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Synthesis and Reactivity of *N*-Aminotroponiminatogermylenepyrrole and Its Derivatives

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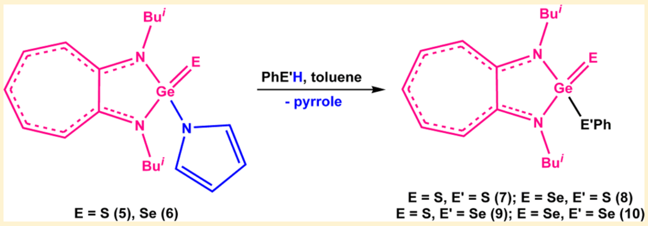
Supporting Information



ABSTRACT: Through the reaction of the aminotroponiminatogermylene monochloride complex [(Bu$^i_2$ATI)GeCl] (**1**) with sodium pyrrolide, the stable *N*-germylene pyrrole complex [(Bu$^i_2$ATI)GeNC$_4$H$_4$] (**2**) has been isolated. The reaction of compound **2** with thiophenol and selenophenol afforded the first germylene thio- and selenophenoxide complexes [(Bu$^i_2$ATI)GeSPh] (**3**) and [(Bu$^i_2$ATI)GeSePh] (**4**) through the substitution of the pyrrole moiety (NC$_4$H$_4$) with an EPh moiety (E = S (**3**), Se (**4**)), respectively. Interestingly, the chalcogenide derivatives of compound **2**, such as the *N*-germathioacylpyrrole complex [(Bu$^i_2$ATI)Ge(S)NC$_4$H$_4$] (**5**) and *N*-germaselenoacylpyrrole complex [(Bu$^i_2$ATI)Ge(Se)NC$_4$H$_4$] (**6**), also underwent the aforementioned substitution reaction with thiophenol and selenophenol, resulting in the first examples of germa thioester complexes ([(Bu$^i_2$ATI)Ge(S)SPh] (**7**) and [(Bu$^i_2$ATI)Ge(Se)SPh] (**8**)) and germa selenoester complexes ([(Bu$^i_2$ATI)Ge(S)SePh] (**9**) and [(Bu$^i_2$ATI)Ge(Se)SePh] (**10**)), respectively. All the novel germanium compounds **3**−**10** have been unequivocally characterized through multinuclear NMR spectroscopy along with the germylene complex **2**. Further, compounds **3**−**5** and **7**−**10** were characterized through single-crystal X-ray diffraction studies. The Ge^{II}−S and Ge^{II}−Se bond lengths in compounds **3** and **4** are 2.367(1) and 2.511(1) Å, respectively. The average Ge^{IV}−S and Ge^{IV}−Se bond lengths in germa thioester (**7** and **8**) and germa selenoester (**9** and **10**) complexes are 2.241(1) and 2.362(1) Å, respectively.

■ INTRODUCTION

Compounds of the type LGeX (L = monoanionic ligand; X = F, Cl, Br, I) are generally called halo-functionalized germylenes, due to the presence of a reactive Ge(II)−X bond apart from the lone pair of electrons on the germanium center.[1] Since the first isolation of LGeI (L = HC(COCH$_3$)$_2$),[2] several halo-functionalized germylenes have been synthesized and characterized.[3] Among them, the chloro-functionalized germylenes (germylene monochlorides) have been widely used and studied because of their easy accessibility. They can show additional reactivity in comparison to the non-functionalized germylenes (L′Ge) (L′ = dianionic ligand) due to the possibility of eliminating or substituting the chloride attached to the germanium(II) center.[4] Jones and Krossing's quasi-one-coordinate amido-germylene monocation[5] [(2,6,4-(HCPh$_2$)$_2$MeC$_6$H$_2$)(Me$_3$Si)N−Ge]$^+$[Al(OC(CF$_3$)$_3$)$_4$]$^-$ and Driess's potassium salt of germacyclopentadienide[6] [HC-(CMe)$_2$N(2,6-Pr$^i_2$C$_6$H$_3$)Ge]$^-$[K(Et$_2$O)$_2$]$^+$ can be cited as examples of unusual germanium compounds[7] obtained from chloro-functionalized germylenes through the elimination of chloride ion. The former compound was isolated from the reaction of RGeCl (R = Me$_3$SiNAr, Ar = 2,6,4-(HCPh$_2$)$_2$MeC$_6$H$_2$) with Ag[Al{OC(CF$_3$)$_3$}$_4$], and the latter was obtained as one of the products during the reduction of LGeCl (L = HC{CMeN(2,6-Pr$^i_2$C$_6$H$_3$)}$_2$) with potassium.[5,6] The substitution reaction on germylene monochlorides is also a very important reaction, because it leads generally to several important non-halo-functionalized germylenes LGeX′ (X′ = OH, OR, NR$_2$, C≡CR, alkyl/aryl, etc.). Roesky and co-workers carried out the reaction of the germylene monochloride complex LGeCl (L = HC{CMeN(2,6-Pr$^i_2$C$_6$H$_3$)}$_2$) with water in the presence of an N-heterocyclic carbene and obtained the hydroxy-functionalized germylene LGeOH.[8] A reaction of the germylene monochloride complex [N(SiMe$_3$)-C(Ph)C(SiMe$_3$)(C$_5$H$_4$N-2)]GeCl with NaCp (Cp = cyclopentadienyl) performed by Leung's group afforded the Cp-substituted germylene [N(SiMe$_3$)C(Ph)C(SiMe$_3$)(C$_5$H$_4$N-2)]GeCp.[9] Thus, the substitution reactions can be carried out on germylene monochlorides using either suitable reagents with an acidic proton in the presence of a base or the metal salts of such reagents. Nevertheless, if the aforementioned substitution reactions can be carried out on non-halo-functionalized germylenes, the advantage would be the possibility to use directly reagents with an acidic proton (without the need for a base or for conversion of the reagents into their metal salts). Such an idea has been pursued with amino-functionalized germylenes containing the Ge^{II}−NR$_2$ moiety (R = acyclic substituent). Thus, the reaction of the amino-functionalized germylene ArGeN(Pr^i)$_2$ (Ar = 2,6-(Et$_2$NCH$_2$)$_2$C$_6$H$_3$) with 2,4,6-trimethylphenol resulted in the germylene aryloxide ArGe[OC$_6$H$_2$(CH$_3$)$_3$] through the cleavage of the Ge^{II}−N

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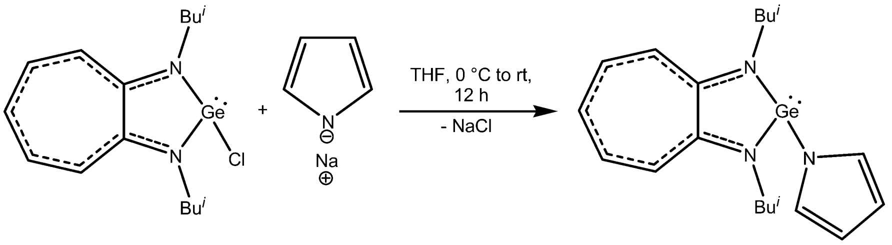
Scheme 1. Synthesis of *N*-Germylene Pyrrole Complex 2 from Aminotroponiminatogermylene Monochloride 1



