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Stepwise and Selective Carborane Substitution in the B(3,6) Positions of a 16*e* CpCo Half-Sandwich Complex Containing a Chelating *ortho*-Carborane-1,2-dithiolate Ligand

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The reactions of the 16*e* half-sandwich complex, CpCo($S_2C_2B_{10}H_{10}$) (**1**), with alkynones at ambient temperature lead to complexes CpCo($S_2C_2B_{10}H_9$)(CH=CH−C(O)R) (R = Ph (**2**), 2-naphthyl (**3**)). Both **2** and **3** are still 16*e* half-sandwich complexes containing a B(3)-substituted *ortho*-carborane-1,2-dithiolate ligand. Treatment of **2** with excess alkynes $R_1C\equiv CR_2$ (R_1 = H, R_2 = Ph, C(O)Ph, CO_2Me; R_1 = R_2 = CO_2Me) affords five complexes, CpCo($S_2C_2B_{10}H_8$)(CH_2CPh)-(CH=CH−C(O)Ph) (**4**), CpCo($S_2C_2B_{10}H_8$)(CH=CH−C(O)Ph)$_2$ (**5**), CpCo($S_2C_2B_{10}H_8$)(CH=CH−CO_2Me)(CH=CH−C(O)Ph) (**6**), CpCo($S_2C_2B_{10}H_9$)(MeO_2C−C=C−CO_2Me)(CH=CH−C(O)Ph) (**7**), and CpCo($S_2C_2B_{10}H_9$)(MeO_2C−C=C−CO_2Me)$_2$(CH=CH−C(O)Ph) (**8**). Complex **4** is an 18*e* complex bearing a B−CH_2 unit. Both **5** and **6** retain a 16*e* half-sandwich structure but contain a B(3,6)-disubstituted *ortho*-carborane-1,2-dithiolate ligand. However, in **7** and **8** one or two alkynes are inserted into one of the Co−S bonds to generate 18*e* species, respectively. Heating **7** leads to the 16*e* complex, CpCo($S_2C_2B_{10}H_8$)(MeO_2C−C=CH−CO_2Me)(CH=CH−C(O)Ph) (**9**), having a B(3,6)-disubstituted *ortho*-carborane-1,2-dithiolate ligand as in **5** and **6**. All complexes were fully characterized by spectroscopic techniques and elemental analysis. The solid-state structures of **2** and **3** and **5**−**9** were further characterized by X-ray structural analysis.

Introduction

Mononuclear 16*e* half-sandwich complexes Cp$^\#$M-($E_2C_2B_{10}H_{10}$) (Cp$^\#$ = Cp, Cp*; M = Co, Rh, Ir; and E = S, Se) and (*p*-cymene)M($S_2C_2B_{10}H_{10}$) (M = Ru, Os) possessing an *ortho*-carborane-1,2-dichalcogenolate ligand have been described extensively.[1−14] These sterically congested, coordinatively unsaturated complexes are stable starting materials and exhibit rich chemistries. For example, they are capable of combining metal species to generate new types of metal−metal binding complexes with one or two *ortho*-carborane-1,2-dichalcogenolate ligands[1] and with Lewis

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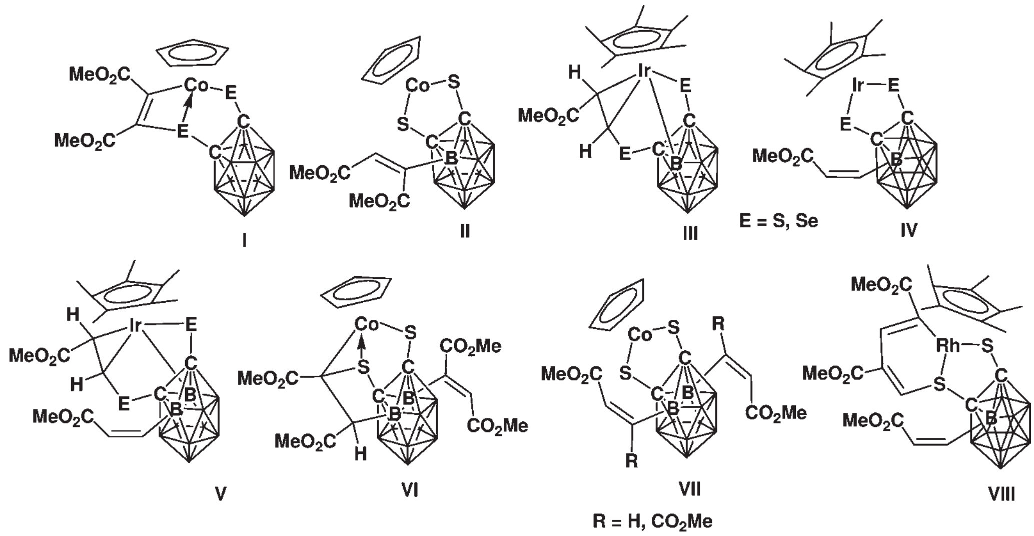
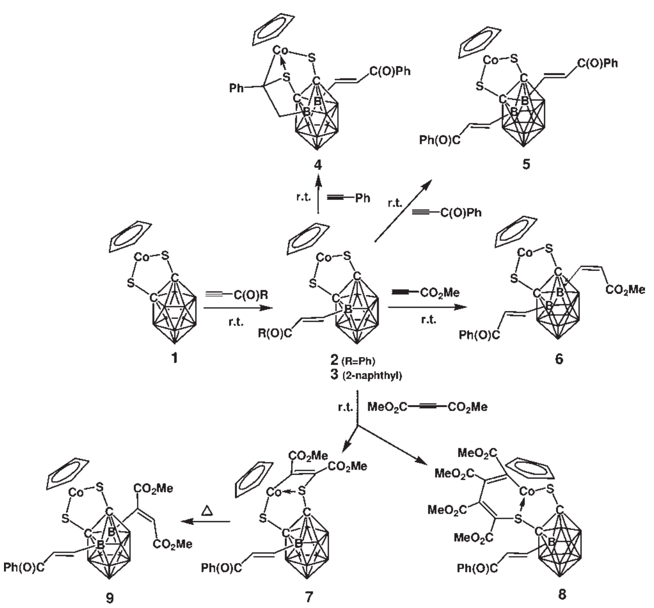
Scheme 1. Some Reported Examples[6,7,11] Possessing an *ortho*-Carborane-1,2-dichalcogenolate Ligand



bases including biologically interesting substrates, such as NH_3, CO, and diazenes, to generate their 18*e* congeners.[2,3] Furthermore, the combination of electron deficiency at the metal center and reactivity of metal−chalcogen bonds renders these complexes interesting candidates for reactions with unsaturated substrates, such as alkynes.[4−14] Additionally, both the bulky ancillary aromatic ligand and the *closo*-dicarba-dodecaborane unit could protect the inner coordination sphere and make the catalytic oligmerization of alkyne possible.[10−13] Very recently we have reported the interesting anticancer actions of two ruthenium complexes with an *ortho*-carborane-1,2-dithiolate ligand.[14]

