Inorganic Chemistry
Article
pubs.acs.org/IC

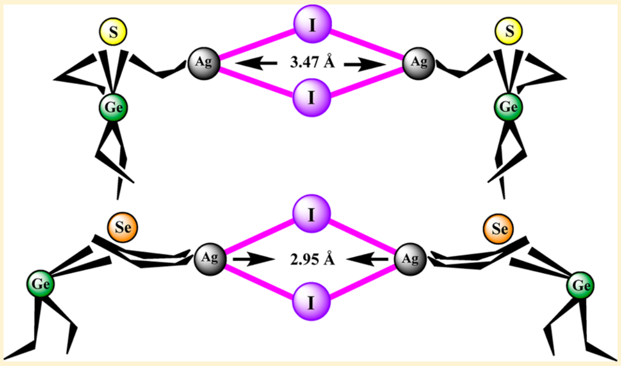
Use of Thio and Seleno Germanones as Ligands: Silver(I) Halide Complexes with Ge═E→Ag–I (E = S, Se) Moieties and Chalcogen-Dependent Argentophilic Interaction

Dhirendra Yadav,[†] Rahul Kumar Siwatch,[†] Goutam Mukherjee,[†] Gopalan Rajaraman,[‡] and Selvarajan Nagendran*,[†]

[†]Department of Chemistry, Indian Institute of Technology Delhi, Hauz Khas, New Delhi 110 016, India
[‡]Department of Chemistry, Indian Institute of Technology Bombay, Powai, Mumbai 400 076, India

Supporting Information

ABSTRACT: The potential of thio and seleno germanones [LPhGe═E] (L = aminotroponiminate (ATI) ligand, E = S **3**, Se **4**) to function as ligands has been demonstrated through the isolation of their silver(I) iodide complexes [{(*t*-Bu)$_2$ATIGe(E)-Ph}$_2$(Ag$_2$I$_2$)] (E = S **5**, Se **6**) with a planar and discrete Ag$_2$I$_2$ core. Compounds **5** and **6** possess the hitherto unknown Ge═E→Ag–I moieties and the crystallographic data reveals the presence of a strong argentophilic interaction (2.950(1) Å) in complex **6**, but is inconclusive in complex **5** (3.470(1) Å). Using theoretical studies, proof for the presence and absence of argentophilic interactions in complexes **6** and **5** was obtained, respectively. Further, it is disclosed that the donor ability of the chalcogen atoms in the Ge═E→Ag–I moieties dictate the Ag···Ag interaction in these complexes.



INTRODUCTION

Like carbenes, germylenes form a number of complexes with transition metals, and their coordination chemistry is very rich.[1] Likewise, their oxidative addition products with polarized Ge═E bonds (E = O, S, Se, Te) can also be visualized as σ-donors based on the chalcogen lone pairs of electrons; however, such possibilities have never been reported.[2] Even the germylenes that possess a matured coordination chemistry have not stabilized a silver(I) halide complex till date. This lacuna, if addressed, may lead to interesting compounds of germanium in view of the emerging importance of donor stabilized silver(I) halide complexes.[3] Therefore, to showcase the utility of germylenes and their oxidative addition products with formal Ge═E bonds as ligands to stabilize silver(I) halide complexes, we explored the reaction of compounds [(*t*-Bu)$_2$ATIGePh] (**2**), [(*t*-Bu)$_2$ATIGe(S)Ph] (**3**), and [(*t*-Bu)$_2$ATIGe(Se)Ph] (**4**) with AgI. Accordingly, we report here the first examples of thio and seleno germanone (**3** and **4**) stabilized silver(I) iodide complexes [{(*t*-Bu)$_2$ATIGe(S)Ph}$_2$(Ag$_2$I$_2$)] (**5**) and [{(*t*-Bu)$_2$ATIGe(Se)Ph}$_2$(Ag$_2$I$_2$)] (**6**), respectively) with hitherto unknown Ge═E→Ag–I moieties and their structural characterization. The bonding features of the Ge═E → Ag–I moieties in these compounds (E = S **5**, Se **6**) and the existence of argentophilic interaction have been delineated and substantiated through DFT calculations. AIM calculations were also carried out for the additional corroboration of the conclusions on argentophilic interaction obtained through DFT studies.

RESULTS AND DISCUSSION

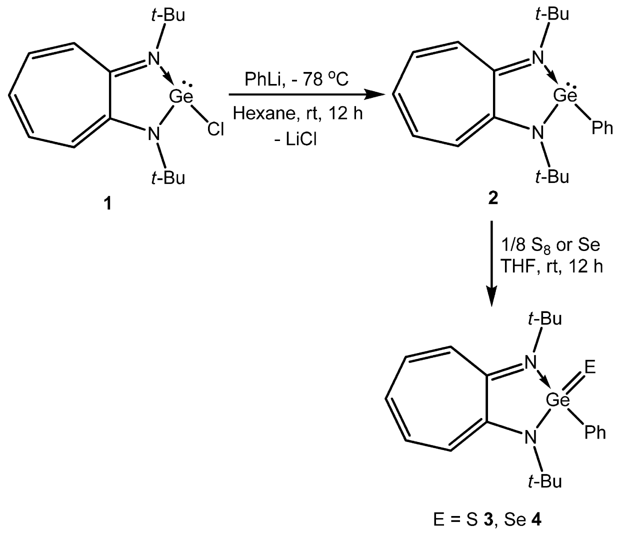
Synthesis and Spectra. Phenyl germylene complex [(*t*-Bu)$_2$ATIGePh] (**2**) was synthesized by reacting a suspension of compound **1** in hexane with a solution of phenyllithium (1.9 M) in di-*n*-butylether at −78 °C (Scheme 1). The reaction of compound **2** with AgI in tetrahydrofuran at room temperature did result in a silver(I) iodide complex, nevertheless, its insolubility in almost all the common organic solvents made its unambiguous characterization impossible. Thio and seleno germanone complexes **3** and **4** were prepared by the oxidative addition reaction of elemental sulfur and selenium to compound **2** at room temperature in tetrahydrofuran, respectively (Scheme 1).

