

# Azametallatranes of Group 14 Elements. Syntheses and X-ray Studies

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Syntheses of a series of the title compounds, viz.,  $N(\text{CH}_2\text{CH}_2\text{NR})_3\text{M}-\text{X}$  (**1**,  $\text{M} = \text{Si}$ ,  $\text{X} = \text{Me}$ ,  $\text{R} = \text{SiMe}_3$ ; **2**,  $\text{M} = \text{Si}$ ,  $\text{X} = \text{Et}$ ,  $\text{R} = \text{SiMe}_3$ ; **3**,  $\text{M} = \text{Si}$ ,  $\text{X} = n\text{-Bu}$ ,  $\text{R} = \text{SiMe}_3$ ; **4**,  $\text{M} = \text{Si}$ ,  $\text{X} = \text{vinyl}$ ,  $\text{R} = \text{SiMe}_3$ ; **5**,  $\text{M} = \text{Si}$ ,  $\text{X} = \text{Ph}$ ,  $\text{R} = \text{SiMe}_3$ ; **6**,  $\text{M} = \text{Ge}$ ,  $\text{X} = \text{Me}$ ,  $\text{R} = \text{SiMe}_3$ ; **7**,  $\text{M} = \text{Ge}$ ,  $\text{X} = n\text{-Bu}$ ,  $\text{R} = \text{SiMe}_3$ ; **8**,  $\text{M} = \text{Ge}$ ,  $\text{X} = \text{Ph}$ ,  $\text{R} = \text{SiMe}_3$ ; **9**,  $\text{M} = \text{Sn}$ ,  $\text{X} = n\text{-Bu}$ ,  $\text{R} = \text{SiMe}_3$ ; **10**,  $\text{M} = \text{Sn}$ ,  $\text{X} = \text{Ph}$ ,  $\text{R} = \text{SiMe}_3$ ; **11**,  $\text{M} = \text{Si}$ ,  $\text{X} = \text{vinyl}$ ,  $\text{R} = \text{Me}$ ; **12**,  $\text{M} = \text{Ge}$ ,  $\text{X} = \text{Me}$ ,  $\text{R} = \text{Me}$ ) by the reaction of  $\text{X}-\text{MCl}_3$  with  $N(\text{CH}_2\text{CH}_2\text{NSiMe}_3\text{Li})_3$  or with  $N(\text{CH}_2\text{CH}_2\text{NMeLi})_3$  are reported. Reactions of the novel compounds  $\text{X}-\text{Ge}(\text{NMe}_2)_3$  (**15**,  $\text{X} = \text{Ph}$ ; **16**,  $\text{X} = 1\text{-naphthyl}$ ; **17**,  $\text{X} = 9\text{-anthracenyl}$ ; **18**,  $\text{X} = 9\text{-phenantrenyl}$ ) with  $N(\text{CH}_2\text{CH}_2\text{NHMe})_3$  or  $N(\text{CH}_2\text{CH}_2\text{NH}_2)_3$  resulted in new 1-arylazagermatranes,  $N(\text{CH}_2\text{CH}_2\text{NMe})_3\text{Ge}-\text{X}$  (**19**,  $\text{X} = \text{Ph}$ ; **20**,  $\text{X} = 1\text{-naphthyl}$ ; **21**,  $\text{X} = 9\text{-anthracenyl}$ ; **22**,  $\text{X} = 9\text{-phenantrenyl}$ ) and  $N(\text{CH}_2\text{CH}_2\text{NH})_3\text{Ge}-\text{X}$  (**23**,  $\text{X} = \text{Ph}$ ; **24**,  $\text{X} = 1\text{-naphthyl}$ ; **25**,  $\text{X} = 9\text{-phenantrenyl}$ ), respectively. 1-Phenylazagermatrane (**23**) is transformed to **8** by treatment with  $n\text{-BuLi}/\text{Me}_3\text{SiCl}$ . Composition and structures of novel compounds were established by elemental analyses,  $^1\text{H}$ ,  $^{13}\text{C}$ , and  $^{29}\text{Si}$  NMR spectroscopy, and mass spectrometry. The X-ray structural studies of **10** and **19** clearly indicated the presence of a transannular interaction  $\text{M}\cdots\text{N}_{\text{ax}}$  for both compounds. *quasi*-Azametallatranes **5** and **8** possess extremely long  $\text{M}\cdots\text{N}_{\text{ax}}$  distances.

## Introduction

The structure and chemical behavior of metallatranes,  $N(\text{CH}_2\text{CH}_2\text{O})_3\text{M}-\text{X}$  (**A**)—cyclic derivatives of trialkanolamines—have been extensively studied,<sup>1–4</sup> and compounds of elements have been reported all over the periodic table. By contrast, azametallatranes,  $N(\text{CH}_2\text{CH}_2\text{NR})_3\text{M}-\text{X}$  (**B**), which are the product of a formal substitution of the oxygen atoms in molecule (**A**) by NR groups, are less well-known;<sup>1,4,5</sup> however, interest in azametallatranes (**B**) has grown steadily over the two past decades: one of the reasons is their potential application as MOCVD precursors for metal and non-metal nitrides,<sup>1,6–8</sup> and another is their wide scope of

chemistry by varying the substitution pattern at both the metal center and the equatorial nitrogen substituents in **B**.<sup>5</sup>

Among azametallatranes of the group 14 elements azasilatranes (**B**,  $\text{M} = \text{Si}$ ), first prepared by Le Grow in 1971, are the most extensively studied.<sup>9–22</sup> Azastan-

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natranes (**B**, M = Sn) and especially azagermatranes (**B**, M = Ge) are quite rare.<sup>23–28</sup> In contrast to metallatrane,<sup>1,4,29,30</sup> the structure of azametallatrane of the group 14 elements was rarely explored by X-ray diffraction studies.

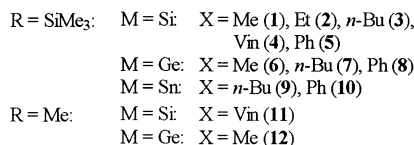
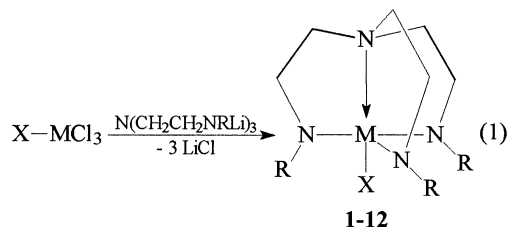
As a part of our program to investigate the chemical behavior of both metallatrane and azametallatrane and the degree of strength of the transannular M←N interactions in these compounds,<sup>31–40</sup> we recently reported a new approach to 1-haloazagermatranes and 1-haloazastannatrane, viz., treatment of MHal<sub>4</sub> (M = Ge, Sn) with N(CH<sub>2</sub>CH<sub>2</sub>NMeLi)<sub>3</sub> (Li<sub>3</sub>-Me-tren) and with N(CH<sub>2</sub>CH<sub>2</sub>NSiMe<sub>3</sub>Li)<sub>3</sub> (Li<sub>3</sub>-Me<sub>3</sub>Si-tren).<sup>41</sup> In this report we present the use of lithium salts Li<sub>3</sub>-Me-tren and Li<sub>3</sub>-Me<sub>3</sub>Si-tren in metathetical reactions of these salts with X-MCl<sub>3</sub> (M = Si, Ge, Sn) for the synthesis of 1-alkyl-, 1-vinyl-, and 1-arylametallatrane of the group 14 elements. A number of 1-arylametallatrane were obtained by transamination reactions between X-M(NMe<sub>2</sub>)<sub>3</sub> and N(CH<sub>2</sub>CH<sub>2</sub>NHR)<sub>3</sub>. The <sup>29</sup>Si NMR spectra of these compounds are discussed. X-ray structural investigations of four azametallatrane are presented.

