



Carbenes Hot Paper

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Carbene-Stabilized Dithiolene (L^0) Zwitterions

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Abstract: A series of reactions between Lewis bases and an imidazole-based dithione dimer (**1**) has been investigated. Both cyclic(alkyl)(amino)carbene (CAAC) (**2**) and *N*-heterocyclic carbene (NHC) (**4**), in addition to *N*-heterocyclic silylene (NHSi) (**6**), demonstrate the capability to cleave the sulphur–sulphur bonds in **1**, giving carbene-stabilized dithiolene (L^0) zwitterions (**3** and **5**) and a spirocyclic silicon–dithiolene compound (**7**), respectively. The bonding nature of **3**, **5**, and **7** are probed by both experimental and theoretical methods.

Largely due to the interplay of variable oxidation states of transition metals and the non-innocent character of the dithiolene ligand,^[1] the intriguing redox behavior of transition metal-based dithiolene complexes has fascinated chemists for more than a half-century.^[1,2] The oxidation state of the dithiolene ligand has previously been reported to vary between three ligand forms: dithiolate dianion (L^{2-}), radical monoanion (L^{-}), and neutral dithione (or dithiete) (L^0) (Figure 1).^[2f,3]

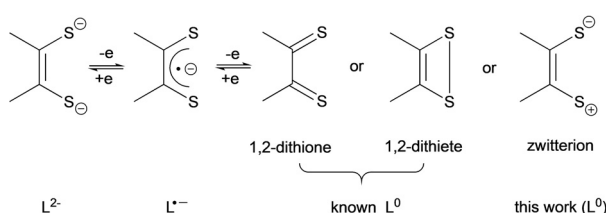
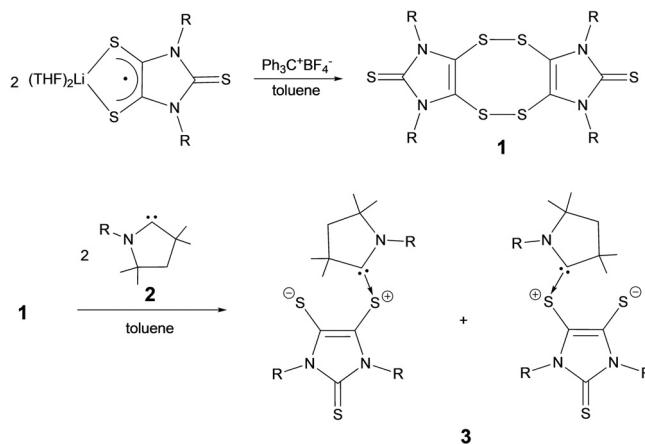


Figure 1. Redox states of dithiolene ligands.

In contrast to the dominant roles of dithiolate (L^{2-}) ligands in transition metal dithiolene chemistry,^[2a] dithiolene ligands with monoanionic radical character (L^{-}) are receiving increasing attention.^[2f] For example, this laboratory recently reported the synthesis and molecular structure of lithium dithiolene radical (Scheme 1),^[4] which provides a unique synthetic platform for accessing the largely unexplored dithiolene chemistry of main group elements.^[5] In contrast to dithiolate dianions (L^{2-} , containing six π -electrons), the 4π -electron-containing neutral dithiolene (L^0) is an electron-deficient



Scheme 1. Synthesis of **3** ($R = 2,6$ -diisopropylphenyl).

system, thus inclined to seek electron-rich species.^[2j] Neutral dithiolenes (L^0) have been reported to exist as dithiones and dithietes (Figure 1).^[2a,g,i,6] While structurally characterized dithiones and dithietes have been reported,^[6d,e,7] zwitterionic dithiolenes (L^0) (Figure 1) remain synthetic targets. Considering its electron deficiency, the dithiolene (L^0) system may employ one of its two sulphur atoms to accept one pair of electrons from a Lewis base ligand. This would result in charge separation, giving a Lewis base-stabilized dithiolene (L^0) zwitterion. To this end, we report the syntheses,^[8] structures^[8] and computations^[8] of the first carbene-stabilized neutral dithiolene (L^0) zwitterions (**3** and **5**). Notably, when employing NHSi as the Lewis base, a spirocyclic silicon–dithiolene complex (**7**) was achieved.

