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Reactions of Bis[bis(trimethylsilyl)methyl]germylene and the Corresponding Stannylene with Diazidosilanes

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ABSTRACT

*The reactions of bis[bis(trimethylsilyl)methyl]-germylene (**1**) and the corresponding stannylene (**2**) with di-tert-butyldiazidosilane gave N-(azidosilyl)germanimine (**4**) and the stannanimine (**5**) in quantitative yields. The structures have been confirmed by single-crystal X-ray diffraction. Crystal data for **4**: space group* $P\bar{1}$, $Z = 2$, $a = 9.236\ (1)$, $b = 12.066\ (1)$, $c = 17.068\ (1)$ Å, $\alpha = 98.45\ (1)$, $\beta = 90.43$, $\gamma = 110.27\ (1)^\circ$. $V = 1761.3$ Å^3, $R = 0.051$, *and* $Rw = 0.069$ *based on 4218 reflections with* $|Fo^2| \geq 3\sigma|Fo^2|$. *For **5**: space group* $P\bar{1}$, $Z = 2$, $a = 9.183\ (1)$, $b = 12.193\ (1)$, $c = 17.292\ (1)$ Å, $\alpha = 98.74\ (1)$, $\beta = 90.21$, $\gamma = 109.96\ (1)^\circ$, $V = 1795.5$ Å^3, $R = 0.040$, *and* $Rw = 0.051$ *based on 4795 reflections. The similar reactions of **1** and **2** with 1,3-diazidohexamethyltrisilane (**16**) provided azatrisilacyclobutanes quantitatively.*

INTRODUCTION

Over the last few years, interest in the chemistry of group 14 element-heteroatom multiple bonds has increased. In particular, it has been established that silanimines (Si=N) [1], germanimines (Ge=N) [2], and stannanimines (Sn=N) [3] are easily accessible by reactions of silylenes (R_2Si:), germylenes (R_2Ge:), and stannylenes (R_2Sn:) with azides (Equation 1). In a recent article [4,5], we reported preparation of *N*-(azidosilyl)germanimines by conversion of bis[bis(trimethylsilyl)methyl]germylene (**1**) [6] with di-*tert*-butyl- and dimesityldiazidosilane and reactions of **1** with dimethyl- and diphenyldiazidosilane. Herein, we wish to report the synthesis and structural features of the stable *N*-(azidosilyl)stannanimine (**5**) which was obtained by treatment of the corresponding stannylene (**2**) with di-*tert*-butyldiazidosilane (**3**) and also the corresponding *N*-(azidosilyl)germanimine (**4**) prepared and studied in an analogous manner. Furthermore, similar reactions of **1** and **2** with 1,1-diazidosilanes and with methyl substituted 1,2- and 1,3-diazidosilanes were performed.

RESULTS AND DISCUSSION

Syntheses and Structures of the N-(Azidosilyl)germanimine (**4**) *and the stannanimine* (**5**)

Treatment of a yellow colored solution of **1** with an equimolar amount of di-*tert*-butyldiazidosilane (**3**) at ambient temperature resulted in rapid decolorization of the solution. After removal of the solvent, colorless crystals of **4** were obtained (Equation 2). Compound **4** is stable in solution in the absence of air. In the ^1H NMR spectrum, the appearance of only one signal for the trimethylsilyl groups is similar to the observations with other stable germanimines [7]. The low field shifted ^{13}C resonance at $\delta = 32$ (in C_6D_6) of the methine carbon atom, as well as the high field shifted ^{29}Si res-

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Dedicated to Prof. Adrian Gibbs Brook on the occasion of his seventieth birthday.

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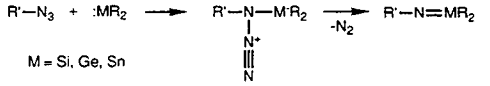
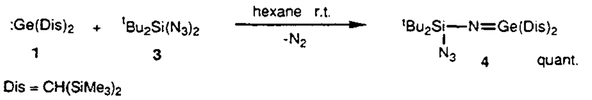


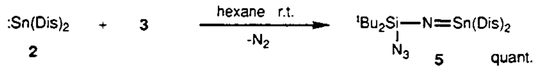
$$\mathrm{R'{-}N_3 + {:}MR_2 \longrightarrow R'{-}\underset{\substack{|\\ N^{+}\\ |||\\ N}}{N}{-}MR_2 \xrightarrow[-N_2]{} R'{-}N{=}MR_2} \qquad (1)$$

M = Si, Ge, Sn



$$\underset{\mathbf{1}}{\mathrm{{:}Ge(Dis)_2}} + \underset{\mathbf{3}}{\mathrm{{}^tBu_2Si(N_3)_2}} \xrightarrow[-N_2]{\text{hexane r.t.}} \mathrm{{}^tBu_2\underset{\substack{|\\ N_3}}{Si}{-}N{=}Ge(Dis)_2} \quad \mathbf{4} \ \text{quant.} \qquad (2)$$

Dis = CH(SiMe$_3$)$_2$



$$\underset{\mathbf{2}}{\mathrm{{:}Sn(Dis)_2}} + \mathbf{3} \xrightarrow[-N_2]{\text{hexane r.t.}} \mathrm{{}^tBu_2\underset{\substack{|\\ N_3}}{Si}{-}N{=}Sn(Dis)_2} \quad \mathbf{5} \ \text{quant.} \qquad (3)$$

onance of the ^{t}Bu$_2$Si unit at $\delta = -10$, indicates a strong polarity of the germanimine moiety (Ge$^+$–N$^-$).

