

Cobalt(III)-Mediated Disulfuration and Hydrosulfuration of Alkynes

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Disulfuration and hydrosulfuration of alkynes mediated by an unusual square-planar tetrathiolate cobalt(III) complex $[\text{Cp}_2\text{Co}]^+[\text{Co}(\text{S}_2\text{C}_2\text{B}_{10}\text{H}_{10})_2]^-$, **1**, lead to a series of cobalt-free carboranyl vinyl sulfides **2–9**. All new complexes **1**, **2**, **3**, **4**, **5**, **6**, **7**, **8**, and **9** were characterized by NMR spectroscopy (^1H , ^{11}B , ^{13}C), and X-ray structural analyses were performed for **1**, **2**, **3**, **5**, **6**, **7**, and **9**.

Introduction

Alkyl vinyl sulfides and their oxidized derivatives are used in a wide range of synthetic transformations, for instance, in cross-coupling,¹ Heck reactions,² sigmatropic rearrangements,³ Diels–Alder reactions,⁴ and Pauson–Khand reactions⁵ and as ligands for a number of transformations,⁶ including C–H activation⁷ and allylic alkylation.⁸ On the other hand, icosahedral carboranes are considered to be versatile building blocks because of their promising applications in materials⁹ and pharmaceuticals.^{10,11} These provide significant impetus to search for an efficient synthetic strategy for the introduction of a carborane entity into a vinyl sulfide backbone.

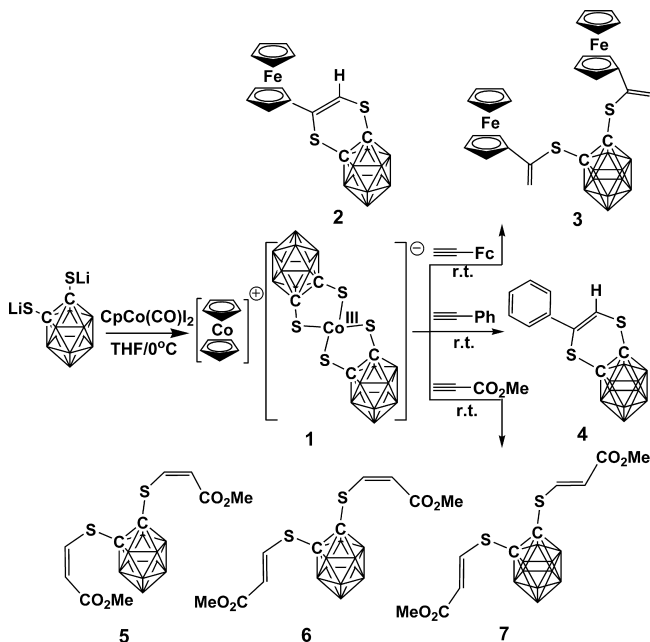
A class of electronically unsaturated ($16e$) complexes $\text{Cp}^*\text{M}(\text{E}_2\text{C}_2\text{B}_{10}\text{H}_{10})$ ($\text{M} = \text{Co}, \text{Rh}, \text{Ir}$; $\text{E} = \text{S}, \text{Se}$) containing a chelating 1,2-dicarba-*closo*-dodecaborane-1,2-dichalcogenolate ligand were reported to mediate selective B–H functionalization of the intramolecular *o*-carborane cage in the presence of alkynes that led to novel B-substitution.^{12,13} The process involved metal-induced B–H activation and M–B formation. In the present paper we report a novel square-planar tetrathiolate cobalt(III) ionic complex $[\text{Cp}_2\text{Co}]^+[\text{Co}(\text{S}_2\text{C}_2\text{B}_{10}\text{H}_{10})_2]^-$, **1** (Scheme 1) and its reactivity toward alkynes to generate a series of cobalt-free carboranyl vinyl sulfides.

The reaction of $\text{Li}_2\text{S}_2\text{C}_2\text{B}_{10}\text{H}_{10}$ with $\text{CpCo}(\text{CO})\text{I}_2$ caused replacement of the Cp ligand by a $[\text{S}_2\text{C}_2\text{B}_{10}\text{H}_{10}]^{2-}$ moiety. This led to a square-planar cobalt(III) complex **1** with two bidentate *o*-carborane dithiolate ligands as shown in Scheme 1 and Figure 1. The displaced Cp combined with a CpCo moiety to give the observed counteranion Cp_2Co^+ . Presumably the formation of this stable cation is the driving force for the generation of the unusual square-planar anion $[\text{Co}(\text{S}_2\text{C}_2\text{B}_{10}\text{H}_{10})_2]^-$ that was also detected by ESI-MS at m/z 470.95. Note that only very few square-planar cobalt(III)

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Scheme 1. Formation of **1** and Its Reactions with Terminal Alkynes

complexes with tetrathiolate ligands are known¹⁴ since the majority of cobalt(III) complexes are observed with an octahedral ligand configuration at the metal center. $[\text{Co}(\text{S}_2\text{C}_2\text{B}_{10}\text{H}_{10})_2]^{2-}$ with a cobalt(II) center possesses tetrahedral geometry.¹⁵

