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Reactivity of N-Heterocyclic Germylene Toward Ammonia and Water

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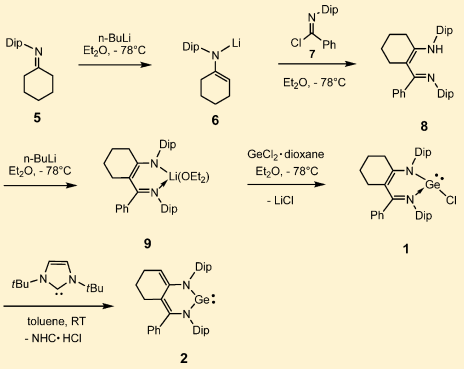
Supporting Information

ABSTRACT: The new N-heterocyclic chlorogermylene **1** has been synthesized in a four-step procedure starting from *N*-cyclohexylidene-2,6-diisopropyl-benzenamine. Dehydrochlorination of **1** with an N-heterocyclic carbene furnished the corresponding germylene **2** in good yield. The Ge(II) centers in **1** and **2** are stabilized by nitrogen π-donors and two bulky aryl groups. The reactivity of germylene **2** toward ammonia and water was investigated. Thus, ammonolysis and hydrolysis of **2** at ambient temperature led to the germylene amide **3** and the first monomeric germylene hydroxide **4**, respectively. The new compounds **1**−**4** were fully characterized, including X-ray diffraction analyses.



The first stable N-heterocyclic carbenes (NHCs) by Arduengo et al. have raised great interest in divalent carbon ligands.[1] NHCs play a vital role in a broad range of applications in organometallic chemistry, organic synthesis, and homogeneous catalysis.[2] In addition, N-heterocyclic germylenes (NHGes), representing heavier analogues of NHCs, have been utilized as versatile ligands as well since the isolation of the first isolable germylene by Lappert and co-workers in 1974.[3,4] More recently, a number of stable germanium(II) derivatives have been synthesized by taking advantage of the intramolecular stabilization with the β-diketiminate ligand.[4a] Interestingly, although a large number of stable low-valent germanium compounds have been reported,[4] there are only a few examples of stable aminogermylenes featuring the parent NH_2 group[5] and germylene hydroxide with a terminal OH group.[6] These compounds deserve particular attention because of their functionizable terminal groups. For example, germylene hydroxides are potential precursors for the synthesis of new functional materials bearing heterobimetallic Ge(II)−O−M moieties. The access to Ge(II)−NH_2 and Ge(II)−OH compounds is also linked to the topic of activation of the N−H bonds of ammonia and O−H bonds of water employing low-valent main-group compounds. In line with that, Bertrand's group reported on the splitting of ammonia with an N-heterocyclic carbene.[7] Furthermore, Power and Stephan et al. independently showed that the activation of ammonia can be achieved using diarylstannylene and frustrated Lewis pairs (FLPs), respectively.[8,9] Recently, we have reported the synthesis, isolation, and peculiar reactivity of the zwitterionic N-heterocyclic silylene **I**[10] and germylene **II**[11] bearing a modified *dianionic* β-diketiminato ligand (Scheme 1).[12,13] The activation of N−H and O−H bonds with silylene **I** and germylene **II** has been investigated by our group and Roesky et al. independently.[5b,6,14,15] Thus, compounds **I** and **II** react with ammonia and water, resulting in the formation of **A**,[14] **B**,[15] aminogermylene **C**,[5b] and germylene hydroxide **D**[6] (Scheme 1). Inspired by the latter work, we decided to synthesize a new type of stable and unsymmetric germylene and to probe its suitability for the formation of aminogermylene and germylene hydroxide through activation of ammonia and water. Herein, we report the synthesis and isolation of germylene chloride **1** and its conversion into germylene **2**. In fact, the latter turned out to be suitable for activation of ammonia and water at ambient temperature to produce the desired aminogermylene **3** and germylene hydroxide **4**, respectively. The molecular structures of **1**−**4** have been elucidated by multinucler NMR spectroscopy and confirmed by X-ray crystallographic analyses.

