

## Synthesis and X-Ray Crystal Structure of Germainines

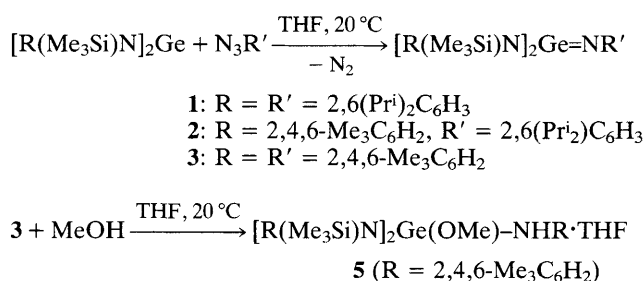
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Three new germainines have been synthesized and two of them characterized by X-ray diffraction; the Ge=N bond lengths agree well with an *ab initio* prediction for H<sub>2</sub>Ge=NH.

The Ge=N distance in unsubstituted germainine (H<sub>2</sub>Ge=NH) has been predicted to be 169.5 pm by *ab initio* calculation with double- $\zeta$  (DZ) plus polarization basis sets.<sup>1</sup> Germainines have been observed as transient species (and trapped by various substrates) since 1978 (see ref. 2 for a recent review). Only a few examples have been isolated and spectroscopically characterized within the last few years.<sup>3–8</sup> Here we report the synthesis of three new germainines prepared from highly sterically hindered diazagermylenes<sup>9</sup> and 2,6-disubstituted phenylazides as shown in Scheme 1.† In the <sup>15</sup>N NMR spectrum of **3** two signals with 2 : 1 intensity ratio at  $\delta = -295$  and  $-193$  (rel. to MeNO<sub>2</sub>) have been detected.

Compounds **1–3** crystallized easily from hot THF (tetrahydrofuran) to give well-shaped amber crystals, which change from yellow at  $-196$  °C to red at  $150$  °C. Compound **1** hydrolyses in air to give [(2,6-(Pr<sup>i</sup>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>(Me<sub>3</sub>Si)N)<sub>2</sub>Ge(OH)–NHC<sub>6</sub>H<sub>3</sub>–2,6-(Pr<sup>i</sup>)<sub>2</sub>]**4** (from spectroscopic evidence). Likewise, methanol is added across the (Ge=N) double bond of **3** thus



Scheme 1

forming **5** which crystallizes with 1 mol of THF.‡ The structures of **1** and **3** have been determined by single crystal X-ray diffraction.§ In these molecules, which are stable for months under dry nitrogen at room temperature, the (Ge=N) bond lengths are found to be 170.3(2) pm and 169.1(3) pm, which are in excellent agreement with the calculated value for germainine.<sup>1</sup> The C–N=Ge–N torsion angles [1.5(5), 178.4(3)° **1** and  $-1.5(5)$ , 178.1(3)° **3**] are consistent with a

† *Preparative details and spectroscopic data:* To a solution of the appropriate diazagermylene (0.020 mol) {bis[(2,6-diisopropylphenyl)-(trimethylsilyl)amino]germane(II) for **1**, bis[(2,4,6-trimethylphenyl)-(trimethylsilyl)amino]germane(II) for **2** and **3**} in 80 ml THF the equimolar amount of arylazide (2,6-diisopropylphenylazide for **1** and **2**, 2,4,6-trimethylphenylazide for **3**) dissolved in 40 ml THF was added dropwise, with stirring, at ambient temperature and maintained at  $25$  °C for 2 h. The clear, deep-red reaction mixtures was concentrated under reduced pressure, the amber crystals formed were filtered off and dried *in vacuo*. Satisfactory C,H,N elemental analyses were obtained for **1–3** and **5**.

