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**Group 14 Chemistry**

# Group II Metal Complexes of the Germylidendiide Dianion Radical and Germylidenide Anion**

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***Abstract:*** *The two-electron reduction of a Group 14-element(I) complex [RË·] (E = Ge, R = supporting ligand) to form a novel low-valent dianion radical with the composition [RË:]$^{\cdot 2-}$ is reported. The reaction of [LGeCl] (**1**, L = 2,6-(CH=NAr)$_2$C$_6$H$_3$, Ar = 2,6-iPr$_2$C$_6$H$_3$) with excess calcium in THF at room temperature afforded the germylidenediide dianion radical complex [LGe]$^{\cdot 2-}$·Ca(THF)$_3$$^{2+}$ (**2**). The reaction proceeds through the formation of the germanium(I) radical [LGe·], which then undergoes a two-electron reduction with calcium to form **2**. EPR spectroscopy, X-ray crystallography, and theoretical studies show that the germanium center in **2** has two lone pairs of electrons and the radical is delocalized over the germanium-containing heterocycle. In contrast, the magnesium derivative of the germylidendiide dianion radical is unstable and undergoes dimerization with concurrent dearomatization to form the germylidenide anion complex [C$_6$H$_3$-2-{C(H)=NAr}Ge-Mg-6-{C(H)-NAr}]$_2$ (**3**).*

**B**ase-stabilized heavier Group 14-element(I) dimers of the composition [LË–ËL] (E = Si, Ge, Sn, and Pb; L = supporting ligand) have attracted much attention in the past few years due to their unique structures and reactivities.[1] They are stabilized kinetically by a variety of ligands such as amidinate, guanidinate, β-diketiminate, N-functionalized aryl and P-functionalized amide, and usually prepared by the reduction of the heavier halocarbene analogues [LËX] (X = Cl, Br, I) with alkali metal or the magnesium(I) dimer [HC(CMeNMes)$_2$Mg]$_2$ (Mes = 2,4,6-Me$_3$C$_6$H$_2$). X-ray crystallography and theoretical studies show that they comprise an Ë–Ë single bond and a lone pair of electrons on each E atom and resemble the heavier alkyne analogues of composition REER (R = aryl or silyl) with a single-bond structure.[2] Their reactivities were also studied and it was found that they are powerful reagents, e.g. for the activation of small molecules and unsaturated substrates.[3] In addition, they serve as building blocks for the construction of complex molecules, for example, disila-1,3-diphosphacyclobutadiene, germatrisilacyclobutadiene, and 2,4-diimino-1,3-disilacyclobutanediyl.[4] Moreover, the reduction of base-stabilized heavier Group 14-element(I) dimers has also been studied. Recently, we reported the reduction of [LË–ËL] or [LËX], which are supported by a 2,6-diiminophenyl ligand (E = Ge, Sn, and Pb; L = 2,6-(CH=NAr)$_2$C$_6$H$_3$, Ar = 2,6-*i*Pr$_2$C$_6$H$_3$ or *t*Bu; X = Cl or Br), with an alkali metal to form the germylidenide, stannylidenide, and plumbylidenide anions [LË:]$^-$, respectively.[1] These reactions proceed through the one-electron reduction of the Group 14-element(I) intermediate [LË·] to form [LË:]$^-$ and the negative charge is stabilized by the electron delocalization in the low-valent Group 14-element heterocycle. These results inspired us to investigate whether a Group 14-element(I) complex [LË·] can undergo a two-electron reduction to form a novel low-valent dianion radical of the composition [LË:]$^{\cdot 2-}$, which is as yet unknown. In contrast, stable neutral heavier Group 14 radicals such as Gomberg-type radicals [R$_3$E·] are well established and two examples of stable low-valent Group 14 neutral and charged radicals, [HC{C(*t*Bu)N(Ar)}$_2$Ge:]$^\cdot$ and [(*t*Bu$_2$MeSi)$_2$Si:]$^{\cdot -}$ have been reported.[5]

The chemistry of low-valent heavier main-group complexes has rapidly expanded in recent years, because their frontier electronic properties and reactivity resemble those of transition metal complexes.[6] Since open-shell transition metal complexes are involved in many catalytic reactions and the activation of small molecules, a better understanding of low-valent main-group radicals would greatly advance their emerging transition-metal-like reactivity. Thus, stable low-valent Group 14 dianion radicals should be worthwhile synthetic targets both for fundamental reasons and for their potential application as initiators/reagents in radical substitution and addition reactions. Herein, we report the synthesis and characterization of a stable calcium derivative of the germylidendiide dianion radical [LGe]$^{\cdot 2-}$·Ca(THF)$_3$$^{2+}$. We also describe the preparation of a magnesium germylidenide complex, which is derived from the dimerization of a magnesium germylidendiide radical intermediate.