Reaction of these compounds **3** and **4** with stoichiometric amounts of AgI in tetrahydrofuran at 50 °C afforded reasonably soluble thio and seleno germanone stabilized silver(I) iodide complexes [{(*t*-Bu)$_2$ATIGe(S)Ph}$_2$(Ag$_2$I$_2$)] (**5**) and [{(*t*-Bu)$_2$ATIGe(Se)Ph}$_2$(Ag$_2$I$_2$)] (**6**) in about 78 and 84% yields, respectively (Scheme 2). Compounds **5** and **6** are stable under an inert atmosphere of N$_2$ and few solvents in which they have limited solubility are tetrahydrofuran, chloroform, dimethyl

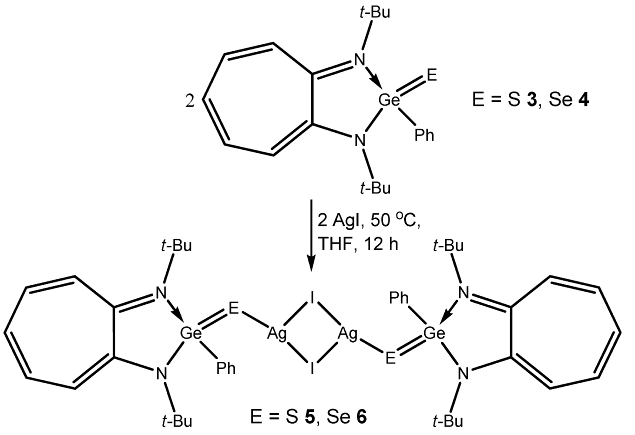
Received: February 19, 2014
Published: September 8, 2014

dx.doi.org/10.1021/ic5008389 | *Inorg. Chem.* 2014, 53, 10054−10059

Scheme 1. Synthesis of Compounds 2−4



Scheme 2. Synthesis of Thio and Seleno Germanones (3 and 4) Stabilized Silver(I) Iodide Complexes (5 and 6)



sulfoxide, and so forth. They were characterized in solution by multinuclear NMR (^{1}H and ^{13}C) spectroscopy.[4] In the ^{1}H NMR spectra of compounds **5** and **6**, a singlet for the *t*-butyl groups is seen at 1.55 ppm. The two C4 protons (Figure 1) in compounds **5** and **6** appear as a broad singlet (7.19 ppm) and triplet (7.14 ppm), respectively. The signals due to other protons of the seven-membered rings merge with the phenyl signals and appear as (a) two broad singlets (7.53, 7.69 ppm) in compound **5** and (b) a broad singlet (7.51 ppm) and multiplet (7.60−7.71 ppm) in compound **6**. Ten signals anticipated for these compounds in their ^{13}C NMR spectra were seen clearly. From these studies, it can be inferred that the thio and seleno germanone ligands in compounds **5** and **6** are symmetric in solution state. This is in agreement with the crystallographic data obtained for compounds **5** and **6** through single-crystal X-ray diffraction studies (vide infra).

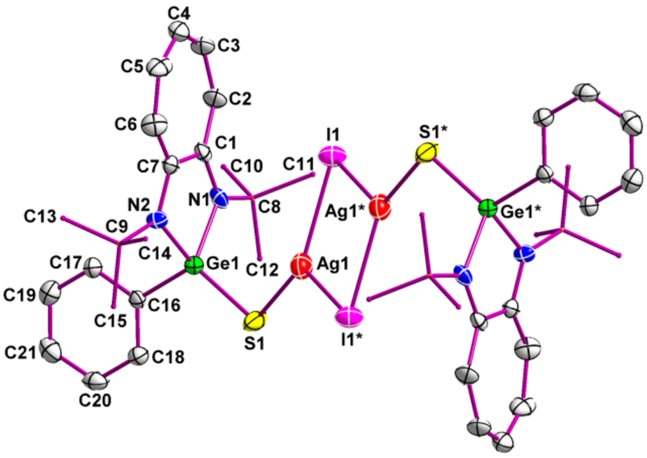


Figure 1. Molecular structure of compound **5**. Thermal ellipsoids are drawn at the 30% probability level. All hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Ge1−N1 1.890(6), Ge1−N2 1.896(5), Ge1−C16 1.952(6), Ge1−S1 2.126(2), S1−Ag1 2.421(2), Ag1−I1* 2.750(1), Ag1−I1 2.852(1); Ge1−S1−Ag1 103.25(9), S1−Ag1−I1* 135.04(7), S1−Ag1−I1 121.23(7), I1*−Ag1−I1 103.47(3), Ag1*−I1−Ag1 76.53(3). *Symmetry transformation used to generate equivalent atoms: −*x* + 2, −*y*, −*z* + 1.

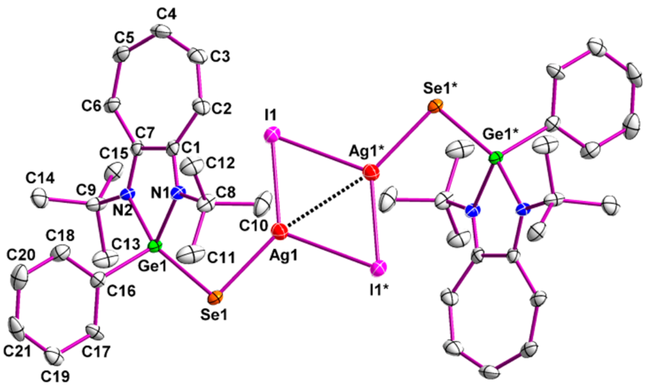
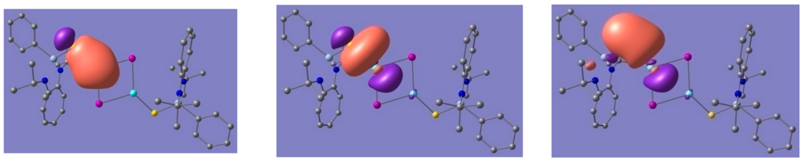
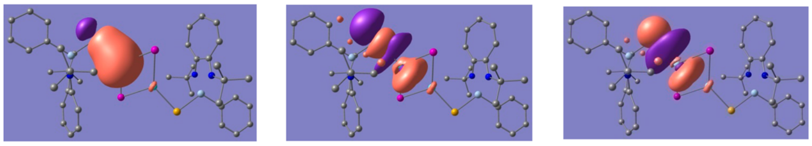