**1:** Bis[(2,6-diisopropylphenyl)-(trimethylsilyl)amino]-(2,6-diisopropylphenylimino)germane: m.p.  $195$  °C (decomp.); yield 11.0 g (74%); C<sub>42</sub>H<sub>69</sub>GeN<sub>3</sub>Si<sub>2</sub> (744.79); MS [*m/z* (%)]: EI 745 (20) [M<sup>+</sup>], 73 (100); NMR (in C<sub>6</sub>D<sub>6</sub>):  $\delta$ (<sup>1</sup>H) 0.33 (s, 18H, SiMe<sub>3</sub>); 1.06, 1.28, 1.32 (3 × d, <sup>3</sup>J<sub>HH</sub> 6.6 Hz, 3 × 6H, 6 × CH<sub>3</sub>-Pr<sup>i</sup>); 1.40–1.60 (br, 18H, 6 × CH<sub>3</sub>-Pr<sup>i</sup>); 2.90, 3.80, 4.06 (3 × sept., 3 × 2H, 6 × CH-Pr<sup>i</sup>); 6.70–7.10, 7.24–7.32 (2 × br, 9H, arom.);  $\delta$ (<sup>13</sup>C) 3.57 (SiMe<sub>3</sub>); 24.63, 24.73, 25.36, 25.68 (threefold intensity) (all CH<sub>3</sub>-Pr<sup>i</sup>); 28.71, 29.06, 29.15 (all CH-Pr<sup>i</sup>); 120.05, 123.25, 124.93, 125.47, 127.08, 139.30, 141.67, 147.15, 147.52, 148.65 (10 signals apparently due to non-equivalence of the 2/6 and 3/5 positions of the imino-bonded aromatic ring) (all arom.);  $\delta$ (<sup>29</sup>Si) 16.2.

**2:** Bis[(2,4,6-trimethylphenyl)-(trimethylsilyl)amino]-(2,6-diisopropylphenylimino)germane: m.p.  $162$  °C; yield 9.2 g (70%); C<sub>36</sub>H<sub>57</sub>GeN<sub>3</sub>Si<sub>2</sub> (660.63); MS [*m/z* (%)]: EI 661 (22) [M<sup>+</sup>], 351 (100); NMR (in C<sub>6</sub>D<sub>6</sub>):  $\delta$ (<sup>1</sup>H) 0.08 (s, 18H, SiMe<sub>3</sub>); 1.50 (d, <sup>3</sup>J<sub>HH</sub> 6.8 Hz, 12H, 4 × CH<sub>3</sub>-Pr<sup>i</sup>); 1.97 (s, 12H, 4 × *o*-CH<sub>3</sub>); 2.08 (s, 6H, 2 × *p*-CH<sub>3</sub>); 3.86 (sept., 2H, 2 × CH-Pr<sup>i</sup>); 6.46–6.52 (m, 4H, C<sub>6</sub>H<sub>2</sub>); 7.05–7.13, 7.28–7.34 (2 × m, 3H, C<sub>6</sub>H<sub>3</sub>);  $\delta$ (<sup>13</sup>C) 2.12 (SiMe<sub>3</sub>); 20.11 (*o*-CH<sub>3</sub>); 20.72 (*p*-CH<sub>3</sub>); 23.98 (CH<sub>3</sub>-Pr<sup>i</sup>); 29.38 (CH-Pr<sup>i</sup>); 119.92, 122.63, 129.37, 134.00, 136.42, 139.20, 140.58, 149.54 (all arom.);  $\delta$ (<sup>29</sup>Si) 14.1.

