

# Isomerization of an N-Heterocyclic Germylene to an Azagermabenzen-1-ylidene and Its Coupling to a Unique Bis(germylene)<sup>§</sup>

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N-Heterocyclic germylene LGe  $[L = CH\{(C=CH_2)(CMe)(N(aryl))_2\}$ , aryl = 2,6-<sup>*i*</sup>Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>] **1** reacts with HN(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub> solely to give the 1,4-addition product L'GeN(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub> **2** (L' = CH(CMe)<sub>2</sub>[N(aryl)]<sub>2</sub>), which contains a Ge(II)-N(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub> moiety. In contrast, HN(SiMe<sub>3</sub>)<sub>2</sub> does not add to **1** but induces isomerization of **1** to generate the first N(aryl)H-substituted, heteroaromatic azagermabenzen-1-ylidene intermediate. The latter readily undergoes 1,4-addition to a second equivalent of **1** to form the unprecedented bis(germylene) **3**, which contains two- and three-coordinate Ge(II) centers. The isomerization process and the nature of the six  $\pi$ -electron aromatic character of the C<sub>4</sub>NGe heterocycle in **2** are explored and supported by DFT calculations.

#### Introduction

The preparative chemistry and reactivity of divalent, two-coordinate germanium(II) compounds (germylenes) have received considerable interest due to their carbenelike properties.<sup>1</sup> Most of the isolable germylenes are stabilized kinetically by sterically demanding substituents and/ or thermodynamically by both  $\pi$ -electron-donating and  $\sigma$ -electron-withdrawing substituents (amido ligands, etc.) bonded to the divalent germanium(II) atom. In some cases, heteroaromatic six  $\pi$ -electron delocalization may also contribute to the remarkable stabilization of N-heterocyclic germylenes.<sup>2</sup>

Using  $\beta$ -diketiminate ligands, bearing sterically congested aryl substituents at the nitrogen atoms, enabled the synthesis

of stable germanium(II) complexes  $A^{1k,3}$  and  $C^4$  (Scheme 1), and these findings initiated renewed interest in investigating N-heterocyclic Ge(II) systems with two- and three-coordinate Ge atoms. Recently, we succeeded in the synthesis and isolation of a new type of Ge(II) heterocycle, the cyclopenta-dienide analogue  $\mathbf{D}$ ,<sup>5</sup> via reduction of  $\mathbf{A}$  (X = Cl)<sup>6a</sup> by elemental potassium and subsequent ring contraction. Moreover, we prepared the N-heterocyclic germylene  $1^7$  through dehydrohalogenation of A. Interestingly, the betaine-like germylene 1 reacts readily with 1,2-dibromoethane, affording the bis(bromogermylene) **B** as a vellow solid.<sup>7</sup> While the Ge(II) centers in A and B are stabilized additionally by intramolecular N $\rightarrow$ Ge coordination, the significant stabilization of C and **D** originates from a heteroaromatic six  $\pi$ -electron delocalization over the respective ring systems. However, in contrast to C and D, while containing dicoordinate Ge(II) and enjoying a planar structure with potentially six  $\pi$ -electrons, DFT calculations indicate no heteroaromatic character for 1. Rather, reactivity investigations of germylene 1 revealed that the vlide-like betaine resonance structure 1' (Scheme 1) plays an important role and determines largely its intriguing reactivity toward electrophiles. For instance, reaction of 1 with trimethylsilyl triflate (Me<sub>3</sub>SiOTf, OTf =  $OSO_2CF_3$ ) leads exclusively to a 1,4-addition product, with addition of the Me<sub>3</sub>Si group to the nucleophilic carbon atom of the terminal methylene moiety and OTf to the electrophilic Ge(II) site, affording a Ge(II) complex of type A.<sup>7</sup> Germylene 1 is even capable of activating N-H bonds of ammonia, giving the

