

Structure Elucidation

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Isolation and Structure of Germylene-Germylumidenes Stabilized by N-Heterocyclic Imines

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

Abstract: The ditopic germanium complex $FGe(NIPr)_2Ge-[BF_4]$ (**3**[BF_4]; $IPr = 1,3$ -bis(2,6-diisopropylphenyl)imidazo-*lin*-2-ylidene) is prepared by the reaction of the amino(imino)germylene ($Me_3Si)_2NGeNIPr$ (**1**) with $BF_3 \cdot OEt_2$. This monocation is converted into the germylene-germyliumylidene **3**[BAR^F_4] [$Ar^F = 3,5-(CF_3)_2-C_6H_3$] by treatment with $Na[BAR^F_4]$. The tetrafluoroborate salt **3**[BF_4] reacts with 2 equivalents of Me_3SiOTf to give the novel complex $(OTf)-(GeNIPr)_2[OTf]$ (**4**[OTf]), which affords **4**[BAR^F_4] and **4**[$Al(OR^F)_4$] [$R^F = C(CF_3)_3$] after 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.

Germylumidenes, 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 [$(\eta^5-C_5Me_5)Ge$]⁺,^[2] various types of donor-stabilized germylumidenes have been reported.^[3] Of the diverse types of synthetic methods for the preparation of germylumidenes which have been studied, the halide abstraction from suitable germylene precursors is found to be the most popular one. For instance, the aminotroponimate Ge^{II} monocation **A** was synthesized by removal of chloride from a respective chlorogermylene using $(\eta^5-C_5H_5)ZrCl_3$ 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 germylumylidene.^[3g]

It is reasonable to assume that the cationic charge would increase the electrophilicity of germylumidenes as compared to their neutral congeners and render these compounds

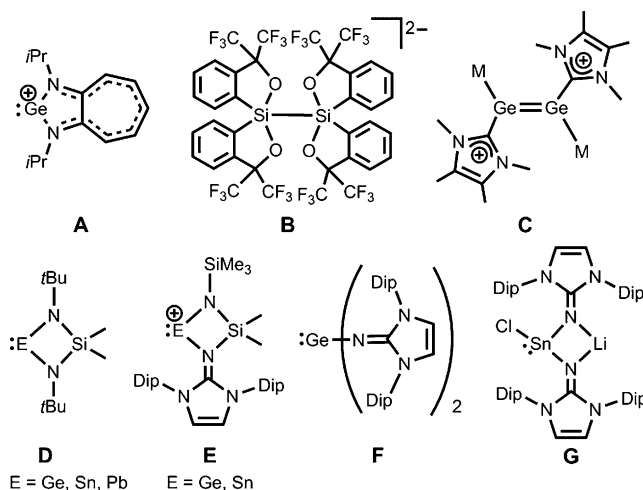


Figure 1. Selected group 14 element compounds: the monocationic germanium(II) compounds **A**, **D**, **E**, **F**, the dimeric compound **C**; $M = C_5Me_5(CO)_3W$, as well as the dianionic disilicate **B** and the stannylene **G**. Dip = 2,6-diisopropylphenyl.

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 Coulombic repulsion between the metal centers. In sharp contrast, neutral interconnected 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]

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

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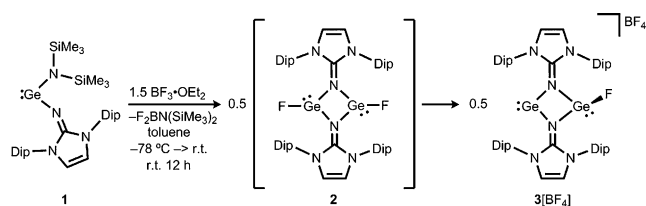
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Since the seminal report on monomeric bis(amido)germylene and stannylene comprising a EN_2Si ($\text{E} = \text{Ge}, \text{Sn}, \text{Pb}$) scaffold by Veith and co-workers (**D**, Figure 1),^[11] a rapidly growing number of papers have been published concerning the research on N-heterocyclic metallylenes. Interestingly, the solid structure of **D** was not reported before 2014.^[12]

