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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, $\beta = 92.77(2)$, $V = 4400(2)$ Å^3; $R = 0.046$, $Rw = 0.050$.[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 $RGeBr_3$ ($R = iPr_2C_6H_3NSiMe_3$) with Ammonia To Give $(RGe)_2(NH_2)_4(NH)$: A Compound Containing Terminal NH_2 Groups**

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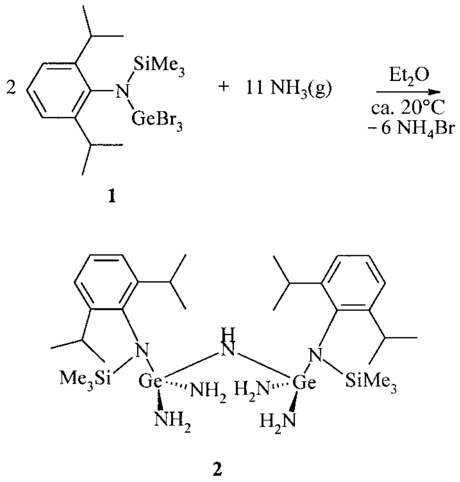
In memory of Jean Rouxel

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, $RSi(NH_2)_3$ compounds react with $AlMe_3$ and $[Cp^*TiMe_3]$ ($Cp^* = C_5Me_5$) 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, $RGeCl_3$ ($R = iPr_2C_6H_3NSiMe_3$)—is not accessible in a pure form. Until now, only one monoaminogermanium compound with the composition Mes_3GeNH_2 ($Mes = Me_3C_6H_2$) 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.

To obtain a suitable reagent for the synthesis of an amino derivative, we first prepared tribromogermanium compounds of the type $RGeBr_3$. The compound $iPr_2C_6H_3NSiMe_3GeBr_3$ (**1**) was obtained by reaction of $iPr_2C_6H_3NSiMe_3Li$ with $GeBr_4$ 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 $RSi(NH_2)_3$ 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, $(RGe)_2(NH_2)_4(NH)$ (**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 NH_2 protons are recognizable as broad singlets ($\delta = 0.65$ for $(RGe)_2(NH_2)_4(NH)$ and $\delta = 0.75$ for $(RGe)_2(NH_2)_4NH$). 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 NH_2 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 $RGe(NH_2)_2$ fragments bridged by a NH group are shown in the asymmetric unit in Figure 1 a. 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 NH_2 groups on the opposite side. This cisoid arrangement is the result of a network of bridging hydrogen bonds (Figure 1 b). The centrosymmetric dimer has four weak N···H-N bridges.[7] The N···H distances are 250.5 pm (H21···N5A, H21A···N5; Figure 1 b) and 267.8 pm (H31···N2A, H31A···N2; Figure 1 b). 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 $[Me_2Si(NtBu)_2Ge(tBu)]NH[(C_5H_4N)Ge(NtBu)_2SiMe_2]$ described by Veith et al. and the cyclotris(dithiolato)germanium imide $[\{(tBuS)_2Ge(NH)\}_3]$ described by George et al., have

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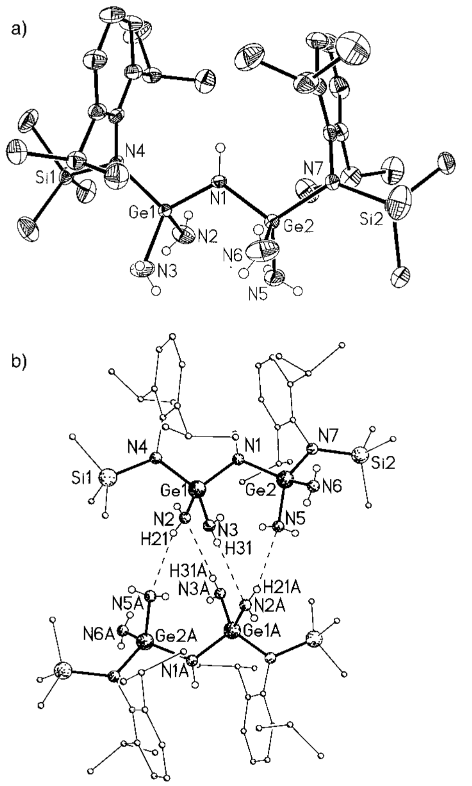

