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Synthesis and Tunable Reactivity of N-Heterocyclic Germylene

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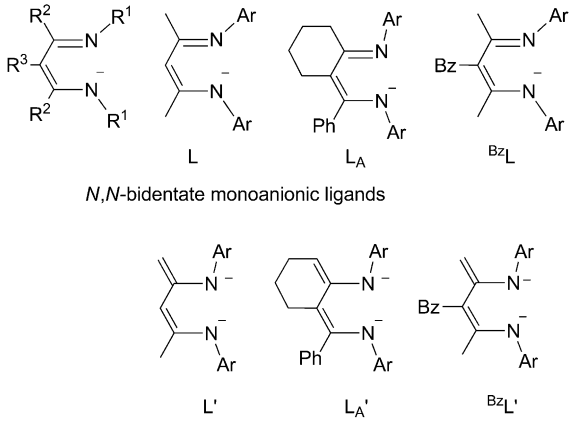
Abstract: Modifying the β-diketimine ligand LH **1** (LH = [ArN=C(Me)−CH=C(Me)−NHAr], Ar = 2,6-*i*Pr$_2$C$_6$H$_3$) through replacement of the proton in 3-position by a benzyl group (Bz) leads to the new ^{Bz}LH ligand **2**, which could be isolated in 77% yield. According to ^{1}H NMR spectroscopy, **2** is a mixture of the bis(imino) form [(ArN=C(Me)]$_2$CH(Bz) **2a** and its tautomer [ArN=C(Me)−C(Bz)=C(Me)NHAr] **2b**. Nevertheless, lithiation of the mixture of **2a** and **2b** affords solely the *N*-lithiated β-diketiminate [ArN=C(Me)−C(Bz)=C(Me)−NLiAr], ^{Bz}LLi **3**. The latter reacts readily with $GeCl_2$·dioxane to form the chlorogermylene ^{Bz}LGeCl **4**, which serves as a precursor for a new zwitterionic germylene by dehydrochlorination with LiN(SiMe$_3$)$_2$. This reaction leads to the zwitterionic germylene ^{Bz}L′Ge: **5** (^{Bz}L′ = ArNC(=CH$_2$)C(Bz)=C(Me)NAr) which could be isolated in 83% yield. The benzyl group has a distinct influence on the reactivity of zwitterionic **5** in comparison to its benzyl-free analogue, as shown by the reaction of **5** with phenylacetylene, which yields solely the 1,4-addition product **6**, that is, the alkynyl germylene ^{Bz}LGeCCPh. Compounds **2**–**6** have been fully characterized by multinuclear NMR spectroscopy, mass spectrometry, elemental analyses, and single-crystal X-ray diffraction analyses.

Keywords: 1,4-addition · bond activation · carbene homologues · diketiminates · germanium

Introduction

Heavier carbene analogues are very reactive and thus indispensable building blocks in synthetic chemistry.[1] In general, kinetic or thermodynamic stabilization (or both) is needed for the successful preparation of isolable heavier carbene analogues, especially for the synthesis of silylenes and germylenes.

It has been shown that β-diketiminate (nacnac) chelate ligands bearing bulky *ortho*-substituted aryl groups at the nitrogen atoms can be applied to the synthesis of a variety of low-valent transition-metal and main-group-element complexes, including silicon(II) and germanium(II) species.[1–4] Among the nacnac ligand systems, LH (Scheme 1, R^1 = Ar = 2,6-*i*Pr$_2$C$_6$H$_3$, R^2 = Me, R^3 = H) represents one of the most suitable ligands used to date for the synthesis of isolable complexes with mono- and divalent heavier Group 14 elements.[5] Meanwhile, it has been demonstrated that the subtle changes of steric demand in the *ortho*-substituted group R^1 as well as in the groups R^2 and R^3 at the C$_3$N$_2$ unit (Scheme 1) can lead to significantly different chemistry. For instance, starting from LH a zwitterionic silylene L′Si:[5a] and its analogous germylene L′Ge:[5b] are easily accessible. However, when smaller groups such as R^1 = 2,6-Et$_2$C$_6$H$_3$ or 2,6-Me$_2$C$_6$H$_3$ were employed as substituents at the nitrogen atom under the same reaction conditions, no corresponding silylene could be obtained.[5c] Moreover, using the modified nacnac ligand with *tert*-butyl group at nitrogen (R^1 position), merely a dimerized silylene could be isolated.[6] It is noteworthy that the influence of different substituents at the R^2 and especially at the R^3 positions on the reactivity of nacnac complexes bearing divalent Si and Ge is far less explored in comparison to that of position R^1, presumably owing to the rather limited access to such modified nacnac ligands. Most recently, the altered ligand L$_A$ with different R^2 and R^3 groups (Scheme 1) was synthesized, from which the corre-



Scheme 1. *N*,*N*-bidentate ligands derived from the β-diketiminate (nacnac) system. Bz = benzyl.