Discussion

It is well-known that cobalt(III) complexes of square-planar geometry with acacen or salen ligands have been successfully employed as chiral Lewis acid catalysts in the enantioselective hetero-Diels–Alder reaction,¹⁶ the carbonylene reaction,¹⁷ 1,3-dipolar cycloaddition of nitrones,¹⁸ and ring opening of epoxides.¹⁹ Thus, the square-planar complex **1** with an electron-deficient cobalt center (14e), reactive Co–S bonds, and the vacant axial positions may offer similarly diverse reaction chemistries. The terminal alkyne ethynylferrocene was used to test its reactivity. Unexpectedly, the ferrocene-substituted dithio-*o*-carboranes **2** and **3** were generated (Scheme 1). In **2**, one alkyne molecule is added to the *o*-carborane dithiolate ligand at two sulfur sites. This leads to a cobalt-free species containing a bent six-membered ring with a dihedral angle (128.4°) at the $\text{S}(1)\cdots\text{S}(2)$ vector (Figure 2.) The ^1H NMR spectrum shows a singlet at 6.53 ppm assigned to the $=\text{CH}$ unit, and its ^{13}C signal is identified at 112.36 ppm. The carbon atom connected to the ferrocene unit ($\text{Fc}-\text{C}=\text{CH}$) is assigned at 141.92 ppm. A similar

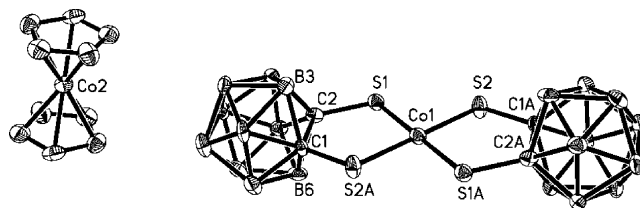


Figure 1. Molecular structure of **1**. Selected bond lengths [Å] and angles [deg]: C(1)–C(2) 1.614(5), Co(1)–S(1) 2.1728(15), Co(1)–S(2) 2.1806(15), C(2)–S(1) 1.794(4), C(1)–S(2A) 1.798(4); S(1)Co(1)S(2) $84.74(4)$, S(1)Co(1)S(2A) $95.26(4)$.

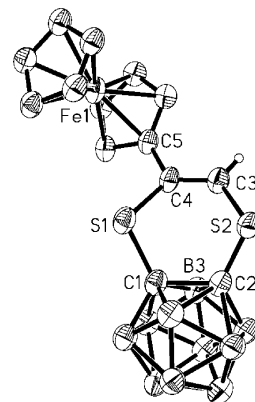


Figure 2. Molecular structure of **2**. Selected bond lengths [Å] and angles [deg]: C(1)–C(2) 1.683(4), S(1)–C(4) 1.743(3), S(2)–C(3) 1.806(3), S(1)–C(1) 1.814(3), S(2)–C(2) 1.720(3), C(3)–C(4) 1.310(4), C(4)–C(5) 1.492(4); S(1)C(1)C(2)S(2)/S(1)C(4)C(3)S(2) 128.4 .

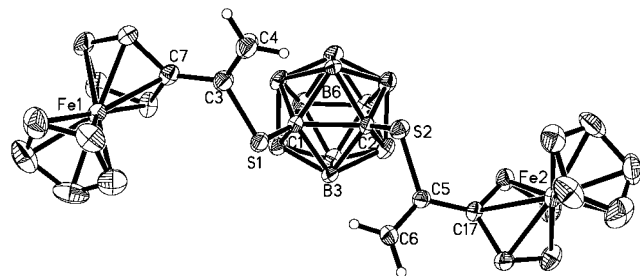


Figure 3. Molecular structure of **3**. Selected bond lengths [Å] and angles [deg]: C(1)–C(2) 1.820(6), S(1)–C(1) 1.731(4), S(1)–C(3) 1.781(4), C(3)–C(4) 1.351(7), S(2)–C(2) 1.740(4), S(2)–C(5) 1.782(5), C(5)–C(6) 1.352(6); C(1)S(1)C(3) $103.5(2)$, S(1)C(3)C(4) $116.2(4)$, S(1)C(3)C(7) $117.3(3)$, C(2)S(2)C(5) $104.9(2)$, S(2)C(5)C(6) $116.4(3)$, S(2)C(5)C(17) $115.7(4)$.

structural type with silicon, instead of sulfur, from the reaction of a 1,2-bis(dimethylsilyl)carborane nickel species with alkynes has been described.²⁰

The solid-state structure of **3** indicates that the *o*-carborane dithiolate ligand is combined with two vinylferrocenes (Figure 3). Interestingly, two extra hydrogen atoms are observed in **3** compared to the starting compounds. S(1)–C(1)–C(2)–S(2) is nearly planar, and the two thiovinyl units are in a *transoid* arrangement. The orientations of the vinylferrocenes are different in the dihedral angles between the Cp ring of the individual ferrocene moieties and the plane S(1)C(1)C(2)S(2), 120.6° for Fe(1)- and 57.7° for Fe(2)-vinylferrocene, respectively. In **3**, the C(1)–C(2) distance (1.820 Å) is exceptionally long, as compared with

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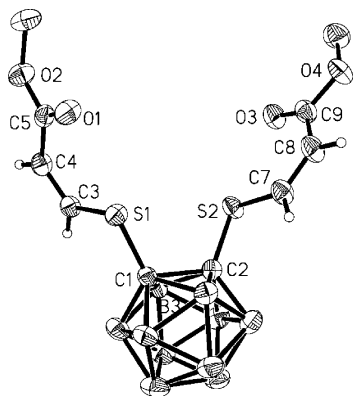


Figure 4. Molecular structure of **5**. Selected bond lengths [Å] and angles [deg]: C(1)–C(2) 1.790(4), S(1)–C(1) 1.774(3), S(1)–C(3) 1.740(3), C(3)–C(4) 1.316(4); C(1)S(1)C(3) 101.90(16).

