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Metal-Induced B−H Bond Activation: Addition of Methyl Acetylene Monocarboxylate to CpCo Half-Sandwich Complexes Containing a Chelating 1,2-Dicarba-*closo*-dodecaborane-1,2-dichalcogenolate Ligand

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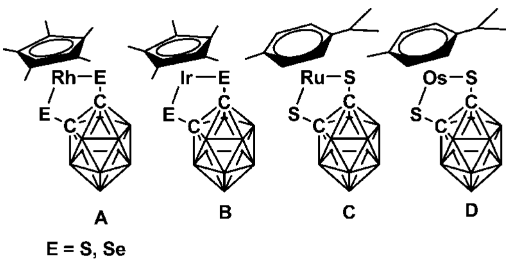
The reaction of the 16*e* half-sandwich complex {CpCo[$S_2C_2B_{10}H_{10}$]} (**1S**) with methyl acetylene monocarboxylate at ambient temperature led to {CpCo[$S_2C_2B_{10}H_{10}$] [CHC(CO_2Me)CHC(CO_2Me)]} (**2S**) and {CpCo[$S_2C_2B_{10}H_8$][CHCH(CO_2Me)]$_2$} (**3S**). In**2S** the alkyne is 2-fold inserted into one of the Co−S bonds. **3S** is a 16*e* B-disubstituted complex with the olefinic units in a *Z*/*Z* configuration. In comparison, {CpCo[$Se_2C_2B_{10}H_{10}$]} (**1Se**) reacted with the alkyne to give rise to {CpCo[$Se_2C_2B_{10}H_{10}$]-[CHC(CO_2Me)CHC(CO_2Me)]} (**2Se**), {CpCo[$Se_2C_2B_{10}H_9$] [CH_2C(CO_2Me)]} (**4Se**), and {CpCo[$Se_2C_2B_{10}H_8$]-[CH_2C(CO_2Me)][CHCH(CO_2Me)]} (**5Se**). **2Se** is the analogue of **2S**. Upon heating, **2S** and **2Se** catalyze cyclotrimerization of the alkyne to generate 1,3,5- and 1,2,4-tricarboxylatebenzenes. **4Se** is an 18*e* B-substituted species with a B−CH_2 unit. **5Se** is analogous to **4Se**, but contains an olefinic substituent at the B(3)/B(6) site of the carborane in a *Z* configuration. Mechanistic implications on metal-induced B−H bond activation and catalytic cyclotrimerization of alkyne were elucidated. All new complexes were characterized by NMR spectroscopy (^1H, ^{11}B, ^{13}C), and X-ray structural analyses were reported for **2S**, **2Se**, **3S**, **4Se**, and **5Se**.

Introduction

The icosahedral 12-vertex 1,2-*ortho*-, 1,7-*meta*-, and 1,12-*para*-carboranes ($C_2B_{10}H_{12}$) have been proved to be versatile precursors to novel structures. The derivatives, 13-, 14-vertex carboranes, and the largest heteroborane, a 15-vertex metallacarborane, have been prepared and studied for development of polyhedral clusters of extraordinary size.[1] The *nido*-carborane, 7,8-dicarba-*nido*-undecaborate anion [$C_2B_9H_{12}$]$^-$, was used as a boron moiety for attachment to biomolecules for BNCT (boron neutron capture therapy), and the research in this field becomes more active.[2] Recently developed constrained-geometry ligands containing both monocyclopentadienyl and σ-heteroatom components have attracted considerable attention.[3] The potential applications of these superclusters as effective catalysts or cocatalysts are attractive.

Scheme 1. 16*e* Half-Sandwich Species Containing a Chelating 1,2-Dicarba-*closo*-dodecaborane-1,2-dichalcogenolate Ligand



The reported results suggest that the 16*e* "pseudoaromatic" half-sandwich species containing a chelating 1,2-dicarba-*closo*-dodecaborane-1,2-dichalcogenolate ligand, {Cp*M[E_2C_2($B_{10}H_{10}$)]}(M = Co, Rh, Ir; E = S, Se)[4–6] and {(*p*-cymene)M-[S_2C_2($B_{10}H_{10}$)]}(M = Ru, Os)[7] (Scheme 1), may be promising for further transformations owing to their electron deficiency

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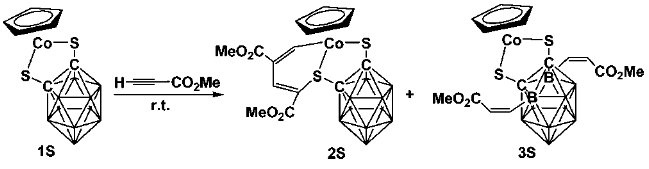
at the metal centers, reactive M−E bonds, and potentially reactive carborane cage. For instance, they could serve as precursors for synthesis of mixed-metal clusters, of which oligonuclear frameworks including heterometallic clusters with metal−metal bonds were built up.[8] On the other hand, the study of their reaction chemistries with organic substrates is of significance.[9–12] The metal center, the chalcogen element, and the reaction conditions strongly influence the reactivity of the 16*e* complexes.[8–12]

The complexes **A** and **D** (Scheme 1) have shown diverse reactivities with alkynes, such as methyl acetylene carboxylates,[9] phenylacetylene,[10] and ferrocenylacetylene[11] in numerous ways depending upon the metal, the chalcogen, and the conditions used. The types of reactions observed turn out to be rather wide, ranging from catalytic oligomerization of alkynes to activation of the B−H bond, formation of a metal−boron bond, and stepwise functionalization in the B(3,6) positions of the *o*-carborane cage. Our preliminary results show that the 16*e* complexes, {CpCo[$E_2C_2B_{10}H_{10}$]} (**1S**, E = S; **1Se**, E = Se) are more reactive than the analogous rhodium and iridium species and could be used as models for further transformations, especially for the reactions with alkynes.[5] In our continuous and systematic studies of the roles of metal in the reaction chemistries of the 16*e* series {Cp*M[$E_2C_2B_{10}H_{10}$]} (M = Co, Rh, Ir; E = S, Se) complexes, we examined the reactivity of the cobalt species {CpCo[$E_2C_2B_{10}H_{10}$]} with the reactive alkyne methyl acetylene monocarboxylate in order to explore the reaction chemistries of the cobalt complexes. In the present paper, five new complexes, **2S**, **2Se**, **3S**, **4Se**, and **5Se**, and the catalytic cyclotrimerization of alkynes by the 16*e* complexes **1S** and **1Se** are reported.

