Synthesis of a germanium analogue of a dithiocarboxylic acid anhydride from the Ge(I) pyridyl-1-azaallyl dimer†

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The reaction of pyridyl-1-azaallyl germanium(II) chloride RGeCl (1) [R = {N(SiMe$_3$)C(Ph)C(SiMe$_3$)(C$_5$H$_4$N-2)}] with lithium metal afforded the dimeric germanium(I) compound [(RGe)$_2$] (2); compound 2 reacts with an excess of elemental sulfur to afford the novel germanium analogue of a dithiocarboxylic acid anhydride [{Ge(S)R}$_2$S] (4) *via* the insertion of elemental sulfur into the Ge(I)–Ge(I) bond followed by the oxidative-addition of elemental sulfur to the germanium(II) centres.

The synthesis of novel dimeric Ge(I) compound was first reported by Jones and co-workers in which the Ge(I) dimers exhibit a *trans*-bent geometry.[1] By using smaller substituents on the amidinato ligand, Roesky reported the synthesis of a germanium(I) dimer in a *gauche*-bent geometry.[2] Recently, Driess and co-workers have prepared a novel unsymmetrically substituted digermylene with a Ge(I)–Ge(I) bond.[3] One common feature among these Ge(I) compounds is that they show Ge–Ge interactions with a lone pair of electrons on each germanium atom. Theoretical studies indicate that multiple bond is not present in these Ge(I) dimers.

We have recently reported the synthesis and reactivities of pyridyl-1-azaallyl germanium(II) chloride **1**.[4–6] Herein, we report the synthesis of the germanium(I) pyridyl-1-azaallyl dimer **2** from the reduction of **1**. The reaction of **2** with an excess of sulfur afforded the unprecedented germanium analogue of a dithiocarboxylic acid anhydride **4**.

Treatment of [Ge{N(SiMe$_3$)C(Ph)C(SiMe$_3$)(C$_5$H$_4$N-2)}Cl] (**1**) with 1 equiv. of lithium metal in THF for 12 h afforded a dark green mixture. Dark green crystals of germanium(I) dimer [{[N(SiMe$_3$)C(Ph)C(SiMe$_3$)(C$_5$H$_4$N-2)]Ge}$_2$] (**2**) were obtained by extraction of the crude product with Et$_2$O followed by concentration and cooling at 0 °C (Scheme 1).

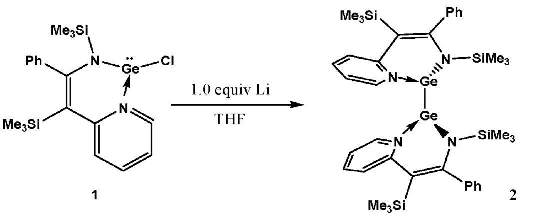
Compound **2** showed good solubility in THF, toluene, Et$_2$O and CH$_2$Cl$_2$. It remains stable in solution or in the solid state at room temperature in an inert atmosphere. Compound **2** has been characterized by elemental analysis, NMR spectroscopy‡ and X-ray structure analysis.§

The molecular structure of **2** is shown in Fig. 1. The coordination environment of the Ge(I) atoms exhibits a distorted tetrahedral geometry. The pyridyl-1-azaallyl ligand is bonded to the germanium centre in a N,N′-chelate fashion. The coordination sites of the Ge(I) centres are each occupied by the two N atoms of the azaallyl ligand and by the other Ge(I) atom. The lone pair of the Ge(I) occupies the remaining coordination site of the tetrahedron. The Ge–Ge bond length in **2** is 2.6021(8) Å, which is very close to the single Ge–Ge interaction (2.61 Å mean[7]), but significantly longer than that for typical digermenes, R$_2$GeGeR$_2$ (2.21–2.51 Å)[7] and the two structurally characterized digermynes (2.2850(6) and 2.2060(8) Å).[8,9] The Ge–Ge bond distance in **2** is in fact comparable to that of the structurally characterized amidinato Ge(I) dimer (2.6380(8) Å)[1] and that of the less bulky Ge(I) dimer (2.569(5) Å).[2] Like the bulky amidinato Ge(I) dimer,[1] compound **2** exhibits a *trans*-bent geometry. These observations suggest that Ge–Ge multiple bond is not present in **2**.

