

Reactivity of CpCo 16e Half-Sandwich Complexes Containing a Chelating 1,2-Dicarba-*closo*-dodecaborane-1,2-dichalcogenolate Ligand toward Phenylacetylene

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The reaction of the 16e half-sandwich complex CpCo[S₂C₂B₁₀H₁₀] (**1S**) with phenylacetylene at ambient temperature led to **2S**, **3S**, and **4S**. In **3S** the alkyne is twofold inserted into one of the Co–S bonds. In **4S** B-substitution occurs at the *ortho*-carborane cage in the position B(3)/B(6) with the formation of a C–B bond. Upon heating, **3S** catalyzed the cyclotrimerization of alkyne to give rise to 1,3,5- and 1,2,4-triphenylbenzenes. In comparison, CpCo[Se₂C₂B₁₀H₁₀] (**1Se**) did not react with the alkyne at ambient temperature. However, if heated to 80 °C, **2Se** and **4Se** (an analogue to **4S**) were generated. Mechanistic implications on metal-induced B–H bond activation and catalytic cyclotrimerization of alkynes were elucidated. The solid-state structures of **2Se**, **3S**, and **4S** have been determined by X-ray crystallography.

Introduction

The transition metal complexes containing chelating 1,2-dicarba-*closo*-dodecaborane-1,2-dichalcogenolate ligands, [E₂C₂B₁₀H₁₀]^{2–} (E = S, Se) have been extensively investigated, and in some cases their reaction chemistries with metal fragments and organic substrates have been reported.^{1–9} Recently, a novel carboranyl-thiol-appended cyclopentadiene ligand, 1-SH-2-[HCpCH(Ph)]-*closo*-1,2-C₂B₁₀H₁₀, was prepared, and its reaction with Ti(NMe₂)₄ generated the corresponding titanium complex [1-(*σ*-S)-2-(*η*⁵-C₅H₄CH(Ph))-1,2-C₂B₁₀H₁₀]-Ti(NMe₂)₂.¹⁰ A type of 16e half-sandwich complexes Cp*M-[E₂C₂B₁₀H₁₀] (M = Co, Rh, Ir; E = S, Se), for instance, could serve as promising precursors for synthesis of mixed-metal

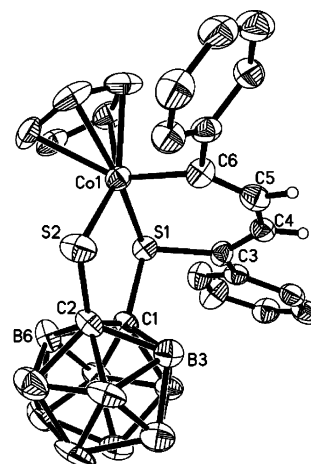


Figure 1. Molecular structure of **3S**. Ellipsoids are shown at the 30% probability level, and hydrogen atoms have been omitted for clarity. Selected bond lengths [Å] and angles [deg]: Co(1)–ring centroid 1.705, Co(1)–S(1) 2.187(2), Co(1)–S(2) 2.271(2), Co(1)–C(6) 1.962(4), S(1)–C(1) 1.839(4), S(1)–C(3) 1.757(4), C(1)–C(2) 1.663(5), C(3)–C(4) 1.372(5), C(4)–C(5) 1.451(5), C(5)–C(6) 1.363(5), C(6)–C(7) 1.475(5), C(3)–C(13) 1.497(5), S(2)–C(2) 1.778(4), S(1)Co(1)C(6) 96.36(12), Co(1)C(6)C(5) 124.0(3), C(3)C(4)C(5) 130.8(3), C(4)C(5)C(6) 130.8(3), Co(1)S(1)C(3) 115.12(13), S(1)C(3)C(4) 117.8(3), S(1)Co(1)S(2) 95.01(6), Co(1)S(1)C(1) 107.00(12), S(1)C(1)C(2) 114.2(2), S(2)C(2)C(1) 119.1(2), Co(1)S(2)C(2) 104.46(13).

clusters, of which oligonuclear frameworks including heterometallic clusters with metal–metal bonds were built up.^{11–15} On the other hand, the study of addition and substitution reactions of such complexes with organic molecules is of great interest. The metal center, the chalcogen element, and the

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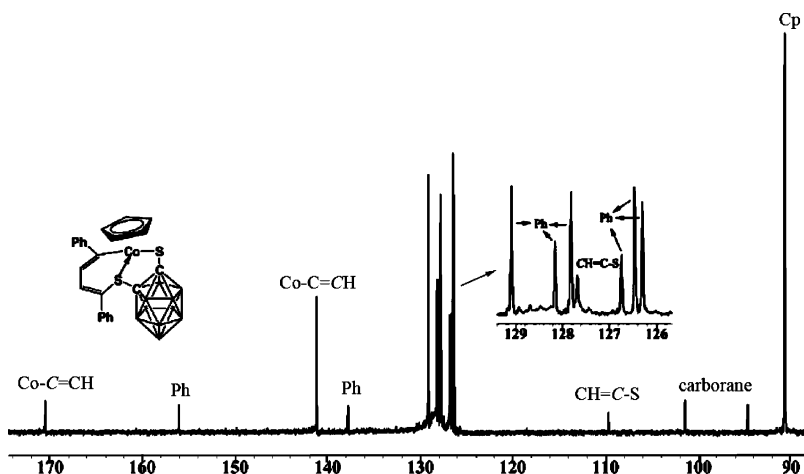


Figure 2. 125.76 MHz $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **3S** in CDCl_3 at 22 °C.

