

A Ditetrylyne as a π -Electron Donor: Synthesis and Characterization of $[\text{AgAr}'\text{GeGeAr}']^+\text{SbF}_6^-$ and $[\text{Ag}_2\text{Ar}'\text{GeGe}(\text{F})\text{Ar}']^+\text{SbF}_6^-$ ($\text{Ar}' = \text{C}_6\text{H}_3\text{-2,6}(\text{C}_6\text{H}_3\text{-2,6-Pr}^i_2)_2$)

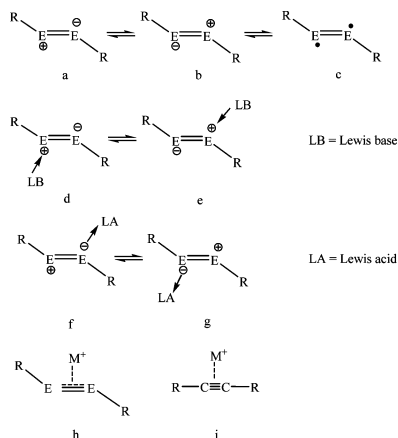
Xinping Wang, Yang Peng, Marilyn M. Olmstead, Håkon Hope, and Philip P. Power*

Department of Chemistry, University of California, Davis, One Shields Avenue, Davis, California 95616

Received June 11, 2010; E-mail: pppower@ucdavis.edu

Abstract: The reaction of a digermynes $\text{Ar}'\text{GeGeAr}'$ ($\text{Ar}' = \text{C}_6\text{H}_3\text{-2,6}(\text{C}_6\text{H}_3\text{-2,6-Pr}^i_2)_2$) with AgSbF_6 at -40°C forms the complex $(\text{AgAr}'\text{GeGeAr}')^+\text{SbF}_6^-$, which provides the first example of a heavier group 14 element alkyne analogue behaving as a π donor to a transition metal. The cation $(\text{AgAr}'\text{GeGeAr}')^+$ is best described as a hybrid of a π -complex and a σ -metallacyclopropene structure.

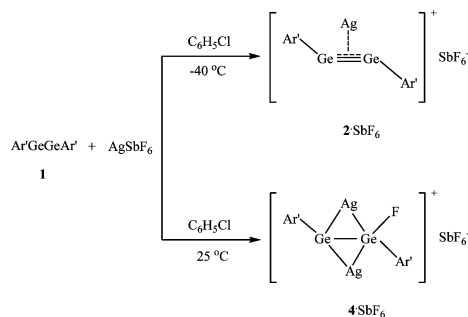
Several alkyne analogues (REER , $\text{E} = \text{Si, Ge, Sn, Pb}$; $\text{R} = \text{aryl}$ or silyl ligand) of heavier group 14 elements have been isolated and characterized.¹ Calculations on the Ge and Sn species show that their bonding can be represented by a or b.² In valence bond terms, there is an approximate $\text{E}=\text{E}$ double bond and a nonbonded,



resonating lone pair at an E. It is also possible to represent the structure as the singlet diradicaloid form c.² Their Lewis acidic character has been supported by reactions of REER ($\text{E} = \text{Si, Ge, Sn}$) with $\text{R}'\text{NC}$ ($\text{R}' = \text{Bu}^t, \text{Mes, SiMe}_3$) that led to the formation of adducts shown by d or e.³ In contrast, complexes such as f or g demonstrating Lewis basic properties and species such as h, in which REER acts as a π electron donor resembling the alkyne congener i, have not been described.⁴ We now report that the reaction of $\text{Ar}'\text{GeGeAr}'$ (**1**, $\text{Ar}' = \text{C}_6\text{H}_3\text{-2,6}(\text{C}_6\text{H}_3\text{-2,6-Pr}^i_2)_2$)^{1b} with AgSbF_6 at -40°C (Scheme 1) leads to a metal cation REER adduct $(\text{AgAr}'\text{GeGeAr}')^+\text{SbF}_6^-$ (**2**· SbF_6^-) with an SbF_6^- counteranion, the first example of a heavier group 14 element alkyne analogue-transition-metal π -complex.⁵