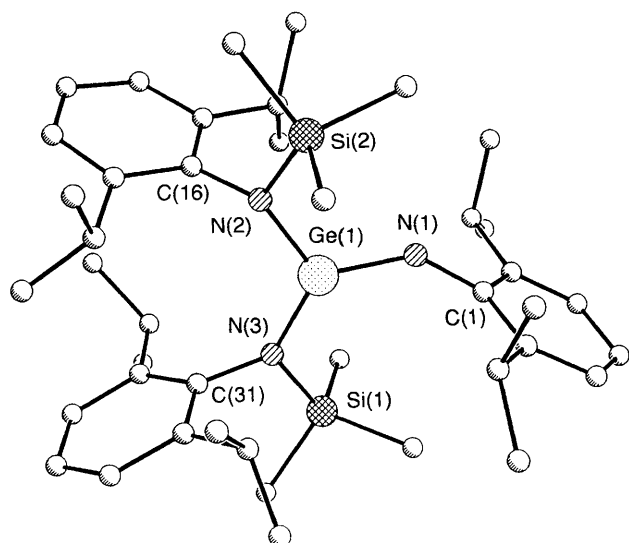
**3:** Bis[(2,4,6-trimethylphenyl)-(trimethylsilyl)amino]-(2,4,6-trimethylphenylimino)germane: m.p.  $177$  °C; yield 8.54 g (69%); C<sub>33</sub>H<sub>51</sub>GeN<sub>3</sub>Si<sub>2</sub> (618.55); MS [*m/z* (%)]: EI 619 (21) [M<sup>+</sup>], 351 (100); NMR (in C<sub>6</sub>D<sub>6</sub>):  $\delta$ (<sup>1</sup>H) 0.11 (s, 18H, SiMe<sub>3</sub>); 2.03 (s, 18H, *o*-CH<sub>3</sub> of mes/amino); 2.33 (s, 3H, *p*-CH<sub>3</sub> of mes'/imino); 2.61 (s, 6H, *p*-CH<sub>3</sub> of mes/amino); 6.380, 6.382 (2s, 4H, C<sub>6</sub>H<sub>2</sub> of mes); 7.064, 7.066 (2s, 2H, C<sub>6</sub>H<sub>2</sub> of mes);  $\delta$ (<sup>13</sup>C) 1.95 (SiMe<sub>3</sub>); 20.66 (*o*-CH<sub>3</sub>, mes/amino); 20.73 (*o*-CH<sub>3</sub>, mes'/imino); 21.04 (*p*-CH<sub>3</sub>, mes); 21.06 (*p*-CH<sub>3</sub>, mes'); 127.30, 128.21, 129.09, 129.25, 133.63, 135.66, 140.61, 150.11, (C<sub>6</sub>H<sub>2</sub> mes + mes');  $\delta$ (<sup>29</sup>Si) 13.4.— $\delta$ (<sup>15</sup>N)-NMR (40% sol. in THF, standard CH<sub>3</sub>NO<sub>2</sub> ext.):  $-295$  (2N),  $-193$  (1N).

‡ **4** m.p.  $236$  °C; C<sub>42</sub>H<sub>71</sub>GeN<sub>3</sub>O<sub>2</sub>Si<sub>2</sub> (762.81); MS [*m/z* (%)]: 763 (2), 73 (100); IR (KBr): 3583 (νOH), 3390 (νNH).

**5:** Bis[2,4,6-trimethylphenyl-(trimethylsilyl)amino]methoxy(2,4,6-trimethylphenylamino)germane was prepared by dropwise addition of a solution of 0.10 g (0.003 mol) MeOH in 5 ml THF to 0.93 g (0.0015 mol) of **3** in 10 ml THF with stirring. After 1 h volatiles were removed *in vacuo* and the colourless residue recrystallized from THF: m.p.  $130$  °C; yield 0.72 g (67%); C<sub>38</sub>H<sub>63</sub>GeN<sub>3</sub>O<sub>2</sub>Si<sub>2</sub> (722.70); MS [*m/z* (%)]: EI 651 (8) [M – THF]<sup>+</sup>, 42 (100).

NMR (in C<sub>6</sub>D<sub>6</sub>):  $\delta$ (<sup>1</sup>H) 0.30 (s, 18H, SiMe<sub>3</sub>); 1.41 (m, 4H, H-3 and H-4 of THF); 1.95, 2.06, 2.14, 2.18 (4s, 27H, *o*-CH<sub>3</sub> + *p*-CH<sub>3</sub>); 2.91 (s, 1H, NH); 3.56 (m, 4H, H-2 and H-5 of THF); 3.91 (s, 3H, OMe); 6.60–6.80 (br, 6H, C<sub>6</sub>H<sub>2</sub>); IR (in Nujol) 3350 (νNH).