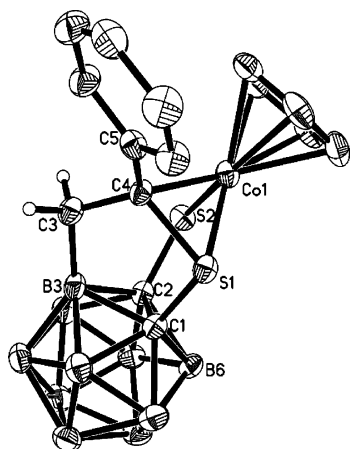


Figure 3. Molecular structure of **4S**. Ellipsoids are shown at the 30% probability level, and hydrogen atoms have been omitted for clarity. Selected bond lengths [Å] and angles [deg]: Co(1)–ring centroid 1.698, Co(1)–S(1) 2.1694(17), Co(1)–S(2) 2.2330(15), Co(1)–C(4) 2.008(5), C(4)–C(5) 1.497(7), C(3)–C(4) 1.518(7), C(1)–C(2) 1.668(8), S(1)–C(1) 1.786(5), S(2)–C(2) 1.750(5), C(3)–B(3) 1.560(8), C(1)–B(3) 1.726(8), C(2)–B(3) 1.771(8), Co(1)S(2)C(2) 103.85(18), S(1)Co(1)S(2) 95.78(5), Co(1)S(1)C(1) 106.6(2), S(2)C(2)C(1) 118.5(3), S(1)C(1)C(2) 114.4(4), C(4)C(3)B(3) 112.1(4), C(1)B(3)C(3) 108.4(4), S(1)C(1)B(3) 108.6(3), C(1)S(1)C(4) 96.6(2), S(1)C(4)C(3) 113.7(4), Co(1)C(4)C(5) 116.0(4), S(1)C(4)C(5) 114.8(4), C(3)C(4)C(5) 116.0(4).

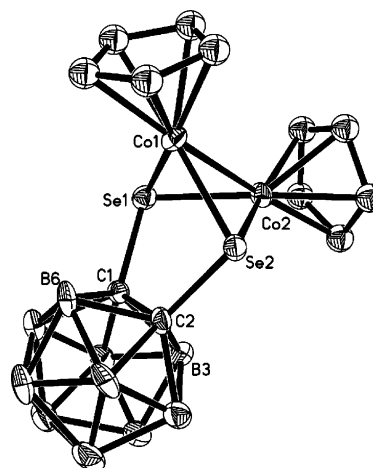


Figure 4. Molecular structure of **2Se**. Ellipsoids are shown at the 30% probability levels, and hydrogen atoms have been omitted for clarity. Selected bond lengths [Å] and angles [deg]: Co(1)–ring centroid 1.693, Co(2)–ring centroid 1.681, Co(1)–Co(2) 2.414, Se(1)–Co(1) 2.3089(12), Se(1)–Co(2) 2.3062(12), Se(1)–C(1) 1.965(5), Se(2)–Co(1) 2.3048(12), Se(2)–Co(2) 2.3090(12), Se(2)–C(2) 1.985(6), C(1)–C(2) 1.598(8), Co(1)Se(2)C(2) 100.69(16), Co(1)Se(1)C(1) 101.56(15), Co(2)Se(1)C(1) 100.38(14), Co(2)Se(2)C(2) 99.96(17), Co(1)Se(2)Co(2) 63.09(3), Co(1)Se(1)–Co(2) 63.07(3), Se(1)C(1)C(2) 113.5(3), Se(2)C(2)C(1) 113.7(3).

reaction conditions strongly influence the reactivity of the analogous unsaturated 16e complexes.^{1–7,16}

