Isolation and Structure of Germylene–Germyliumylidenes stabilized by N-Heterocyclic Imine

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Dedicated to Professor F. Ekkehardt Hahn on the occasion of his 60th birthday

Abstract: The ditopic germanium complex [FGe(NIPr)$_2$Ge][BF$_4$] (**3**[BF$_4$], IPr = 1,3-bis(2,6-diisopropylphenyl)imidazolin-2-ylidene) is prepared by the reaction of the amino(imino)germylene (Me$_3$Si)$_2$NGeNIPr (**1**) with 2 equiv of BF$_3$•OEt$_2$. This monocation is converted to the germylene-germyliumylidene **3**[BAr$^F_4$] (Ar^F = 3,5-(CF$_3$)$_2$-C$_6$H$_3$) by treatment with Na[BAr$^F_4$]. The tetrafluoroborate salt **3**[BF$_4$] reacts with 2 equiv of Me$_3$SiOTf to give the novel complex [(OTf)(GeNIPr)$_2$][OTf] (**4**[OTf]), which affords **4**[BAr$^F_4$] and **4**[Al(OR^F)$_4$] (R^F = C(CF$_3$)$_3$) anion exchange with Na[BAr$^F_4$] or Ag[Al(OR^F)$_4$], respectively. The computational, as well as crystallographic study reveals that **4$^+$** has significant bis(germyliumylidene) dication character.

Germyliumylidenes, germanium(II) monocations, have been attractive targets for fundamental research because they may exhibit both electrophilic and nucleophilic character.[1] Since the seminal work on the half-sandwich germanocene cation [(η^5-C$_5$Me$_5$)Ge:]$^+$,[2] various types of donor-stabilized germyliumylidenes have been reported.[3] Of the diverse types of synthetic methods for the preparation of germyliumylidenes that have been studied, the halide abstraction from suitable germylene precursors is found to be the most popular one. For instance, the aminotroponiminate Ge(II) monocation **I** was synthesized via removal of chloride from a respective chlorogermylene using (η^5-C$_5$H$_5$)ZrCl$_3$ as a halide scavenger (Figure 1).[3a] In another example, chloride abstraction with Li[Al(OR^F)$_4$] (R^F = C(CF$_3$)$_3$) furnished a bulky amide-substituted germyliumylidene.[3g]

It is reasonable to assume that the cationic charge would increase the electrophilicity of germyliumylidenes as compared to their neutral congeners and render these compounds particularly prone to aggregation. In fact, highly charged

dicationic germanium(II) complexes require strong donor ligands and a large coordination number of the metal for isolation.[4] Accordingly, reports on dicationic bis(germyliumylidene) complexes which comprise two cationic metal atoms in the same molecule are scarcely found in the literature. One would expect that the stability of such compounds is additionally impaired by severe Coulomb repulsion between the metal centers. In sharp contrast, neutral inter-connected and spacer-separated bis(germylene) compounds have been investigated thoroughly and several representatives of this compound class were described.[5,6] In addition, the use of bis(germylene) as a chelating ligand towards transition metals[7] contributed to the development of this field.[7,8] In fact, some of the reported bis(germylene)-metal complexes, showed pronounced catalytic activity for C—C coupling [8d] or hydroboration.[8b]

As an intriguing example as to how charge distribution into the adjacent ligand system can reduce Coulomb repulsion between metal centers serves the dianionic disilicate **II** (Figure 1).[9] In analogy to this dianionic complex (**II**), Tobita and co-workers synthesized the NHC-stabilized dicationic complexes of type **III** in which the repulsion between the two central germanium atoms is decreased by delocalization of a positive charge into the imidazoline rings (Figure 1).[10] These complexes (**III**) can be regarded as dimers of the respective parent metallogermylene monocations that form a Ge=Ge double bond.

