

Synthesis and structure of the azidogermylumylidene azide complex $[L(N_3)Ge:]^+N_3^-$ with covalently and ionically bonded azide ligands at germanium(II) $[L = \text{bis}(N\text{-heterocyclic carbene})]^\dagger$

Yun Xiong, Shenglai Yao and Matthias Driess*

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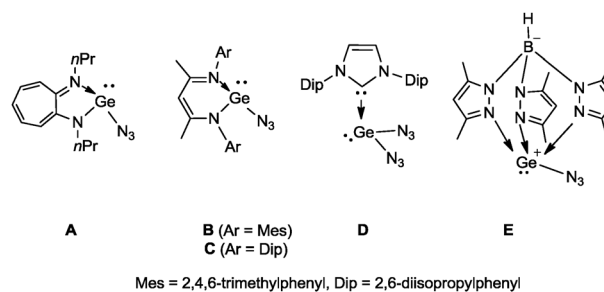
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Starting from the chlorogermylumylidene chloride salt $[L(Cl)Ge:]Cl$ (**1**) ($L = 1,1'$ -methylene-3,3'-di-2,6-diisopropyl-phenylimidazole-2,2'-diylidene), the chloride ion can be easily substituted by BPh_4 to yield $[L(Cl)Ge:]BPh_4$ (**3**). Reaction of the latter with NaN_3 furnishes $[L(N_3)Ge:]BPh_4$ (**4**). In contrast, the direct reaction of **1** with NaN_3 affords exclusively the first azidogermylumylidene azide salt $[L(N_3)Ge:]N_3$ (**2**). The latter represents the first isolable diazido Ge(II) complex with a covalently bonded azido ligand and a weakly coordinating azide anion as the counterion. All new compounds **2**, **3**, and **4** were fully characterized, including using X-ray diffraction analysis.

Azido species containing the azide group (N_3) have been known for many years.¹ Owing to their sensitivity to heat and shock some of them have found applications as explosives.² On the other hand, they have been used in synthetic chemistry as azido transfer reagents.³ In fact, the versatility of the azido bridge for building molecular-based materials enables them to be used in the field of new magnetic materials.⁴ Among the azido complexes of group 14 elements, azides of carbon were the most well studied species.^{1,2,5} Even the heavier analogues, namely azides of E(IV) centres ($E = Si, Ge, Sn$), are also relatively well known.⁶ In contrast, the azides of low-valent group 14 elements are relatively scarcely reported. By taking Ge(II) azides into consideration, to the best of our knowledge not many three-coordinate germanium(II) azides (Scheme 1, A–D) and only a few four-coordinate germanium(II) azides^{7a–e} have been described. Among the latter compounds a four-coordinate zwitterionic germanium(II) azide **E** was successfully isolated and fully characterized by the group of Filippou (Scheme 1, E).⁸

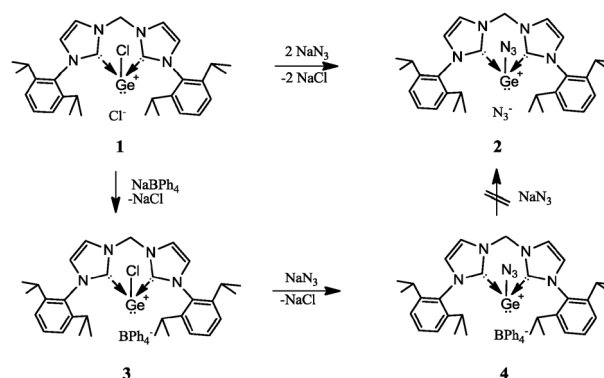
Very recently, we prepared the chelate bis(N -heterocyclic carbene) (abbrev. bNHC) stabilized complex $[bNHC(Cl)Ge:]Cl$ (**1**) (bNHC =



Scheme 1 Selected divalent azidogermanium(II) complexes A–E.

$1,1'$ -methylene-3,3'-di-2,6-diisopropylphenylimidazole-2,2'-diylidene) (Scheme 2).⁹ The existence of chlorine atoms both in the outer- and inner-sphere of **1** prompted us to investigate the substitution possibility of Cl atoms by other functional groups. According to the pseudohalide properties of the azido group, we investigated the reactivity of **1** towards NaN_3 . Herein we report the synthesis and characterisation of two unprecedented azidogermylumylidene complexes.

It is found that from the direct reaction of **1** with an equimolar amount of NaN_3 both chlorine atoms in **1** are always simultaneously substituted by two azide groups to yield the azidogermylumylidene



Scheme 2 Synthesis of azidogermylumylidene azide complex **2** and azidogermylumylidene tetraphenylborate complex **4**.

