JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

Article

pubs.acs.org/JACS

Acyclic Germylones: Congeners of Allenes with a Central Germanium Atom

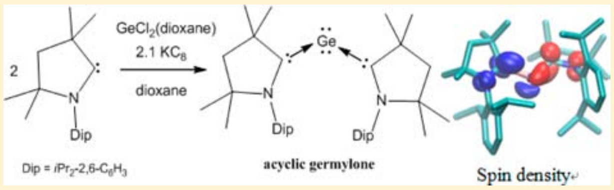
Yan Li,[†,‡] Kartik Chandra Mondal,[‡] Herbert W. Roesky,*[,‡] Hongping Zhu,*[,†] Peter Stollberg,[‡] Regine Herbst-Irmer,[‡] Dietmar Stalke,*[,‡] and Diego M. Andrada*[,§,⊥]

[†]State Key Laboratory of Physical Chemistry of Solid Surfaces, National Engineering Laboratory for Green Chemical Productions of Alcohols—Ethers—Esters, College of Chemistry and Chemical Engineering, Xiamen University, Xiamen, Fujian, 361005, China

[‡]Institut für Anorganische Chemie, Georg-August-Universität, Tammannstraβe 4, and [§]Institut für Physikalische Chemie, Georg-August-Universität, Tammannstraβe 6, 37077-Göttingen, Germany

[⊥]Instituto de Investigaciones en Fisicoquímica de Córdoba, Departamento de Química Orgánica, Facultad de Ciencias Químicas, Universidad Nacional de Córdoba, Ciudad Universitaria 5016, Córdoba, Argentina

Ⓢ *Supporting Information*

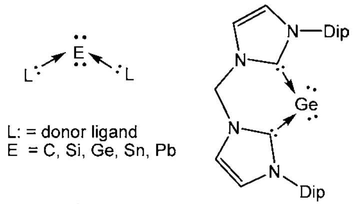


ABSTRACT: The cyclic alkyl(amino) carbene (cAAC:)-stabilized acyclic germylones (Me$_2$-cAAC:)$_2$Ge (**1**) and (Cy$_2$-cAAC:)$_2$Ge (**2**) were prepared utilizing a one-pot synthesis of GeCl$_2$(dioxane), cAAC:, and KC$_8$ in a 1:2:2.1 molar ratio. Dark green crystals of compounds **1** and **2** were produced in 75 and 70% yields, respectively. The reported methods for the preparation of the corresponding silicon compounds turned out to be not applicable in the case of germanium. The single-crystal X-ray structures of **1** and **2** feature the C—Ge—C bent backbone, which possesses a three-center two-electron π-bond system. Compounds **1** and **2** are the first acyclic germylones containing each one germanium atom and two cAAC: molecules. EPR measurements on compounds **1** and **2** confirmed the singlet spin ground state. DFT calculations on **1**/**2** revealed that the singlet ground state is more stable by ~16 to 18 kcal mol^{-1} than that of the triplet state. First and second proton affinity values were theoretically calculated to be of 265.8 (**1**)/267.1 (**2**) and 180.4 (**1**)/183.8 (**2**) kcal mol^{-1}, respectively. Further calculations, which were performed at different levels suggest a singlet diradicaloid character of **1** and **2**. The TD-DFT calculations exhibit an absorption band at ~655 nm in *n*-hexane solution that originates from the diradicaloid character of germylones **1** and **2**.

■ INTRODUCTION

Allenes are compounds with a fascinating $R_2C{=}C{=}CR_2$ backbone and have attracted organic chemists for several decades because of their exciting structures and reactivities.[1] On the basis of DFT calculations,[2] Frenking et al. proposed that the allenes with a heavier central element of group 14 form a ylidone structure with the L:→E←:L (**A**) arrangement (Scheme 1) featuring a bent configuration with the formal oxidation state of zero of the central atom E. According to their theoretical calculations, the bonding situation can be considered as a donor—acceptor interaction between two donor ligands L: and the central acceptor E, whereas the two lone pairs at the E atom are retained.

Scheme 1. Representation of Ylidone



A **B**

The pioneering work on the homo- and heteroallenes has been done by Kira et al. and Escudié et al.[3] The chemistry of this class of allenes has been intensively explored by them and others.[3] However, so far the related heavier allenes with two terminal carbons were rarely documented, although some of the bent allenes (carbodicarbene) have been prepared.[4] The heavier analogues of carbene were utilized for the syntheses of such interesting compounds.[3] Very recently, Driess et al. reported[5a] a bis-*N*-heterocyclic carbene (bNHC) stabilized cyclic germadicarbene (**B**) through the reductive dehalogenation of its precursor chlorogermyliumylidene cation by sodium naphthalenide in moderate yield (Scheme 1). The highest occupied molecular orbital (HOMO) of **B** consists of the π-type orbital including Ge—C π-bonding interaction (back-bonding) and a σ-lone-pair orbital at the Ge center. The calculated values of proton affinities (PA) support the germylone character of **B**. Subsequently, corresponding cyclic siladicarbene was published by the same group.[5]

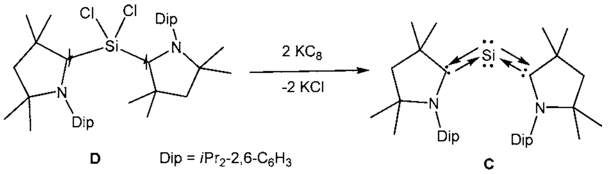
NHCs play a crucial role in the stabilization of compounds of E with formal oxidation state of zero.[6] Since the first synthesis

Received: June 18, 2013
Published: July 19, 2013

of cyclic alkyl(amino) carbene (cAAC:) by Bertrand et al.,[7] activation of small molecules such as NH_3 has been achieved, which was not successful with NHCs.

