

A Cyclopentadienide Analogue Containing Divalent Germanium and a Heavy Cyclobutadiene-like Dianion with an Unusual Ge₄ Core

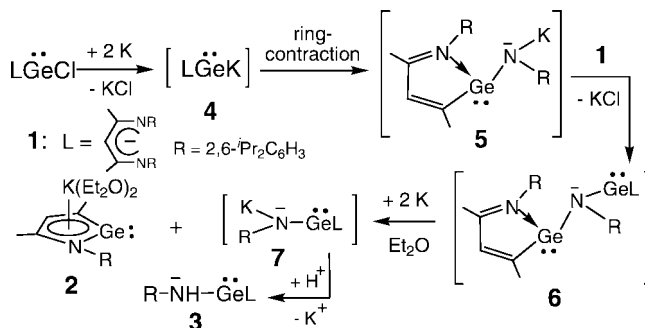
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Cyclopentadienides (Cp[−]) are aromatic charged 6π electron ligands of importance in organometallic chemistry and beyond.¹ In particular, a vast number of transition-metal (half)sandwich complexes of Cp[−] have found extensive applications in catalysis (i.e., electron transfer catalysis, asymmetric catalysis) as well as in materials synthesis (i.e., olefin polymerization, synthesis of redox-active conducting polymers). In order to extend the intriguingly broad range of applications and to explore strikingly new ones, tremendous efforts have been undertaken to gain access to Cp[−] congeners containing heavier group 14 elements (Si, Ge, Sn, Pb).² Recently, substantial progress has been achieved in synthesizing isolable sila-,³ germa-,^{3e,4} and tin analogues⁵ of Cp[−]. Moreover, even cyclobutadiene dianions (CBD^{2−}), representing another class of fascinating but much less explored 6π aromatic ligands, and their analogues consisting of heavier group 14 elements attract a great deal of attention.² Milestones comprise also the synthesis of heavier metallocenes containing Si and/or Ge atoms,⁶ and quite recently, the first transition-metal complexes of a tetrasil-CBD^{2−} ligand have been reported, as well.⁷ We are particularly interested in the synthesis of new types of Cp[−] analogues containing divalent group 14 elements, which may lead to electron-rich transition-metal complexes with unusually high reduction potential, owing to the presence of strong electropositive low-valent group 14 metals. To our knowledge, no Cp[−] analogues containing low-valent heavier group 14 elements are known as yet.

We now learned that reduction of the sterically encumbered but coordinatively flexible β-diketiminato Ge(II) chloride, LGeCl **1** (L = CH[CMe(NR)]₂, R = 2,6-*i*-Pr₂C₆H₃),^{8a} with potassium in THF at ambient temperature furnishes the first cyclogermylidenide derivative in the form of its potassium salt **2**; the latter has been isolated by fractional crystallization in diethylether in the form of the highly air- and water-sensitive pale yellow crystals in 33% yield (Scheme 1). Additionally, the reduction leads at the same time to the β-diketiminato Ge(II) amide **3**, LGe(NHR), which has been isolated by fractional crystallization in hexane in the form of yellow crystals in 31% yield. The new compounds have been characterized by NMR spectroscopy (¹H, ¹³C), EI-mass spectrometry (**3**), and correct elemental analyses (see Supporting Information). Although the mechanism is still unknown, we propose the formation of the N-heterocyclic potassium germylidenide **4** as initial transient species by halogen–metal exchange reaction. The latter undergoes a ring contraction to give the transient germylene amide **5**, which reacts with **1** in a salt metathesis reaction, affording the NR-bridged digermylene **6**. Reductive fission of a Ge–N bond in **6** by elemental K leads to **2** and formation of the K salt of **3**, that is, compound **7**; its subsequent protonation at nitrogen by ether cleavage affords **3** (Scheme 1).