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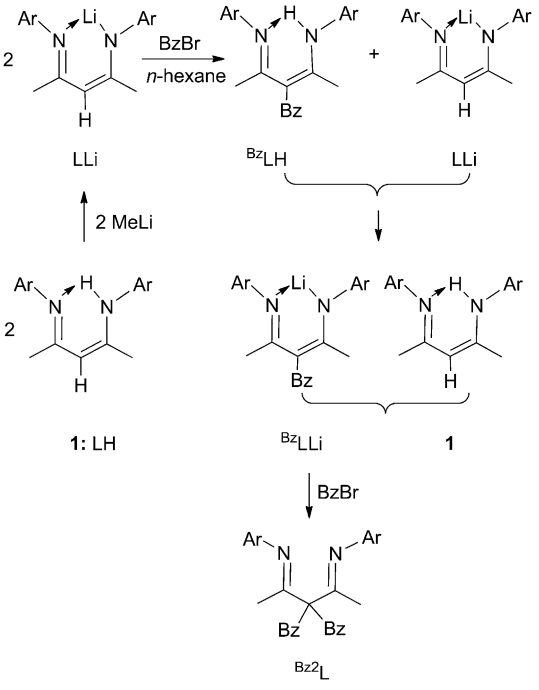
sponding zwitterionic N-heterocyclic germylene $L_A'Ge$: could be produced.[7] In order to understand the influence of substituents at the ring carbon atoms of the C_3N_2 framework of the β-diketimine ligand in more detail, we synthesized the new ligand ^{Bz}LH bearing a benzyl group in the 3-position of the C_3N_2 skeleton (Scheme 1). Herein we report the synthesis of the new zwitterionic germylene ^{Bz}L′Ge: (^{Bz}L′ = ArNC(=CH_2)C(Bz)=C(Me)NAr, Ar = 2,6-*i*$Pr_2C_6H_3$) based on the benzyl-modified ligand ^{Bz}LH and its markedly different reactivity towards phenylacetylene in comparison to that of L′Ge:.

Results and Discussion

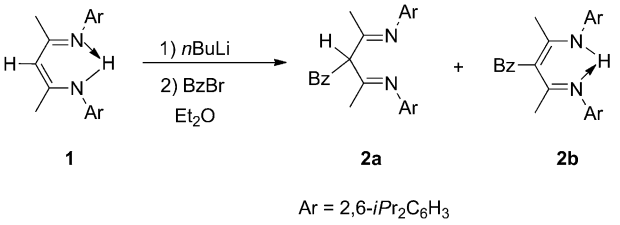
Synthesis of ^{Bz}LH 2a,b and ^{Bz}LLi 3

According to previous reports, attempts to synthesize the benzyl-modified β-diketimine ^{Bz}LH by stepwise lithiation and subsequent benzylation of LH **1** in *n*-hexane as solvent failed but led merely to small amounts of 3,3-dibenzylated β-diketimine ^{Bz2}L and unreacted LH (**1**; Scheme 2)[8]



Scheme 2. Introduction of benzyl groups (Bz) at the nacnac ligand L by reaction of LLi with $PhCH_2Br$ (BzBr). Ar = 2,6-*i*$Pr_2C_6H_3$.

We learned that choosing a more polar aprotic solvent is key to synthesize the desired monobenzylated β-diketimine ^{Bz}LH. Since LLi has a higher solubility in diethyl ether than in *n*-hexane, ^{Bz}LH is now accessible because the unwanted translithiation of ^{Bz}LH by LLi and thus the second benzylation of ^{Bz}LH can be suppressed in diethyl ether. Therefore, the reaction using a slightly molar excess of BzBr (2%) in diethyl ether furnishes the desired monobenzylated β-diketimine ^{Bz}LH in 77% yield (Scheme 3).



Scheme 3. Synthesis of ^{Bz}LH **2a** and **2b**.

Owing to the facile tautomerization in solutions, ^{Bz}LH can be formed as a mixture of isomers **2a** and **2b**. This result is evident in the ^{1}H NMR spectrum of the isolated product ^{Bz}LH in C_6D_6, which shows two sets of signals corresponding to the tautomers **2a** and **2b** (Scheme 3 and Experimental Section). The CH(Bz) moiety in **2a** (Scheme 3) exhibits a triplet at $\delta = 4.20$ ppm for the methine proton and a doublet at $\delta = 3.46$ ppm for the methylene protons of the Bz group. In contrast, the isomer **2b** with a cyclic structure similar to **1** exhibits a singlet at $\delta = 3.70$ ppm for the CH_2Ph protons and a characteristic downfield singlet resonance at $\delta = 14.0$ ppm for the N*H* proton. From *n*-hexane solutions the isomer **2a** could be isolated by crystallization as colorless plates at −20 °C; its structure has been confirmed by single-crystal X-ray diffraction analysis (Figure 1).

