Synthesis and X-Ray Crystal Structure of Germaimines

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Three new germaimines 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 $H_2Ge{=}NH$.

The Ge=N distance in unsubstituted germaimine ($H_2Ge{=}NH$) has been predicted to be 169.5 pm by *ab initio* calculation with double-ζ (DZ) plus polarization basis sets.[1] Germaimines 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 germaimines prepared from highly sterically hindered diazagermylenes[9] and 2,6-disubstituted phenylazides as shown in Scheme 1.† In the ^{15}N NMR spectrum of **3** two signals with 2 : 1 intensity ratio at δ = −295 and −193 (rel. to $MeNO_2$) 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 $[(2,6(Pr^i)_2C_6H_3(Me_3Si)N]_2Ge(OH){-}NHC_6H_3{-}2,6(Pr^i)_2$ **4** (from spectroscopic evidence). Likewise, methanol is added across the (Ge=N) double bond of **3** thus 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 germaimine.[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

$$[R(Me_3Si)N]_2Ge + N_3R' \xrightarrow[-\,N_2]{THF,\,20\,^{\circ}C} [R(Me_3Si)N]_2Ge{=}NR'$$

1: $R = R' = 2,6(Pr^i)_2C_6H_3$
2: $R = 2,4,6\text{-}Me_3C_6H_2,\ R' = 2,6(Pr^i{}_2)C_6H_3$
3: $R = R' = 2,4,6\text{-}Me_3C_6H_2$

$$3 + MeOH \xrightarrow{THF,\,20\,^{\circ}C} [R(Me_3Si)N]_2Ge(OMe){-}NHR{\cdot}THF$$

5 ($R = 2,4,6\text{-}Me_3C_6H_2$)

Scheme 1

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† *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%); $C_{42}H_{69}GeN_3Si_2$ (744.79); MS [*m/z* (%)]: EI 745 (20) [M$^+$], 73 (100); NMR (in C_6D_6): δ(^{1}H) 0.33 (s, 18H, $SiMe_3$); 1.06, 1.28, 1.32 (3 × d, $^3J_{HH}$ 6.6 Hz, 3 × 6H, 6 × CH_3-Pr^i); 1.40–1.60 (br, 18H, 6 × CH_3-Pr^i); 2.90, 3.80, 4.06 (3 × sept., 3 × 2H, 6 × CH-Pr^i); 6.70–7.10, 7.24–7.32 (2 × br, 9H, arom.); δ(^{13}C) 3.57 ($SiMe_3$); 24.63, 24.73, 25.36, 25.68 (threefold intensity) (all CH_3-Pr^i); 28.71, 29.06, 29.15 (all CH-Pr^i); 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(^{29}Si) 16.2.

2: Bis[(2,4,6-trimethylphenyl)(trimethylsilyl)amino]-(2,6-diisopropylphenylimino)germane: m.p. 162 °C; yield 9.2 g (70%); $C_{36}H_{57}GeN_3Si_2$ (660.63); MS [*m/z* (%)]: EI 661 (22) [M$^+$], 351 (100); NMR (in C_6D_6): δ(^{1}H) 0.08 (s, 18H, $SiMe_3$); 1.50 (d, $^3J_{HH}$ 6.8 Hz, 12H, 4 × CH_3-Pr^i); 1.97 (s, 12H, 4 × *o*-CH_3); 2.08 (s, 6H, 2 × *p*-CH_3), 3.86 (sept., 2H, 2 × CH-Pr^i); 6.46–6.52 (m, 4H, C_6H_2); 7.05–7.13, 7.28–7.34 (2 × m, 3H, C_6H_3); δ(^{13}C) 2.12 ($SiMe_3$); 20.11 (*o*-CH_3); 20.72 (*p*-CH_3); 23.98 (CH_3-Pr^i); 29.38 (CH-Pr^i); 119.92, 122.63, 129.37, 134.00, 136.42, 139.20, 140.58, 149.54 (all arom.); δ(^{29}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%); $C_{33}H_{51}GeN_3Si_2$ (618.55); MS [*m/z* (%)]: EI 619 (21) [M$^+$], 351 (100); NMR (in C_6D_6): δ(^{1}H) 0.11 (s, 18H, $SiMe_3$); 2.03 (s, 18H, *o*-CH_3 of mes + mes′); 2.33 (s, 3H, *p*-CH_3 of mes′/imino); 2.61 (s, 6H, *p*-CH_3 of mes/amino); 6.380, 6.382 (2s, 4H, C_6H_2 of mes); 7.064, 7.066 (2s, 2H, C_6H_2 of mes); δ(^{13}C) 1.95 ($SiMe_3$); 20.66 (*o*-CH_3, mes/amino); 20.73 (*o*-CH_3, mes′/imino); 21.04 (*p*-CH_3, mes); 21.06 (*p*-CH_3, mes′); 127.30, 128.21, 129.09, 129.25, 133.63, 135.66, 140.61, 150.11, (C_6H_2 mes + mes′); δ(^{29}Si) 13.4.—δ(^{15}N)-NMR (40% sol. in THF, standard CH_3NO_2 ext.): −295 (2N), −193 (1N).

