Low-Valent Germanylidene Anions: Efficient Single-Site Nucleophiles for Activation of Small Molecules

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Abstract: Rare mononuclear and helical chain low-valent germanylidene anions supported by cyclic (alkyl)(amino) carbene and hypermetallyl ligands were synthesised by stepwise reduction from corresponding germylene precursors via stable and isolable germanium radicals. The electronic structures of the anions can be described with ylidene and yliden resonance forms with the Ge–C π-electrons capable of binding even weak electrophiles. The germanylidene anions reacted with CO to give μ-CO₂-xC₆O complexes, a rare coordination mode for low-valent germanium and inaccessible for the related neutral germynes. These results implicate low-valent germanylidene anions as efficient single-site nucleophiles for activation of small molecules.

Mononuclear complexes of germanium have garnered attention as congeners of transition metals in bond activation processes. The most intensely studied chemistries in this class involve Ge IV, Ge IV reactivity in which germanium functions primarily as a single-site amiphile via a Lewis acidic p-orbital and an electron pair.[1–11] More recently, ylidones (cAAC)₂E (cAAC = cyclic (alkyl)(amino)carbene; E = Si, Ge) A (Figure 1) featuring electron-rich Group 14 elements formally in oxidation state zero have been put to the fore. Akin to transition metals, increased nucleophilicity at the metalloid is critical to effect bond activation. These low-valent species are supported by ancillary ligands combining good σ-donor quality and capacity for accepting back-donation.[12–15] As such, carbenes and carbenoids are commonly employed in designs which range from simple monodentate ligands[16–21] to more exotic chelating[22–28] and pincer-type frameworks.[29–31] Despite the growing collection of ylidones, their chemistry is still in its infancy and dominated by coordination of Lewis acids and oxidative addition reactions with polar substrates.[26,30,32–35] Advancements in this regard include isolated incidents of frustrated Lewis pair reactivity with H₂,[36] activation of CO,[37–43] and metal-ligand cooperation.[31]

Contrasting the number of neutral ylidone compounds, related germanium-centred anions are scarce. This is surprising given the popularity of low-valent anionic aluminium nucleophiles[44] and is perhaps associated with the limited profile of anionic ligands in the chemistry of zero-valent germanium. Replacing a neutral cAAC unit in germylone A for a charge bearing amido ligand allows the stabilization of radicals B.[44] Although electrochemical evidence suggests that anions may be obtained by reduction of B,[44] the only known example, C, has been independently reported and its reactivity remains unexplored.[45]

Aiming to develop the chemistry of low-valent germanium further, we deployed the electronic stabilization afforded by Me₂-cAAC (1-(2,6-diisopropylphenyl)-3,3,5,5-tetramethylvypyrrolidine-2-ylidene, 2,6-diisopropylphenyl = Dipp) in combination with sterically encumbering hypermetallyl ligands E-(SiMe₃)₃ (E = Si, Ge) that are not significantly π-withdrawing; cf. the cAAC ligand and aryI group in A and C, respectively. This led to the synthesis of potassium salts of germaniyldene anions ([Me₂-cAAC]GeE(SiMe₃)₃] via corresponding germanium-centred radicals. Subsequent computational analyses and reactivity

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studies showed the electronic structures of [(Me₂-cAAC)GeE(SiMe₃)₂] (E = Si, Ge) to reside between ylidene and ylidone extremes, and the anions are able to function as efficient nucleophiles even with weak electrophiles, such as CO₂.

The reaction of (Me₂-cAAC)GeCl₂, [20] with a half equivalent of Mg[E(SiMe₃)₂](THF), [44,47] at −78 °C in THF (Scheme 1) yielded hypermetallyl germylene complexes 2a (E = Si) and 2b (E = Ge). Complexes 2 can be isolated in good yields by crystallization from hot heptane and stored for several months at −20 °C. NMR spectroscopy showed the expected resonances for 2 with ¹³C chemical shifts for the carbenic carbon at 248.0 and 249.8 ppm for 2a and 2b, respectively. These signals are in-line with that of (Me₂-cAAC)GeCl₂ (245.2 ppm), [20] but significantly deshielded compared to related N-heterocyclic carbene (NHC) complexes (NHC)GeClE(SiMe₃)₂ (E = Si, 173.1 ppm; E = Ge, 174.0 ppm). [48]

The molecular structures of 2 were confirmed by single crystal X-ray diffraction, revealing pyramidal geometry around germanium (Figures S18 and S19). The measured Ge–C bond lengths (2.015(2) and 2.025(3) Å in 2a and 2b, respectively) are slightly shortened as compared to (NHC)GeClSi(SiMe₃)₂ (2.093(3) Å), [46] indicating Ge–C back-bonding typical of cAAC-supported complexes that is also evident in their calculated HOMOs (Figure S32). Despite the different atomic properties of germanium and silicon, [46,49] varying the hypermetallyl ligand does not lead to significant structural or spectroscopic changes between 2a and 2b (cf. 4 and 5, see below).