It should be noted that the M–N contact distance in atrane is influenced by the nature of the metal, the electronic and steric properties of the apical substituent on the metal atom, and, of course, the structure of the atrane moiety. Motivation in our work was to study structural changes in azametallatrane arising from both the formal replacement of NMe or NH groups with NSiMe<sub>3</sub> groups in the azaatrane skeleton and the nature of apical substituents on the metal atom.

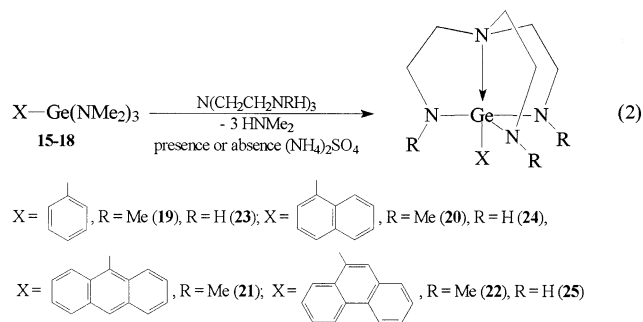
## Results and Discussion

The smooth reaction of X-MCl<sub>3</sub> (M = Si, Ge, Sn; X = organyl substituent) with Li<sub>3</sub>-Me<sub>3</sub>Si-tren during 24 h

at room temperature led to azametallatrane **1–10** in good yields (eq 1). The reaction of Li<sub>3</sub>-Me-tren with X-MCl<sub>3</sub> is less specific. We prepared azaatrane **11** and **12** as colorless liquids only in minor yields by the reaction of Li<sub>3</sub>-Me-tren with vinyl-SiCl<sub>3</sub> and Me-GeCl<sub>3</sub>, respectively (eq 1). Li<sub>3</sub>-Me<sub>3</sub>Si-tren and Li<sub>3</sub>-Me-tren were generated in situ by treatment of Me<sub>3</sub>Si-tren (**13**) and Me-tren (**14**) with 3 equiv of *n*-BuLi, respectively.



Due to small yields of azametallatrane **11** and **12** [N(CH<sub>2</sub>CH<sub>2</sub>NMe)<sub>3</sub>M–X], obtained from the reaction of Li<sub>3</sub>-Me-tren with X-MCl<sub>3</sub>, the usual approach to azametallatrane–transamination reaction (eq 2)—was used for preparation of 1-aryl-*N,N,N'*-trimethylazagermatranes (**19–22**). Tetraamine **14** reacts in several hours with X-Ge(NMe<sub>2</sub>)<sub>3</sub> (X = phenyl (**15**); 1-naphthyl (**16**); 9-antracenylyl (**17**); 9-phenantrenyl (**18**)) at high temperature without any solvent. The starting materials **15–18**, also unknown before, were readily synthesized by an exchange reaction between lithium or magnesium derivatives and Cl-Ge(NMe<sub>2</sub>)<sub>3</sub>. In a similar manner transamination reactions of X-Ge(NMe<sub>2</sub>)<sub>3</sub> (**15**, **16**, **18**) with the tetraamine **26** [N(CH<sub>2</sub>CH<sub>2</sub>NH<sub>2</sub>)<sub>3</sub>, tren] lead to the formation of azagermatranes **23–25** in satisfactory yields (eq 2). In contrast, reaction of trisamide **17** with tren **26** gives after workup procedure only polymeric products. Although Verkade et al. have demonstrated that transamination reactions between X-Ge(NMe<sub>2</sub>)<sub>3</sub> and **14** in the case of X = Me, *tert*-Bu demand the presence of a catalyst,<sup>23</sup> we have shown that it is not necessary in transamination reactions of aryltris(dimethylamino)germanes with the tetraamine **14**.



We also studied an alternative approach for the formation of azagermatranes containing trimethylsilyl substituents at the equatorial nitrogen atoms, viz., silylation reactions of azagermatranes N(CH<sub>2</sub>CH<sub>2</sub>NH)<sub>3</sub>Ge–X with a *n*-BuLi/Me<sub>3</sub>SiCl system (eq 3). The

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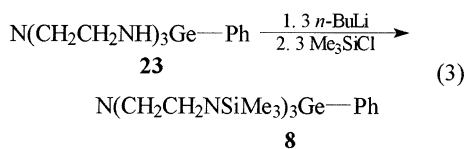
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**Table 1.** Crystal Data, Data Collection, Structure Solution, and Refinement Parameters for **5**, **8**, **10**, and **19**

	<b>5</b>	<b>8</b>	<b>10</b>	<b>19</b>
empirical formula	C <sub>21</sub> H <sub>44</sub> N <sub>4</sub> Si <sub>4</sub>	C <sub>21</sub> H <sub>44</sub> GeN <sub>4</sub> Si <sub>3</sub>	C <sub>21</sub> H <sub>44</sub> N <sub>4</sub> Si <sub>3</sub> Sn	C <sub>15</sub> H <sub>26</sub> GeN <sub>4</sub>
fw	464.96	509.46	555.56	334.99
color, habit	plate, colorless	prism, colorless	nugget, colorless	block, colorless
crystal size [mm]	0.60 × 0.30 × 0.21	0.35 × 0.25 × 0.18	0.48 × 0.30 × 0.27	0.40 × 0.30 × 0.20
crystal system	rhombohedral	rhombohedral	triclinic	orthorhombic
space group, Z	R3c, Z = 18	R3c, Z = 18	P1, Z = 4	P2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub> , Z = 4
unit cell dimens [Å and deg]	a = 20.3499(9) b = 20.3499(9) c = 34.489(3) α = 90 β = 90 γ = 120	a = 20.3810(6) b = 20.3810(6) c = 34.732(2) α = 90 β = 90 γ = 120	a = 10.7581(8) b = 16.267(1) c = 17.826(1) α = 73.644(6) β = 88.022(6) γ = 72.245(5)	a = 8.3466(6) b = 11.2962(8) c = 16.363(1) α = 90 β = 90 γ = 90
volume [Å <sup>3</sup> ]	12368.9(12)	12494.4(7)	2846.3(4)	1542.8(2)
density (calc), [g cm <sup>-3</sup> ]	1.124	1.219	1.296	1.442
abs coeff [mm <sup>-1</sup> ]	0.231	1.247	1.038	1.983
F(000)	4572	4896	1160	704
diffractometer	Stoe IPDS	Stoe IPDS	Stoe IPDS-II	Bruker SMART
temperature [K]	193(2)	193(2)	193(2)	110(2)
radiation [λ, Å]		graphite monochromatized Mo Kα, 0.71073		
θ-range [deg]	2.60 to 25.96	2.00 to 25.90	1.37 to 24.92	2.19 to 26.99
index ranges	-24 ≤ h ≤ 24 -24 ≤ k ≤ 24 -42 ≤ l ≤ 42	-24 < h ≤ 24 -25 ≤ k ≤ 25 -42 ≤ l ≤ 42	-12 ≤ h ≤ 12 -19 ≤ k ≤ 19 -21 ≤ l ≤ 21	-11 < h ≤ 11 -15 ≤ k ≤ 15 -23 ≤ l ≤ 13
no. of reflns collected	28 420	38 778	36 345	11 023
no. of ind reflns	5323 [R <sub>int</sub> = 0.0456]	5389 [R <sub>int</sub> = 0.0567]	9878 [R <sub>int</sub> = 0.0469]	3369 [R <sub>int</sub> = 0.0746]
data reduction	Stoe Integrate <sup>46a</sup>	Stoe Integrate <sup>46a</sup>	Stoe WinIntegrate <sup>46b</sup>	Bruker SAINT <sup>45a</sup>
abs corr	none	none	none	SADABS <sup>45b</sup>
min./max. transmn				0.4298/1.0000
no. of data/restraints/param	5323/1/272	5389/1/271	9878/0/541	3347/0/284
GOOF on F <sup>2</sup>	0.987	0.921	0.952	1.033
R <sub>1</sub> [I > 2σ(I)]	0.0272	0.0257	0.0204	0.0383
wR <sub>2</sub> (all data)	0.0656	0.0532	0.0508	0.0956
Flack param	0.00(7)	-0002(6)		-0.02(1)
largest diff peak and hole [e Å <sup>-3</sup> ]	0.217/-0.172	0.248/-0.342	0.537/-0.563	1.193/-1.168

small yield in the reaction above (<sup>1</sup>H NMR spectroscopy data) is probably due to steric hindrance in azagermatrane **23** in comparison with that of N(CH<sub>2</sub>CH<sub>2</sub>-NH)<sub>3</sub>Si-Me, which recently was used as a starting material for the synthesis of azasilatrane **1**.<sup>14</sup>