Since the seminal report on monomeric bis(amido) germylene and stannylene comprising a EN$_2$Si (E = Ge, Sn, Pb) scaffold by Veith and co-workers (**IV**, Figure 1),[11] a rapidly growing number of papers have been published concerning the research on N-heterocyclic metallylenes. Interestingly, the solid structure of the germylene (**IV**) was not reported before 2014.[12]
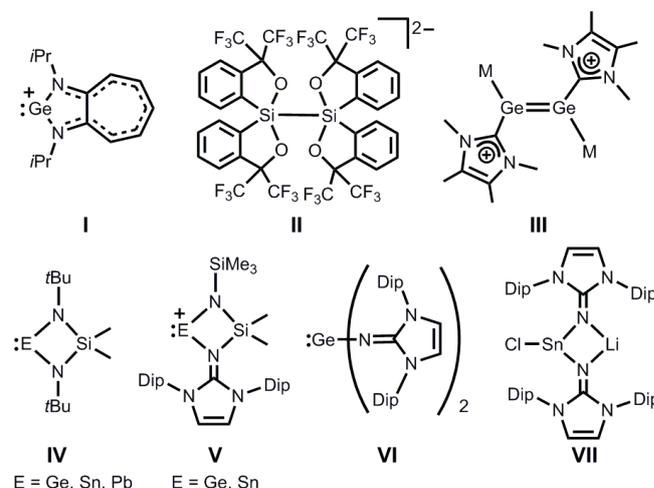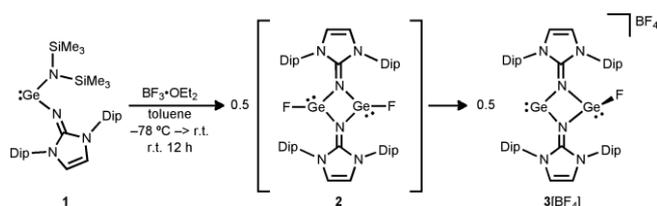
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Figure 1. Selected group 14 element compounds: the monotopic germanium(II) compounds **I**, **IV**, **V**, **VI** the dimeric compound (**III**; M = C$_5$Me$_5$(CO)$_3$W), as well as the dianionic disilicate **II** and the stannylenoid **VII**.

Scheme 1. Synthesis of the germyliumylidene salt **3**[BF$_4$].

We reported the isolation of the imidazolin-2-imino-substituted Ge(II) and Sn(II) monocations **V** containing a four-membered EN$_2$Si (E = Ge, Sn) ring system (Figure 1). Their formation is promoted by the delocalization of positive charge density into the imidazoline ring.[13,14] Notably, this imino system was also implemented in the bis(imino)germylene **VI**[15] and the bis(imino)stannylenoid **VII**[16] and the strongly related imidazolidine-2-iminato ligand (saturated in the ligand backbone) has been successfully used for the synthesis of a phosphorus mononitride radical cation.[17] These studies reveal that the imidazolin-2-imino group is particularly efficient in the stabilization of electron-deficient species. Herein we describe the isolation of hitherto unknown cationic germanium heterocycles and a new spacer-separated bis(germylene) bistriflate with pronounced bis(germyliumylidene) character.

Treatment of the amino(imino)germylene **1** with 2 equiv of BF$_3$·OEt$_2$ afforded the tetrafluoroborate salt **3**[BF$_4$] the formation of which proceeds via the intermediate fluorogermylene dimer [FGeNIPr]$_2$ (**2**) as suggested by DFT calculations (Scheme 1, Figure S35).[18] Thus, the boron trifluoride subsequently assumes the role of a fluorination reagent, as well as a fluoride abstraction agent. The formulation of **3**[BF$_4$] was confirmed by multinuclear NMR spectroscopy and high resolution mass spectrometry. In the X-ray single crystal structure analysis we find a highly disordered germanium-bonded fluorine atom which possesses a 50% site-occupancy factor at each of the two Ge-atoms. Due to this disorder, we could not assign the germylene site and the germyliumylidene site in the solid-state structure of **3**[BF$_4$] (Figure S28).[18]