Reaction of AgSbF_6 and 1 equiv of **1** in chlorobenzene at -40°C yielded, after workup, green crystals of compound **2**· SbF_6^- in 23% yield (Scheme 1). The UV–vis spectrum of **2**· SbF_6^- in $\text{C}_6\text{H}_5\text{Cl}$ displays an absorption maximum at $\lambda_{\text{max}} = 412 \text{ nm}$ ($\epsilon = 640$), which differs considerably from that of uncomplexed **1** ($\lambda_{\text{max}} = 501 \text{ nm}$ ($\epsilon = 7500$), 371 nm ($34\,000$)).^{1b}

Scheme 1. Reactions of **1** with AgSbF_6 at -40 and 25°C



The structure of **2**· SbF_6^- consists of well-separated cations and anions. The cation (Figure 1) is characterized by a C_2 axis through the silver atom and midpoint of the $\text{Ge}-\text{Ge}$ bond. The $\text{C}-\text{Ge}-\text{Ge}-\text{C}$ core of **2** has a trans configuration ($\text{Ge}-\text{Ge}-\text{C} = 130.4(3)^\circ$) featuring a near-planar $\text{Ge}_2\{\text{C}(\text{ipso})\}_2$ array. The silver bridges the two Ge atoms in a symmetric fashion. The $\text{Ag}-\text{Ge}$ bonds ($2.6501(14) \text{ \AA}$) are ca. $0.2 \text{ \AA}$ longer than the $\text{Ag}-\text{Ge}(\text{II})$ bonds in complexes $\text{Ag}[\text{Ge}(\text{OC}_6\text{HPh}_4\text{-2,3,5,6})_3(\text{AgOSO}_2\text{CF}_3)] \cdot 4\text{C}_6\text{H}_6$, $\text{HB}\{3,5(\text{CF}_3)_2\text{Pz}\}_3\text{AgGeCl}[(\text{Me})_2\text{-ATI}]$ and $[\text{HB}\{3,5-(\text{CF}_3)_2\text{Pz}\}_3\text{AgGe}(\text{OSO}_2\text{CF}_3)][(\text{Me})_2\text{-ATI}]$ ($(\text{Me})_2\text{-ATI} = N\text{-methyl-2-methylamino-troponimine}$), consistent with their bridging character.⁶ In addition, silver is coordinated by four C atoms from two flanking rings with $\text{Ag}-\text{C}$ distances of $2.636(10)$ and $2.680(10) \text{ \AA}$ that are considerably longer than $\text{Ag}-\text{arene}$ bonds ($\sim 2.4 \text{ \AA}$) in $\text{Ag}(\eta^2\text{-PhMe})_2(\text{Al}(\text{OCH}(\text{CF}_3)_2)_4$.⁷ The $\text{Ge}-\text{Ge}$ distance ($2.303(2) \text{ \AA}$) is within the range ($2.2060(7)$ – $2.307(1) \text{ \AA}$) for digermynes^{1b,8,9} and is slightly longer than the $2.2850(6) \text{ \AA}$ of the $\text{Ge}-\text{Ge}$ bond in uncomplexed **1**.^{1b} The closest previously known structure to **2** is that of $\text{NaAr}'\text{GeGeAr}'$ ¹⁰ (cf. very similar effective radii of four coordinate Ag^+ ($1.00 \text{ \AA}$) and Na^+ ($0.99 \text{ \AA}$)).¹¹ In that compound, however, the $\text{Na}\cdots\text{Ge}$ distances ($3.1391(15)$ and $3.1596(15) \text{ \AA}$) are ca. $0.5 \text{ \AA}$ longer although the closest $\text{Na}-\text{C}$ distances are 0.15 – $0.2 \text{ \AA}$ longer than $\text{Ag}-\text{C}$ in **2**. These distances suggest a significantly stronger $\text{Ge}-\text{M}$

