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A functionalized Ge_3-compound with a dual character of the central germanium atom†

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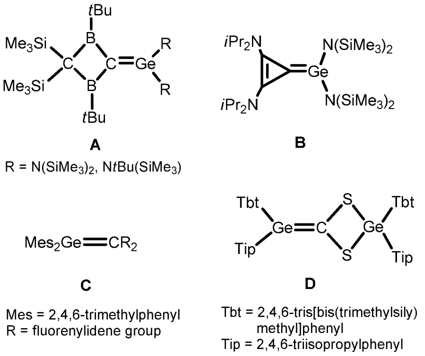
$(cAAC)Ge(GeL)_2$ (1) (cAAC = cyclic alkyl(amino) carbene; L = PhC-(tBuN)$_2$), a functionalized Ge_3-compound was prepared. Quantum mechanical studies on 1 show a reciprocal relationship between the electronic state of the central tri-coordinated Ge atom and its reactivity towards protons, *viz.* tetravalent Ge(0) in terms of bonding and divalent Ge(0) in terms of reactivity. Thus the central Ge atom can be considered as having a hidden but highly reactive lone pair of electrons. However, the terminal Ge atoms can be considered as tri-coordinated divalent Ge(I) with an active lone pair of electrons.

The formation of multiple bonds between carbon and heavier group 14 elements (Si, Ge, and Sn) has been an attractive research topic for decades.[1] Stable germenes (>C=Ge<) can be accessed by protecting both carbon and germanium centers using sterically demanding ligands (Scheme 1). The approaches to germenes **A**[2] and **B**[3] are assumed *via* transient carbenes, while **B** is best described as an adduct of cyclopropenylidene and germylene. Compound **C**[4] is prepared by treating $Mes_2Ge(F)–C(H)R_2$ with *t*BuLi, and **D**[5] is probably produced by the insertion of CS_2 into a Ge=Ge double bond. A germylone[6a,b] with composition $(cAAC)_2Ge(0)$ shows an interesting biradicaloid character.[6c] The NBO study demonstrates that the principal orbitals of $(cAAC)_2Ge$ are a lone pair on Ge and a three-center C–Ge–C π-type orbital where 43% is at the Ge atom and 28.5% at each carbene carbon, different from the C → Ge donor–acceptor bond present in the cyclic germylone.[7] This is mainly attributed to the singlet spin ground state and the smaller HOMO–LUMO energy gap of cAAC, when compared with that of NHC (N-heterocyclic carbene).[8] This finding enriches the carbene–Ge chemistry, and a similar bonding situation is theoretically reported for the Si analogues.[9] Although $(cAAC)_2Ge$ can be prepared easily by using $GeCl_2$(dioxane) as the Ge source,[6c] we are curious to study the reaction behavior when a substituted germanium precursor is employed. Herein, we report a novel Ge_3-compound (**1**) which shows for the first time the direct formation of a Ge=C bond using a stable cAAC. Moreover, theoretical studies predict an unusual dual character of the central Ge atom.



Scheme 1 Representatives of the stable >C=Ge< species.

The reaction of LGeCl (L = PhC(tBuN)$_2$),[10] cAAC and KC_8 in a molar ratio of 1 : 0.5 : 1.2 in THF at −78 °C for 1 h gives compound $(cAAC)Ge(GeL)_2$ (**1**) isolated as red crystals in 35% yield (based on Ge) (Scheme 2). The molar ratio mentioned above is tested to be necessary for the formation of **1**. Interestingly, stirring the reaction overnight at room temperature affords a mixture of **1**, dark green plates of $(cAAC)_2Ge$ (**2**) and a small amount of colorless crystals of $(cAACH)_2O$.[11] **2** is also slowly generated from the mother liquid of **1** (Scheme 2). However, when NHC (1,3-bis(isopropyl)imidazol-2-ylidene) is used instead of cAAC, only LGe–GeL[10] is produced.

