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- [20] This species was originally detected in an inseparable mixture of complexes resulting from a metal-mediated degradation of methyl formate.^[6]
- [21] Crystal data for [PPN]-**4c**: Monoclinic, space group $P2_1/n$; $a = 29.322(4)$, $b = 15.558(2)$, $c = 9.656(2)$ Å, $\beta = 92.77(2)$, $V = 4400(2)$ Å³; $R = 0.046$, $R_w = 0.050$.^[11b]
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- [23] Carbenoid species derived from simple carbonyl-chloro Ru^{II} complexes have been recently proposed by Murai et al. as intermediates in the construction of polycyclic ring systems from enynes.^[4a]

Reaction of RGeBr₃ (R = *i*Pr₂C₆H₃NSiMe₃) with Ammonia To Give (RGe)₂(NH₂)₄(NH): A Compound Containing Terminal NH₂ Groups**

Karsten Wraage, Lutz Lameyer, Dietmar Stalke, and Herbert W. Roesky*

In memory of Jean Rouxel

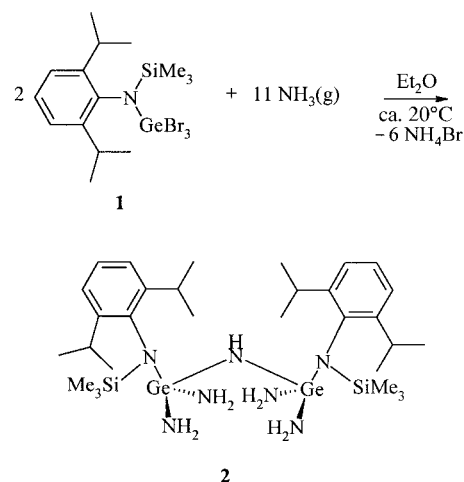
In the past few years Power et al.,^[1] Schnick et al.,^[2] and others^[3, 4] have shown that amino and imino derivatives containing silicon can undergo interesting reactions. In this respect they resemble the oxygen derivatives to some extent, but they can also differ from them quite considerably.^[5] For example, RSi(NH₂)₃ compounds react with AlMe₃ and [Cp*TiMe₃] (Cp* = C₅Me₅) with elimination of methane to form interesting, new, soluble heterocycles. We were interested in finding out whether there is a similar successive chemistry for germanium derivatives. We quickly discovered that the preferred starting compound for the reaction with ammonia—namely, RGeCl₃ (R = *i*Pr₂C₆H₃NSiMe₃)—is not accessible in a pure form. Until now, only one monoamino-germanium compound with the composition Mes₃GeNH₂ (Mes = Me₃C₆H₂) was known which is stable with regard to condensation reactions.^[6] We report here on the preparation and structure of an amino-iminogermanium compound with free amino groups that have not undergone condensation reactions.

[*] Prof. H. W. Roesky, Dipl.-Chem. K. Wraage
Institut für Anorganische Chemie der Universität
Tammannstrasse 4, D-37077 Göttingen (Germany)
Fax: (+49) 551-393-373
E-mail: hroesky@gwdg.de

Dipl.-Chem. L. Lameyer, Prof. D. Stalke
Institut für Anorganische Chemie der Universität Würzburg
(Germany)

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To obtain a suitable reagent for the synthesis of an amino derivative, we first prepared tribromogermanium compounds of the type RGeBr₃. The compound *i*Pr₂C₆H₃NSiMe₃GeBr₃ (**1**) was obtained by reaction of *i*Pr₂C₆H₃NSiMe₃Li with GeBr₄ in diethyl ether at –78 °C under elimination of LiBr. The reaction of **1** in liquid ammonia, which was performed analogous to the synthesis of RSi(NH₂)₃ derivatives,^[1, 3] proved to be unsuccessful; due to condensation reactions no definitive product could be isolated. If **1** is dissolved at room temperature in diethyl ether and ammonia is passed through the reaction solution, however, (RGe)₂(NH₂)₄(NH) (**2**) is obtained in good yield (Scheme 1).



Scheme 1. Synthesis of **2** from **1**.

Compound **2** was studied by NMR spectroscopy, mass spectrometry, and structure analysis. In the ¹H NMR spectrum the characteristic signals for the NH and NH₂ protons are recognizable as broad singlets ($\delta = 0.65$ for (RGe)₂(NH₂)₄–(NH) and $\delta = 0.75$ for (RGe)₂(NH₂)₄NH). The IR spectrum shows three N–H bands in the bond stretching region (3325–3402 cm^{–1}), and the bands at 1540 and 1578 cm^{–1} have been provisionally assigned to the NH₂ bending vibrations.