Theoretical calculations demonstrate that cAAC: possesses a singlet spin ground state, and in contrast to NHC:, a smaller energy gap between the HOMO and the lowest unoccupied molecular orbital (LUMO).[7c,d] Because of the electronic disparity of nitrogen (σ-electron-withdrawing and π-donating) and carbon (σ-electron-donating and non-π-donating), the difference of neighboring atoms at the carbene carbon leads to a remarkable change in the reactivities of cAAC:. In our previous work, we reported on a unique diradicaloid siladicarbene $(cAAC:)_2Si$ (**C**),[8a] which is easily accessible through the reduction of $(cAAC\cdot)_2SiCl_2$ (**D**)[8b] with two equivalents of KC_8.[8] Compound **C** is the first report of a silylone (Scheme 2), which was confirmed by theoretical calculations. The singlet spin ground state of **C** was assigned by EPR spectroscopy and the diradicaloid character was shown by theoretical calculation, which originated from the small HOMO−LUMO energy gap. This breakthrough opens a new field of main group chemistry. Inspired by the facile access[8] of $(cAAC:)_2Si$, we extended our work to germanium. Herein, we report on the preparation, characterization, and detailed theoretical investigation of the first acyclic germylones $(Me_2\text{-}cAAC:)_2Ge$ (**1**) and $(Cy\text{-}cAAC:)_2Ge$ (**2**).

Scheme 2. Synthetic Route for Silylone C[8a,c]

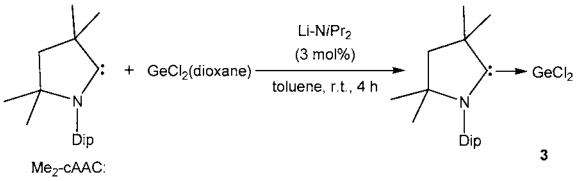


■ RESULTS AND DISCUSSION

Recently, we have observed that the dark blue colored diradical $(cAAC\cdot)_2SiCl_2$ is formed in high yield when cAAC: is reacted with $NHC{:}\rightarrow SiCl_2$ in a 3:1 molar ratio. This reaction is exothermic and always easily produces $(cAAC\cdot)_2SiCl_2$. The bond between each carbene carbon and silicon in the diradical $(cAAC\cdot)_2SiCl_2$ is found to be an electron sharing single bond rather than a usual coordinate bond. The corresponding reaction of $NHC{:}\rightarrow GeCl_2$[6b,10] with cAAC: does not proceed, independent of the molar ratio or temperature (up to 60 °C). The formation of $(cAAC\cdot)_2GeCl_2$ is not favored because of the lower Ge−C bond energy of 80 kJ mol^{-1}, when compared with that of the Si−C bond.

When the $GeCl_2(dioxane)$ adduct was treated with cAAC: in a 1:1 molar ratio in THF or toluene or diethylether, the $cAAC{:}H^+$ cation was exclusively obtained. This was concluded from NMR studies. The analogous $NHC{:}H^+$ is also formed ($NHC{:}H^+GeCl_3^-$, NHC: = 1,3-bis(2,6-diisopropylphenyl)-imidazol-2-ylidene) in 2% yield when $GeCl_2(dioxane)$ was treated with NHC: while $NHC{:}\rightarrow GeCl_2$ is produced in 98% in this reaction.[6b,10] Because cAAC: is more nucleophilic[7a,9a] than NHC:, it abstracts a proton possibly from the coordinated dioxane ligand of $GeCl_2(dioxane)$. The protons of the CH_2 groups of dioxane in $GeCl_2(dioxane)$ are as expected more acidic than those of uncoordinated dioxane. However, we observed that $Me_2\text{-}cAAC{:}\rightarrow GeCl_2$ (**3**) can be successfully prepared in 50% yield when $GeCl_2(dioxane)$ is treated with Me_2-cAAC: in a 1:1 molar ratio in the presence of 10 mol % of $[Na_4(Et_2O)_4(IPy)_2]$.[9b] The yield of the reaction remains almost unaltered (47−50%) even though 100 mol % of $[Na_4(Et_2O)_4(IPy)_2]$ are employed. Compound **3** can also be synthesized in 51% yield by utilizing a catalytic amount (3 mol %) of commercially available lithium diisopropylamide (LDA) (Scheme 3). This result suggests that the formation of $Me_2\text{-}cAAC{:}\rightarrow GeCl_2$ (**3**) is possibly triggered by a cation such as Li^+ or Na^+. Compound **3** is colorless and soluble in THF and toluene. It crystallizes in two shapes, colorless plates and rods. The single crystal X-ray diffraction on both types of crystals showed similar structures but different space groups (see the Supporting Information). The ^{13}C NMR spectrum of **3** exhibits a resonance of the carbene carbon atom (245.2 ppm), which is significantly upfield shifted (304.2 ppm) when compared with that of Me_2-cAAC:,[7a] whereas it is downfield shifted when compared with that of the reported $aNHC{:}\rightarrow GeCl_2$ (155.8 ppm, aNHC: = 1,3-bis(2,6-diisopropylphenyl)-2,4-diphenylimidazol-5-ylidene).[11]

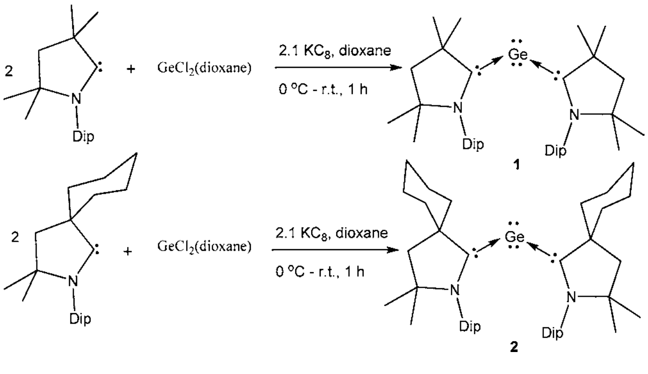
Scheme 3. Synthetic Strategy for the Preparation of Compound 3



The reduction of $Me_2\text{-}cAAC{:}\rightarrow GeCl_2$ (**3**) with two equivalents of KC_8 in the presence of an additional equivalent of Me_2-cAAC: was not successful for the preparation of compound **1**. This result reveals that $Me_2\text{-}cAAC{:}\rightarrow GeCl_2$ (**3**) is not the right precursor for the germanium analogue of $(Me_2\text{-}cAAC:)_2Si$.

