**Main-Group Elements**

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# Stabilization of a Two-Coordinate $[\mathrm{GeCl}]^+$ Cation by Simultaneous σ and π Donation from a Monodentate Carbodiphosphorane**

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There are two classical synthetic strategies aimed towards the isolation of Ge$^{\text{II}}$-derived monocations:[1] the use of neutral ancillary ligands, such as N-heterocyclic carbenes,[2] macrocycles,[3] arene rings,[4] or pyridine-based chelating ligands[5] that electronically saturate the germanium center (Figure 1; **A**), or the embedding of germanium in a heterocyclic scaffold employing bidentate monoanionic ligands (**B**).[6] It was only recently that Krossing and Jones reported a third approach, which relies on the simultaneous use of an anionic, sterically very demanding amido ligand and a weakly coordinating counteranion. Thus, they were able to isolate and structurally characterize two-coordinate Ge$^{\text{II}}$ monocations of formula $[\mathrm{RGe}\leftarrow\mathrm{L}]^+$ in which L indicates a weak intramolecular $\eta^2$-arene interaction of one of the two benzhydryl substituents of R with the Ge center (**C**).[7]

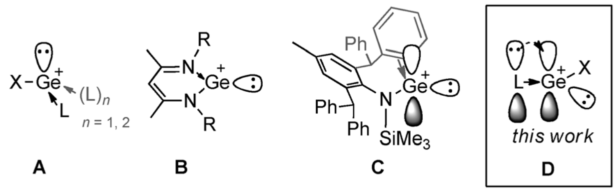
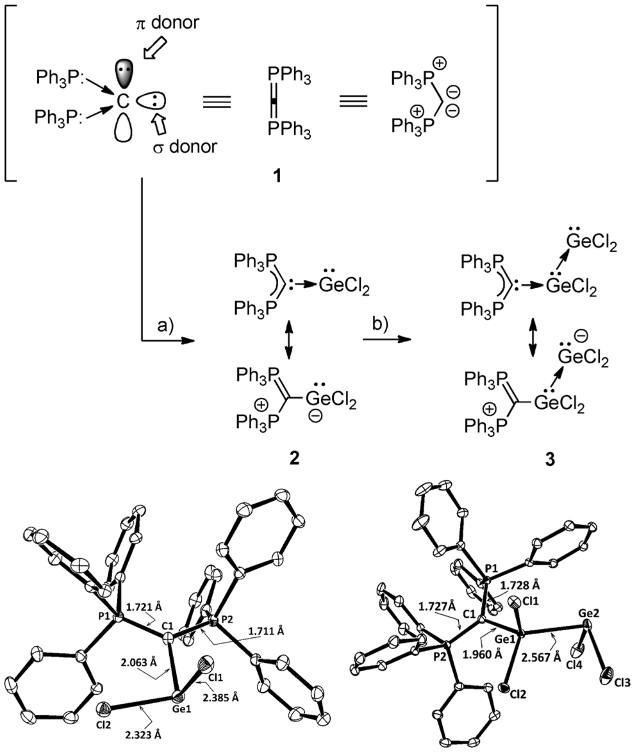


*Figure 1.* Bonding environments of known cationic Ge$^{\text{II}}$ centers (**A**–**C**) and new synthetic strategy (**D**).

Alternatively, displacement of a halide by a neutral monodentate ligand L in Ge$^{\text{II}}$ dihalides should render simpler two-coordinate structures $[\mathrm{L}\rightarrow\mathrm{GeX}]^+$ (X = Cl, Br, or I). However, despite their synthetic potential, no such compound has yet been reported to the best of our knowledge. Their isolation is probably impeded by the reduced steric protection provided by a halide substituent and the highly electrophilic nature of these species, which carry both an empty p orbital and a positive charge. In this regard, we envisaged that a monodentate neutral ligand that is formally able to simultaneously engage in σ and π donation to the Ge$^{\text{II}}$ center may provide sufficient stabilization to attenuate the high reactivity of $[\mathrm{L}\rightarrow\mathrm{GeX}]^+$ species to a level that permits their isolation and the study of their reactivity (**D**).

