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Synthesis of Boron-Fused 1,4-Dithiin via Cobalt-Mediated Disulfuration of Alkyne at the *o*-Carborane-9,12-dithiolate Unit

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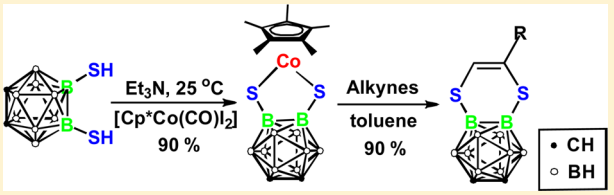
Supporting Information

ABSTRACT: We present the first synthesis and characterization of a series of boron-fused 1,4-dithiin compounds through the reactions of newly established boron-substituted 16*e* half-sandwich complex Cp*Co(9,12-$S_2C_2B_{10}H_{10}$) with alkynes. The generated $C_2S_2B_2$ ring in these 1,4-dithiin species is a stable structural motif with electron-negative sulfur atoms, as evidenced by theoretical calculation and its solid-state self-assembly. Single-crystal X-ray analysis indicates that C_{carb}–H···S hydrogen bonding is involved in the self-assemblies of these compounds, which serves as a compatible interaction with stronger C_{carb}–H···π, C_{carb}–H···O, or C_{carb}–H···F hydrogen bonding. All new compounds are characterized by NMR, mass spectroscopy, and X-ray structural analysis.

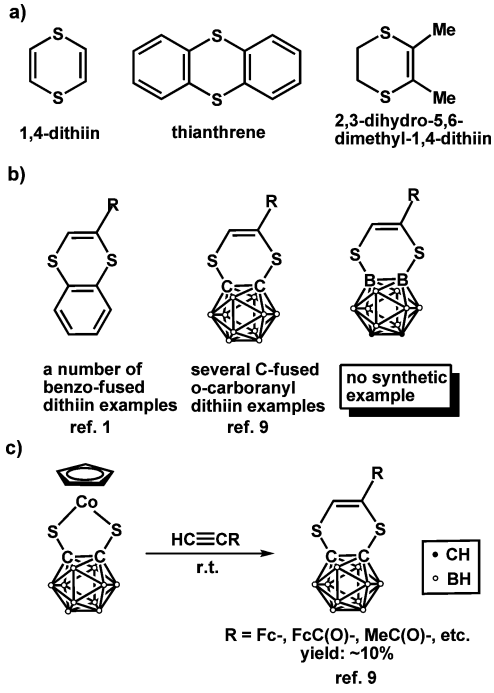


INTRODUCTION

1,4-Dithiin[1] compounds (a class of heterocyclic compounds with a $C_2S_2C_2$ ring) have attracted renewed interest since the discovery that plants of the sunflower family contain dimethipin,[2] a commercial plant growth regulant. These 1,4-dithiin derivatives have been reported to exhibit a wide range of biological activity[2,3] (Chart 1a). The substitution on the 1,4-dithiin ring plays an important role in governing the chemical reactivity[4] and biological activity[5] of these compounds. On the other hand, icosahedral carborane derivatives have been applied in the areas of catalysis,[6] materials,[7] and drugs.[8] These provide significant impetus to search for an efficient synthetic strategy for the construction of carborane-based 1,4-dithiin derivatives. Indeed, several carbon-fused *o*-carboranyl-1,4-dithiin compounds have already been synthesized and characterized[9] that were found to bind to myoglobin via the dithio units and influenced the native conformation of the protein.[10] Furthermore, these conjugates also show selective antineoplastic activity and may serve as potential anticancer agents.[11] Nevertheless, the expansion of structural diversity beyond what can be achieved by nature is one of the main goals of synthetic chemistry. Carbon or boron fusion has emerged as a viable strategy to increase the chemical space of compounds relevant to biomedical research and materials science.[12] If 1,4-dithiin is combined with the three-dimensional pseudoaromatic *o*-carborane cluster, two structural isomers might be generated depending on the attachment of S atoms on carbon or boron vertexes (Chart 1b).

The known synthetic routes toward carbon-fused *o*-carboranyl-1,4-dithiin compounds[9] were mainly based on the square-planar cobalt complex $[Co(S_2C_2B_{10}H_{10})_2]^-$ [9a] or mononuclear 16*e* half-sanwich complex [CpCo(1,2-$S_2C_2B_{10}H_{12}$)] [Cp = cyclopentadienyl][9b,c] (Chart 1c). The analogous metal complexes (Ru, Os, Co, Rh, and Ir) containing 1,2-dicarba-*closo*-dodecaborane-1,2-dithiolate ligand have exhibited rich reaction chemistries[13−15] toward metal fragments, Lewis bases, alkynes, and others. However, similar dithiolato complexes based on the *o*-carborane-9,12-dithiolate ligand[16] are still rare,[17] and the synthesis of a

