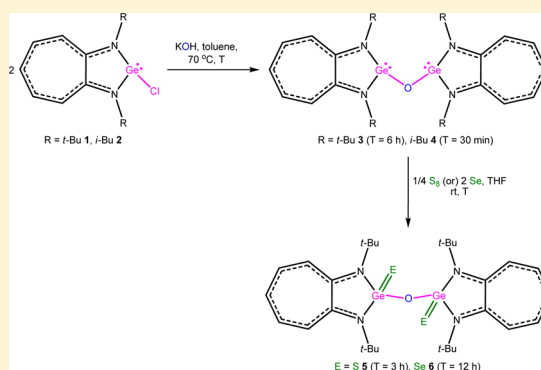


Digermylene Oxide Complexes: Facile Synthesis and Reactivity

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Supporting Information

ABSTRACT: A simple heating of aminotroponimate (ATI) ligand stabilized germylene monochlorides [(R)₂ATIGeCl] (R = *t*-Bu **1**, *i*-Bu **2**) with an excess of potassium hydroxide in toluene resulted in the first ATI ligand stabilized digermylene oxides [(R)₂ATIGe]₂O (R = *t*-Bu **3**, *i*-Bu **4**), respectively. Reaction of compound **3** with elemental sulfur and selenium gave the first germaacid anhydride complexes [(*t*-Bu)₂-ATIGe(E)]₂O (E = S **5**, Se **6**) with (S)Ge–O–Ge(S) and (Se)Ge–O–Ge(Se) moieties, respectively. The digermylene oxide complexes **3** and **4** and germaacid anhydride complexes **5** and **6** were characterized by multinuclear NMR spectroscopy and single-crystal X-ray diffraction analysis. In its ⁷⁷Se NMR spectrum, compound **6** showed a resonance at –78.9 ppm. The Ge–O–Ge bond angles in compounds **5** and **6** are 178.66(2)° and 179.81(2)°, respectively. To understand further the bonding features, DFT calculations followed by MO, AIM, and NBO analysis were carried out on compounds **3**, **5**, and **6**. The computed Wiberg bond indices of Ge–O bonds are slightly less than 0.5 in all the aforementioned compounds, and the same for the Ge=E bonds in compounds **5** and **6** are close to 1.4.



INTRODUCTION

Compounds of the type [LGe(I)–Ge(I)L] that contain monoanionic bidentate ligands and bulky monoanionic substituents as “L” are referred to as germanium(I) dimers¹ and digermynes,² respectively. When an oxygen atom is introduced in between the two germanium atoms in the aforementioned compounds, they are then referred to as digermylene oxides.^{3–5} The digermylene oxides are relatively new to the low-valent germanium chemistry,⁶ and three of them (**I**, **III**, and **V**) have been isolated recently (Chart 1).^{3–5} So and co-worker reported that the reaction of amidinatogermylene monochloride^{1a} [L¹GeCl] (L¹ = *t*-BuC(NAr)₂; Ar = 2,6-*i*-Pr₂C₆H₃) with potassium graphite and half of an equivalent of trimethylamine *N*-oxide afforded digermylene oxide complex [L¹Ge–O–GeL¹] (**I**) in 11% yield through the intermediacy of an amidinatogermanium(I) species [L¹Ge(I)].³ The reaction of digermyne [L²Ge≡GeL²] (**II**) (L² = 2,6-(2,6-*i*-Pr₂C₆H₃)₂C₆H₃) with pyridine *N*-oxide in toluene was exploited by Power and co-workers for the isolation of digermylene oxide [L²Ge–O–GeL²] (**III**) in 42% yield.⁴ Compound **II** was synthesized by Power's group through the reduction of germylene monochloride [L²GeCl] with potassium in THF or benzene.^{2a} The reaction of carbon dioxide/nitrous oxide with digermyne [L³Ge–GeL³] (**IV**) (L³ = N(Ar')(SiMe₃); Ar' = 4-(Me)-2,6-(CHPh₂)₂C₆H₂) in toluene at low temperatures investigated by the groups of Jones and Frenking resulted in the quantitative formation of digermylene oxide [L³Ge–O–GeL³] (**V**).⁵ Compound **V** was also obtained

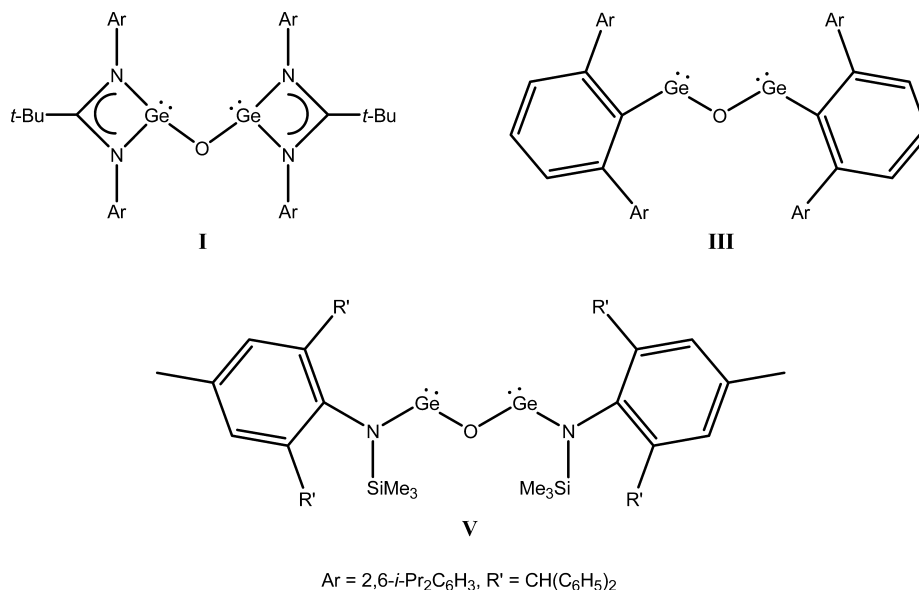
in a low yield (12%) from the reaction of digermyne **IV** with *t*-BuNCO in toluene at ambient temperatures. The digermyne **IV** used for the synthesis of compound **V** was obtained by reducing the corresponding germylene monochloride [L³GeCl] with magnesium(I) dimer [{(MesNCMe)₂CH₂Mg₂] in toluene (Mes = mesityl).^{2e}

