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COMMUNICATION

A Single-Step Conversion of Silathiogermylene to Germaacid Anhydrides: An Unusual Reactivity

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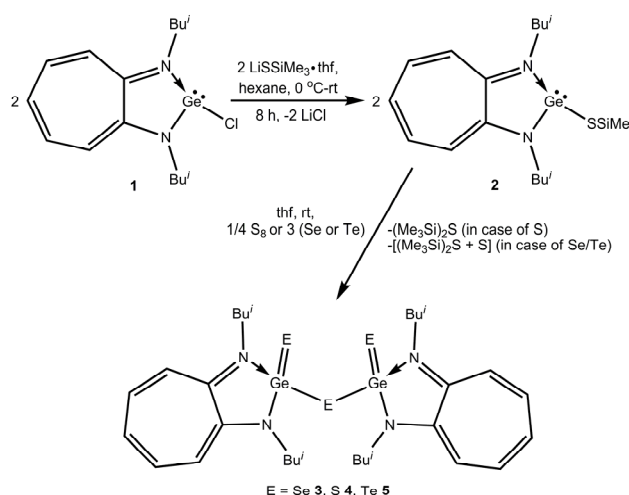
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A novel silathiogermylene $[\text{Bu}'_2(\text{ATI})\text{GeSSiMe}_3]$ (**2**) containing a reactive $\text{Ge(II)}-\text{SSiMe}_3$ moiety showed an unusual reaction when treated with elemental selenium and sulfur to afford the germaacid anhydrides $[\{\text{Bu}'_2(\text{ATI})\text{Ge}(\text{Se})\}_2\text{Se}]$ (**3**) and $[\{\text{Bu}'_2(\text{ATI})\text{Ge}(\text{S})\}_2\text{S}]$ (**4**) in excellent yields, respectively. This single-step conversion of compound **2** to compounds **3** and **4** involves condensation along with insertion and oxidative addition reactions and such reactivity of a germylene with elemental chalcogens is observed for the first time.

Germylenes are known to undergo a variety of reactions such as oxidative addition, insertion, Lewis acid-base adduct formation, and so forth.¹⁻³ Reactions of sterically bulky ligand stabilized germylenes with chalcogens have frequently offered oxidative addition products with $\text{Ge(IV)}=\text{E}$ bonds ($\text{E} = \text{O}, \text{S}, \text{Se}, \text{Te}$).⁴ Therefore, it can be asked, apart from the usual oxidative addition, can germylenes undergo other kinds of reactivity with chalcogens? Although examples are rare, the answer is yes and it depends on the substituents on the low-valent germanium centers. The substituents such as hydride and dicyclohexylphosphide on the low-valent germanium center have resulted in insertion along with/without the oxidative addition reactions.^{5,6} Nevertheless, there is no reaction of a germylene with chalcogens that involves condensation along with/without oxidative addition and insertion reactions. Therefore, we became interested in incorporating a labile functionality on the germylene center and studying the reactivity of the resultant novel functionalized germylene with elemental chalcogens. Accordingly, we report herein the synthesis and unusual reactivity of a novel aminotroponiminato(trimethylsilathio)germylene $[\text{Bu}'_2(\text{ATI})\text{GeS-SiMe}_3]$ (**2**) with elemental selenium and sulfur.