1 **2**

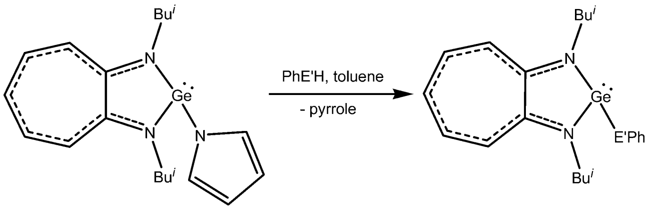
bond.[10] However, for cases where the N atom is a part of an aromatic ring, the possibility of substituting such an N-heterocyclic ring (with a suitable group) by cleaving the $Ge^{II}-N_{ring}$ bond has not yet been explored. Further, the feasibility of substituting the NR_2 group/N-heterocycle attached to a Ge(IV) center formally double bonded to an E atom (E = S, Se) has also never been studied. To address these issues and to expand the scope of the substitution reactions on non-halo-functionalized germylenes, we report here the pyrrole-functionalized germylene complex $[(Bu^i_2ATI)GeNC_4H_4]$ (**2**) stabilized by a bulky aminotroponiminate ligand and substitution reactions on it to result in the first germylene thiophenoxide, $[(Bu^i_2ATI)GeSPh]$ (**3**), and selenophenoxide, $[(Bu^i_2ATI)GeSePh]$ (**4**), complexes. Further, we also demonstrate the feasibility of carrying out the same substitution reaction on chalcogenide derivatives (*N*-germathioacylpyrrole complex $[(Bu^i_2ATI)Ge(S)NC_4H_4]$ (**5**) and *N*-germaselenoacylpyrrole complex $[(Bu^i_2ATI)Ge(Se)NC_4H_4]$ (**6**)) of compound **2** and isolating the germa thioester and selenoester complexes ($[(Bu^i_2ATI)Ge(E)SPh]$ (E = S (**7**), Se (**8**)) and $[(Bu^i_2ATI)Ge(E)SePh]$ (E = S (**9**), Se (**10**)), respectively). Compounds **7** and **8** and **9** and **10** are the first examples of germa thioester and selenoester complexes, respectively. The synthesis of germa ester complexes **9** and **10** gains further importance due to the absence of any heavier group 14 selenoester complexes.

RESULTS AND DISCUSSION

Synthesis and Spectra. The desired germylene complex **2** with a pyrrole substituent was synthesized using the aminotroponiminatogermylene monochloride **1** isolated by us.[4a] Accordingly, the reaction of 1 equiv of germylene monochloride complex **1** with 1.2 equiv of sodium pyrrolide at 0 °C in THF afforded the *N*-germylenepyrrole complex **2** in a quantitative yield (Scheme 1). The other known germylene complex with a pyrrole moiety is $Ge(NC_4H_3COR)_2$ (R = Me_2N, Me, H). It contains a pyrrole derivative as a ligand and was obtained by reacting germylenediamide $Ge[N(TMS)_2]_2$ with the pyrrole-based ligand HNC_4H_3COR.[11]

To test the feasibility of substitution reactions on a heterocycle-functionalized germylene, compound **2** was reacted with various reagents with acidic protons. Eventually, it was identified that such reactivity on compound **2** is possible cleanly with thio- and selenophenol. Thus, the reaction of 1 equiv of the *N*-germylenepyrrole complex **2** with a slight excess of thiophenol in toluene at room temperature led to the cleavage of the $Ge^{II}-N_{ring}$ bond and resulted in the first germylene thiophenoxide complex $[(Bu^i_2ATI)GeSPh]$ (**3**) with an excellent yield of 99% (Scheme 2). Similarly, the reaction of compound **2** with selenophenol also occurred smoothly at 0 °C and afforded the first germylene selenophenoxide complex $[(Bu^i_2ATI)GeSePh]$ (**4**) in 97% yield (Scheme 2). It is important to mention here that such metallylene thio and seleno alkoxide/aryloxide complexes of other group 14 elements are rare. The only known example of a group 14 metallylene thio-alkoxide/aryloxide is the stannylene thiophenoxide[12] $[4\text{-}Bu^t\text{-}2,6\text{-}\{P(O)(OPr^i)_2\}_2C_6H_2]SnSPh$, and there is no example of a group 14 metallylene seleno alkoxide/aryloxide. Interestingly, the germylene thio- and selenophenoxide complexes $[(Bu^i_2ATI)GeSPh]$ (**3**) and $[(Bu^i_2ATI)GeSePh]$ (**4**) are also obtainable quantitatively through the reaction of germylene monochloride complex **1** with the lithium salts of thiophenol and selenophenol (obtained by reacting thiophenol and selenophenol with *n*-BuLi), respectively.

Scheme 2. Synthesis of Aminotroponiminatogermylene Thiophenoxide and Selenophenoxide Complexes 3 and 4 from *N*-Germylenepyrrole Complex 2

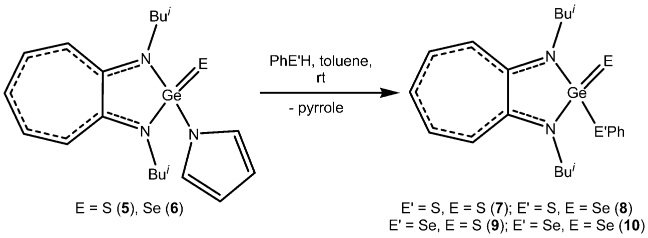


2

E' = S (**3**), Se (**4**)

In these reactions, the feasibility of substituting the pyrrole moiety (NC_4H_4) in compound **2** with an E′Ph group has been witnessed. With this success, the possibility of carrying out the aforementioned substitution reactions on compounds of the type $LGe(E)NC_4H_4$ (L = monoanionic ligand; E = S, Se) that contain a pyrrole moiety attached to the germanium(IV) center was checked. To obtain the germanium(IV) compounds $[(Bu^i_2ATI)Ge(E)NC_4H_4]$ (E = S (**5**), Se (**6**)) required for this study, the oxidative addition reaction of compound **2** was carried out with elemental sulfur and selenium, respectively. Interestingly, in the reaction of *N*-germaacylpyrrole complexes **5** and **6** with a slight excess of thiophenol, the substitution reaction occurred to afford the first examples of germa thioester complexes **7** and **8** ($(Bu^i_2ATI)Ge(E)SPh$; E = S (**7**), Se (**8**)) in about 94% and 96% yields, respectively (Scheme 3). The only known heavier group 14 thioester complex, $[\{PhC(NBu^t)_2\}Si(S)SBu^t]$, was obtained when amidinatosilyldichlorothio-*tert*-butoxide $[\{PhC(NBu^t)_2\}SiCl_2SBu^t]$ was reduced with potassium.[13] The aforementioned substitution of the pyrrole moiety in complexes **5** and **6** was observed with selenophenol also. Thus, the reaction of selenophenol with complexes **5** and **6** in a 1.1:1 ratio resulted in the first germa selenoester complexes $(Bu^i_2ATI)Ge(S)SePh$ (**9**) and $(Bu^i_2ATI)Ge(Se)SePh$ (**10**) in excellent yields (95% and 92%), respectively (Scheme 3). Further, it has been found that the germa ester complexes **7**–**10** can also be obtained through the following two conventional

Scheme 3. Synthesis of Aminotroponiminatogerma Thioester and Selenoester Complexes 7−10 from *N*-Germaacylpyrrole Complexes 5 and 6



synthetic routes in about quantitative yields: (a) an oxidative addition reaction of compounds **3** and **4** with elemental sulfur and selenium and (b) reaction of germa acid chloride complexes $(Bu^i_2ATI)Ge(S)Cl$ and $(Bu^i_2ATI)Ge(Se)Cl$ with the lithium thio- and selenophenoxides.

Compounds **2**−**10** are all stable at room temperature under a dry N_2 atmosphere. Compounds **2** and **3** are freely soluble in most of the organic solvents, whereas compound **4** is soluble in hexane, toluene, and THF but decomposes in dichloromethane and chloroform. Compounds **5**−**8** are soluble in toluene, dichloromethane, chloroform, and THF, whereas compounds **9** and **10** decompose in dichloromethane and chloroform but are freely soluble in toluene and THF. Further, it has been observed that compound **7** in chloroform and dichloromethane starts to decompose after a period of about 2 h. Compounds **2**, **3** and **4**, and **5**−**10** are orange, red, and yellow solids, respectively.

