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Aminotroponiminatogermaacid Halides with a Ge(E)X Moiety (E = S, Se; X = F, Cl)

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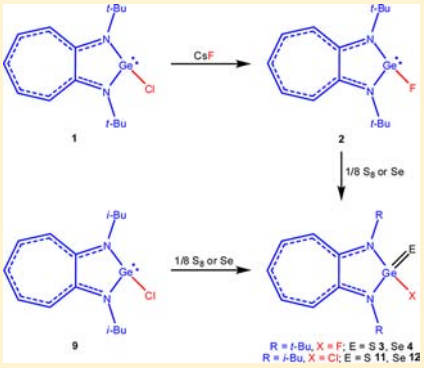
Supporting Information

ABSTRACT: Fluorination of aminotroponiminate (ATI) ligand-stabilized germylene monochloride [(*t*-Bu)$_2$ATI]GeCl (**1**) with CsF gave the aminotroponiminatogermylene monofluoride [(*t*-Bu)$_2$ATI]GeF (**2**). Oxidative addition reaction of compound **2** with elemental sulfur and selenium led to isolation of the corresponding germathioacid fluoride [(*t*-Bu)$_2$ATI]Ge(S)F (**3**) and germaselenoacid fluoride [(*t*-Bu)$_2$ATI]Ge(Se)F (**4**), respectively. Similarly, reaction of aminotroponiminatogermylene monochloride [(*i*-Bu)$_2$ATI]GeCl (**9**) with elemental sulfur and selenium gave the aminotroponiminatogermathioacid chloride [(*i*-Bu)$_2$ATI]Ge(S)Cl (**11**) and aminotroponiminatogermaselenoacid chloride [(*i*-Bu)$_2$ATI]Ge(Se)Cl (**12**), respectively. Compound **9** has been prepared through a multistep synthetic route starting from 2-(tosyloxy)tropone **5**. All compounds (**2**−**4** and **6**−**12**) were characterized through the multinuclear NMR spectroscopy, and single-crystal X-ray diffraction studies were performed on compounds **2**, **4**, and **8**−**12**. The germaselenoacid halide complexes **4** and **12** showed doublet (−142.37 ppm) and singlet (−213.13 ppm) resonances in their ^{77}Se NMR spectra, respectively. Germylene monohalide complexes **2** and **9** have a germanium center in distorted trigonal pyramidal geometry, whereas a distorted tetrahedral geometry is seen around the germanium center in germaacid halide complexes **4**, **11**, and **12**. The length of the Ge═E bond in germathioacid chloride (**11**) and germaselenoacid halide (**4** and **12**) complexes is 2.065(1) and 2.194$_{av}$ Å, respectively. Theoretical studies (based on the DFT methods) on complexes **4**, **11**, and **12** reveal the nature of the Ge═E multiple bond in these germaacid halide complexes with computed Wiberg bond indices (WBI) being 1.480, 1.508, and 1.541, respectively.



INTRODUCTION

Interest toward compounds containing low-valent germanium center(s) is growing continuously due to the breakthroughs that this area of research has seen over the past two decades.[1] A few of the recent accomplishments include the following: (a) Driess, Jones, and co-workers synthesis of a *β*-diketiminatogermanium(I) radical complex [{HC(C(*t*-Bu)NAr)$_2$}Ge]$^•$ (Ar = 2,6-*i*-Pr$_2$C$_6$H$_3$)[2a] by reducing the germylene monochloride [{HC(C(*t*-Bu)NAr)$_2$}GeCl][2b] with sodium naphthalenide, (b) reaction of a NHC-stabilized germanium dichloride tungsten pentacarbonyl complex [NHC→GeCl$_2$→W(CO)$_5$][3] with lithium borohydride carried out by Rivard and co-workers for isolation of a germamethylene tungsten pentacarbonyl complex [NHC→GeH$_2$→W(CO)$_5$] (NHC = [(HCNAr)$_2$C]),[3a] and (c) synthesis of a hypersilyl(chloro)-germylene−NHC′ complex [NHC′→Ge(Cl)Si(SiMe$_3$)$_3$] (NHC′ = [{(Me)CN(*i*-Pr)}$_2$C])[4] by Escudié and Castel's group through reaction of a NHC′−germanium dichloride complex [NHC′→GeCl$_2$][5] with Mg[Si(SiMe$_3$)$_3$]$_2$·(THF)$_2$.[6] Apart from the inherent importance of these and various other low-valent germanium compounds, most of the germanium(II) compounds can provide access to germanium(IV) compounds of significance.[1,7] Essentially, synthesis of compounds containing a double bond between the germanium and chalcogen centers utilizes this strategy.[8−10] Driess and co-workers isolated a germanone complex [L(DMAP)Ge═O] (L = [CH{(C═CH$_2$)(CMe)(NAr)$_2$}]; DMAP = 4-dimethylaminopyridine) from reaction of a germylene−dimethylaminopyridine adduct [L(DMAP)Ge] (**I**) with N$_2$O in toluene.[8a] The base-free germanone [R$_2$Ge═O] (R = 1,1,3,3,5,5,7,7-octaethyl-*s*-hydrindacen-4-yl) has been synthesized by the group of Tamao through reaction of a germylene [R$_2$Ge] (which contains very bulky aryl substituents) with Me$_3$NO.[10] Oxidative addition reaction performed by Meller's group on bis[(2-pyridyl)bis(trimethylsilyl)methyl-*C*, *N*]germanium(II) [{C$_5$H$_4$NC(SiMe$_3$)$_2$}$_2$Ge] (**II**) using sulfur at room temperature gave a germanethione complex [{C$_5$H$_4$NC(SiMe$_3$)$_2$}$_2$Ge(S)].[11] Compounds **I** and **II** contain a bidentate dianionic and two bidentate monoanionic ligands[1f,g,12] around the germanium(II) center, respectively. Instead, use of a germylene complex with a bidentate monoanionic ligand and fluoride substituent for oxidative addition reaction with a chalcogen (such as sulfur/selenium) can be visualized as a way to obtain

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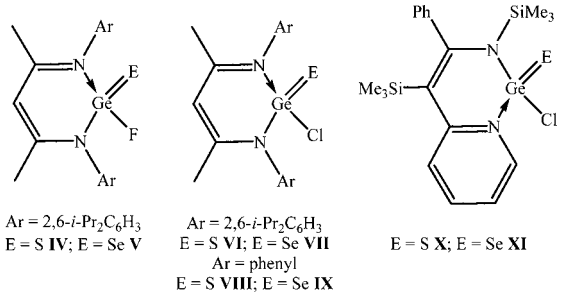
the germanium analogue of acid fluoride stabilized intramolecularly by a donor ligand system.[13] This strategy was employed by Roesky and co-workers for isolation of germathioacid and germaselenoacid fluorides (**IV** and **V**)[13] (Chart 1) through reaction of a β-diketiminatogermanium(II)

Chart 1. Structure of Compounds IV−XI



fluoride [{HC(C(Me)NAr)$_2$}GeF] (**III**)[14] with sulfur and selenium, respectively.[1f] Apart from these single examples of germathioacid and germaselenoacid fluorides, there is no further example of germathio- and germaselenoacid fluoride complexes. To address this issue, we planned to synthesize germathioacid and germaselenoacid fluorides stabilized by an aminotroponiminate (ATI) ligand[15] with the intent to diversify the chemistry of germaacid fluoride complexes. Consequently, we report the first ATI ligand-stabilized germathioacid fluoride [(*t*-Bu)$_2$ATI]Ge(S)F (**3**) and germaselenoacid fluoride [(*t*-Bu)$_2$ATI]Ge(Se)F (**4**). The germylene monofluoride complex [(*t*-Bu)$_2$ATI]GeF (**2**), required as a precursor for the synthesis of these compounds (**3** and **4**), has been obtained through an interesting and hitherto unknown synthetic route (for low-valent group 14 chemistry) that uses an aminotroponiminatogermylene monochloride [(*t*-Bu)$_2$ATI]GeCl (**1**)[16] and cesium fluoride.