Crystals which were suitable for X-ray analysis were obtained by slow evaporation of a hexane solution of **4**. The ORTEP plot is shown in Figure 1, and the crystal data, positional parameters, and selected bonding parameters are summarized in Tables 1, 2, and 3, respectively. The Ge=N bond distance of 1.704(5) Å is comparable with those of other germanimines prepared by Meller and co-workers (1.691(1), 1.703(2) Å) [8] and is in good agreement with an ab initio calculation (1.695 Å) [9]. The torsional angles C1–Ge=N–Si of 1.0° and C2–Ge=N–Si of 177.9° show an almost planar arrangement of the germanimine unit, as expected for a normal *pπ-pπ* double bond. The angle of Ge=N–Si (136.0°) is bent, presumably to decrease repulsion between bulky substituents on the silicon and germanium atoms.

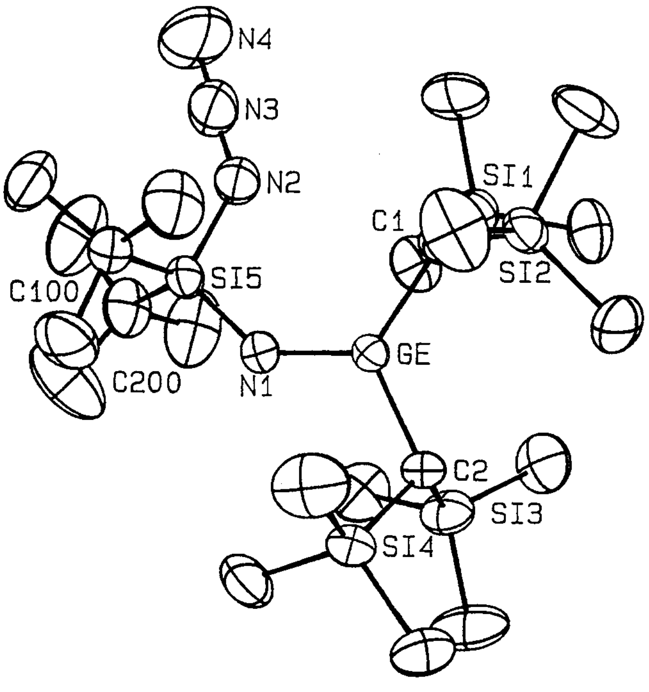


FIGURE 1 ORTEP drawing of **4**.

The reaction of the stannylene **2**, a higher group 14 of analog of **1**, with diazidosilane **3** proceeded in the same manner as that of the reaction of **1** with **3** and afforded the N-(azidosilyl)stannanimine (**5**) as yellow crystals in quantitative yield (Equation 3). As in the case of compound **4**, the low field shifted methine ^{13}C resonance at $\delta = 35.43$ and ^{29}Si resonance upfield at $\delta = -18.6$ indicate the presence of a polarized stannanimine moiety (Sn$^+$–N$^-$). The most intriguing value is the chemical shift of the ^{119}Sn, which appeared at 340 ppm higher field than Me$_4$Sn. By comparison with other doubly bonded tin derivatives, this value is relatively highly shifted (725 and 740 ppm for Dis$_2$Sn=SnDis$_2$ [10], 658 ppm for Dis$_2$Sn=PMes* (Mes* = 2,4,6-tri-*tert*-butylphenyl) [11], and 499.5 ppm for Is$_2$Sn=PMes* (Is = 2,4,6-triisopropylphenyl) [12]). However, a ^{119}Sn chemical shift of a stannanimine which had been prepared by Meller and co-workers was reported to show a high field shifted signal (δc −3.5 in toluene-d$_8$ at −40°C) [3].

Crystals which were suitable for X-ray analysis were obtained by slow evaporation of a hexane solution of **5**, much the same as for the preparation of crystals of compound **4**. The ORTEP plot is shown in Figure 2, and positional parameters and selected bonding parameters are shown in Tables 4 and 5. Interestingly, the crystal of compound **5** is isomorphous to that of compound **4** (unit cell parameters of the two compounds being about the same). The Sn=N bond distance of 1.905(5) Å is slightly shortened compared to that of other stannanimines (1.921(2) Å) [3] and further shortened by 0.1 Å than that found in the usual Si–N single bond. Similar to the germanimine, torsional angles for C1–Ge=N–Si of 1.9° and for C2–Ge=N–Si of 178.4° indicate that the stannanimine unit is almost planar.

Reactions of N-(Azidosilyl)germanimine (4)

Compound **4** is hydrolyzed easily in air to give the germanol **6** and reacts with methanol very easily to afford the corresponding adduct **7**. Although there is a Ge = N double bond and one azido group in the same molecule, compound **4** is thermally stable and can be recovered unchanged after having been heated to 140°C in C$_6$D$_6$ for 10 hours (sealed NMR tube). The photolysis of **4** with a high pressure Hg lamp for several hours gave the cyclic germanimine (**8**) in 60% yield, and the structure was based on NMR spectroscopic data. (Scheme 1) Compound **8** seems to be formed by intramolecular C–H insertion of a nitrene moiety, although photolysis of silylazide derivatives usually gives silanimines via migration of a substituent on silicon to the nitrene [13]. Recently, we reported that the reaction of **4** with an equivalent amount of **1**

