

## Synthesis and Structure of $[\{\text{PhC}(\text{N}t\text{Bu})_2\}_2\text{Ge}_2(\mu\text{-S})_2\text{Cl}_2]$ and a Germanium Dithiocarboxylate Analogue

Sakya S. Sen, Rajendra S. Ghadwal, Daniel Kratzert, Daniel Stern, Herbert W. Roesky,\* and Dietmar Stalke

*Institut für Anorganische Chemie der Universität Göttingen, Tammannstrasse 4, 37077 Göttingen, Germany*

Received November 15, 2010

$\text{LGeCl}$  ( $\text{L} = \text{PhC}(\text{N}t\text{Bu})_2$ ) was treated with elemental sulfur in THF to afford  $[\{\text{PhC}(\text{N}t\text{Bu})_2\}_2\text{Ge}_2(\mu\text{-S})_2\text{Cl}_2]$  (**2**) in 44% yield instead of yielding a compound containing a  $\text{Ge}=\text{S}$  double bond. It was revealed by the X-ray single-crystal structure that there is no  $\text{Ge}=\text{S}$  unit in **2**. Instead, **2** features a four-membered ring containing two germanium and two sulfur atoms. The four-membered  $\text{Ge}_2\text{S}_2$  ring is planar and is formed by a weak  $[2 + 2]$  cycloaddition interaction. Within the ring skeleton the two germanium atoms are arranged opposite to each other. Furthermore, **2** was reduced with 2 equiv of potassium graphite in THF to yield a potassium salt of a germathiocarboxylate analogue of composition  $[\{\text{PhC}(\text{N}t\text{Bu})_2\}_2\text{Ge}(\text{S})\text{SK}(\text{THF})_2]$  (**3**). Compounds **2** and **3** were characterized by single-crystal X-ray diffraction studies, NMR spectroscopy, EI-MS spectrometry, and elemental analysis.

### Introduction

The chemistry of sulfur complexes shows a rich diversity. Metal sulfur clusters are of considerable interest because of their remarkable chemical and physical properties.<sup>1</sup> Transition-metal clusters are among those which have been intensely studied in recent years.<sup>2</sup> In comparison to that, main group sulfur clusters are less common in the literature.<sup>3</sup> Network compounds that consist of group 14 elements linked by sulfur atoms have received considerable

attention, due to the great variety of interesting chemical and physical properties as well as applications.<sup>4</sup> Several synthetic approaches to this class of compounds have been developed. Thiostannates have been synthesized through a solvothermal route using different amines as structure-directing agents such as  $[\text{SnS}_2 \cdot \text{en}]$  ( $\text{en} = \text{ethylenediamine}$ ),<sup>5</sup>  $(\text{C}_6\text{H}_{20}\text{N}_4)_2[\text{SnS}_2] \cdot 2\text{H}_2\text{O}$ ,<sup>6</sup>  $(\text{C}_2\text{H}_{10}\text{N}_2)(\text{C}_2\text{H}_9\text{N}_2)_2[\text{Sn}_2\text{S}_6]$ ,<sup>7</sup>  $\text{R}_2\text{Sn}_3\text{S}_7$  ( $\text{R} = \text{tetramethylammonium (TMA)}$ ),<sup>8</sup> diazabicyclooctane (DABCO),<sup>9</sup> ammonium/tetraethylammonium (ATEA), tetraethylammonium (TEA)<sup>10</sup>,  $\text{R}'_2\text{Sn}_4\text{S}_9$  ( $\text{R}' = \text{tetrapropylammonium (TPA)}$ ), tetrabutylammonium (TBA)<sup>10</sup>, and  $(\text{enH})_4[\text{Sn}_2\text{S}_6]$ .<sup>11</sup> In this series of compounds thiogermanates were neglected. Moreover, a well-known problem in solvothermal syntheses is that many parameters such as temperature, time, solvent, and concentration influence the product formation. Although several efforts have been undertaken, chemists are still far from achieving a deeper understanding of the reaction mechanism occurring under solvothermal conditions.<sup>12</sup> As a result, there has been a great quest for an alternative

\*To whom correspondence should be addressed: E-mail: hroesky@gwdg.de.