The reaction of [LGeCl] (**1**) with excess calcium in THF at room temperature afforded [LGe]$^{\cdot 2-}$·Ca(THF)$_3$$^{2+}$ (**2**, Scheme 1).[7] It can also be prepared by the reaction of the germanium(I) dimer [LGe:]$_2$ with excess calcium in THF. The reactions appear to proceed through the formation of the germanium(I) radical [LGe·]. It then undergoes a two-electron reduction with calcium, which results in the formation of two lone pairs of electrons on the germanium center and an unpaired electron, which is delocalized over the germanium-containing heterocycle (see below), to form **2**.

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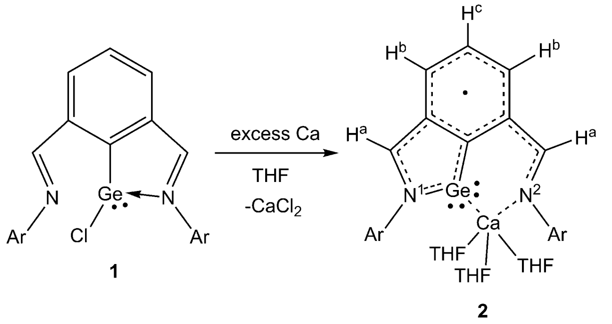


***Scheme 1.*** Synthesis of [LGe]$^{\bullet 2-}$·Ca(THF)$_3^{2+}$ (**2**).

Compound **2** is isolated as an extremely air- and moisture-sensitive red crystalline solid in low yield (25.6 %). Under an inert atmosphere, it is stable in the solid state at room temperature. In solution, it is unstable and gradually decomposes within a day to form a mixture of unidentified products, which were observed by NMR spectroscopy. In this regard, a freshly prepared solution of **2** in THF is necessary for electron paramagnetic resonance (EPR) characterization. The isotropic continuous-wave (CW) EPR spectrum and the corresponding simulation are shown in Figure 1. A satisfactory fit to the experimental data was achieved with the spin Hamiltonian parameters listed in Table 1. The simulation was performed with the Easyspin toolbox for Matlab.[8] The simulation revealed the contributions of two in-equivalent nitrogen nuclei ($N^1$ and $N^2$; see Scheme 1) along with two groups of two-equivalent protons ($H^a$ and $H^b$). The final unique proton ($H^c$) produced a clearly resolved doublet structure in the spectrum. Any possible in-equivalencies in the couplings to the $H^{a,b}$ protons was not visible in the X-band EPR spectrum. The weak signal intensities observed in the wings of the spectrum, highlighted in the low-field region of Figure 1, arise from hyperfine coupling to the germanium nucleus ($I(^{73}Ge) = 9/2$, 7.7 % abundance). As expected, no hyperfine interaction could be detected to the $Ca^{2+}$ nucleus or to the protons of the two Ar groups. The EPR data therefore confirms the delocalized nature of the radical and the small spin density on the Ge center (s character = 0.1 %).

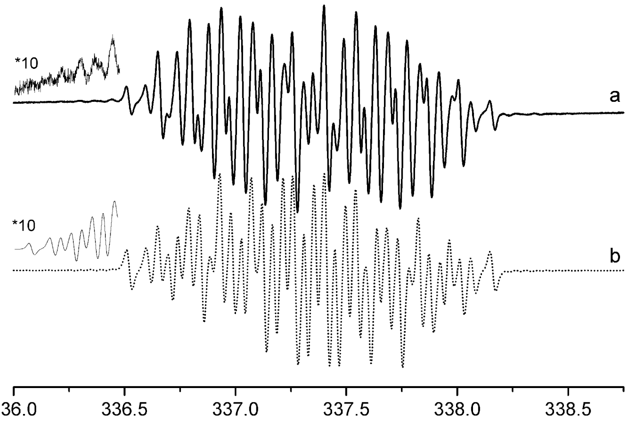


***Figure 1.*** X-band CW EPR spectrum of compound **2**, recorded at 298 K. a) Experimental. b) Simulation.

***Table 1:*** The spin Hamiltonian parameters of compound **2**.[a]

| | $^{73}$Ge | $^{14}$N$_1$ | $^{14}$N$_2$ | $^1$H$^a$ | $^1$H$^b$ | $^1$H$^c$ |
|---|---|---|---|---|---|---|
| $n$[b] | 1 | 1 | 1 | 2 | 2 | 1 |
| $a_{iso}$ [MHz][c] | 2.77 | 7.98 | 4.60 | 5.24 | 3.90 | 2.50 |