The conversion of **3**[BF$_4$] with Na[BAr$^F_4$] (Ar^F = 3,5-bis(trifluoromethyl)phenyl) led to the formation of **3**[BAr$^F_4$] by anion exchange. In the molecular structure derived from X-ray single crystal analysis the disorder of the Ge-bonded fluorine atom as in **3**[BF$_4$] is not observed. We find that the cation is marked by a distorted square planar Ge$_2$N$_2$ ring as a main structural feature (Figure 2). It exhibits two longer Ge–N$_{imine}$ distances at the Ge1 atom that bears a fluoride substituent (2.025(3) Å, 2.030(3) Å) and two shorter Ge–N$_{imine}$ bond lengths at the Ge2 center (1.876(3) Å, 1.897(3) Å). In compliance with this finding the N1–Ge1–N4 angle of 74.90(11)º is smaller than the N1–Ge2–N4 angle of 81.64(11)º. The Ge–F bond length of 1.800(4) Å falls within the range for germanium–fluorine single bonds.[19] We suggest that the bonding situation in **3**$^+$ is described in high approximation by the resonance structure **A1** rather than the formulation **A2** (Scheme 2). The former represents a bis(imino)germylene-stabilized fluorogermyliumylidene and the

latter an iminogermyliumylidene aggregated with an iminofluorogermylene via two germanium-nitrogen dative bonds. Interestingly, the coordinating properties of ligand systems that comprise divalent metal atoms of the group 14 elements but bond via adjacent functionalities rather than the ylidenic centers have scarcely been investigated. Breher and co-workers reported unique bis(stannylenes), where two tin(II) centers are linked head-to-tail via the pyrazole fragments.[20] This arrangement is energetically favored over distannene composed of an Sn=Sn double bond. Furthermore, Power and co-workers used the metallylene compound **VIII** for the synthesis of the molybdenum complex **IX** in which the transition metal prefers chelate-fashioned coordination by the two sulfur atoms instead of binding to the low-valent metal center (Scheme 3).[21] A notable change in the SES fragment (E = Ge or Sn) upon transformation of **VIII** into **IX** is the elongation of the E–S bond with concomitant decrease of the S–E–S bond angle. Accordingly, the Ge2–N$_{imine}$ distances in the ditopic cation **3**$^+$ are increased with respect to the monotopic bis(imino)germylene **VI** (1.876(3) Å and 1.897(3) Å vs. 1.8194(15) Å).[21] Moreover, the N1–Ge2–N4 angle of 81.64(11)º is considerably more acute than the N–Ge–N angle of 99.48(10)º in **VI**. These comparisons between **VIII** and **IX**, as well as **VI** and **3**$^+$ affirm the suggested resonance structure **A1** for **3**$^+$ with its marked cationic fluorogermyliumylidene moiety. We conclude that the bis(imino)germylene group functions as a bidentate ligand that bonds to the Ge(II)$^+$ center via the nitrogen atoms of the imino functionalities. The efficiency of the bis(imino) group to stabilize the cationic metal center is shown by the C$_{NHC}$–N$_{imine}$ distances (NHC = N-heterocyclic carbene = imidazoline-2-ylidene) of 1.324(4) Å and 1.334(4) Å in **3**$^+$ which exceed the 1.273(2) Å reported for **VI**.[15] The delocalization of positive charge density into the imidazoline ring is illustrated by resonance structure **A3**, as well as **A4** (Scheme 2).
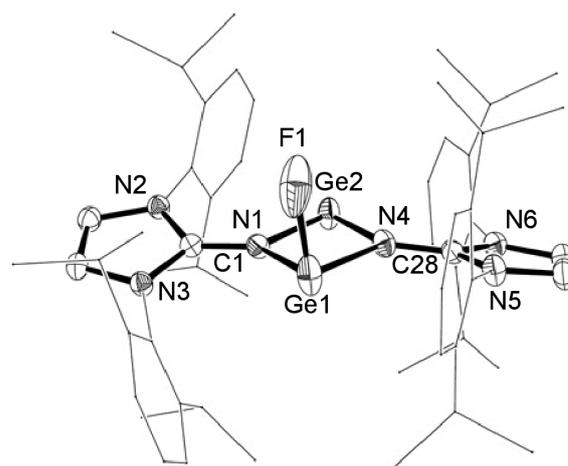