Compounds **2**−**10** have been characterized in solution by multinuclear (^1H, ^{13}C, and ^{77}Se) NMR spectroscopy. In the ^1H NMR spectrum of compound **2**, methyl protons of isobutyl groups appeared as two doublets (0.89 and 0.97 ppm). Its methylene protons were observed as two doublets of doublets (3.22 and 3.37 ppm) due to their diastereotopic nature, whereas methine protons were observed as a multiplet (2.05−2.19 ppm). All these resonances are shifted upfield if a comparison is made with respect to the isobutyl groups of germylene monochloride complex **1**.[4a] The aforementioned splitting pattern of the isobutyl groups in compound **2** was also observed for the same groups in compounds **3**−**10**. Two singlets were seen at 6.17 and 6.59 ppm for the pyrrole protons of compound **2**, although the latter resonance overlaps with the signals due to seven-membered-ring protons (6.52−6.68 ppm). The pyrrole ring protons of compounds **5** (6.23 and 6.76 ppm) and **6** (6.23 and 6.76 ppm) also appeared as two singlets but without the aforementioned overlap with seven-membered-ring resonances (**5**, 7.01−7.59 ppm; **6**, 7.00−7.58 ppm). In compounds **7**−**10**, the ten protons of phenyl and seven-membered rings were seen in the range 6.02−7.32 ppm. In the ^{13}C NMR spectra of compounds **2**−**10**, methyl, methylene, and methine carbons were observed as two, one, and one singlet, respectively. Two singlets were seen for the pyrrole carbons of compounds **2** (108.17, 123.34 ppm), **5** (110.62, 123.06 ppm), and **6** (110.50, 123.08 ppm). As anticipated, eight singlet resonances were observed for the phenyl and seven-membered-ring carbons of compounds **3**, **4**, **7**, and **8**. In compounds **9** and **10**, only six and seven singlets were seen, respectively, as the rest merged into the resonance for C_6D_6. In the ^{77}Se NMR spectra of compounds **6**, **8**, and **10**, the resonance for the selenium center in the Ge═Se bond appeared at −436.60, −253.86, and −165.49 ppm, respectively. These values are between the selenium resonances seen in tetracoordinate germanium(IV) complexes **II**−**V** (Table 1) with polar Ge═Se bonds. Nevertheless, the tricoordinate germanium(IV) compound (Tbt)(Tip)Ge═Se (**I**; Tbt = 2,4,6-tris(bis(trimethylsilyl)methyl)phenyl; Tip = 2,4,6-triisopropylphenyl) with an electronically unperturbed Ge═Se bond shows a singlet resonance at 940.60 ppm (Table 1). The singlet resonances due to the Ge−SePh moiety in compounds **4**, **9**, and **10** were observed at 329.74, 257.76, and 288.15 ppm in their ^{77}Se NMR spectra, respectively.

Table 1. ^{77}Se NMR Chemical Shifts of Compounds I−V, 4, 6, and 8−10

entry	compd	δ(Ge═Se) (ppm)	δ(Ge−Se) (ppm)	ref
1	(Tbt)(Tip)Ge═Se (**I**)	940.60[a]		4j
2	$[N(SiMe_3)C(Ph)C(SiMe_3)(C_5H_4N\text{-}2)]Ge(Se)Cl$ (**II**)	−266.21[b]		4d
3	$\{HC[CMeN(2,6\text{-}Pr^i_2C_6H_3)]_2\}Ge(Se)OH$ (**III**)	−439.80[a]		4c
4	$(Bu^i_2ATI)Ge(Se)Cl$ (**IV**)	−213.13[c]		4a
5	$(Bu^t_2ATI)Ge(Se)OBu^t$ (**V**)	−77.76[c]		4b
6	$(Bu^i_2ATI)GeSePh$ (**4**)		329.74[a]	this work
7	$(Bu^i_2ATI)Ge(Se)NC_4H_4$ (**6**)	−436.60[c]		this work
8	$(Bu^i_2ATI)Ge(Se)SPh$ (**8**)	−253.86[c]		this work
9	$(Bu^i_2ATI)Ge(S)SePh$ (**9**)		257.76[a]	this work
10	$(Bu^i_2ATI)Ge(Se)SePh$ (**10**)	−165.49[a]	288.15[a]	this work

[a] In C_6D_6. [b] In THF-d_8. [c] In $CDCl_3$.

X-ray Crystal Structures of Compounds 3−5 and 7−10. The molecular structure of compounds **3**−**5** and **7**−**10** were further confirmed by single-crystal X-ray diffraction analysis. The crystallographic data for these compounds are summarized in Table S1 (see the Supporting Information). Compounds **3** and **4** crystallized in the monoclinic space group $P2_1/n$. In the molecular structure of germylene complexes **3** (Figure 1) and **4** (Figure S1; see the Supporting Information), the germanium atom is bonded to two nitrogen atoms and one sulfur/selenium (sulfur (**3**), selenium (**4**)) atom in a distorted-trigonal-pyramidal geometry. The sums of the bond angles around the germanium center in compounds **3** and **4** are 274.8(2) and 275.4(4)°, respectively. The orientations of the SPh (in compound **3**) and SePh (in compound **4**) moieties with respect to the fused five- and seven-membered rings are different; in the former it is away, and in the latter it is above. The dihedral angles between the five- and seven-membered ring mean planes in compounds **3** and **4** are 4.0(1) and 2.7(1)°, respectively, and these values hint at the nearly planar nature of the fused rings in these compounds. The average Ge−N bond lengths in compounds **3** and **4** are 1.958(4) and 1.950(2) Å, respectively. Further, the Ge−S and Ge−Se bond lengths are 2.367(1) and 2.511(1) Å in compounds **3** and **4**, respectively. The average S−Ge−N (97.9(2)°) and Se−Ge−N (97.9(7)°) bond angles in compounds **3** and **4** are almost equal.

Compounds **5**, **9**, **7**, **8**, and **10** crystallized in the monoclinic $P2_1/n$, monoclinic $P2_1/n$, monoclinic $C2/c$, monoclinic $C2/c$, and triclinic $P\bar{1}$ space groups, respectively. In all of these compounds, the geometry around the germanium center is distorted tetrahedral. In compound **5** (Figure 2), the Ge−

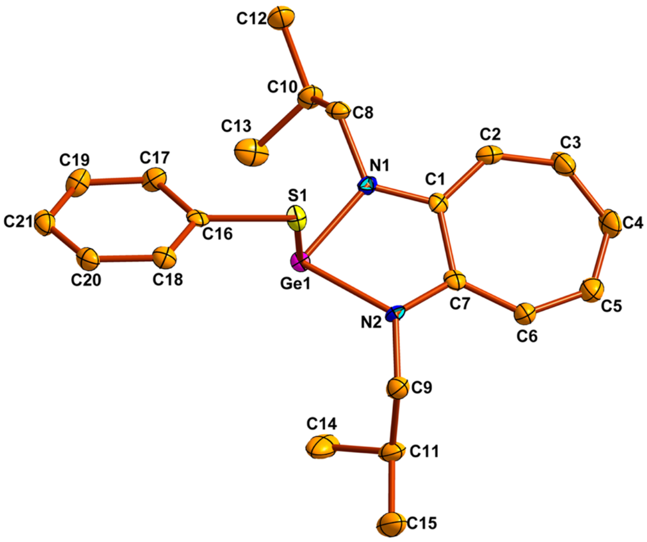


Figure 1. Molecular structure of (Bu$^{i}_{2}$ATI)GeSPh (**3**). All of the hydrogen atoms are omitted for clarity, and thermal ellipsoids are drawn at the 40% probability level. Selected bond lengths (Å) and angles (deg): Ge(1)−S(1) = 2.367(1), Ge(1)−N(1) = 1.962(4), Ge(1)−N(2) = 1.953(4); S(1)−Ge(1)−N(1) = 97.3(1), S(1)−Ge(1)−N(2) = 98.5(1), N(1)−Ge(1)−N(2) = 79.0(2), Ge(1)−S(1)−C(16) = 96.4(2).