Finally, when a 1:2:2.1 molar ratio of $GeCl_2(dioxane)$, Me_2-cAAC: and KC_8 was reacted in THF at −78 °C, the resultant suspension was slowly warmed up to room temperature. It afforded a dark blue solution. The resultant solution was dried and extracted with *n*-hexane. The dark greenish plates of $(Me_2\text{-}cAAC:)_2Ge$ (**1**) were formed in 75% yield (Scheme 4) from the filtrate, which was stored at 0 °C in a refrigerator. Moreover a small amount (about 3%) of $(Me_2\text{-}cAACH)_2O$ (**4**) was also isolated as colorless plates which were characterized both by NMR and single crystal X-ray diffraction (see the Supporting Information). The source of H_2O in $(Me_2\text{-}cAACH)_2O$ is possibly THF. Nevertheless, the formation of $(Me_2\text{-}cAACH)_2O$

Scheme 4. Preparation of Compounds 1 and 2

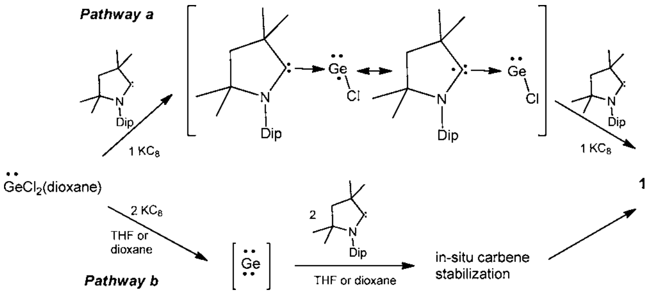


was less than 0.5% when the reaction was carried out in dioxane at 0 °C for one hour. The yield of compound **1** remains almost the same. A one-pot reaction utilizing potassium metal failed to produce **1** instead $(Me_2\text{-cAACH})_2O$ was obtained in 40% yield (see the Supporting Information). A similar synthetic strategy was also applied in the successful preparation of 2-germadisilaallene.[3c] Compound **2** was synthesized following the similar procedure as given in Scheme 4. The yields of compounds **1** and **2** are higher than that of the reported cyclic germylone **B** (45% yield).[5a] This is surprising because cyclic species are in general more easily formed than the corresponding acyclic ones. Thus it can be argued that cAAC: is superior when compared with NHC: toward the stabilization of germylones, because cAAC: is more nucleophilic and electrophilic than NHC:.[7]

Compounds **1** and **2** are less stable than the corresponding silicon molecule $(\text{cAAC:})_2Si$. A slow decomposition to an unknown black powder is observed during the crystallization. The green crystals of **1** and **2** are stable in an inert atmosphere at room temperature for at least 2 weeks. However, **1** and **2** can be stored in air for several hours and then slowly oxidize to $Me_2\text{-cAAC}{=}O$ and Cy-cAAC=O, respectively. When N_2O gas was passed through the THF solution of **1** and **2** for 1 hour, the latter compounds were obtained in 90–92% yield.[8c] The carbene carbon atoms of compounds **1** and **2** show a upfield shift (232.6 (**1**) and 232.8 ppm (**2**)) relative to that of compound **3** (245.2 ppm) in the ^{13}C NMR spectra. The carbene carbon resonances of **1** and **2** appear downfield shifted when compared with those of **C** (210.9 ppm)[8b,c] and cyclic germylone **B** (196 ppm).[5a]

A proposed mechanism for the formation of compound **1** is given in Scheme 5. The reaction of $GeCl_2$(dioxane), Me_2-cAAC: and KC_8 in 1:1:1 molar ratio resulted in a brown mixture. The identification of both the intermediate species of cAAC:→Ge(·)Cl and the final product of $(\text{cAAC:})_2Ge$ was not successful (*pathway a*). The cAAC:→Ge(·)Cl radical might be unstable and decompose rapidly after its formation. As mentioned above, the direct reaction of $GeCl_2$(dioxane) and Me_2-cAAC: did not result in compound **3**. Moreover, in the one-pot reaction the cAAC:H$^+$ cation was not found, which was confirmed by NMR. Obviously the interaction between $GeCl_2$(dioxane) and Me_2-cAAC: at the early stage of the reaction is not preferred, when THF or dioxane is used as a donor solvent. However, the use of a noncoordinating solvent such as toluene in preparation of **1** led to the decomposition of **1**. It is rational that in the environment of donor solvent, $GeCl_2$ first reacts with two equivalents of KC_8 to generate solvated Ge(0) atoms which are in situ coordinated and stabilized by cAAC: (*pathway b*). Under this condition, the formation of elemental germanium is not observed, instead $(\text{cAAC:})_2Ge$ is formed.

Scheme 5. Plausible Mechanism for the Formation of 1



Compounds **1** and **2** are EPR silent confirming that their singlet ground state is like that of **C**.[8b,c] Compounds **1** and **2** exhibit UV–visible absorption bands at 310 (values of **2**, 320), 410 (414), 495 (503), and 653 (657) nm. These values are comparable to those found for the red colored cyclic germylone **B**[5a] (286, 420, and 564 nm), 2-germadisilaallene[3c] (409 and 599 nm), and trigermaallene[3e] (280, 380, 435, 496, and 630 nm). **B** does not show any absorption band above 600 nm.