Results and Discussion

Reactions of {CpCo[$E_2C_2B_{10}H_{10}$]} (1S, E = S; 1Se, E = Se) with methyl acetylene monocarboxylate (HC≡C−CO_2Me). The reactions of 16*e* half-sandwich rhodium, iridium, ruthenium, and osmium complexes containing a chelating 1,2-dicarba-*closo*-dodecaborane-1,2-dichalcogenolate ligand with HC≡C−CO_2Me have been fully studied, and varieties of intermediates and products were isolated and characterized.[9] In contrast, the analogous 16*e* cobalt complexes have not been investigated. To develop a picture of this complex reaction system, the reactions of **1S** and **1Se** with HC≡C−CO_2Me are discussed sequentially.

Scheme 2



Reaction of 1S with HC≡C−CO_2Me. The reaction of **1S** with HC≡C−CO_2Me at ambient temperature afforded two new complexes, **2S** and **3S**, as shown in Scheme 2.

2S was isolated in a yield of 30%. Its X-ray structure as shown in Figure 1 displays that the alkyne is 2-fold inserted into one of the Co−S bonds in a head-to-tail mode. The generated six-membered ring S(1)Co(1)C(4)C(5)C(6)C(7) is fused at one Co−S bond with the five-membered ring S(1)Co(1)S(2)C(2)C(1) with an angle close to 90°. The former is almost planar with a dihedral angle at the C(4)···C(7) vector of 175.9°, while the later is slightly bent at the S(1)···S(2) vector (168.9°) compared to the planar ring in **1S**. The coordinative S(1)→Co bond is slightly shorter (0.057 Å) than the covalent S(2)−Co bond. Clearly, if the coordinative bond is sufficiently weak, the cobalt atom could be approached by a third alkyne with subsequent reductive elimination to give cyclotrimers of the alkyne. A couple of related structures have been reported from the reactions of {Cp*Rh[$E_2C_2B_{10}H_{10}$]} (E = S, Se) with HC≡C–CO_2Me.[9a,d] An analogue was also isolated from the reaction of **1S** with HC≡C−Ph in a head-to-head mode in the alkyne addition.[5]

The NMR spectroscopic data of **2S** in solution are fully in accord with its solid-state structure. Two singlets at 5.27 and 6.63 ppm in the ^1H NMR spectrum were assigned to the vinyl protons of the six-membered ring. Straightforward assignments for the ^{13}C signals were made by using 2D $^{13}C/^1H$ HETCOR (HMQC and HMBC) experiments based on coupling constants $^1J(^{13}C, ^1H)$ and long-range coupling couplings $^nJ(^{13}C, ^1H)$ (n = 2, 3). As a result, the four ring carbon signals were assigned to 105.35 (S−C=*C*H), 128.65 (=CH−Co), 151.58 (S−C=), and 155.52 (*C*=CH−Co). The signals for the carborane carbon atoms were recognized as 94.61 and 101.44 ppm owing to

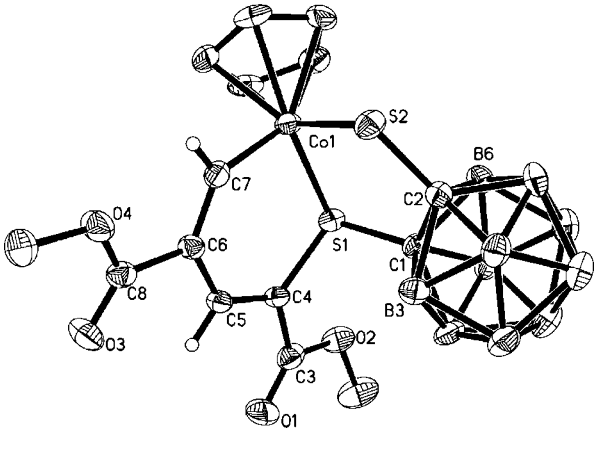


Figure 1. Molecular structure of **2S**; ellipsoids show 30% probability levels, and hydrogen atoms have been omitted for clarity. Selected bond lengths [Å] and angles [deg]: Co(1)−S(1) 2.1870(11), Co(1)−S(2) 2.2439(11), C(1)−C(2) 1.662(5), Co(1)−C(7) 1.875(4), C(7)−C(6) 1.347(6), C(6)−C(5) 1.447(6), C(5)−C(4) 1.333(5), S(1)−C(4) 1.770(4), C(7)C(6)C(5)C(4)/C(4)S(1)Co(1)C(7) 175.9, S(1)C(1)C(2)S(2) /S(1)Co(1)S(2) 168.9.