In view of the limited examples of known germaacid chloride complexes **VI**−**XI**[1f,13,17] (Chart 1), we report the first ATI ligand-stabilized germathioacid chloride [(*i*-Bu)$_2$ATI]Ge(S)Cl (**11**) and germaselenoacid chloride [(*i*-Bu)$_2$ATI]Ge(Se)Cl (**12**). Complexes **11** and **12** were obtained using a novel aminotroponiminatogermylene monochloride [(*i*-Bu)$_2$ATI]-GeCl (**9**) with *i*-butyl substituents on the nitrogen atoms. Therefore, its isolation through a multistep synthetic route from 2-(tosyloxy)tropone **5**[18] is reported.

EXPERIMENTAL SECTION

All experiments and manipulations were performed under an atmosphere of dry N_2 using either standard Schlenk or glovebox [GP(Concept)-T2, Jacomex] techniques. Dry solvents were either prepared using conventional procedures or purchased directly from Aldrich. [(*t*-Bu)$_2$ATI]GeCl (**1**)[16] and 2-(tosyloxy)tropone **5**[18] were prepared according to literature procedures. *i*-Butylamine, $Et_3O{\cdot}BF_4$, *n*-BuLi (1.6 M solution in hexane), $GeCl_2{\cdot}$(1,4-dioxane), sulfur, and selenium were purchased from Aldrich and used without any further purification. Cesium fluoride purchased from Acros Organics was dried prior to use by heating it at 150 °C for 4 h under vacuum. Melting points of the solid samples were recorded (by sealing the samples in glass capillary tubes) using an Ambassador melting point apparatus and are uncorrected. Elemental analyses were carried out using a Perkin-Elmer CHN analyzer. IR spectroscopic studies were performed through a Thermo-Nicolet Protege-460 FT-IR spectrometer as KBr pellets. ^{1}H, ^{13}C, ^{19}F, and ^{77}Se NMR spectra were recorded on a 300 MHz Bruker Topspin/400 MHz JEOL JNM-ECA NMR spectrometer using either dry $CDCl_3$ or C_6D_6. Chemical shifts δ are reported in ppm and referenced either internally to residual solvent (^{1}H NMR) and solvent (^{13}C NMR) resonances[19] or externally to suitable standards [^{19}F NMR ($CFCl_3$) and ^{77}Se NMR (Me_2Se)]. Mass spectroscopic studies were carried out using a Bruker ESI-MS system (micrOTOF-Q II).

Synthesis of [(*t*-Bu)$_2$ATI]GeF (2). To a mixture of compound **1** (1.00 g, 2.95 mmol) and cesium fluoride (3.58 g, 23.57 mmol), THF (25 mL) was added and stirred at room temperature for 3 days. All volatiles were then removed under reduced pressure to yield an orange solid. It was extracted using toluene (40 mL) and filtered through a G4 frit. Removal of the solvent from the filtrate in vacuo afforded compound **2** as an orange solid. Single crystals of compound **2** suitable for X-ray diffraction studies were grown from its toluene solution at −40 °C. Yield: 0.78 g, 82%. Mp: 112 °C. Anal. Calcd for $C_{15}H_{23}FGeN_2$ (M = 322.99): C, 55.78; H, 7.18; N, 8.67. Found: C, 55.71; H, 7.24; N, 8.58. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.72 (s, 18H, C(C*H*$_3$)$_3$), 6.59 (t, $^3J_{HH}$ = 8.7 Hz, 1H, C*H*), 7.03 (d, $^3J_{HH}$ = 11.1 Hz, 2H, C*H*), 7.13−7.20 (m, 2H, C*H*). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 31.05 (C(*C*H$_3$)$_3$), 56.52 (*C*(CH$_3$)$_3$), 117.83 (C_4), 121.40 ($C_{2,6}$), 134.65 ($C_{3,5}$), 159.76 ($C_{1,7}$). ^{19}F{^{1}H} NMR (282 MHz, $CDCl_3$): δ −101.37.

Synthesis of [(*t*-Bu)$_2$ATI]Ge(S)F (3). A solution of compound **2** (0.20 g, 0.62 mmol) in THF (10 mL) was transferred to a solution of elemental sulfur (0.02 g, 0.62 mmol) in THF (5 mL) at 0 °C. Then the reaction mixture was stirred for 4 h at room temperature, and all volatiles were removed under reduced pressure to get a yellow solid. It was washed with hexane (10 mL) and dried in vacuo to result in an analytically pure sample of compound **3** as a yellow solid. Yield: 0.19 g, 86%. Mp: 169 °C. Anal. Calcd for $C_{15}H_{23}FGeN_2S$ (M = 355.06): C, 50.74; H, 6.53; N, 7.89. Found: C, 50.66; H, 7.01; N, 7.86. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.86 (s, 18H, C(C*H*$_3$)$_3$), 6.98−7.03 (m, 1H, C*H*), 7.39−7.50 (m, 4H, C*H*). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 30.04 (C(*C*H$_3$)$_3$), 58.22 (*C*(CH$_3$)$_3$), 120.12 (C_4), 126.64 ($C_{2,6}$), 137.41 ($C_{3,5}$), 156.42 ($C_{1,7}$). ^{19}F{^{1}H} NMR (282 MHz, $CDCl_3$): δ −91.37.

Synthesis of [(*t*-Bu)$_2$ATI]Ge(Se)F (4). A 100 mL Schlenk flask was charged with compound **2** (0.20 g, 0.62 mmol), elemental selenium (0.05 g, 0.62 mmol), and THF (15 mL). This mixture was stirred at 40 °C for 24 h and filtered through a G4 frit, and the solvent from the filtrate was removed under reduced pressure to get a solid residue. It was washed with toluene (10 mL) and dried in vacuo to afford compound **4** as a yellow solid. Single crystals of compound **4** suitable for X-ray diffraction studies were grown by cooling its THF solution at −40 °C. Yield: 0.17 g, 68%. Mp: 176 °C. Anal. Calcd for $C_{15}H_{23}FGeN_2Se$ (M = 401.95): C, 44.82; H, 5.77; N, 6.97. Found: C, 44.91; H, 5.62; N, 7.04. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.87 (s, 18H, C(C*H*$_3$)$_3$), 6.97−7.02 (m, 1H, C*H*), 7.37−7.52 (m, 4H, C*H*). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 30.29 (C(*C*H$_3$)$_3$), 58.37 (*C*(CH$_3$)$_3$), 120.34 (C_4), 126.82 ($C_{2,6}$), 137.19 ($C_{3,5}$), 156.20 ($C_{1,7}$). ^{19}F{^{1}H} NMR (282 MHz, $CDCl_3$): δ −86.20. ^{77}Se{^{1}H} (57 MHz, $CDCl_3$): δ −142.37 (d, $^2J_{SeF}$ = 91.0 Hz).