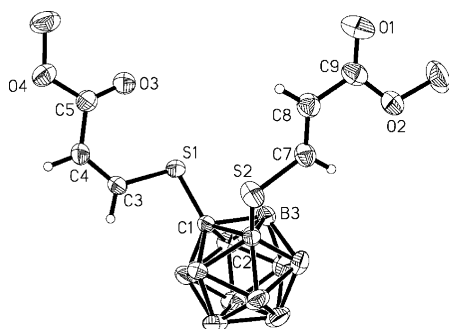


Figure 5. Molecular structure of **6**. Selected bond lengths [Å] and angles [deg]: C(1)–C(2) 1.793(3), S(1)–C(1) 1.771(2), S(1)–C(3) 1.731(2), C(3)–C(4) 1.323(3), C(4)–C(5) 1.451(3), C(8)–C(9) 1.455(3), C(7)–C(8) 1.311(3), S(2)–C(7) 1.740(2), C(2)–S(2) 1.762(2); C(1)S(1)C(3) 101.96(11), C(2)S(2)C(7) 102.48(11).

the typical range found in *o*-carborane derivatives of 1.62–1.70 Å.²¹ This reflects a considerable distortion of the carborane cage that may be attributed to the steric factor of the two vinylferrocene units. The ¹H NMR spectrum of **3** contains two singlets at δ 5.78 and 6.13 owing to the geminal ¹H nuclei of the respective vinyl protons. The ¹³C signals at 124.99 (=CH₂) and 139.31 ppm (=C–Fc) are also indicative of the presence of the terminal alkene. The EI-MS analysis shows the molecular ion peak. These are consistent with the solid-state structure.

In the case of phenyl acetylene, the structural type **3** was not generated, and only one product **4**, an analogue of **2**, was observed (Scheme 1) based on the spectroscopic data and microanalysis. In the case of the activated alkyne, methyl carboxylate acetylene, three hydrosulfuration products **5–7** with the two C=C bonds in *Z/Z*, *Z/E*, *E/E* configurations, respectively, were isolated in a ratio of appropriate 1:1:1, as shown in Scheme 1 and Figure 4–6. Again, extra hydrogen atoms were observed in **5–7**. The ¹H NMR spectra of the three structural isomers are similar, showing the vinyl doublets in a range from 6.02 to 7.51 ppm and different coupling constants of 16 Hz for *E* configuration versus 10 Hz for *Z* configuration. The ¹³C signals of the carbon atoms linked to sulfur are shifted to low field approximately 20 ppm relative to the ones linked to C(O) in the S–CH=CH–C(O) unit. Note that the structural type **2** or **4** was not generated

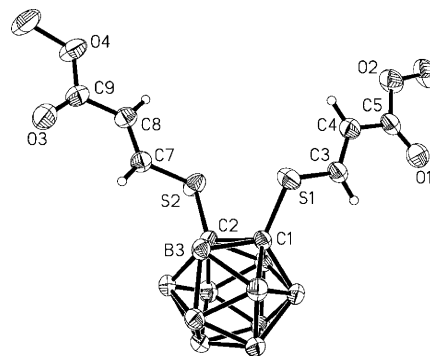


Figure 6. Molecular structure of **7**. Selected bond lengths [Å] and angles [deg]: C(1)–C(2) 1.777(3), S(1)–C(1) 1.766(2), S(1)–C(3) 1.737(2), C(3)–C(4) 1.307(3); C(1)S(1)C(3) 104.28(10).

in this reaction. These suggest that a product type is determined by the nature of an alkyne. Moreover, the generation of **3** and **5–7** reflects the regio- and stereoselective addition of terminal alkynes and is mechanistic in origin. Very recently, a dithio derivative 1,12-[HS(CH₂)₃]₂-1,12-C₂B₁₀H₁₀ has been reported from a dibromo derivative of *p*-carborane.²² However, the hydrosulfuration products of the types described in this paper are unknown.

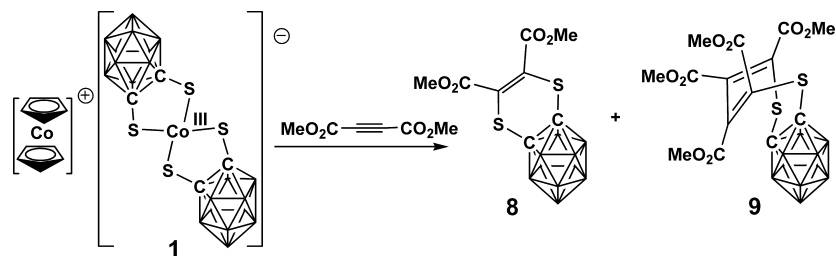
The terminal hydrogen atom in the alkynes used above may be responsible for the two “extra” hydrogen atoms in the generation of hydrosulfuration species **3**, **5–7**. To test this hypothesis, the internal alkyne, dimethyl acetylenedicarboxylate, was chosen to react with **1** that led to only disulfuration products **8** and **9** (Scheme 2.)