Scheme 1. Synthesis of **2** and **3**



In contrast, reaction of **1** with K in toluene even at 0 °C leads merely to the complete replacement of Ge by K via reduction of Ge(II) to elemental Ge powder and concomitant formation of the corresponding known β-diketiminato potassium complex, LK,^{8b} which has been isolated in 72% yield and identified by ¹H NMR and X-ray diffraction. According to NMR spectroscopy, **2** is a K(Et₂O)₂ salt. This is confirmed by a single-crystal X-ray diffraction analysis (Figure 1): **2** crystallizes in the triclinic space group *P* $\bar{1}$ and consists of a dimeric half-sandwich complex interconnected via intermolecular Ge→K dative bonds. Each half-sandwich moiety consists of a K(Et₂O)₂ cation which is η⁵-coordinated to the anionic five-membered planar C₃NGe ring.

As expected, the K1–Ge1 distance of 344.9(1) pm is much shorter than the intermolecular K1–Ge1' distance of 357.3(1) pm. Somewhat shorter K–Ge distances have been observed in a related dipotassium(18-crown-6) tetraphenylgermol dianion (330, 335 pm)^{4b,9a} and in a (18-crown-6)-solvated potassium silylgermanides (342 pm) both containing tetravalent germanium atoms.^{9b} Accordingly, the K–C(ring) distances in **2** (309.2(2)–333.0(2) pm) are also longer than that in the aforementioned dipotassium germol dianion (288–317 pm). The Ge1–N1 distance of 194.4(2) pm are

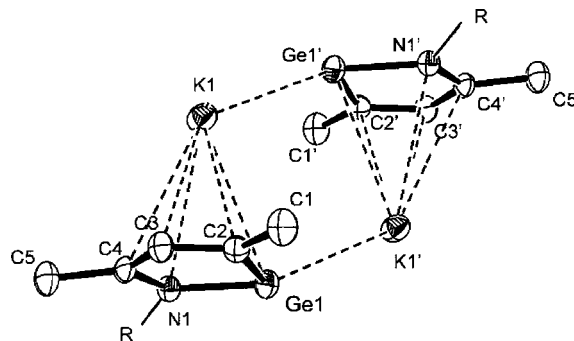
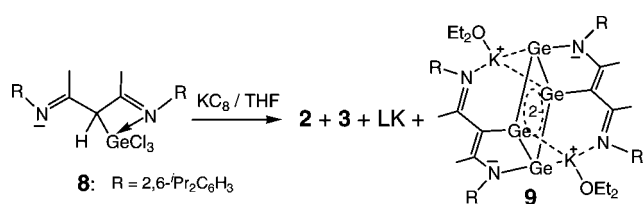


Figure 1. Molecular core structure of dimeric **2** (R = 2,6-*i*-Pr₂C₆H₃). The Et₂O donor molecules coordinated to K1 and K1' and the H atoms were omitted for clarity; for details see Supporting Information.

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Scheme 2. Facile Synthesis of **2**, **3**, and **9** from **8**