*N,N,N'*-Tris(trimethylsilyl)azasilatranes **2–5** were investigated by <sup>29</sup>Si NMR spectroscopy to establish the structure of these compounds in solution. The δ <sup>29</sup>Si<sub>central</sub> values (C<sub>6</sub>D<sub>6</sub>) of **2–5** [-24.7-(−21.4) ppm] shift to low field as compared with related *N,N,N'*-trimethylazasilatranes [-44.4-(−40.9) ppm].<sup>21</sup> In general, this fact underlines the decrease of coordination number at the silicon atom.<sup>42</sup> Consequently, the transannular Si<sub>central</sub> ← N<sub>ax</sub> interaction in *N,N,N'*-tris(trimethylsilyl)azasilatranes **2–5** in solution is weaker than that in the related *N,N,N'*-trimethylazasilatranes.

The same trend of weakness of this interaction for azametallatranes of the group 14 elements is observed in the solid state. To the best of our knowledge, compound **1** was the only one to be structurally characterized by X-ray studies<sup>14</sup> among the N(CH<sub>2</sub>CH<sub>2</sub>-NSiMe<sub>3</sub>)<sub>3</sub>Si-X series prior to our investigations. Recently we have prepared and characterized by X-ray analysis N(CH<sub>2</sub>CH<sub>2</sub>NSiMe<sub>3</sub>)<sub>3</sub>Ge-Cl.<sup>41</sup> Herein we report the crystal structures of N(CH<sub>2</sub>CH<sub>2</sub>NSiMe<sub>3</sub>)<sub>3</sub>M-C<sub>6</sub>H<sub>5</sub>

[M = Si (**5**), Ge (**8**), Sn (**10**)] and N(CH<sub>2</sub>CH<sub>2</sub>NMe)<sub>3</sub>Ge-C<sub>6</sub>H<sub>5</sub> (**19**). Table 2 summarizes crystal data as well as details of the data collection and structure refinement for compounds **5**, **8**, **10**, and **19**.<sup>43–46</sup>

Important bond lengths and angles for studied compounds are summarized in Table 2. The primary coordination environment at the Si(1) atom in **5** is formed by three covalently linked nitrogen atoms [N<sub>eq</sub>: N(1), N(7), N(10)] and the carbon atom C(11) and may be regarded as tetrahedral. Similarly, the coordination polyhedron at the germanium atom in **8** represents a slightly distorted tetrahedron with [N<sub>eq</sub>: N(1), N(3), N(4)] and C(7) atoms in the vertexes. However, both compounds may also be considered as the derivatives of pentacoordinated silicon and germanium with weak M←N<sub>ax</sub> interactions based on the following intramolecular distances [N(4)-Si(1) (2.792(1) Å) for **5** and N(2)-Ge(1) (2.766(2) Å) for **8**]. The latter values are considerably shorter than the sum of the van der Waals radii of Si and N (3.65 Å) and Ge and N (3.75 Å), respectively.<sup>47</sup> According to Verkade, these compounds have to be treated as *quasi*-azametallatranes.<sup>1</sup> The distances differ from the typical ranges for “normal” azasilatranes (2.034(2)–2.214(3) Å)<sup>15,21</sup> and azagermatranes (2.167(4)–2.278(2) Å).<sup>41</sup> A similar long distance Si←N<sub>ax</sub> was previously only found in the single

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(44) Sheldrick, G. M. *SHELXL-97, Program for the Refinement of Crystal Structures*; University of Göttingen: Germany, 1997.

(45) (a) *SAINT Version 5.0*; Bruker AXS Inc.: Madison, WI, 1997.

(b) *SHELXTL Version 5.0*; Bruker AXS Inc.: Madison, WI, 1997.

(46) (a) *Stoe-Integrate STOE IPDS Software Version 2.90*; STOE & CIE GmbH: Darmstadt, 1999. (b) *Stoe Win-Integrate STOE X-Area Version 1.15*; STOE & CIE GmbH: Darmstadt, 2001.

(47) Bondi, A. J. *Phys. Chem.* **1964**, *68*, 441–451.

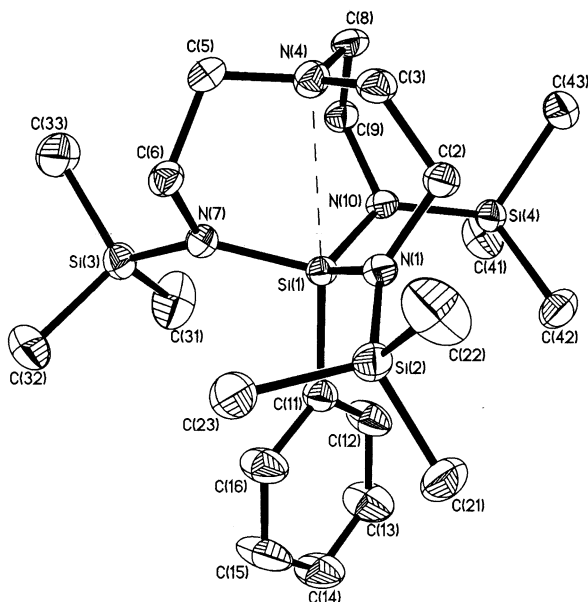
(42) Tandura, S. N.; Voronkov, M. G.; Alekseev, N. V. *Top. Curr. Chem.* **1986**, *131*, 99–189.



