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A Bis(germyliumylidene)silver(I) Complex Dication

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Supporting Information Placeholder

ABSTRACT: The reaction of the 2,6-bis(imino)phenylchlorogermylene [LGeCl] (**1**, L = C₆H₃-2,6-(HC=NtBu)₂) with silver(I) trifluoromethanesulfonate (AgOTf) in a molar ratio of 2:3 in toluene afforded a mixture of the bis(germylene)silver(I) complex [L(TfO)Ge]₂Ag(OTf)] (**2**) and AgCl. Compound **2** was then reacted with 2 equiv of 1,3-dimethyl-4,5-dimethylimidazol-2-ylidene (I_{Me}, :C{N(Me)C(Me)}₂) in toluene to afford **3**, which comprises the bis(germyliumylidene)silver(I) complex dication [L(I_{Me})Ge]₂Ag(OTf)²⁺. Compounds **2** and **3** were characterized by NMR spectroscopy and X-ray crystallography. [L(I_{Me})Ge]₂Ag(OTf)²⁺ in compound **3** was further elucidated by DFT studies.

INTRODUCTION

Germlyumylidene cations of composition [RGe:]⁺ have attracted much attention owing to their distinctive properties.¹ They consist of two vacant orbitals and a lone pair of electrons on the germanium(II) cations, possessing the properties of highly Lewis acidic germyl cations and the amphiphilic character of germynes. In this context, they are highly reactive and difficult to isolate. In the past decades, several research groups tackled the difficulties and utilized the concepts of thermodynamic and/or kinetic stabilization to afford stable germlyumylidene cations. The most spectacular example is the amido germlyumylidene cation [Ar*(Me₃Si)NGe]⁺ (**I**, Chart 1),² in which the low-valent germanium cation is stabilized by a steric hindered monodentate ligand and weak arene interaction. In addition, a series of germlyumylidene cations such as **II** – **VII** were synthesized with the aid of strong electron pair donors.^{3–16}

Chart 1. Germlyumylidene cations

Recently, germynes were used as ancillary ligands to coordinate with transition metals^{17–20} such as group 11 met-

als.^{21–33} The resulting transition metal-germylene complexes were capable of catalyzing organic transformations.^{34–37} As such, it is anticipated that transition metal-germyliumylidene cation complexes may have beneficial application in homogeneous catalysis due to the increased Lewis acidity of transition metal centres. However, such complexes are still unknown as yet.

Previously, we showed the reduction of the 2,6-bis(imino)phenylchlorogermylene [LGeCl] (**1**, L = C₆H₃-2,6-(HC=NtBu)₂, Scheme 1) with alkali metal to afford the 2,6-bis(imino)phenylgermylidenide anion [LGe][–].³⁸ It is suggested that **1** could possibly undergo halide abstraction to form a 2,6-bis(imino)phenylgermyliumylidene cation, which can be used as a ligand to coordinate with transition metal. Herein, we report the synthesis of a bis(germyliumylidene)silver(I) complex dication.

RESULTS AND DISCUSSION

The reaction of the 2,6-bis(imino)phenylchlorogermylene [LGeCl] (**1**) with sodium trifluoromethanesulfonate NaOTf (OTf = CF₃SO₃[–]), sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate or methyl trifluoromethanesulfonate MeOTf afforded an insoluble white precipitate, which cannot be dissolved in any organic solvents. In contrast, when compound **1** was reacted with silver(I) trifluoromethanesulfonate (AgOTf) in a molar ratio of 2:3 in toluene, a mixture of the bis(germylene)silver(I) complex [L(TfO)Ge]₂Ag(OTf)] (**2**, Scheme 1) and AgCl was afforded. Other germylene-silver(I) complexes were not observed in the reaction mixture, which was confirmed by ¹H NMR spectroscopy. In addition, when **1** reacted with one equiv of AgOTf, [L(Cl)Ge-AgOTf] was not afforded and instead, compound **2** was formed. On the basis of experimental results, it is proposed that AgOTf simultaneously

undergoes salt elimination reaction and coordination with **1** to form **2**.