Synthesis of [(*i*-Bu)$_2$ATI]GeCl (9). A solution of compound **8** (1.00 g, 2.61 mmol) was prepared in THF (35 mL) and transferred to a suspension of $GeCl_2{\cdot}$(1,4-dioxane) (0.61 g, 2.61 mmol) in THF (20 mL) at −78 °C. The reaction mixture was brought to room temperature and stirred overnight. All volatiles were then removed under reduced pressure to yield an orange solid, extracted with toluene (20 mL), and filtered through a G4 frit. Removal of toluene from the filtrate yielded compound **9** as an orange solid. Single crystals of compound **9** suitable for X-ray diffraction analysis were grown in toluene at −40 °C. Yield: 0.82 g, 92%. Mp: 104 °C. Anal. Calcd for $C_{15}H_{23}ClGeN_2$ (M = 339.45): C, 53.07; H, 6.83; N, 8.25. Found: C, 52.97; H, 6.88; N, 8.32. ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.98 (d, $^3J_{HH}$ = 6.0 Hz, 12H, CH(C*H*$_3$)$_2$), 2.15−2.24 (m, 2H, C*H*(CH$_3$)$_2$), 3.49 (d, $^3J_{HH}$ = 7.2 Hz, 4H, C*H*$_2$), 6.70 (t, $^3J_{HH}$ = 9.3 Hz, 1H, C*H*), 6.81 (d, $^3J_{HH}$ = 11.1 Hz, 2H, C*H*), 7.19−7.28 (m, 2H, C*H*). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 21.13 (CH(*C*H$_3$)$_2$), 27.95 (*C*H(CH$_3$)$_2$), 53.93 (*C*H$_2$), 116.17 (C_4), 123.48 ($C_{2,6}$), 136.76 ($C_{3,5}$), 161.08 ($C_{1,7}$).

Synthesis of [(*i*-Bu)$_2$ATI]GeF (10). To a mixture of compound **9** (1.50 g, 4.42 mmol) and cesium fluoride (5.37 g, 35.35 mmol), THF (30 mL) was added and stirred at room temperature for 3 days. All

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volatiles were then removed under reduced pressure to yield an orange solid. It was extracted using toluene (50 mL) and filtered through a G4 frit. Removal of solvent from the filtrate in vacuo yielded compound **10** as an orange solid. Single crystals of compound **10** suitable for X-ray diffraction studies were grown from its toluene solution at −40 °C. Yield: 1.10 g, 77%. Mp: 68 °C. Anal. Calcd for $C_{15}H_{23}FGeN_2$ (M = 322.99): C, 55.78; H, 7.18; N, 8.67. Found: C, 55.86; H, 7.13; N, 8.54. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.02 (d, $^3J_{HH}$ = 6.4 Hz, 6H, $CH(CH_3)_2$), 1.04 (d, $^3J_{HH}$ = 6.9 Hz, 6H, $CH(CH_3)_2$), 2.18−2.27 (m, 2H, $CH(CH_3)_2$), 3.55 (d, $^3J_{HH}$ = 7.3 Hz, 4H, CH_2), 6.67 (t, $^3J_{HH}$ = 9.1 Hz, 1H, CH), 6.78 (d, $^3J_{HH}$ = 11.0 Hz, 2H, CH), 7.23−7.29 (m, 2H, CH). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 21.23 ($CH(CH_3)_2$), 21.36 ($CH(CH_3)_2$), 28.01 ($CH(CH_3)_2$), 54.20 (CH_2), 114.75 (C_4), 122.32 ($C_{2,6}$), 136.42 ($C_{3,5}$), 160.97 ($C_{1,7}$). $^{19}F\{^1H\}$ NMR (282 MHz, $CDCl_3$): δ −98.91.

Synthesis of [(*i*-Bu)$_2$ATI]Ge(S)Cl (11). A solution of compound **9** (2.00 g, 5.89 mmol) in THF (40 mL) was transferred to a solution of elemental sulfur (0.19 g, 5.89 mmol) in THF (30 mL) at room temperature. The reaction mixture was stirred for 12 h, and solvent was removed under reduced pressure to get a yellow solid. It was washed with toluene (15 mL) and dried in vacuo to afford compound **11** as a yellow solid. Single crystals of compound **11** suitable for X-ray diffraction studies were grown from its acetonitrile solution containing a few drops of toluene at −40 °C. Yield: 2.01 g, 92%. Mp: 123 °C. Anal. Calcd for $C_{15}H_{23}ClGeN_2S$ (M = 371.51): C, 48.49; H, 6.24; N, 7.54. Found: C, 48.59; H, 6.31; N, 7.66. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.06 (d, $^3J_{HH}$ = 6.3 Hz, 12H, $CH(CH_3)_2$), 2.34−2.47 (m, 2H, $CH(CH_3)_2$), 3.60 (dd, $^3J_{HH}$ = 14.1, 8.1 Hz, 2H, CH_2), 3.78 (dd, $^3J_{HH}$ = 14.1, 6.9 Hz, 2H, CH_2), 7.07 (t, $^3J_{HH}$ = 9.3 Hz, 1H, CH), 7.16 (d, $^3J_{HH}$ = 11.1 Hz, 2H, CH), 7.56 (t, $^3J_{HH}$ = 10.2 Hz, 2H, CH). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 21.03 ($CH(CH_3)_2$), 28.11 ($CH(CH_3)_2$), 53.47 (CH_2), 117.70 (C_4), 127.20 ($C_{2,6}$), 139.12 ($C_{3,5}$), 156.75 ($C_{1,7}$).