TABLE 1 Crystallographic Data for **4** and **5**

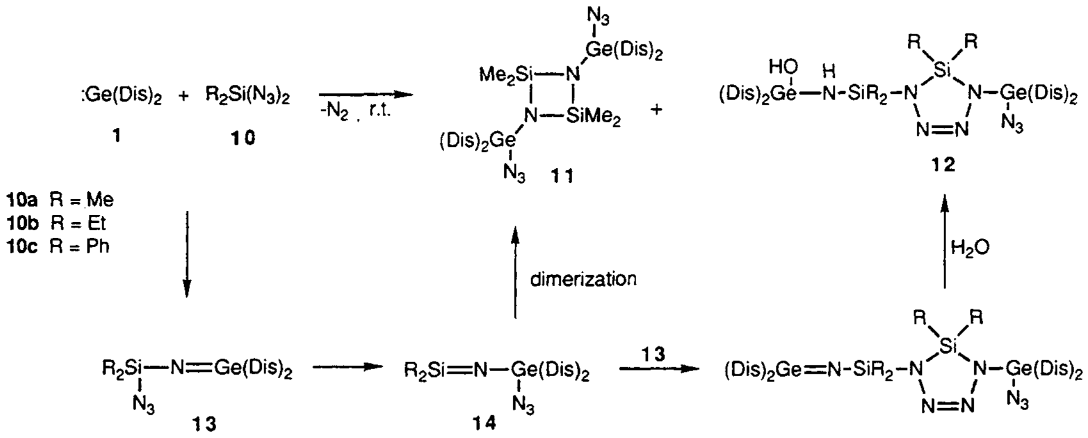
	4	**5**
Formula	$C_{22}H_{56}N_4Si_5Ge$	$C_{22}H_{56}N_4Si_5Sn$
FW	589.74	635.84
Color, habit	colorless, rod	yellow, rod
Cryst dimension, mm	0.5 × 0.5 × 0.3	0.5 × 0.5 × 0.3
Space group	$P\bar{1}$	$P\bar{1}$
a, Å	9.236(1)	9.183(1)
b, Å	12.066(1)	12.193(1)
c, Å	17.068(1)	17.292(1)
α, deg	98.45(1)	98.74(1)
β, deg	90.43(1)	90.21(1)
γ, deg	110.27(1)	109.96(1)
Cell volume, Å^3	1761.3	1795.5
Z	2	2
D_{calcd}, g/cm^3	1.11	1.18
F000	636	672
Temp, °C	23	23
Scan range, deg	$0.5 + 0.740 \tan\theta$	$0.7 + 0.620 \tan\theta$
Radiation	Mo $K_\alpha(\lambda = 0.71073$ Å)	Mo $K_\alpha(\lambda = 0.71073$ Å)
2θ max, deg	50	50
m, cm	10.4	8.9
No. of obsd reflections ($I < 3\sigma(I)$)	4218	4795
R	0.051	0.040
Rw	0.069	0.051
Largest/lowest peak in final diffraction map, e/Å^3	0.53/−0.17	0.55/−0.15

furnished a bis(germanimine) system **9** in quantitative yield [4], and this is the first molecule that includes two group 14 heavy element-heteroatom multiple bonds. The high field shifted ^{29}Si resonance at δ −19.3 for **9** supports the concept of a strong polarity of each of the two germanimine moieties.

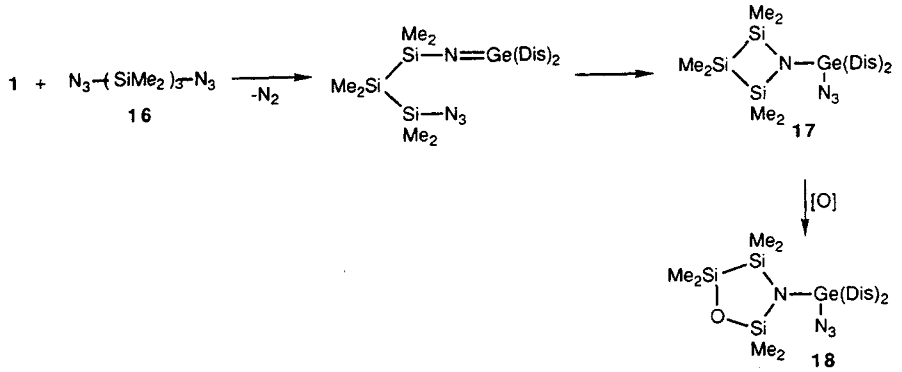
Reactions of **1** *and* **2** *with Other Diazidosilanes*

The treatment of a solution of **1** with 1 equiv of dimethyldiazidosilane (**10a**) in a hydrocarbon solvent at room temperature resulted in rapid decolorization of the solution, accompanied by evolution of nitrogen gas. The solvent was removed, and then the residue was separated by preparative HPLC to give the cyclodisilazane **11** (23%) and the siladihydrotetrazole derivative **12a** (27%) as major products (Equation 4). Most likely, the first step of this reaction is the formation of *N*-(azidosilyl)germanimine (**13a**) and the second step is rearrangement of **13a** to *N*-(azidogermyl)silanimine (**14a**) by azide group migration. Dimerization of compound **13a** produces **11**, while [2 + 3] cycloaddition of **13a** with **14a** affords a siladihydrotetrazole which is hydrolyzed in air to give **12a**. Interestingly, the reaction of **1** with diethyldiazidosilane (**10b**) furnished only **12b** (60%, separated by HPLC). This result suggests that the bulkiness of substituents on silicon makes a rate of the migration of the azide group slow. There are a few examples of such a rearrangement of a group 14 element-heteroatom double bond to another double bond, e.g., silene (Si = C) to ketene [14] and germanimine to nitrilimine [15]. It is also noteworthy that Wiberg and co-workers reported a germanimine-silanimine rearrangement with a phenyl group as the migration group [16]. In our case, when **1** was reacted with diphenyldiazidosilane (**10c**), the only isolated product was **12c**; no product derived from phenyl group migration could be observed. This result clearly demonstrates that the azide group has a higher migration ability than the phenyl group in the germanimine-silanimine rearrangement.