Radical complexes 3 were prepared by reduction of germynes 2 using an excess of 10% potassium naphthaleneide ([K][C₆H₄]) at −78 °C (Scheme 1). Recrystallization from pentane at −30 °C afforded analytically pure products. Room temperature EPR spectra of 3 (pantaneg, Figure S16) show broad singlets with g ≈ 2.0 and linewidths of approximately 40 G owing to the coupling of the mostly germanium-centred (50%, Figure S33) unpaired electron to ¹⁴N (−3.5 G) and ¹H nuclei on the methyl groups of both Me₂-cAAC and SiMe₃ (0.1–3.4 G). The redox properties of 3 were characterised by cyclic voltammetry ([NBu₄]PF₆ in THF, Figure S17), with both species showing an electrochemically reversible one-electron reduction attributed to the formation of anions 4 and 5 (E₁/₂ = −2.02 V and −2.07 V vs. Fc/Fc⁺ for 3a and 3b, respectively).

Single crystal X-ray diffraction studies of 3 show two-coordinate germainium in a classic bent-geometry (Figures S20 and S21). Buried volume estimates suggest well protected metal coordination pockets, as imposed by Dipp and SiMe₃ substituents (V₉₋₁₃₇% in 3a and 3b, respectively). [31–34] Measured Ge–C bond lengths in 3 are comparable to those reported for B [(1.993(3) and 1.985(1) Å in 3a and 3b, respectively, vs. 1.986(2) Å in B) [44]] and only slightly shorter than in germylenes 2. As indicated by the frontier orbitals of 2 and 3 (Figure S32), the removal of chloride and addition of an electron to 2 results in enhanced σ-type Ge–C back-bonding in the SOMO of 3 vs. the HOMO of 2. However, since the SOMO of 3 is occupied by a single electron whereas the HOMO of 2 is occupied by two, the Ge–C bonds in 2 and 3 have comparable lengths.

The anions 4 and 5 can be chemically accessed by reaction of 2 with excess (2.2 equivalents) of [K][C₆H₄] in THF or, alternatively, by direct reduction of 3 with KC₆ or [K][C₆H₄] (Scheme 2). Solvate-free 4 and 5 were isolated by careful purification of the reaction products with pentane, while 4-(THF) and 4-(THF)₂ could be crystallised as a result from the presence of adventitious solvent molecules (Figures S28 and S29). The carbenic carbon signal appears at 226.3 ppm in the ¹³C NMR spectrum of 4, matching with literature data for C (212.1 ppm). This observation is reconciled by changes in the
frontier orbitals of 2, 3, and 4 (Figure S32), and consistent with greater shielding relative to 2a (248.0 ppm).

Unlike C, which exists as a dimer in the solid-state, complex 4 crystallizes as a discrete mononuclear species (Figure 2) that, however, forms pseudo-1D polymeric chains held together by anagostic \( \text{C} - \text{H} \cdot \cdot \cdot \text{K} \) interactions. In the crystal structure of 4, the germanium atom is flanked by Me\(_2\)cAAC and hypersilyl ligands, with potassium completing a trigonal planar coordination sphere. As suggested by the doubly occupied \( \pi \)-type HOMO of 4 (Figure S32), the Ge\( - \text{C} \) bond, 1.879(2) \( \text{Å} \), is significantly shortened relative to 3a (1.993(3) \( \text{Å} \)), while on par with that in C (1.874(2) \( \text{Å} \)). The Ge\( - \text{K} \) distance in 4 (3.1878(6) \( \text{Å} \)) is considerably shorter than in C (3.2555(6) \( \text{Å} \)), indicating strong electrostatic interaction between the lone pair on germanium and potassium cation. The cation is further \( \eta^3 \)-coordinated to the Dipp substituent and can readily participate in other coordinative interactions (the formation of 4-(THF) and 4-(THF)_2, see below).