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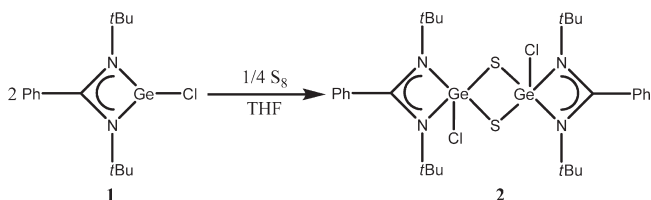
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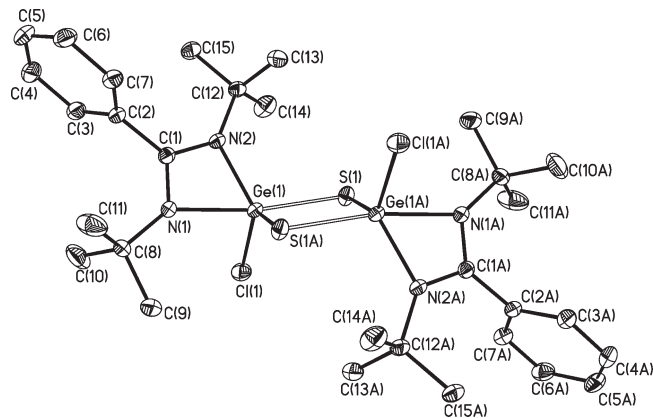
## Scheme 1. Preparation of 2



route. It has been found that the introduction of organic ligands with a designed functionality is a convenient route to prepare a variety of new main group sulfur clusters.<sup>4,13,14</sup> In view of these literature studies we were interested in synthesizing a thiogermanate bound with terminal halide, because the halide can easily be replaced to open a wide avenue to various new compounds. We have been interested in germanium polysulfides, due to their applicability as precursors for novel heteropolynuclear sulfur complexes composed of germanium and various transition metals. Earlier we treated the  $\beta$ -diketaminato germanium halide  $[\{\text{HC}(\text{CMeNAr})_2\}\text{GeX}]$  ( $\text{Ar} = 2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3$ ,  $\text{X} = \text{Cl}, \text{F}$ ) with elemental sulfur and obtained  $[\{\text{HC}(\text{CMeNAr})_2\}\text{Ge}(\text{S})\text{X}]$ <sup>15</sup> instead of a  $\text{Ge}_2\text{S}_2$  four-membered ring. Very recently we reported on the synthesis of a monomeric germanium(II) chloride of composition  $(\text{PhC}(\text{N}t\text{Bu})_2\text{GeCl})$  (**1**) with the support of a bulky benzamidinato ligand with *t*Bu substituents on the nitrogen atoms.<sup>16</sup> Furthermore, we were able to isolate a Ge(I) dimer by the reduction of **1** with finely divided potassium metal.<sup>16</sup> These results prompted us to study the oxidation reaction of **1** with elemental sulfur. Instead of obtaining the germathione analogue ( $> \text{Ge}=\text{S}$ ), we isolated  $[\{\text{PhC}(\text{N}t\text{Bu})_2\}_2\text{Ge}_2(\mu\text{-S})_2\text{Cl}_2]$  (**2**), containing two germanium atoms bridged by two sulfur atoms. Furthermore, each germanium atom is coordinated by a terminal chlorine atom.

