Inorganic Chemistry
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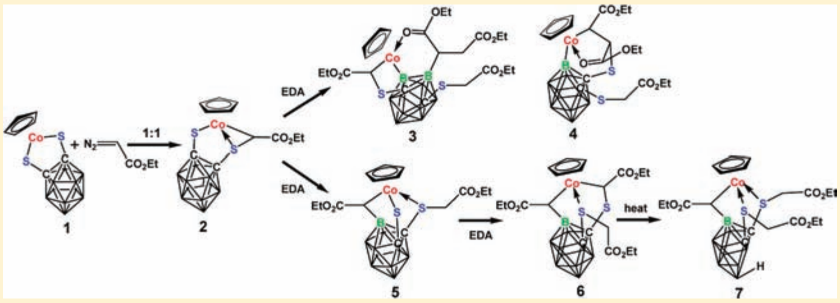
Cobalt-Mediated Selective B−H Activation and Formation of a Co−B Bond in the Reaction of the 16-Electron CpCo Half-Sandwich Complex Containing an *o*-Carborane-1,2-dithiolate Ligand with Ethyl Diazoacetate

Guifeng Liu, Jiurong Hu, Jialin Wen, Huimin Dai, Yizhi Li, and Hong Yan*

State Key Laboratory of Coordination Chemistry, School of Chemistry and Chemical Engineering, Nanjing University, Jiangsu 210093, China

S *Supporting Information*

ABSTRACT:



The reaction of the 16-electron half-sandwich complex $CpCo(S_2C_2B_{10}H_{10})$ (**1**; Cp = cyclopentadienyl) with ethyl diazoacetate (EDA) at ambient temperature leads to compounds $CpCo(S_2C_2B_{10}H_{10})(CHCO_2Et)$ (**2**), $CpCo(S_2C_2B_{10}H_8)(CHCO_2Et)(CH_2CO_2Et)[CH(CO_2Et)(CH_2CO_2Et)]$ (**3**), $CpCo(S_2C_2B_{10}H_9)(CH_2CO_2Et)(CHCO_2Et)_2$ (**4**), $CpCo(S_2C_2B_{10}H_9)(CHCO_2Et)(CH_2CO_2Et)$ (**5**), and $CpCo(S_2C_2B_{10}H_9)(CHCO_2Et)_2(CH_2CO_2Et)$ (**6**). In **2**, the EDA molecule has been inserted into one Co−S bond in **1** with the loss of N_2 to form an 18-electron compound containing a three-membered metallacyclic ring. In **3**, two B−H bonds of the carborane cage have been activated and the unusual B4−H bond activation leads to the formation of a stable Co−B bond. Two EDA molecules are inserted into the Co−B3 bond to generate an unexpected six-membered heterocyclic ring Co−B−B−C−C−O. In **4**, a stable Co−B bond is present as well but in the position B3/B6, and two EDA molecules are inserted into one Co−S bond to produce a five-membered heterocyclic ring Co−C−C−C−O. In **5**, one EDA is inserted into the Co−B bond with the formation of a C−B bond in the position B3/B6. One more EDA is inserted into the Co−S bond in **5** to generate **6**. Upon heating, **6** loses the BH vertex close to the two carbon atoms to lead to $CpCo(S_2C_2B_9H_9)(CHCO_2Et)(CH_2CO_2Et)_2$ (**7**) containing a *nido*-C_2B_9 unit. All of the new compounds **2**−**7** were characterized by NMR spectroscopy (^1H, ^{11}B, and ^{13}C), mass spectrometry, IR spectroscopy, and elemental analysis, and their solid-state structures were further characterized by X-ray structural analysis.

■ INTRODUCTION

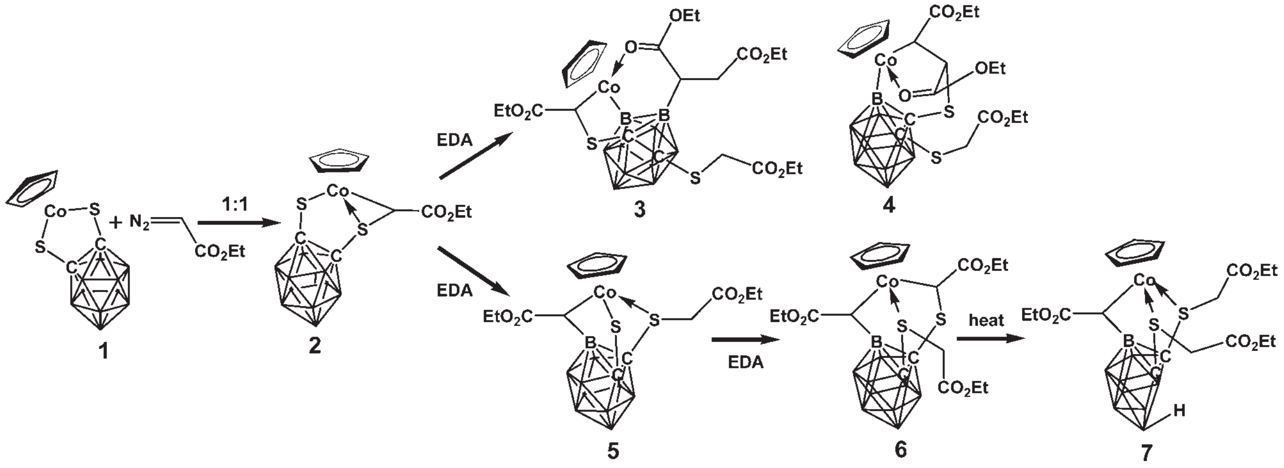
The mononuclear 16-electron half-sandwich complexes $Cp^{\#}M(E_2C_2B_{10}H_{10})$ ($Cp^{\#}$ = Cp, Cp*; M = Co, Rh, Ir; E = S, Se) and (*p*-cymene)$M(S_2C_2B_{10}H_{10})$ (M = Ru, Os) possessing an *o*-carborane-1,2-dichalcogenolate ligand have been described extensively as a kind of attractive starting material: they could serve as precursors for the synthesis of multimetal clusters including heterometallic clusters with metal−metal bonds;[1] they could react with Lewis bases such as NH_3, CO, and N-heterocyclic ligands to construct their 18-electron congeners;[2,3] they could react with selected alkynes to generate novel compounds that result from insertion of alkyne into a M−E bond, followed by B−H activation, M−B bond formation, and further chemical transformations.[4−12] Also, our previous results have demonstrated that the cobalt species $CpCo(S_2C_2B_{10}H_{10})$ (**1**) is more reactive than its analogous rhodium and iridium species if an alkyne is used as a substrate.[4−6]