On the basis of the aforementioned synthetic routes for the isolation of digermylene oxides, it can be anticipated that a facile and high yielding route for their synthesis from germylene monochlorides will tremendously aid in the development of their chemistry.⁶ With this objective, we studied the reactivity of aminotroponinatogermylene monochlorides^{7,8} [(R)₂-ATIGeCl] (R = *t*-Bu **1**, *i*-Bu **2**) with reagents such as Ag₂O, LiOH, etc. and found, to our surprise, that a common laboratory reagent, potassium hydroxide, is the most suitable candidate. Accordingly, we report herein a novel and simple route for the synthesis of ATI ligand stabilized digermylene oxides [(*t*-Bu)₂ATIGe]₂O (**3**) and [(*i*-Bu)₂ATIGe]₂O (**4**) in high yields, directly from the corresponding germylene monochlorides. Further, to the best of our knowledge, there is no report on the direct reactivity of digermylene oxide complexes.^{3–6} Therefore, we report on the first reactivity, through the oxidative addition reaction on compound **3** with elemental sulfur and selenium. This reaction resulted in the first dithiogermaacid anhydride [(*t*-Bu)₂ATIGe(S)]₂O (**5**) and

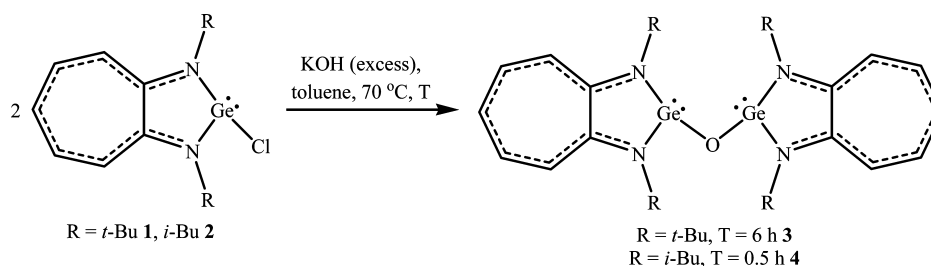
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Chart 1. Structures of Digermylene Oxides I, III, and V



Scheme 1. Synthesis of Digermylene Oxide Complexes 3 and 4



diselenogermaacid anhydride $[(t\text{-Bu})_2\text{ATIGe}(\text{Se})_2\text{O}]$ (**6**) complexes with an almost linear Ge(IV)–O–Ge(IV) moiety. Additionally, the nature of the bonding in digermylene oxide **3** and germaacid anhydride **5** and **6** complexes with Ge–O–Ge and (E)Ge–O–Ge(E) (E = S **5**, Se **6**) moieties was studied through DFT and AIM calculations for the first time and the details are furnished, respectively.

RESULTS AND DISCUSSION

Synthesis and Spectra. The reaction of an aminotroponinimatogermylene monochloride **1** with an excess of potassium hydroxide in toluene at 70 °C for 6 h led to the isolation of the analytically pure digermylene oxide complex **3** as a red solid in about 84% yield (Scheme 1). In contrast, when the aforementioned reaction was carried out with an aminotroponinimatogermylene monochloride **2** with less bulky *i*-butyl substituents,⁸ the reaction took only 30 min for completion and the yield of the expected digermylene oxide complex **4** was almost quantitative (Scheme 1). It is anticipated that the reaction of germylene monochloride complexes **1** and **2** with KOH results in germylene monohydroxide complexes⁹ $[(t\text{-Bu})_2\text{ATIGeOH}]$ (**1***) and $[(i\text{-Bu})_2\text{ATIGeOH}]$ (**2***), as intermediates along with KCl (Scheme S1; see the Supporting Information). These intermediates are expected to react further with one more equivalent of KOH and result in the intermediates $[(t\text{-Bu})_2\text{ATIGeOK}]$ (**1****) and $[(i\text{-Bu})_2\text{ATIGeOK}]$ (**2****) along with H₂O as the side product (Scheme S1; see Supporting Information). Finally, the reaction of the intermediates **1**** and **2**** with another equivalent of

compounds **1** and **2** is likely to afford the digermylene oxide complexes **3** and **4**, respectively (Scheme S1; see the Supporting Information). The formation of the intermediates **1*** and **1**** is supported by theoretical studies (for details, see the Supporting Information), wherein the free energy changes for the reactions $[(t\text{-Bu})_2\text{ATIGeCl} + \text{KOH} \rightarrow (t\text{-Bu})_2\text{ATIGeOH} + \text{KCl}]$ and $(t\text{-Bu})_2\text{ATIGeOH} + \text{KOH} \rightarrow (t\text{-Bu})_2\text{ATIGeOK} + \text{H}_2\text{O}]$ (at 1 atm and 343 K) that lead to their formations are –22.4 and –6.4 kcal/mol, respectively (Table S1; see the Supporting Information).