**Table 2.** Selected Bond Lengths (Å) and Angles (deg) for **5**, **8**, **10**, and **19**,  $N(CH_2CH_2NR)_3M-C_6H_5$ 

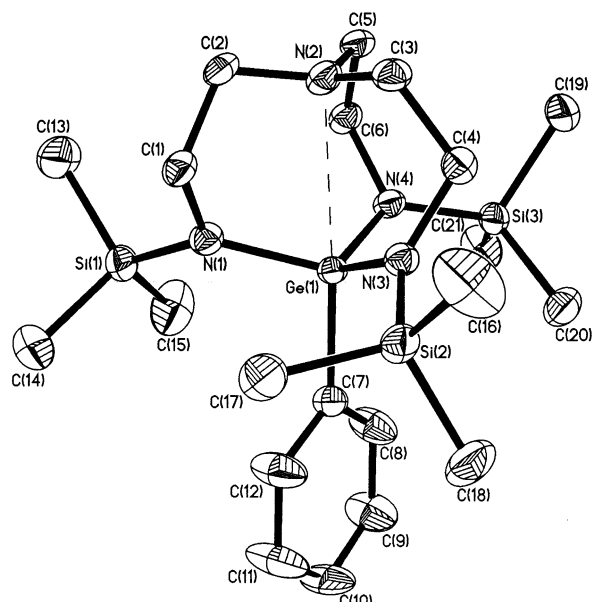
	<b>5</b> ; M = Si, R = SiMe <sub>3</sub>	<b>8</b> ; M = Ge, R = SiMe <sub>3</sub>	<b>10</b> ; M = Sn, R = SiMe <sub>3</sub>		<b>19</b> ; M = Ge, R = Me
			molecule A	molecule B	
M←N <sub>ax</sub>	2.792(1)	2.766(2)	2.509(2)	2.523(2)	2.307(2)
M←N <sub>eq</sub>	1.743(1)	1.850(2)	2.057(2)	2.052(2)	1.869(2)
	1.750(1)	1.855(2)	2.061(1)	2.054(2)	1.879(3)
	1.753(1)	1.862(2)	2.064(2)	2.057(2)	1.890(2)
M←C <sub>Ph</sub>	1.910(2)	1.985(2)	2.172(2)	2.169(2)	1.984(2)
ΔM <sup>a</sup>	0.50	0.54	0.51	0.51	0.32
ΔN <sub>ax</sub> <sup>b</sup>	0.17	0.22	0.38	0.38	0.38
N <sub>ax</sub> ←M←C <sub>Ph</sub>	176.2	176.4	172.50(6)	172.39(7)	176.15(9)
N <sub>eq</sub> ←M←N <sub>eq</sub>	113.74(6)	113.41(8)	112.10(6)	113.56(8)	120.4(1)
	111.96(6)	111.44(8)	111.38(6)	117.64(7)	115.3(1)
	110.87(6)	110.69(8)	118.89(6)	110.98(7)	115.8(1)
N <sub>eq</sub> ←M←C <sub>Ph</sub>	103.75(6)	104.28(9)	110.25(6)	100.18(7)	98.0(1)
	107.46(6)	107.39(8)	98.71(6)	111.24(7)	101.6(1)
	108.60(6)	109.28(9)	104.17(6)	101.90(7)	99.8(1)
C←N <sub>ax</sub> ←C	118.8(2)	117.6(2)	114.0(2)	113.6(2)	114.7(2)
	118.4(2)	117.7(2)	113.2(1)	113.8(2)	113.1(3)
	118.8(2)	117.9(2)	113.3(2)	113.5(2)	112.8(2)

<sup>a</sup> Displacement of M atom from the plane defined by the three N<sub>eq</sub> atoms toward the Ph substituent. <sup>b</sup> Displacement of N<sub>ax</sub> atom from the plane defined by the three carbon atoms toward the metal atom.



**Figure 1.** Molecular structure of complex **5**. Hydrogen atoms are omitted for clarity. Displacement ellipsoids are shown at the 50% probability level.

X-ray study of a *quasi*-azasilatrane,  $N(CH_2CH_2NSiMe_3)_3Si-Me$  (**1**) (2.775(7) Å).<sup>14</sup> The formal substitution of the Me<sub>3</sub>Si group by a hydrogen atom in compound **5** sharply shortens the transannular Si←N<sub>ax</sub> distance (2.132(4) Å for  $N(CH_2CH_2NH)_3Si-C_6H_5$ ).<sup>12</sup> The Si←C distance observed in **5** (1.910(2) Å) is somewhat longer than that in the closely related 1-phenylsilatrane  $N(CH_2CH_2O)_3Si-C_6H_5$  (1.882(6), 1.894(5), and 1.908(4) Å for different crystal modifications)<sup>48–50</sup> but slightly shorter than that in 1-phenylazasilatrane  $N(CH_2CH_2NH)_3Si-C_6H_5$  (1.922–(5) Å).<sup>12</sup> Analogously, the Ge←C bond (1.985(2) Å) for compound **8** is also longer than that in 1-phenylgermatrane  $N(CH_2CH_2O)_3Ge-C_6H_5$  (1.947(6) Å).<sup>51</sup> In con-



**Figure 2.** Molecular structure of complex **8**. Hydrogen atoms are omitted for clarity. Displacement ellipsoids are shown at the 50% probability level.

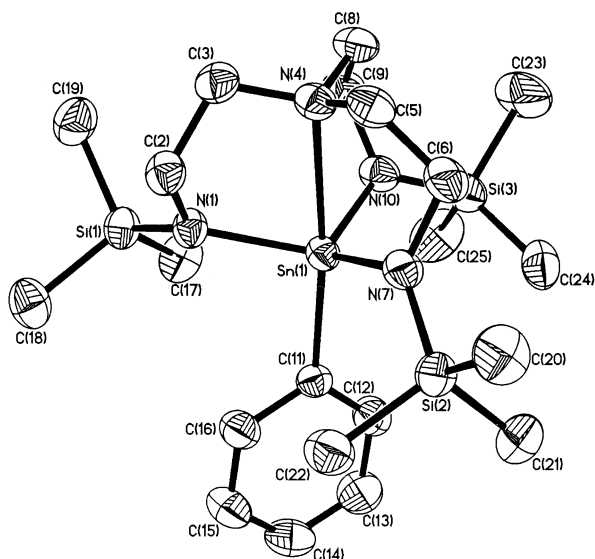
trast to **5** and **8**, the coordination polyhedron of the Ge atom in compound **19** and the Sn atom in compound **10** represents a distorted trigonal bipyramid with N(1) (for compound **19**) or N(4) (for compound **10**) and carbon atoms C(11) (for **10**) or C(1) (for **19**) occupying the axial positions and the three nitrogen atoms lying in equatorial sites. The Sn←C<sub>Ph</sub> distances observed in two independent molecules of **10** (2.172(2), 2.169(2) Å) are comparable to those found for the related 1-phenylazastannatrane  $N(CH_2CH_2NH)_3Sn-C_6H_5$ , 2.155(3) and 2.177(3) Å.<sup>26</sup> The Sn←N<sub>ax</sub> bonds (2.509(2) and 2.523(4) Å) in **10** are much longer than those in the single X-ray study of the azastannatrane  $N(CH_2CH_2NH)_3Sn-C_6H_5$ , 2.380(2) and 2.453(2) Å.<sup>26</sup> Similarly, the Ge←C<sub>Ph</sub> bond distance found in **19** (1.984(2) Å) is equal to that in **8**, and the Ge←N<sub>ax</sub> distances in **19** (2.307(2) Å) are shorter than that in **8**. The Si←N<sub>eq</sub> bond distances in **5** (average 1.749 Å) are slightly longer than that in  $N(CH_2CH_2NH)_3Si-C_6H_5$  (average 1.739 Å).<sup>12</sup> At the same time Ge←N<sub>eq</sub> bond distances in **8** (average 1.856 Å) are

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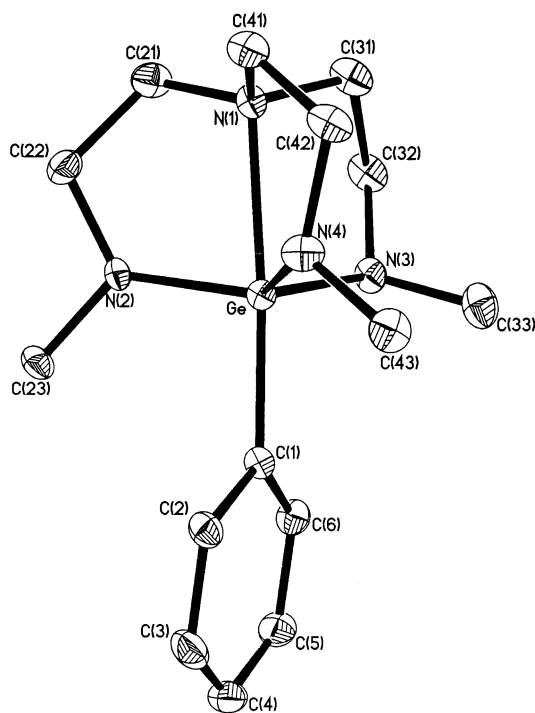
(49) Parkanyi, L.; Simon, K.; Nagy, J. *Acta Crystallogr.* **1974**, *B30*, 2328–2332.

