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Isolation of a germanium(II) cation and a germylene iron carbonyl complex utilizing an imidazolin-2-iminato ligand†

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The novel amino(imino)germylene 1 was prepared by the conversion of HNIPr (NIPr = bis(2,6-diisopropylphenyl)imidazolin-2-imino) with 1 equiv. of $Ge[N(SiMe_3)_2]_2$. Germylene 1 reacts with $B(C_6F_5)_3$ to afford the borate salt $2^+[MeB(C_6F_5)_3]^-$ in a methyl-abstraction and ring-closing reaction. The conversion of 2 with $Fe_2(CO)_9$ furnishes the germylene iron carbonyl complex 3 with a trigonal planar-coordinate germanium atom.

For decades, divalent compounds of germanium, mostly referred to as germylenes, have been attractive targets for fundamental, as well as applied research. Succeeding the seminal report of Harris and Lappert on the bis(amino)germylene $Ge[N(SiMe_3)_2]_2$ in 1974,[1] a huge variety of germylenes are known to date.[2]

In sharp contrast to the neutral germylenes, the field of germyliumylidenes, that is, germanium(II) monocations of the type $[RGe:]^+$ (R = anionic ligand), is still in its infancy. This may be due to the poor thermodynamic stability of this system which demands for additional electron pair donor ligands at the metal center. Despite the synthetic challenges, this class of compounds has received great attention because of its pronounced Lewis ambiphilic nature. Since the characterisation of the half-sandwich germanocene cation $[(C_5Me_5)Ge:]^+$ by Jutzi and co-workers in 1980,[3] several types of donor-stabilised germyliumylidenes have been described. For example, Dias and co-workers implemented an aminotroponiminate ligand to stabilise the highly reactive Ge(II) cation species (**I**, Fig. 1),[4] whereas a β-diketiminate ligand was introduced by Power (**II**, Fig. 1).[5] Müller and co-workers synthesised the germyliumylidene **III** (Fig. 1) by protonation of the respective uncharged germylene at the ligand backbone.[6] Following a different synthetic approach, a number of germyliumylidenes have been described that were formed *via* auto-ionisation of germanium dichloride imposed by neutral chelate systems[7–10] or a carbodiphosphorane[11] ligand. Recently, Jones, Krossing and co-workers reported a germanium(II) monocation stabilised by a weak arene interaction.[12] Remarkably, germanium(II) dications have also been reported.[13]

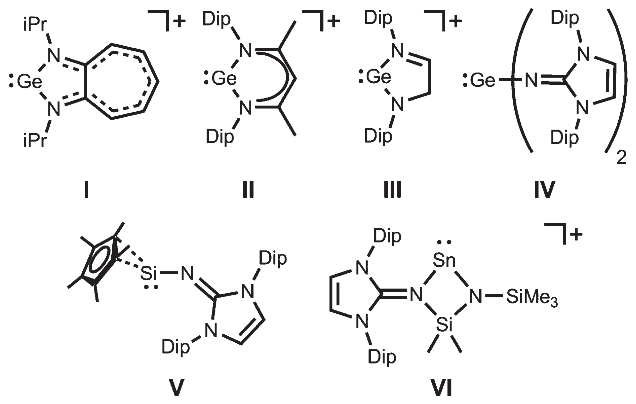

Fig. 1 Selected low-valent group 14 element compounds: the germanium(II) compounds **I–IV** (top), as well as imidazoline-2-iminato complexes of silicon(II) and tin(II) (**V**, **VI**, bottom).

