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Desulfurization of isothiocyanates by a divalent germanium amide†

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Ge[N(SiMe₃)₂]₂ reacts with isocyanates but its reactivity with the related heavier congeners has not been explored. Its reaction with tertiary isothiocyanates results in the abstraction of the sulfur atom to yield a germanium(IV) dimer [(SiMe₃)₂N]₂GeSe]₂ in high yield. The reaction with *tert*-butylisoselecyanate produced the related dimer [(SiMe₃)₂N]₂GeSe]₂ within 5 minutes as shown using ⁷⁷Se NMR spectroscopy.

Germanium(II) amides are divalent germanium compounds that are stabilized by the presence of sterically encumbering substituents. These compounds can function as both Lewis acids and Lewis bases as they possess a vacant p-orbital and also a lone pair of electrons at germanium. In terms of reactivity, one of the most versatile germanium(II) amides is Ge[N(SiMe₃)₂]₂ (**1**) that was first reported in 1974.^{1,2} Compound **1** along with its tin analogue Sn[N(SiMe₃)₂]₂ has been shown to react with a variety of heterocumulenes including carbon dioxide and *N*-substituted isocyanates.^{3–5} Treatment of Ge[N(SiMe₃)₂]₂ with CO₂ resulted in the formation of the dimer [Ge(OSiMe₃)₂]₂ with the concomitant formation of both an isocyanate Me₃SiNCO and a symmetric carbodiimide Me₃SiNCNSiMe₃. In reactions with isocyanates RNCO only an unsymmetrical carbodiimide Me₃SiNCNR was generated along with the dimer.

However, efforts directed at the reaction of **1** with heavier chalcogen-containing compounds such as carbon disulfide CS₂ and isothiocyanates RNCS were found to be unsuccessful, despite the fact that the tin(IV) amide MeN(SnMe₃)₂ reacts with CS₂ to yield the isothiocyanate MeNCS and (Me₃Sn)₂S⁶ and N(SnMe₃)₃ reacts with CS₂ to yield Me₃SnNCS and (Me₃Sn)₂S.⁷

There are similarities in the chemistry of metal(II) amides in Groups 12 and 14, and it was shown that the cadmium(II) amide Cd[N(SiMe₃)₂]₂ reacts with ^tBuNCS and CyNCSe to yield the corresponding chalcogenides Cd[Q(SiMe₃)₂]₂ (Q = S or Se) and Me₃SiNCR (R = ^tBu or Cy).⁸ The reaction of Sn[N(SiMe₃)₂]₂ with CS₂ or Bu^tNCS did not produce any products even at elevated temperatures, the reaction of Sn[N(SiMe₃)₂]₂ with CyNCSe was also unsuccessful, and no attempts of reacting germylene **1** with these types of reagents were reported.⁹ However, the germylene (i-Pr)₂NB(NDmp)₂Ge was shown to react with RNCS reagents (R = ^tBu or adamantyl) to yield a product containing a Ge₃S ring formed by the desulfurization of the isothiocyanates.¹⁰

In order to determine if **1** would react with isothiocyanates, a benzene solution of **1** was combined with two equiv. of *tert*-butylisothiocyanate (^tBuNCS) at room temperature, which resulted in the immediate fading of the orange color of **1**. After a reaction time of 2 h a large amount of needle-like colorless crystals precipitated from the reaction mixture when the solution was concentrated, which were washed with hexane, isolated, and analyzed by ¹H and ¹³C NMR spectroscopy in benzene-*d*₆. Under more dilute conditions, the crystalline product precipitated from the solution during the removal of the solvent under reduced pressure. A singlet at δ 0.51 ppm was observed in the ¹H NMR spectrum of the product and a single feature at δ 7.08 ppm was present in the ¹³C NMR spectrum. Both these features were sharp, in contrast to the broad resonances that were observed for the [Ge(OSiMe₃)₂]₂ dimer.⁵