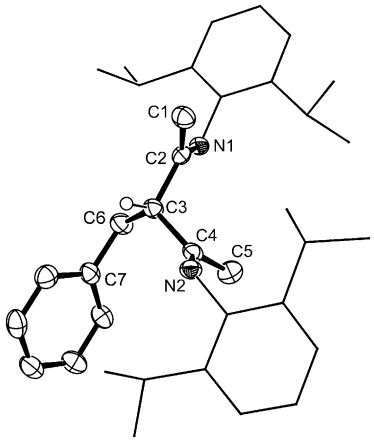
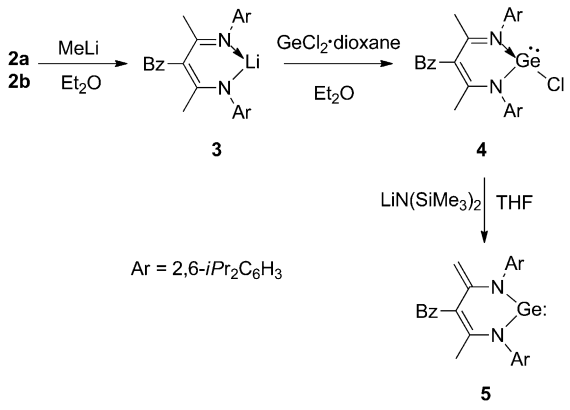


Figure 1. Molecular structure of the tautomer **2a**. Thermal ellipsoids are drawn at 50% probability level. H atoms (except the H at C3) are omitted for clarity. Selected bond lengths (Å) and angles (°): C1–C2 1.490(2), C2–C3 1.524(2), C3–C4 1.525(2), C4–C5 1.501(2), C2–N1 1.275(2), N2–C4 1.276(2), C3–C6 1.535(2), C6–C7 1.507(2); C1-C2-N1 126.3(2), N2-C4-C5 125.6(1), C5-C4-C3 117.9(1), C1-C2-C3 115.4(1), C2-C3-C4 111.2(1), C2-C3-C6 111.4(1), C4-C3-C6 112.9(1), C3-C6-C7 112.9(1).

Compound **2a** crystallizes in the triclinic space group $P\bar{1}$. The molecule possesses an acyclic structure with the C3 atom being tetrahedrally surrounded by three carbon atoms and a hydrogen atom. As expected, the relatively short C2–N1 (1.275(2) Å) and N2–C4 distances (1.276(2) Å) indicate C–N double bonds, while the C1–C2 (1.490(2) Å), C2–C3 (1.524(2) Å), C3–C4 (1.525(2) Å), C4–C5 (1.501(2) Å), C3–C6, (1.535(2) Å), and C6–C7 distances (1.507(2) Å) reflect C–C single bonds.

Lithiation of both isomers **2a** and **2b** with MeLi is straightforward and gives the desired β-diketiminate lithium salt **3** in quantitative yield (Scheme 4), which can be unambiguously identified by ^{1}H and ^{13}C NMR spectroscopy. Accordingly, the ^{1}H NMR spectrum of **3** shows only a downfield-shifted singlet for the PhCH_2 protons at $\delta = 4.04$ ppm.



Scheme 4. Synthesis of ^{Bz}LLi (**3**),^{Bz}LGeCl (**4**), and ^{Bz}L′Ge: (**5**).

Synthesis of ^{Bz}LGeCl (4) and ^{Bz}L′Ge: (5)

Compound **3** reacts readily with $GeCl_2$·dioxane in diethyl ether to form the chlorogermylene **4**, which could be isolated as a yellow powder in 81% yield (Scheme 4). The latter is insoluble in *n*-hexane, sparingly soluble in diethyl ether, but well soluble in THF. Its composition has been confirmed by ^{1}H and ^{13}C NMR spectroscopy, EI-MS spectrometry and elemental analysis. Compound **4** crystallized from diethyl ether at room temperature in the triclinic space group $P\bar{1}$. Its molecular structure consists of a six-membered, puckered C_3N_2Ge ring with a pyramidally coordinated Ge^{II} atom (Figure 2). The bond lengths are very similar to those observed for the analogous N-heterocyclic chlorogermylene LGeCl.[9]

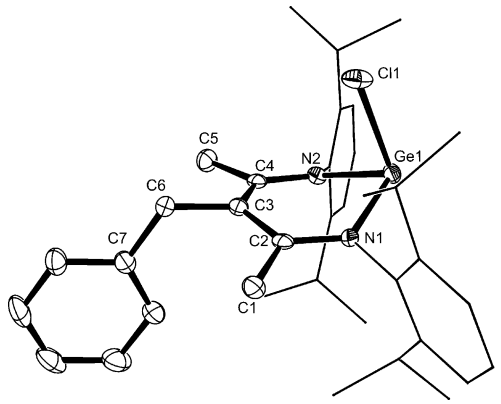


Figure 2. Molecular structure of ^{Bz}LGeCl (**4**). Thermal ellipsoids are drawn at 50% probability level. H atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Ge1–N1 1.964(2), Ge1–N2 1.962(2), Ge1–Cl1 2.329(1), C1–C2 1.502(3), C2–C3 1.420(3), C3–C4 1.404(3), C4–C5 1.513(3), C3–C6 1.511(3), C6–C7 1.523(3), N2–C4 1.343(3), N1–C2 1.338(2); N2-Ge1-N1 89.93(7), N2-Ge1-Cl1 94.22(5), N1-Ge1-Cl1 94.06(5), C2-N1-Ge1 123.6(1), C4-N2-Ge1 122.8(1), C3-C6-C7 117.0(2), C2-C3-C6 118.1(2), C4-C3-C6 117.8(2).

