Main-Group Elements

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Isolation of an Imino-N-heterocyclic Carbene/Germanium(0) Adduct: A Mesoionic Germylene Equivalent**

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Abstract: *An autoionization of germanium dichloride/dioxane complex with an imino-N-heterocyclic carbene ligand (**L**) afforded a novel germyliumylidene ion, $[(\mathbf{L})\mathrm{GeCl}]^+[\mathrm{GeCl}_3]^-$, which was fully characterized. Reduction of the germyliumylidene ion with potassium graphite produced a cyclic species $[(\mathbf{L})\mathrm{Ge}]$, which can be viewed as both a Ge^0 species and a mesoionic germylene. X-ray diffraction analysis and computational studies revealed one of the lone pairs on the Ge atom is involved in the π system on the $\mathrm{GeC_2N_2}$ five-membered ring. It was also confirmed that the nucleophilic behavior of $[(\mathbf{L})\mathrm{Ge}]$ as a two lone-pair donor.*

Chemistry of stable singlet carbenes has dramatically developed over the past two decades since the discovery of the first isolable species.[1] In addition to the extensive study on N-heterocyclic carbenes (NHCs),[2] various types of carbenes other than NHCs, are known, and has enriched this field.[3] Among them, Bertrand et al. isolated the free imidazol-5-ylidene **A** (Figure 1 a), termed an abnormal N-heterocyclic carbene (*a*NHC) or mesoionic carbene (MIC),[4] and has led the further diversity in the applications of singlet carbenes for catalysis.[5] Meanwhile, the corresponding heavier group 14 analogues **Ba** (E = Si, Ge, Sn, Pb; Figure 1 b) have not been described before despite the long history of tetrylene chemistry,[6] probably because of the lack of the suitable synthetic methodology.

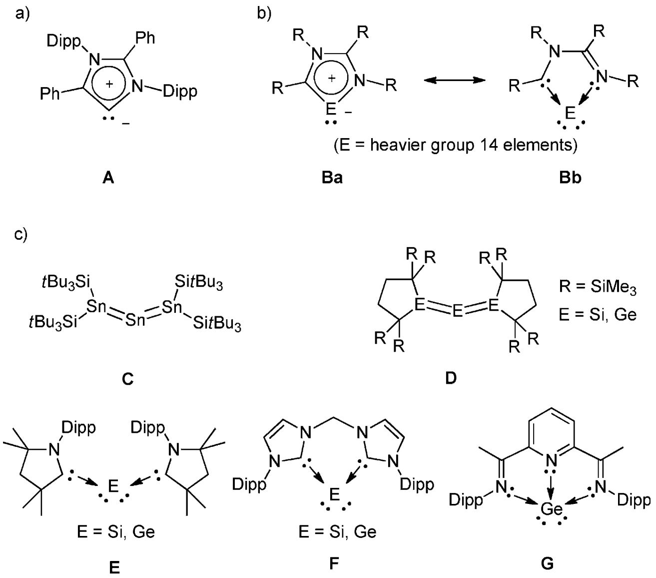

Figure 1. a) The first isolable abnormal-N-heterocyclic carbene **A**. b) Two canonical forms of **B**. c) Structurally characterized heavier group 14 molecules featuring an element in the zero-oxidation state **C**–**G**. Dipp = 2,6-diisopropylphenyl.

