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A Cyclic Germadicarbene (“Germylone”) from Germyliumylidene

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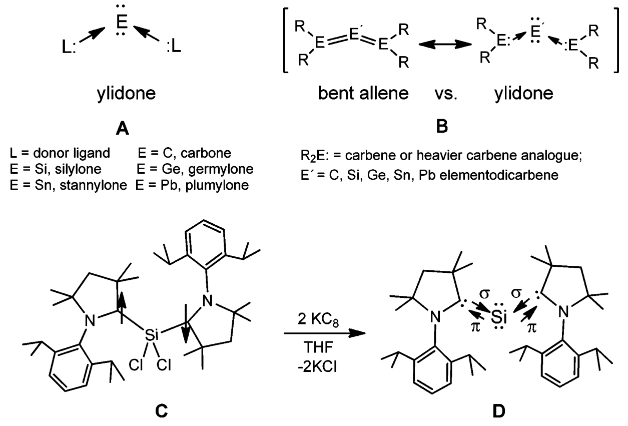
Supporting Information

ABSTRACT: By employing the chelate dicarbene **1**, the new chlorogermyliumylidene complex **2** could be synthesized and isolated in 95% yield. Dechlorination of **2** with sodium naphthalenide furnishes the unique cyclic germadicarbene **3** which could be isolated in 45% yield. Compound **3** is the first isolable Ge(0) complex with a single germanium atom stabilized by a dicarbene. Its molecular structure is in accordance with DFT calculations which underline the peculiar electronic structure of **3** with two lone pairs of electrons at the Ge atom.

Recently, the use of N-heterocyclic carbenes (NHCs) as ligands to stabilize Group 14 elements in the zero oxidation state has attracted significant research interest. For example, through dechlorination of the NHC-stabilized compounds NHC→$SiCl_4$ and NHC→$GeCl_2$ (NHC = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene) the groups of Robinson[1] and Jones[2] were able to isolate the fascinating Si(0) and Ge(0) species L:→Si═Si←:L and L:→Ge═Ge←:L (L = NHC), respectively. In the latter compounds each Si(0) and Ge(0) atom features one lone pair of electrons. Another striking new class of compounds with Group 14 atoms represents the so-called ylidones L:→E←:L (Scheme 1, **A**), (L: = donor ligand, E = C − Pb),[3] in which the E atom retains its valence electrons as two lone pairs and the bonding situation between the two donor ligands L: and the single atom E can be best described in terms of donor−acceptor interactions; they are expected to possess unusual reactivity owing to the peculiar electronic structures in accordance with results from theoretical calculations reported by the research groups of Frenking[3a−g] and Apeloig.[3h] Accordingly, the isolated and structurally characterized bent allenes reported by the groups of Bertrand[4a] and Regitz,[4b] as well as the heavier Group 14 analogues (trisilaallene, trigermaallene, and 1,3-digermasilaallene) published by the groups of Kira[5] and Wiberg (tristannaallene),[6] should rather be interpreted as ylidones (Scheme 1, **B**), since these compounds have bent structures with nonlinear E−E−E bond angles (E = C − Sn) ranging from 122 to 156°, and the four substituents at the terminal E atoms deviate from orthogonal arrangement as in genuine allenes.[3−6]

Scheme 1. Dicoordinate E(0) Complexes



In order to synthesize isolable ylidones, carbenes have proven to serve as suitable donors, although even phosphanes[7] and heavier carbene analogues have been employed successfully as mentioned above. Very recently, Roesky and Frenking et al. reported the first silylone $(L:)_2Si$ **D** (Scheme 1),[8a] bearing the cyclic alkyl amino carbene (cAAC) L:. Compound **D** results from dechlorination of the precursor **C** with KC_8 (Scheme 1).[8b] The latter investigations revealed that, in contrast to the remarkable biradical electronic structure of precursor **C**, the siladicarbene **D** is a silylone instead of a Si(II) silylene. However, **D** has a closed-shell singlet ground state with a non-negligible contribution from the singly excited state owing to the low electronic excitation energy (small HOMO−LUMO gap). In other words, **D** has a biradicaloid character. The two carbene ligands L: in **D** coordinate to the Si atom in a much more acute C−Si−C bond angle of 117° compared with those observed for **B** (122−156°). The slightly shorter Si−C bond distance of 1.841(2) Å in **D** than the calculated value for $(NHC)_2Si$ (1.869 Å)[3e−g] exhibits the better π acceptor properties of the cAAC ligand than NHC,[8a] which is reflected by its frontier orbitals: its HOMO is a π-type orbital which has the largest extension at Si but exhibits significant Si−C π bonding. NBO analysis of the siladicarbene **D** gives one σ lone-pair orbital and a three-center C−Si−C π orbital with 40% at Si and 30% at each C atom as shown in Scheme 1.[8a]