Figure 2. Molecular structure of compound **6**. Thermal ellipsoids are drawn at the 50% probability level. All hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Ge1−N1 1.901(3), Ge1−N2 1.898(3), Ge1−C16 1.939(4), Ge1−Se1 2.267(1), Ag1−Se1 2.545(1), Ag1···Ag1* 2.950(1), Ag1−I1 2.739(1), Ag1−I1* 2.853(1); Ge1−Se1−Ag1 98.13(2), Se1−Ag1−I1 133.44(2), Se1−Ag1−I1* 110.20(2), I1−Ag1−I1* 116.35(1), Ag1−I1−Ag1* 63.65(1). *Symmetry transformation used to generate equivalent atoms: −*x* + 1, −*y*, −*z*.

X-ray Structures of Compounds 3−6. Compounds **3** and **4** crystallized in the orthorhombic space group $P2_12_12_1$ (see Table S1 and Figure S1 in the Supporting Information). Though compounds **3** and **4** are achiral they crystallize in a chiral space group due to the lattice forces. Low values of the Flack parameter[5] in compounds **3** (0.010(9)) and **4** (0.002(8)) are suggestive of homochirality in their crystals. The helices formed along the 2_1 axes are shown in Figures S2 and S3 (see the Supporting Information). Compounds **5** and **6** crystallized in the orthorhombic and monoclinic space groups *P*bca and $P2_1/n$, respectively (see Table S1 in the Supporting Information). Their molecular structures (Figure 1 (**5**), 2 (**6**)) reveal the presence of Ge=E→Ag−I moieties (E = S **5**, Se **6**). The germanium atoms in these compounds are tetracoordinate with a carbon atom of the phenyl group, two nitrogen atoms, and a chalcogen atom (S **5**, Se **6**)) and possess distorted tetrahedral geometries. The silver atoms are tricoordinate (with one chalcogen (S **5** and Se **6**) and two iodine atoms) and have trigonal planar geometries (the sum of bond angles around them is very close 360°). Compounds **5** and **6** possess a planar and discrete Ag_2I_2 core with *μ*-bridged iodine atoms. Compound $[L_2(Ag_2I_2)]$ (L = 1-((6-mesitylpyr-



(a) 50 kcal/mol (b) 32 kcal/mol (c) 20 kcal/mol



(d) 53 kcal/mol (e) 41 kcal/mol (f) 25 kcal/mol

Figure 3. NBO interactions between the chalcogen (E) and silver atoms in compounds **5** (E = S) and **6** (E = Se).

Table 1. Values of Intramolecular Ag···Ag distances, WBI, Electron Density ($\rho(r_c)$), Laplacian of Electron Density ($\nabla^2\rho(r_c)$), Kinetic Energy Density ($G(r_c)$), Potential Energy Density ($V(r_c)$), and Total Energy Density ($H(r_c)$) between the Two Silver Atoms in Compounds 5 and 6

compds	Ag···Ag distance[a]	WBI	$\rho(r_c)$[b]	$\nabla^2\rho(r_c)$[b]	$G(r_c)$[b]	$V(r_c)$[b]	$H(r_c)$[b]
5	3.470	0.052					
6	2.951	0.130	0.0185	0.0706	0.01734	−0.0170	0.0003

[a] In Å. [b] In a.u.

idin-2-yl)methyl)-3-methyl-1H-imidazol-2(3H)-ylidene) reported by Liu and co-workers contains a similar Ag_2I_2 core with tricoordinate silver atoms.[6] The Ge1−S1−Ag1 and Ge1−Se1−Ag1 bond angles in these compounds are found to be 103.25(9) and 98.13(2)°, respectively.

The observed I−Ag−I angles in compound **6** (116.35(1)°) are greater than same angles in compound **5** (103.47(3)°). But the Ag−I−Ag angles in compound **6** (63.65(1)°) are smaller than same angles in compound **5** (76.53(3)°). The Ge−N (1.890(6) and 1.896(5) Å) bond distances are slightly shortened while the Ge═S (2.126(6) Å) bond is elongated in compound **5** in comparison to those in compound **3** (Ge−N 1.902(2) and 1.918(2), Ge═S 2.102(1) Å). These are anticipated effects because of the donation of electrons by sulfur atoms to the silver atoms and a similar trend is observed in compound **6** also. The E1−Ag1 bond lengths in compounds **5** (E = S) and **6** (E = Se) are 2.421(2) and 2.545(1) Å, respectively. These values are comparable to the lengths of the same bonds in related donor stabilized silver(I) iodide complexes.[7] The Ag−I bond lengths (2.750(1) and 2.852(1) Å) in compound **5** are comparable to the same values seen in compound **6** (2.739(1) and 2.853(1) Å). The interatomic distance between the two silver atoms in compound **5** is 3.470(1) Å and it is slightly greater than the sum of the van der Waals radii of two silver atoms (3.40 Å). Therefore, a concrete conclusion on the existence of argentophilic interaction cannot be made using this data and requires further corroboration (vide infra). However, there is a strong argentophilic interaction between the silver atoms in compound **6** as the distance of 2.950(1) Å between them is much shorter than the sum of their van der Waals radii.[8] This is the strongest argentophilic interaction among the donor stabilized AgX (X = Cl, Br, I) complexes with a planar and discrete Ag_2X_2 core. Nevertheless, it should be noted that the compound $[Ag_2(Me_2pipdt)I_2]_n$ (Me_2pipdt = N, N′-dimethyl-piperazine-2,3-dithione) with an extended structure (reported by Serpe, Marchiò, Deplano, and co-workers) has a further less separation of 2.8139(9) Å between the two closest silver atoms.[9] To the best of our knowledge, there is no report on the chalcogen dependent argentophilic interactions in donor stabilized silver(I) iodide complexes. Therefore, to understand the effect of chalcogen donations in the Ge═E→Ag−I moieties to induce argentophilic interaction, theoretical studies were performed.[10−12]