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Ar =  $2,6^{-i}$ Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub> X = halide, hydride, alkyl, OR, NR<sub>2</sub>, PR<sub>2</sub>

Scheme 2. Synthesis of 2 and 3 from Germylene 1



same type of 1,4-addition product A (X = NH<sub>2</sub>).<sup>6b</sup> Likewise, germylene 1 reacts also with the secondary amine HN(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>, to give the amido-substituted germylene 2 as an expected 1,4addition product. To our surprise, HN(SiMe<sub>3</sub>)<sub>2</sub> exhibits different behavior, serving as a catalyst for the rearrangement of 1 to an azagermabenzen-1-ylidene intermediate, which undergoes coupling with one additional molecule of 1 to give the unique bis(germylene) 3 (Scheme 2). The latter features both two- and three-coordinate Ge(II) moieties connected by an N(aryl) group. Herein we describe the facile addition of secondary amine HN(C<sub>6</sub>F<sub>5</sub>) to give the Ge(II)-amido complex 2 and the remarkably different result for the conversion  $1 \rightarrow 3$  in the presence of HN(SiMe<sub>3</sub>)<sub>2</sub>.

### **Results and Discussion**

Bis(pentafluorophenyl)amine reacts readily with 1 in hexane at room temperature, affording the expected 1,4-addition product 2 (Scheme 2). As reported earlier, similar reactions have been observed for 1 employing different substrates.<sup>6b,7,8</sup> Compound 2 has been isolated as yellow crystals in 91% yield and has been fully characterized by spectroscopic means (see below).

The molecular structure of 2 obtained from a single-crystal X-ray diffraction analysis (Figure 1) revealed, as expected, that the three-coordinate Ge atom adopts a pseudo-tetra-



Figure 1. Molecular structure of 2. Thermal ellipsoids are drawn at a 50% probability level. Hydrogen atoms are omitted for the sake of clarity. Selected bond lengths [Å] and angles [deg]: Ge1-N2 1.987(2), Ge1-N1 1.990(2), Ge1-N3 2.054(2), N1-C2 1.338(2), C1-C2 1.500(2), N2-C4 1.339(2), C2-C3 1.390(3), N3-C30 1.395(2), N3-C41 1.422(2), C3-C4 1.390(3), C4-C5 1.506(2), N2-Ge1-N1 92.03(6), N2-Ge1-N3 104.76(6), N1-Ge1-N3 104.67(6), C2-N1-Ge1 126.3(1), C4-N2-Ge1 125.8(1), N1-C2-C3 123.0(2), N1-C2-C1 119.4(2), C30-N3-C41 116.7(1), C30-N3-Ge1 139.9(1), C41-N3-Ge1 103.0(1).

hedral geometry. Two sites are occupied by nitrogen atoms from the  $\beta$ -diketiminate ligand, and one site is occupied by the exocyclic N atom of the N(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub> group. The lone pair of electrons occupies presumably the remaining coordination site of the tetrahedron. While the bond lengths within the C<sub>3</sub>N<sub>2</sub>Ge ring of **2** are comparable to those found in related structures, the exocyclic Ge1–N3 distance of 2.054(2) Å, however, is about 0.2 Å longer than the corresponding Ge–N bond length (1.845(2) Å) in **A** (X = NH<sub>2</sub>),<sup>6b</sup> presumably due to the electron-withdrawing character of the electronegative N(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub> subunit, which favors an enhanced Ge<sup>+</sup>–N<sup>-</sup> polarization.

