Monomeric Germanium(II) Amides Bearing β-Diketiminato Ligands: Synthesis, Structural Characterization, and Thermal Properties

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Germanium(II) compounds featuring β-diketiminate-type ligands are attractive for applications as nanoparticle precursors, imaging agents, and components of electronic devices. In this work, we report the synthesis of β-diketiminatogermanium(II) amides L'Ge(NHPh) [**1**, L' = {HC(CMeN–2,4,6-Me$_3$C$_6$H$_2$)$_2$}$^-$], L'Ge(4-NHPy) (**2**), L'Ge(2-NHPy) (**3**), and LGe(2-NHPy) (**4**), L = {HC(CMeN–2,6-iPr$_2$C$_6$H$_3$)$_2$}$^-$], which were obtained by the reaction of a low-valent organogermanium halide (L'GeCl or LGeCl) with a lithium salt of the respective aromatic amine (LiNHPh) or aminopyridine [Li(4-

NHPy) and Li(2-NHPy)]. Compounds **1–4** were characterized with several techniques such as melting point, FTIR, ^{1}H and ^{13}C NMR spectroscopy, elemental analysis, X-ray diffraction, and thermogravimetric analysis (TGA). Compounds **1–3** and **4** crystallized in the orthorhombic (space group *Pnma*) and monoclinic (space group *P*2$_1$/*c*) crystal systems, respectively. In all cases, the geometry around the central germanium atom was highly tetrahedrally distorted. According to TGA data, **1–4** do not sublime intact but rather exhibit thermal decomposition.

Introduction

Germylenes are low-valent species with a lone electron pair and acid–base behavior that is reminiscent of the carbon(II) atom localized in carbenes.[1] As opposed to carbenes, several neutral germylenes have been isolated and characterized that feature functional groups such as chloride,[2] fluoride,[3] hydroxide,[4] hydride,[3,5] amide,[6] and azide.[7] In this regard, the utilization of monoanionic and bidentate β-diketiminato ligands {L, L = [HC(CMeN–2,6-iPr$_2$C$_6$H$_3$)$_2$]$^-$; Scheme 1}[2–7] provides electronic and steric characteristics that allow the chemical stabilization of highly reactive moieties.[8] These low-valent germanium compounds are also used as versatile precursors toward novel chemical compounds.[1] In our case, we are interested in germylene amides bearing β-diketiminato ligands.

Previous reports disclosed the preparation of LGeNH(2,6-iPr$_2$C$_6$H$_3$)[9] and L*GeNH(2,6-iPr$_2$C$_6$H$_3$)[10] (Scheme 1 for L*) amides, which were obtained unexpec-

tedly in modest yields following the reduction of LGeCl[9] or L*GeCl[10] with alkaline reducing agents and subsequent ligand rearrangement. The reaction of L^{x}Ge germylene with ammonia[6] or HN(C$_6$F$_5$)$_2$[11] in nonpolar organic solvents afforded LGeNH$_2$[6] and LGeN(C$_6$F$_5$)$_2$,[11] respectively (Scheme 1). Use of sterically encumbered lithium amine salts with an organogermanium(II) halide led to metathesis products LGeNMe$_2$[12] and LGeNH(2,6-iPr$_2$C$_6$H$_3$)[13] and ligand intramolecular C–H activation to form L^{x}Ge[13,14] depending on the identity of the salt (Scheme 2). It should be noted that the amide nitrogen atom in the former compounds bears two methyl group substituents that act as electron-density donors, and a 2,6-iPr$_2$C$_6$H$_3$ substituent that behaves like an electron-density acceptor. However, in the latter example, relatively larger (SiMe$_3$)$_2$, Et$_2$, and iPr$_2$ substituents favor donation of electron density.[15]

Conversely, L''GeCl (see Scheme 1 for L'') readily reacts with LiN(SiMe$_3$)$_2$ to give L''GeN(SiMe$_3$)$_2$ product.[16] These examples clearly demonstrate how easily the chemical composition of the product can be changed by fine-tuning the steric or electronic features of the ligands employed in the germanium(II) or lithium amide precursors.

Germylene amides are not only of interest for purely synthetic or mechanistic pursuits, they also exhibit chemical functionalities that are relevant for Ge-based nanomaterials, electronic devices,[17] co-sensitizers in dye-sensitized solar cells,[18] and as biological markers.[19] In this context, a variety of synthetic approaches have emerged related to