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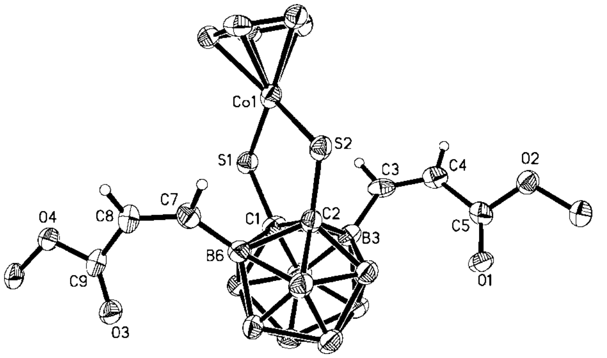

Figure 2. Molecular structure of *trans*-**3S**. Ellipsoids show 30% probability levels, and hydrogen atoms have been omitted for clarity. Selected bond lengths [Å] and angles [deg]: Co(1)−S(1) 2.1243(13), Co(1)−S(2) 2.1422(13), S(1)−C(1) 1.792(4), S(2)−C(2) 1.774(4), C(1)−C(2) 1.642(6), C(3)−B(3) 1.546(7), C(7)−B(6) 1.542(7), C(3)−C(4) 1.334(6), C(7)−C(8) 1.321(6), S(1)Co(1)S(2) 96.48(5), B(3)C(3)C(4)C(5) 3.4(8), B(6)C(7)C(8)C(9) 1.4(8), S(1)Co(1)S(2)/S(2)C(2)C(1)S(1) 177.1.

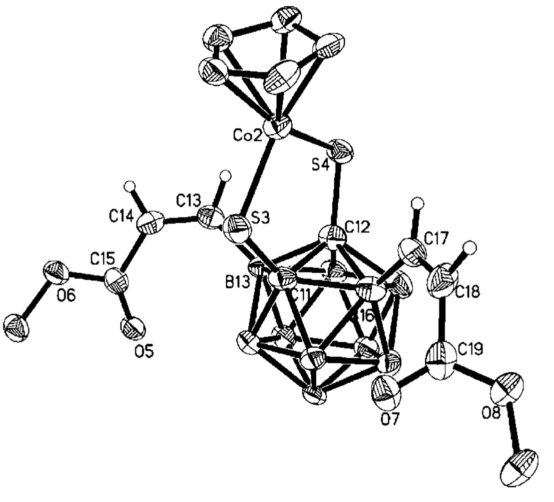

Figure 3. Molecule structure of *cis*-**3S**. Ellipsoids show 30% probability levels, and hydrogen atoms have been omitted for clarity. Selected bond lengths [Å] and angles [deg]: Co(2)−S(3) 2.1312(14), Co(2)−S(4) 2.1443(13), S(3)−C(11) 1.777(4), S(4)−C(12) 1.777(4), C(11)−C(12) 1.623(6), C(13)−B(13) 1.542(7), C(17)−B(16) 1.590(7), C(14)−C(15) 1.453(7), C(17)−C(18) 1.324(7), S(3)Co(2)S(4) 96.60(5), B(13)C(13)C(14)C(15) 0.5(8), B(16)C(17)C(18)C(19) −2.7(9), S(3)Co(2)S(4)/ S(4)C(12)C(11)S(3) 174.8.

broadening by partially relaxed scalar ^{13}C−^{11}B coupling. **3S** was isolated in a yield of 30%. The solid-state structure shows three discrete molecules in one unit cell assigned to a 16*e* complex with disubstitution at B(3)/B(6) sites of the carborane cage. Two molecules have the olefinic substituents in a *trans* arrangement (i.e., two substituents point in opposite directions), numbered in Co(1) and Co(3) by metal, respectively. Their subtle difference lies in the orientation of one carboxylate group (Figure 2). One molecule with the olefinic substituents in a *cis* arrangement (i.e., two substituents point in the same direction) is defined as Co(2) (Figure 3). Here, Co(1) (*trans*-**3S**) and Co(2) (*cis*-**3S**) are chosen for comparison. In *trans*-**3S**, the dihedral angle between B(3)C(3)C(4)C(5) and B(6)C(7)C(8)C(9) is 112.0°, in contrast to 51.9° between B(13)C(13)C(14)C(15) and B(16)C(17)C(18)C(19) in *cis*-**3S**. The coexistence of *cis–trans* conformers in one unit cell has been observed in a rhodium analogue,[9c] but this lacks proof. In this paper we used DFT calculations at a UB3LYP hybrid functional level to study both complexes and found that *cis*-**3S** is slightly lower than *trans*-**3S** by 0.45 kcal/mol, and the cause of coexistence in one unit cell could be attributed to a low barrier of 3.81 kcal/mol for conversion (Figure 4).

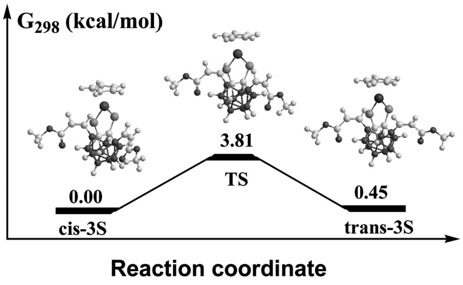

Figure 4. Free energy profile for the conversion between species of *cis*-**3S** and *trans*-**3S** in the gas phase.

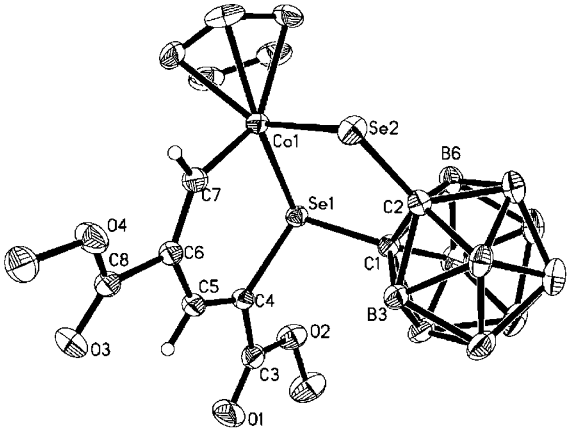

Figure 5. Molecular structure of **2Se**. Ellipsoids show 30% probability levels, and hydrogen atoms have been omitted for clarity. Selected bond lengths [Å] and angles [deg]: Co(1)−Se(1) 2.2913(7), Co(1)−Se(2) 2.3526(7), Co(1)−C(7) 1.888(4), C(6)−C(7) 1.367(6), C(5)−C(6) 1.433(6), C(4)−C(5) 1.340(5), Se(1)−C(4) 1.901(4), C(1)−C(2) 1.646(5), C(4)C(5)C(6)C(7)/C(7)Co(1)Se(1)C(4) 176.6, Se(1)C(1)C(2)Se(2)/Se(2)Co(1)Se(1) 171.0.