We have shown that 16e complexes $\text{Cp}^*\text{M}[\text{E}_2\text{C}_2\text{B}_{10}\text{H}_{10}]$ ($\text{M} = \text{Rh}, \text{Ir}; \text{E} = \text{S}, \text{Se}$) and (*p*-cymene) $\text{M}[\text{S}_2\text{C}_2\text{B}_{10}\text{H}_{10}]$ ($\text{M} = \text{Ru}, \text{Os}$) reacted with alkynes to generate numerous novel complexes that resulted from the insertion of alkyne into one of the M–E bonds, followed by B–H bond activation, M–B bond formation,

and further transformations.¹⁷ In the case of phenylacetylene, one type of *ortho*-metalation compound with a M–B bond was isolated at ambient temperature in a *cisoid* arrangement with respect to the relative positions of $\text{E}-\eta^2\text{-(Ph)C}\equiv\text{C}$ and C(1)–B(M) units (see **A**, Scheme 1). If heated, the *cisoid* species of different metal centers behave differently. For instance, the ruthenium and osmium species converted to a *transoid* arrangement; the rhodium species with sulfur atoms led to cleavage of a M–B bond and the formation of a C–B bond (see **B**, Scheme 1); and the Ir species retained the *cisoid* skeleton and showed no transformations.¹⁸ Surprisingly, the 16e complex $\text{Cp}^*\text{Rh}[\text{Se}_2\text{C}_2\text{B}_{10}\text{H}_{10}]$ did not react with phenylacetylene.

In our continuous and systematic studies of the roles of metal in the chemistries in these 16e series $\text{Cp}^*\text{M}[\text{E}_2\text{C}_2\text{B}_{10}\text{H}_{10}]$ (M

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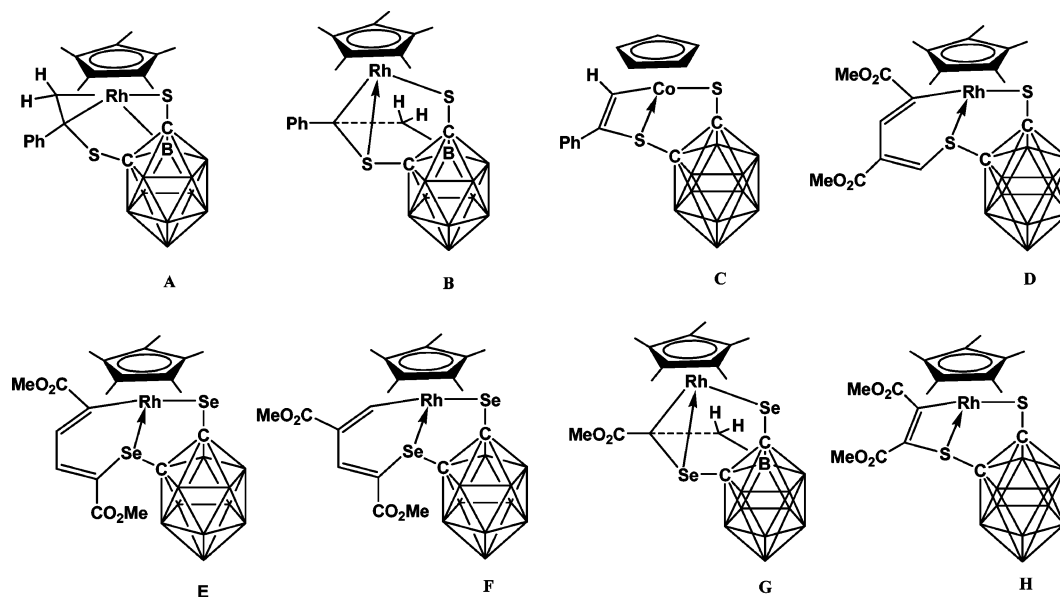
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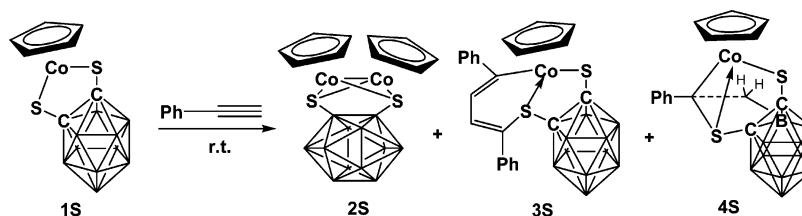
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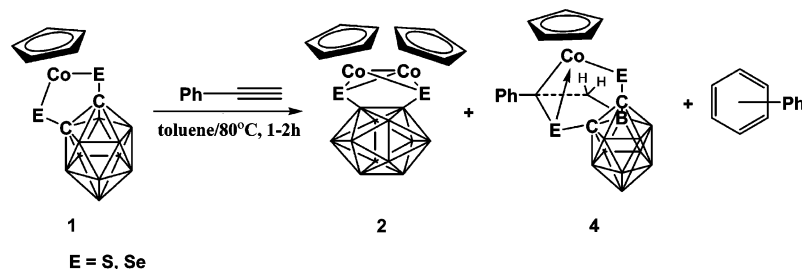
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Scheme 1. Some Examples of Structurally Characterized Complexes (A,¹⁹ B,¹⁹ C,¹ D,⁷ E,² F,² G,² H³)

Scheme 2



Scheme 3



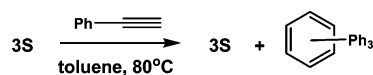
(Co , Rh , Ir ; $\text{E} = \text{S}$, Se) complexes, we now report the reactivity of $\text{CpCo}[\text{E}_2\text{C}_2\text{B}_{10}\text{H}_{10}]$ ($\text{E} = \text{S}$, Se), **1**, with $\text{HC}\equiv\text{CPh}$ in order to obtain more evidence for transition metal induced B–H bond activation, *ortho*-metalation, and B(3,6)-substitution of the carborane cluster as well as to explore the chemistries of the cobalt complex. Previously, Kang's group described one addition product, **C** (Scheme 1), from the reaction of **1S** with phenyl acetylene.^{1a} In this paper, we report the isolation of new complexes **3S**, **4S**, **2Se**, and **4Se** and the catalytic cyclotrimerization of alkyne by the 16e complexes **1S** and **1Se**. The reactivity of the 18e dicobalt complexes **2S** and **2Se** with $\text{HC}\equiv\text{CPh}$ has also been studied.