Technische Universität Berlin, Department of Chemistry, Metalorganics and Inorganic Materials, Sekr. C2, Strasse des 17. Juni 135 D-10623, Berlin, Germany. E-mail: matthias.driess@tu-berlin.de; Web: <http://www.driess.tu-berlin.de>;

Fax: +49-30-314-29732

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azide complex [bNHC(N₃)Ge:]N₃ (**2**) (Scheme 2), instead of [bNHC(Cl)Ge:]N₃ and/or [bNHC(N₃)Ge:]Cl. Compound **2** was isolated as an off-white solid in high yield (82%). It is soluble in acetonitrile, but insoluble in THF. The ¹H and ¹³C{¹H} NMR spectra of **2** display resonances for the ligand bNHC (see ESI†). The IR spectrum of **2** in KBr exhibits absorption bands at $\nu = 2077\text{ cm}^{-1}$ for the azido group of the Ge(II)N₃ moiety and at 2003 cm^{-1} for the N₃⁻ counterion (asymmetric N–N–N stretching vibrations), respectively. The stretching vibration band at $\nu_{\text{asym}}(\text{N}_3) = 2077\text{ cm}^{-1}$ in **2** is close to those of the three-coordinate Ge(II) azides **B** ($\nu_{\text{asym}}(\text{N}_3) = 2062\text{ cm}^{-1}$),^{7b} **C** ($\nu_{\text{asym}}(\text{N}_3) = 2068\text{ cm}^{-1}$),^{7c} and **D** ($\nu_{\text{asym}}(\text{N}_3) = 2075\text{ cm}^{-1}$),^{7d} and higher than those of **E** ($\nu_{\text{asym}}(\text{N}_3) = 2043\text{ cm}^{-1}$)⁹ and **A** ($\nu_{\text{asym}}(\text{N}_3) = 2048\text{ cm}^{-1}$).^{7a} However, it is still at lower frequency when compared with those of Ge(IV) tri-, tetra-, or hexaazides (>2080 cm⁻¹)⁶ due to the ionic properties and thus higher polarity of the Ge–N bond in **2**. On the other hand, the ν_{asym} absorption band at $\nu = 2003\text{ cm}^{-1}$ for the N₃⁻ counterion in **2** is close to that found for the matrix-isolated N₃⁻ anion [$\nu_{\text{asym}}(\text{N}_3) = 2005\text{ cm}^{-1}$].¹⁰ It is noteworthy that the solution IR spectrum of **2** in acetonitrile displays also two sets of absorption bands with similar wavenumbers at $\nu_{\text{asym}}(\text{N}_3) = 2077\text{ cm}^{-1}$ and $\nu_{\text{asym}}(\text{N}_3) = 2005\text{ cm}^{-1}$, respectively, for the two different azide groups, indicating the similar structure of **2** both in solution and in the solid state.

Crystals of **2** were grown in acetonitrile at $-20\text{ }^\circ\text{C}$ and crystallize in the monoclinic space group *P*₂₁/*c* (Fig. 1). In compound **2** the Ge(II) atom is three coordinated by two carbon atoms of the bNHC ligand and one nitrogen atom of the azide group N₃. Owing to the chelate coordination a six-membered C₃N₂Ge ring is formed, and the coordinated N₃ group occupies a site above the ring system with *trans*-arrangement. Although the six-membered C₃N₂Ge ring is puckered as in **1** in a boat conformation with N2, N4, C1, and C2 being nearly coplanar, the Ge1 and C7 atoms displaced away from that plane in the opposite direction as the Ge1–N5 bonding vector is pointing. The latter deformation presumably results from the interaction between the Ge atom and the N₃⁻ counterion, which is located under the ring system close to the center of the six-

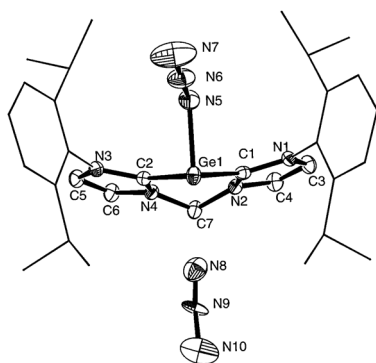


Fig. 1 Molecular structure of **2**. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms and three acetonitrile molecules are omitted for clarity. Selected bond distances (Å) and angles (°): Ge1–N5 2.037(2), Ge1–C2 2.046(2), Ge1–C1 2.051(2), N5–N6 1.199(3), N6–N7 1.148(3), N8–N9 1.098(3), N9–N10 1.185(3); N7–N6–N5 177.0(3), N8–N9–N10 173.0(3), N6–N5–Ge1 114.4(2), N5–Ge1–C2 89.1(1), N5–Ge1–C1 89.4(1), C1–Ge1–C2 89.5(1), Ge1–C2–N3 127.0(2), Ge1–C2–N4 128.0(2), N3–C2–N4 104.9(2), Ge1–C1–N1 127.3(2), Ge1–C1–N2 127.8(2), N1–C1–N2 104.9(2).

