A Ditetrylyne as a π-Electron Donor: Synthesis and Characterization of [AgAr′GeGeAr′]⁺SbF₆⁻ and [Ag₂Ar′GeGe(F)Ar′]⁺SbF₆⁻ (Ar′ = C₆H₃-2,6(C₆H₃-2,6-Pr$^i_2$)₂)

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Abstract: The reaction of a digermyne Ar′GeGeAr′ (Ar′ = C₆H₃-2,6-(C₆H₃-2,6-Pr$^i_2$)₂) with AgSbF₆ at −40 °C forms the complex (AgAr′GeGeAr′)⁺SbF₆⁻, which provides the first example of a heavier group 14 element alkyne analogue behaving as a π donor to a transition metal. The cation (AgAr′GeGeAr′)⁺ is best described as a hybrid of a π-complex and a σ-metallacyclopropene structure.

Several alkyne analogues (REER, E = Si, Ge, Sn, Pb; R = 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 E−E double bond and a nonbonded,
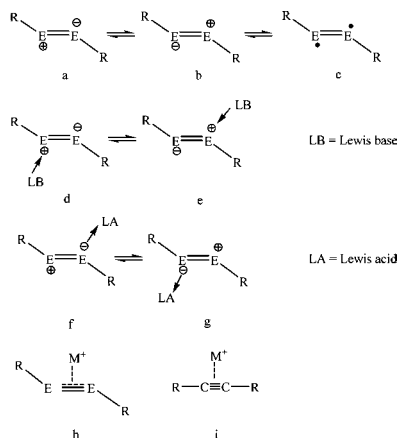
resonating lone pair at an E. It is also possible to represent the structure as the singlet diradicaloid form c.[2] Their Lewis acidic character has been supported by reactions of REER (E = Si, Ge, Sn) with R′NC: (R′ = Bu^t, Mes, SiMe₃) that led to the formation of adducts shown by d or e.[3] In contrast, 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 Ar′GeGeAr′ (**1**, Ar′ = C₆H₃-2,6-(C₆H₃-2,6-Pr$^i_2$)₂)[1b] with AgSbF₆ at −40 °C (Scheme 1) leads to a metal cation REER adduct (AgAr′GeGeAr′)⁺SbF₆⁻ (**2**·SbF₆) with an SbF₆⁻ counteranion, the first example of a heavier group 14 element alkyne analogue-transition-metal π-complex.[5]

Reaction of AgSbF₆ and 1 equiv of **1** in chlorobenzene at −40 °C yielded, after workup, green crystals of compound **2**·SbF₆ in 23% yield (Scheme 1). The UV−vis spectrum of **2**·SbF₆ in C₆H₅Cl displays an absorption maximum at $\lambda_{max} = 412$ nm ($\varepsilon = 640$), which differs considerably from that of uncomplexed **1** ($\lambda_{max} = 501$ nm ($\varepsilon = 7500$), 371 nm (34 000)).[1b]

Scheme 1. Reactions of **1** with AgSbF₆ at −40 and 25 °C
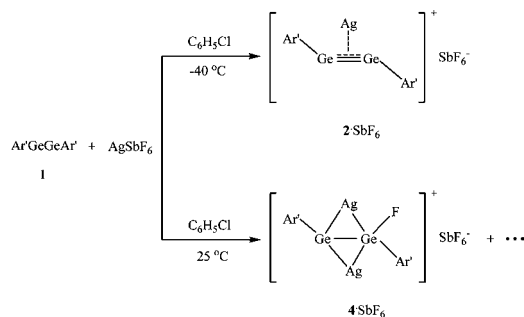
The structure of **2**·SbF₆ consists of well-separated cations and anions. The cation (Figure 1) is characterized by a C_2 axis through the silver atom and midpoint of the Ge−Ge bond. The C−Ge−Ge−C core of **2** has a trans configuration (Ge−Ge−C = 130.4(3)°) featuring a near-planar Ge₂{C(ipso)}₂ array. The silver bridges the two Ge atoms in a symmetric fashion. The Ag−Ge bonds (2.6501(14) Å) are ca. 0.2 Å longer than the Ag−Ge(II) bonds in complexes Ag[Ge(OC₆HPh₄-2,3,5,6)₃(AgOSO₂CF₃)]·4C₆H₆, HB{3,5(CF₃)₂Pz}₃AgGeCl[(Me)₂-ATI] and [HB{3,5-(CF₃)₂Pz}₃]AgGe-(OSO₂CF₃)[(Me)₂ATI] ((Me)₂-ATI = *N*-methyl-2-methylamino-troponiminate), consistent with their bridging character.[6] In addition, silver is coordinated by four C atoms from two flanking rings with Ag−C distances of 2.636(10) and 2.680(10) Å that are considerably longer than Ag−arene bonds (~2.4 Å) in Ag(η^2-PhMe)₂(Al(OCH(CF₃)₂)₄).[7] The Ge−Ge distance (2.303(2) Å) is within the range (2.2060(7)−2.307(1) Å) for digermynes[1b,8,9] and is slightly longer than the 2.2850(6) Å of the Ge−Ge bond in uncomplexed **1**.[1b] The closest previously known structure to **2** is that of NaAr′GeGeAr′[10] (cf. very similar effective radii of four coordinate Ag⁺ (1.00 Å) and Na⁺ (0.99 Å)).[11] In that compound, however, the Na···Ge distances (3.1391(15) and 3.1596(15) Å) are ca. 0.5 Å longer although the closest Na−C distances are 0.15−0.2 Å longer than Ag−C in **2**. These distances suggest a significantly stronger Ge−M
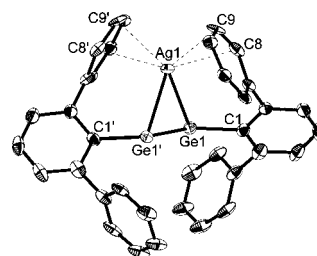