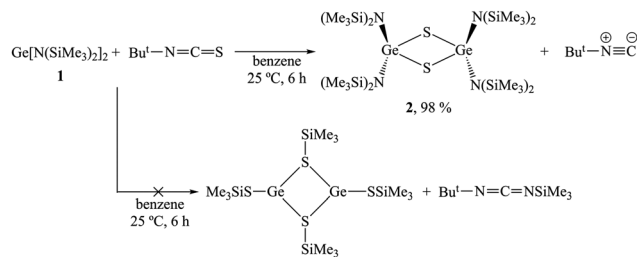
In order to unambiguously identify the product the crystals obtained were analyzed by X-ray diffraction. Instead of being the sulfur analogue of [Ge(OSiMe₃)₂]₂, the product formed was identified to be [Ge(N(SiMe₃)₂)₂(μ-S)]₂ (**2**), which was obtained in 98% overall yield (Scheme 1). The synthesis of **2** was previously reported in 1991 by the oxidative addition reaction of **1** with elemental sulfur.¹¹ However in this case the sulfur atoms in **2** must originate from the ^tBuNCS reagent.

An ORTEP diagram of **2** is shown in Fig. 1. The Ge₂S₂ framework in **2** is planar, with the Ge–S bond distances

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Scheme 1 Synthesis of $[\text{Ge}(\text{N}(\text{SiMe}_3)_2)_2(\mu\text{-S})]_2$ (**2**).

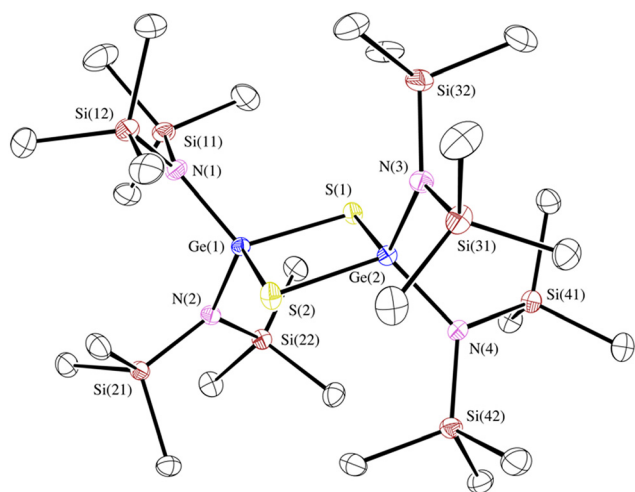


Fig. 1 ORTEP diagram of **2**. Thermal ellipsoids are drawn at 50% probability. Selected bond distances (Å): Ge(1)–S(1) 2.2482(7), Ge(1)–S(2) 2.2358(6), Ge(2)–S(1) 2.2355(6), Ge(2)–S(2) 2.2303(7), Ge(1)–N(1) 1.852(2), Ge(1)–N(4) 1.857(2), Ge(2)–N(2) 1.947(3), Ge(2)–N(3) 1.852(3). Selected bond angles ($^\circ$): Ge(1)–S(1)–Ge(2) 85.65(2), Ge(1)–S(2)–Ge(2) 86.07(2), S(1)–Ge(1)–S(2) 93.84(2), S(1)–Ge(2)–S(2) 94.34(2).

averaging 2.2375 Å and the Ge–N bond distances averaging 1.852(3) Å. The Ge–N bond distances are shorter than those in **1** that have an average distance of 1.876(5) Å¹² since germanium is in the tetravalent oxidation state in **2** rather than the divalent oxidation state in **1**. In the Ge_2S_2 framework of **2** the bond angles are slightly distorted from an ideal value of 90° by an average of $4.14(2)^\circ$ for the Ge–S–Ge bond angles and $4.09(2)^\circ$ for the S–Ge–S bond angles. The structure obtained is consistent with the previously reported structure.¹³

In order to ascertain the pathway for the formation of **2**, a sample of **1** was treated with two equiv. of $^t\text{BuNCS}$ at room temperature in benzene- d_6 on an NMR scale. Since the NMR samples were dilute no precipitation of **2** was observed. The ^1H NMR spectrum of the reaction mixture was recorded after 30 minutes and three features were visible including a singlet at δ 0.49 ppm, a second singlet at δ 0.82 ppm, and a feature centered at δ 0.90 ppm consisting of three individual lines as shown in Fig. 2. These three features are present in an intensity ratio of 8 : 1 : 1, respectively, and the spectrum remained unchanged after 12 h at room temperature.