We further probed HN(SiMe<sub>3</sub>)<sub>2</sub> as a potential substrate for 1,4-addition to 1. We assumed that, if addition of the amine occurs at all, the desired process would be relatively slow because of the more demanding steric congestion of the amino group as compared to  $N(C_6F_5)_2$ . In fact, conversion of 1 in the presence of a catalytic amount (12 mol %) of bis(trimethylsilyl)amine occurs with only moderate progress, irrespective of the polarity of the nonprotic organic solvent used (hexane, diethyl ether, or benzene), and it takes about three weeks for the complete conversion of 1. Notably, no significant change has been observed by using additional amounts of bis(trimethylsilyl)amine. Moreover, at elevated temperature the reaction led to a complex mixture. Unexpectedly, the novel bis(germylene) 3 crystallized at room temperature in hexane as yellow crystals and was isolated from the reaction mixture in 48% yield (Scheme 2). In accordance with its <sup>1</sup>H and <sup>13</sup>C NMR spectroscopic features and mass spectrometric data, 3 constitutes a coupling product that contains two different Ge(II) subunits as distinct N-heterocyclic ligands. The most notable resonances in the <sup>1</sup>H NMR spectrum of 3 recorded in  $d_8$ -THF are two doublets in the aromatic proton region at  $\delta = 7.06$  and 6.69 ppm with  ${}^{4}J_{\rm HH} = 2.8$  Hz.

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**Figure 2.** (a) Molecular structure of **3**. Thermal ellipsoids are drawn at a 50% probability level. Hydrogen atoms are omitted for the sake of clarity. (b) The six-membered C<sub>4</sub>NGe ring is disordered over two orientations. Selected bond lengths [Å] and angles [deg]: Ge1–N3 1.959(3), Ge1–N1 2.038(3), Ge1–N2 2.073(3), Ge2–C30 1.869(5), Ge2–N4 1.919(9), N1–C2 1.343(4), N2–C4 1.310(4), N2–C12 1.456(4), N3–C31 1.405(5), N4–C33 1.334(9), C2–C3 1.381(5), C3–C4 1.398(5), C30–C31 1.397(6), C31–C32 1.407(6), C32–C33 1.380(7), N3–Ge1–N1 105.1(1), N3–Ge1–N2 105.4(1), N1–Ge1–N2 88.7(1), C30–Ge2–N4 95.6(3), C31–C30–Ge2 126.5(4), C30–C31–C32 122.5(4), C(30)–C(31)–N(3) 124.2(5), C(31)–N(3)–Ge(1) 137.6(3).

The latter could be unambiguously assigned to a  $\alpha$ -CH and its adjacent  $\gamma$ -CH proton in 3, respectively, indicating the presence of an heteroaromatic six  $\pi$ -electron system (see below). However, the structure of 3 could be unequivocally determined only by a single-crystal X-ray diffraction analysis (Figure 2). Compound 3 crystallizes in the triclinic space group  $P\overline{1}$  and consists of two six-membered N-heterocyclic germylenes connected by an N(aryl) group. While one of the germylene subunits in 3 represents a complex of type A with a six-membered C<sub>3</sub>N<sub>2</sub>Ge ring and a three-coordinate Ge(II) site, the other one corresponds to a unique azagermabenzen-1-ylidene heterocycle that contains a six-membered C<sub>4</sub>NGe ring bearing a two-coordinate Ge(II) center. The six-membered C<sub>3</sub>N<sub>2</sub>Ge ring in **3** is slightly puckered, and the geometric parameters are quite similar to those of related complexes of type A, including an N(H)aryl-substituted (aryl =  $2,6^{-i}$ Pr<sub>2</sub>- $C_6H_3$ ) derivative,<sup>5</sup> which resulted as a side product from the reduction of the corresponding chloro Ge(II) complex<sup>6a</sup> with elemental potassium. However, the Ge1-N3 bond length (1.959(3) Å) in **3** is slightly longer than that in the N(H)aryl derivative mentioned above (1.906(2) Å), owing to the larger steric congestion of 3. The most noteworthy structural feature of 3 concerns the planar six-membered C<sub>4</sub>NGe ring derived from a rearangement of the  $\beta$ -diketiminate-like ligand in precursor 1. The C<sub>4</sub>NGe ring is orthogonally positioned to the C3N2Ge ring and disordered over two orientations in a population ratio of 0.74:0.26 (Figure 2b); only the major form is shown in Figure 2a. Interestingly, the C-C distances within the C<sub>4</sub>NGe ring are similar to one another (1.397(6), 1.407(6), and 1.380(7) Å), thus suggesting the presence of strongly delocalized  $\pi$ -bonds. In addition, the Ge2-C30 distance of 1.869(5) Å is significantly shorter than that of a normal Ge-C single-bond length, and the Ge2-N4



