



Stable Boron Dithiolene Radicals

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Abstract: Whereas low-temperature (-78°C) reaction of the lithium dithiolene radical **1**[•] with boron bromide gives the dibromoboron dithiolene radical **2**[•], the parallel reaction of **1**[•] with $(\text{C}_6\text{H}_{11})_2\text{BCl}$ (0°C) affords the dicyclohexylboron dithiolene radical **3**[•]. Radicals **2**[•] and **3**[•] were characterized by single-crystal X-ray diffraction, UV/Vis, and EPR spectroscopy. The nature of these radicals was also probed computationally. Under mild conditions, **3**[•] undergoes unexpected thiourea-mediated B–C bond activation to give zwitterion **4**, which may be regarded as an anionic dithiolene-modified carbene complex of the sulphenyl cation RS^+ ($\text{R} = \text{cyclohexyl}$).

The unique optical, conductive, magnetic, and catalytic properties of transition-metal dithiolene complexes have long fascinated chemists.^[1] The “non-innocent” character^[1c] of dithiolene ligands (Figure 1) has been shown to play a pivotal role in such disparate fields as materials science^[1d,j] and biological systems.^[1b,k] Indeed, the non-innocent character of transition-metal dithiolenes was recently probed by sulfur K-edge X-ray absorption spectroscopy (XAS).^[1h]

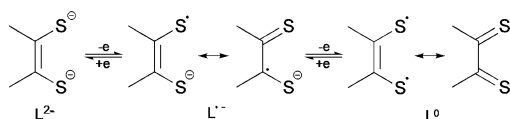
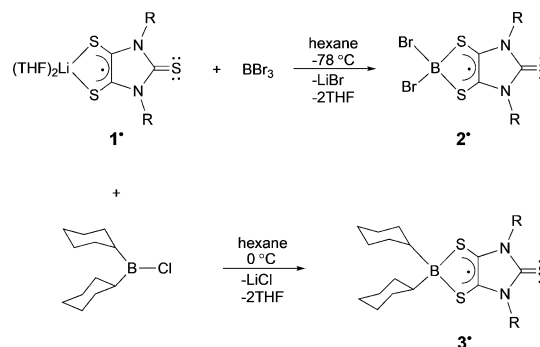


Figure 1. Redox non-innocence of a dithiolene ligand.^[2]

The presence of radical anionic ligands ($\text{L}^{\cdot-}$) in transition-metal dithiolene complexes was notably predicted by Gray and co-workers more than five decades ago.^[3] Subsequently, the radical character of ligands in transition-metal dithiolene complexes has been extensively studied.^[1h,4] Notably, the literature does not reveal reports of p block element containing dithiolene radicals. Our group recently reported the first structurally characterized anionic dithiolene radical **1**[•] (Scheme 1), which was obtained by trisulfurization of the corresponding anionic N-heterocyclic dicarbene (NHDC).^[6] Significantly, **1**[•] provides a unique platform for the generation of a variety of dithiolene-based p block species.

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Supporting information and the ORCID identification number(s) for the author(s) of this article can be found under:
<https://doi.org/10.1002/anie.201804298>.



Scheme 1. Synthesis of boron dithiolene radicals **2**[•] and **3**[•]. $\text{R} = 2,6$ -diisopropylphenyl.

Radicals involving boron atoms^[7] are intriguing not only for their interesting structures and bonding motifs, but also owing to their potentially broad applications as chemical sensors, polymerization initiators, reagents for organic synthesis, and building blocks for magnetic systems.^[8] Compared to anionic boron radicals ($\text{BR}_3^{\cdot-}$), neutral radicals (BR_2^{\cdot}) are more reactive owing to the enhanced electron deficiency of the two-coordinate boron atom (usually complexed by Lewis bases). The reported neutral three-coordinate LBR_2^{\cdot} species usually employ amines, phosphines, N-heteroarenes, and carbenes as the Lewis base ligands (L).^[7b] In addition, a neutral β -diiminate-based three-coordinate diazaborocyclic radical (Figure 2a) has been reported, wherein the unpaired electron is delocalized over the six-membered $\text{C}_3\text{N}_2\text{B}$ ring.^[9] Bidentate heterocyclic ligands are effective for achieving boron-containing radicals. Indeed, five-membered diazaborocyclic (Figure 2b, c)^[10] and dioxoborocyclic (Figure 2d)^[11] radicals containing four-coordinate boron atoms have been synthesized. Interestingly, the syntheses of the dioxoboro-