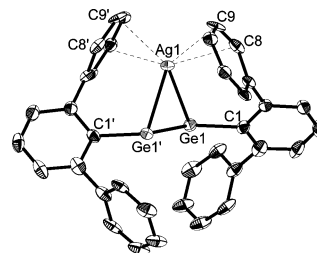
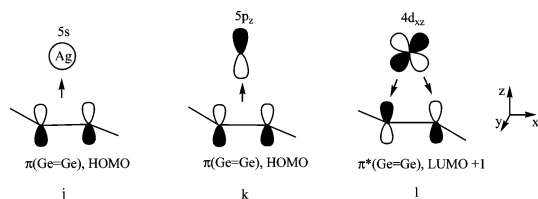


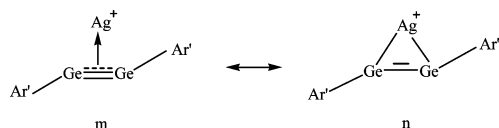
Figure 1. Thermal ellipsoid (50%) drawing of **2**. H atoms and Pr^i groups are not shown. Selected bond distances ($\text{\AA}$) and angles ($^\circ$): $\text{Ag1}-\text{C9}$ $2.636(10)$, $\text{Ag1}-\text{Ge1}$ $2.6501(14)$, $\text{Ag1}-\text{C8}$ $2.680(10)$, $\text{Ge1}-\text{C1}$ $1.972(9)$, $\text{Ge1}-\text{Ge1'}$ $2.303(2)$, $\text{Ge1}-\text{Ag1}-\text{Ge1'}$ $51.51(5)$, $\text{C1}-\text{Ge1}-\text{Ge1'}$ $130.4(3)$, $\text{C1}-\text{Ge1}-\text{Ag1}$ $108.6(3)$, $\text{Ge1}-\text{Ge1'}-\text{Ag1}$ $64.24(2)$.

interaction for the silver species especially in view of the fact that, in NaAr'GeGeAr' , the “ Ar'GeGeAr' ” unit formally carries the negative charge.¹⁰

To further understand **2**, we performed DFT calculations¹² for the model complex cation $\text{Ag}(\text{MeGeGeMe})^+$ (**3**). This was found to have an energy minimum whose geometrical parameters compare well with those found in the X-ray structure of **2**. The calculated HOMO–LUMO gap (71.0 kcal/mol) for **3** is close to the energy difference of 69.4 kcal/mol suggested by the experimental UV/vis absorption at 412 nm. Natural bond orbital (NBO) calculations



reveal that 0.43 electrons are donated from the digermine MeGeGeMe to Ag^+ . According to the calculated second-order perturbation interaction energies, the strongest orbital interaction (54.0 kcal/mol) in **3** (and thus in **2**) is between the π orbital (HOMO) of the Ge–Ge bond and the empty 5s or 5p orbitals of the Ag^+ cation, shown above as **j** and **k**. The back-donation (**l**) from the $4d_{xz}$ orbital of Ag^+ into the empty π^* orbital (LUMO+1) of Ge–Ge (**l**) is relatively weak (5.5 kcal/mol). Complex **2** is best described as a hybrid of a π -complex **m** and a σ -metallacyclopentene structure **n** shown below.