Figure 3. Potential energy surface for the isomerization  $1 \rightarrow 1b$ . To compare with TS1a/1b, the energy of NH<sub>3</sub> was added to 1, TS1/1a, 1a, and 1b. [Relative energies (with zero-point energy corrections) are given in kcal mol<sup>-1</sup> and the bond distances in Å.]

Scheme 3. Proposed DFT-Based Mechanism for the Isomerization of 1, via 1a and 1b, and Its Coupling (1,4-Addition) with 1 to Give 3



distance of 1.919(9) Å lies very close to those Ge-N bonds (1.894(2) Å) found in cation **B** as reported by Power and coworkers.<sup>4</sup> Accordingly and in line with NMR data, this suggests aromatic character for the novel C<sub>4</sub>NGe ring system resulting from a planar (Hückel-like) heteroaromatic six  $\pi$ electron delocalization. This notion is supported by density functional theory (DFT) calculations, which reproduced well the geometric parameters of 3. In fact, the calculated negative NICS values for 3 (NICS(0) = -1.6 ppm, NICS(1) = -3.9 ppm) clearly indicate significant aromatic stabilization in the C<sub>4</sub>NGe ring. In contrast, no aromatic stabilization is predicted for the C<sub>3</sub>N<sub>2</sub>Ge ring, as shown by the computed positive NICS values (NICS(0) = 3.5 ppm, NICS(1) = 2.3ppm), owing to the presence of three-coordinate Ge(II) in the type A germylene subunit. Compound 3 represents a unique bis(germylene) bearing the first heteroleptic, two-coordinate Ge(II) center in a six-membered C<sub>4</sub>NGe ring system with only one adjacent nitrogen donor atom and stabilized additionally by six  $\pi$ -electron delocalization.

In order to rationalize the formation of 3, which obviously occurs via isomerization of 1 in the presence of  $HN(SiMe_3)_2$ 

and its subsequent coupling with another molecule of 1, DFT calculations have been performed. The proposed mechanism involving the reactive intermediates 1a and 1b and part of the calculated potential energy surface are shown in Scheme 3 and Figure 3, respectively. The isomerization is initiated by a nucleophilic attack of the methylene subunit in resonance structure 1' to the Ge(II) center and the concomitant formation of an excocyclic imine group to give the intermediate 1a.

The barrier for the isomerization step  $1 \rightarrow 1a$  was calculated to 29.4 kcal mol<sup>-1</sup>, thus indicating a slow but yet achievable process at room temperature. **1a** is ca. 9.4 kcal mol<sup>-1</sup> higher in energy than 1 due to sacrificing one of the stabilizing N-Ge interactions. However, transient **1a** can undergo an imine-enamine tautomerization by transferring a proton from C1 to N1 to give **1b**; the latter gains extra stabilization through six  $\pi$ -electron delocalization. Such a proton-transfer process can be accelerated in the presence of a suitable base. With NH<sub>3</sub>, acting as an external model to mimic HN(SiMe<sub>3</sub>)<sub>2</sub>, the relative energy of **TS1a/1b** amounts to 28.8 kcal mol<sup>-1</sup>, which is slightly lower than that of **TS1/1a**. The N1 atom of the NH(aryl) moiety in **1b** is sterically less congested than that of HN(SiMe<sub>3</sub>)<sub>2</sub> and thus easily accessible for a 1,4-addition to **1** to give the bis(germylene) **3**.