We reported the isolation of the imidazolin-2-imino-substituted Ge^{II} and Sn^{II} monocations **E** containing a four-membered EN_2Si ($\text{E} = \text{Ge}, \text{Sn}$) 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 **F**^[15] and the bis(imino)stannylene **G**^[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 $\text{BF}_3 \cdot \text{OEt}_2$ afforded the tetrafluoroborate salt **3** $[\text{BF}_4]$, the formation of which proceeds via the intermediate fluorogermylene dimer $[\text{FGeNIPr}]_2$ (**2**) as suggested by DFT calculations (Scheme 1; see Figure S35 in the Supporting Informa-



Scheme 1. Synthesis of the germyliumylidene salt **3** $[\text{BF}_4]$.

tion).^[18] Thus, the boron trifluoride subsequently assumes the role of a fluorination reagent, as well as a fluoride abstraction agent. The formulation of **3** $[\text{BF}_4]$ was confirmed by multinuclear NMR spectroscopy and high-resolution mass spectrometry. In the single-crystal X-ray 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. Because of this disorder, we could not assign the germylene site and the germyliumylidene site in the solid-state structure of **3** $[\text{BF}_4]$ (see Figure S28).^[18]

The conversion of **3** $[\text{BF}_4]$ with $\text{Na}[\text{BAR}^{\text{F}}_4]$ ($\text{Ar}^{\text{F}} = 3,5$ -bis(trifluoromethyl)phenyl) led to the formation of **3** $[\text{BAR}^{\text{F}}_4]$ by anion exchange. In the molecular structure derived from single-crystal X-ray analysis the disorder of the Ge-bonded fluorine atom as in **3** $[\text{BF}_4]$ is not observed. We find that the cation is marked by a distorted square-planar Ge_2N_2 ring as a main structural feature (Figure 2). It exhibits two longer $\text{Ge}-\text{N}_{\text{imine}}$ distances at the Ge1 atom which bears a fluoride substituent (2.025(3) Å, 2.030(3) Å) and two shorter $\text{Ge}-\text{N}_{\text{imine}}$ bond lengths at the Ge2 center (1.876(3) Å, 1.897(3) Å).

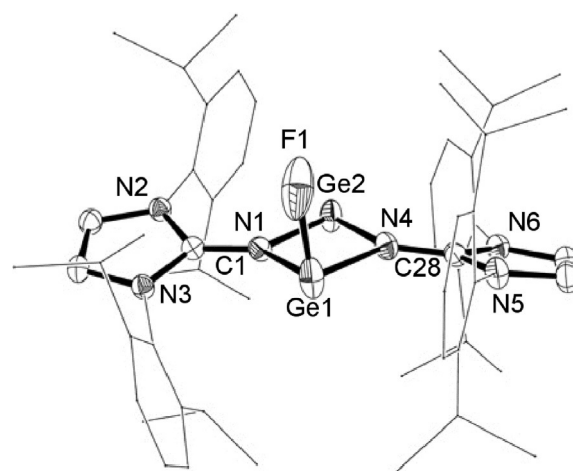
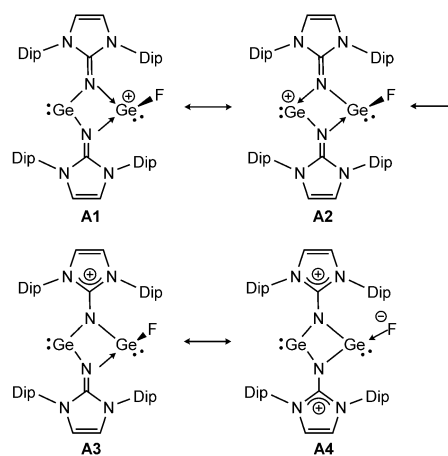


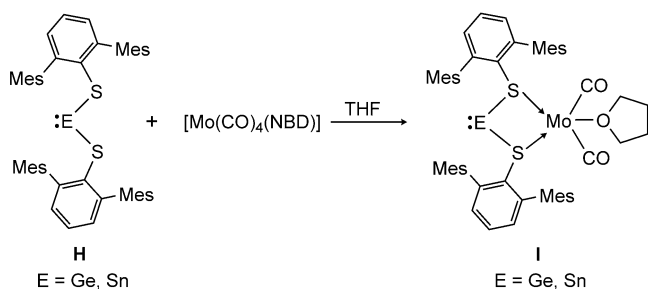
Figure 2. ORTEP representation of the molecular structure of the cation in **3** $[\text{BAR}^{\text{F}}_4]$.^[25] The thermal ellipsoids are at the 40% probability level. Hydrogen atoms are omitted for clarity. For disordered atoms only the higher occupied site is shown. Dip groups are depicted as stick 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).