We have investigated the reactivity of **2** in order to study the bonding character between the Ge(I) centres in **2**. Treatment of **2** with an excess of sulfur afforded a yellowish-orange mixture. Extraction of the crude product with CH$_2$Cl$_2$ followed by concentration of filtrate afforded yellow crystals of [{Ge(S)[N(SiMe$_3$)C(Ph)C(SiMe$_3$)(C$_5$H$_4$N-2)]}$_2$S] (**4**).

The reaction of **2** with an excess of sulfur (Scheme 2) demonstrates that the Ge–Ge interaction in **2** is prone to insertion and the Ge(I) dimers can undergo an oxidative-addition reaction. The germanium compound **4** obtained is the first example of a heavier group 14 element analogue of a dithiocarboxylic acid anhydride. The germanium analogue of dithiocarboxylic acid has been recently prepared by Roesky and co-workers.[10]

The molecular structure of **4** is shown in Fig. 2. Each germanium atom is bonded to a pyridyl-1-azaallyl ligand in a N,N′-chelate fashion and to two sulfur atoms. The single bond distances between the germanium atoms and the central sulfur are 2.222(3) and 2.226(3) Å, respectively. The Ge=S bond distances on each side are 2.070(3) and 2.062(4) Å, which are similar to that of 2.056(2) Å in [Ge(S){N(SiMe$_3$)C(Ph)C(SiMe$_3$)(C$_5$H$_4$N-2)}Cl][6] and 2.053(6) Å in [{HC(CMeNAr)$_2$}Ge(S)Cl] (Ar = 2,6-Pr$^i_2$C$_6$H$_3$).[11] The bond distances are also close to the calculated Ge=S bond distance of 2.06 Å,[12] indicating the double bond nature between germanium and sulfur on each side of the molecule.



Scheme 1 Synthesis of compound **2**.

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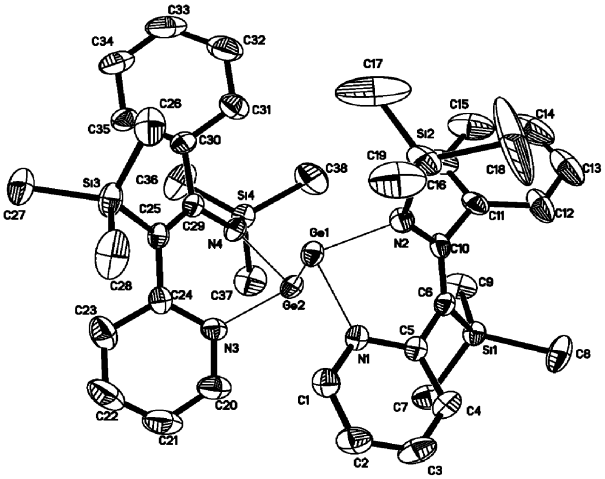
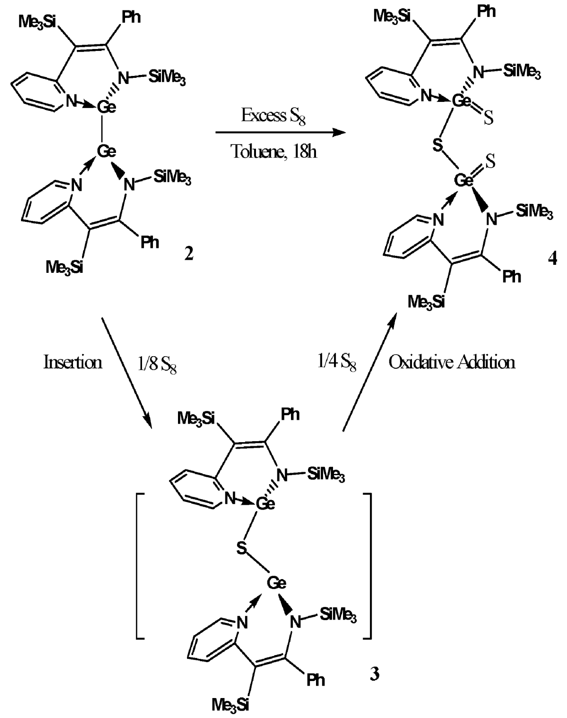