On the other hand, diazo compounds have been extensively utilized in organic synthesis on the basis of their diverse reactivities.[13] In particular, they can be readily decomposed by transition-metal complexes to generate Fischer-type metal carbene intermediates, which can subsequently undergo various chemical transformations, for instance, X−H (X = C, O, S, N, etc.) insertion,[14] cyclopropanation,[15] and ylide formation.[16] On the basis of the electron deficiency at the metal center, the reactive

Received: February 17, 2011
Published: March 28, 2011

dx.doi.org/10.1021/ic200333q

Scheme 1. Reaction of 1 with EDA



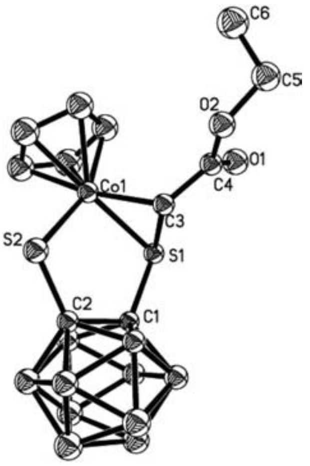


Figure 1. Molecular structure of **2**. Ellipsoids show 30% probability levels, and some of the hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Co1−C3 1.968(3), Co1−S1 2.1758(9), Co1−S2 2.2626(10), C1−C2 1.651(4), C1−S1 1.789(3), C2−S2 1.783(3), C3−S1 1.759(3), C3−C4 1.482(4); C1−S1−Co1 104.78(10), C1−C2−S2 116.52(19), C2−C1−S1 117.72(19), C2−S2−Co1 103.04(10), C3−Co1−S1 49.94(8), C3−S1−C1 107.68(13), C4−C3−S1 112.8(2), C4−C3−Co1 119.7(2), S1−C3−Co1 71.18(11).

metal−sulfur bonds, the potentially reactive B−H bonds at carborane of the 16-electron half-sandwich compound **1**, we expect that its reaction with ethyl diazoacetate (EDA) would produce more chemical transformations. Herein, we report on the six novel products (**2**−**7**).

■ RESULTS AND DISCUSSION

Reaction of 1 with EDA. The 16-electron complex **1** immediately reacts with EDA in the molar ratio 1:1 at ambient temperature to lead to **2** in a yield of 78%, as shown in Scheme 1.

The structure of **2** was determined by single-crystal X-ray analysis (Figure 1). It shows an insertion of EDA after the loss of N_2 into one Co−S bond to give rise to an 18-electron compound. The newly generated three-membered ring (Co−S−C) shares one Co−S bond with the existing five-membered metallacyclic ring (Co−S−C−C−S), which is no longer planar after the ligand insertion. The NMR data of the ^{1}H singlet at 4.38 ppm and the ^{13}C signal at 45.4 ppm correspond to the newly formed S−C*H*−Co unit. Two species with a similar structural type have been seen, but no further reactivity was described.[17] However, here **2** still has reactivity toward EDA.

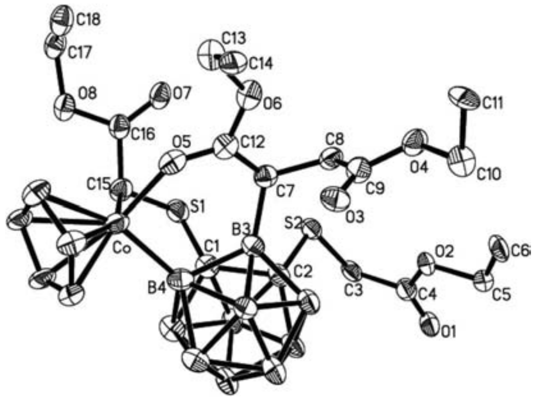


Figure 2. Molecular structure of **3**. Ellipsoids show 30% probability levels, and some of the hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Co−B4 1.975(5), Co−O5 1.948(2), Co−C15 2.035(4), C1−C2 1.714(5), C1−S1 1.760(4), C2−S2 1.775(4), C1−B3 1.793(5), C1−B4 1.699(6), C2−B3 1.758(6), C3−S2 1.789(4), C3−C4 1.516(5), C7−C8 1.528(5), C7−B3 1.596(6), C7−C12 1.494(5), C15−S1 1.815(4), C12−O5 1.229(4), B3−B4 1.814(6); C1−B4−Co 115.1(3), C2−S2−C3 103.81(18), S1−C15−Co 119.6(2), B3−B4−Co 113.8(3), B4−C1−S1 116.5(3), B4−Co−C15 88.95(17), C7−B3−B4 123.5(3), O5−Co−B4 94.52(15), O5−C12−C7 126.5(3), C12−O5−Co 136.0(3), C12−C7−C8 112.0(3), C12−C7−B3 112.8(3).

Reaction of 2 with Excess EDA. **2** reacts with excess EDA at ambient temperature to give rise to **3**−**6** in the yields of 23%, 6%, 4%, and 45%, respectively, as shown in Scheme 1.

As seen in Figure 2, the solid-state structure of **3** shows a unique six-membered metallacyclic ring Co−B−B−C−C−O, which is generated by the insertion of two EDA molecules into the Co−B3 bond accompanied by carbonyl coordination to metal (O → Co). Here two adjacent B−H bond activations at the B3/B4 sites of the carborane have occurred. Also, the five-membered

