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Single-step conversion of silathiogermylene to germaacid anhydrides: unusual reactivity†‡

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A novel silathiogermylene [Bu$^i_2$(ATI)GeSSiMe$_3$] (**2**) containing a reactive Ge(II)-SSiMe$_3$ moiety showed an unusual reaction when treated with elemental selenium and sulfur to afford the germaacid anhydrides [{Bu$^i_2$(ATI)Ge(Se)}$_2$Se] (**3**) and [{Bu$^i_2$(ATI)Ge(S)}$_2$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 Ge(IV)=E bonds (E = O, S, Se, Te).[4] Therefore, it can be asked, apart from the usual oxidative addition, can germylenes undergo other kinds of reactions 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 hydrides and dicyclohexylphosphides 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 reaction of the resultant novel functionalized germylene with elemental chalcogens. Accordingly, we report herein the synthesis and unusual reactivity of a novel aminotroponiminato(trimethylsilathio)germylene [Bu$^i_2$(ATI)Ge-SSiMe$_3$] (**2**) with elemental selenium and sulfur.

Aminotroponiminato(trimethylsilathio)germylene [Bu$^i_2$(ATI)Ge-SSiMe$_3$] (**2**) was obtained by the reaction of the germylene monochloride complex [Bu$^i_2$(ATI)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]

With the isolation of compound **2**, we carried out its reaction with elemental chalcogens with interest in finding 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

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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 {(Bu$^i_2$ATI)Ge(S)}$_2$S (**4**) (Fig. S1), ^{125}Te NMR spectrum of compound **5** (Fig. S2), computational details, and coordinates of the optimized geometries for compounds **2**, **3**, **I**, **II**, **A–E**, Se$_8$, S$_8$, (Me$_3$SiS)$_2$ and (Me$_3$Si)$_2$S. CCDC 1017826 (**3**) and 1028134 (**4**). For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c5cc00169b
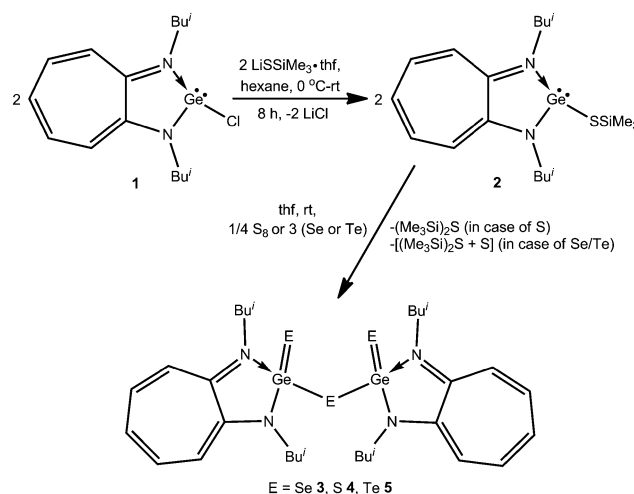
Scheme 1 Synthesis of aminotroponiminato(trimethylsilathio)germylene **2** and its reaction with elemental chalcogens.
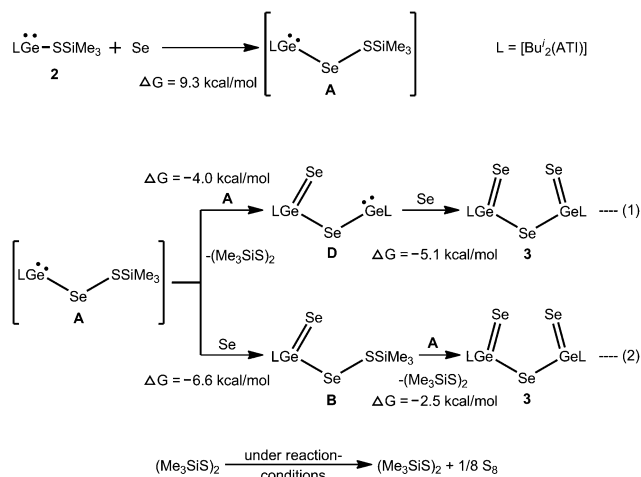
Scheme 2 A plausible mechanism showing energetics (ΔG) for each step in the formation of compound **3**. Note: under the actual reaction conditions, as selenium goes into solution from the solid state (that is not taken into consideration during computations), the associated increase in entropy should make the overall ΔG value negative for the conversion of **2** to **3**.

simple oxidative addition reaction took place and afforded the first triselenogermaacid anhydride [{(Bu$^i_2$ATI)Ge(Se)}$_2$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 in Scheme 2. The initial reaction of compound **2** with elemental selenium can occur in two possible ways: either an oxidative addition to afford compound [Bu$_2$(ATI)Ge(Se)-S-SiMe$_3$] (**I**) or an insertion to give compound **A** (Scheme S1, ESI‡). 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, ESI‡).