To find out the nature of chalcogen-silver bonds in these compounds, NBO second order perturbation theory analyses were carried out and the results are shown in Figure 3. It is revealed that there are three major stabilizing interactions between the chalcogen and silver atoms in these compounds (**5** and **6**) and their origin is due to the overlap of the sp^x-hybrid orbitals of chalcogen (E = S **5**, Se **6**) and s- or p-orbitals of silver atoms. Overlap between the $sp^{4.05}$-hybrid orbital of sulfur and s-orbital of silver atoms in compound **5** gave a maximum stabilization of 50 kcal/mol (Figure 3a) to the S−Ag bond and the stabilization due to the same type of interaction between selenium and silver atoms in compound **6** is 53 kcal/mol (Figure 3d). The second interaction (32 kcal/mol **5** (Figure 3b), 41 kcal/mol **6** (Figure 3e)) in these compounds result from the head-on overlap of the sp^x-hybrid orbitals of chalcogens (x = 4.05 (**5**), x = 3.62 (**6**)) and p-orbitals of silver atoms. The third significant interaction (20 kcal/mol **5** (Figure 3c), 25 kcal/mol **6** (Figure 3f)) is due to the overlap of the sp^x−hybrid orbitals of chalcogens (x = 0.65 (**5**), x = 0.59 (**6**)) and p-orbitals of silver atoms.

On the basis of these interactions, it can be understood that the donations from selenium to silver atoms in compound **6** is enhanced by 17 kcal/mol than the sulfur and silver interactions in compound **5**. Computed Natural Population Analysis (NPA) charges on the silver atoms in compounds **5** (+0.228 e) and **6** (+0.152 e) also support this observation. The contributions of the E atoms to the HOMOs of complexes **5** (E = S) and **6** (E = Se) are 3 and 12%, respectively. These values support the results obtained from NBO calculations. Whereas, the contributions of the E atoms to the HOMOs of the corresponding ligands **3** (E = S, 84%) and **4** (E = Se, 86%) are almost the same. Further, it is to be mentioned here that the donor−acceptor interactions shown in Figure 3 are not reflected in MOs.

The closed shell d^{10}−d^{10} interaction is dispersive in nature and its origin can also be accounted through orbital mixing.[13] Therefore, a greater degree of σ-donations to the 5s- and 5p-orbitals of the silver by selenium justifies the stronger argentophilic interaction in compound **6** than in compound **5** (found through structural studies).[13] Wiberg Bond Index (WBI) analysis also predicts a bond order of 0.130 between the silver atoms in compound **6**, which is in line with the reported bond orders for argentophilic interactions.[14] At the same time a negligible bond order between the silver atoms has been computed for compound **5**. Thus, this WBI analysis reiterates the presence and absence of argentophilic interaction in compounds **6** and **5**, respectively. Further, to support these findings, AIM calculations were carried out and the results are tabulated (Table 1).[15]

Electron density ($\rho(r_c)$) at the bond critical point (r_c) of two silver atoms in compound **6** is 0.0185. This low and nonzero value of $\rho(r_c)$ clearly indicates the accumulation of electron density and substantiates the presence of argentophilic interaction between them in compound **6** (Figure 4b).

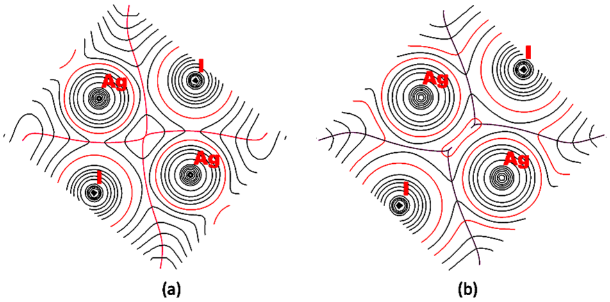


Figure 4. 2D contour plots that show the charge densities of the Ag_2I_2 cores in compounds (a) **5** and (b) **6**.

A positive value of laplacian of electron density ($\nabla^2\rho(r_c)$) and total energy density ($H(r_c)$) at the bond critical point indicate that the interaction is noncovalent. Absence of a bond critical point between the two silver atoms in compound **5** and the node that passes through them in the 2D contour plot (Figure 4a) indicates the nonexistence of argentophilic interaction.

■ CONCLUSION

In conclusion, we successfully demonstrated the first utility of thio and seleno germanones **3** and **4** as ligands for the isolation of rare silver(I) iodide complexes (**5** and **6**) with Ge═E→Ag−I moieties (E = S **5**, Se **6**). Compound **6** shows a strong ligand supported argentophilic interaction and it is the shortest among the silver(I) halide complexes with a planar and discrete Ag_2I_2 core. The role of chalcogen atom in inducing argentophilic interaction has been explained by theoretical studies.

■ EXPERIMENTAL SECTION

All the manipulations involving air- and moisture-sensitive compounds were performed under a dry N_2 atmosphere using either standard Schlenk or glovebox [Jacomex (GP Concept)-T2 workstation] techniques. Sulfur, selenium, silver iodide, and phenyllithium (1.9 M in di-*n*-butylether) were purchased from Sigma-Aldrich and Alfa Aesar, respectively. Tetrahydrofuran and hexane were dried using potassium mirror. Dichloromethane was refluxed over P_2O_5 and distilled prior to use. Compound [(*t*-Bu)$_2$ATIGeCl] (**1**) was synthesized according to the literature procedure.[16] Melting points of the pure compounds were recorded using an Ambassador melting point apparatus by sealing the samples in glass capillaries, and the reported melting points are uncorrected. Elemental analyses were carried out on a PerkinElmer CHN analyzer. Multinuclear NMR spectroscopic studies were carried out on a 300 MHz Bruker Topspin NMR spectrometer using benzene-d_6 and dimethyl sulfoxide-d_6. The chemical shifts δ are reported in ppm and are referenced internally with respect to the residual solvent (^{1}H NMR) and solvent (^{13}C NMR) resonances.[17]