membered C₃N₂Ge ring with the closest Ge1–N8 contact of 2.706 Å. Both N₃ groups in **2** are almost linear with the N5–N6–N7 bond angle of 177.0(3)° and the N8–N9–N10 angle of 173.0(3)°, respectively. The N5–N6 bond distance of 1.199(3) Å and the N6–N7 bond distance of 1.148(3) Å of the Ge–N₃ moiety in **2** are close to those in **A** (1.197(3) Å, 1.144(4) Å),^{7a} **B** (1.199(7) Å, 1.152(8) Å),^{7b} **C** (1.198(4) Å, 1.149(4) Å),^{7c} and **D** (1.209 Å, 1.152 Å).^{7d} In contrast to the almost identical N–N distances in ionic N₃ groups,⁶ the counterion N₃⁻ in **2** gives rise to two slightly different N–N bond lengths (N8–N9 1.098(3) Å and N9–N10 1.185(3) Å) owing to the slight disorder of N₃⁻ in **2**. The Ge1–N5–N6 bond angle of 114.2(2)° is slightly smaller than the ideal value for an sp²-hybridized α -nitrogen atom. The covalent Ge1–N5 bond distance of 2.037(2) Å in **2** is comparable to those in **A–E** (**E** 2.034(3) Å, **A** 2.047(2) Å, **B** 1.979(5) Å, **C** 2.002(3) Å, **D** 1.969 Å).⁷ The Ge1–N5 bond in **2** is oriented nearly perpendicular to both Ge–C bonds with the N5–Ge1–C1 and N5–Ge1–C2 bond angle of 89.4(1)° and 89.1(1)°, respectively. The latter are slightly smaller than those in **1** (90.5(1)° and 91.8(1)°). The Ge–C bond distances (2.046(2) Å, 2.051(2) Å) in **2** are close to those in **1** (2.058(3) Å and 2.057(3) Å), but significantly shorter than that in NHC–GeCl₂ (2.112(2) Å).¹¹

In order to further examine the substitution ability of chlorine atoms in **1** toward other substrates, sodium tetraphenylborate NaBPh₄ was employed to react with **1**. It is found that the equimolar reaction of **1** with NaBPh₄ affords the [bNHC(Cl)Ge:]BPh₄ complex **3** (Scheme 2), in which only the chloride anion in the outer sphere of **1** was substituted by BPh₄⁻. In fact, the reaction of an excess amount of NaBPh₄ with **1** yields exclusively compound **3**. Compound **3** was isolated as an off-white solid in high yield (83%). Featuring the larger and lipophilic BPh₄ anion, the ion pair **3** is soluble even in THF (Fig. 2). The ESI-MS of compound **3** (negative ion mode) exhibits a signal for the BPh₄⁻ ion at $m/z = 319.16512$ (calc. 319.16526). In addition, the positive ion mode electrospray-MS of **3** shows the corresponding ion peak for the [bNHC–GeCl]⁺ cation at $m/z = 577.21492$ (calc. 577.21478). The ¹H- and ¹³C NMR spectra of **3** display resonances for the bNHC ligand and the BPh₄⁻ counter anion (see ESI†). Whereas compound **1** crystallizes in the orthorhombic space group *P*₂₁2₁2₁, compound **3** leads to crystals in the monoclinic space group *P*₂₁/*c*. The slight differences in the corresponding bond lengths and angles between **1** and **3** are shown in Table 1. In comparison to the N₃⁻ counterion in **2**, the BPh₄⁻ counterion in **3** is located far away from the Ge(II) site. Thus, akin to

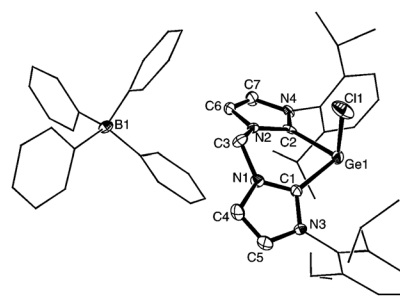


Fig. 2 Molecular structure of **3**. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms and acetonitrile molecules are omitted for clarity.