CRYSTAL STRUCTURE DESCRIPTION

Compounds **1** and **2** crystallize from *n*-hexane solutions in the triclinic space group $P\overline{1}$ and are isostructural to the analogous silicon compounds. Both the compounds have similar (Figure 1 and 2) molecular structures containing one germanium coordinated by two cAAC: molecules. The asymmetric unit of **1** contains two molecules of $(Me_2\text{-cAAC:})_2Ge$ and one lattice solvent molecule (*n*-hexane), whereas the asymmetric unit of **2** contains one molecule of $(Cy_2\text{-cAAC:})_2Ge$ and half of a lattice solvent molecule (*n*-hexane).

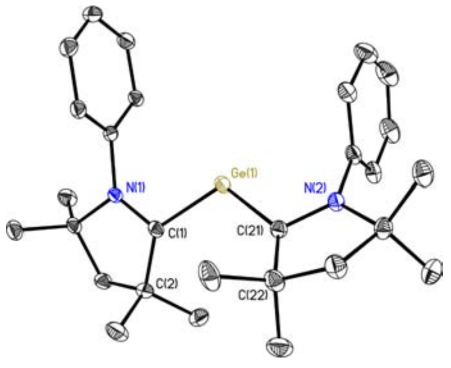


Figure 1. Molecular structure of compound **1** with the anisotropic displacement parameters drawn at the 50% probability level. The hydrogen atoms and isopropyl groups are omitted for clarity.

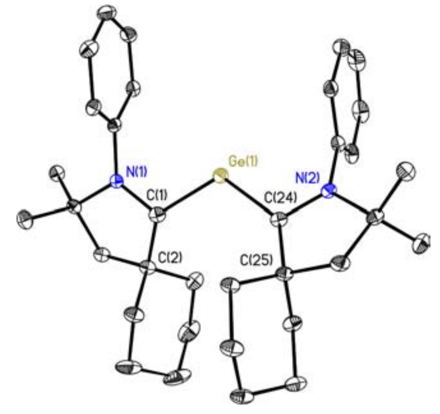


Figure 2. Molecular structure of compound **2** with the anisotropic displacement parameters drawn at the 50% probability level. The hydrogen atoms and isopropyl groups are omitted for clarity.

Selected bond lengths and angles of compounds **1**, **2**, and **B** are shown in Table 1. The Ge–C_{carbene} bond distances of **1** (1.9386(16), 1.9417(15) Å) and **2** (1.954(2), 1.9386(18) Å) are slightly shorter than those found in germylone **B** (1.965(3), 1.961(3) Å).[5a] It is important to note that both Ge–C bond

Table 1. Selected Bond Lengths and Angles of Compounds 1, 2, and B

	1	2	B^{5a}
Ge–$C_{carbene}$	1.9386(16)–1.9417(15)	1.954(2)–1.9386(18)	1.965(3)–1.961(3)
N1–C1 (Å)	1.367(19)	1.365(2)	1.378(4)
N2–C21/C24 (Å)	1.3666(19)	1.369(3)	1.377(4)
N–$C_{carbene}$–C/N (deg)	107.22(12)–107.07(12)	107.56(16)–107.15(15)	102.9(2)–103.3(1)
C–Si/Ge–C (deg)	114.71(6) –115.27(6)	117.24(8)	86.5(1)
N–$C_{carbene}$ –Si/Ge (deg)	113.55(10)–113.89(11)	112.94(13)–113.74(13)	128.6(2)
N/Me_2C–$C_{carbene}$–Si/Ge (deg)	136.53(11)–136.26(11)	135.80(14)–136.78(14)	128.1(2)
sum of angles at $C_{carbene}$ (deg)	357.30–357.22	356.30–357.67	359.6–360.0
sum of angles at N (deg)	359.83–359.90	359.92–359.90	

distances differ significantly in **2**, while they are almost identical in **1**. This is first observed in the analogous silicon compounds. A purple-colored $\{C_6H_3\text{-}2,6\text{-}Mes_2\}_2Ge$ with two coordinate germanium has been reported with Ge–C bond length of 2.033(4) Å which is slightly longer than those of **1** and **2**.[13]

The DFT calculation on **B** revealed that the HOMO consists of the π-type orbital at the germanium center including Ge–C π-bonding and the short Ge–C bond was explained by π-back-bonding like that in **C**. This could be explained by the fact that the cAAC: is a much better π-acceptor[7] than the bNHC: of **B**.[5a] The C–Ge–C bond angles of compounds **1** and **2** are 114.71(6)–115.27(6)° and 117.24(8)°, respectively. In comparison the C–Si–C angles are 117.18(8)–117.70(8)/118.16(6)° for **C**.[8a,c] In contrast, the C–Ge–C bond angle (86.5(1)°) in **B** is sharper[5a] by 28.5°/30.7° (Table 1) when compared with those of **1** and **2** indicating a stronger π-bond in the C–Ge–C part of **1**/**2** like that of **C**, than that of **B**. Thus the C–Ge–C backbone of **1** and **2** is significantly less bent than that of cyclic **B**. The reported $\{C_6H_3\text{-}2,6\text{-}Mes_2\}_2Ge$ compound has a similar C–Ge–C bond angle (114.4(2)°),[12] whereas larger bent angles are observed in compounds 2-germadisilaallene[3c] (132.38(2)°) and trigermaallene[3e] (122.61(6)°), respectively. Unlike the configuration of the heavy analogues of trisilaallene,[3a−f] the central Ge atoms in **1** and **2** are fixed without dynamic disorders detected. The $C_{carbene}$–N bond lengths of **1** and **2** are 1.3670(19)-1.3666(19) and 1.365(2)–1.369(3) Å which are similar to those values found in **B** and **C**.[6,7] As we could show recently the geometry at the nitrogen atoms in the cAAC is an indicator for the bonding situation in $(cAAC\cdot)_2X$, X = $SiCl_2$, Si, BH, species.[8c] A deviation from the planar geometry at the nitrogen atom like in the free carbene should be observed if the bond between the central atom and the carbene is an electron sharing bond. With an angular sum close to 360° (Table 1) we anticipate the carbenes in both compounds **1** and **2** to be in the singlet state. Full tables of bond lengths and bond angles of compounds **1**–**4** are given in the Supporting Information.