In compliance with this finding the N1-Ge1-N4 angle of $74.90(11)^\circ$ is smaller than the N1-Ge2-N4 angle of $81.64(11)^\circ$. The $\text{Ge}-\text{F}$ bond length of 1.800(4) Å falls within the range for $\text{Ge}-\text{F}$ 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 fluoro-germyliumylidene, and the latter an iminogermyliumylidene aggregated with an iminofluorogermylene by two germanium–nitrogen dative bonds. Interestingly, the coordinating properties of ligand systems which comprise divalent metal atoms of the group 14 elements, but bond by adjacent functionalities rather than the ylidenic centers, have scarcely been investigated. Breher and co-workers reported unique



Scheme 2. Selected resonance structures of **3**⁺.

bis(stannylenes), where two Sn^{II} centers are linked head-to-tail by the pyrazole fragments.^[20] This arrangement is energetically favored over distannene, composed of an $\text{Sn}=\text{Sn}$ bond. Furthermore, Power and co-workers used the metallylene compound **H** for the synthesis of the molybdenum complex **I** 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 ($\text{E}=\text{Ge}$ or Sn) upon

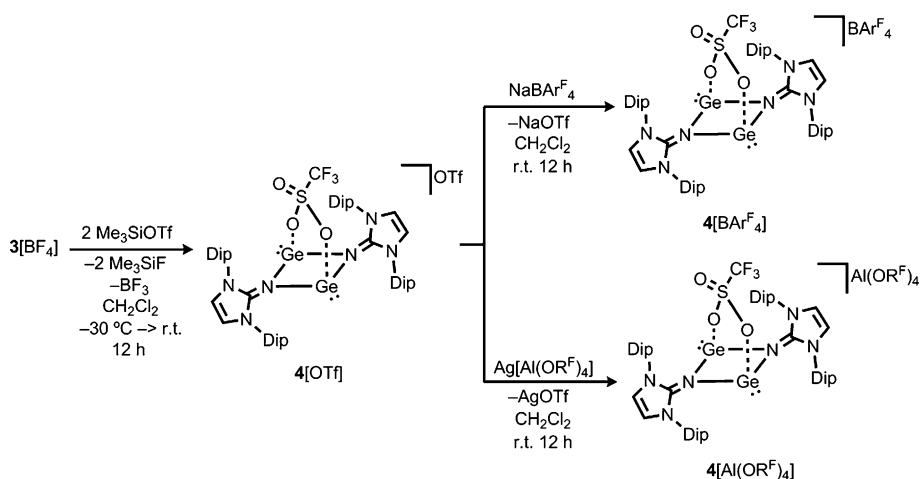


Scheme 3. Conversion of **H** into the metal complex **I** as reported by Power and co-workers. Mes = 2,4-trimethylphenyl, NBD = bicyclo[2.2.1]hepta-2,5-diene,^[21] THF = tetrahydrofuran.

transformation of **H** into **I** is the elongation of the E–S bond with concomitant decrease of the S–E–S bond angle. Accordingly, the $\text{Ge2-N}_{\text{imine}}$ distances in the ditopic cation 3^+ are increased with respect to **F** [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)° is considerably more acute than the N–Ge–N angle of 99.48(10)° in **F**. These comparisons between **H** and **I**, as well as **F** and 3^+ affirm the suggested resonance structure **A1** for 3^+ with its marked cationic fluorogermylumylidene moiety. We conclude that the bis(imino)germylene group functions as a bidentate ligand which bonds to the $\text{Ge}^{\text{II}+}$ center through the nitrogen atoms of the imino functionalities. The efficiency of the bis(imino) group to stabilize the cationic metal center is shown by the $\text{C}_{\text{NHC}}\text{--N}_{\text{imine}}$ 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 **F**.^[15] The delocalization of positive charge density into the imidazoline ring is illustrated by the resonance structure **A3**, as well as **A4** (Scheme 2).