Chart 1. Illustration of a 1,4-Dithiin Compound and Its Derivatives Containing Benzo-Fused Dithiin Examples and C/B-Fused *o*-Carboranyl Dithiin Examples



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boron-fused 1,4-dithiin has remained unknown to date. In this contribution, we first report the efficient route to boron-fused 1,4-dithiin compounds starting from the mononuclear 16*e* half-sandwich cobalt complex containing an *o*-carborane-9,12-dithiolate. We also demonstrate that negative charge is significantly increased at the S atoms owing to the boron substitution. As a result, the nonconventional C_{carb}–H···S hydrogen bonding is involved in the self-assembly of these compounds and acts in a role compatible with the conventional C_{carb}–H···O or C_{carb}–H···F hydrogen bonding.

RESULTS AND DISCUSSION

The reaction of boron-substituted dithiol **1** and Cp*Co(CO)I_2 [Cp* = pentamethylcyclopentadienyl] gave rise to the orange product **2** in excellent isolated yield (90%). Note that complex **2** is stable both in solution and in the solid state, in contrast to the similarly prepared CpCo(9,12-$S_2C_2B_{10}H_{12}$), which is not stable enough in solution.[17] The X-ray crystal structure of **2** (Figure 1) validates the formation of a five-membered metallacycle

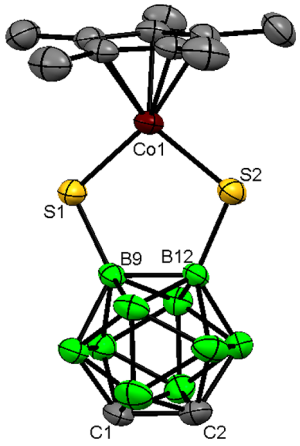
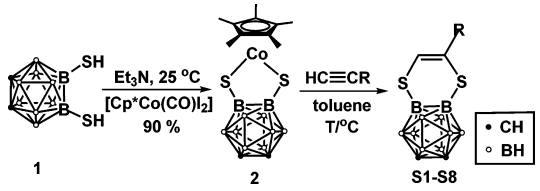


Figure 1. Molecular structure of complex **2**. For clarity, the hydrogen atoms are not shown. Selected bond distances [Å] and bond angles [deg]: C1–C2 1.632(5), B9–S1 1.843(4), B12–S2 1.844(4), Co1–S1 2.1930(10), Co1–S2 2.1745(10), S1–Co1–S2 100.14(3).

ring CoS_2B_2, and the electron count confirms the 16*e* cobalt center. The NMR data are in agreement with the solid-state structure. For example, the ^{11}B NMR spectrum shows one type of $cage_{B-S}$ resonance at 18.1 ppm in comparison to 8.5 ppm in the parent ligand **1**. The ^{1}H NMR spectrum also exhibits the $cage_{C-H}$ signal at 2.86 ppm. Here, the steric and electronic effect of the Cp* unit may play an important role in stabilizing the CoS_2B_2 ring in contrast to the Cp unit.

Reactions of **2** toward PhC≡CH in boiling toluene led to the alkyne disulfurated product **S1** as the sole product in an excellent yield (90%) (Scheme 1 and Figure 2). The scope of alkynes was expanded (Scheme 1), and similar reactivity was observed for (*o*, *m*, *p*-F)-PhC≡CH and FcC≡CH, leading to **S2-1**, **S2-2**, **S2-3**, and **S3**. In the case of alkynes with an electron-withdrawing group such as HC≡CC(O)R, the reactions proceeded smoothly at room temperature to give rise to **S4**–**S8** in yields of 88–92% (Scheme 1 and Table 1). Note that boron-substituted dithiol **1** does not react with alkynes in the absence of a metal fragment. Similar reactions of alkynes with the carbon-substituted 16*e* half-sandwich complex [Cp*Co{1,2-$S_2C_2B_{10}H_{10}$}] led only to double-alkyne-inserted products at M–S bonds, and its Cp analogue, [CpCo{1,2-$S_2C_2B_{10}H_{10}$}], led to carbon-fused 1,4-dithiins[9] in lower yields

Scheme 1. Synthetic Route toward Boron-Substituted 1,4-Dithiin Compounds S1–S8 via a 16*e* Half-Sandwich Cobalt Dithiolato Complex 2



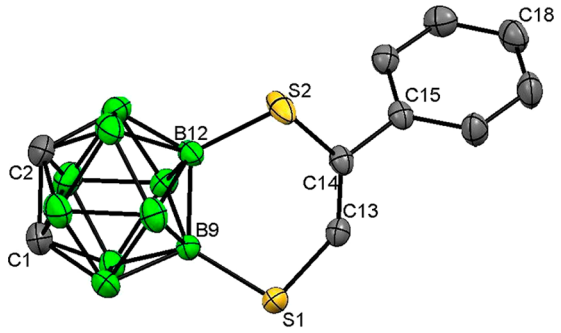


Figure 2. Molecular structure of compound **S1**. For clarity, the hydrogen atoms are not shown. Selected bond distances [Å] and bond angles [deg]: C1–C2 1.625(3), B9–S1 1.852(2), B12–S2 1.854(2), C13–S1 1.7659(19), C14–S2 1.7687(19), C13–C14 1.328(3), C13–S1–B9 102.28(9), C14–S2–B12 103.32(9).