The syntheses of **1** and **2** are shown in Scheme 2. The new chlorogermylene **1** is easily accessible from the *N*-cyclohexylidene-2,6-diisopropyl-benzenamine **5**[16] in a four-step procedure. In the first step, the deprotonation of **5** with *n*-BuLi in diethylether leads to the corresponding lithium amide **6**. The salt metathesis reaction of **6** with (*Z*)-*N*-(2,6-diisopropylphenyl)benzimidoyl chloride **7**[17] in diethylether afforded the novel β-diketiminato-type ligand **8**. Its lithium salt **9** can be isolated in high yield through lithiation of **8** with *n*-BuLi. The subsequent reaction of **9** with the dichlorogermylene dioxane complex affords the desired chlorogermylene **1** in 82% yield. Furthermore, germylene **2** was obtained by dehydrochloration of **1** with 1,3-di-*tert*-butylimidazol-2-ylidene as a base in 78% yield. The composition and constitution of **1** and **2** were fully characterized by elemental analysis, IR and multinuclear NMR spectroscopies, and X-ray crystallography.

The molecular structures of compounds **1** and **2** are shown in Figure 1. In compound **1**, the six-membered C_3N_2Ge ring

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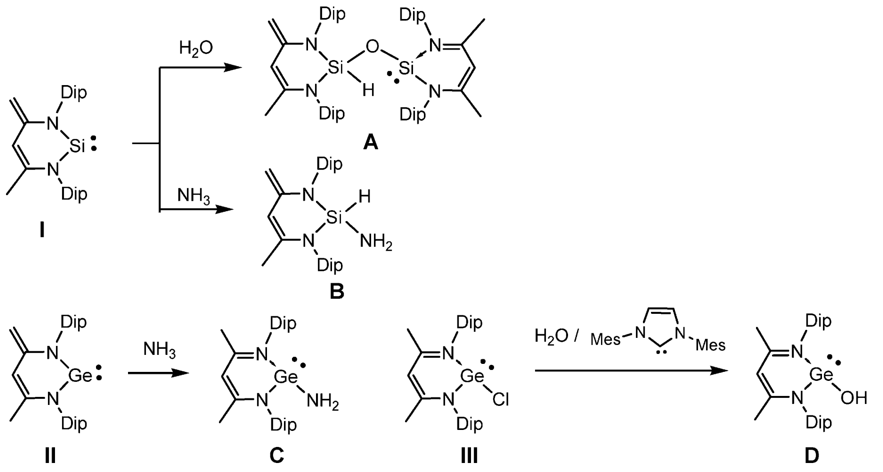
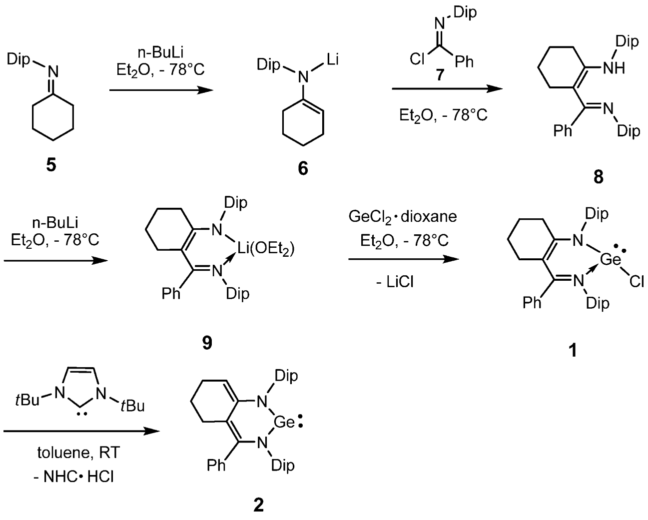
Scheme 1. Examples of the N−H and O−H Bond Activation with Silylene I and Germylenes II and III[a]



[a]Dip = 2,6-$iPr_2C_6H_3$; Mes = 2,4,6-$Me_3C_6H_2$.