Results and Discussion

The reactions of $\text{CpCo}[\text{E}_2\text{C}_2\text{B}_{10}\text{H}_{10}]$, **1**, with phenylacetylene were explored at three different temperatures (25, 80, and 110 °C). The products were isolated by chromatography and characterized with NMR spectroscopic data and X-ray crystal structure analysis.

Reaction of $\text{CpCo}[\text{S}_2\text{C}_2\text{B}_{10}\text{H}_{10}]$ (1S**) with Phenylacetylene at 25 °C.** The reaction of **1S** with $\text{HC}\equiv\text{CPh}$ at 25 °C led to a

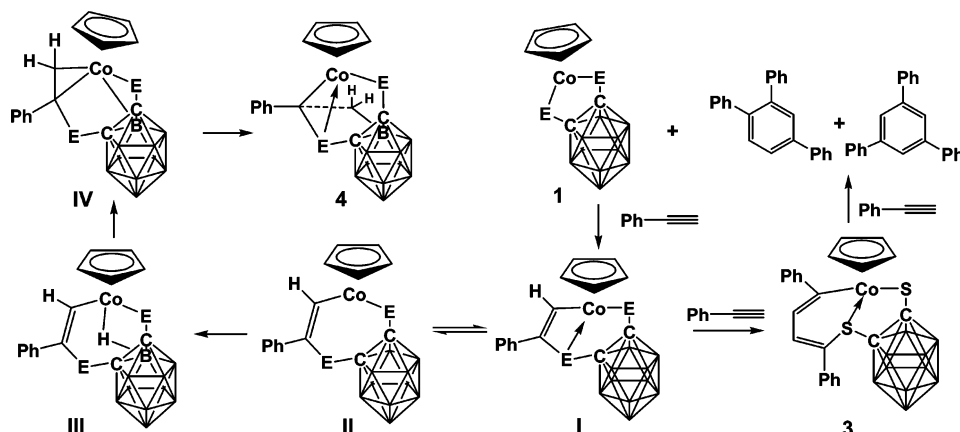
Scheme 4



mixture from which **2S**, **3S**, and **4S** were isolated. **2S** was obtained as a byproduct in a yield of 11%. Its solid-state structure has been described.¹ In the present paper its ¹¹B and ¹³C NMR data are first reported for comparison with the selenium analogue.

3S was isolated in a yield of 40%. Its X-ray structure as shown in Figure 1 shows that the alkyne is twofold inserted into one of the Co–S bonds in a head–head mode. The generated six-membered ring S(1)Co(1)C(6)C(5)C(4)C(3) is fused at one Co–S bond with the five-membered ring S(1)Co(1)S(2)C(2)C(1). The five-membered ring is no longer planar as in **1S** due to the alkyne insertion. The coordinative S→Co bond length (2.187 Å) is significantly shorter than the other covalent S–Co bond (2.271 Å). This probably determines the presence of the six-membered ring from the double insertion of the alkyne. In **3S** the bond length of C(1)–C(2) (1.663 Å) of the carborane cage falls in the typical range (1.62–1.70 Å)

Scheme 5. Proposed Mechanisms for Products 3 and 4 and Cyclotrimerization of Alkyne



of *o*-carborane derivatives.²⁰ The configuration in **3S** does not induce significant strain. A couple of analogous examples have been isolated from the reactions of Cp*Rh[E₂C₂B₁₀H₁₀] with HC≡CCO₂Me (see D–F, Scheme 1);^{2,7} however, no such structure was isolated with HC≡CPh in the Rh and Ir systems.

The NMR data of **3S** are in agreement with its solid-state structure. The ¹H chemical shifts of the CH=CH unit of the six-membered ring appear at 6.17 and 7.51 ppm, as confirmed by a homonuclear decoupling experiment. The magnitude of ³J_{H–H} (8 Hz) is characteristic of ¹H nuclei in a *cis* position of an alkene group. Figure 2 shows the ¹³C NMR spectrum. Straightforward assignments were made by using 2D ¹³C/¹H HETCOR (HMQC and HMBC) experiments based on coupling constants ¹J(¹³C, ¹H) and long-range couplings ^{*n*}J(¹³C, ¹H) (*n* = 2, 3). As a result, the CH=CH unit was identified at 127.68 and 141.15 ppm. The carbon atom adjacent to the metal center (C–M) and the one close to sulfur (C–S) were assigned at 170.45 and 109.65 ppm, respectively. The signals for C(1) and C(2) of the carborane were readily recognized owing to broadening by partially relaxed scalar ¹³C–¹¹B coupling.