8 was identified on the basis of spectroscopic data and microanalysis. The NMR data demonstrate a symmetric structure, and the mass spectrum displays a strong peak at 348.1 corresponding to the molecular ion. In **9** the alkyne is a 2-fold addition to the *o*-carborane dithiolate ligand at the two sulfur sites that results in an eight-membered ring as indicated in Figure 7. The ¹H and ¹³C data show two types of signals from the alkyne and only one ¹³C signal from the carborane. The EI-MS spectrum gives a molecular ion peak at 490.0. Thus, the spectroscopic data support the solid-state structure. A 2-fold alkyne insertion into an M–E bond occurred in the 16e complexes Cp^{*}M(E₂C₂B₁₀H₁₀) (M = Co, Rh; E = S, Se), and the resulting complexes acted as intermediates in the generation of benzene derivatives from alkynes.^{12,13} We therefore envision that **1** may have a potential for catalytic cyclotrimerization of alkynes. Indeed, hexamethyl benzene-hexacarboxylate was isolated in a yield of 10% (based on dimethyl acetylenedicarboxylate used).

Mechanistic Implications. As **3** and **5–7** are unique, their origins are of interest. The mechanistic implications are summarized in Scheme 3. The alkyne insertion into one of the Co–S bonds in **1** may lead to **II**, in analogy to reported examples of alkyne insertion into M–S bonds.¹² **III** is reasonable provided the generated S→Co coordinative bond is weak enough. The next step is the release of **2** or **4** via reductive elimination. Both a new alkyne addition to a Co–S bond and the oxidative addition of a second terminal alkyne

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Scheme 2. Reaction of **1** with Dimethyl Acetylenedicarboxylate

to the metal center may give rise to the metal hydride species **V**. Hydrogen transfer from the metal to the adjacent olefinic carbon atom in **V** then generates the vinyl compound **VI**, and repetition from **IV** to **VI** may lead to the final products **3**, **5**, **6**, and **7**.

On the basis of this mechanism, production of **3** requires excess alkyne. Indeed, experimentally, we observe that **3** can not be generated for stoichiometric alkyne addition. The

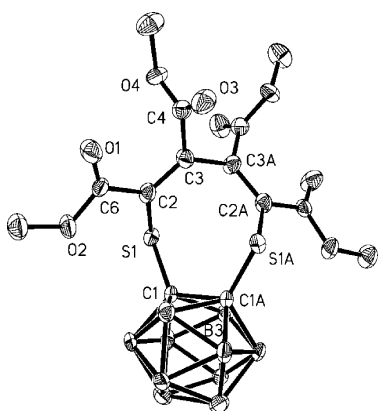
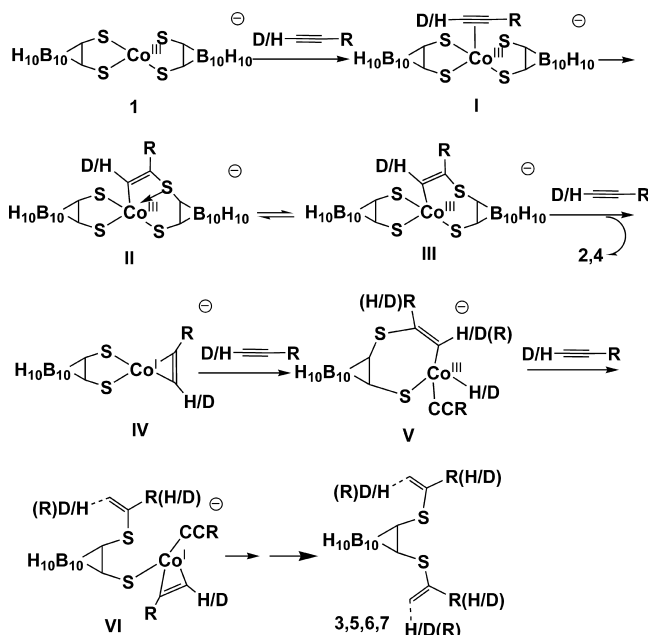


Figure 7. Molecular structure of **9**. Selected bond lengths [Å] and angles [deg]: C(1)–C(1A) 1.717(3), S(1)–C(1) 1.786(3), S(1)–C(2) 1.769(3), C(2)–C(3) 1.360(4); C(1)C(1A)S(1A)S(1)/S(1)C(2)C(3)C(3A) 76.3, C(1)C(1A)S(1A)S(1)/C(3)C(3A)C(2A)S(1A) 76.3, S(1)C(2)C(3)C(3A)/C(3)C(3A)C(2A)S(1A) 77.6.