### **Experimental Section**

**General Considerations.** All experiments were carried out under dry, oxygen-free dinitrogen using standard Schlenk techniques or in an MBraun inert atmosphere drybox containing an atmosphere of purified nitrogen. Solvents were dried by standard methods and freshly distilled prior to use. The starting material LGe was prepared according to literature procedures.<sup>7</sup> <sup>1</sup>H, <sup>13</sup>C, and <sup>19</sup>F NMR spectra were recorded with the Bruker spectrometers ARX 200 and AV 400, respectively. EI-MS spectra were taken on a Finnigan-MAT 955 instrument. Elemental analyses were performed on a FlashEA 1112 CHNS analyzer.

**Syntheses.** Compound 2. A solution of  $HN(C_6F_5)_2$  (0.29 g, 0.81 mmol) in hexane (10 mL) was added to a solution of 1 (0.40 g, 0.81 mmol) in hexane (15 mL) at room temperature. The brownred color of the reaction mixture changed to yellow immediately. After concentration and cooling to  $-20 \,^{\circ}C$  for 24 h, compound 2 crystallized from the solution as yellow crystals (0.62 g, 0.74 mmol, 91%). Mp: 191  $^{\circ}C$  (dec). <sup>1</sup>H NMR (200.13 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K):  $\delta$  1.06 (d, <sup>3</sup>*J*<sub>HH</sub> = 7 Hz, 6 H, CH*M*e<sub>2</sub>), 1.12 (d, <sup>3</sup>*J*<sub>HH</sub> = 7 Hz, 6 H, CH*M*e<sub>2</sub>), 1.23 (d, <sup>3</sup>*J*<sub>HH</sub> = 7 Hz, 6 H, CH*M*e<sub>2</sub>), 1.33 (d, <sup>3</sup>*J*<sub>HH</sub> = 7 Hz, 6 H, CH*M*e<sub>2</sub>), 1.23 (d, <sup>3</sup>*J*<sub>HH</sub> = 7 Hz, 6 H, CH*M*e<sub>2</sub>), 3.37 (sept., 2H, <sup>3</sup>*J*<sub>HH</sub> = 7 Hz, C*H*Me<sub>2</sub>), 5.01 (s, 1 H,  $\gamma$ -C*H*), 7.02–7.20 (m, br, 6 H, aroma-*H*). <sup>13</sup>C{<sup>1</sup>H} NMR (50.61 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K):  $\delta$  24.4, 24.7, 24.8, 25.7, 28.3, 29.3 (<sup>i</sup>*Pr*, NC*M*e), 101.7 ( $\gamma$ -C), 125.0–146.2 (2,6-<sup>i</sup>Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>, C<sub>6</sub>F<sub>5</sub>), 167.8 (NCMe). <sup>19</sup>F{<sup>1</sup>H} NMR (188.31 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K):  $\delta$  –146 (br), –149 (br), –165.5 (br). Anal. (%) calcd for C<sub>41</sub>H<sub>41</sub>N<sub>3</sub>GeF<sub>10</sub>: C 58.74; H 4.93; N 5.01. Found: C 59.31; H 5.05; N 4.96. EI-MS: *m*/*z*(%) 491 (15, [M – N(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>]<sup>+</sup>), 475 (73, [M – N(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub> – Me]<sup>+</sup>), 349 (100, [N(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>]<sup>+</sup>).