Taking into account that chelate ligands with strong push−pull effect[4a,9] will lead automatically to acute bending angles, we planned to synthesize ylidones of type **E** (Scheme 2). Recently, we described the coordination properties of the chelate ligand 1,8-bis(tributylphosphazenyl)naphthalene toward Si(II) and Ge(II) which furnishes the potential chlorosilyliumylidene precursors **F** and its Ge analogue **G**, respectively (Scheme 2).[10] However, their reduction reactions with KC_8 did not lead to the desired ylidone **H** but to reduction of the chelate ligand. This can be explained by DFT calculations which revealed that the

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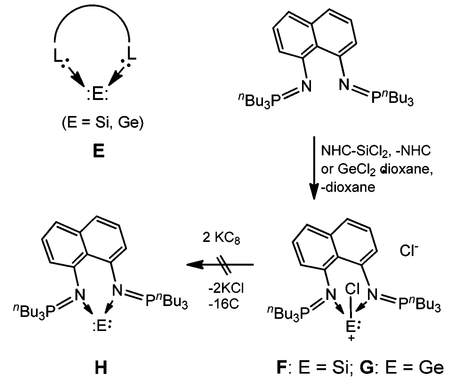
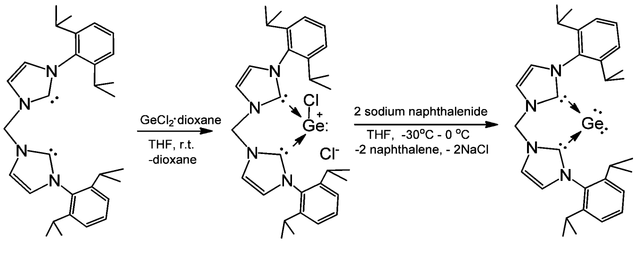
Scheme 2. Attempts To Prepare Ylidones Featuring Chelate Ligands



LUMOs of **F** and **G** are mainly represented by the π system of the naphthalene moiety.

Based on the formation of **F** and **G** and inspired by the successful preparation of **D** we explored the reactivity of the bis-N-heterocyclic carbene (bNHC) **1** (Scheme 3) toward $GeCl_2$·dioxane, aiming at synthesizing the first germadicarbene ("germylone") **E** through dehalogenation (Scheme 2). To our best knowledge, the coordination ability of **1** has merely been investigated toward a few transition metals such as chromium[11] and iron,[12] but its utilization to stabilize low-valent p-block main-group elements has not yet been reported.

Scheme 3. Generation of the Chlorogermyliumylidene Chloride 2, Starting from bNHC 1, and Its Dechlorination to the Cyclic Germadicarbene ("Germylone") 3