Synthesis of [(*i*-Bu)$_2$ATI]Ge(Se)Cl (12). A solution of compound **9** (0.30 g, 0.88 mmol) was prepared in toluene (30 mL), and selenium powder (0.10 g, 1.33 mmol) was added to it at room temperature. This mixture was allowed to stir for 2 days at 50 °C. It was then filtered through a G4 frit, and the filtrate was reduced to 10 mL. Storage of this solution at −40 °C for 24 h afforded a yellow precipitate. It was dried in vacuo to afford compound **12** as a yellow solid. Single crystals of compound **12** suitable for X-ray diffraction studies were grown from its THF solution at −40 °C. Yield: 0.20 g, 54%. Mp: 129 °C. Anal. Calcd for $C_{15}H_{23}ClGeN_2Se$ (M = 418.41): C, 43.06; H, 5.54; N, 6.70. Found: C, 43.16; H, 5.43; N, 6.89. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.05 (d, $^3J_{HH}$ = 2.7 Hz, 6H, $CH(CH_3)_2$), 1.08 (d, $^3J_{HH}$ = 3.0 Hz, 6H, $CH(CH_3)_2$), 2.38−2.50 (m, 2H, $CH(CH_3)_2$), 3.60 (dd, $^3J_{HH}$ = 14.1, 8.1 Hz, 2H, CH_2), 3.81 (dd, $^3J_{HH}$ = 14.1, 6.9 Hz, 2H, CH_2) 7.05 (t, $^3J_{HH}$ = 9.6 Hz, 1H, CH), 7.16 (d, $^3J_{HH}$ = 11.1 Hz, 2H, CH), 7.51−7.58 (m, 2H, CH). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 20.92 ($CH(CH_3)_2$), 21.11 ($CH(CH_3)_2$), 28.03 ($CH(CH_3)_2$), 53.31 (CH_2), 117.57 (C_4), 127.27 ($C_{2,6}$), 139.15 ($C_{3,5}$), 156.84 ($C_{1,7}$). $^{77}Se\{^1H\}$ (57 MHz, $CDCl_3$): δ −213.31.

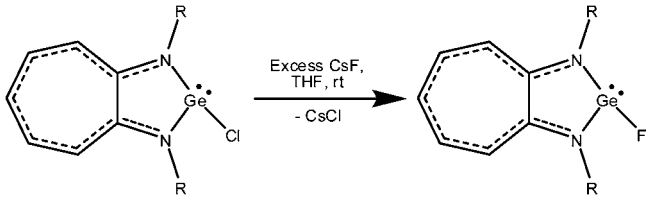
X-ray Structure Determination of Compounds 2, 4, and 8−12. X-ray data of compounds **2**, **4**, and **8−12** (Table S1; see Supporting Information) were collected through a Bruker SMART APEX diffractometer equipped with a 3-axis goniometer.[20] Crystals were covered with a cryoprotectant and mounted on a glass fiber. Data were collected either at room temperature or under a steady flow of cold dinitrogen. Integration of the data was carried out using SAINT, and an empirical absorption correction was applied using SADABS.[21] Structures were solved by direct methods and refined by full matrix least-squares on F^2 using SHELXTL software.[22] All non-hydrogen atoms were refined anisotropically, whereas the positions of the hydrogen atoms were fixed according to a riding model and isotropically refined.

Computational Details. All calculations were carried out using GAUSSIAN-03 programs.[23] The geometry of compounds **4**, **11**, and **12** was optimized at the B3LYP level of theory[24] using a LANL2DZ basis set[25] for germanium and chalcogens (S or Se) and 6-31+G** basis set[26,27] for the rest of the elements. Geometry optimizations were carried out using the coordinates obtained from single-crystal X-ray diffraction studies without any symmetry restriction. The harmonic force constants were computed at the optimized geometries to characterize the stationary points as minima. Weinhold's natural bond orbital (NBO) analysis[28,29] was performed at the aforementioned level of theory, and this approach was used to calculate the natural population analysis (NPA) charges, orbital populations, and other bonding analyses. NBO orbital plots were made using the Chemcraft software (http://www.chemcraftprog.com). Energy decomposition analysis (EDA) was performed at the B3LYP/6-31G*/LANL2DZ level of theory using AOMix software.[30]

RESULTS AND DISSCUSSION

Synthesis and Spectra. In order to synthesize aminotroponiminatogermylene monofluoride **2**, reaction of germylene monochloride complex **1** was carried out with cesium fluoride in THF at room temperature for 3 days. Compound **2** was obtained as an orange solid in 82% yield (Scheme 1).

Scheme 1. Synthesis of Germylene Monofluoride Complexes 2 and 10



Interestingly, cesium fluoride has been used as a fluorinating agent for the first time to prepare a group 14 metallylene monofluoride complex. Germylene monofluoride complexes [{HC(C(Me)NAr)$_2$}GeF] (**III**) (Ar = 2,6-*i*-Pr$_2$C$_6$H$_3$) and [{HC(C(Me)NAr′)$_2$}GeF] (**XII**) (Ar′ = 2,6-Me$_2$C$_6$H$_3$)[14] reported by Roesky and co-workers were obtained by fluorination of [{HC(C(Me)NAr)$_2$}GeCl][31] and [{HC(C(Me)NAr′)$_2$}GeCl][14] using Me$_3$SnF, respectively. Fluorinating agents used for preparation of other group 14 metallylene fluoride complexes such as the silylene, stannylene, and plumbylene monofluorides are summarized in Table 1.

Table 1 clearly reveals the unknown use of CsF in low-valent group 14 chemistry as a fluorinating agent. Compound **2** is soluble in common organic solvents such as hexane, toluene, diethyl ether, tetrahydrofuran, and chloroform. For preparation of the first ATI ligand-stabilized germathioacid fluoride **3** and germaselenoacid fluoride **4**, compound **2** was reacted with elemental sulfur and selenium, respectively. Thus, a stoichiometric reaction of compound **2** with elemental sulfur in THF afforded the desired germathioacid fluoride complex **3** as a yellow solid in 86% yield (Scheme 2). Similarly, reaction of elemental selenium with compound **2** gave germaselenoacid fluoride complex **4** as a yellow solid in a yield of 68% (Scheme 2). Compounds **3** and **4** are soluble in polar organic solvents such as THF, chloroform, dichloromethane, etc. and are sparingly soluble in the solvents like benzene and toluene. Compounds **2−4** are stable at room temperature in an inert atmosphere.

To synthesize germaacid chloride complexes we used aminotroponiminatogermylene monochloride **9** with *i*-butyl substituents on the nitrogen atoms as the precursor. Compound **9** was synthesized from 2-(tosyloxy)tropone **5** (see Supporting Information) by means of a slightly modified multistep synthetic route used for synthesis of compound **1**

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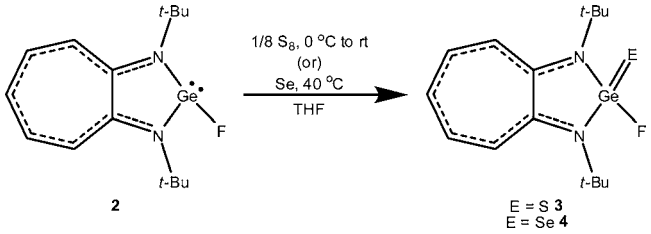
Table 1. Fluorinating Agents Used for Synthesis of Group 14 Metallylene Fluoride Complexes[a]