The B−H activation of the polyhedral carborane is conceivable if the electron deficient metal atom is located in close proximity to the B−H vertices.[15] Recently, some highly substituted carborane derivatives have been prepared by metal-mediated catalytic dehydrogenative borylation,[16] and the polyethylated icosahedral carborane monoanions may be potentially used as weakly coordinating anions.[17] In the presence of selected alkynes, the electronically unsaturated (16*e*) complexes $Cp^*M(E_2C_2B_{10}H_{10})$ (Cp^* = pentamethylcyclopentadienyl; M = Rh, Ir; and E = S, Se) have been reported to promote hydroboration of the *ortho*-carborane cage in the B(3,6) positions (Scheme 1).[5−12] Other selective substitution at the icosahedral *ortho*-carborane cage has been accomplished as well.[18]

Scheme 2. Reactions of **1** with $HC{\equiv}C{-}C(O)R$ (R = Ph (**2**), 2-Naphthyl (**3**)) and the Further Reactions of **2** with Alkynes



Recently, we have extended the reaction system to cobalt and found that the 16*e* complexes $CpCo(E_2C_2B_{10}H_{10})$ (Cp = cyclopentadienyl; and E = S, Se) are more reactive than the analogous rhodium and iridium species (Scheme 1).[5−12] Even so, through choice of the compatibility between the 16*e* species and alkyne as well as of the reaction ratio, we could control the selective B−H functionalization at the *ortho*-carborane cage step by step. Herein, we report such an example that the reactions of the 16*e* complex $CpCo(S_2C_2B_{10}H_{10})$ (**1**) with $HC{\equiv}C{-}C(O)R$ (R = Ph, 2-naphthyl) lead to 16*e* half-sandwich complexes **2** and **3** containing a B(3)-monosubstituted *ortho*-carborane-1,2-dithiolate ligand and then **2** further reacts with different alkynes.

Results and Discussion

Synthesis of 2 and 3. The reactions of the 16*e* complex, $[CpCo(S_2C_2B_{10}H_{10})]$ (**1**), with alkynones $HC{\equiv}C{-}C(O)R$ (R = Ph, 2-naphthyl) in a 1:1 ratio at ambient temperature lead to complexes **2** and **3**, respectively (Scheme 2). Their solid-state structures are shown in Figures 1 and 2,

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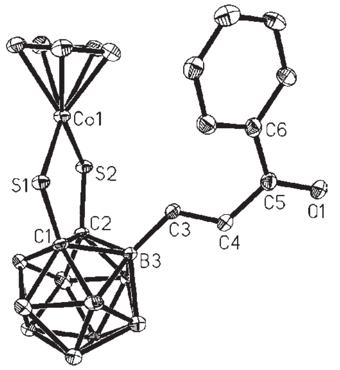

Figure 1. Molecular structure of **2**. Selected bond lengths (Å) and angles (°): Co1−S1, 2.1425(8); Co1−S2, 2.1244(8); C1−C2, 1.633(4); C1−S1, 1.774(3); C2−S2, 1.790(3); C3−C4, 1.323(4); B3−C3, 1.543(5); S2−Co1−S1, 96.69(3); C1−S1−Co1, 105.37(10); and C2−S2−Co1, 105.87(10).

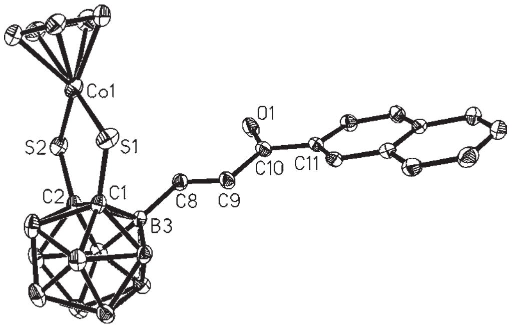

Figure 2. Molecular structure of **3**. Selected bond lengths (Å) and angles (°): Co1−S1, 2.1164(9); Co1−S2, 2.1435(11); S1−C1, 1.779(3); S2−C2, 1.780(3); C1−C2, 1.654(3); B3−C8, 1.548(4); C8−C9, 1.300(4); S1−Co1−S2, 97.26(4); C1−S1−Co1, 105.78(9); and C2−S2−Co1, 105.23(9).

respectively. Both are 16*e* half-sandwich complexes possessing B(3)-substituted *ortho*-carborane-1,2-dithiolate ligand, and the C=C bond in the B−H functionalized group of the alkyne takes an *E* configuration.

In the ^{1}H NMR spectra the two doublets at 6.47 and 7.45 ppm in **2** and at 6.52 and 7.62 ppm in **3** are assigned to the individual B−CH=CH unit (Table 1), and the large coupling constant (J = 18 Hz) corresponds to an *E* configuration. Note that the resonance of the proton adjacent to the boron atom shows the characteristic broader doublet due to partially relaxed ^{1}H−^{11}B coupling. In the ^{13}C NMR spectrum of **2**, the sharp ^{13}C signal at 138.2 ppm and the broader resonance at 140.4 ppm of the carbon nuclei linked directly to B are indicative of the B−CH=CH unit, as further confirmed by ^{13}C/^{1}H HETCOR (HMQC) experiments. In **3**, the corresponding ^{13}C data are 138.2 and 140.1 ppm (Table 1). Therefore, the spectroscopic data are consistent with their solid-state structures. Also, the molecular ion peaks in the mass spectra and the elemental analysis data further verify their structures.

We have previously reported this type of the 16*e* species, for example, **II** and **IV** in Scheme 1.[6,11] However, they were obtained from conversions of corresponding precursors, for example, **I**→**II** and **III**→**IV** (Scheme 1) upon heating. In this paper, the reactions of **1** with alkynones provide a facile route to the selectively B-monosubstituted *ortho*-carborane in one step.