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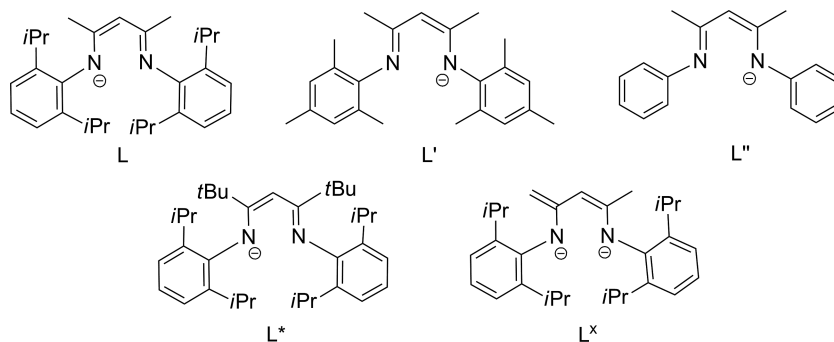
Scheme 1. Structure of some β-diketiminato ligands.
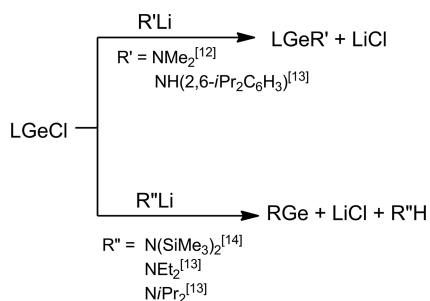
Scheme 2. Reactivity of LGeCl with some Li amides.

germanium nanoparticle growth (e.g., high and mild temperatures, high pressures, and seed catalysts).[17]

For thin-film growth applications, β-diketiminato ligands are widely reported to enhance the thermal stability of molecular compounds.[20] For example, β-diketiminato zirconium(VI) complexes were utilized as versatile precursors for the chemical vapor deposition (CVD) of Zr-based materials.[21] Previously, we have studied the structures and volatilities of β-ketoiminato hafnium(IV) precursors for the growth of HfO$_2$ thin films.[22] Herein we report the synthesis and characterization of germanium(II) analogues. Our interest in this system is based on the ability of β-diketiminato ligands to stabilize germanium compounds in low oxidation states and low coordination numbers, and the dearth of germanium(II)-based CVD precursors, which should lead to interesting synthetic strategies for advanced materials.

The amines selected for this current study include aniline (H$_2$NPh, b.p. 184.17 °C), 2-aminopyridine (2-H$_2$NPy, b.p. 210 °C), and 4-aminopyridine (4-H$_2$NPy, b.p. 273 °C). Our rationale for choosing these amines are twofold: first, both exhibit a relatively low vaporization temperature that is desirable for CVD applications; second, the aminopyridines have both a primary amine and a pyridine moiety that can be used as an additional coordination site. Herein, we report the syntheses, X-ray structural characterization, and thermogravimetric analyses (TGA) of L′Ge(NHPh) {1, L′ = [HC(CMeN–2,4,6-Me$_3$C$_6$H$_2$)$_2$]$^-$, Scheme 1}; L′Ge(4-NHPy) (2), L′Ge(2-NHPy) (3); and LGe(2-NHPy) {4, L = [HC(CMeN-2,6-iPr$_2$C$_6$H$_3$)$_2$]$^-$}, accomplished by reacting L′GeCl or LGeCl and the lithium salt of the corresponding aromatic amine (LiNHPh) or aminopyridine [Li(2-NHPy)

and Li(4-NHPy)]. Compound 4 was prepared to determine the steric effect of the ligand relative to 1–3. Additionally, we report the FTIR and ^{1}H/^{13}C NMR spectroscopy, thermal stabilities, and elemental analyses for 1–4.

Results and Discussion

Lithium salt amides were prepared by mixing an equivalent amount of amine and alkyllithium salt in THF at –78 °C with concomitant methane evolution as a byproduct, then used in situ because of their high reactivity and instability.[23] In the case of LiNHPh and Li(2-NHPy), a clear solution was obtained, whereas for 4-NH$_2$Py, the resultant lithium salt was a white suspension. The metathesis reaction of lithium amide in the presence of L′GeCl or LGeCl in THF furnished a pale yellow solution for 1, 3, and 4, whereas the reaction mixture to make 2 changed from green to a yellow solution after stirring 5 h from –78 °C to ambient temperature (Scheme 3).
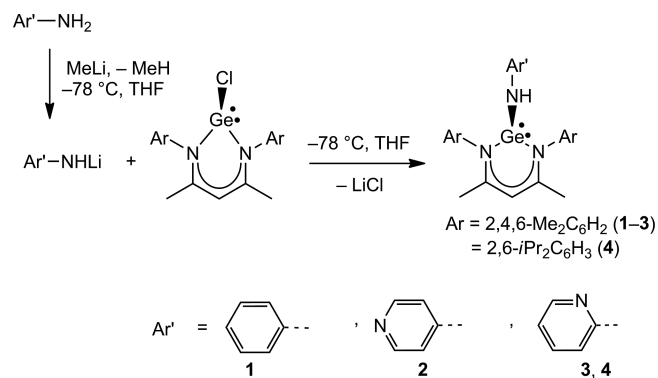
Scheme 3. Synthesis of 1–4.

