Germanium(II) Dications

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# Splendid Isolation for a Nonmetallic Dication**

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carbene homologues · cations · cryptands · germanium · reactive intermediates

*In memory of Peter Köll*

The quest for organometallic cations $R_3E^+$ of the heavier Group 14 elements E has been a central theme in element-organic chemistry for the last twenty years.[1] Several examples of these analogues of classical carbenium ions were recently synthesized, and some have found applications in synthesis and catalysis.[1,2] In light of the high electrophilicity of the cations of Group 14 elements in the oxidation state +IV, it is intriguing to imagine the reactivity and the synthetic potential of species that combine the principal properties of carbene analogues with those of cations, that is, compounds of the composition $RE{:}^{+}$ with the Group 14 element in the oxidation state +II.[3]

Some highly stabilized examples of this class of compounds have been synthesized (Figure 1), including the *nido*-cluster cations **1**[4a–d] and the intra- or intermolecularly stabilized species **2**–**5**.[4e–j] It is a formidable challenge to synthetic methodology and experimental skills to synthesize these compounds, in which the central atom possesses only four valence electrons. In particular, for the nonmetallic elements of Group 14 (C, Si, and Ge), it seemed out of reach to strip off the last substituent and generate atomic dications $E{:}^{2+}$ with only two valence electrons. The open-shell nature of nonmetallic cations $E{:}^{2+}$ is decidedly different from the classical omnipresent closed-shell metallic cations such as $K^+$ and $Ca^{2+}$. The occurrence of three empty orbitals leads to an enormous electrophilicity, and instantaneous reaction with any nucleophile or solvent molecule is expected. Even more remarkable and exciting is therefore the recent report on a germanium(II) dication encapsulated in [2.2.2]cryptand (abbreviated herein as *222*) by Baines and co-workers.[5] The cryptand cage provides stabilization and protection for the nonmetallic dication and allows its isolation and characterization in the form of the triflate salt [Ge(*222*)](OTf)$_2$ (OTf = $CF_3SO_3$).

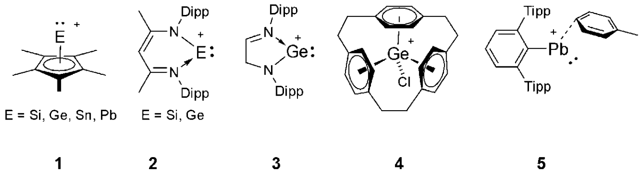
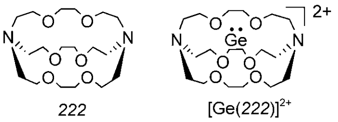
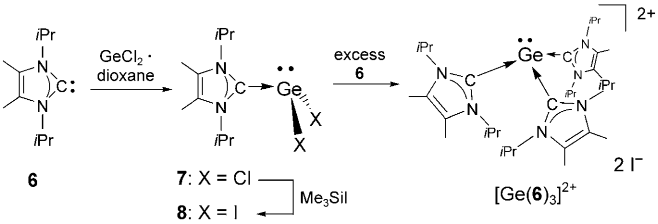


***Figure 1.*** Examples of cations of the general composition $RE^+$. (Dipp: 2,6-diisopropylphenyl, Tipp: 2,4,6-triisopropylphenyl).



Prerequisite for this success was work by the groups of Arduengo and Lappert, who demonstrated that reactions of N-heterocyclic singlet carbenes (NHCs) with germylenes (carbene analogues of germanium) do not afford germenes (compounds with Ge=C double bonds) but rather result in the formation of base-stabilized germylenes with the NHC acting as a Lewis base.[6] In continuation of this work, Baines and co-workers reported recently that NHC **6** is able to stabilize transient diarylgermylenes[7] and that it forms complex **7** with $GeCl_2$·dioxane (see Scheme 1). Complex **7** serves as the starting material for a whole series of NHC-stabilized germylenes GeXY,[8] which adopt a trigonal-pyramidal molecular structure typical for an $AB_3E$ configuration. Therefore, these complexes can be seen as the neutral analogues of the trihalogermanite anions $[Ge^{II}X_3]^-$.[9]



***Scheme 1.*** Synthesis of the germanium(II)-centered dication $[Ge(\mathbf{6})_3]^{2+}$.[10]

The ground-breaking idea pursued by Baines and co-workers was to remove the chlorine substituents in the neutral complex **7** as chloride anions and to replace them by neutral NHC ligands, thereby formally generating a germanium(II) dication. This work parallels recent results from the groups of

