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A Stable Anionic Dithiolene Radical

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Supporting Information

ABSTRACT: Sulfurization of anionic N-heterocyclic dicarbene, $[:C\{[N(2,6\text{-}Pr^i_2C_6H_3)]_2CHCLi\}]_n$ (**2**), with elemental sulfur (in a 1:2 ratio) in Et_2O at low temperature gives **3** by inserting two sulfur atoms into the Li−C (i.e., C2 and C4) bonds in polymeric **2**. Further reaction of **3** with 2 equiv of elemental sulfur in THF affords $\mathbf{4}^{\bullet}$ via unexpected C−H bond activation, which represents the first anionic dithiolene radical to be structurally characterized in the solid state. Alternatively, $\mathbf{4}^{\bullet}$ may also be synthesized directly by reaction of **1** with sulfur (in a 1:4 ratio) in THF. Reaction of $\mathbf{4}^{\bullet}$ with $GeCl_2\cdot$dioxane gives an anionic germanium(IV)−bis(dithiolene) complex (**5**). The nature of the bonding in $\mathbf{4}^{\bullet}$ and **5** was probed by experimental and theoretical methods.

Metal−dithiolene complexes, extensively studied since the early 1960s,[1−10] are intriguing not only due to their unique structural and bonding motifs but also for their remarkable capabilities in such disparate fields as materials science[4,10] and biological systems.[2,11] While both molybdenum and tungsten enzymes contain the dithiolene unit,[2,5] transition metal−bis-dithiolenes, possessing unique optical, conductive, and magnetic properties, have shown promise in the development of optoelectronic devices.[4,7,10]

The fascinating redox chemistry demonstrated by metal−dithiolenes may largely be attributed to the *non-innocent* behavior of dithiolene ligands (Figure 1).[3] Gray boldly proposed the likely presence of dithiolate radical anion moieties ($L^{\bullet-}$) in transition metal−dithiolene complexes more than five decades ago.[13,14] The electronic structures of transition metal−dithiolene complexes were recently probed by sulfur K-edge X-ray absorption spectroscopy (XAS), providing the strong support for the *non-innocence* of dithiolene ligands.[8] While the radical character of the ligands in transition metal−dithiolene complexes has been extensively explored,[8,15−24] free anionic dithiolene radicals are highly reactive and have only been studied computationally and by electron paramagnetic resonance (EPR).[25−28] Indeed, the electronic absorption spectrum of the prototype dithiolene radical anion ($C_2H_2S_2^{\bullet-}$) was recently observed in a low-temperature matrix.[29] Consequently, the captivating chemistry of anionic dithiolene radicals remains highly relevant. Herein, we report the synthesis, structure, spectra, computations,[30] and reactivity of the lithium salt of anionic dithiolene radical ($\mathbf{4}^{\bullet}$), an R_2timdt-type ligand (R_2timdt = disubstituted imidazolidine-2,4,5-trithione).[31−36] Notably, $\mathbf{4}^{\bullet}$ is uniquely synthesized via a carbene-based strategy and represents the first stable anionic dithiolene radical to be structurally characterized.

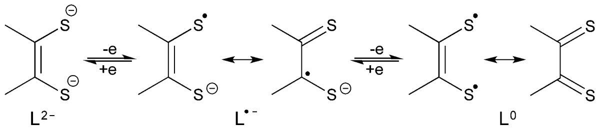
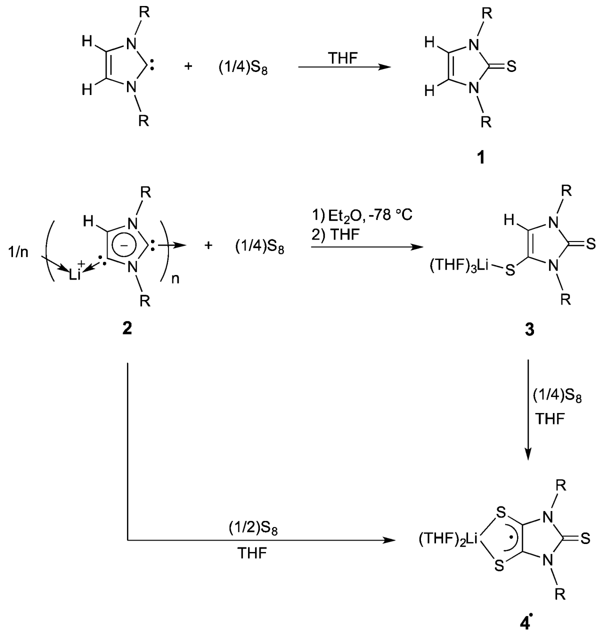