[a] $g_{iso} = 2.0040$. [b] $n$ = Number of equivalent nuclei. [c] ±0.005 MHz. Protons labeled $^1H^{a-c}$ are shown in Scheme 1.

The molecular structure of **2** (Figure 2) shows that the germanium-containing five-membered ring (Ge1C1C6C7N1) is planar, whereas that in **1** is puckered. The sum of the interior bond angles is 540°. The Ca1 atom is $\eta^5$-coordinated with the Ge1C1C2C20N2 skeleton, which displaces from the Ge1C1C2C20 least squares plane by 2.368 Å. The coordination sphere on the Ca1 atom is further supplemented by the oxygen atoms of three THF molecules. The N2 atom also displaces from the Ge1C1C2C20 least squares plane by 0.801 Å. The bond lengths in **2** indicate that there is an appreciable electron delocalization in the ligand skeleton when compared with those in compound **1** (Figure 3). Moreover, the Ge1–Ca1 bond (3.229(1) Å) is longer than the sum of the covalent radii (2.96 Å) and those in the calcium–germyl complex [Ca(THF)$_3${Ge(SiMe$_3$)$_3$}$_2$] (3.022(2) Å)[9] and in the calcium derivative of 1,3-disila-2,4-digermabicyclo[1.1.0]butane-2,4-diide (3.0372(14), 3.0388(14) Å).[10] This indicates that the Ge–Ca bond is ionic. The Ca–N bond length (2.290(8) Å) is comparable with that in the calcium amide complex [Ca(DME){N(SiMe$_3$)$_2$}$_2$] (2.271(3) Å).[11]

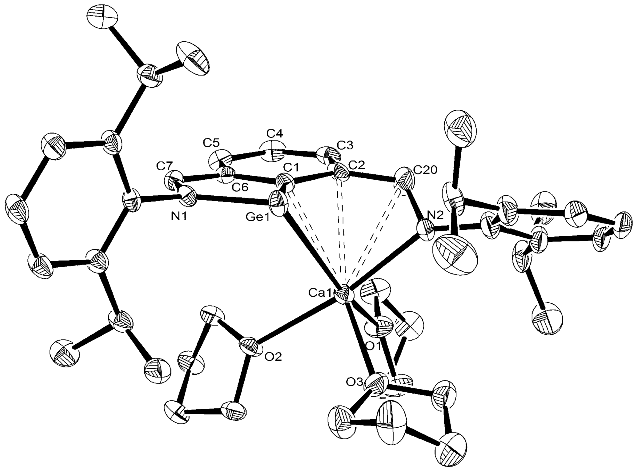


***Figure 2.*** Molecular structure of compound **2** (ellipsoids set at 30% probability). Hydrogen atoms and disorder in the Ar substituents and THF molecules are omitted for clarity. Selected bond lengths [Å] and angles [°]: Ge1–Ca1 3.2292(10), Ge1–C1 1.947(4), Ge1–N1 1.911(3), N1–C7 1.368(5), C7–C6 1.376(5), C6–C1 1.436(5), Ca1–N2 2.290(8), N2–C20 1.361(10), C20–C2 1.463(10), C2–C1 1.453(5), C2–C3 1.395(6), C3–C4 1.389(6), C4–C5 1.399(6), C5–C6 1.450(5); N1-Ge1-C1 83.33(14), N1-Ge1-Ca1 110.99(9), C1-Ge1-Ca1 57.16(11), C7-N1-Ge1 115.1(2), N1-C7-C6 115.3(3), C7-C6-C1 114.9(3), C6-C1-Ge1 111.4(3), Ge1-Ca1-N2 77.8(5), Ca1-N2-C20 95.3(8), C2-C20-N2 122.9(11), C20-C2-C1 126.9(7), C2-C1-Ge1 130.9(3).