Compounds 1–4 are pale yellow microcrystalline solids soluble in THF, toluene, and benzene, 1–3 are insoluble in hexane, but 4 solubilizes only slightly. Compounds 1–3 have melting points above 200 °C, and 4 melts at about 168 °C. In the FTIR spectra of 1–4, N–H stretching bands appear at 3377, 3321, 3365, and 3348 cm^{-1}, respectively, and are comparable to the N–H group of LGeNH$_2$ (3333 cm^{-1})[6] and LGa(NH$_2$)$_2$ (3359 cm^{-1}),[24] and the N–H vibrations observed for LGa(NHEt)$_2$, LGa(NHiPr)$_2$, LGa(NHnBu)$_2$, LGa(NHPh)$_2$, and LAl(NHEt)$_2$ (3371–3381 cm^{-1}).[23d] For

1–4, the ^{1}H NMR spectra exhibit broad signals (δ = 5.00 ppm for **1**, 5.08 ppm for **2**, 6.13 ppm for **3**, and 6.06 ppm for **4**), which can be assigned to the N–H proton. Interestingly, the position of the N_{endo} atom in the pyridine ring relative to the amide N–H bond for **2** and **3** brings about a larger chemical shift. This is likely due to more pronounced deshielding caused by interactions between the lone electron pair on the pyridinic nitrogen atom and the π-electron system of the aromatic ring with an N–H fragment. Such electronic interactions are not present in the aniline molecule of **1**, which gives rise to a smaller chemical shift relative to **2** and **3**. By comparison, the N–H bond chemical shift in **4** is smaller than that of **3**, which is likely due to bulky isopropyl groups on the aromatic rings. These chemical shifts are in good agreement with previously reported N–H signals for LGeNH(2,6-iPr$_2$C$_6$H$_3$) (δ = 5.64 ppm),[9] L*GeNH(2,6-iPr$_2$C$_6$H$_3$) (δ = 4.85 ppm),[10] and the gallium(III) amide LGa(NHPh)$_2$ (δ = 6.16 ppm).[23d]

Compounds **1–3** form X-ray-suitable microcrystalline solids from solution in toluene and crystallize in the orthorhombic space group *Pnma*, whereas **4** crystallizes from hexane in the monoclinic space group $P2_1/c$. The respective crystal data and collection parameters are listed in Table 1. The molecular structure of **1** (Figure 1), **2** (Figure 2), **3** (Figure 3), and **4** (Figure 4) show a three-coordinate germanium(II) center with two Ge–N_{ligand} bond lengths (*endo*) and one Ge–N_{amide} bond length (*exo*). For these compounds, the coordination geometry about germanium is derived from a distorted tetrahedron. The asymmetric unit of **1–3** has a mirror plane that passes through C2, Ge1, and the phenyl or pyridine ring; this parameter for **4** is a complete molecule.

Equivalent Ge–N_{ligand} bond lengths are 1.9971(10), 1.9835(11), and 1.9914(12) Å for **1**, **2** and **3**, respectively; in **4** these nonequivalent bond lengths are 1.9935(13) and 2.0046(13) Å, which are consistent with the analogous bond lengths of LGeN(C$_6$F$_5$)$_2$ [avg. 1.988(2) Å],[11] LGeNH(2,6-iPr$_2$C$_6$H$_3$) (avg. 2.038 Å),[9] LGeNH$_2$ [2.030(2) Å],[6] L*GeNH(2,6-iPr$_2$C$_6$H$_3$) [avg. 2.0170(11) Å],[10] and LGeNMe$_2$ [2.0309(16) Å][12] and are slightly longer than the Ge–N_{ligand} bond length of azide L′GeN$_3$ [1.974(4) Å].[23] Also, Ge–N_{amide} bond lengths for **1** [1.8954(16) Å], **2** [1.9100(16) Å], **3** [1.9052(19) Å], and **4** [1.9186(14) Å] agree well with the Ge–N_{exo} bond lengths of LGeNH(2,6-iPr$_2$C$_6$H$_3$) [1.906(2) Å],[9] L*GeNH(2,6-iPr$_2$C$_6$H$_3$) [1.9097(12) Å],[10] and LGeNHNH$_2$ [1.909(5) Å],[12] but they are slightly longer than bond lengths of LGeNH$_2$ [1.845(2) Å][6] and LGeNMe$_2$ (1.8712(14) Å).[12] In addition, they are slightly shorter than the Ge–N_{exo} bond

Table 1. Crystal data and structure refinement details for compounds **1–4**.