Fig. 1 ORTEP view (30% ellipsoid probability) of [{[N(SiMe$_3$)C(Ph)C(SiMe$_3$)(C$_5$H$_4$N-2)]Ge}$_2$] (**2**). Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (°): Ge(1)–Ge(2) 2.602(8), Ge(1)–N(1) 2.057(3), Ge(1)–N(2) 1.955(4), Ge(2)–N(4) 1.957(3), Ge(2)–N(3) 2.054(4), Si(1)–C(6) 1.907(4), Si(2)–N(2) 1.746(4), N(1)–C(5) 1.366(5), N(2)–C(10) 1.381(5), N(1)–C(1) 1.352(5), C(5)–C(6) 1.471(6), C(6)–C(10), 1.355(6); N(2)–Ge(1)–N(1) 86.9(2), N(2)–Ge(1)–Ge(2) 102.7(1), N(1)–Ge(1)–Ge(2) 83.4(1), N(4)–Ge(2)–N(3) 87.1(1), N(4)–Ge(2)–Ge(1) 102.8(1), N(3)–Ge(2)–Ge(1) 85.1(1), C(1)–N(1)–C(5) 120.3(4), C(1)–N(1)–Ge(1) 117.8(3), C(5)–N(1)–Ge(1) 121.8(3), C(10)–N(2)–Ge(1) 116.1(3).



Scheme 2 Synthesis of compound **4**.

In conclusion, we have prepared a germanium(I) dimer from the reduction of pyridyl-1-azaallyl germanium (II) chloride with lithium metal. Structural studies support that there are no multiple bond characters in the Ge(I) dimer. The reaction of the Ge(I) dimer with an excess of elemental sulfur afforded a novel germanium analogue of a dithiocarboxylic acid anhydride.

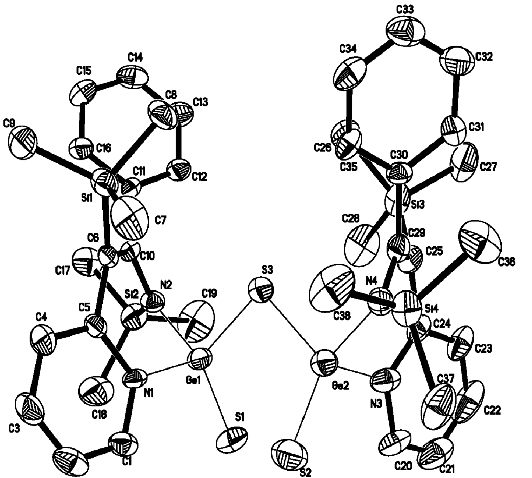


Fig. 2 ORTEP view (30% ellipsoid probability) of [{Ge(S)[N(SiMe$_3$)C(Ph)C(SiMe$_3$)(C$_5$H$_4$N-2)]}$_2$S] (**4**). Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (°): S(3)–Ge(1) 2.222(3), S(3)–Ge(2) 2.226(3), Ge(1)–S(1) 2.070(3), Ge(2)–S(2) 2.062(4), Ge(1)–N(2) 1.842(8), Ge(1)–N(1) 1.947(8), Ge(2)–N(4) 1.846(7), Ge(2)–N(3) 1.963(9), N(1)–C(5) 1.380(1), N(2)–C(10) 1.396(1), C(5)–C(6) 1.476(1), C(6)–C(10) 1.370(1); Ge(1)–S(3)–Ge(2) 101.4(1), N(2)–Ge(1)–S(1) 122.0(2), N(1)–Ge(1)–S(1) 113.0(2), N(2)–Ge(1)–S(3) 101.4(2), N(1)–Ge(1)–S(3) 101.9(2), S(1)–Ge(1)–S(3) 121.3(1), N(2)–Ge(1)–N(1) 91.8(3), C(1)–N(1)–Ge(1) 121.1(7), C(5)–N(1)–Ge(1) 118.5(6), N(4)–Ge(2)–S(2) 121.5(3), N(3)–Ge(2)–S(2) 113.8(3), N(4)–Ge(2)–S(3) 100.8(2), N(3)–Ge(2)–S(3) 102.7(2), S(2)–Ge(2)–S(3) 121.4(1).