Scission of sulphur–sulphur bonds is important in biological processes and organic synthesis,^[9] which usually involves transition metals or main group species (i.e., nucleophiles, electrophiles, and FLPs).^[9,10] Carbene-insertion into the S–S bond is attracting increasing attention.^[11] In particular, transient donor/acceptor-free carbenes have been shown to cleave the S–S bond through ylide formation or radical mechanisms.^[11d] This laboratory recently synthesized the imidazole-based dithione dimer, containing S–S bonds, (**1**) by one-electron oxidation of the corresponding lithium dithiolene radical anion (Scheme 1).^[12] The analogues of **1** have been synthesized by both sulfurization of imidazole-based dione with Lawesson's reagent and Br_2 oxidation of nickel bis-dithiolene complex.^[13] Dissociation of these dithione dimers in solution has not been observed. Dithione was only documented as a reactive intermediate in the synthesis of stable analogue of **1** ($R = iPr$).^[13a] The 1:2 reaction of **1** with $MeCAAC$ (**2**)^[14] in toluene results in the cleavage of the S–S bonds in **1**, affording the carbene-

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stabilized dithiolene (L^0) zwitterion (**3**) as a purple-blue powder in 94.0% yield (Scheme 1).^[8] X-ray single crystals of **3** were obtained by recrystallization from hot toluene (or from a 1,2-difluorobenzene/hexane mixed solvent). The UV–Vis absorption spectrum of **3** in toluene reveals one strong broad absorption ($\lambda_{\text{max}} = 611$ nm) and one weak broad absorption ($\lambda_{\text{max}} = 451$ nm) (Figure S1).^[8] Due to poor solubility in benzene (or toluene) at room temperature, the ^{13}C NMR spectrum of **3** (in C_6D_6) was determined at an elevated temperature ($T = 68^\circ\text{C}$).^[8] The ^{13}C NMR resonance of the carbene carbon in **3** [C(28) in Figure 2] (in C_6D_6) is observed at 208.53 ppm, which shifts upfield compared to that (313.6 ppm) of the free $^{\text{Me}}\text{CAAC}$ ligand (in C_6D_6).^[14a]

X-ray structural analysis^[8] reveals that **3** exists as a pair of enantiomers (with identical bonding parameters) (Figure 2), which may be attributed to the steric congestion of **3**, thereby restricting the rotation about the C(2)–S(2) bond (see the space filling model of **3** in Figure S2).^[8] In addition, the two 2,6-diisopropylphenyl substituents of the imidazole ring are bent toward the opposite sides of the five-membered ring. While being marginally shorter than the corresponding theoretical values in **3** model ($d_{\text{C-C}} = 1.393$ Å, $d_{\text{C-S}} = 1.704$ and 1.735 Å),^[8] the C_2S_2 unit in **3** shows an elongated C–C bond [1.374(2) Å] and concomitantly shortened C–S bonds