	1	**2**	**3**	**4**
Empirical formula	C$_{29}$H$_{35}$GeN$_3$	C$_{28}$H$_{34}$GeN$_4$	C$_{28}$H$_{34}$GeN$_4$	C$_{34}$H$_{46}$GeN$_4$
M_r	498.19	499.18	499.18	583.34
T [K]	100(2)	100(2)	100(2)	100(2)
λ [Å]	0.71073	0.71073	0.71073	0.71073
Crystal system	orthorhombic	orthorhombic	orthorhombic	monoclinic
Space group	*Pnma*	*Pnma*	*Pnma*	$P2_1/c$
a [Å]	14.1876(3)	13.8592(11)	14.1502(2)	16.5066(6)
b [Å]	19.8449(5)	20.0377(15)	19.8948(5)	8.7441(3)
c [Å]	9.1635(2)	9.2178(7)	8.9860(3)	22.2179(6)
α [°]	90	90	90	90
β [°]	90	90	90	96.937(2)
γ [°]	90	90	90	90
V [Å^3]	2580.00(10)	2559.8(3)	2529.70(13)	3183.35(18)
Z	4	4	4	4
$D_{calcd.}$ [Mg m^{-3}]	1.283	1.295	1.311	1.217
μ [mm^{-1}]	1.208	1.219	1.234	0.990
$F(000)$	1048	1048	1048	1240
Crystal size [mm^3]	0.48 × 0.25 × 0.24	0.35 × 0.24 × 0.14	0.23 × 0.15 × 0.08	0.28 × 0.12 × 0.10
θ range [°]	2.05–27.50	2.03–27.50	2.05–27.50	1.243–27.499
Index range	–18 ≤ h ≤ 18	–18 ≤ h ≤ 11	–18 ≤ h ≤ 14	–15 ≤ h ≤ 21
	–24 ≤ k ≤ 25	–25 ≤ k ≤ 16	–25 ≤ k ≤ 25	–11 ≤ k ≤ 11
	–11 ≤ l ≤ 11	–11 ≤ l ≤ 11	–11 ≤ l ≤ 9	–28 ≤ l ≤ 28
Reflections collected	22563	12942	12738	29282
Completeness [%] to θ = 27.50° (**1–3**)	100.0	99.7	100.0	100.0
θ = 25.242° (**4**)				
Absorption correction	semiempirical	semiempirical	semiempirical	multiscan
Max./min. transmission	0.7602/0.5947	0.8479/0.6749	0.9078/0.7645	
Refinement method	full-matrix least-squares on F^2 for all compounds			
Data/restraints/parameters	3046/0/167	3007/0/167	2995/0/167	7321/0/366
GOF[a] on F^2	1.076	1.068	1.035	1.012
R indices [$I > 2\sigma(I)$][b]	R_1 = 0.0219, $wR2$ = 0.0604	R_1 = 0.0229, $wR2$ = 0.0600	R_1 = 0.0252, $wR2$ = 0.0629	R_1 = 0.0296, $wR2$ = 0.0654
R indices (all data)	R_1 = 0.0232, $wR2$ = 0.0609	R_1 = 0.0266, $wR2$ = 0.0618	R_1 = 0.0303, $wR2$ = 0.0650	R_1 = 0.0414, $wR2$ = 0.0698
Largest diff. peak/hole [e Å^{-3}]	0.329/–0.300	0.378/–0.269	0.398/–0.290	0.385/–0.306

[a] GOF = $[\Sigma\omega(F_o^2 - F_c^2)^2/(n - p)]^{1/2}$. [b] R1 = $\Sigma||F_o| - |F_c||/\Sigma|F_o|$, ωR2 = $[\Sigma\omega(F_o^2 - F_c^2)^2/\Sigma\omega F_o^2]^{1/2}$.
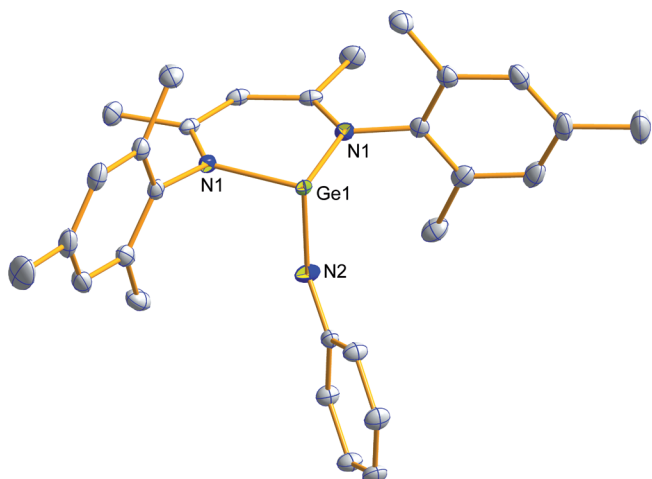
Figure 1. Molecular structure of **1**. Anisotropic displacement parameters are depicted at 50% probability level, and all restrained refined hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°] are Ge1–N2 1.8954(16), Ge1–N1 1.9971(10); N2–Ge1–N1 94.09(4), N1#1-Ge1–N1 90.14(6).
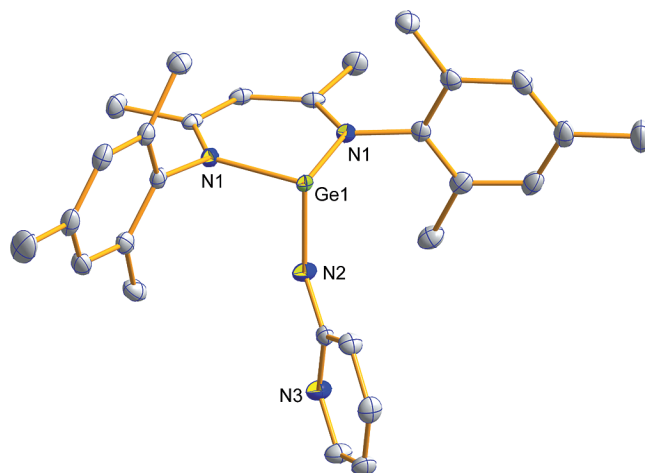