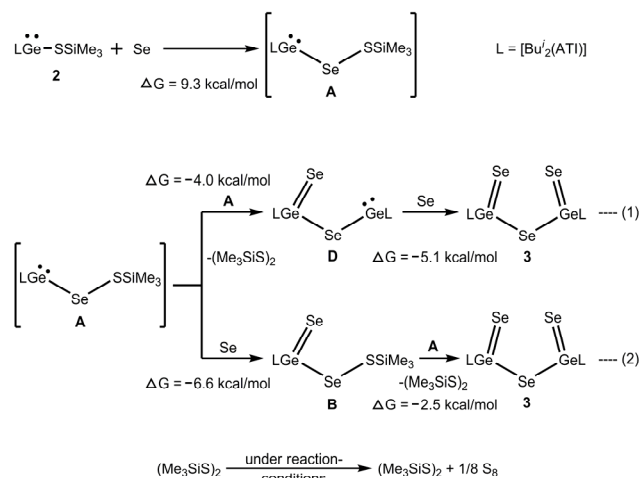
Aminotroponiminato(trimethylsilathio)germylene $[\text{Bu}'_2(\text{ATI})\text{GeS-SiMe}_3]$ (**2**) was obtained from the reaction of germylene monochloride complex $[\text{Bu}'_2(\text{ATI})\text{GeCl}]$ ^{7,8} (**1**) with LiSSiMe_3 in hexane at low temperature for 8 h (Scheme 1). Notably, compound **2** is the first example of a silathiogermylene and its synthesis gains further importance due to the absence of a free siloxygermylene.⁹



Scheme 1. Synthesis of aminotroponiminato(trimethylsilathio)germylene **2** and its reaction with elemental chalcogens.

With the isolation of compound **2**, we carried out its reaction with elemental chalcogens with an interest to find out the nature of reactivity. Thus, when compound **2** was reacted with selenium in a 2:3 molar ratio in tetrahydrofuran at room temperature for 12 hours, an unusual reaction apart from the simple oxidative addition reaction took place and afforded the first triselenogermaacid anhydride $[\{\text{Bu}'_2(\text{ATI})\text{Ge}(\text{Se})\}_2\text{Se}]$ (**3**) in an excellent yield (95.8%). A plausible mechanism for this reaction that involves condensation and insertion reactions apart from oxidative addition reaction is shown below (Scheme 2). The initial reaction of compound **2** with elemental selenium can occur in two possible ways: either an oxidative addition to afford compound $[\text{Bu}'_2(\text{ATI})\text{Ge}(\text{Se})-\text{S-SiMe}_3]$ (**I**) or an insertion to give compound **A** (Scheme S1, see supporting information). The thermodynamic stability calculations suggest that the anticipated oxidative addition product **I** is thermodynamically stable, nevertheless, further reaction sequences that we could think

of for the formation of compound **3** from **I** are all energetically unfavorable (Scheme S1).



Scheme 2. A plausible mechanism showing energetics (ΔG) for each step in the formation of compound **3**. Note: Under the actual reaction conditions, as selenium goes into solution from the solid state (that is not taken into consideration during computations), the associated increase in entropy should make the overall ΔG value negative for the conversion of **2** to **3**.

Whereas, the intermediate **A** either can self-condense to give **D** or can undergo oxidative addition with selenium to give **B** (Scheme 2). Both of these possibilities have favorable energetics (exothermic in nature). Intermediate **D** results in compound **3** through oxidative addition with selenium ($\Delta G = -5.1$ kcal/mol) while **B** condenses with **A** to afford the end-product **3** ($\Delta G = -2.5$ kcal/mol). It could be the anionic character of the sulfide stabilized by Lewis acidic silicon center that enables compound **2** to take the insertion path when reacted with elemental selenium as observed in case of the phosphide substituted germylene.⁶ If any of these pathways operates the reaction, the side product should be $\text{Me}_3\text{Si-S-SiMe}_3$. To check that the ^{29}Si NMR spectrum of the crude reaction mixture that afforded compound **3** was recorded. A signal at 13.1 ppm in CDCl_3 (10.9 in DMSO-d_6) was observed which is in the same region reported for $\text{Me}_3\text{Si-S-SiMe}_3$ (14.7 ppm in CDCl_3). As the ^{29}Si NMR spectroscopic data for $\text{Me}_3\text{Si-S-SiMe}_3$ is not reported, the observed value stands for either the expected side product $\text{Me}_3\text{Si-S-SiMe}_3$ or $\text{Me}_3\text{Si-S-SiMe}_3$ (if $\text{Me}_3\text{Si-S-SiMe}_3$ is decomposing to $\text{Me}_3\text{Si-S-SiMe}_3$ and sulfur under the reaction conditions).