Table 1. Scope of Terminal Alkynes

compound	R-	*T*/°C	yield
S1	Ph-	110	90%
S2-1, S2-2, S2-3	(*o*, *m*, *p*)-F-Ph-	110	87–90%
S3	Fc-	110	88%
S4	Me-C(O)-	25	92%
S5	2-furyl-C(O)-	25	93%
S6	Ph-C(O)-	25	91%
S7	MeO-C(O)-	25	90%
S8	Fc-C(O)-	25	89%

(<10%) with predominantly competing B–H activation.[18] Therefore, the reactivity of the carbon-substituted 16*e* complexes [$Cp^{\#}$Co{1,2-$S_2C_2B_{10}H_{10}$}] ($Cp^{\#}$ = Cp, Cp*) toward alkynes differs. Here we provide a clean reaction to boron-fused 1,4-dithiins with excellent yields from the boron-substituted 16*e* complex [Cp*Co{9,12-$S_2C_2B_{10}H_{10}$}].

Single-crystal X-ray analysis ambiguously confirms the newly formed compounds **S1**–**S8**. For example, the solid-state structure of **S1** (Figure 2) shows an alkyne added to the *o*-caborane-9,12-dithiolate ligand at the two sulfur atoms. The generated six-membered ring C(13)C(14)S(1)S(2)B(9)B(12) is bent at the S(1)···S(2) vector at a dihedral angle of 141.8°. The C13–C14 is measured as 1.328(3) Å, in the range of carbon–carbon double bonds, and the C1–C2 distance of the *o*-carborane is observed at 1.625(3) Å. The other X-ray structures of **S2**–**S8** are found in the SI, Figures s6–13. A DFT-optimized structure of **S6** based on its crystal structure indicates that the $C_2S_2B_2$ six-membered ring is a stable structural motif, as its HOMO–LUMO gap (0.142 eV) is similar to that in the carbon-fused species (SI, Figures s2–4).

Consistent with the solid-state structures, the ^{1}H NMR spectra of all products show a quartet in the olefinic area, which is assigned to the C=C*H* unit. The splitting of the hydrogen

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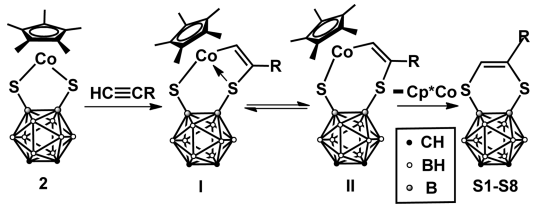
signal is attributed to the remote coupling from the two B atoms of the B−S bonds with J_{B-H} = 5 Hz via the comparison of the boron-coupled and boron-decoupled ^{1}H NMR measurements (SI, Figure s5). The cage$_{C-H}$ proton signal is observed around 3.70 ppm. The ^{13}C NMR signals of the newly generated C═CH unit are located in the normal range for olefinic carbon atoms. Selected ^{1}H, ^{13}C, and ^{11}B data for compounds **S1**−**S8** are listed in Table 2.

Table 2. ^{1}H, ^{13}C, and ^{11}B NMR Data of the $C_2S_2B_2$ Six-Membered Rings in S1−S8

compound	C═C−H (^{1}H)	S−C═C−H (^{13}C)	B−B−S (^{11}B)
S1	6.15	114.5, 130.8	8.4, 7.4
S2-1	6.12	118.2, 130.4	8.5, 7.5
S2-2	6.15	114.2, 130.1	8.5, 7.4
S2-3	6.09	114.5, 129.0	8.2, 7.4
S3	6.10	109.3, 129.2	8.7, 8.1
S4	7.24	130.8, 149.0	7.2, 4.7
S5	7.33	132.0, 151.1	7.1, 5.0
S6	6.94	118.8, 129.1	8.4, 7.4
S7	7.37	118.7, 129.2	7.1, 5.0
S8	7.08	126.2, 130.8	7.8, 6.0

As shown in Scheme 2, a plausible mechanism has been proposed to illustrate the disulfuration of alkyne at *o*-carborane-9,12-dithiolate.

