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Carbene-mediated synthesis of a germanium tris(dithiolene)dianion[†]

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While the 1:1 reaction of 3 with an N-heterocyclic carbene $(\{(Me)CN(i-Pr)\}_2C:)$ in THF resulted in ligand-substituted product 4, the corresponding 1:2 reaction (in the presence of H₂O) gives the first structurally characterized germanium tris(dithiolene)dianion 5 as the major product and the "naked" dithiolene radical 6[•] as a minor by-product. The structure and bonding of 4 and 5 were probed by experimental and theoretical methods. Our study suggests that carbene-mediated partial hydrolysis may represent a new method to access tris(dithiolene) complexes of main-group elements.

The intriguing non-innocent character of dithiolene ligands has fascinated chemists for more than five decades.¹⁻⁴ In contrast to the well documented dithiolene chemistry of transition metals,⁵⁻⁷ the corresponding dithiolene-based chemistry of main group elements remains quite limited.^{1,4} In particular, the literature reveals only a few tris(dithiolene) complexes of main group elements.^{4,8-17} This laboratory recently reported a stable lithium dithiolene radical anion (1°), via the reaction of the N-heterocyclic dicarbene (NHDC)¹⁸ with elemental sulphur (Scheme 1).¹⁹ Interestingly, radical 1[•] may well serve as a novel platform to explore the dithiolene chemistry of the main group elements. To this end, a series of magnesium²⁰ and boron²¹ dithiolene complexes have been reported. In addition, the first "naked" dithiolene radical anion (6•) (Scheme 1) was recently synthesized (by reaction of 1^{\bullet} with an imidazolium salt $[{(Me)CN(i-Pr)}_2CH]^+Cl^-, ^{22}$ which, surprisingly, participated in a synergic THF ring-open reaction with N-heterocyclic silvlene and the hexasulphide dianion. In addition, we recently reported the reaction of 1º with carbene-stabilized disilicon, which afforded the first silicon tris(dithiolene)dianion (2) (Scheme 1).¹⁶ Notably,

the carbene-stabilized disilicon complex functioned as a silicon transfer agent in this reaction.

Complexes of hypervalent group 14 elements are intriguing due to their unique structural/bonding nature, high reactivity, and possible utility in studying dynamic processes.²³ Interestingly, six-coordinate germanium(iv)-diketonate complexes have been explored as anticancer agents.²⁴ Notably, six-coordinate germanium atoms residing in an S₆ coordination environment are quite rare, the literature revealing only a germanium tris(dithiolene) complex reported nearly half a century ago.¹⁷ However, compelling structural detail of such compounds is lacking. Herein, we report the synthesis,²⁵ molecular structure,²⁵ and computations²⁵ of the first structurally characterized germanium tris(dithiolene)dianion (5).

The anionic chlorogermanium bis(dithiolene) complex 3 was prepared via a 2:1 reaction of 1° with GeCl₂ dioxane in THF.¹⁹ The subsequent 1:1 reaction of 3 with the N-heterocyclic carbene {(Me)CN(i-Pr)}₂C:²⁶ afforded a reddish slurry, from which 4 was isolated as a red solid (87.5% yield) (Scheme 1). X-ray quality single crystals of 4 were ultimately obtained by crystallization in 1,2-difluorobenzene. Compound 4 demonstrates poor solubility in common polar solvents. Consequently, an ideal ¹³C NMR spectrum proved difficult to obtain. The 1:2 reaction of 3 with {(Me)CN(i-Pr)}₂C: gave 4 first (which was confirmed by the ¹H NMR tube reaction in THF-d₈) and finally resulted in the formation of 5 over 24 h. While 5 was isolated as dark blue microcrystals from the parent solution as major product (75.7% yield) (Scheme 1), the dark purple radical $6^{\circ 22}$ was obtained as a minor by-product. 5 can be readily separated from 6° due to their different solubility in THF. Recrystallization in 1,2-difluorobenzene gives X-ray quality single crystals of 5. The free imidazolium salt [{(Me)CN(i-Pr)}₂CH]⁺Cl⁻, as another by-product, was isolated and confirmed by the ¹H NMR spectroscopy in D₂O. The 8.75 ppm singlet ¹H NMR resonance of 5 indicates the presence of the imidazolium moiety in this molecule. The synthesis of 5 in polar solvents such as THF or 1,2-difluorobenzene may involve carbene-mediated partial hydrolysis of 4. Indeed, partial hydrolysis of the carbenecomplexed magnesium dithiolene complex has been previously

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(a) NHC-stabilized Si(0)₂ as a silicon transfer agent