1
bNHC
2
3

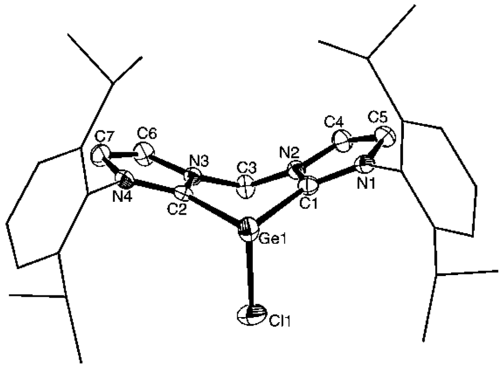


Figure 1. Molecular structure of the chlorogermyliumylidene cation in **2**. Thermal ellipsoids are drawn at the 50% probability level. H atoms, counteranion (Cl^-), and one acetonitrile lattice solvent molecule are omitted for clarity. Selected interatomic distances (Å) and angles (°): Ge1−Cl1 2.310(1), Ge1−C1 2.058(3), Ge1−C2 2.057(3), C1−N1 1.349(4), C1−N2 1.341(4), C2−N3 1.347(4), C2−N4 1.385(5), C1−Ge1−C2 85.2(1), C1−Ge1−Cl1 91.8(1), C2−Ge1−Cl1 90.5(1), Ge1−C1−N1 129.1(2), Ge1−C1−N2 126.0(2), N1−C1−N2 104.8(3), Ge1−C2−N3 126.2(2), Ge1−C2−N4 128.8(2), N3−C2−N4 104.9(3).

Similar to the formation of **G**, treatment of an equimolar amount of bNHC **1** with $GeCl_2$·dioxane in THF at room temperature furnished the desired Ge(II) salt $[\text{bNHC-GeCl}]^+Cl^-$ **2** as an off-white powder in 95% yield (Scheme 3). Compound **2** is the first germyliumylidene cation supported by a chelating bis-carbene. In contrast to **G**, compound **2** is insoluble in THF but soluble in acetonitrile, exhibiting its stronger ionicity. The high-resolution ESI-mass spectrum of **2** dissolved in acetonitrile gives in the positive mode a peak at m/z = 577.21484 (calcd 577.21478) corresponding to the $[\text{bNHC-GeCl}]^+$ cation. In comparison to **1**, the donor ^{13}C carbene nuclei in **2** show an upfield shift (δ = 166 ppm for **2** vs 220 ppm for **1**) in the ^{13}C NMR spectrum. Single crystals of **2** suitable for X-ray diffraction analysis were grown in actonitrile solutions at −20 °C. Similar to **G**, the Ge(II) atom in **2** is threefold coordinated by two carbon atoms from the bis-carbene ligand **1** and one chlorine atom (Figure 1); the chloride counterion is located far away from the Ge center (6.53 Å). The six-membered C_3N_2Ge ring is puckered in a boat conformation with N2, N3, C1, and C2 being nearly coplanar, and Ge1 and C3 displaced away from that plane in the same direction as the Ge−Cl bonding vector is pointing. The dihedral angle between the plane defined by C3, N2, N3 and the plane defined by N2, N3, C2, C1 is 38.7°, whereas the dihedral angle between the plane defined by Ge1, C1, C2 and the plane defined by N2, N3, C2, C1 is 18.4°. The Ge1−Cl1 bond in **2** is oriented nearly perpendicular to both Ge−C bonds, with Cl1−Ge1−C1 and Cl1−Ge1−C2 bond angles of 90.(1)° and 91.8(1)°, respectively, which are smaller than those in **G** (average 95.8°). The sum of angles around the carbene carbon atoms in **2** is 359.90° and 359.88°, respectively, indicating a nearly ideal trigonal-planar geometry. The Ge1−Cl1 distance of 2.310(1) Å in **2** is longer than those in **G** (2.278(1) Å), in the NHC-$GeCl_2$ adduct (average 2.277 Å[13]), and in the related four-coordinate Ge(II) species 1,2,3,4-tetrakis(di-*tert*-butylmethylsilyl)-3,4-dichlorotetragermetene (2.248(1) Å[14]) and $[\text{GeCl(pmdta)}][\text{GeCl}_3]$ (2.266(2) Å[15]). In contrast, the Ge1−C1 (2.058(3) Å) and Ge1−C2 (2.057(3) Å) bond lengths in **2** are significantly shorter than that in NHC-$GeCl_2$ (2.112(2) Å),[13] indicating a stronger interaction of the chelate carbene carbon atoms toward the Ge atom in **2** than that in NHC-$GeCl_2$.