Figure 3. Molecular structure of **3**. Anisotropic displacement parameters are depicted at 50% probability level, and all restrained refined hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°] are Ge1–N2 1.9052(19), Ge1–N1 1.9914(12); N2–Ge1–N1 94.52(5), N1–Ge1–N1#1 90.23(7).
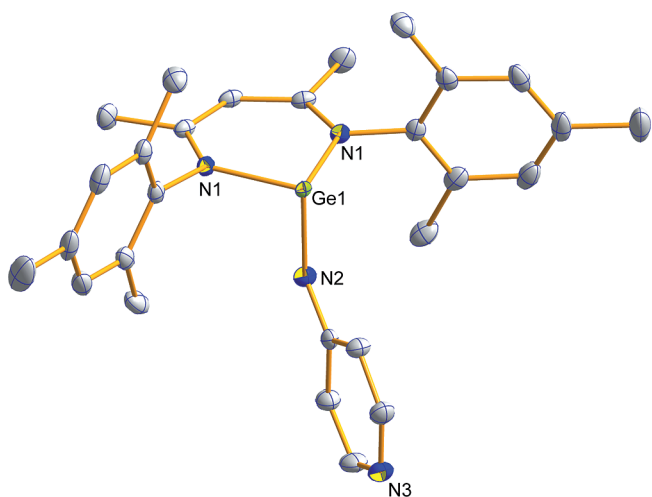

Figure 2. Molecular structure of **2**. Anisotropic displacement parameters are depicted at 50% probability level, and all restrained refined hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°] are Ge1–N2 1.9100(16), Ge1–N1 1.9835(11); N2–Ge1–N1 94.69(5), N1–Ge1–N1#1 90.95(6).
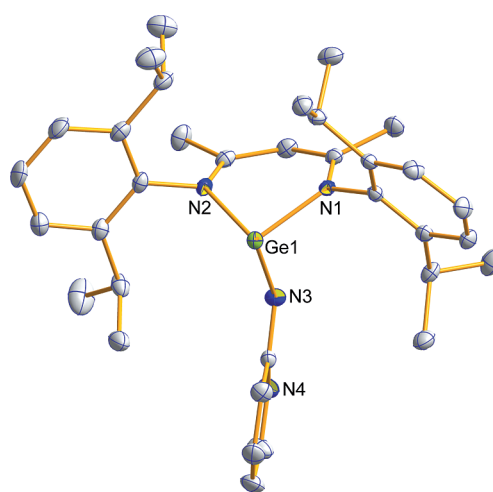

Figure 4. Molecular structure of **4**. Anisotropic displacement parameters are depicted at 50% probability level, and all restrained refined hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°] are Ge1–N2 1.9935(13), Ge1–N1 2.0046(13), Ge1–N3 1.9186(14); N3–Ge1–N2 95.33(6), N3–Ge1–N1 92.11(6), N2–Ge1–N1 89.00.

lengths of L′GeN$_3$ [1.979(5) Å][23] and LGeN(C$_6$F$_5$)$_2$ [2.054(2) Å].[11]

The bond angles around the germanium atom in complexes **1–4** are within the values reported for β-diketiminato germylene amides such as LGeNH(2,6-iPr$_2$C$_6$H$_3$),[9] L*GeNH(2,6-iPr$_2$C$_6$H$_3$),[10] LGeNH$_2$,[6] LGeN(C$_6$F$_5$)$_2$,[11] and LGeNMe$_2$.[12] The bond angles between the germanium atom and ligand nitrogen atoms (N1#1–Ge1–N1) of **1**, **2**, and **3** are 90.14(6), 90.95(6), and 90.23(7)°, respectively, and are slightly shorter than the bond angle (N2–Ge1–N1) for **4** [89.00(5)°]. Moreover, the equivalent bond angles between the N$_{amide}$ atom, germanium atom, and nitrogen ligand atoms (N1#1–Ge1–N2 and N1–Ge1–N2) of **1**, **2**, and **3**, [94.09(4), 94.69(5), and 94.52(5)°, respectively] compare well with **4**, N2–Ge1–N3 95.33(6)°; but the other

fragment is slightly longer, N1–Ge1–N3 92.11(6)°. In fact, the tetrahedral geometry around the germanium atom in **4** has larger distortion than that of **1–3**, probably as a result of ligand steric constraints.