To put this concept into practice, hexaphenylcarbodiphosphorane **1** was chosen as ancillary ligand that might fulfill the necessary electronic requirements (Scheme 1). According to computational studies by Frenking and co-workers, the two internal phosphines in this compound coordinate to the central carbon atom, which thus keeps its own four valence electrons in the form of two orthogonal lone pairs.[9] However, when acting as four-electron donor, the central carbon of **1** prefers to donate each electron pair to a different electrophile. Simultaneous σ- and π-donation to the same Lewis acid center is very rarely observed.[10]



*Scheme 1.* Synthesis and molecular structure of **2** (left) and **3** (right) in the solid state (hydrogen atoms and solvent molecules removed for clarity; ellipsoids set at 50% probability).[8] Reagents and conditions: a) $\mathrm{GeCl_2}$·dioxane, toluene, RT, quantitative; b) $\mathrm{GeCl_2}$·dioxane, $\mathrm{CH_2Cl_2}$, RT, 60%.

Addition of $\mathrm{GeCl_2}$·dioxane complex to a toluene solution of **1** afforded a white solid in quantitative yield. Complete spectroscopic characterization of this new compound could

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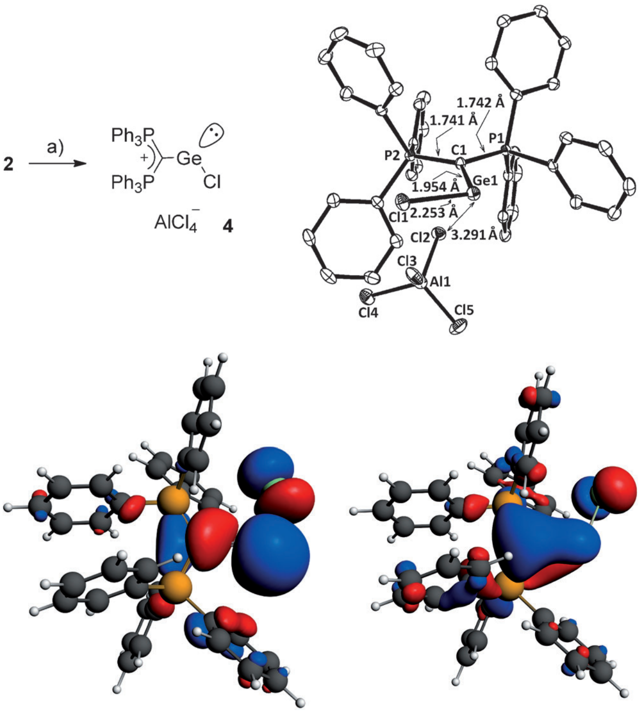
not be achieved owing to its high insolubility in all common organic solvents. However, its ${}^{31}$P NMR spectrum displays a new resonance at $\delta = 22.2$ ppm, suggesting coordination of the carbodiphosphorane ligand. X-ray diffraction analysis of the crystals obtained from the reaction bulk confirmed the formation of the expected adduct **2** (Scheme 1).

Interestingly, addition of a second equivalent of $GeCl_2$·dioxane complex to a suspension of **2** in $CH_2Cl_2$ caused complete dissolution of all of the solids. Furthermore, the original ${}^{31}$P NMR signal disappeared and a new signal at $\delta = 23.3$ ppm cleanly emerged. Colorless crystals were grown by diffusion of pentane into a saturated dichloromethane solution of the crude reaction mixture and were analyzed by X-ray diffraction. The structure was determined to be complex **3** in which the central $Ge^{II}$ atom formally accepts an electron pair from **1** and donates a second pair to the terminal Ge atom. While $Ge^{II} \rightarrow Ge^{II}$ donor–acceptor interactions have been previously described,[11] unsupported $Ge^{II} \rightarrow Ge^{II}$ dative bonds have no precedent. Their occurrence in **3** is probably a consequence of the privileged donor capacity of **1** that renders the Ge atom in **2** basic enough to react with a second $GeCl_2$ fragment. This view of the Ge−Ge interaction is consistent with the observed shortening of the C1−Ge1 bond upon going from compound **2** (2.063 Å) to **3** (1.960 Å).[12]