In contrast, **2** and **3** still have a coordinatively and electronically unsaturated metal center (16*e*), reactive metal−sulfur bonds, and potentially reactive BH vertice of the carborane cage, thus may still possess the potential to complete further chemical transformations. In this manuscript, we examined the reactivity of **2** with alkynes.

Table 1. ^{1}H and ^{13}C NMR Data of the B−CH=CH−C(O)R unit (R = Ph, 2-naphthyl) in **2**−**9**

	^{1}H		^{13}C	
complex	B−C*H*=CH	B−CH=C*H*	B−C=*C*	B−*C*=C
2	6.47	7.45	138.2	140.4 (br)
3	6.52	7.62	138.2	140.1 (br)
4	7.39	7.71	139.4	140.1 (br)
5	6.37	7.47	138.4	139.8 (br)
6	6.51	7.47	137.9	140.6 (br)
7	7.68	7.91	139.1	140.1 (br)
8	6.72	7.53	137.1	140.4 (br)
9	6.39	7.41	138.2	140.2 (br)

Reaction of 2 with Phenylacetylene. The reaction of **2** with excess HC≡C−Ph at ambient temperature leads to the only product **4** in a yield of 69%. Unfortunately, attempts to grow suitable single crystals for structural determination failed. However, the spectroscopic data support its structure, as proposed in Scheme 2. In the ^{1}H NMR spectrum the broader doublets at 2.03 and 2.36 ppm are assigned to the new generated alkyl group of the B−CH$_2$ unit, and the large value (16 Hz) of the geminal coupling constants $^2J(^1\text{H}, ^1\text{H})$ is typical for diastereotopic ^{1}H nuclei of the B−CH$_2$ group. The broader ^{13}C signal at 34.3 ppm also reflects that the CH$_2$ group is linked to a boron atom. Thus, the NMR data demonstrate that the second B-substitution occurs with the generation of an alkyl B−CH$_2$ unit. Another noticeable feature includes that the second phenyl group appears in one broad signal at 7.29 ppm, hence a ^{13}C/^{1}H HETCOR (HMQC) experiment has to be used to recognize the ^{13}C signals. The proton signal broadening of the phenyl ring might be caused by its fast rotation in solution at ambient temperature. Some examples with a similar structure of a B−CH$_2$ unit have been reported,[7−11] including the one generated from the reaction of **1** with HC≡C−Ph.[12] Additionally, in this system, the reaction of phenyl acetylene leads to significant effects on the ^{1}H data of the existing B−CH=CH−C(O)Ph unit from 6.47 and 7.45 ppm in **1** to 7.39 and 7.71 ppm in **4** (Table 1).

Reaction of 2 with Phenyl Ethynyl Ketone. The reaction of **2** with excess HC≡C−C(O)Ph at ambient temperature leads to **5** as the sole product in a yield of 63%. Its solid-state structure (Figure 3) reveals that **5** is still a 16*e* half-sandwich complex containing a B(3,6)-disubstituted *ortho*-carborane-1,2-dithiolate ligand, and the olefinic substituents in B(3,6) positions take *E*/*E* configurations.

The NMR data show that only one type of B−CH=CH unit is present as only two doublets at 6.37 and 7.47 ppm appear in the ^{1}H NMR spectrum. The coupling constant (J = 18 Hz) corresponds to an *E* configuration. Correspondingly, in the ^{13}C NMR spectrum one sharp ^{13}C signal at 138.4 ppm and one broader resonance at 139.8 ppm are assigned to the B−CH=CH unit, as confirmed by ^{13}C/^{1}H HETCOR (HMQC) experiment. The chemical shifts in **5** are similar to those in **2** (Table 1). However, its molecular ion peak in the mass spectrum and the elemental analysis data can further verify B(3,6)-disubstitution at carborane.

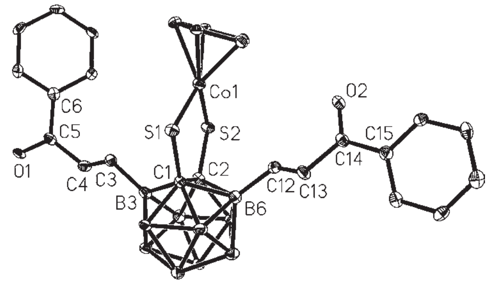

Figure 3. Molecular structure of **5**. Selected bond lengths (Å) and angles (°): Co1−S1, 2.1443(10); Co1−S2, 2.1387(10); C1−C2, 1.639(5); C1−S1, 1.776(3); C2−S2, 1.788(4); C3−C4, 1.312(5); B3−C3, 1.553(5); B6−C12, 1.550(6); C12−C13, 1.306(5); S2−Co1−S1, 96.90(4); C1−S1−Co1, 104.98(12); and C2−S2−Co1, 104.95(11).

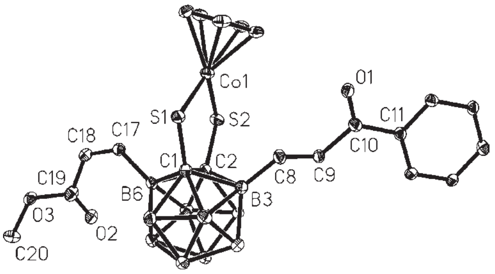

Figure 4. Molecular structure of **6**. Selected bond lengths (Å) and angles (°): Co1−S1, 2.1373(9); Co1−S2, 2.1309(9); C1−S1, 1.777(3); C2−S2, 1.779(3); C1−C2, 1.626(4); B6−C17, 1.552(3); B3−C8, 1.523(5); C8−C9, 1.328(4); C17−C18, 1.332(4); S2−Co1−S1, 97.00(3); C1−S1−Co1, 104.69(9); and C2−S2−Co1 105.03(9).

Complex **5** can be also obtained from the reaction of **1** with excess HC≡C−C(O)Ph at ambient temperature. We have previously reported similar structures with two equal substituents at B(3) and B(6) sites of *ortho*-carborane in the Co, Rh, and Ir systems by use of activated alkynes.[5,6,11]

Reaction of 2 with Methyl Acetylene Monocarboxylate. As shown in Scheme 2, the reaction of **2** with excess HC≡C−CO_2Me at ambient temperature leads to **6** in a yield of 66%. Its solid-state structure shows a 16*e* complex, similar to **5**, but contains two different olefinic substituents in the B(3) and B(6) positions of *ortho*-carborane in *E* and *Z* configurations, respectively (Figure 4).