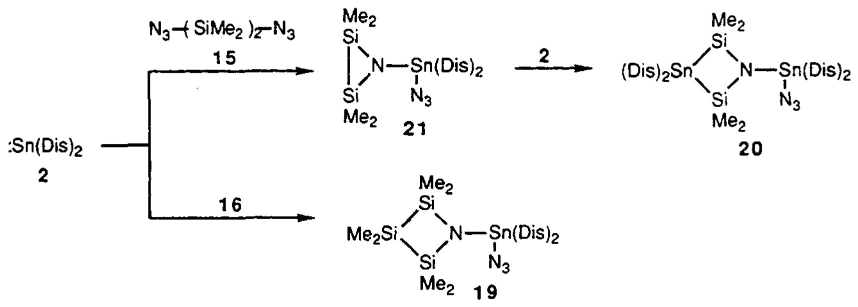
Compound **1** was treated with 1,2-diazidotetramethyldisilane (**15**) for further possible study of the migration ability of the azide group; however, no major products could be observed by HPLC and NMR spectroscopic methods. In contrast, the reaction of **1** with 1,3-diazidohexamethyltrisilane (**16**) gave the azatrisilacyclobutane (**17**) in quantitative yield. Compound **17** is easily oxidized to the siloxane **18** in air (Equation 5). As expected, when stannylene **2** was treated with **16**, the azatrisilacyclobutane (**19**) was obtained. However, the reaction of **2** with **15** gave the four-membered ring compound **20** (50%). Incidentally, the use of a 2 equiv amount of the stannylene increased the yield of **20** to 90%. A reasonable first step of the pathway



(4)



(5)



(6)

whereby **20** is produced is the formation of the azadisilacyclopropane (**21**) by azido group migration, compound **20** then being produced by insertion of the stannylene moiety into **21** (Equation 6). It is noteworthy that highly strained cycloazapolysila compounds are easily prepared under mild conditions.

SUMMARY

Reactions of stable germylene and stannylene compounds with a diazidosilane bearing bulky substituents produce the *N*-(azidosilyl)germanimine (**4**) and, respectively, the stannanimine (**5**). This is the first report of the syntheses and structures of the two group 14 element-heteroatom double bond species containing entirely the same substituents.

N-(azidosilyl)germanimine exhibited not merely thermal stability but a variety of reactivities, e.g. to furnish a cyclic germanimine by photolysis and to give a bis(germanimine) by the reaction with a germylene.

The azide group in methyl substituted *N*-(azidosilyl)germanimines and stannanimines showed a high migration ability, thereby transforming the unstable double bonds to transient silanimines or highly strained ring systems.

TABLE 2 Positional Parameters and Their Estimated Standard Deviations for **4**

	x	*y*	*z*	B_{iso}[a]
Ge	0.16820(8)	0.32828(6)	0.22706(4)	2.73(1)
Si1	−0.0608(2)	0.1231(2)	0.3185(1)	3.76(4)
Si2	0.2958(2)	0.2618(2)	0.3844(1)	3.97(5)
Si3	0.3642(2)	0.2335(2)	0.0970(1)	4.87(5)
Si4	0.0526(2)	0.2744(2)	0.0475(1)	4.03(5)
Si5	0.2196(2)	0.5966(2)	0.2917(1)	3.43(4)
N1	0.2070(6)	0.4765(4)	0.2252(3)	3.7(1)
N2	0.2456(8)	0.5667(5)	0.3895(4)	5.4(2)
N3	0.216(1)	0.6091(6)	0.4517(4)	7.8(2)
N4	0.194(2)	0.646(1)	0.5134(6)	15.6(4)
C1	0.1204(7)	0.2600(5)	0.3248(4)	3.2(1)
C2	0.1642(7)	0.2313(6)	0.1240(4)	3.3(1)
C11	−0.095(1)	0.0740(8)	0.4189(5)	6.4(2)
C12	−0.052(1)	−0.0053(7)	0.2444(6)	6.7(3)
C13	−0.230(1)	0.1654(8)	0.2903(6)	6.8(2)
C21	0.4806(9)	0.3698(8)	0.3530(6)	5.7(2)
C22	0.317(1)	0.1098(7)	0.3762(6)	6.5(2)
C23	0.274(1)	0.3166(9)	0.4913(5)	6.9(3)
C31	0.415(1)	0.1278(8)	0.1538(6)	6.8(2)
C32	0.368(1)	0.174(1)	−0.0119(6)	8.6(3)
C33	0.513(1)	0.3885(9)	0.1198(6)	7.0(3)
C41	−0.132(1)	0.2873(9)	0.0868(6)	6.6(3)
C42	0.172(1)	0.4201(7)	0.0166(5)	6.1(2)
C43	−0.012(1)	0.1496(8)	−0.0410(5)	6.7(3)
C100	0.0310(8)	0.6277(6)	0.2886(4)	4.0(2)
C101	−0.0989(9)	0.5199(8)	0.3141(6)	6.1(2)
C102	0.038(1)	0.7437(7)	0.3450(6)	6.0(2)
C103	−0.015(1)	0.6361(8)	0.2029(5)	6.2(2)
C200	0.404(1)	0.7258(7)	0.2798(6)	5.8(2)
C201	0.441(1)	0.8300(9)	0.3530(9)	9.8(4)
C202	0.540(1)	0.6769(9)	0.2783(8)	8.9(4)
C203	0.388(1)	0.776(1)	0.2030(7)	10.7(4)

[a] B_{iso} is the mean of the principal axes of the thermal ellipsoid.