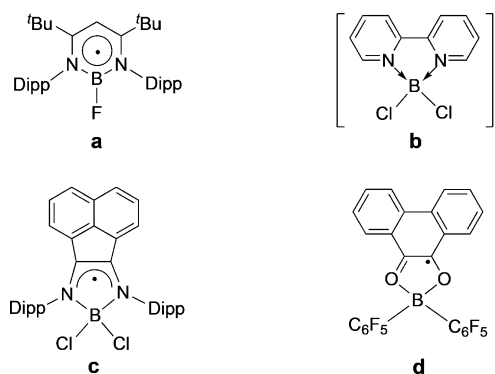
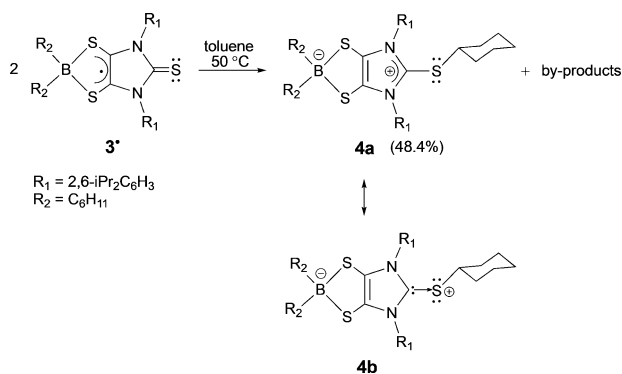


Figure 2. Representative neutral diazaborocyclic (a–c) and dioxoborocyclic (d) radicals. Dipp = 2,6-diisopropylphenyl.

cycle (Figure 2d) and its 4,5-pyrenedione-derived analogues involved H₂ activation with polyaromatic diones and B(C₆F₅)₃ as frustrated Lewis pairs.^[11] Notably, dithioborocyclic radicals have not been reported. Herein, we report the synthesis,^[12] structures,^[12] EPR^[12] and UV/Vis spectra,^[12] and computations^[12] of the first boron dithiolene radicals **2**[•] and **3**[•] (Scheme 1). Surprisingly, **3**[•] readily undergoes thiourea-mediated boron–carbon bond activation under mild conditions to give diamagnetic zwitterion **4** (Scheme 2), which may be



Scheme 2. Synthesis of zwitterion **4** by thiourea-mediated B–C bond activation. Compound **4** has two major resonance forms, **4a** and **4b** (anionic boron-dithiolene-modified carbene complex of a sulfenyl cation).

regarded as an anionic dithiolene-modified carbene complex of the sulfenyl cation RS⁺ (R = cyclohexyl). The activation of boron–carbon bonds with high bond dissociation energies (BDE_{B–C} ≈ 360 kJ mol^{−1} vs. BDE_{C–C} ≈ 350 kJ mol^{−1}) under mild conditions has been well explored.^[13] Transition-metal species are well known for their utility in boron–carbon bond activation (e.g., Pd⁰ species in Suzuki couplings^[14] between organoboranes and organic halides).^[15] In contrast, B–C bond activation mediated by main group species has only been scarcely documented.^[13,16] The synthesis of **4** represents the first example of thiourea-mediated B–C bond activation.

Reaction of the purple lithium dithiolene radical **1**[•] with excess BBr₃ in hexane (−78 °C) gave **2**[•] as dark blue crystals (upon recrystallization from a toluene solution; Scheme 1). The parallel reaction of **1**[•] with (C₆H₁₁)₂BCl (0 °C) afforded the dark blue radical **3**[•] (Scheme 1). Two strong UV/Vis absorption bands were observed for **2**[•] (λ = 606 and 654 nm) and **3**[•] (λ = 596 and 630 nm).^[12] The paramagnetic properties of radicals **2**[•] and **3**[•] were analyzed by room-temperature EPR spectroscopy in toluene. The EPR spectrum of **2**[•] (Figure 3A) displays an S = 1/2 septet due to hyperfine coupling with two equivalent bromine atoms. Spectral simulations give g_{av} = 2.008 and hyperfine coupling constants of A_{av} = 28.95 MHz for ⁷⁹Br (I = 3/2, g_n = 1.404) and A_{av} = 31.20 MHz for ⁸¹Br (I = 3/2, g_n = 1.514). Molecular orbital calculations indicate that the SOMOs of **2**[•] (Figure 3C) and **[3-Ph]**[•] (Figure 3D) are predominantly ligand-based, with C–C π-bonding and C–S π-antibonding character. While computations suggest that the majority of the spin density of **2**[•] (0.71) and **[3-Ph]**[•] (0.77), similar to that for **1**[•] (0.88),^[5] resides on the C₂S₂ unit of the dithiolene ligand, the hyperfine coupling constants suggest

