ORGANOMETALLICS
Article
pubs.acs.org/Organometallics

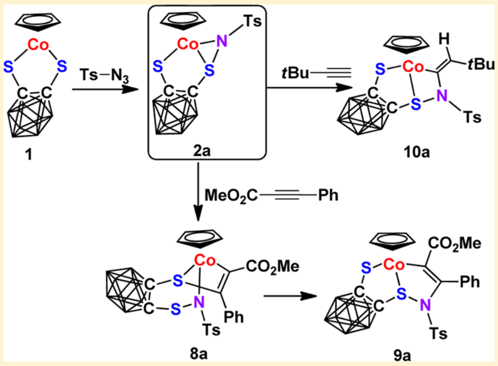
Synthesis and Reactivity of the Imido-Bridged Metallothiocarboranes $CpCo(S_2C_2B_{10}H_{10})(NSO_2R)$

Wei Zhong,[†] Qiwu Yang,[‡] Yi Shang,[†] Guifeng Liu,[†] Haitao Zhao,*[,‡] Yizhi Li,[†] and Hong Yan*[,†]

[†]State Key Laboratory of Coordination Chemistry, School of Chemistry and Chemical Engineering, Nanjing University, Nanjing, Jiangsu 210093, P. R. China

[‡]Department of Chemistry, School of Science, Tianjin University, Tianjin 300072, P. R. China

Ⓢ *Supporting Information*



ABSTRACT: The reactions of the 16-electron half-sandwich complex $CpCo(S_2C_2B_{10}H_{10})$ (**1**) (Cp: cyclopentadienyl) with sulfonyl azides (*p*-toluenesulfonyl azide, TsN_3; methanesulfonyl azide, MsN_3) in refluxing dichloromethane or at ambient temperature lead to imido-bridged adducts $CpCo(S_2C_2B_{10}H_{10})$ (NSO_2R) (**2a**, R = 4-MePh; **2b**, R = Me) which can convert to the tetraazadiene cobalt complexes $CpCoN_4(SO_2R)_2$ (**3a**, R = 4-MePh; **3b**, R = Me) in the presence of excess azide if heated. The reactions of **1** with acyl azides (methyl azidoformate and benzoyl azide) lead to $CpCo(S_2C_2B_{10}H_{10})(CONR)$ (**4a**, R = OMe; **4b**, R = Ph) with a newly-generated five-membered metallacyclic ring Co−S−N−C−O. Complexes **2a** and **2b** show further reactivity toward alkynes to give rise to the insertion products $CpCo(S_2C_2B_{10}H_{10})(R_1C{=}CR_2)$ (NSO_2R) (R_1 = COOMe, R_2 = H, R = 4-MePh, **5a**, R = Me, **5b**; $R_1 = R_2$ = COOMe, R = 4-MePh, **6a**, R = Me, **6b**; R_1 = COOMe, R_2 = Ph, R = 4-MePh, **8a**, R = Me, **8b**) formed by alkyne addition to a Co−S bond to generate a Co−C−C−S four-membered ring and $CpCo(S_2C_2B_{10}H_{10})(R_1C{=}CR_2NSO_2R)$ (R_1 = H, R_2 = Ph, R = 4-MePh, **7a**, R = Me, **7b**; R_1 = COOMe, R_2 = Ph, R = 4-MePh, **9a**, R = Me, **9b**) formed by alkyne insertion into a Co−N bond to generate a Co−C−C−N−S five-membered ring. In the case of $PhC{\equiv}CCO_2Me$, the products with insertion into both Co−S and Co−N bonds are isolated. Interestingly, if *tert*-butylacetylene is used, $CpCo(S_2C_2B_{10}H_{10})(R_1R_2C{=}CNSO_2R)$ (R_1 = *t*Bu, R_2 = H, R = 4-MePh, **10a**, R = Me, **10b**) are generated by insertion of terminal carbon into a Co−N bond to form four-membered ring Co−C−N−S. The insertion pathways of these reactions have been discussed on the basis of DFT calculations. All the new complexes were fully characterized, and X-ray structural analyses were performed for **2a**, **3a**, **3b**, **4a**, **4b**, **5a**, **6a**, **7a**, **7b**, **8a**, **9a**, **9b**, and **10b**.