Scheme 3. Proposed Mechanism for the Reaction of **1** with Terminal Alkynes



competitive formation of **3** in CH_2Cl_2 is less favored than that of **2**, as demonstrated by yields of 10% for **3** versus 70% for **2**. The yield of **3** was increased by addition of polar solvents, for example, an increase in the yield of **3** by 50% in THF/ CH_2Cl_2 (1:1). This can be attributed to a solvent-stabilized agostic intermediate, a prerequisite of C–H oxidative addition that involves an elongation of an agostic C–H bond.²³ Thus, the solvent effect suggests the presence of a metal hydride. In comparison, $\text{HC}\equiv\text{CCO}_2\text{Me}$ leads only to oxidative addition products **5**–**7** whereas $\text{HC}\equiv\text{CPh}$ gives only reductive elimination product **4**. This further demonstrates that the type of alkyne plays a crucial role in generating and stabilizing the intermediate metal hydride species that ultimately determines the variety and yield of the products. Thus, the consumption of excess terminal alkynes provides the extra hydrogen atoms for hydrosulfuration. To further confirm this, we used 1-deuterio-2-ferrocenylethyne to react with **1**, and as a consequence, **3** was obtained with a deuterium content of approximate 83%; this value exactly parallels to the deuterium contents for **2** and the deuterated alkyne. Therefore, the result substantiates our proposal for the origin of the additional hydrogen atoms in the hydrosulfuration products (see the Supporting Information for the detailed NMR data).

In summary, an unusual square-planar tetrathiolate cobalt(III) complex $[\text{Cp}_2\text{Co}]^+[\text{Co}(\text{S}_2\text{C}_2\text{B}_{10}\text{H}_{10})_2]^-$ (**1**) was synthesized and used for the disulfuration and hydrosulfuration of alkynes. An effective synthetic route that incorporates an alkyne into an *o*-carborane dithiolate unit for carboranyl vinyl sulfides in a one-pot reaction has proved successful. The resulting novel products may be served as valuable synthetic intermediates or precursors to materials and bioactive molecules.

Experimental Section

General Information. *n*-Butyllithium (2.0 M in hexanes, Aldrich), *o*-carborane (Katchem, Czech), methyl acetylene monocarboxylate (Alfa Aesar), phenylacetylene (Alfa Aesar), and dimethylacetylenedicarboxylate (Aldrich) were used as supplied. Ethynylferrocene,²⁴ 1-deuterio-2-ferrocenylethyne,²⁵ and CpCo –

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Table 1. Crystallographic Data and Structure Refinement Information for **1**, **2**, **3**, and **5**

	1	2	3	5
formula	C ₄ H ₂₀ B ₂₀ CoS ₄ ·C ₁₀ H ₁₀ Co	C ₁₄ H ₂₀ B ₁₀ FeS ₂	C ₂₆ H ₃₂ B ₁₀ Fe ₂ S ₂	C ₁₀ H ₂₀ B ₁₀ O ₄ S ₂
formula weight	660.72	416.39	628.46	376.50
color	green	yellow	yellow	white
size, mm	0.24 × 0.26 × 0.30	0.24 × 0.26 × 0.30	0.24 × 0.26 × 0.30	0.24 × 0.26 × 0.30
crystal system	triclinic	orthorhombic	triclinic	triclinic
space group	<i>P</i> $\bar{1}$	<i>Pbcn</i>	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$
<i>a</i> , Å	7.153(4)	16.585(4)	10.2696(12)	10.028(3)
<i>b</i> , Å	10.580(5)	16.254(4)	10.668(3)	10.509(3)
<i>c</i> , Å	11.339(8)	14.786(3)	14.0596(17)	11.515(4)
α (deg)	62.240(6)	90	74.060(2)	65.152(4)
β (deg)	82.802(10)	90	88.1300(10)	84.841(5)
γ (deg)	84.983(6)	90	82.311(3)	61.930(4)
<i>V</i> (Å ³)	753.0(8)	3985.9(16)	1467.8(5)	962.8(5)
<i>z</i>	1	8	2	2
θ range (deg)	2.0–26.0	1.8–26.0	1.5–26.0	2.0–26.0
<i>D</i> (calc) [g/cm ³]	1.457	1.388	1.422	1.299
μ (mm ^{−1})	1.389	0.962	1.149	0.288
min, max trans	0.665, 0.715	0.7612, 0.8019	0.7161, 0.7610	0.9163, 0.9312
data/restraints/parameters	2849/0/184	3919/0/244	5642/0/361	3699/0/237
<i>F</i> (000)	332	1696	644	388
no. reflns. collected	3913	20343	8056	5280
no. unique reflns. (<i>R</i> _{int})	2849 (0.024)	3919 (0.056)	5642 (0.023)	3699 (0.042)
GOF	1.02	1.01	1.03	0.97
<i>R</i> indices (<i>I</i> > 2 σ (<i>I</i>))	<i>R</i> ₁ = 0.0511 w <i>R</i> ₂ = 0.1168	<i>R</i> ₁ = 0.0499 w <i>R</i> ₂ = 0.0970	<i>R</i> ₁ = 0.0493 w <i>R</i> ₂ = 0.1009	<i>R</i> ₁ = 0.0469 w <i>R</i> ₂ = 0.1204
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0619 w <i>R</i> ₂ = 0.1198	<i>R</i> ₁ = 0.0923 w <i>R</i> ₂ = 0.1072	<i>R</i> ₁ = 0.0652 w <i>R</i> ₂ = 0.1045	<i>R</i> ₁ = 0.0743 w <i>R</i> ₂ = 0.1425
largest diff. peak and hole	0.497, −0.829	0.301, −0.228	0.296, −0.433	0.271, −0.203