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(51) Lukevics, E.; Ignatovich, L.; Belyakov, S. *J. Organomet. Chem.* **1999**, *588*, 222–230.



**Figure 3.** Molecular structure of complex **10** (one independent molecule). Hydrogen atoms are omitted for clarity. Displacement ellipsoids are shown at the 50% probability level.



**Figure 4.** Molecular structure of complex **19**. Hydrogen atoms are omitted for clarity. Displacement ellipsoids are shown at the 50% probability level.

shorter than that in **19** (average 1.877 Å). The formal substitution of Me<sub>3</sub>Si groups by hydrogen atoms in **10** and N(CH<sub>2</sub>CH<sub>2</sub>NH)<sub>3</sub>Si–C<sub>6</sub>H<sub>5</sub> does not influence significantly the Sn–N<sub>eq</sub> bond distances (average for two independent molecules: 2.058 and 2.058 Å, respectively). The environment of the N<sub>ax</sub> atom in compounds **10** and **19** is approximately tetrahedral. For both compounds, the axial nitrogen atoms are displaced by 0.38 Å from the plane defined by the three carbon atoms toward the metal atom. In contrast, the deviations of the N<sub>ax</sub> atom from the same planes in compounds **5** and **8** are significantly smaller (0.17 and 0.22 Å, respectively).

In conclusion, metathetical exchange reactions between X–MCl<sub>3</sub> (M = Si, Ge, Sn) and lithiated parent amines afforded compounds **1–12** in high yields. Transamination reactions of X–M(NMe<sub>2</sub>)<sub>3</sub> with Me-tren and tren resulted in azagermatranes **19–25**. The presence of a transannular M–N<sub>ax</sub> interaction in **10** and **19** was proven by X-ray diffraction analysis; according to the X-ray data, azametallatranes **5** and **8** possess extremely weak transannular bonds.

## Experimental Section

**General Comments.** All solvents were dried by standard methods and distilled before use. All reactions were carried out under argon atmosphere using standard Schlenk techniques. NMR spectra were recorded at 25 °C on Bruker AC 300 and Varian VXR 400 spectrometers; C<sub>6</sub>D<sub>6</sub> was used as the solvent and as internal deuterium lock in all cases except where indicated. The chemical shifts in the <sup>1</sup>H and <sup>13</sup>C NMR spectra are given in ppm relative to TMS. Elemental analyses were carried out by the Microanalytical Laboratory of the Chemistry Department of the Moscow State University and by that of the Fachbereich Chemie of the Philipps-University of Marburg (Heraeus-Rapid-Analyser). Mass spectra (EI-MS) were recorded on a Varian CH-7a device using electron impact ionization at 70 eV; mass spectra (FD-MS) were recorded on a HP-5989B device; all assignments were made with reference to the most abundant isotopes. X–MCl<sub>3</sub> (M = Si, Ge, Sn; R = Me, Et, *n*-Bu, vinyl, and Ph) (Aldrich) were used as supplied. Cl–Ge(NMe<sub>2</sub>)<sub>3</sub>,<sup>40</sup> Me<sub>3</sub>-tren,<sup>52</sup> and MeSi<sub>3</sub>-tren<sup>35</sup> were prepared according to the literature. C<sub>6</sub>D<sub>6</sub> was obtained from Deutero GmbH and dried over sodium/potassium alloy. The experimental details of synthesis of **15–18** are given in the Supporting Information.

**Synthesis of 1-Phenyl-*N,N,N'*-tris(trimethylsilyl)azasilatrane, N(CH<sub>2</sub>CH<sub>2</sub>NSiMe<sub>3</sub>)<sub>3</sub>Si–Ph (**5**).** To a stirred solution of the tetraamine **13** (1.74 g, 4.8 mmol) in toluene (40 mL) was added dropwise *n*-butyllithium (1.6 M in hexane, 6.1 mL, 9.8 mmol) at room temperature. The solution was stirred for 5 h. To this was added dropwise a solution of Ph–SiCl<sub>3</sub> (0.69 g, 3.3 mmol) in toluene (10 mL) at room temperature with stirring. The reaction mixture was stirred for a further 24 h, and then all volatiles were removed under reduced pressure. *n*-Pentane (20 mL) was added to the residue, and insoluble substances were removed by filtration. The solution was reduced in volume to one half and stored at –30 °C to obtain colorless crystals of **5** (yield 0.82 g, 54%). <sup>1</sup>H NMR (300.13 MHz): δ 0.13 (s, 27H, SiMe<sub>3</sub>), 2.40 (br s, 6H, NCH<sub>2</sub>), 2.82 (t, 6H, NCH<sub>2</sub>), 7.18–7.29 (m, 3H), 8.11–8.13 (m, 2H) Ph-hydrogens. <sup>13</sup>C NMR (75.47 MHz): δ 2.61 (SiMe<sub>3</sub>), 44.49 (N(Si)CH<sub>2</sub>), 58.21 (NCH<sub>2</sub>), 126.61, 127.75, 128.77, 137.46 (Ph-carbons). <sup>29</sup>Si NMR (79.49 MHz): δ –22.02 (SiN<sub>3</sub>), 3.57 (SiMe<sub>3</sub>). Anal. Calcd for C<sub>21</sub>H<sub>44</sub>N<sub>4</sub>Si<sub>4</sub> (464.94): C, 54.25; H, 9.54; N, 12.05. Found: C, 41.90; H, 6.16; N, 7.95. EI-MS: 465 (7.2, M<sup>+</sup>), 450 (2.1, M<sup>+</sup> – Me), 388 (5.8, M<sup>+</sup> – Ph).

A procedure similar to that for **5** was used for preparation of **1–4** and **6–10**.

**1-Methyl-*N,N,N'*-tris(trimethylsilyl)azasilatrane, N(CH<sub>2</sub>CH<sub>2</sub>NSiMe<sub>3</sub>)<sub>3</sub>Si–Me (**1**).** Yield: 87%. <sup>1</sup>H and <sup>13</sup>C NMR data are consistent with those already published.<sup>14</sup>

**1-Ethyl-*N,N,N'*-tris(trimethylsilyl)azasilatrane, N(CH<sub>2</sub>CH<sub>2</sub>NSiMe<sub>3</sub>)<sub>3</sub>Si–Et (**2**).** Yield: 83%. <sup>1</sup>H NMR (300.13 MHz): δ 0.22 (s, 27H, SiMe<sub>3</sub>), 0.98 (q, 2H, SiCH<sub>2</sub>), 1.27 (t, 3H, CH<sub>2</sub>CH<sub>3</sub>), 2.36 (br s, 6H, NCH<sub>2</sub>), 2.68 (t, 6H, NCH<sub>2</sub>). <sup>13</sup>C NMR (75.47 MHz): δ 1.94 (SiMe<sub>3</sub>), 10.63 (SiCH<sub>2</sub>), 14.95 (CH<sub>2</sub>CH<sub>3</sub>),

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44.45 (NCH<sub>2</sub>), 57.92 (NCH<sub>2</sub>). <sup>29</sup>Si NMR (79.49 MHz): δ -21.44 (SiN<sub>3</sub>), 2.23 (SiMe<sub>3</sub>). Anal. Calcd for C<sub>17</sub>H<sub>44</sub>N<sub>4</sub>Si<sub>4</sub> (416.90): C, 48.98; H, 10.64; N, 13.44. Found: C, 48.53; H, 10.25; N, 13.36. EI-MS: 417 (0.5, M<sup>+</sup>), 402 (8.8, M<sup>+</sup> - Me), 387 (100, M<sup>+</sup> - Et).