The purpose to use excess KOH in the aforementioned reactions can now be clearly understood as it aids in the removal of water molecules generated during these reactions (Scheme S1; see the Supporting Information). The water molecules, if not removed, will decompose the germylene monochloride and digermylene oxide complexes to the corresponding aminotroponimines $[(\text{ATI})\text{H}]$ and considerably reduce the yields of the desired bisgermylene oxide complexes. This was confirmed by carrying out the aforementioned reactions with stoichiometric amounts of KOH.

Compounds **3** and **4** are stable at ambient temperatures when stored under an argon or nitrogen atmosphere. They are freely soluble and stable in various nonchlorinated organic solvents, such as benzene, toluene, diethyl ether, and tetrahydrofuran.

With the successful isolation of digermylene oxide complexes through a facile synthetic route, we turned our focus toward their reactivity. As mentioned (*vide supra*), there is no direct reactivity study on digermylene oxide complexes. Nevertheless,

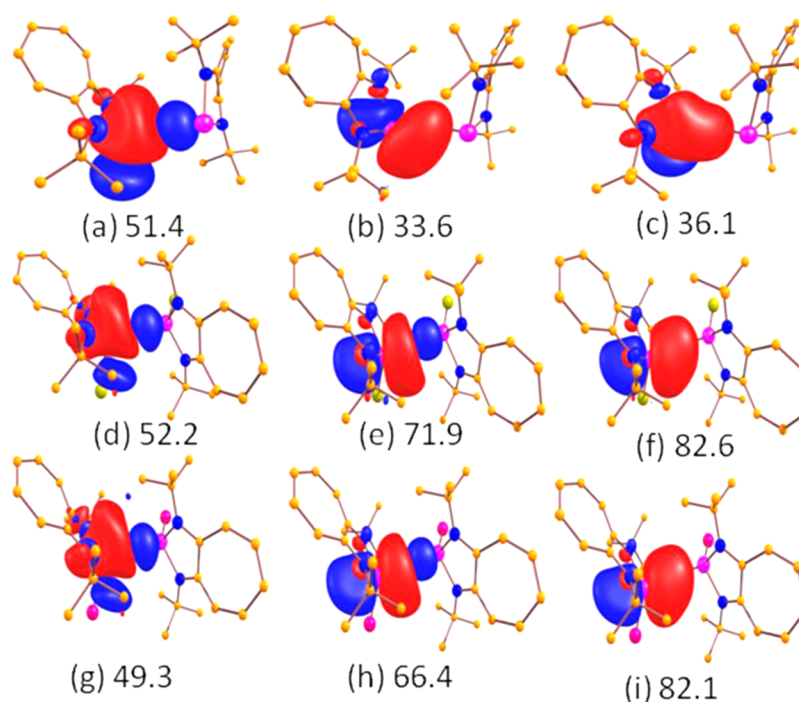


Figure 3. NBO orbitals of compounds **3** [(a)–(c)], **5** [(d)–(f)], and **6** [(g)–(i)] showing the significant oxygen to germanium donor interactions along with their stabilization energies in kcal/mol. The hydrogen atoms are omitted for clarity.

spectrum. This is reminiscent of the situation found in germaester complex $[(t\text{-Bu})_2\text{ATiGe}(\text{Se})\text{O}t\text{-Bu}]$,¹³ where the selenium resonance occurs at -77.76 ppm and confirms the attachment of selenium atoms to tetracoordinate germanium(IV) atoms.^{6,11}

X-ray Crystal Structures of Compounds 3–6. Single crystals of compounds **3–6** suitable for X-ray diffraction studies were grown according to the procedures given in the Experimental Section (vide infra). Compounds **3** and **4** crystallized in the triclinic $[P\bar{1}]$ and orthorhombic $[P2_12_12_1]$ space groups, respectively. As the latter space group is acentric, the Flack parameter was checked and found to be close to zero (Table S2; see the Supporting Information). This is suggestive of the homochirality in the crystals of compound **4**. Their molecular structures [Figure 1 (for compound **3**) and Figure S1 (for compound **4**, see the Supporting Information)] reveal the presence of an oxide bridge between the two amino-tropinimatogermylene moieties.

Each tricoordinate germanium atom in compounds **3** and **4** contains two nitrogen and one oxygen atoms in its immediate environment. The sum of the bond angles around each germanium atom in compound **3** is almost the same (272.8°); nevertheless, it varies slightly for the germanium atoms of compound **4** (Ge1: 279.0° and Ge2: 277.1°). Therefore, all the germanium(II) atoms have a distorted trigonal-pyramidal geometry and a stereochemically active lone pair of electrons.⁶ In compound **3**, the average Ge–N⁶ and Ge–O^{3–6} bond lengths are 2.015 Å and 1.790 Å, respectively, and almost similar averages are seen in compound **4** also (Ge–N bond: 1.99 Å and Ge–O bond: 1.791 Å) (Figure S1; see the Supporting Information). The lengths of the Ge–O bonds in compounds **3** and **4** are slightly longer than the Ge–O bonds [1.760(2) Å] present in Power's compound **III**.⁴ The Ge(1)–O–Ge(2) bond angles in compounds **3** and **4** [$154.4(2)^\circ$ and $154.9(3)^\circ$, respectively] are comparable to the same angle

found in compound **III** [$154.8(1)^\circ$].⁴ The fused (five- and seven-membered) rings in compound **3** are not coplanar; nevertheless, these rings in compound **4** are almost planar (Figure S2; see the Supporting Information).