The structural parameters of the three independent molecules of **3S** are identical; thus, only *trans*-**3S** is discussed here. In **3S** the olefinic substituents in B(3) and B(6) positions take *Z/Z* configurations. The five-membered ring Co(1)S(1)C(1)C(2)S(2) is planar within experimental error as in **1S**. The C(1)–C(2) bond distance (1.605 Å) is similar to that observed in the rhodium and iridium analogues,[9] but shorter than in other *o*-carborane derivatives (1.62–1.70 Å).[13]

The solid-state structure of **3S** with B-disubstitution at B(3) and B(6) sites of the carborane is reflected by its NMR spectroscopy. The **^{1}**H NMR spectrum shows two doublets at 5.35 and 6.30 ppm owing to ^3J(^{1}H, ^{1}H) across the C═C bond. The large coupling constant (J = 15 Hz) corresponds to a *Z* configuration, as revealed by the solid-state structure. This was also observed in analogous rhodium and iridium complexes containing a 3,6-disubstituted carborane cage.[9] 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. The sharp ^{13}C signal at 133.85 ppm and the broad resonance at 136.65 ppm of the carbon nuclei linked directly to B(3)/B(6) are indicative of the B−CH═CH unit. The slightly broadened signal at 97.07 ppm was assigned to the carbon atoms of the carborane. A systematic investigation demonstrates that

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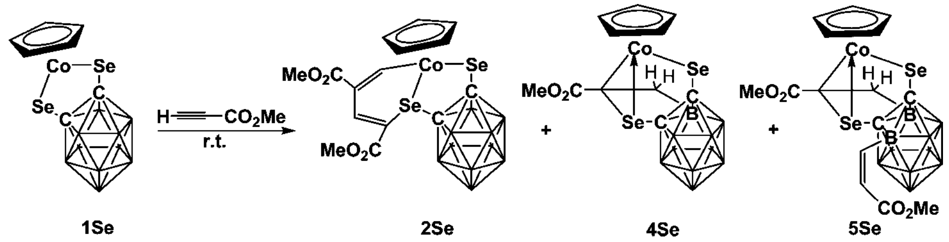
Scheme 3



a *Z/Z* configuration complex, such as **3S**, is readily recognized on the basis of its NMR data.

Reaction of 1Se with HC≡C–CO$_2$Me. Different from **1S**, the reaction of **1Se** with HC≡C–CO$_2$Me at ambient temperature gave rise to three new products, **2Se**, **4Se**, and **5Se**, as shown in Scheme 3.

2Se was isolated in a yield of 5%. Its solid-state structure shows an analogue of **2S**; that is, the alkyne is 2-fold inserted into one of the Co−Se bonds. The NMR spectroscopic data correspond closely to those of **2S** as well. The mass spectrum displays a molecular ion peak, together with the microanalysis data, further verifying the proposed structure of **2Se** in Scheme 3.

4Se was isolated in a yield of 50%. The X-ray structure as shown in Figure 6 displays a B−C bond, generated from functionalization of the B−H bond at B(3)/B(6) sites of the carborane cage. The hydrogen atom of the carborane is regio- and stereoselectively transferred to the terminal carbon atom of the alkyne that eventually is reduced to a C−C single bond (1.517 Å). The newly generated five-membered ring C(3)B(6)C(1)-Se(1)C(4) is nearly planar, whereas the five-membered ring Se(1)Co(1)Se(2)C(2)C(1) is nonplanar, in contrast to the 16*e* starting complex. One rhodium analogue of **4Se** was previously prepared.[9d]

The NMR data of **4Se** support its solid-state structure. In the ^{1}H NMR spectrum the broader doublets at 1.40 and 2.58 ppm were assigned to the alkyl group of the B−CH$_2$ unit. The large germinal coupling constant (J = 16 Hz) is typical for diastereotopic ^{1}H nuclei of the B−CH$_2$ group. The ^{11}B 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 4.3 ppm relative to negative values of the other boron signals. Similar downfield shifts of boron chemical shifts appeared in B-substituted carboranes.[5,10a] In the ^{13}C NMR spectrum the low, broad resonance at 31.17 ppm indicates that the CH$_2$ group is linked to a boron atom. The ^{13}C signals of the carborane at 69.62 and 86.77 ppm and the sp^3 hybrid carbon at 89.48 ppm from the reduced alkyne shift to high-field owing to the heavy atom effect.

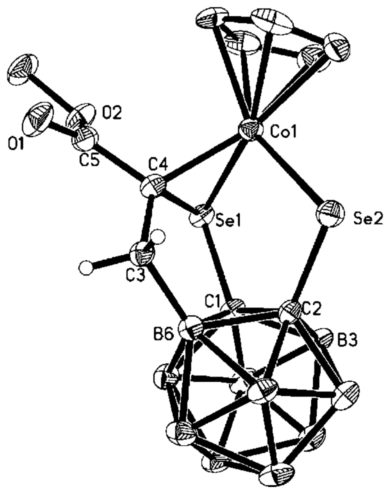


Figure 6. Molecular structure of **4Se**. Ellipsoids show 30% probability levels, and hydrogen atoms have been omitted for clarity. Selected bond lengths [Å] and angles [deg]: Co(1)−C(4) 2.003(5), Co(1)−Se(1) 2.2846(9), Co(1)−Se(2) 2.3450(9), C(3)−C(4) 1.517(6), C(1)−C(2) 1.660(7), Se(1)−C(4) 1.969(5), C(3)−B(6) 1.580(8), Se(1)−C(1) 1.941(4) Se(2)−C(2) 1.922(5), C(3)C(4)Se(1)/Se(1)C(1)B(6)C(3) 166.0, Se(1)C(2)C(1)Se(2)/Se(1)Co(1)Se(2) 167.4.