(b) carbene-mediated formation of germanium tris(dithiolene)dianion



Scheme 1 (a) previous work: synthesis of 2 using NHC-stabilized Si(0)₂ as a silicon transfer agent. (b) Synthesis of 4 and 5 (note: H_2O is either added or from THF).

proposed by this laboratory.²⁰ To support this deduction, two equivalent water (as a 0.1% v/v solution in THF) was added to the 1:2 mixture of 3 with {(Me)CN(i-Pr)}₂C: in THF, which led to the rapid change of the solution colour from red (for 4) into dark blue (for the mixture of 5 and 6°). The compounds 5 and 6°, which were achieved from this 'water-added' route, were characterized by X-ray single crystal diffraction technique. By comparison, without the addition of water, the 4-to-5 conversion undergoes obviously slower due to the lower concentration of H₂O in the original THF solution. Indeed, we observed that without adding water, large amount of THF have to be employed in order to effectively synthesize 5. While the mechanism remains obscured, it is plausible that an *in situ* produced OH species (from protonation of the carbene by H_2O) would react with germanium or lithium cations (affording the corresponding metal hydroxides). Consequently, a free dithiolate dianion could be eliminated from one germanium bis(dithiolene) complex, and

subsequently captured by a second germanium bis(dithiolene) complex, giving **5**. The isolation of (minor by-product) **6**[•] supports the *in situ* formation of the free dithiolate species. The free dithiolate species may either participate in the formation of **5** or undergo one-electron oxidation (by trace amount of O_2 in the system) to give **6**[•].

X-ray structural analysis confirms that, in contrast to 3,¹⁹ wherein the five-coordinate Ge(IV) centre adopts an approximate square pyramidal geometry ($\tau^{29} = 0.02$), the germanium atom in 4 assumes a slightly distorted trigonal bipyramidal geometry ($\tau = 0.98$) (Fig. 1).²⁵ While the Ge–S bond distances in 3 are in a range from 2.3290(8) Å to 2.3561(8) Å, the Ge–S_{eq} bonds in 4 [2.2610(4) and 2.2667(4) Å] are obviously shorter than the Ge–S_{ax} bonds [2.4052(4) and 2.4136(4) Å]. Concomitantly, the C–S_{eq} bonds [1.7445(15) Å, av] are *ca.* 0.02 Å longer than the C–S_{ax} bonds [1.7266(14) Å, av] in 4.²⁵ The NHC ligand resides at an equatorial position with a 2.0101(14) Å Ge–C_{NHC} bond, which is in the range (1.90–2.05 Å) of typical Ge–C single bonds.³⁰ The bend angle¹ (η) between the GeS₂ plane and S₂C₂ plane in 4 (14.0°, av) is obviously less than those in 3 (37.3°, av).¹⁹

X-ray structural analysis²⁵ reveals the presence of one pair of Λ - and Δ -enantiomers of 5 in the asymmetric unit (Fig. 1; for clarity, only the structural parameters of the Δ enantiomer of 5 are shown in the caption of Fig. 1). In 5 the germanium tris(dithiolene) moiety exists as a dianion with a rare [{(Me)CN (i-Pr)₂CH⁺]₃Cl⁻ counter-dication (Fig. 1). In the dicationic unit of 5, the central chloride is bound by three imidazolium cations via C-H···Cl hydrogen bonds $[d_{\text{H···Cl}} = 2.49 \text{ Å (av)}, \theta_{\text{C-H···Cl}} = 155^{\circ} \text{ (av)}]^{.31}$ All hydrogen atoms at the C2 carbons of imidazolium fragments in 5 were located from difference Fourier maps. Both 2 [trigonal twist angle $(\phi) = 56.5^{\circ}$, s/h = 1.14]^{16,32} and 5 $[(\phi) = 53.6^{\circ}$ (av), s/h = 1.17 (av)] adopt an octahedral geometry, which involves the elongated distortion considering their less than 1.22 s/h ratios [For a regular octahedron, $(\phi) = 60^{\circ}$, s/h = 1.22].²⁷ For 5, the bend angle (η) between the GeS₂ plane and the C_2S_2 plane (34.8°, av) is between those for 3 $(37.3^{\circ}, av)^{19}$ and those for 4 (14.0°, av). The olefinic C-C bonds [1.345(5)–1.353(5) Å] and C-S bonds [1.712(4)–1.731(4) Å] in the C₂S₂ units of 5 are consistent with those in reported dithiolates.¹ Thus, like that in 3,¹⁹ the central germanium atom in dianionic 5 has an oxidation state of +4. The Ge-S bonds in 5 [2.3887(10)-2.4381(11) Å] are comparable to those in 3 and 4 [2.2610(4)-2.4052(4) Å].^{19,25}