Scheme 1. Synthesis of **2** and **3**

Compound **2** was isolated as a highly air- and moisture-sensitive colourless crystalline solid and its purity was confirmed by elemental analysis. It is soluble in THF and CH_2Cl_2 . It was characterized by NMR spectroscopy and X-ray crystallography. Its ^1H NMR spectrum exhibits a singlet at δ 1.62 ppm for the *t*Bu substituents, a singlet at δ 7.90 ppm and triplet at δ 7.70 ppm for the phenyl protons, and another singlet at δ 8.86 ppm corresponding to $\text{HC}=\text{N}$ protons. The $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum shows one set of resonances due to the ligand backbone and another quartet arising from the OTf substituents. The $^{19}\text{F}\{^1\text{H}\}$ NMR spectrum exhibits a signal at δ -78.61 ppm, which is inconsistent with the solid-state structure, suggesting that the triflate groups dissociate in solution ($\text{THF}-d_8$) at room temperature. In this context, the $^{19}\text{F}\{^1\text{H}\}$ NMR spectroscopy was performed at -100 $^\circ\text{C}$, which shows a signal at δ -67.8 ppm, suggesting that the triflate groups are bound to the metal centres.

Figure 1. X-ray crystal structure of **2** with thermal ellipsoids at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Ag1–Ge1 2.5009(5), Ag1–Ge2 2.4782(5), Ge1–O1

1.951(3), Ag1–O4 2.492(5), Ge2–O7 1.930(13), C1–Ge1 1.933(3), C18–Ge2 1.933(4); Ge1–Ag1–Ge2 139.459(18), Ge1–Ag1–O4 97.26(12), Ge2–Ag1–O4 123.27(12), C1–Ge1–Ag1 145.58(10), C1–Ge1–O1 102.9(2), O1–Ge1–Ag1 111.5(2), C18–Ge2–Ag1 137.59(10), Ag1–Ge2–O7 116.8(7), C18–Ge2–O7 105.6(7).

The X-ray crystal structure of **2** (Figure 1) shows that the 2,6-bis(imino)phenyl ligands are in a staggered conformation. The germanium atom adopts a distorted trigonal bipyramidal geometry with the imino nitrogen atoms at the axial position, while the silver atom adopts a trigonal planar geometry. The $\text{C}_{\text{aryl}}\text{--Ge}$ (1.933(3) – 1.933(4) Å) and $\text{Ge--N}_{\text{imino}}$ (2.309(3) – 2.358(3) Å) bond lengths are comparable to those of **1** (Ge--C : 2.0004(19) Å; Ge--N : 2.2981(17) Å). The Ge--O bond lengths (1.930(13), 1.951(3) Å) are slightly shorter than that of the aminotroponiminato triflatogermylene-silver(I) complex (Ge--O : 2.020(6) Å).²⁷ The Ag1–O4 bond length (2.492(5) Å) is comparable to that of AgOTf (Ag--O : 2.485(5), 2.504(5) Å).⁴⁰ The Ag–Ge bond lengths (2.5009(5), 2.4782(5) Å) are unequal, but they are comparable to those of base-stabilized germylene-silver(I) cation complexes such as $[\{\text{R}(\text{tBu})\text{Ge}\}_2\text{Ag}]^+$ ($\text{R} = \text{PhC}(\text{NtBu})_2$, 2.4539(3) Å)³³ and $[\{\text{R}(\text{PhC}\equiv\text{C})\text{Ge}\}_2\text{Ag}][\text{Ag}(\text{C}_6\text{F}_5)_2]$ ($\text{R} = \text{HC}(\text{C}(\text{Me})\text{NAr})_2$, 2.4732(10), 2.4731(10) Å).²⁸