The ^{1}H NMR spectrum displays two pairs of two doublets. One pair at 5.18 and 6.31 ppm is assigned to the B−CH═CH−CO_2Me unit with a coupling constant of J = 15 Hz, corresponding to a *Z* configuration. The other at 6.51 and 7.47 ppm is assigned to the B−CH═CH−C(O)Ph unit with a coupling constant of J = 18 Hz, corresponding to an *E* configuration. A ^{13}C/^{1}H heteronuclear correlation (HMQC) experiment was used to allow a complete assignment of the ^{13}C signals. As a result, the ^{13}C signals at 134.4 and 134.8 (br. C−B) ppm and 137.9 and 140.6 (br. C−B) ppm are, respectively, assigned to the olefinic carbon atoms of the B−CH═CH−CO_2Me and B−CH═CH−C(O)Ph groups. The NMR data are parallel to those in **5** and in the B-disubstituted complex $CpCo(S_2C_2B_{10}H_8)(CH{=}CH{-}CO_2Me)_2$.[10] Clearly, the NMR data are in agreement with its solid-state structure. The stepwise reaction provides an efficient route in generation of B-disubstitution at carborane with differing functional groups. In contrast to **5**, **6** may be predicted as a more efficient catalyst in alkyne cyclotrimerization with higher regioselectivity owing to different coordination environments around the metal center that is generated by two different substituents at carborane.

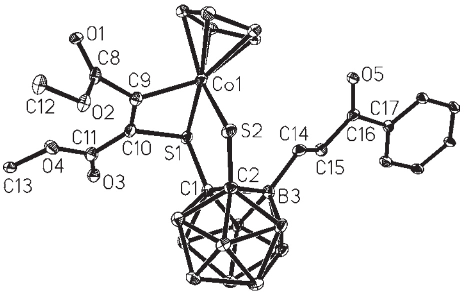

Figure 5. Molecular structure of **7**. Selected bond lengths (Å) and angles (°): Co1−S1, 2.2722(10); Co1−S2, 2.2551(10); C1−C2, 1.651(4); C1−S1, 1.810(3); C2−S2, 1.774(3); B3−C14, 1.558(5); C9−C10, 1.297(4); C9−Co1, 1.904(3); C10−S1, 1.802(3); C14−C15, 1.318(4); C1−S1−Co1, 104.91(11); C2−S2−Co1, 105.07(11); S2−Co1−S1, 94.14(3); C10−S1−Co1, 77.98(11); C10−S1−C1, 102.44(13); C9−Co1−S1, 71.58(10); C9−Co1−S2, 93.98(9); C10−C9−Co1, 106.5(2); and C9−C10−S1, 103.9(2).

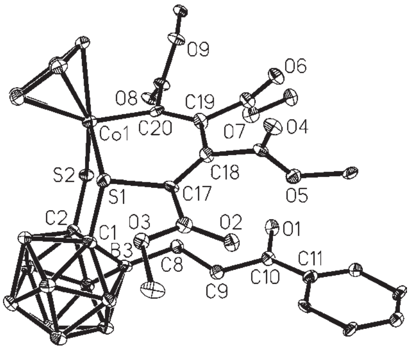

Figure 6. Molecular structure of **8**. Selected bond lengths (Å) and angles (°): Co1−S1, 2.1821(10); Co1−S2, 2.2589(10); C1−C2, 1.641(5); C1−S1, 1.864(4); C2−S2, 1.784(4); B3−C8, 1.559(5); C8−C9, 1.327(5); C17−C18, 1.369(5); C17−S1, 1.783(4); C18−C19, 1.504(4); C19−C20, 1.375(5); C20−Co1, 1.910(4); S1−Co1−S2, 93.78(4); C1−S1−Co1, 106.96(11); C2−S2−Co1, 102.77(12); C17−S1−C1, 103.89(16); C17−S1−Co1, 113.93(11); C17−C18−C19, 130.2(3); C20−C19−C18, 124.1(3); and C19−C20−Co1 130.4(3).

Reaction of 2 with Dimethyl Acetylene Dicarboxylate. The reaction of **2** with excess $MeO_2C{-}C{\equiv}C{-}CO_2Me$ at ambient temperature leads to **7** and **8** in the yields of 62% and 32%, respectively (Scheme 2). Their solid-state structures are shown in Figures 5 and 6, respectively. In each case, the olefinic substituent in the B(3) position of carborane retains an *E* configuration, as observed in **2**. But interestingly in **7**, one alkyne is inserted into one of the Co−S bonds to generate a four-membered ring CoCCS which is on the opposite side with the B−CH═CH−C(O)Ph unit. Whereas in **8**, two alkynes are inserted into one Co−S bond to form a six-membered ring CoCCCCS which is on the same side, in contrast, to the B−CH═CH−C(O)Ph unit.

The NMR data support their solid-state structures. The ^{1}H NMR spectra show characteristic doublets at 7.68 and 7.91 ppm in **7** and 6.72 and 7.53 ppm in **8** for the individual B−CH═CH unit with a coupling constant of J = 18 Hz, corresponding to the *E* configuration for both. Compared to **2**, considerable changes in the ^{1}H values are

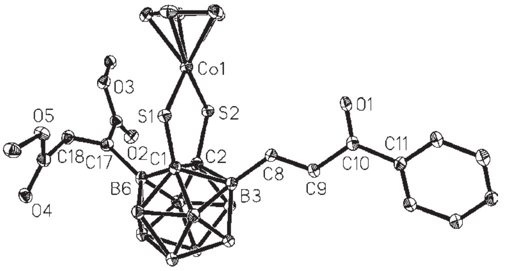

Figure 7. Molecular structure of **9**. Selected bond lengths (Å) and angles (°): Co1−S1, 2.1261(8); Co1−S2, 2.1405(8); S1−C1, 1.776(3); S2−C2, 1.786(3); C1−C2, 1.656(4); C8−B3, 1.552(4); C8−C9, 1.335(4); C17−B6, 1.586(4); C17−C18, 1.302(4); S1−Co1−S2, 96.80(3); C1−S1−Co1, 105.70(10); and C2−S2−Co1 106.37(10).

