

From Carbene-Dithiolene Zwitterion Mediated B–H Bond Activation to $\text{BH}_3\cdot\text{SMe}_2$ -Assisted Boron–Boron Bond Formation

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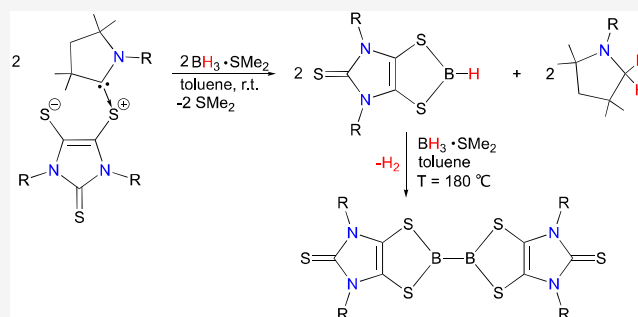
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ABSTRACT: The 1:1 reaction of the carbene-stabilized dithiolene zwitterion **1** with $\text{BH}_3\cdot\text{SMe}_2$ gave the dithiolene-based hydroborane **2** and the doubly hydrogen-capped CAAC species **3** via hydride-coupled reverse electron transfer processes. The mechanism of this transformation was probed computationally using density functional theory. The subsequent 2:1 reaction of **2** with **1** resulted in **4** and **3**, suggesting that **1** can mediate the B–H bond activation not only for BH_3 but also for monohydroboranes. In the presence of $\text{BH}_3\cdot\text{SMe}_2$, **2** was unexpectedly converted to the corresponding diborane(4) complex **5** through a dehydrocoupling reaction at an elevated temperature.

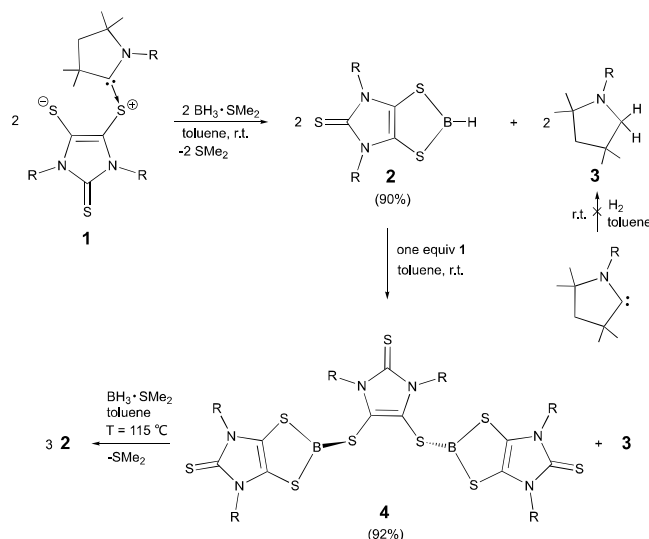


INTRODUCTION

The chemistry of boranes, compounds with boron–hydrogen bonds, has progressed significantly over the past century.^{1–3} Correspondingly, due to the pivotal role of boranes in a myriad of synthetic applications,⁴ coupled with the potential of ammonia–borane and related compounds as carbon-free energy sources,⁵ activation of the B–H bond steadfastly remains extremely relevant. Although higher order boranes are readily obtained from the pyrolysis of diborane (B_2H_6),⁶ the B–H bond is among the strongest two-electron σ -bonds on record (B–H bond dissociation energy (BDE): ca. 106 kcal mol⁻¹).^{6,7} Traditionally, transition-metal species have played a dominant role in B–H bond activation, wherein the B–H bond is commonly activated through an oxidative addition mechanism. Indeed, oxidative addition of a borane B–H unit to a metal center has been reported as a key step in transition-metal-catalyzed hydroboration.^{8,9} Furthermore, metal–ligand cooperative B–H bond activation reactions are receiving increased attention.¹⁰ While main-group-species^{11–18}-mediated B–H bond activation mainly involves 1,1-addition at a low-valent main-group species (such as carbenes,¹¹ carbenoid species,¹² and amidosilylenes¹³), frustrated Lewis pairs (FLPs)^{14,15} and boron-containing heterocycles^{16,17} have also been reported for this utility. In addition, boranes may demonstrate reduced B–H BDE values when being complexed by Lewis bases (such as NHCs).^{19,20} Consequently, NHC-complexed boranes have been employed as hydrogen atom donors via homolytic B–H cleavage.^{20–22} Notably, nitrogen-centered radical-mediated B–H activation of icosahedral carboranes via hydrogen atom transfer (HAT) has recently been reported.²³ This laboratory recently reported a cyclic