(CO)₂²⁶ were prepared by modified literature procedures. All reactions were carried out under argon using standard Schlenk techniques. All solvents were dried and deoxygenated prior to use. Diethyl ether, tetrahydrofuran (THF), and petroleum ether toluene were refluxed and distilled over sodium/benzophenone ketyl under nitrogen. CH₂Cl₂ was refluxed and distilled over CaH₂ under nitrogen. The NMR measurements were performed on a Bruker DRX 500 spectrometer. Chemical shifts were given with respect to CHCl₃/CDCl₃ (δ ¹H = 7.24; δ ¹³C = 77.0) and external Et₂O-BF₃ (δ ¹B = 0). The IR spectra were recorded on a Bruker Vector 22 spectrophotometer with KBr pellets in the region of 4000–400 cm^{−1}. The C and H microanalyses were carried out with Elementar Vario EL III elemental analyzer. The mass spectra (MS) was recorded in a Micromass GC-TOF for EI-MS (70 eV).

Preparation of 1. A solution of *o*-C₂B₁₀H₁₂ (50 mg, 0.32 mmol) in diethylether (10 mL) was lithiated by addition of a 2.0 M solution of *n*-butyllithium (0.32 mL, 0.64 mmol) in hexanes. Then sulfur (21 mg, 0.64 mmol) was added to the above mixture to generate Li₂S₂C₂B₁₀H₁₀ which reacted with CpCo(CO)I₂ (120 mg, 0.30 mmol) in THF (20 mL) at 0 °C for 1 h. After removal of the solvents the residue was chromatographed on silica. Elution with CH₂Cl₂ gave **1**. Green solid, yield 40 mg (40%). mp 210 °C dec. ¹H NMR (CDCl₃): δ 4.19 (s, Cp), ¹¹B{¹H} NMR (CDCl₃): δ 1.5 (2B), −3.8 (1B), −4.8 (4B), −7.1 (2B), −9.3 (1B). ESI-MS: *m/z* 471 ([M − (Cp₂Co)]⁺, 100%). IR (KBr): ν (cm^{−1}) 2585 (B–H). Elemental analysis: calcd (%) for C₁₄H₃₀B₂₀Co₂S₄: C 25.45, H 4.58; found: C 25.91, H 4.77.

Preparation of 2 and 3. A mixture of **1** (66 mg, 0.1 mmol) and ethynylferrocene (210 mg, 1.0 mmol) in CH₂Cl₂ (20 mL) was stirred for 24 h at ambient temperature. The color turned from green to yellow. After removal of the solvent the residue was chromatographed on silica. Elution with petrol ether gave **2** and **3**. **2**. Yellow solid, yield 58 mg (70%), mp 155 °C dec. ¹H NMR (CDCl₃): δ 4.21 (s, 5H, Cp), 4.45 (m, 2H, Fc), 4.40 (m, 2H, Fc), 6.53 (s, 1H,

HC=C). ¹¹B{¹H} NMR (CDCl₃): δ −6.6 (3B), −6.0 (3B), −4.2 (2B), −1.6 (2B). ¹³C NMR (CDCl₃): δ 67.02, 69.82, 70.48, 81.79 (Fc), 77.13, 112.29 (carborane), 112.36 (CH=C), 141.92 (=C–Fc). EI-MS (70 eV): *m/z* 416 (M⁺, 100%). IR (KBr): ν (cm^{−1}) 1633 (C=C), 2587 (B–H). Elemental analysis, calcd (%) for C₁₄H₂₀B₁₀FeS₂: C 40.38, H 4.84; found: C 39.87, H 4.53. **3**. Yellow solid, yield 13 mg (10%), mp 183 °C dec. ¹H NMR (CDCl₃): δ 4.16 (s, 10H, Cp), 4.65 (m, 4H, Fc), 4.35 (m, 4H, Fc), 5.78 (s, 2H, C=CH₂), 6.13 (s, 2H, C=CH₂). ¹³C NMR (CDCl₃): δ 68.36, 69.82, 69.99, 84.26 (Fc), 93.52 (carborane), 124.99 (C=CH₂), 139.31 (=C–Fc). ¹¹B{¹H} NMR (CDCl₃): δ −8.7 (1B), −6.2 (7B), −0.6 (2B). EI-MS (70 eV): *m/z* 628 (M⁺, 21%). IR (KBr): ν (cm^{−1}) 1594 (FcC=CH₂), 2575 (B–H). Elemental analysis: calcd (%) for C₂₆H₃₂B₁₀Fe₂S₂: C 49.69, H 5.13; found: C 49.17, H 5.44.