The solution of **1** is highly air sensitive, but it is stable in the solid state, even when exposed to air for two days. **1** decomposes above 183 °C. **1** is soluble in THF and toluene, but sparingly soluble in *n*-hexane. The ^1H NMR spectrum shows the resonances corresponding to iPr-*H* (septet at 3.41 ppm) and >CH_2 (singlet at 1.42 ppm)

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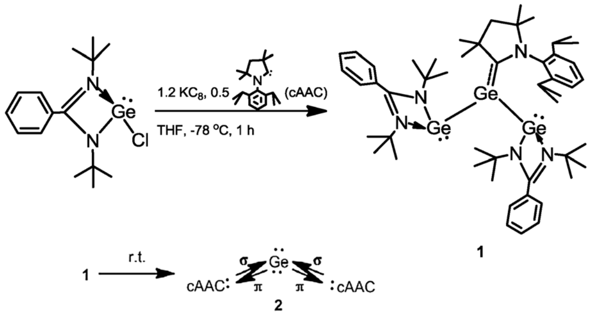


Scheme 2 Synthesis of **1** and its transformation to germylone **2**.

of cAAC. The amidinate ligand exhibits two *t*Bu-*H* resonances (1.34 and 1.32 ppm), indicating the asymmetric structure of the molecule. In the ^{13}C NMR spectrum, the resonance for the carbene carbon (C–Ge) is observed at 219.4 ppm which shifts upfield when compared with that of the free cAAC (304.2 ppm)[9] and **2** (232.6 ppm).[6c] This resonance is significantly low field shifted relative to those reported for the stable germaethene **A** (115 and 93 ppm) and the conjugated $Ar_2Ge{=}C(R)C{\equiv}C(R)C{=}GeAr_2$ (Ar = 2,3,4-trimethyl-6-*t*Bu-phenyl; R = *n*Bu and C_6H_5).[12] The UV-visible spectrum of **1** recorded in C_6D_6 shows a strong absorption band at 490 nm.

The structure of **1** (Fig. 1) exhibits an asymmetric Ge_3 backbone, in which the central Ge1 atom adopts a three coordinate geometry with one C and two Ge atoms. The geometry around the Ge1 atom is nearly planar, which indicates the absence of a stereoactive lone pair at Ge1. In contrast, the Ge2 and Ge3 atoms are both pyramidalized due to the presence of a lone pair of electrons at the apex of a distorted trigonal pyramid. The N2–Ge2–N3 and N4–Ge3–N5 planes are nearly perpendicular (*ca.* 88°). The Ge2–Ge1–Ge3 bond angle is 107.65(2)° which is comparable to those reported for the four-membered zwitterionic ring L_4Ge_6,[13] while it is smaller than that of the bent trigermaallene (122.61(6)°).[14] The Ge1–Ge3 (2.4929(6) Å) and Ge1–Ge2 bond lengths (2.4746(7) Å) are close to that of the Ge–Ge single bonds (2.43–2.47 Å),[15] while shorter than that of the Ge–Ge bond (2.5439(7) Å) in 2,6-$Mes_2C_6H_3Ge$–Ge*t*Bu_3.[16] Notably, the Ge1–C1 bond distance (1.881(3) Å) is comparable to that of the reported Ge–C double bond, while it is shorter than that of 2 (*ca.* 1.94 Å)[6c] and the donating C → Ge (*ca.* 2.13 Å) bond in the cAAC($GeCl_2$) adduct.[6c] The torsion angle of the N1–C1–C2–Ge1 and Ge3–Ge1–Ge2–C1 planes is *ca.* 3.7°, which is smaller than those of **A** (av. 36°)[2] and **C** (av. 6°),[4] but close to that of **D** (4°).[5] This flatness allows a π-bonding between the carbene carbon (C1) and the central Ge1 atom.

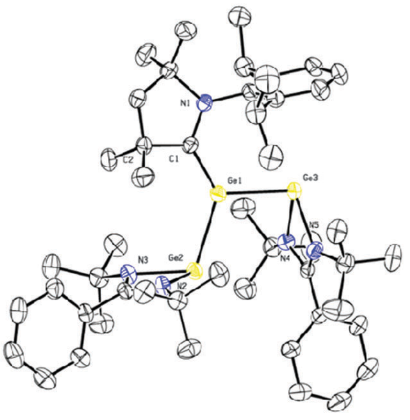


Fig. 1 Molecular structure of **1**. Selected bond lengths (Å) and angles (°): Ge1–C1 1.881(3), Ge1–Ge2 2.4746(7), Ge1–Ge3 2.4929(6), C1–N1 1.375(5), Ge2–N2 2.015(3), Ge2–N3 2.029(3); Ge2–Ge1–Ge3 107.65(2), C1–Ge1–Ge2 128.95(11), C1–Ge1–Ge3 122.68(11), N1–C1–C2 107.3(3), N1–C1–Ge1 127.5(2), C2–C1–Ge1 124.9(3). The sum of angles around C1 and Ge1 are *ca.* 359.7 and 359.3°, respectively.