(alkyl)(amino)carbene (CAAC)-stabilized dithiolene zwitterion (**1**, in Scheme 1),²⁴ a new type of metal-free bifunctional molecular system which has been shown to activate ammonia

Scheme 1. Synthesis of **2** and **4** (R = 2,6-Diisopropylphenyl)



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via both single-electron-transfer (SET) and HAT processes.²⁵ Therein the 4π -electron neutral dithiolene moiety serves as an electron reservoir, while the in situ released CAAC ligand acts as a nucleophile. Herein, we report the CAAC-dithiolene zwitterion (**1**) mediated double and triple B–H bond activation of BH_3 via hydride-coupled reverse electron transfer (HCRET) processes. Interestingly, the $^{\text{Me}}\text{CAAC}^{26-28}$ ligand in **1** may serve as a two-hydrogen-atom acceptor in these transformations. Although the 1,2-hydride migration from a boron center to the adjacent carbene carbon of the CAAC ligand has been documented,^{29,30} observation of CAAC as a double-hydrogen-atom acceptor via HCRET has not been reported yet.

RESULTS AND DISCUSSION

The room-temperature reaction of **1** with $\text{BH}_3\cdot\text{SMe}_2$ (in a 1:1 ratio) in toluene rapidly gave the dithiolene-based hydroborane **2** as an off-white powder in 90% yield (Scheme 1)³¹ and the byproduct **3**.³² The ^1H NMR spectroscopic study shows that **2** and **3** are formed in a ca. 1:1 ratio. The doublet ^{11}B NMR resonance of the B(H) unit for **2** at 51.5 ppm ($J_{\text{BH}} = 152$ Hz, in toluene- d_8 , at 100 °C) compares to that (61.3 ppm ($J_{\text{BH}} = 140$ Hz)) for $(\text{CH}_2\text{S})_2\text{BH}$ (1,3,2-dithiaborolane).³³ In addition, the B–H stretching absorption (2469 cm^{-1}) in the infrared (IR) spectrum (Figure S14) of **2** (in KBr) is comparable with that (2435 cm^{-1}) of $(\text{CH}_2\text{S})_2\text{BH}$.³⁴ Further reaction of **2** with **1** (in a 2:1 ratio) in toluene at room temperature gave **4** as an off-white powder (in 92% yield) and byproduct **3** (Scheme 1).³¹ The ^{11}B NMR resonance (in C_6D_6) of **4** displays a broad singlet at 59.3 ppm ($w_{1/2} = 991$ Hz). Compound **4** may also be directly prepared by the reaction of **1** with $\text{BH}_3\cdot\text{SMe}_2$ in a 3:2 ratio. Compound **4** was quantitatively converted to **2** via a 1:1 reaction with $\text{BH}_3\cdot\text{SMe}_2$ at an elevated temperature ($T = 115\text{ °C}$) (Scheme 1). Isolation of the doubly-hydrogen-capped CAAC species **3** as a byproduct in the 1-to-2 and 2-to-4 conversions suggests that two hydrogen atoms are ultimately transferred to the CAAC ligand.

Compounds **2** and **4** were further characterized by single-crystal X-ray diffraction analysis.³¹ The hydrogen atom bound to the boron atom in **2** (Figure 1) was located from difference Fourier maps. The three-coordinate boron atom in **2** adopts a trigonal-planar geometry. The experimental (1.792(3) Å) and theoretical (1.808 Å) values of the S–B bond distance of **2** are considerably shorter than those in four-coordinate boron-based dithiolene complexes (1.927(4)–2.031(2) Å)³⁵ due to the S–B π interaction (The S–B Wiberg bond index (WBI) of **2** is 1.29). In the solid state, compound **4** exists as a pair of enantiomers with identical bonding parameters (for clarity, only one of the enantiomers is shown in Figure 1). The X-ray structural analysis of **4** shows that the dithiolene unit serves as a bridging ligand to bind two boron dithiolene species via two S–B single bonds (1.815(5) Å) on opposite sides of the dithiolene (C_2S_2) plane (in C_2 symmetry), confirming exhaustive B–H bond activation of BH_3 .