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 orders) of the $\text{Ge1-N}_{\text{imine}}$ bonds were both calculated to be 0.55 and this value is significantly smaller than the corresponding one of **F** (1.12),^[18] and even reduced relative to the respective MBO of the germylumylidene cation **E** (0.68),^[14,18] and underlines the high dative-bond character of the $\text{Ge1-N}_{\text{imine}}$ interactions. In comparison, we determined MBOs of 0.89 for the $\text{Ge2-N}_{\text{imine}}$ bonds in 3^+ . In accordance with our structural discussion these data verify the germylene-germyliumylidene formulation **A1** (Scheme 2). In line with the expectation the MBO of the $\text{C}_{\text{NHC}}\text{--N}_{\text{imine}}$ bond (1.32) in 3^+ is comparable to that of **E** (1.24). In addition, we performed NRT (natural resonance theory) analysis to gain deeper insight into the bonding situation 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%). The HOMO for 3^+ is mainly the antisymmetric combination of the two lone pairs of the Ge centers (see Figure S30).^[18] The LUMO for 3^+ is essentially the vacant p-type atomic orbital on the Ge^{II} atom (Ge2) and supports **2** as an intermediate during the formation of 3^+ (Figure S30).^[18]

With the intention to synthesize a conceivable dicationic $[\text{GeNIPr}]_2^{2+}$ species, referred to as bis(germyliumylidene), we converted $3[\text{BF}_4]$ using two equivalents of Me_3SiOTf as a fluoride scavenger. This reaction resulted in the formation of the triflate salt $4[\text{OTf}]$ (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 CD_3CN solution of $4[\text{OTf}]$ is stable at temperatures up to 60 °C. Unfortunately, X-ray diffraction-quality crystals of $4[\text{OTf}]$ could not be obtained. The salt $4[\text{OTf}]$ was converted into $4[\text{BAR}^{\text{F}}_4]$ by anion exchange with $\text{Na}[\text{BAR}^{\text{F}}_4]$ (Scheme 4). It is of note that the dicationic complex $[\text{GeNIPr}]_2[\text{BAR}^{\text{F}}_4]_2$ was not generated by treatment with an excess amount of $\text{Na}[\text{BAR}^{\text{F}}_4]$.^[18] Single crystals of



Scheme 4. Synthesis of the bis(triflate) $4[\text{OTf}]$ and its conversion into the borate salt $4[\text{BAR}^{\text{F}}_4]$, as well as the perfluoroalkoxyalane $4[\text{Al}(\text{OR}^{\text{F}})_4]$. $\text{Ar}^{\text{F}} = 3,5\text{-(CF}_3)_2\text{-C}_6\text{H}_3$, $\text{R}^{\text{F}} = \text{C}(\text{CF}_3)_3$, Tf = trifluoromethanesulfonyl.

$4[\text{BAR}^{\text{F}}_4]$ suitable for X-ray diffraction analysis were retrieved from a CH_2Cl_2 solution at -30°C . Similarly, the reaction of $4[\text{OTf}]$ with the silver salt of the perfluorinated aluminate anion, $[\text{Al}(\text{OR}^{\text{F}})_4]^-$ afforded the aluminate salt $4[\text{Al}(\text{OR}^{\text{F}})_4]$ (Scheme 4). This reactivity between $4[\text{OTf}]$ and $\text{Ag}[\text{Al}(\text{OR}^{\text{F}})_4]$ is contrasted by the treatment of amido-substituted chlorogermylene with $\text{Ag}[\text{Al}(\text{OR}^{\text{F}})_4]$, after which formation of a chlorogermylene silver complex was observed.^[3g] The Ge_2N_2 germacycle unit possesses the same structure in $4[\text{BAR}^{\text{F}}_4]$ and $4[\text{Al}(\text{OR}^{\text{F}})_4]$. Therefore, only the structure of the cation of $4[\text{BAR}^{\text{F}}_4]$ is depicted in Figure 3. The structural