■ INTRODUCTION

Metal dithiolene complexes have been extensively investigated due to their versatile reaction chemistries,[1] specific geometries,[1a,2] useful physical properties,[3] and important biological role in enzymes.[4] Among a number of dithiolene complexes which have been developed so far, compounds involving η^5-cyclopentadienyl (Cp) have attracted much attention due to the diverse chemical reactivities which are derived from aromatic and unsaturated characters of the five-membered metallacycle (MS_2C_2).[1a,2] A typical reaction of this type is an addition reaction occurring between the M−S bond of a metalladithiolene ring, which has been addressed for many substrates including diazo compounds,[5] alkynes,[6] quadricyclane,[7] and azides.[8] In addition, substitution reactions due to the aromaticity of the metalladithiolene ring have been also reported.[9]

Mononuclear 16-electron half-sandwich complexes of Co, Rh, Ir, Ru, and Os containing a chelating 1,2-dicarba-*closo*-dodecaborane-1,2-dichalcogenolate ligand, $[E_2C_2B_{10}H_{10}]^{2-}$ (E = S, Se), are analogues of metal dithiolene complexes and have attracted particular attention due to their rich reaction chemistry.[10−13] For example, these complexes could serve as precursors for synthesis of mixed-metal clusters to construct metal−metal bonds.[12b−f] Meanwhile, the study of addition and substitution reactions of such complexes with organic substrates has been widely explored.[10,11,13] In particular, systematical study of the reactivity of $[CpCo(E_2C_2B_{10}H_{10})]$ (E = S, Se), $[Cp^*M(E_2C_2B_{10}H_{10})]$ (M = Co, Rh, Ir; E = S, Se), and $[(p\text{-cymene})M(S_2C_2B_{10}H_{10})]$ (M = Ru, Os) with alkynes have been reported.[10,11a,b,13] A representative characterization of these reactions is that the insertion of alkynes into metal−chalcogen bonds led to B−H bond activation, formation of a metal−boron bond, and selective functionalization of a carborane cage in the positions of B(3)/B(6).[10,13a−e] Recently, our group reported the reactivity of 16-electron half-sandwich complex $CpCo(S_2C_2B_{10}H_{10})$ with ethyl diazoacetate and gained a series of unpredictable products with Co−B bond formation.[14] It is clear from these studies that the nature of the metal center, the chalcogen element, organic substrates, and reaction conditions strongly influence the reactivity of the analogous unsaturated 16-electron complexes.

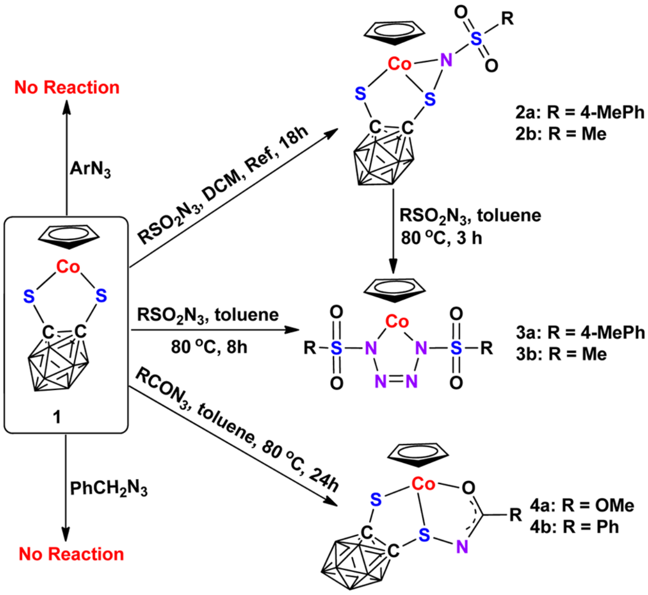
Received: August 1, 2012
Published: September 6, 2012