We figured that a strongly electron-donating ligand would grant thermodynamic stability to a highly electrophilic germyliumylidene species. The imidazolin-2-iminato ligand may act as a 2σ- and either a 2π- or a 4π-electron donor and, hence, suits this criterion. Also, variation of its steric bulk may be used to fine-tune the kinetic protection of a metal center. Over the last two decades the properties of transition-metal complexes of the imidazolin-2-iminato ligand have been investigated thoroughly by Tamm and co-workers.[14] In contrast, research on main group element compounds comprising this system has been neglected in recent years. Rivard and co-workers reported on the bis(imino)germylene **IV** (Fig. 1) and a related silicon compound.[15] Our group isolated the Cp*-substituted iminosilylene **V**[16] (Fig. 1) and discovered a number of applications for boron-,[17] as well as aluminium[18] complexes of this ligand. Prior to this work we described the tin(II) mono-

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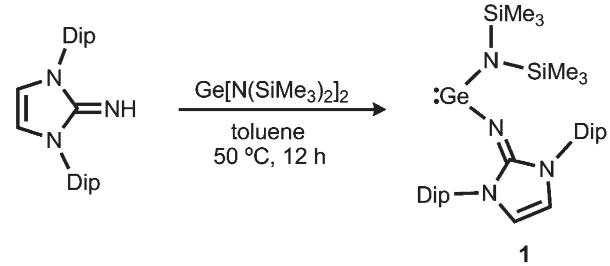


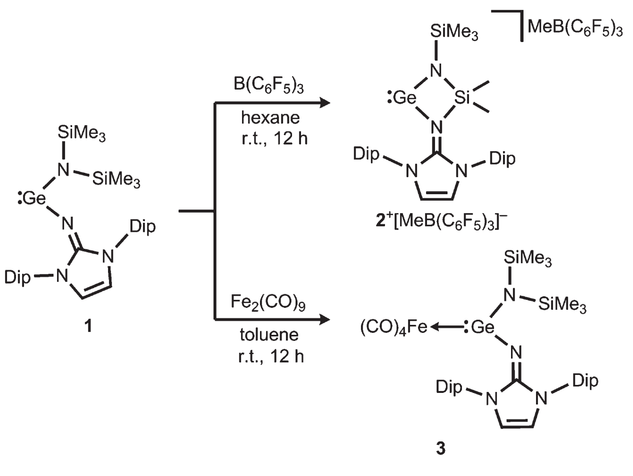
Scheme 1 Synthesis of amino(imino)germylene **1** (Dip = 2,6-diisopropylphenyl).

cation **VI** (Fig. 1).[19] The straightforward synthesis of **VI** by conversion of its amino(imino)stannylene precursor with tris(pentafluorophenyl)borane prompted us to examine the germanium chemistry of this ligand system. Herein we describe the synthesis and structural characterisation of the germanium analogue of **VI** and an amino(imino)germylene iron carbonyl complex.

The reaction of HNIPr with $Ge[N(SiMe_3)_2]_2$ in toluene at 50 °C furnishes the novel amino(imino)germylene **1** in high yield (87%, Scheme 1) which was confirmed by ^{1}H-, ^{13}C-, and ^{29}Si NMR analysis, as well as high resolution mass spectrometry. As already reported, a very similar synthetic approach grants access to the tin congener of **1**.[19]

Following our established concept for the synthesis of **VI** (Fig. 1) equimolar amounts of amino(imino)germylene **1** and $B(C_6F_5)_3$ were brought into contact in hexane solution (Scheme 2). After work-up $\mathbf{2}^+[MeB(C_6F_5)_3]^-$ was obtained as a crystalline solid in moderate yield (48%). The multinuclear NMR study, as well as a single crystal X-ray diffraction analysis verified our formulation of this borate salt and high resolution mass spectrometry complemented its characterisation.