Table 1 Selected bond lengths (Å) and angles (°) for compounds **3** and **1**

	3	1
Ge1–Cl1	2.308(1)	2.310(1)
Ge1–C1	2.045(4)	2.057(3)
Ge1–C2	2.048(4)	2.058(3)
Cl1–Ge1–C1	92.0(1)	91.8(1)
Cl1–Ge1–C2	91.7(1)	90.5(1)
C1–Ge1–C2	84.9(2)	85.2(1)

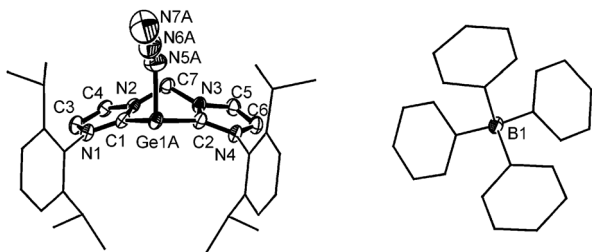


Fig. 3 Molecular structure of **4**. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms and three acetonitrile molecules are omitted for clarity. Ge and N₃ are in disorder, and Ge1B, N5B, N6B, and N7B are omitted for clarity. Selected bond distances (Å) and angles (°): Ge1A–N5A 2.003(5), G1A–C1 2.050(3), Ge1A–C2 2.054(3), N5A–N6A 1.179(6), N6A–N7A 1.155(5); N5A–N6A–N7A 175.7(8), N6A–N5A–Ge1A 117.9(4), N5A–Ge1A–C1 90.2(2), N5A–Ge1A–C2 90.4(2), C1–Ge1A–C2 84.4(1).

the situation in **1**, in the puckered six-membered C₃N₂Ge ring in **3** the Ge1 and C3 atoms are displaced away from the plane defined by C1, N1, N2, C2 in the same direction as the Ge1–Cl1 bonding vector is pointing (Fig. 2).

With **3** in hand, its reaction with an equimolar amount of NaN₃ yielded the expected [bNHC(N₃)Ge]:BPh₄ species **4**, in which the covalently bonded chlorine atom of **3** was replaced by the N₃ ligand, whereas the BPh₄[−] counter anion remained (Scheme 2). The reaction is very clean, and compound **4** can be isolated in 88% yield as an off-white solid. Similar to **3**, featuring a large BPh₄[−] anion, compound **4** is well soluble in THF. The IR spectrum of **4** (KBr pellets) exhibits the characteristic absorption at $\nu = 2078\text{ cm}^{-1}$ for the asymmetric N₃ stretching mode, which is in nearly the same position as that in **2** ($\nu_{\text{asym}}(\text{N}_3) = 2077\text{ cm}^{-1}$) and close to that in **D** ($\nu_{\text{asym}}(\text{N}_3) = 2075\text{ cm}^{-1}$).

Compound **4** has the same cation as **2**, but featuring a different anion (Fig. 3), which enables it to possess much different properties. The electrospray-MS of compound **4** (negative ion mode) exhibits a signal for BPh₄[−] at $m/z = 319.16515$ (calc. 319.16526). In addition, in the positive ion mode **4** shows an ion peak for the [bNHC–GeN₃]⁺ cation at $m/z = 584.25512$ (calc. 584.25515). The ¹H- and ¹³C NMR spectra of **4** display resonances for the bNHC ligand and the BPh₄[−] counter anion (see ESI[†]). Akin to **2** and **3**, compound **4** crystallizes in the monoclinic space group *P*2₁/*c*. There is disorder in the GeN₃ moiety (Fig. 3, only part A (GeA–N5A–N6A–N7A) is shown for clarity). The corresponding bond lengths and angles in the cations of **2** and **4** show only slight differences (Fig. 1 and 3). However, different from the N₃[−] counterion in **2**, but similar to that in **3**, the BPh₄[−] counterion in **4** is located far away from the cation. The six-membered C₃N₂Ge ring in **4** is puckered as in **1** and **3** and adopts a boat conformation with N2, N4, C1, and C2 being nearly coplanar,

and the atoms Ge1 and C7 displaced away from that plane in the same direction as the Ge1–N5 bonding vector is pointing.

In summary, the first azidogermiumylidene azide complex **2** with covalently and ionically bonded azides could be synthesized and successfully isolated by direct reaction of **1** with NaN₃. In contrast, by employing the weakly coordinating BPh₄[−] counterion the facile formation of the isolable chlorogermiumylidene tetraphenylborate complex **3** could be achieved, starting from the chlorogermiumylidene chloride **1**. Compound **3** can react with NaN₃ to afford the azidogermiumylidene tetraphenylborate complex **4** in high yield. Compounds **2–4** could be potential building blocks in the synthesis of novel germanium species and azido-containing materials. Respective studies are currently in progress.

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