Synthesis, Structure, and Photoreaction of Bis(germanimines)

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*Summary: The reaction of bis[bis(trimethylsilyl)methyl]germylene (**1**) with N-(azidosilyl)germanimines **3a,b** at room temperature gave bis(germanimines) **4a,b** in quantitative yield whose structures have been confirmed by single-crystal X-ray diffraction. The photolysis of **4a** gave the cyclic silanimine **6** as an unexpected product.*

Recently, there has been great interest in molecules which contain group 14 element–heteroatom multiple bonds. However, examples of compounds which contain more than one such multiple bond are rare. In this paper attention is focused on germanimines[1] (Ge═N) which are easily accessible by reaction of azides with germylenes. Herein we report the synthesis of the first *N*-(azidosilyl)germanimines and bis(germanimines) as well as a photochemical transformation of the latter.

The reaction of bis[bis(trimethylsilyl)methyl]germylene (**1**)[2] with 1 equiv of a diazidosilane[3] (**2a,b**) in pentane at ambient temperature resulted in rapid decolorization of the solution with evolution of nitrogen gas. Evaporation of the solvent afforded colorless crystals of the *N*-(azidosilyl)germanimines **3a,b**,[4] whose structures were determined by X-ray analysis[5] (Figure 1). Compounds **3a,b** exhibit an unusual thermal stability; e.g., they can be heated to 140 °C in C_6D_6 for 10 h (sealed NMR tube) without decomposition, although a Ge═N bond and an azide group are present in one molecule.

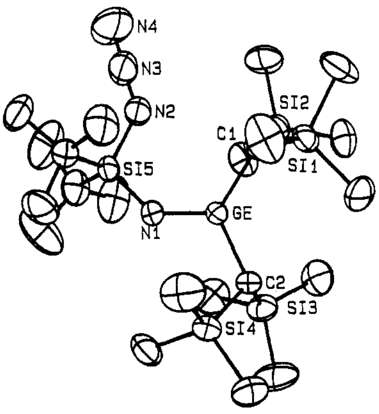
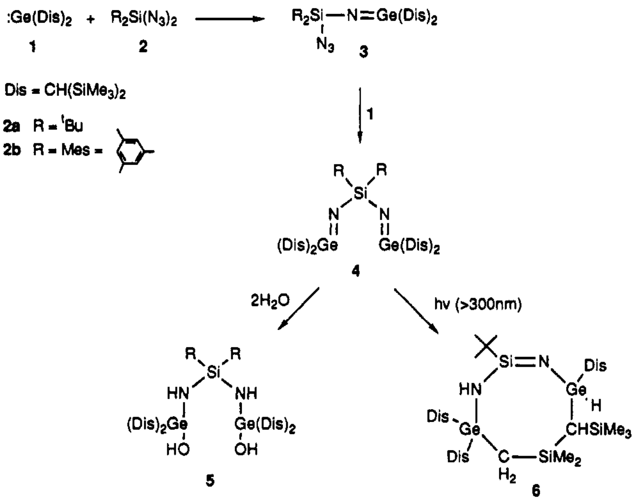


Figure 1. ORTEP drawing of **3a**. Selected bond distances (Å) and angles (deg): Ge–N1 = 1.704(5), Ge–C1 = 1.955(6), Ge–C2 = 1.957(6), Si5–N1 = 1.673(5), Si5–N2 = 1.791(7); Si5–N1–Ge = 136.0(4), C1–Ge–C2 = 122.9(3), N1–Ge–C1 = 121.8(3), N1–Ge–C2 = 115.2(3).

Scheme 1



Interestingly, further treatment of **1** with a second equivalent of **3a,b** at room temperature gave bis(germanimines) **4a,b**, which were purified by recrystallization from pentane (isolated yields: **4a**, 86%; **4b**, 86%).[6] In the ^1H NMR spectra of **4a,b**, the appearance of only one