Thus, for the first time, a condensation reaction has also been observed during the reaction of a chalcogen with a germylene apart from oxidative addition reaction which leads to a single step isolation of triselenogermaacid anhydride **3**. The importance of SiMe_3 group in the Ge(II)-SSiMe_3 moiety to bring out this unusual reactivity can be inferred from the observation that a stable and usual oxidative addition product $[(\text{Bu}^i_2\text{ATI})\text{Ge}(\text{Se})\text{SPh}]$ (**III**) has been isolated through the reaction of elemental selenium with $[(\text{Bu}^i_2\text{ATI})\text{GeSPh}]$ (**IV**) where a phenyl group is attached to the sulfur atom instead of the SiMe_3 group as in compound **2**.¹⁰ Further, to understand the role of sulfur atom in the SSiMe_3 group, the reaction of siloxygermylene $[(\text{Bu}^i_2\text{ATI})\text{GeOSiMe}_3]$ (**6**), an oxygen analogue of compound **2**, was carried out with elemental selenium and sulfur to obtain the usual and expected oxidative addition products $[(\text{Bu}^i_2\text{ATI})\text{Ge}(\text{E})\text{OSiMe}_3]$ (E = Se **7**, S **8**).¹¹ Therefore, it can be concluded that the observed unusual reactivity is a combined effect of the sulfur atom and SiMe_3 group.

To check whether this reaction is unique for selenium only or not, the reaction of compound **2** with elemental sulfur and tellurium were also carried out. The reaction of compound **2** with elemental sulfur (in a 1:1 molar ratio) and tellurium (in a 2:3 molar ratio) in tetrahydrofuran at room temperature also underwent in the aforementioned unusual fashion leading to $[(\text{Bu}^i_2\text{ATI})\text{Ge}(\text{S})_2\text{S}]$ (**4**) and $[(\text{Bu}^i_2\text{ATI})\text{Ge}(\text{Te})_2\text{Te}]$ (**5**) that are sulfur and tellurium analogues of compound **3**, respectively (Scheme 1). Therefore, the mechanism proposed for the formation of compound **3** should operate in the formation of the compounds **4** and **5** also. This is supported by the ^{29}Si NMR spectra on crude reaction mixtures that afforded compounds **4** and **5** which exactly matches with the same value (10.9 in DMSO-d_6) obtained for the side product in the case of compound **3**. On the basis of this NMR spectroscopic data and the stoichiometry of the reaction of compound **2** with elemental sulfur (1:1), it may be safely stated that $\text{Me}_3\text{Si-S-SiMe}_3$ is the side product. As indicated earlier, the decomposition of the expected side product, $\text{Me}_3\text{Si-S-SiMe}_3$, under the reaction conditions leads to the formation of $\text{Me}_3\text{Si-S-SiMe}_3$ with the elimination of sulfur. This sulfur is consumed in the reaction that results in compound **4**, but not in the reactions that afford compounds **3** and **5** when the required stoichiometry (2:3) is maintained.