ca. 6 pm shorter than those in **1**^{8a} but longer than that in an N-heterocyclic, 6π aromatic germyliumylidene cation (189 pm) and related compounds.¹⁰ Correspondingly, the Ge1–C2 distance (188.7(2) pm), the endocyclic C–C distances (C3–C4 137.1(3), C2–C3 141.1(3) pm), and the C4–N1 bond length (138.2(3) pm) suggest appreciable π -resonance stabilization in the C_3NGe ring. In line with that, the remarkable deshielding of the resonance signal for the γ -H atom at the C3 ring atom in the ^1H NMR spectrum (δ 6.18 ppm) is consistent with a considerable Cp^- -like resonance stabilization in the C_3NGe ring. This is supported by density functional theory (DFT) calculations, which reveal pronounced aromaticity of the C_3GeN ring, indicated by the negative nucleus-independent chemical shift (NICS) values [NICS(1) = -7.4 ppm and NICS(0) = -7.7 ppm; see Supporting Information]. The molecular structure of **3** has also been determined by X-ray diffraction (here not shown; see Supporting Information). Compound **3** consists of a puckered six-membered $\text{C}_3\text{N}_2\text{Ge}$ ring with bond lengths and angles similar to those observed in **1**^{8a} and related systems.¹⁰ Interestingly, the terminal Ge–N distance of 190.5(2) pm is considerably shorter than the endocyclic ones (202.6(2), 205.1(2) pm). It is striking that **2** and **3** are also accessible by dehalogenation of the related β -diketiminate-substituted organogermanium trichloride **8**^{8c} employing KC_8 as a gentle reducing agent. In fact, this method is more convenient (no application of Ge(II) starting materials) and improves the yield for **2** and **3** by 42 and 39%, respectively (Scheme 2). Additionally, colorless crystals of the known β -diketiminato potassium complex, LK, have been isolated as side products along with deep-red crystals of the remarkable novel cluster compound **9** in 3% yield.

According to an X-ray diffraction analysis (Figure 2), **9** represents a dipotassium salt of the first “heavy” cyclobutadiene-like dianion (CBD^{2-}) consisting of a Ge_4 core. Up to now, only a few metal complexes of “heavy” CBD^{2-} have been reported, featuring a Si_4 and Si_2Ge_2 core.⁷ Compound **9** consists of a planar $\text{L}'_2\text{Ge}_4^{2-}$ dianion ($\text{L}' = \text{C}[\text{CMe}(\text{NR})]_2$; R = 2,6- $\text{Pr}_2\text{C}_6\text{H}_3$), in which the two unusual

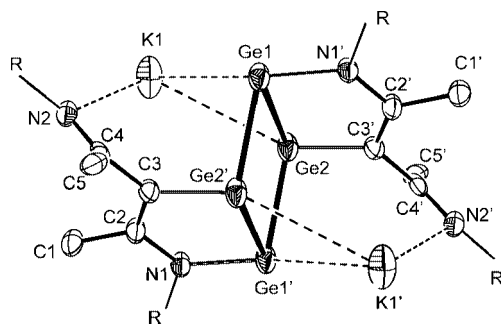


Figure 2. Molecular core structure of **9** (R = 2,6- $\text{Pr}_2\text{C}_6\text{H}_3$). The Et_2O donor molecules coordinated to K1 and K1' and the H atoms were omitted for clarity; for details see Supporting Information.

chelate ligands L' are attached to the Ge_4 core each with terminal Ge–C and Ge–N σ -bonds. The dianion accommodates two η^3 -coordinated $\text{K}(\text{Et}_2\text{O})$ cations each coordinated to Ge1, Ge2, and N2, and Ge1', Ge2', and N2', respectively. The K–Ge distances of 335.5(1) pm (K1–Ge1) and 347.7(1) pm (K1–Ge2) are similar to those in **2** and in related potassium germanides.⁹ The structure is also notable for the parallelogram configuration of the planar Ge_4 core and the unusual coordination of the Ge atoms. The Ge1–Ge2 (251.2(1) pm) and Ge1–Ge2' distances (255.3(1) pm) represent Ge–Ge single bonds close to values observed in bulky substituted cyclotetragermanes (ca. 251 pm),¹¹ while the transannular Ge2–Ge2' distance of 274.7(1) pm is much larger. Remarkably, despite of the pyramidal coordination of the Ge atoms, the Ge_4^{2-} in **9** shows extremely strong aromaticity as shown by the negative NICS (1) of -21.5 ppm and NICS (0) value of -38.9 ppm, respectively, determined by DFT calculations (see Supporting Information).

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Supporting Information Available: Experimental details for the synthesis and spectroscopic data of **2**, **3**, and **9**, DFT calculations of the NICS values and Cartesian coordinates of **2** and **9** (PDF); crystallographic data for **2**, **3**, and **9** (CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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