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[1] Reviews: (a) Wiberg, N. *J. Organomet. Chem.* **1984**, *273*, 141. (b) Barrau, J.; Escudié, J.; Satgé, J. *Chem. Rev.* **1990**, *90*, 283. (c) Rivière, P.; Cazes, A.; Castel, A.; Rivière-Baudet, M.; Satgé, J. *J. Organomet. Chem.* **1978**, *155*, C58. (d) Glidewell, C.; Lloyd, D., Lumbard, K. W.; McKechnie, J. S. *Tetrahedron Lett.* **1987**, *28*, 343. (e) Pfeiffer, J.; Maringgele, W., Noltemeyer, M.; Meller, A. *Chem. Ber.* **1989**, *122*, 245. (f) Tsumuraya, T.; Ando, W. *Chem. Lett.* **1989**, 1043. (g) Lazraq, M.; Couret, C.; Declercq, J. P.; Dubourg, A.; Escudié, J.; Rivière-Baudet, M. *Organometallics* **1990**, *9*, 845. (h) Veith, M.; Beoker, S.; Hush, V. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 216. (i) Meller, A.; Ossig, G.; Maringgele, W.; Stalke, D.; Herbst-Irmer, R.; Freitag, S.; Sheldrick, G. M. *J. Chem. Soc., Chem. Commun.* **1991**, 1123. (j) Rivière-Baudet, M.; Khallaayoun, A.; Satgé, J. *Organometallics* **1993**, *12*, 1003.

[2] (a) Davidson, P. J.; Harris, D. H.; Lappert, M. F. *J. Chem. Soc., Dalton Trans.* **1976**, 2268. (b) Fjeldberg, T.; Haaland, A.; Schilling, B. E. R.; Lappert, M. F.; Thorne, A. J. *J. Chem. Soc., Dalton Trans.* **1986**, 1551.

[3] The diazidosilanes were synthesized from the corresponding dichlorosilanes and NaN_3: (a) Wiberg, N.; Neruda, B. *J. Organomet. Chem.* **1966**, *99*, 740. (b) Welsh, K. M.; Michl, J.; West, R. *J. Am. Chem. Soc.* **1988**, *110*, 6689.

[4] **3a**: colorless crystals; mp 120–121 °C; ^1H NMR (400 MHz, C_6D_6) δ 0.48 (s, 36 H), 1.33 (s, 2 H), 1.49 (s, 18 H); ^{13}C NMR (100 MHz, C_6D_6) δ 3.57 (q), 23.31 (s), 29.00 (q), 32.56 (d); ^{29}Si NMR (79.5 MHz, C_6D_6) δ −10.8 ($^tBu_2Si$), −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. **3b**: colorless crystals; ^1H NMR (400 MHz, C_6D_6, 30 °C) δ 0.25 (s, 36 H), 1.36 (s, 2 H), 2.15 (s, 6 H), 2.76 (s, 12 H), 6.81 (s, 4 H); ^{13}C NMR (100 MHz, C_6D_6) δ 3.27 (q), 21.05 (q), 24.45 (q), 31.94 (d), 129.85 (d), 134.21 (s), 138.38 (s), 143.68 (s); ^{29}Si NMR (79.5 MHz, C_6D_6) δ −29.8 ($(Mes)_2Si$), −0.7. Anal. Calcd for $C_{32}H_{60}N_4Si_5Ge$: C, 53.84; H, 8.47; N, 7.85. Found: C, 52.86; H, 8.70; N, 7.21.

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

[6] **4a**: pale yellow crystals; mp 157–159 °C; ^1H NMR (400 MHz, C_6D_6) δ 0.33 (s, 4 H), 0.41 (s, 72 H), 1.51 (s, 18 H); ^{13}C NMR (100 MHz, C_6D_6) δ 1.36 (d), 4.21 (q), 22.92 (s), 31.31 (q); ^{29}Si NMR (79.5 MHz, C_6D_6) δ −19.3 ($^tBu_2Si$), −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. **4b**: pale yellow crystals, dec pt 189 °C; ^1H NMR (400 MHz, C_6D_6, 30 °C) δ 0.14–0.51 (76 H), 2.23 (s, 6 H), 2.37 (s, 6 H), 3.37 (s, 6 H), 6.68 (s, 2 H), 6.93 (s, 2 H); ^{13}C NMR (100 MHz, C_6D_6) δ 4.51 (q), 20.96 (q), 25.86 (q), 26.40 (q). 27.64 (d), 31.07 (d), 130.12 (d), 130.49 (d), 135.72 (s), 143.20 (s), 144.13 (s); ^{29}Si NMR (79.5 MHz, C_6D_6) δ −38.0 ($(Mes)_2Si$), 1.2. Anal. Calcd for $C_{46}H_{98}N_2Si_9Ge_2$: C, 51.29; H, 9.17; N, 2.60. Found: C, 50.69; H, 9.40; N, 2.48.