Both the germaacid anhydride complexes (**5** and **6**) crystallized in the orthorhombic space group $Fdd2$, which is also acentric. Like in compound **4** (vide supra), the Flack parameters for these compounds are also close to zero (Table S2; see the Supporting Information). The molecular structures of these compounds clearly show the existence of (S)Ge–O–Ge(S) and (Se)Ge–O–Ge(Se) moieties in compounds **5** (Figure S3; see the Supporting Information) and **6** (Figure 2), respectively. Each germanium atom in these compounds is tetracoordinate and possesses a distorted tetrahedral environment of two nitrogen, an oxygen, and a chalcogen (S **5**, Se **6**) atoms. The anticipated decrease in the average Ge–N [1.909 Å (**5**), 1.904 Å (**6**)] and Ge–O [1.7333(5) Å (**5**), 1.7340(5) Å (**6**)] bond lengths in these compounds from the corresponding values found for compound **3** (vide supra) [in view of the increased oxidation state of germanium atoms from +2 (in compound **3**) to +4 (in compounds **5** and **6**)] has been observed clearly.^{6,8,11,12d,13} The Ge=S bond length [2.080(1) Å] in compound **5** is comparable to the average length of the Ge=S bonds (2.066 Å) in Leung's derivative $[\text{L}^4\text{Ge}(\text{S})\text{S}(\text{S})\text{GeL}^4]$ and is considerably shorter than the average length of the Ge–S single bonds (2.224 Å) present in the same compound.^{1c,6l} The length of the Ge=Se bonds [2.2124(8) Å] in compound **6** is close to the Ge=Se bond length [2.2197(7) Å] reported for gemaseleneoester complex $[(t\text{-Bu})_2\text{ATiGe}(\text{Se})\text{O}t\text{-Bu}]$.¹³ On the basis of these discussions and other reports on tetracoordinate germanium(IV) compounds with Ge=E bonds,^{6,8,11,12d,13} compounds **5** and **6** can be considered to contain polarized Ge=E (E = S **5**, Se **6**) double bonds (vide infra).

Interestingly, the Ge–O–Ge moieties in germaacid anhydride complexes **5** and **6** are almost linear with the bond angles of 178.6(4)° and 179.8(4)°, respectively. Apart from the reasons mentioned in the computational details (vide infra), it is anticipated that the steric requirement of the *t*-butyl groups in the presence of E atoms (E = S **5**, Se **6**) may also contribute to the linear nature of the Ge–O–Ge moiety in these compounds. This can be tested by the structural analysis on the less bulky analogues of compounds **5** and **6** with *i*-butyl groups; nevertheless, we are unable to get the suitable single crystals of these analogues till now. The orientation of the two Ge=S bonds in compound **5** is almost orthogonal to each other, and the same feature is seen with respect to the Ge=Se bonds in compound **6** also. Like in compound **3**, the fused rings of compounds **5** and **6** are not planar (Figure S2; see the Supporting Information).

Theoretical Studies on Compounds **3**, **5**, and **6**.

Theoretical studies were carried out with an objective to understand the nature of bonding in Ge–O–Ge and (E)Ge–O–Ge(E) moieties in compounds **3**, **5**, and **6** (E = S **5**, Se **6**) respectively. To probe the bonding features, DFT calculations followed by NBO and MO analyses,^{14,15} were performed on all the three compounds. The NBO analysis reveals that, in compound **3**, the Ge–O σ -bond is formed by the overlap of the sp^{9.55} hybridized orbital of germanium and sp^{1.05} hybridized orbital of oxygen. The NBO computed orbital interactions from the second-order perturbation analysis are shown in Figure 3. This interaction between the s orbital of germanium and p orbital of oxygen is found to be stabilized by 51.4 kcal/mol (Figure 3a). In addition to this, there are two more interactions of significant stabilization that result from the overlap of the s orbital of oxygen with either the p or the s orbital of germanium (Figure 3b,c). The Ge–O σ -bonds in compound **5** are formed by the overlap of the sp^{5.42} hybridized orbital of germanium and sp^{0.89} hybridized orbital of oxygen. In compound **6**, the sp^{5.09} hybridized orbital of germanium and the sp^{0.83} hybridized orbital of oxygen are used for the formation of Ge–O σ -bonds. In line with compound **3**, the NBO donor–acceptor interactions in compounds **5** and **6** are also plotted in Figure 3d–i. The first oxygen to germanium interaction detected in these compounds (**5** and **6**) (Figure 3d,g, respectively) is similar to that in compound **3** (Figure 3a) with almost the same stabilization strength. However, the other two interactions in compounds **5** and **6** (Figure 3e,f and Figure 3h,i, respectively) have gained significant stability in comparison to those in compound **3** (Figure 3b,c).

These enhanced σ -donations from oxygen to germanium in compounds **5** (E = S) and **6** (E = Se) are a result of the increased charge separation between them (oxygen and germanium atoms) in the presence of the electron-withdrawing E atoms (Table 1).