Our previous results showed that the reactions of 16-electron complex Cp*Ir($S_2C_2B_{10}H_{10}$) with substituted aryl azides led to C(sp^3)−H activation and ortho-substituted electron-withdrawing group migration in the final products.[15] As part of our systematic study of the role of metal in the reaction chemistry, herein we examine the reactivity of CpCo($S_2C_2B_{10}H_{10}$) (**1**) toward different kinds of organic azides and the insertion reactions of the imido-bridged adducts with selected alkynes.

RESULTS AND DISCUSSION

Reactivity of CpCo($S_2C_2B_{10}H_{10}$) toward Organic Azides. As outlined in Scheme 1, reactions of CpCo($S_2C_2B_{10}H_{10}$) (**1**) with excess sulfonyl azides (*p*-toluenesulfonyl azide, TsN_3, and methanesulfonyl azide, MsN_3) in refluxing dichloromethane afford imido-bridged adducts **2a** and **2b** in good yields. The formation of such compounds should be similar to that of alkylidene-bridging by diazo compounds[5a] and result from 1,3-dipolar addition of sulfonyl azides to the Co−S bond which has been previously reported.[8a] The reactions also can be performed in dichloromethane at room temperature. In such a case, the reaction time proceeds over four days but the yield is lower. When the reactions are conducted in toluene at 80 °C for 8 h, tetraazadiene cobalt complexes (**3a** and **3b**) are formed in moderate yields. Interestingly, complex **3a** or **3b** can also be obtained via the reaction of **2a** or **2b** with excess corresponding sulfonyl azide, and heating at 80 °C in toluene. This fact suggests that complexes **3a** and **3b** are formed via cycloaddition of **2a** and **2b** to corresponding sulfonyl azide. Such tetraazadiene derivatives are common products in the reaction of organic azides with transition metal complexes.[16] To the best of our knowledge, the reactions in this study are the first examples of tetraazadiene complexes formed from the reaction of organic azides with transition metal complexes with dithiolate ligands.

Scheme 1. The Reactivity of CpCo($S_2C_2B_{10}H_{10}$) (1) toward Organic Azides



Treatment complex **1** with excess methyl azidoformate in toluene at 80 °C for 24 h led to a five-membered chelate metallacycle, **4a**, in a yield of 60%. But when the reaction of complex **1** with excess benzoyl azide was conducted under the same conditions, only ∼5% complex **4b** could be isolated as a yellow-green solid. An attempt of heating at higher temperature and prolonging the reaction time did not improve the yield of **4b**. In this case, most of complex **1** remains in the mixture since benzoyl azide readily forms nitrene, then rearranges to form phenyl isocyanate, which react with each other readily to form carbamoyl urea (named as *N*,*N*′,*N*″-triphenylbiuret).[17] It is obvious that the formations of **4b** and carbamoyl urea are two competitive reactions and the latter predominates to result in a lower yield of **4b**. Other than the formation of complexes **2a** and **2b** via 1,3-dipolar addition, complexes **4a** and **4b** should be formed via nitrene, which rearranges to form a conjugated N−C−O $^{4}_{3}\pi$ system to coordinate to the center metal (see the structural analysis vide infra).

The reaction of complex **1** was extended to other azides, such as phenyl azide, substituted aryl azides (2,6-$Me_2C_6H_3N_3$ and 2-Me-6-$NO_2C_6H_3N_3$), and benzyl azide. The results showed that, no matter which conditions were attempted, e.g., excess azide, different solvent, prolonging the reaction time, or refluxing in xylene, the reaction did not work at all with these azides.