S. no.	metallylene fluoride	fluorinating agent	ref
1	$[\{HC(C(Me)NAr')_2\}GeF]$ (**XII**)	Me_3SnF	14
2	$[\{HC(C(Me)NAr)_2\}GeF]$ (**III**)	Me_3SnF	14
3	$L(F)Si{\rightarrow}M(CO)_5$	Me_3SnF	32
4	$[\{HC(C(Me)NAr)_2\}SnF]$	Me_3SnF	33
5	4-*t*-Bu-2,6-$[P(O)(Oi\text{-}Pr)_2]_2C_6H_2Sn(F)W(CO)_5$	KF	34
6	$[\{HC(C(Me)NAr)_2\}PbF]$	C_5F_5N	35
7	$L(F)Si{\rightarrow}BH_3$	$[\{HC(C(Me)NAr)_2\}PbF]$	35
8	$[(t\text{-}Bu)_2ATI]GeF$ (**2**)	CsF	This work
9	$[(i\text{-}Bu)_2ATI]GeF$ (**10**)	CsF	This work

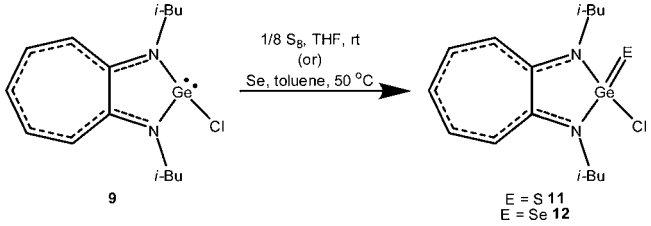
[a]M = Cr, Mo, W; L = $PhC(Nt\text{-}Bu)_2$.

Scheme 2. Synthesis of ATI Ligand-Stabilized Germathioacid and Germaselenoacid Fluorides (3 and 4)



(Scheme S1, see Supporting Information). Oxidative addition reaction of compound **9** with elemental sulfur at room temperature gave germathioacid chloride complex **11** with a yield of 92% (Scheme 3). Reaction of compound **9** with

Scheme 3. Synthesis of Germaacid Chloride Complexes 11 and 12



elemental selenium at 50 °C afforded germaselenoacid chloride complex **12** as a yellow powder in 54% yield (Scheme 3). Compounds **11** and **12** are freely soluble in polar organic solvents such as THF, chloroform, and dichloromethane.

Interestingly, our efforts to isolate germathioacid and germaselenoacid fluorides stabilized by the ATI ligand with *i*-butyl substituents on its nitrogen atoms did not work. Thus, reaction of compound **9** with cesium fluoride gave germylene monofluoride complex **10** (Scheme 1), but oxidative addition reaction of compound **10** with elemental sulfur and selenium gave only a mixture of unidentified products. Proton-decoupled ^{19}F NMR spectra of the crude products obtained from reaction of compound **10** with sulfur and selenium contained three and four resonances (against the anticipation of a single resonance), respectively. Complete consumption of compound **10** in these reactions was noticed through the absence of the singlet resonance corresponding to it in the aforementioned ^{19}F NMR spectra. Our efforts to separate different compounds in the crude products and optimize the reactions for exclusive formation of the desired products through varied reaction conditions were not successful until now.

All compounds (**2**–**4** and **6**–**12**) were characterized by various spectroscopic techniques. The ^1H NMR spectrum of compound **2** in $CDCl_3$ shows a sharp singlet at 1.72 ppm for the *tert*-butyl groups, and this trend is seen in the ^1H NMR spectra of compounds **3** and **4** also. This shows the chemically equivalent nature of the *tert*-butyl groups in solution; nevertheless, the *tert*-butyl resonances of compounds **3** (1.86 ppm) and **4** (1.87 ppm) are slightly downfield shifted with respect to that of compound **2**. In the ^1H NMR spectrum of compound **9** (in $CDCl_3$) the methyl, methine, and methylene protons of the *i*-butyl substituents appear as a doublet (0.98 ppm), multiplet (2.15–2.24 ppm), and doublet (3.49 ppm), respectively. This resonance pattern for the *i*-butyl substituents is not retained in the ^1H NMR spectra of compound **10** due to the appearance of two doublets for its methyl protons. The methyl groups of the *i*-butyl substituents in compounds **11** and **12** appear as one (1.06 ppm) and two doublets (1.05 and 1.08 ppm), respectively. The methine and methylene groups of the *i*-butyl substituents in the aforementioned compounds resonate as one multiplet (2.34–2.47 **11** and 2.38–2.50 ppm **12**) and two double doublets (3.60, 3.78 **11** and 3.60, 3.81 ppm **12**), respectively. These characteristic patterns reveal the nonequivalence of the *i*-butyl substituents in compounds **11** and **12**. In the ^{13}C NMR spectrum of compound **2**, the carbon atoms of the *tert*-butyl groups appear as two singlets (31.05 and 56.52 ppm), and this pattern is retained in the ^{13}C NMR spectra of compounds **3** and **4** also. In the ^{13}C NMR spectrum of compounds **9** and **11** the methyl, methine, and methylene carbons resonate as three singlets, whereas in compounds **10** and **12** the same carbon atoms resonate as four singlets due to the nonequivalent methyl groups. In the ^{19}F NMR spectra of germylene monofluoride complexes **2** and **10**, a singlet resonance at −101.37 and −98.91 ppm can be seen as anticipated, respectively. The ^{19}F NMR resonances of germathioacid fluoride **3** (−91.37 ppm) and germaselenoacid fluoride **4** (−86.20 ppm) complexes are downfield shifted in comparison to that observed for compound **2**. The magnitude of the shift in compounds **3** and **4** (with respect to compound **2**) is large in comparison to the shift observed by Roesky and co-workers in derivatives **IV** and **V** (with respect to compound **III**) (Table S2; see Supporting Information). The ^{77}Se NMR spectrum of compound **4** shows a doublet at −142.37 ppm due to the germinal coupling of selenium with fluorine. This value is largely downfield shifted in comparison to that found for the germaselenoacid fluoride complex **V** (−465.10 ppm). The selenium center in compound **12** resonates at −213.13 ppm and this value is slightly downfield shifted in comparison to those found for compounds **VII** and **XI** (Table S2; see Supporting Information). The aforementioned selenium

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resonances (−142.37 and −213.13 ppm for compounds **4** and **12**, respectively) lie in between the resonances seen in compounds $(H_3Ge)_2Se$ (−612 ppm)[36] and (Tbt)(Tip)Ge═Se (940 ppm)[9b] with the Ge−Se single and electronically unperturbed Ge═Se double bonds, respectively (Tbt = 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl; Tip = 2,4,6-tris-(isopropyl)phenyl).

X-ray Crystal Structure of Compounds 2, 4, and 8−12. Structures of compounds **2**, **4**, and **8−12** were further confirmed by single-crystal X-ray diffraction studies. Single crystals of these compounds were grown by cooling their concentrated solutions in a low-temperature refrigerator maintained at −40 °C. Important structural parameters for these compounds are summarized in Table S1 (see Supporting Information).

The germylene monohalide complexes **2**, **9**, and **10** crystallized in the orthorhombic, monoclinic, and orthorhombic space groups $P2_12_12_1$, $P2_1/c$, and *Pbca*, respectively. The molecular structure of these compounds [**2** and **9** (Figures 1 and 2), **10** (Figure S1; see Supporting Information)] reveals their monomeric nature. The germanium center in compounds **2**, **9**, and **10** adopts a distorted trigonal-pyramidal geometry [with two nitrogen and one halogen (F **2** and **10**, Cl **9**) atoms in the coordination sphere], and the sum of the bond angles around the germanium center is 270.9, 274.72, and 270.6°, respectively. These features point to the presence of a stereochemically active lone pair of electrons on the germanium center in these compounds.