Colourless crystals of $\mathbf{2}^+[MeB(C_6F_5)_3]^-$ were grown in toluene at −30 °C and the solid-state structure shows discrete cations and anions (Fig. 2). We find the shortest distance between the germanium center and a fluorine atom at 3.96 Å. In comparison, the sum of the van der Waals radii of these atoms amounts to 3.38 Å (1.98 Å for Ge and 1.40 Å for F).[20] The four-membered N_2SiGe ring in the cation of $\mathbf{2}^+$ is planar (the sum of the internal angles of the N_2SiGe ring amounts to 360°). Interestingly, the Ge1–N4 bond length of 1.8437(15) Å in $\mathbf{2}^+$ resembles the Ge–N distances in uncharged $Ge[N(SiMe_3)_2]_2$ (1.878(5) Å and 1.873(5) Å).[1c] However, it is clearly reduced as compared to **I** and **II** in which the Ge–N bond lengths range from 1.894(2) Å to 1.917(5) Å.[4,5] In contrast, the Ge1–N1 distance of 1.9694(14) Å is significantly increased with respect to that in **I** and **II**. Note that the germanium(II) cation **III** also exhibits a longer Ge–N distance to the imino nitrogen-atom (1.9884(18) Å) and a shorter Ge–N contact to the amino nitrogen-atom (1.8286(21) Å).[6] In accordance with the conclusions drawn by Müller for **III**, the X-ray study of $\mathbf{2}^+$ suggests a high dative character of the Ge1–N1 bond and a significantly stronger interaction between Ge1 and N4 in comparison. As a result, one approximation to describe the bonding situation in the germyliumylidene $\mathbf{2}^+$ is represented by resonance structure **A1** with the imino ligand functioning as an intramolecular electron-pair donor to the germanium center (Scheme 3).



Scheme 2 Synthesis of the four-membered germyliumylidene salt $\mathbf{2}^+[MeB(C_6F_5)_3]^-$ and the germylene iron carbonyl complex **3** (Dip = 2,6-diisopropylphenyl).

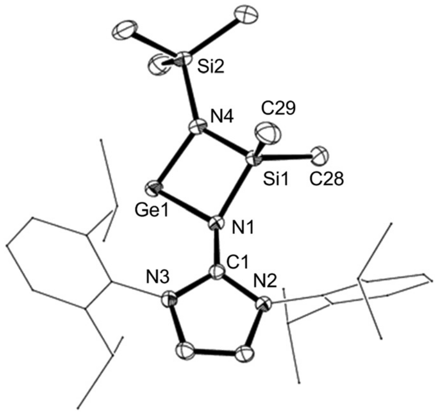
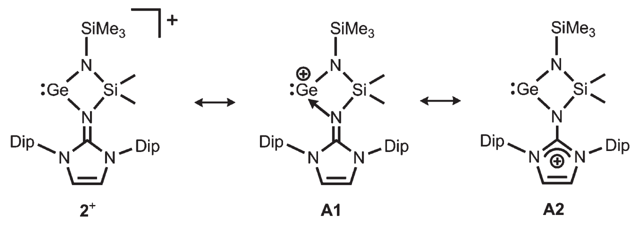


Fig. 2 ORTEP representation of the molecular structure of the cation of $\mathbf{2}^+[MeB(C_6F_5)_3]^-$ in the solid state. Thermal ellipsoids are at the 40% probability level. Dip groups are depicted as stick models. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and bond angles (°): Ge1–N1, 1.9694(14); Ge1–N4, 1.8437(15); Si1–N1, 1.7814(14); Si1–N4, 1.7332(16); Si1–C28, 1.8426(19); Si1–C29, 1.849(2); Si2–N4, 1.7499(15); C1–N1, 1.335(2); C1–N2, 1.358(2); C1–N3, 1.357(2); N1–Ge1–N4, 80.54(6); N1–Si1–N4, 89.13(7); Si1–N1–Ge1, 92.09(6); Si1–N4–Ge1, 98.14(7).



Scheme 3 Selected resonance structures of $\mathbf{2}^+$ (Dip = 2,6-diisopropylphenyl).

The C1–N1 distance of 1.335(2) Å in $\mathbf{2}^+$ is very similar to the one observed for the imino group in its tin congener **VI** (1.331(3) Å) and lies between that of a typical C–N single and a C═N double bond.[21] As it had been demonstrated for **VI**[19] this indicates the delocalisation of the positive charge of $\mathbf{2}^+$ into the imidazoline moiety which is illustrated by the structural formula **A2** (Scheme 3).