Figure 2. ORTEP representation of the molecular structure of the cation in **3**[BAr$^F_4$]; The thermal ellipsoids are at the 40% probability level. Hydrogen atoms and solvent molecules are omitted for clarity. For disordered atoms only the higher occupied site is shown. Dip groups are depicted as stick models. Selected bond lengths (Å) and bond angles (deg): Ge1–F1, 1.800(4); Ge1–N1, 2.030(3); Ge1–N4, 2.025(3); Ge2–N1, 1.876(3); Ge2–N4, 1.897(3); N1–C1, 1.324(4); N2–C1, 1.365(4); N3–C1, 1.357(4); N4–C28, 1.334(4); N5–C28, 1.344(5); N6–C28, 1.357(4); F1-Ge1-N4, 94.78(15); F1-Ge1-N1, 90.70(14); N1-Ge1-N4, 74.90(11); N1-Ge2-N4, 81.64(11).
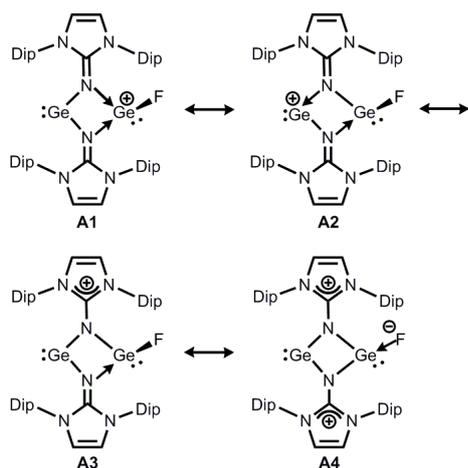
Scheme 2. Selected resonance structures of **3⁺** (Dip = 2,6-diisopropylphenyl).
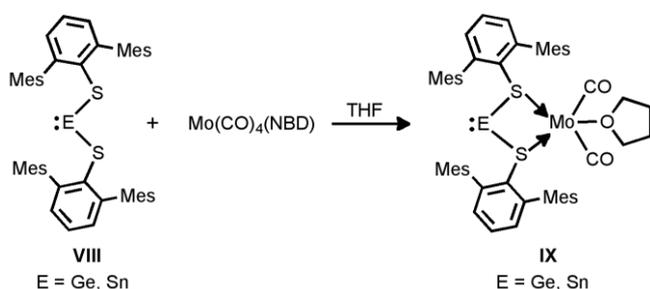

Scheme 3. Conversion of **VIII** to the metal complex **IX** as reported by Power (NBD = bicyclo[2.2.1]hepta-2,5-diene).[21]

In order to shed light on the validity of the suggested resonance structures theoretical calculations for **3⁺** were carried out at the B3LYP level.[18] The MBOs (Mayer Bond Order) of the Ge1−N_{imine} bonds were both calculated to be 0.55 and this value is significantly smaller than the corresponding one of the bis(imino)germylene **VI** (1.12),[18] and even reduced relative to the germyliumylidene cation in **V** (0.68),[14,18] which underlines the high dative bond character of the Ge1–N_{imine} interactions. In comparison, we determined MBOs of 0.89 for the Ge2–N_{imine} bonds in **3⁺**. In accordance with our structural discussion these data verify the germylene-germyliumylidene formulation **A1**. In line with the expectation the MBO of the C_{NHC}–N_{imine} bond (1.32) in **3⁺** is comparable to that of **V** (1.24). In addition, we performed NRT (Natural Resonance Theory) analysis in order to gain deeper insight into the nature of the structure of **3⁺**. Evaluation of the relative contributions of all important resonance structures for compound **3⁺** elucidates that the germylene-germyliumylidene formulation **A1** (53.7%) is dominant over the resonance structure **A2** (8.9%) to a large degree. Additionally, **3⁺** possesses relevant imidazolium cation character (**A3**, 27.6%). Interestingly, resonance structures of type **A4**, in which formal positive charge is located at both imidazolium rings with a fluoride anion coordinated to Ge1, have a non-negligible role in the description of **3⁺** (9.8%, Scheme 2). The HOMO for **3⁺** is mainly the antisymmetric combination of the two lone pairs of the Ge centers (Figure S30).[18] The LUMO for **3⁺** is essentially

the vacant p-type atomic orbital on the Ge(II) atom (Ge2) which supports **2** as an intermediate during the formation of **3⁺** (Figure S30).[18]

