Synthesis and Unexpected Reactivity of Germyliumylidene Hydride [:GeH]+ Stabilized by a Bis(N-heterocyclic carbene)borate Ligand

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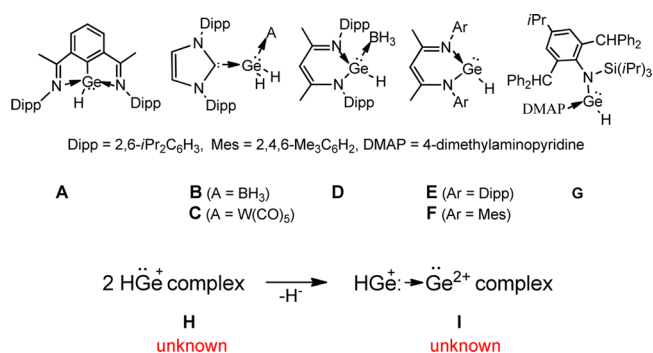
S *Supporting Information*

ABSTRACT: Employing the potassium salt of the monoanionic bis(NHC)borate **1** (NHC = N-Heterocyclic Carbene) enables the synthesis and isolation of the bis(NHC)borate-stabilized chlorogermyliumylidene precursor **2** in 61% yield. A Cl/H exchange reaction of **2** using potassium tri*sec.*-butylborhydride as a hydride source leads to the isolation of the first germyliumylidene hydride [HGe:+] complex **3** in 91% yield. The Ge(II)−H bond in the latter compound has an unexpected reactivity as shown by the reaction with the potential hydride scavenger $[Ph_3C]^+[B(C_6F_5)_4]^-$, furnishing the corresponding HGe: → CPh3 cation in the ion pair **4** as initial product. Compound **4** liberates HCPh3 in the presence of **3** to give the unusual dinuclear HGe: → Ge: cation in **5**. The latter represents the first three-coordinate dicationic Ge(II) species stabilized by an anionic bis(NHC) chelate ligand and a Ge(II) donor. All novel compounds were fully characterized, including X-ray diffraction analyses.

Akin to transition-metal hydrides, Group 14 hydrides such as R_3EH (E = Si, Ge, and Sn) are found to be important intermediates in some industrial and catalytic processes.[1] Moreover, the low-valent Group 14 hydrides such as R(H)E: and H_2E: possess more fascinating properties owing to the lone electron pairs at the E atoms. However, due to the high reactivity of these species, their preparation is challenging. By taking advantage of kinetic and thermodynamic stabilization several Lewis base- and/or acid-stabilized four-coordinate germylene hydrides **A−D**,[2] and three-coordinate germylene hydrides **E−G** (Scheme 1) could be prepared[3] and their reactivity toward selected small molecules has been explored.[2,3] However, the hydride abstraction of **A−G** to yield corresponding Ge(II) cations has not yet been reported to our best knowledge. Although cations of Ge(II), owing to their Lewis ambiphilic nature of carbene analogues, have received considerable research interest,[4−6] Ge(II) hydride cations such as the monoanionic bis(carbene) supported three-coordinate germyliumylidene hydride **H** and its corresponding Ge(II) dication complex **I** are currently unknown (Scheme 1).

Commonly, the synthesis of a Ge(II) hydride can be achieved via Cl/H exchange reaction of the corresponding Ge(II) chloride with a hydride source.[2,3] Recently, we reported neutral bidentate bis(NHC) (NHC = N-Heterocyclic Carbene)

**Scheme 1. Known Monomeric Germylene Hydride Complexes A−G vs Unknown Germyliumylidene Hydride Complex H and Ge(II) Complex I**

Dipp = 2,6-*iPr*2C6H3, Mes = 2,4,6-Me3C6H2, DMAP = 4-dimethylaminopyridine

| A | B (A = BH3) | D | E (Ar = Dipp) | G |
| | C (A = W(CO)5) | | F (Ar = Mes) | |

or bis(iminophosphorane) supported chlorogermyliumylidene chlorides.[5b,c] Unfortunately, the Cl/H exchange for the latter with common hydride sources does not lead to the respective Ge(II) hydride species, presumably, due to the outer-sphere chloride in the precursors which intervenes the desired Cl/H exchange. The interference of the outer-sphere chloride prompted us to synthesize a zwitterionic germyliumylidene chloride supported by a bis(NHC)borate for the access to the corresponding germyliumylidene hydride.