Scheme 2. Syntheses of the Modified ß-Diketiminate Ligand 8 and the New Germylenes 1 and 2



exhibits a boat-like conformation. The C_2N_2 moiety of the chelating ligand [N1, N2, C1, C3] is nearly planar, and the Ge and C2 atoms are out-of-plane [Ge, 0.37 Å; C2, 0.13 Å]. In compound **2**, the C_3N_2Ge ring is almost planar. The Ge−N bond lengths in **1** (1.980(2) and 1.976(2) Å) are longer than those in **2** (1.843(3) and 1.861(3) Å), and the N1−Ge1−N2 bond angle (91.23°) in **1** is smaller than that of compound **2** (95.09°). This is probably owing to the dative nature of the Ge−N bonds and the three-coordinate Ge(II) atom in **1**. The Ge−Cl bond length of 2.296(1) Å in **1** is consistent with the value observed in the N-heterocyclic β-diketiminato chlorogermylene LGeCl [L = HC(CMeNAr)$_2$, Ar = 2,6-$iPr_2C_6H_3$].[18] The fused cyclohexyl moiety of **1** is distorted, and the phenyl group is oriented in nearly the same direction as the aryl group on the N2 atom, while the C2, C3, C4, and C7 atoms of the fused C_6 ring in **1** are coplanar with the C_3N_2 ring [C1, C2, C3, N1, N2] while the C5 and C6 atoms deviate above the plane of the C_3N_2 ring. This conformation of the cyclohexyl moiety is also observed in compound **2**. It is of note that the buta-1,3-diene moiety [C1, C2, C3, C4, C32] of compound **2** clearly has alternating C−C distances [C32−C1, 1.498(4); C1−C2, 1.359(4); C2−C3, 1.461(4); and C3−C4, 1.360(4) Å], which is not the case in germylene **II**.[11]

Germylene **2** undergoes controllable ammonolysis and hydrolysis (Scheme 3). Thus, treatment of **2** with ammonia gas at room temperature in toluene resulted in the formation of the corresponding aminogermylene **3** in high yield (92%). Likewise, germylene **2** also readily reacts with water to produce germylene hydroxide **4** nearly quantitatively (95%).

The ^{1}H and ^{13}C NMR spectroscopic data of **4** are very similar to the corresponding resonances of **3** appearing at or near the same chemical shifts. In the ^{1}H NMR spectrum of **3**, the protons of the NH_2 group appear at δ = 1.54 ppm. This chemical shift is close to that of the dimeric aminogermylene $(Ar'GeNH_2)_2$ [Ar′ = C_6H_3-2,6(C_6H_2-2,4,6-iPr_3)$_2$] (δ = 1.62 ppm).[8] The ^{1}H NMR spectrum of **4** displays a singlet for the hydroxide proton at δ = 1.60 ppm, which is close to the respective value observed for the dimeric germylene hydroxide **D** (δ = 1.54 ppm).[6] The IR spectrum of **3** clearly shows two N−H stretching modes of the NH_2 group at ν = 3430 and 3343 cm^{-1}, respectively. These values are similar to those observed for related aminogermylenes $(Ar^*GeNH_2)_2$ [Ar* = C_6H_3-2,6(C_6H_2-2,6-iPr_3)$_2$] (3380 and 3308 cm^{-1}) and **C** (3431 and 3333 cm^{-1}).[5b,8] A sharp absorption at ν = 3643 cm^{-1} that can be attributed to the O−H stretching frequency was observed in the IR spectrum of **4**. This value resembles that of germylene hydroxide **D** (3571 cm^{-1}).[6]

Both compounds **3** and **4** are monomeric species. The structure of **3** is shown in Figure 2. The structural features of **3** and **4** are very similar and show close structural parameters compared with that of chlorogermylene **1**. As in **1**, the Ge1 and C2 atoms of **3** and **4** slightly deviate from the C_2N_2 ring (N1, N2, C1, C3) plane [**3**: Ge, 0.46 Å and C2, 0.13 Å. **4**: Ge, 0.49 Å and C2, 0.13 Å]. The Ge−N$_{\text{ligand}}$ bond lengths (**3**: 2.017(2) and 2.021(2) Å. **4**: 2.0054(17) and 2.0071(16) Å) of **3** and **4** are longer than the Ge−N$_{\text{amide}}$ bond length of **3** [1.829(3) Å]. In each case, there is clearly a difference between the dative bond and covalent bond. Compound **4** represents the first monomeric three-coordinate Ge(II) hydroxide in the solid state (Figure 2) owing the larger steric congestion around the Ge(II) center, in contrast to compound **D**.[6]