In order to gain further insight into the electronic properties of the germanium(II) cation $\mathbf{2}^+$, quantum-mechanical calculations were carried out (see the ESI†). The Natural Population Analysis (NPA) of $\mathbf{2}^+$ determines the charges at the germanium center, the C_{imine} atom and the two nitrogen atoms of the imidazoline ring to +1.240, +0.609 and −0.348/−0.352 (Fig. S15†). The relation to the less positive/more negative NPA charges in **1** (+1.135, +0.580 and 0.399/−0.410) points out the germanium(II) cation character of $\mathbf{2}^+$ and supports our charge assignment in the structural formulations **A1** and **A2** (Scheme 3). The calculated Wiberg Bond Index (WBI) for the Ge–N_{imine} bond in $\mathbf{2}^+$ amounts to 0.476 which is considerably lower than that of the Ge–N_{amine} interaction (0.729). For comparison, we calculated a WBI of 0.774 for the Ge–N_{imine} bond in **1**. The WBI of the C_{NHC}–N_{imine} bond in $\mathbf{2}^+$ (1.291) is lower than that of the C_{NHC}–N_{imine} bond in **1** (1.590). These results underline the conclusion of our X-ray study on $\mathbf{2}^+$ (*vide supra*). The LUMO+1 of $\mathbf{2}^+$ majorly exhibits orbital lobes at the five- and six-membered rings of the iminato ligand and a p-type orbital at the Ge(II) atom (Fig. 3). In the LUMO a p-orbital at the germanium(II) center engages in non-bonding interaction with π-symmetric components at the adjacent N_{amine} atom, as well as the imino group. In the HOMO of $\mathbf{2}^+$ an orbital lobe observed at the Ge(II) center hints towards an expected lone pair in an s-type orbital. However, the major contributions to the HOMO derive from orbital components with high p-character at the N atoms and the imidazoline moiety.

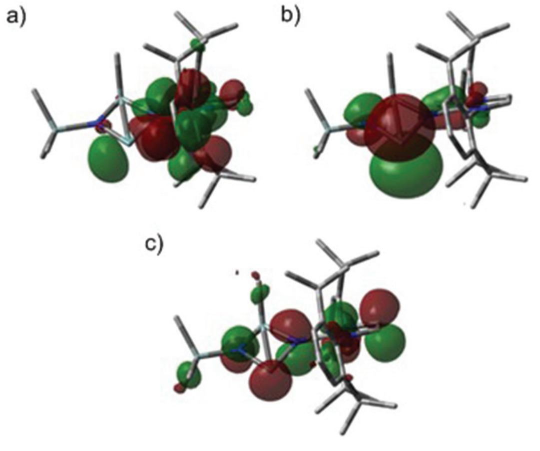


Fig. 3 (a) LUMO+1, (b) LUMO and (c) HOMO of $\mathbf{2}^+$.

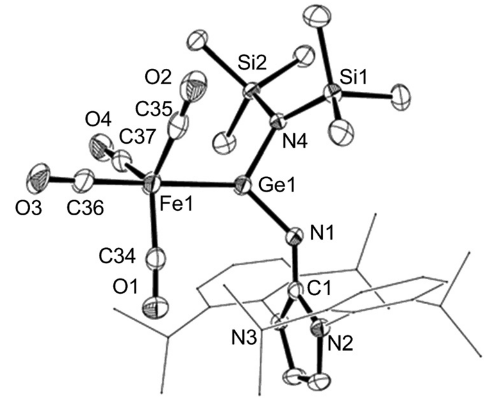


Fig. 4 ORTEP representation of the molecular structure of one of the two independent molecules of **3** in the solid state. Thermal ellipsoids are at the 40% probability level. Hydrogen atoms are omitted for clarity. Dip groups are depicted as stick models. Selected bond lengths (Å) and bond angles (°); values for the not depicted molecules are given in square brackets: Ge1–N1, 1.755(2), [1.752(2)]; Ge1–N4, 1.839(2), [1.835(2)]; Ge1–Fe1, 2.3026(5), [2.3041(5)]; N1–C1, 1.296(3), [1.300(3)]; N2–C1, 1.381(3), [1.377(3)]; N3–C1, 1.378(3), [1.373(3)]; N1–Ge1–N4, 104.87(10), [105.54(10)]; Fe1–Ge1–N1, 131.97(7), [132.89(7)]; Fe1–Ge1–N4, 121.69(7), [120.87(7)]; Ge1–N1–C1, 136.12(19), [133.75(18)].