Germaselenoacid fluoride **4** and germaselenoacid chloride **12** complexes crystallized in the tetragonal and orthorhombic space groups $P4_32_12$ and *Pbca*, respectively. The molecular structure of these compounds [Figures 3 and S2 (see Supporting Information)] reveals the presence of a tetracoordinate germanium center with a distorted tetrahedral environment of two nitrogen, one halogen (F **4**, Cl **12**), and one selenium atoms.

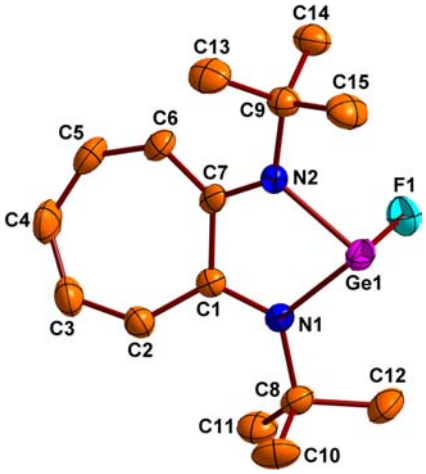

Figure 1. Molecular structure of aminotroponiminatogermylene monofluoride **2**. All hydrogen atoms are omitted for clarity, and thermal ellipsoids are drawn at the 40% probability level. Selected bond lengths (Angstroms) and angles (degrees): Ge(1)−F(1) 1.835(2), Ge(1)−N(1) 1.986(3), Ge(1)−N(2) 1.973(3); N(1)−Ge(1)−F(1) 94.9(1), N(2)−Ge(1)−F(1) 94.7(1), N(2)−Ge(1)−N(1) 81.3(1), C(1)−N(1)−Ge(1) 114.3(2), C(7)−N(2)−Ge(1) 113.8(2).

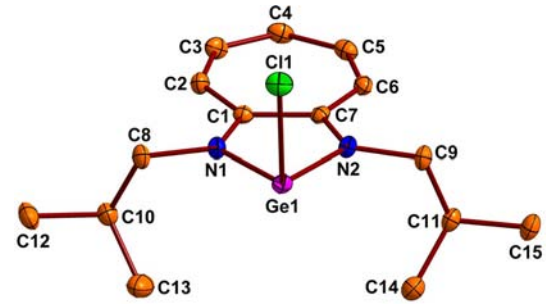

Figure 2. Molecular structure of aminotroponiminatogermylene monochloride **9**. All hydrogen atoms are omitted for clarity, and thermal ellipsoids are drawn at the 40% probability level. Selected bond lengths (Angstroms) and angles (degrees): Ge(1)−Cl(1) 2.3598(5), Ge(1)−N(1) 1.933(1), Ge(1)−N(2) 1.943(1); N(1)−Ge(1)−Cl(1) 96.71(4), N(2)−Ge(1)−Cl(1) 97.97(4), N(1)−Ge(1)−N(2) 80.04(6), C(1)−N(1)−Ge(1) 117.7(1), C(7)−N(2)−Ge(1) 117.4(1).

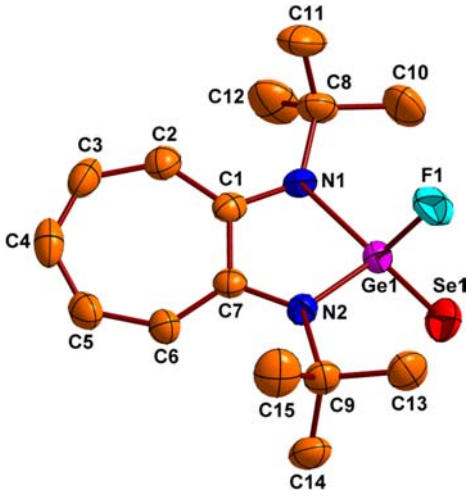

Figure 3. Molecular structure of aminotroponiminatogermaselenoacid fluoride **4**. All hydrogen atoms are omitted for clarity, and thermal ellipsoids are drawn at the 40% probability level. Selected bond lengths (Angstroms) and angles (degrees): Ge(1)−Se(1) 2.198(1), Ge(1)−F(1) 1.763(4), Ge(1)−N(1) 1.888(5), Ge(1)−N(2) 1.879(5); N(1)−Ge(1)−Se(1) 123.8(2), N(2)−Ge(1)−Se(1) 120.0(2), N(1)−Ge(1)−F(1) 100.9(2), N(2)−Ge(1)−F(1) 104.2(2), N(1)−Ge(1)−N(2) 86.7(2), Se(1)−Ge(1)−F(1) 116.1(2).

The Ge═Se bond [2.198(1) Å **4**; 2.190(1) Å **12**] is appreciably shorter than the Ge−Se single bond [2.433(1) Å] found in $[Tbt(Mes)GeSe]_2$ (Mes = 2,4,6-trimethylphenyl)[9b] and slightly longer than the electronically unperturbed Ge═Se double bond [2.180(2) Å] seen in the kinetically stabilized germaselenone (Tbt)(Tip)Ge═Se.[9b] On the basis of these facts, it can be mentioned that the nature of bonding between the germanium and selenium atoms in compounds **4** and **12** is essentially a double bond with partial ionic character. The Ge−X bond in these compounds [1.763(4) Å **4** (X = F); 2.178(2) Å **12** (X = Cl)] is considerably shorter than the corresponding bond length observed in their starting materials [1.835(2) Å **2**; 2.3598(5) Å **9**]. This is anticipated in view of the increased formal oxidation state of the germanium center from +2 (in compounds **2** and **9**) to +4 (in compounds **4** and **12**) upon oxidation. The average N−Ge−X bond angle in compounds **4** (102.55°) and **12** (103.9°) is larger than the same bond angle seen in compounds **2** (94.8°) and **9** (97.34°), respectively. The

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average N−Ge−Se bond angle in compounds **4** and **12** is 121.9° and 123.1°, respectively.

The germathioacid chloride complex **11** crystallized in an orthorhombic space group *Pbca*. The germanium center is tetracoordinate and adopts a distorted tetrahedral geometry with two nitrogen, one sulfur, and one chlorine atoms in its coordination sphere (Figure 4). The Ge═S bond [2.065(1) Å] is slightly longer than the electronically unperturbed Ge═S bond [2.049(3) Å] observed in Tbt(Tip)Ge═S.[9b] Nevertheless, it is considerably shorter than the Ge−S single bond present in [{(TMS)$_2$C(2-Py)}{(TMS)C(2-Py)}]GeS(TMS) by a margin of 0.174 Å (Py = pyridyl).[11] These arguments are suggestive of a partial ionic character in the Ge═S double bond in compound **11**. In accordance with a formal +4 oxidation state of the germanium center in compound **11**, the Ge−Cl [2.1893(9) Å] and average Ge−N (1.879 Å) bond lengths are shorter than those found in germanium(II) monochloride complex **9** [2.3598(5) and 1.938 Å, respectively]. The average N−Ge−Cl and N−Ge−S bond angles are 103.74° and 123.04°, respectively.