Compound **2** was then reacted with 2 equiv of 1,3-dimethyl-4,5-dimethylimidazol-2-ylidene ($\text{I}_{\text{Me}} = \text{:C}\{\text{N}(\text{Me})\text{C}(\text{Me})\}_2$) in toluene to afford **3**, which is the first example comprising a bis(germyliumylidene)silver(I) complex dication $[\{\text{L}(\text{I}_{\text{Me}})\text{Ge}\}_2\text{Ag}(\text{OTf})]^{2+}$ (Scheme 1), following a previous example of the bis(germanium(II) dication)-silver(I) complex $[\{(\text{H}_2\text{CN}=\text{C}(\text{Me})\text{C}_5\text{H}_4\text{N})_2\text{Ge}\}_2\text{Ag}(\text{OTf})]^{4+}$.²⁹ Compound **3** was isolated as an extremely air- and moisture-sensitive yellow crystalline solid and its purity was confirmed by elemental analysis. It is soluble in CH_2Cl_2 and 1,2-difluorobenzene. It was characterized by NMR spectroscopy. Its ^1H NMR spectrum shows a singlet at δ 1.11 ppm for the *t*Bu substituents, four other singlets at δ 2.08, 2.27, 2.57 and 4.28 ppm for the methyl protons on I_{Me} , a triplet at δ 7.95 ppm and a doublet at δ 8.09 ppm for the phenyl protons, and another singlet at δ 8.56 ppm for the $\text{HC}=\text{N}$ protons. These signals suggest that the imino substituents are chemically equivalent in solution but otherwise in the solid state structure (Figure 2). In addition, the four singlets corresponding to the methyl protons on I_{Me} suggest that the I_{Me} ligands do not freely rotate, resulting in chemically inequivalent in solution. The $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum shows one set of resonances due to the ligand backbone, one set of resonances due to the I_{Me} ligand and another quartet arising from the OTf substituents. The $^{19}\text{F}\{^1\text{H}\}$ NMR spectra at room temperature and -70 $^\circ\text{C}$ exhibit a signal at δ -78.6 ppm, indicating the exchange between free and bound triflate groups to be fast on the NMR time scale. A similar observation was made for the 2,6-bis(imino)pyridine-bound stannylumylidene cation $[\text{C}_5\text{H}_3\text{N-2,6-}\{\text{C}(\text{Me})\text{N}(\text{Ar})\}_2\text{SnOTf}]\text{OTf}$.³⁹

The X-ray crystal structure of **3** (Figure 2) comprises two molecules in the asymmetric unit and only one of them is

discussed herein. The silver atom adopts a distorted trigonal planar geometry, while the germanium atoms adopt a pseudo trigonal bipyramidal geometry with the N_{imino} atoms at the axial position. The Ge1-N3 (2.081(6) Å) and Ge2-N7 (2.099(5) Å) bond lengths are significantly shorter than the $\text{Ge1}\cdots\text{N4}$ (2.740(7) Å) and $\text{Ge2}\cdots\text{N8}$ (2.704(6) Å) distances. The Ge1-N3 (2.081(6) Å) and Ge2-N7 (2.099(5) Å) bond lengths are intermediate values between those of the $\text{Ge-N}_{\text{imino}}$ coordinative covalent bonds in the pyridinylimino-stabilized chlorogermylumylidene cations $[\{\text{C}_5\text{H}_3\text{N-2-OMe-6-(MeCNAr)}\}\text{GeCl}]^+$ (Ge-N : 2.045(4), 2.070(4) Å; $\text{Ar} = 2,6\text{-iPr}_2\text{C}_6\text{H}_3$),¹⁰ and $[\{\text{C}_5\text{H}_3\text{N-2,6-(MeCNAr)}_2\}\text{GeCl}]^+$ (Ge-N : 2.255(2), 2.267(2) Å).¹¹ The $\text{Ge1}\cdots\text{N4}$ (2.740(7) Å) and $\text{Ge2}\cdots\text{N8}$ (2.704(6) Å) distances are shorter than the sum of their van der Waals radii (ca. 3.55 Å), indicating a weak interaction between these germanium and nitrogen atoms. The $\text{C}_{\text{aryl}}\text{-Ge}$ (C8-Ge1 : 1.941(7), C31-Ge2 : 1.937(7) Å) and Ag-Ge (Ag1-Ge1 : 2.5003(8), Ag1-Ge2 : 2.4881(8) Å) bond lengths are comparable to those of **2**. The $\text{C}_{\text{Ime}}\text{-Ge}$ bond lengths (C1-Ge1 : 2.0016, C24-Ge2 : 1.987(6) Å) are intermediate values between the $\text{C}_{\text{aryl}}\text{-Ge}$ bond lengths in **3** and the $\text{C}_{\text{Ar}}\text{-Ge}$ bond length in the NHC-germylumylidene cation complex $[\text{I}_{\text{Ar}}\text{-GeCH}(\text{SiMe}_3)_2]^+$ (2.082(1) Å, $\text{I}_{\text{Ar}} = \text{:C}(\text{N}(\text{Ar})\text{CH})_2$).⁷

Figure 2. X-ray crystal structure of the cation $[\{\text{L}(\text{Ime})\text{Ge}\}_2\text{Ag}(\text{OTf})]^{2+}$ in compound **3** with thermal ellipsoids at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Ag1-Ge1 2.5003(8), Ag1-Ge2 2.4881(8), C8-Ge1 1.941(7), C31-Ge2 1.937(7), N3-Ge1 2.081(6), N7-Ge2 2.099(5), C1-Ge1 2.001(6), C24-Ge2 1.987(6), Ag1-O1 2.417(12); Ge1-Ag1-Ge2 134.33(3), Ge1-Ag1-O1 102.8(10), Ge2-Ag1-O1 122.9(10), C31-Ge2-Ag1 116.14(18), C31-Ge2-N7 81.8(2), C31-Ge2-C24 109.9(3), Ag1-Ge2-C24 126.47(18), C24-Ge2-N7 97.5(2), Ag1-Ge2-N7 114.35(14), C8-Ge1-Ag1 115.69(19), C8-Ge1-N3 82.4(3), C8-Ge1-C1 109.9(3), N3-Ge1-Ag1 111.84(16), N3-Ge1-C1 98.6(2), C1-Ge1-Ag1 127.41(19).