Compounds **2**, **3**, and **4** are stable under N_2 atmosphere at room temperature. After isolation from the mother liquid, compound **5** started decomposing immediately and within half an hour, the isolated red free flowing powder turned blackish. Nevertheless, it was found to be stable in the mother liquid for up to our checking period of 12 h at $\sim 25^\circ\text{C}$. Compound **2** is freely soluble and stable in hexane, toluene, and tetrahydrofuran but decomposes in CDCl_3 . Whereas, compounds **3** and **4** are poorly soluble in toluene, tetrahydrofuran, and acetonitrile. Further, they are moderately soluble in dimethylsulfoxide but decompose in CDCl_3 . Compounds **2-5** were characterized in solution by NMR (^1H , ^{13}C , ^{29}Si , ^{77}Se , and ^{125}Te) spectroscopy. In the ^1H NMR spectrum, one singlet for nine methyl protons of the characteristic trimethylsilyl group of compound **2** was observed at 0.63 ppm that disappeared in case of compounds **3**, **4**, and **5**. In the ^{13}C NMR spectra of compounds **2** and **3-4**, nine and seven signals were observed, respectively. For the silicon atom of the trimethylsilyl group in compound **2**, a resonance at 10.16 ppm was observed in the ^{29}Si NMR spectrum. In the ^{77}Se NMR spectrum of compound **3**, two resonances were observed for the terminal and bridging selenium atoms at -370.4 and -324.1 ppm upon addition of a few milligrams (10 mg) of $\text{Cr}(\text{acac})_3$ (acac = acetylacetonate) as a relaxing agent for the ^{77}Se nuclei. These values are comparable to the selenium resonances in bidentate monoanionic ligand stabilized germanium compounds with formal $\text{Ge}=\text{Se}$ bonds.^{3h,i,6} Nevertheless, the selenium resonance in compound $[(\text{Bu}^i_2\text{ATI})\text{Ge}(\text{Se})\text{SePh}]$ (**V**) with a $\text{Ge}-\text{Se}$ single bond appears in a relatively downfield region (288.2 ppm).¹⁰ Two resonances were observed for bridging and terminal tellurium atom of compound **5** at -217.9 (for bridging Te) and -933.2 (for terminal Te) in its ^{125}Te NMR spectrum. The peaks are assigned based on the ^{125}Te NMR resonance reported (-884.1 ppm) for a similar compound $[(\text{Bu}^i_2\text{ATI})\text{Ge}(\text{Te})_2\text{O}]$ (**VI**).¹² Compounds **3** and **4** have been further structurally characterized through single crystal X-ray diffraction studies.¹³⁻¹⁵ The germanium centers in compounds **3** and **4** (Figure 1 and S1, respectively) are in distorted tetrahedral geometry. The average N-Ge-N bond angles in compounds **3** ($84.1(3)^\circ_{\text{av}}$) and **4** ($84.2(1)^\circ_{\text{av}}$) are almost similar to the same bond angles in compounds $[(\text{Bu}^i_2\text{ATI})\text{Ge}(\text{Se})\text{SePh}]$ (**V**) ($83.6(3)^\circ$) and $[(\text{Bu}^i_2\text{ATI})\text{Ge}(\text{S})\text{SPh}]$ (**VII**) ($84.1(1)^\circ$), respectively.^{3r} The Se-Ge-Se ($123.3(1)$ and $118.6(1)^\circ$) and S-Ge-S ($123.4(1)$ and $118.3(1)^\circ$) bond angles in compounds **3** and **4** are greater than those in compounds **V** ($114.5(1)^\circ$) and **VII** ($110.0(1)^\circ$), respectively.