The green color of solutions of $\text{2} \cdot \text{SbF}_6$ becomes brown when warmed above ca. 0 °C. Brown crystals of compound $[\text{Ag}_2\text{Ar'GeGe}(\text{F})\text{Ar'}]\text{SbF}_6$ (**4**· SbF_6) in 30% yield were obtained upon cooling (Scheme 1). The reaction of **1** with AgSbF_6 at room temperature also gave **4**· SbF_6 in a similar yield. The mechanism of formation of **4** is unclear, but an abstraction of F from SbF_6^- to form what may be a stronger Ge–F bond (bond energy: Ge–F 473, Sb–F 405 kJ/mol) is a possibility.¹³ In addition, the fluorophilicity of the three-coordinate Ge atoms in **2** is probably quite high. The unique structure of **4** (Figure 2) features a near-planar AgGeAgGe core. The atoms Ge1, Ge2, and

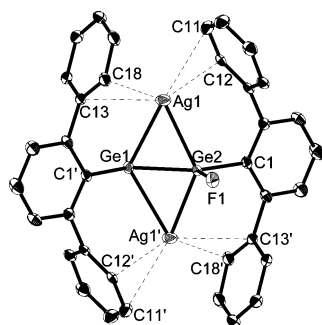
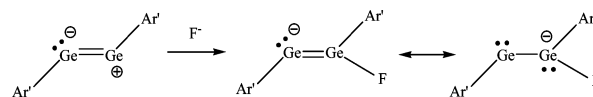


Figure 2. Thermal ellipsoid (50%) drawing of **4** (only one of the disordered core arrangements is illustrated). H atoms and Pr' groups are not shown. Selected bond distances (Å) and angles (deg): $\text{Ag1}–\text{Ge2}$ 2.5710(11), $\text{Ag1}–\text{Ge1}$ 2.7650(12), $\text{Ag1}'–\text{Ge2}$ 2.4908(11), $\text{Ag1}'–\text{Ge1}$ 2.7182(11), $\text{Ge1}–\text{Ge2}$ 2.4861(16), $\text{Ge2}–\text{F1}$ 1.795(5), $\text{Ag1}–\text{C11}$ 2.814(4), $\text{Ag1}–\text{C12}$ 2.562(3), $\text{Ag1}–\text{C13}$ 2.820(3), $\text{Ag1}–\text{C18}$ 2.642(3), $\text{Ag1}–\text{Ge2}–\text{Ge1}$ 66.274(1), $\text{Ag1}–\text{Ge1}–\text{Ge2}$ 58.3(3), $\text{Ge1}–\text{Ag1}–\text{Ge2}$ 55.4(4), $\text{C1}–\text{Ge2}–\text{Ge1}$ 124.8(1), $\text{F1}–\text{Ge2}–\text{Ge1}$ 130.8(1), $\text{F1}–\text{Ge2}–\text{Ag1}$ 102.6(1), $\text{C1}'–\text{Ge2}–\text{Ge1}$ 108.5(1).

F1 are disordered with respect to a crystallographic inversion center, and each atom was refined at half-occupancy at the two disordered sites (see Supporting Information). The Ge–Ag distances (avg. 2.5310(11), 2.7415(12) Å) are unequal with the shorter bond distance to the fluorinated Ge. The Ge–F distance (1.795(5) Å) is close to that in compounds (e.g., 1.805(17) Å in $[\{\text{HC}(\text{CMeNAr})_2\}\text{GeF}]$ ($\text{Ar} = 2,6\text{-iPr}_2\text{C}_6\text{H}_3$)).¹⁴ The Ge–Ge distance (2.4861(12) Å) may be compared with the 2.44 Å of a single Ge–Ge bond.¹⁵ **4** can be viewed as an anionic digermine fluoride adduct that is π -bonded to two Ag^+ ions.¹⁶ Its formation and possible resonance structures of the $\text{Ar'GeGe}(\text{F})\text{Ar'}$ monoanion are shown in Scheme 2.

Scheme 2



In summary, it has been shown that digermine Ar'GeGeAr' (**1**) reacts with Ag^+ at low temperature to form the side-on complex **2**. Its geometry, the Ge–Ge bond lengthening, and calculated electron densities indicate that the digermine **1** is acting as a π electron donor. The exploration of its chemistry is in hand.

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Supporting Information Available: CIF for **2** and **4**, experimental data, and DFT calculations. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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