With the intention to synthesize a conceivable dicationic [GeNIPr]₂²⁺ species, referred to as bis(germyliumylidene), we converted **3**[BF₄] with two equivalents of Me₃SiOTf as a fluoride scavenger. This resulted in the formation of the triflate salt **4**[OTf] in (Scheme 4). At ambient temperature no decomposition of this compound was detected in the solid state, even after storage for weeks under an inert atmosphere. A CD₃CN solution of **4**[OTf] is stable at temperatures up to 60 °C. Unfortunately, X-ray diffraction-quality crystals of **4**[OTf] could not be obtained. The salt (**4**[OTf]) was converted to **4**[BArF₄] by anion exchange with Na[BArF₄]. It is of note that the dicationic complex [GeNIPr]₂-[BArF₄]₂ was not generated by treatment with an excess amount of Na[BArF₄].[18] Single crystals of **4**[BArF₄] suitable for X-ray diffraction analysis were retrieved from a CH₂Cl₂ solution at −30 °C. Similarly, the reaction of **4**[OTf] with the silver salt of the perfluorinated aluminate anion, [Al(ORF)₄]⁻ afforded the aluminate salt **4**[Al(ORF)₄]. This reactivity between **4**[OTf] and Ag[Al(ORF)₄] is contrasted by the treatment of amido-substituted chlorogermylene with Ag[Al(ORF)₄], after which formation of a chlorogermylene-silver complex was observed.[3g] The Ge₂N₂ germacycle unit possesses the same structure in **4**[BArF₄] and **4**[Al(ORF)₄]. Therefore, only the structure of the cation of **4**[BArF₄] is depicted in Figure 3. The structural features of **4**[Al(ORF)₄] are reported in the Supporting Information (Figure S29).[18] The molecular structure revealed that, akin to **3⁺**, the Ge₂N₂ ring in **4⁺** is distorted from square planarity to rhombic geometry. The distances between the Ge- and N_{imine} atoms range from 1.949(2) Å to 1.960(2) Å, which is longer than that of the neutral bis(imino)germylene **VI** (1.8194(15) Å).[15] This emphasizes the partial dative-bond character for the germanium−nitrogen interactions in **4⁺**. The C_{NHC}−N_{imine} bonds (1.329(4) Å, 1.335(4) Å) are elongated as compared to those of neutral iminogermylenes (1.296(3) Å, 1.273(2) Å),[14,15] but fall well inside the range of those of the cationic compounds **V**[13,14] and **3⁺** (1.32–1.34 Å), suggesting the delocalization of positive charge into the imidazoline rings. Interestingly, the triflato group in
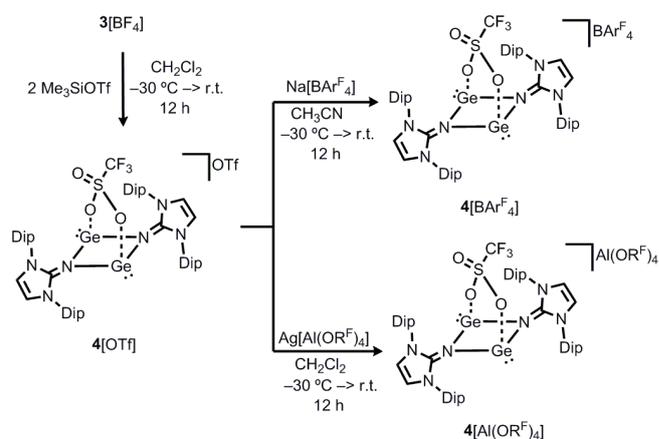
Scheme 4. Synthesis of the bis(triflate) **4**[OTf] and its conversion to the borate salt **4**[BArF₄], as well as the perfluoroalkoxyalanate **4**[Al(ORF)₄] (Dip = 2,6-diisopropylphenyl, ArF = 3,5-(CF₃)₂-C₆H₃, RF = C(CF₃)₃).