The dehydrochlorination of **4** with $LiN(SiMe_3)_2$ in THF led to the quantitative formation (as determined by ^{1}H NMR spectroscopy) of the expected germylene ^{Bz}L′Ge: **5** (Scheme 4), which could be isolated in 83% yield. The ^{1}H NMR spectrum of **5** exhibits two singlets at $\delta = 3.49$ and 4.09 ppm, respectively, for the diastereotopic exocyclic CH_2 protons and a singlet at $\delta = 3.77$ ppm for the methylene protons of the benzyl group. Compound **5** crystallized in *n*-hexane as red single crystals that were suitable for an X-ray diffraction analysis. In contrast to the molecular structure of **4**, the six-membered C_3N_2Ge ring in **5** is almost planar (Figure 3). The phenyl ring of the benzyl group is perpendicular to the C_3N_2Ge ring plane. The Ge–N bonds (average 1.849 Å) become shorter than those in its precursor **4** (1.963 Å), and the same is true for the C1–C2 distance. Despite the benzyl group at the 4-postion in **5**, the geometric parameters are quite similar to those observed in germylene L′Ge:.[5b] For instance, the C2–C3 and C3–C4 bond lengths in the C_3N_2Ge ring in **5** (1.422(4), 1.400(4) Å) are comparable to the corresponding values in L′Ge: (1.402(3), 1.392(3) Å). The Ge–N distances in **5** (1.847(2), 1.851(2) Å) are also close to those observed in L′Ge: (1.866(2), 1.865(2) Å).

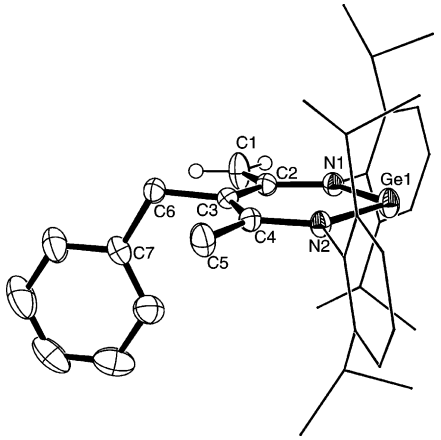
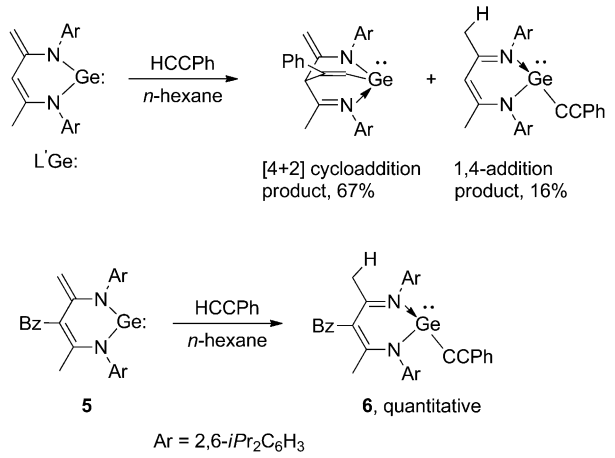


Figure 3. Molecular structure of ^{Bz}L′Ge: (**5**). Thermal ellipsoids are drawn at 50% probability level. H atoms (except those at C1) are omitted for clarity. Selected bond lengths (Å) and angles (°): Ge1–N1 1.847(2), Ge1–N2 1.851(2), C1–C2 1.425(4), C2–C3 1.422(4), C3–C4 1.400(4), C4–C5 1.444(4), C3–C6 1.515(4), C6–C7 1.517(4), C2–N1 1.406(3), C4–N2 1.410(3); N2-Ge1-N1 94.98(9), C2-N1-Ge1 128.5(2), C4-N2-Ge1 128.1(2), C2-C3-C6 116.3(2), C4-C3-C6 117.0(2), C3-C6-C7 116.2(2), C1-C2-C3 122.1(2), C3-C4-C5 122.2(3).

Reaction of ^{Bz}L′Ge: (5) with Phenylacetylene

In our previous work we showed that germylene L′Ge: can react with phenylacetylene to yield two products, namely a [4+2] cycloaddition product in 67% yield and a C–H activation product (1,4-addition) in 16% yield (Scheme 5).[10]



Scheme 5. Different reactivity of the new germylene **5** versus L′Ge:[10]

The latter ambivalent reactivity of the zwitterionic L′Ge: is strikingly different from that of the analogous silylene L′Si:. To examine the change of reactivity for the benzyl-modified germylene **5**, phenylacetylene was employed under the same reaction conditions. Interestingly, the conversion afforded exclusively the C–H activation product **6**, as indicated by the disappearance of the two characteristic singlets for the exocyclic CH_2 protons in **5** in the ^{1}H NMR spectrum (Scheme 5).