Scheme 2. Proposed Mechanism for the Formation of Boron-Fused 1,4-Dithiin Compounds



The first step should be insertion of alkyne into a Co−S bond to form the 18*e* species **I** since the addition of alkyne to the M−E bond of the 16*e* half-sandwich complexes Cp$^{\#}$M(1,2-E$_2$C$_2$B$_{10}$H$_{10}$) (Cp$^{\#}$ = Cp, Cp*; M = Co, Rh, Ir; E = S, Se) and (*p*-cymene)M(S$_2$C$_2$B$_{10}$H$_{10}$) (M = Ru, Os) has been well reported.[14,19] If the coordinative Co←S bonding is not strong enough, the 16*e* species **II** might be present, followed by loss of the Cp*Co fragment to give boron-fused 1,4-dithiin compounds. It is noteworthy that the one-fold alkyne insertion intermediate **I** was not observed in this system, probably owing to the fast Cp*Co reductive elimination. This also might be the reason that no other competitive reactions could occur in this reaction system.

Moreover, DFT calculations demonstrate the electron-negative property on the S atoms in these boron-fused 1,4-dithiin compounds, in contrast to the carbon-fused analogues (SI, Table s1). Correspondingly, the C$_{carb}$−H···S hydrogen bonding[20] involved in self-assembly has been observed in the solid state, which is comparable to the C$_{carb}$−H···π,[21] C$_{carb}$−H···O,[22] or C$_{carb}$−H···F[23] hydrogen bonding in these compounds. For example, in **S1** each molecule has been linked by one C$_{carb}$−H···π interaction (2.468 Å) and one C$_{carb}$−H···S (2.678 Å) bonding with two adjacent molecules in a triangular fashion (Figure 3) to form a two-dimensional polymeric plane. The observed C$_{carb}$−H···S distance of 2.678 Å is shorter than 3.0 Å,

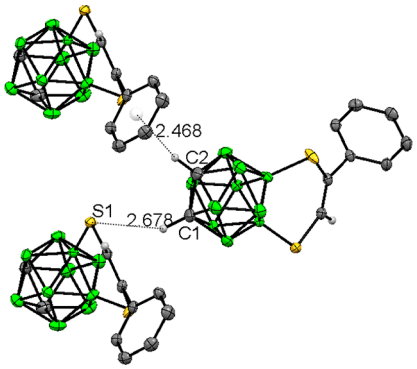


Figure 3. C−H···π and C−H···S hydrogen bonding involved in self-assembly of **S1** in the solid state. For clarity, partial hydrogen atoms are not shown. Green: boron, black: carbon, yellow: sulfur, white: hydrogen.

corresponding to the sum of the van der Waals radii of hydrogen and sulfur atoms,[20f] and the nearly linear C$_{carb}$−H···S angle (147.66°) qualifies it to be a hydrogen bond. Another shorter and stronger contact is also seen in **S4** (C$_{carb}$−H···S 2.518 Å, 164.68°) in a cooperative fashion with the C$_{carb}$−H···O interaction (2.255 Å, 123.42°), which leads to a one-dimensional S-type polymeric chain (Figure 4). However, in **S2-3** the C$_{carb}$−H···S

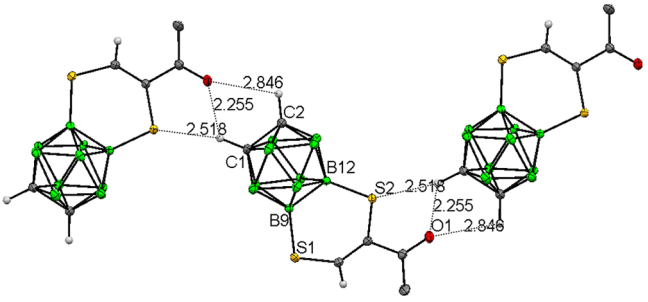


Figure 4. C−H···O and C−H···S hydrogen bonding involved in self-assembly of **S4** in the solid state. For clarity, partial hydrogen atoms are not shown. Green: boron, black: carbon, yellow: sulfur, white: hydrogen, red: oxygen.

interaction (2.944 Å, 149.71°) turns out to be very weak in comparison with the stronger C$_{carb}$−H···F interaction (2.347 Å, 121.21°); thus the molecules form a one-dimensional linear polymeric chain dominated by C$_{carb}$−H···F bonding (Figure 5). Our results indicate that the boron-attached S atoms in 1,4-dithiin compounds may serve as a compatible hydrogen acceptor in multiforce-involved supramolecular self-assembly. The related C−H···S−H···H−B hydrogen bonding interaction based on the boron-attached SH group has been reported.[24]

CONCLUSION

In summary, we first found an efficient synthetic route to the boron-fused 1,4-dithiin compounds through the reactions of a 16*e* half-sandwich cobalt complex and alkynes in excellent yields. The $C_2S_2B_2$ six-membered ring in these species is a thermally stable and isolatable heterocycle with considerably negatively charged sulfur atoms. Single-crystal X-ray diffration analysis indicates that the C$_{carb}$−H···S hydrogen bonding is involved in self-assemblies of these products in the solid state. In view of the recent advances in developing new ferrocenyl-substituted carborane conjugates as potential anticancer