5Se was isolated in a yield of 10%. The crystal structure in Figure 7 shows both a B−CH$_2$ unit and one B-substitution by an olefinic unit in a Z configuration. The two types of substitution in B(3) and B(6) positions reflect nonregioselective addition of the terminal alkyne. This is the first example for B-disubstitution of different types at the carborane cage in the B(3)/B(6) positions. The solid-state structure of **5Se** is consistent with the NMR spectroscopic data in solution. The two broader doublets at 1.43 and 2.56 ppm with a characteristic coupling constant (J = 16 Hz) for the B−CH$_2$ unit and the doublets at 6.31 and 6.54 (br) ppm with a coupling constant of J = 15 Hz in the olefinic unit were observed in the ^{1}H NMR spectra. The ^{13}C NMR spectrum as shown in Figure 8 displays two broad resonances at 31.21 and 139.52 ppm, corresponding to the methylene and the vinyl carbon atoms bonded to boron atoms, respectively. The chemical shifts of the three carbon atoms

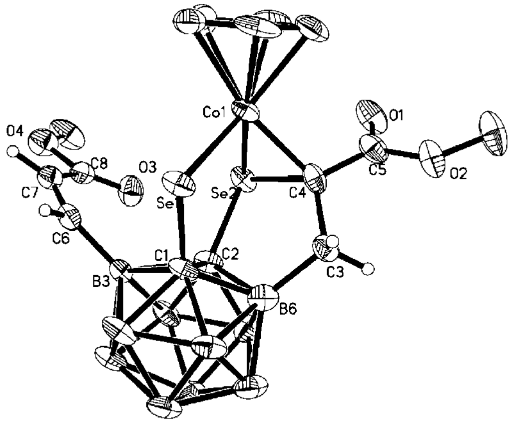


Figure 7. Molecular structure of **5Se**. Ellipsoids show 30% probability levels, and hydrogen atoms have been omitted for clarity. Selected bond lengths [Å] and angles [deg]: Co(1)–C(4) 1.967(7), Co(1)–Se(1) 2.3404(14), Co(1)–Se(2) 2.3021(13), Se(1)–C(1) 1.930(7), Se(2)–C(2) 1.940(7), Se(2)–C(4) 1.935(8), C(1)–C(2) 1.665(10), C(3)–C(4) 1.546(12), C(3)–B(6) 1.572(13), C(6)–C(7) 1.324(13), C(7)–C(8) 1.502(12), Se(2)Co(1)C(4) 53.2(2), Se(1)Co(1)C(4) 97.1(3), Se(1)Co(1)Se(2) 97.99(5), C(2)Se(2)C(4) 91.6(3), Se(2)C(2)C(1) 116.7(5), Se(1)C(1)C(2) 119.7(5), Co(1)Se(2)C(2) 102.8(2), Co(1)Se(1)C(1) 100.3(2), C(4)C(3)B(6) 111.5(7), C(1)B(3)C(6) 116.5(6), C(2)B(3)C(6) 127.3(7), C(7)C(6)B(3) 134.6(7), C(6)C(7)C(8) 124.7(7), C(3)C(4)Co(1)Se(2)/C(3)B(6)C(2)Se(2) 116.4.

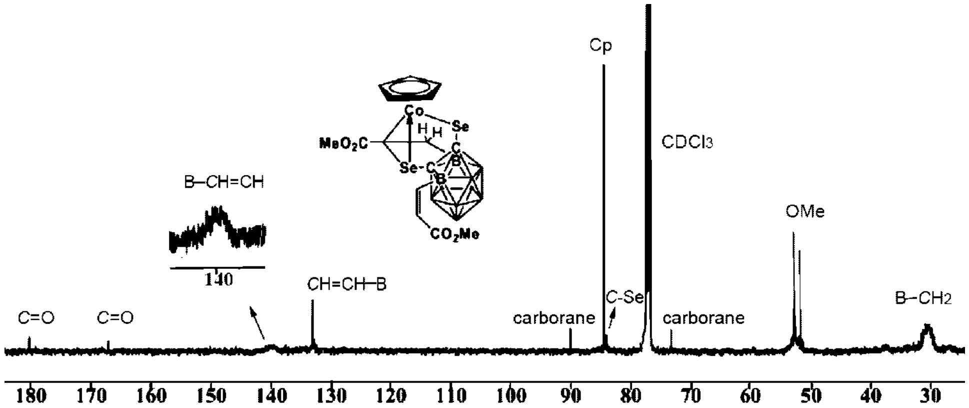
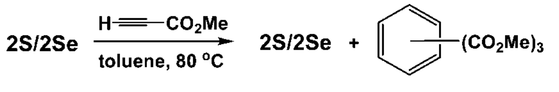
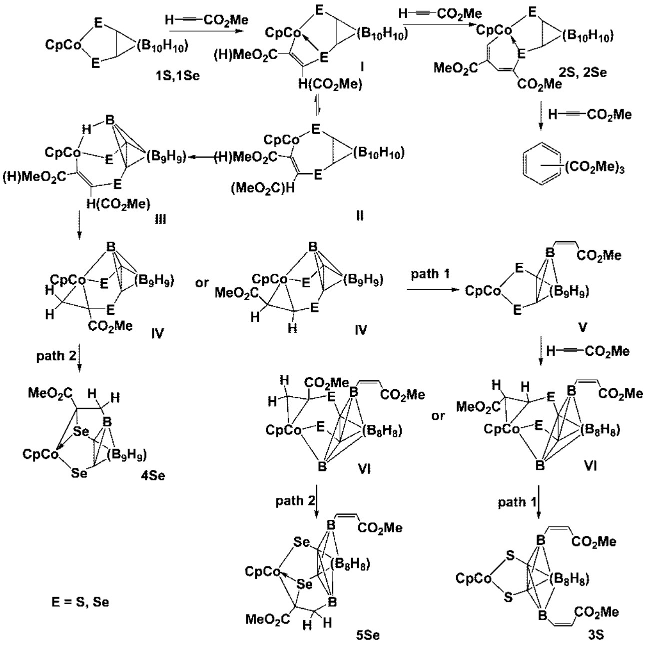


Figure 8. 125.76 MHz $^{13}C\{^1H\}$ NMR spectrum of **5Se**in $CDCl_3$ at 22 °C.