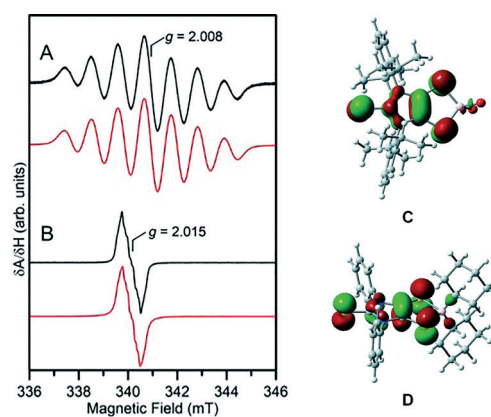


Figure 3. Room-temperature X-band EPR spectra of A) **2**[•] and B) **3**[•] in toluene. Spectra (black lines) were recorded at 9.581 GHz with a modulation amplitude of 0.02 mT and a microwave power of 0.1 mW for **2**[•] and 1.0 mW for **3**[•]. Spectral simulations (red lines) used the following parameters: A) Linewidth: 0.6 mT; g_{av} = 2.008; ⁷⁹Br (I = 3/2): A_{av} = 28.95 MHz; ⁸¹Br (I = 3/2): A_{av} = 31.20 MHz. B) Linewidth: 0.137 mT, g_{av} = 2.015; ¹⁰B (I = 3): A_{av} = 1.97 MHz; ¹¹B (I = 3/2): A_{av} = 5.64 MHz; ¹⁴N (I = 1) A_{av} = 2.80 MHz. C) SOMO of **2**[•] and D) SOMO of the simplified model **[3-Ph]**[•].

that significant spin density resides on the two equivalent bromine atoms in **2**[•]. For instance, after correcting for the difference in g_n values, the bromine atoms have two- to threefold higher spin density than the two equivalent nitrogen atoms in **2**[•] and its precursor **1**[•].^[5] The large linewidths (0.6 mT); Figure 3A) reflect the presence of two I = 3/2 bromine isotopes with different g_n values and, most likely, the presence of unresolved ¹⁰B (I = 3), ¹¹B (I = 3/2), and ¹⁴N (I = 1) hyperfine interactions. Although **3**[•] exhibits a complex EPR spectrum with partially resolved hyperfine splitting (Figure 3B), it was well simulated with g_{av} = 2.015, a linewidth of 0.137 mT, and hyperfine coupling constants of A_{av} = 5.64 MHz for ¹¹B (I = 3/2, g_n = 1.404), A_{av} = 1.97 MHz for ¹⁰B (I = 3, g_n = 0.600), and A_{av} = 2.8 MHz for two equivalent ¹⁴N nuclei (I = 1, g_n = 0.404). After correction for the differences in the g_n values, the hyperfine interactions indicate approximately twofold greater spin density on the two equivalent nitrogen atoms than on the boron atom.