In conclusion, we have presented the synthesis and structure of new types of N-heterocyclic germylenes **1** and **2** employing the novel asymmetric ligand **8**. Germylene **2** is capable of

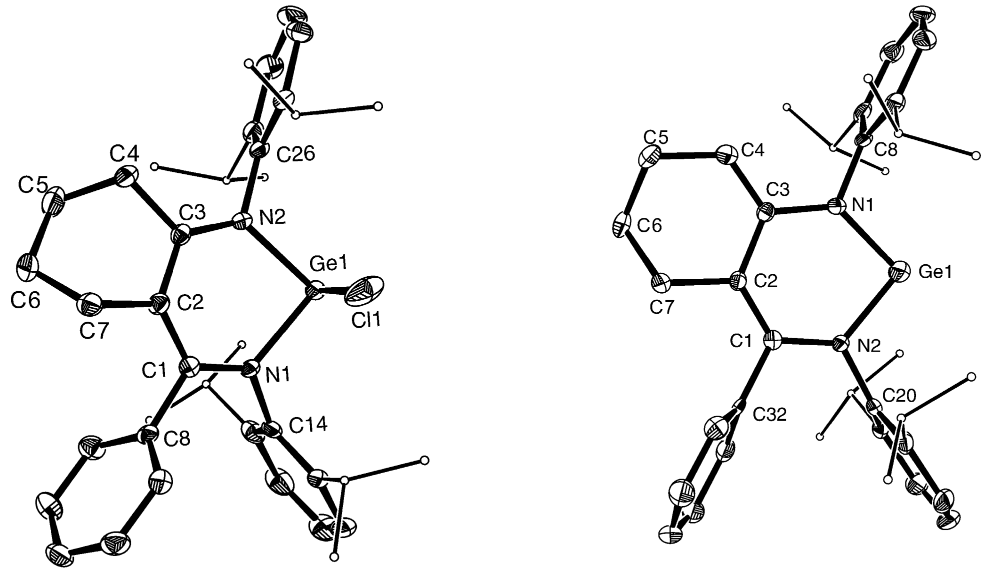
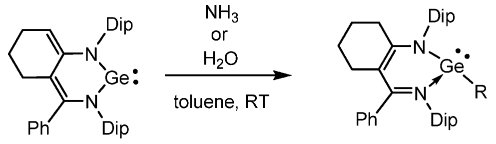


Figure 1. ORTEP drawing of compounds **1** (left) and **2** (right). Thermal ellipsoids are shown with 50% probability (except the C atoms of the *i*Pr groups at the aryl groups at nitrogen), and hydrogen atoms have been omitted for clarity.

Scheme 3. Syntheses of Aminogermylene 3 and Germylene Hydroxide 4



2

3: R = NH_2
4: R = OH

readily activating N−H and O−H bonds of ammonia and water to produce the corresponding aminogermylene **3** and germylene hydroxide **4**, respectively. Compound **8** is a promising ancillary chelate ligand for the synthesis and preparation of novel isolable silylenes, stannylenes, and plumbylenes. Their respective synthesis and reactivity is currently under investigation.

■ EXPERIMENTAL SECTION

All experiments and manipulations were carried out under dry oxygen-free nitrogen 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 materials *N*-cyclohexylidene-2,6-diisopropyl-benzenamine, **5**,[19] (*Z*)-*N*-(2,6-diisopropylphenyl)benzimidoyl chloride, **7**,[20] and 1,3-bis-*tert*-butylimidazol-2-ylidene[21] were prepared according to the literature procedure. ^1H and ^{13}C NMR spectra were recorded on Bruker Spectrometers AV 400 and ARX 200.

