NMe_2)_3$, only 60% conversion was evident by ^{1}H NMR spectroscopy even after 44 h at reflux temperature.

Discussion

Syntheses. An effective route to two new tris(dimethylamino)-germanes synthesized in this work is shown in reactions 1 and 2.

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

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

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

79% yield

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

The conditions for the syntheses of **4–7** (reactions 3–6) reflect the steric properties of the reactants. Thus, whereas tren reacts in minutes in reaction 3 to give **4** at room temperature, the formation of **5–7** requires heating for 2–3 h above 100 °C in the

$$MeGe(NMe_2)_3 \xrightarrow[\text{rt, ~1 min.}]{\text{tren}} \textbf{4} \text{ (74\% yield)} \quad (3)$$

$$MeGe(NMe_2)_3 \xrightarrow[125\ ^\circ C,\ 3\ h]{Me_3\text{-tren},\ (NH_4)_2SO_4} \textbf{5} \text{ (63\% yield)} \quad (4)$$

$$t\text{-BuGe}(NMe_2)_3 \xrightarrow[120\ ^\circ C,\ 2\ h]{\text{tren},\ (NH_4)_2SO_4} \textbf{6} \text{ (54\% yield)} \quad (5)$$

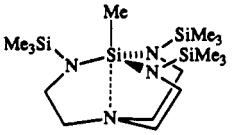
$$t\text{-BuGe}(NMe_2)_3 \xrightarrow[120\ ^\circ C,\ 2\ h]{Me_3\text{-tren}\ (NH_4)_2SO_4} \textbf{7} \text{ (61\% yield)} \quad (6)$$

presence of a catalyst. NMR tube reactions in C_6D_6 of the two reactants in eqs 3–6 (without catalyst) revealed formation of **4** within minutes at room temperature, partial conversion to **5** after 10 h at reflux temperature, and no detectable **6** or **7** after 10 h at reflux temperature. Interestingly, reaction 7 for the preparation

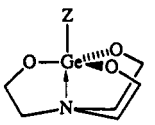
$$Ge(NMe_2)_4 + (MeHNCH_2CH_2)_3N \xrightarrow[(NH_4)_2SO_4]{120\ ^\circ C,\ 3\ h} \underset{(19\%\ \text{yield})}{\textbf{8}} \quad (7)$$

of **8** (albeit in low yield) gives only a polymeric material when tren is used instead of Me_3tren. This contrasting behavior between the two tetramines has also been noted with other $M(NMe_2)_x$ species in our laboratories (e.g., M = B,[8] Al,[8] Ti,[5] and Si[12]). It may be that these atoms activate the second hydrogen on the primary amine nitrogens to further substitution, thus leading to oligomers.

Because sterically unhindered azasilatranes[4] and azastannatranes[7] possess transannular bonds, it is expected that the same is true for **4** and **5**. In view of the quasi-azasilatrane structure of **11** established by X-ray means, however,[4a] it is possible that



11



	Z
12	Et
13	α-naphthyl
14	ICH_2
15	(-)-1-menthoxy

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

Azagermatrane Interconversions. Although germanium compounds are well-known to undergo monodentate ligand exchange in thermodynamically controlled equilibrium reactions,[13] reactions 8 and 9 demonstrate that a tetradentate amino ligand can be quantitatively replaced by another. Interestingly this reaction is

$$\textbf{5} + (H_2NCH_2CH_2)_3N \xrightarrow[\text{tren}]{} \textbf{4} + (MeHNCH_2CH_2)_3N \quad (8)$$

$$\textbf{7} + (H_2NCH_2CH_2)_3N \longrightarrow \textbf{6} + (MeHNCH_2CH_2)_3N \quad (9)$$

not reversible to any detectable extent, suggesting that steric factors probably dominate in the replacement of the more sterically hindered $(MeNCH_2CH_2)_3N$ moiety by the $(HNCH_2CH_2)_3N$ fragment. Such a replacement may also permit a stronger transannular interaction. It is worth noting that reaction 9 was carried out at room temperature in C_6D_6 and was ~50% complete in 0.5 h, whereas reaction 5 produced no detectable product at 120 °C for 2 h unless a catalyst was present. (That a solvent effect is not operative here was shown by the absence of a detectable amount of **6** when reaction 5 was carried out for 10 h in refluxing C_6D_6). This result is contrary to expectation, since reaction 5 is entropically and thermodynamically favored, and the reactant *t*-BuGe$(NMe_2)_3$ is less sterically encumbered than **7** in reaction 9. We are presently unable to explain this result satisfactorily. It is possible that if there is significant (albeit strained) transannular bonding in **7**, the hybridizational promotion energy from a tetrahedral to a trigonal bipyramidal Ge geometry required in reaction 5 interconversion in reaction 9.

Reactions 10 and 11, carried out as NMR tube experiments, are quantitative at room temperature. For **4**, **5**, and **7** the reaction

$$\textbf{4 or 5} + (HOCH_2CH_2)_3N \xrightarrow[\text{TEA}]{C_6D_6} \textbf{9} + \text{tren or } Me_3\text{-tren} \quad (10)$$

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

was complete in minutes whereas for **6** it required ~14 h. The reason for the slowness of **6** to react may be due to steric inhibition. Although this factor is expected to be larger in the case of **7**, it may be sufficiently large that the transannular bond is weakened or broken in this compound, thus rendering the Ge center more electrophilic. The replacement of three Ge–N linkages by three stronger Ge–O bonds favors these reactions, as does the reduction in the steric requirements of the $(OCH_2CH_2)_3N$ group. The structures for **10**, **12**, and **13** determined by X-ray means reveal the presence of Ge←N transannular bonds (2.238 (6), 2.24, and 2.24 Å, respectively[14]). This distance appears to be slightly shorter in **14** (2.19 (3) Å[15]) and **15** (2.150 (7) Å[16]). These data strongly suggest that **9** and **10** also contain transannular bonds, whose strengths are probably enhanced by the three electronegative alkoxy oxygens over the three less electronegative amido nitrogens present in azagermatranes. The reaction of **8** with TEA gave a complicated mixture, undoubtedly owing to competitive departure of the Me_2N substituent and the MeN nitrogens in the $(MeNCH_2CH_2)_3N$ moiety during nucleophilic displacement by the triol.

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(12) Here $Si(NMe_2)_4$, whether heated with or without a catalyst in the presence of tren or Me_3tren, does not give the corresponding (dimethylamino)-azasilatrane,[4a] although $Me_2NSi(HNCH_2CH_2)_3N$ has been claimed to be formed in this manner: LeGrow, G. E. U.S. Patent 3,576,026, 1971.

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