The electronic property of $[\{\text{L}(\text{Ime})\text{Ge}\}_2\text{Ag}(\text{OTf})]^{2+}$ in compound **3** is further elucidated by Density Functional Theory (DFT) studies and Natural Bond Orbital (NBO) analysis. First, Natural Population Analysis (NPA) charges

of the Ge centres are positive (0.93, 0.92 e). Second, the donor-acceptor interaction from the Ge^+ cations to the Ag centre in $[\{\text{L}(\text{Ime})\text{Ge}\}_2\text{Ag}(\text{OTf})]^{2+}$ is undoubtedly illustrated by the HOMO (Figure 3). In addition, the Ge-Ag bonds are polarized in such a way that NBO analysis dissects them into a lone pair (LP, $sp^{0.63}$) localized on the Ge cations and vacant acceptor orbitals (s and p) on the Ag cation (the second order perturbation energies, $\text{LP}_{\text{Ge}} \rightarrow s_{\text{Ag}}$: 66.5, 67.7 kcal/mol; $\text{LP}_{\text{Ge}} \rightarrow p_{\text{Ag}}$: 20.4, 26.0 kcal/mol). Moreover, Wiberg bond index (WBI) of the Ge-Ag bonds is significantly small (WBI: 0.29). Third, NBO analysis shows that the $\text{C}_{\text{Ime}}\text{-Ge}$ bonds are highly polarized toward the C_{Ime} atoms (77.5 % C + 22.6 % Ge; 77.4 % C + 22.6 % Ge) with WBI of 0.65. They are formed by the overlapping of the sp^2 hybridized lone pair orbitals on the C_{NHC} atoms ($sp^{1.43}$; $sp^{1.42}$) with the vacant p -rich hybrids ($sp^{4.58}$; $sp^{4.58}$) on the Ge centres.

Figure 3. The HOMO of $[\{\text{L}(\text{Ime})\text{Ge}\}_2\text{Ag}(\text{OTf})]^{2+}$

CONCLUSION

The first example of the bis(germylumylidene)silver(I) complex dication $[\{\text{L}(\text{Ime})\text{Ge}\}_2\text{Ag}(\text{OTf})]^{2+}$ was synthesized by a simple synthetic methodology. X-ray crystallography and DFT studies conclusively show that the $\text{Ge}(\text{II})$ cations in $[\{\text{L}(\text{Ime})\text{Ge}\}_2\text{Ag}(\text{OTf})]^{2+}$ form donor-acceptor interaction with both Ime and AgOTf . The catalysis mediated by **2** and **3** is currently under investigation.

EXPERIMENTAL SECTION

General Procedures. All manipulations were carried out under an inert atmosphere of argon gas using standard Schlenk techniques. THF, toluene, and Et_2O were dried over and distilled over Na/K alloy prior to use. CH_2Cl_2 was dried over and distilled over CaH_2 prior to use. Compound **1** was prepared as described in the literature.³⁸ The ^1H , ^{13}C and ^{19}F NMR spectra were recorded on a JEOL ECA 400 spectrometer. The chemical shifts (δ) are relative to SiMe_4 for ^1H and ^{13}C , and CFCl_3 for ^{19}F . The purity of compounds **2** and **3** was characterized by elemental analysis, which was performed by Nanyang Technological University, Division of Chemistry and Biological Chemistry. Melting points were measured in sealed glass tubes and were uncorrected.