**1-*n*-Butyl-*N,N,N'*-tris(trimethylsilyl)azasilatrane, N(CH<sub>2</sub>CH<sub>2</sub>NSiMe<sub>3</sub>)<sub>3</sub>Si-*n*-Bu (3).** Yield: 65%. <sup>1</sup>H NMR (300.13 MHz): δ 0.25 (s, 27H, SiMe<sub>3</sub>), 0.97–1.77 (m, 9H, *n*-C<sub>4</sub>H<sub>9</sub>), 2.36 (br s, 6H, NCH<sub>2</sub>), 2.69 (t, 6H, NCH<sub>2</sub>). <sup>13</sup>C NMR (75.47 MHz): δ 1.99 (SiMe<sub>3</sub>), 14.07, 24.30, 27.87, 28.64 (CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 44.47 (NCH<sub>2</sub>), 57.94 (NCH<sub>2</sub>). <sup>29</sup>Si NMR (79.49 MHz): δ -21.47 (SiN<sub>3</sub>), 2.35 (SiMe<sub>3</sub>). Anal. Calcd for C<sub>19</sub>H<sub>48</sub>N<sub>4</sub>Si<sub>4</sub> (444.95): C, 51.29; H, 10.87; N, 12.59. Found: C, 50.88; H, 10.53; N, 12.18. EI-MS: 444 (0.1, M<sup>+</sup>), 429 (8.8, M<sup>+</sup> - Me), 387 (100, M<sup>+</sup> - C<sub>4</sub>H<sub>9</sub>).

**1-Vinyl-*N,N,N'*-tris(trimethylsilyl)azasilatrane, N(CH<sub>2</sub>CH<sub>2</sub>NSiMe<sub>3</sub>)<sub>3</sub>Si-Vinyl (4).** Yield: 79%. <sup>1</sup>H NMR (300.13 MHz): δ 0.23 (s, 27H, SiMe<sub>3</sub>), 2.28 (br s, 6H, NCH<sub>2</sub>), 2.65 (t, 6H, NCH<sub>2</sub>), 5.91–6.03 (m, 2H, =CH<sub>2</sub>), 6.37–6.55 (m, 1H, =C(Si)H). <sup>13</sup>C NMR (75.47 MHz): δ 2.41 (SiMe<sub>3</sub>), 43.23 (NCH<sub>2</sub>), 58.26 (NCH<sub>2</sub>), 131.05 (SiCH=), 144.80 (CH<sub>2</sub>=). <sup>29</sup>Si NMR (79.49 MHz): δ -24.71 (SiN<sub>3</sub>), 3.28 (SiMe<sub>3</sub>). Anal. Calcd for C<sub>17</sub>H<sub>42</sub>N<sub>4</sub>Si<sub>4</sub> (414.88): C, 49.21; H, 10.20; N, 13.50. Found: C, 48.89; H, 9.95; N, 12.96. FD-MS: 414 (100, M<sup>+</sup>).

**1-Methyl-*N,N,N'*-tris(trimethylsilyl)azagermatrane, N(CH<sub>2</sub>CH<sub>2</sub>NSiMe<sub>3</sub>)<sub>3</sub>Ge-Me (6).** Yield: 44%. <sup>1</sup>H NMR (300.13 MHz): δ 0.20 (s, 27H, SiMe<sub>3</sub>), 0.72 (s, 3H, GeMe), 2.23 (br s, 6H, NCH<sub>2</sub>), 2.68 (t, 6H, NCH<sub>2</sub>). <sup>13</sup>C NMR (75.47 MHz): δ -3.07 (GeMe), 1.78 (SiMe<sub>3</sub>), 42.32 (NCH<sub>2</sub>), 58.75 (NCH<sub>2</sub>). Anal. Calcd for C<sub>16</sub>H<sub>42</sub>GeN<sub>4</sub>Si<sub>3</sub> (447.38): C, 42.96; H, 9.64; N, 12.52. Found: C, 43.45; H, 9.94; N, 12.31. EI-MS: 433 (3.2, M<sup>+</sup> - Me), 408 (7.1, M<sup>+</sup> - Me - Me<sub>3</sub>SiNCH<sub>2</sub>).

**1-*n*-Butyl-*N,N,N'*-tris(trimethylsilyl)azagermatrane, N(CH<sub>2</sub>CH<sub>2</sub>NSiMe<sub>3</sub>)<sub>3</sub>Ge-*n*-Bu (7).** Yield: 71%. <sup>1</sup>H NMR (300.13 MHz): δ 0.24 (s, 27H, SiMe<sub>3</sub>), 0.96–1.84 (m, 9H, *n*-C<sub>4</sub>H<sub>9</sub>), 2.31 (br s, 6H, NCH<sub>2</sub>), 2.72 (t, 6H, NCH<sub>2</sub>). <sup>13</sup>C NMR (75.47 MHz): δ 2.01 (SiMe<sub>3</sub>), 13.94, 27.29, 27.80, 28.42 (CH<sub>2</sub>-CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 43.20 (NCH<sub>2</sub>), 59.13 (NCH<sub>2</sub>). Anal. Calcd for C<sub>19</sub>H<sub>48</sub>GeN<sub>4</sub>Si<sub>3</sub> (489.46): C, 46.62; H, 9.88; N, 11.45. Found: C, 46.08; H, 9.74; N, 11.12. EI-MS: 491 (4.5, M<sup>+</sup>), 476 (12.3, M<sup>+</sup> - Me), 433 (100, M<sup>+</sup> - C<sub>4</sub>H<sub>9</sub>), 389 (54.1, M<sup>+</sup> - Me<sub>3</sub>SiNCH<sub>2</sub>).

**1-Phenyl-*N,N,N'*-tris(trimethylsilyl)azagermatrane, N(CH<sub>2</sub>CH<sub>2</sub>NSiMe<sub>3</sub>)<sub>3</sub>Ge-Ph (8).** Yield: 49%. <sup>1</sup>H NMR (300.13 MHz): δ 0.15 (s, 27H, SiMe<sub>3</sub>), 2.34 (br s, 6H, N(Si)CH<sub>2</sub>), 2.83 (t, 6H, NCH<sub>2</sub>), 7.16–7.27 (m, 3H), 8.10–8.13 (m, 2H) Ph-hydrogens. <sup>13</sup>C NMR (75.47 MHz): δ 2.59 (SiMe<sub>3</sub>), 43.28 (N(Si)-CH<sub>2</sub>), 59.31 (NCH<sub>2</sub>), 127.23, 128.35, 129.03, 136.19 (Ph-carbons). Anal. Calcd for C<sub>21</sub>H<sub>44</sub>GeN<sub>4</sub>Si<sub>3</sub> (509.45): C, 49.51; H, 8.71; N, 11.00. Found: C, 49.30; H, 8.64; N, 10.46. EI-MS: 510 (2.1, M<sup>+</sup>), 450 (7.7, M<sup>+</sup> - Me), 433 (2.3, M<sup>+</sup> - Ph), 408 (95.5, M<sup>+</sup> - Me<sub>3</sub>SiNCH<sub>2</sub>).

**1-*n*-Butyl-*N,N,N'*-tris(trimethylsilyl)azastannatrane, N(CH<sub>2</sub>CH<sub>2</sub>NSiMe<sub>3</sub>)<sub>3</sub>Sn-*n*-Bu (9).** Yield: 61%. <sup>1</sup>H NMR (300.13 MHz): δ 0.24 (s, 27H, SiMe<sub>3</sub>), 0.94–1.63 (m, 9H, *n*-C<sub>4</sub>H<sub>9</sub>), 2.06 (t, 6H, NCH<sub>2</sub>), 2.77 (t, 6H, NCH<sub>2</sub>). <sup>13</sup>C NMR (75.47 MHz): δ 2.19 (SiMe<sub>3</sub>), 13.88, 26.51, 28.27, 29.14 (CH<sub>2</sub>-CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 41.45 (NCH<sub>2</sub>), 60.58 (NCH<sub>2</sub>). Anal. Calcd for C<sub>19</sub>H<sub>48</sub>N<sub>4</sub>Si<sub>3</sub>Sn (435.56): C, 42.61; H, 9.03; N, 10.46. Found: C, 42.29; H, 8.78; N, 10.22. EI-MS: 322 (7.1, M<sup>+</sup> - C<sub>4</sub>H<sub>9</sub> - Me<sub>3</sub>SiN - Me<sub>3</sub>Si).