Figure 1. Three oxidation levels of a dithiolene ligand.[12]

Reaction of N-heterocyclic carbene [NHC = $:C\{N(2,6\text{-}Pr^i_2C_6H_3)CH\}_2$] with an excess of elemental sulfur gives thione (**1**) (Scheme 1).[37] However, di- and tri- sulfurization of the imidazole ring may be achieved by sulfurization of C4-metalated N-heterocyclic carbenes. The first anionic N-heterocyclic dicarbene (NHDC, **2**) was synthesized by this laboratory in 2010 via C4-lithiation of a NHC ligand [L: = $:C\{N(2,6\text{-}Pr^i_2C_6H_3)CH\}_2$].[38] Reaction of **2** with two equivalents of elemental sulfur in Et_2O at low-temperature and

Scheme 1. Synthesis of 1, 3, and $\mathbf{4}^{\bullet}$



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subsequent workup in THF gives colorless disulfurized product **3** (in 73.5% yield) (Scheme 1, R = 2,6-diisopropylphenyl). Compound **3** may be purified by recrystallization in THF/hexane mixed solvent at −40 °C. Further reaction of crystalline **3** with elemental sulfur (in a 1:2 ratio) in THF at room temperature gives **4**$^\bullet$ as a crystalline purple powder in quantitative yield, which can be employed for synthesis without further purification. Notably, **4**$^\bullet$ may also be synthesized by directly reacting **2** with elemental sulfur in a 1:4 ratio (Scheme 1). However, the purity of the product **4**$^\bullet$ from the 1:4 route is relative low. Radical **4**$^\bullet$ solid is stable indefinitely under an inert atmosphere of argon. Interestingly, the transformation of **3** to **4**$^\bullet$ involves unexpected C−H bond activation. The metal-catalyzed C−S bond formation via C−H bond functionalization has received substantial attention.[39] In addition, the disulfide bridge in dinuclear Ru(III) complexes has been reported to be involved in C−S bond formation.[40] Notably, elemental sulfur has been utilized in copper-mediated C−S bond forming reactions via C−H activation.[41] While the mechanism of the transformation of **3** to **4**$^\bullet$ remains unclear, our study reveals that this reaction requires two equivalents of elemental sulfur (Scheme 1). The corresponding 1:1 reaction only affords a mixture containing **4**$^\bullet$ and unreacted **3**.

Although the ^{1}H NMR imidazole resonance of **3** (6.14 ppm) is similar to that of **2** (6.16 ppm),[38] single crystal X-ray structural analysis reveals that the two carbene carbons of **3** are sulfurized (Figure 2). The C(1)═S(1) bond distance in **3** [1.678(4) Å], comparing well to that of **1** [1.670(3) Å],[42] is ca. 0.04 Å shorter than that of the C(3)−S(2) single bond in **3** [1.716(4) Å]. While the S(1) atom is terminal, the S(2) atom is bridged between the C4 carbon [i.e., C(3)] and a THF-solvated lithium cation. In addition, the Li−S bond is nearly coplanar with the imidazole ring [Li(1)−S(2)−C(3)−C(2) torsion angle = 2.1°].

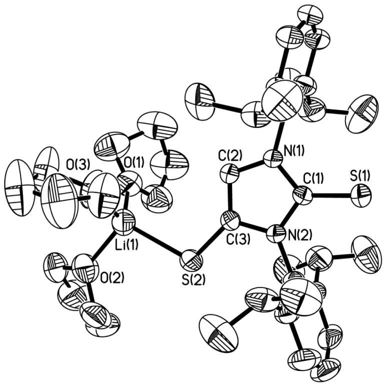


Figure 2. Molecular structure of **3**. Thermal ellipsoids represent 30% probability. Hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (deg): C(1)−S(1), 1.678(4); C(2)−C(3), 1.355(5); C(3)−S(2), 1.716(4); Li(1)−S(2), 2.369(8); S(1)−C(1)−N(1), 128.8(3); C(2)−C(3)−S(2), 134.7(3); Li(1)−S(2)−C(3), 108.4(2).