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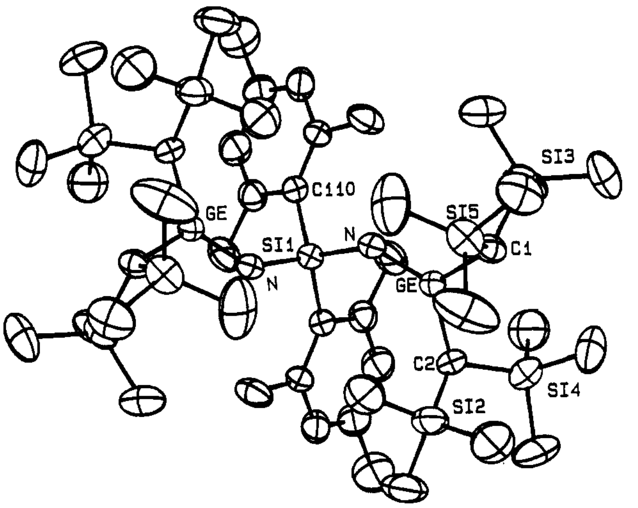
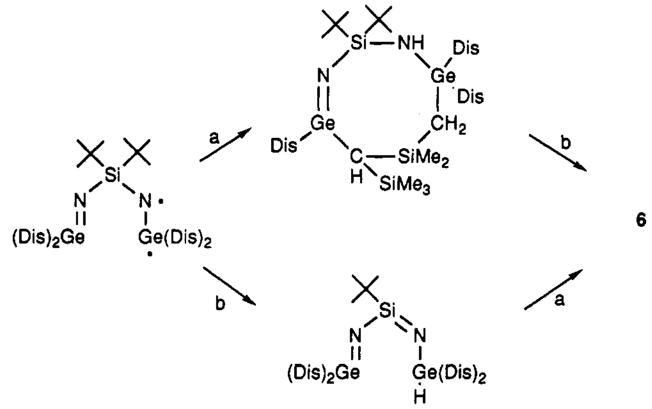


Figure 2. ORTEP drawing of the C_2-symmetric **4b**. Selected bond distances (Å) and angles (deg): Ge–N = 1.681(8), Ge–C1 = 1.97(1), Ge–C2 = 1.97(1), Si1–N = 1.717(9); Si1–N–Ge = 137.3(5), N–Ge–C1 = 119.1(5), N–Ge–C2 = 124.6(4), C1–Ge–C2 = 116.3(5), N–Si1–C110 = 108.6(4), N–Si1–N = 110.4(5).

signal for the trimethylsilyl groups is agreement with the symmetrical structures of **4a,b**. Relatively high field shifted ^{29}Si resonances at –19.3 and –38.0 ppm for **4a,b** indicate a strong polarity (Ge^+–N^-) of the two germanimine moieties. As expected, **5a,b** are formed as hydrolysis products of **4a,b**.[7] Slow evaporation of a benzene solution of **4b** gave crystals which were suitable for X-ray analysis[8] (Figure 2). The Ge═N bond distance of 1.681(8) Å is comparable with those of other germanimine derivatives prepared by Meller and co-workers[11] and is in agreement with ab initio calculations.[9] The torsion angles C1—Ge═N—Si = 178.7° and C2—Ge═N—Si = 3.2° show a nearly planar arrangement of the germanimine unit, as expected for a normal pπ–pπ double bond. In accord with the C_2 symmetry of the molecule, the two Ge═N bonds are not coplanar. Similar to **3a,b**, compounds **4a,b** are extraordinarily thermally stable; heating to 140 °C in C_6D_6 in a sealed NMR tube does not lead to any decomposition. On the other hand, photolysis of **4a** in hexane (λ > 300 nm) gave exclusively the cyclic silanimine **6**, which was isolated in 55% yield.[10] The structure was assigned on the basis of ^{1}H, ^{13}C, ^{29}Si, and C-H COSY NMR spectroscopic data. In particular, a low-field ^{29}Si resonance at 38.4 ppm is ascribed to the silanimine structure. The formation of **6** suggests two alternative reaction modes for the excited germanimine moieties in Scheme 2: (a) insertion into the C—H bond of a trimethylsilyl group to give an aminogermane and (b) ene-type elimination of isobutene with formation of a silanimine and a germanium hydride. Although it is not known whether or not these two reactions occurred simultaneously, it is clear that the excited germanimine has a highly radical character.[11]

Scheme 2. Possible Mechanism: (a) C—H Insertion of Excited Germanimine; (b) Ene-Type Elimination of Butene



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Supplementary Material Available: Text describing crystallographic procedures, tables of crystallographic data, atomic coordinates, thermal parameters, and bond lengths and angles for **3a** and **4b**, and figures of ^{1}H, ^{13}C, ^{29}Si, and C-H COSY NMR spectra for **6** (32 pages). Ordering information is given on any current masthead page.