The room-temperature NMR-tube reaction of **1** with $\text{BH}_3\cdot\text{SMe}_2$ (in a 1:1 ratio) in C_6D_6 did not exhibit the singlet ^1H NMR resonance of $\text{H}_2(\text{g})$ at 4.47 ppm (Figure S13)³¹ and thus does not support the evolution of dihydrogen gas in the formation of **2**. Although CAAC-mediated dihydrogen splitting has been observed at 35 °C,³⁶ the free $^{\text{Me}}\text{CAAC}$ ligand does not react with $\text{H}_2(\text{g})$ in toluene at room temperature (Scheme 1).

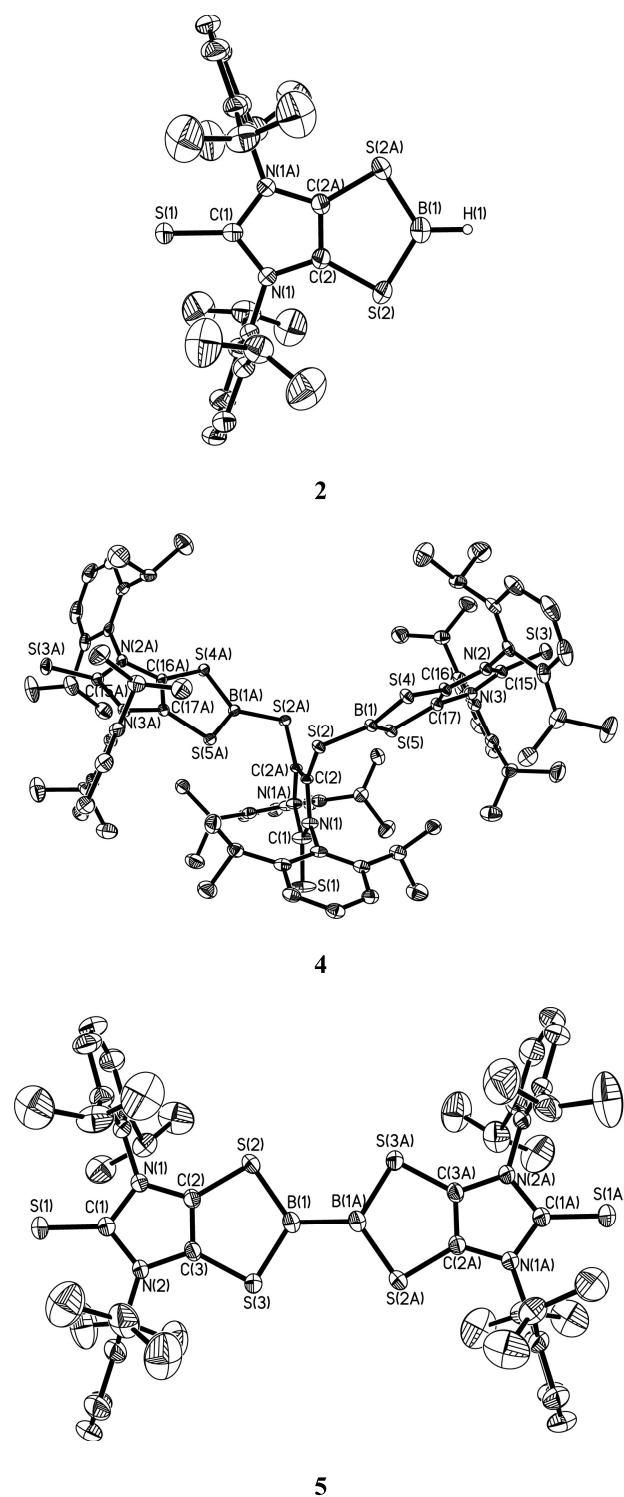


Figure 1. Molecular structures of **2**, **4**, and **5**. Thermal ellipsoids represent 30% probability. Hydrogen atoms on carbon have been omitted for clarity. Selected bond distances (Å) and angles (deg) for **2**: C(2)–C(2A) 1.331(5); C(2)–S(2) 1.724(2); S(2)–B(1) 1.792(3); C(2A)–C(2)–S(2) 119.74(8); S(2A)–B(1)–S(2) 116.1(3). Selected bond distances (Å) and angles (deg) for **4**: C(2)–C(2A) 1.342(8); C(2)–S(2) 1.759(4); S(2)–B(1) 1.815(5); C(2A)–C(2)–S(2) 130.58(14); C(2)–S(2)–B(1) 100.4(2). Selected bond distances (Å) and angles (deg) for **5**: B(1)–B(1A) 1.645(6); S(2)–B(1) 1.796(3); C(2)–S(2) 1.715(3); S(2)–B(1)–S(3) 113.88(16); S(2)–B(1)–B(1A) 123.6(3); S(3)–B(1)–B(1A) 122.5(3).

