Changing the Reactivity of Zero- and Mono-Valent Germanium with a Redox Non-Innocent Bis(silylenyl)carborane Ligand

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Dedicated to Professor Hansgeorg Schnöckel

Abstract: Using the chelating C,C-bis(silylenyl)-ortho-dicarborane ligand, 1,2-(RSi)$_2$-1,2-C$_2$B$_{10}$H$_{12}$, in redox reactions leads to the monoatomic zero-valent Ge complex ("germylone") 3. The redox non-innocent character of the carborane scaffold has a drastic influence on the reactivity of 3 towards reductants and oxidants. Reduction of 3 with one molar equivalent of potassium naphthalenide (KC$_{10}$H$_8$) causes facile oxidation of Ge$^0$ to Ge$^0$ along with a two-electron reduction of the C$_2$B$_{10}$ cluster core and subsequent Ge$^0$-Ge$^0$ coupling to form the dianionic bis(silylene)-supported Ge$_2$ complex 4. In contrast, the oxidation of 3 with one molar equivalent of [Cp$_2$Fe]-[BF$_4$] as a one-electron oxidant furnishes the dicaticonic bis(silylene)-supported Ge$_2$ complex 5. The Ge$^0$ atom in 3 acts as donor towards GeCl$_2$ to form the trinuclear mixed-valent Ge$^0$-Ge$^0$-Ge$^0$ complex 6, from which dechlorination with KC$_{10}$H$_8$ affords the neutral Ge$_2$ complex 7 as a diradical species.

Tetraylones have emerged recently which represent a new class of molecules featuring monoatomic, zero-valent Group 14 elements directly stabilized by two donor ligands (L) through Lewis donor–acceptor interaction (L:···E···L, E = C, Si, Ge, Sn, Pb).

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Akin to the analogous silylene with the same bis(silylene) ligand \(1\),[22] the HOMO and the HOMO-1 in \(3\) correspond to the germylene lone pairs with \(\pi\)- and \(\sigma\)-symmetry, respectively (Figure 2). NBO analysis shows that in \(3\) the Ge\(^0\) \(\pi\)-symmetry lone pair, with occupancy of 1.11 el., exhibits strong donor-acceptor interaction with the low-valent 3p orbitals of the amidinato-silylene Si atoms (175.2 kcalmol \(^{-1}\)). The \(\pi\)-symmetry lone pair with occupancy of 1.80 el. mainly interacts with the low-valent \(sp^3\) orbitals of the amidino-silylene Si atoms (25.7 kcalmol \(^{-1}\), Figure S18 in the Supporting Information).

We investigated the redox behavior of \(3\) with cyclic voltammetry, which shows multiple irreversible redox events (Figure S5). The complexity of the latter is presumably due to a facile oxidation-state change of the Ge center and electronic structure variation involving the redox non-innocent amidinato ligand and the \(C_2B_{10}\) cluster core. In order to achieve a controllable single-electron reduction of \(3\), we conducted the reaction with one molar equiv of potassium naphthalenide, which, in fact, led to the isolation of the Ge\(^1\)-Ge\(^1\) coupling product \(4\) as a dark red crystalline solid in 95% yields (Scheme 2).

The crystal structure of \(4\) reveals a one-dimensional ionic polymer in which the dianionic units feature a Ge–Ge core coordinated by one bis(silylene)-nido-dicarborane ligand at each Ge site (Figure 3) and two K cations linked to two dicarborane units via agostic interaction with the B–H bonds of the \(C_2B_{10}H_{10}\) clusters. Both Ge atoms possess a lone pair of electrons and are three-coordinated. The Ge–Si distances [Ge1–Si1 2.4294(8) and Ge1–Si2 2.4105(8) Å] are significantly longer than those Ge–Si distances in \(3\) [2.2896(5) and 2.2846(5) Å]. Representing the first bis(silylene)-supported \([\text{Ge}^1–\text{Ge}^1]\)\(^{2+}\), compound \(4\) features a Ge–Ge distance of 2.5161(6) Å which is shorter than that in a bis(NHC) borate-stabilized \([\text{Ge}^1–\text{Ge}^1]\)\(^{2+}\) [2.673(1) Å],[29] but comparable to the value in the amidinato digermylene \([\text{PhC}(N\text{tBu})_2]\text{Ge}:\text{2},[30] The C1–C2 distance of 2.68 Å indicates that the two silylene units in \(4\) are bridged by a dianionic nido-\(C_2B_{10}\) cluster core.

The Ge–Ge coupling of \(4\) is reminiscent of the formation of the analogous \([\text{Si}^1–\text{Si}^1]\)\(^{2+}\) complex.[22] According to DFT calculations reported previously for the latter Si homologue, the one-electron reduction transforms the closo-\(C_2B_{10}H_{10}\) bridge to the opened dianionic nido-cluster and the Ge\(^0\) center to a Ge\(^1\) radical (Figure 4), which undergoes Ge\(^1\)-Ge\(^1\) coupling.
coupling to furnish 4 as an isolable product. The electronic structure of 4 closely resembles that of the aforementioned Si$_2$ homologue (Figure S20).\[22\]

To investigate the one-electron oxidation, 3 was allowed to react with one molar equiv of [Cp$_2$Fe][B(C$_6$H$_3$(CF$_3$)$_2$)$_4$] in THF at room temperature, which led to the isolation of a new [Ge$^+$-Ge$^+$] coupling compound 5 as an orange solid in 92\% yield (Scheme 2). This product is also insoluble in diethyl ether, but well soluble in THF. The $^1$H NMR spectrum of 5 in [D$_8$]THF exhibits only one singlet at $\delta$ = 1.46 ppm for the tBu groups, while the $^{29}$Si [$^1$H] NMR spectrum shows a broad resonance at $\delta$ = 68.0 ppm.

