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A Germanium(II)-Centered Dication

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Understanding the structure and reactivity of carbenium ions has been critical in the development of many areas of organic chemistry. Given the long-standing interest in the fundamental differences and similarities between carbon and its heavier congeners, cationic compounds of the heavier group 14 elements, particularly, in the condensed phase, have also been the subject of intense research and much controversy.[1] The nature of the interaction between the cation and the counterion and/or neutral ligands has been at the center of the debate.[1] Until now, only heavier monocationic group 14 species (Ge, Sn, Pb) have been successfully isolated and characterized; more highly charged species are unknown, although they, too, hold much potential as useful compounds.[1c]

In the case of germanium, four types of cationic compounds have been unambiguously characterized (Chart 1): Type **A** relies on the steric protection and the electronic effects of the substituents for stabilization,[1] whereas types **B**[2] and **C**[3] utilize neutral donors to occupy vacant coordination sites on germanium. Type **D**[4] also contains a neutral donor. Since germanium is in the 2+ oxidation state, the lone pair of electrons provides additional shielding from potential nucleophiles. Undoubtedly, in Types **B**, **C**, and **D**, the charge is delocalized to some extent onto the donor molecules. In this context, we now report on a new class of group 14 centered cations with a unique bonding arrangement in p-block chemistry: a dicationic complex with a central germanium atom coordinated by three N-heterocyclic carbene (NHC) ligands (Chart 2, Type **E**).[5]

Recently, we have shown that an NHC can stabilize an otherwise transient diorganogermylene by complexation.[6] The strong donor ability of NHCs should enable the synthesis and isolation of other novel germanium(II) species,[7] and thus, we explored the synthesis and reactivity of carbene−dihalogermylene complexes.[7b]

The addition of a stoichiometric amount of carbene **1** to GeCl₂· dioxane produced **2** in high yield. Our initial attempt to displace the chlorines with excess **1** was not successful, and thus, the chlorines were replaced with iodines via halogen exchange using Me₃SiI to afford **3** (Scheme 1).[8] Upon addition of excess **1** to a yellow THF solution of **3**, the color of the solution quickly faded and a white precipitate formed. Colorless crystals were grown by diffusion of diethyl ether into a saturated pyridine solution of the bulk powder and were analyzed by single-crystal X-ray diffraction. The structure was determined to be the diiodide salt of **4²⁺** in which three crystallographically identical carbenes are bonded to the germanium center forming a pyramidal C_3 propeller consistent with an AX_3E[9] configuration (Figure 1).[10] The pyramidal geometry at germanium, the carbenic C−Ge bond length of 2.070(6) Å, which is slightly longer than an average C−Ge single bond (range 1.90− 2.05 Å),[11] and the lack of color suggests that back-bonding from the germanium lone pair to the carbenes is absent in **4²⁺**.[12]

The two iodide anions in the asymmetric unit show no significant bonding interaction with the germanium of **4²⁺**. The closest approach of the iodides is 3.11 Å from a methyl hydrogen, which is barely within the sum of the van der Waals radii (3.18 Å).[13] Iodide is usually considered a nucleophilic anion; exclusion of

Chart 1. Cations of Germanium, D = Neutral Donor
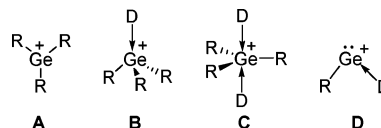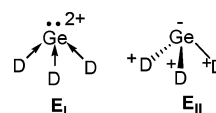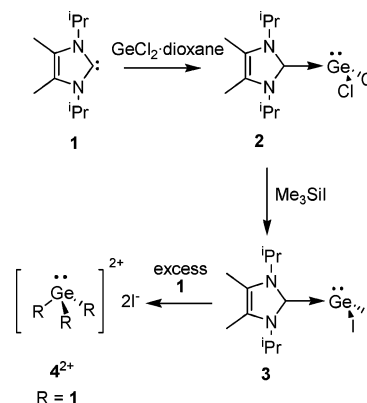

Chart 2. Representations of a Ge-Centered Dication

Scheme 1

iodide from germanium (the closest Ge−I approach is 5.96 Å) can be attributed to steric protection from the carbenes and the stereochemically active lone pair of electrons. A disordered pyridine solvate is also present in the unit cell but is distant from the germanium with the closest approach being 3.78 Å.