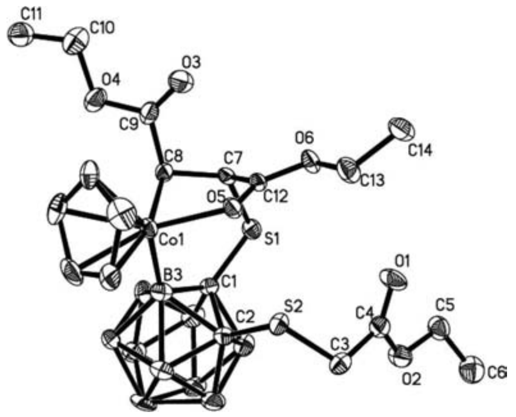


Figure 3. Molecular structure of **4**. Ellipsoids show 30% probability levels, and some of the hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Co1−B3 2.008(4), Co1−O5 1.977(2), Co1−C8 2.014(3), C1−C2 1.709(5), C1−S1 1.778(3), C2−S2 1.762(3), C3−S2 1.806(4), C3−C4 1.502(5), C7−S1 1.811(3), C7−C8 1.515(4), C7−C12 1.523(4), C8−C9 1.475(5), C12−O5 1.234(4); C1−B3−Co1 123.8(2), C1−S1−C7 105.17(15), B3−Co1−C8 89.22(16), C7−C8−Co1 105.4(2), C8−C7−C12 105.4(3), C9−C8−Co1 109.6(2), O5−C12−C7 118.8(3), O5−Co1−B3 101.60(15), O5−Co1−C8 82.62(11).

metallacyclic ring Co−B−C−S−C is nearly planar and is generated by one EDA molecule insertion into the Co−S bond. Both heterocyclic rings share one Co−B4 bond. Another EDA molecule is used to form a sulfide ylide. Such a solid-state structure is consistent with the solution structure, as revealed by spectroscopic data. The ^{1}H NMR spectrum indicates a singlet at 5.53 ppm assigned to the S−C*H*−Co unit; the two doublets at 3.63 and 3.69 ppm with $J = 16$ Hz are assigned to the S−CH_2 unit of the sulfide ylide; the double of doublets at 2.57 ppm is assigned to the B−C*H*−CH_2 unit; the two double of doublets at 3.03 and 2.81 ppm are assigned to the B−CH−CH_2 unit with $J = 17.5$ Hz. In the ^{13}C NMR spectrum, the characteristic broad resonance at 28.6 ppm is indicative of a carbon atom connected to boron in the B−CH−CH_2 unit, the signal at 31.0 ppm is assigned to the S−CH−Co group, and the signals at 34.2 and 38.4 ppm are assigned to B−CH−CH_2 and S−CH_2 units, respectively. All of the assignments are confirmed by ^{13}C/^{1}H HETCOR (HMQC) experiments. The mass spectroscopy shows the molecular ion peak.

It is noted that in **3** a stable Co−B bond is present. This is the first example in the reaction system using the 16-electron half-sandwich complexes Cp$^\#$M($E_2C_2B_{10}H_{10}$) (Cp$^\#$ = Cp, Cp*; M = Co, Rh, Ir; E = S, Se) and (*p*-cymene)M($S_2C_2B_{10}H_{10}$) (M = Ru, Os) bearing an *o*-carborane-1,2-dichalcogenolate ligand as starting materials,[4−12] even though stable Co−B bonds are generally observed in species such as cobaltabisdicarbollides,[18] cobaltacarboranes,[19] cobaltaboranes,[20] dinuclear cobalt complexes bridged by nonsubstituted borylene−trimethylphosphine,[21] and cobalt borylene complexes.[22] In particular, the selective B−H activation at the B4 site and the Co−B bond formation have occurred as readily as in the position of B3/B6. In sharp contrast, previous studies demonstrated that metal-induced B−H activation and the formation of the M−B bond (M = Rh, Ir, Ru, Os) were always observed in the positions of B3/B6.[7−10] Thus, in **3**, the formation of the Co−B bond at the site B4 is unusual. Additionally, **3** is also the first example to see a direct insertion in a M−B bond, different from the cleavage of a M−B bond and formation of a C−B bond as reported in the reaction system with alkynes.[4−12]

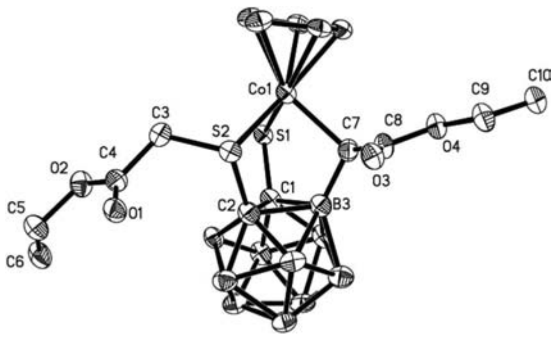


Figure 4. Molecular structure of **5**. Ellipsoids show 30% probability levels, and some of the hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Co1−S1 2.259(12), Co1−S2 2.2287(13), Co1−C7 2.048(5), C1−C2 1.718(6), C1−S1 1.763(5), C2−S2 1.784(5), C3−S2 1.815(5), C3−C4 1.531(7), C7−B3 1.526(7); C1−S1−Co1 96.09(15), C2−S2−Co1 98.36(16), B3−C7−Co1 105.6(3), C7−Co1−S2 88.28(14), C7−Co1−S1 87.31(14), S2−Co1−S1 90.19(5).

The core structure of **4** consists of five-membered (Co−O−C−C−C) and six-membered (Co−B−C−S−C−C) metallacyclic rings (Figure 3). The former is generated by the insertion of two EDA molecules into one Co−S bond followed by O → Co formation. A stable Co−B bond is present as well, but the B−H activation occurs in the position of B3. It appears that the hydrogen atom of the activated B−H bond might be immigrated to the initially inserted EDA unit in **2** to create the sulfide ylide. The spectroscopic data support its solid-state structure. For instance, the ^{1}H NMR spectrum shows two singlets at 3.60 and 3.02 ppm assigned to C*H*−Co and S−C*H* units, respectively. These two adjacent hydrogen atoms do not show any coupling because the two C−H bonds are close to perpendicular, as reflected by its solid-state structure. The two doublets at 3.63 and 3.76 ppm are assigned to the alkyl group of the S−CH_2 unit with $J = 16$ Hz. The ^{13}C signals at 50.3 and 40.1 ppm are respectively assigned to the S−CH and S−CH_2 units, and the signal at 22.4 ppm is assigned to the CH−Co group, as further confirmed by ^{13}C/^{1}H HETCOR (HMQC) experiments. Mass spectroscopy shows the molecular ion peak.