Table 1. NPA Charges on the Germanium Atoms and Other Atoms Connected to Them in Compounds **3**, **5**, and **6**

atom	compound 3	compound 4 (E = S)	compound 5 (E = Se)
Ge	1.260	1.959	1.858
E	–	–0.828	–0.717
O	–1.406	–1.392	–1.4
N	–0.697 ^a	–0.743 ^a	–0.745 ^a

^aAverage values.

The aforementioned Ge–O σ -donations are also visible in the computed MOs for compounds **3**, **5** and **6** (Figure 4).

To understand the polarity of the Ge–O bonds in compound **3**, the bond ionicity ($i_{\text{Ge-O}}$) was calculated and found to be 0.79 with 10.48% and 89.52% donation from the germanium and oxygen atoms, respectively. The ionicity ($i_{\text{Ge-O}}$) of the Ge–O bonds in compounds **5** (0.84) and **6** (0.85) are higher than that seen in compound **3**. Accordingly, the contributions of the germanium and oxygen atoms in compounds **5** are 7.93% and 92.07%, respectively. Similarly, the contributions of the same atoms in compound **6** are 7.55% and 92.45%, respectively. These data suggest that the Ge–O bonds in these compounds (**3**, **5**, and **6**) are significantly polar; nevertheless, the polarity in compounds **5** and **6** is greater than that in compound **3**. In view of this, AIM calculations¹⁶ (Figures S4–S6; see the Supporting Information) were performed to further probe the covalent/ionic nature of the Ge–O bonds in these compounds. The presence of a bond critical point (bcp) and the negative energy density at the bcp confirms the covalent nature of the Ge–O bonds (Table 2).¹⁷ Similar calculations were extended to the Ge=E bonds in compounds **5** (E = S) and **6** (E = Se) and found to be covalent (Table 2).

To determine the bond order of the Ge–O (in compounds **3**, **5**, and **6**) and Ge=E (in compounds **5** and **6**) bonds, the Wiberg bond index (WBI) analysis was performed. The WBI for the Ge–O bonds in compound **3** is 0.49, and a very close value of 0.47 was observed for compounds **5** and **6**. Although these values are smaller than what is expected for a conventional Ge–O single bond, such a small bond order between two heteroatoms of different sizes has been observed earlier.¹⁸ Besides this, the low values of WBI in all of these cases are most likely due to the presence of antibonding interactions (Figure S7; see the Supporting Information) between oxygen and germanium atoms. Further, to account for the WBI values that are almost the same in compounds **3**, **5**, and **6**, the aforementioned oxygen to germanium donor strength/bond ionicity should be considered. The increased donor strength/higher Ge–O bond ionicity in compounds **5** and **6** (than in compound **3**) is likely to reduce the Ge–O bond order in compounds **5** and **6** than in compound **3**. However, the MO analysis reveals that the Ge–O bonding/antibonding orbitals are significantly stabilized/destabilized by the Ge=E orbitals, and this interaction (Figure S8; see the Supporting Information) enhances the Ge–O bond order in compounds **5** and **6** to be on par with that of the complex **3**.

The WBI values of the Ge=E bonds in compounds **5** (E = S, 1.43), and **6** (E = Se, 1.40) are almost the same. This clearly indicates that there is only a partial double bond character, and it is explained through the NBO analysis.⁸ The Ge–S σ -bond in compound **5** is formed by the overlap of the sp^{0.51} hybridized orbital of germanium and sp^{5.87} hybridized orbitals of sulfur. The contributions from the germanium and sulfur atoms are 40% and 60%, respectively, and the computed bond ionicity ($i_{\text{Ge-S}}$) is 0.21. Similarly, in compound **6**, the Ge–Se σ -bond is formed by the overlap of the sp^{0.50} hybridized orbital of germanium and sp^{7.14} hybridized orbital of selenium, and the contributions from the germanium and selenium atoms are 45% and 55%, respectively, with a bond ionicity ($i_{\text{Ge-Se}}$) of 0.10. The NBO second-order perturbation analysis shows the presence of Ge=E π -bonding interactions in compounds **5** (E = S) and **6** (E = Se), and they are stabilized by 30.8 and 30.3 kcal/mol, respectively (Figure S9; see the Supporting

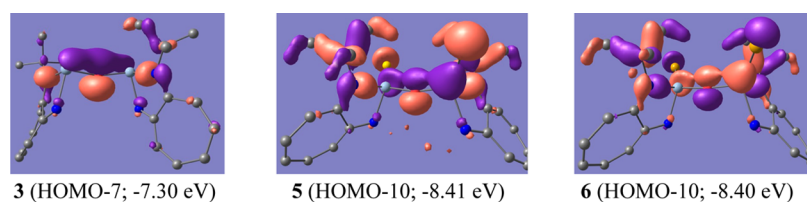


Figure 4. Molecular orbitals showing the overlap between oxygen and germanium atoms in compounds **3**, **5**, and **6**. All the hydrogen atoms and a few of the *t*-butyl groups are omitted for clarity.