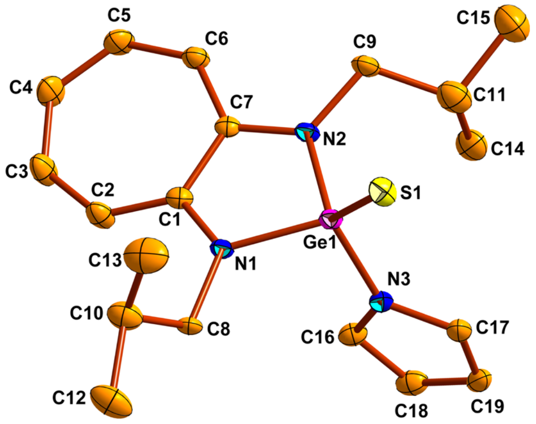


Figure 2. Molecular structure of (Bu$^{i}_{2}$ATI)Ge(S)NC$_4$H$_4$ (**5**). All of the hydrogen atoms are omitted for clarity, and thermal ellipsoids are drawn at the 40% probability level. One of the two molecules present in the asymmetric unit is shown here. Selected bond lengths (Å) and angles (deg): molecule 1, Ge(1)−S(1) = 2.069(1), Ge(1)−N(1) = 1.874(2), Ge(1)−N(2) = 1.884(2), Ge(1)−N(3) = 1.867(2), S(1)−Ge(1)−N(3) = 116.2(1), S(1)−Ge(1)−N(1) = 125.1(1), S(1)−Ge(1)−N(2) = 118.2(1), N(1)−Ge(1)−N(2) = 84.9(1); molecule 2, Ge(2)−S(2) = 2.064(1), Ge(2)−N(4) = 1.879(2), Ge(2)−N(5) = 1.878(2), Ge(2)−N(6) = 1.873(2), S(2)−Ge(2)−N(6) = 115.2(1), S(2)−Ge(2)−N(4) = 123.7(1), S(2)−Ge(2)−N(5) = 120.9(1), N(4)−Ge(2)−N(5) = 84.8(1).

N$_{\text{pyrrole}}$ bond length (average 1.870(2) Å) is almost equal to the average Ge−N$_{\text{ligand}}$ bond length (1.878(2) Å). As anticipated, the latter average is shorter than the corresponding value seen in the germylene complexes **3** (1.958(4) Å) and **4** (1.950(2) Å) due to an increase in the formal oxidation state of the germanium center from +2 (in **3** and **4**) to +4 (in **5**). In compound **5**, the average S−Ge−N$_{\text{ligand}}$ bond angle (122.0(7)°) is greater than the S−Ge−N$_{\text{pyrrole}}$ bond angle (average 115.7(8)°). The dihedral angle (average 5.9(7)°) between the mean planes of five- and seven-membered rings is greater than the same angle found in germylene complexes **3** and **4** and reveals a greater puckering in the fused rings of compound **5**. The C$_2$N$_2$Ge five-membered ring is almost perpendicular to the pyrrole ring, and the dihedral angle between the mean planes of these rings is 87.6(9)° (average).

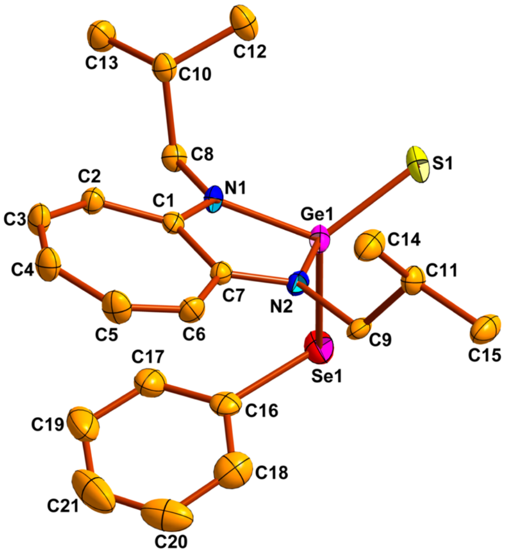


Figure 3. Molecular structure of (Bu$^{i}_{2}$ATI)Ge(S)SePh (**9**). All of the hydrogen atoms are omitted for clarity, and thermal ellipsoids are drawn at the 30% probability level. Selected bond lengths (Å) and angles (deg): Ge(1)−S(1) = 2.075(1), Ge(1)−Se(1) = 2.356(1), Ge(1)−N(1) = 1.886(3), Ge(1)−N(2) = 1.884(4); S(1)−Ge(1)−Se(1) = 111.4(1), S(1)−Ge(1)−N(1) = 122.4(1), S(1)−Ge(1)−N(2) = 120.9(1), N(1)−Ge(1)−N(2) = 84.7(1), Ge(1)−Se(1)−C(16) = 99.9(1).

The Ge=S bond length in *N*-germaacyl pyrrole complex **5** (average 2.067(1) Å) is very close to that in the germa thioacid chloride complex [(Bu$^{i}_{2}$ATI)Ge(S)Cl] (2.065(1) Å).[4a] The length of the Ge=S bond in compounds **7** (2.071(1) Å, Figure S2 (see the Supporting Information)) and **9** (2.075(1) Å, Figure 3) is comparable to the length of the same bond present in germanium complexes of the type LGe(S)X (Table S2 (see the Supporting Information)). The length of the Ge=Se bond in compounds **8** (2.202(1) Å, Figure 4) and **10** (2.205(1) Å, Figure S3 (see the Supporting Information)) is almost the same and it matches with the corresponding bond length in germanium(IV) complexes of general formula LGe(Se)X (Table S2 (see the Supporting Information)). The aforementioned comparisons suggest that the Ge=E bond (E = S (**5**, **7**, **9**), Se (**8**, **10**)) in these compounds is polarized and can be considered as a formal double bond.[4a,e,f,m−p] Nevertheless, these polar Ge=S (in compounds **5**, **7**, and **9**) and Ge=Se (in compounds **8** and **10**) bonds are longer than the electronically unperturbed Ge=E (E = S, Se) bond present in the kinetically stabilized compounds Tbt(Tip)Ge=S (2.049(3) Å)[4j] and Tbt(Tip)Ge=Se (2.180(2) Å),[4j] respectively. The length of the Ge−S bond in compounds **7** and **8** (2.240(1) and 2.242(1) Å, respectively) is comparable to the length of the Ge−S single bond (2.242(4) Å) present in the *β*-diketiminato germa thioacid LGe(S)SH.[3d] The Ge−Se single bond lengths in compounds **9** and **10** are 2.356(1) and 2.367(1) Å, respectively. As there is no reported compound that has a Ge(E)Se (E = S, Se) moiety, the aforementioned bond lengths have been

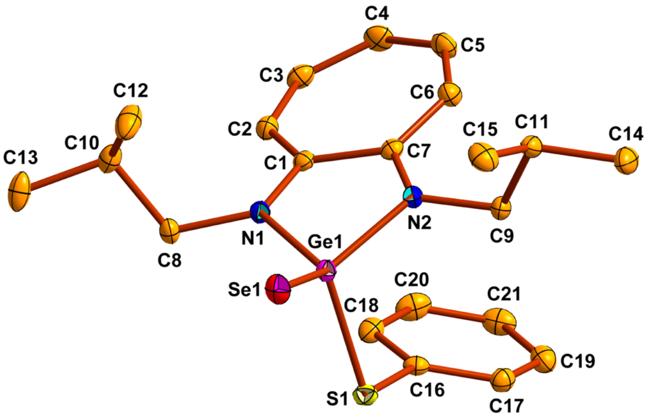


Figure 4. Molecular structure of (Bu$^i_2$ATI)Ge(Se)SPh (**8**). One solvent molecule (THF) and all of the hydrogen atoms are omitted for clarity, and thermal ellipsoids are drawn at the 40% probability level. Selected bond lengths (Å) and angles (deg): Ge(1)−Se(1) = 2.202(1), Ge(1)−S(1) = 2.242(1), Ge(1)−N(1) = 1.882(1), Ge(1)−N(2) = 1.892(1); Se(1)−Ge(1)−S(1) = 109.5(1), Se(1)−Ge(1)−N(1) = 119.4(1), Se(1)−Ge(1)−N(2) = 127.7(1), N(1)−Ge(1)−N(2) = 84.2(1), Ge(1)−S(1)−C(16) = 102.8(1).

compared with those of the germanium compound [C_6H_{11}NC(Me)NC_6H_{11}]$_2$Ge[SeC_6H_5]$_2$, which has Ge^{IV}−Se single bonds (average 2.474(2) Å),[14] and are found to be quite shorter. The S=Ge−S and Se=Ge−S bond angles in compounds **7** and **8** are 110.0(1) and 109.5(1)°, respectively. These are shorter than the S=Ge−Se (111.4(1)°) and Se=Ge−Se (114.5(1)°) bond angles in compounds **9** and **10**, respectively. As in compound **4**, the phenyl group in compounds **7**−**10** lies above the fused rings. The dihedral angles between the five- and seven-membered rings in compounds **7**, **8**, and **10** are 9.7(1), 10.2(1), and 9.3(2)°, respectively, and these values are close to that seen in compound **5** (vide supra). Nevertheless, the dihedral angle between the aforementioned rings in compound **9** is 4.2(2)° and close to the same angle found in compound **3** (vide supra).