4S was isolated in a yield of 35%. The X-ray structure as shown in Figure 3 displays a B–C bond, and the hydrogen atom of the B–H bond of the carborane has been transferred to the terminal carbon of the alkyne. Moreover, the C≡C triple bond of the alkyne has been extended to the range of a C–C single bond (1.518 Å). The newly generated five-membered ring C(3)B(3)C(1)S(1)C(4) is nearly planar, whereas the five-membered ring S(1)Co(1)S(2)C(2)C(1) is nonplanar, in contrast to the 16e starting complex. Note that **A** rearranged to **B** upon heating in boiling CHCl₃, as shown in Scheme 1. In contrast, **4S** was synthesized and isolated as a final product at 25 °C. An analogous species of **A** with a M–B bond was not seen in the cobalt case, indicating the 16e cobalt starting material is more reactive.

The ¹H NMR data of **4S** support its solid-state structure. The broader doublets at 1.98 and 2.32 ppm were assigned to the alkyl group of the B–CH₂ unit. The large value (16 Hz) of the geminal coupling constants ²J_{H–H} is typical for diastereotopic ¹H nuclei of the B–CH₂ group. The ¹¹B NMR spectrum shows the pattern of overlapping signals as expected for unsymmetrically substituted *o*-carborane derivatives; however, a low-field shift for the substituted boron atom was observed at 1.5 ppm relative to negative values for the other boron signals. A similar chemical shift appeared in **B**¹⁸ and **G**² (Scheme 1) for B-

substituted carboranes. In the ¹³C NMR spectrum, the low, broad peak at 33.93 ppm shows that the CH₂ group is linked to a boron atom.

Reaction of 1S with Phenylacetylene at Higher Temperature. The reaction of **1S** with HC≡CPh at 80 °C in toluene led to **2S**, **4S**, and 1,2,4- and 1,3,5-triphenylbenzenes (Scheme 3). **3S** was not isolated at 80 °C. In a separate experiment, heating **3S** at 80 °C led to decomposition. At 80 °C the competitive catalytic cyclotrimerization of alkyne becomes significant, in contrast to that at ambient temperature. If the temperature was raised to 110 °C, **2S** was isolated with a large amount of triphenylbenzenes and **4S** decomposed at 110 °C. It needs to be mentioned that the species **C**, shown in Scheme 1, was not isolated at both ambient and higher temperatures with the same reaction conditions as described in the literature.¹

3S as Catalytic Intermediate. As discussed above, **3S** decomposes at 80 °C. However, in the presence of phenylacetylene, **3S** acts as a catalyst to generate triphenylbenzenes. **3S** was isolated as the predominant product in the mixture with traces of **2S** and **4S** (Scheme 4).

Reaction of CpCo[Se₂C₂B₁₀H₁₀] (1Se) with Phenylacetylene. **1Se** did not react with HC≡CPh at ambient temperature. If heated at 80 °C in toluene for 2 h, **2Se** and **4Se** were isolated together with 1,3,5- and 1,2,4-triphenylbenzenes in about 1:1 ratio (Scheme 3). **3Se** (analogue of **3S**) was not isolated at 80 °C. If the reaction was carried out in boiling toluene, **2Se** was the only complex isolated, accompanied by triphenylbenzenes. **4Se** decomposed at 110 °C.

2Se was isolated in a yield of 73% at 80 °C and showed high thermal stability (mp = 245 °C, dec). The X-ray analysis displays (Figure 4) a symmetric dinuclear molecular structure analogous to **2S**. The addition of a CpCo moiety to the Se–Co–Se unit in **1Se** generates **2Se** with Co–Co bonding. Two similar dinuclear structures, [(*tert*-Bu)₂(C₅H₃)Rh]₂[E₂C₂B₁₀H₁₀] (E = S, Se), were reported by Jin's group.^{13a} However, in the rhodium and iridium series with a larger pentamethylcyclopentadienyl (Cp*) unit such a species was never isolated. It appears that the generation of **2S** and **2Se** depends on the size of the auxiliary ligand. Its ¹H NMR spectrum consists of a single sharp signal of Cp, consistent with the symmetric structure. The ¹³C data of the carborane (66.7 ppm) shifts to a high field of about 20 ppm relative to **2S** (87.1 ppm) owing to the typical heavy atom effect exerted by Se versus S. This was observed in Rh and Ir complexes as well.^{2,18}

4Se was isolated in a yield of 4% from the reaction at 80 °C. It was identified on the basis of spectral data and elemental analysis. The NMR spectroscopic properties of **4Se** correspond

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Table 1. Crystallographic Data and Structure Refinement Information for 3S, 4S, and 2Se