In order to gain more insight into the electronic features, DFT calculations (B3LYP/6-31G(d) level of theory) have been performed for the chlorogermyliumylidene cation in **2**.Geometry optimization of the latter yielded a structure similar to that observed experimentally. Its HOMO and LUMO are depicted in Figure 2. The HOMO is essentially a σ lone-pair orbital at the Ge(II) center. Strikingly, the LUMO consists mainly of a π-type orbital at Ge, which is in marked contrast to the situation of compounds **F** and **G**. In addition, a strong interaction between the chelate carbene carbons and the Ge center in the germyliumylidene in **2** is supported by the Wiberg bond index values of the Ge−C bonds (0.608 and 0.611). We expected that these features may facilitate the two-electron reduction of the Ge(II) atom of the chlorogermyliumylidene in **2** to give the desired germylone **3**.

In fact, the dechlorination of **2** with sodium naphthalenide leads to the cyclic germadicarbene **3** (Scheme 3). When a cold

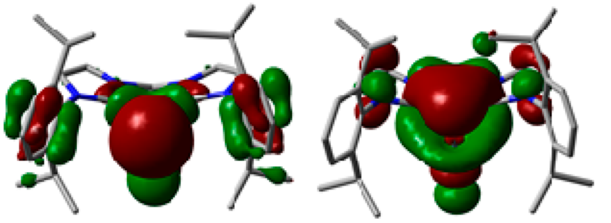


Figure 2. HOMO (left) and LUMO (right) of the chlorogermyliumylidene cation in **2**. Hydrogen atoms are omitted for clarity.

solution of 2 molar equiv of sodium naphthalenide in THF (−30 °C) was added to the suspension of **2** in THF (−30 °C), the reaction mixture turned immediately dark red. Compound **3** could be isolated from toluene solutions of the reaction mixtures as dark red crystals in 45% yield. The dark red crystals of **3** dissolved in toluene showed UV−vis absorption bands at λ = 286, 420, and 564 nm which are comparable with those found for the bent trigermaallene (trigermaylidone, λ = 280, 380, 435, 496, and 630 nm)[5b] and **D** (390 and 584 nm).[8a] Interestingly, the chemical shift of the carbene carbons in **3**, compared to that of the precursor **2** (δ = 166 ppm), appears downfield (δ = 196 ppm) in the ^{13}C NMR spectrum, which is relatively close to that observed for the silylone **D** (δ = 210.9 ppm).[8a]

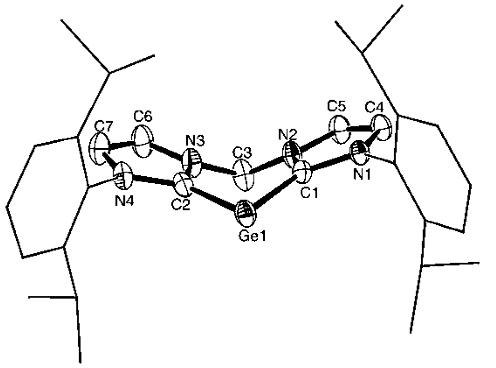


Figure 3. Molecular structure of **3**. Thermal ellipsoids are drawn at the 50% probability level. H atoms and toluene lattice solvent molecules are omitted for clarity. Selected interatomic distances (Å) and angles (°): Ge1−C1 1.965(3), Ge1−C2 1.961(3), C1−N1 1.382(4), C1−N2 1.378(4), C2−N3 1.377(4), C2−N4 1.375(4), C1−Ge1−C2 86.5(1), Ge1−C1−N2 128.6(2), Ge1−C1−N1 128.1(2), N1−C1−C2 103.3(1), Ge1−C2−N3 127.7(2), Ge1−C2−N4 129.0(2), N3−C2−N4 102.9(2).