Synthesis of 2. Toluene (20 mL) was added to a mixture of **1** (0.351 g, 1.00 mmol) and AgOTf (0.385 g, 1.50 mmol) at 0 °C. The reaction mixture was then warmed to room temperature and stirred for 15 h in the absence of ambient light. Solvent was removed under vacuum, and the residue was extracted with dichloromethane. AgCl was filtered off, and the pale yellow filtrate was concentrated to afford colourless crystals of **2**. (0.200 g, 31%). M.p.: 170 °C (dec). Elemental analysis (%) calcd for $\text{C}_{36}\text{H}_{48}\text{AgCl}_2\text{F}_9\text{Ge}_2\text{N}_4\text{O}_3$ ($2 \cdot \text{CH}_2\text{Cl}_2$): C, 34.01; H, 3.81; N, 4.41; S, 7.57. Found: C, 34.05; H, 3.92; N, 4.34; S, 7.90. ^1H NMR (399.5 MHz, THF-d_8 , 27.2 °C): δ 1.62 (s, 36H, $\text{C}(\text{CH}_3)_3$), 7.90 (s, 4H, Ph), 7.70 (t, $3J_{\text{HH}} = 7.55$ Hz, 2H, Ph), 8.86 (s, 4H, $\text{CH}=\text{N}$). $^{13}\text{C}\{^1\text{H}\}$ NMR (100.5

MHz, THF-*d*₈, 27.4 °C): δ 30.92 (CH₃), 60.97 (C(CH₃)₃), 120.6 (q, ³J_{CF} = 319.81 Hz, CF₃), 132.76, 140.28 (Ph), 161.99 ppm (C=N–C). ¹⁹F{¹H} NMR (375.9 MHz, THF-*d*₈, 27.0 °C): δ -78.6 ppm.

Synthesis of 3. I_{Me} (0.127 g, 1.03 mmol) in toluene (10 mL) was added dropwise to 2 (0.636 g, 0.50 mmol) in toluene (20 mL) at room temperature. The resulting yellow solution was stirred for 15 h. Solvent was removed under vacuum, and the residue was extracted with 1,2-difluorobenzene. Insoluble precipitate was filtered off and the yellow filtrate was concentrated to afford yellow crystals of 3 (0.300 g, 32%). M.p.: 207 °C (dec). Elemental analysis (%) calcd for C₆₁H₇₈AgF₁₃Ge₂N₈O₉S₃ (3.2(1,2-C₆H₄F₂)): C, 44.04; H, 4.73; N, 6.74; S, 5.78. Found: C, 44.31; H, 4.49; N, 6.67; S, 5.47. ¹H NMR (399.5 MHz, CD₂Cl₂, 22.9 °C): δ 1.11 (s, 36H, C(CH₃)₃), 2.08 (s, 6H, I_{Me}), 2.27 (s, 6H, I_{Me}), 2.57 (s, 6H, I_{Me}), 4.28 (s, 6H, I_{Me}), 7.95 (t, ³J_{HH} = 7.55 Hz, 2H, Ph), 8.09 (d, ³J_{HH} = 319.81 Hz, 4H, Ph), 8.56 (s, 4H, CH=N). ¹³C{¹H} NMR (100.5 MHz, CD₂Cl₂, 23.2 °C): δ 9.23 (C–CH₃), 9.43 (C–CH₃), 31.15 (C(CH₃)₃), 33.70 (N–CH₃), 36.40 (N–CH₃), 60.56 (C(CH₃)₃), 116.47 (CF₃), 119.66, 122.86 (C=C), 126.05, 129.46, 130.29, 132.16 (Ph), 134.69, 138.16 (NCN), 160.80 ppm (C=N–C). ¹⁹F{¹H} NMR (375.9 MHz, CD₂Cl₂, 23.3 °C): δ -78.5 ppm.

X-ray data collection and structural refinement: Intensity data for all compounds were collected by using a Bruker APEX II diffractometer. The structures were solved by direct-phase determination (SHELXS-97) and refined for all data by full-matrix least-squares methods on *F*².⁴¹ All non-hydrogen atoms were subjected to anisotropic refinement. The hydrogen atoms were generated geometrically and allowed to ride on their respective parent atoms; they were assigned appropriate isotropic thermal parameters and included in the structure-factor calculations.

DFT studies:⁴² [(L(I_{Me}))Ge]₂Ag(OTf)₂²⁺ in compound 3 was investigated using DFT Mo6-2X method with the LanLo8 basis set for Ag and 6-311G(d) for other atoms. All calculations were carried out using the Gaussian 09 packages. The optimized geometries are in good agreement with their X-ray crystallographic data. NPA, NBO analysis and WBI bond index were performed with DFT-Mo6-2X wave functions and the calculations were carried out with NBO 5.0 package.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.

Selected NMR spectra and theoretical data (PDF)
Cartesian coordinates of calculated compound 3 (xyz)
X-ray crystallographic data (CIF)

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Notes

The authors declare no competing financial interests.