Whereas, 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^{-1}) while **B** condenses with **A** to afford the end-product **3** ($\Delta G = -2.5$ kcal mol^{-1}). 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 the case of the phosphide substituted germylene.[6] If any of these pathways operate the reaction, the side product should be Me$_3$Si–S–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 Me$_3$Si–S–SiMe$_3$ (14.7 ppm in CDCl$_3$). As the ^{29}Si NMR spectroscopic data for Me$_3$Si–S–S–SiMe$_3$ are not reported, the observed value stands for either the expected side product Me$_3$Si–S–S–SiMe$_3$ or Me$_3$Si–S–SiMe$_3$ (if Me$_3$Si–S–S–SiMe$_3$ decomposes to Me$_3$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 and insertion reactions which leads to a single-step isolation of triselenogermaacid anhydride **3**. The importance of the SiMe$_3$ group in the Ge(II)-SSiMe$_3$ moiety to bring about this unusual reactivity can be inferred from the observation that a stable and usual oxidative addition product [(Bu$^i_2$ATI)Ge(Se)SPh] (**III**) has been isolated through the reaction of elemental selenium with [(Bu$^i_2$ATI)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 the sulfur atom in the SSiMe$_3$ group, the reaction of siloxygermylene [Bu$^i_2$(ATI)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 [Bu$^i_2$(ATI)Ge(E)-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 was 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 [{(Bu$^i_2$ATI)Ge(S)}$_2$S] (**4**) and [{(Bu$^i_2$ATI)Ge(Te)}$_2$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 also operate in the formation of the compounds **4** and **5**. This is supported by the ^{29}Si NMR spectra of 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 reaction that gave compound **3**. On the basis of these NMR spectroscopic data and the stoichiometry of the reaction of compound **2** with elemental sulfur (1 : 1), it may be safely stated that Me$_3$Si–S–SiMe$_3$ is the side product. As indicated earlier, the decomposition of the expected side product, Me$_3$Si–S–S–SiMe$_3$, under the reaction conditions leads to the formation of Me$_3$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 of germylene and chalcogen (2 : 3) is maintained.

Compounds **2**, **3**, and **4** are stable under a dry 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 ~ 25 °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 (^{1}H, ^{13}C, ^{29}Si, ^{77}Se, and ^{125}Te) spectroscopy. In the ^{1}H 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 compounds **3**, **4**, and **5**. In the ^{13}C NMR spectra of compounds **2**, **3** and **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 Cr(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 Ge=Se bonds.[3h,i,6] Nevertheless, the selenium resonance in compound [(Bu$^i_2$ATI)Ge(Se)SePh] (**V**) with a Ge−Se single bond appears in a relatively downfield region (288.2 ppm).[10] Two resonances were observed for bridging and terminal tellurium atoms 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 [{(Bu$^i_2$ATI)Ge(Te)}$_2$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** (Fig. 1 and Fig. S1, ESI‡ respectively) are in distorted tetrahedral geometry. The average N–Ge–N bond angles in compounds **3** (84.1(3)$°_{av}$) and **4** (84.2(1)$°_{av}$) are almost similar to the same bond angles in compounds [(Bu$^i_2$ATI)Ge(Se)SePh] (**V**) (83.6(3)°) and [(Bu$^i_2$ATI)-Ge(S)SPh] (**VII**) (84.1(1)°), respectively.[10] The Se–Ge–Se (123.3(1) and 118.6(1)°) and S–Ge–S (123.4(1) and 118.3(1)°) bond angles in compounds **3** and **4** are greater than those in compounds **V** (114.5(1)°) and **VII** (110.0(1)°), respectively.

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)°. The torsional angle between the formal Ge(1)=Se(1) and Ge(2)=Se(2) bonds is 76.8(1)°.
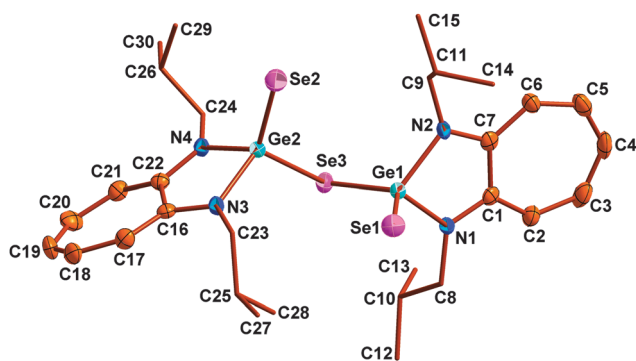
Fig. 1 Molecular structure of [{(Bu$^i_2$ATI)Ge(Se)}$_2$Se] (**3**). All the hydrogen atoms are omitted for clarity. Thermal ellipsoids are drawn at 50% probability. Selected bond lengths (Å) and angles (°): Ge(1)−Se(1) 2.202(1), Ge(2)−Se(2) 2.194(1), Ge(1)−Se(3) 2.291(2), Ge(2)−Se(3) 2.289(2), Ge(1)−N(1) 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 **4**, the average Ge=S bond length (2.080(1)$_{av}$ Å) is comparable to that in compounds **VII** (2.070(1) Å) and {[N(SiMe$_3$)C(Ph)C(SiMe$_3$)(C$_5$H$_4$N-2)]Ge(S)}$_2$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).[4h] The average length of the Ge−S bond is 2.220(1)$_{av}$ Å and the Ge−S−Ge bond angle is 105.7(1)°. The torsional angle between the formal Ge(1)=S(1) and Ge(2)=S(2) bonds is 77.1(1)°.

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11 The characteristic nine methyl protons of SiMe$_3$ group in compounds **7** and **8** were observed in their ^{1}H 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 along with other results will be published elsewhere.

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