Single crystals of **2** are obtained on recrystallization from *n*-hexane. Compound **2** crystallizes in the space group $P\bar{1}$;^[11] two RGe(NH₂)₂ fragments bridged by a NH group are shown in the asymmetric unit in Figure 1a. In spite of their comparatively large spatial requirement, both of the *N*-(2,6-diisopropylphenyl)-*N*-(trimethylsilyl)amino groups are located on one side of the molecule and the four NH₂ groups on the opposite side. This cisoid arrangement is the result of a network of bridging hydrogen bonds (Figure 1b). The centrosymmetric dimer has four weak N···H–N bridges.^[7] The N···H distances are 250.5 pm (H21···N5A, H21A···N5; Figure 1b) and 267.8 pm (H31···N2A, H31A···N2; Figure 1b). All the Ge–N bond lengths to the hydrogen-substituted nitrogen atoms N1, N2, N3, N5, and N6 lie in the range from 181.1(2) to 182.4(2) pm, the bonds to the aryl-substituted nitrogen atoms N4 and N7 (both 184.2(2) pm) are about 3 pm longer.

The Ge–N bond lengths all lie in the expected region. Similar derivatives, such as the NH-bridged compound [Me₂Si(N*t*Bu)₂Ge(*t*Bu)]NH[(C₅H₄N)Ge(N*t*Bu)₂SiMe₂] described by Veith et al. and the cyclotris(dithiolato)germanium imide [(*t*BuS)₂Ge(NH)]₃ described by George et al., have

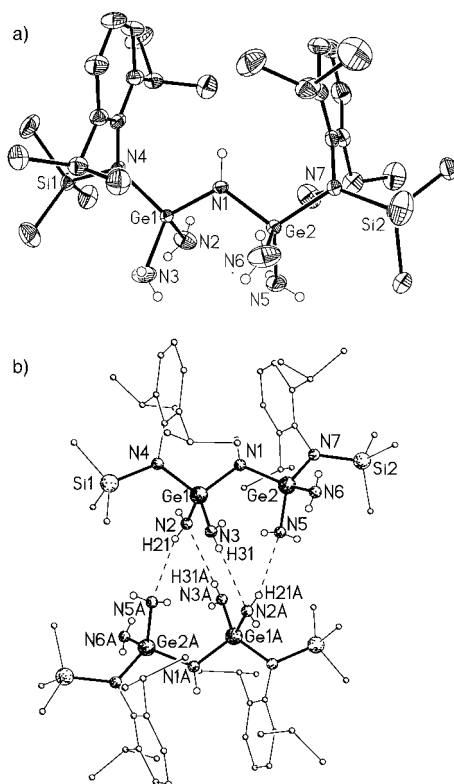


Figure 1. a) Structure of **2** in the crystal. Selected bond lengths [pm] and angles [°]: Ge1–N1 181.8(2), Ge1–N2 181.8(2), Ge1–N3 181.5(2), Ge1–N4 184.2(2), Ge2–N1 181.1(2), Ge2–N5 182.4(2), Ge2–N6 181.4(2), Ge2–N7 184.2(2); Ge1–N1–Ge2 120.89(9), N1–Ge1–N4 108.61(8), N2–Ge1–N3 101.80(10), N1–Ge2–N7 109.55(8), N5–Ge2–N6 104.54(11). b) Bridging hydrogen bonds between two molecules of **2**. Distances [pm] and angles [°] (the hydrogen atom positions were determined by difference Fourier synthesis and freely refined): H21...N5A 250.5, H31...N2A 267.8; N2–H21...N5A 164.28, N3–H31...N2A 174.08.

Ge–N bond lengths similar to those in **2**.^[8,9] In the *Nt*Bu-bridged amide [*t*BuN(CH₂)₂*Nt*Bu](Me)Si[N(*t*Bu)[Ge(N(H)–SiMe₃)(OSiMe₃){OCH₂N(CH₃)₂}], which contains sterically more demanding substituents on the nitrogen atom, the Ge–N bond is 184.2 pm long, and thus lies in the same range as the Ge–NAr(SiMe₃) bond lengths in **2** (Ge1–N4, Ge2–N7).^[10] The dimers exist in the solid as isolated molecules, however, and there are no bridging intermolecular hydrogen bonds.

The synthesis of **2** demonstrates that stable amino-imino-germanium derivatives can be prepared through the ammonolysis of a RGeBr₃ compound. Compound **2** contains reactive hydrogen atoms which should prove predestined for the synthesis of heterocycles containing germanium. The reaction of **2** with trimethylaluminum leads to the formation of a six-membered (GeN)₃ heterocycle and methane. Terminal NH₂ groups are located on each of the germanium atoms in the ring. The high hydrogen content should favor the elimination of the organic groups in **2**, so that new Ge–N phases should become accessible.