Preparation of 4. A mixture of **1** (66 mg, 0.1 mmol) and phenylacetylene (0.22 mL, 2 mmol) in CH₂Cl₂ (20 mL) was stirred for 24 h at ambient temperature. The color turned from green to brown. After removal of the solvent, the residue was chromatographed on TLC, and elution with petrol ether gave **4**. White solid, yield 50 mg (81%). ¹H NMR (CDCl₃): δ 6.85 (s, 1H, C=CH), 7.41 (m, 3H, Ph), 7.47 (m, 2H, Ph). ¹³C NMR (CDCl₃): δ 126.23, 129.09, 130.09, 136.35 (Ph), 118.46 (CH=C), 124.87 (=C–Ph). ¹¹B{¹H} NMR (CDCl₃): δ −6.4 (3B), −5.1 (3B), −3.6 (2B), −1.2 (2B). EI-MS (70 eV): *m/z* 308.3 (M⁺, 100%). IR (KBr): ν (cm^{−1}) 1633 (C=CH), 2593 (B–H). Elemental analysis, calcd (%) for C₁₀H₁₆B₁₀S₂: C 38.94, H 5.23; found: C 38.43, H 5.64.

Preparation of 5, 6, and 7. A mixture of **1** (66 mg, 0.1 mmol) and methyl acetylene monocarboxylate (0.17 mL, 2.0 mmol) in CH₂Cl₂ (20 mL) was stirred for 24 h at ambient temperature. The color turned from green to brown. After removal of the solvent, the residue was chromatographed on TLC, and elution with petrol ether/CH₂Cl₂ (1:1) gave **5**, **6**, and **7**. **5**. White solid, yield 23 mg (30%), mp 100 °C dec. ¹H NMR (CDCl₃): δ 3.76 (s, 3H, OMe), 6.02 (d, *J* = 10 Hz, 1H, HC=CH–C(O)), 7.14 (d, *J* = 10 Hz, 1H, S–CH=CH). ¹³C NMR (CDCl₃): δ 51.96, (OMe), 89.44 (carborane), 116.14 (HC=CH–C(O)), 144.33 (S–CH=CH), 166.53 (C=O). ¹¹B{¹H} NMR (CDCl₃): δ −11.1 (2B), −8.2 (6B), −1.8

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Table 2. Crystallographic Data and Structure Refinement Information for **6**, **7**, and **9**

	6	7	9
formula	C ₁₀ H ₂₀ B ₁₀ O ₄ S ₂	C ₁₀ H ₂₀ B ₁₀ O ₄ S ₂	C ₁₄ H ₂₂ B ₁₀ O ₈ S ₂
formula weight	376.50	376.50	490.56
color	white	white	white
size, mm	0.24 × 0.26 × 0.30	0.24 × 0.26 × 0.30	0.24 × 0.26 × 0.30
crystal system	triclinic	monoclinic	monoclinic
space group	<i>P</i> $\bar{1}$	<i>C</i> 2/ <i>c</i>	<i>C</i> 2/ <i>c</i>
<i>a</i> , Å	10.9663(10)	22.857(2)	12.356(7)
<i>b</i> , Å	12.7759(12)	13.6124(13)	12.873(7)
<i>c</i> , Å	14.7343(14)	13.2963(12)	14.575(10)
α (deg)	83.9590(10)	90	90
β (deg)	76.6780(10)	106.9170(10)	93.926(12)
γ (deg)	83.3300(10)	90	90
<i>V</i> (Å ³)	1988.6(3)	3958.0(6)	2313(2)
<i>z</i>	4	8	4
θ range (deg)	1.6–26.0	1.8–26.0	2.3–26.0
<i>D</i> (calc) [g/cm ³]	1.258	1.264	1.409
μ (mm ^{−1})	0.279	0.280	0.273
min, max trans	0.9163, 0.9312	0.9163, 0.9312	0.9132, 0.9279
data/restraints/parameters	7664/0/473	3887/0/237	2261/0/156
<i>F</i> (000)	776	1552	1008
no. reflns. collected	10900	10609	6248
no. unique reflns. (<i>R</i> _{int})	7664 (0.061)	3887 (0.052)	2261 (0.053)
GOF	0.93	1.09	1.08
<i>R</i> indices (<i>I</i> > 2 σ (<i>I</i>))	<i>R</i> ₁ = 0.0478 <i>wR</i> ₂ = 0.1156	<i>R</i> ₁ = 0.0441 <i>wR</i> ₂ = 0.1251	<i>R</i> ₁ = 0.0528 <i>wR</i> ₂ = 0.1206
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0725 <i>wR</i> ₂ = 0.1257	<i>R</i> ₁ = 0.0628 <i>wR</i> ₂ = 0.1351	<i>R</i> ₁ = 0.0633 <i>wR</i> ₂ = 0.1240
largest diff. peak and hole	0.390, −0.229	0.357, −0.206	0.223, −0.353