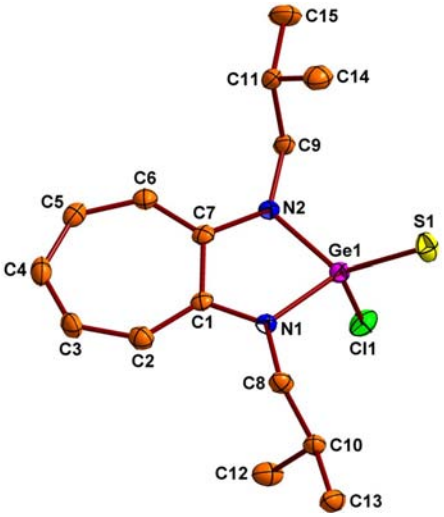

Figure 4. Molecular structure of aminotroponiminatogermathioacid chloride **11**. All hydrogen atoms are omitted for clarity, and thermal ellipsoids are drawn at the 40% probability level. Selected bond lengths (Angstroms) and angles (degrees): Ge(1)−S(1) 2.065(1), Ge(1)−Cl(1) 2.1893(9), Ge(1)−N(1) 1.881(2), Ge(1)−N(2) 1.877(2); N(1)−Ge(1)−S(1) 120.19(8), N(2)−Ge(1)−S(1) 125.90(8), N(1)−Ge(1)−Cl(1) 106.74(8), N(2)−Ge(1)−Cl(1) 100.73(8), N(1)−Ge(1)−N(2) 84.8(1), S(1)−Ge(1)−Cl(1) 113.75(4).

To illustrate the nature of the C_7 seven-membered and C_2N_2X (X = Ge **2**, **4**, **9**−**12**; X = Li **8**) five-membered rings in compounds **2**, **4**, and **8**−**12**, the side view of these molecules through the C1−C7 bond axis (along with the dihedral angle information) is shown in Figure S4 (see Supporting Information). A general feature that can be seen in these molecules is the high and low degree of ring puckering in the presence of the bulky *tert*-butyl (as in compounds **2** and **4**) and less bulky *i*-butyl (as in compounds **9** to **12**) substituents on the nitrogen atoms of the ATI ligand backbone, respectively. The dihedral angle of 21.14(8)° between the seven- and five-membered rings present in the germylene monofluoride complex **2** is the highest that has been seen to date in the ATI ligand-stabilized compounds with a low-valent germanium center; nevertheless, its *i*-butyl analogue **10** is nearly planar [with a dihedral angle of 3.87(1)°]. The latter situation also prevails in the germylene monochloride complex **9** as the dihedral angle between its ring systems is 2.09(4)° only. The scenario with respect to the five- and seven-membered rings in compounds **11** and **12** is quite unique in the sense that except the germanium atom all other ring atoms lie almost in the same plane, and this is evocative of an envelope conformation.

Theoretical Studies on Compounds 4, 11, and 12. Theoretical studies were carried out with an objective to identify the nature of the Ge═E (E = S or Se) bond present in compounds **4**, **11**, and **12**. The effect of the halogen atom on the aforementioned bond has also been looked upon. All calculated bond lengths and angles for compounds **4**, **11**, and **12** are in good agreement with the experimental data obtained from single-crystal X-ray diffraction studies (vide supra). Weinhold's NBO analysis indicates a strong germanium- and chalcogen-bonding interaction in compounds **4**, **11**, and **12**. In compound **4**, NBO analysis reveals that the Ge−Se σ interaction is formed by the overlap of the $sp^{0.45}$-hybridized orbital of germanium and $sp^{7.88}$-hybridized orbital of selenium (see Figure 5a). This σ interaction is found to be significantly covalent in character (the natural bond ionicity i_{Ge-Se} is computed to be −0.08)[37] with 46% donation from germanium and 54% from selenium. Besides, the NBO second-order perturbation theory analysis reveals important clues regarding the π-bonding and antibonding characters present in the Ge═Se bond. The Ge(p_x)−Se(p_x) orbitals overlap laterally to form a π-bond that is perpendicular to the Ge−F bond and is stabilized by 29.8 kcal/mol (Figure 5b). Further, a significant donor−acceptor (Se→Ge) π-antibonding interaction formed by the lateral overlap of Ge(p_y)−Se(p_y) (35 kcal/mol; along Ge−F bond) (Figure 5c) perpendicular to the aforementioned π bond has been detected. In this interaction, a fluorine p orbital also tends to participate and accounts for a partial π

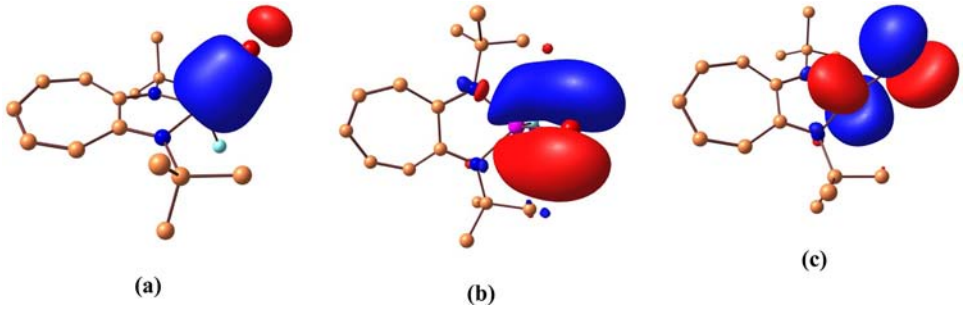

Figure 5. NBO orbitals of compound **4** showing (a) Ge−Se σ, (b) Ge−Se π, and (c) Ge−Se π^* interactions. Hydrogen atoms are omitted for clarity.

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character in the Ge═Se bond. Since this donor−acceptor interaction is antibonding in character, the net π bonding present in the Ge═Se bond is thus expected to be reduced. It is to be noted here that the HOMO and HOMO−1 (9.1 kJ/mol lower in energy from HOMO) orbitals of **4** are found to be the π-bonding and π-antibonding orbitals of the Ge═Se bond described in Figure 5b and 5c, respectively.