## Results and Discussion

The reaction of **1** with elemental sulfur in THF at ambient temperature for 2 days smoothly afforded  $[\{\text{PhC}(\text{N}t\text{Bu})_2\}_2\text{Ge}_2(\mu\text{-S})_2\text{Cl}_2]$  (**2**) in moderate yield (0.18 g, 44%) (Scheme 1). The isolation of a compound with a terminal  $> \text{Ge}=\text{S}$  moiety is probably due to the reactivity of the  $> \text{Ge}=\text{S}$  unit, which can be assumed as an intermediate, that rapidly undergoes a  $[2 + 2]$  cycloaddition to yield **2**. Yellow crystals of **2** were obtained from a THF solution at  $-32^\circ\text{C}$ . The  $^1\text{H}$  NMR spectrum of **2** shows a singlet at  $\delta$  1.18 ppm for the 36 protons of the four *t*Bu groups and a multiplet resonance for the 10 aromatic protons ( $\delta$  6.86–7.26 ppm). The *t*Bu protons resonance in **2** exhibits a small downfield shift in comparison with that of the precursor **1** ( $\delta$  1.08 ppm for *t*Bu protons). The most abundant peak in the EI-MS spectrum of **2** appeared with the highest relative intensity at  $m/z$  371, which corresponds to the half-fragment of **2**. To understand the bonding situation of **2**, it was structurally characterized by single-crystal X-ray diffraction studies.



**Figure 1.** X-ray structure of **2**·2THF. Hydrogen atoms and two THF molecules are not shown for clarity. Selected bond distances (Å) and bond angles (deg):  $\text{Ge}(1)\text{—N}(2) = 1.9245(11)$ ,  $\text{Ge}(1)\text{—N}(1) = 2.0774(10)$ ,  $\text{Ge}(1)\text{—S}(1\text{A}) = 2.2090(4)$ ,  $\text{Ge}(1)\text{—Cl}(1) = 2.2096(4)$ ,  $\text{Ge}(1)\text{—S}(1) = 2.2978(4)$ ;  $\text{N}(2)\text{—Ge}(1)\text{—N}(1) = 65.48(4)$ ,  $\text{N}(2)\text{—Ge}(1)\text{—S}(1\text{A}) = 118.27(3)$ ,  $\text{N}(1)\text{—Ge}(1)\text{—S}(1\text{A}) = 90.37(3)$ ,  $\text{N}(2)\text{—Ge}(1)\text{—Cl}(1) = 112.55(3)$ ,  $\text{N}(1)\text{—Ge}(1)\text{—Cl}(1) = 91.92(3)$ ,  $\text{S}(1\text{A})\text{—Ge}(1)\text{—Cl}(1) = 124.808(14)$ ,  $\text{N}(2)\text{—Ge}(1)\text{—S}(1) = 106.02(3)$ ,  $\text{N}(1)\text{—Ge}(1)\text{—S}(1) = 170.89(3)$ ,  $\text{S}(1\text{A})\text{—Ge}(1)\text{—S}(1) = 91.121(13)$ ,  $\text{Cl}(1)\text{—Ge}(1)\text{—S}(1) = 94.599(14)$ ,  $\text{S}(1\text{A})\text{—Ge}(1)\text{—C}(1) = 103.99(3)$ ,  $\text{Cl}(1)\text{—Ge}(1)\text{—C}(1) = 106.61(3)$ ,  $\text{S}(1)\text{—Ge}(1)\text{—C}(1) = 138.95(3)$ ,  $\text{Ge}(1\text{A})\text{—S}(1)\text{—Ge}(1) = 88.881(13)$ .