Contrasting 4, the solid-state structure of 5 depicts germanium in a pseudo-tetrahedral coordination environment with distortion towards disphenoidal (distorted tetrahedral) geometry (Figure 2). The long Ge\( - \text{K} \) contacts (3.6253(7)–3.725(2) \( \text{Å} \)) work together with bridging \( \text{K} \)\( - \cdot \cdot \cdot (\eta^1\)-arene) interactions to connect adjacent complexes in 1-D helical chains (Figures S24 and S25). The extended structure of 5 arises, at least in part, from relaxed steric, that is, from longer Ge\( - \text{E} \) bond distance (Ge1–Si1 = 2.4428(6) \( \text{Å} \)) in 4 vs. Ge1–Ge2 = 2.5362(6) \( \text{Å} \) and Ge3–Ge4 = 2.5345(7) \( \text{Å} \) in 5). The formation of 1-D chain structure of 5 is accompanied by elongation of the Ge\( - \text{C} \) bond relative to 4 (1.922(4) and 1.913(4) \( \text{Å} \) in 5 vs. 1.879(2) \( \text{Å} \) in 4) due to attraction of the bridging potassium cation to electrons formally in the Ge\( - \text{C} \) \( \pi \)-bond and consequent enhancement of ylidone character on germanium (Scheme 3, right).

The \(^1\)H NMR spectra of poorly soluble 5 (C\(_6\)D\(_6\) and THF-d\(_8\)) show visible broadening, indicating that an extended structure is present also in solution. The broad resonances can, however, be resolved by introducing stoichiometric amounts of bis(2-methoxyethyl) ether (diglyme) to NMR solutions of 5, yielding spectra that are comparable to those measured for 4 (Figure S57). The resolved solution NMR spectra of 5 show signals for free diglyme and adducts 5-(diglyme) and 5\(_2\)-(diglyme) could be crystallographically identified (Figures S30 and S31). This supports decomposition of the extended structure of 5 to a dynamic equilibrium of monomeric and dimeric subunits upon addition of diglyme.

The electronic structures of 4 and monomeric 5 were analysed by computational methods. The Ge\( - \text{C} \) bond has significant double bond character arising from \( \pi \)-type Ge\( - \text{C} \) back-bonding, as evidenced by the calculated Wiberg Bond Indices (WBIs) for the series 2a, 3a, 4, and 5: 1.04, 1.04, 1.44, and 1.45, respectively (Figure S34). For comparison, the WBI of the corresponding Ge\( - \text{C} \) bond in C is 1.40,

\[^{[55]}\]

while that of each of the two equivalent Ge\( - \text{C} \) bonds in the gemylene A is 1.15.

\[^{[55]}\]

Natural population analyses of 4 and 5 reveal a highly electron rich germanium centre with a negative partial charge of \( -0.21 \) and \( -0.17 \) \( e \), respectively; cf. \( +0.16 \) \( e \) in C and \( +0.33 \) \( e \) in the gemylene A.

\[^{[45,55]}\]

Subsequent Natural Bond Orbital (NBO) analyses found the ylidene description (Scheme 3, left) to be the best single Lewis-type depiction of the electronic structure of both 4 and monomeric 5. However, a more detailed inspection of NBOs revealed the Ge\( - \text{E} \) \( \pi \)-orbital in 4 and monomeric 5 to be occupied by as much as 0.23 \( e \), indicating deviation from the ideally localised Lewis-model. In similar fashion, Electron Localization Function (ELF) analyses (Figure S53) further emphasised the importance of delocalization effects and the ylidene description for 4 and monomeric 5 (Scheme 3, right) by showing a significant flux of electrons between the monosynaptic V(\( \text{Ge} \),\( \text{C} \)) lone pair basin and the disynaptic V(\( \text{Ge} \),\( \text{C} \)) bond basin, each occupied on average by approximately three electrons. Taken as a whole, the electronic structures of 4 and monomeric 5 are between those of the two extremes shown in Scheme 3, and the Ge\( - \text{E} \) \( \pi \)-electrons can be viewed as an electron pair reservoir that is readily accessed by germanium to effect nucleophilicity. This behaviour parallels with that observed by Roesky in cAAC supported phosphine-
denes/phosphaalkenes, and emphasizes the valence-isoelectronic relationship between (cAAC)PR and [(cAAC)GeR]· [R = organic substituent].