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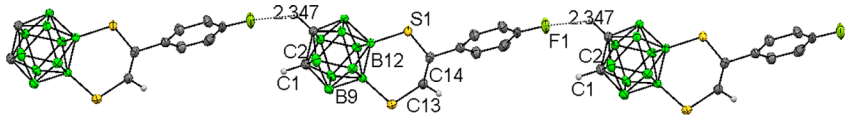


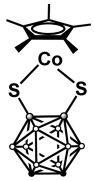
Figure 5. C−H···F hydrogen bonding involved in self-assembly of **S2-3** in the solid state. For clarity, partial hydrogen atoms are not shown. Green: boron, black: carbon, yellow: sulfur, white: hydrogen, grass green: fluorine.

agents,[11] this work opens the door to the preparation of structural diversity of these species for potential use in the biomedical field.

EXPERIMENTAL SECTION

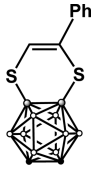
General Procedures. All workup was performed under an argon atmosphere using standard Schlenk techniques. Solvents were dried by refluxing over sodium (petroleum ether, ether, and toluene) or calcium hydride (dichloromethane) under nitrogen and then were distilled prior to use. Cp*Co(CO)I_2[25] and HC≡CC(O)Fc[26] were prepared according to the literature methods. The other alkynes were used as commercial products without further purification. 9,12-Dithiol-*o*-carborane was prepared according to the reported literature methods.[16] Elemental analysis was performed in an Elementar Vario EL III elemental analyzer. NMR data were recorded on a Bruker DRX-500 spectrometer. ^{1}H NMR and ^{13}C NMR spectra were reported in ppm with respect to $CHCl_3/CDCl_3$ (σ ^{1}H = 7.24, σ ^{13}C = 77.0), and ^{11}B NMR spectra were reported in ppm with respect to external $Et_2O{\cdot}BF_3$ (σ ^{11}B = 0). The IR spectra were recorded on a Bruker Tensor 27 spectrophotometer with KBr pellets in the 4000−400 cm^{-1} region. The mass spectra were recorded on a Finnigan MAT TSQ7000 for ESI-MS.

Synthesis of 16e Complex ***2*** *[Cp*Co(9,12-$S_2C_2B_{10}H_{10}$)].* 9,12-Dithiol-1,2-*o*-carborane (60 mg, 0.3 mmol) was dissolved in CH_2Cl_2 (30 mL),



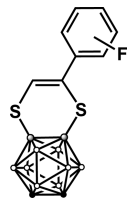
Et_3N (90 μL, 0.6 mmol) was added to the solution, and the mixture was stirred for 20 min at room temperature. A CH_2Cl_2 solution of Cp*Co(CO)I_2 (144 mg, 0.3 mmol) was added to the mixture. The resulting solution turned orange instantly. After 30 min, the solvent was removed *in vacuo* and the residue was chromatographed on silica gel by CH_2Cl_2 to give complex **2** (108 mg, 90%). Single crystals suitable for single-crystal analysis were obtained by slow evaporation of a solution of CH_2Cl_2/hexanes. Color: orange. Mp: 234−235 °C. ^{1}H NMR ($CDCl_3$): δ 2.86 (s, 2H, cage−C*H*), 1.70−2.81 (br, 8H, cage−B*H*), 1.68 (s, 15H, CH_3), ^{11}B{^{1}H} NMR (CD_2Cl_2): δ 18.1 (2B, B−S), −6.0 (2B), −11.5 (4B), −13.5 (2B). ^{13}C NMR ($CDCl_3$): δ 89.9 (Cp*), 37.1 (cage−C), 10.6 (Cp*). ESI-MS (positive ion mode) *m*/*z*: 423.50 (M + Na$^+$, 100%). IR (KBr): ν (cm^{-1}) 2557 (B−H). Anal. Calcd for $C_{12}H_{25}B_{10}S_2Co$: C, 35.99; H, 6.29. Found: C, 35.63; H, 6.18.

Synthesis of ***S1****.* HC≡CPh (0.2 mL, 2 mmol) was added to a toluene (20 mL) solution of complex **2** (40.0 mg, 0.2 mmol), and the