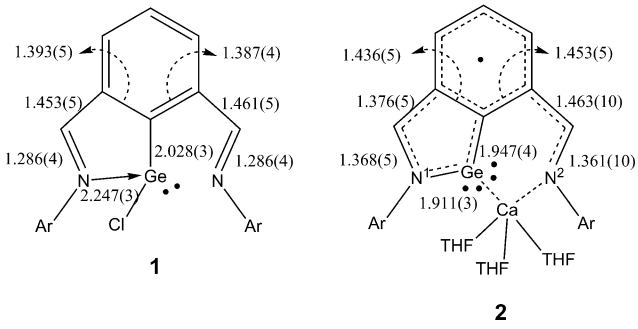
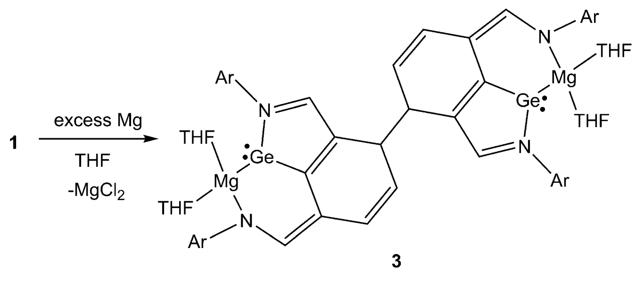


***Figure 3.*** Comparison of the bond lengths of compounds **1** and **2**.

To understand the bonding nature in compound **2**, density functional calculations were conducted.[12] The optimized geometry (B3LYP/6-31+G(d) level, Figure S1, see the Supporting Information) is in good agreement with the X-ray crystallographic data, although the calculated Ge–Ca bond (3.032 Å) was underestimated by about 6%. The singly occupied molecular orbital (α-SOMO, Figure S2) shows precisely that the radical is delocalized over the ligand core. The highest occupied molecular orbitals (HOMO and HOMO−1) show primarily that the germanium atom comprises two lone-pair orbitals, which are perpendicular to and lie in the same plane as the germanium-containing five-membered ring, respectively. Moreover, the Wiberg bond index (Ge–Ca: 0.29) and large difference in the NPA charges between the Ge (0.46) and Ca (1.48) atoms illustrate that the Ge–Ca bond is ionic.

Recently, Jones et al. reported that a magnesium germylidenide complex [RGe–MgR] (R = HC{C(*t*Bu)NMes}$_2$) supported by a β-diketiminate ligand is unstable, and undergoes a ring contraction rearrangement.[1] It has been suggested that the synthesis of a complex comprising a low-valent germanium–magnesium bond is a formidable challenge and no example has been reported yet. After the successful isolation of compound **2**, it is anticipated that a low-valent Ge–Mg-bonded compound can be prepared by a similar strategy. The reaction of **1** with excess magnesium in THF at room temperature afforded the magnesium germylidenide **3** (Scheme 2). It can also be prepared by the reaction of the germanium(I) dimer [LGe:]$_2$ with excess magnesium in THF. Although the reaction mechanism is still unknown, on the basis of experimental results, we propose that the reaction proceeds through the formation of a magnesium derivative of the germylidendiide dianion radical "[LGe]$^{\cdot 2-}\cdot$Mg$^{2+}$", which then dimerizes at the *meta*-position of the phenyl ring and dearomatizes to form **3**. The result is in contrast to that of the reaction of **1** with calcium. We suggest that the electropositive calcium centre in **2** may lead to a higher negative charge density in the ligand, which hinders the dimerization.



***Scheme 2.*** Synthesis of [C$_6$H$_3$-2-{C(H)=NAr}Ge-Mg-6-{C(H)−NAr}]$_2$ (**3**).

Compound **3** was isolated as a highly air- and moisture-sensitive red crystalline solid in moderate yield (58.5%). It is stable in solution and the solid state under an inert atmosphere. There is no EPR signal for compound **3** in solution, which implies that it cannot dissociate in solution to form the germylidendiide dianion radical "[LGe]$^{\cdot 2-}\cdot$Mg$^{2+}$". The $^1$H NMR spectrum shows a set of signals, which are attributed to the ligand backbone. There is a broad signal at δ 3.16 ppm and multiplets at δ 6.36–6.64 ppm for the methine and methylene protons of the dearomatized six-membered ring, respectively. It is noteworthy that the signals for *H*C=NAr (δ 7.82, 7.91 ppm) show an upfield shift compared with those of **1** (δ 8.06, 8.08 ppm) and fall in the aromatic proton region. The results indicate that the lone-pair electrons on the Ge atom are stabilized by an electron delocalization in the GeC$_3$N five-membered ring.