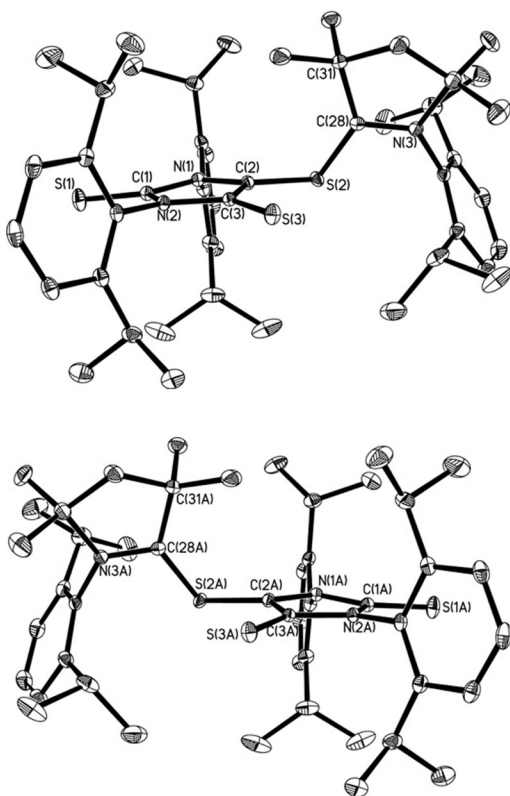


Figure 2. Molecular structures of the enantiomers of **3**. Thermal ellipsoids represent 30% probability. Hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (deg): S(1)–C(1), 1.6718(16); C(2)–C(3), 1.374(2); C(2)–S(2), 1.7137(15); C(3)–S(3), 1.6941(16); S(2)–C(28), 1.7285(16); C(28)–C(31), 1.524(2); C(28)–N(3), 1.304(2); C(2)–C(3)–S(3), 131.42(12); C(2)–S(2)–C(28), 106.69(8).

[1.6941(16) and 1.7137(15) Å] compared to those in **1** [$d_{\text{C-C}} = 1.362(8)$ Å, $d_{\text{C-S}} = 1.724$ (6) and 1.733(6) Å].^[12] By comparison, the C–S bonds in the C_2S_2 unit of **3** [1.6941(16) and 1.7137(15) Å] are longer than the C(1)=S(1) double bond of **3** [1.6718(16) Å], however, shorter than the typical C–S single bonds (such as those in $\text{PtPh}_2(9\text{S3})$ ($9\text{S3} = 1,4,7\text{-trithiacyclononane}$) [1.815(8)–1.848(8) Å].^[15] The C(3)–C(2)–S(2)–C(28) torsion angle (-63.7°) of **3** is comparable to that (-63.1°) in **3** model, whereas the S(2)–C(2)–C(3)–S(3) torsion angle (9.0°) of **3** is somewhat smaller than its theoretical value (16.5°) (which may be due to packing effects).^[16] The carbene carbon in **3** [i.e., C(28)] exhibits a trigonal planar geometry [the sum of bond angles around C(28) = 359.7°].

The DFT computations^[8] of **3** at the B3LYP/6–311G** level show that the HOMO is predominantly dithiolene-based, involving polarized C–C π -bonding and C–S π -antibonding character, whereas the LUMO is mainly CAAC-based with $\text{C}_{\text{CAAC}}\text{-N}$ π -antibonding character (Figure 3). NBO natural population analysis reveals a positive charge of +0.43 at the S(2) atom and a negative charge of -0.35 at the S(3) atom of **3**, supporting **3A** (Figure 4) as the major resonance contributor. It is reasonable to deduce that formation of **3** may be through CAAC-mediated heterolytic cleavage of S–S bonds in **1**. The diradical product **3 $^{\bullet}$** would be expected if CAAC-mediated cleavage of S–S bonds in **1** is homolytic and involves a radical mechanism. However, our computations reveal that the triplet diradical **3 $^{\bullet}$** is 15.32 kcal mol^{-1} higher in energy than the singlet zwitterionic **3 $^{\bullet}$** .^[8]

We also investigated the corresponding reactions of **1** with other Lewis bases (i.e., NHC and NHSi). The 1:2 reaction of **1** with NHC^{IPr} ^[17] (**4**) gave enantiomeric **5** (the NHC analogue of **3**) as a yellow powder (in 84.4% yield) (Scheme 2). Unexpectedly, the parallel reaction of **1** with sterically demanding $\text{NHSi}^{\text{Dipp}}$ ^[18] (Dipp = 2,6-diisopropylphenyl) (**6**)