**1-Phenyl-*N,N,N'*-tris(trimethylsilyl)azastannatrane, N(CH<sub>2</sub>CH<sub>2</sub>NSiMe<sub>3</sub>)<sub>3</sub>Sn-Ph (10).** Yield: 47%. <sup>1</sup>H NMR (300.13 MHz): δ 0.17 (s, 27H, SiMe<sub>3</sub>), 2.10 (t, 6H, NCH<sub>2</sub>), 2.85 (t, 6H, NCH<sub>2</sub>), 7.24–7.32 (m, 3H), 8.10–8.11 (m, 2H) Ph-hydrogens. <sup>13</sup>C NMR (75.47 MHz): δ 1.33 (SiMe<sub>3</sub>), 42.75 (N(Si)-CH<sub>2</sub>), 60.73 (NCH<sub>2</sub>), 126.12, 127.45, 128.83, 134.90 (Ph-carbons). Anal. Calcd for C<sub>21</sub>H<sub>44</sub>N<sub>4</sub>Si<sub>3</sub>Sn (555.55): C, 45.40; H, 7.98; N, 10.08. Found: C, 45.11; H, 8.30; N, 10.21. EI-MS: 147 (100).

**Synthesis of 1-Vinyl-*N,N,N'*-trimethylazasilatrane, N(CH<sub>2</sub>CH<sub>2</sub>NMe)<sub>3</sub>Si-Vinyl (11).** To a stirred solution of the

tetraamine **14** (0.52 g, 2.8 mmol) in hexane (25 mL) was added dropwise *n*-butyllithium (1.6 M in hexane, 5.25 mL, 8.4 mmol) at room temperature. The mixture was stirred for 0.5 h. To this was added dropwise a solution of vinyl-SiCl<sub>3</sub> (0.45 g, 2.8 mmol) in toluene (10 mL) at room temperature with stirring. The reaction mixture was stirred for a further 24 h, and all volatiles were removed under reduced pressure. Toluene (20 mL) was added to the residue, and insoluble substances were removed by filtration. All volatiles were removed in vacuo to obtain **11** as a colorless oil (yield 0.18 g, 27%). <sup>1</sup>H NMR (300.13 MHz): δ 2.22 (t, 6H, NCH<sub>2</sub>), 2.58 (t, 6H, NCH<sub>2</sub>), 2.67 (s, 9H, CH<sub>3</sub>), 5.98–6.15 (m, 2H, =CH<sub>2</sub>), 6.39–6.52 (m, 1H, =C(Si)H). <sup>13</sup>C NMR (75.47 MHz): δ 37.55 (Me), 49.75 (NCH<sub>2</sub>), 49.88 (NCH<sub>2</sub>), 129.20 (SiCH=), 141.73 (CH<sub>2</sub>=). Anal. Calcd for C<sub>11</sub>H<sub>24</sub>N<sub>4</sub>Si (240.42): C, 54.95; H, 10.06; N, 23.30. Found: C, 55.31; H, 9.89; N, 23.47.

**Synthesis of 1-Methyl-*N,N,N'*-trimethylazagermatrane, N(CH<sub>2</sub>CH<sub>2</sub>NMe)<sub>3</sub>Ge-Me (12).** A procedure similar to that for **11** was used. Yield: 52%. <sup>1</sup>H and <sup>13</sup>C NMR data are consistent with those already published.<sup>23</sup>

**Synthesis of 1-Phenyl-*N,N,N'*-trimethylazagermatrane, N(CH<sub>2</sub>CH<sub>2</sub>NMe)<sub>3</sub>Ge-Ph (19).** A mixture of phenyltris(dimethylamino)germane (**15**) (1.21 g, 4.3 mmol) and tetraamine (**14**) (0.76 g, 4.04 mmol) was stirred at 130–135 °C for 2 h. Evolution of dimethylamine was observed during heating. The reaction mixture was allowed to cool to room temperature and colorless liquid crystallized to a white solid. Crude product was recrystallized from hot *n*-heptane to give 0.73 g (54%) of **19** as a white solid. <sup>1</sup>H NMR (400.13 MHz): δ 2.26 (t, NCH<sub>2</sub>, 6H), 2.59 (s, NMe, 9H), 2.72 (t, NCH<sub>2</sub>, 6H), 7.20–7.35 (m, aromatic protons), 8.08 (d, aromatic protons, 2H). <sup>13</sup>C NMR (100.61 MHz): δ 39.74 (NMe), 50.38 (NCH<sub>2</sub>), 50.58 (NCH<sub>2</sub>), 122.01, 127.91, 136.34, 141.76 (aromatic carbons). Anal. Calcd for C<sub>15</sub>H<sub>26</sub>GeN<sub>4</sub> (334.98): C, 53.78; H, 7.82; N, 16.73. Found: C, 54.30; H, 8.28; N, 17.32. EI-MS: 336 (1.5, M<sup>+</sup>), 280 (6.0, M<sup>+</sup> - CH<sub>2</sub>CH<sub>2</sub>NCH<sub>2</sub>), 259 (6.0, M<sup>+</sup> - Ph).

A procedure similar to that for **19** was used for the preparation of **20–24**.

**1-(1-Naphthyl)-*N,N,N'*-trimethylazagermatrane, N(CH<sub>2</sub>CH<sub>2</sub>NMe)<sub>3</sub>Ge-(1-naphthyl) (20).** Yield: 53%. <sup>1</sup>H NMR (400.13 MHz): δ 2.29 (t, NCH<sub>2</sub>, 6H), 2.49 (s, NMe, 9H), 2.76 (t, NCH<sub>2</sub>, 6H), 7.29–7.51 (m, aromatic protons), 7.72–7.75 (m, aromatic protons), 8.59 (d, aromatic proton, 1H), 8.81 (d, aromatic proton, 1H). <sup>13</sup>C NMR (100.61 MHz): δ 39.67 (NMe), 50.35 (NCH<sub>2</sub>), 50.64 (NCH<sub>2</sub>), 125.34, 125.78, 125.88, 128.88, 129.23, 130.81, 134.21, 134.98, 138.68, 140.76 (aromatic carbons). Anal. Calcd for C<sub>19</sub>H<sub>28</sub>GeN<sub>4</sub> (385.04): C, 59.26; H, 7.33; N, 14.55. Found: C, 59.16; H, 7.35; N, 14.13. EI-MS: 386 (4.5, M<sup>+</sup>), 330 (23.0, M<sup>+</sup> - CH<sub>2</sub>CH<sub>2</sub>NCH<sub>2</sub>), 259 (24.3, M<sup>+</sup> - C<sub>10</sub>H<sub>7</sub>).

**1-(9-Anthracenyl)-*N,N,N'*-trimethylazagermatrane, N(CH<sub>2</sub>CH<sub>2</sub>NMe)<sub>3</sub>Ge-(9-anthracenyl) (21).** Yield: 34%. <sup>1</sup>H NMR (400.13 MHz): δ 2.29 (t, NCH<sub>2</sub>, 6H), 2.37 (s, NMe, 9H), 2.82 (t, NCH<sub>2</sub>, 6H), 7.23 (d, aromatic protons, 2H), 7.32–7.36 (m, aromatic protons), 7.52–7.55 (m, aromatic protons), 7.90 (d, aromatic protons, 2H), 8.32 (s, aromatic proton, 1H). <sup>13</sup>C NMR (100.61 MHz): δ 39.55 (NMe), 50.56 (NCH<sub>2</sub>), 50.80 (NCH<sub>2</sub>), 124.89, 125.09, 129.21, 129.38, 131.03, 132.19, 138.48, 139.89 (aromatic carbons). Anal. Calcd for C<sub>23</sub>H<sub>30</sub>GeN<sub>4</sub> (435.10): C, 63.49; H, 6.95; N, 12.88. Found: C, 63.70; H, 6.88; N, 12.54. EI-MS: 436 (5.5, M<sup>+</sup>), 379 (10.7, M<sup>+</sup> - CH<sub>2</sub>CH<sub>2</sub>NMe), 259 (11.0, M<sup>+</sup> - C<sub>14</sub>H<sub>9</sub>).