■ COMPUTATIONAL STUDIES

To gain further insight into the electronic structure of the studied compounds, theoretical calculations have been carried out. Specifically, we have performed geometry optimizations on compounds **1** and **2** at the M05-2X/def2-SVP[13] level of theory considering three electronic states, namely, singlet closed-shell, singlet broken-symmetry and triplet state. For a better visualization, we have prepared superposition plots of the X-ray structures with the optimized ones (see Figures S3–S10, Supporting Information). Our theoretical geometries show that both singlet states are in a better agreement with the X-ray structures than the triplet state. The latter structure has a good representation of the side ligands but presents a significant deviation on the bridge $C_{carbene}$–Ge–$C_{carbene}$.

An improvement of the electronic energies of each species has been done at several levels of theory, namely, M05-2X/def2-TZVPP, B3LYP/def2-TZVPP,[14] PBE/def2-TZVPP[15] and BP86/def2-TZVPP.[16] All these methods predict that both the singlet states have almost the same energy while the triplet form is 16.6 kcal mol^{-1} (M05-2X), 18.6 kcal mol^{-1} (B3LYP), 22.0 kcal mol^{-1} (BP86), and 17.4 kcal mol^{-1} (PBE) higher in energy for compound **1**. Likewise, the computed singlet-triplet electronic energy differences for compound **2** are 16.7 kcal mol^{-1} (M05-2X), 18.3 kcal mol^{-1} (B3LYP), 21.5 kcal mol^{-1} (BP86), and 17.1 kcal mol^{-1} (PBE). These results support the experimental EPR outcome of a singlet state. However, it is important to stress that among all the functionals used M05-2X was only one which recognized a singlet broken symmetry state, which would fall in agreement with the observation of a diradical species (see Tables S3 and S4 in the Supporting Information).

In Figure 3, we have depicted the shape of the molecular orbitals HOMO-1, HOMO and LUMO of the singlet state form for compound **1**. Additionally, in Figure S11 in the Supporting Information, the frontier molecular orbitals are displayed for the broken symmetry state.

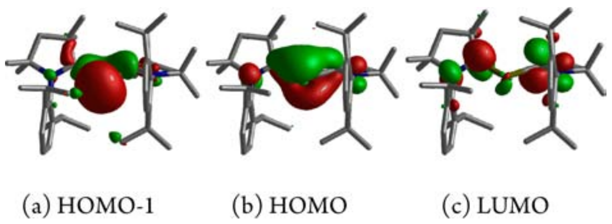


Figure 3. Frontier KS molecular orbitals (isocontour 0.045 au) of compounds **1** (M05-2X/def2-TZVPP). Hydrogen atoms are omitted for clarity.

The shapes of the orbitals fall into the typical features of the carbone(0) and silylone(0) compounds giving hints into their nature.[2] The HOMO-1 is a σ-type lone pair orbital located on Ge. On the other hand, the HOMO is a π-type orbital with the largest contribution on Ge, which is normal for back-donation. Interestingly, the LUMO orbital has a great contribution of the π-antibonding orbital N–$C_{carbene}$ of each carbene moiety and a smaller one on the Ge atom. Additionally, the frontier degenerate singly occupied molecular orbitals of the singlet diradicaloid systems are shown in Figure S11 in the Supporting Information. Strikingly, the HOMO is split up in two different spatial orbitals which mainly involve a π-type Ge–$C_{carbene}$ orbital, each one with a cAAC: ligand.

The Natural Bond Orbital (NBO)[17] analysis on compounds **1** and **2** as closed-shell species has been carried out including a three-center bond search. The results pointed out that the principal orbitals are a lone pair on Ge with occupancy of 1.770 electrons (1.760 electrons for compound **2**) and a three-center C−Ge−C π-type orbital where 43% is at the Ge atom and 28.5% at each of the carbene carbon atoms with occupancy of 1.935 electrons (1.933 electrons). Strikingly, the NBO analysis also indicated the presence of two three-center π-antibonding orbitals at the C−Ge−C bridge, the first one with an occupancy of 0.628 electrons and located on the two carbene carbon atoms; the second one is a π-type orbital placed on Ge (57%) and $C_{carbene}$ (21.5%), which has an occupancy of 0.200 electrons. Indeed, application of the second-order perturbation theory of the NBO method revealed the occurrence of the strong stabilizing two-electron donor−acceptor interactions from the lone pair of Ge (LP(Ge)) into the three center antibonding orbitals (π^*(C−Ge−C)), and from the lone pair of the N atoms (LP(N)), at the cAAC: moieties, into the (π^*(C−Ge−C)). For instance, the computed energies are 42.3 kcal mol^{-1} for LP(Ge)→π^*(C−Ge−C) donor−acceptor interaction and 26 kcal mol^{-1} for the two LP(N)→π^*(C−Ge−C) donor−acceptor interactions, which indicate a high stabilization effect by delocalization. The Wiberg bond order[18] of the Ge−$C_{carbene}$ bonds are 1.146 and 1.148 au for compounds **1** and **2** (in that order), explaining the short distances observed in the X-ray structures. Furthermore, the computed NPA charge on the Ge is 0.36 au for **1** and 0.37 au for **2** supporting the nature of these compounds as Ge(0) germylones.