TABLE 3 Selected Bond Lengths and Angles for **4**

	Bond Lengths (Å)		
Ge–N1	1.704(5)	Si5–N1	1.673(5)
Ge–C1	1.955(6)	Si5–N2	1.791(7)
Ge–C2	1.957(6)	Si5–C100	1.907(8)
Si1–C1	1.889(6)	Si5–C200	1.908(8)
Si2–C1	1.899(7)	N2–N3	1.18(1)
Si3–C2	1.899(7)	N3–N4	1.13(1)
Si4–C2	1.894(8)		
	Bond Angles (deg)		
N1–Ge–C1	121.8(3)	Si5–N2–N3	130.5(7)
N1–Ge–C2	115.2(3)	N2–N3–N4	175.(1)
C1–Ge–C2	122.9(3)	Ge–C1–Si1	115.7(3)
N1–Si5–N2	109.4(3)	Ge–C1–Si2	114.3(3)
N1–Si5–C100	110.2(3)	Si1–C1–Si2	112.3(3)
N1–Si5–C200	109.7(3)	Ge–C2–Si3	112.3(3)
C100–Si5–C200	116.7(4)	Ge–C2–Si4	109.1(4)
Ge–N1–Si5	136.0(4)	Si3–C2–Si4	115.6(3)

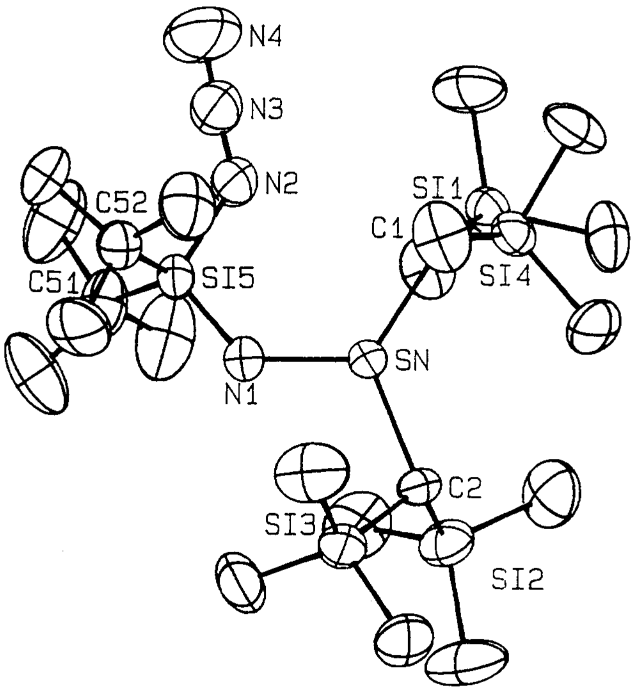


FIGURE 2 ORTEP drawing of **5**.

EXPERIMENTAL

General

All reactions involving air-sensitive reagents were carried out in a glove box (VAC DRI-LAB-08/85). Hydrocarbon solvents were distilled from $LiAlH_4$ under an Ar atmosphere. Bis[bis(trimethylsilyl)-methyl]germylene and bis[bis(trimethylsilyl)-methyl]stannylene were prepared according to literature procedures and purified by sublimation. The diazidosilanes were synthesized from the corresponding dichlorosilanes and NaN_3. Photoreactions were performed with use of a high pressure mercury lamp (Ushio, 450W). NMR spectra were recorded on an AC400 Bruker spectrometer operating at 400 MHz (^1H), 100 MHz (^{13}C) 79.5 MHz (^{29}Si), and 149 MHz (^{119}Sn); the solvent (C_6D_6) was dried by use of a potassium mirror under reduced pressure. Preparative gel permeation liquid chromatography was performed with an LC908 on JAIGEL 1H and 2H columns (Japan Analytical Industry Co. LTD.) with toluene as eluent.

N-(Azidosilyl)germanimine (**4**) *and N-(Azidosilyl)stannanimine* (**5**)

Di-*tert*-butyl-diazidosilane (**3**) (58 mg, 0.26 mmol) was added to a solution of 100 mg (0.26 mmol) of **1** in 15 mL of hexane at room temperature, and rapid decolorization of the germylene under evolution of dinitrogen gas was observed. Evaporation of the solvent afforded colorless crystals of **4**. **4**: mp

TABLE 4 Positional Parameters and Their Estimated Standard Deviations for **5**

	x	*y*	*z*	B_{iso}[a]
Sn	0.67035(4)	0.82781(3)	0.22677(2)	2.963(7)
Si1	0.8002(2)	0.7623(2)	0.3902(1)	4.12(4)
Si2	0.8707(2)	0.7258(2)	0.0921(1)	5.21(5)
Si3	0.5574(2)	0.7672(2)	0.0399(1)	4.50(4)
Si4	0.4386(2)	0.6244(2)	0.3262(1)	4.03(4)
Si5	0.7182(2)	1.1033(1)	0.2898(1)	3.62(4)
N1	0.7097(6)	0.9899(4)	0.2204(3)	4.2(1)
N2	0.7445(7)	0.0682(5)	0.3846(3)	5.6(1)
N3	0.7153(9)	0.1066(5)	0.4471(4)	7.7(2)
N4	0.692(1)	0.1409(8)	0.5092(5)	14.9(3)
C1	0.6197(6)	0.7589(5)	0.3351(3)	3.4(1)
C2	0.6684(6)	0.7231(5)	0.1146(3)	3.5(1)
C11	0.9802(8)	0.8682(6)	0.3549(5)	5.8(2)
C12	0.8219(9)	0.6122(6)	0.3805(5)	6.9(2)
C13	0.785(1)	0.8198(8)	0.4967(4)	7.6(3)
C21	0.9191(9)	0.6247(7)	0.1526(6)	7.4(2)
C22	0.881(1)	0.665(1)	0.9854(5)	9.3(3)
C23	0.9843(9)	0.1192(8)	0.8832(6)	7.8(3)
C31	0.6273(9)	0.2215(8)	0.9197(5)	7.6(2)
C32	0.675(1)	0.9315(6)	0.0115(5)	7.1(2)
C33	0.504(1)	0.3549(7)	0.0486(4)	7.1(2)
C41	0.602(1)	0.4277(7)	0.5770(4)	6.6(2)
C42	0.547(1)	0.5000(6)	0.7486(5)	7.0(2)
C43	0.7281(9)	0.3324(7)	0.7048(5)	6.9(2)
C51	0.9014(8)	0.2339(6)	0.2819(5)	6.0(2)
C52	0.5277(7)	0.1326(5)	0.2891(4)	4.4(1)
C511	0.939(1)	0.3315(8)	0.3563(7)	9.5(3)
C512	0.884(1)	0.2901(8)	0.2092(6)	10.2(3)
C513	0.9616(9)	0.8152(8)	0.7256(7)	9.0(3)
C521	0.5332(9)	0.2469(6)	0.3461(5)	6.4(2)
C522	0.6012(9)	0.9749(7)	0.6854(6)	6.9(2)
C523	0.5199(9)	0.8572(7)	0.7947(5)	7.1(2)

[a] B_{iso} is the mean of the principal axes of the thermal ellipsoid.