observed, especially for **7** (Table 1). However, in the ^{13}C NMR spectra the two olefinic carbon data of the B−CH=CH units both in **7** and **8** are close to those in **2**. The ^{13}C values of the carbon atoms linked to cobalt are shifted to a lower field, for example, at 189.4 ppm in **7** and 187.1 ppm in **8**, owing to the metal effect on the ^{13}C nuclear shielding. This parallels to the cases of previously reported Co, Rh, Ir, Ru, and Os analogues.[7−12]

Note that addition of one or two alkynes to a M−E bond of the 16*e* species $Cp^{\#}M(E_2C_2B_{10}H_{10})$ ($Cp^{\#}$ = Cp, Cp*; M = Co, Rh, Ir; and E = S, Se) and (*p*-cymene)-$M(S_2C_2B_{10}H_{10})$ (M = Ru, Os) to generate a four- or six-membered ring has been extensively described.[7−12] However, **7** is the first isolated example bearing both a four-membered ring and a B−CH=CH−C(O)R group at carborane. And **8** is the second example (the first is **XIII** in Scheme 1) for such a structural type. Both are the key intermediates to the metal-mediated B-disubstitution at carborane and alkyne cyclotrimerization, respectively. So far, this is the first reaction to produce both one- and two-alkyne inserted complexes.

Transformation of 7 at a Higher Temperature. In Scheme 1 the one-alkyne inserted species **I** (E = S) could convert to the B-monosubstituted species **II**.[11] This provides direct evidence that the alkyne inserted species is the early stage intermediate to metal-induced B−H activation and selective B-functionalization at carborane.[5−12] As the coordinative S→Co bond distance of 2.272 Å in **7** is longer than that of 2.246 Å in **I** (E = S), **7** might further convert as well. Indeed, **7** could cleanly convert to its geometrical isomer **9** upon heating at 70 °C (Scheme 2). Its solid-state structure is shown in Figure 7.

Similar to **5** and **6**, **9** is also a 16*e* half-sandwich complex containing a B(3,6)-disubstituted *ortho*-carborane-1,2-dithiolate ligand where both the olefinic substituents in the B(3) and B(6) positions take *E* configurations. The ^{1}H NMR spectrum shows a singlet at 6.79 ppm for the vinyl proton and two singlets at 3.80 and 3.86 ppm for the OMe groups of the new generated $B-C(CO_2Me)=CH-CO_2Me$ unit. The olefinic ^{13}C signal at 141.1 ppm for the =*C*H unit of the $B-C(CO_2Me)=CH-CO_2Me$ group is identified by ^{13}C/^{1}H heteronuclear correlation. The ^{1}H and ^{13}C data of the existing B−CH=CH−C(O)Ph unit are similar to those in **2**, parallel to the analogues of **5** and **6** as well.

Alternatively, **9** could be generated from the reaction of the 16*e* complex **II** (Scheme 1) with HC≡C−C(O)Ph at ambient temperature. Therefore, a 16*e* complex with B-monosubstitution at carborane could continue to react with alkynes to generate 16*e* B-disubstituted species, such as **5**, **6**, and **9**, depending on the alkyne used. And the different functional groups at carborane may induce stereoselectivity of substrates to improve regioselectivity of the products in alkyne cyclotrimerization mediated by such species.

Conclusion

Through control of the ratio of the starting 16*e* complex $CpCo(S_2C_2B_{10}H_{10})$ (**1**) and alkynone HC≡C−C(O)R (R = Ph, 2-naphthyl), the 16*e* half-sandwich complexes **2** and **3** possessing a B-monosubstituted *ortho*-carborane-1,2-dithiolate ligand have been synthesized at ambient temperature. Since these molecules still have a coordinatively and electronically unsaturated metal center, reactive metal−sulfur bonds as well as potentially reactive B−H bonds of the carborane cage, they have shown further reactivity toward alkynes to generate three types of products at ambient temperature, depending on the alkyne used. The first type is the alkyne insertion product including one or two alkynes inserted 18*e* species when dimethyl acetylene dicarboxylate is applied; the second type is the 18*e* product with a second B−H functionalized group of a $B-CH_2$ unit when a nonactivated terminal alkyne, phenylacetylene, is used; and the third is the 16*e* half-sandwich complex with B(3,6)-disubstitution at *ortho*-carborane if an activated terminal alkyne is used, for instance, phenyl ethynyl ketone and methyl acetylene monocarboxylate. Through this investigation different products could be obtained by choosing alkyne type. The most important point is that this study provides a facile and straightforward way for the stepwise and selective B−H functionalization at the carborane cage.

Experimental Section

General Procedures. The preparative work was carried out under an argon atmosphere using standard Schlenk techniques. Solvents were freshly distilled under nitrogen from either sodium or calcium hydride prior to use. Aromatic alkynones HC≡C−C(O)R[19] (R = Ph, 2-naphthyl) and $CpCoS_2C_2B_{10}H_{10}$ (**1**)[20,4a] were prepared according to the literature methods. *n*-Butyllithium (2.0 M in cyclohexane, Aldrich), phenylacetylene (Alfa Aesar), methyl acetylene monocarboxylate (Alfa Aesar), and dimethyl acetylene dicarboxylate (Aldrich) were used as commercial products without further purification.

Elemental analysis was performed in an elementar vario EL III elemental analyzer. NMR data were obtained on a Bruker DRX-500 spectrometer. Chemical shifts were given with respect to $CHCl_3/CDCl_3$ (δ ^{1}H = 7.24, δ ^{13}C = 77.0) and external Et_2O-BF_3 (δ ^{11}B = 0). The IR spectra were recorded on a Bruker Vector 22 spectrophotometer with KBr pellets in the 4000−400 cm^{-1} region. The mass spectra were recorded on either a Micromass GC-TOF for EI-MS (70 ev). Finnigan MAT TSQ7000 was used for ESI-MS. X-ray crystallographic data[21] were collected on a Bruker SMART Apex II CCD diffractometer using graphite-monochromated Mo Kα (λ = 0.71073 Å) radiation. The intensities were corrected for Lorentz polarization effects and empirical absorption with the SADABS program. The structures were solved by direct methods using the SHELXL-97 program. Details regarding data

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(19) (a) Mortier, J.; Vaultier, M.; Carreaux, F.; Douin, J. M. *J. Org. Chem.* **1998**, *63*, 3515–3516. (b) Caliendo, G.; Fiorino, F.; Perissutti, E.; Severino, B.; Scolaro, D.; Gessi, S.; Cattabriga, E.; Borea, P. A.; Santagada, V. *Eur. J. Pharm. Sci.* **2002**, *16*, 15–28.