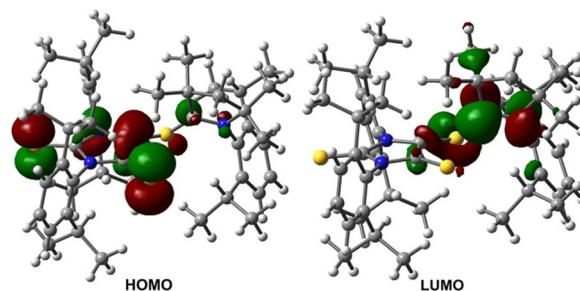


Figure 3. Frontier molecular orbitals of **3**.

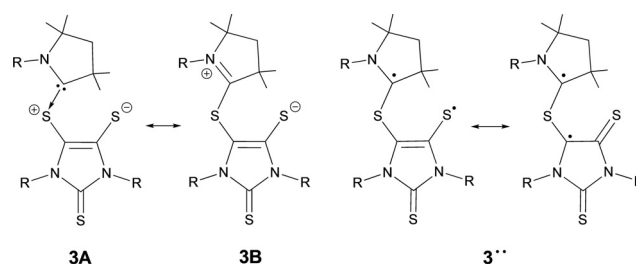
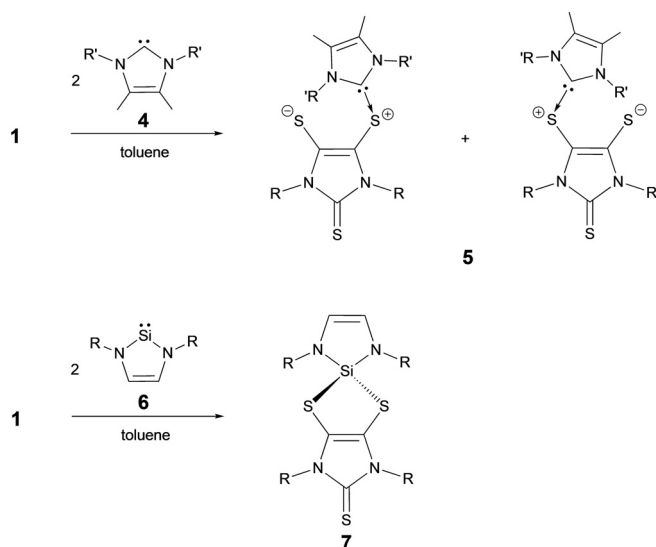


Figure 4. Canonical structures of **3** and **3 $^{\bullet}$** .



Scheme 2. Synthesis of NHC-stabilized **5** and spiro silicon-dithiolene **7** ($R=2,6$ -diisopropylphenyl, R' = isopropyl).

quantitatively resulted in colourless spirocyclic silicon–dithiolene complex (**7**) (Scheme 2).^[8] Consequently, **7** joins a small group of structurally characterized silicon–dithiolene complexes.^[5c,19] To the best of our knowledge, the literature does not reveal a report of stable carbene-, or silylene-, mediated cleavage of a sulphur–sulphur bond (in a molecular compound). The dramatic colour difference between **3** and **5** may be related to their distinct HOMO–LUMO energy gaps [$\Delta E_{\text{HOMO-LUMO}} = 2.08$ eV (**3**) and 2.88 eV (**5**)].^[8] Compound **5** is largely insoluble in benzene and toluene. The ^1H NMR spectrum of **5** (Figure S6) in $\text{C}_6\text{D}_5\text{Br}$ at room temperature shows broad lines. Notably, the methine proton resonance of the NHC^{Pr} ligand in **5** cannot be even distinguished from the baseline. Variable-temperature (VT) ^1H NMR experiments of **5** (Figure S5) show that with the temperature increasing from 25 to 80 °C, the methyl proton resonances at 0.74 and 1.04 ppm evolve from broad singlets to sharp doublets. Meanwhile, the methine proton resonance of the NHC^{Pr} unit of **5** is observed as a broad singlet at 5.68 ppm (Figure S7). Such dynamic behaviour of **5** in $\text{C}_6\text{D}_5\text{Br}$ should be due to steric congestion of this compound, which restricts the ligand rotation (see the space filling model of **5** in Figure S2). In contrast to carbene-complexed zwitterions (**3** and **5**), spirocyclic compound **7** is readily soluble in toluene. The four-coordinate silicon atom in **7** exhibits a ^{29}Si NMR resonance at -4.67 ppm. By comparison, the ^{29}Si NMR resonance of the silicon bis(dithiolene) complex, $\text{Si}[\text{S}_2(o\text{-C}_6\text{H}_4)]_2$,^[19a] is observed at 45.4 ppm, while those for the alkoxy-functionalized NHSi sulphides were observed at -24.3 and -24.4 ppm.^[20] Spirocyclic silanes have been obtained via 4 + 1 cyclization reactions of silylenes with various dienes.^[21] Thus, **7**, may also be accessed through 1,2-dithiones (Figure 1).