Figure 1. Thermal ellipsoid (50%) drawing of **2**. H atoms and Pr^i groups are not shown. Selected bond distances (Å) and angles (deg): Ag1−C9 2.636(10), Ag1−Ge1 2.6501(14), Ag1−C8 2.680(10), Ge1−C1 1.972(9), Ge1−Ge1′ 2.303(2), Ge1−Ag1−Ge1′ 51.51(5), C1−Ge1−Ge1′ 130.4(3), C1−Ge1−Ag1 108.6(3), Ge1−Ge1′−Ag1 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 calculations[12] for the model complex cation Ag(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
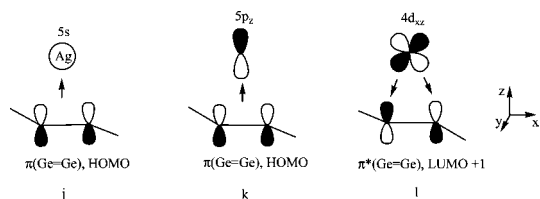
reveal that 0.43 electrons are donated from the digermyne MeGeGeMe to Ag$^+$. According to the calculated second-order perturbation interaction energies, the strongest orbital interaction (54.0 kcal/mol) in **3** (and thus in **2**) is between the π orbital (HOMO) of the Ge−Ge bond and the empty 5s or 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-metallacyclopropene structure n shown below.
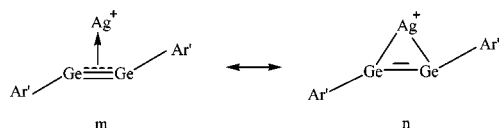
The green color of solutions of **2**·SbF$_6$ becomes brown when warmed above *ca.* 0 °C. Brown crystals of compound [Ag$_2$Ar′GeGe-(F)Ar′]SbF$_6$ (**4**·SbF$_6$) in 30% yield were obtained upon cooling (Scheme 1). The reaction of **1** with AgSbF$_6$ at room temperature also gave **4**·SbF$_6$ in a 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
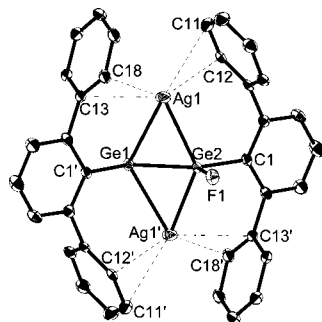
F1 are disordered with respect to a crystallographic inversion center, and each atom was refined at half-occupancy at the two disordered sites (see Supporting Information). The Ge−Ag distances (avg. 2.5310(11), 2.7415(12) Å) are unequal with the shorter bond distance to the fluorinated Ge. The Ge−F distance (1.795(5) Å) is close to that in compounds (e.g., 1.805(17) Å in [{HC-(CMeNAr)$_2$}GeF] (Ar = 2,6-^{i}Pr$_2$C$_6$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 digermyne fluoride adduct that is π-bonded to two Ag$^+$ ions.[16] Its formation and possible resonance structures of the Ar′GeGe(F)Ar′ monoanion are shown in Scheme 2.

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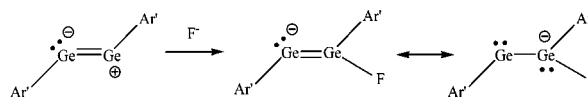
In summary, it has been shown that digermyne Ar′GeGeAr′ (**1**) reacts with Ag$^+$ at low temperature to form the side-on complex **2**. Its geometry, the Ge−Ge bond lengthening, and calculated electron densities indicate that the digermyne **1** is acting as a π electron donor. The exploration of its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

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.

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

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