TABLE 5 Selected Bond Lengths and Angles for **5**

	Bond Lengths (Å)		
Sn–N1	1.905(5)	Si5–N1	1.667(5)
Sn–C1	2.155(6)	Si5–N2	1.792(6)
Sn–C2	2.150(5)	Si5–C51	1.903(8)
Si1–C1	1.894(6)	Si5–C52	1.902(8)
Si2–C2	1.890(6)	N2–N3	1.179(9)
Si3–C2	1.891(7)	N3–N4	1.14(1)
Si4–C1	1.882(5)		
	Bond Angles (deg)		
N1–Sn–C1	122.3(2)	Si5–N2–N3	130.9(3)
N1–Sn–C2	112.7(2)	N2–N3–N4	175.(1)
C1–Sn–C2	124.8(2)	Sn–C1–Si1	112.5(3)
N1–Si5–N2	110.1(3)	Sn–C1–Si4	113.0(2)
N1–Si5–C51	109.6(3)	Si1–C1–Si4	119.8(3)
N1–Si5–C52	110.4(3)	Sn–C2–Si2	110.7(3)
C51–Si5–C52	116.5(4)	Sn–C2–Si3	108.6(3)
Sn–N1–Si5	130.6(3)	Si2–C2–Si3	117.7(3)

120–121°C; ^{1}H NMR 0.48 (s, 36H), 1.33 (s, 2H), 1.49 (s, 18H); ^{13}C NMR 3.57 (q), 23.31 (s), 29.00 (q), 32.56 (d); ^{29}Si NMR −10.8 (^{t}Bu$_2$Si), −0.7. Anal. calcd for $C_{22}H_{56}N_4Si_5Ge$: C, 44.80; H, 9.57; N, 9.50. Found: C, 44.39; H, 9.54; N, 9.08. Compound **5** was prepared in an analogous manner. **5**: yellow crystals; mp 117–120°C; ^{1}H NMR 0.27 (s, 36H), 0.97 (s, 2H), 1.38 (s, 18H); ^{13}C NMR 3.73 (q), 23.34 (s), 28.97 (q), 35.43 (d); ^{29}Si NMR −18.6 (^{t}Bu$_2$Si), −0.7; ^{119}Sn NMR 340.4. Anal. calcd for $C_{22}H_{56}N_4Si_5Sn$: C, 41.56; H, 8.88; N, 8.81. Found: C, 40.65; H, 9.05; N, 8.81.

Hydrolysis and Methanolysis of 4

Exposure of a solution of compound **4** to air produced the germanol **6** rapidly, **6**: colorless crystals, mp 93–94°C; ^{1}H NMR 0.26 (s, 2H), 0.30 (s, 18H), 0.32 (s, 18H), 0.74 (s, 1H, NH), 1.11 (s, 18H), 1.38 (s, 1H, OH); ^{13}C NMR 3.56 (q), 4.04 (q), 13.17 (d), 23.04 (s), 28.26 (q). Anal. calcd for $C_{22}H_{58}N_4OSi_5Ge$: C, 43.48; H, 9.62; N, 9.22. Found: C, 43.67; H, 9.33; N, 9.11.

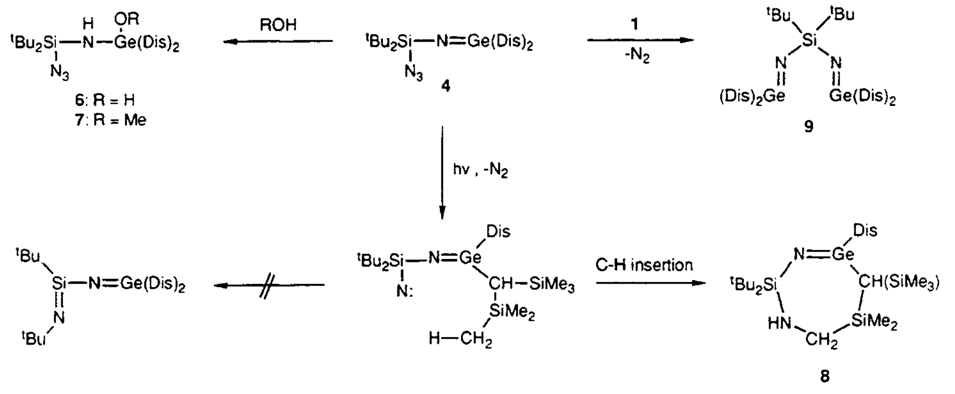
Methanol (20 mg, 0.63 mmol) was added to a solution of 150 mg (0.255 mmol) of **4** in 10 mL of hexane. The solvent was removed immediately, and the residue was purified by preparative HPLC. **7**: waxy solid (147 mg, 93%), ^{1}H NMR 0.37 (s, 18H), 0.38 (s, 18H), 0.51 (s, 2H), 0.77 (s, 1H, NH), 1.19 (s, 18H), 3.56 (s, 3H); ^{13}C NMR 3.71 (q), 4.49 (q), 11.90 (d), 22.99(s), 28.36 (q), 51.85 (q). Anal. calcd for $C_{23}H_{60}N_4OSi_5Ge$: C, 44.43; H, 9.73; N, 9.01. Found: C, 44.05; H, 9.35; N, 8.35.