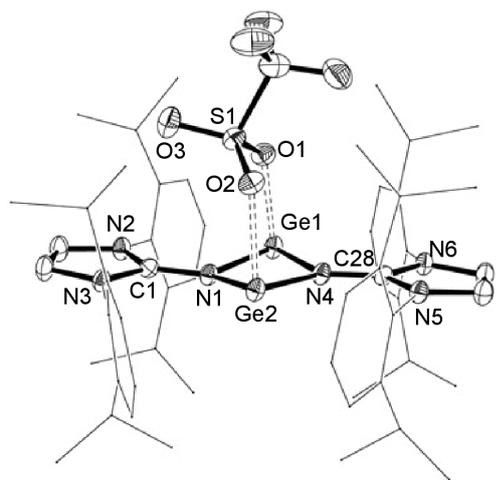**Figure 3.** ORTEP representation of the molecular structure of the cation in **4**[BAr$^F_4$] in the solid state. Thermal ellipsoids are at the 40% probability level. Dip groups are depicted as stick models. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and bond angles (deg): Ge1-N4, 1.956(2); Ge1-N1, 1.959(2); Ge1-O1, 2.250(2); Ge2-N4, 1.949(2); Ge2-N1, 1.960(2); Ge2-O2, 2.269(2); N1-C1, 1.329(4); N2-C1, 1.363(4); N3-C1, 1.367(4); N4-C28, 1.335(4); N5-C28, 1.363(4); N6-C28, 1.362(4); N1-Ge1-N4, 78.18(10); N1-Ge1-O1, 87.53(9); N4-Ge1-O1, 90.10(9); N1-Ge2-N4, 78.34(10); N1-Ge2-O2, 88.22(9); N4-Ge2-O2, 88.60(9); C1-N1-Ge1, 128.0(2); C1-N1-Ge2, 128.5(2); Ge1-N1-Ge2, 100.80(10); C28-N4-Ge2, 129.3(2); C28-N4-Ge1, 129.1(2); Ge1-N4-Ge2 101.31(10).
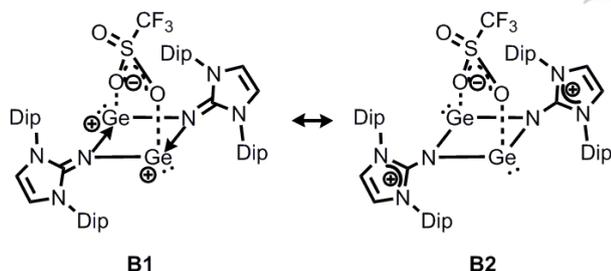
Scheme 5. Selected resonance structures of **4**$^+$ (Dip = 2,6-diisopropylphenyl).

4[BAr$^F_4$] bridges the two germanium centers with the formation of two $\mu_1{}^1$ type coordinative interactions between the metals and two oxygen atoms. The Ge–O$_{triflate}$ distances in **4**$^+$ (2.250(2) Å, 2.269(2) Å) exceed the scope of typical Ge–O bond lengths (1.75–1.85 Å)[22] and fall within the common range of Ge−O$_{triflate}$ distances (1.91–2.58 Å),[23] demonstrating the bidentate coordination mode of the triflate ligand. A related structural motif has been reported for cyclic bis(triflate)dibismadiazane [(TfO)Bi(NTer)]$_2$ (Ter = 2,6-bis(2,4,6-trimethylphenyl)phenyl).[24]

In order to gain further insight into the electronic properties of the germanium(II) cation **4**$^+$, quantum chemical calculations were carried out. The calculated MBOs for the Ge–N$_{imine}$ bonds in **4**$^+$ amount to 0.74 each, which is significantly smaller than that of **VI** (1.12) though somewhat larger than the germanium-imino dative bond of **V** (0.68). Moreover, the bonding characteristics of **4**$^+$ were analyzed by means of NRT. The study shows that the