With the intention to assess the properties of amino(imino) germylene **1** as a ligand to transition metals we treated it with 1.1 equiv. of $Fe_2(CO)_9$ in toluene (Scheme 2). After work-up, yellow crystals of the iron carbonyl compound **3** were obtained in 62% yield from hexane (Fig. 4, two independent molecules were found in the asymmetric unit). The germylene iron complex **3** features a trigonal-bipyramidal coordinated Fe atom and a trigonal planar Ge moiety (the sum of the bond angles around the Ge center amounts to 359°). Notably, most related iron carbonyls exhibit a germanium center that is either tetracoordinate (germylene–iron complexes)[22] or found at the apex of a trigonal pyramid (ferrogermylenes).[23] From our literature search[24] we retrieved the germylene complex $(2,6\text{-}t\mathrm{Bu}_2\text{-}4\text{-Me-}C_6H_2O)_2GeFe(CO)_4$ as the only respective example with a trigonal planar-coordinate germanium center.[25] The Fe1–Ge1 bond length in **3** was determined to be 2.3026(5) Å [2.3041(5) Å] which is longer than that reported for $(2,6\text{-tBu}_2\text{-4-Me-}C_6H_2O)_2GeFe(CO)_4$ (2.240(2) Å)[25] but does not exceed the range found for the majority of related iron carbonyls (germylene–iron complexes: 2.298(2)–2.348(1) Å; ferrogermylenes: 2.4415(11) Å, 2.496(2) Å).[22,23]

Interestingly, the Ge–N_{imine} distance in **3** (Ge1–N1 = 1.755(2) Å [1.752(2) Å]) is considerably decreased in comparison with those in Rivard's bis(imino)germylene **IV** (1.8194(15) Å)[15] and approaches the typical Ge═N bond lengths in germaimines (1.691(3)–1.704(5) Å).[26] Moreover, we determined the WBI of the Ge–N_{imine} bond in **3** to 0.857 which is larger than that calculated for **1** (0.774, see the ESI, Fig. S16†). We conceived that this might hint towards a significant 1-germa-2-azaallene character of **3** resembling the 1-sila-2-azaallene nature reported for the tris(pentafluorophenyl)borane adduct of the iminosilylene **V**[16] (Fig. 1, adduct not shown). As another indicator of a possible 1-germa-2-azaallene character the C_{NHC}–N_{imine} bond length in **3** (1.296(3) Å [1.300(3) Å]) is longer than the one in $Ge(NIPr)_2$ (**IV**, 1.273(2) Å).[15] However, the Ge1–N1–C1 bond angle in **3** amounts to 136.12(19)°

[133.75(18)°] which is more similar to that in bent Ge(NIPr)$_2$ (**IV**, 131.21(13)°) than it resembles the wider C_{NHC}–N_{imine}–Si bond angle (158.7(3)°) in the silylene–borane adduct of **V**. Consequently, the relevant 1-germa-2-azaallene character of **3** is negligible.

Conclusions

In summary, we synthesised the amino(imino)germylene **1** which serves as a precursor to the novel Ge(II) cation salt $2^+[MeB(C_6F_5)_3]^-$. Compound 2^+ features a two-coordinate germanium atom incorporated into a four-membered metallacycle and is formed *via* a rare type of methyl-abstraction and ring-closing reaction using $B(C_6F_5)_3$ as a Lewis acid. This synthetic approach to monocationic complexes of germanium(II) is without precedence in the literature. Moreover, conversion of **1** with $Fe_2(CO)_9$ affords the germylene iron carbonyl complex **3**. In the latter, the germanium atom is found in a trigonal planar coordination environment which is a scarce structure motive for this type of compound. In future research we will examine the use of 2^+ as a ligand in transition metal complexes.

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