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REFERENCES

- Fang, H.; Wang, Z.; Fu, X. Beyond Carbocations: Synthesis, Structure and Reactivity of Heavier Group 14 Element Cations. *Coord. Chem. Rev.* **2017**, *344*, 214–237.
- Li, J.; Schenk, C.; Winter, F.; Scherer, H.; Trapp, N.; Higelin, A.; Keller, S.; Poettgen, R.; Krossing, I.; Jones, C. Weak Arene Stabilization of Bulky Amido-Germanium(II) and Tin(II) Monocations. *Angew. Chem., Int. Ed.* **2012**, *51*, 9557–9561.
- Stender, M.; Phillips, A. D.; Power, P. P. Characterization and Bonding of the Cation [Ge{N(C₆H₃-2,6-*i*-Pr₂)CMe₂CH}]+: Comparison with the Isoelectronic Ga{N(C₆H₃-2,6-*i*-Pr₂)CMe₂CH}. *Inorg. Chem.* **2001**, *40*, 5314–5315.
- Dias, H. V. R.; Wang, Z. Germanium-Containing Heterobicyclic 10-π-Electron Ring Systems. Synthesis and Characterization of Neutral and Cationic Germanium(II) Derivatives of Aminotroponimines. *J. Am. Chem. Soc.* **1997**, *119*, 4650–4655.
- Schäfer, A.; Saak, W.; Haase, D.; Müller, T. A Germanium(II) Cation with [1+1] Coordination. *Chem. - Eur. J.* **2009**, *15*, 3945–3950.
- Ochiai, T.; Franz, D.; Wu, X.-N.; Inoue, S. Isolation of a Germanium(II) Cation and a Germylene Iron Carbonyl Complex Utilizing an Imidazolin-2-iminato Ligand. *Dalton Trans.* **2015**, *44*, 10952–10956.
- Rit, A.; Tirfoin, R.; Aldridge, S. Exploiting Electrostatics to Generate Unsaturation: Oxidative Ge=E Bond Formation Using a Non π-Donor Stabilized [R(L)Ge:]⁺ Cation. *Angew. Chem., Int. Ed.* **2016**, *55*, 378–382.
- Arii, H.; Nakadate, F.; Mochida, K.; Kawashima, T. Lewis Base Complexes of an Enantiomeric Germanium(II) Cation Bearing a Bis(oxazoline) Ligand. *Organometallics* **2011**, *30*, 4471–4474.
- Paul, D.; Heins, F.; Krupski, S.; Hepp, A.; Daniliuc, C. G.; Klahr, K.; Neugebauer, J.; Glorius, F.; Hahn, F. E. Synthesis and Reactivity of Intramolecularly NHC-stabilized Germynes and Stannylenes. *Organometallics* **2017**, *36*, 1001–1008.
- Bouška, M.; Dostál, L.; Růžička, A.; Jambor, R. Stabilization of Three-Coordinated Germanium(II) and Tin(II) Cations by a Neutral Chelating Ligand. *Organometallics* **2013**, *32*, 1995–1999.
- Singh, A. P.; Roesky, H. W.; Carl, E.; Stalke, D.; Demers, J.-P.; Lange, A. Lewis Base Mediated Autoionization of GeCl₂ and SnCl₂. *J. Am. Chem. Soc.* **2012**, *134*, 4998–5003.
- Roy, M. M. D.; Lummis, P. A.; Ferguson, M. J.; McDonald, R.; Rivard, E. Accessing Low-Valent Inorganic Cations by Using an Extremely Bulky N-Heterocyclic Carbene. *Chem. - Eur. J.* **2017**, *23*, 11249–11252.
- Su, Y.; Li, Y.; Ganguly, R.; Kinjo, R. Isolation and Reactivity of a Chlorogermylumylidene Featuring Two Ge–Cl Units. *Eur. J. Inorg. Chem.* **2018**, DOI: 10.1002/ejic.201701482.
- Khan, S.; Gopakumar, G.; Thiel, W.; Alcarazo, M., Stabilization of a Two-Coordinate [GeCl]⁺ Cation by Simultaneous σ and π Donation from a Monodentate Carbodiphosphorane. *Angew. Chem., Int. Ed.* **2013**, *52*, 5644–5647.
- Su, B.; Ganguly, R.; Li, Y.; Kinjo, R. Isolation of an Imino-N-heterocyclic Carbene/Germanium(o) Adduct: A Mesoionic Germylene Equivalent. *Angew. Chem., Int. Ed.* **2014**, *53*, 13106–13109.
- Su, B.; Ganguly, R.; Li, Y.; Kinjo, R. Synthesis, Characterization, and Electronic Structures of a Methyl Germylumylidene Ion and Germylene-group VI Metal Complexes. *Chem. Commun.* **2016**, *52*, 613–616.
- Baumgartner, J.; Marschner, C. Coordination of Non-stabilized Germynes, Stannylenes, and Plumbynes to Transition Metals. *Rev. Inorg. Chem.* **2014**, *34*, 119–152.
- Álvarez-Rodríguez, L.; Cabeza, J. A.; García-Álvarez, P.; Polo, D. The Transition-metal Chemistry of Amidinatosilylenes, -