Synthesis of [(*t*-Bu)$_2$ATIGePh] (2). To a suspension of compound **1** (1.00 g, 2.95 mmol) in hexane (60 mL) was added phenyllithium (1.9 M in di-*n*-butylether) (1.55 mL, 2.95 mmol) dropwise at −78 °C, and the resultant mixture was brought to room temperature. It was stirred for 12 h and all the volatiles were then removed under reduced pressure to yield a dark brown solid. This solid was dissolved in hexane and filtered through a G-4 frit. Removal of solvent from the filtrate under reduced pressure afforded an analytically pure sample of compound **2** as a dark brown solid. Yield: 1.05 g, 94%. Mp: 81 °C. Anal. Calcd for $C_{21}H_{28}GeN_2$ (M = 381.10): C, 66.18; H, 7.41; N, 7.35 Found: C, 66.14; H, 7.38; N, 7.39. ^{1}H NMR (300 MHz, C_6D_6): δ 1.28 (s, 18H, C(CH_3)$_3$), 5.99 (t, $^3J_{HH}$ = 9.0 Hz, 1H, C*H*), 6.40 (d, $^3J_{HH}$ = 11.4 Hz, 2H, C*H*), 6.55 (t, $^3J_{HH}$ = 11.4 Hz, 2H, C*H*), 7.19 (t, $^3J_{HH}$ = 7.2 Hz, 1H, *Ph*), 7.29 (t, $^3J_{HH}$ = 7.2 Hz, 2H, *Ph*), 7.86 (d, $^3J_{HH}$ = 6.6 Hz, 2H, *Ph*). ^{13}C{^{1}H} NMR (75 MHz, C_6D_6): δ 29.44 (CH_3), 20.68 (*C*(CH_3)$_3$), 116.89, 117.47, 127.88, 128.22, 133.31, 135.45, 161.04, 161.72 (C_{Ar}).

Synthesis of [(*t*-Bu)$_2$ATIGe(S)Ph] (3). To a solution of compound **2** (0.50 g, 1.31 mmol) in tetrahydrofuran (50 mL) was added sulfur (0.04 g, 1.31 mmol), and the solution was stirred for 12 h at room temperature. All the volatiles were then removed under reduced pressure to yield a solid product. It was washed with hexane (10 mL) and dried under reduced pressure to give an analytically pure sample of compound **3** as a yellow solid. Single crystals of compound **3** suitable for X-ray diffraction studies were grown by the slow evaporation of its solution (in a mixture of dichloromethane and hexane) at room temperature. Yield: 0.53 g, 98%. Mp: 244 °C. Anal. Calcd for $C_{21}H_{28}GeN_2S$ (M = 413.17): C, 61.05; H, 6.83; N, 6.78. Found: C, 61.01; H, 6.78; N, 6.77. ^{1}H NMR (300 MHz, $(CD_3)_2SO$): δ 1.51 (s, 18H, C(CH_3)$_3$), 6.95 (t, 1H, $^3J_{HH}$ = 8.7 Hz, C*H*), 7.44−7.58 (m, 7H, C*H*), 7.67 (bs, 2H, C*H*). ^{13}C{^{1}H} NMR (75 MHz, $(CD_3)_2SO$): δ 29.27 (CH_3), 57.40 (*C*(CH_3)$_3$), 119.79, 124.71, 128.60, 129.85, 131.77, 137.46, 145.72, 157.39 (C_{Ar}).

Synthesis of [(*t*-Bu)$_2$ATIGe(Se)Ph] (4). To a solution of compound **2** (0.50 g, 1.31 mmol) in tetrahydrofuran (30 mL) was added selenium (0.10 g, 1.31 mmol), and the solution was stirred for 12 h at room temperature. All the volatiles were then removed under reduced pressure to yield a solid product. It was washed with hexane (5 mL) and dried under reduced pressure to give an analytically pure sample of compound **4** as a pale yellow solid. Single crystals of compound **4** suitable for X-ray diffraction studies were grown by the slow evaporation of its solution (in a mixture of dichloromethane and tetrahydrofuran) at room temperature. Yield: 0.59 g, 99%. Mp: 238 °C. Anal. Calcd for $C_{21}H_{28}GeN_2Se$ (M = 460.06): C, 54.82; H, 6.13; N, 6.09. Found: C, 54.79; H, 6.11; N, 6.05. ^{1}H NMR (300 MHz, $(CD_3)_2SO$): δ 1.51 (s, 18H, C(CH_3)$_3$), 6.96 (t, 1H, $^3J_{HH}$ = 8.7 Hz, C*H*), 7.44−7.58 (m, 7H, C*H*), 7.68 (bs, 2H, C*H*). ^{13}C{^{1}H} NMR (75 MHz, $(CD_3)_2SO$): δ 29.26 (CH_3), 57.40 (*C*(CH_3)$_3$), 119.80, 124.71, 128.61, 129.85, 131.77, 137.47, 145.73, 157.38 (C_{Ar}). ^{77}Se{^{1}H} NMR (57 MHz, $(CD_3)_2SO$, Me_2Se): δ −216.97 (Ge═*Se*).

Synthesis of [{(*t*-Bu)$_2$ATIGe(S)Ph}$_2$(Ag$_2$I$_2$)] (5). A Schlenk flask was charged with compound **3** (0.50 g, 1.21 mmol), AgI (0.28 g, 1.21 mmol), and tetrahydrofuran (50 mL). The resultant mixture was stirred for 12 h at 50 °C and filtered through a G-4 frit (while it was at the same temperature) to get a dark yellow solution. Removal of solvent under reduced pressure afforded a yellow solid and it was washed with hexane (10 mL). Finally, drying under reduced pressure afforded an analytically pure sample of compound **5** as a yellow solid. Single crystals of compound **5** suitable for X-ray diffraction studies were grown from its dilute solution in tetrahydrofuran by slow evaporation at room temperature. Yield: 0.61 g, 78%. Mp: 178 °C. Anal. Calcd for $C_{42}H_{56}Ag_2Ge_2I_2N_4S_2$ (M = 1295.88): C, 38.93; H, 4.36; N, 4.32. Found: C, 38.88; H, 4.33; N, 4.30. ^1H NMR (300 MHz, $(CD_3)_2SO$): δ 1.55 (s, 36H, C(CH_3)$_3$), 7.19 (bs, 2H, C*H*), 7.53 (bs, 6H, C*H*), 7.69 (bs, 12H, C*H*). $^{13}C\{^1H\}$ NMR (75 MHz, $(CD_3)_2SO$): δ 29.60 (CH_3), 58.04 ($C(CH_3)_3$), 121.92, 127.23, 129.22, 130.98, 131.59, 138.42, 142.40, 157.66 (C_{Ar}).