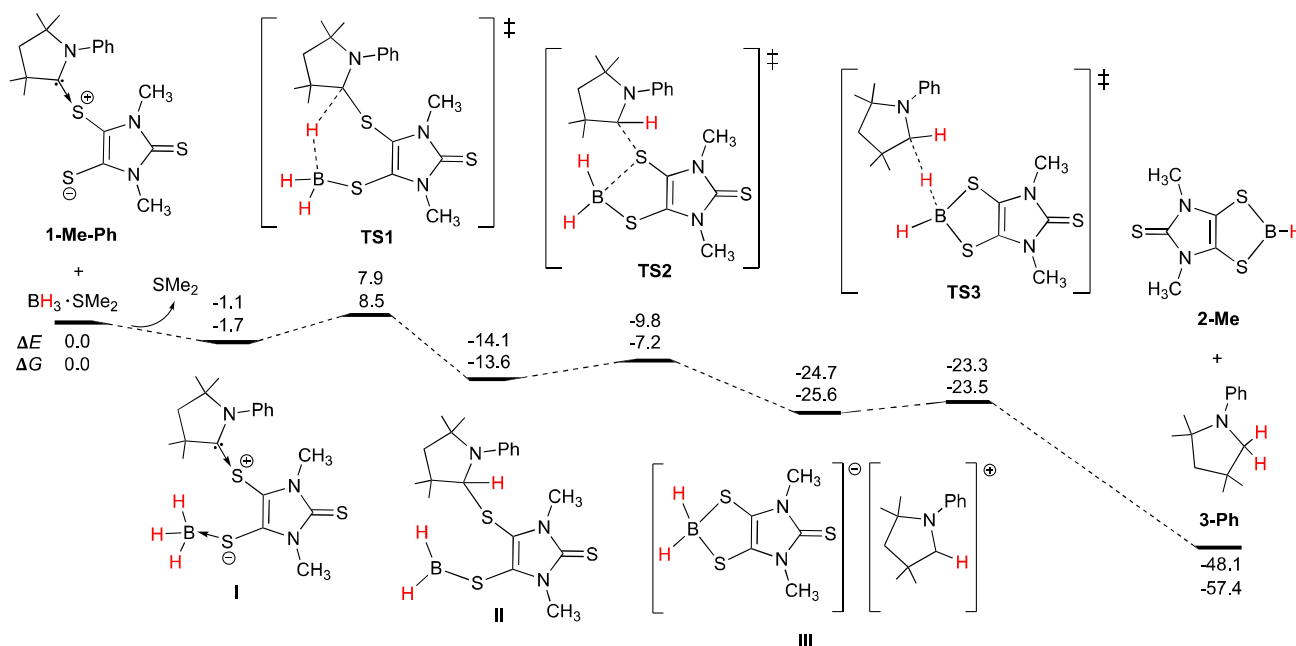


Figure 2. Computed relative energies (ΔE , in kcal mol⁻¹) and free energies (ΔG , in kcal mol⁻¹) for the reaction of the simplified 1-Me-Ph model with $\text{BH}_3 \cdot \text{SMe}_2$ at the B3LYP/6-311G** (SMD, toluene) level.

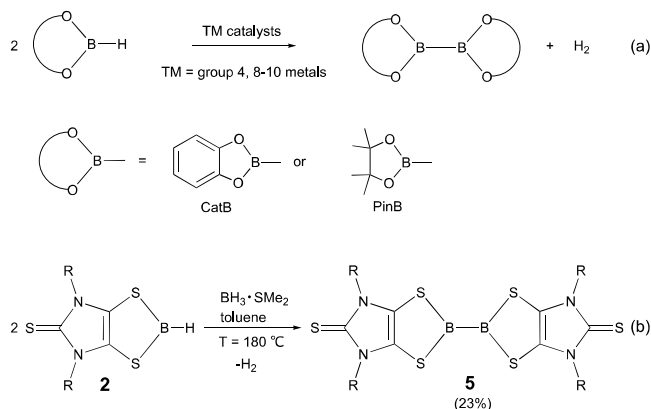
Toward a plausible mechanism, the reaction of the simplified 1-Me-Ph model with $\text{BH}_3 \cdot \text{SMe}_2$ was probed using density functional theory (DFT) at the B3LYP/6-311G** (SMD, toluene) level (Figure 2).³¹