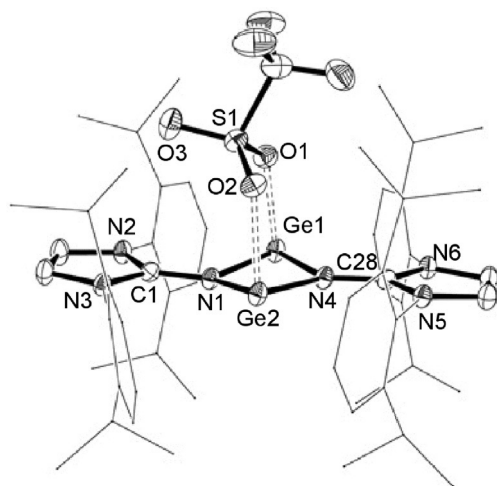
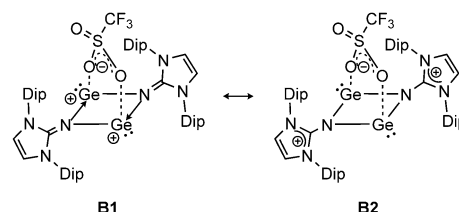


Figure 3. ORTEP representation of the molecular structure of the cation in $4[\text{BAr}^{\text{F}}_4]$ in the solid state.^[25] Thermal ellipsoids are at the 40% probability level. Dip groups are depicted as stick models. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and bond angles (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).

features of $4[\text{Al}(\text{OR}^{\text{F}})_4]$ are reported in the Supporting Information (see Figure S29).^[18] The molecular structure revealed that, akin to 3^+ , the Ge_2N_2 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 **F** [1.8194(15) Å].^[15] This difference emphasizes the partial dative-bond character for the germanium–nitrogen atom interactions in 4^+ . The $\text{C}_{\text{NHC}}\text{--N}_{\text{imine}}$ bonds [1.329(4) Å, 1.335(4) Å] are elongated as compared to those of neutral iminogermynes [1.296(3) Å, 1.273(2) Å],^[14,15] but fall well inside the range of those of the cationic compounds **E**^[13,14] and **3**⁺ (1.32–1.34 Å), thus suggesting the delocalization of positive charge into the imidazoline rings. Interestingly, the triflate group in $4[\text{BAr}^{\text{F}}_4]$ bridges the two germanium centers with the formation of two μ_1 -type coordinative interactions between the metals and two oxygen

atoms. The Ge– $\text{O}_{\text{triflate}}$ 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– $\text{O}_{\text{triflate}}$ distances (1.91–2.58 Å),^[23] thus 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]

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 **F** (1.12) though somewhat larger than the germanium-imino dative bond of **E** (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 triflate moiety bears a negative charge (Scheme 5). Resonance structures of type



Scheme 5. Selected resonance structures of 4^+ .

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 $[\text{GeNIPr}]_2^{2+}$ by removing the bridging triflate anion from 4^+ . We found that the structural parameters of $[\text{GeNIPr}]_2^{2+}$ are in good agreement with those of the triflate-germyliumylidene 4^+ , and indicates that the bridging triflate has a minor effect on the geometry of the dicationic moiety. However, the presumed bis(germyliumylidene) character for $[\text{GeNIPr}]_2^{2+}$ 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%; see Figure S34). This difference 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 (see 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 and indicates picture consistent 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-dimethylamino-pyridine, 1,3,4,5-tetramethylimidazolin-2-ylidene), Lewis acids (e.g. Me_3SiCl , Me_3SiBr), small-molecule substrates

(e.g. Me_3SiCN , Me_3SiN_3 , S_8), as well as selected transition-metal complexes (e.g. $[\text{Fe}_2(\text{CO})_9]$, $[\text{Ni}(\text{cod})_2]$, $(\text{Ph}_3\text{P})_2\text{Pt}(\text{C}_2\text{H}_4)$; $\text{cod} = 1,4\text{-cyclooctadiene}$).

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

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