Compound **6** crystallized as yellowish plates in *n*-hexane. The structure of **6**, which is quite similar to that of **4**, was confirmed by X-ray diffraction analysis (Figure 4). The six-membered C_3N_2Ge ring again exhibits a puckered conformation. The alkynyl moiety at the three-coordinate Ge^{II} atom and the benzyl group are oriented away from each other. Due to statistical disorder of the GeCCPh moiety, a discussion of structural parameters is not meaningful.

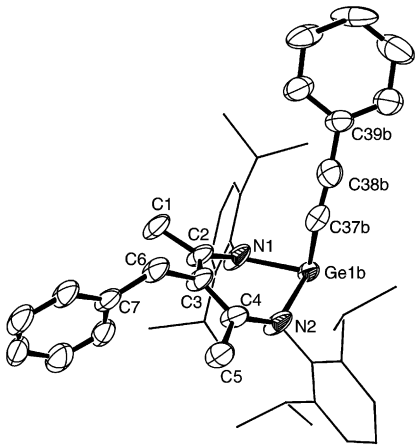


Figure 4. Molecular structure of ^{Bz}LGe(CCPh) (**6**). Thermal ellipsoids are drawn at 50% probability level. H atoms and the disordered part of the C≡CPh moiety are omitted for clarity. Selected bond lengths (Å): N1–Ge1a 1.815(5), N1–Ge1b 2.132(5), Ge1a–C37a 1.94(3), G1b–C37b 1.97(2), Ge1a–N2 2.002(5), Ge1b–N2 2.033(5), N1–C2 1.344(5), N2–C4 1.330(6), C1–C2 1.507(6), C2–C3 1.400(6), C3–C4 1.415(6), C4–C5 1.520(6), C3–C6 1.522(6), C6–C7 1.511(8).

The preferred C–H activation of phenylacetylene by **5** to yield the 1,4-addition product **6** indicates that the benzyl group in 4-position of the C_3N_2Ge ring facilitates an ylide-like reactivity as suggested for L′Ge: by DFT calculations and disfavors a [4+2] cycloaddition for steric reasons.[5b,10]

Conclusions

In summary, the newly benzyl-modified nacnac ligand in ^{Bz}LH (**2**) could be synthesized, which is easily accessible by stepwise lithiation of LH (**1**) with *n*BuLi in diethyl ether and single benzylation with BzBr, to afford a tautomeric mixture of ^{Bz}LH (**2a**/**2b**); subsequent lithiation of the mixture with MeLi furnished **3**. Reaction of **3** with $GeCl_2$·dioxane led to the N-heterocyclic chlorogermylene **4**, which could be converted by dehydrochlorination into the zwitterionic germylene **5** in quantitative yield. Remarkably, the benzyl group at the C_3N_2Ge ring facilitates an ylide-like reactivity towards phenylacetylene to yield exclusively the 1,4-addition product (alkynylgermylene, ^{Bz}LGe(CCPh)) **6**.

Experimental Section

General Considerations

All experiments and manipulations were carried out under dry oxygen-free nitrogen using standard Schlenk techniques or in an MBraun inert atmosphere dry-box containing an atmosphere of purified nitrogen. Solvents were dried by standard methods and freshly distilled prior to use. The NMR spectra were recorded with Bruker spectrometers ARX200, AV400 and with residual solvent signals as internal references (^{1}H and ^{13}C{H}) or with an external reference ($SiMe_4$ for ^{29}Si). Abbreviations: s = singlet; d = doublet; t = triplet; sept = septet; m = multiplet; br = broad. Elemental analyses were performed on a FlashEA 1112 CHNS Analyzer.

Single-Crystal X-ray Structure Determination

Crystals were each mounted on a glass capillary in perfluorinated oil and measured in a cold N_2 flow. The data of **2a**, **4**, **5**, and **6** were collected on an Oxford Diffraction Xcalibur S Sapphire at 150 K ($Mo_{K\alpha}$-radiation, λ = 0.71073 Å). The structures were solved by direct methods and refined on F^2 with the SHELX-97 [11] software package. The positions of the H atoms were calculated and considered isotropically according to a riding model. CCDC 878533 (**2a**), CCDC 878534 (**4**), CCDC 878535 (**5**), and CCDC 878536 (**6**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre at www.ccdc.cam.ac.uk./data_request/cif.

*^{Bz}LH (**2a**)*

Triclinic, space group $P\bar{1}$, a = 11.0830(5), b = 12.2132(8), c = 13.7190(9) Å, α = 67.998(6), β = 67.580(5), γ = 89.060(4)°, V = 1574.18(16) Å^3, Z = 2, ρ_{calcd} = 1.073 Mg m^{-3}, $\mu(Mo_{K\alpha})$ = 0.061 mm^{-1}, 15264 collected reflections, 5536 crystallographically independent reflections [R_{int} = 0.0389], 3395 reflections with $I > 2\sigma(I)$, θ_{max} = 25°, $R(F_o)$ = 0.0426 ($I > 2\sigma(I)$), wR(F_o^2) = 0.0941 (all data), 353 refined parameters.