- Germynes and -Stannynes. *Coord. Chem. Rev.* **2015**, 300, 1-28.
- (19) Cabeza, J. A.; García-Álvarez, P.; Polo, D. Intramolecularly Stabilized Heavier Tetrylenes: From Monodentate to Bidentate -Ligands. *Eur. J. Inorg. Chem.* **2016**, 2016, 10-22.
- (20) Alvarez-Rodríguez, L.; Brugos, J.; Cabeza, J. A.; Garcia-Alvarez, P.; Perez-Carreno, E.; Polo, D. Synthesis and Initial Transition Metal Chemistry of the First PGeP Pincer-type Germylene. *Chem. Commun.* **2017**, 53, 893-896.
- (21) York, J. T.; Young, V. G.; Tolman, W. B. Heterobimetallic Activation of Dioxxygen: Characterization and Reactivity of Novel Cu(I)-Ge(II) Complexes. *Inorg. Chem.* **2006**, 45, 4191-4198.
- (22) Yadav, D.; Siwatch, R. K.; Sinhababu, S.; Nagendran, S. Aminotroponiminato(chloro)germylene Stabilized Copper(I) Iodide Complexes: Synthesis and Structure. *Inorg. Chem.* **2014**, 53, 600-606.
- (23) Zhao, N.; Zhang, J.; Yang, Y.; Zhu, H.; Li, Y.; Fu, G. β -Diketiminato Germylene-Supported Pentafluorophenylcopper(I) and -silver(I) Complexes $[LGe(Me)(CuC_6F_5)_n]_2$ ($n = 1, 2$), $LGe[C(SiMe_3)N_2][AgC_6F_5]$, and $\{LGe[C(SiMe_3)N_2](AgC_6F_5)_2\}_2$ ($L = HC[C(Me)N-2,6-iPr_2C_6H_3]_2$): Synthesis and Structural Characterization. *Inorg. Chem.* **2012**, 51, 8710-8718.
- (24) Ferro, L.; Hitchcock, P. B.; Coles, M. P.; Fulton, J. R. Reactivity of Divalent Germanium Alkoxide Complexes Is in Sharp Contrast to the Heavier Tin and Lead Analogues. *Inorg. Chem.* **2012**, 51, 1544-1551.
- (25) Arii, H.; Nakadate, F.; Mochida, K. Arii, H.; Nakadate, F.; Mochida, K., Spectroscopic and Structural Characterization of Copper-Germylene Complexes Bearing an Isopropyl-Substituted β -Diketiminato Ligand. *Organometallics* **2009**, 28, 4909-4911.
- (26) Leung, W.-P.; So, C.-W.; Chong, K.-H.; Kan, K.-W.; Chan, H.-S.; Mak, T. C. W. Reactivity of Pyridyl-1-azaallyl Germanium(II) Chloride: Synthesis of Novel Lithium Germinate $[(PhC\equiv C)_3Ge]_3GeLi(Et_2O)_3$ and Ge(II)-M(I) ($M = Cu$ and Au) Adducts. *Organometallics* **2006**, 25, 2851-2858.
- (27) Dias, H. V. R.; Wang, Z. Adduct Formation or Metathesis Reactions of Silver Complexes Containing the Fluorinated Ligands $[HB(3,5-(CF_3)_2Pz)_3]^-$ and $[CF_3SO_3]^-$: Formation of Silver Adducts Containing Unsupported Silver-Germanium Bonds. *Inorg. Chem.* **2000**, 39, 3890-3893.
- (28) Zhao, N.; Zhang, J.; Yang, Y.; Chen, G.; Zhu, H.; Roesky, H. W. Reactivity Studies of (Phenylethynyl)germylene $LGeC\equiv CPh$ ($L = HC[C(Me)N-2,6-iPr_2C_6H_3]_2$) toward Pentafluorophenylcopper(I), -silver(I), and -gold(I) Complexes. *Organometallics* **2013**, 32, 762-769.
- (29) Raut, R. K.; Majumdar, M. Direct Coordination of a Germanium(II) Dicationic Center to Transition Metals. *Chem. Commun.* **2017**, 53, 1467-1469.