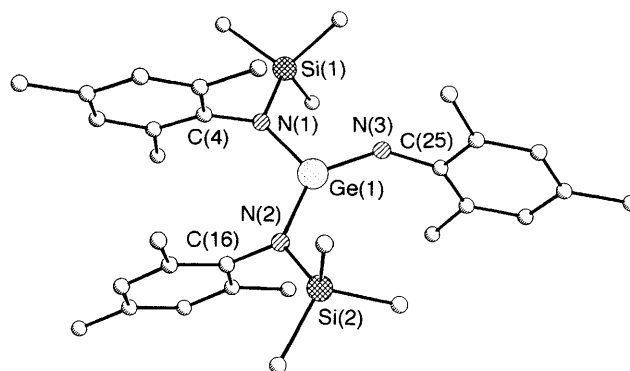
§ *Crystal data* for **1**: C<sub>42</sub>H<sub>69</sub>GeN<sub>3</sub>Si<sub>2</sub>, triclinic, space group  $P\bar{1}$ ,  $a = 1144.6(2)$ ,  $b = 1178.7(2)$ ,  $c = 1728.6(3)$  pm,  $\alpha = 88.84(1)$ ,  $\beta = 80.67(1)$ ,  $\gamma = 68.20(1)^\circ$ ,  $U = 2.13$  nm<sup>3</sup>,  $Z = 2$ ,  $D_c = 1.16$  g cm<sup>-3</sup>,  $\mu = 0.80$  mm<sup>-1</sup>,  $F(000) = 804$ , crystal dimensions  $0.5 \times 0.5 \times 0.6$  mm, 8471 reflections collected with  $8 < 2\theta < 50^\circ$ , 7488 unique and 6099 with  $F > 3\sigma(F)$  used in the structural analysis. **3**: C<sub>33</sub>H<sub>51</sub>GeN<sub>3</sub>Si<sub>2</sub>, monoclinic, space group  $P2_1/n$ ,  $a = 852.3(2)$ ,  $b = 2961.1(4)$ ,  $c = 1382.1(2)$  pm,  $\beta = 100.30(2)^\circ$ ,  $U = 3.43$  nm<sup>3</sup>,  $Z = 4$ ,  $D_c = 1.20$  g cm<sup>-3</sup>,  $\mu = 0.99$  mm<sup>-1</sup>,  $F(000) = 1320$ , crystal dimensions  $0.4 \times 0.4 \times 0.6$  mm, 7086 reflections collected with  $8 < 2\theta < 50^\circ$ , 5991 unique and 4589 with  $F > 3\sigma(F)$  used in the structural analysis. Both data sets were collected on a Siemens-Stoe AED diffractometer using Mo-K $\alpha$  radiation ( $\lambda = 71.073$  pm) at a temperature of 153 K. Semiempirical absorption corrections were applied. The structures were solved by Patterson and Direct methods. All non-hydrogen atoms were refined anisotropically, and a riding model starting from calculated positions was employed for the hydrogen atoms. 437 **1** and 356 **3** parameters were refined with a weighting scheme [ $w^{-1} = \sigma^2(F) + 0.0002 F_o^2$ ] **1** and [ $w^{-1} = \sigma^2(F) + 0.00015 F_o^2$ ] **3**. The refinement converged with  $R = 0.041$ ,  $R_w = 0.037$  **1** and  $R = 0.048$ ,  $R_w = 0.040$  **3** and final difference electron density maxima of 0.51 **1** and 0.42 **3** and minima of  $-0.42$  **1** and  $-0.41$  10<sup>-6</sup> epm<sup>-3</sup> **3**. Atomic coordinates, bond lengths and angles, and anisotropic displacement parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.



**Fig. 1** Molecular structure of **1**; selected bond distances (pm) and angles ( $^{\circ}$ ): Ge(1)–N(1) 170.3(2), Ge(1)–N(2) 181.9(3), Ge(1)–N(3) 182.6(3), N(1)–C(1) 141.1(4), N(2)–C(16) 145.3(3), N(3)–C(31) 145.5(3); N(1)–Ge(1)–N(2) 108.4(1), N(1)–Ge(1)–N(3) 130.9(1), N(2)–Ge(1)–N(3) 120.7(1)

normal  $\pi\text{-}\pi$  double bond. The difference between the mean Ge–N and Ge=N distances in these compounds is only 12 pm; for most pairs of atoms a double bond is about 20 pm shorter than a single bond. In view of the Ge–N distances reported here,  $[\text{GeN}(2,6\text{-Pr}_2\text{C}_6\text{H}_3)]_3$  [mean Ge–N 185.9(2) pm]<sup>10</sup> should be regarded as a  $\text{Ge}^{\text{II}}$  derivative without significant multiple bonding.

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**Fig. 2** Molecular structure of **3**; selected bond distances (pm) and angles ( $^{\circ}$ ): Ge(1)–N(3) 169.1(3), Ge(1)–N(1) 180.8(3), Ge(1)–N(2) 182.8(3), N(3)–C(25) 139.9(4), N(1)–C(4) 145.2(4), N(2)–C(16) 145.7(4); N(3)–Ge(1)–N(1) 110.6(1), N(3)–Ge(1)–N(2) 134.0(1), N(1)–Ge(1)–N(2) 115.4(1)

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