This clearly shows that the reactivity of complex **1** is very different from that of Cp*Ir($S_2C_2B_{10}H_{10}$).[15] Moreover, compared to alkynes and diazo compounds, organic azides are less reactive to complex **1**. Our preliminary study of the reactivity of complex **1** toward alkynes showed that the cobalt complex **1** is more reactive than their analogous rhodium and iridium species,[13a−c] but for organic azides, the opposite reactivity of the 16-electron complexes was observed.

Good analytical data were obtained for these complexes, which were isolated as green (**2a**, **2b**, **4a**, and **4b**) or yellow solids (**3a** and **3b**) and are soluble in common organic solvents. IR and NMR (^1H, ^{11}B, ^{13}C) data confirmed the proposed formulations, which were further supported by X-ray crystal structure determination with the exception of **2b**.

The ORTEP plot and selected bond parameters for **2a** are shown in Figure 1. Similar to the reported alkylidene-

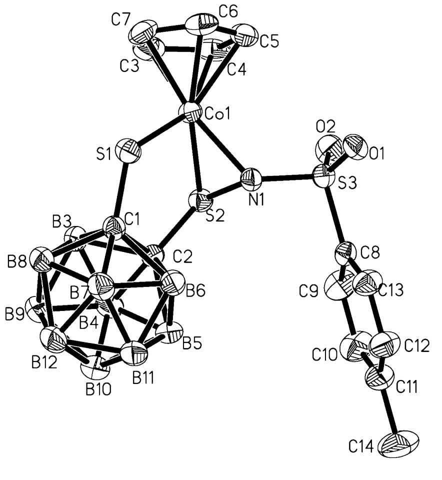


Figure 1. ORTEP plot (30% probability thermal ellipsoids) of **2a** with hydrogen atoms omitted for clarity. Selected bond lengths (Å) and angles (deg): Co1−N1 = 1.974(2), Co1−S1 = 2.2556(9), Co1−S2 = 2.2000(8), S1−C1 = 1.773(3), S2−C2 = 1.798(3), S2−N1 = 1.695(2); S1−Co1−S2 = 94.48(3), S1−Co1−N1 = 93.57(6), S2−Co1−N1 = 47.54(6), Co1−S1−C1 = 104.55(9), Co1−S2−N1 = 59.21(7), Co1−S2−C2 = 107.01(8), N1−S2−C2 = 101.99(11), Co1−N1−S2 = 73.25(8), S1−C1−C2 = 118.49(17), S2−C2−C1 = 115.01(17).

bridged[5a,14] and imido-bridged complexes,[8a] the generated three-membered ring (Co1−N1−S2) is almost perpendicular to the five-membered cobaltadithia-*o*-carborane ring (Co1−S1−C1−C2−S2), which almost remained planar (within 0.034°), with the dihedral angle of 93.1° between the two planes. The Co−S bond lengths (Co1−S2, 2.2000(8) Å, Co1−S1, 2.2556(9) Å) are slightly longer than those in complex **1** (Co−S, 2.139(8) and 2.129(8) Å),[11a] but similar to alkylidene-bridged complexes[5a,14] and other imido-bridged complexes.[8a]

ORTEP representations of **3a** and **3b** with selected bond distances and angles are shown in Figure S1 in the Supporting Information. In **3a**, the tetraazabutadiene ligand adopts a syn conformation, with toluenesulfonyl substituents oriented on the same sides with respect to the five-membered chelation ring, which is planar within 0.03°. In contrast, the tetraazabutadiene ligand in **3b** adopts an anti conformation, with methanesulfonyl substituents oriented on the opposite side with respect to the five-membered chelation ring, which is planar within 0.01°. A search of tetraazadiene metal complexes contained in the Cambridge Structure Database found that all the four similar tetraazadiene metal complexes adopt an anti conformation.[18] In the tetraaza system of **3a** and **3b**, the centeral N−N bond is shorter than the lateral ones by 0.11 Å on average, which is analogous to reported tetraazadiene metal complexes.[18,19] The average Co−N bond distance is 1.829(7) Å in both compounds, slightly longer than those found for other tetraazadiene cobalt complexes.[20]