Similar to **3**, the NHC-complexed dithiolene (L^0) zwitterion (**5**) also exists as an enantiomeric pair (with identical bonding parameters) (Figure 5 a).^[8] By comparison with **3**, the most obvious structural changes for **5** are the $\text{C}(3)\text{--}\text{C}(2)\text{--}\text{S}(2)$ -

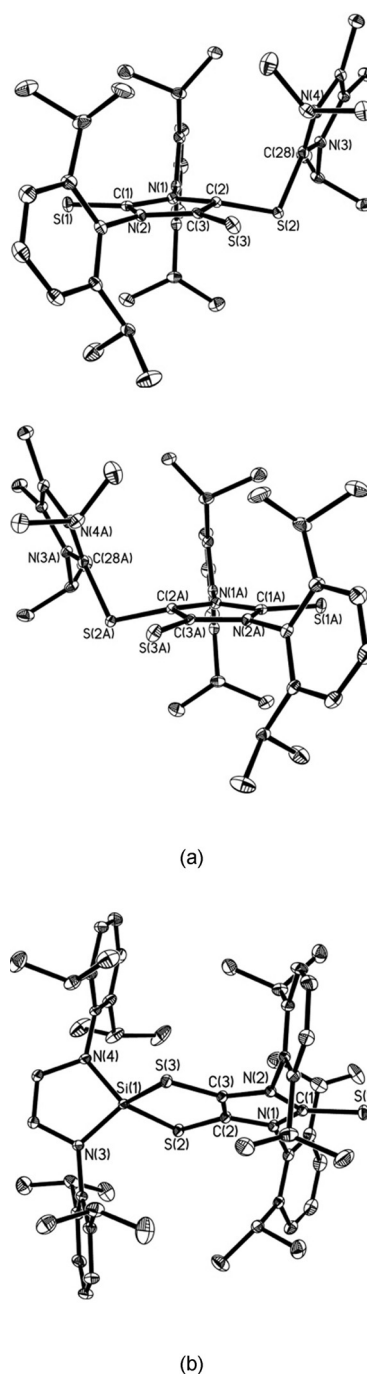


Figure 5. Molecular structures of enantiomeric **5** (a) and spiro silicon-dithiolene **7** (b). Thermal ellipsoids represent 30% probability. Hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (deg): For **5**, $\text{S}(1)\text{--}\text{C}(1)$, 1.673(2); $\text{C}(2)\text{--}\text{C}(3)$, 1.380(3); $\text{C}(2)\text{--}\text{S}(2)$, 1.718(2); $\text{C}(3)\text{--}\text{S}(3)$, 1.690(2); $\text{S}(2)\text{--}\text{C}(28)$, 1.757(2); $\text{C}(2)\text{--}\text{C}(3)\text{--}\text{S}(3)$, 131.22(17); $\text{C}(3)\text{--}\text{C}(2)\text{--}\text{S}(2)$, 125.84(17); $\text{C}(2)\text{--}\text{S}(2)\text{--}\text{C}(28)$, 106.62(11). For **7**, $\text{S}(1)\text{--}\text{C}(1)$, 1.6638(9); $\text{C}(2)\text{--}\text{C}(3)$, 1.3468(12); $\text{C}(2)\text{--}\text{S}(2)$, 1.7374(9); $\text{C}(3)\text{--}\text{S}(3)$, 1.7339(9); $\text{S}(2)\text{--}\text{Si}(1)$, 2.1591(4); $\text{N}(3)\text{--}\text{Si}(1)$, 1.7118(9); $\text{C}(2)\text{--}\text{C}(3)\text{--}\text{S}(3)$, 125.12(7); $\text{C}(2)\text{--}\text{S}(2)\text{--}\text{Si}(1)$, 94.73(3); $\text{S}(2)\text{--}\text{Si}(1)\text{--}\text{S}(3)$, 100.893(15).

$\text{C}(28)$ torsion angle (-63.7° for **3**, -114.8° for **5**) and $\text{N}(3)\text{--}\text{C}(28)\text{--}\text{S}(2)\text{--}\text{C}(2)$ torsion angle ($+154.1^\circ$ for **3**, -126.5° for **5**). These structural distinctions between **3** and **5** are largely due