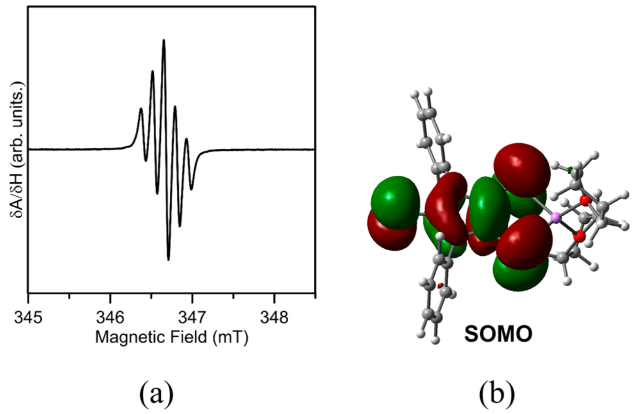


Figure 3. (a) Room-temperature X-band EPR spectrum of **4**$^\bullet$ in THF recorded at 9.78 GHz with a modulation amplitude of 0.02 mT and a microwave power of 0.1 mW. (b) SOMO of the simplified model [**4-Ph**]$^\bullet$.

While the UV−vis absorption spectrum (Figure S1)[30] of radical **4**$^\bullet$ (purple) in toluene shows two broad absorptions at 554 and 579 nm, the paramagnetic properties of radical **4**$^\bullet$ are characterized by EPR spectroscopy in THF at 298 K (Figure 3a). The EPR spectrum displays a $S = 1/2$ quintet ($g_{\mathrm{av}} = 2.016$) due to weak hyperfine coupling with two equivalent $I = 1$ ^{14}N nuclei, $A_{\mathrm{av}}(^{14}\mathrm{N}) = 3.9$ MHz. Molecular orbital calculations of the simplified [**4-Ph**]$^\bullet$ model suggest that the SOMO (Figure 3b) is primarily ligand-based, involving C−S π-antibonding and C−C π-bonding character. The total spin density (0.88) of the C_2S_2 unit in [**4-Ph**]$^\bullet$ [$\rho(S_2) = \rho(S_3) = 0.31$, $\rho = 0.26$ for the olefinic carbons] indicates that the unpaired electron is largely localized on the C_2S_2 moieties.

X-ray structural analysis (Figure 4) shows that a THF-solvated four-coordinate lithium cation is bound to two sulfur atoms of the dithiolene moiety in **4**$^\bullet$, giving a five-membered LiS_2C_2 ring. The LiS_2C_2 ring of [**4-Ph**]$^\bullet$ model is almost planar,[30] rather than having the lithium atom obviously puckered out of plane, as observed in **4**$^\bullet$ [bend angle (η) between the MS_2 (M = Li) plane and the S_2C_2 plane = 14.2°]. This may be due to the steric bulk of the ligand and the packing effects.[43,44] The Li−S bond distances in **4**$^\bullet$ [2.442(5) Å, av], similar to that of [**4-Ph**]$^\bullet$ (2.455 Å, av), is approximately 0.07 Å longer than that in monothiolate **3** [2.369(8)Å]. The Wiberg bond indices (WBIs) of the Li−S bonds in [**4-Ph**]$^\bullet$ (0.28, av), coupled with the +0.66 natural charges of $[(\mathrm{THF})_2\mathrm{Li}]^+$, indicate both the ionic bonding essence of the Li−S bonds and the anionic character of the $[\mathrm{S{=}C\{N(2{,}6\text{-}Pr^i_2C_6H_3)\text{-}CS\}_2}]^{\bullet-}$ fragment in **4**$^\bullet$. While comparing well with the