*^{Bz}LGeCl (**4**)*

Triclinic, space group $P\bar{1}$, a = 12.1310(8), b = 12.3090(9), c = 12.7248(10) Å, α = 90.016(6), β = 108.196(6), γ = 113.830(7)°, V = 1633.6(2) Å^3, Z = 2, ρ_{calcd} = 1.252 Mg m^{-3}, $\mu(Mo_{K\alpha})$ = 1.046 mm^{-1}, 12347

collected reflections, 5732 crystallographically independent reflections [$R_{int}=0.03391$], 5201 reflections with $I>2\sigma(I)$, $\theta_{max}=25°$, $R(F_o)=0.0319$ ($I>2\sigma(I)$), $wR(F_o^2)=0.0758$ (all data), 371 refined parameters.

*^{Bz}L′Ge: (**5**)*

Monoclinic, space group $P2_1/n$, $a=12.5423(17)$, $b=19.345(2)$, $c=13.9173(19)$ Å, $\beta=102.880(15)°$, $V=3291.8(7)$ Å^3, $Z=4$, $\rho_{calcd}=1.169$ Mg m^{-3}, $\mu(Mo_{K\alpha})=0.955$ mm^{-1}, 26068 collected reflections, 5791 crystallographically independent reflections [$R_{int}=0.0677$], 4855 reflections with $I>2\sigma(I)$, $\theta_{max}=25°$, $R(F_o)=0.0455$ ($I>2\sigma(I)$), $wR(F_o^2)=0.1107$ (all data), 361 refined parameters.

*^{Bz}LGeC≡CPh (**6**)*

Monoclinic, space group $C2/c$, $a=33.690(2)$, $b=13.655(1)$, $c=22.091(1)$ Å, $\beta=117.869(7)°$, $V=8984.1(1)$ Å^3, $Z=4$, $\rho_{calcd}=1.008$ Mg m^{-3}, $\mu(Mo_{K\alpha})=0.709$ mm^{-1}, 29622 collected reflections, 7890 crystallographically independent reflections [$R_{int}=0.0414$], 5313 reflections with $I>2\sigma(I)$, $\theta_{max}=25°$, $R(F_o)=0.0856$ ($I>2\sigma(I)$), $wR(F_o^2)=0.2897$ (all data), 516 refined parameters.

Syntheses

*Compounds **2a** and **2b***

To a solution of compound **1** (7.08 g, 16.9 mmol) in diethyl ether (50 mL) was added *n*-butyllithium (6.76 mL, 2.5 M solution in *n*-hexane) at −20 °C under stirring. The reaction solution was allowed to warm to room temperature. After 2 h the reaction was finished. Benzylbromide (2.10 mL, 98 %, 17.2 mmol) was added to the yellow solution in situ at room temperature. The reaction mixture was stirred for three days. The solution was dried under vacuum. The product was extracted with *n*-hexane. From the concentrated solution compound **2a** crystallized as colorless plates at −20 °C. The remaining solution was dried under vacuum and the residue was dissolved in methanol (5 mL), which yielded colorless crystals of a mixture of **2a** and **2b**. The first and second crops of **2a** and **2b** amounted 6.62 g, 13.0 mmol (77 % yield). M.p. 82 °C; ^{1}H NMR (200.13 MHz, C_6D_6, 25 °C): for **2a**: $\delta=1.06$ (d, ^3J(H,H) = 7 Hz, 6H; CH*Me*$_2$), 1.09 (d, ^3J(H,H) = 7 Hz, 6H; CH*Me*$_2$), 1.12 (d, ^3J(H,H) = 7 Hz, 6H; CH*Me*$_2$), 1.16-(d, ^3J(H,H) = 7 Hz, 6H; CH*Me*$_2$), 1.68 (s, 6H; NC*Me*), 2.51 (sept, ^3J-(H,H) = 7.0 Hz, 2H; C*H*Me$_2$), 2.75 (sept, ^3J(H,H) = 7.0 Hz, 2H; C*H*Me$_2$), 3.46 (d, ^3J(H,H) = 7 Hz, 2H, CH_2Ph), 4.20 (t, ^3J(H,H) = 7 Hz, 1H, γ-C*H*), 7.03–7.21 ppm (m, br, 11H; *Ph*); for **2b**: 1.18 (d, ^3J(H,H) = 7 Hz, 12H; CH*Me*$_2$), 1.19 (d, ^3J(H,H) = 7 Hz, 12H; CH*Me*$_2$), 1.69 (s, 6H; NC*Me*), 3.36 (sept, ^3J(H,H) = 7 Hz, 4H; C*H*Me$_2$), 3.70 (s, 2H, PhCH_2), 7.04–7.32 (m, br, 11H; *Ph*), 14.0 ppm (s, 1H, N*H*); HR-ESI: *m*/*z* (%): 509.38848 [*M*+H]$^+$, calcd 509.38120; elemental analysis calcd (%) for $C_{36}H_{48}N_2$: C 84.99, H 9.51, N 5.51; found: C 84.74, H 9.32, N 5.41.