Compound 8. To a solution of **5** (20.0 g, 77.7 mmol) in 200 mL of Et_2O at −78 °C was added 1.6 M *n*-butyllithium (48.6 mL, 77.7 mmol) in hexane, and the reaction mixture was stirred at room temperature overnight, resulting in a slightly yellow slurry. The reaction mixture was cooled to −78 °C again, and the solution of **7**

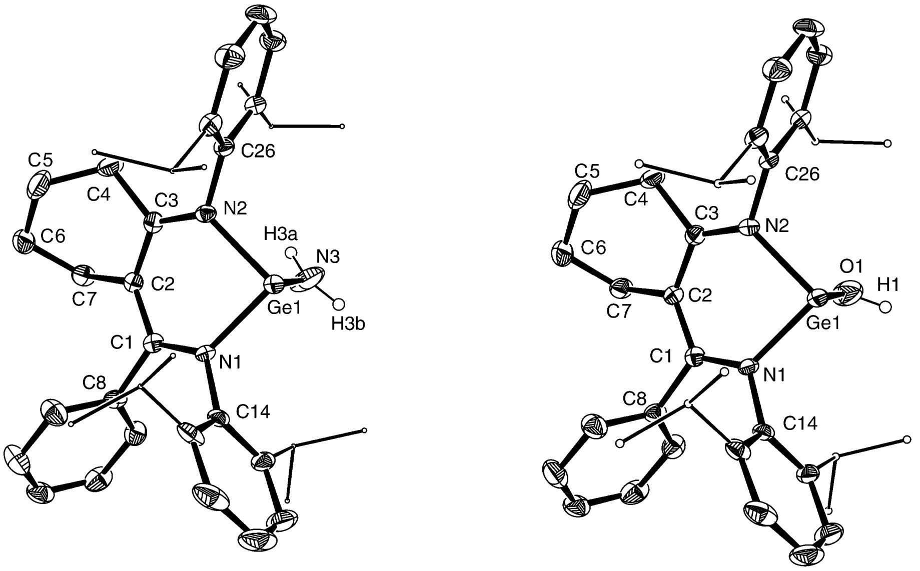


Figure 2. ORTEP drawing of compounds **3** (left) and **4** (right). Thermal ellipsoids are shown with 50% probability (except the C atoms of the *i*Pr groups at the aryl groups at nitrogen), and hydrogen atoms have been omitted for clarity.

(21.0 g, 70.0 mmol) in Et$_2$O (100 mL) was added. The reaction mixture was stirred at room temperature for 2 h and then refluxed for 1 h. Water-free Et$_3$NHCl (1.08 g, 7.77 mmol) was added to the reaction mixture and stirred. All solvents were evaporated in vacuo. The residue was extracted with warm hexane and crystallized at −30 °C to obtain 22.9 g (44.0 mmol, 63%) of **8** as colorless crystals. mp: 148−150 °C. ^{1}H NMR (400.13 MHz, CDCl$_3$, 298 K): δ = 1.17 (d, $^3J_{HH}$ = 7 Hz, 6H, CH*Me*$_2$), 1.22 (d, $^3J_{HH}$ = 7 Hz, 6H, CH*Me*$_2$), 1.25 (d, $^3J_{HH}$ = 7 Hz, 6H, CH*Me*$_2$), 1.34 (d, $^3J_{HH}$ = 7 Hz, 6H, CH*Me*$_2$), 1.64 (m, 4H, Cy-C*H*$_2$), 1.87 (s, 1H, N*H*), 2.17 (m, 4H, Cy-C*H*$_2$), 3.35 (m, 4H, C*H*Me$_2$), 6.96 (s, 3H, arom. *H*), 7.15−7.27 (m, 8H, arom. *H*). ^{13}C{^{1}H} NMR (100.61 MHz, CDCl$_3$, 298 K): δ = 21.8 (Cy-*C*H$_2$), 22.1 (CH*Me*$_2$), 23.6 (CH*Me*$_2$), 23.8 (Cy-*C*H$_2$), 24.7 (CH*Me*$_2$), 25.6 (CH*Me*$_2$), 28.0 (*C*HMe$_2$), 28.2 (*C*HMe$_2$), 28.5 (Cy-*C*H$_2$), 28.6 (Cy-*C*H$_2$), 97.7 (Cy-*C*CN), 122.2−144.1 (arom. *C*), 160.0 (Cy-*C*N), 165.8 (Ph-*C*N). Anal. Calcd for $C_{37}H_{48}N_2$: C, 85.33; H, 9.29; N, 5.38. Found: C, 85.18; H, 9.27; N, 5.47.