The solid-state structures of both **2**[•] and **3**[•] (Figure 4)^[12] feature a bent five-membered BS₂C₂ ring. However, the BS₂C₂ rings of the **2**[•] and **[3-Ph]**[•] models were computed as planar in the gas phase.^[12] The bent angle (η) between the BS₂ plane and the S₂C₂ plane [13.5° (**2**[•]), 16.2° (**3**[•])] in the solid state may be a consequence of a combination of packing effects and the steric repulsion between the substituents of boron and the dithiolene ligand.^[17] The experimental B–S bond lengths of **2**[•] [1.927 (4) Å] and **3**[•] [2.027(4) Å, avg.] are comparable to the values calculated for **2**[•] (1.985 Å) and **[3-Ph]**[•] (2.058 Å).^[12] The boron atoms in **2**[•] and **3**[•] are four-coordinate and adopt a distorted tetrahedral geometry. As those in precursor **1**[•] [d_{C–C} = 1.417(3) Å, d_{C–S} = 1.677(3) Å, avg.],^[5] the C₂S₂ units in both **2**[•] [d_{C–C} = 1.394(7) Å, d_{C–S} = 1.682(3) Å] and **3**[•] [d_{C–C} = 1.388(4) Å, d_{C–S} = 1.687(3) Å, avg.] exhibit elongated carbon–carbon bonds and shortened carbon–sulfur bonds compared to those in dithiolates [e.g., (NMe₄)₂(C₃S₅):^[18] d_{C–C} = 1.371(8) Å, d_{C–S} = 1.724(6) Å, avg.].^[1b] This is consistent

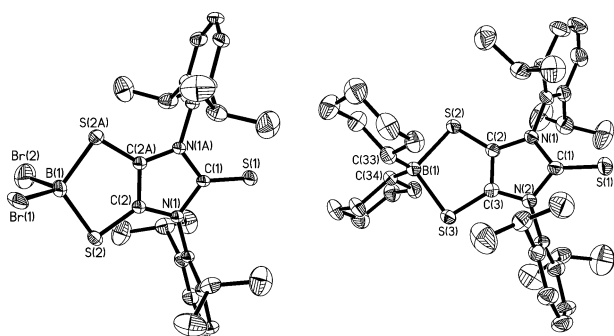


Figure 4. Molecular structures of **2⁺** and **3[•]**: Thermal ellipsoids set at 30% probability. Hydrogen atoms on carbon atoms omitted for clarity. Selected bond lengths [Å] and angles [°] for **2⁺**: S(1)–C(1) 1.623(5), C(2)–C(2A) 1.394(7), S(2)–C(2) 1.682(3), S(2)–B(1) 1.927(4), B(1)–Br 1.982(8) (avg), B(1)–Br(2) 1.984(10) (avg); B(1)–S(2)–C(2) 92.4(2), S(2)–C(2)–C(2A) 121.69(12), S(2)–B(1)–S(2A) 110.3(3), Br(1)–B(1)–Br(2) 107.4(4) (avg); for **3[•]**: S(1)–C(1) 1.633(4), C(2)–C(3) 1.388(4), S(2)–C(2) 1.680(3), S(3)–C(3) 1.694(3), S(2)–B(1) 2.026(4), S(3)–B(1) 2.028(4), B(1)–C(33) 1.607(6); B(1)–S(2)–C(2) 94.94(16), S(2)–C(2)–C(3) 122.9(3), S(2)–B(1)–S(3) 103.27(18), C(33)–B(1)–C(34) 118.8(3).

with the presence of a SOMO in **2⁺** (Figure 3C) and **3[•]** (Figure 3D) that has both C–C π -bonding and C–S π -antibonding character.^[12]

In contrast to **2⁺**, radical **3[•]** readily undergoes thiourea-mediated boron–carbon bond activation, resulting in diamagnetic zwitterion **4** (48.4% yield; Scheme 2).^[12] While the mechanism remains unclear, the formation of **4** appears to involve thiourea-mediated intermolecular cyclohexyl radical transfer. Notably, the spin density^[12] residing on S(1) (0.228) in **3[•]** (Figure 4) is comparable to that of S(2) (0.234) and S(3) (0.234). Furthermore, reactions of thioureas with carbon-centered radicals have previously been reported.^[19] Whereas compound **4** was routinely isolated as pale yellow-green crystals (Scheme 2), repeated attempts to isolate and characterize other side products from the thick residue were unsuccessful. Interestingly, Stephan and co-workers recently reported that phenanthrene-dione- (Figure 2d) and pyrene-dione-derived borocyclic radicals exhibit unique reactivity with nucleophiles (phosphines, carbenes, amines, and pyridines).^[20]