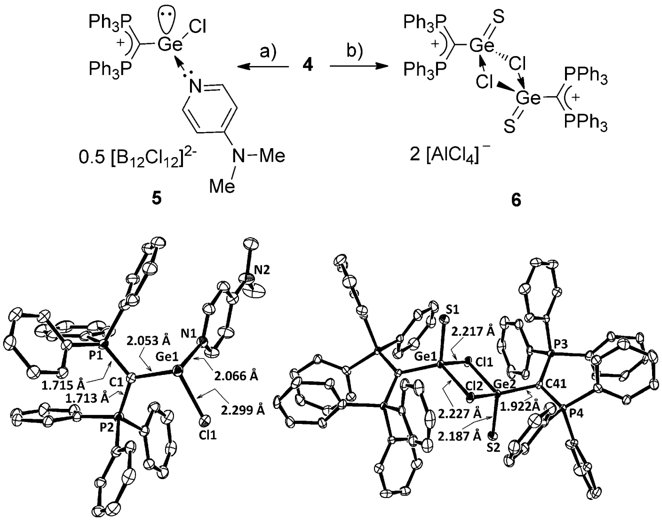
Upon treatment of a dichloromethane suspension of **2** with one equivalent of $AlCl_3$, a transparent bright-yellow solution displaying a ${}^{31}$P NMR resonance at $\delta = 23.1$ ppm slowly appeared. Scheme 2 depicts the ORTEP diagram of the newly formed compound **4**. Abstraction of a chloride from **2** generates a $[GeCl]^+$ moiety that is stabilized by the carbodiphosphorane ligand. The most interesting feature in this structure is the P2-C1-Ge1-Cl1 torsion angle of only 8.1°, which allows good overlap between the full p orbital at C1 and the empty orbital at Ge. Apparently, this stabilizing interaction seems to prevail over adverse steric repulsions. As a result, the C1−Ge1 distance in **4** (1.954 Å) is shorter than in **2** (2.063 Å) although still longer than in typical Ge=C bonds that are non-dative in nature.[13,14]



***Scheme 2.*** Synthesis, frontier orbitals (HOMO, left; HOMO−1, right) and molecular structure of **4** in the solid state (hydrogen atoms and solvent molecules removed for clarity; ellipsoids set at 50% probability).[8] C black, H white, P orange, Cl green, Ge violet (not visible). Reagents and conditions: a) $AlCl_3$, $CH_2Cl_2$, RT, 68%.

To better ascertain the unusual electronic nature of these compounds, density functional theory (DFT) calculations at the BP86/def2-TZVP level were carried out. There is a close match between the DFT and X-ray structures (Supporting Information, Figures S1–S4). Scheme 2 shows the shapes of the frontier orbitals of **4**. The HOMO is a mainly σ lone-pair orbital with its major coefficient at Ge, while the HOMO−1 is a π orbital strongly polarized towards the carbon atom but still exhibiting significant C−Ge π bonding. For a quantification of the strength of this π interaction, a fragment orbital analysis was carried out as implemented in the ADF package.[15] Based on this analysis, the amount of C→Ge π donation is estimated to be 0.47 $e$ (Supporting Information, Table S8). Furthermore, Wiberg bond indices (*Wi*) were calculated (Supporting Information, Tables S1–S7). The C1−Ge1 value was found to be substantially higher in **4** (0.84) than in **2** (0.54). These numbers, although still low on an absolute scale owing to the dative nature of the interactions, indicate an increase in the bond strength between carbon and germanium when going from **2** to **4** that can be attributed to the π interaction.[16]

The reactivity of **4** was further investigated. It readily reacts with Lewis bases, such as 4-dimethylaminopyridine (DMAP) to yield the corresponding adduct **5**, the X-ray structure of which could be obtained after exchanging the original $[AlCl_4]^-$ anion against $[B_{12}Cl_{12}]^{2-}$ (Scheme 3). Coor-

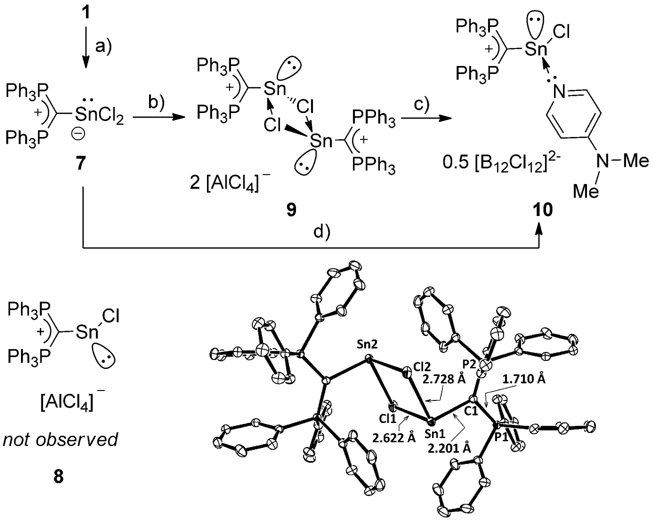


***Scheme 3.*** Synthesis and molecular structure of **5** (left) and **6** (right) in the solid state (hydrogen atoms, solvent molecules, and anions removed for clarity; ellipsoids at 50% probability).[8] Reagents and conditions: a) DMAP, $CH_2Cl_2$, $K_2[B_{12}Cl_{12}]$ (0.5 equiv), 56%; b) $S_8$ (0.125 equiv), $CH_2Cl_2$, 61%.

dination of DMAP populates the LUMO of **4** that corresponds to the π*(C–Ge) orbital (Supporting Information, Figure S6). This eliminates any possible π component of the C–Ge interaction, and accordingly the C–Ge distance (2.053 Å) and *Wi* value (0.64) in **5** are similar to those found in **2** (Scheme 3).