Recently, a series of molecules featuring heavier group 14 elements in the zero-oxidation state have been reported (Figure 1 c).[7] In 1999, Wiberg et al. synthesized the tristannaallene **C** bearing a tin(0) atom.[8] Kira and co-workers isolated the trisilaallene, 1,3-digermasilaallene and trigermaallene (**D**) which contain silicon(0) and germanium(0), respectively.[9] The groups of Roesky and Driess revealed that two strong σ-donating carbenes can effectively support the E^0 species (E = Si, Ge) **E** and **F**.[10,11] Significantly, Nikonov et al. demonstrated that germanium(0) can be prepared even in the absence of carbene ligands. Thus, they synthesized the first tricoordinate compound (**G**) of germanium(0) stabilized by a bis(imino)pyridine, wherein partial delocalization of one of the germanium lone pairs onto the π*(C=N) orbitals was observed, and contributes to the strong interaction between germanium(0) and the ligand.[12] These pioneering studies prompted us to investigate whether even the combination of one singlet carbene and one imino group can stabilize such species. In particular, we were interested in employing imino-N-heterocyclic carbene[13] as the ligand because the resulting E^0 species **Bb** may correspond to an equivalent of the synthetically challenging **Ba** (Figure 1 b). Herein, we report the synthesis, single-crystal X-ray diffraction analysis, and computational studies of a novel germanium(0) derivative supported by an imino-N-heterocyclic carbene.

First, we synthesized a new imino-N-heterocyclic carbene by following the procedures previously reported, with slight modification.[13] The nitrilium cation $[\mathrm{MesN{\equiv}C}t\mathrm{Bu}]^+$, generated in situ by the reaction of the corresponding imidoyl chloride with $\mathrm{NaBF_4}$, was coupled with *N*-adamantyl-dihydroimidazole, which afforded the imidazolium salt **1** in 68 % yield (Scheme 1). Deprotonation of **1** with potassium hexamethyldisilazide (KHMDS) in THF cleanly proceeded, and after work-up the free imino-N-heterocyclic carbene **2** was

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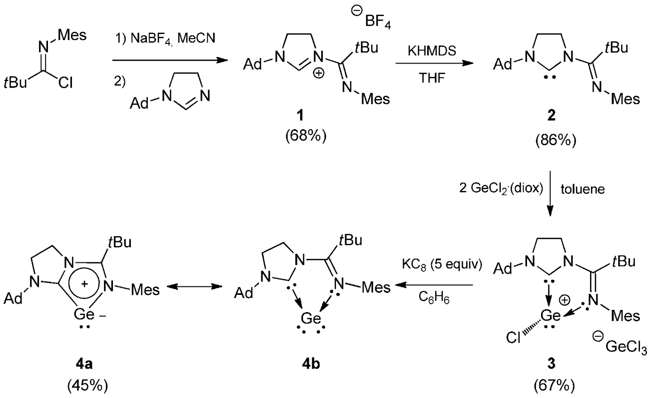


Scheme 1. Synthesis of **3** and **4**. Ad = 1-adamantyl, Mes = 2,4,6-trimethylphenyl.

obtained in 86 % yield. Compound **2** was fully characterized by NMR spectroscopy and a single-crystal X-ray diffraction study.[14] Next, we attempted autoionization[15] of germanium dichloride using **2**. Treatment of a toluene solution of **2** with two equivalents of a germanium dichloride/1,4-dioxane complex led a white precipitate. After evaporation of the solvent under vacuum, the residue was washed with cold toluene to afford compound **3** in 67 % yield. Compound **3** is the first chlorogermyliumylidene ion[11a,15,16] chelated by an imino-N-heterocyclic carbene. In the ^{13}C NMR spectrum of **3**, an upfield shift of the carbene peak ($\delta = 198.4$ ppm), compared to that of the precursor **2** ($\delta = 242.3$ ppm), was observed. The complex **3** is thermally stable both in solid state and in solution at ambient temperature but it gradually decomposes upon exposure to air.