X-ray structural analysis^[12] (Figure 5) shows that, in contrast to the bent boron dithiolene ring in **3[•]** [d_{C-C} = 1.388(4) Å, d_{C-S} = 1.687(3) Å, avg.], the five-membered BS₂C₂ ring in **4** is almost planar, containing a shortened carbon–carbon bond and concomitantly elongated carbon–sulfur bonds [d_{C-C} = 1.365(2) Å, d_{C-S} = 1.7099(18) Å, avg.]. The C(2)–C(3) bond in **4** [1.365(2) Å] compares well with reported imidazole C=C double bonds.^[21] The four-coordinate boron atom in **4** exhibits a ¹¹B NMR resonance at δ = 18.9 ppm, which is comparable to the values reported for the zwitterions containing dioxaborocyclic moieties (δ = 10.2–11.1 ppm).^[20] While comparing well to those [1.732(4)–1.737(2) Å] in carbene-stabilized sulfenyl cations,^[22] the C(1)–S(1) bond in **4** [1.7256(18) Å] is about 0.09 Å longer than that in **3[•]** [1.633(9) Å], but approximately 0.11 Å shorter than the C(40)–S(1) single bond in **4** [1.834(4) Å]. Our

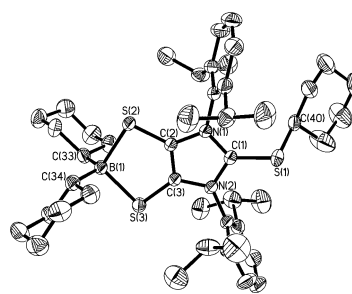


Figure 5. Molecular structure of **4**. Thermal ellipsoids set at 30% probability. Hydrogen atoms on carbon atoms omitted for clarity. Selected bond lengths [Å] and angles [°]: S(1)–C(1) 1.7256(18), S(1)–C(40) 1.834(4), C(2)–C(3) 1.365(2), S(2)–C(2) 1.7078(18), S(3)–C(3) 1.7120(18), S(2)–B(1) 2.027(2), S(3)–B(1) 2.031(2), B(1)–C(33) 1.611(3); B(1)–S(2)–C(2) 94.96(8), S(2)–C(2)–C(3) 123.01(14), S(2)–B(1)–S(3) 104.64(9), C(33)–B(1)–C(34) 117.05(16).

computations^[12] indicate that the C(1)–S(1) bond of **4** is polarized predominantly toward the C(1) atom (55.7%). The C(1) and S(1) atoms bear positive charges of +0.21 and +0.23, respectively. The Wiberg bond index (1.12) of the C(1)–S(1) bond in **4** is only marginally smaller than that (1.17) of the carbene-stabilized parent sulfenyl cation (HS⁺),^[22] thereby suggesting modest electron back-donation from the S(1) atom to the empty p orbital of the C(1) atom. Consequently, two resonance structures (**4a** and **4b** in Scheme 2) may be proposed for **4**. Resonance form **4b** represents an anionic boron-dithiolene-modified carbene complex of the sulfenyl cation RS⁺ (R = cyclohexyl). In both the solid state and the gas phase, the C(1)–S(1) bond of **4** is slightly puckered out of the imidazole plane [S(1)–C(1)–N(1)–C(2) torsion angle: –168.7° (solid state), –162.5° (gas phase)], which may be ascribed to the steric repulsion between two flanking 2,6-diisopropylphenyl moieties and the sulfur-bonded cyclohexyl group.

In conclusion, the first boron dithiolene radicals **2⁺** and **3[•]** have been synthesized by combining **1[•]** with the corresponding borane agents at low temperature. Under mild conditions, radical **3[•]** was further converted into zwitterion **4** by thiourea-mediated B–C bond activation. Notably, **4** may be regarded as an anionic dithiolene-modified carbene complex. The unique redox-active character of dithiolenes and the diverse utility of carbenes have both been well documented. This study demonstrates the possibility of developing novel chemistry at the dithiolene–carbene interface. The utility of zwitterion **4** is being explored in our laboratory.

Acknowledgements

We are grateful to the National Science Foundation for support (CHE-1565676 to G.H.R. and Y.W. and CHE-1661604 to H.F.S.). EPR studies were supported by a grant from the National Institutes of Health (R37-GM62524 to M.K.J.).

Conflict of interest

The authors declare no conflict of interest.

Keywords: B–C activation · boron · carbenes · dithiolenes · radicals

How to cite: *Angew. Chem. Int. Ed.* **2018**, *57*, 7865–7868
Angew. Chem. **2018**, *130*, 7991–7994

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Manuscript received: April 11, 2018

Accepted manuscript online: May 14, 2018

Version of record online: May 22, 2018