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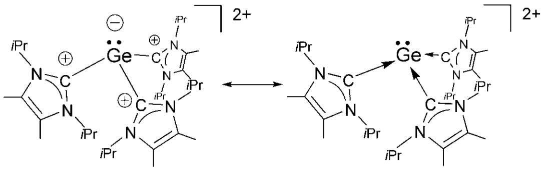
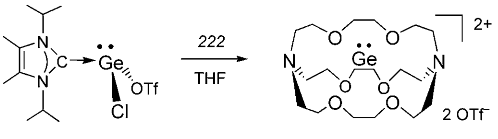
Macdonald, Robinson, Bertrand, and Fürstner, which demonstrate that singlet carbenes such as NHC **6** are able to stabilize main-group elements in low oxidation states.[11] The displacement of chloride in complex **7** was not possible, but reaction of the diiodo compound **8** with excess NHC **6** affords the salt $[\mathrm{Ge}(\mathbf{6})_3]\mathrm{I}_2$ in 84 % yield (Scheme 1).[10] Clearly, this salt contains a germanium-centered dication, but what is the nature of this dication? A single-crystal X-ray structure determination of the pyridine solvate of the salt $[\mathrm{Ge}(\mathbf{6})_3]\mathrm{I}_2$ shows the cation to have a propeller-like $C_3$ symmetry with Ge–C bonds of $r(\mathrm{GeC}) = 207.0(6)$ pm. This $\mathrm{Ge^{II}}$–C bond is slightly longer than the average $\mathrm{Ge^{IV}}$–C bond (195–205 pm)[12] but is well within the range of $\mathrm{Ge^{II}}$–C bonds (201–208 pm),[12] and it is even shorter than the Ge–C bond in the sterically less encumbered complex **8** (210.6(3) pm). DFT calculations at the B3LYP/6-31G(d) level revealed that the highest occupied molecular orbital (HOMO) of the dication $[\mathrm{Ge}(\mathbf{6})_3]^{2+}$ is oriented along the molecular $C_3$ axis, pointing away from the NHC ligands; it corresponds to the stereochemically active lone pair of the germanium atom. It is also interesting to note that neither the iodide anion nor the pyridine solvent can efficiently compete with the NHC as a ligand for the germanium(II) dication. These experimental and theoretical results suggest that the ylidic valence-bond representation **A** of $[\mathrm{Ge}(\mathbf{6})_3]^{2+}$ (Scheme 2), which illustrates the close relationship between the dication and trihalogermanite anions, strongly contributes to the electronic situation in $[\mathrm{Ge}(\mathbf{6})_3]^{2+}$. Therefore, the bonding in the dication $[\mathrm{Ge}(\mathbf{6})_3]^{2+}$ closely resembles that of related NHC-stabilized subvalent main-group compounds that have been synthesized recently.[11]

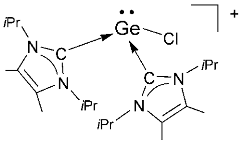


***Scheme 2.*** Resonance structures **A** and **B** of dication $[\mathrm{Ge}(\mathbf{6})_3]^{2+}$.

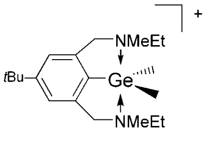
Apparently, it is necessary to distribute the electron donation by the neutral ligand over more donor atoms to decrease the interaction between individual donor atoms and the central germanium dication. Crown ethers and cryptands fulfill this requirement.[13] Moreover, cryptands provide three-dimensional protection of the reactive center. Indeed, in a subsequent report, Baines and co-workers were able to demonstrate that [2.2.2]cryptand is a suitable replacement for the tightly bound NHC ligands.[5] Thus, reaction of the NHC-stabilized germylene **9**, featuring chloride and triflate as labile substituents, with *222* in THF resulted in rapid precipitation of a white powder, which was identified as the triflate $[\mathrm{Ge}(222)](\mathrm{OTf})_2$, in an optimized yield of 88 % (Scheme 3). The neutral NHC germylene complex **7** and the NHC-stabilized germanium(II) monocation **10** were identified as by-products. A single crystal X-ray structure determination of the salt $[\mathrm{Ge}(222)](\mathrm{OTf})_2$ reveals that the germanium atom is encapsulated in the cryptand molecule and that it is well-separated from the triflate anions; the shortest $\mathrm{O_{triflate}}$–Ge separation is 532 pm. The germanium atom is located in the center between the two nitrogen atoms and equidistant from the six oxygen atoms of the cryptand. This highly symmetric arrangement of the encapsulated dication is also conserved in acetonitrile solution, as indicated by $^1$H NMR spectroscopy. Furthermore, $^{19}$F NMR investigations reveal the presence of only non-coordinated triflate anions.



