

Synthesis and X-Ray Crystal Structure of Germainines

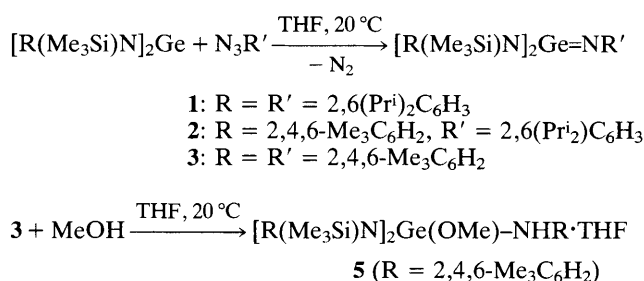
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Three new germainines have been synthesized and two of them characterized by X-ray diffraction; the Ge=N bond lengths agree well with an *ab initio* prediction for H₂Ge=NH.

The Ge=N distance in unsubstituted germainine (H₂Ge=NH) has been predicted to be 169.5 pm by *ab initio* calculation with double- ζ (DZ) plus polarization basis sets.¹ 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.^{3–8} Here we report the synthesis of three new germainines prepared from highly sterically hindered diazagermylenes⁹ and 2,6-disubstituted phenylazides as shown in Scheme 1.† In the ¹⁵N NMR spectrum of **3** two signals with 2 : 1 intensity ratio at $\delta = -295$ and -193 (rel. to MeNO₂) 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)₂C₆H₃(Me₃Si)N)₂Ge(OH)–NHC₆H₃–2,6-(Pr)₂]**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.¹ 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%); C₄₂H₆₉GeN₃Si₂ (744.79); MS [*m/z* (%): EI 745 (20) [M⁺], 73 (100); NMR (in C₆D₆): δ (¹H) 0.33 (s, 18H, SiMe₃); 1.06, 1.28, 1.32 (3 × d, ³J_{HH} 6.6 Hz, 3 × 6H, 6 × CH₃-Pr); 1.40–1.60 (br, 18H, 6 × CH₃-Pr); 2.90, 3.80, 4.06 (3 × sept., 3 × 2H, 6 × CH-Pr); 6.70–7.10, 7.24–7.32 (2 × br, 9H, arom.); δ (¹³C) 3.57 (SiMe₃); 24.63, 24.73, 25.36, 25.68 (threefold intensity) (all CH₃-Pr); 28.71, 29.06, 29.15 (all CH-Pr); 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.); δ (²⁹Si) 16.2.

2: Bis[(2,4,6-trimethylphenyl)(trimethylsilyl)amino]-(2,6-diisopropylphenylimino)germane: m.p. 162 °C; yield 9.2 g (70%); C₃₆H₅₇GeN₃Si₂ (660.63); MS [*m/z* (%): EI 661 (22) [M⁺], 351 (100); NMR (in C₆D₆): δ (¹H) 0.08 (s, 18H, SiMe₃); 1.50 (d, ³J_{HH} 6.8 Hz, 12H, 4 × CH₃-Pr); 1.97 (s, 12H, 4 × *o*-CH₃); 2.08 (s, 6H, 2 × *p*-CH₃), 3.86 (sept., 2H, 2 × CH-Pr); 6.46–6.52 (m, 4H, C₆H₂); 7.05–7.13, 7.28–7.34 (2 × m, 3H, C₆H₃); δ (¹³C) 2.12 (SiMe₃); 20.11 (*o*-CH₃); 20.72 (*p*-CH₃); 23.98 (CH₃-Pr); 29.38 (CH-Pr); 119.92, 122.63, 129.37, 134.00, 136.42, 139.20, 140.58, 149.54 (all arom.); δ (²⁹Si) 14.1.

3: Bis[(2,4,6-trimethylphenyl)(trimethylsilyl)amino]-(2,4,6-trimethylphenylimino)germane: m.p. 177 °C; yield 8.54 g (69%); C₃₃H₅₁GeN₃Si₂ (618.55); MS [*m/z* (%): EI 619 (21) [M⁺], 351 (100); NMR (in C₆D₆): δ (¹H) 0.11 (s, 18H, SiMe₃); 2.03 (s, 18H, *o*-CH₃ of mes/amino); 2.33 (s, 3H, *p*-CH₃ of mes'/imino); 2.61 (s, 6H, *p*-CH₃ of mes/amino); 6.380, 6.382 (2s, 4H, C₆H₂ of mes); 7.064, 7.066 (2s, 2H, C₆H₂ of mes); δ (¹³C) 1.95 (SiMe₃); 20.66 (*o*-CH₃, mes/amino); 20.73 (*o*-CH₃, mes'/imino); 21.04 (*p*-CH₃, mes); 21.06 (*p*-CH₃, mes'); 127.30, 128.21, 129.09, 129.25, 133.63, 135.66, 140.61, 150.11, (C₆H₂ mes + mes'); δ (²⁹Si) 13.4.— δ (¹⁵N)-NMR (40% sol. in THF, standard CH₃NO₂ ext.): -295 (2N), -193 (1N).