Even though **4** is a cation, its HOMO still has significant lone-pair character localized at Ge. This prompted us to study its reactivity towards oxidants. Treatment of **4** with elemental sulfur in dichloromethane afforded a new compound **6** in which the original $Ge^{II}$ center has been oxidized to $Ge^{IV}$ and a formal S=Ge double bond has been formed. Previously reported compounds containing the $[Ge(S)Cl]^+$ unit are monomeric owing to intramolecular coordination of a base.[17] However, in the absence of base, the $Ge^{IV}$ centers in **6** satisfy their electrophilicity through the formation of chloride bridges. Therefore, the structure of **6** is dimeric despite the cationic nature of its two components.

Finally, the extension of this chemistry to $Sn^{II}$ was also attempted. Reaction of **1** with $SnCl_2$ afforded the extremely insoluble and air-sensitive adduct **7**[18] that was subsequently treated with $AlCl_3$. In sharp contrast to the Ge analogue previously described, abstraction of a chloride anion from **7** did not yield the expected cation **8** but its dimer **9** (Scheme 4).



*Scheme 4.* Synthesis of **7**, **9**, and **10** and molecular structure of **9** in the solid state (hydrogen atoms, solvent molecules, and anions removed for clarity; ellipsoids set at 50% probability).[8] Reagents and conditions: a) **1**, $GeCl_2$·dioxane, $CH_2Cl_2$, RT, quantitative; b) **7**, $AlCl_3$, $CH_2Cl_2$, 67%; c) **9**, DMAP, $CH_2Cl_2$, $K_2[B_{12}Cl_{12}]$ (0.5 equiv); d) **7**, DMAP, $CH_2Cl_2$, $K_2[B_{12}Cl_{12}]$ (0.5 equiv), 53%.

The steric hindrance around Ge in **4** and Sn in a hypothetical complex **8** (see calculated structure, Figure 2) are basically identical. Therefore, the isolation of **9** indicates that the plausible stabilization provided by a π(C–Sn) bond in **8** is so weak that it is overridden by formation of chloride bridges between the Sn atoms.

A less-efficient overlap between the C(2p) and Sn(5p) orbitals may be responsible for the weakness of the dative C→Sn π interaction.[19] Consequently, the calculated C–Sn *Wi* values in **7** and **8** are quite similar (0.41 and 0.49, respectively). However, for synthetic purposes, **9** shows the same reactivity as expected for its monomer **8**. For example, it readily reacts with bases, such as DMAP to afford adduct **10**.[20]

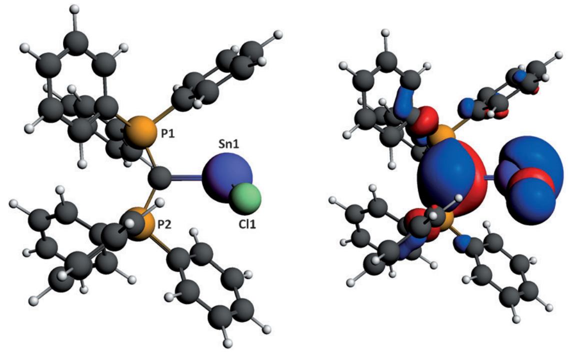


*Figure 2.* Calculated gas-phase structure of cation **8** (left) and plot of its HOMO (right) at BP86/def2-TZVP.

In summary, the synthesis of a $[L\rightarrow GeCl]^+$ structure has been achieved by employing hexaphenylcarbodiphosphorane as a neutral monodentate ligand able to donate two electron pairs. Thus, compound **4** is an unusual example of a bonding situation where double dative C=E σ and π bonds are formed (E = main group element). Moreover, the reactivity of this compound towards bases and oxidants has been studied. Conversely, our attempts to extend the same strategy to the preparation of $Sn^{II}$ analogues afforded dimeric structures in which only the σ(C–Sn) dative bond is present. The synthetic applications of these two types of compounds are now under study in our laboratories.

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[18] Owing to the high insolubility of **7** in organic solvents, only elemental analysis and reactivity data support the proposed formulation.

[19] As a consequence, the calculated P2-C1-Sn1-Cl1 torsion angle in **8** is 62.3°.

[20] For the X-ray structure of this compound, see the Supporting Information.