The molecular structure of **3** (Figure 4) shows that the germanium-containing five-membered ring (Ge1C1C2C20-N2) is planar, which is similar to that of **2**. The sum of the interior bond angles is 540°. The Mg1 atom is coordinated with the Ge1, N1, and the oxygen atoms of two THF molecules, which displaces from the Ge1C1C2C20N2 plane by 1.886 Å. The Ge–Mg bond (2.6068(15) Å) is comparable to the sum of the covalent radii (2.61 Å) and that in the

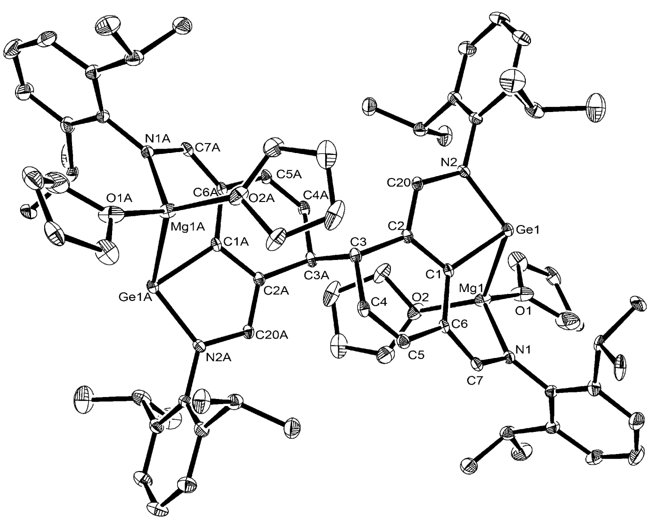


***Figure 4.*** Molecular structure of compound **3** (ellipsoids set at 30% probability). Hydrogen atoms and disorder in the THF molecules are omitted for clarity. Selected bond lengths [Å] and angles [°]: Ge1–Mg1 2.6068(15), Ge1–C1 1.957(4), Ge1–N2 1.905(3), N2–C20 1.355(5), C20–C2 1.373(5), C2–C1 1.432(5), Mg1–N1 2.001(3), N1–C7 1.367(5), C7–C6 1.378(5), C6–C1 1.471(5), C2–C3 1.526(5), C3–C4 1.497(5), C4–C5 1.341(5), C5–C6 1.454(5), C3–C3A 1.577(8); N2-Ge1-C1 84.71(15), N2-Ge1-Mg1 121.88(10), C1-Ge1-Mg1 68.92(12), C20-N2-Ge1 113.1(2), N2-C20-C2 117.2(3), C1-C2-C20 115.1(3), C2-C1-Ge1 109.6(3), Ge1-Mg1-N1 93.52(11), Mg1-N2-C7 108.7(3), C6-C7-N1 125.0(4), C7-C6-C1 124.4(3), C6-C1-Ge1 131.0(3).

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germyl magnesium complex $[\{(\mathrm{SiMe_3})_3\mathrm{Ge}\}_2\mathrm{Mg(THF)_2}]$ (2.679(1) Å).[13] The Mg–N bond (2.001(3) Å) is similar to that in the amido–magnesium complex $[\mathrm{Mg(THF)_2}\{\mathrm{N(SiMe_3)_2}\}_2]$ (2.015(5), 2.027(5) Å).[14] In addition, the C3–C3A bond (1.577(8) Å) is a typical C–C single bond (average 1.53 Å). Moreover, comparing the bonding in the $\mathrm{GeC_3N}$ five-membered ring [Ge1–N2: 1.905(3) Å, N2–C20: 1.355(5) Å, C2–C20: 1.373(5) Å, C1–C2: 1.432(5) Å, Ge1–C1: 1.957(4) Å] with those in compound **1**, it is suggested that the lone-pair electrons on the Ge atom are stabilized by an electron delocalization in the $\mathrm{GeC_3N}$ five-membered ring.

In conclusion, we have reported the synthesis of the first calcium complex of the germylidendiide dianion radical **2** by a simple procedure. X-ray crystallography and EPR spectroscopy show conclusively that the radical is delocalized over the low-valent germanium-containing heterocycle. In contrast, the magnesium derivative of the germylidendiide dianion radical is unstable and its dimerization is accompanied by dearomatization, forming the germylidenide anion complex **3**. The synthesis of other heavier Group II metal analogues and the reactivity of compounds **2** and **3** toward transition metals are currently under investigation.

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