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(7) **5a**: colorless crystals; mp 106–108 °C; ^{1}H NMR (400 MHz, C_6D_6) δ 0.39 (s, 36 H), 0.44 (s, 4 H), 1.45 (s, 36 H), 1.36 (s, 18 H); ^{13}C NMR (100 MHz, C_6D_6) δ 4.25 (q), 4.94 (q), 15.25 (d), 22.07 (s), 30.44 (q); ^{29}Si NMR (79.5 MHz, C_6D_6) δ –0.3, 0.1 (^{t}Bu$_2$Si). Anal. Calcd for $C_{36}H_{98}N_2O_2Si_9Ge_2$: C, 43.71; H, 9.98; N, 2.83. Found: C, 43.25; H, 9.58; N, 2.45. **5b**: colorless crystals; ^{1}H NMR (400 MHz, C_6D_6, 30 °C) δ 0.19 (s, 4 H), 0.29 (s, 36 H), 0.40 (s, 36 H), 2.13 (s, 6 H), 2.61 (s, 12 H), 6.71 (s, 4 H); ^{13}C NMR (100 MHz, C_6D_6) δ 4.49 (q), 4.80 (q), 13.52 (q), 20.88 (d), 26.39 (q), 130.58 (d), 137.64 (s), 138.75 (s), 143.89 (s). Anal. Calcd for $C_{46}H_{102}N_2O_2Si_9Ge_2$: C, 49.63; H, 9.23; N, 2.52. Found: C, 49.56; H, 9.34; N, 2.22.

(8) Crystallographic data for **4b**: $C_{46}H_{98}N_2Si_9Ge_2$, orthorhombic, space group *Pbcn*, $a = 15.459(4)$ Å, $b = 21.628(5)$ Å, $c = 19.201(8)$ Å, $V = 6419.8$ Å^3, $\rho_{calcd} = 1.11$ g/cm^3, $\mu = 11.2$ cm^{-1}, $Z = 4$. The structure was solved from 2224 collected independent reflections ($2\theta \le 50°$, $|F_o^2| > 3\sigma|F_o^2|$) measured on an Enraf-Nonius CAD4 diffractometer using Mo Kα irradiation and an ω–2θ scan. The structure was solved by direct methods, and all non-hydrogen atoms were refined anisotropically to $R = 0.059$ and $R_w = 0.071$.

(9) Trinquier, G.; Barthelat, J. C.; Satgé, J. *J. Am. Chem. Soc.* 1982, *104*, 5931.

(10) **6**: colorless crystals; dec pt 88 °C; ^{1}H NMR (400 MHz, C_6D_6) δ –0.25 (s, 1 H), –0.06 (s, 1 H), 0.02 (s, 1 H), 0.19 (d, 1 H, J = 6.8 Hz), 0.24 (s, 9 H), 0.25 (s, 9 H), 0.26 (s, 9 H), 0.44 (s, 9 H), 0.46 (s, 3 H), 0.47 (s, 9 H), 0.54 (s, 9 H), 0.55 (s, 9 H), 0.63 (d, 1 H, J = 13.5 Hz), 0.80 (s, 3 H), 0.90 (d, 1 H, J = 13.5 Hz), 1.32 (s, 9 H), 1.64 (s, 1 H, NH), 5.92 (d, 1 H, J = 6.8 Hz, GeH); ^{13}C NMR (100 MHz, C_6D_6) δ 2.28 (q), 3.20 (q), 3.73 (q), 4.33 (q), 4.49 (q), 4.52 (q), 5.53 (q), 6.61 (d), 6.73 (q), 7.78 (q), 11.09 (d), 11.65 (d), 12.95 (d), 16.11 (t), 23.73 (s), 29.33 (q); ^{29}Si NMR (79.5 MHz, C_6D_6) δ –1.2, –0.7, 0.4, 0.5, 0.8, 0.9, 1.0, 1.4 (SiMe$_2$), 38.4 (Si═N). Anal. Calcd for $C_{32}H_{86}N_2Si_9Ge_2$: C, 42.85; H, 9.66; N, 3.12. Found: C, 43.63; H, 9.80; N, 2.94.

(11) Photoreactions of silanimines: Weidenbruch, M.; Brand-Roth, B.; Pohl, S.; Saak, W. *J. Organomet. Chem.* 1989, *379*, 217.