Single crystals of **3** were obtained from an acetonitrile solvent at room temperature, and X-ray diffraction analysis revealed that the shortest distance between the cation [**2**-Ge^{II}Cl]$^+$ and the anion [Ge^{II}Cl$_3$]$^-$ is greater than 6.5 Å, thus indicating no interaction between them (Figure 2).[14] In the cation part, the Ge atom in **3** is coordinated by the carbene carbon atom, the imine nitrogen atom, and one chlorine atom. The sum of the bond angles around carbene carbon atom is 359.1°. All five atoms of the central C_2N_2Ge ring are nearly coplanar (the sum of internal pentagon angles = 537.38°) but Ge1 slightly deviates from the plane in the opposite direction of the Ge1–Cl1 bonding vector. The Cl1 atom is located out of the C_2N_2Ge plane with bond angles of 95.25(5)° for C1-Ge1-Cl1 and 95.79(5)° for N3-Ge1-Cl1. The Ge1-Cl1 distance of 2.2646(6) Å is comparable to those (2.243–2.310 Å) observed in previously reported germyliumylidene ions.[11a,15,16] The Ge1–C1 distance of 2.0588(19) Å is nearly identical to those [2.058(3) and 2.057(3) Å] of a cyclic germadicarbene.[11a] The Ge1–N3 distance of 2.0560(16) Å is longer than those [1.981(3) and 1.960(3) Å][16b] of [LClGe:]$^+$ [L = 1,8-bis(tri-n-butylphosphanzenyl)naphthalene] but slightly shorter than those [2.114(5)–2.428(5) Å][16c] in [(pmdta)ClGe:]$^+$ and those [2.071(2)–2.267(2) Å][15] in [L′ClGe:]$^+$ [L′ = 2,6-diacetylpyridinebis(2,6-diisopropylanil)], thus suggesting a relatively strong interaction between the Ge1 atom and the N3 atom in **3**. To gain insight into the electronic properties, we performed quantum chemical calculations for the cationic fragment of **3**.[17] Geometry optimization reproduced the experimental result. A lone-pair orbital on Ge was confirmed in the HOMO−2 (Figure 3, left) whereas the LUMO mainly corresponds to a π-type orbital (Figure 3, right). Natural bond order (NBO) analysis gave Wiberg bond index (WBI) values of the Ge–C bond (0.61) and the Ge–N bond (0.39), thus indicating a pronounced interaction between the imino-carbene ligand and the [:GeCl]$^+$ fragment in **3**. Indeed, Natural population analysis (NPA) revealed an overall charge transfer of 0.57 e from the imino-carbene ligand **2** to [:GeCl]$^+$ in **3**.

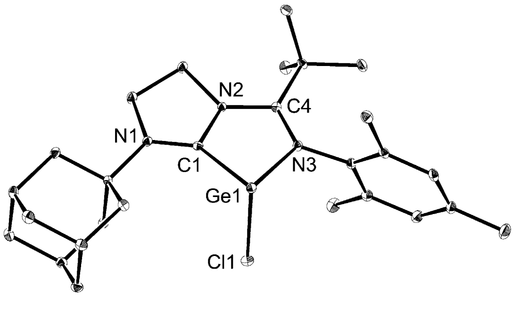


Figure 2. Solid-state structure of **3** (hydrogen atoms, solvent molecules, and counteranion (GeCl$_3^-$) are omitted for clarity). Thermal ellipsoids are set at the 30 % probability. Selected bond lengths [Å] and angles [°]: Ge1-Cl1 2.2646(6), Ge1-C1 2.0588(19), Ge1-N3 2.0560(16), C1-N1 1.301(2), C1-N2 1.375(2), C4-N2 1.391(2), C4-N3 1.300(2), C1-Ge1-N3 76.88(7), Ge1-C1-N2 111.34(13), C1-N2-C4 118.67(16), N2-C4-N3 112.97(16), Ge1-N3-C4 117.52(12), C1-Ge1-Cl1 95.25(5), N3-Ge1-Cl1 95.79(5).

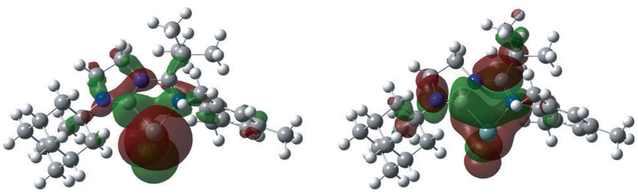


Figure 3. Plots of the HOMO−2 (left) and LUMO (right) of **3** calculated at the B3LYP/6-311G(d,p) level of theory.