Compound **3** is extremely air and moisture sensitive. It exhibits also slight temperature sensitivity. Solutions of **3** in THF are stable for 2 days in a sealed NMR tube at room temperature and then show traces of "free" bNHC **1** (^{1}H NMR). Compound **3** crystallizes at −20 °C in toluene solutions in the monoclinic space group $P2_1/c$ (Figure 3). X-ray diffraction analysis reveals that the Ge atom in **3** is two-coordinate with a C−Ge−C angle of 86.6(1)°. This angle is only slightly smaller than the corresponding value for the precursor **2** (85.2(1)°), but much more acute than the Ge−Ge−Ge bond angle of the trigermaylidone of type **B** (Scheme 1) reported by Kira and co-workers (122.6°).[5b] In fact, compound **3** represents the most bent allene or ylidone hitherto structurally characterized (117−156°).[4−6,8] Similar to **2**, the six-membered C_3N_2Ge ring in **3** is also puckered in a boat conformation, but exhibits a larger dihedral angle between the plane defined by C3, N2, N3 and the plane defined by N2, N3, C1, C2 (46° in **3** vs 38.7° in **2**), and a smaller dihedral angle between the plane defined by Ge1, C1, C2 and the plane defined by C1, C2, N2, N3 (13° in **3** vs 18.4° in **2**). In addition, the sum of angles around each carbene carbon atom in **3** (359.95° and 359.59°), just as in **2**, indicates an almost ideal trigonal-planar coordination geometry. The Ge−C bond distances of 1.967(2) and 1.962(2) Å in **3** are significantly shorter by about 0.10 Å than those in the precursor **2** (2.058(3) and 2.057(3) Å), and distinctly shorter by about 0.15 Å than that in NHC-GeCl$_2$ (2.112(2) Å).[12] The short Ge−C bond distances in **3** are comparable to the Ge−C$_{sp^2}$ single bond in Ph3GeC(F)═CF2 (1.969(6) Å)[16] but slightly longer than the Ge−C$_{sp^3}$ single bonds in 9,10-dihydro-10-germa-9-sila-anthracene (1.903−1.913 Å)[17] and 2,3,5,6-tetrakis(trimethylgermyl)-1,4-benzoquinones (1.941(6)−1.965(7) Å).[18]

In order to shed light on the electronic nature of compound **3**, DFT calculations [B3LYP/6-31G(d)] were performed. The optimized structure of **3** in the singlet ground state is in good agreement with the metric data observed by X-ray analysis. Furthermore, it was found through DFT calculation that the structure with the first triplet state is by 33.2 kcal mol^{-1} less stable than the singlet ground state. The HOMO of **3** consists of the π-type orbital at the Ge center, including Ge−C π bonding (Figure 4, left). This π interaction (back-bonding) may explain the relatively short Ge−C bond lengths in **3**. On the other hand, the HOMO−1 represents a σ lone-pair orbital at Ge (Figure 4, right). In addition, the proton affinities (PA) of compound **3** were calculated to certificate the germylone character. The first and second values PA(1) PA(2) were estimated to be 279.6 and 175.0 kcal mol^{-1}, respectively. It follows from the relatively large value for PA(2) that compound **3** clearly possesses germylone character. These trends can also be observed in the acyclic silylone **D**,[8a] and similar structural and electronic features of related species (carbone, silylone, germylone, etc.) have been theoretically predicted by Frenking and co-workers.[3]

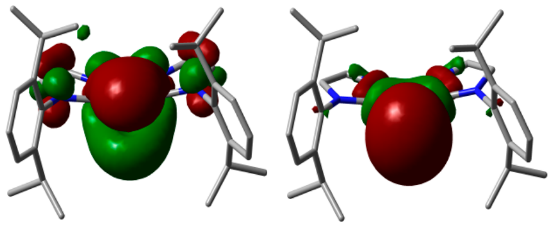


Figure 4. HOMO (left) and HOMO−1 (right) of cyclic germaylidone **3**. Hydrogen atoms are omitted for clarity.

In summary, we report here for the first time the bis-carbene-stabilized chlorogermyliumylidene cation **2** which could be successfully dehalogenated by sodium naphthalenide to give the unique isolable cyclic germadicarbene (germylone) **3**. The latter contains a single Ge atom in the formal oxidation state zero which is coordinated by the bis-carbene chelate ligand **1**.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental details for the synthesis, and spectroscopic and crystallographic (CIF) data for **2** and **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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