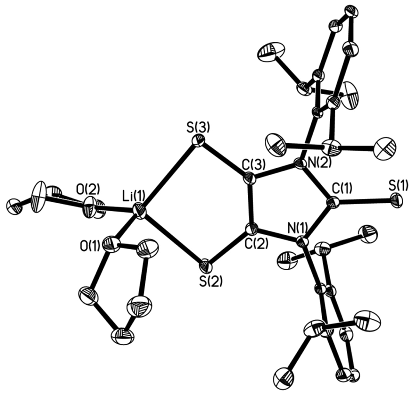
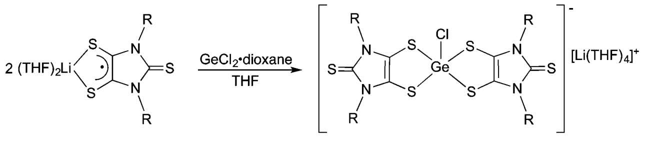


Figure 4. Molecular structure of **4**$^\bullet$. Thermal ellipsoids represent 30% probability. Hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (deg): S(1)−C(1), 1.654(2); C(2)−C(3), 1.417(3); C(2)−S(2), 1.674(3); C(3)−S(3), 1.680(3); Li(1)−S(2), 2.437(5); Li(1)−S(3), 2.446(5); C(2)−C(3)−S(3), 129.54(19); Li(1)−S(2)−C(2), 93.08(14); S(2)−Li(1)−S(3), 93.31(16).

theoretical values for [**4-Ph**]$^{\bullet}$ ($d_{\text{C–C}}$ = 1.426 Å, $d_{\text{C–S}}$ = 1.697 Å) and for *cis*-$C_2H_2S_2^{\bullet-}$ ($d_{\text{C–C}}$ = 1.411 Å, $d_{\text{C–S}}$ = 1.693 Å),[29] the C(2)−C(3) bond distance [1.417(3)Å] and C−S bond distances [1.677(3) Å, av] in the C_2S_2 moieties of **4**$^{\bullet}$ are in contrast to those in **3** [$d_{\text{C–C}}$ = 1.355(5)Å, $d_{\text{C–S}}$ = 1.716(4) Å] and in various dithiolates[2] such as uncomplexed dithiolate ligand [i.e., $(NMe_4)_2(C_3S_5)$, $d_{\text{C–C}}$ = 1.371(8) Å, $d_{\text{C–S}}$ = 1.724(6) Å, av][45] and silver dithiolate complex $[NBu_4]_4[Ag(mnt)]_4$ (mnt = 1,2-maleonitrile-1,2-dithiolate) [$d_{\text{C–C}}$ = 1.373(8) Å, $d_{\text{C–S}}$ = 1.736(6) Å, av].[46] By comparison with those in dithiolates (L^{2-}, Figure 1),[2] the elongation of the carbon−carbon bond and concomitant shortening of the carbon−sulfur bonds observed in **4**$^{\bullet}$ may be attributed to the SOMO (Figure 3b) of **4**$^{\bullet}$, which has C−C π-bonding and C−S π-antibonding character. The WBI values of the C(2)−C(3) bond (1.22) and C−S bonds (1.34, av) in the C_2S_2 moieties of **4**$^{\bullet}$ indicate that these bonds have a modest double bond character, which is consistent with the resonance structures of $L^{\bullet-}$ in Figure 1.

Although synthetic routes for dithiolene complexes have been reported,[2] **4**$^{\bullet}$, as a bidentate ligand with both anionic and radical character, provides a unique platform to access a variety of dithiolene compounds. To this end, we allowed **4**$^{\bullet}$ to react with $GeCl_2$·dioxane in THF (in a ratio of 2:1). The anionic chlorogermanium-bis(dithiolene) complex (**5**) was isolated as a dark-blue diamagnetic crystalline solid (83.3% yield) (Scheme 2).