In a separate NMR experiment, **1** was treated with one equiv. of $^t\text{BuNCS}$ at room temperature in benzene- d_6 . In this

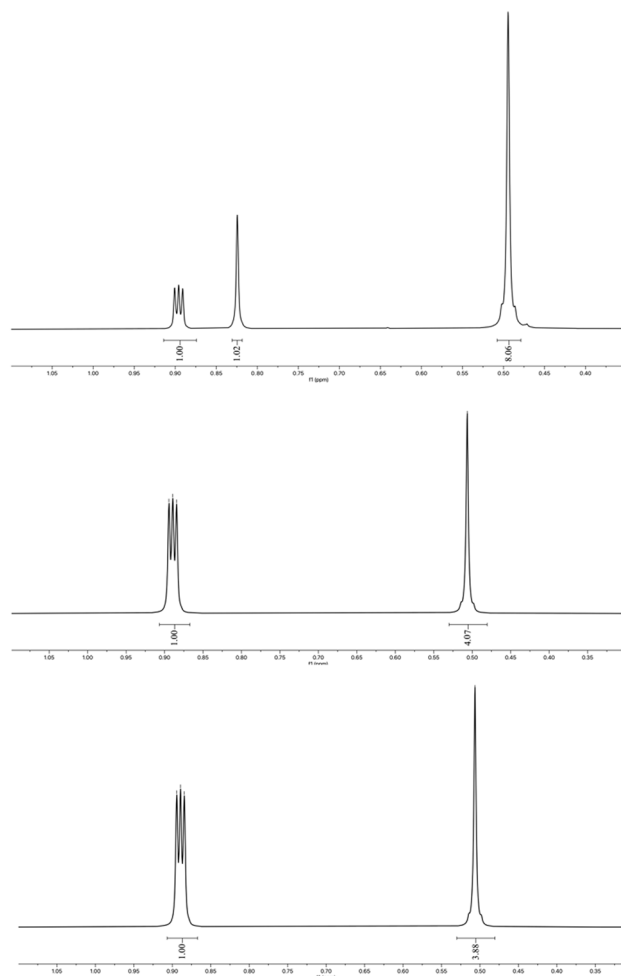
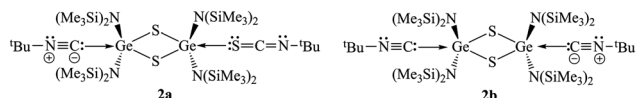


Fig. 2 ^1H NMR spectra of the NMR scale reaction of **1** with two equiv. of $^t\text{BuNCS}$ (top), the NMR scale reaction of **1** with one equiv. of $^t\text{BuNCS}$ (middle), and the addition of two equiv. of $^t\text{BuNC}$ to **2** (bottom).

case, the resulting ^1H NMR spectrum was similar to the previous experiment except that the singlet at δ 0.82 ppm was absent, the upfield resonance appeared at δ 0.51 ppm, and the grouping of three lines was again centered at δ 0.90 ppm. The two resonances were present in an intensity ratio of 4 : 1. In a third experiment, two equiv. of $^t\text{BuNC}$ were added to a sample of pure crystalline **2** in benzene- d_6 . The ^1H NMR spectrum for this sample was essentially identical to that obtained for the reaction of **1** with one equiv. of $^t\text{BuNCS}$, with a singlet at δ 0.51 ppm and a grouping of three lines centered at δ 0.90 ppm, again in an intensity ratio of 4 : 1 (Fig. 2).

These data indicate that the $^t\text{BuNC}$ formed in the reaction coordinates to the germanium centers in solution and also that only one equivalent of the isothiocyanate is needed to generate **2**. The complex present in solution after the reaction of **1** with two equiv. of $^t\text{BuNCS}$ is likely **2a** (Scheme 2) where both $^t\text{BuNC}$ formed in the reaction and the excess $^t\text{BuNCS}$ competes for coordination to the germanium atoms of **2**. This results in a slight shift of the ^1H NMR resonances for **2** as well as for the coordinated $^t\text{BuNCS}$ and $^t\text{BuNC}$. Two equiv. of the