Scheme 4



Scheme 5. Mechanisms Proposed for the Reactions of 1S and 1Se with HC≡C–CO$_2$Me (complexes assigned to Roman numerals were not isolated)



directly connected to selenium atoms shift to high-field, for instance, 73.28 and 90.02 ppm for carborane and 84.05 ppm for Se–*C*–CO$_2$Me due to the heavy atom effect.

2S and 2Se as Catalytic Intermediates. 2S and **2Se** decompose at 80 °C. However, in the presence of HC≡C–CO$_2$Me, they act as catalysts to generate trisubstituted benzene derivatives in a 1:1 ratio. **2S** and **2Se** remain in the mixture, along with traces of $\{(CpCo)_2[E_2C_2B_{10}H_{10}]\}$ (E = S, Se), respectively (see Scheme 4).

Mechanistic Implications. The mechanisms proposed for the reactions of **1S** and **1Se** with HC≡C–CO$_2$Me are illustrated in Scheme 5. Although some species shown in Scheme 5 were never isolated, most of them have been identified or even characterized in other reaction systems (except II and III).

Despite not isolated from the reactions with HC≡C–CO$_2$Me, **I** could be considered as the key intermediates, formed by initial addition of the C≡C bond to the 16*e* metal centers, followed by insertion into one of the metal–chalcogen bonds. Such a structural type has been reported from the reactions of analogous 16*e* rhodium, iridium, ruthenium, and osmium complexes with MeO$_2$C–C≡C–CO$_2$Me.[9] Obviously, the second carboxylate substituent can strengthen the coordinative E→M bond since these derivatives are exceptionally stable examples of type **I**. Complexes **I** are subjected to reaction with a second alkyne, leading to 2-fold insertion compounds **2S/2Se**, of which the strength of the coordinative E→M bond is increased by forming a six-membered ring. Indeed, in **2S/2Se** and the reported analogues[9] the coordinative E→M bond distance is shorter than that of the other covalent E–Co bond. Addition of one alkyne to **2S/2Se** leads to release of **1S/1Se** and benzenetricarboxylates, thus completing a catalytic cycle. Higher temperature favors the catalytic pathway. Apparently, rearrangement of **I** via **II** and **III** to **IV** competes with the pathway from **I** to **2S/2Se**. The 18*e* structure in **I** appears to be fairly rigid, and thus the cobalt atom cannot get close to the carborane cage. To attain a more flexible core skeleton (**II**), the coordinative E→M bond needs to be weak enough so that the metal center can approach the B(3)/B(6) positions to activate B–H bonds, as a result, to generate M–H–B bonding (**III**). Note that such a bonding type is well-known in metallaborane and metallacarborane complexes which are stable enough and could be isolated.[14] 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**. These species were not isolated in this reaction; however, numerous complexes of such a type have been reported with other alkynes and metal centers.[9–12] Cleavage of the M–B bond in **IV** leads to formation of a C–B bond in the 18*e* complex **4Se** and 16*e* complex **V**, depending on the stereochemistry of alkyne addition in **I**. As to **V**, repetition of the sequence from **1S/1Se** to **IV** leads to two types of final products of **3S** and **5Se** with disubstitution in B(3) and B(6) positions.

Conclusion

The reactions of the 16*e* half-sandwich complexes $\{CpCo[E_2C_2B_{10}H_{10}]\}$ (**1S** and **1Se**) with the activated alkyne HC≡C–CO$_2$Me at ambient temperature led to new complexes **2S**, **2Se**, **3S**, **4Se**, and **5Se**. However, the two starting materials generate markedly different final products. It is conceivable that selenium instead of sulfur affects the regio- and stereoselectivity of the terminal alkyne insertion owing to the larger covalent radius of selenium. This parallels the observation in analogous

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Table 1. Crystallographic Data and Structure Refinement Information for 2S, 2Se, 3S, 4Se, and 5Se