As expected, the FT Raman spectrum of the bulk powder of **4²⁺** 2I⁻ lacked a signal attributable to a germanium−iodine covalent bond which was clearly evident in the FT Raman spectrum of **3** (205 cm⁻¹). The ¹H NMR spectrum of **4²⁺** is rather complex at room temperature, showing multiple broad signals which, at 90 °C, simplify into resonances consistent with one type of carbene moiety. The ¹H NMR spectrum of a solution containing both **1** and **4²⁺** at room temperature shows sharp peaks attributable to free carbene **1** superimposed on the signals of **4²⁺**, suggesting that ligand exchange is not responsible for the broadening of the ¹H NMR signals of **4²⁺**. At −20 °C, the ¹H NMR spectrum of **4²⁺** revealed signals attributable to two nonequivalent isopropyl methyne ¹H's, four isopropyl methyl groups, and two backbone methyl groups which is consistent with the C_3 symmetry of **4²⁺** in the solid state (Figure 1).[8] Therefore, we can conclude that hindered rotation is the most likely explanation for the complex ¹H NMR spectrum of **4²⁺** observed at room temperature.

Electronic structure calculations[14] reveal that the HOMO of **4²⁺** is the lone electron pair on germanium, which is consistent with a
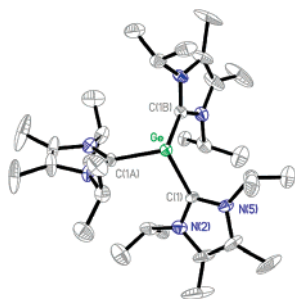
Figure 1. Thermal ellipsoid plot (30% probability surface) of 4^{2+}. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): C(1)−Ge = 2.070(6), N(2)−C(1) = 1.319(9), N(5)−C(1) = 1.358(9), N(2)−C(1)−N(5) = 106.5(6), C(1)−Ge−C(1A) = 103.1(2).
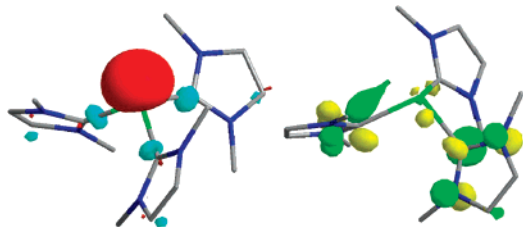

Figure 2. The HOMO and one of the degenerate LUMOs at an isosurface value of 0.075 for 4^{2+}. For clarity, the methyl groups and hydrogen atoms are not shown.

Ge(II) species, while the LUMO is a pair of degenerate π^* orbitals localized on the carbenes (Figure 2). In agreement with experimental observations, the lone pair of electrons on germanium shows no tendency for π bonding with the carbenes.

Two opposite interpretations of the bonding for 4^{2+} are possible. In 4^{2+}, the germanium can be considered dicationic with three neutral ligands (Chart 2, $\mathbf{E_I}$) or anionic with each ligand adopting a charge of +1 (Chart 2, $\mathbf{E_{II}}$). To determine which Lewis structure describes the electronic structure of 4^{2+} more accurately, the atomic charge on germanium was calculated using three population analysis schemes. The Mulliken charge on Ge is +0.05, natural population analysis[15] gives a charge of +0.64, and the atomic polar tensor[16] scheme predicts a charge of +1.02.[17] Since none of these charges are close to +2.0 or −1.0, the true nature of 4^{2+} must be somewhere between the two extremes ($\mathbf{E_I}$ and $\mathbf{E_{II}}$).[18]

In summary, we have reported the relatively straightforward synthesis of 4^{2+}, a germanium-centered dication. Spectroscopic evidence of the new complex is consistent with a discrete cation anion pair despite the dicationic charge and the presence of the relatively nucleophilic iodide anions. The combination of a metal-centered lone pair of electrons and a large positive charge make this complex unique in group 14 chemistry and an important contribution to known p-block-centered dications.[19] The ease of synthesis for 4^{2+} should make it a useful reagent for the synthesis of many germanium-containing compounds;[20] we are actively exploring its reactivity and synthetic utility.

Supporting Information Available: Experimental details, NMR spectra, computational details including complete ref 14, CIFs, and thermal ellipsoid plots for **2**, **3**, and 4^{2+} 2I⁻·pyridine. This material is available free of charge via the Internet at http://pubs.acs.org.

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