Published in final edited form as:

J Am Chem Soc. 2017 May 24; 139(20): 6859–6862. doi:10.1021/jacs.7b03794.

A Stable Anionic Dithiolene Radical

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Abstract

Sulfurization of anionic N-heterocyclic dicarbene, $[\text{C}\{\text{N}(\text{2,6-Pr}_2\text{C}_6\text{H}_3)\}_2\text{CHCLi}]_n$ (**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 **4**[•] via unexpected C–H bond activation, which represents the first anionic dithiolene radical to be structurally characterized in the solid state. Alternatively, **4**[•] may also be synthesized directly by reaction of **1** with sulfur (in a 1:4 ratio) in THF. Reaction of **4**[•] with $\text{GeCl}_2 \cdot \text{dioxane}$ gives an anionic germanium(IV)–bis(dithiolene) complex (**5**). The nature of the bonding in **4**[•] 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 ($\text{L}^{\bullet-}$) 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

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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**[•], 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.

have only been studied computationally and by electron paramagnetic resonance (EPR).^{25–28} Indeed, the electronic absorption spectrum of the prototype dithiolenic radical anion ($C_2H_2S_2^{\bullet-}$) was recently observed in a low-temperature matrix.²⁹ Consequently, the captivating chemistry of anionic dithiolenic radicals remains highly relevant. Herein, we report the synthesis, structure, spectra, computations,³⁰ and reactivity of the lithium salt of anionic dithiolenic radical (**4**[•]), an R_2 timdt-type ligand (R_2 timdt = disubstituted imidazolidine-2,4,5-trithione).^{31–36} Notably, **4**[•] is uniquely synthesized via a carbene-based strategy and represents the first stable anionic dithiolenic radical to be structurally characterized.

Reaction of N-heterocyclic carbene [NHC = :C{N(2,6- $Pr^i_2C_6H_3$)CH}₂] with an excess of elemental sulfur gives thione (**1**) (Scheme 1).³⁷ However, di- and tri- sulfuration 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- $Pr^i_2C_6H_3$)CH}₂].³⁸ Reaction of **2** with two equivalents of elemental sulfur in Et₂O at low-temperature and 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**[•] as a crystalline purple powder in quantitative yield, which can be employed for synthesis without further purification. Notably, **4**[•] 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**[•] from the 1:4 route is relative low. Radical **4**[•] solid is stable indefinitely under an inert atmosphere of argon. Interestingly, the transformation of **3** to **4**[•] 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**[•] 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**[•] and unreacted **3**.

Although the ¹H 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°].

While the UV–vis absorption spectrum (Figure S1)³⁰ of radical **4**[•] (purple) in toluene shows two broad absorptions at 554 and 579 nm, the paramagnetic properties of radical **4**[•] are characterized by EPR spectroscopy in THF at 298 K (Figure 3a). The EPR spectrum displays a $S = 1/2$ quintet ($g_{av} = 2.016$) due to weak hyperfine coupling with two equivalent

$I = 1$ ^{14}N nuclei, $A_{\text{av}}(^{14}\text{N}) = 3.9$ 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]** $^{\bullet}$ [$\rho(\text{S}_2) = \rho(\text{S}_3) = 0.31$, $\rho = 0.26$ 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 ($\text{M} = \text{Li}$) 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 $[(\text{THF})_2\text{Li}]^+$, indicate both the ionic bonding essence of the Li–S bonds and the anionic character of the $[\text{S}=\text{C}\{\text{N}(2,6\text{-Pr}_2\text{C}_6\text{H}_3)\text{-CS}\}_2]^{\bullet-}$ fragment in **4** $^{\bullet}$. While comparing well with the theoretical values for **[4-Ph]** $^{\bullet}$ ($d_{\text{C-C}} = 1.426$ Å, $d_{\text{C-S}} = 1.697$ Å) and for *cis*- $\text{C}_2\text{H}_2\text{S}_2^{\bullet-}$ ($d_{\text{C-C}} = 1.411$ 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 dithiolates² such as uncomplexed dithiolate ligand [i.e., $(\text{NMe}_4)_2(\text{C}_3\text{S}_5)$, $d_{\text{C-C}} = 1.371(8)$ Å, $d_{\text{C-S}} = 1.724(6)$ Å, av]⁴⁵ and silver dithiolate complex $[\text{NBu}_4]_4[\text{Ag}(\text{mnt})]_4$ (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 $\text{L}^{\bullet-}$ 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).

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 ($d_{\text{S} \cdots \text{S}} = 3.134\text{--}3.309$ 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 ($\text{S}_4\text{--Ge}_1\text{--S}_8$ angle = 167.2° ; $\text{S}_5\text{--Ge}_1\text{--S}_7$ angle = 127.7°), which is comparable to that for anionic fluorogermanate $[(\text{C}_7\text{H}_6\text{S}_2)_2\text{GeF}]^-$ ($\text{S}_{\text{ax}}\text{--Ge--S}_{\text{ax}} = 171.1^\circ$, $\text{S}_{\text{eq}}\text{--Ge--S}_{\text{eq}} = 136.2^\circ$).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**[•] [1.417(3) Å]. Meanwhile, the C–S bonds [1.719(3)–1.729(3) Å] in the C₂S₂ moieties of **5** are concomitantly elongated compared to those in **4**[•] [1.677(3) Å, av]. Thus, the germanium atom in **5** may be assigned an oxidation state of +4. In addition, the C₂S₂Ge rings in **5** ($\eta = 37.3^\circ$, av) are more bent than those in [5-H][−] ($\eta = 29.6^\circ$) and the C₂S₂Li ring in **4**[•] ($\eta = 14.2^\circ$). 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**[•], respectively. Compound **3** may be further transformed into **4**[•] via C–H bond activation. The effective transformation of **4**[•] to **5** suggests that **4**[•], 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**[•] is being studied in this laboratory.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

We are grateful to the National Science Foundation for support: CHE-1565676 (G.H.R., Y.W.) and CHE-1361178 (H.F.S.). EPR studies were supported by a grant from the National Institutes of Health: R37-GM62524 (M.K.J.).

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

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**[•] 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**][•].

Figure 4.

Molecular structure of **4•**. 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).

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.

Scheme 1.
Synthesis of 1, 3, and 4*

Scheme 2.
Synthesis of 5