**Compound 3.** To a solution of **1** (0.47 g, 0.96 mmol) in hexane (20 mL) was added HN(SiMe<sub>3</sub>)<sub>2</sub> (12 mol %) at room temperature. During the course of 3 weeks yellow crystals of compound **3** were formed (0.23 g, 0.23 mmol, 48%). Mp: 181 °C (dec). <sup>1</sup>H NMR (200.13 MHz, D<sub>8</sub>-THF, 298 K):  $\delta$  0.10 (d, <sup>3</sup>*J*<sub>HH</sub> = 7 Hz, 6 H, CH*Me*<sub>2</sub>), 0.85 (d, <sup>3</sup>*J*<sub>HH</sub> = 7 Hz, 6 H, CH*Me*<sub>2</sub>), 1.08 (d, <sup>3</sup>*J*<sub>HH</sub> = 7 Hz, 6 H, CH*Me*<sub>2</sub>), 1.10 (d, <sup>3</sup>*J*<sub>HH</sub> = 7 Hz, 6 H, CH*Me*<sub>2</sub>), 1.18 (d, <sup>3</sup>*J*<sub>HH</sub> = 7 Hz, 6 H, CH*Me*<sub>2</sub>), 1.10 (d, <sup>3</sup>*J*<sub>HH</sub> = 7 Hz, 6 H, CH*Me*<sub>2</sub>), 1.18 (d, <sup>3</sup>*J*<sub>HH</sub> = 7 Hz, 6 H, CH*Me*<sub>2</sub>), 1.25 (d, <sup>3</sup>*J*<sub>HH</sub> = 7 Hz, 6 H, CH*Me*<sub>2</sub>), 1.31 (d, <sup>3</sup>*J*<sub>HH</sub> = 7 Hz, 6 H, CH*Me*<sub>2</sub>), 1.75 (s, 6 H, C*Me*), 2.18 (s, 3 H, C*Me*), 2.53 (sept., <sup>3</sup>*J*<sub>HH</sub> = 7 Hz, 2 H, C*H*Me<sub>2</sub>), 3.39 (sept., <sup>3</sup>*J*<sub>HH</sub> = 7 Hz, 2 H, C*H*Me<sub>2</sub>), 3.39 (sept., <sup>3</sup>*J*<sub>HH</sub> = 7 Hz, 2 H, C*H*Me<sub>2</sub>), 5.27 (s, 1 H,  $\gamma$ -C*H*), 6.69 (d, <sup>4</sup>*J*<sub>HH</sub> = 2.8 Hz, 1 H,  $\gamma$ -C*H*),

7.06 (d,  ${}^{4}J_{HH} = 2.8$  Hz, 1 H, α-*CH*), 6.89 - 7.32 (m, 12 H, 2,6- ${}^{1}Pr_{2}C_{6}H_{3}$ ).  ${}^{13}C{}^{1}H{}$ NMR (100.61 MHz, D<sub>8</sub>-THF, 298 K): δ 24.1, 26.0, 26.2, 27.2, 28.3, 28.7, 29.7, 30.4 ( ${}^{i}Pr$ , NC*Me*); 97.3, 110.1 ( $\gamma$ -*C*); 152.1 (α-*C*); 124.2 - 153.8 (2,6- ${}^{1}Pr_{2}C_{6}H_{3}$ ); 160.7, 170.3 (NCMe). Anal. (%) Calcd for C<sub>58</sub>H<sub>82</sub>N<sub>4</sub>Ge<sub>2</sub>: C 71.20; H 8.24; N 5.73. Found: C 70.97; H 8.27; N 5.37. EI-MS: *m/z* (%) 978 (0.5, [M]<sup>+</sup>), 490 (33, [1/2M]<sup>+</sup>), 475 (100, [1/2M - Me]<sup>+</sup>).

Single-Crystal X-ray Structure Determinations. Crystals were each mounted on a glass capillary in perfluorinated oil and measured in a cold N<sub>2</sub> flow. The data of compounds **2** and **3** were collected on an Oxford Diffraction Xcalibur S Sapphire at 150 K (Mo K $\alpha$  radiation,  $\lambda = 0.71073$  Å). The structures were solved by direct methods and refined on  $F^2$  with the SHELX-97<sup>9</sup> software package. The positions of the H atoms were calculated and considered isotropically according to a riding model.