Treatment of $GeCl_2 \cdot$dioxane with potassium bis(NHC)-borate **1**, which can be prepared *in situ* from an imidazolium salt[7] with 2 mol equiv of $PhCH_2K$[8] in THF, led to the formation of zwitterionic germyliumylidene chloride **2** in moderate yield (61%, Scheme 2). The yellowish compound **2** is soluble in toluene and THF. Its composition was proven by elemental analysis, consistent ^1H, ^{13}C, ^{11}B NMR and HR-APCI-MS spectroscopy (see Supporting Information [SI]).

Scheme 2. Synthesis of the Zwitterionic Germyliumylidene Chloride 2 and the Corresponding Hydride 3
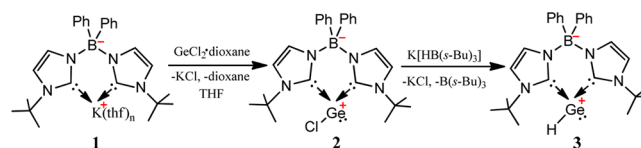
Compound **2** crystallizes as colorless rods in the orthorhombic space group *Fdd*2 (Figure 1, left). The Ge
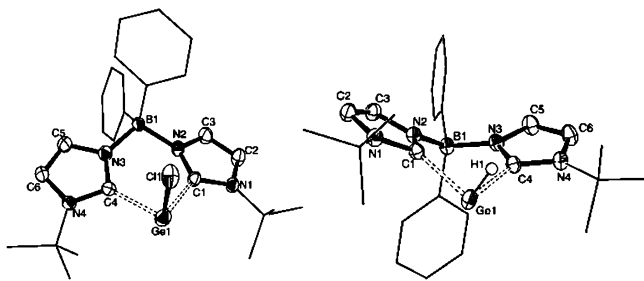

Figure 1. Molecular structures of **2** (left) and **3** (right). Thermal ellipsoids are drawn at 50% probability level. H atoms (except that at Ge atom in **3**) are omitted for clarity. Selected interatomic distances (Å) and angles (deg) for **2**: Ge1−Cl1 2.304(1), Ge1−C1 2.036(5), Ge1−C4 2.038(5); C4−Ge1−C1 91.2(2), C4−Ge1−Cl1 91.3(1), C1−Ge1−Cl1 96.5(1). For **3**: Ge1−C1 2.049(2), Ge1−C4 2.044(2), C1−Ge1−C4 90.8(1).

atom is three-coordinated by two ligating carbene-carbon atoms and one chlorine atom, featuring a distorted trigonal pyramidal geometry with the three Ge1−C1, Ge1−C4, and Ge1−Cl1 bonds nearly perpendicular to each other (ranging from 91.2 to 96.5°). The average Ge−C bond length of 2.037(5) Å in **2** is close to that in [L′(Cl)Ge:]Cl (Ge−C 2.057(3) Å) (L′= neutral bis(*NHC*) chelate ligand),[5c] but significantly longer than a Ge−C single bond (∼1.95 Å). Similarly, the Ge−Cl bond (2.304(1) Å) in **2** is comparable to that in [L′(Cl)Ge:]Cl (2.310(1) Å).[5c]

The Cl/H exchange reaction of **2** with K[HB(*s*Bu)₃] in THF at ambient temperature furnishes quantitatively the corresponding germyliumylidene hydride **3** (Scheme 2). The molecular ion peak of **3** is found at *m/z* = 487.20905 (calcd 487.20828, [M + H]⁺) in the HR-APCI-MS spectrum. In the ¹H NMR spectrum of **3** the proton resonance of Ge*H* (δ = 5.69 ppm) shows a dramatic upfield shift compared with the monomeric species **E** (δ = 8.08 ppm), **F** (δ = 8.25 ppm), and **G** (δ = 9.04 ppm).[3a,b,e] Moreover, a very strong stretching vibration at 1809 cm⁻¹ is observed in the IR spectrum of **3**. This corresponds to the Ge−H moiety, which is significantly shifted to higher wave numbers than those observed for **E** (1733 cm⁻¹), and **F** (1722 cm⁻¹), comparable to that for **G** (1812 cm⁻¹),[3a,b,e] but yet lower than those found for the four-coordinate Ge(II) hydrides **A** (1985 cm⁻¹) and **B** (1928 cm⁻¹).[2a,b]