To further understand the electronic structure and bonding of **1**, quantum chemical calculations were performed at the M06/def2-TZVPP//BP86/def2-SVP level of theory.[17a] The calculated singlet geometry (**3**) (Fig. S3, see ESI†) is in good agreement with the crystal structure. The singlet state is more stable than the triplet state by 24.6 kcal mol^{-1}. The calculated pyramidalization angle (θ_p = 360° − sum of the three angles around Ge atoms) indicates the planar coordination around Ge1 (θ_p = 0°) and pyramidal coordination around Ge2 (θ_p = 75.0°) and Ge3 (θ_p = 101.2°) implying the presence of a lone pair on Ge2 as well as on Ge3. The HOMO − 1 and HOMO − 2 (Fig. 2) represent the combinations of the lone pairs on the terminal Ge atoms. It is to be noted that the C1–N1 bond length (1.394 Å) is significantly elongated when compared with the corresponding bond length (1.320 Å) in the free cAAC. This can be understood from the HOMO which shows the back donation of the lone pair on Ge1 to the C1–N1 π*–MO (Fig. 2).

The significant back donation from Ge1 to the C1–N1 π*–MO can also be understood from the NBO charge and population analysis (Table S2, see ESI†).[17a] The group charge of cAAC is −0.32 e^- which indicates a net charge flow from the Ge_3L_2 fragment to the carbene ligand. This signifies that the π-back donation from Ge1 to the C1–N1 π*–MO of cAAC is much stronger than the σ-donation from cAAC to Ge1 of the Ge_3L_2 fragment. The Wiberg bond index of the Ge1–C1 bond (1.35) also indicates the partial double bond character.[18] The Wiberg bond index of the C1–N1 bond in **3** (1.12) is significantly reduced as compared to that of free cAAC (1.50). Interestingly, the NBO calculations suggest the presence of a p-type lone pair (100% p-character) on Ge1 and a sp-hybrid type lone pair on Ge2 (81.5% s-character and 18.5% p-character) and Ge3 (80.0% s-character and 20.0% p-character). Moreover, the occupancy of the lone pair on Ge1 is only 1.02 e^-, whereas on Ge2 and Ge3 is 1.93 e^- and 1.94 e^-, respectively. The molecular orbitals and the NBO charge and population analysis suggest that Ge2 and Ge3 can be considered as divalent Ge(I), where each Ge atom utilizes one electron for forming an electron sharing bond with the central Ge1 atom and one electron for the electron sharing bond with one N-atom of the amidinate ligand. The second N-atom of the amidinate ligand donates two

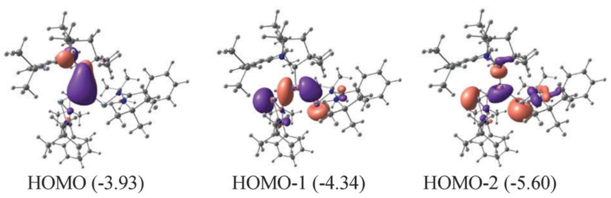
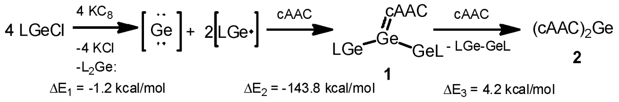


Fig. 2 Plot of important molecular orbitals of **3** showing the back donation from Ge1 to the C1–N1 π*–MO (HOMO) and the lone pair combinations of Ge2 and Ge3 (HOMO − 1 and HOMO − 2) at the M06/def2-TZVPP//BP86/def2-SVP level of theory. The eigenvalues (eV) are given in parentheses.