‡ **4** m.p. 236 °C; C₄₂H₇₁GeN₃O₂Si₂ (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%); C₃₈H₆₃GeN₃O₂Si₂ (722.70); MS [*m/z* (%): EI 651(8) [M – THF]⁺, 42 (100).

NMR (in C₆D₆): δ (¹H) 0.30 (s, 18H, SiMe₃); 1.41 (m, 4H, H-3 and H-4 of THF); 1.95, 2.06, 2.14, 2.18 (4s, 27H, *o*-CH₃ + *p*-CH₃); 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, C₆H₂); IR (in Nujol) 3350 (νNH).

§ *Crystal data* for **1**: C₄₂H₆₉GeN₃Si₂, triclinic, space group $P\bar{1}$, $a = 1144.6(2)$, $b = 1178.7(2)$, $c = 1728.6(3)$ pm, $\alpha = 88.84(1)$, $\beta = 80.67(1)$, $\gamma = 68.20(1)^\circ$, $U = 2.13$ nm³, $Z = 2$, $D_c = 1.16$ g cm⁻³, $\mu = 0.80$ mm⁻¹, $F(000) = 804$, 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**: C₃₃H₅₁GeN₃Si₂, monoclinic, space group $P2_1/n$, $a = 852.3(2)$, $b = 2961.1(4)$, $c = 1382.1(2)$ pm, $\beta = 100.30(2)^\circ$, $U = 3.43$ nm³, $Z = 4$, $D_c = 1.20$ g cm⁻³, $\mu = 0.99$ mm⁻¹, $F(000) = 1320$, 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 α 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 10⁻⁶ epm⁻³ **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.

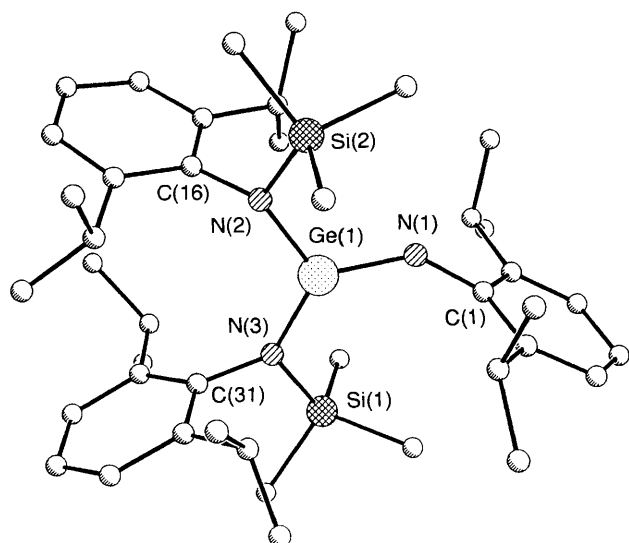


Fig. 1 Molecular structure of **1**; selected bond distances (pm) and angles ($^{\circ}$): Ge(1)–N(1) 170.3(2), Ge(1)–N(2) 181.9(3), Ge(1)–N(3) 182.6(3), N(1)–C(1) 141.1(4), N(2)–C(16) 145.3(3), N(3)–C(31) 145.5(3); N(1)–Ge(1)–N(2) 108.4(1), N(1)–Ge(1)–N(3) 130.9(1), N(2)–Ge(1)–N(3) 120.7(1)

normal π – π 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, $[\text{GeN}(\text{2,6-Pr}_2\text{C}_6\text{H}_3)]_3$ [mean Ge–N 185.9(2) pm]¹⁰ should be regarded as a Ge^{II} derivative without significant multiple bonding.

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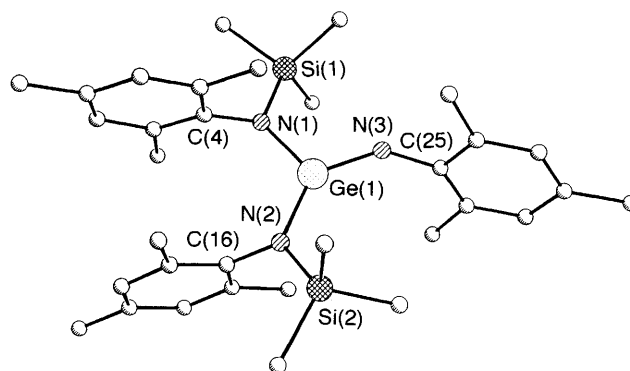


Fig. 2 Molecular structure of **3**; selected bond distances (pm) and angles ($^{\circ}$): Ge(1)–N(3) 169.1(3), Ge(1)–N(1) 180.8(3), Ge(1)–N(2) 182.8(3), N(3)–C(25) 139.9(4), N(1)–C(4) 145.2(4), N(2)–C(16) 145.7(4); N(3)–Ge(1)–N(1) 110.6(1), N(3)–Ge(1)–N(2) 134.0(1), N(1)–Ge(1)–N(2) 115.4(1)

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