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Notes and references

‡ *Selected spectroscopic data* for **2**: ^{1}H NMR (benzene-d_6): δ 0.24 (s, 9H, SiMe$_3$), 0.26 (s, 9H, SiMe$_3$), 6.06–6.12 (m, 1H, 5-py), 7.17–7.39 (m, 5H, Ph), 7.41–7.45 (m, 1H, 3-py), 7.78–7.82 (m, 1H, 4-py), 8.09–8.11 (d, 1H, 6-py). ^{13}C{^{1}H} NMR (benzene-d_6): δ 2.63, 3.74 (SiMe$_3$), 114.215 (*C*SiMe$_3$), 124.65, 130.01, 138.08, 142.23, 143.54, 145.94, 147.97, 156.45, 159.53 (Ph and Py), 164.60 (N*C*Ph). **4**: ^{1}H NMR (THF-d_8): δ −0.01 (s, 9H, SiMe$_3$), 0.16 (s, 9H, SiMe$_3$), 6.60–6.64 (t, 1H, 5-py), 7.02–7.28 (m, 5H, Ph), 7.36–7.40 (d, 1H, 3-py), 7.50–7.52 (t, 1H, 4-py), 7.81–7.83 (d, 1H, 6-py). ^{13}C{^{1}H} NMR (THF-d_8): δ 2.63, 3.31 (SiMe$_3$), 118.66 (*C*SiMe$_3$), 125.18, 128.08, 129.56, 131.50, 136.63, 137.37, 144.60, 146.18, 147.16 (Ph and Py), 159.18 (N*C*Ph).

§ *Crystal data* for **2**: $C_{38}H_{54}Ge_2N_4Si_4$, M = 824.39, crystal size = 0.50 × 0.40 × 0.30 mm, Flack parameter = −0.008(9), monoclinic, space group $P2_1$, a = 13.346(3), b = 11.006(3), c = 15.589(4) Å, β = 108.301(4)°, V = 2173.8(9) Å^3, Z = 2, D_c = 1.259 g cm^{-3}, μ = 1.523 mm^{-1}, λ = 0.71073 Å, T = 293(2) K, $2\theta_{max}$ = 25.00°, $F(000)$ = 860, 7263 independent reflections (R_{int} = 0.0342), $R1$ = 0.0397, $wR2$ = 0.0913 ($I > 2\sigma(I)$), largest diff. peak and hole: 0.597 and −0.281 e Å^{-3}. **4**: $C_{38}H_{54}Ge_2N_4S_3Si_4$, M = 920.57, crystal size = 0.40 × 0.30 × 0.20 mm, Flack parameter = 0.027(17), orthorhombic, space group $Pna2_1$, a = 24.360(6), b = 11.062(3), c = 17.424(5) Å, V = 4695(2) Å^3, Z = 4, D_c = 1.302 g cm^{-3}, μ = 1.546 mm^{-1}, λ = 0.71073 Å, T = 293(2) K, $2\theta_{max}$ = 28.07°, $F(000)$ = 1912, 11252 independent reflections (R_{int} = 0.1514), $R1$ = 0.0694, $wR2$ = 0.1370 ($I > 2\sigma(I)$), largest diff. peak and hole: 0.602 and −1.095 e Å^{-3}.

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