Compound **3** is very stable both in the solid state and in solutions. From toluene at room temperature it crystallizes as colorless rods in the triclinic space group *P*1̄. The single crystal X-ray diffraction analysis confirms the deduced structure of **3** (Figure 1, right). The Ge−H moiety is disordered in two orientations with a 90:10 occupation ratio, and only the major component is shown in Figure 1. Similar to its precursor **2**, the Ge center in **3** is three-coordinate with a distorted trigonal pyramidal geometry. The six-membered ring C2N2BGe is strongly puckered in a boat conformation with N2, N3, C1, and C4 being nearly coplanar, and Ge1 and B1 displaced away in the same direction from that plane. The average Ge−C distance of 2.046 Å is close to that in its precursor **2** (2.037 Å).

The electronic nature of **3** has been analyzed by DFT calculations [B97-D/6-31G(d) Ge:cc-pVTZ-PP] (see SI for details). The calculated metric parameters of **3** are in good agreement with those obtained by X-ray diffraction (Ge−C

2.079 Å, C−Ge−C 88.9°). The HOMO (−4.01 eV) is depicted in Figure 3 (left) which clearly represents the lone pair of the Ge though it has considerable contribution from the Ge−H bond. The calculated Ge−H vibrational frequency (1802 cm⁻¹) is in excellent agreement with the experimental value (1809 cm⁻¹). The calculations reveal that the unusually strong Ge−H bond is attributed to the symmetric combination of the lone pairs of the *NHC*'s ligands and the Ge−H bond represented by HOMO-49 with relatively downshift in energy (−11.39 eV, Figure S8 in the SI). The NBO analysis reveals a large positive charge at the Ge center (+0.43) and a negative value for the H atom of the Ge−H moiety (−0.21) as well as a negative charge for the NHC rings (−0.11). The Wiberg Bond Indices show three bonds of the Ge atom (Ge−C: 0.75, Ge−H: 0.86), and the overall valence electrons of the Ge atom, according to NBO analysis, amount to 3.46 including the lone pair. Therefore, compound **3** can be best described as a zwitterionic species with two *NHC* donors stabilizing the [GeH]⁺ moiety (Scheme 2).

The hydridic character of the Ge−H moiety in **3** prompted us to examine its reactivity toward the trityl cation in [Ph₃C]⁺[B(C₆F₅)₄]⁻ as a potential hydride scavenger. The equimolar reaction of **3** with Ph₃C[B(C₆F₅)₄] furnishes two compounds **4** and **5** which could be isolated by fractional crystallization (Scheme 3). The orange compound **4** is the

Scheme 3. Reactivity of 3 towards [Ph₃C]⁺[B(C₆F₅)₄]⁻
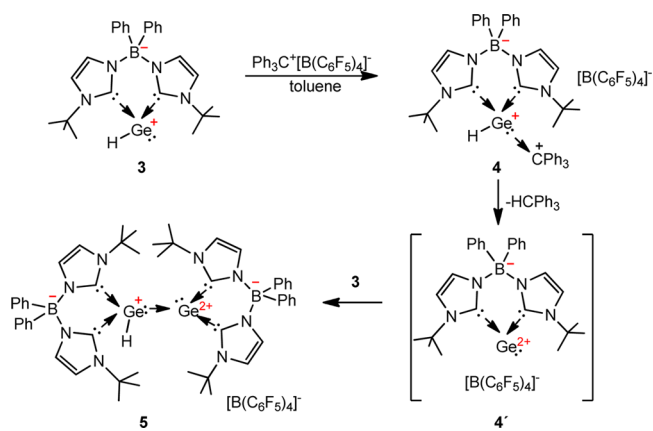
Ge(II) → CPh₃⁺ adduct of **3**, while compound **5** represents the unexpected adduct of **3** with the desired corresponding Ge(II) dication. Obviously, the desired two-coordinate Ge(II) dication is too reactive which precludes its isolation; it readily undergoes donor−acceptor stabilization by unreacted **3**. Accordingly, heating of the solution of **4** in acetonitrile at 80 °C affords HCPh₃ (¹H NMR) and a mixture of unidentified products; the corresponding two-coordinate Ge(II) dication in **4′** (Scheme 3) could not be detected under these reaction conditions. However, when compound **4** is allowed to react with an equimolar amount of **3** in acetonitrile solution at ambient temperature, it smoothly furnishes compound **5** along with HCPh₃. Consistently, the reaction of **3** with Ph₃C⁺[B(C₆F₅)₄]⁻ in the molar ratio of 2:1 in toluene affords compound **5** quantitatively. The yellowish compound **5** is stable even in boiling dry acetonitrile under nitrogen.