Figure 1. a) Structure of **2** in the crystal. Selected bond lengths [pm] and angles [°]: Ge1–N1 181.8(2), Ge1–N2 181.8(2), Ge1–N3 181.5(2), Ge1–N4 184.2(2), Ge2–N1 181.1(2), Ge2–N5 182.4(2), Ge2–N6 181.4(2), Ge2–N7 184.2(2); Ge1-N1-Ge2 120.89(9), N1-Ge1-N4 108.61(8), N2-Ge1-N3 101.80(10), N1-Ge2-N7 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 N*t*Bu-bridged amide [{*t*BuN(CH$_2$)$_2$N*t*Bu}(Me)Si]N(*t*Bu)[Ge{N(H)-SiMe$_3$}(OSiMe$_3$){OCH$_2$N(CH$_3$)$_2$}], 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(SiMe$_3$) 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 RGeBr$_3$ 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 NH$_2$ 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: GeBr$_4$ (5.2 g, 16.6 mmol) was dissolved in diethyl ether (100 mL). A solution of *i*Pr$_2$C$_6$H$_3$NSiMe$_3$Li (3.8 g, 14.9 mmol, 0.9 equiv.) dissolved in diethyl ether (80 mL) was added slowly to the GeBr$_4$ solution at $-78\,^{\circ}$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**. C$_{15}$H$_{26}$Br$_3$GeNSi ($M = 560.8$ g mol^{-1}); sublimation at 150–160 °C; ^{1}H NMR (200 MHz, C$_6$D$_6$, TMS$_{\text{ext.}}$): $\delta = 0.32$ (s, 9H; Si(C*H*$_3$)$_3$), 1.15 (d, ^3J(H,H) = 6.9 Hz, 6H; CH(C*H*$_3$)$_2$), 1.25 (d, ^3J(H,H) = 6.9 Hz, 6H; CH(C*H*$_3$)$_2$), 3.45 (sept, 2H; C*H*(CH$_3$)$_2$), 7.05 (m, 3H; H$_{\text{arom.}}$); ^{29}Si NMR (49 MHz, C$_6$D$_6$, TMS$_{\text{ext.}}$): $\delta = 13.1$ (*Si*(CH$_3$)$_3$); MS (EI, 70 eV): *m/z* (%): 560.9 (100) [M^+], 545.8 (90) [$M^+ - \text{CH}_3$]; correct elemental analysis.

2: *i*Pr$_2$C$_6$H$_3$NSiMe$_3$GeBr$_3$ (**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**. C$_{30}$H$_{61}$Ge$_2$N$_7$Si$_2$ ($M = 721.3$ g mol^{-1}); m.p. 139 °C; ^{1}H NMR (250 MHz, CDCl$_3$, TMS$_{\text{ext.}}$): $\delta = 0.07$ (s, 18H; Si(C*H*$_3$)$_3$), 0.65 (s, 1H; (H$_2$N)$_2$GeN*H*Ge(NH$_2$)$_2$), 0.75 (s, 8H; (*H*$_2$N)$_2$GeNHGe(N*H*$_2$)$_2$), 1.15 (dd, 24H; CH(C*H*$_3$)$_2$), 3.45 (sept, 4H; C*H*(CH$_3$)$_2$), 7.05 (m, 6H; H$_{\text{arom.}}$); ^{29}Si NMR (79 MHz, CDCl$_3$, TMS$_{\text{ext.}}$): $\delta = 4.9$ (*Si*(CH$_3$)$_3$); IR (KBr): $\tilde{\nu} = 1540$, 1578, 3325, 3389, 3402 cm^{-1}; MS (EI, 70 eV): *m/z* (%): 705 (2) [$M^+ - \text{CH}_3$], 473 (100) [$M^+ - i\text{Pr}_2\text{C}_6\text{H}_3\text{NSiMe}_3$]; correct elemental analysis.

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[11] Crystal structure analysis of **2**: C$_{30}$H$_{61}$Ge$_2$N$_7$Si$_2$, $M_r = 721.22$, triclinic, space group $P\bar{1}$, $a = 1035.0(2)$, $b = 1264.3(3)$, $c = 1556.7(3)$ pm, $\alpha = 101.59(3)$, $\beta = 90.86(3)$, $\gamma = 109.39(3)^{\circ}$, $V = 1.8749(6)$ nm^3, $Z = 2$, $\rho_{\text{calcd}} = 1.278$ Mg m^{-3}, $F(000) = 764$, $\lambda = 71.073$ pm, $T = 173(2)$ K, absorption coefficient 1.696 mm^{-1}. Crystal size: $0.40 \times 0.30 \times 0.30$ mm^3, measured θ region 2.09–25.99°; of 26875 reflections measured, 6810 were independent ($R_{\text{int}} = 0.1052$); 62 restraints, 408 refined parameters, R values [$I > 2\sigma(I)$]: $R1 = 0.0290$, $wR2 = 0.0741$, R values (for all data): $R1 = 0.0354$, $wR2 = 0.0764$; weighting scheme $w = 1/[\sigma^2(F_o^2) + (0.0560P)^2]$ with $P = (\max(F_o^2,0) + 2F_c^2)/3$; 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 CB21EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).