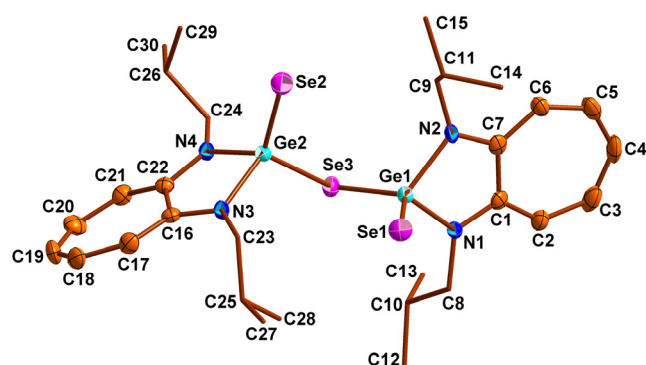


Figure 1. Molecular structure of $[(\text{Bu}'_2\text{ATI})\text{Ge}(\text{Se})_2\text{Se}]$ (**3**). All the hydrogen atoms are omitted for clarity. Thermal ellipsoids are drawn at 50% probability. Selected bond lengths (Å) and angles ($^\circ$): Ge(1)-Se(1) 2.202(1), Ge(2)-Se(2) 2.194(1), Ge(1)-Se(3) 2.291(2), Ge(2)-Se(3) 2.289(2), Ge(1)-N(1) 1.894(7), Ge(1)-N(2) 1.885(7), Ge(2)-N(3) 1.888(8), Ge(2)-N(4) 1.895(7); Se(1)-Ge(1)-Se(3) 123.3(1), Se(2)-Ge(2)-Se(3) 118.6(1), Ge(1)-Se(3)-Ge(2) 104.3(1), N(1)-Ge(1)-N(2) 83.8(3), N(3)-Ge(2)-N(4) 84.4(3).

In compound **3**, the average length of the formal Ge=Se bonds is 2.198(1) Å which is almost similar to the length of the same bond in compound **V** (2.205(1) Å). However, it is longer than that in the kinetically stabilized germanesellone Tbt(Tip)Ge=Se (**VIII**) (2.180(2) Å) [Tbt = 2,4,6-tris{bis(trimethylsilyl)methyl}phenyl; Tip = 2,4,6-tri(isopropyl)phenyl].^{4h} The average length of the Ge-Se bonds is 2.290(2)_{av} Å and the Ge-Se-Ge angle is 104.3(1) $^\circ$. The torsional angle between the formal Ge(1)=Se(1) and Ge(2)=Se(2) bonds is 76.8(1) $^\circ$.

In compound **4**, the average Ge=S bond length (2.080(1)_{av} Å) is comparable to that in compounds **VII** (2.070(1) Å) and $\{\text{N}(\text{SiMe}_3)\text{C}(\text{Ph})\text{C}(\text{SiMe}_3)(\text{C}_3\text{H}_4\text{N}-2)\}\text{Ge}(\text{S})_2\text{S}$ (**IX**) (2.066(4)_{av} Å).^{4c} But, it is longer than the same bond in the kinetically stabilized germanethione [Tbt(Tip)Ge=S] (**X**) (2.049(3) Å) [Tbt = 2,4,6-tris{bis-(trimethylsilyl)methyl}-phenyl; Tip = 2,4,6-tris(isopropyl)phenyl].^{4h} The average length of the Ge-S bonds is 2.220(1)_{av} Å and the Ge-S-Ge bond angle is 105.7(1) $^\circ$. The torsional angle between the formal Ge(1)=S(1) and Ge(2)=S(2) bonds is 77.1(1) $^\circ$.

Notes and references

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Electronic Supplementary Information (ESI) available: experimental procedures, various reaction pathways and their thermochemical feasibility for the formation of compound **3** from compound **2** and elemental selenium (Scheme S1), thermochemical variables for reactants, products, and reaction steps shown in scheme S1 (Table S1), X-ray data collection for compounds **3** and **4**, crystal data and refinement parameters for compounds **3** and **4** (Table S2), molecular structure of $\{(\text{Bu}'_2\text{ATI})\text{Ge}(\text{S})_2\text{S}\}_2$ (**4**) (Figure S1), ¹²⁵Te NMR spectrum of compound **5** (Figure S2), computational details, and coordinates of the optimized geometries for compounds **2**, **3**, **I**, **II**, **A-E**, Se₈, S₈, (Me₃SiS)₂, and (Me₃Si)₂S. See DOI: 10.1039/c000000x/

†† CCDC 1017826 (for **3**) and CCDC 1028134 (for **4**) contain crystallographic information files which can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif

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- 11 The characteristic nine methyl protons of SiMe₃ group in compounds **7** and **8** were observed in their ¹H NMR spectra (0.17 and 0.16 ppm, respectively). Compound **6** was structurally characterized by single crystal X-ray diffraction method also. The experimental details and results along with other results will be published elsewhere.
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