Synthesis of [{(*t*-Bu)$_2$ATIGe(Se)Ph}$_2$(Ag$_2$I$_2$)] (6). A Schlenk flask was charged with compound **4** (0.50 g, 1.08 mmol), AgI (0.26 g, 1.08 mmol), and tetrahydrofuran (50 mL). The resultant mixture was stirred for 12 h at 50 °C and filtered through a G-4 frit (while it was at the same temperature) to give a dark yellow solution. Removal of the solvent under reduced pressure afforded a yellow solid and it was washed with hexane (10 mL). Finally, drying under reduced pressure afforded an analytically pure sample of compound **6** as a yellow solid. Single crystals of compound **6** suitable for X-ray diffraction studies were grown from its dilute solution in tetrahydrofuran by the slow evaporation at room temperature. Yield: 0.63 g, 84%. Mp: 169 °C. Anal. Calcd for $C_{42}H_{56}Ag_2Ge_2I_2N_4Se_2$ (M = 1389.67): C, 36.30; H, 4.06; N, 4.03. Found: C, 36.28; H, 4.03; N, 4.00. ^1H NMR (300 MHz, $(CD_3)_2SO$): δ 1.55 (s, 36H, C(CH_3)$_3$), 7.14 (t, 2H, $^3J_{HH}$ = 8.7 Hz, C*H*), 7.51 (bs, 6H, C*H*), 7.60−7.71 (m, 12H, C*H*). $^{13}C\{^1H\}$ NMR (75 MHz, $(CD_3)_2SO$): δ 29.66 (CH_3), 58.13 ($C(CH_3)_3$), 121.99, 126.94, 129.04, 130.79, 131.51, 138.05, 143.19, 157.79 (C_{Ar}).

X-ray Data Collection for Compounds 3−6. Single crystals of compounds **3**−**6** suitable for X-ray diffraction studies were coated with Paratone-N and mounted on a glass fiber. Data were collected using a Bruker SMART APEX CCD diffractometer using Mo Kα radiation (λ = 0.71073 Å).[18] The data were integrated using SAINT and an empirical absorption correction was applied using SADABS.[19] The structures were solved by direct methods and refined by full matrix least-squares on F^2 using SHELXTL software.[20] All non-hydrogen atoms were refined anisotropically. The positions of the hydrogen atoms were fixed according to a riding model and were isotropically refined. The important crystallographic data for compounds **3**−**6** are summarized in Table S1 in the Supporting Information.

Computational Details. DFT calculations were performed using B3LYP functional by using Gaussian-09 software. Coordinates obtained from single crystal X-ray diffraction studies (to take care of the dispersion interaction) were directly used for the Natural Bond Orbital (NBO) analysis (using NBO (version 3.1) implemented in the Gaussian-09) and Atoms in Molecules (AIM) calculation (by AIM 2000 (version 2)). For NBO analysis the following basis sets were employed for different atoms: 3-21G* for carbon and hydrogen, 6-311+G* for nitrogen, and LANL2DZ for germanium, chalcogens (E = S **5**, Se **6**), silver, and iodine. AIM calculations were performed using the following basis sets for different atoms: 3-21G* for carbon and hydrogen, 6-311+G* for the nitrogen, and WBTS for germanium, chalcogens (E = S **5**, Se **6**), silver and iodine. Chemcraft software (http://www.chemcraftprog.com) was used for plotting the NBO interactions.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Crystallographic information file (CIF) for compounds **3**−**6**, data and structure refinement parameters for compounds **3**−**6** (Table S1), molecular structures of compounds **3** and **4** (Figure S1), helix formation in compounds **3** (E = S, Figure S2) and **4** (E = Se, Figure S3) via C−H···E interactions, metric parameters for the weak C−H···E interactions in compounds **3** (E = S) and **4** (E = Se) (Table S2), representation of bond critical point between two silver atoms in compound **6**, and complete list of authors for ref 10. This material is available free of charge via the Internet at http://pubs.acs.org

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: sisn@chemistry.iitd.ac.in. Phone: +91-11-2659 1523. Fax: +91-11-2658 1102.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

D.Y. and R.K.S. thank the UGC and CSIR for the fellowship, respectively. We thank Prof. B. Jayaram (Coordinator, Supercomputing Facility for Bioinformatics and Computational Biology (SCFBio) and Professor, Department of Chemistry, IIT Delhi, New Delhi, India), for providing us the access to his computational facilities. We thank Prof. R. P. Ojha, Deen Dayal Upadhyay Gorakhpur University, Uttar Pradesh, India, for allowing us to use the GAUSSIAN-09 software. We thank Prof. P. Venuvanalingam, School of Chemistry, Bharathidasan University, Tamilnadu, India, for his help in generating Figure 4. S.N. thanks the SERB (SB/S1/IC-46/2013), DST, New Delhi, India, for financial support. Further, he thanks the DST for providing financial support (through the DST-FIST program) to the Department of Chemistry, IIT Delhi, New Delhi, India, for establishing the single-crystal X-ray diffraction and ESI-MS facilities.