To confirm the classification of compounds **1** and **2**, we have computed their proton affinity at the BP86/def2-SVP level of theory. The results suggest a high first proton affinity, namely, 265.8 kcal mol^{-1} and 267.1 kcal mol^{-1} for **1** and **2**, respectively. Moreover, the second proton affinity is lower but still high, i.e., 180.4 and 183.8 kcal mol^{-1} for **1** and **2**, respectively. These values of the proton affinities are in the normal range for germylones.[2b,c,5a]

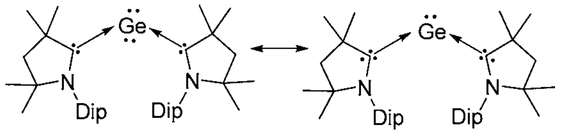
To have a better understanding of the electronic ground state CASSCF(2,2)/def2-SVP//M05-2X/def2-SVP[19] calculations were performed. These multireference calculations led to a CI vector having coefficients of 0.96 (**1** and **2**) for the closed-shell 2,0 configuration, 0.0 (**1** and **2**) for the 1,1 configuration, and −0.28 (**1** and **2**) for the 0,2 configuration. Therefore, compounds **1** and **2** are closed-shell singlet species having a contribution of double excited state which gives a singlet diradicaloid character. In this regard, the singlet diradical index, proposed by Neese and co-workers,[20,21] can be calculated, for an ab initio CI calculation with the canonical MOs, by the following equation:

$$d = 200\sqrt{\frac{c_0^2 c_d^2}{c_0^2 + c_d^2}}$$

where c_0^2 is the weight of the closed-shell configuration in the CI wave function and c_d^2 is weight of the double excitation. According with our values the diradicaloid character is 54% for **1** and **2**.

Finally, to help in interpreting the UV−visible spectra band assignment, we have carried out TD-CAM-B3LYP/def2-SVP[22] calculations with the both the singlet configurations in the gas phase and in the solvent *n*-hexane (PCM model).[23] The results are gathered in the Tables S3 and S4. The results for the closed-shell configuration yield three main excitations, namely, for compound **1** at 565.3 nm (568.6 nm; results for compound **2**), 325.6 nm (328.2 nm), and 280.6 nm (282.9 nm) with the oscillator strengths of 0.280 (0.258), 0.026 (0.025), and 0.166 (0.157), respectively. They mainly correspond to the electron promotion HOMO→LUMO, HOMO→LUMO+5, and HOMO-1→LUMO+1, in that order (see the Supporting Information, Figure S12). In *n*-hexane, the absorption bands are slightly shifted and the oscillator strength is slightly stronger. In addition, when the TD-DFT calculation was performed on compound **1** and **2** in their broken symmetry state a band appeared at 618.1 nm (628.8 nm in *n*-hexane) and 628.2 (637.6 nm in *n*-hexane) for compounds **1** and **2**, respectively. This is in good agreement with the experimental UV−visible spectra that give a diradicaloid band at 653 nm for **1** and 657 nm for **2**. The assignation of these bands are the promotion of one electron SHOMO-$\alpha(\beta)$ into LUMO-$\alpha(\beta)$ (see Figure S13 in the Supporting Information). On the basis of the theoretical evidence, the resonance structures of **1** are given in Scheme 6.

Scheme 6. Resonance Structures of 1[a]



[a]Schematic representation drawn in the right formula shows the results of a proposed three-center two-electron π bond.[8b,c]

CONCLUSION

We have developed novel methodologies for the synthesis of acyclic germylones $(Me_2\text{-cAAC:})_2Ge$ (**1**) and $(Cy\text{-cAAC:})_2Ge$ (**2**) and germylenedichloride Me_2-cAAC:→$GeCl_2$ (**3**). We have experienced that the germanium analogue of the diradical $(Me_2\text{-cAAC}\cdot)_2SiCl_2$ is not formed due to the weaker Ge−C single bond energy. An adduct between the Me_2-cAAC: and $GeCl_2$, Me_2-cAAC:→$GeCl_2$ (**3**), was obtained. However, the reduction of **3** with KC_8 in the presence of Me_2-cAAC: did not give the desired germylone $(Me_2\text{-cAAC:})_2Ge$. This suggests that **3** is not the right precursor for the synthesis of $(Me_2\text{-cAAC:})_2Ge$ (**1**). Hence in the search for an alternative method we have demonstrated that a one-pot reaction of $GeCl_2$(dioxane), Me_2-cAAC: and KC_8 led to the germylones **1** and **2** yielding 75 and 70%, respectively. The dark greenish crystals of **1** and **2** are stable in an inert atmosphere at room temperature for at least two weeks and can be stored in air for several hours. DFT calculation showed that single ground state of **1**/**2** is more stable by ∼16 to 18 kcal mol^{-1} than that of triplet state. Two proton affinity values were theoretically calculated to be 265.8 (**1**)/267.1 (**2**) and 180.4 (**1**)/183.8 (**2**) kcal mol^{-1}, respectively. Importantly, the computed NPA charges on the Ge are 0.36 au for **1** and 0.37 au for **2**, which suggest that the formal oxidation state of germanium atom in **1**/**2** is zero. The theoretical results pointed out that the principal orbitals are a lone pair on Ge with occupancy of 1.770 electrons (1.760 electrons for **2**) and a three-center C−Ge−C π-type orbital where 43% is at Ge atom and 28.5% at each of the carbene carbon with the occupancy of 1.935 electrons (1.933 electrons for **2**). Further calculations demonstrated that these compounds are germylones in nature and possess 54% of a diradicaloid character, which is due to the stronger π-accepting ability of cAAC: carbenes. The absorption band at 653 nm for **1** and 657 nm for **2** originated because of diradicaloid character of **1** and **2**. Studies of the chemistry of the new compounds $(Me_2\text{-cAAC:})_2Ge$ (**1**) and $(Cy_2\text{-cAAC:})_2Ge$ (**2**) are currently in progress.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental details for the synthesis, crystallographic data, tables of bond lengths and angles, UV−visible spectra, and theoretical calculation details. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: hroesky@gwdg.de (H.W.R.); hpzhu@xmu.edu.cn (H.Z.); dstalke@chemie.uni-goettingen.de (D.S.); die@mail.fcq.unc.edu.ar (D.M.A.).