(20) King, R. B. *Inorg. Chem.* **1966**, *5*, 82–87.

(21) *Bruker*; *SMART*, version 5.0; *SAINT*, version 6; *SHELXTL*, version 6.1; *SADABS*, version 2.03; Bruker AXS Inc.: Madison, WI, **2000**.

Table 2. Crystallographic Data and Structural Refinement Details of **2**, **3**, **5**, and **6**

	2	**3**	**5**	**6**
chemical formula	$C_{16}H_{21}B_{10}CoOS_2$	$C_{20}H_{23}B_{10}CoOS_2$	$C_{25}H_{27}B_{10}CoO_2S_2$	$C_{40}H_{52}B_{20}Co_2O_7S_4$
crystal size (mm)	0.30 × 0.26 × 0.24	0.40 × 0.36 × 0.28	0.30 × 0.26 × 0.22	0.30 × 0.25 × 0.24
formula weight	460.48	510.53	590.62	1107.12
temperature (K)	291(2)	293(2)	291(2)	291(2)
radiation	Mo Kα (0.71073 Å)	Mo Kα (0.71073 Å)	Mo Kα (0.71073 Å)	Mo Kα (0.71073 Å)
crystal system	monoclinic	triclinic	orthorhombic	monoclinic
space group	*P*2(1)/*c*	*P*-1	*P*2(1)2(1)2(1)	*P*2(1)/*c*
a (Å)	11.0395(11)	7.071(3)	7.9575(8)	9.2832(9)
b (Å)	11.9960(12)	11.578(3)	15.6813(14)	22.806(2)
c (Å)	16.9848(17)	14.990(5)	22.837(2)	24.997(3)
α (°)	90.00	83.297(4)	90.00	90.00
β (°)	99.827(2)	78.928(4)	90.00	95.409(2)
γ (°)	90.00	86.111(2)	90.00	90.00
V (Å^3)	2216.3(4)	1194.8(6)	2849.7(5)	5268.7(9)
Z	4	2	4	4
ρ_{calc} (g·cm^{-3})	1.380	1.419	1.377	1.396
absorp. coeff. (mm^{-1})	0.969	0.907	0.773	0.835
F(000)	936	520	1208	2264
θ range (°)	2.09−26.00	1.77−26.00	1.78−26.00	1.64−26.00
reflns collected	11 924 (R_{int} = 0.0442)	6549 (R_{int} = 0.0571)	15 685 (R_{int} = 0.0433)	28 460 (R_{int} = 0.0465)
indep. reflns	4346	4617	5599	10 295
refns obs. [$I > 2\sigma(I)$]	2840	3288	4294	7482
data /restr./paras	4346/0/271	4617/0/307	5599/0/361	10 295/0/660
GOF	1.044	1.029	0.992	1.029
$R_1/wR_2I > 2\sigma(I)$]	0.0405/0.0841	0.0422/0.0924	0.0420/0.0865	0.0542/0.1186
R_1/wR_2 (all data)	0.0725/0.0936	0.0603/0.0969	0.0585/0.0934	0.0748/0.1232
larg. peak/hole (e·Å^{-3})	0.446/−0.372	0.339/−0.302	0.245/−0.264	0.328/−0.951

Table 3. Crystallographic Data and Structural Refinement Details of **7**−**9**

	7	**8**	**9**
chemical formula	$C_{22}H_{27}B_{10}CoO_5S_2$	$C_{29}H_{35}B_{10}Cl_2CoO_9S_2$	$C_{22}H_{27}B_{10}CoO_5S_2$
crystal size (mm)	0.28 × 0.24 × 0.22	0.28 × 0.24 × 0.23	0.26 × 0.22 × 0.20
formula weight	602.59	829.62	602.59
temperature (K)	291(2)	291(2)	291(2)
radiation	Mo Kα (0.71073 Å)	Mo Kα (0.71073 Å)	Mo Kα (0.71073 Å)
crystal system	monoclinic	triclinic	monoclinic
space group	*P*2(1)/*n*	*P*-1	*P*2(1)/*c*
a (Å)	16.357(3)	8.1563(11)	10.927(2)
b (Å)	8.5356(17)	13.1739(18)	14.171(3)
c (Å)	21.208(4)	18.120(3)	19.382(4)
α (°)	90.00	86.919(3)	90.00
β (°)	106.691(3)	85.606(2)	102.610(3)
γ (°)	90.00	85.532(2)	90.00
V (Å^3)	2836.2(9)	1933.1(5)	2928.9(10)
Z	4	2	4
ρ_{calc} (g·cm^{-3})	1.411	1.425	1.367
absorp. coeff. (mm^{-1})	0.786	0.739	0.761
F(000)	1232	848	1232
θ range (°)	1.86−26.00	1.96−26.00	1.80−26.00
reflns collected	15 060 (R_{int} = 0.0443)	10 734 (R_{int} = 0.0335)	15 587 (R_{int} = 0.0383)
indep. reflns	5564	7460	5680
refns obs. [$I > 2\sigma(I)$]	3977	4873	4839
data /restr./paras	5564/0/363	7460/0/482	5680/0/363
GOF	0.978	1.014	1.023
$R_1/wR_2I > 2\sigma(I)$]	0.0452/0.1073	0.0532/0.1010	0.0474/0.1194
R_1/wR_2 (all data)	0.0726/0.1183	0.0932/0.1092	0.0568/0.1234
larg. peak/hole (e·Å^{-3})	0.310/−0.370	0.592/−0.316	0.268/−0.603

collection of complexes (**2** and **3** and **5**−**9**) are provided in the Supporting Information (CIF files CCDC 738001, 738000, and 738002−738006) and Tables 2 and 3. Thermal ellipsoids are shown at the 30% probability level and all hydrogen atoms are omitted for clarity in ORTEP drawings of **2**, **3**, and **5**−**9**.

Synthesis of 2 and 3. HC≡C−C(O)R (R = Ph (26.0 mg, 0.2 mmol) or 2-naphthyl (36.0 mg, 0.2 mmol)) was added to the red solution of complex **1** (660 mg, 2 mmol) in CH_2Cl_2 (20 mL), and the resultant mixture was stirred for 12 h at ambient temperature. After removal of solvent, the residue was chromatographed on silica gel. Elution with petroleum ether/CH_2Cl_2 (2:3) gave **2** (35.0 mg, 38%) or **3** (35.7 mg, 35%).