(2B). EI-MS (70 eV): *m/z* 376.1 (*M*⁺, 3%). IR (KBr): ν (cm^{−1}) 1633 (C=C), 1692 (C=O), 2572 (B–H). Elemental analysis, calcd (%) for C₁₀H₂₀B₁₀O₄S₂: C 31.90, H 5.35; found: C 32.53, H 5.89. **6**. White solid, yield 21 mg (27%), mp 102 °C dec ¹H NMR (CDCl₃): δ 3.78 (s, 3H, OMe), 3.79 (s, 3H, OMe), 6.04 (d, *J* = 10 Hz, 1H, HC=CH–C(O)(Z)), 6.09 (d, *J* = 16 Hz, 1H, HC=CH–C(O)(E)), 7.14 (d, *J* = 10 Hz, 1H, S–CH=CH (Z)), 7.51 (d, *J* = 16 Hz, 1H, S–CH=CH (E)). ¹³C NMR (CDCl₃): δ 52.06, 52.07 (OMe), 87.35, 89.29 (carborane), 116.31 (HC=CH–C(O) (Z)), 121.45 (HC=CH–C(O) (E)), 140.73 (S–CH=CH (E)), 144.33 (S–CH=CH (Z)), 164.14, 166.53 (C=O). ¹¹B{¹H} NMR (CDCl₃): δ −10.8 (2B), −8.3 (6B), −1.7 (2B). EI-MS (70 eV): *m/z* 376.2 (*M*⁺, 2%). IR (KBr): ν (cm^{−1}) 1592 (C=C), 1699, 1724 (C=O), 2599 (B–H). Elemental analysis, calcd (%) for C₁₀H₂₀B₁₀O₄S₂: C 31.90, H 5.35; found: C 32.64, H 5.76. **7**. White solid, yield 26 mg (34%), mp 105 °C dec ¹H NMR (CDCl₃): δ 3.79 (s, 3H, OMe), 6.12 (d, *J* = 16 Hz, 1H, HC=CH–C(O)), 7.50 (d, *J* = 16 Hz, 1H, S–CH=CH). ¹³C NMR (CDCl₃): δ 52.15 (OMe), 87.31 (carborane), 121.61 (HC=CH–C(O)), 140.60 (S–CH=CH), 164.09 (C=O). ¹¹B{¹H} NMR (CDCl₃): −10.8 (2B), −8.3 (6B), −1.6 (2B). EI-MS (70 eV): *m/z* 376.2 (*M*⁺, 1%). IR (KBr): ν (cm^{−1}) 1630 (C=C), 1725 (C=O), 2598 (B–H). Elemental analysis, calcd (%) for C₁₀H₂₀B₁₀O₄S₂: C 31.90, H 5.35; found: C 31.43, H 5.83.

Preparation of 8 and 9. A mixture of **1** (66 mg, 0.1 mmol) and dimethyl acetylenedicarboxylate (0.25 mL, 2.0 mmol) in CH₂Cl₂ (200 mL) was stirred for 24 h at ambient temperature. The color turned from green to deep red. After removal of the solvent, the residue was chromatographed on TLC, and elution with petrol ether/CH₂Cl₂ (1: 2) gave **8**, **9**, and hexamethyl benzene-hexacarboxylate (171 mg, 10%, based on dimethyl acetylenedicarboxylate used). **8**. White solid, yield 21 mg (30%). ¹H NMR (CDCl₃): δ 3.87 (s, 6H, OMe). ¹³C NMR (CDCl₃): δ 53.91 (OMe), 72.63 (carborane), 133.31 (C–C(O)), 162.18 (C=O). ¹¹B{¹H} NMR (CDCl₃): δ −7.9 (5B), −5.7 (2B), −2.9 (3B). EI-MS (70 eV): *m/z* 348.1 (*M*⁺, 100%). IR (KBr): ν (cm^{−1}) 1568 (C=C), 1733 (C=O), 2593 (B–H). Elemental analysis, calcd (%) for C₈H₁₆B₁₀O₄S₂: C 27.58, H 4.63; found: C 28.26, H 4.39. **9**. White solid, yield 33 mg (30%), mp 110 °C dec. ¹H NMR (CDCl₃): δ 3.86 (s, 6H, OMe), 3.95 (s, 6H, OMe). ¹³C NMR (CDCl₃): δ 53.83, 53.90 (OMe), 72.52 (carborane), 127.51 (C=C–C(O)), 151.35 (S–C=C), 162.04, 163.35 (C=O).

¹¹B{¹H} NMR (CDCl₃): δ −9.5 (5B), −8.1 (2B), −5.2 (1B), −2.5 (2B). EI-MS (70 eV): *m/z* 490.0 (*M*⁺, 25%). IR (KBr): ν (cm^{−1}) 1741 (C=O), 2586 (B–H). Elemental analysis, calcd (%) for C₁₄H₂₂B₁₀O₈S₂: C 34.28, H 4.52; found: C 33.76, H 4.83.

X-ray Crystallography. Crystals suitable for X-ray analysis were obtained by slow evaporation of a solution in petroleum ether/dichloromethane. Diffraction data were collected on a Bruker SMART Apex II CCD diffractometer using graphite-monochromated Mo K α (λ = 0.71073 Å) radiation at 273 K. During the intensity data collection, no significant decay was observed. The intensities were corrected for Lorentz-polarization effects and empirical absorption with the SADABS program.²⁷ The structures were solved by direct methods using the SHELXL-97 program.²⁸ All non-hydrogen atoms were found from the difference Fourier syntheses. The H atoms were included in calculated positions with isotropic thermal parameters related to those of the supporting carbon atoms but were not included in the refinement. All calculations were performed using the Bruker SMART program (Tables 1 and 2).

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Supporting Information Available: X-ray crystallographic files in CIF format for the compounds **1**, **2**, **3**, **5**, **6**, **7**, **9**, the CheckCIF and the ¹H NMR spectra for **2** and **3** isolated from the reactions of deuterated and nondeuterated FcC≡CH with **1** for comparison. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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