In *d₃*-acetonitrile compound **5** displays two sets of NMR signals for the bis(*NHC*)borates in the ¹H NMR spectrum corresponding to the moieties of **4′** and **3**, respectively (see SI). The Ge−*H* subunit in **5** resonates at δ = 5.20 ppm in the ¹H

NMR spectrum, showing only a slight upfield shift compared with that in **3** (δ = 5.69 ppm). Owing to the Ge $\rightarrow$ Ge coordination, the Ge–H stretching vibration in the IR spectrum of **5** gives rise to an absorption at 2050 cm^{-1}, which is at a much higher frequency compared with that for **3** (1809 cm^{-1}) and falls in the range of four-coordinate Ge(II)H and Ge(IV)H species (1953–2175 cm^{-1}).[9] In contrast, the proton of the Ge–H subunit of **4** resonates at δ = 7.28 ppm, exhibiting a strong downfield shift compared with that of **3** (δ = 5.69 ppm) and **5** (δ = 5.20 ppm). Due to the four-coordinate Ge center, the stretching vibration mode of the Ge–H moiety in **4** amounts 2152 cm^{-1}.

Single crystals of compound **4** can be obtained in acetonitrile solutions at 4 °C. The X-ray diffraction analysis of **4** reveals that the Ge atom in the cation (Figure 2, left) is four-coordinated by
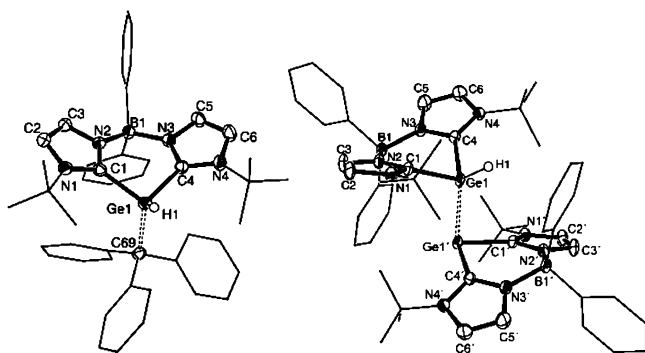

Figure 2. Structures of the cations in **4** (left) and **5** (right). Thermal ellipsoids are drawn at 50% probability level. H atoms (except those at Ge atoms) are omitted for clarity. Selected interatomic distances (Å) and angles (deg) for **4**: Ge1–C1 1.968(2), Ge1–C4 1.974(2), Ge1–C69 2.063(2), C1–Ge1–C4 97.9(1), C1–Ge1–C69 114.8(1), C4–Ge1–C69 116.5(1). For **5**: Ge1–Ge1′ 2.556, Ge1–C1 1.999(2), Ge1–C4 1.993(2), Ge1′–C1′ 2.046(2), Ge1′–C4′ 2.046(2), C1–Ge1–C4 92.5(1), C1′–Ge1′–C4′ 89.56.

the two carbene-carbon atoms C1 and C4, the hydrogen atom H1, and the alkyl carbon atom C69 of the Ph$_3$C$^+$ group. The Ge–C69 (2.063(2) Å) bond is significantly longer than a Ge–C single bond (around 1.95 Å), exhibiting its weak Ge–C interaction. It is likely that this weak Ge–C interaction makes the hydride abstraction of **4** possible upon addition of **3** as a donor. The Ge–C$_{carbene}$ distances of 1.968(2) and 1.974(2) Å in **4** are similar to those observed in the bis(*NHC*) coordinated Ge(0) species (1.967(2) and 1.962(2) Å).[5c]

From concentrated acetonitrile solutions, compound **5** crystallizes as yellowish crystals in the monoclinic space group $I2/a$. As shown by the results of the X-ray diffraction analysis, **5** comprises an ion pair of the novel Ge: $\rightarrow$ Ge cation (Figure 2, right) and the [B(C$_6$F$_5$)$_4$] anion. Both Ge atoms are disordered in two positions with a 50:50 occupation ratio and only one set of them is shown in Figure 2. The L(H)Ge and LGe moieties are linked via a Ge–Ge bond. The Ge–Ge distance of 2.556 Å in **5** is comparable to that in *NHC*-(Cl)$_2$Ge: $\rightarrow$ GeCl$_2$ (2.630(1) Å),[10] but significantly longer than that observed for a Ge–Ge single bond in digermanes (around 2.41 Å). The Ge atom in L(H)Ge is tetrahedrally coordinated, whereas that in the LGe subunit is three-coordinated and adopts a trigonal pyramidal geometry. Remarkably, the geometric parameters around both germanium centers are quite different. In the L(H)Ge moiety, the Ge–C distances of 1.993(2) and 1.999(2) Å are shorter than those in the LGe