Complexes **1–4** were also characterized by TGA to assess their thermal robustness and decomposition behavior that result from the substituent groups on the phenyl ring of the β-diketiminato ligand and the bonding of the amide fragment. TGA curves of **1–3** (Figure 5) show a slight mass loss about 150–200 °C, which further decreases to reach a plateau at approximately 600 °C, thus indicating a thermal decomposition. In the case of **4**, the onset of thermal decomposition is 130–200 °C, but it further declines significantly at a lower temperature relative to **1–3**.
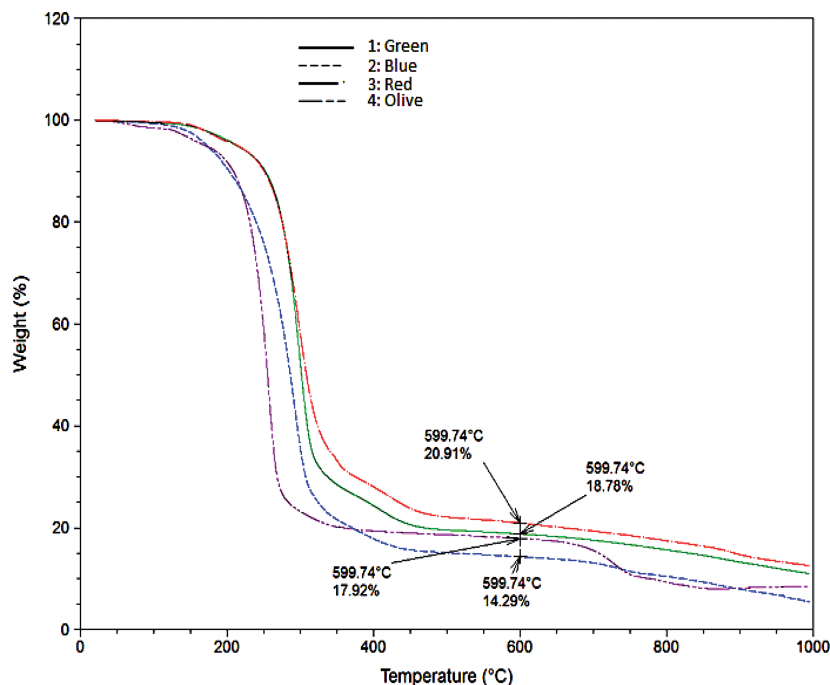
Figure 5. TGA data for compounds **1**–**4**.

Furthermore, **4** was chosen to verify the occurrence of a sublimation or decomposition process during the weight loss at about 130–200 °C.[21] The temperature of the sublimation apparatus was set to 140 °C and kept under vacuum (10^{-2} Torr), with the collection of a white solid after 2 h. No signals of compound **4** were detected in the ^{1}H NMR spectrum. Instead free-ligand signals and traces of unidentified products were observed, thus confirming its thermal decomposition at 140 °C. It is probable that the bulkier nature of the isopropyl aromatic substituents on the ligand relative to the less sterically hindered methyl groups on ligands **1**–**3** eases the cleavage of Ge–N$_{\text{ligand}}$ fragment as temperature increases. In fact, the bite angle in **4** is more acute [89.00(5)°] than analogous angles for **1**–**3**. Indeed, these findings could be of interest if one assumes the formation of germanium nitride (GeN$_x$) as the stable product from the decomposition of **1**–**4** (Figure 5, residual mass at 600 °C).

Conclusion

In summary, a facile preparation of germylene amides supported by β-diketiminato ligands was demonstrated. In fact, spectroscopic and metrical data for **1**–**4** confirm the chemical composition in which the geometry at the germanium atom is a distorted tetrahedron, which denotes both ligand bulkiness and an amide fragment affect. According to TGA, compounds **1**–**4** all thermally decompose to form GeN$_x$ rather than subliming intact, with the Ge–N$_{\text{ligand}}$ bond of **4** being cleaved more easily, presumably on account of greater ligand bulkiness. Future work in this area will focus on the synthesis of compounds bearing transition-metal fragments [e.g., Cu$_2$R$_4$(THF)$_2$] coordinated to the nitrogen of the pyridine fragment in compounds **2**–**4**.