The X-ray structure of **2**·2THF is shown in Figure 1. **2** crystallizes in the monoclinic space group  $P2_1/n$ .<sup>17</sup> The structure of **2**·2THF consists of a  $\text{Ge}_2\text{S}_2$  four-membered ring, and each germanium atom exhibits a trigonal-bipyramidal coordination polyhedron. Selected bond lengths and bond angles are given in the legend of Figure 1. The four-membered ring is planar, due to its inversion center. Two germanium atoms are arranged opposite to each other in the  $\text{Ge}_2\text{S}_2$  four-membered ring. To explain the coordination environment of the germanium atoms, Ge(1) is discussed in detail. The three equatorial positions of the trigonal-bipyramidal geometry are occupied by one nitrogen atom (N(2)) of the amidinato ligand, by one sulfur atom (S(1A)), and one chlorine atom (Cl(1)). The axial positions are occupied by the second sulfur atom (S(1)) and the remaining nitrogen atom (N(1)) of the amidinato ligand. The most striking features are the Ge—S bond lengths. The Ge—S bond distances of **2** are 2.2090(4)–2.2978(4) Å; they match well with those found for the Ge(IV) compound reported by Meller et al.<sup>18</sup> and are similar to those bond lengths reported for typical Ge—S single bonds (2.17–2.25 Å).<sup>19</sup> The Ge—S bond distances in **2** are longer when compared with that of the germathione  $\text{Tbt}(\text{Tip})\text{Ge}=\text{S}$  (2.049(3) Å).<sup>20</sup> Subsequently the Ge=S bond distance found in  $[\{\text{HC}(\text{CMeNAr})_2\}\text{Ge}(\text{S})\text{Cl}]$  ( $\text{Ar} = 2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3$ )<sup>15</sup> is 0.15 and 0.24 Å shorter than those in **2**, respectively. Recently Leung et al. reported the synthesis of sulfur-bridged dimers of the germaketene analogues

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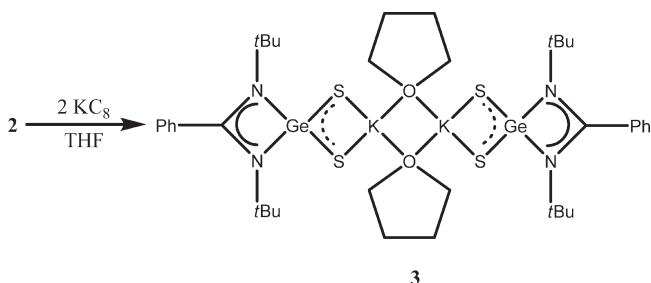
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Scheme 2. Preparation of **3**

[[ $(\text{TMS})\text{N}=\text{PPh}_2$ ] $_2\text{C}=\text{Ge}(\mu\text{-S})$ ] $_2$ .<sup>21</sup> In this compound the two Ge–S bond distances (2.230(2) and 2.236(2) Å) are almost identical, whereas those of **2** differ significantly. Therefore we assume that **2** forms a weak [2 + 2] cycloaddition product. The Ge–Cl<sub>av</sub> bond length of 2.2096(4) Å in **2** is marginally shorter than that of **1** (2.2572(13) Å)<sup>16</sup> and comparable to the Ge<sup>IV</sup>–Cl bond distance reported by Willey et al.<sup>22</sup>

Recently, we were able to isolate a silicon thioester analogue, [ $\{\text{PhC}(\text{N}t\text{Bu})_2\}\text{Si}(\text{S})\text{S}t\text{Bu}$ ], with a Si(=S)–S skeleton from the reduction of [ $\{\text{PhC}(\text{N}t\text{Bu})_2\}\text{SiCl}_2\text{S}t\text{Bu}$ ] with finely divided potassium metal.<sup>23</sup> Following this, we successfully isolated the germanium carboxylic acid analogue [ $\{\text{HC}(\text{CMeNAr})_2\}\text{Ge}(\text{E})\text{OH}$ ] (E = S, Se) by oxidative addition of elemental sulfur and selenium to the corresponding Ge–OH compound<sup>24a</sup> and also the germanium thiocarboxylic acid [ $\{\text{HC}(\text{CMeNAr})_2\}\text{Ge}(\text{S})\text{SH}$ ] (Ar = 2,6-*i*Pr<sub>2</sub>C<sub>6</sub>H<sub>32</sub>)<sup>24b</sup> by insertion of elemental sulfur into the germylene–hydrogen bond and simultaneous oxidative addition with elemental sulfur. In view of these results, we became interested to see whether benzamidinato-stabilized **2** is also capable of forming the thiocarboxylate analogue or the LGe(S)–Ge(S)L compound.