dominant resonance structures are represented by **B1** (71.6 %), in which a positive charge resides on each Ge(II) center and a coordinated triflato moiety bears a negative charge (Scheme 5). Resonance structures of type **B2** (28.4%) have also considerable weight and account for the imidazolium cation character of **4**$^+$. For comparison, we calculated the optimized structure of the hypothetical dication [(GeNIPr)$_2$]$^{2+}$ by removing the bridging triflate anion from **4**$^+$. We found that the structural parameters of [(GeNIPr)$_2$]$^{2+}$ are in good agreement with those of the triflate-germyliumylidene **4**$^+$, which indicates that the bridging triflate has a minor effect on the geometry of the dicationic moiety. However, the presumed bis(germyliumylidine) character for [(GeNIPr)$_2$]$^{2+}$ is mitigated by its NRT analysis for which the contribution of imidazolium cation resonance structures as represented by **B2** has higher weight (39.1%) in comparison with that in **4**$^+$ (28.4%) (Figure S34). This is probably due to destabilization of the hypothetical bis(germyliumylidene) dication by the electronic repulsion between the two Ge(II) centers.[18] This result implies that the coordinated triflate anion is crucial for the stabilization of the bis(germyliumylidene) form **B1**. The LUMO and the LUMO+1 for **4**$^+$ exhibit vacant p-orbitals on the Ge(II) centers (Figure S31).[18] The HOMO corresponds to the π-orbitals of the imino ligands while HOMO−1 shows mainly the antisymmetric combination of the lone pair orbitals on the germanium centers which indicates consistent picture with the NRT analysis.

Preliminary investigations of the reactivity of **4**$^+$ revealed its remarkably high stability: no reactions proceeded upon conversion with strong Lewis bases (e.g. 4-dimethylaminopyridine, 1,3,4,5-tetramethylimidazolin-2-ylidene), Lewis acids (e.g. Me$_3$SiCl, Me$_3$SiBr), small molecule substrates (e.g. Me$_3$SiCN, Me$_3$SiN$_3$, S$_8$), as well as selected transition metal complexes (e.g. Fe$_2$(CO)$_9$, Ni(cod)$_2$, (Ph$_3$P)$_2$Pt(C$_2$H$_4$); cod = 1,4-cyclooctadiene).

In summary, we report the syntheses of the imino-stabilized bisgermanium monocation **3**[BF$_4$] and its derivative **3**[BAr$^F_4$] obtained via anion exchange. The cation **3**$^+$ marks a unique germylene-germyliumylidene species which features a two-coordinate germylene and a three-coordinated germyliumylidene functionality incorporated into a four-membered digermametallacycle. Additionally, the substitution of fluoride in **3**[BF$_4$] by triflate yields **4**[OTf], which can be converted via salt metathesis to **4**[BAr$^F_4$], as well as **4**[Al(OR^F)$_4$] with one triflato group coordinated to the germanium centers in a bridging fashion and a non-coordinated counteranion. Computational study of **4**$^+$ show that the [GeNIPr]$_2$ moiety possesses properties of a dication which suggests considerable bis(germyliumylidene) character for this ionic compound.

Acknowledgements

Keywords: germanium • germylene • germyliumylidene • dication • imine

[1] For review on germyliumylidenes see: V. S. V. S. N. Swamy, S. Pal, S. Khan, S. S. Sen, *Dalton Trans.* **2015**, *44*, 12903 and references cited therein.

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COMMUNICATION

Germylene-Fluorogermyliumylidene   Germylene-Triflatogermyliumylidene
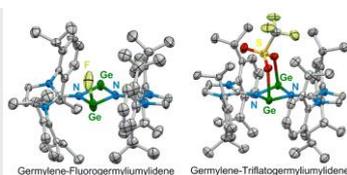
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Isolation and Structure of Germylene–Germyliumylidenes stabilized by N-Heterocyclic Imine

Double charge: A monocationic four-membered germacycle is prepared by fluorination of an amino(imino)germylene followed by fluoride abstraction. The nature of the bonding situation is analyzed computationally and indicates that the germylene-stabilized germyliumylidene character is dominant. Reaction of germylene-germyliumylidene with Me$_3$SiOTf affords a unique triflate-substituted germylene-germyliumylidene with pronounced dicationic bis(germyliumylidene) character.