Compound 1. *n*-Butyllithium (8.81 mL, 14.1 mmol, 1.6 M) was added to a solution of **8** (7.20 g, 13.8 mmol) in 80 mL of Et$_2$O at −78 °C. The solution was allowed to slowly warm to room temperature and stirred for 4 h. GeCl$_2$·dioxane (3.30 g, 14.2 mmol) was added to the reaction solution at −78 °C. The resulting suspension was stirred overnight at room temperature. Volatiles were removed under reduced pressure, and the residue was extracted with warm toluene two times. The filtrate was concentrated and stored at −30 °C, yielding **1** as yellow crystals (7.10 g, 11.3 mmol, 82%). mp: 203 °C. ^{1}H NMR (400.13 MHz, C$_6$D$_6$, 298 K): δ = 0.97 (d, $^3J_{HH}$ = 7 Hz, 3H, CH*Me*$_2$), 1.07 (d, $^3J_{HH}$ = 7 Hz, 3H, CH*Me*$_2$), 1.16 (d, $^3J_{HH}$ = 7 Hz, 3H, CH*Me*$_2$), 1.21−1.27 (m, 9H, CH*Me*$_2$), 1.28−1.39 (m, 4H, Cy-C*H*$_2$), 1.44 (d, $^3J_{HH}$ = 7 Hz, 3H, CH*Me*$_2$), 1.55 (d, $^3J_{HH}$ = 7 Hz, 3H, CH*Me*$_2$), 2.03−2.27 (m, 4H, Cy-C*H*$_2$), 3.17 (sept, $^3J_{HH}$ = 7 Hz, 1H, C*H*Me$_2$), 3.27 (sept, $^3J_{HH}$ = 7 Hz, 1H, C*H*Me$_2$), 3.94 (sept, $^3J_{HH}$ = 7 Hz, 1H, C*H*Me$_2$), 4.17 (sept, $^3J_{HH}$ = 7 Hz, 1H, C*H*Me$_2$), 6.80−7.39 (m, 11H, arom. *H*). ^{13}C{^{1}H} NMR (100.61 MHz, C$_6$D$_6$, 298 K): δ = 21.3 (CH*Me*$_2$), 22.6 (CH*Me*$_2$), 23.1 (Cy-*C*H$_2$), 23.9 (CH*Me*$_2$), 24.5 (CH*Me*$_2$), 24.6 (Cy-*C*H$_2$), 24.9 (CH*Me*$_2$), 27.4 (CH*Me*$_2$), 27.7 (CH*Me*$_2$), 28.4 (*C*HMe$_2$), 28.6 (*C*HMe$_2$), 28.9 (*C*HMe$_2$), 29.1 (CH*Me*$_2$), 29.3 (*C*HMe$_2$), 29.5 (Cy-*C*H$_2$), 31.5 (Cy-*C*H$_2$), 108.9 (Cy-*C*CN), 123.4−147.6 (arom. *C*), 165.1 (Cy-*C*N), 168.8 (Ph-*C*N). Anal. Calcd for $C_{37}H_{47}ClGeN_2$: C, 70.78; H, 7.54; N, 4.46. Found: C, 70.73; H, 7.62; N, 4.57.