The bonding nature of **4** and **5** were further probed by B3LYP/6-311G**density functional theory (DFT) computations on the simplified **4-Me** and Δ -[**5-Me**]²⁻ models, respectively.²⁵ The optimized structures of **4-Me** and Δ -[**5-Me**]²⁻ models are consistent with the solid-state structures of **4** and **5**. Notably, the Ge-C_{NHC} bond (2.088 Å), Ge-S_{eq} bonds (2.348 Å, av), and Ge-S_{ax} bonds (2.442 Å, av) of **4-Me** are slightly longer than those of **4** ($d_{Ge-C(NHC)} = 2.010$ Å; $d_{Ge-S(eq)} = 2.264$ Å, av; $d_{Ge-S(ax)} = 2.409$ Å, av). The Ge-S bonds (2.499–2.526 Å) of Δ -[**5-Me**]²⁻ are also somewhat longer than those in **5** [2.3887(10)–2.4381(11) Å]. While LUMOs of **4-Me** and Δ -[**5-Me**]²⁻ involve germanium–sulphur and germanium–carbon (for **4-Me** only) antibonding interactions, HOMOs of **4-Me** and Δ -[**5-Me**]²⁻ are mainly dithiolene ligand-based, bearing both C-C π -bonding and C-S π -antibonding features (Fig. 2). Natural bond orbital (NBO) analysis shows that both Ge-S bonds and Ge-C_{NHC}



Fig. 1 Molecular structures of **4** and **5** dianion (thermal ellipsoids represent 30% probability; hydrogen atoms on carbons are omitted for clarity). Selected bond distances (Å) and angles (deg): for **4**, C(2)-C(3) 1.350(2), C(2)-S(2) 1.7269(15), C(3)-S(3) 1.7459(15), S(2)-Ge(1) 2.4052(4), S(3)-Ge(1) 2.2667(4), S(5)-Ge(1) 2.2610(4), S(6)-Ge(1) 2.4136(4), C(55)-Ge(1) 2.0101(14); S(2)-Ge(1)-S(6) 175.03(1), S(3)-Ge(1)-C(55) 122.13(4), S(5)-Ge(1)-C(55) 121.80(4), S(3)-Ge(1)-S(5) 116.07(2). For Δ -**5**, C(2)-C(3) 1.352(5), C(2)-S(2) 1.719(4), C(3)-S(3) 1.721(4), S(2)-Ge(1) 2.4161(11), S(3)-Ge(1) 2.4286(11); S(2)-Ge(1)-S(3) 89.07(4), S(2)-Ge(1)-S(8) 173.99(4), S(2)-Ge(1)-S(5) 94.63(4). Schematic representation of enantiomers of **[5]**²⁻ (trigonal twist angle ϕ , triangle side s, intertriangle distance h, Dipp₂timdt = diisopropylphenyl-substituted imidazolidine-2,4,5-trithione).^{27,28}

bond in **4-Me** and Ge–S bonds in Λ -[**5-Me**]^{2–} are polarized. For **4-Me**, while the Ge–C_{NHC} σ bond polarization is 23.5% toward germanium and 76.5% toward carbon, the Ge–S_{ax} σ bond polarization [23.1% (av) toward germanium and 76.9% (av) toward sulphur] is stronger than that of the Ge–S_{eq} σ bonds [30.9% (av) toward germanium and 69.1% (av) toward sulphur]. For Λ -[**5-Me**]^{2–}, the average Ge–S σ bond polarization is 20.4% toward germanium and 79.6% toward sulphur. The positive natural charges of the germanium atoms in **4-Me** and Λ -[**5-Me**]^{2–} are +0.82 and +0.65, respectively. Notably, the equatorial sulphur atoms in **4-Me** bear an average negative charge of –0.07, which is somewhat less than that of the

axial sulphur atoms in 4-Me (-0.16) and each sulphur atom bound to the central germanium atom in Δ -[5-Me]²⁻ (-0.15, av).²⁵

In a 1:1 reaction of 3 with $\{(Me)CN(i-Pr)\}_2C$:, the N-heterocyclic carbene may replace the axial chloride ligand in the five-coordinate germanium bis(dithiolene) complex (3), giving a carbene-complexed germanium bis(dithiolene) (4). However, the corresponding 1:2 reaction gave a mixture containing both the first structurally characterized germanium tris(dithiolene)dianion 5 (the major product) and 6• (the minor by-product). This chemical transformation may involve carbene-mediated partial hydrolysis of the germanium bis(dithiolene) species.



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Conflicts of interest

There are no conflicts to declare.

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