■ REFERENCES

(1) (a) Yadav, D.; Siwatch, R. K.; Sinhababu, S.; Nagendran, S. *Inorg. Chem.* **2014**, *53*, 600. (b) Gallego, D.; Brück, A.; Irran, E.; Meier, F.; Kaupp, M.; Driess, M.; Hartwig, J. F. *J. Am. Chem. Soc.* **2013**, *135*, 15617. (c) Hlina, J.; Baumgartner, J.; Marschner, C.; Zark, P.; Müller, T. *Organometallics* **2013**, *32*, 3300. (d) Al-Rafia, S. M. I.; Momeni, M. R.; Ferguson, M. J.; McDonald, R.; Brown, A.; Rivard, E. *Organometallics* **2013**, *32*, 6658. (e) Cabeza, J. A.; García-Álvarez, P.; Polo, D. *Dalton Trans.* **2013**, *42*, 1329. (f) García, J. M.; Ocando-Mavárez, E.; Kato, T.; Coll, D. S.; Briceño, A.; Saffon-Merceron, N.; Baceiredo, A. *Inorg. Chem.* **2012**, *51*, 8187. (g) Wang, W.; Inoue, S.; Enthaler, S.; Driess, M. *Angew. Chem., Int. Ed.* **2012**, *51*, 6167. (h) Zabula, A. V.; Hahn, F. E.; Pape, T.; Hepp, A. *Organometallics* **2007**, *26*, 1972. (i) Pineda, L. W.; Jancik, V.; Colunga-Valladares, J. F.; Roesky, H. W.; Hofmeister, A.; Magull, J. *Organometallics* **2006**, *25*, 2381. (j) Saur, I.; Alonso, S. G.; Gornitzka, H.; Lemierre, V.; Chrostowska, A.; Barrau, J. *Organometallics* **2005**, *24*, 2988. (k) Bibal, C.; Mazières, S.; Gornitzka, H.; Couret, C. *Organometallics* **2002**, *21*, 2940. (l) Bazinet, P.; Yap, G. P. A.; Richeson, D. S. *J. Am. Chem. Soc.* **2001**, *123*, 11162. (m) Knorr, M.; Hallauer, E.; Huch, V.; Veith, M.; Braunstein, P. *Organometallics* **1996**, *15*, 3868. (n) Jacobsen, H.; Ziegler, T. *Inorg. Chem.* **1996**, *35*, 775. (o) Veith, V. M.; Stuhl, L. *Angew. Chem.* **1993**, *105*, 123. (p) Petz, W. *Chem. Rev.* **1986**, *86*, 1019. (q) Lappert, M. F.; Power, P. P. *J. Chem. Soc., Dalton Trans.* **1985**, 51. (r) Campbell, G. K.; Hitchcock, P. B.; Lappert, M. F.; Misra, M. C. *J. Organomet. Chem.* **1985**, *289*, C1.

(2) (a) Tam, E. C. Y.; Harris, L. M.; Borren, E. S.; Smith, J. D.; Lein, M.; Coles, M. P.; Fulton, J. R. *Chem. Commun.* **2013**, *49*, 10278. (b) Kocsor, T.-G.; Matioszek, D.; Nemeş, G.; Castel, A.; Escudié, J.; Petrar, P. M.; Saffon, N.; Haiduc, I. *Inorg. Chem.* **2012**, *51*, 7782. (c) Li, L.; Fukawa, T.; Matsuo, T.; Hashizume, D.; Fueno, H.; Tanaka, K.; Tamao, K. *Nat. Chem.* **2012**, *4*, 361. (d) Yao, S.; Xiong, Y.; Driess, M. *Chem. Commun.* **2009**, 6466. (e) Pineda, L. W.; Jancik, V.; Oswald, R. B.; Roesky, H. W. *Organometallics* **2006**, *25*, 2384. (f) Leung, W.-P.; Chong, K.-H.; Wu, Y.-S.; So, C.-W.; Chan, H.-S.; Mak, T. C. W. *Eur. J. Inorg. Chem.* **2006**, 808. (g) Pineda, L. W.; Jancik, V.; Roesky, H. W.; Herbst-Irmer, R. *Angew. Chem., Int. Ed.* **2004**, *43*, 5534. (h) Ding, Y.; Ma, Q.; Roesky, H. W.; Usón, I.; Noltemeyer, M.; Schmidt, H.-G. *Dalton Trans.* **2003**, 1094. (i) Saur, I.; Rima, G.; Gornitzka, H.; Miqueu, K.; Barrau, J. *Organometallics* **2003**, *22*, 1106. (j) Ding, Y.; Ma, Q.; Usón, I.; Roesky, H. W.; Noltemeyer, M.; Schmidt, H.-G. *J. Am. Chem. Soc.* **2002**, *124*, 8542. (k) Okazaki, R.; Tokitoh, N. *Acc.*

Chem. Res. **2000**, *33*, 625. (l) Matsumoto, T.; Tokitoh, N.; Okazaki, R. *J. Am. Chem. Soc.* **1999**, *121*, 8811. (m) Ossig, G.; Meller, A.; Brönneke, C.; Müller, O.; Schäfer, M.; Herbst-Irmer, R. *Organometallics* **1997**, *16*, 2116. (n) Kuchta, M. C.; Parkin, G. *J. Chem. Soc., Chem. Commun.* **1994**, 1351. (o) Tokitoh, N.; Matsumoto, T.; Manmaru, K.; Okazaki, R. *J. Am. Chem. Soc.* **1993**, *115*, 8855. (p) Veith, M.; Becker, S.; Huch, V. *Angew. Chem., Int. Ed.* **1989**, *28*, 1237. (q) During revision, the following work was published: Li, B.; Li, Y.; Zhao, N.; Chen, Y.; Chen, Y.; Fu, G.; Zhu, H.; Ding, Y. *Dalton Trans.* **2014**, *43*, 12100.

(3) (a) Hindi, K. M.; Panzner, M. J.; Tessier, C. A.; Cannon, C. L.; Youngs, W. J. *Chem. Rev.* **2009**, *109*, 3859. (b) Lin, J. C. Y.; Huang, R. T. W.; Lee, C. S.; Bhattacharyya, A.; Hwang, W. S.; Lin, I. J. B. *Chem. Rev.* **2009**, *109*, 3561. (c) Panneerselvam, A.; Nguyen, C. Q.; Malik, M. A.; O'Brien, P.; Raftery, J. *J. Mater. Chem.* **2009**, *19*, 419. (d) Meijbooma, R.; Bowenb, R. J.; Berners-Price, S. J. *Coord. Chem. Rev.* **2009**, *253*, 325. (e) Lin, I. J. B.; Vasam, C. S. *Coord. Chem. Rev.* **2007**, *251*, 642. (f) Garrison, J. C.; Youngs, W. J. *Chem. Rev.* **2005**, *105*, 3978.