Compound **3**: To a solution of **2a** and **2b** (2.90 g, 5.70 mmol) in diethyl ether (50 mL) was added *n*-butyllithium (2.5 M in diethyl ether, 2.28 mL, 5.70 mmol) at −10 °C under stirring. The reaction was completed in 2 h and the solvent was changed to THF. From THF compound **3** was obtained at −20 °C as yellow crystals with yield of 2.70 g (5.24 mmol, 92 %). M.p. 130 °C (decomposed); ^{1}H NMR (200.13 MHz, C_6D_6, 25 °C): $\delta=1.21$ (d, ^3J(H,H) = 7.0 Hz, 12H; CH*Me*$_2$), 1.23 (d, ^3J(H,H) = 7.0 Hz, 12H; CH*Me*$_2$), 1.90 (s, 6H; NC*Me*), 3.38 (sept, ^3J(H,H) = 7.0 Hz, 4H; C*H*Me$_2$), 4.04 (s, 2H; CH_2Ph), 6.99–7.10 (m, br, 7H; Ph), 7.30 (t, ^3J(H,H) = 7.3 Hz, 2H, Ph), 7.48 ppm (d, ^3J(H,H) = 7.3 Hz, 2H; Ph); ^{13}C{^{1}H} NMR (100.61 MHz, C_6D_6, 25 °C): $\delta=21.1$ (NC*Me*), 23.9, 24.1 (CH*Me*$_2$), 28.2 (C*H*Me$_2$), 38.1 (CH_2Ph), 96.6 (γ-*C*), 122.8, 123.4, 125.6, 127.9, 128.3, 140.9, 145.2, 150.2, 164.5 ppm (N*C*Me, *Ph*); HR-ESI: *m*/*z* (%): 509.38793 [*M*−Li+H]$^+$, calcd 509.38120 elemental analysis calcd (%) for $C_{36}H_{47}N_2Li$·THF: C 81.87, H 9.45, N 4.77, found: C 81.86, H 9.48, N 4.73.

Compound **4**: $GeCl_2$·dioxane (0.66 g, 2.85 mmol) was added to a yellow solution of **3** (1.47 g, 2.85 mmol) in toluene (80 mL) at room temperature. From the solution colorless precipitate formed immediately. After six hours the salt LiCl was filtered away, and the solution was dried in vacuum and washed with *n*-hexane (2×8 mL), which yielded yellowish powder of **5** with yield of 1.42 g (2.30 mmol, 81 %). Single crystals of **4** suitable for X-ray analysis were obtained from diethyl ether. M.p. 172 °C (decomposed); ^{1}H NMR (200.13 MHz, C_6D_6, 25 °C): $\delta=1.05$ (d, ^3J-(H,H) = 7.0 Hz, 6H; CH*Me*$_2$), 1.12 (d, ^3J(H,H) = 7.0 Hz, 6H; CH*Me*$_2$), 1.24 (d, ^3J(H,H) = 7.0 Hz, 6H; CH*Me*$_2$), 1.51 (d, ^3J(H,H) = 7.0 Hz, 6H; CH*Me*$_2$), 1.71 (s, 6H; NC*Me*), 3.24 (sept., ^3J(H,H) = 7.0 Hz, 2H; C*H*Me$_2$), 3.60 (s, 2H; CH_2Ph), 3.92 (sept., ^3J(H,H) = 7.0 Hz, 2H; C*H*Me$_2$), 7.00–7.31 ppm (m, 11H, Ph); ^{13}C{^{1}H} NMR (100.61 MHz, C_6D_6, 25 °C): $\delta=21.5$ (NC*Me*), 24.2, 24.3, 24.8, 27.5, 28.4, 29.4 (CH*Me*$_2$), 36.9 (CH_2Ph), 107.0 (γ-*C*), 124.1, 125.8, 126.4, 127.8, 128.1, 128.3, 128.9, 140.7, 141.0, 143.7, 147.3, 165.5 ppm (N*C*Me, Ph); EI-MS: *m*/*z* (%): 615 [*M*−H]$^+$; elemental analysis calcd (%) for $C_{36}H_{47}N_2GeCl$: C 70.21, H 7.69, N 4.55; found: C 69.95, H 7.53, N 4.64.