electrons to the Ge2/Ge3 atom. Thus two electrons of the terminal Ge atoms are retained as a lone pair. In contrast, the central Ge1 atom utilizes two electrons for electron sharing bonds with the terminal Ge atoms. The vacant in-plane σ-orbital accepts a pair of electrons from cAAC and the remaining two electrons on the p-orbital of Ge1 are back donated to the empty C1–N1 π*–MO of cAAC. Hence the tri-coordinated Ge1 atom can be considered as tetravalent Ge(0).[17b,19]

The EDA-NOCV method was employed to deeply study the nature of the interaction of cAAC with the Ge_3L_2 fragment.[17b] The donor–acceptor interaction between the singlet cAAC and the singlet Ge_3L_2 is found to be the most favorable bonding description and the corresponding EDA data are shown in Table S4 (see ESI†).[17b] The Ge1–C bond has a higher percentage of electrostatic interaction (54.0%) as compared to covalent interaction (46.0%). The two NOCV pairs of orbitals (Ψ_{-1}/Ψ_1 and Ψ_{-2}/Ψ_2) having a major contribution to the total orbital interaction energy (Fig. S4, ESI†) and their corresponding deformation density indicate mixing between the σ-type and π-type fragment orbitals on the Ge_3L_2 and cAAC. The NOCV pairs of orbitals do not have an appropriate σ- or π-symmetry.[17b] The corresponding deformation density plots $\Delta\rho_1$ ($\Delta E_1 = -62.1$ kcal mol^{-1}) and $\Delta\rho_2$ ($\Delta E_2 = -77.2$ kcal mol^{-1}) do not show any significant variation of electron density along the Ge1–C_{cAAC} bond. However, significant accumulation and depletion of electron density above and below the plane of the Ge1–C bond are observed. Hence, the bonding situation in the Ge1–C bond can be considered to be formed by two bent donor–acceptor bonds.[17b] This is also reflected in the low bond dissociation energy ($D_e = 26.9$ kcal mol^{-1}).

We have also calculated the proton affinity at each Ge center to understand the reactivity of the lone pairs. The proton affinities of Ge1 (267.6 kcal mol^{-1}), Ge2 (264.8 kcal mol^{-1}) and Ge3 (266.2 kcal mol^{-1}) are similar, which are quite higher than the calculated value for a five-membered N-heterocyclic germylene (196.0 kcal mol^{-1}) at the same level of theory and close to that of germylone (266.1 kcal mol^{-1}).[6c] Even though the lone pair on Ge1 is utilized for the π-bond formation with the carbene carbon atom, it is as equally available as those on Ge2 and Ge3 towards protonation. This can be attributed to the compensative π back donation of N1 → C1 within the cAAC ring and the more accessible 100% p-type lone pair on Ge1 as compared to the less accessible sp-hybrid type lone pair (approximately 80% s-character) on Ge2 and Ge3 atoms. Thus, as per the structure and bonding analysis, tri-coordinated Ge1 can be considered as tetravalent Ge(0) while the high proton affinity indicates its divalent Ge(0) nature. Hence, Ge1 shows a dual character for the electronic state and the lone pair on Ge1 can be considered as a hidden-type. We have recently reported a similar type of bonding and reactivity pattern for tri-coordinated beryllium complexes.[19] A similar type of bonding and reactivity pattern of divalent carbon(0) is also reported by Frenking and co-workers.[20]



Scheme 3 Proposed mechanism for the formation of **1** and **2**.

The proposed reaction mechanism for the formation of **1–2** (Scheme 3) was theoretically studied (see the ESI† for detailed discussion).

In summary, we have synthesized and characterized a novel Ge_3-compound $(cAAC)Ge(GeL)_2$ (**1**) in the singlet state. It is stable at room temperature in solid state under an inert atmosphere. Compound **1** can slowly convert to germylone **2** in solution. Notably, cAAC exclusively favors the generation of **1**, while NHC does not. Compound **1** is the first example of direct formation of a Ge═C bond by using a stable cAAC. Quantum mechanical studies show a reciprocal relationship between the bonding and reactivity of the central Ge atom. The bonding pattern of the central Ge atom is substantially different as compared to the terminal Ge atoms. However, the reactivity of all Ge atoms towards protonation is similar. The EDA-NOCV analysis suggests two bent bonds for the Ge1–C_{cAAC} bond.

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