Scheme 2. Synthesis of 5



4$^{\bullet}$

5

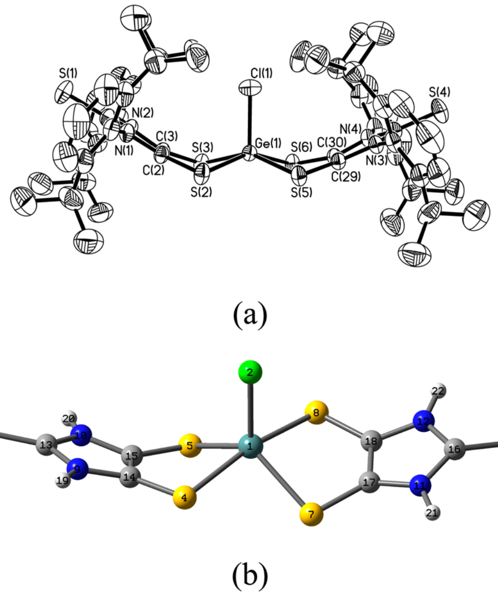


Figure 5. (a) Molecular structure of [**5**]$^-$. Thermal ellipsoids represent 30% probability. Hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (deg): Ge(1)−Cl(1), 2.1902(9); Ge−S, 2.3290(8)−2.3561(8); C(2)−C(3), 1.349(4); C(2)−S(2), 1.724(3); C(3)−S(3), 1.727(3); S(2)−Ge(1)−Cl(1), 103.13(4); S(2)−Ge(1)−S(6), 153.89(4); S(3)−Ge(1)−S(5), 152.66(3). (b) The optimized structure of [**5-H**]$^-$ model in C_2 symmetry.

X-ray structural analysis (Figure 5a) shows that the central five-coordinate germanium atom in **5** adopts an approximate square pyramidal geometry, having four coplanar basal sulfur atoms ($d_{\text{S}\cdots\text{S}}$ = 3.134−3.309 Å) and an apical chlorine atom. In contrast, the optimized structure (Figure 5b) of the simplified [**5-H**]$^-$ model (in C_2 symmetry) features a distorted trigonal bipyramidal geometry around the germanium atom (S_4−Ge_1−S_8 angle = 167.2°; S_5−Ge_1−S_7 angle = 127.7°), which is comparable to that for anionic fluorogermanate $[(C_7H_6S_2)_2GeF]^-$ (S_{ax}−Ge−S_{ax} = 171.1°, S_{eq}−Ge−S_{eq} = 136.2°).[47] The square pyramidal geometry about the germanium atom in **5** may well be a consequence of steric repulsion of the bulky ligands (see space-filling model of **5**, Figure S2). The Ge−S bonds in **5** [2.3290(8)−2.3561(8) Å] are similar to the Ge−S_{eq} bonds (2.361 Å), but obviously shorter than the Ge−S_{ax} bonds (2.465 Å) in [**5-H**]$^-$. It is noteworthy that, while comparing well to those of dithiolates (L^{2-}, Figure 1),[2,45,46] the olefinic C−C bonds [1.347(4) Å, av] in **5** are shorter than that in **4**$^{\bullet}$ [1.417(3) Å]. Meanwhile, the C−S bonds [1.719(3)−1.729(3) Å] in the C_2S_2 moieties of **5** are concomitantly elongated compared to those in **4**$^{\bullet}$ [1.677(3) Å, av]. Thus, the germanium atom in **5** may be assigned an oxidation state of +4. In addition, the C_2S_2Ge rings in **5** (η = 37.3°, av) are more bent than those in [**5-H**]$^-$ (η = 29.6°) and the C_2S_2Li ring in **4**$^{\bullet}$ (η = 14.2°). The axial Ge(1)−Cl(1) bond in **5** [2.1902(9) Å] is only slightly shorter than that in [**5-H**]$^-$ (2.265 Å).

The anionic NHDC ligand (**2**) may be di- and trisulfurized to give **3** and **4**$^{\bullet}$, respectively. Compound **3** may be further transformed into **4**$^{\bullet}$ via C−H bond activation. The effective transformation of **4**$^{\bullet}$ to **5** suggests that **4**$^{\bullet}$, as a stable monoanionic dithiolene radical, may serve as a new platform to access a variety of unexplored dithiolene chemistry. The reactivity of both **3** and **4**$^{\bullet}$ is being studied in this laboratory.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.7b03794.

Syntheses, computations, and X-ray crystal determination, including Figures S1 and S2 and Tables S1−S12 (PDF)

Crystallographic data for compounds **3**, **4**$^{\bullet}$, and **5** (CIF)

Crystallographic data for compound (CIF) Crystallographic data for compound **5** (CIF) (CIF)

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Notes

The authors declare no competing financial interest.

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