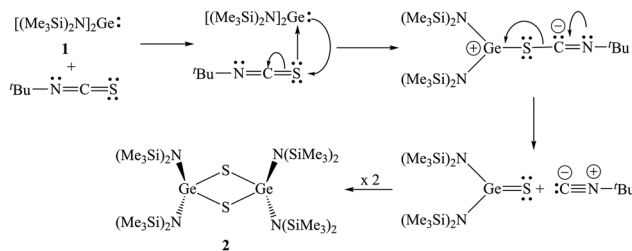
Scheme 2 Proposed structures of the hypervalent complexes of **2** formed in solution.

stronger donor 3-dimethylaminopyridine (DMAP) were added to **2** in benzene-*d*₆ and the ¹H and ¹³C NMR spectra were recorded. No complexation of DMAP to **2** was observed, likely because DMAP is too large of a ligand to fit into the sterically encumbered environment around the germanium atoms of **2**.

The resonances for free ^tBuNCS and ^tBuNC appear at δ 0.90 and 0.96 ppm, respectively. In the reaction of **1** with one equiv. of ^tBuNCS, the structure of the complex present in solution is **2b** (Scheme 2). This was confirmed by the identical ¹H NMR spectrum obtained by the addition of two equiv. of ^tBuNC to **2**, where **2** had been isolated on a preparative scale. The resonance for the coordinated ^tBuNC in both **2a** and **2b** appears as a grouping of three singlets and this suggests that there is restricted rotation about the C–N bond in the molecule due to the steric environment at the germanium centers, which renders the three methyl groups magnetically nonequivalent. When a sample of **2b** in benzene-*d*₆ was heated to 50 °C the three resonances disappeared and a singlet at δ 0.96 ppm was present indicating that the ^tBuNC is no longer coordinated to the germanium centers. Unfortunately, attempts to isolate **2b** by crystallization or precipitation were not successful.

Since only one equiv. of ^tBuNCS is required for the formation of **2** from **1**, it is possible that the formation of **2** might occur *via* the dimerization of a germathione that is formed as an intermediate in the reaction. These types of compounds are known but they require sterically encumbering ligands attached to the germanium center to kinetically stabilize the Ge=S double bond. The germathione Tbt(Tip)R'Ge=S employed the bulky Tbt and Tip ligands to stabilize the germanium–sulfur double bond. The germathione Tbt(Dis)Ge=S,¹⁴ This moiety could also be stabilized by using the less bulky Dis (–CH(SiMe₃)₂) ligand in place of the Tip ligand in Tbt(Dis)Ge=S,¹⁵ and recently the germathione (Eind)₂Ge=S that makes use of two annulated ring systems to stabilize the germanium–sulfur double bond has been reported.¹⁶ Since the –N(SiMe₃)₂ ligands are not sufficiently bulky to stabilize the Ge=S double bond, the germathione dimerizes to yield **2**.

A proposed pathway for the formation of **2** from **1** and ^tBuNCS is shown in Scheme 3. Initial coordination of ^tBuNCS to **1** through the sulfur atom occurs by the donation of one lone pair of electrons to the vacant p-orbital in **1**. Next a rearrangement ensues where the lone pair of electrons on germanium attacks the sulfur atom of the coordinated ^tBuNCS molecule, and a pair of electrons in the carbon–sulfur bond migrates to the carbon atom to form the zwitterionic species. The migration of the electrons in the sulfur–carbon bond then leads to the formation of the germanium–sulfur double bond in the germathione with the concomitant formation of ^tBuNC. The germathione subsequently dimerizes to generate **2**.

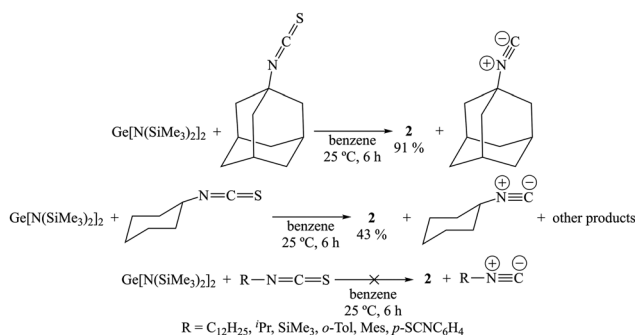


Scheme 3 Proposed pathway for the formation of **2**.