Photolysis of the N-(Azidosilyl)germanimine (4)

A solution of **4** (15 mg, 0.025 mmol) in C_6D_6 (0.4 mL) in a sealed pyrex NMR tube was irradiated with a high-pressure Hg lamp. After 4 hours, NMR spectra showed the presence of the cyclic germanimine **8** as the major product (60%, based on intensity of C_6H_6). **8**: ^{1}H NMR −0.01 (s, 1H), 0.20 (s, 9H), 0.21 (s, 9H), 0.31 (s, 9H), 0.34 (s, 3H), 0.48 (s, 3H), 0.98 (s, 1H), 1.09 (d, 1H, J = 15 Hz), 1.12 (s, 9H), 1.13 (s, 9H), 1.32 (s, 1H, NH), 1.46 (d, 1H, J = 15 Hz); ^{13}C NMR 1.56 (q), 2.82 (q), 3.33 (q), 3.64 (q), 3.84 (q), 8.66 (d), 18.98 (t), 22.83 (s), 22.93 (s), 23.15 (d), 28.02 (q), 28.03 (q).

Bis(germanimines) (9)

A solution of **1** (50 mg, 0.13 mmol) in 10 mL of hexane was added to a solution of **4** (75 mg, 0.13 mmol) in 15 mL of hexane. After the new solution had been stirred for 24 hours at room temperature, the solvent was removed under reduced pressure. The obtained residue was crystallized by dissolution in pentane and slow evaporation of the solution. **9**: pale yellow crystals (105 mg, 86%), mp 157–159°C; ^{1}H NMR 0.33 (s, 4H), 0.41 (s, 72H), 1.51 (s,



SCHEME 1

18H); ^{13}C NMR 1.36 (d), 4.21 (q), 22.92 (s), 31.31 (q); ^{29}Si NMR −19.3 ($^{t}Bu_2Si$), −1.4. Anal. calcd for $C_{36}H_{94}N_2Si_9Ge_2$: C, 45.38; H, 9.94; N, 2.94. Found: C, 45.06; H, 10.18; N, 3.10.

Cyclodisilazane **11** *and the Siladihydrotetrazole Derivative* **12a**

Dimethyldiazidosilane (**10a**) (25 mg, 0.18 mmol) was added to a solution of the germylene (70 mg, 0.18 mmol) in hexane (12 mL). After the mixture had been stirred for 12 hours, the solvent was removed under reduced pressure and the residue was separated by preparative HPLC. **11** (23%): colorless crystals, mp 205–206°C (hexane); ^{1}H NMR 0.38 (s, 36H), 0.41 (s, 36H), 0.48 (s, 4H), 0.80 (s, 12H); ^{13}C NMR 4.48 (q), 4.63 (q), 9.39 (q), 16.06 (d); ^{29}Si NMR 0.4, 0.7, 9.2 ($SiMe_2$). Anal. calcd for $C_{32}H_{88}N_8Si_{10}Ge_2$: C, 38.01; H, 8.77; N, 11.08. Found: C, 37.65; H, 8.61; N, 11.04. **12a** (27%): colorless solid, mp 128–130°C; ^{1}H NMR 0.01 (s, 2H), 0.31 (s, 36H), 0.36 (s, 18H), 0.41 (s, 18H), 0.47 (s, 6H), 0.51 (s, 2H), 0.54 (s, 6H), 1.40 (s, 1H, NH), 2.92 (s, 1H, OH); ^{13}C NMR 2.93 (q), 3.49 (q), 3.61 (q), 3.88 (q), 3.90 (q), 4.48 (q), 14.38 (d), 14.43 (d). Anal. calcd for $C_{32}H_{90}N_8OSi_{10}Ge_2$: C, 37.37; H, 8.75; N, 10.89. Found: C, 38.23; H, 8.93; N, 11.01.

The Siladihydrotetrazole Derivative **12b**

Compound **12b** is a colorless solid, mp 77–81°C; ^{1}H NMR 0.13 (s, 2H), 0.29 (s, 2H), 0.32 (s, 18H), 0.33 (s, 18H), 0.40 (s, 18H), 0.44 (s, 18H), 0.49 (s, 1H, NH), 0.87–1.17 (m, 20H), 3.42 (s, 1H, OH); ^{13}C NMR 3.69 (q), 3.75 (q), 3.94 (q), 4.18 (q), 7.66 (d), 7.76 (t), 7.78 (d), 10.27 (t), 14.31 (q), 14.50 (q); ^{29}Si NMR −0.1, 0.1, 0.3, 0.6, 0.7. Anal. calcd for $C_{36}H_{98}N_8OSi_{10}Ge_2$: C, 39.84; H, 9.10; N, 10.33. Found: C, 40.49; H, 9.21; N, 9.38.

The Siladihydrotetrazole Derivative **12c**

Compound **12c** is a colorless solid, mp 163–164°C; ^{1}H NMR 0.20 (s, 18H), 0.27 (s, 18H), 0.29 (s, 2H), 0.35 (s, 2H), 0.40 (s, 18H), 0.42 (s, 18H), 2.16 (s, 1H, NH), 2.73 (s, 1H, OH), 7.02–7.16 (m, 12H), 7.57–7.71 (m, 8H); ^{13}C NMR 3.66 (q), 3.72 (q), 3.74 (q), 4.27 (q), 12.40 (d), 14.51 (d), 127.70 (d), 128.34 (d), 130.22 (d), 130.80 (d), 132.64 (s), 135.03 (s), 136.69 (d), 137.16 (d). Anal. calcd for $C_{48}H_{98}N_8OSi_{10}Ge_2$: C, 46.89; H, 8.03; N, 9.11. Found: C, 47.58; H, 7.98; N; 8.28.