■ CONCLUSION

We have demonstrated for the first time the possibility of substituting the pyrrole moiety in a pyrrole-functionalized germylene with SPh and SePh groups that involves Ge^{II}−N$_{ring}$ bond cleavage. Thus, by reacting the *N*-germylenepyrrole complex **2** with thiophenol and selenophenol, the first examples of germylene thiophenoxide (**3**) and selenophenoxide (**4**) complexes have been obtained, respectively. Further, we have found that the aforementioned substitution of the pyrrole moiety is possible even when it is bonded to the Ge(IV) center in LGe(E)NC_4H_4 compounds that have a polar Ge=E bond. Accordingly, when *N*-germaacylpyrrole complexes with a polar Ge=E bond (E = S (**5**), Se (**6**)) were reacted with thiophenol and selenophenol, the first examples of germa thioester and selenoester complexes (**7**−**10**) were obtained. Preparation of the silicon analogues of compounds **2**, **5**, and **6** and examination of their amenability to similar substitution reactions are being pursued currently in our laboratory.

■ EXPERIMENTAL SECTION

The synthesis and handling of air- and moisture-sensitive compounds were performed under a dry dinitrogen atmosphere using either standard Schlenk or glovebox techniques (Jacomex (GP Concept)-T2 workstation). Solvents for synthesis were dried by following the conventional procedures. Hexane, THF, and toluene were further dried over potassium. $CDCl_3$ and C_6D_6 were dried over 4 Å molecular sieves and potassium, respectively. Sulfur, selenium, thiophenol, and selenophenol were purchased from Aldrich and used without any further purification. Compound **1** and sodium pyrrolide were synthesized according to the literature procedures.[4a,15,16] Melting points 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 Perkin-Elmer CHN analyzer. Multinuclear (^{1}H, ^{13}C, and ^{77}Se) NMR spectroscopic studies were carried out on a 300 MHz Bruker Topspin NMR spectrometer using dry $CDCl_3$ or C_6D_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] In the case of ^{77}Se NMR spectroscopic studies, Me_2Se was used as an external reference.

Synthesis of (Bu$^i_2$ATI)GeNC_4H_4 (2). To a solution of compound **1** (2.40 g, 7.07 mmol) in THF (40 mL) was added sodium pyrrolide (0.76 g, 8.48 mmol) at 0 °C; the mixture was then warmed to room temperature and stirred for 12 h. All the volatiles were then removed under reduced pressure, the resultant residue was extracted into hexane, and the extract was filtered using a G4 frit containing Celite. Removal of hexane from the filtrate under reduced pressure afforded an analytically pure sample of compound **2** as an orange solid. Yield: 2.60 g (7.02 mmol, 99%). Mp: 93 °C. Anal. Calcd for $C_{19}H_{27}GeN_3$ (*M* = 370.08): C, 61.66; H, 7.35; N, 11.35. Found: C, 61.42; H, 7.18; N, 11.05. ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.89 (d, $^3J_{HH}$ = 6.6 Hz, 6H, CH(C*H*$_3$)$_2$), 0.97 (d, $^3J_{HH}$ = 6.3 Hz, 6H, CH(C*H*$_3$)$_2$), 2.05−2.19 (m, 2H, C*H*(CH$_3$)$_2$), 3.22 (dd, J_{HH} = 13.8, 8.1 Hz, 2H, C*H*$_2$), 3.37 (dd, J_{HH} = 13.8, 6.0 Hz, 2H, C*H*$_2$), 6.17 (s, 2H, C*H*$_{pyrrole}$), 6.59 (s, 2H, C*H*$_{pyrrole}$), 6.52−6.68 (m, 3H, C*H*$_{ring}$), 7.14−7.21 (m, 2H, C*H*$_{ring}$). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 20.70 (CH(CH$_3$)$_2$), 21.06 (CH(CH$_3$)$_2$), 27.60 (CH(CH$_3$)$_2$), 53.93 (CH$_2$), 108.09 (pyrrole), 114.30 (tp), 121.10 (tp), 123.26 (pyrrole), 136.85 (tp), 161.23 (tp) (tp = seven-membered tropylium ring).

Synthesis of (Bu$^i_2$ATI)GeSPh (3). To a solution of compound **2** (0.90 g, 2.43 mmol) in toluene (15 mL) was added thiophenol (0.26 mL, 2.55 mmol) at room temperature, and the mixture was stirred for 8 h. Removal of the volatiles from the resultant solution under reduced pressure resulted in an analytically pure sample of compound **3** as a red solid. Single crystals of compound **3**, suitable for X-ray diffraction studies, were obtained from its hexane solution by the slow evaporation method at room temperature. Yield: 0.97 g (2.36 mmol, 99%). Mp: 81 °C. Anal. Calcd for $C_{21}H_{28}GeN_2S$ (*M* = 413.13): C, 61.05; H, 6.83; N, 6.78. Found: C, 60.71; H, 6.64; N, 6.45. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.02 (d, $^3J_{HH}$ = 1.5 Hz, 6H, CH(C*H*$_3$)$_2$), 1.04 (d, $^3J_{HH}$ = 1.2 Hz, 6H, CH(C*H*$_3$)$_2$), 2.12−2.26 (m, 2H, C*H*(CH$_3$)$_2$), 3.33 (dd, J_{HH} = 13.5, 5.7 Hz, 2H, C*H*$_2$), 3.42 (dd, J_{HH} = 13.5, 8.4 Hz, 2H, C*H*$_2$), 6.31−6.38 (m, 3H, C*H*$_{ring}$), 6.84−7.00 (m, 5H, C*H*$_{ring}$), 7.12 (d, $^3J_{HH}$ = 6.9 Hz, 2H, C*H*$_{ring}$). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 21.19 (CH(CH$_3$)$_2$), 21.42 (CH(CH$_3$)$_2$), 27.58 (CH(CH$_3$)$_2$), 54.03 (CH$_2$), 114.58 (tp), 121.02 (tp), 124.98 (Ph), 127.87 (Ph), 134.47 (tp), 136.68 (Ph), 138.07 (Ph), 161.14 (tp).

Synthesis of (Bu$^i_2$ATI)GeSePh (4). To a solution of compound **2** (0.80 g, 2.16 mmol) in toluene (15 mL) was added selenophenol (0.24 mL, 2.26 mmol) at 0 °C, and the mixture was stirred for 7 h at room temperature. Removal of the volatiles under reduced pressure resulted in an analytically pure sample of compound **4** as a red solid. Single crystals of compound **4** were obtained by cooling its hexane solution at −40 °C. Yield: 0.96 g (2.10 mmol, 97%). Mp: 71 °C. Anal. Calcd for $C_{21}H_{28}GeN_2Se$ (*M* = 460.02): C, 54.82; H, 6.13; N, 6.09. Found: C, 54.70; H, 5.82; N, 5.78. ^{1}H NMR (300 MHz, C_6D_6): δ 0.77 (d, $^3J_{HH}$ = 6.6 Hz, 6H, CH(C*H*$_3$)$_2$), 0.88 (d, $^3J_{HH}$ = 6.6 Hz, 6H, CH(C*H*$_3$)$_2$), 1.97−2.11 (m, 2H, C*H*(CH$_3$)$_2$), 3.08 (dd, J_{HH} = 13.5, 5.4 Hz, 2H, C*H*$_2$), 3.38 (dd, J_{HH} = 13.5, 8.4 Hz, 2H, C*H*$_2$), 5.95−6.03 (m, 3H, C*H*$_{ring}$), 6.50 (t, $^3J_{HH}$ = 9.6 Hz, 2H, C*H*$_{ring}$), 6.86−6.88 (m, 3H, C*H*$_{ring}$), 7.63−7.66 (m, 2H, C*H*$_{ring}$). ^{13}C{^{1}H} NMR (75 MHz, C_6D_6): δ 20.98 (CH(CH$_3$)$_2$), 21.29 (CH(CH$_3$)$_2$), 27.69 (CH(CH$_3$)$_2$), 54.15 (CH$_2$), 114.90 (tp), 120.60 (tp), 125.68 (Ph), 128.25 (Ph), 132.56

(Ph), 136.66 (tp), 137.14 (Ph), 161.32 (tp). ^{77}Se{^{1}H} NMR (57 MHz, C$_6$D$_6$): δ 329.74 (Ge–*Se*).