Experimental Section

General Methods: All manipulations were carried out using standard Schlenk and glovebox techniques under a dry atmosphere of nitrogen. The compounds LGeCl[2] and L′GeCl[25] were prepared by variations on the literature procedures, and aniline was distilled from potassium hydroxide under vacuum before use. Toluene and C$_6$D$_6$ were dried with the sodium benzophenone mixture; tetrahydrofuran and diethyl ether were dried with MBraun Solvent Purification Systems (MB-SPS). Dry hexane (95%), methyllithium (1.6 M in Et$_2$O), 4-aminopyridine, and 2-aminopyridine were used as received from Aldrich. ^{1}H and ^{13}C NMR spectra were recorded with a Bruker 400 MHz spectrometer and were referenced to the resonances of the solvent used. IR spectra were recorded with a Perkin–Elmer Spectrum 1000FT spectrometer as Nujol mulls between NaCl plates. Elemental analysis measurements were carried out by Atlantic Microlab Inc. Melting points were determined in sealed glass capillaries under nitrogen. TGA experiments were performed with a TA Instruments SDT 2960 using a 4 °C min^{-1} temperature ramp and 100 mL min^{-1} dry nitrogen flux.

General Preparation of L′Ge(NHPh) (1), L′Ge(4-NHPy) (2), and L′Ge(2-NHPy) (3): Methyllithium (1.6 M, 1.82 mL, 2.9 mmol) was added to a solution of the respective aromatic amine (0.27 g, 2.9 mmol) in THF (50 mL) at –78 °C, whereupon the reaction mixture was warmed to room temperature and stirred for 0.5 h. A solution of L′GeCl (1.29 g, 2.9 mmol) in THF (50 mL) was transferred by cannula to a precooled (–78 °C) mixture that contained the amine lithium salt. The reaction mixture was warmed to room temperature and stirred for 5 h. All volatiles were subsequently removed under vacuum. The residue was extracted into toluene (80 mL for **2** and 60 mL for **1** and **3**), filtered through Celite, and the resultant solution was slowly concentrated under vacuum until reaching the minimal volume of saturation.

Compound 1: Blocklike microcrystals were obtained from a saturated solution in toluene at 5 °C after 2 h, yield 62% (0.90 g, 1.8 mmol), m.p. 205–208 °C. ^{1}H NMR (400 MHz, C$_6$D$_6$, 298 K): δ

= 1.55 (s, 6 H, NCCH_3), 2.08, 2.21, 2.28 (3s, 3×6 H, *o*-CH_3, *p*-CH_3), 4.91 (s, 1 H, NCCHCN), 5.00 (br. s, 1 H, N*H*), 6.63 (t, 1 H, *p*-Ph–*H*), 6.67, 6.75 (2s, 2×2 H, *m*-Ar–*H*), 6.79 (d, 2 H, *o*-Ph–*H*), 7.07 (t, 2 H, *m*-Ph–*H*) ppm. ^{13}C NMR (100 MHz, C$_6$D$_6$, 298 K): δ = 19.20, 19.27, 20.80 (*o*-CH_3, *p*-CH_3), 22.54 (NCCH_3), 96.48 (NCCHCN), 115.76 (*p*-C of Ph), 115.92 (*i*-C of Ph), 129.45, 129.53, 130.24, 132.65, 134.80, 135.69, 141.57, 151.63 (*o*-, *m*-C of Ph and *i*-, *o*-, *m*-, *p*-C of Ar), 163.56 (*C*=N) ppm. FTIR (Nujol): ṽ = 3377 (w, N–H) cm^{-1}. C$_{29}$H$_{35}$GeN$_3$ (498.21): calcd. 69.9, H 7.1, N 8.4; found C 67.9, H 6.9, N 8.1.

Compound 2: Blocklike microcrystals were obtained from a saturated solution in toluene at room temperature after 10 h, yield 68% (0.99 g, 2.0 mmol), m.p. 243–245 °C. ^{1}H NMR (400 MHz, C$_6$D$_6$, 298 K): δ = 1.50 (s, 6 H, NCCH_3), 2.07, 2.15, 2.16 (3 s, 3×6 H, *o*-CH_3, *p*-CH_3), 4.88 (s, 1 H, NCCHCN), 5.08 (br. s, 1 H, N*H*), 6.44 (d, 2 H, α-Py-*H*), 6.68, 6.74 (2s, 2×2 H, *m*-Ar–*H*), 8.32 (d, 2 H, β-Py-*H*) ppm. ^{13}C NMR (100 MHz, C$_6$D$_6$, 298 K): δ = 18.95, 19.19, 20.78 (*o*-CH_3, *p*-CH_3), 22.47 (NCCH_3), 96.88 (NCCHCN), 110.95 (γ-C of Py), 129.56, 130.33, 132.58, 134.58, 136.09, 141.10, 150.89, 157.18 (α-, β-C of Py and *i*-, *o*-, *m*-, *p*-C of Ar), 164.08 (*C*=N) ppm. FTIR (Nujol): ṽ = 3321 (vw, N–H) cm^{-1}. C$_{28}$H$_{34}$GeN$_4$ (499.19): calcd. C 67.4, H 6.9, N 11.2; found C 65.3, H 7.0, N 10.3.