Interestingly, different from one EDA insertion into a Co−S bond in **2**, the insertion of two EDA molecules into one Co−S bond happens in a head-to-head mode in **4**. This is analogous to the insertion of 2-fold alkyne into one of the two Co−S bonds in the compounds Cp$^\#$M($E_2C_2B_{10}H_{10}$) (Cp$^\#$ = Cp, Cp*; M = Co, Rh, Ir; E = S, Se).[5−12]

Figure 4 shows that two EDA molecules are involved in the generation of **5**. One is inserted into the Co−B bond to generate a B−C bond, and the other is the one that was originally inserted in **2**. As assumed in **4**, the hydrogen atom of the activated B−H bond might be transferred to the initially inserted EDA unit in **2** to yield the sulfide ylide, but here it is further coordinated to metal to meet the 18-electron configuration. ^{1}H NMR spectrum displays a singlet at 3.59 ppm assigned to the B−C*H* unit, and the two doublets at 3.87 and 4.37 ppm are assigned to the S−CH_2 unit. The ^{13}C signals at 8.1 (broad) and 42.8 ppm are assigned to B−CH and S−CH_2, respectively.

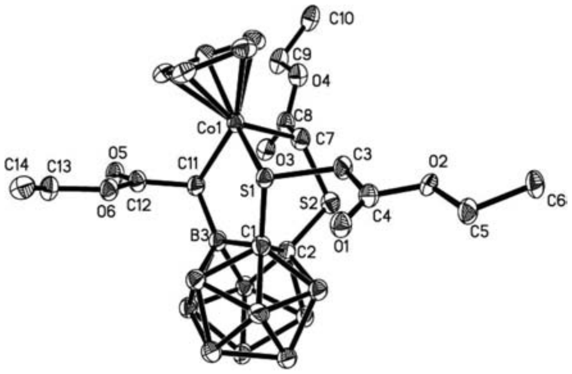


Figure 5. Molecular structure of **6**. Ellipsoids show 30% probability levels, and some of the hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Co1−S1 2.2297(6), Co1−C7 2.054(2), Co1−C11 2.067(3), C1−C2 1.657(3), C1−S1 1.772(2), C2−S2 1.759(2), C3−C4 1.531(3), C3−S1 1.814(2), C7−C8 1.511(3), C7−S2 1.781(3), C11−C12 1.460(3), C11−B3 1.541(4); C2−S2−C7 109.06(12), S2−C7−Co1 120.44(13), C3−S1−Co1 109.18(8), B3−C11−Co1 108.98(17), C7−Co1−C11 88.30(11), C7−Co1−S1 95.51(8), C11−B3−C2 117.8(2), C11−B3−C1 120.0(2).

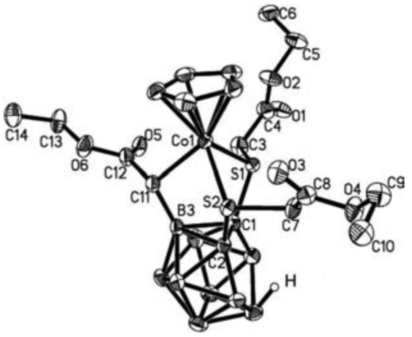


Figure 6. Molecular structure of **7**. Ellipsoids show 30% probability levels, and some of the hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Co1−S1 2.2357(12), Co1−S2 2.2257(12), Co1−C11 2.076(4), C1−C2 1.562(6), C1−S1 1.806(4), C2−S2 1.784(4), C3−C4 1.480(6), C3−S1 1.822(5), C7−C8 1.509(6), C7−S2 1.813(4), C11−C12 1.492(6), C11−B3 1.555(7); C1−S1−C3 100.0(2), C1−S1−Co1 98.59(14), C2−S2−C7 100.2(2), C2−S2−Co1 98.06(14), C3−S1−Co1 116.42(17), S2−Co1−S1 84.77(4), B3−C11−Co1 105.9(3), B3−C1−S1 109.4(3), B3−C2−S2 106.5(3), C7−S2−Co1 111.12(17), C11−Co1−S2 83.64(12), C11−Co1−S1 92.01(13).

Different from **3** and **4**, **5** still has one reactive Co−S bond, and the sulfur atom of the newly generated sulfide ylide unit is coordinated to metal rather than in an idle style. As occurred in **3**, the EDA insertion in the Co−B bond is observed again. It is well-known that transition-metal boryl (M−B) complexes played an important role as reactive intermediates.[23] In carborane chemistry, the Xie group reported numerous samples concerning the insertion of alkynes into the M−C bond of the carborane cage,[24] and very recently the alkyne insertion into the Ni−B bond of carborane in the catalytic preparation of C,B-functionalization of carboranes was proposed by this group;[25] however, no intermediates could be isolated. In our reaction system, the species not only with a stable Co−B bond but with EDA insertion into a Co−B bond can be isolated as well.