**1-(9-Phenanthrenyl)-*N,N,N'*-trimethylazagermatrane, N(CH<sub>2</sub>CH<sub>2</sub>NMe)<sub>3</sub>Ge-(9-phenanthrenyl) (22).** Yield: 23% ((NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>, 10 mol %, was added to the reaction mixture). <sup>1</sup>H NMR (400.13 MHz): δ 2.28 (t, NCH<sub>2</sub>, 6H), 2.53 (s, NMe, 9H), 2.77 (t, NCH<sub>2</sub>, 6H), 7.36–7.59 (m, aromatic protons) 7.90 (d, aromatic proton, 1H), 8.54 (d, aromatic proton, 1H), 8.60 (d, aromatic proton, 1H), 8.90 (s, aromatic proton, 1H). <sup>13</sup>C NMR (100.61 MHz): δ 39.76 (NMe), 50.32 (NCH<sub>2</sub>), 50.67 (NCH<sub>2</sub>), 122.86, 123.01, 123.13, 126.09, 126.59, 126.83, 129.34,



130.66, 131.43, 131.52, 132.54, 136.77, 136.82, 139.39 (aromatic carbons). Anal. Calcd for  $C_{23}H_{30}GeN_4$  (435.10): C, 63.49; H, 6.95; N, 12.88. Found: C, 63.54; H, 7.23; N, 12.48. EI-MS: 436 (3.6,  $M^+$ ), 259 (7.9,  $M^+ - C_{14}H_9$ ).

**1-Phenylazagermatrane,  $N(CH_2CH_2NH)_3Ge-Ph$  (23).** Yield: 79%.  $^1H$  NMR (400.13 MHz):  $\delta$  0.68 (br s,  $GeNH$ , 3H), 2.20 (t,  $NCH_2$ , 6H), 2.78 (t,  $NCH_2$ , 6H), 7.21–7.28 (m, aromatic protons, 3H), 7.79 (d, aromatic protons, 2H).  $^{13}C$  NMR (100.61 MHz):  $\delta$  38.47 ( $NCH_2$ ), 52.53 ( $NCH_2$ ), 127.94, 128.33, 133.51, 146.87 (aromatic carbons). Anal. Calcd for  $C_{12}H_{20}GeN_4$  (292.90): C, 49.21; H, 6.88; N, 19.13. Found: C, 49.47; H, 6.81; N, 19.29. EI-MS: 292 (2.0,  $M^+$ ), 277 (5.5,  $M^+ - CH_3$ ), 217 (9.6,  $M^+ - Ph$ ).

**1-(1-Naphthyl)azagermatrane,  $N(CH_2CH_2NH)_3Ge-(1-naphthyl)$  (24).** Yield: 65%.  $^1H$  NMR (400.13 MHz):  $\delta$  0.82 (s,  $GeNH$ , 3H), 2.30 (t,  $NCH_2$ , 6H), 2.85 (t,  $NCH_2$ , 6H), 7.39–7.55 (m, aromatic protons, 3H), 7.82 (t, aromatic protons, 2H), 8.24 (d, aromatic proton, 1H), 9.17 (d, aromatic proton, 1H).  $^{13}C$  NMR (100.61 MHz):  $\delta$  38.86 ( $NCH_2$ ), 53.55 ( $NCH_2$ ), 121.73, 125.34, 128.93, 129.05, 131.03, 132.82, 134.63, 137.91, 144.90 (aromatic carbons, one crossed with  $C_6D_6$  signals). Anal. Calcd for  $C_{16}H_{22}GeN_4$  (342.96): C, 56.03; H, 6.47; N, 16.34. Found: C, 55.85; H, 6.13; N, 16.56. EI-MS: 344 (4.5,  $M^+$ ), 217 (13.0,  $M^+ - C_{10}H_7$ ).

**Synthesis of 1-(9-Phenanthrenyl)azagermatrane,  $N(CH_2CH_2NMe)_3Ge-(9-phenanthrenyl)$  (25).** A mixture of 9-phenanthrenyltris(dimethylamino)germane (2.62 g, 6.8 mmol) and tren (0.95 g, 6.5 mmol) was stirred and heated at 170–180 °C for 11 h. Slow evolution of dimethylamine was observed. The reaction mixture was allowed to cool to room temperature, and brown oil crystallized to solid. The reaction mixture was treated with toluene (25 mL), and insoluble residue was filtered off. Toluene was removed in vacuo, and residue was recrystallized from hot *n*-heptane. **25** was obtained as a yellow solid in 22% yield (0.57 g).  $^1H$  NMR (400.13 MHz):  $\delta$  0.73 (s,  $GeNH$ , 3H), 2.19 (t,  $NCH_2$ , 6H), 2.76 (t,  $NCH_2$ , 6H), 7.38–7.58 (m, aromatic protons, 4H), 7.84 (d, aromatic proton, 1H), 8.54 (d, aromatic proton, 1H), 8.55 (s, aromatic proton, 1H), 8.62 (d, aromatic proton, 1H), 9.14 (d, aromatic proton, 1H).  $^{13}C$  NMR (100.61 MHz):  $\delta$  38.94 ( $NCH_2$ ), 53.67 ( $NCH_2$ ), 122.81, 123.27, 126.03, 126.21, 126.65, 126.73, 129.14, 131.11,

131.29, 131.67, 132.05, 134.75, 136.18, 143.14 (aromatic carbons). Anal. Calcd for  $C_{20}H_{24}GeN_4$  (393.02): C, 61.12; H, 6.15; N, 14.25. Found: C, 60.81; H, 6.23; N, 14.39. EI-MS: 217 (1.3,  $M^+ - C_{10}H_7$ ).

**Sylation Reaction of 1-Phenylazagermatrane (24).** To a stirred solution of **24** (0.30 g, 1.0 mmol) in THF (15 mL) was added dropwise *n*-butyllithium (1.6 M in hexane, 2.00 mL, 3.2 mmol) at –78 °C. The mixture was stirred for 10 min at this temperature and an additional 4 h at room temperature. To this was added dropwise a solution of  $Me_3SiCl$  (0.45 mL, 3.7 mmol) in THF (5 mL) at –40 °C with stirring. The reaction mixture was stirred for a further 12 h at room temperature, and all volatiles were removed under reduced pressure. *n*-Hexane (20 mL) was added to the residue, and insoluble substances were removed by filtration. All volatiles were removed in vacuo to obtain a yellow oil, containing according to  $^1H$  NMR spectroscopy data a minor quantity of azagermatrane **8**.

**X-ray Crystallography.** Table 2 summarizes crystal data as well as details of the data collection and structure refinement for compounds **5**, **8**, **10**, and **19**. All presented structures were solved by direct methods<sup>43</sup> and refined by full matrix least-squares on  $F^2$  with anisotropic thermal parameters for all non-hydrogen atoms.<sup>44</sup> In the structures of **5**, **8**, and **10** hydrogen atoms were placed in calculated positions and refined using a riding model. As for **19**, all hydrogen atoms were refined isotropically.

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**Supporting Information Available:** X-ray crystallographic files, in CIF format, for the structures of **5**, **8**, **10**, and **19** as well as experimental details of the syntheses of **15**–**18**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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