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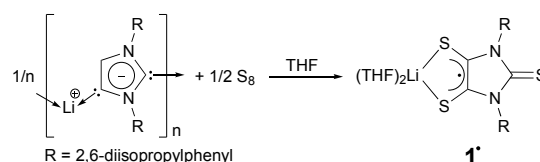
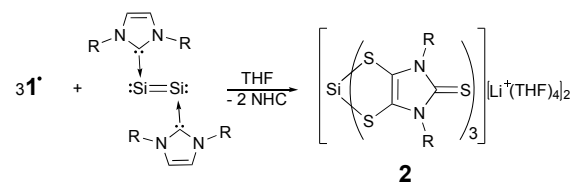
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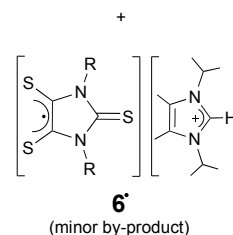
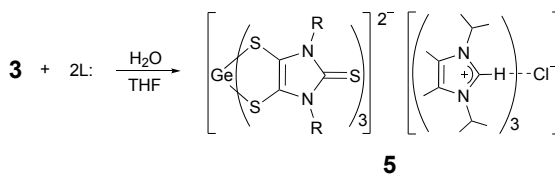
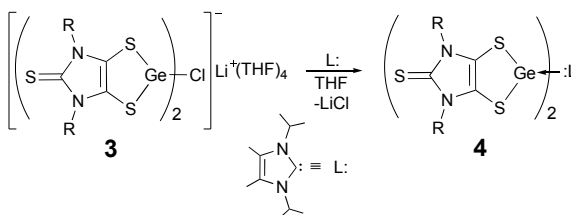
While the 1:1 reaction of **3** with an N-heterocyclic carbene $\{(\text{Me})\text{CN}(i\text{-Pr})\}_2\text{C}$: in THF resulted in ligand-substituted product **4**, the corresponding 1:2 reaction (in the presence of H_2O) gives the first structurally characterized germanium tris(dithiolene) dianion **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 is 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*** with an imidazolium salt $\{[(\text{Me})\text{CN}(i\text{-Pr})_2\text{CH}]^+\text{Cl}^-\}$,²² which, surprisingly, participated in a synergic THF ring-open reaction with N-heterocyclic silylene and the hexasulphide dianion. In addition, we recently reported the reaction of **1*** 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.

(a) NHC-stabilized $\text{Si}(0)_2$ as a silicon transfer agent

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



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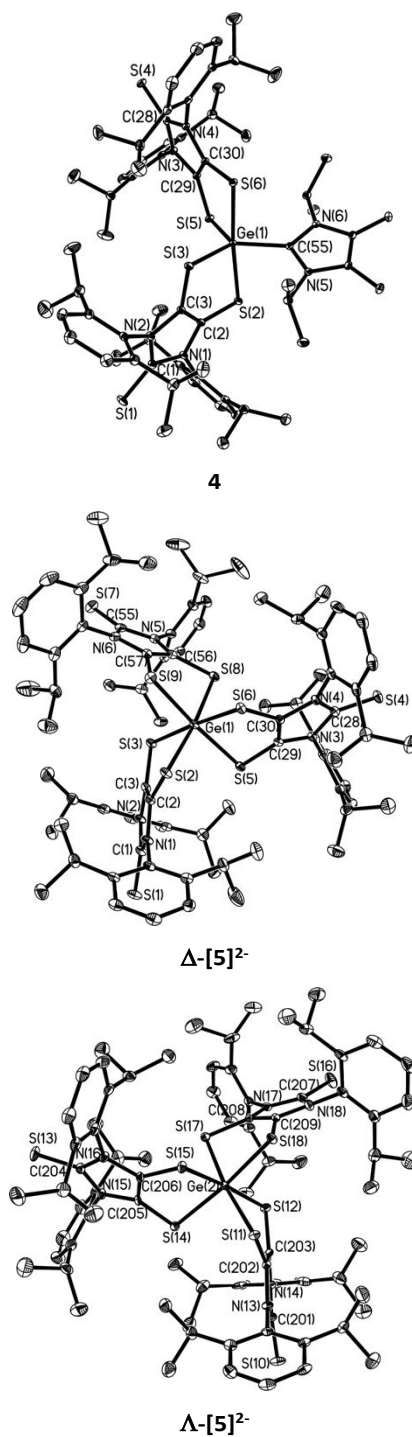
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Scheme 1 (a) previous work: Synthesis of **2** using NHC-stabilized Si(O)₂ as a silicon transfer agent. (b) synthesis of **4** and **5** (note: H₂O is either added or from THF).