***Scheme 3.*** Synthesis of $[\mathrm{Ge}(222)]^{2+}$.[5]



**10**

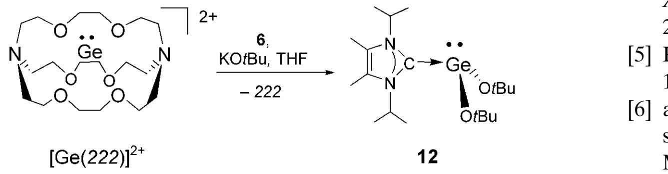


**11**

The experimentally determined Ge–N and Ge–O distances in $[\mathrm{Ge}(222)]^{2+}$ ($r(\mathrm{GeN}) = 252.4(3)$ pm, $r(\mathrm{GeO}) = 248.56(16)$ pm) are significantly longer than typical Ge–N (185–186 pm) and Ge–O (170–180 pm) single bonds.[12] The Ge–N separation in $[\mathrm{Ge}(222)]^{2+}$ is also significantly longer than coordinative N→$\mathrm{Ge^{IV}}$ interactions, for example in germonium ions such as **11** (231, 236 pm),[14] while the Ge–O distances are similar to the intermolecular Ge–O separation in the dioxane complex of dichlorogermylene (239.9(1) pm).[15] Therefore, the molecular structure of $[\mathrm{Ge}(222)]^{2+}$ does not indicate any significant covalent interaction between the donor atoms of the cryptand and the central germanium atom. Similarly, a computational natural bond orbital analysis of a DFT-derived wavefunction of the dication $[\mathrm{Ge}(222)]^{2+}$ assigned nearly pure 4s character to the remaining lone pair at the germanium atom and revealed only noncovalent interactions between the lone pairs of the donor atoms of the cryptand cage and the central germanium atom. Consequently, only fractional bond orders between these atoms are computed. This analysis implies that the electron-rich, nearly spherical cavity supplied by the cryptand satisfies the extreme electron demand of the central germanium ion without the need for localized bonding. Nevertheless, the interaction between the cryptand and the germanium ion is large, and the protection efficiently competes with moderately nucleophilic solvent such as acetonitrile. This situation contrasts the behavior of trisubstituted germylium ions $\mathrm{R_3Ge^+}$ (R = silyl, aryl),[16] which react with nitriles instantaneously to afford germylated nitrilium ions.[16a]

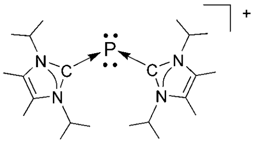
In light of this unexpected lack of reactivity of $[\mathrm{Ge}(222)]^{2+}$, more extended experimental studies and refined theoretical investigations seem appropriate. $^{17}$O and in particular $^{15}$N NMR spectroscopy experiments would provide important insights into the host–guest interaction, and, considering the highly symmetric $D_3$ molecular structure of the cryptand/dication complex, even $^{73}$Ge NMR spectroscopy could provide useful information. Electronic structure calculations that do not explicitly exclude a delocalized bonding scheme and, in particular, a careful assessment of the thermodynamics of the binding process between the cryptand cage and the guest cation[17] would certainly add important pieces to the understanding of the nature of this intriguing encapsulated germanium(II) dication.

The dication $[Ge(222)]^{2+}$ is clearly not a new superelectrophile, and trisubstituted organometallic cations of the Group 14 elements have proven to be much more efficient.[1] $[Ge(222)]^{2+}$ may, however, have synthetic applications as a reagent in germanium(II) chemistry. A first proof of principle is given by the reaction of $[Ge(222)]^{2+}(OTf_2)$ with KO*t*Bu in the presence of **6**, which afforded the NHC-stabilized germylene **12** (Scheme 4). Further work is certainly required to assess the scope of the reactivity of $[Ge(222)]^{2+}$. A crucial point will be how efficiently it competes with other Ge$^{II}$ sources, such as NHC-stabilized germylenes like **7** or even the GeCl$_2$ dioxane complex, as starting materials or storage materials for Ge$^{II}$ chemistry.



***Scheme 4.*** Reactivity of $[Ge^{2+}(222)]$ with KO*t*Bu.[5]

The use of cryptands to protect and stabilize atomic cations is without precedence in nonmetal chemistry, and the successful synthesis and isolation of $[Ge(222)]^{2+}(OTf)_2$ are breakthroughs that open a synthetic avenue to novel cations of nonmetallic elements with all their perspective applications in synthesis. In light of the wide variety of available cryptands and comparable host molecules, it is tempting to speculate that the synthesis of similarly remarkable cations—such as $Al^+$, $Ga^+$, $Si^{2+}$, $P^+$, $P^{3+}$, $As^{3+}$—by encapsulation in cryptands is in reach. In this respect it is interesting to note that the synthesis of the NHC-stabilized phosphorous(I) cation



$[P(\mathbf{6})_2]^+$

$[P(\mathbf{6})_2]^+$ was reported several years ago[11a] by Macdonald and co-workers.[18]

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[17] For a recent example, see: J. W. Su, R. R. Burnette, *ChemPhysChem* **2008**, *9*, 1989.

[18] Note added in proof: As a sequel to this work, Baines, MacDonald, and co-workers recently reported results that describe the synthesis and characterization of novel crown ether complexes of X–$Ge^+$ ($X = Cl^-$ and $OTf^-$) and of $Ge^{2+}$. By using different crown ethers, the authors convincingly show the interrelation between the cavity size of the crown ether and the stability of the $Ge^{2+}$ dication or the $GeX^+$ monocation complex, and they impressively demonstrate the general applicability of this synthetic approach to isolated subvalent germanium cations. See P. A. Rupar, R. Bandyopadhyay, B. F. T. Cooper, M. R. Stinchcombe, P. J. Ragogna, C. L. B. Macdonald, K. M. Baines, *Angew. Chem. Int. Ed.* **2009**, DOI: 10.1002/anie.200901351.