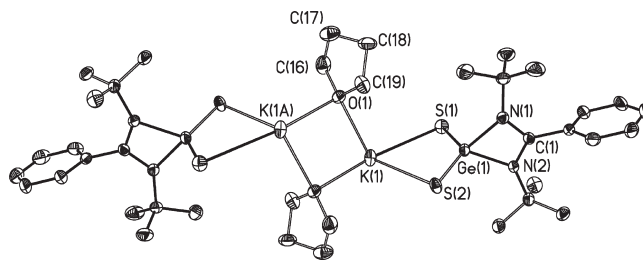
Treatment of **2** with 2 equiv of KC<sub>8</sub> in THF afforded a potassium salt of a germanium thiocarboxylic acid analogue, [ $\{\text{PhC}(\text{N}t\text{Bu})_2\}\text{Ge}(\text{S})\text{SK}(\text{THF})$ ] (**3**), in 39% yield (Scheme 2) instead of forming the anticipated LGe(S)–Ge(S)L (L = PhC(N*t*Bu)<sub>2</sub>). **3** is stable in solution and in the solid state at room temperature under an inert atmosphere. It is soluble in solvents such as toluene, THF, and diethyl ether. **3** was characterized by NMR spectroscopy, EI-MS spectrometry, elemental analysis, and single-crystal X-ray studies. The <sup>1</sup>H and <sup>13</sup>C NMR spectra of **3** display two sets of resonances from the benzamidinate ligand. In the <sup>1</sup>H NMR spectrum a downfield shift of the *t*Bu protons (δ 1.39 ppm) is observed in comparison with those of **2** (δ 1.18 ppm). In addition, **3** displays two more resonances at δ 1.72 and 3.56 ppm, which indicates the existence of coordinated THF in the complex. This was further confirmed by the <sup>13</sup>C NMR

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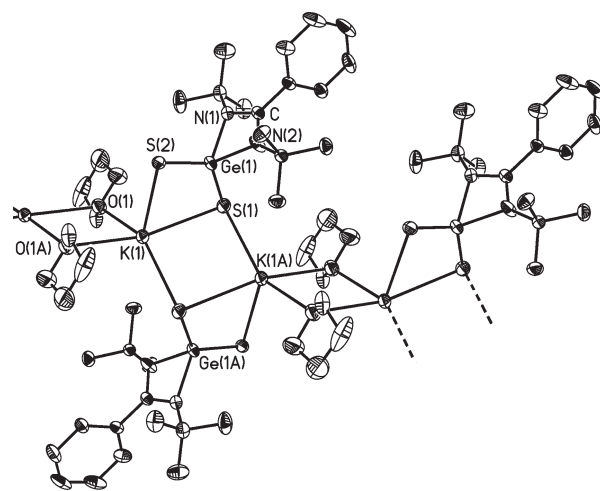
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**Figure 2.** X-ray structure of **3** at the 50% probability level. Hydrogen atoms are not shown for clarity. Selected bond distances (Å) and bond angles (deg): Ge(1)–N(2) = 1.9595(17), Ge(1)–N(1) = 1.9744(16), Ge(1)–S(2) = 2.1601(10), Ge(1)–S(2′) = 2.067(7), Ge(1)–S(1) = 2.1184(6), K(1)–O(1) = 2.852(12), K(1)–O(1′) = 2.74(2), K(1)–S(1) = 3.1743(7), K(1)–S(2) = 3.185(9), K(1)–S(2′) = 3.203(6); N(2)–Ge(1)–N(1) = 66.83(7), N(2)–Ge(1)–S(2′) = 112.7(3), N(2)–Ge(1)–S(1) = 113.16(6), N(1)–Ge(1)–S(1) = 110.93(5), S(2′)–Ge(1)–S(1) = 123.10(18).



**Figure 3.** Molecular structure of **3** in the solid state, elucidating the head-to-tail connection between the dimers to give the overall coordination polymer.

spectrum, which exhibits resonances at δ 26.8 and 67.8 ppm. The molecular ion was not observed in the EI-MS spectrum, although it exhibited a fragment at *m/z* 479 as the ion with the highest mass, which indicates the half-fragment of **3**.