	2S	2Se	3S	4Se	5Se
formula	$C_{15}H_{23}B_{10}CoO_4S_2$	$C_{15}H_{23}B_{10}CoO_4Se_2$	$C_{15}H_{23}B_{10}CoO_4S_2$	$C_{11}H_{19}B_{10}CoO_2Se_2$	$C_{15}H_{23}B_{10}CoO_4Se_2$
fw	498.50	592.28	498.50	508.21	592.28
color	red	red	red	blue	blue
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	0.24 × 0.26 × 0.30
cryst syst	monoclinic	monoclinic	monoclinic	monoclinic	triclinic
space group	$P2_1/n$	$P2_1/n$	$P2_1/c$	$P2_1/c$	$P\bar{1}$
a, Å	9.9360(17)	10.0659(9)	26.917(3)	6.6368(7)	9.5889(13)
b, Å	18.012(3)	18.0533(16)	19.900(2)	21.230(2)	9.6525(13)
c, Å	13.344(2)	13.4238(12)	13.2375(15)	13.4715(14)	13.9915(19)
α (deg)	90	90	90	90	72.157(2)
β (deg)	110.741(2)	110.9220(10)	93.859(2)	96.437(2)	75.856(2)
γ (deg)	90	90	90	90	73.250(2)
V (Å^3)	2233.4(6)	2278.6(4)	7074.6(13)	1886.2(3)	1163.0(3)
Z	4	4	12	4	2
θ range (deg)	2.0−26.0	2.0−26.0	1.5−26.0	1.8−26.0	1.5−26.0
D(calc) [g/cm^3]	1.483	1.727	1.404	1.790	1.691
μ (mm^{-1})	0.977	3.970	0.926	4.771	3.889
min., max. transmn	0.75, 0.79	0.30, 0.39	0.7687, 0.8084	0.24, 0.32	0.32, 0.39
no. of data/restraints/params	4389/1/289	4483/0/291	13 854/0/871	3696/0/236	4484/1/291
F(000)	1016	1160	3048	984	580
no. reflns collected	12 020	12 275	38 588	10 289	6404
no. unique reflns (R_{int})	4389 (0.085)	4483 (0.108)	13 854 (0.047)	3696 (0.101)	4568 (0.097)
GOF	0.88	1.05	1.06	0.86	1.00
R indices ($I > 2\sigma(I)$)	$R_1 = 0.0451$, $wR_2 = 0.0663$	$R_1 = 0.0368$, $wR_2 = 0.0923$	$R_1 = 0.0698$, $wR_2 = 0.\ 1361$	$R_1 = 0.0388$, $wR_2 = 0.0635$	$R_1 = 0.0580$, $wR_2 = 0.1037$
R indices (all data)	$R_1 = 0.0914$, $wR_2 = 0.0721$	$R_1 = 0.0439$, $wR_2 = 0.0947$	$R_1 = 0.1117$, $wR_2 = 0.1461$	$R_1 = 0.0663$, $wR_2 = 0.0666$	$R_1 = 0.0999$, $wR_2 = 0.1037$
largest diff peak and hole (e/Å^3)	0.353, −0.421	0.987, −0.867	0.307, −0.827	0.804, −0.648	0.813, −0.868

rhodium and iridium systems. The activated alkyne HC≡C−CO_2Me makes no significant difference in reaction rates of **1S** versus **1Se**, in contrast to a terminal alkyne with an alkyl group, where the reaction rate order is **1S** > > **1Se**. On the other hand, the 16*e* cobalt species **1S** and **1Se** are more reactive than the analogous 16*e* rhodium and iridium complexes, as revealed in the reactions with HC≡C−CO_2Me. This is reflected by generation of a C−B bond even at ambient temperature for 16*e* cobalt species, rather than a M−B bond, as occurred in rhodium and iridium complexes. These 16*e* cobalt compounds seem to be promising for various transformations with other reagents.

Experimental Section

General Procedures. *n*-Butyllithium (2.0 M in hexanes, Aldrich), *o*-carborane (Katchem, Czech), and methyl acetylene monocarboxylate (Alfa Aesar) were used as supplied. $CpCo(CO)I_2$[15] and 16*e* complexes $\{CpCo[E_2C_2(B_{10}H_{10})]\}$ (E = S, Se)[16] 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, THF, petroleum ether, and toluene were refluxed and distilled over sodium/benzophenone ketyl under nitrogen. CH_2Cl_2 was refluxed and distilled over CaH_2 under nitrogen. The NMR measurements were performed on a Bruker AC 500 spectrometer. Chemical shifts were given with respect to $CHCl_3/CDCl_3$ (δ ^1H = 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 region of 4000−400 cm^{-1}. The C and H microanalyses were carried out with a Perkin-Elmer 240C elemental analyzer. The mass spectra (MS) was recorded in a Micromass GC-TOF for EI-MS (70 eV).

Syntheses of 2S and 3S. HC≡C−CO_2Me (0.17 mL, 2.0 mmol) was added to the red solution of **1S** (66.0 mg, 0.2 mmol) in CH_2Cl_2 (20 mL), and the mixture was stirred for 24 h at ambient temperature to give a brown-red solution. After removal of solvent, the residue was chromatographed on TLC, and elution with CH_2Cl_2 gave **2S** and **3S**. **2S**: Red solid, yield 30.0 mg (30%), mp 176 °C dec. ^{1}H NMR ($CDCl_3$): δ 3.80 (s, 3H, OMe), 3.92 (s, 3H, OMe), 5.27 (s, 5H, Cp), 6.63 (s, 1H, Co−CH), 7.21 (s, 1H, CH). ^{13}C NMR ($CDCl_3$): δ 53.23, 53.63 (OMe), 90.13 (Cp), 94.61, 101.44 (carborane), 105.35 (S−C═*C*H), 128.65 (═CH−Co), 151.58 (S−C═), 155.52 (*C*═CH−Co), 165.34, 174.57 (C═O). ^{11}B NMR ($CDCl_3$): δ −10.3 (1B), −7.0 (3B), −4.9 (3B), −1.9 (3B). EI-MS (70 eV): *m*/*z* 498 (M$^+$, 10%). IR (KBr): ν (cm^{-1}) 2589 (B−H). Anal. Calcd (%) for $C_{15}H_{23}B_{10}Co_1O_4S_2$: C 36.14, H 4.65. Found: C 36.78,H 4.94. **3S**: Red solid, yield 30.0 mg (30%), mp 197 °C dec. ^{1}H NMR ($CDCl_3$): δ 3.78 (s, 6H, OMe), 5.35 (br, d, J = 15 Hz, 1H, ═CH−B), 5.38 (s, 5H, Cp), 6.30 (d, J = 15 Hz, 1H, ═CH). ^{13}C NMR ($CDCl_3$): δ 51.15 (OMe), 97.07 (carborane), 81.79 (Cp), 133.85 (═CH), 136.65 (br, ═CH–B), 166.99 (C═O). ^{11}B NMR ($CDCl_3$): δ −7.8 (3B), −6.4 (3B), −4.7 (4B). EI-MS (70 eV): *m*/*z* 498 (M$^+$, 5%). IR (KBr): ν (cm^{-1}) 2585 (B−H). Anal. Calcd (%) for $C_{15}H_{23}B_{10}Co_1O_4S_2$: C 36.14, H 4.65. Found: C 35.59, H 4.87.