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 24h. 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**^{*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** in polar solvents. Indeed, partial hydrolysis of the carbene-complexed magnesium dithiolene complex has been previously 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 H₂O) 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 O₂ in the system) to give **6**^{*}.



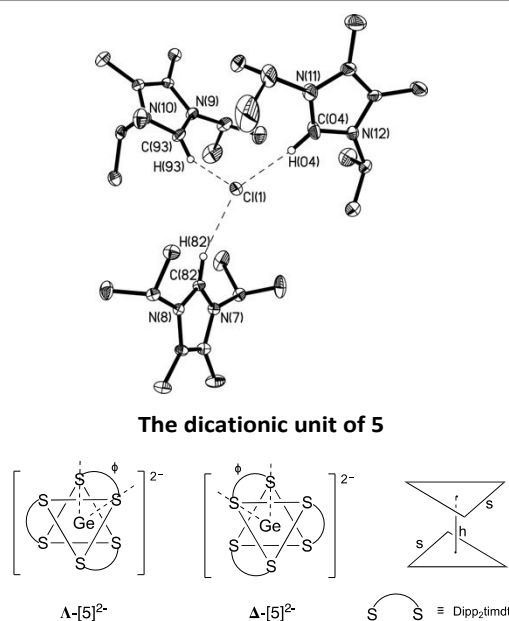


Fig. 1 Molecular structures of **4** and **5** dianion (thermal ellipsoids represent 30% probability; hydrogen atoms on carbons are omitted for clarity). Selected bond distances (Å) and angles (deg): For **4**, C(2)–C(3) 1.350(2), C(2)–S(2) 1.7269(15), C(3)–S(3) 1.7459(15), S(2)–Ge(1) 2.4052(4), S(3)–Ge(1) 2.2667(4), S(5)–Ge(1) 2.2610(4), S(6)–Ge(1) 2.4136(4), S(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}

X-ray structural analysis confirms that, in contrast to **3**,¹⁹ wherein the five-coordinate Ge(IV) centre adopts an approximate square pyramidal geometry (τ ²⁹ = 0.02), the germanium atom in **4** assumes a slightly distorted trigonal bipyramidal geometry (τ = 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 Å–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 [$d_{\text{H}\cdots\text{Cl}}$ = 2.49 Å (av), $\theta_{\text{C}\cdots\text{H}\cdots\text{Cl}}$ = 155° (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 (ϕ) = 56.5°, s/h = 1.14]^{16,32} and **5** [(ϕ) = 53.6° (av), s/h = 1.17 (av)] adopt an octahedral geometry, which

involve the elongated distortion considering their less than 1.22 s/h ratios [For a regular octahedron, (ϕ) = 60°, s/h = 1.22].²⁷ For **5**, the bend angle (η) between the GeS₂ plane and the C₂S₂ plane (34.8°, av) is between those for **3** (37.3°, 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}

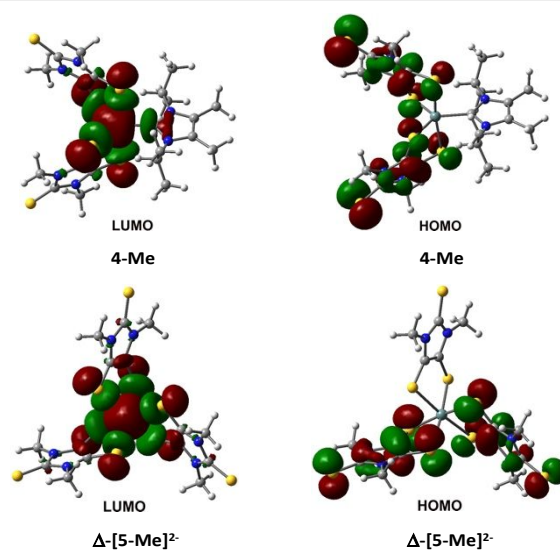


Fig. 2 Frontier molecular orbitals of **4-Me** and Δ -**[5-Me]²⁻** models.

The bonding character 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** ($d_{\text{Ge-C(NHC)}}$ = 2.010 Å; $d_{\text{Ge-S(eq)}}$ = 2.264 Å, av; $d_{\text{Ge-S(ax)}}$ = 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} bond in **4-Me** and Ge–S bonds in Δ -**[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 Δ -**[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 Δ -**[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.

Conflicts of interest

There are no conflicts to declare.

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