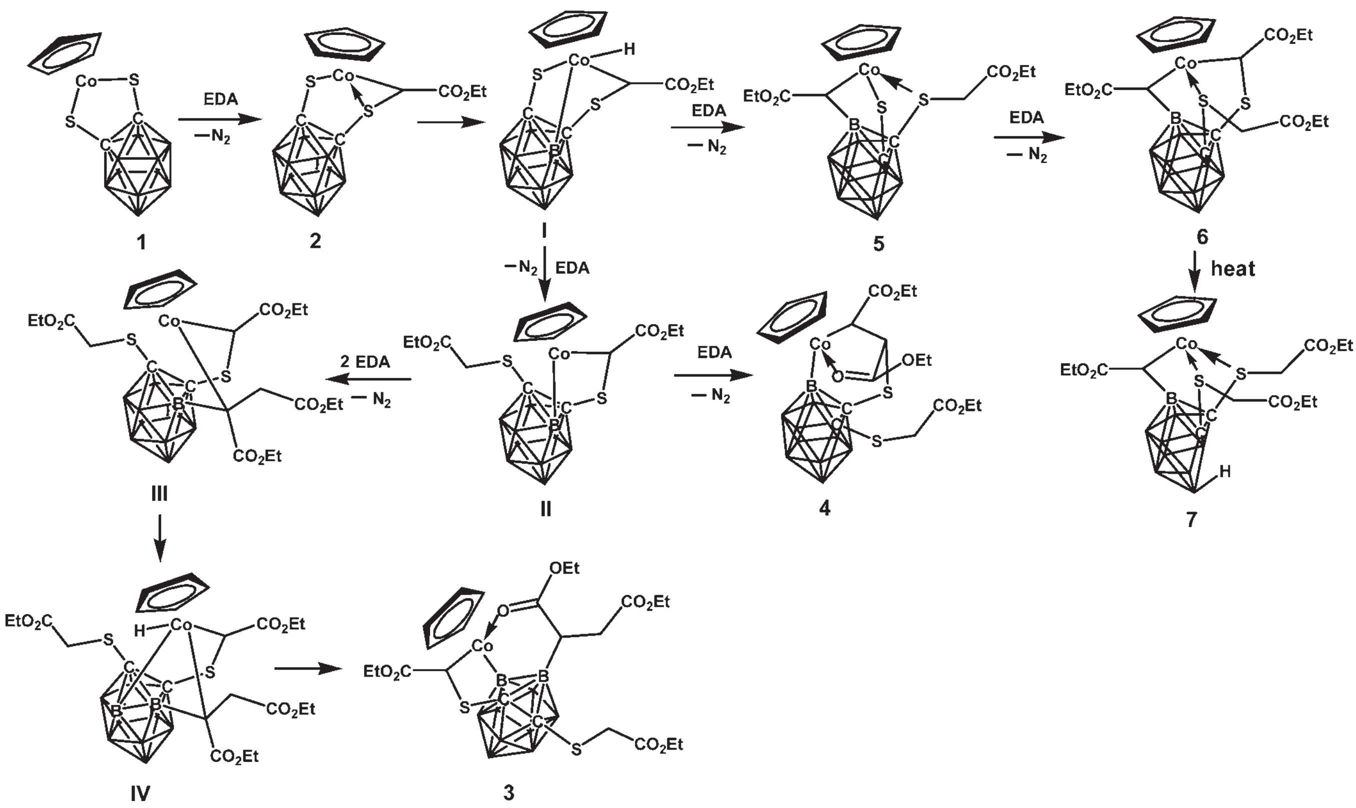
In a comparison to **5**, the solid-state structure of **6**, as shown in Figure 5, displays one more EDA insertion into the Co−S bond in **5**. The NMR data show the resonances at 4.84 (^{1}H) and 29.1 (^{13}C) ppm for the new insertion unit Co−*CH*−S. The singlet at 2.23 ppm is assigned to the B−C*H* unit, and the two doublets at 4.09 and 4.71 ppm are ascribed to the alkyl group of the S−C*H*$_2$ unit with *J* = 16 Hz. These ^{1}H data demonstrate significant shifts, in contrast to those in **5**. However, the ^{13}C signal at 41.1 ppm corresponding to S−*C*H$_2$ and the broad signal at 8.6 ppm assigned to B−*C*H are close to those in **5**. One more EDA addition is also confirmed by the molecular ion peak in mass spectroscopy. Thus, both the solution and solid-state structures are consistent.

Transformation of 6 at a Higher Temperature. Upon heating in boiling CHCl$_3$, **6** can readily lose one apex BH and rearrange to **7** (Scheme 1). Its solid-state structure (Figure 6) demonstrates a *nido*-C$_2$B$_9$ unit and the coordination of two sulfide ylide units in order to meet an 18-electron configuration at the metal center. The NMR data support its solid-state structure. The characteristic well-separated ^{11}B signals in the range from +4.8 to −33.4 ppm present a sharp contrast with those of the *closo*-*o*-carborane derivatives,[4−12] indicating the lowered symmetry of the carborane cage. The broad singlet at −2.26 ppm in the ^{1}H NMR spectrum is the feature of the face-hydride binding mode on three boron atoms as supported by the solid-state structure. The four separate ^{1}H doublets at 3.80, 3.87, 3.94, and 5.27 ppm with *J* = 16 Hz and the two ^{13}C signals at 39.6 and 41.8 ppm are indicative of the two S−*C*H$_2$ units. Compared to **6**, the loss of one BH vertex and cleavage of the Co−C bond to form the S−Co bond in **7** lead to significant effects on the ^{1}H and ^{13}C data of the existing B−C*H* unit from 2.23 and 8.6 ppm in **6** to 2.87 and 11.4 ppm in **7**.

Mechanistic Implications. The mechanistic suggestions for the generation of **2**−**7** are assumed and shown in Scheme 2. The first step is the EDA addition into one Co−S bond to generate the isolable species **2**, which is analogous to alkyne addition to the 16-electron compounds published by our group.[4−12] In **2**, the metal center could come close to the carborane cage to activate the B−H bond to generate intermediate **I**. One EDA insertion into the Co−B bond followed by hydride transfer to the inserted EDA could lead to **5**. If one extra EDA is inserted into the Co−S bond in **5**, **6** could be generated, as confirmed by experimental evidence. **6** can be converted to **7** if heated. However, one competitive pathway is present, that is, one EDA could be alternatively inserted into Co−S in **I** to give rise to **II**. After this, if one more EDA is inserted into the Co−C bond in **II**, **4** could be produced; alternatively, if two EDA molecules are inserted into the Co−B bond in **II**, **III** could be formed. The skeleton in **III** might be more flexible; thus, the metal center could approach the carborane cage to activate the adjacent B−H bond at the B4 site and, as a result, yield a Co−B bond, as shown in **IV**, which could give rise to **3** after hydride transfer.

CONCLUSION

This work demonstrates an unexpected reactivity of the 16-electron compound **1** toward EDA that leads to novel chemical transformations. If the molar ratio 1:1 is used, **2** is isolated as the major product. As the early precursor, it further reacts with excess EDA in two competitive pathways to produce **3**/**4** and **5**/**6**, respectively. **6** is converted to **7** after heating. In this reaction, stepwise and selective B−H activation at carborane has occurred, Scheme 2. Proposed Mechanism for the Formation of 2−7



and for the first time, B−H activation at the B4 site has taken place as well but coming after B−H activation at the B3 site. Furthermore, both stable Co−B bonds and EDA insertion into Co−B bonds are observed for the first time. In sharp contrast, in this reaction system stable M−B bonds were reported only for Rh, Ir, Ru, and Os, and no insertion into these M−B bonds was described. As a reactive species, EDA insertion into a Co−S bond starts a fascinating reaction followed by metal-induced B−H activation, Co−B formation, and EDA reinsertion into Co−B, Co−S, and Co−C, which eventually lead to a series of unpredictable products. This study greatly enriches the reaction chemistry of both 16-electron starting compounds and diazoacetates.