To this end, Lewis adduct I is generated via the weakly exergonic reaction of 1-Me-Ph with $\text{BH}_3 \cdot \text{SMe}_2$ ($\Delta G = -1.7$ kcal mol⁻¹). The formation of I involves the coordination of the terminal sulfur atom of the C_2S_2 unit in 1-Me-Ph to one BH_3 molecule, while releasing dimethyl sulfide (SMe_2) as a byproduct. The adduct I may be readily converted to intermediate II via intramolecular B-to- C_{CAAC} hydrogen migration (TS1 (transition state) energy barrier 10.2 kcal mol⁻¹). The I-to-II conversion is exergonic by 11.9 kcal mol⁻¹. Compound II could be subsequently converted to intermediate III (with an energy of -25.6 kcal mol⁻¹) via an intramolecular cyclization transition state (i.e., TS2 with an energy barrier of 6.4 kcal mol⁻¹). In the II-to-III conversion, accompanying the formation of the five-membered $\text{C}_2\text{S}_2\text{B}$ ring (as observed in III), the S- C_{CAAC} bond is gradually elongated ($d_{\text{S-C(CAAC)}} = 1.948$ Å for TS2 vs $d_{\text{S-C(CAAC)}} = 1.901$ Å for II) and finally heterolytically cleaved, which is supported by a natural bond orbital (NBO) analysis of III. NBO analysis shows that the CAAC-H and dithiolene- BH_2 moieties in III have a positive charge of +0.88 and a negative charge of -0.88, respectively. Thus, the formation of III involves CAAC-H-to-dithiolene- BH_2 one-electron transfer. Subsequently, the cationic CAAC-H unit of III may readily take one hydride group from the boron atom (via the transition state TS3 with an energy barrier of 2.1 kcal mol⁻¹), rendering the final products 2-Me and 3-Ph. This conversion is also thermodynamically favored ($\Delta G = -31.8$ kcal mol⁻¹). The DFT computations indicate that the net transfer of two hydrogen atoms from borane to the CAAC ligand (as observed in the formation of 3) may go through a hydride-coupled reverse electron transfer (HCRET) process in which the hydride migrates from the boron atom to the CAAC ligand, while one electron is transferred from the CAAC unit back to the

dithiolene fragment. It is noteworthy that both the electrophilic property of the CAAC ligand³⁷ and the redox-active character of the dithiolene ligand³⁸ play pivotal roles in the hydride-coupled reverse electron transfer reaction. For example, in the 1-to-2 conversion the dithiolene fragment is reduced from a neutral dithiolene zwitterion (as shown in 1) to a dithiolate (as shown in 2). The 2-to-4 conversion shows that I can activate the boron-hydrogen bond not only for BH_3 but also for monohydroboranes via similar HCRET processes. In contrast to the high energy barrier for the homolytic B-H cleavage in HAT, the HCRET process provides an energetically effective route for net “hydrogen atom” transfer.

Diboranes(4) have demonstrated extensive utility in organic synthesis.³⁹ While haloborane reduction remains the principal synthetic means for electron-precise boron-boron bond formation, the borane dehydrocoupling method has received increasing attention.⁴⁰ For example, catecholborane (CatBH) and pinacolborane (PinBH) have been converted to the corresponding diboranes(4) via transition-metal-catalyzed dehydrocoupling reactions (Scheme 2a).^{41,42} Metal-free formation of boron-boron bonds via borane dehydrocoupling reactions is rare.^{43,44} The calculated B-H bond dissociation energy in 2 (112.2 kcal mol⁻¹)³¹ compares well to that of catecholborane (CatBH) (111.3 kcal mol⁻¹).⁷ This study demonstrated that, in the presence of a small amount of $\text{BH}_3 \cdot \text{SMe}_2$, pyrolysis of 2 in toluene at 180 °C in a sealed Schlenk tube for 30 min gave an orange-red mixture, consisting of the dithiolene-based diborane(4) 5, the unreacted 2, and other unidentified byproducts (Scheme 2b). 5 was isolated as orange-red crystals (in 23% yield) from the concentrated parent solution. It is noteworthy that, in the absence of $\text{BH}_3 \cdot \text{SMe}_2$, the 2-to-5 conversion in toluene did not occur even at a high temperature. The NMR-tube reactions indicate that the reaction stoichiometry influences the 2-to-5 conversion. Reaction of 2 with $\text{BH}_3 \cdot \text{SMe}_2$ (in a molar ratio of 6:1) gave a relatively high 2-to-5 conversion. The resulting reaction mixture contains both 2 and 5 in a 1:1.2 molar ratio. Notably,