1,2-Diazidotetramethyldisilane (**15**) *and 1,3-Diazidohexamethyltrisilane* (**16**)

A toluene solution (20 mL) of 1,2-dichlorotetramethylsilane (4.0 g, 21 mmol) and sodium azide (5.5 g, 85 mmol) was heated to reflux for 8 hours. Salts were removed by decantation, and then the solvent was evaporated. The residue was distilled to give **15** in 50% yield: colorless oil, bp. 75–78°C/20 mmHg; ^{1}H NMR ($CDCl_3$) 0.08 (s, 12H). Similarly, 1,3-diazidohexamethyltrisilane was prepared by the reaction of 1,3-dichlorotrisilane and sodium azide. **16** (53%): colorless oil, bp 80–84°C/1 mmHg; ^{1}H NMR ($CDCl_3$) 0.32 (s, 6H), 0.45 (s, 12H).

The Azatrisilacyclobutanes (**17** *and* **19**)

1,3-Diazidohexamethyltrisilane (**16**) (65 mg, 0.26 mmol) was added to a solution of 100 mg (0.26 mmol) of **1** in 15 mL of hexane at room temperature. Evaporation of the solvent afforded **17**: a colorless solid, decomp point 155°C; ^{1}H NMR 0.36 (s, 18H), 0.37 (s, 6H), 0.41 (s, 18H), 0.43 (s, 2H), 0.62 (s, 12H); ^{13}C NMR −7.80 (q), 4.67 (q), 4.79 (q), 5.67 (q), 15.97 (d); ^{29}Si NMR −31.2, 0.3, 1.2, 9.9. Anal. calcd for $C_{20}H_{56}N_4Si_7Ge$: C, 38.63; H, 9.08; N, 9.01. Found: C, 38.94; H, 9.35; N, 8.13. Similarly, compound **19** was prepared by the reaction of **2** with **16**. **19**: a colorless solid; ^{1}H NMR 0.32 (s, 18H), 0.33 (s, 2H), 0.39 (s, 18H), 0.40 (s, 6H), 0.61 (s, 12H); ^{13}C NMR −7.80 (q), 4.67 (q), 4.79 (q), 5.67 (q), 15.97 (d). Anal. calcd for $C_{20}H_{56}N_4Si_7Sn$: C, 35.96; H, 8.45; N, 8.39. Found: C, 36.16; H, 8.67; N, 8.46. Compound **17** was oxidized in air to give siloxane **18**: colorless solid, mp 98–100°C ^{1}H NMR 0.32 (s, 1H), 0.34 (s, 18H), 0.37 (s, 6H), 0.38 (s, 9H), 0.41 (s, 9H), 0.42 (s, 1H), 0.50 (s, 3H), 0.52 (s, 3H), 0.53 (s, 3H), 0.55 (s, 3H); ^{13}C NMR 1.13 (q), 1.58 (q), 2.86 (q), 4.49 (q), 4.58 (q), 4.64 (q), 4.81 (q), 4.89 (q), 4.91 (q), 6.39 (q), 15.77 (d), 15.80 (d). Anal. calcd for $C_{20}H_{56}N_4OSi_7Ge$: C, 37.68; H, 8.79; N, 8.79. Found: C, 38.37; H, 8.97; N, 7.94.

Aza-2,4-disila-3-stannacyclobutane (**20**)

1,2-diazidotetramethyldisilane (**15**) (46 mg, 0.23 mmol) was added to a solution of 100 mg (0.23 mmol) of **2** in 15 mL of hexane. After the solvent was removed, the residue was separated by HPLC. **20** (60 mg, 50%): colorless crystals; ^{1}H NMR 0.07 (s, 2H), 0.33 (s, 18H), 0.36 (s, 36H), 0.41 (s, 18H), 0.44 (s, 2H), 0.84 (s, 12H); ^{13}C NMR 1.75 (d), 4.41 (q), 4.64 (q), 4.77 (q), 9.73 (q), 16.65 (d). Anal. calcd for $C_{32}H_{88}N_4Si_{10}Sn_2$: C, 36.71; H, 8.41; N, 5.35. Found: C, 36.60; H, 8.50; N, 5.32.

X-Ray Structure Analyses of **4** *and* **5**

Data for **4**: $C_{22}H_{56}N_4Si_5Ge$, triclinic, space group $P\bar{1}$, $a = 9.236$ (1), $b = 12.066$ (1), $c = 17.068$ (1) Å, $\alpha = 98.45$ (1), $\beta = 90.43$, $\gamma = 110.27$ (1)°, $V = 1761.3$ Å^3, $D_{calcd} = 1.11$ g/cm^3, $\mu = 10.4$ cm^{-1}, and $Z = 2$. The structure was solved from 4218 collected independent reflections [$2\theta \leq 50°$, $|Fo^2| > 3\sigma|Fo^2|$] measured on an Enraf–Nonius CAD4 diffractometer using MoK_α irradiation and an $\omega - 2\theta$ scan. The structure was solved by direct methods, and all nonhydrogen atoms were refined anisotropically to $R = 0.051$ and $Rw = 0.069$.

The analysis of **5** was carried out in a manner similar to **4**. Data for **5**: $C_{22}H_{56}N_4Si_5Sn$, triclinic, space group $P\bar{1}$, $a = 9.183$ (1), $b = 12.193$ (1), $c = 17.292$ (1) Å, $\alpha = 98.74$ (1), $\beta = 90.21$, $\gamma = 109.96$ (1)°, V = 1795.5 Å^3, $D_{calcd} = 1.18$ g/cm^3, $\mu = 8.9$ cm^{-1}, $Z = 2$, 4795 collected reflections, and $R = 0.040$ ($Rw = 0.051$).

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SUPPLEMENTARY MATERIAL AVAILABLE

A text describing crystallographic procedures, tables of crystallographic data, atomic coordinates and thermal parameters, bond lengths and angles, and figures showing ORTEP structures for **4** and **5** (41 pages) may be ordered by writing to Prof. Wataru Ando.

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