A Stable Anionic Dithiolene Radical

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Supporting Information

ABSTRACT: Sulfurization of anionic N-heterocyclic dicarbene, 

\[ \text{[C(N(2,6-Pr\text{II}_2C_6H_3)CH)]_2Cl} \] 2, with elemental sulfur (in a 1:2 ratio) in Et\textsubscript{2}O at low temperature gives \( 3 \) by inserting two sulfur atoms into the Li\textsuperscript{−}C (i.e., C\textsubscript{2} and C\textsubscript{4}) 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 GeCl\textsubscript{2}·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,\textsuperscript{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\textsuperscript{4,10} and biological systems.\textsuperscript{2,11} While both molybdenum and tungsten enzymes contain the dithiolene unit,\textsuperscript{2,5} transition metal−bis-dithiolenes, possessing unique optical, conductive, and magnetic properties, have shown promise in the development of optoelectronic devices.\textsuperscript{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).\textsuperscript{3} Gray boldly proposed the likely presence of dithiolate radical anion moieties (L\textsuperscript{−}) in transition metal−dithiolene complexes more than five decades ago.\textsuperscript{3,14} 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.\textsuperscript{4} While the radical character of the ligands in transition metal−dithiolene complexes has been extensively explored,\textsuperscript{4,13−24} free anionic dithiolene radicals are highly reactive and have only been studied computationally and by electron paramagnetic resonance (EPR).\textsuperscript{25−28} Indeed, the electronic absorption spectrum of the prototype dithiolene radical anion (C\textsubscript{2}H\textsubscript{2}S\textsubscript{−}) was recently observed in a low-temperature matrix.\textsuperscript{29} Consequently, the captivating chemistry of anionic dithiolene radicals remains highly relevant. Herein, we report the synthesis, structure, spectra, computations,\textsuperscript{30} and reactivity of the lithium salt of anionic dithiolene radical (\( 4^\text{−} \)), an R\textsubscript{2}timdt-type ligand (R\textsubscript{2}timdt = disubstituted imidazolidine-2,4,5-trithione).\textsuperscript{31−36} Notably, \( 4^\text{−} \) is uniquely synthesized via a carbene-based strategy and represents the first stable anionic dithiolene radical to be structurally characterized.

Reaction of N-heterocyclic carbene [NHC = :C(N(2,6-Pr\text{II}_2C_6H_3)CH)] with an excess of elemental sulfur gives thione (1) (Scheme 1).\textsuperscript{37} However, di- and tri-sulfurization of the imidazole ring may be achieved by sulfurization of C4-metalated N-heterocyclic carbene. The first anionic N-heterocyclic dicarbene (NHDC, 2) was synthesized by this laboratory in 2010 via C4-lithiation of a NHC ligand [L\textsubscript{1} = :C(N(2,6-Pr\text{II}_2C_6H_3)CH)]\textsubscript{2}].\textsuperscript{38} Reaction of 2 with two equivalents of elemental sulfur gives thione (1) (Scheme 1).\textsuperscript{37} However, di- and tri-sulfurization of the

Figure 1. Three oxidation levels of a dithiolene ligand.\textsuperscript{12}

Scheme 1. Synthesis of 1, 3, and 4

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subsequent workup in THF gives colorless disulfurized product 3 (in 73.5% yield) (Scheme 1, R = 2,6-dimethylphenyl). 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),48 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); G(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).

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 14N nuclei, $A_{av}(^{14N}) = 3.9$ MHz. Molecular orbital calculations of the simplified [4-Ph]* model suggest that the SOMO (Figure 3b) is primarily ligand-based, involving C−S $\pi$-antibonding and C−C $\pi$-bonding character. The total spin density (0.88) of the C4S2 unit in [4-Ph]* [$\rho(S_{2}) = \rho(S_{3}) = 0.31, \rho = 0.26$ for the olefinic carbons] indicates that the unpaired electron is largely localized on the C4S2 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*, giving a five-membered LiS2C2 ring. The LiS2C2 ring of [4-Ph]* model is almost planar,40 rather than having the lithium atom obviously puckered out of plane, as observed in 4* [bend angle (η) between the MS2 (M = Li) plane and the S2C2 plane = 14.2°]. This may be due to the steric bulk of the ligand and the packing effects.45 The Li−S bond distances in 4* [2.442(5) Å, av], similar to that of [4-Ph]* (2.455 Å, av), is approximately 0.07 Å longer than that in monothiolate 3 [2.369(8) Å]. The Wiberg bond indices (WBI)s of the Li−S bonds in [4-Ph]* (0.28, av), coupled with the +0.66 natural charges of [(THF)2Li]+, indicate both the ionic bonding essence of the Li−S bonds and the anionic character of the [S≡C(N(2,6-Pr2C6H4)−CS)2]+ fragment in 4*. While comparing well with the
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Theoretical values for [4-Ph]* (d_{C=C} = 1.426 Å, d_{C-S} = 1.697 Å) and for cis-C_{4}H_{2}S_{2}* (d_{C-C} = 1.411 Å, d_{C-S} = 1.693 Å), the C(2)–C(3) bond distance [1.417(3) Å] and C–S bond distances [1.677(3) Å, av] in the C_{5}S_{2} moieties of 4* are in contrast to those in 3 [d_{C-C} = 1.355(5)Å, d_{C-S} = 1.716(4) Å] and in various dithiolates such as uncomplexed dithiolate ligand [i.e., (NMe_{2})_{2}(C_{5}S_{2})], d_{C-C} = 1.371(8) Å, d_{C-S} = 1.724(6) Å, av] and silver dithiolate complex [NBu_{4}]_{4}[Ag-(mnt)]_{4} (mnt = 1,2-maleonitrile-1,2-dithiolate) [d_{C-C} = 1.373(8) Å, d_{C-S} = 1.736(6) Å, av]. By comparison with those in dithiolates (L_{2}S_{2}, Figure 1), the elongation of the carbon–carbon bond and concomitant shortening of the carbon–sulfur bonds observed in 4* may be attributed to the SOMO (Figure 3b) of 4*, 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_{5}S_{2} moieties of 4* indicate that these bonds have a modest double bond character, which is consistent with the resonance structures of L* in Figure 1.

Although synthetic routes for dithiolene complexes have been reported, 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* to react with GeCl_{2}/dioxane in THF (in a ratio of 2:1). The anionic chlorogermainium-bis(dithiolene) complex (5) was isolated as a dark-blue diamagnetic crystalline solid (83.3% yield) (Scheme 2).

Scheme 2. Synthesis of 5

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_{C-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_{3} symmetry) features a distorted trigonal bipyramidal geometry around the germanium atom (S_{a}-Ge_{a}-S_{a} angle = 167.25°; S_{a}-Ge_{a}-S_{eq} angle = 127.7°), which is comparable to that for anionic fluorogermainate ([C_{4}H_{2}S_{2}]_{2}GeF) (S_{a}-Ge-S_{ax} = 171.1°, S_{eq}-Ge-S_{eq} = 136.2°). The square pyramidal geometry around 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), 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 C_{5}S_{2} 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 C_{5}S_{2}Ge rings in 5 (η = 37.3°, av) are more bent than those in [5-H]− (η = 29.6°) and the C_{5}S_{2}Li ring in 4* (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*, 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 monomeric 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.

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

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Notes

The authors declare no competing financial interest.
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REFERENCES

(30) See the Supporting Information for synthetic, spectral, computational, and crystallographic details.