Scheme 2. Electron-Precise Boron–Boron Bond Formation: (a) Transition-Metal-Catalyzed Borane Dehydrocoupling Reactions; (b) Borane-Mediated Dehydrocoupling of 2 (R = 2,6-Diisopropylphenyl)



$\text{BH}_3\cdot\text{SMe}_2$ is expected to decompose in toluene at 180 °C (BDE of the B–S bond in $\text{BH}_3\cdot\text{SMe}_2$: 21.2 kcal mol⁻¹).³¹ The released BH_3 species may be further transformed into a complicated mixture of higher order boranes, even polymeric BH_x materials.⁶ Due to the complexity of this pyrolysis reaction, mechanistic aspects of the 2-to-5 conversion remain unclear. H_2 gas is expected to be formed as a byproduct in the 2-to-5 conversion (Scheme 2). The ¹H NMR signal of H_2 was indeed observed as a singlet at 4.51 ppm (in toluene-*d*₈) in the high-temperature NMR-tube reaction of 2 with $\text{BH}_3\cdot\text{SMe}_2$. However, the pyrolysis of $\text{BH}_3\cdot\text{SMe}_2$ itself can also produce H_2 .

The UV–vis absorption spectrum of 5 (orange-red) in toluene shows one strong broad absorption at 478 nm (Figure S1). It compares to the TD-DFT calculated value of 536 nm (B3LYP/6-311G**, SMD, toluene), corresponding to the excitation from HOMO to LUMO. While the HOMO is dithiolene ligand based, the LUMO mainly involves B–B π -bonding and S–B π -antibonding character (Figure 3). The X-

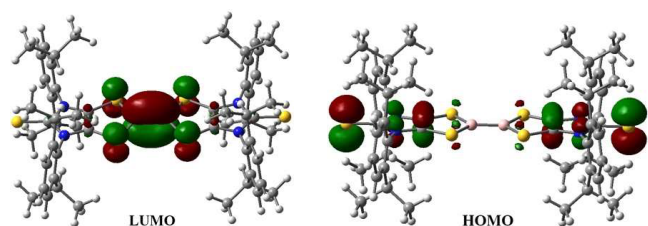


Figure 3. Frontier molecular orbitals of 5.

ray structural analysis of 5 (Figure 1) shows that all atoms are essentially coplanar, except for those of the four flanking Dipp substituents (Dipp = 2,6-diisopropylphenyl). Like 2 and 4, each three-coordinate boron atom in 5 adopts a trigonal-planar geometry. The B–B (1.645(6) Å) and B–S (1.798 Å, av) bonds in 5 are comparable with the calculated values of 5 ($d_{\text{B-B}} = 1.665$ Å; $d_{\text{B-S}} = 1.825$ Å) and those of bis-(dithiocatecholato)diborane, $\text{B}_2(1,2\text{-S}_2\text{C}_6\text{H}_4)_2$ (6) ($d_{\text{B-B}} = 1.672$ Å, av; $d_{\text{B-S}} = 1.794$ Å, av).⁴⁵ The ¹¹B NMR spectrum of 5 (in toluene-*d*₈, 100 °C) exhibits a singlet resonance at 54.6 ppm ($w_{1/2} = 471$ Hz), which is comparable with that of 6 (57.9 ppm).⁴⁶

CONCLUSION

The CAAC-stabilized neutral dithiolene 1 may react with $\text{BH}_3\cdot\text{SMe}_2$, giving the dithiolene-based boranes (2 and 4) and doubly hydrogen-capped CAAC species 3 (as a byproduct) via a hydride-coupled reverse electron transfer (HCRET). The borane-mediated boron–boron bond formation in 5 via the high-temperature dehydrocoupling of dithiolene-based hydroborane (2) represents yet another surprise. The unique synergic interaction between the noninnocent dithiolene unit and the electrophilic CAAC ligand in 1 is expected to exhibit other unusual applications for small-molecule activation.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.organomet.3c00361>.

Syntheses, computations, and X-ray crystal determination (PDF)

Cartesian coordinates for the calculated structures (XYZ)

Accession Codes

CCDC 2269318 and 2269320–2269321 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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