2: orange solid, mp 190 °C dec ^{1}H NMR ($CDCl_3$): *δ* 5.38 (s, 5H, Cp), 6.47 (d, *J* = 18 Hz, 1H, B−C*H*=CH), 7.45 (d, *J* = 18 Hz, 1H, B−CH=C*H*), 7.54 (t, 2H, Ph), 7.62 (t, 1H, Ph), 8.04 (d, 2H, Ph). ^{11}B NMR ($CDCl_3$): *δ* −4.1 (1B), −4.4 (2B), −4.7 (2B), −6.6 (3B), −7.7 (2B). ^{13}C NMR ($CDCl_3$): *δ* 81.5 (Cp), 97.0 (carborane), 128.7, 128.8, 133.2, 137.3 (Ph), 138.2 (B−CH=*C*H), 140.4 (br, B−*C*H=CH), 190.1 (C=O). EI-MS (70 eV): *m*/*z* 460 (M^+, 15%). IR (KBr): *ν* (cm^{-1}) 1638 (C=O), 2579 (B−H). Anal. calcd for $C_{16}H_{21}B_{10}CoOS_2$: C, 41.73; H, 4.60. Found: C, 41.27; H, 4.49%.

3: orange solid, mp 203 °C dec ^{1}H NMR ($CDCl_3$): *δ* 5.37 (s, 5H, Cp), 6.52 (d, *J* = 18 Hz, 1H, B−C*H*=CH), 7.62 (d, *J* = 18 Hz, 1H, B−CH=C*H*), 7.61−7.66 (2H), 7.91−7.97 (2H), 8.06−8.10 (3H), 8.58 (s, 1H) (2-naphthyl). ^{11}B NMR ($CDCl_3$): δ −6.3 (1B), −6.7 (2B), −6.9 (2B), −8.7 (3B), −9.8 (2B). ^{13}C NMR ($CDCl_3$): δ 81.6 (Cp), 97.0 (carborane), 124.4, 127.0, 127.9, 128.7, 128.8, 129.7, 130.7, 130.9, 132.5, 135.6 (2-naphthyl), 138.2 (B−CH=*C*H), 140.1 (br, B−*C*H=CH), 190.1 (C=O). EI-MS (70 eV): *m*/*z* 510 (M^+, 3%). IR (KBr): ν (cm^{-1}) 1648 (C=O), 2577 (B−H). Anal. calcd for $C_{20}H_{23}B_{10}CoOS_2$: C, 47.05; H, 4.54. Found: C, 46.44; H, 4.71%.

Synthesis of 4−8. General procedure: Alkyne (2 mmol) was added to the red solution of complex **2** (92.1 mg, 0.2 mmol) in CH_2Cl_2 (20 mL), and the resultant mixture was stirred for 12 h at ambient temperature. After removal of solvent, the residue was chromatographed on silica gel. Elution with petroleum ether/CH_2Cl_2 gave the corresponding product.

4: Purple solid, yield 77.6 mg (69%). ^{1}H NMR ($CDCl_3$): δ 2.03 (d, *J* = 16.0 Hz, 1H, B−C*H*$_2$), 2.36 (d, *J* = 16.0 Hz, 1H, B−C*H*$_2$), 4.49 (s, 5H, Cp), 7.29 (br s, 5H, Ph), 7.39 (d, *J* = 18.0 Hz, 1H, B−C*H*=CH), 7.71 (d, *J* = 18.0 Hz, 1H, B−CH=C*H*), 7.58 (t, 2H, Ph), 7.66 (t, 1H, Ph), 8.12 (d, 2H, Ph). ^{11}B{^{1}H} NMR ($CDCl_3$): δ −2.5 (1B), −8.9 (1B), −12.0 (2B), −13.9 (5B), −18.5 (1B). ^{13}C NMR($CDCl_3$): δ 34.3 (br, B−*C*H$_2$), 85.3 (Co−*C*−Ph), 86.6 (Cp), 96.6, 99.5 (carborane), 124.5 (br), 126.3, 129.1, 152.8 (Co−C−*Ph*), 128.8, 128.9, 133.2, 137.4 (*Ph*−C(O)), 139.4 (B−CH=*C*H), 140.1 (br, B−*C*H=CH), 190.2 (C=O). EI-MS (70 eV): *m*/*z* 562 (M^+, 2%). IR (KBr): ν (cm^{-1}) 1638 (C=O), 2584 (B−H). Anal. calcd for $C_{24}H_{27}B_{10}CoOS_2$: C, 51.23; H, 4.84. Found: C, 50.61; H, 4.89%.

5: Red solid, yield 74.4 mg (63%), mp 192 °C dec ^{1}HNMR ($CDCl_3$): δ 5.42 (s, 5H, Cp), 6.37 (d, *J* = 18.0 Hz, 2H, B−C*H*=CH), 7.47 (d, *J* = 18.0 Hz, 2H, B−CH=C*H*), 7.54 (t, 4H, Ph), 7.63 (t, 2H, Ph), 8.04 (d, 4H, Ph). ^{11}B{^{1}H} NMR ($CDCl_3$): δ −11.8 (5B), −14.0 (2B), −14.9 (3B). ^{13}CNMR ($CDCl_3$): δ 81.4 (Cp), 98.4 (carborane), 128.7, 128.8, 133.2, 137.7 (Ph), 138.4 (B−CH= *C*H), 139.8 (br, B−*C* H=CH), 190.0 (C=O). EI-MS (70 eV): *m*/*z* 590 (M^+, 4%). IR (KBr): ν (cm^{-1}) 1617, 1639 (C=O), 2589 (B−H). Anal. calcd for $C_{25}H_{27}B_{10}CoO_2S_2$: C, 50.84; H, 4.61. Found: C, 51.23; H, 4.87%.