Next we attempted the reduction of **3**. A benzene solution of **3** with five equivalents of potassium graphite was stirred at ambient temperature for 1 hour. After removing the solvent in vacuo and work-up, **4** was obtained as a yellow solid in 45 % yield (Scheme 1). Note that **4** can be illustrated as both the abnormal N-heterocyclic germylene **4a** and the Ge^0 species **4b**, which is the first example of a dicoordinate Ge^0 analogue supported by a carbene and an imine ligand.[18] In the ^{13}C NMR spectrum of **4**, the carbene peak appeared at $\delta = 194.3$ ppm which is similar to that of **3** and shifted upfield with respect to that of **2** ($\delta = 242.3$ ppm). The complex **4** is thermally stable both in solid state and in solution, and even after heating at 110 °C for several hours in toluene no decomposition was detected. However, it rapidly decomposed upon exposure to air or moisture. Recrystallization from a benzene solution of **4** stored at 10 °C under argon afforded single crystals, and the solid-state structure of **4** was confirmed

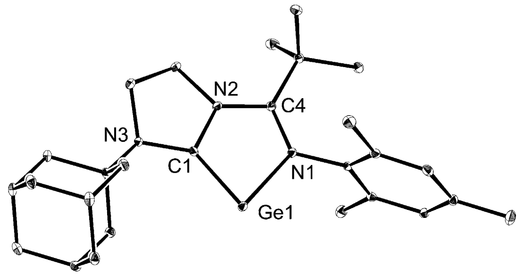


Figure 4. Solid-state structure of **4** (hydrogen atoms and solvent molecules are omitted for clarity). Thermal ellipsoids are set at the 30% probability. Selected bond lengths [Å] and angles [°]: Ge1-C1 1.8870(15), Ge1-N1 1.9680(13), C1-N2 1.392(2), C1-N3 1.4062(19), C4-N1 1.3427(19), C4-N2 1.366(2), C1-Ge1-N1 80.59(6), Ge1-C1-N2 113.23(11), C1-N2-C4 118.93(13), N1-C4-N2 109.73(13), Ge1-N1-C4 117.49(11).

by a single-crystal X-ray diffraction study (Figure 4).[14] The Ge1 atom is two-coordinate with the carbene carbon atom and the imine nitrogen atom, and a C1-Ge1-N1 angle of 80.59(6)°. This angle is slightly larger than that [76.88(7)°] of **3**, but smaller than the corresponding C-Ge-C angle [86.6(1)°] of a cyclic germadicarbene **F**[11a] or those [83.44(12)° and 85.62(7)°] of tetraphenylgermole dianions $(thf)_nLi_2[(PhC)_4Ge]$[19a] which are isoelectronic species of **4**. The five-membered C_2N_2Ge ring is nearly coplanar (the sum of internal pentagon angles = 539.97°) with a trigonal-planar geometry around the carbene carbon atom (the sum of bond angles = 359.98°). The Ge1-C1 distance of 1.8870(15) Å is significantly shorter by 0.3776 Å than that in **3**, and it ranges between typical Ge−C bonds and Ge=C bonds.[20] There is shortening of the Ge1−N1 bond and the C4−N2 bond, and slight lengthening of the C4−N1 bond and the C1−N2 bond, compared to those of **3**. These structural features suggest the delocalization of π electrons over the five-membered C_2N_2Ge ring in **4**. A similar geometrical property has been reported on germole dianions $M_2[(RC)_4Ge]$ displaying a planar C_4Ge ring structure as well as cyclic C−C bond equalization, which indicates the delocalization of the negative charge over the entire ring system.[19] Analoguously, cyclic delocalization of the π electrons on the skeletal five-membered ring was also proposed in the N-heterocyclic germanediyl derivatives $[(H)C(R)N]_2Ge$: which are alternative isomers of **4**, based on experimental analysis and theoretical studies.[21]