Table 2. Electron Charge Density and Electronic Energy Density for Ge–O (in Compounds **3**, **5**, and **6**) and Ge=E (in Compounds **5** and **6**) Bonds at the Bond Critical Points (bcp's)

bond	$\rho(r_c)$ [e/a_0^3]	$G(r_c)$ [hartree/ a_0^3]	$V(r_c)$ [hartree/ a_0^3]	$H(r_c)$ [hartree/ a_0^3]
Ge–O (compound 3)	0.1140	0.1766	–0.2056	–0.0290
Ge–O (compound 5)	0.1294	0.2203	–0.2573	–0.0370
Ge–O (compound 6)	0.1284	0.2184	–0.2544	–0.0360
Ge–S (compound 5)	0.0956	0.0493	–0.0902	–0.0409
Ge–Se (compound 6)	0.0839	0.0359	–0.0686	–0.0327

Information). Apart from these π -bonding interactions in compounds (**5** and **6**), there are Ge=E π -antibonding interactions (Figure S9; see the Supporting Information) in compounds **5** (E = S) and **6** (E = Se) that are stabilized by 28.8 and 28.5 kcal/mol, respectively. Besides the aforementioned π -bonding and π -antibonding interactions, there is also an interaction between the lone pair of electrons of nitrogen and oxygen atoms (directed toward germanium atom) and the antibonding orbital of the Ge–E bond (Figure S9; see the Supporting Information) in each of these two compounds. This interaction in compounds **5** and **6** has stabilized the systems by 36.5 and 30.0 kcal/mol, respectively. Thus, the Ge=E π -antibonding interaction and electronic population in the antibonding Ge–E orbital are responsible for the reduction in the Ge=E bond order (vide supra) in compounds **5** (E = S) and **6** (E = Se). Further, with an average Ge–N bond order of around 0.4 and an overall bond order around each germanium atom that is less than 3 in these compounds (**5** and **6**), the need for the germanium atoms to use any d orbital for bonding is obviated.

Apart from the aforementioned NBO and MO analyses, the composition of the FMO in all of these compounds **3**, **5**, and **6** was also looked at. In compound **3**, the HOMO is composed of the π -electron cloud of the seven-membered rings and lone pairs of electrons of germanium and oxygen atoms (Figure S10; see the Supporting Information). The overall contributions of the two germanium atoms, one oxygen atom, and two seven-membered rings are 32.09%, 10.63%, and 57.28% respectively. However, the HOMOs of compounds **4** and **5** are mainly composed of the lone pairs of electrons of the chalcogen atoms [S1: 38.54% and S2: 37.13% (**5**), Se1: 41.59% and Se2: 41.59% (**6**)] (Figure S10; see the Supporting Information).

CONCLUSIONS

In brief, we have shown a simple and high yielding route for the synthesis of digermylene oxide complexes **3** and **4** from

germylene monochloride complexes **1** and **2**, respectively. The first direct reactivity study on a digermylene oxide has been demonstrated through the reaction of compound **3** with elemental sulfur and selenium, wherein the hitherto unknown germaacid anhydride complexes (**5** and **6**) with an almost linear Ge–O–Ge moiety have been obtained and characterized, respectively. The NBO calculations on compounds **3**, **5**, and **6** reveal the presence of significant oxygen to germanium donations and high ionicity of the Ge–O bonds in them. Nevertheless, the aforementioned donations and ionicity are greater in compounds **5** (E = S) and **6** (E = Se) than those in compound **3** due to the presence of the electron-withdrawing E atoms. Although the Ge–O and Ge=E bonds are polar based on the NBO analysis, the AIM calculations on them predict that they are still covalent. Further, the synthesis and reactivity studies on the silicon analogues of compounds **3** and **4** are in progress in our laboratory.

EXPERIMENTAL SECTION

The synthesis and handling of air- and moisture-sensitive compounds were performed under an inert atmosphere of dry nitrogen gas by means of the standard Schlenk and/or glovebox techniques. The drying of the required solvents was performed according to the usual procedures. Deuterated solvents C_6D_6 and $CDCl_3$ for NMR spectroscopic studies were dried over potassium and phosphorus pentoxide, respectively. Germylene monochloride complexes [(*t*-Bu) $_2$ ATiGeCl] (**1**)⁷ and [(*i*-Bu) $_2$ ATiGeCl] (**2**)⁸ were prepared according to the literature procedures. Anhydrous potassium hydroxide was purchased from SD Fine Chemicals and dried under vacuum at 100 °C before use. Sulfur and selenium were purchased from Aldrich and used as such without any further purification. Melting points of the new compounds were measured using an Ambassador melting point apparatus, and the reported values are uncorrected. Elemental analysis was performed using a PerkinElmer CHN analyzer. Multinuclear NMR (1H , ^{13}C , and ^{77}Se) spectroscopic studies were carried out on a 300 MHz Bruker Topsin NMR spectrometer. The reported values of chemical shifts δ are in parts per million. The referencing was done internally with respect to the residual solvent and solvent resonances in the case of 1H and ^{13}C NMR spectra, respectively.¹⁹ For the ^{77}Se NMR spectroscopic study, dimethyl selenide was used as the external reference.