In order to elucidate the bonding situation in **3**, it was further structurally characterized by single-crystal X-ray diffraction studies.<sup>17</sup> The molecular structure of **3** is shown in Figure 2. Selected bond lengths and angles are given in the caption to the figure. **3** crystallizes in the monoclinic space group *P*2<sub>1</sub>/*c*. The solid-state structure consists of the dimer [LGeS<sub>2</sub>K·THF]<sub>2</sub>, generated by a center of inversion in the middle of the K<sub>2</sub>O<sub>2</sub> four-membered ring. The two potassium atoms are slightly asymmetrically bridged (K–O = 2.85 vs 2.75 Å) by the two THF molecules in the dimer. This bridging is quite rare in THF coordination to potassium.<sup>25</sup> The potassium atom is five-coordinate. Two oxygen atoms of the THF molecules and three

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sulfur atoms (K(1)–S(1) = 3.1743(7) Å, K(1)–S(2) = 3.1208(69) Å, K(1)–S(2') = 3.2030(6) Å) reside in its coordination environment. The symmetry equivalent of S(1) ( $[+x, 1 + y, +z]$ ) at a distance of 3.17 Å of the closest neighboring dimer provides the link to give a coordination polymer along the *b* axis, depicted in Figure 3.

The potassium (K(1)), the two sulfur atoms (S(1) and S(2)), and the germanium atom (Ge(1)) form another four-membered ring, which is oriented perpendicularly to the neighboring GeN<sub>2</sub>C unit. The central Ge atom is almost ideally tetrahedrally coordinated by the two nitrogen atoms of the amidinato ring and two sulfur atoms.

The structure is disordered with respect to the bridging THF molecule, one of the *t*Bu groups, and one of the sulfur atoms (S(2)) bridging the potassium and germanium atoms. Nevertheless, this disorder could successfully be modeled and all non-hydrogen atoms were refined anisotropically. The site occupation factors were refined to 0.59/0.41 (*t*Bu), 0.66/0.34 (THF), and 0.57/0.43 (S2), respectively.

### Conclusion

In summary,  $[\{\text{PhC}(\text{N}t\text{Bu})_2\}_2\text{Ge}_2(\mu\text{-S})_2\text{Cl}_2]$  (**2**) has been prepared and fully characterized. It was reduced with potassium graphite to afford a potassium salt of a dithiocarboxylate analogue of composition  $[\{\text{PhC}(\text{N}t\text{Bu})_2\}\text{Ge}(\text{S})\text{-SK}(\text{THF})_2]$  (**3**). The potassium cation was introduced from the reducing agent K<sub>2</sub>C<sub>8</sub>, to give a coordination polymer.

### Experimental Section

All manipulations were carried out under an inert gas atmosphere of dinitrogen using standard Schlenk techniques and in a dinitrogen-filled glovebox. Solvents were purified by a MBRAUN MB SPS-800 solvent purification system. All chemicals purchased from Aldrich were used without further purification. Compound **1** was prepared according to the literature method.<sup>16</sup> <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded using a Bruker Avance DPX 200 or a Bruker Avance DRX 500 spectrometer. The NMR spectra were recorded in C<sub>6</sub>D<sub>6</sub>. The chemical shifts  $\delta$  are given relative to SiMe<sub>4</sub>. EI-MS spectra were obtained using a Finnigan MAT 8230 instrument. Elemental analyses were performed by the Institut für Anorganische Chemie, Universität Göttingen. Melting points were measured in a sealed glass tube on a Büchi B-540 melting point apparatus.