	3S	4S	2Se
formula	C ₂₃ H ₂₇ B ₁₀ CoS ₂	C ₁₅ H ₂₁ B ₁₀ CoS ₂	C ₁₂ H ₂₀ B ₁₀ Co ₂ Se ₂
fw	534.62	432.49	548.16
color	yellow	purple	green
size, mm	0.24 × 0.26 × 0.30	0.24 × 0.26 × 0.30	0.24 × 0.26 × 0.30
cryst syst	monoclinic	triclinic	monoclinic
space group	P2 ₁ /c	P1	P2 ₁ /n
a (Å)	11.152 (10)	11.962(3)	12.250(3)
b (Å)	12.074(10)	13.029(3)	9.259(3)
c (Å)	20.855(16)	15.174(4)	17.685(5)
α (deg)	90	115.007(3)	90
β (deg)	105.51(4)	103.298(5)	99.682(4)
γ (deg)	90	98.994(4)	90
V (Å ³)	2706(4)	1997.7(9)	1977.3(10)
z	2	4	4
θ range (deg)	1.9–26.0	1.8–26.0	1.9–26.0
D(calc) [g/cm ³]	1.334	1.438	1.841
μ (mm ⁻¹)	0.804	1.066	5.352
min., max. transmn	0.7945, 0.8305	0.7403, 0.7839	0.22, 0.28
no. of data/restraints/params	5314/0/334	7662/0/505	3882/0/235
F(000)	1116	880	1056
no. of reflns collected	14 286	10 816	10 451
no. of unique reflns (R _{int})	5314 (0.038)	7662 (0.035)	3882 (0.040)
GOF	1.03	1.01	1.10
R indices (I > 2σ(I))	R ₁ = 0.0546 wR ₂ = 0.1272	R ₁ = 0.0676 wR ₂ = 0.1529	R ₁ = 0.0510 wR ₂ = 0.1257
R indices (all data)	R ₁ = 0.0712 wR ₂ = 0.1320	R ₁ = 0.0902 wR ₂ = 0.1589	R ₁ = 0.0624 wR ₂ = 0.1293
largest diff peak and hole (e/Å ³)	0.526, -0.515	0.500, -0.928	0.564, -0.728

closely to those of **4S**. The mass spectrum displayed a molecular ion peak, together with microanalysis data, further verifying the proposed structure for **4Se** in Scheme 3.

Reactions of (CpCo)₂[E₂C₂B₁₀H₁₀] (2S, 2Se) with Phenylacetylene. In the present report, **2S** and **2Se** were generated as byproducts from the reactions of 16e complexes **1S** and **1Se**, respectively, and HC≡CPh. Alternatively, they were isolated from the reactions of CpCo(CO)I₂ and Li₂[E₂C₂B₁₀H₁₀] for the preparation of **1S** and **1Se**, respectively. The 16e complexes **1S** and **1Se** have demonstrated interesting reactivities with HC≡CPh. In contrast, the corresponding **2S** and **2Se** did not react with HC≡CPh even at 110 °C.

Mechanism Implications. The two reaction pathways leading from **1** to **3** and **4**, as had been suggested in part previously,^{3,7} are summarized in Scheme 5. Although some species shown were never isolated, some were identified and even characterized by X-ray analysis from other reactions. The complex **I** was not isolated in this reaction; however, two analogues generated from MeCO₂C≡CCO₂Me are stable and characterized by their solid-state structure.^{1,3} The 18e structure in **I** appears to be fairly rigid, and the cobalt atom cannot get close to the carborane cage. The equilibrium between **I** and **II** is possible if the coordinative E→M bond is weak enough. The core skeleton in **II** is more flexible so that the metal center can approach the B(3)/B(6) positions of the carborane cage to activate the B–H bond, as a result, to generate M–H–B bonding as shown in **III**. The bridging hydrogen atom is passed stereoselectively to the olefinic carbon atom, accompanied by formation of a M–B bond to give rise to **IV**. **IV** was not detected even by monitoring the reaction by NMR spectroscopy at ambient temperature; however, numerous complexes of such type have been reported with other alkynes and metal centers by our group.^{7,18} The cleavage of a M–B bond leads to a C–B bond to afford **4**.

Apparently, the insertion of a second alkyne competes with the pathway from **I** to **4**, and in **3** the strength of the coordinative S→Co bond may be increased by forming a six-membered ring relative to a four-membered ring in **I**. Indeed, as reported in **D**,

E, and **F** (Scheme 1) together with **3S**, the coordinative S→Co bond is about 0.1 Å shorter than the other covalent S–Co bond in a six-membered ring, whereas the coordinative S→Co bond is nearly the same as the other S–Co bond in length in the four-membered-ring complexes **H** (Scheme 1)³ and [CpCo-(S₂C₂B₁₀H₁₀)(MeCO₂C≡CCO₂Me)].¹ Addition of one more alkyne to **3** leads to release of **1** and generation of 1,2,4-triphenylbenzene, thus completing a catalytic cycle. Here, it is needed to mention that the similar **D** and **F** complexes (Scheme 1) with a phenyl group as a substituent were not isolated in this reaction; however, they are the intermediates to the catalytic products of both 1,3,5- and 1,2,4-triphenylbenzenes since the two substituted benzene derivatives were experimentally obtained. Higher temperature favors the catalytic pathway.