Synthesis of [(*t*-Bu) $_2$ ATiGe] $_2$ O (3**).** To a solution of [(*t*-Bu) $_2$ ATiGeCl] (**1**) (0.50 g, 1.47 mmol) in toluene (5 mL) was added excess KOH (1.65 g, 29.41 mmol). This mixture was heated at 70 °C for 6 h, cooled, and filtered through a G4 frit. Removal of all volatiles from the filtrate resulted in a red solid. It was washed with cold hexane (10 mL) and dried under reduced pressure to afford an analytically pure sample of compound **3** as a red solid. Single crystals of compound **3** suitable for X-ray diffraction analysis were grown by cooling its toluene solution at –40 °C. Yield: 0.39 g (0.62 mmol), 84%. mp: 162 °C. Anal. Calcd for $C_{30}H_{46}Ge_2N_4O$ (M = 623.99): C, 57.74; H, 7.43; N, 8.98. Found: C, 57.81; H, 7.38; N, 9.07. 1H NMR (300 MHz, C_6D_6): δ 1.61 (s, 36H, C(CH $_3$) $_3$), 6.20 (t, $^3J_{HH}$ = 8.7 Hz, 2H, CH), 6.64–6.80 (m, 8H, CH). $^{13}C\{^1H\}$ NMR (75.48 MHz, C_6D_6): δ 30.57 (C(CH $_3$) $_3$), 56.29 (C(CH $_3$) $_3$), 116.22 (C $_4$), 117.51 (C $_{2,6}$), 133.62 (C $_{3,5}$), 159.33 (C $_{1,7}$).

Synthesis of [(*i*-Bu)₂ATiGe₂O] (4). To a solution of [(*i*-Bu)₂ATiGeCl] (2) (0.80 g, 2.36 mmol) in toluene (8 mL) was added excess KOH (2.65 g, 47.23 mmol). This mixture was heated at 70 °C for 30 min, cooled, and filtered through a G4 frit. Removal of all the volatiles from the filtrate resulted in a red solid. It was washed with cold pentane (3 mL) and dried under reduced pressure to afford an analytically pure sample of compound 4 as a red solid. Single crystals of compound 4 suitable for X-ray diffraction analysis were grown by cooling its toluene solution at -40 °C. Yield: 0.73 g (1.17 mmol), 99%. mp: 97 °C. Anal. Calcd for C₃₀H₄₆Ge₂N₄O (M = 623.99): C, 57.74; H, 7.43; N, 8.98. Found: C, 57.75; H, 7.49; N, 8.90. ¹H NMR (300 MHz, C₆D₆): δ 0.87 (d, ³J_{HH} = 6.3 Hz, 12H, CH₃), 0.95 (d, ³J_{HH} = 6.6 Hz, 12H, CH₃), 2.13–2.27 (m, 4H, CH(CH₃)₂), 3.27 (dd, ³J_{HH} = 13.2, 6.0 Hz, 4H, CH₂), 3.40 (dd, ³J_{HH} = 13.5, 8.1 Hz, 4H, CH₂), 6.18 (t, ³J_{HH} = 9.3 Hz, 2H, CH), 6.34 (d, ³J_{HH} = 11.4 Hz, 4H, CH), 6.76 (t, ³J_{HH} = 10.2 Hz, 4H, CH). ¹³C{¹H} NMR (75.48 MHz, C₆D₆): δ 21.34 (CH₃), 21.58 (CH₃), 27.86 (CH(CH₃)₂), 54.48 (CH₂), 113.05 (C₄), 118.53 (C_{2,6}), 135.85 (C_{3,5}), 161.03 (C_{1,7}).

Synthesis of [(*t*-Bu)₂ATiGe(S)₂O] (5). To a solution of compound 3 (0.35 g, 0.56 mmol) in THF (15 mL) was added elemental sulfur (0.036 g, 1.12 mmol), and the mixture was stirred for 3 h. Then, the solvent was removed under reduced pressure to result in a yellow solid. It was washed with hexane (5 mL) and dried in vacuo to get an analytically pure sample of compound 5. Single crystals of compound 5 suitable for X-ray diffraction analysis were grown by the slow evaporation of its dichloromethane solution at room temperature. Yield: 0.38 g (0.55 mmol), 98%. mp: 270 °C (dec.). Anal. Calcd for C₃₀H₄₆Ge₂N₄OS₂ (M = 688.12): C, 52.36; H, 6.74; N, 8.14. Found: C, 52.29; H, 6.68; N, 8.19. ¹H NMR (300 MHz, CDCl₃): δ 1.87 (s, 36H, C(CH₃)₃), 6.84 (t, ³J_{HH} = 7.8 Hz, 2H, CH), 7.28–7.39 (m, 8H, CH). ¹³C{¹H} NMR (75.48 MHz, CDCl₃): δ 30.12 (C(CH₃)₃), 58.36 (C(CH₃)₃), 118.64 (C₄), 124.66 (C_{2,6}), 136.53 (C_{3,5}), 155.77 (C_{1,7}).

Synthesis of [(*t*-Bu)₂ATiGe(Se)₂O] (6). To a solution of compound 3 (0.45 g, 0.72 mmol) in THF (20 mL) was added elemental selenium (0.114 g, 1.44 mmol), and the mixture was stirred for 12 h. Then, the solution was filtered through a G4 frit with a thick bed of Celite. The solvent from the filtrate was removed under reduced pressure, and the product was washed with hexane (5 mL) and dried in vacuo to get an analytically pure sample of compound 6. Single crystals of compound 6 suitable for X-ray diffraction analysis were grown by slow evaporation of its dichloromethane solution at room temperature. Yield: 0.50 g (0.64 mmol), 88%. mp: 211 °C (dec.). Anal. Calcd for C₃₀H₄₆Ge₂N₄OSe₂ (M = 781.91): C, 46.08; H, 5.93; N, 7.17. Found: C, 46.16; H, 5.88; N, 7.23. ¹H NMR (300 MHz, CDCl₃): δ 1.82 (s, 36H, C(CH₃)₃), 6.75 (t, ³J_{HH} = 8.4 Hz, 2H, CH), 7.18–7.32 (m, 8H, CH). ¹³C{¹H} NMR (75.48 MHz, CDCl₃): δ 30.52 (C(CH₃)₃), 58.71 (C(CH₃)₃), 119.01 (C₄), 124.79 (C_{2,6}), 136.35 (C_{3,5}), 155.61 (C_{1,7}). ⁷⁷Se{¹H} NMR (57 MHz, CDCl₃): δ -78.88 (Ge=Se).