Syntheses of 2Se, 4Se, and 5Se. HC≡C−CO_2Me (0.17 mL, 2.0 mmol) was added to the suspension of **1Se** (85.0 mg, 0.2 mmol) in CH_2Cl_2 (20 mL), and the mixture was stirred for 48 h at ambient temperature to give a green solution. After removal of solvent, the residue was chromatographed on TLC, and elution with CH_2Cl_2 gave **2Se**, **4Se** and **5Se**. **2Se**: Red solid, yield 6.0 mg (5%), mp 197 °C dec. ^{1}H NMR ($CDCl_3$): δ 3.86 (s, 3H, OMe), 3.94 (s, 3H, OMe), 5.13 (s, 1H, Co–CH), 5.25 (s, 5H, Cp), 5.48 (s, 1H, CH). ^{11}B NMR ($CDCl_3$): δ −8.0 (1B), −7.2 (3B), −5.4 (3B), −4.7 (3B). EI-MS (70 eV): *m*/*z* 592 (M$^+$, 4%). IR (KBr): ν (cm^{-1}) 2585 (B−H). Anal. Calcd (%) for $C_{15}H_{23}B_{10}Co_1O_4Se_2$: C 30.42, H 3.91. Found: C 29.66, H 3.56. **4Se**: Blue solid, yield 51.0 mg (50%), mp 190 °C dec. ^{1}H NMR ($CDCl_3$): δ 1.40 (br, d, J = 16 Hz, 1H, B–CH_2), 2.58 (br, d, J = 16 Hz, 1H, B−CH_2), 3.87 (s, 3H, OMe), 4.88 (s, 5H, Cp). ^{13}C NMR ($CDCl_3$): δ 31.17 (br, B−CH_2), 52.93 (OMe), 69.62, 86.77 (carborane), 84.66 (Cp), 89.48 (C−Se), 180.01 (C═O). ^{11}B NMR ($CDCl_3$): δ −11.3 (1B), −6.4 (1B), −5.5 (3B), −5.0 (4B), 4.3 (B–CH_2, 1B). EI-MS (70 eV): *m*/*z* 508 (M$^+$, 26%). IR (KBr): ν (cm^{-1}) 2579 (B−H). Anal. Calcd (%) for

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$C_{11}H_{19}B_{10}Co_1O_2Se_2$: C 26.00, H 2.18. Found: C 25.33, H 2.46. **5Se**: Blue solid, yield 12.0 mg (10%), mp 210 °C dec. ^{1}H NMR ($CDCl_3$): δ 1.43 (br, d, J = 16 Hz, 1H, B−CH_2), 2.56 (br, d, J = 16 Hz, 1H, B−CH_2), 3.83 (s, 3H, OMe), 3.84 (s, 3H, OMe), 4.81 (s, 5H, Cp), 6.31 (d, 1H, J = 15 Hz, =CH), 6.54 (br, d, 1H, J = 15 Hz, B−CH=). ^{13}C NMR ($CDCl_3$): δ 31.21 (br, B−CH_2), 52.61, 52.77 (OCH_3), 73.28, 90.02 (carborane), 84.05 (C–Se), 84.45 (Cp), 132.97 (=CH), 139.52 (br, B−CH=), 166.53, 180.23 (C=O). ^{11}B NMR ($CDCl_3$): δ −14.2 (1B), −13.1 (1B), −9.1 (2B), −8.3 (2B), −7.7 (2B), −5.9 (1B), 2.1 (B−CH_2, 1B). EI-MS (70 eV): m/z 592 (M^+, 3%). IR (KBr): ν (cm^{-1}) 2575 (B−H). Anal. Calcd (%) for $C_{15}H_{23}B_{10}Co_1O_4Se_2$: C 30.42, H 3.91. Found: C 29.97, H 3.58.

Reactions of 2 with HC≡C–CO_2Me in Toluene at 80 °C. HC≡C–CO_2Me (0.22 mL, 2 mmol) was added to the red solution of **2S** (50.0 mg, 0.1 mmol) or **2Se** (59.0 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, **2** remained and benzenetricarboxylates were the major products in the mixture.

X-ray Crystallography. Crystals suitable for X-ray analysis were obtained by slow evaporation of a solution in petroleum ether/dicloromethene. Diffraction data were collected on a Bruker SMART Apex II CCD diffractometer using graphite-monochromated Mo Kα (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.[17] The structures were solved by direct methods using the SHELXL-97 program.[18] 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.

Computational Details. Stationary points on the potential energy surfaces were calculated with the Gaussian03 package.[19] The UB3LYP hybrid density functional was employed for all of the DFT calculations. This functional is comprised of Becke's hybrid exchange functional[20] and the correlation functional of Lee, Yang, and Parr.[21] For cobalt and sulfur, the relativistic effective core potential (ECP)[22,23] was employed in all UB3LYP calculations. The basis set for Co was a modified LANL2DZ double-ζ basis set plus an f-type polarization function,[24] in which the two 4p functions of the standard LANL2DZ have been replaced by the optimized 4p functions from Couty and Hall,[25] and for sulfur, one d function with an exponent of 0.503[26] was added. For all other atoms a 6-31G(d, p) basis was employed. Full geometry optimizations have been carried out to obtain the structures of reactants and transition state. For each species, harmonic vibrational frequencies were calculated to obtain zero-point energies (ZPE) and verified whether it is a minimum or a transition state by the absence or presence a single imaginary frequency. Then the energies, enthalpies, and Gibbs free energies of the stationary points were calculated at 298 K.

Acknowledgment. Financial support by the National Natural Science Foundation of China (No. 20471017) is gratefully acknowledged.

Supporting Information Available: X-ray crystallographic files in CIF format for the structure determination of compounds **2S**, **2Se**, **3S**, **4Se**, and **5Se** are available free of charge via the Internet at http://pubs.acs.org.

OM7009864

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