Synthesis of (Bu$^{i}_{2}$ATI)Ge(S)NC$_4$H$_4$ (5). To a solution of compound **2** (1.00 g, 2.70 mmol) in toluene (20 mL) was added elemental sulfur (0.08 g, 2.70 mmol) at room temperature, and the mixture was stirred for 4 h. Removal of the volatiles under reduced pressure led to the formation of a yellow solid. The solid was washed with cold hexane (5 mL) and dried to give an analytically pure sample of compound **5** as a yellow solid. Keeping a saturated solution of compound **5** in THF at −40 °C afforded single crystals suitable for X-ray diffraction studies. Yield: 1.02 g (2.54 mmol, 93.6%). Mp: 108 °C. Anal. Calcd for $C_{19}H_{27}GeN_3S$ (*M* = 402.12): C, 56.75; H, 6.77; N, 10.45. Found: C, 56.59; H, 6.50; N, 10.16. ^{1}H NMR (300 MHz, CDCl$_3$): δ 0.78 (d, $^{3}J_{HH}$ = 6.6 Hz, 6H, CH(C*H*$_3$)$_2$), 0.93 (d, $^{3}J_{HH}$ = 6.6 Hz, 6H, CH(C*H*$_3$)$_2$), 2.00–2.14 (m, 2H, C*H*(CH$_3$)$_2$), 3.42 (dd, J_{HH} = 14.1, 7.8 Hz, 2H, C*H*$_2$), 3.70 (dd, J_{HH} = 13.8, 6.9 Hz, 2H, C*H*$_2$), 6.22 (s, 2H, C*H*$_{\mathrm{pyrrole}}$), 6.76 (s, 2H, C*H*$_{\mathrm{pyrrole}}$), 7.01–7.08 (m, 1H, C*H*$_{\mathrm{ring}}$), 7.16 (d, $^{3}J_{HH}$ = 11.1 Hz, 2H, C*H*$_{\mathrm{ring}}$), 7.52–7.58 (m, 2H, C*H*$_{\mathrm{ring}}$). ^{13}C{^{1}H} NMR (75 MHz, CDCl$_3$): δ 20.38 (CH(CH$_3$)$_2$), 21.07 (CH(CH$_3$)$_2$), 28.03 (CH(CH$_3$)$_2$), 53.77 (CH$_2$), 110.62 (pyrrole), 117.34 (tp), 123.06 (pyrrole), 126.54 (tp), 139.09 (tp), 157.46 (tp).

Synthesis of (Bu$^{i}_{2}$ATI)Ge(Se)NC$_4$H$_4$ (6). To a solution of compound **2** (1.00 g, 2.70 mmol) in toluene (20 mL) was added selenium powder (0.21 g, 2.70 mmol) at room temperature, and the mixture was stirred for 6 h. Then, the reaction mixture was filtered through a G4 frit. Removal of the volatiles from the filtrate under reduced pressure resulted in a solid residue. The residue was washed with cold hexane (5 mL) and dried under reduced pressure to yield an analytically pure sample of compound **6** as a yellow solid. Yield: 1.05 g (2.34 mmol, 86.5%). Mp: 149 °C. Anal. Calcd for $C_{19}H_{27}GeN_3Se$ (*M* = 449.04): C, 50.82; H, 6.06; N, 9.36. Found: C, 50.57; H, 5.94; N, 9.06. ^{1}H NMR (300 MHz, CDCl$_3$): δ 0.76 (d, $^{3}J_{HH}$ = 6.6 Hz, 6H, CH(C*H*$_3$)$_2$), 0.93 (d, $^{3}J_{HH}$ = 6.6 Hz, 6H, CH(C*H*$_3$)$_2$), 2.00–2.13 (m, 2H, C*H*(CH$_3$)$_2$), 3.42 (dd, J_{HH} = 14.1, 7.8 Hz, 2H, C*H*$_2$), 3.71 (dd, J_{HH} = 14.1, 6.9 Hz, 2H, C*H*$_2$), 6.23 (s, 2H, C*H*$_{\mathrm{pyrrole}}$), 6.76 (s, 2H, C*H*$_{\mathrm{pyrrole}}$), 7.00–7.04 (m, 1H, C*H*$_{\mathrm{ring}}$), 7.14 (d, $^{3}J_{HH}$ = 11.4 Hz, 2H, C*H*$_{\mathrm{ring}}$), 7.51–7.58 (m, 2H, C*H*$_{\mathrm{ring}}$). ^{13}C{^{1}H} NMR (75 MHz, CDCl$_3$): δ 20.34 (CH(CH$_3$)$_2$), 21.13 (CH(CH$_3$)$_2$), 28.05 (CH(CH$_3$)$_2$), 53.71 (CH$_2$), 110.50 (pyrrole), 117.40 (tp), 123.08 (pyrrole), 126.58 (tp), 138.94 (tp), 157.53 (tp). ^{77}Se{^{1}H} NMR (57 MHz, CDCl$_3$): δ −436.60 (Ge=*Se*).

Synthesis of (Bu$^{i}_{2}$ATI)Ge(S)SPh (7). To a solution of compound **5** (0.50 g, 1.24 mmol) in toluene (30 mL) was added thiophenol (0.14 mL, 1.36 mmol) at room temperature, and the mixture was stirred for 12 h. All the volatiles were then removed under reduced pressure, the resultant residue was washed with hexane (5 mL), and dried under reduced pressure to result in an analytically pure sample of compound **7** as a yellow solid. Keeping a saturated solution of compound **7** in THF at −40 °C afforded single crystals suitable for X-ray diffraction studies. Yield: 0.52 g (1.16 mmol, 94%). Mp: 145 °C. Anal. Calcd for $C_{21}H_{28}GeN_2S_2$ (*M* = 445.23): C, 56.65; H, 6.34; N, 6.29. Found: C, 56.81; H, 6.32; N, 6.10. ^{1}H NMR (300 MHz, CDCl$_3$): δ 1.03 (d, $^{3}J_{HH}$ = 6.6 Hz, 6H, CH(C*H*$_3$)$_2$), 1.08 (d, $^{3}J_{HH}$ = 6.6 Hz, 6H, CH(C*H*$_3$)$_2$), 2.28–2.41 (m, 2H, C*H*(CH$_3$)$_2$), 3.47 (dd, J_{HH} = 13.5, 6.3 Hz, 2H, C*H*$_2$), 3.59 (dd, J_{HH} = 13.5, 8.1 Hz, 2H, C*H*$_2$), 6.70–6.80 (m, 3H, C*H*$_{\mathrm{ring}}$), 6.90 (b, 3H, C*H*$_{\mathrm{ring}}$), 7.10 (b, 2H, C*H*$_{\mathrm{ring}}$), 7.22–7.30 (m, 2H, C*H*$_{\mathrm{ring}}$). ^{13}C{^{1}H} NMR (75 MHz, CDCl$_3$): δ 21.22 (CH(CH$_3$)$_2$), 21.42 (CH(CH$_3$)$_2$), 27.79 (CH(CH$_3$)$_2$), 53.39 (CH$_2$), 116.10 (tp), 125.46 (tp), 127.45 (Ph), 128.36 (Ph), 131.16 (Ph), 134.96 (Ph), 138.21 (tp), 157.42 (tp).