To gain further insight into the electronic features of **4**, geometry optimization, NBO analysis, and NPA calculation for **4** were performed.[17] Geometry optimization provided similar structural parameters to those observed experimentally. Figure 5 displays the two highest occupied molecular orbitals of **4**. The HOMO is mainly a C–Ge π-bonding orbital which exhibits antibonding conjugation with the N=C(*t*Bu) π orbital in the C_2N_2Ge ring (Figure 5, top). Meanwhile, the HOMO−1 is a σ-type lone-pair orbital at the Ge atom (Figure 5, bottom). WBI values of the Ge−C bond (1.21) supports the π-bonding property of the Ge−C bond. WBI values larger than 1 for the $C_{(carbene)}$−N bond (1.08) and the N−C(*t*Bu) bonds (1.20 and 1.35) in the C_2N_2Ge ring were also obtained, thus indicating the delocalization of the π system.

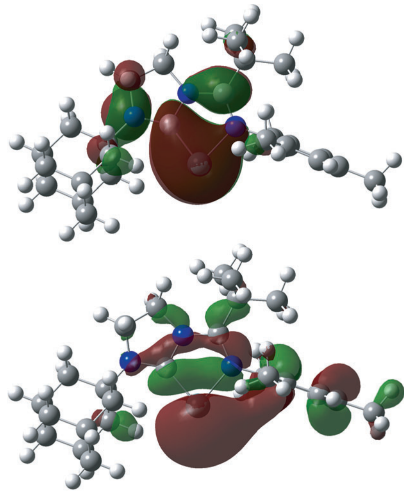
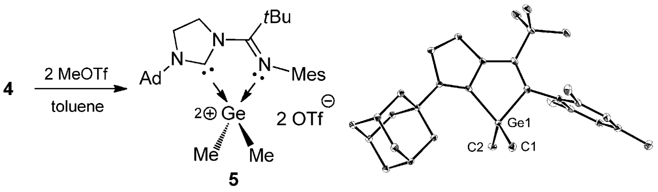


Figure 5. Plots of the HOMO (top) and HOMO−1 (bottom) of **4** calculated at the B3LYP/6-311G(d,p) level of theory.

In the UV-Vis spectrum of **4**, a strong absorption band with $\lambda_{max} = 415$ nm was observed and corresponds to the π–π* transition (see the Supporting Information).

Similar to the reactivity of germole dianions, $M_2[(RC)_4Ge]$, in the facile derivatization with electrophiles (R′X) which afforded the corresponding germoles $(RC)_4GeR'_2$,[19] the reaction of **4** with two equivalents of methyl trifluoromethanesulfonate (MeOTf) gave the corresponding dicationic species **5** [= (**2**$GeMe_2$)·2OTf] (80%) which was fully characterized by NMR spectroscopy and X-ray diffraction analysis (Scheme 2).[14] This result demonstrated a nucleophilic property of **4** where the Ge center donated two lone pairs to form two Ge−Me bonds of **5**.



Scheme 2. Reaction of **4** with 2 equivalents of MeOTf, and solid-state structure of **5** (hydrogen atoms, the counteranions, and solvent molecules are omitted for clarity). Thermal ellipsoids are set at the 30% probability. Tf = trifluoromethanesulfonyl.

In conclusion, we demonstrated that the imino-N-heterocyclic carbene ligand-supported chlorogermyliumylidene cation **3** could be synthesized through autoionization of a germanium dichloride/1,4-dioxane complex. Reduction of **3** successfully produced the novel germanium compound **4** which can be viewed as both a mesoionic germylene and a germanium(0) species. X-ray diffraction analysis and computational studies revealed the electron delocalization over the five-membered C_2N_2Ge ring involving one of the lone pairs on Ge, thus supporting the electronic properties of the resonance structure **4a**. In addition, the reaction of **4** with two equivalents of MeOTf afforded the dicationic species **5**, thus demonstrating the property of **4** as a donor of two lone pairs and supporting a contribution of the resonance structure **4b**. Investigation of the ligand property of **4** as well as the synthesis of congeners containing other heavier 14 elements is currently underway in our group.

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