6: Red solid, yield 71.8 mg (66%), mp 191 °C dec ^{1}H NMR ($CDCl_3$): δ 3.77 (s, 3H, OC*H*$_3$), 5.18 (d, *J* = 15.0 Hz, 1H, B−C*H*=CH), 5.44 (s, 5H, Cp), 6.31 (d, *J* = 15.0 Hz, 1H, B−CH=C*H*), 6.51 (d, *J* = 18.0 Hz, 1H, B−C*H*=CH), 7.47 (d, *J* = 18.0 Hz, 1H, B−CH=C*H*), 7.54 (t, 2H, Ph), 7.63 (t, 1H, Ph), 8.05 (d, 2H, Ph). ^{11}B{^{1}H} NMR ($CDCl_3$): δ −6.5 (4B), −7.3 (3B), −9.9 (3B). ^{13}C NMR ($CDCl_3$): δ 51.1 (O*C*H$_3$), 81.5 (Cp), 97.9 (carborane), 128.8, 133.3, 137.3 (Ph), 134.4 (B-CH=*C*HCO$_2$Me), 134.8 (br, B−*C* H=CHCO$_2$Me), 137.9 (B−CH=*C*HC(O)Ph), 140.6 (br, B−*C*H=CHC(O)Ph), 166.8, 190.1 (C=O). EI-MS (70 eV): *m*/*z* 544 (M^+, 1%). IR (KBr): ν (cm^{-1}) 1629, 1645 (C=O), 2579 (B−H). Anal. calcd for **6**·0.5H_2O, $C_{20}H_{26}B_{10}CoO_{3.5}S_2$: C, 43.39; H, 4.73. Found: C, 43.01; H, 4.52%.

7: Purple solid, yield 61.5 mg (51%), mp 189 °C dec ^{1}H NMR ($CDCl_3$): δ 3.81 (s, 3H, OC*H*$_3$), 4.00 (s, 3H, OC*H*$_3$), 5.34 (s, 5H, Cp), 7.68 (d, *J* = 18.0 Hz, 1H, B−C*H*=CH), 7.91 (d, *J* = 18.0 Hz, 1H, B−CH=C*H*), 7.59 (t, 2H, Ph), 7.68 (t, 1H, Ph), 8.16 (d, 2H, Ph). ^{11}B{^{1}H} NMR ($CDCl_3$): δ −0.9 (2B), −2.6 (2B), −3.9 (1B), −5.4 (3B), −7.1 (2B). ^{13}C NMR($CDCl_3$): δ 52.7, 52.9 (O*C*H$_3$), 81.9, 99.5 (carborane), 87.3 (Cp), 119.6 (S−*C*=C), 128.9, 129.0, 133.7, 137.1 (Ph), 139.1 (B−CH=*C*H), 140.1 (br, B−*C*H=CH), 154.9, 171.1, 178.2 (C=O), 189.4 (Co− *C*=C). EI-MS (70 eV): *m*/*z* 602 (M^+, 10%). IR (KBr): ν (cm^{-1}) 1650, 1709, 1717 (C=O), 2587 (B−H). Anal. calcd for $C_{22}H_{27}B_{10}CoO_5S_2$: C, 43.85; H, 4.52. Found: C, 43.21; H, 4.33%.

8: Red solid, yield 47.7 mg (32%), mp 195 °C dec ^{1}H NMR ($CDCl_3$): δ 3.24 (s, 3H, OC*H*$_3$), 3.61 (s, 3H, OC*H*$_3$), 3.80 (s, 3H, OC*H*$_3$), 3.94 (s, 3H, OC*H*$_3$), 5.35 (s, 5H, Cp), 6.72 (d, *J* = 18.0 Hz, 1H, B−C*H*=CH), 7.53 (d, *J* = 18.0 Hz, 1H, B−CH=C*H*), 7.48 (t, 2H, Ph), 7.55 (t, 1H, Ph), 8.00 (d, 2H, Ph). ^{11}B{^{1}H} NMR ($CDCl_3$): δ 4.8 (1B), 2.2 (1B), −0.9 (1B), −4.7 (2B), −7.1 (4B), −10.3 (1B). ^{13}C NMR($CDCl_3$): δ 52.2, 52.4, 52.8, 53.6 (O*C*H$_3$), 91.5, 98.6 (carborane), 91.9 (Cp), 102.3 (S−*C*=C), 128.4, 128.8, 132.4, 138.1 (Ph), 131.7 (S−C=*C*), 137.1 (B−CH=*C*H), 140.4 (br, B−*C*H=CH), 154.0 (Co−C=*C*), 162.7, 163.4, 166.2, 175.8, 177.1 (C=O), 187.1 (Co−*C*=C). ESI-MS (positive ion mode, *m*/*z*): 768.3, $[M + Na]^+$. IR (KBr): ν (cm^{-1}) 1665, 1720 (s), 1725, 1746 (C=O), 2591 (B−H). Anal. calcd for **8**·CH_2Cl_2, $C_{29}H_{35}B_{10}Cl_2CoO_9S_2$: C, 41.98; H, 4.25. Found: C, 41.52; H, 4.36.

Synthesis of 9. A red solution of **7** (120.5 mg, 0.2 mmol) in toluene was heated to 70 °C for 12 h. After removal of solvent, the residue was chromatographed on silica gel. Elution with petroleum ether/CH_2Cl_2 (1:50) gave **9** (92.8 mg, 77%). Red solid, mp 178 °C dec ^{1}H NMR ($CDCl_3$): δ 3.80 (s, 3H, OC*H*$_3$), 3.86 (s, 3H, OC*H*$_3$), 5.43 (s, 5H, Cp), 6.39 (d, *J* = 18.0 Hz, 1H, B−C*H*=CH), 6.79 (s, 1H, B−C=C*H*), 7.41 (d, *J* = 18.0 Hz, 1H, B−CH=C*H*), 7.53 (t, 2H, Ph), 7.62 (t, 1H, Ph), 8.03 (d, 2H, Ph). ^{11}B{^{1}H} NMR ($CDCl_3$): δ −4.3 (2B), −5.7 (5B), −7.2 (3B). ^{13}C NMR($CDCl_3$): δ 51.8, 52.3 (O*C*H$_3$), 81.5 (Cp), 98.7 (carborane), 128.7, 128.8, 133.2, 137.3 (Ph), 138.2 (B−CH=*C*H), 140.2 (br, B− *C* H=CH), 141.1 (B−C= *C*H), 166.9, 170.9, 190.1 (C=O). EI-MS (70 eV): *m*/*z* 602 (M^+, 7%). IR (KBr): ν (cm^{-1}) 1659, 1728 (C=O), 2575 (B−H). Anal. calcd for $C_{22}H_{27}B_{10}CoO_5S_2$: C, 43.85; H, 4.52. Found: C, 43.37; H, 4.24%.

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Supporting Information Available: CIF files giving X-ray crystallographic data for the structure determinations of compounds **2**, **3**, and **5**−**9**. This material is available free of charge via the Internet at http://pubs.acs.org.