X-ray Structure Determination for Compounds 3–6. For all the compounds 3–6, the X-ray data were collected using a Bruker SMART APEX diffractometer equipped with a 3-axis goniometer operating at room temperature.²⁰ The crystals were mounted on a glass fiber after covering them with a cryoprotectant. SAINT and SADABS were used to integrate the data and apply an empirical absorption correction, respectively.²¹ SHELXTL was used for structural solution by direct methods and refinement by full-matrix least-squares on *F*².²² Anisotropic refinement was performed for all the non-hydrogen atoms. A riding model was used to fix the positions of the hydrogen atoms, and they were refined isotropically. The crystallographic data for these compounds (3–6) are given in Table S2 (see the Supporting Information).

COMPUTATIONAL DETAILS

All the calculations were carried out using GAUSSIAN 09 programs.²³ The geometry of compounds 5 and 6 was optimized initially at the B3LYP level of theory using a LANL2DZ basis set for germanium and chalcogens (S or Se) and a 6-311+G* basis set for the rest of the elements. As the computed Ge–O–Ge bond angles deviated from the

experimentally observed values by a large value of 22.65° and 17.58° in compounds 5 and 6, we planned to use other basis sets, respectively. Accordingly, further optimizations were carried out by sequentially lowering the basis set used for carbon and hydrogen atoms (Table S3; see the Supporting Information). As a 3-21G* basis set for these elements gave better Ge–O–Ge bond angles than the other basis sets (Table S3; see the Supporting Information), the results obtained by using this basis set have been taken for discussion. To further probe this deviation, we have performed a partial optimization by freezing the Ge–O–Ge bond angle to the experimentally observed value. The fully relaxed geometries in both the cases are found to be only ~2 kcal/mol lower in energy compared to the partially optimized structures. This suggests that the Ge–O–Ge bond angle is quite flexible, and thus, the near-linear structure observed in the experiments could be due to other factors, such as crystal packing and intermolecular interactions. The difference in the bond angles may also be attributed to the difference in the oxygen to germanium donations as described (vide supra) in the NBO analysis.^{14,15} Except for this bond angle parameter, other parameters are in acceptable agreement to the single-crystal X-ray diffraction data (Table S4; see the Supporting Information). Though not the best (Table S3; see the Supporting Information), for a meaningful comparison of the results, the data obtained by optimizing the compound 3 using the basis set employed for compounds 5 and 6 have been considered for discussion.

Full and partial 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. The Weinhold's natural bond orbital (NBO) analysis was performed at the aforementioned level of theory using the coordinates obtained from fully optimized geometries.^{14,15} The same approach was used to calculate the natural population analysis (NPA) charges and orbital populations. NBO orbital plots were made using the Chemcraft software (<http://www.chemcraftprog.com>). AIM calculations¹⁶ were carried out starting from the aforementioned optimized geometry of these compounds at the B3LYP level of theory using a WBTS basis set for germanium and chalcogens (S or Se), a 6-311+G* basis set for N and O, and a 3-21G* basis set for C and H atoms.

ASSOCIATED CONTENT

Supporting Information

Plausible mechanism for the formation of compounds 3 and 4 (Scheme S1); computational details for calculating the free energy change for steps 1 and 2 shown in Scheme S1; B3LYP computed total energies along with the reaction enthalpies and free energies for the steps 1 and 2 in Scheme S1 (Table S1); molecular structure of digermylene oxide complex 4 (Figure S1); dihedral angle information for compounds 3–6 (Figure S2); molecular structure of dithiogermanic anhydride complex 5 (Figure S3); AIM calculations showing critical points for compound 3, 5, and 6 (Figures S4–S6); π -antibonding interaction between oxygen and germanium atoms in compounds 3, 5, and 6 (Figure S7); MOs of compounds 5 and 6 that show the mixing of Ge–O and Ge=E antibonding orbitals (Figure S8); π -bonding interaction between germanium and sulfur atoms in compound 5, π -antibonding interaction between germanium and sulfur atoms in compound 5, π -bonding interaction between germanium and selenium atoms in compound 6, π -antibonding interaction between germanium and selenium atoms in compound 6, interaction of the lone pair of electrons of nitrogen atom with Ge–S antibonding orbital in compound 5, interaction of the lone pair of electrons of oxygen atom with Ge–S antibonding orbital in compound 5, interaction of the lone pair of electrons of nitrogen atom with Ge–Se antibonding orbital in compound 6, interaction of the lone pair of electrons of oxygen atom with

Ge–Se antibonding orbital in compound **6** (Figure S9); HOMO and LUMO diagrams for compounds **3**, **5**, and **6** (Figure S10); crystal data and structure refinement parameters for compounds **3–6** (Table S2); variation of the Ge–O–Ge bond angles in compounds **3**, **5**, and **6** based on the basis set used with respect to the experimental values (Table S3); comparison of the important bond angles and lengths in compounds **3**, **5**, and **6** obtained from experimental studies with the corresponding values calculated using DFT calculations (Table S4); complete authors list for ref 23; and crystallographic information file (CIF) for compounds **3–6**. 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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