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This manuscript is dedicated to Professor Helmut Schwarz on the occasion of his 70th birthday. This work was funded by the Deutsche Forschungsgemeinschaft (RO 224/60-1, H.W.R.) and the Danish National Research Foundation (DNRF93) funded Center for Materials Crystallography (D.S.). We thank Prof. Dr. Ricardo A. Mata for his valuable comments and guidance in carrying out the theoretical calculation. We thank Prof. Dr. F. Meyer and N. Bruckner for UV−visible and Dr. A. C. Stückl for EPR measurements. Y. L. thanks the Chinese Scholarship Council for a fellowship.

■ REFERENCES

(1) Smith, M. B.; March, J. *March's Advanced Organic Chemistry: Reactions, Mechanisms, and Structure*, 6th ed; Wiley-Interscience: New York, 2007.

(2) (a) Tonner, R.; Frenking, G. *Angew. Chem., Int. Ed.* **2007**, *46*, 8695−8698; *Angew. Chem.* **2007**, *119*, 8850−8853. (b) Takagi, N.; Shimizu, T.; Frenking, G. *Chem.—Eur. J.* **2009**, *15*, 8593−8604. (c) Takagi, N.; Shimizu, T.; Frenking, G. *Chem.—Eur. J.* **2012**, *18*, 1772−1780. (d) Tonner, R.; Öxler, F.; Neumüller, B.; Petz, W.; Frenking, G. *Angew. Chem., Int. Ed.* **2006**, *45*, 8038−8042; *Angew. Chem.* **2006**, *118*, 8206−8211. (e) Frenking, G.; Neumüller, B.; Petz, W.; Tonner, R.; Öxler, F. *Angew. Chem, Int. Ed.* **2007**, *46*, 2986−2987; *Angew. Chem.* **2007**, *119*, 3044−3045. (f) Frenking, G.; Tonner, R. *Pure Appl. Chem.* **2009**, *81*, 597−614. (g) Klein, S.; Tonner, R.; Frenking, G. *Chem.—Eur. J.* **2010**, *16*, 10160−10170. (h) Frenking, G.; Tonner, R. *Wiley Interdisciplinary Rev.: Comput. Mol. Sci.* **2011**, *1*, 869−878. (i) Takagi, N.; Frenking, G. *Theor. Chem. Acc.* **2011**, *129*, 615−623. (j) Takagi, N.; Shimizu, T.; Frenking, G. *Chem.—Eur. J.* **2009**, *15*, 3448−3456.

(3) For reviews on heteroallenes, see: (a) Ishida, S.; Iwamoto, T.; Kabuto, C.; Kira, M. *Nature* **2003**, *421*, 725−727. (b) Kira, M.; Iwamoto, T.; Ishida, S.; Masuda, H. *J. Am. Chem. Soc.* **2009**, *131*, 17135−17144. (c) Iwamoto, T.; Abe, T.; Kabuto, C.; Kira, M. *Chem. Commun.* **2005**, 5190−5192. (d) Kira, M. *Chem. Comunm.* **2010**, *46*, 2893−2903. (e) Iwamoto, T.; Masuda, H.; Kabuto, C.; Kira, M. *Organometallics* **2005**, *24*, 197−199. (f) Escudié, J.; Ranaivonjatovo, H.; Rigon, L. *Chem. Rev.* **2000**, *100*, 3639−3696. (g) Ghereg, D.; Saffon, N.; Escudié, J.; Miqueu, K.; Sotiropoulos, J.-M. *J. Am. Chem. Soc.* **2011**, *133*, 2366−2369.

(4) (a) Weber, E.; Seichter, W.; Hess, B.; Will, G.; Dasting, H. J. *J. Phys. Org. Chem.* **1995**, *8*, 94−96. (b) Dyker, C. A.; Lavallo, V.; Donnadieu, B.; Bertrand, G. *Angew. Chem., Int. Ed.* **2008**, *47*, 3206−3209; *Angew. Chem.* **2008**, *120*, 3250−3253. (c) Hofmann, M. A.; Bergsträsser, U.; Reiss, G. J.; Nyulaszi, L.; Regitz, M. *Angew. Chem., Int. Ed.* **2000**, *39*, 1261−1263; *Angew. Chem.* **2000**, *112*, 1318−1320. (d) Chen, W.-C.; Hsu, Y.-C.; Lee, C.-Y.; Yap, G. P. A.; Ong, T.-G. *Organometallics* **2013**, *32*, 2435−2442.

(5) (a) Xiong, Y.; Yao, S.; Tan, G.; Inoue, S.; Driess, M. *J. Am. Chem. Soc.* **2013**, *135*, 5004−5007. (b) Xiong, Y.; Yao, S.; Inoue, S.; Epping, J. D.; Driess, M. *Angew. Chem., Int. Ed.* **2013**, *52*, 7147−7150; *Angew. Chem.* **2013**, *125*, 7287−7291.

(6) (a) Wang, Y.; Xie, Y.; Wei, P.; King, R. B.; Schaefer, H. F., III.; Schleyer, P. v. R.; Robinson, G. H. *Science* **2008**, *321*, 1069−1071. (b) Sidiropoulos, A.; Jones, C.; Stasch, A.; Klein, S.; Frenking, G. *Angew. Chem., Int. Ed.* **2009**, *48*, 9701−9704; *Angew. Chem.* **2009**, *121*, 9881−9884. (c) Wang, Y.; Robinson, G. H. *Chem. Commun.* **2009**, 5201−5213 and the references therein.