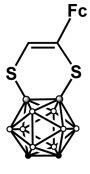
mixture was stirred for 24 h at 110 °C. After removal of the solvent, the residue was chromatographed on TLC. Elution with petroleum ether/CH_2Cl_2 (2:1) gave compound **S1** in a yield of 90%. Color: white solid. Mp: 117−118 °C. ^{1}H NMR ($CDCl_3$): δ 7.42−7.21 (m, 5H, Ph), 6.15 (q, J_{B-H} = 5 Hz, 1H, C═CH), 3.51 (s, 2H, cage−C*H*), 1.60−3.14 (br, 8H, cage−B*H*). ^{11}B{^{1}H} NMR ($CDCl_3$): δ 8.4 (1B, B−S), 7.4 (1B, B−S), −2.0 (2B), −11.4 (4B), −13.0 (2B). ^{13}C NMR ($CDCl_3$): δ 143.0 (Ph), 130.8 (S−*C*═C) 128.1 (Ph), 127.0 (Ph), 126.7 (Ph), 114.5 (S−C═*C*H) 47.1 (cage−*C*). ESI-MS (positive ion mode) *m*/*z*: 331.44 (M + Na$^+$, 100%). IR (KBr): ν (cm^{-1}) 2587 (B−H). Anal. Calcd for $C_{10}H_{16}B_{10}S_2$: C, 35.77; H, 4.86. Found: C, 35.32; H, 5.01.

Synthesis of ***S2-1****,* ***S2-2****, and* ***S2-3****.* HC≡C(2F-Ph) (HC≡C(3F-Ph) or HC≡C(4F-Ph)) (0.2 mL, 2 mmol) was added to a toluene (20 mL)



solution of complex **2** (40.0 mg, 0.2 mmol), and the mixture was stirred for 24 h at 110 °C. After removal of the solvent, the residue was chromatographed on TLC. Elution with petroleum ether/CH_2Cl_2 (2:1) gave compounds **S2-1**, **S2-2**, and **S2-3** in yields of 87−90%. Compound **S2-1**, yield: 87%. Color: white solid. Mp: 123−124 °C. ^{1}H NMR ($CDCl_3$): δ 7.32−7.00 (m, 4H, Ph), 6.12 (q, J_{B-H} = 5 Hz, 1H, C═CH), 3.53 (s, 2H, cage−C*H*), 1.60−3.14 (br, 8H, cage−B*H*). ^{11}B{^{1}H} NMR ($CDCl_3$): δ 8.5 (1B, B−S), 7.5 (1B, B−S), −2.0 (2B), −11.4 (4B), −13.0 (2B). ^{19}F NMR ($CDCl_3$): δ −115.1. ^{13}C NMR ($CDCl_3$): δ 159.3 (d, J_{C-F} = 250 Hz, *C*−F), 130.4 (S−*C*═C), 129.0 (d, J_{C-F} = 3 Hz, Ph), 128.8 (d, J_{C-F} = 12 Hz, Ph), 123.8 (d, J_{C-F} = 3 Hz, Ph), 118.2 (S−C═*C*H), 115.7 (d, J_{C-F} = 12 Hz, Ph), 114.9 (d, J_{C-F} = 25 Hz, Ph), 47.1 (cage−*C*). ESI-MS (positive ion mode) *m*/*z*: 349.44 (M + Na$^+$, 100%). IR (KBr): ν (cm^{-1}) 2587 (B−H). Anal. Calcd for $C_{10}H_{15}B_{10}S_2F$: C, 36.79; H, 4.63. Found: C, 36.46; H, 4.83. Compound **S2-2**, yield: 87%. Color: white solid. Mp: 123−124 °C. ^{1}H NMR ($CDCl_3$): δ 7.42−7.21 (m, 4H, Ph), 6.15 (q, J_{B-H} = 5 Hz, 1H, C═CH), 3.51 (s, 2H, cage−C*H*), 1.60−3.14 (br, 8H, cage−B*H*). ^{11}B{^{1}H} NMR ($CDCl_3$): δ 8.5 (1B, B−S), 7.4 (1B, B−S), −2.1 (2B), −11.3 (4B), −13.1 (2B). ^{19}F NMR ($CDCl_3$): δ −111.9. ^{13}C NMR ($CDCl_3$): δ 160.3 (d, J_{C-F} = 250 Hz, *C*−F), 138.9 (d, J_{C-F} = 12 Hz, Ph), 130.1 (S−*C*═C) 128.8 (d, J_{C-F} = 12 Hz, Ph), 126.3 (d, J_{C-F} = 3 Hz, Ph), 116.9 (d, J_{C-F} = 25 Hz, Ph), 115.7 (d, J_{C-F} = 25 Hz, Ph), 114.2 (S−C═*C*H), 47.2 (cage−*C*). ESI-MS (positive ion mode) *m*/*z*: 349.45 (M + Na$^+$, 100%). IR (KBr): ν (cm^{-1}) 2587 (B−H). Anal. Calcd for $C_{10}H_{15}B_{10}S_2F$: C, 36.79; H, 4.63. Found: C, 36.45; H, 4.80. Compound **S2-3**, yield: 90%. Color: white solid. Mp: 123−124 °C. ^{1}H NMR ($CDCl_3$): δ 6.96−7.38 (m, 4H, Ph), 6.09 (q, J_{B-H} = 5 Hz, 1H, C═CH), 3.53 (s, 2H, cage−C*H*), 1.60−3.14 (br, 8H, cage−B*H*). ^{11}B{^{1}H} NMR ($CDCl_3$): δ 8.2 (1B, B−S), 7.4 (1B, B−S), −2.0 (2B), −11.3 (4B), −12.9 (2B). ^{19}F NMR ($CDCl_3$): δ −114.9. ^{13}C NMR ($CDCl_3$): δ 162.5 (d, J_{C-F} = 250 Hz, *C*−F), 129.0 (S−*C*═C), 128.4 (d, J_{C-F} = 12 Hz, Ph), 125.3 (Ph), 115.0 (d, J_{C-F} = 25 Hz, Ph), 114.5 (S−C═*C*H), 47.3 (cage−*C*). ESI-MS (positive ion mode) *m*/*z*: 349.46 (M + Na$^+$, 100%). IR (KBr): ν (cm^{-1}) 2587 (B−H). Anal. Calcd for $C_{10}H_{15}B_{10}S_2F$: C, 36.79; H, 4.63. Found: C, 36.48; H, 4.74.