(4) Attempts to obtain the ^{77}Se NMR spectrum of compound **6** are not fruitful till now. As suggested by one of the reviewers, the low temperature studies also did not give any result. This may be due to the low solubility of compound **6** in common organic solvents (vide supra).

(5) Flack, H. D. *Acta Crystallogr., Sect. A* **1983**, *39*, 876.

(6) Wang, C.-Y.; Fu, C.-F.; Liu, Y.-H.; Peng, S.-M.; Liu, S.-T. *Inorg. Chem.* **2007**, *46*, 5779.

(7) (a) Santra, B. K.; Chen, J.-L.; Sarkar, B.; Liu, C. W. *Dalton Trans.* **2008**, 2270. (b) Zhang, Q.-F.; Ding, J.; Yu, Z.; Song, Y.; Rothenberger, A.; Fenske, D.; Leung, W.-H. *Inorg. Chem.* **2006**, *45*, 8638. (c) Matrosov, E. I.; Starikova, Z. A.; Yanovsky, A. I.; Lobanov, D. I.; Aladzheva, I. M.; Bykhovskaya, O. V.; Struchkov, Y. T.; Mastryukova, T. A.; Kabachnik, M. I. *J. Organomet. Chem.* **1997**, *535*, 121. (d) Huang, S.-P.; Kanatzidis, M. G. *Inorg. Chem.* **1991**, *30*, 1455.

(8) (a) Sánchez, A.; Sordo, J.; López, E. M. V. *Dalton Trans.* **2013**, *42*, 5916. (b) Jin, J.; Wang, W.; Liu, Y.; Hou, H.; Fan, Y. *Chem. Commun.* **2011**, *47*, 7461. (c) Yang, C.; Elbjeirami, O.; Gamage, C. S. P.; Dias, H. V. R; Omary, M. A. *Chem. Commun.* **2011**, *47*, 7434. (d) Vittal, J. J. *Coord. Chem. Rev.* **2007**, *251*, 1781. (e) Chu, Q.; Swenson, D. C.; MacGillivray, L. R. *Angew. Chem., Int. Ed.* **2005**, *44*, 3569. (f) Dobrzańska, L.; Raubenheimer, H. G.; Barbour, L. J. *Chem. Commun.* **2005**, 5050. (g) Singh, K.; Long, J. R.; Stavropoulos, P. *J. Am. Chem. Soc.* **1997**, *119*, 2942. (h) Barreiro, E.; Casas, J. S.; Couce, M. D.; Laguna, A.; López-de-Luzuriaga, J. M.; Monge, M.; Jansen, M. *Angew. Chem., Int. Ed.* **1987**, *26*, 1098.

(9) Serpe, A.; Artizzu, F.; Marchiò, L.; Mercuri, M. L.; Pilia, L.; Deplano, P. *Cryst. Growth Des.* **2011**, *11*, 1278.

(10) Frisch, M. J., et al.; *Gaussian 09*, revision C. 01; Gaussian, Inc.: Wallingford, CT, 2010.

(11) Weinhold, F.; Landis, C. R. *Valency and Bonding*; Cambridge: Cambridge, U.K., 2005.

(12) (a) Carranza, M. P.; Manzano, B. R.; Jalón, F. A.; Rodríguez, A. M.; Santos, L.; Moreno, M. *New J. Chem.* **2013**, *37*, 3183. (b) Mukherjee, G.; Singh, P.; Ganguri, C.; Sharma, S.; Singh, H. B.; Goel, N.; Singh, U. P.; Butcher, R. J. *Inorg. Chem.* **2012**, *51*, 8128.

(13) (a) Bezuidenhout, D. I.; Westhuizen, B.; van der; Rosenthal, A. J.; Wörle, M.; Liles, D. C.; Fernández, I. *Dalton Trans.* **2014**, *43*, 398. (b) Schmidbaur, H.; Schier, A. *Chem. Soc. Rev.* **2012**, *41*, 370. (c) Sculfort, S.; Braunstein, P. *Chem. Soc. Rev.* **2011**, *40*, 2741. (d) Pyykkö, P. *Chem. Rev.* **1997**, *97*, 597.

(14) (a) Carranza, M. P.; Manzano, B. R.; Jalón, F. A.; Rodríguez, A. M.; Santos, L.; Moreno, M. *New J. Chem.* **2013**, *37*, 3183. (b) Mukherjee, G.; Singh, P.; Ganguri, C.; Sharma, S.; Singh, H. B.; Goel, N.; Singh, U. P.; Butcher, R. J. *Inorg. Chem.* **2012**, *51*, 8128.

(15) (a) Biegler-König, F.; Schönbohm, J.; Bayles, D. *J. Comput. Chem.* **2001**, *22*, 545. (b) Bader, R. F. W. *Chem. Rev.* **1991**, *91*, 893. (c) Bader, R. F. W. *Atoms in Molecules: A Quantum Theory*; Oxford University Press: New York, 1990. (d) Bader, R. F. W. In *Encyclopedia of Computational Chemistry*; Schleyer, P. v. R., Allinger, N. L., Clark, T., Gasteiger, J., Kollman, P. A., Schaefer, H. F. S., III, Schreiner, P. R., Eds.; Wiley: Chichester, U.K., 1998; Vol. *1*, pp 64−86. (e) http://www.AIM2000.de.20.

(16) Siwatch, R. K.; Kundu, S.; Kumar, D.; Nagendran, S. *Organometallics* **2011**, *30*, 1998.

(17) Fulmer, G. R.; Miller, A. J. M.; Sherden, N. H.; Gottlieb, H. E.; Nudelman, A.; Stoltz, B. M.; Bercaw, J. E.; Goldberg, K. I. *Organometallics* **2010**, *29*, 2176.

(18) *SMART, Bruker Molecular Analysis Research Tool*, version 5.618; Bruker AXS: Madison, WI, 2000.

(19) *SAINT-NT*, version 6.04; Bruker AXS: Madison, WI, 2001.

(20) *SHELXTL-NT*, version 6.10; Bruker AXS: Madison, WI, 2000.