■ EXPERIMENTAL SECTION

General Procedures. *n*-BuLi (2.0 M in hexanes, Aldrich) was used as supplied. $CpCo(CO)I_2$,[26] $CpCoS_2C_2B_{10}H_{10}$,[27] and ethyl diazoacetate (EDA)[28] were prepared by literature procedures. All reactions were carried out under argon by using standard Schlenk techniques. All solvents were dried and deoxygenated prior to use. Diethyl ether, tetrahydrofuran, and petroleum ether were refluxed and distilled over sodium/benzophenone under nitrogen. CH_2Cl_2 was distilled over CaH_2 under nitrogen. The NMR measurements were performed on a Bruker DRX 500 spectrometer. Chemical shifts were given with respect to $CHCl_3/CDCl_3$ (δ ^1H = 7.24 ppm; δ ^{13}C = 77.0 ppm) and external $Et_2O \cdot BF_3$ (δ ^{11}B = 0 ppm). 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 an Elementar Vario EL III elemental analyzer. Mass spectra were recorded in a Micromass time-of-flight gas chromatograph for electron impact mass spectrometry (70 eV).

Synthesis of 2. To a solution of **1** (132.0 mg, 0.4 mmol) in CH_2Cl_2 (20 mL) was added using a syringe ethyl diazoethanoate (0.04 mL, 0.4 mmol) in 4 mL of CH_2Cl_2. The mixture was stirred for 5 min at ambient temperature. The color changed from red to blue. After removal of solvent, the residue was chromatographed on silica, and elution with petroleum ether/CH_2Cl_2 gave **2** in a yield of 128 mg, 78%.

2: blue solid. Mp: 156 °C. ^1H NMR ($CDCl_3$): δ 1.38 (t, 3H, J = 7.0 Hz, CH_3), 4.26 (q, 2H, J = 7.0 Hz, $O{-}CH_2$), 4.38 (s, 1H, S−CH−Co), 5.02 (s, 5H, Cp). $^{11}B\{^1H\}$ NMR ($CDCl_3$): δ −1.2 (2B), −2.2 (3B), −5.0 (1B), −6.6 (2B), −8.1 (2B). ^{13}C NMR ($CDCl_3$): δ 14.4 (CH_3), 45.4 (S−CH−Co), 61.9 ($O{-}CH_2$), 84.9 (Cp), 88.5, 92.9 (carborane), 174.5 (C=O). MS (70 eV): m/z 416.1 (M^+, 33%). IR (KBr): ν 1694 (C=O), 2587 (B−H) cm^{-1}. Elem anal. Calcd for $C_{11}H_{21}B_{10}CoO_2S_2$: C, 31.72; H, 5.08. Found: C, 31.46; H, 4.93.

Syntheses of 3−6. *Method 1*. Ethyl diazoethanoate (0.2 mL, 2 mmol) was added to the blue solution of **2** (83.4 mg, 0.2 mmol) in CH_2Cl_2 (20 mL). The mixture was stirred for 6 h at ambient temperature. The color gradually turned from blue to deep purple. After removal of the solvent, the residue was chromatographed on silica, and elution with petroleum ether/ethyl acetate gave **3** (31 mg, 23%), **4** (7 mg, 6%), **5** (4 mg, 4%), and **6** (52.9 mg, 45%).

Method 2. Ethyl diazoethanoate (0.2 mL, 2 mmol) was added to the red solution of complex **1** (66 mg, 0.2 mmol) in CH_2Cl_2 (20 mL), the color is changed immediately to blue and then gradually to deep purple. After 6 h the solvent was removed and the resultant residue was chromatographed on silica. Elution with petroleum ether/ethyl acetate gave **3** (28 mg, 20.7%), **4** (8 mg, 6.8%), **5** (4 mg, 4%) and **6** (51.5 mg, 43.8%).

3: green solid. Mp: 121 °C. ^1H NMR ($CDCl_3$): δ 1.21 (t, 3H, J = 7.0 Hz, CH_3), 1.24 (t, 3H, J = 7.0 Hz, CH_3), 1.29 (t, 3H, J = 7.0 Hz, CH_3), 1.40 (t, 3H, J = 7.0 Hz, CH_3), 2.57 (dd, 1H, J_1 = 4.5 Hz, J_2 = 6 Hz, B−CH−CH_2), 2.81 (dd, 1H, J_1 = 6 Hz, J_2 = 17.5 Hz, B−CH−CH_2),

Table 1. Crystallographic Data and Structural Refinement Details of Compounds 2−7

	2	3	4	5	6	7
formula	$C_{11}H_{21}B_{10}CoO_2S_2$	$2(C_{23}H_{39}B_{10}CoO_8S_2)\cdot CH_2Cl_2\cdot H_2O$	$C_{19}H_{33}B_{10}CoO_6S_2$	$C_{15}H_{27}B_{10}CoO_4S_2$	$2(C_{19}H_{33}B_{10}CoO_6S_2)\cdot H_2O$	$C_{19}H_{34}B_9CoO_6S_2$
cryst size (mm)	0.28 × 0.23 × 0.22	0.13 × 0.12 × 0.10	0.28 × 0.22 × 0.20	0.28 × 0.24 × 0.22	0.23 × 0.21 × 0.18	0.30 × 0.26 × 0.24
fw	416.43	1452.33	588.60	502.52	1195.22	578.80
temperature (K)	291(2)	291(2)	291(2)	291(2)	291(2)	293(2)
cryst syst	monoclinic	orthorhombic	triclinic	triclinic	monoclinic	orthorhombic
space group	*P*2(1)/*n*	*Pbca*	$P\bar{1}$	$P\bar{1}$	*P*2(1)/*n*	*Pbca*
a (Å)	13.098(3)	16.0580(17)	11.0279(11)	10.601(2)	20.301(2)	10.1943(13)
b (Å)	16.643(4)	13.4281(15)	11.9237(11)	10.875(2)	14.401(4)	16.673(2)
c (Å)	18.050(4)	33.516(4)	12.4112(12)	11.161(3)	21.577(2)	32.4719(12)
α (deg)	90.00	90.00	83.1470(10)	80.060(2)	90.00	90.00
β (deg)	96.439(3)	90.00	69.0500(10)	84.133(2)	102.193(3)	90.00
γ (deg)	90.00	90.00	67.7690(10)	70.847(3)	90.00	90.00
V ($Å^3$)	3909.8(16)	7227.1(13)	1410.6(2)	1195.8(4)	6165.5(18)	5519.3(10)
Z	8	4	2	2	4	8
ρ_{calcd} ($g\cdot cm^{-3}$)	1.415	1.335	1.386	1.396	1.288	1.393
abs coeff (mm^{-1})	1.094	0.707	0.790	0.913	0.725	0.807
F	1696	3008	608	516	2472	2400
θ range (deg)	1.67−26.00	1.76−26.00	1.85−26.00	2.00−26.00	1.71−26.00	2.36−26.00
reflns collected	21 012 [*R*(int) = 0.0402]	37 732 [*R*(int) = 0.0834]	7769 [*R*(int) = 0.0299]	6593 [*R*(int) = 0.0319]	32 566 [*R*(int) = 0.0259]	28 415 [*R*(int) = 0.0892]
indep reflns	7655	7104	5442	4610	12 072	5418
reflns obsd [$I > 2\sigma(I)$]	5514	4506	3746	3268	10 686	3376
data/restraints/param	7655/0/471	7104/31/428	5442/0/346	4610/0/291	12 072/0/709	5418/0/351
GOF	1.059	1.035	1.022	1.087	1.145	1.012
R1/R2 [$I > 2\sigma(I)$]	0.0502/0.1108	0.0583/0.1300	0.0489/0.1103	0.0624/0.1340	0.0384/0.0873	0.0614/0.1421
R1/R2 (all data)	0.0660/0.1140	0.0915/0.1379	0.0704/0.1173	0.0838/0.1389	0.0449/0.0893	0.0926/0.1511
largest peak/hole ($e\cdot Å^{-3}$)	0.259/−0.442	0.229/−0.323	0.367/−0.294	0.589/−0.906	0.173/−0.222	0.570/−0.778