Compound 2. Germylene chloride **1** (3.00 g, 4.79 mmol) and 1,3-bis-*tert*-butylimidazol-2-ylidene (0.91 g, 5.02 mmol) were dissolved in toluene (25 mL) at room temperature and stirred for 48 h, resulting in a white precipitate of the corresponding NHC·HCl salt. The color of the solution changed from yellow to brown-red. The solvent was removed under reduced pressure and the residue extracted with warm hexane two times. The combined filtrate was concentrated and stored at −30 °C, yielding **2** as red crystals (2.20 g, 3.73 mmol, 78%). mp: 167−168 °C. ^{1}H NMR (400.13 MHz, C$_6$D$_6$, 298 K): δ = 1.15 (d, $^3J_{HH}$ = 7 Hz, 6H, CH*Me*$_2$), 1.26 (d, $^3J_{HH}$ = 7 Hz, 6H, CH*Me*$_2$), 1.35 (d, $^3J_{HH}$ = 7 Hz, 12H, CH*Me*$_2$), 1.55 (m, 2H, Cy-C*H*$_2$), 2.04 (m, 2H, Cy-C*H*$_2$), 2.21 (m, 2H, Cy-C*H*$_2$), 3.69 (sept, $^3J_{HH}$ = 7 Hz, 2H, C*H*Me$_2$), 3.80 (sept, $^3J_{HH}$ = 7 Hz, 2H, C*H*Me$_2$), 4.15 (t, $^3J_{HH}$ = 4.4 Hz, 1H, C=C*H*), 6.75−7.25 (m, 11H, arom. *H*). ^{13}C{^{1}H} NMR (100.61 MHz, C$_6$D$_6$, 298 K): δ = 22.6 (CH*Me*$_2$), 23.4 (Cy-*C*H$_2$), 24.7 (CH*Me*$_2$), 25.8 (Cy-*C*H$_2$), 25.9 (CH*Me*$_2$), 27.3 (CH*Me*$_2$), 28.3 (*C*HMe$_2$), 28.4 (*C*HMe$_2$), 31.5 (Cy-*C*H$_2$), 98.7 (Cy-*C*H), 111.7 (Cy-*C*CN), 123.6−143.1 (arom. *C*), 147.3, 147.4 (Cy-*C*N, Ph-*C*N). IR (KBr, cm^{-1}): 704 (s), 787 (s), 939 (m), 1104 (s), 1135 (s), 1204 (s), 1248 (s), 1296 (s), 1322 (s), 1365 (s), 1439 (s), 1461 (s), 1535 (m), 1600 (s), 2822 (m), 2865 (s), 2922 (s), 2957 (w), 3022 (w), 3061 (m). Anal. Calcd for $C_{37}H_{46}GeN_2$: C, 75.14; H, 7.84; N, 4.74. Found: C, 74.95; H, 8.00; N, 4.84.

Compound 3. A red solution of **2** (591 mg, 1.00 mmol) in toluene (15 mL) was exposed to dry ammonia gas for 10 min at room temperature. The solution turned to a yellow color and was stirred for 6 h at ambient temperature. The solvent was removed and the residue redissolved in hexane (40 mL). The concentrated solution was stored at 0 °C, yielding **3** as yellow crystals (0.560 g, 0.92 mmol, 92%). mp: 173 °C. ^{1}H NMR (400.13 MHz, C$_6$D$_6$, 298 K): δ = 1.06 (d, $^3J_{HH}$ = 7 Hz, 3H, CH*Me*$_2$), 1.17 (d, $^3J_{HH}$ = 7 Hz, 3H, CH*Me*$_2$), 1.20−1.36 (m, 15H, CH*Me*$_2$; 4H, Cy-C*H*$_2$), 1.42 (d, $^3J_{HH}$ = 7 Hz, 3H, CH*Me*$_2$), 1.54 (s, 2H, N*H*$_2$), 2.00−2.13 (m, 4H, Cy-C*H*$_2$), 3.46 (sept, $^3J_{HH}$ = 7 Hz, 1H, C*H*Me$_2$), 3.57 (sept, $^3J_{HH}$ = 7 Hz, 1H, C*H*Me$_2$), 3.63 (sept, $^3J_{HH}$ = 7 Hz, 1H, C*H*Me$_2$), 3.88 (sept, $^3J_{HH}$ = 7 Hz, 1H, C*H*Me$_2$), 6.79−7.24 (m, 11H, arom. *H*). ^{13}C{^{1}H} NMR (100.61 MHz, C$_6$D$_6$, 298 K): δ = 21.4 (CH*Me*$_2$), 23.0 (CH*Me*$_2$), 23.4 (CH*Me*$_2$), 23.7 (Cy-*C*H$_2$), 24.4 (CH*Me*$_2$), 24.6 (Cy-*C*H$_2$), 24.8 (CH*Me*$_2$), 27.2 (CH*Me*$_2$), 27.6 (CH*Me*$_2$), 28.4 (*C*HMe$_2$), 28.5 (*C*HMe$_2$), 28.8 (*C*HMe$_2$), 28.9 (CH*Me*$_2$), 29.0 (*C*HMe$_2$), 29.3 (Cy-*C*H$_2$), 31.5 (Cy-*C*H$_2$), 102.3 (Cy-*C*CN), 123.4−146.2 (arom. *C*), 164.3 (Cy-*C*N), 166.9 (Ph-*C*N). IR (KBr, cm^{-1}): 561 (s), 704 (s), 752 (s), 796 (s), 839 (m), 922 (s), 1052 (s), 1096 (s), 1143 (s), 1174 (s), 1252 (s), 1304 (s), 1360 (s), 1430 (s), 1470 (s), 1543 (s), 2865 (m), 2961 (s), 3021 (w), 3048 (m), 3343 (w), 3430 (w). Anal. Calcd for $C_{37}H_{49}GeN_3$: C, 73.04; H, 8.12; N, 6.91. Found: C, 72.72; H, 8.10; N, 6.83.