**2**: triclinic, space group  $P\overline{1}$ , a = 10.8593(3) Å, b = 13.1638(4) Å, c = 14.4489(3) Å,  $\alpha = 92.576(2)^\circ$ ,  $\beta = 101.490(2)^\circ$ ,  $\gamma = 102.174(2)^\circ$ , V = 1970.39(9) Å<sup>3</sup>, Z = 2,  $\rho_{calc} = 1.413$  Mg/m<sup>3</sup>,  $\mu$ (Mo K $\alpha$ ) = 0.858 mm<sup>-1</sup>, 16016 collected reflections, 6886 crystallographically independent reflections [ $R_{int} = 0.0142$ ], 6064 reflections with  $I > 2\sigma(I)$ ,  $\theta_{max} = 25^\circ$ ,  $R(F_o) = 0.0264$ ( $I > 2\sigma(I)$ ),  $wR(F_o^2) = 0.0716$  (all data), 506 refined parameters.

**3**: triclinic, space group  $P\overline{1}$ , a = 11.403(3) Å, b = 14.520(2) Å, c = 18.793(3) Å,  $\alpha = 78.926(12)^\circ$ ,  $\beta = 82.882(17)^\circ$ ,  $\gamma = 78.326(16)^\circ$ , V = 2978.7(10) Å<sup>3</sup>, Z = 2,  $\rho_{calc} = 1.187$  Mg/m<sup>3</sup>,  $\mu$ (Mo K $\alpha$ ) = 1.050 mm<sup>-1</sup>, 23 925 collected reflections, 10 182 crystallographically independent reflections [ $R_{int} = 0.0489$ ], 5230 reflections with  $I > 2\sigma(I)$ ,  $\theta_{max} = 25^\circ$ ,  $R(F_o) = 0.0455$ ( $I > 2\sigma(I)$ ),  $wR(F_o^2) = 0.0938$  (all data), 787 refined parameters.

## **Computational Details**

All calculations were performed at the B3LYP level of theory<sup>10</sup> as implemented in the Gaussian03 program package.<sup>11</sup>

The geometry of compound **2** was optimized with the basis sets BSI (def2-TZVP for Ge, N, and the C atoms at the two core rings  $C_4GeN$ ,  $C_3GeN_2$ ,<sup>12</sup> and with 6-31G for the other atoms). The NICS values were calculated by the GIAO method with the Ahlrichs basis set BSII, with VTZ for all the elements.<sup>13</sup> The ring centers were defined by a nonweighted mean of the atom coordinates. The ring plane is defined as the plane through the ring center for which the sum of the squares of the distance of that plane to the positions of the atoms forming the ring is minimal. The positions of the NICS centers are aligned through the ring center and are orthogonal to the ring plane. All relevant oordinates can be found in the Supporting Information.

To study the isomerization  $1 \rightarrow 1a \rightarrow 1b$ , the two-layer ONIOM-(B3LYP/BSIII: B3LYP/3-21G) approach was employed.<sup>14</sup> As shown in Figure 3, the higher layer consists of the core ring and was calculated with basis sets BSIII (6-311G+(d,p) for N and 6-311G+(d,p) for other elements). The lower layer consists of the

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two substituents (2,6- ${}^{i}Pr_{2}C_{6}H_{3}$ -), as calculated with the 3-21G basis sets. The quality of the two-layer scheme was tested with the *S*-value,  ${}^{14g,15}$  and we obtained for 1, TS1/1a, 1a, TS1a/1b, and 1b the following data: -5.2879, -5.2815, -5.2826, -5.2817, and -5.2898 hartree, indicating that the two-layer ONIOM setup is reasonable. Frequency calculations were carried out for all optimized structures with the same method to verify the nature of the stationary points on the potential-energy surfaces and to obtain the zero-point energy corrections.

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**Supporting Information Available:** Crystallographic data for **2** and **3** (CIF); details of NICS calculations and coordinates of optimized structure. This material is available free of charge via the Internet at http://pubs.acs.org.