(7) (a) Lavallo, V.; Canac, Y.; Präsang, C.; Donnadieu, B.; Bertrand, G. *Angew. Chem., Int. Ed.* **2005**, *44*, 5705−5709; *Angew. Chem.* **2005**, *117*, 5851−5855. (b) Martin, C. D.; Soleilhavoup, M.; Bertrand, G. *Chem. Sci.* **2013**, *4*, 3020−3030. (c) Martin, D.; Melaimi, M.; Soleilhavoup, M.; Bertrand, G. *Organometallics* **2011**, *30*, 5304−5313. (d) Back, O.; Henry-Ellinger, M.; Martin, C. D.; Martin, D.; Bertrand, G. *Angew. Chem., Int. Ed.* **2013**, *52*, 2939−2943; *Angew. Chem.* **2013**, *125*, 3011−3015.

(8) (a) Mondal, K. C.; Roesky, H. W.; Schwarzer, M. C.; Frenking, G.; Niepötter, B.; Wolf, H.; Herbst−Irmer, R.; Stalke, D. *Angew. Chem., Int. Ed.* **2013**, *52*, 2963−2967; *Angew. Chem.* **2013**, *125*, 3036−3040. (b) Mondal, K. C.; Roesky, H. W.; Schwarzer, M. C.; Frenking, G.; Tkach, I.; Wolf, H.; Kratzert, D.; Herbst-Irmer, R.; Niepötter, B.; Stalke, D. *Angew. Chem., Int. Ed.* **2013**, *52*, 1801−1805; *Angew. Chem.* **2013**, *125*, 1845−1850. (c) Mondal, K. C.; Samuel, P. P.; Tretiakov, M.; Singh, A. P.; Roesky, H. W.; Stückl, A. C.; Niepötter, B.; Carl, E.; Wolf, H.; Herbst-Irmer, R.; Stalke, D. *Inorg. Chem.* **2013**, *52*, 4736−4743.

(9) (a) Martin, D.; Soleilhavoup, M.; Bertrand, G. *Chem. Sci.* **2011**, *2*, 389−399. (b) Nayek, H. P.; Arleth, N.; Trapp, I.; Löble, M.; Ona-Burgos, P.; Kuzdrowska, M.; Lan, Y.; Powell, A. K.; Breher, F.; Roesky, P. W. *Chem.—Eur. J.* **2011**, *17*, 10814−10819.

(10) Thimer, K. C.; Al-Rafia, S. M. I.; Ferguson, M. J.; McDonald, R.; Rivard, E. *Chem. Commun.* **2009**, 7119−7121.

(11) Singh, A. P.; Ghadwal, R. S.; Roesky, H. W.; Holstein, J. J.; Dittrich, B.; Demers, J.-P.; Chevelkov, V.; Lange, A. *Chem. Commun.* **2012**, *48*, 7574−7576.

(12) Simons, R. S.; Pu, L.; Olmstead, M. M.; Power, P. P. *Organometallics* **1997**, *16*, 1920−1925.

(13) (a) Zhao, Y.; Schultz, N. E.; Truhlar, D. G. *J. Chem. Theory Comput.* **2006**, *2*, 364−382. (b) Zhao, Y.; Schultz, N. E.; Truhlar, D. G. *J. Chem. Phys.* **2005**, *123*, 161103−161106. (c) Weigend, F.; Ahlrichs, R. *Phys. Chem. Chem. Phys.* **2005**, *7*, 3297−3305.

(14) (a) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648−5652. (b) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785−789.

(15) (a) Perdew, J. P.; Burke, K.; Ernzerhof, M. *Phys. Rev. Lett.* **1996**, *77*, 3865−3868. (b) Adamo, C.; Barone, V. *J. Chem. Phys.* **1999**, *110*, 6158−6170.

(16) (a) Perdew, J. P. *Phys. Rev. B* **1986**, *33*, 8822−8824. (b) Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098−3100.

(17) (a) Reed, A. E.; Curtiss, L. A.; Weinhold, F. *Chem. Rev.* **1988**, *88*, 899−926. (b) Reed, A. E.; Weinstock, R. B.; Weinhold, F. *J. Chem. Phys.* **1985**, *83*, 735−746. (c) Reed, A. E.; Weinhold, F. *J. Chem. Phys.* **1985**, *83*, 1736−1740. (d) Foster, J. P.; Weinhold, F. *J. Am. Chem. Soc.* **1980**, *102*, 7211−7218.

(18) Wiberg, K. B. *Tetrahedron* **1968**, *24*, 1083−1096.

(19) (a) Hegarty, D.; Robb, M. A. *Mol. Phys.* **1979**, *38*, 1795−1812. (b) Eade, R. H. A.; Robb, M. A. *Chem. Phys. Lett.* **1981**, *83*, 362−368. (c) Yamamoto, N.; Vreven, T.; Robb, M. A.; Frisch, M. J.; Schlegel, H. B. *Chem. Phys. Lett.* **1996**, *250*, 373−378. (d) Frisch, M.; Ragazos, I. N.; Robb, M. A.; Bernhard Schlegel, H. *Chem. Phys. Lett.* **1992**, *189*, 524−528.

(20) Bachler, V.; Olbrich, G.; Neese, F.; Wieghardt, K. *Inorg. Chem.* **2002**, *41*, 4179−4193.
(21) (a) Herebian, D.; Bothe, E.; Neese, F.; Weyhermüller, T.; Wieghardt, K. *J. Am. Chem. Soc.* **2003**, *125*, 9116−9128. (b) Herebian, D.; Wieghardt, K. E.; Neese, F. *J. Am. Chem. Soc.* **2003**, *125*, 10997−11005. (c) Neese, F. *J. Phys. Chem. Solids* **2004**, *65*, 781−785.
(22) Yanai, T.; Tew, D. P.; Handy, N. C. *Chem. Phys. Lett.* **2004**, *393*, 51−57.
(23) Miertš, S.; Scrocco, E.; Tomasi, J. *J. Chem. Phys.* **1981**, *55*, 117−129.