Compound 4. A diluted solution of H$_2$O in THF (1.79 mL, 1.00 mmol, 0.56 M) was dropped into a solution of **2** (591 mg, 1.00 mmol) in toluene (10 mL) at −30 °C. The solution turned to a yellow color and was stirred for 6 h at ambient temperature. The solvents were removed and the residue redissolved in hexane (40 mL). The concentrated solution was stored at 0 °C, yielding **4** as yellow crystals (0.580 g, 0.95 mmol, 95%). mp: 188 °C. ^{1}H NMR (400.13 MHz, C$_6$D$_6$, 298 K): δ = 1.11 (d, $^3J_{HH}$ = 7 Hz, 3H, CH*Me*$_2$), 1.16 (d, $^3J_{HH}$ = 7 Hz, 3H, CH*Me*$_2$), 1.19−1.36 (m, 15H, CH*Me*$_2$; 4H, Cy-C*H*$_2$), 1.39 (d, $^3J_{HH}$ = 7 Hz, 3H, CH*Me*$_2$), 1.66 (s, 1H, O*H*), 1.95−2.21 (m, 4H, Cy-C*H*$_2$), 3.35 (sept, $^3J_{HH}$ = 7 Hz, 1H, C*H*Me$_2$), 3.46 (sept, $^3J_{HH}$ = 7 Hz, 1H, C*H*Me$_2$), 3.84 (sept, $^3J_{HH}$ = 7 Hz, 1H, C*H*Me$_2$), 3.97 (sept, $^3J_{HH}$ = 7 Hz, 1H, C*H*Me$_2$), 6.75−7.26 (m, 11H, arom. *H*). ^{13}C{^{1}H} NMR (100.61 MHz, C$_6$D$_6$, 298 K): δ = 21.3 (CH*Me*$_2$), 22.9 (CH*Me*$_2$), 23.3 (CH*Me*$_2$), 23.4 (Cy-*C*H$_2$), 24.3 (CH*Me*$_2$), 24.6 (Cy-*C*H$_2$), 24.7 (CH*Me*$_2$), 26.9 (CH*Me*$_2$), 27.6 (CH*Me*$_2$), 28.1 (*C*HMe$_2$), 28.3 (*C*HMe$_2$), 28.8 (CH*Me*$_2$), 28.9 (*C*HMe$_2$), 29.0 (*C*HMe$_2$), 29.1 (Cy-*C*H$_2$), 31.4 (Cy-*C*H$_2$), 102.8 (Cy-*C*CN), 123.3−146.4 (arom. *C*), 164.7 (Cy-*C*N), 166.6 (Ph-*C*N). IR (KBr, cm^{-1}): ν = 561 (s), 713 (s), 743 (s), 770 (s), 791 (s), 839 (s), 926 (m), 1056 (m), 1104 (s), 1148 (s), 1170 (s), 1257 (s), 1313 (s), 1339 (s), 1365 (s), 1430 (s), 1470 (s), 1539 (s), 2861 (s), 2961 (s), 3018 (w), 3057 (m), 3643 (m). Anal. Calcd for $C_{37}H_{48}GeN_2O$: C, 72.92; H, 7.94; N, 4.60. Found: C, 73.00; H, 7.86; N, 4.64.

■ ASSOCIATED CONTENT

S Supporting Information

Full details of the crystal structure determinations for **1−4** (CIF) are available. This material is available free of charge via the Internet at http://pubs.acs.org.

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