Experimental Section

1: GeBr₄ (5.2 g, 16.6 mmol) was dissolved in diethyl ether (100 mL). A solution of *i*Pr₂C₆H₃NSiMe₃Li (3.8 g, 14.9 mmol, 0.9 equiv.) dissolved in

diethyl ether (80 mL) was added slowly to the GeBr₄ solution at –78 °C. After the mixture was warmed slowly and stirred for about 12 h, the solvent was removed under reduced pressure and the residue taken up in *n*-hexane (70 mL). Insoluble components were filtered off, and the product subsequently recrystallized from *n*-hexane (5 mL). Yield: 7.5 g (80%) of **1**. C₁₅H₂₆Br₃GeNSi (*M* = 560.8 g mol^{–1}); sublimation at 150–160 °C; ¹H NMR (200 MHz, C₆D₆, TMS_{ext}): δ = 0.32 (s, 9H; Si(CH₃)₃), 1.15 (d, ³J(H,H) = 6.9 Hz, 6H; CH(CH₃)₂), 1.25 (d, ³J(H,H) = 6.9 Hz, 6H; CH(CH₃)₂), 3.45 (sept, 2H; CH(CH₃)₂), 7.05 (m, 3H; H_{arom}); ²⁹Si NMR (49 MHz, C₆D₆, TMS_{ext}): δ = 13.1 (Si(CH₃)₃); MS (EI, 70 eV): *m/z* (%): 560.9 (100) [*M*⁺], 545.8 (90) [*M*⁺ – CH₃]; correct elemental analysis.

2: *i*Pr₂C₆H₃NSiMe₃GeBr₃ (**1**, 0.56 g, 1 mmol) was dissolved in diethyl ether (10 mL). Ammonia (120 mL min^{–1}) was introduced under continuous stirring at room temperature. After 1 min the originally orange solution had turned colorless and a white precipitate formed. The reaction mixture was stirred for a further 0.5 h, and the precipitate then filtered off and recrystallized from *n*-hexane (5 mL). Yield: 0.3 g (81%) of **2**. C₃₀H₆₁Ge₂N₇Si₂ (*M* = 721.3 g mol^{–1}); m.p. 139 °C; ¹H NMR (250 MHz, CDCl₃, TMS_{ext}): δ = 0.07 (s, 18H; Si(CH₃)₃), 0.65 (s, 1H; (H₂N)₂GeNHGe(NH₂)₂), 0.75 (s, 8H; (H₂N)₂GeNHGe(NH₂)₂), 1.15 (dd, 24H; CH(CH₃)₂), 3.45 (sept, 4H; CH(CH₃)₂), 7.05 (m, 6H; H_{arom}); ²⁹Si NMR (79 MHz, CDCl₃, TMS_{ext}): δ = 4.9 (Si(CH₃)₃); IR (KBr): $\tilde{\nu}$ = 1540, 1578, 3325, 3389, 3402 cm^{–1}; MS (EI, 70 eV): *m/z* (%): 705 (2) [*M*⁺ – CH₃], 473 (100) [*M*⁺ – *i*Pr₂C₆H₃NSiMe₃]; correct elemental analysis.

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- [11] Crystal structure analysis of **2**: C₃₀H₆₁Ge₂N₇Si₂, *M*_r = 721.22, triclinic, space group *P* $\bar{1}$, *a* = 1035.0(2), *b* = 1264.3(3), *c* = 1556.7(3) pm, α = 101.59(3), β = 90.86(3), γ = 109.39(3)°, *V* = 1.8749(6) nm³, *Z* = 2, ρ_{calcd} = 1.278 Mg m^{–3}, *F*(000) = 764, λ = 71.073 pm, *T* = 173(2) K, absorption coefficient 1.696 mm^{–1}. Crystal size: 0.40 × 0.30 × 0.30 mm³, measured θ region 2.09–25.99°; of 26875 reflections measured, 6810 were independent (*R*_{int} = 0.1052); 62 restraints, 408 refined parameters, *R* values [*I* > 2σ(*I*)]: *R*1 = 0.0290, *wR*2 = 0.0741, *R* values (for all data): *R*1 = 0.0354, *wR*2 = 0.0764; weighting scheme *w* = 1/[σ²(*F*_o²) + (0.0560 *P*)²] with *P* = (max(*F*_o², 0) + 2 *F*_c²)/3; max./min. residual electron density: 559/–734 e nm^{–3}. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms on N2, N3, N5, and N6 (H21, H22, H31, H32, H51, H52, H61, and H62) were localized by difference Fourier syntheses and freely refined using distance restraints. The ideal geometrical positions of all the other hydrogen atoms were calculated and refined using a riding model. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-103202. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).