to the different steric effects of the carbene ligands (**2** and **4**). The +0.33 positive charge of the S(2) atom and −0.35 negative charge of the S(3) atom in **5** compare well to that in **3** [+0.43 for S(2) and −0.35 for S(3)], suggesting its zwitterionic character. The 1.34–1.48 Wiberg bond index of the C–S_{terminal} bonds [i.e., C(1)–S(1) and C(3)–S(3) bonds] in **3** and **5** indicate that these two bonds have modest double bond character. The C_{carbene}–S bond in **5** [1.757(2) Å; 57.5% toward C and 42.5% toward S] is somewhat longer and more polarized than that in **3** [1.7285(16) Å; 55.3% toward C and 44.7% toward S]. Frontier molecular orbitals of **5** (Figure S12) are comparable with those of **3**.^[8]

X-ray structural analysis^[8] (Figure 5b) shows that the four-coordinate silicon atom in **7** adopts a distorted tetrahedral geometry ($\tau = 0.78$).^[22] Similar to that [2.1381(6) Å] of Si[S₂(*o*-C₆H₄)₂] containing a four-coordinate silicon atom,^[19a] the Si–S bond distances of **7** [2.1604(4) Å, av] are much shorter than those [2.3195(12)–2.3374(12) Å] in the reported silicon tris(dithiolene) dianion containing a six-coordinate silicon atom.^[5c] The bonding parameters of the C₂S₂ unit [*d*_{C–S} = 1.7357(9) Å, av; *d*_{C=C} = 1.3468(12) Å] of **7** are consistent with those for the reported dithiolates.^[2a,23] Thus, the Si^{II} atom in NHSi^{Dipp} (**6**) is oxidized to Si^{IV} when forming **7**. The natural charge residing at the central silicon of **7** is +1.59. While the HOMO of **7** is dithiolene-based (containing both C–C π -bonding and C–S π -antibonding character), the LUMO involves silicon–sulphur σ -antibonding interactions (Figure S13).^[8]

The sulphur–sulphur bonds in the imidazole-based dithione dimer (**1**) have successfully been cleaved using a series of stable Lewis bases [^{Me}CAAC (**2**), NHC^{Pr} (**4**), and NHSi^{Dipp} (**6**)], which gives carbene-stabilized dithiolene (L⁰) zwitterions (**3** and **5**) and spirocyclic silicon–dithiolene complex (**7**), respectively. The intriguing redox reactivity of these compounds are being further investigated in this laboratory.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords: carbenes · dithiolenes · silicon · silylenes · sulphur

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