The importance of the ylidone resonance form in the chemistry of 4 and 5 is best exemplified by their reactions with weak electrophiles, such as CO₂. Under 1 atm of CO₂, solutions of 4 and 5 undergo an instantaneous colour change from red to purple. Reaction atmospheres were subsequently degassed to limit deleterious side reactivity. After work-up, single crystal X-ray diffraction analysis revealed the products to be isostructural μ-CO₂·κ-C≡Cκ·O complexes 6 (Scheme 2 and Figure 3). The concomitant intermolecular silyl group transfer eventuates low isolated yields (~20%). 13C NMR shows carbenic carbon resonances at 246.5 and 247.8 ppm for 6a and 6b, respectively, matching those measured for 2a and 2b. Characteristic νCO stretches are observed in the IR spectra of 6a and 6b at 1613 and 1614 and cm⁻¹, respectively.

Computational analysis of the reaction mechanism suggested that CO₂ initially binds to the electrons flowing from the Ge–C π-bond in 4 and 5 in π-C≡Cκ·O fashion. Subsequent migration of the potassium cation yields intermolecular complexes exhibiting a μ-C≡Cκ·O,O'-bonding mode (Scheme 2 and Figure S36). The calculated gas phase reaction energies were found to be exothermic by ~50 kJ mol⁻¹ but become approximately energy neutral upon inclusion of entropy terms and solvent effects. This is not unexpected as π-C≡Cκ·O adducts are extremely rare and potassium cation is a weak Lewis acid, providing significantly less electronic stabilization to the bound CO₂ molecule than the silyl group in 6.

The aforementioned observations implicate germanium as a nucelophile in the addition of CO₂ and are reminiscent of early reports on in situ prepared triorganogermanecarboxylates. Complexes 6 are also rare examples of μ-CO₂·κ-C≡Cκ·O bonding involving a heavy Group 14 element. The only other crystallographically characterised example for germanium is a [4 + 2] cycloadduct of 1,4-digermabenzenec with CO₂ in which the two metalloid centres work in tandem as a Lewis acid and a base. Germanium mediated CO₂ transformations typically involve insertion to a Ge–H bond to give Ge–O bound formic acid derivatives. Other reported examples include the conversion of heavy Group 14 ketones to k²O,O'-bound carbonates in the presence of CO₂ and side-on insertion of CO₂ to the Ge–Ge single bond of a digermyne to give a bis(germylene) oxide after CO release. The high nucleophilic character of germanium in 4 and 5 is highlighted by comparison with germylones A that have not been reported to react with CO₂. In agreement with these observations, or the lack thereof, computational analyses probing the potential energy surface of cAAC·Ge and CO₂ failed to locate a stable adduct between the two.

To summarize, mononuclear germanylidene complex 4 and coordination polymer 5 bearing cAAC and hypermetall ligands were synthesised by stepwise reduction from germylene precursors 2 through stable and isolable germanium radicals. The germanium atom in 4 and 5 is highly electron-rich, with electrons formally in the Ge–C π-bond readily available for forming new intermolecular interactions, as illustrated by computational analyses, the extended solid-state structure of 5, and the reactivity of 4 and 5 towards CO₂. Bridged μ-CO₂·κ-C≡Cκ·O adducts 6 were obtained that display a common binding mode for CO₂ in transition metal complexes but rare for germanium. The reported efforts expand the portfolio of known cAAC-stabilised germanylidene anions and demonstrate their utility as efficient single-site nucleophiles that surpass ylidones of type A. Further reactivity studies of 4 and 5 with small molecules are currently underway.

**Experimental Section**

Deposition Number(s) 2090119 (for 2a), 2090120 (for 3a), 2090121 (for 4), 2090122 (for 4·(THF)), 2090123 (for 4·(THF)₂), 2090124 (for 6a), 2090125 (for 2b), 2090126 (for 3b), 2090127 (for 5), 2090128 (for 5·(diglyme)), 2090129 (for 5·(diglyme)) and 2090130 (for 6b) contain(s) the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service.

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**Conflict of Interest**

The authors declare no conflict of interest.

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Stepwise reduction of germynes via stable and isolable germanium radicals yields germanylidene anions supported by cyclic (alkyl)(amino) carbene and hypermetaldehyde ligands. The anions contain a highly electron-rich germanium centre with significant ylidone character and are efficient single-site nucleophiles that react even with weak electrophiles.