- (30) Cabeza, J. A.; Fernandez-Colinas, J. M.; Garcia-Alvarez, P.; Polo, D. Diaminogermylene and Diaminostannylene Derivatives of Gold(I): Novel AuM and AuM_2 ($M = Ge, Sn$) Complexes. *Inorg. Chem.* **2012**, 51, 3896-3903.
- (31) Matioszek, D.; Kocsor, T.-G.; Castel, A.; Nemes, G.; Escudie, J.; Saffon, N. Phosphaalkenyl Germynes and Their Gold, Tungsten and Molybdenum Complexes. *Chem. Commun.* **2012**, 48, 3629-3631.
- (32) Yadav, D.; Kumar Siwatch, R.; Sinhababu, S.; Karwasara, S.; Singh, D.; Rajaraman, G.; Nagendran, S. Digermylene Oxide Stabilized Group 11 Metal Iodide Complexes. *Inorg. Chem.* **2015**, 54, 11067-11076.
- (33) Álvarez-Rodríguez, L.; Cabeza, J. A.; García-Álvarez, P.; Polo, D. Amidinatogermylene Complexes of Copper, Silver, and Gold. *Organometallics* **2015**, 34, 5479-5484.
- (34) Litz, K. E.; Bender, J. E.; Kampf, J. W.; Holl, M. M. B. Transition Metal Germylene Complexes as Hydrogenation Catalysts: the Synthesis of a Rare Bis(amino)germane. *Angew. Chem., Int. Ed. Engl.* **1997**, 36, 496-498.
- (35) Álvarez-Rodríguez, L.; Cabeza, J. A.; Fernández-Colinas, J. M.; García-Álvarez, P.; Polo, D. Amidinatogermylene Metal Complexes as Homogeneous Catalysts in Alcoholic Media. *Organometallics* **2016**, 35, 2516-2523.
- (36) Kireenko, M. M.; Zaitsev, K. V.; Oprunenko, Y. F.; Churakov, A. V.; Tafeenko, V. A.; Karlov, S. S.; Zaitseva, G. S. Palladium Complexes with Stabilized Germylene and Stannylene Ligands. *Dalton Trans.* **2013**, 42, 7901-7912.
- (37) Gallego, D.; Brück, A.; Irran, E.; Meier, F.; Kaupp, M.; Driess, M.; Hartwig, J. F. From Bis(silylene) and Bis(germylene) Pincer-Type Nickel(II) Complexes to Isolable Intermediates of the Nickel-Catalyzed Sonogashira Cross-Coupling Reaction. *J. Am. Chem. Soc.* **2013**, 135, 15617-15626.
- (38) Seow, C.; Xi, H.-W.; Li, Y.; So, C.-W. Synthesis of a Germylidenide Anion from the C-C Bond Activation of a Bis(germylene). *Organometallics* **2016**, 35, 1060-1063.
- (39) Bouska, M.; Dostál, L.; Lutter, M.; Glowacki, B.; Ruzickova, Z.; Beck, D.; Jambor, R.; Jurkschat, K. N-Coordinated Tin(II) Trifluoromethanesulfonates and Their Reactions with Transition Metal Carbonyls. *Inorg. Chem.* **2015**, 54, 6792-6800.
- (40) Grochala, W.; Cyranski, M. K.; Derzsi, M.; Michalowski, T.; Malinowski, P. J.; Mazej, Z.; Kurzydowski, D.; Kozminski, W.; Budzianowski, A.; Leszczynski, P. J. Crystal and Electronic Structure, Lattice Dynamics and Thermal Properties of $Ag(I)(SO_3)R$ ($R = F, CF_3$) Lewis acids in the Solid State. *Dalton Trans.* **2012**, 41, 2034-2047.
- (41) Sheldrick, G. M. SHELXL-97, Universität Göttingen, Göttingen.
- (42) For the details of DFT and NBO calculations and references, see the supporting information.

The reaction of compound **1** with $AgOTf$ and $:C[N(Me)C(Me)]_2$ in toluene afforded the bis(germyliumylidene)silver(I) complex dication in compound **3**.