**Preparation of 2.** A solution of **1** (0.40 g, 1.02 mmol) in THF (20 mL) was added to a stirred suspension of sulfur (0.038 g, 1.02 mmol) in THF (10 mL). The reaction mixture was stirred at room temperature for 2 days until the solution became transparent. Storage of the reaction mixture at –32 °C in a freezer for 7 days afforded the crystals of **2**·2THF, suitable for a X-ray structure determination (yield 0.18 g, 43.42%). Mp: 165–170 °C. For the elemental analysis **2**·2THF was kept overnight

under vacuum to remove the two noncoordinated THF molecules. Anal. Calcd for C<sub>30</sub>H<sub>46</sub>Cl<sub>2</sub>Ge<sub>2</sub>N<sub>4</sub>S<sub>2</sub> (743.1): C, 48.49; H, 6.24; N, 7.54. Found: C, 47.66; H, 6.63; N, 7.36. <sup>1</sup>H NMR (200 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C):  $\delta$  1.18 (s, 36H, *t*Bu), 6.86–7.26 (m, 10H, Ph) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (125.75 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C):  $\delta$  29.6 (CMe<sub>3</sub>), 42.8 (CMe<sub>3</sub>), 128.8, 131.8, 133.0, 137.2 (*Ph*), 164.4 (NCN) ppm. EI-MS: *m/z* (%) 371 [(M/2)<sup>+</sup>] (100).

**Preparation of 3.** THF (50 mL) was added to a mixture of **2** (1.09 g, 2.94 mmol) and potassium graphite (0.59, 4.41 mmol) at –78 °C. The resulting red mixture was stirred overnight. The solvent was then removed in vacuo, and the residue was extracted with THF (50 mL). The insoluble precipitate was filtered off, and the colorless filtrate was concentrated to yield colorless crystals of **3**, suitable for an X-ray structure determination (0.46 g, 38.65%). Mp: 192–198 °C. Anal. Calcd for C<sub>38</sub>H<sub>62</sub>Ge<sub>2</sub>K<sub>2</sub>N<sub>4</sub>O<sub>2</sub>S<sub>4</sub> (960.15): C, 47.61; H, 6.52; N, 5.84. Found: C, 47.12; H, 6.42; N, 6.27. <sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C):  $\delta$  1.39 (br, 36H, *t*Bu), 1.72 (br, 8H, THF), 3.56 (br, 8H, THF), 6.93–7.14 (m, 10H, Ph) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (125.75 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C):  $\delta$  26.8 (THF), 32.1 (CMe<sub>3</sub>), 53.7 (CMe<sub>3</sub>), 67.8 (THF), 128.9, 129.83, 136.68, 143.2 (*Ph*), 166.6 (NCN) ppm. EI-MS: *m/z* (%) 479 [M<sup>+</sup> – C<sub>19</sub>H<sub>31</sub>GeKN<sub>2</sub>OS<sub>2</sub>] (100).

**Crystal Structure Determination.** Shock-cooled crystals were selected and mounted under a nitrogen atmosphere using the X-TEMP device.<sup>17</sup> Data were collected at 100(2) K. Those for **2** were measured on a Bruker TXS-Mo rotating anode with Helios mirror optics and APEX II detector on a D8 goniometer, while those for **3** were collected on a INCOATEC Mo Microsource<sup>26</sup> with Quazar mirror optics and APEX II detector on a D8 goniometer. Both diffractometers were equipped with a low-temperature device and used Mo K $\alpha$  radiation ( $\lambda = 0.7173$  Å). The data for **2** and **3** were integrated with SAINT,<sup>27</sup> and an empirical absorption correction (SADABS) was applied.<sup>28</sup> The structures were solved by direct methods (SHELXS-97) and refined by full-matrix least-squares methods against *F*<sup>2</sup> (SHELXL-97).<sup>29</sup> All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were refined isotropically on calculated positions using a riding model with their *U*<sub>iso</sub> values constrained to equal to 1.5 times the *U*<sub>eq</sub> values of their pivot atoms for terminal sp<sup>3</sup> carbon atoms and 1.2 times these values for all other carbon atoms. Disordered moieties were refined using bond length restraints and isotropic displacement parameter restraints.

**Acknowledgment.** We are grateful to the Deutsche Forschungsgemeinschaft, the DNRFF, and the Center for Materials Crystallography for supporting this work.

**Supporting Information Available:** A table and CIF files giving crystal data for **2** and **3**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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