Synthesis of ***S3****.* Compound **S3** was synthesized similarly to **S1** by using HC≡CFc. Yield: 88%. Color: yellow solid. Mp: 187−188 °C.



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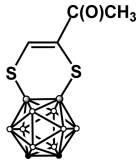
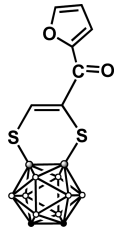
^{1}H NMR ($CDCl_3$): δ 6.10 (q, J_{B-H} = 5 Hz, 1H, C═CH), 4.40 (m, 2H, Fc−CH), 4.19 (s, 5H, Fc−Cp), 4.16 (m, 2H, Fc−CH), 3.51 (s, 2H, cage−C*H*), 1.70−3.02 (br, 8H, cage−B*H*). ^{11}B{^{1}H} NMR ($CDCl_3$): δ 8.7 (1B, B−S), 8.1 (1B, B−S), −2.2 (2B), −11.4 (4B), −12.9 (2B). ^{13}C NMR ($CDCl_3$): δ 129.2 (S−*C*═C), 109.3 (S−C═*C*H), 89.8 (Fc−*C*), 69.4 (Fc−*Cp*), 68.2 (Fc−CH), 66.1 (Fc−*C*H), 46.6 (cage−*C*). ESI-MS (positive ion mode) *m*/*z*: 439.41 (M + Na$^+$, 100%). IR (KBr): ν (cm^{-1}) 2592 (B−H). Anal. Calcd for $C_{14}H_{20}B_{10}S_2Fe$: C, 40.38; H, 4.84. Found: C, 40.11; H, 5.02.

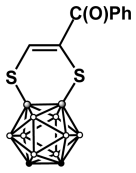
Synthesis of ***S4*****−*****S8*****.** Alkyne (1 mmol) was added to a CH_2Cl_2 (20 mL) solution of complex **2** (40.0 mg, 0.2 mmol), and the mixture was stirred at 25 °C for 4 h. After removal of the solvent, the residue was chromatographed on TLC. Elution with petroleum ether/CH_2Cl_2 (1:2) gave compounds **S4**−**S8**.



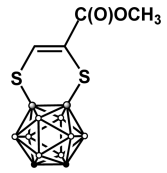
Compound **S4**, yield: 92%, white solid. Mp: 97−98 °C. ^{1}H NMR ($CDCl_3$): δ 7.24 (q, J_{B-H} = 5 Hz, 1H, C═CH), 3.70 (s, 2H, cage−C*H*), 1.70−3.12 (br m, 8H, cage−B*H*), 2.32 (s, 3H, CH_3). ^{11}B{^{1}H} NMR ($CDCl_3$): δ 7.2 (1B, B−S), 4.7 (1B, B−S), −1.1 (2B), −5.6 (1B), −11.1 (3B), −11.6 (2B). ^{13}C NMR ($CDCl_3$): δ 193.8 (*C*═O), 149.0 (S−*C*═C), 130.8 (S−C═*C*H), 48.6 (cage−*C*), 49.1 (cage−*C*), 26.2 (CH_3). ESI-MS (positive ion mode) *m*/*z*: 298.92 (M + Na$^+$, 100%). IR (KBr): ν (cm^{-1}) 2578 (B−H). Anal. Calcd for $C_6H_{14}B_{10}S_2O$: C, 26.26; H, 5.14. Found: C, 26.02; H, 5.34.