The Ge−S σ bond in compound **11** is a result of the overlap between the $sp^{1.99}$- and $sp^{4.14}$-hybridized orbitals on germanium and sulfur, respectively. The contributions from the germanium and sulfur atoms are 39% and 61%, respectively, and the computed bond ionicity i_{Ge-S} is −0.2. Therefore, the Ge−S bond is significantly more ionic in nature compared to the Ge−Se bond in compound **4**. The Ge(p_x)−S(p_x) π-bonding interaction is stabilized only by 14.2 kcal/mol, and this value is smaller in comparison to that seen in compound **4** (vide supra). Nevertheless, the perpendicular antibonding π interaction present in the Ge═S bond is significantly weaker and suggests a net stronger π interaction with an additional π-type interaction between the germanium and chlorine atoms. In compound **12**, the Ge−Se σ bond is formed by the overlap of the $sp^{1.25}$-hybridized orbital of germanium and the $sp^{7.96}$-hybridized orbital of selenium. NBO analysis reveals that this bond is only slightly perturbed due to halogen exchange (bond ionicity i_{Ge-Se} is −0.12 with 44% donation from germanium and 56% from selenium) and is comparable to the situation (vide supra) that prevails in compound **4**. However, the other features (such as the weak π-antibonding interaction in the Ge═Se bond and π-type interaction between chlorine and germanium centers) are similar to that present in compound **11** and lead to a stronger π interaction. To gain further insight, the Wiberg bond index (WBI) for the Ge═E bond in compounds **4** (1.480), **11** (1.508), and **12** (1.541) has been computed. The WBI for the Ge−F bond in compound **4** is 0.439, while the same for the Ge−Cl bond in compounds **11** and **12** is 0.691 and 0.687, respectively. The π-bonding character of chlorine essentially enhances the WBI index and strengthens the Ge═Se bond in compounds **11** and **12** (Figure S5; see Supporting Information). For comparison, the WBI for the Ge═E bond in H_2Ge═E (E = S, 1.845; E = Se, 1.9) and the Ge−E bond in $(H_3Ge)_2E$ (E = S, 0.889; E = Se, 0.938) were calculated. Explicitly, the Wiberg bond indices for compounds **4**, **11**, and **12** stand almost at the middle of the two extreme cases (of double and single bonds) and provide concrete evidence on how the Ge═E bond polarity varies upon halogen and N-heterocyclic ligand substitution. Since the effect of electron donation by the ligand systems is likely to be the same across the series of compounds studied, energy decomposition analysis (EDA) (Table 2) and natural population analysis (NPA) charges (Table 3) can provide additional information about the bonding aspects of the Ge═E and Ge−X bonds in compounds **4**, **11**, and **12**.

Interactions between the two fragments (Table 2) were considered for the EDA analysis on each of the aforementioned bonds. As expected, the E_{orb} and E_{int} values (that are directly related to the bond strength) are larger for the Ge═E bond (entries 1, 3, and 5 in Table 2) in comparison to the same values for the Ge−X bond (entries 2, 4, and 6 in Table 2) in compounds **4**, **11**, and **12**. Due to the greater electronegativity difference between the germanium and the sulfur atoms and weak participation of the chlorine p orbital in the donor−acceptor (S→Ge) π-antibonding interaction, E_{int} between fragments $\{LGeCl\}^{2+}$ and $\{S\}^{2-}$ of compound **11** is the highest (Table 2). Among the compounds **4** and **12**, because of the participation of the fluorine p orbital in the donor−acceptor (Se→Ge) π-antibonding interaction, the value of E_{int} between fragments $\{LGeF\}^{2+}$ and $\{Se\}^{2-}$ of compound **4** is lower than its chloride analogue **12** (where the chlorine p-orbital's participation in the same interaction is weak) (Table 2). A comparatively large positive charge has been noted on the germanium center in compound **4** (Table 3), indicating less electron flow to its orbitals from the donor atoms. This is reflected in the computed WBI index also (vide supra).

Alternatively, substitution of the fluorine by a π-interacting chlorine leads to a picture change, as donation from chlorine essentially decreases the net positive charge on germanium (Table 3) and helps in strengthening the Ge═E bond.

Table 2. EDA[a] on Compounds 4, 11, and 12

entry no.	compound	E_{orb} (kcal/mol)	E_{int} (kcal/mol)	fragments
1	**4**	−419.4	−569.29	$\{LGeF\}^{2+}$ + $\{Se\}^{2-}$
2	**4**	−164.7	−234.69	$\{LGeSe\}^{1+}$ + $\{F\}^{1-}$
3	**11**	−463.7	−609.69	$\{LGeCl\}^{2+}$ + $\{S\}^{2-}$
4	**11**	−125.5	−148.27	$\{LGeS\}^{1+}$ + $\{Cl\}^{1-}$
5	**12**	−453.7	−581.57	$\{LGeCl\}^{2+}$ + $\{Se\}^{2-}$
6	**12**	−124.4	−145.29	$\{LGeSe\}^{1+}$ + $\{Cl\}^{1-}$

[a] E_{orb} = orbital energy, E_{int} = interaction energy, E_{steric} = steric energy, and $E_{int} = E_{steric} + E_{orb}$

Table 3. NPA Charges on the Germanium Center and Atoms Present around It in Compounds 4, 11, and 12

atom	**4** (E = Se; X = F)	**11** (E = S; X = Cl)	**12** (E = Se; X = Cl)
Ge	1.832	1.590	1.480
E	−0.690	−0.728	−0.613
X	−0.704	−0.462	−0.463
N	-0.763_{av}	-0.751_{av}	-0.751_{av}

CONCLUSION

In summary, we demonstrated the feasible synthesis of aminotroponiminatogermylene monofluoride **2** using cesium fluoride as a fluorinating agent. Oxidative addition reaction of compound **2** with elemental sulfur and selenium afforded germaacid fluoride complexes **3** and **4**, respectively. Similarly, using an aminotroponiminatogermylene monochloride **9** we were able to synthesize germaacid chloride complexes **11** and **12**. Compounds **3**, **4**, **11**, and **12** are the first examples of germaacid halides stabilized using ATI ligand systems. The Ge═E bond lengths obtained from the structural studies reveal their double-bond nature with a partial polarization. DFT studies have been carried out for the first time to understand the nature of the Ge═E multiple bond (E = S or Se) in germaacid halide complexes. NBO analysis reveals that the Ge═E bond in compounds **4**, **11**, and **12** is formally a double bond. Although the σ interaction in the Ge═E bond is somewhat less perturbed across the series of compounds studied, the strength of the π interaction varies due to the differences in the π-donating abilities of the halogen substituent. Furthermore, synthesis of the silicon analogues of compounds **2**−**4** and **9**−**12** is being carried out currently in our research laboratory.

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■ ASSOCIATED CONTENT

Supporting Information

Synthesis of compounds **6**−**8**, crystal data and structure refinement parameters for compounds **2**, **4**, and **8**−**12**, scheme for the synthesis of germylene monochloride complex **9**, ^{19}F and ^{77}Se NMR values of germylene monofluoride and germaacid halide complexes, molecular structures of aminotroponiminatogermylene monofluoride **10**, aminotroponiminatogermaselenoacid chloride **12**, and lithium salt **8**, side view of molecules **2**, **4**, and **8**−**12** through the C1−C7 bond axis, detected (a) Ge−Cl σ and (b) Ge−Cl π interactions in the NBO analysis of compound **11**, optimized coordinates of compounds **4**, **11**, and **12**, complete author list for ref 23, and crystallographic information file (CIF) for compounds **2**, **4**, and **8**−**12**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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■ DEDICATION

Dedicated to Prof. V. Chandrasekhar.

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