Synthesis of (Bu$^{i}_{2}$ATI)Ge(Se)SPh (8). To a solution of compound **6** (0.50 g, 1.11 mmol) in toluene (20 mL) was added thiophenol (0.12 mL, 1.22 mmol) at room temperature, and the mixture was stirred for 12 h. After removal of the volatiles under reduced pressure, the residue obtained was washed with hexane (5 mL) and dried under reduced pressure to result in an analytically pure sample of compound **8** as a yellow solid. Single crystals of compound **8**, suitable for X-ray diffraction studies, were obtained from its saturated solution in THF at −40 °C. Yield: 0.52 g (1.05 mmol, 96%). Mp: 101 °C. Anal. Calcd for $C_{21}H_{28}GeN_2SSe$ (*M* = 492.13): C, 51.25; H, 5.73; N, 5.69. Found: C, 50.93; H, 5.81; N, 5.58. ^{1}H NMR (300 MHz, CDCl$_3$): δ 1.06 (d, $^{3}J_{HH}$ = 6.6 Hz, 6H, CH(C*H*$_3$)$_2$), 1.10 (d, $^{3}J_{HH}$ = 6.6 Hz, 6H, CH(C*H*$_3$)$_2$), 2.32–2.46 (m, 2H, C*H*(CH$_3$)$_2$), 3.50 (dd, J_{HH} = 13.8, 6.3 Hz, 2H, C*H*$_2$), 3.62 (dd, J_{HH} = 13.8, 8.1 Hz, 2H, C*H*$_2$), 6.71–6.81 (m, 3H, C*H*$_{\mathrm{ring}}$), 6.88–6.94 (m, 3H, C*H*$_{\mathrm{ring}}$), 7.11–7.14 (m, 2H, C*H*$_{\mathrm{ring}}$), 7.25–7.32 (m, 2H, C*H*$_{\mathrm{ring}}$). ^{13}C{^{1}H} NMR (75 MHz, CDCl$_3$): δ 21.21 (CH(CH$_3$)$_2$), 21.55 (CH(CH$_3$)$_2$), 27.78 (CH(CH$_3$)$_2$), 53.25 (CH$_2$), 116.23 (tp), 125.53 (tp), 127.49 (Ph), 128.39 (Ph), 131.81 (Ph), 134.89 (Ph), 138.08 (tp), 157.53 (tp). ^{77}Se{^{1}H} NMR (57 MHz, CDCl$_3$): δ −253.83 (Ge=*Se*).

Synthesis of (Bu$^{i}_{2}$ATI)Ge(S)SePh (9). To a solution of compound **5** (0.30 g, 0.74 mmol) in toluene (15 mL) was added selenophenol (0.08 mL, 0.78 mmol) at room temperature, and the mixture was stirred for 10 h. All of the volatiles were then removed under reduced pressure; the resultant residue was washed with hexane (2 mL) and dried under reduced pressure to give an analytically pure sample of compound **9** as a yellow solid. Slow diffusion of hexane into a solution of **9** in toluene at room temperature afforded single crystals suitable for X-ray diffraction studies. Yield: 0.35 g (0.71 mmol, 95%). Mp: 96 °C. Anal. Calcd for $C_{21}H_{28}GeN_2SSe$ (*M* = 492.09): C, 51.25; H, 5.73; N, 5.69. Found: C, 51.06; H, 5.88; N, 5.65. ^{1}H NMR (300 MHz, C$_6$D$_6$): δ 0.79 (d, $^{3}J_{HH}$ = 6.6 Hz, 6H, CH(C*H*$_3$)$_2$), 1.06 (d, $^{3}J_{HH}$ = 6.6 Hz, 6H, CH(C*H*$_3$)$_2$), 2.26–2.40 (m, 2H, C*H*(CH$_3$)$_2$), 3.22 (dd, J_{HH} = 13.8, 6.3 Hz, 2H, C*H*$_2$), 3.60 (dd, J_{HH} = 13.8, 8.7 Hz, 2H, C*H*$_2$), 6.04 (t, $^{3}J_{HH}$ = 9.3 Hz, 1H, C*H*$_{\mathrm{ring}}$), 6.14 (d, $^{3}J_{HH}$ = 11.1 Hz, 2H, C*H*$_{\mathrm{ring}}$), 6.46 (t, $^{3}J_{HH}$ = 10.2 Hz, 2H, C*H*$_{\mathrm{ring}}$), 6.60–6.65 (m, 3H, C*H*$_{\mathrm{ring}}$), 7.28 (d, $^{3}J_{HH}$ = 6.3 Hz, 2H, C*H*$_{\mathrm{ring}}$). ^{13}C{^{1}H} NMR (75 MHz, C$_6$D$_6$): δ 20.96 (CH(CH$_3$)$_2$), 21.43 (CH(CH$_3$)$_2$), 27.81 (CH(CH$_3$)$_2$), 53.14 (CH$_2$), 115.40 (tp), 124.00 (tp), 127.30 (Ph), 136.84 (Ph), 137.39 (tp), 157.21 (tp). ^{77}Se{^{1}H} NMR (57 MHz, C$_6$D$_6$): δ 257.76 (Ge–*Se*).

Synthesis of (Bu$^{i}_{2}$ATI)Ge(Se)SePh (10). To a solution of compound **6** (0.32 g, 0.71 mmol) in toluene (15 mL) was added selenophenol (0.08 mL, 0.75 mmol) at room temperature, and the mixture was stirred for 10 h. Removal of volatiles under reduced pressure resulted in a crude product which was washed with hexane (3 mL) and dried under reduced pressure to give an analytically pure sample of compound **10** as a yellow solid. Single crystals of compound **10** were obtained by employing the same method used for compound **9**. Yield: 0.33 g (0.61 mmol, 92%). Mp: 105 °C. Anal. Calcd for $C_{21}H_{28}GeN_2Se_2$ (*M* = 538.98): C, 46.79; H, 5.24; N, 5.20. Found: C, 46.66; H, 5.10; N, 5.03. ^{1}H NMR (300 MHz, C$_6$D$_6$): δ 0.81 (d, $^{3}J_{HH}$ = 6.6 Hz, 6H, CH(C*H*$_3$)$_2$), 1.06 (d, $^{3}J_{HH}$ = 6.6 Hz, 6H, CH(C*H*$_3$)$_2$), 2.30–2.44 (m, 2H, C*H*(CH$_3$)$_2$), 3.26 (dd, J_{HH} = 13.8, 6.3 Hz, 2H, C*H*$_2$), 3.61 (dd, J_{HH} = 13.5, 8.4 Hz, 2H, C*H*$_2$), 6.05–6.12 (m, 1H, C*H*$_{\mathrm{ring}}$), 6.17 (d, $^{3}J_{HH}$ = 11.1 Hz, 2H, C*H*$_{\mathrm{ring}}$), 6.48–6.54 (m, 2H, C*H*$_{\mathrm{ring}}$), 6.60–6.68 (m, 3H, C*H*$_{\mathrm{ring}}$), 7.28 (d, $^{3}J_{HH}$ = 6.3 Hz, 2H, C*H*$_{\mathrm{ring}}$). ^{13}C{^{1}H} NMR (75 MHz, C$_6$D$_6$): δ 20.98 (CH(CH$_3$)$_2$), 21.57 (CH(CH$_3$)$_2$), 27.85 (CH(CH$_3$)$_2$), 53.03 (CH$_2$), 115.70 (tp), 124.34 (tp), 127.43 (Ph), 128.50 (Ph), 136.77 (Ph), 137.39 (tp), 157.38 (tp). ^{77}Se{^{1}H} NMR (57 MHz, C$_6$D$_6$): δ −165.49 (Ge=*Se*), 288.15 (Ge–*Se*).

X-ray Data Collection for Compounds 3–5 and 7–10. Single crystals of the title compounds were each coated with a layer of cryoprotectant and then mounted on a glass fiber. The data for these compounds were collected on a Bruker SMART APEX CCD diffractometer with a three-axis goniometer.[18] SAINT and SADABS were used for data integration and empirical absorption correction, respectively.[19] Using the crystallographic software SHELXTL, the structures of these compounds were solved by direct methods and refined by full matrix least squares on F^2.[20] All of the non-hydrogen atoms were anisotropically refined. The positions of the hydrogen atoms were calculated using a riding model and refined isotropically. Important crystallographic details pertaining to compounds **3–5** and **7–10** are provided in Table S1 (see the Supporting Information).