Compound **5**: To a solution of **4** (0.97 g, 1.58 mmol) in THF (20 mL) was added $LiN(SiMe_3)_2(Et_2O)$ (0.38 g, 1.58 mmol) at room temperature under stirring. The solution was stirred for one hour. The precipitate was filtered away and the solvent was changed to *n*-hexane. From *n*-hexane compound **5** crystallized as red plates with yield of 0.76 g (1.31 mmol, 83 %). M.p. 140 °C (decomposed); ^{1}H NMR (200.13 MHz, C_6D_6, 25 °C): $\delta=1.17$ (d, ^3J(H,H) = 7.0 Hz, 6H; CH*Me*$_2$), 1.24 (d, ^3J(H,H) = 7.0 Hz, 6H; CH*Me*$_2$), 1.28 (d, ^3J(H,H) = 7.0 Hz, 6H; CH*Me*$_2$), 1.29 (d, ^3J(H,H) = 7.0 Hz, 6H; CH*Me*$_2$), 1.58 (s, 3H; NC*Me*), 3.49 (s, 1H, NCCH_2), 3,52–3,77 (m, 4H; C*H*Me$_2$), 3.77 (s, 2H; CH_2Ph), 4.09 (s, 1H; NCCH_2), 7.03–7.35 ppm (m, br, 11H; Ph); ^{13}C{^{1}H} NMR (100.61 MHz, C_6D_6, 25 °C): $\delta=$ 18.6 (NC*Me*), 23.4, 24.5, 25.6, 25.8 (CH*Me*$_2$), 28.4, 28.5 (*C*HMe$_2$), 38.1 (*C*H_2Ph), 84.6 (NC*C*H$_2$), 111.1 (γ-*C*), 124.2, 125.6, 126.0, 127.9, 128.3, 128.7, 140.0, 140.2, 141.2, 141.3, 147.1, 147.3, 151.4 ppm (N*C*Me, N*C*CH$_2$, CH$_2$*Ph* 2,6-*i*Pr$_2$*C*$_6$H$_3$); HR-ESI: *m*/*z* (%): 581.29548 [*M*+H]$^+$, calcd 581.29455; elemental analysis calcd (%) for $C_{36}H_{46}N_2Ge$: C 74.63, H 8.00, N 4.84, found: C 74.81, H 8.05, N 4.84.

Compound **6:** To a solution of **5** (0.65 g, 1.12 mmol) in diethyl ether (10 mL) was added phenylacetylene (0.13 mL, $d=0.92$ g mL^{-1}, 1.12 mmol) at room temperature. The reaction mixture was left to stand for 2 h. The color changed from deep red to orange. From *n*-hexane compound **6** crystallized as colorless plates at 4 °C with yield of 0.59 g (0.87 mmol, 78 %). M.p. 51 °C (decomposed); ^{1}H NMR (200.13 MHz, C_6D_6, 25 °C): $\delta=1.16$ (d, ^3J(H,H) = 7.0 Hz, 6H; CH*Me*$_2$, 1.18 (d, ^3J-(H,H) = 7.0 Hz, 6H; CH*Me*$_2$, 1.34 (d, ^3J(H,H) = 7.0 Hz, 6H; CH*Me*$_2$, 1.50 (d, ^3J(H,H) = 7.0 Hz, 6H; CH*Me*$_2$, 1.71 (s, 6H; NC*Me*), 3.51 (sept., ^3J(H,H) = 7.0 Hz, 2H; C*H*Me$_2$), 3.68 (s, 2H; PhCH_2), 4.06 (sept., ^3J-(H,H) = 7.0 Hz, 2H; C*H*Me$_2$), 6.90–7.19 (m, br, 12H; *Ph*), 7.48–7.62 ppm (m, 4H; *Ph*); ^{13}C{^{1}H} NMR (100.61 MHz, C_6D_6, 25 °C): $\delta=21.4$ (NC*Me*), 24.3, 24.6, 24.8, 27.7, 28.6, 29.2 (CH*Me*$_2$), 37.1 (*C*H$_2$Ph), 104.0, 106.4 (*C*≡ *C*Ph), 113.7 (γ-*C*), 124.2, 125.2, 126.2, 126.4, 127.2, 128.1 128.4, 128.9, 131.9, 141.9, 142.5, 143.6, 147.0, 166.9 ppm (N*C*Me, CH$_2$*Ph* 2,6-*i*Pr$_2$*C*$_6$H$_3$, C≡C*Ph*); HR-ESI: *m*/*z* (%): 683.33953 [*M*+H]$^+$, calcd 683.34150; elemental analysis calcd (%) for $C_{44}H_{52}N_2Ge$: C 77.55, H 7.69, N 4.11, found: C 77.55, H 7.87, N 3.98.

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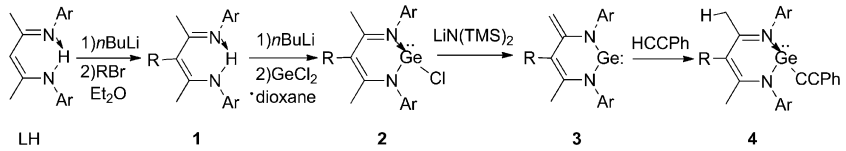

Ar = 2,6-*i*Pr$_2$C$_6$H$_3$, R = CH$_2$Ph, TMS = SiMe$_3$

Good germs: Lithiation and monobenzylation of β-diketimine LH afforded the new benzyl-modified β-diketimine **1a** and its tautomer **1b** (not shown). Lithiation and subsequent reaction with $GeCl_2$·dioxane furnished the chlorogermylene **2**, which could be transformed quantitatively into the new zwitterionic germylene **3**. Remarkably, **3** reacts with phenylacetylene exclusively under 1,4-addition to give the alkynyl germylene **4** owing to the σ-donating benzyl group.

Germanium Chemistry

*Yun Xiong, Shenglai Yao, Matthias Driess** ——— ▮▮▮▮–▮▮▮▮

Synthesis and Tunable Reactivity of N-Heterocyclic Germylene