3.03 (dd, 1H, J_1 = 4.5 Hz, J_2 = 17.5 Hz, B−CH−CH_2), 3.63 (d, 1H, *J* = 16 Hz, S−CH_2), 3.69 (d, 1H, *J* = 16 Hz, S−CH_2), 4.02 (q, 2H, *J* = 7.0 Hz, O−CH_2), 4.15 (q, 2H, *J* = 7.0 Hz, O−CH_2), 4.21 (q, 2H, *J* = 7.0 Hz, O−CH_2), 4.24 (q, 2H, *J* = 7.0 Hz, O−CH_2), 4.75 (s, 5H, Cp), 5.53 (s, 1H, S−CH−Co). $^{11}B\{^1H\}$NMR ($CDCl_3$): *δ* 8.2 (B−C, 1B), 2.1 (1B), 0.35 (1B), −2.3 (3B), −5.1 (1B), −6.5 (2B), −10.8 (B−Co, 1B). ^{13}C NMR ($CDCl_3$): *δ* 13.5, 13.9, 14.1, 14.7 (CH_3), 28.6 (br, B−CH−CH_2), 31.0 (CH−Co), 34.2 (B−CH−CH_2), 38.4 (S−CH_2), 59.8, 60.4, 62.1, 63.4, (O−CH_2), 85.5 (Cp), 80.9, 103.0 (carborane), 167.0, 171.3, 180.2, 183.3 (C=O). MS (70 eV): *m*/*z* 674.1(M^+, 10%). IR (KBr): *ν* 1648, 1733 (C=O), 2574 (B−H) cm^{-1}. Elem anal. Calcd for $C_{23}H_{39}B_{10}CoO_8S_2\cdot 0.5CH_2Cl_2\cdot 0.5H_2O$: C, 38.87; H, 5.69. Found: C, 38.60; H, 5.56. **4**: green solid. Mp: 169 °C. ^1H NMR: *δ* 1.22 (t, 3H, *J* = 7.0 Hz, CH_3), 1.25 (t, 3H, *J* = 7.0 Hz, CH_3), 1.40 (t, 3H, *J* = 7.0 Hz, CH_3), 3.02 (s, 1H, S−CH), 3.60 (s, 1H, CH−Co), 3.63 (d, 1H, *J* = 16 Hz, S−CH_2), 3.76 (d, 1H, *J* = 16 Hz, S−CH_2), 4.00 (q, 2H, *J* = 7.0 Hz, O−CH_2), 4.34 (q, 2H, *J* = 7.0 Hz, O−CH_2), 4.38 (q, 2H, *J* = 7.0 Hz, O−CH_2), 4.86 (s, 5H, Cp). $^{11}B\{^1H\}$ NMR ($CDCl_3$): *δ* 1.3 (3B), −0.8 (3B), −2.7 (1B), −4.6 (2B), −8.8 (B−Co, 1B). ^{13}C NMR ($CDCl_3$): *δ* 13.6, 14.1, 14.8 (CH_3), 22.4 (CH−Co), 40.1 (S−CH_2), 50.3 (S−CH), 59.7, 65.4, 61.9 (O−CH_2), 86.4 (Cp), 80.6, 87.5 (carborane), 165.2, 185.1, 186.5 (C=O). MS (70 eV): *m*/*z* 588.2 (M^+, 31%). IR (KBr): *ν* 1638, 1733 (C=O), 2572 (B−H) cm^{-1}. Elem anal. Calcd for $C_{19}H_{33}B_{10}CoO_6S_2$: C, 38.77; H, 5.65. Found: C, 38.49; H, 5.72. **5**: purple solid. Mp: 143 °C. ^1H NMR ($CDCl_3$): *δ* 1.40 (t, 3H, *J* = 7.0 Hz, CH_3), 1.41 (t, 3H, *J* = 7.0 Hz, CH_3), 3.59 (s, 1H, B−CH), 3.87 (d, 1H, *J* = 16 Hz, S−CH_2), 4.37 (d, 1H, *J* = 16 Hz, S−CH_2), 4.28 (q, 2H, *J* = 7.0 Hz, O−CH_2), 4.35 (q, 2H, *J* = 7.0 Hz, O−CH_2), 4.98 (s, 5H, Cp). $^{11}B\{^1H\}$ NMR ($CDCl_3$): *δ* 8.1 (B−C, 1B), 2.6 (2B), 0.0 (1B), −2.5 (1B), −6.6 (2B), −11.4 (2B), −13.7 (1B). ^{13}C NMR ($CDCl_3$): *δ* 8.1 (br, B−CH), 14.1, 14.8 (CH_3), 42.8 (S−CH_2), 59.9, 63.1 (O−CH_2), 84.3 (Cp), 92.2, 97.6 (carborane), 166.0, 182.2 (C=O). MS (70 eV): *m*/*z* 502.1 (M^+, 39%). IR (KBr): *ν* 1653, 1725 (C=O), 2561 (B−H) cm^{-1}. Elem anal. Calcd for $C_{15}H_{27}B_{10}CoO_4S_2$: C, 35.85; H, 5.42. Found: C, 35.65; H, 5.33. **6**: purple solid. Mp: 166 °C. ^1H NMR ($CDCl_3$): *δ* 1.37 (t, 3H, *J* = 7.0 Hz, CH_3), 1.38 (t, 3H, *J* = 7.0 Hz, CH_3), 1.39 (t, 3H, *J* = 7.0 Hz, CH_3), 2.23 (s, 1H, B−CH), 4.09 (d, 1H, *J* = 16 Hz, S−CH_2), 4.16 (q, 2H, *J* = 7.0 Hz, O−CH_2), 4.27 (q, 2H, *J* = 7.0 Hz, O−CH_2), 4.33 (q, 2H, *J* = 7.0 Hz, O−CH_2), 4.71 (d, 1H, *J* = 16 Hz, S−CH_2), 4.84 (s, 1H, Co−CH−S), 4.87 (s, 5H, Cp). $^{11}B\{^1H\}$ NMR ($CDCl_3$): *δ* 10.8 (B−C, 1B), 0.4 (1B), −0.6 (2B), −4.9 (1B), −8.6 (3B), −12.6 (2B). ^{13}C NMR ($CDCl_3$): *δ* 8.6 (br, B−CH), 14.1, 14.6, 14.8 (CH_3), 29.1 (S−CH), 41.1 (S−CH_2), 59.7, 60.7, 62.6 (O−CH_2), 78.2, 83.2 (carborane), 88.1 (Cp), 166.3, 181.3, 184.5 (C=O). MS (70 eV): *m*/*z* 588.1 (M^+, 12%). IR (KBr): *ν* 1689, 1735 (C=O), 2581 (B−H) cm^{-1}. Elem anal. Calcd for $C_{19}H_{33}B_{10}CoO_6S_2\cdot 0.5H_2O$: C, 38.18; H, 5.73. Found: C, 37.92; H, 5.62.