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Crystallographic data for compounds **3–5** and **7–10** as CIF files, crystal data and structure refinement parameters for compounds **3**−**5** and **7**−**10** (Table S1), Ge═E (E = S, Se) bond lengths in germanium(IV) compounds (Table S2), and molecular structure of (Bu$^{i}_{2}$ATI)GeSePh (**4**), (Bu$^{i}_{2}$ATI)Ge(S)SPh (**7**), and (Bu$^{i}_{2}$ATI)Ge(Se)SePh (**10**) (Figures S1−S3, respectively). 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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■ REFERENCES

(1) (a) Asay, M.; Jones, C.; Driess, M. *Chem. Rev.* **2011**, *111*, 354. (b) Mandal, S. K.; Roesky, H. W. *Chem. Commun.* **2010**, *46*, 6016. (c) Mizuhata, Y.; Sasamori, T.; Tokitoh, N. *Chem. Rev.* **2009**, *109*, 3479. (d) Zabula, A. V.; Hahn, F. E. *Eur. J. Inorg. Chem.* **2008**, 5165. (e) Nagendran, S.; Roesky, H. W. *Organometallics* **2008**, *27*, 457. (f) Leung, W.-P.; Kan, K.-W.; Chong, K.-H. *Coord. Chem. Rev.* **2007**, *251*, 2253. (g) Kühl, O. *Coord. Chem. Rev.* **2004**, *248*, 411. (h) Tokitoh, N.; Okazaki, R. *Coord. Chem. Rev.* **2000**, *210*, 251.

(2) (a) Stobart, S. R.; Churchill, M. R.; Hollander, F. J.; Youngs, W. J. *J. Chem. Soc., Chem. Commun.* **1979**, 911.

(3) (a) Samuel, P. P.; Singh, A. P.; Sarish, S. P.; Matussek, J.; Objartel, I.; Roesky, H. W.; Stalke, D. *Inorg. Chem.* **2013**, *52*, 1544. (b) Yang, Y.; Zhao, N.; Wu, Y.; Zhu, H.; Roesky, H. W. *Inorg. Chem.* **2012**, *51*, 2425. (c) Leung, W.-P.; Chiu, W.-K.; Mak, T. C. W. *Organometallics* **2012**, *31*, 6966. (d) Jana, A.; Ghoshal, D.; Roesky, H. W.; Objartel, I.; Schwab, G.; Stalke, D. *J. Am. Chem. Soc.* **2009**, *131*, 1288. (e) Jones, C.; Rose, R. P.; Stasch, A. *Dalton Trans.* **2008**, 2871. (f) Mcheik, A.; Katir, N.; Castel, A.; Gornitzka, H.; Massou, S.; Rivière, P.; Hamieh, T. *Eur. J. Inorg. Chem.* **2008**, 5397. (g) Saur, I.; Alonso, S. G.; Gornitzka, H.; Lemierre, V.; Chrostowska, A.; Barrau, J. *Organometallics* **2005**, *24*, 2988.

(4) (a) Sinhababu, S.; Siwatch, R. K.; Mukherjee, G.; Rajaraman, G.; Nagendran, S. *Inorg. Chem.* **2012**, *51*, 9240. (b) Siwatch, R. K.; Nagendran, S. *Organometallics* **2012**, *31*, 3389. (c) Pineda, L. W.; Jancik, V.; Oswald, R. B.; Roesky, H. W. *Organometallics* **2006**, *25*, 2384. (d) 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. (e) Pineda, L. W.; Jancik, V.; Roesky, H. W.; Herbst-Irmer, R. *Angew. Chem., Int. Ed.* **2004**, *43*, 5534. (f) Ding, Y.; Ma, Q.; Usón, I.; Roesky, H. W.; Noltemeyer, M.; Schmidt, H.-G. *J. Am. Chem. Soc.* **2002**, *124*, 8542. (g) Li, L.; Fukawa, T.; Matsuo, T.; Hashizume, D.; Fueno, H.; Tanaka, K.; Tamao, K. *Nat. Chem.* **2012**, *4*, 361. (h) Yao, S.; Xiong, Y.; Driess, M. *Chem. Commun.* **2009**, 6466. (i) Okazaki, R.; Tokitoh, N. *Acc. Chem. Res.* **2000**, *33*, 625. (j) Matsumoto, T.; Tokitoh, N.; Okazaki, R. *J. Am. Chem. Soc.* **1999**, *121*, 8811. (k) Tokitoh, N.; Matsumoto, T.; Manmaru, K.; Okazaki, R. *J. Am. Chem. Soc.* **1993**, *115*, 8855−8856. (l) Veith, M.; Becker, S.; Huch, V. *Angew. Chem., Int. Ed.* **1989**, *28*, 1237. (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) Saur, I.; Rima, G.; Gornitzka, H.; Miqueu, K.; Barrau, J. *Organometallics* **2003**, *22*, 1106. (p) Ding, Y.; Ma, Q.; Roesky, H. W.; Usón, I.; Noltemeyer, M.; Schmidt, H.-G. *Dalton Trans.* **2003**, 1094.

(5) Li, J.; Schenk, C.; Winter, F.; Scherer, H.; Trapp, N.; Higelin, A.; Keller, S.; Pöttgen, R.; Krossing, I.; Jones, C. *Angew. Chem., Int. Ed.* **2012**, *51*, 9557.

(6) Wang, W.; Yao, S.; Wüllen, C. V.; Driess, M. *J. Am. Chem. Soc.* **2008**, *130*, 9640.

(7) (a) Li, J.; Hermann, M.; Frenking, G.; Jones, C. *Angew. Chem., Int. Ed.* **2012**, *51*, 8611. (b) Xiong, Y.; Yao, S.; Inoue, S.; Berkefeld, A.; Driess, M. *Chem. Commun.* **2012**, *48*, 12198. (c) Singh, A. P.; Roesky, H. W.; Carl, E.; Stalke, D.; Demers, J.-P.; Lange, A. *J. Am. Chem. Soc.* **2012**, *134*, 4998. (d) Choong, S. L.; Schenk, C.; Stasch, A.; Dange, D.; Jones, C. *Chem. Commun.* **2012**, *48*, 2504. (e) Katir, N.; Matioszek, D.; Ladeira, S.; Escudié, J.; Castel, A. *Angew. Chem., Int. Ed.* **2011**, *50*, 5352. (f) Wang, W.; Inoue, S.; Yao, S.; Driess, M. *Chem. Commun.* **2009**, 2661.

(8) Pineda, L. W.; Jancik, V.; Roesky, H. W.; Neculai, D.; Neculai, A. M. *Angew. Chem., Int. Ed.* **2004**, *43*, 1419−1421.

(9) Leung, W.-P.; Chiu, W.-K.; Mak, T. C. W. *Organometallics* **2012**, *31*, 6966.

(10) Bibal, C.; Mazières, S.; Gornitzka, H.; Couret, C. *Organometallics* **2002**, *21*, 2940.

(11) Hübler, K.; Hübler, U. *Z. Anorg. Allg. Chem.* **2000**, *626*, 1224.

(12) Henn, M.; Deáky, V.; Krabbe, S.; Schürmann, M.; Prosenc, M. H.; Herres-Pawlis, S.; Mahieu, B.; Jurkschat, K. *Z. Anorg. Allg. Chem.* **2011**, *637*, 211.

(13) So, C.-W.; Roesky, H. W.; Oswald, R. B.; Pal, A.; Jones, P. G. *Dalton Trans.* **2007**, 5241.

(14) Foley, S. R.; Yap, G. P. A.; Richeson, D. S. *Dalton Trans.* **2000**, 1663.

(15) (a) Siwatch, R. K.; Kundu, S.; Kumar, D.; Nagendran, S. *Organometallics* **2011**, *30*, 1998. (b) Dias, H. V. R.; Wang, Z. *J. Am. Chem. Soc.* **1997**, *119*, 4650.

(16) Rieth, R. D.; Mankad, N. P.; Callimano, E.; Sadighi, J. P. *Org. Lett.* **2004**, *6*, 22.

(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.