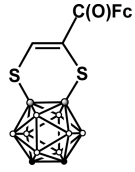
Compound **S5**, yield: 93%, white solid. Mp: 133−134 °C. ^{1}H NMR ($CDCl_3$): δ 7.59 (m, 1H, furyl −CH), 7.33 (q, J_{B-H} = 5 Hz, 1H, C═CH), 7.08 (m, 1H, furyl −CH), 6.50 (m, 1H, furyl −CH), 3.83 (s, 1H, cage−C*H*), 3.78 (s, 1H, cage−C*H*) 1.90−3.42 (br, 8H, cage−B*H*). ^{11}B{^{1}H} NMR ($CDCl_3$): δ 7.1 (1B, B−S), 5.0 (1B, B−S), −1.3 (2B), −11.3 (4B), −12.6 (2B). ^{13}C NMR ($CDCl_3$): δ 179.6 (*C*═O), 151.1 (S−*C*═C), 146.1 (furyl−CH), 132.0 (S−C═*C*H), 128.9 (furyl−C), 119.6 (furyl−CH), 112.2 (furyl−CH), 49.3 (cage−*C*), 48.8 (cage−*C*). ESI-MS (positive ion mode) *m*/*z*: 350.58 (M + Na$^+$, 100%). IR (KBr): ν (cm^{-1}) 2583 (B−H). Anal. Calcd for $C_9H_{14}B_{10}S_2O_2$: C, 33.11; H, 4.32. Found: C, 32.89; H, 4.49.



Compound **S6**, yield: 91%, white solid. Mp: 125−126 °C. ^{1}H NMR ($CDCl_3$): δ 7.54−7.38 (m, 5H, Ph), 6.94 (q, J_{B-H} = 5 Hz, 1H, C═CH), 3.80 (s, 1H, cage−C*H*), 3.75 (s, 1H, cage−C*H*), 1.63−3.39 (br, 8H, cage−B*H*). ^{11}B{^{1}H} NMR ($CDCl_3$): δ 8.4 (1B, B−S), 7.4 (1B, B−S), −1.2 (2B), −11.4 (4B), −12.5 (2B). ^{13}C NMR ($CDCl_3$): δ 193.7 (*C*═O), 143.0 (Ph), 129.1 (S−C═*C*H), 118.8 (S−*C*═C), 131.4 (Ph), 129.8 (Ph), 129.8 (Ph), 128.2 (Ph), 49.3 (cage−*C*), 48.7 (cage−*C*). ESI-MS (positive ion mode) *m*/*z*: 360.50 (M + Na$^+$, 100%). IR (KBr): ν (cm^{-1}) 2572 (B−H). Anal. Calcd for $C_{11}H_{16}B_{10}S_2O$: C, 39.26; H, 4.79. Found: C, 38.99; H, 4.66.



Compound **S7**, yield: 90%, white solid. Mp: 105−106 °C. ^{1}H NMR ($CDCl_3$): δ 7.37 (q, J_{B-H} = 5 Hz, 1H, C═CH), 3.75 (s, 3H, OCH_3), 3.58 (s, 2H, cage−C*H*), 1.63−3.39 (br, 8H, cage−B*H*). ^{11}B{^{1}H} NMR ($CDCl_3$): δ 7.1 (1B, B−S), 5.0 (1B, B−S), −1.1 (2B), −11.5 (4B), −12.6 (2B). ^{13}C NMR ($CDCl_3$): δ 165.3 (*C*═O), 129.2 (S−C═*C*H), 118.7 (S−*C*═C), 52.6 (OCH_3), 48.9 (cage−*C*), 48.5 (cage−*C*). ESI-MS (positive ion mode) *m*/*z*: 314.50 (M + Na$^+$, 100%). IR (KBr): ν (cm^{-1}) 2579 (B−H). Anal. Calcd for $C_6H_{14}B_{10}S_2O_2$: C, 24.81; H, 4.86. Found: C, 24.69; H, 5.05.



Compound **S8**, yield: 89%, red solid. Mp: 125−126 °C. ^{1}H NMR ($CDCl_3$): δ 7.08 (q, J_{B-H} = 5 Hz, 1H, C═CH), 4.81 (m, 2H, Fc−CH), 4.50 (m, 2H, Fc−CH), 4.23 (s, 5H, Fc−*Cp*), 3.70 (s, 2H, cage−C*H*), 1.93−3.49 (br, 8H, cage−B*H*). ^{11}B{^{1}H} NMR ($CDCl_3$): δ 7.8 (1B, B−S), 6.0 (1B, B−S), −1.6 (2B), −11.3 (4B), −12.6 (2B). ^{13}C NMR ($CDCl_3$): δ 195.5 (*C*═O), 130.8 (S−*C*═CH), 126.2 (S−C═*C*), 72.2 (Fc−CH), 71.2 (Fc−CH), 70.3 (Fc−*Cp*), 48.6 (cage−*C*), 48.2 (cage−*C*). ESI-MS (positive ion mode) *m*/*z*: 468.50 (M + Na$^+$, 100%). IR (KBr): ν (cm^{-1}) 2572 (B−H). Anal. Calcd for $C_{15}H_{20}B_{10}S_2OFe$: C, 40.54; H, 4.53. Found: C, 40.33; H, 4.39.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Calculation details and crystallographic data (CIF, CCDC Nos. 996700−996710). This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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