Transformation of 5 to 6 at Ambient Temperature. Ethyl diazoethanoate (0.1 mL, 1 mmol) was added to the solution of **5** (30 mg, 0.06 mmol) in CH_2Cl_2 (10 mL), and the resultant mixture was stirred for 12 h at ambient temperature. After removal of solvent, the residue was chromatographed on silica. Elution with petroleum ether/ethyl acetate gave **6** (33.1 mg, 94%). No **5** was left.

Transformation of 6 to 7 at a Higher Temperature. Upon heating **6** (117.6 mg, 0.2 mmol) in boiling $CHCl_3$ for 24 h, the solution color gradually changed from purple to red. After the solvent was removed, the residue was chromatographed on silica, and elution with CH_2Cl_2/Ac_2O gave **7** (106.3 mg, 92%). No **6** was left.

7: red solid. Mp: 169 °C. ^1H NMR ($CDCl_3$): δ −2.26 (s, 1H, B−H−B), 1.36 (t, 3H, J = 7.0 Hz, CH_3), 1.37 (t, 3H, J = 7.0 Hz, CH_3), 1.38 (t, 3H, J = 7.0 Hz, CH_3), 2.87 (s, 1H, B−CH), 3.80 (d, 1H, J = 16 Hz, S−CH_2), 3.87 (d, 1H, J = 16 Hz, S−CH_2), 3.94 (d, 1H, J = 16 Hz, S−CH_2), 4.23 (q, 2H, J = 7.0 Hz, O−CH_2), 4.29 (q, 2H, J = 7.0 Hz, O−CH_2), 4.32 (q, 2H, J = 7.0 Hz, O−CH_2), 5.17 (s, 5H, Cp), 5.27 (d, 1H, J = 16 Hz, S−CH_2). $^{11}B\{^1H\}$ NMR ($CDCl_3$): δ 4.8 (B−C, 1B), 0.1 (1B), −5.0 (1B), −8.8 (1B), −11.9 (1B), −15.7 (1B), −17.4 (1B), −30.8 (1B), −33.4 (1B). ^{13}C NMR ($CDCl_3$): δ 11.4 (br, B−CH), 13.9, 14.6, 14.7 (CH_3), 39.6 (S−CH_2), 41.8 (S−CH_2), 60.0, 62.6, 62.9 (O−CH_2), 86.2 (Cp), 86.3, 86.6 (carborane), 166.3, 167.5, 182.2 (C═O). MS (70 eV): m/z 578.2 (M^+, 19%). IR (KBr): ν 1676, 1732 (C═O), 2543 (B−H) cm^{-1}. Elem anal. Calcd for $C_{19}H_{34}B_9CoO_6S_2$: C, 39.49; H, 5.76. Found: C, 39.20; H, 5.87.

X-ray Structure Determinations. Crystals suitable for X-ray analysis were obtained by the slow evaporation of a solution in petroleum ether/dichloromethane. Diffraction data were collected on a Bruker SMART Apex II CCD diffractometer by means of graphite-monochromated Mo Kα (λ = 0.710 73 Å) radiation at 291 K. During collection of the intensity data, no significant decay was observed. The intensities were corrected for Lorentz polarization effects and empirical absorption by using the *SADABS* program.[29] The structures were solved by direct methods with the *SHELXL-97* program.[30] All non-hydrogen atoms were found from difference Fourier synthesis. The hydrogen atoms were included in the 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 by using the Bruker *SMART* program. Crystallographic data and the details of data collection and structure refinements of **2**−**7** are provided in Table 1 and the CIF files of the Cambridge Crystallographic Data Centre (CCDC 807093−807098; see the Supporting Information).

■ ASSOCIATED CONTENT

Ⓢ **Supporting Information.** X-ray crystallographic data in CIF format for the structure determinations of compounds **2**−**7**. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: hyan1965@nju.edu.cn. Fax: (+86)-25-83314502.

■ ACKNOWLEDGMENT

This work was supported by the National Natural Science Foundation of China (Grants 20925104 and 21021062), the National Basic Research Program of China (Grants 2007CB925101 and 2010CB923303), the Natural Science Foundation of Jiangsu Province (Grant BK2010052), and the Ministry of Education of China (Grant 20090091110015).

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