Compound 3: Blocklike microcrystals were obtained from a saturated solution in toluene at 5 °C after 4 d, yield 51% (0.75 g, 1.5 mmol), m.p. 208–209 °C. ^{1}H NMR (400 MHz, C$_6$D$_6$, 298 K): δ = 1.52 (s, 6 H, NCCH_3), 2.07, 2.18, 2.33 (3s, 3×6 H, *o*-CH_3, *p*-CH_3), 4.84 (s, 1 H, NCCHCN), 6.13 (br. s, 1 H, N*H*), 6.26 (t, 1 H, 5-Py-*H*), 6.61 (d, 1 H, 3-Py-*H*), 6.77, 6.81 (2 s, 2×2 H, *m*-Ar–*H*), 6.93 (m, 1 H, 4-Py-*H*), 8.21 (d, 1 H, 6-Py-*H*) ppm. ^{13}C NMR (100 MHz, C$_6$D$_6$, 298 K): δ = 19.25, 19.36, 20.80 (*o*-CH_3, *p*-CH_3), 22.48 (NCCH_3), 96.99 (NCCHCN), 108.45, 111.47, 129.41, 130.26, 132.66, 134.91, 135.70, 136.66, 141.54, 149.19 (3-, 4-, 5-, 6-C of Py and *i*-, *o*-, *m*-, *p*-C of Ar), 163.29 (2-C of Py), 163.67 (*C*=N) ppm. FTIR (Nujol): ṽ = 3365 (w, N–H) cm^{-1}. C$_{28}$H$_{34}$GeN$_4$ (499.19): calcd. C 67.4, H 6.9, N 11.2; found C 66.7, H 6.8, N 11.0.

Preparation of LGe(2NHPy) (4): Methyllithium 1.6 M (1.9 mL, 3.0 mmol) was added to a solution of 2-aminopyridine (0.28 g, 3.0 mmol) in THF (50 mL) at –78 °C, and the reaction mixture was warmed to room temperature and stirred for 0.5 h. A solution of LGeCl (1.58 g, 3.0 mmol) in THF (50 mL) was transferred by cannula to a precooled (–78 °C) mixture of the amine lithium salt. The reaction mixture was warmed to room temperature and stirred for 1 h. All volatiles were subsequently removed under vacuum. The residue was extracted into hexane (50 mL), filtered through Celite, and the resultant solution was slowly concentrated under vacuum until all solvent was removed. The resultant product was a high-purity yellow solid, yield 86% (1.52 g, 2.6 mmol). Microcrystals were obtained from a saturated solution in hexane at room temperature after 3 d, m.p. 168–170 °C. ^{1}H NMR (400 MHz, C$_6$D$_6$, 298 K): δ = 1.02, 1.09, 1.17, 1.32 (4d, 4×6 H, CHCH_3CH_3), 1.54 (s, 6 H, NCCH_3), 3.36, 3.55 (2m, 2×2 H, CHCH$_3$CH$_3$), 4.73 (s, 1 H, NCCHCN), 6.06 (br. s, 1 H, N*H*), 6.22 (t, 1 H, 5-Py-*H*), 6.48 (d, 1 H, 3-Py-*H*), 6.85 (d, 1 H, 4-Py-*H*), 7.09 (m, 6 H, *m*-Ar–*H*, *p*-Ar–*H*), 8.12 (d, 1 H, 6-Py-*H*) ppm. ^{13}C NMR (100 MHz, C$_6$D$_6$, 298 K): δ = 23.37 (NCCH_3), 24.10, 24.58, 24.64, 26.42, 28.84, 29.29 (CHCH_3CH_3), 97.14 (NCCHCN), 108.98, 111.41, 124.14, 125.02, 127.61, 136.28, 141.13, 143.53, 146.47, 148.79 (3-, 4-, 5-, 6-C of Py and *i*-, *o*-, *m*-, *p*-C of Ar), 164.02 (2-C of Py), 164.30 (*C*=N) ppm. FTIR (Nujol): ṽ = 3348 (w, N–H) cm^{-1}. C$_{34}$H$_{46}$GeN$_4$ (583.35): calcd. C 70.0, H 8.0, N 9.6; found C 68.8, H 8.0, N 9.2.

Structure Determination: Data for the structures of **1**–**4** were collected with a Bruker three-circle diffractometer equipped with a APEX-II CCD detector with graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å). Intensity measurements were performed on a rapidly cooled crystal using ω scans. Semiempirical absorption correction from equivalents implemented in the SADABS program was applied to the **1**–**4** dataset and led to satisfactory values for both R_{int} and R_σ.[26] Structures **1**–**4** were solved by direct methods (SHELXS-97)[27] and refined with all data by full-matrix least-squares methods on F^2.[28] The hydrogen atoms of C–H bonds in compounds **1**–**4** were placed in idealized positions and refined isotropically with a riding model. The non-hydrogen atoms were refined anisotropically. Crystal data for compounds **1**–**4** are summarized in Table 1.

CCDC-950211 (for **1**), -950213 (for **2**), -950214 (for **3**), and -1002250 (for **4**) contain the supplementary crystallographic data for this paper. This data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk./data_request/cif.

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