‡ **4** m.p. 236 °C; $C_{42}H_{71}GeN_3OSi_2$ (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%); $C_{38}H_{63}GeN_3O_2Si_2$ (722.70); MS [*m/z* (%)]: EI 651(8) [M − THF]$^+$, 42 (100).

NMR (in C_6D_6): δ(^{1}H) 0.30 (s, 18H, $SiMe_3$); 1.41 (m, 4H, H-3 and H-4 of THF); 1.95, 2.06, 2.14, 2.18 (4s, 27H, *o*-CH_3+ *p*-CH_3); 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_6H_2); IR (in Nujol) 3350 (νNH).

§ *Crystal data* for **1**: $C_{42}H_{69}GeN_3Si_2$, triclinic, space group $P\bar{1}$, a = 1144.6(2), b = 1178.7(2), c = 1728.6(3) pm, α = 88.84(1), β = 80.67(1), γ = 68.20(1)°, U = 2.13 nm^3, Z = 2, D_c = 1.16 g cm^{-3}, μ = 0.80 mm^{-1}, F(000) = 804, crystal dimensions 0.5 × 0.5 × 0.6 mm, 8471 reflections collected with 8 < 2θ < 50°, 7488 unique and 6099 with $F > 3\sigma(F)$ used in the structural analysis. **3**: $C_{33}H_{51}GeN_3Si_2$, monoclinic, space group $P2_1/n$, a = 852.3(2), b = 2961.1(4), c = 1382.1(2) pm, β = 100.30(2)°, U = 3.43 nm^3, Z = 4, D_c = 1.20 g cm^{-3}, μ = 0.99 mm^{-1}, F(000) = 1320, crystal dimensions 0.4 × 0.4 × 0.6 mm, 7086 reflections collected with 8 < 2θ < 50°, 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-Kα radiation (λ = 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.

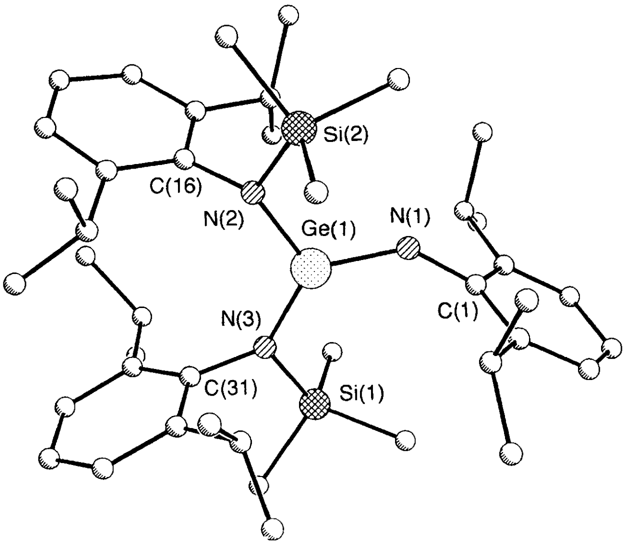

Fig. 1 Molecular structure of **1**; selected bond distances (pm) and angles (°): Ge(1)–N(1) 170.3(2), Ge(1)–N(2) 181.9(3), Ge(1)–N(3) 182.6(3), N(1)–C(1) 141.1(4), N(2)–C(16) 145.3(3), N(3)–C(31) 145.5(3); N(1)–Ge(1)–N(2) 108.4(1), N(1)–Ge(1)–N(3) 130.9(1), N(2)–Ge(1)–N(3) 120.7(1)

normal pπ–pπ 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, $[\mathrm{GeN}(2,6\text{-}\mathrm{Pr^i{}_2C_6H_3})]_3$ [mean Ge–N 185.9(2) pm][10] should be regarded as a $\mathrm{Ge^{II}}$ derivative without significant multiple bonding.

Received, 16th May 1991; Com. 1/02326H

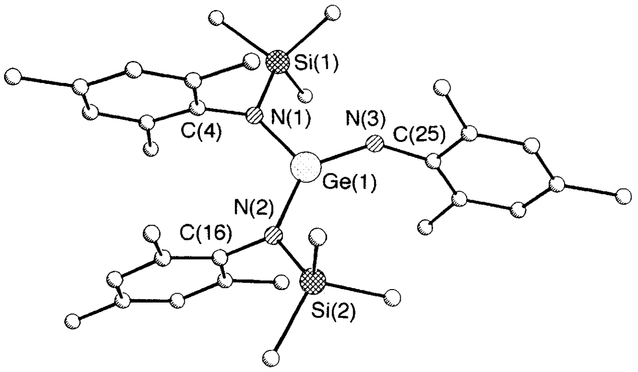

Fig. 2 Molecular structure of **3**; selected bond distances (pm) and angles (°): Ge(1)–N(3) 169.1(3), Ge(1)–N(1) 180.8(3), Ge(1)–N(2) 182.8(3), N(3)–C(25) 139.9(4), N(1)–C(4) 145.2(4), N(2)–C(16) 145.7(4); N(3)–Ge(1)–N(1) 110.6(1), N(3)–Ge(1)–N(2) 134.0(1), N(1)–Ge(1)–N(2) 115.4(1)

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