moiety (2.046(2) Å). In fact, the former are close to those Ge–C distances in **4** (ave. 1.971 Å), but the latter resemble those in **3** (2.044(2) and 2.049(2) Å) and close to the Ge–C bond lengths of cationic Ge(II) compound (2.070(6) Å) described in ref 6a.

These anomalies in Ge–C bond distances can be explained by DFT calculations on the cation of **5**. The optimized structure is in good agreement with that obtained from X-ray diffraction analysis (Ge(H)–C 2.011 Å, Ge(H)–Ge 2.577 Å, Ge–C 2.081 Å). The results of the calculations support the importance of resonance structures to describe the electronic structure of **5** in light of the valence bond theory (Scheme 4);

Scheme 4. Selected resonance structures of the cation of 5
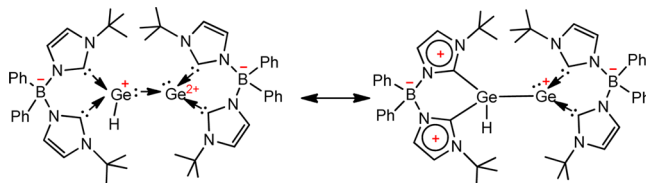
the Ge center of L(H)Ge moiety is close to a regular sp^3 Ge site with four covalent bonds including two covalent Ge–C bonds and the LGe: moiety represents a similar valence bond structure to that of **3**. The HOMO of **5** (−6.81 eV) is depicted in Figure 3 (right) which shows a lone pair at the Ge center of
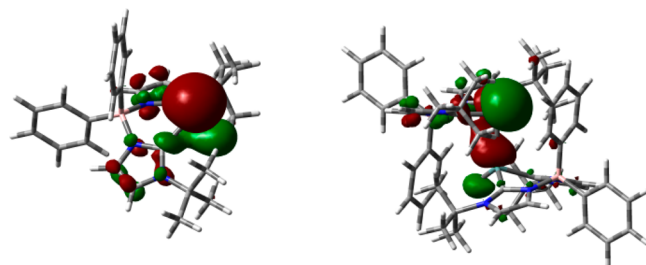

Figure 3. HOMO of **3** (left) and **5** (right).

the LGe moiety coordinated by the Ge center of the L(H)Ge part showing similarities to that of **3**. In fact, all the MOs of the LGe moiety in the cation of **5** closely resemble those of compound **3** described above (see SI). The NBO analysis of the cation of **5** also supports a sp^3 Ge resonance structure; the s character of the Ge–C bond in the LGe moiety is only 6.80%, similar to that in **3** (8.30%), indicating a low hybrid character, and that the lone pair of a *NHC* ligand donates to the vacant 4p-orbital of the Ge center. In contrast, the s character of the Ge–C bond in the L(H)Ge moiety is significantly larger (19.15%), suggesting a more classical Ge–C σ bond character with a sp^3 Ge atom as depicted in the resonance structure in Scheme 4 (right) (see SI for details).

In summary, we reported the synthesis and isolation of the first [HGe:]$^+$ complex **3**, supported by the monoanionic bidentate bis(*NHC*)borate ligand. The latter is easily accessible by Cl/H exchange reaction of the corresponding Ge(II) chloride **2** with K[HB(sBu)$_3$] in THF. Reaction of **3** with the trityl salt [Ph$_3$C]$^+$[B(C$_6$F$_5$)$_4$]$^-$ as a hydride scavenger in the molar ratio of 2:1 furnishes the unprecedented three-coordinate [Ge:]$^{2+}$ complex **5**. The successful protocol to form low-coordinate and low-valent main-group cations could pave the way to even stronger Lewis acid analogues with silicon and

group 13 centers. Respective investigations are currently in progress.

ASSOCIATED CONTENT

ⓢ Supporting Information

Experimental details for the synthesis and spectroscopic data of **2**−-**5** and crystallographic data for **2**−**5**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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