Germylene **1** was also reacted with other isothiocyanates R–NCS (Scheme 4). Of the surveyed reagents the full conversion of **1** to **2** was only successful for 1-adamantylisothiocyanate and **2** was isolated in 91% yield from this reaction. The reaction of **1** with cyclohexylisothiocyanate did produce some **2** but the reaction was not clean and provided **2** in only 43% yield after recrystallization. None of the other isothiocyanates reacted with **1** to yield **2** in any detectable amount. Therefore, it appears that only isothiocyanates that have their nitrogen atom bound to a tertiary carbon react with **1**, while cyclohexylisothiocyanate in which the nitrogen is bound to a secondary carbon does react but not to the extent of the *tert*-butyl and adamantyl derivatives. Therefore, **1** cleanly provides **2** by reacting with the same two isothiocyanates that also reacted with (i-Pr)₂NB(NDmp)₂Ge.¹⁰ Curiously, no formation of **2** was observed in the reaction of **1** with isopropylisothiocyanate, which also has a secondary carbon attached to the –NCS group.

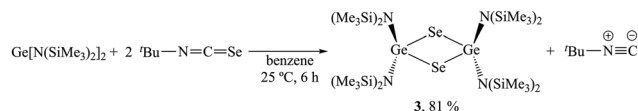
The selenium analogue of **2** [Ge(N(SiMe₃)₂)₂(μ-Se)]₂ (**3**) could also be prepared by the reaction of **1** with two equiv. of ^tBuNCSe (Scheme 5) and **3** was isolated in 78% yield as colorless crystals. The ¹H and ¹³C NMR spectra of **3** each contain a singlet at δ 0.52 and 7.25 ppm, respectively. Compound **3** was previously synthesized from **1** and elemental selenium,^{11,13} and the NMR data obtained in this study are consistent with the published results.¹³

In an attempt to observe the formation of [(Me₃Si)₂N]₂Ge=Se the reaction of **1** with two equiv. of ^tBuNCSe was conducted on an NMR scale and was monitored by ⁷⁷Se NMR spectroscopy. The ⁷⁷Se NMR spectrum of **3** con-



Scheme 4 Reaction of **1** with a variety of isothiocyanates.





Scheme 5 Synthesis of $[\text{Ge}(\text{N}(\text{SiMe}_3)_2)_2(\mu\text{-Se})]_2$ (**3**).

tains a single resonance at δ 573.9 ppm and that of the starting material $^t\text{BuNCSe}$ has a singlet at δ - 346.2 ppm. After *ca.* 5 minutes of mixing, the dimer **3** was already present, indicating that **3** forms very rapidly in the reaction. No resonances were observed in the range where signals for a germaselenone would be expected, such as the two germaselenones $\text{Tbt}(\text{Tip})\text{Ge}=\text{Se}$ and $\text{Tbt}(\text{Dis})\text{Ge}=\text{Se}$ that exhibit ^{77}Se NMR resonances at δ 940.6 and 872.7 ppm, respectively.¹⁵ Presumably, when $[(\text{Me}_3\text{Si})_2\text{N}]_2\text{Ge}=\text{Se}$ is formed in this reaction it immediately dimerizes to yield **3** and a similar process likely occurs with the sulfur analogue.

Conclusions

In conclusion, these findings indicate that **2** is readily formed in high yield from **1** and an isothiocyanate when the carbon bound to the nitrogen of the $-\text{NCS}$ group is tertiary as in $^t\text{BuNCS}$ and 1-adNCS. The dimer **2** is formed from **1** *via* an oxidative addition process involving the abstraction of the sulfur atom from the isothiocyanate. In the case of cyclohexylisothiocyanate CyNCS the carbon attached to the $-\text{NCS}$ group is secondary but the reaction proceeds to generate some **2**, but the reaction did not proceed as rapidly and did not provide **2** in high yield. The other isothiocyanates used in these investigations have a primary carbon or an aromatic carbon attached to the $-\text{NCS}$ group and no conversion of **1** to **2** was observed in any of these cases. Compound **1** also reacts with $^t\text{BuNCSe}$ to yield **3** that is the selenium analogue of **2**, and it was shown that **3** forms from **1** within five minutes by ^{77}Se NMR spectroscopy.

Data availability

The data supporting this article have been included as part of the ESI.† A CIF file for the structure of **2** has been deposited at the Cambridge Crystallographic Data Centre (2351450†).

Conflicts of interest

There are no conflicts to declare.

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