Conclusion

The reactions of CpCo[E₂C₂B₁₀H₁₀] (**1S**, **1Se**) with HC≡CPh led to new complexes **2Se**, **3S**, **4S**, and **4Se**. The two 16e complexes display markedly different reactivity toward phenylacetylene: **1S** > **1Se**. It is conceivable that the selenium atom instead of sulfur changes the kinetics of some of the reactions involved owing to the larger covalent radius of selenium and different strength of the Co–Se bond. This result has been observed in analogous Rh and Ir systems. On the other hand, **1S** and **1Se** are more reactive than the analogous 16e rhodium and iridium complexes, as revealed in the reaction with phenylacetylene. This is reflected by the generation of a C–B bond at ambient temperature, rather than a M–B bond as occurred in Rh and Ir complexes. These 16e cobalt species may be promising for various transformations with other reagents.

Experimental Section

General Procedures. *n*-Butyllithium (2.0 M in cyclohexane, Aldrich), *o*-carborane (Katchem, Czech), and phenylacetylene (Alfa Aesar) were used as supplied. CpCo(CO)I₂²¹ and CpCo[E₂C₂–

(B₁₀H₁₀)] (E = S, Se)^{1,22} were prepared by slightly 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, THF, petroleum ether, and toluene were refluxed and distilled over sodium/benzophenone ketyl under nitrogen. CH₂Cl₂ was refluxed and distilled over CaH₂ under nitrogen. Silica gel (100–200 mesh) was predried at 180 °C before use. The NMR measurements were performed on a Bruker AC 500 spectrometer. Chemical shifts were given with respect to CHCl₃/CDCl₃ (δ ¹H = 7.24; δ ¹³C = 77.0) and external Et₂O–BF₃ (δ ¹¹B = 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 a Perkin-Elmer 240C elemental analyzer. The mass spectra were recorded in a Micromass GC-TOF for EI-MS (70 eV).

Synthesis of 2S, 3S, and 4S. Phenylacetylene (0.22 mL, 2 mmol) was added to the red solution of **1S** (66.0 mg, 0.2 mmol) in CH₂-Cl₂ (20 mL), and the resultant mixture was stirred at ambient temperature for 24 h. The color changed to brown-red within the first 2 h and then gradually to deep brown. After removal of solvent, the residue was chromatographed on silica gel eluting with petroleum ether to give **2S** and then with petroleum ether/CH₂Cl₂ (10:1) to give **3S** and **4S**.

2S: green solid, yield 5.3 mg (11%). ¹H NMR (CDCl₃): δ 5.02 (s, Cp). ¹³C NMR (CDCl₃): δ 77.73 (Cp), 87.14 (carborane). ¹¹B NMR (CDCl₃): δ –9.1 (2B), –5.4 (2B), –1.6 (2B), 6.6 (4B). EI-MS (70 eV): m/z 454 (M⁺, 40%). IR (KBr): 2586 (ν_{B-H}).

3S: yellow solid, yield 43 mg (40%). Mp = 165 °C (dec). ¹H NMR (CDCl₃): δ 4.98 (s, 5H, Cp), 6.17 (d, J = 8 Hz, 1H, CH=CH), 7.51 (d, J = 8 Hz, 1H, CH=CH), 7.27 (m, 1H), 7.29 (m, 1H), 7.34 (m, 2H), 7.45 (m, 2H), 7.46 (m, 2H), 7.77 (m, 2H) (phenyl groups). ¹¹B NMR (CDCl₃): δ –9.2 (1B), –7.4 (1B), –4.8 (4B), –3.0 (2B), –2.4 (2B). ¹³C NMR (CDCl₃): δ 90.63 (Cp), 94.64, 101.40 (carborane), 109.65 (CH=C–S), 126.30, 126.46, 126.75, 127.82, 128.16, 129.10, 137.77, 156.01 (Ph), 127.68 (CH=C–S), 141.15 (Co–C=CH), 170.45 (Co–C=CH). EI-MS (70 eV): m/z 535 (M⁺, 1%). IR (KBr): 2586 (ν_{B-H}). Anal. Calcd for C₂₃H₂₇B₁₀Co₁S₂: C, 51.67; H, 5.09. Found: C, 51.51; H, 5.17.