The single-crystal structure of 5 reveals a separate ion pair with a Ge$_2$-containing dication and two borate counteranions (Figure 5). Similar to the structure of 4, both Ge centers in 5 adopt a trigonal-pyramidal coordination geometry and the Ge-Ge distance of 2.5468(3) Å is close to that in 4 [2.5161(6) Å]. A marked metric difference between the dication in 5 and the dianion in 4 represents the carborane-C-C distance [5: ca.1.67 Å vs. 4: 2.68 Å], due to the presence of a nido- core in 4 vs. a closo-C$_2$B$_{10}$H$_{10}$ cluster in 5. We propose that the formation of 5 upon oxidation of 3 is achieved by a one-electron transfer from the HOMO of 3 (Figure 2), forming the corresponding Ge$^+$ radical cation intermediate in which 74\% of the spin density resides on the Ge atom (Figure 4), and subsequent radical coupling. Similar to the dianion in 4, the dication in 5 contains a Ge-Ge bond with a Wiberg Bond Index (WBI) of 0.86, and retains one o-symmetry lone pair on each of the Ge atoms, as confirmed by the Natural Bond Orbital (NBO) analysis (Figure S19).

To explore the coordination ability of the Ge$^+$ center, compound 3 was allowed to react with GeCl$_2$—dioxane (Scheme 2). The reaction yields exclusively compound 6 as a yellow solid regardless of the ratio of reactants. 6 is insoluble in common aprotic organic solvent. Its $^{29}$Si solid-state NMR spectrum shows a resonance at $\delta$ =
56.0 ppm. The molecular structure of 6 reveals a seesaw coordination geometry for the central Ge center with both chloride atoms located at the axial positions (Cl1-Ge3-Cl2: 163.2°), suggesting that one of the equatorial position is occupied by a lone pair (Figure 6). Compound 6 can be viewed as a Ge\textsuperscript{0}-Ge\textsuperscript{II} adduct, and each Ge\textsuperscript{0} atom features still a stereochemically active lone pair as indicated by its pyramidal coordination geometry (sum of bond angles each ca. 295°). The Ge–Ge distances [Ge1–Ge3 2.412(4) Å and Ge2–Ge3 2.416(5) Å] are considerably shorter than those Ge–Ge bonds in 4 [2.5161(6) Å] and 5 [2.5468(3) Å], suggesting a relatively strong Ge–Ge interaction in 6.

Interestingly, complex 6 can serve as a precursor for the novel bis(NHSi)-supported neutral Ge\textsubscript{2} complex 7, which is obtained as a minor isolable product (28% yields) along with germylone 3 (58% yields) from dechlorination of 6 with two molar equivs of potassium naphthalenide (scheme 2). Compound 7 is NMR silent; its molecular structure has been established by single-crystal X-ray diffraction analysis (Figure 7). 7 features a Ge\textsubscript{2} dumbbell coordinated by two bis(silylene) ligands in a side-on manner. Due to the electronic neutral nature of the Ge\textsubscript{2}\textsuperscript{2+} complex, each of the C\textsubscript{2}B\textsubscript{10}H\textsubscript{10} clusters carries one negative charge and thus is a radical in keeping with the observed NMR silence of 7. In agreement with this, the C–C distance in the C\textsubscript{2}B\textsubscript{10} core in 7 is ca. 2.4 Å, lying closer to the C–C value in 4 (nido-C\textsubscript{2}B\textsubscript{10}, 2.68 Å) than that in 5 (closo-C\textsubscript{2}B\textsubscript{10}, 1.67 Å). The triplet diradical nature of 7 has been confirmed by its electron paramagnetic resonance spectrum (Figure S12), which exhibits an isotropic signal at \( g = 2.004 \) very similar to the spectral signature of known carborane radical anions\([28]\). Furthermore, DFT calculations support the triplet diradical assignment. Optimization of 7 in triplet and singlet states leads to geometries in which the triplet state is lower in energy by 15.8 kcalmol\(^{-1}\). As shown in Figure 8, the spin density (1.92 e\textsuperscript{-}) of 7 in the triplet state is localized at the carborane moieties and NBO analysis shows the Ge–Ge WBI of 0.85. It should be noted, although 7 can be considered as a dimer of germylone 3 and the dimerization reaction is endergonic by 1.8 kcalmol\(^{-1}\), no equilibrium between 3 and 7 has been observed, presumably, due to the difference of their coordination modes.

In summary, a series of unexpected novel low-valent Ge\textsubscript{2} complexes could be synthesized, starting from the monovalent zero-valent Ge\textsuperscript{0} complex 3 supported by the redox non-innocent bis(silylenyl)-ortho-dicarborane ligand. While its one-electron reduction affords the bis(silylene)-supported [Ge\textsuperscript{1}–Ge\textsuperscript{1}] dianion complex in 4, the one-electron oxidation leads to the bis(silylene)-stabilized [Ge\textsuperscript{1}–Ge\textsuperscript{1}] dication complex in 5. Moreover, coordination of two germylone molecules of 3 with one GeCl\textsubscript{2} allowed the isolation of the mixed-valent trinuclear Ge complex 6, which serves as a precursor for the neutral Ge\textsubscript{2} complex 7 with a triplet diradical ground state.
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Conflict of interest

The authors declare no conflict of interest.

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