4S: purple solid, yield 35 mg (40%). Mp = 179 °C (dec). ¹H NMR (CDCl₃): δ 1.98 (br d, J = 16 Hz, 1H, B–CH₂), 2.32 (br d, J = 16 Hz, 1H, B–CH₂), 4.52 (s, 5H, Cp), 7.31 (s, 5H, Ph). ¹³C NMR (CDCl₃): δ 33.93 (br, B–CH₂), 84.86 (Ph–C), 86.47 (Cp), 94.78, 97.91 (carborane), 124.65 (br), 126.31, 129.08, 152.76 (Ph). ¹¹B NMR (CDCl₃): δ –14.1 (1B), –9.9 (1B), –9.1 (1B), –8.2 (5B), –7.6 (1B), 1.5 (B–CH₂, 1B). EI-MS (70 eV): m/z 432 (M⁺, 42%). Anal. Calcd for C₁₅H₂₁B₁₀Co₁S₂: C, 41.66; H, 4.89. Found: C, 41.76; H, 4.95.

Syntheses of 2Se and 4Se. Phenylacetylene (0.22 mL, 2 mmol) was added to the suspension of **1Se** (85.0 mg, 0.2 mmol) in toluene (10 mL), and the mixture was heated at 80 °C for 2 h. The color changed to deep red. After removal of solvent, the residue was chromatographed. Elution with petroleum ether gave **2Se** and **4Se**.

2Se: green solid, yield 40 mg (73%). Mp = 245 °C (dec). ¹H NMR (CDCl₃): δ 4.99 (s, Cp). ¹³C NMR (CDCl₃): δ 66.71 (carborane), 76.54 (Cp). ¹¹B NMR (CDCl₃): δ –8.6 (2B), –4.1 (2B), –1.5 (2B), 3.2 (4B). EI-MS (70 eV): m/z 548 (M⁺, 21%). IR (KBr): 2577 (ν_{B-H}). Anal. Calcd for C₁₂H₂₀B₁₀Co₂Se₂: C, 16.66; H, 3.68. Found: C, 16.78; H, 3.59.

4Se: purple solid, yield 4 mg (4%). ¹H NMR (CDCl₃): δ 2.09 (br d, J = 16 Hz, 1H, B–CH₂), 2.68 (br d, J = 16 Hz, 1H, B–CH₂), 5.35 (s, 5H, Cp), 7.30 (s, 5H, Ph). ¹¹B NMR (CDCl₃): δ –14.2 (1B), –9.4 (1B), –8.1 (5B), –7.2 (2B), 1.7 (B–CH₂, 1B). EI-MS

(70 eV): m/z 526 (M⁺, 9%). Anal. Calcd for C₁₅H₂₁B₁₀Co₁Se₂: C, 34.23; H, 4.02. Found: C, 34.40; H, 4.11.

Reactions of 1Se with Phenylacetylene at Ambient Temperature. Phenylacetylene (0.22 mL, 2 mmol) was added to **1Se** (85.0 mg, 0.2 mmol) in CH₂Cl₂ or toluene (20 mL), and the resultant mixture was stirred at ambient temperature for 24 h. After removal of solvent, the residue contained unreacted **1Se** and traces of 1,3,5- and 1,2,4-triphenylbenzenes.

Reaction of 1S with Phenylacetylene in Toluene at 80 °C. Phenylacetylene (0.22 mL, 2 mmol) was added to the red solution of **1S** (66.0 mg, 0.2 mmol) in toluene (10 mL). Then the mixture was heated at 80 °C for 2 h, and the color changed to deep red. After removal of solvent, the residue was chromatographed to give rise to **2S**, **4S**, and triphenylbenzenes (~1:1).

Reactions of 1S and 1Se with Phenylacetylene in Boiling Toluene. Phenylacetylene (0.22 mL, 2 mmol) was added to **1S** (66.0 mg, 0.2 mmol) or **1Se** (85.0 mg, 0.2 mmol) in toluene (10 mL). Then the mixture was heated at 110 °C for 3 h, and the color changed from red to deep green. After removal of solvent, the residue was chromatographed to give **2S** (35 mg, 75%) and **2Se** (40 mg, 73%), respectively, and triphenylbenzenes (~1:1).

Reaction of 3S with Phenylacetylene in Toluene at 80 °C. Phenylacetylene (0.11 mL, 1 mmol) was added to the yellow solution of **3S** (50 mg, 0.1 mmol) in toluene (5 mL). Then the mixture was heated at 80 °C for 3 h, and the color changed to brown-yellow. After removal of solvent, the residue contained **3S** and triphenylbenzenes as major products and **2S** and **4S** as minor products.

Reactions of 2S and 2Se with Phenylacetylene in Boiling Toluene. Phenylacetylene (0.11 mL, 1 mmol) was added to the green solution of **2S** (45 mg, 0.1 mmol) or **2Se** (55 mg, 0.1 mmol) in toluene (5 mL). The mixture was stirred for 6 h at 110 °C, but no color change occurred. After removal of solvent, the residue was chromatographed to give **2S** (42 mg, 93%) or **2Se** (53 mg, 96%).

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.²³ The structures were solved by direct methods using the SHELXL-97 program.²⁴ 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.

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Supporting Information Available: X-ray crystallographic files in CIF format for the structure determination of compounds **2Se**, **3S**, and **4S** are available free of charge via the Internet at <http://pubs.acs.org>.

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