A perspective view of complexes **4a** and **4b** is present in Figure 2 and Figure S2 in the Supporting Information, respectively. The structure of both compounds shows an unusual five-membered metallacyclic ring Co−S−N−C−O which is generated by one azide molecule insertion Co−S bond with the loss of N_2, followed by carbonyl coordination to the metal. In both compounds, the distances of C8−O1(1.281(4) Å in **4a**, 1.298(3) Å in **4b**) are intermediate between that expected for carbon−oxygen single and double bonds. The distances of C8−N1(1.309(4) Å in **4a** and 1.316(3) Å in **4b**) are also shorter than the usual C−N but longer than the normal C═N. This phenomenon indicates that N1−C8−O1 is a conjugated ${}^{4}_{3}\pi$ system. The five-membered metallacyclic rings (Co1−S2−N1−C8−O1) in both compounds are almost planar within 0.04° on average. Different from the three-membered cobaltathiaziridine ring which is almost located at a perpendicular position with respect to the existing five-membered cobaltadithia-*o*-carborane ring in **2a**, the angles between the two five-membered metallacyclic rings in **4a** and **4b** are 99.4° and 100.3°, respectively.

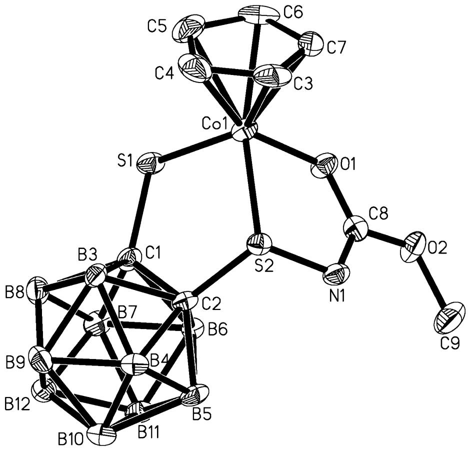


Figure 2. ORTEP plot (30% probability thermal ellipsoids) of **4a** with hydrogen atoms omitted for clarity. Selected bond lengths (Å) and angles (deg): Co1−S1 = 2.2420(10), Co1−S2 = 2.2129(9), Co1−O1 = 1.951(2), O1−C8 = 1.281(4), N1−C8 = 1.309(4), N1−S2 = 1.662(3); S1−Co1−S2 = 95.95(3), S1−Co1−O1 = 93.64(8), S2−Co1−O1 = 82.79(7), Co1−S1−C1 = 104.00(13), Co1−S2−C2 = 104.93(11), Co1−S2−N1 = 100.91(10), N1−S2−C2 = 102.98(15), Co1−O1−C8 = 115.8(2), S2−N1−C8 = 112.3(3), S1−C1−C2 = 117.8(2), S2−C2−C1 = 116.8(2).

Reactivity of Imido-Bridged Adducts 2a and 2b with Alkynes. The insertion of unsaturated organic founctional groups such as alkynes, alkenes, or isocyanides into a metal−heteroatom bond is a key step of transition-metal-catalyzed heterofunctionalization of such organic substrates.[21] Continuous studies for decades on insertions of organometallic complexes with unsaturated organic small molecules and their applications in organic synthesis have experienced extremely important development and displayed many novel structures of the intermediate compounds and reactivity patterns.[21d,f,22] Compared to the numerous insertion reactions with unsaturated organic small molecules only into metal−carbon bond,[23] concerning metal−nitrogen bond[24] or metal−sulfur bond,[25] there are very few cases of an insertion reaction occurring at one complex which contains two active metal−heteroatom bonds.[26−28]

In our case, imido-bridged adducts **2a** and **2b** contain both Co−S and Co−N bonds, which may act as active sites for C≡C bond insertion based on some facts as follows. First, Herberhold's and our groups have investigated the reactivity of 16-electron half-sandwich complexes Cp″M[$E_2C_2B_{10}H_{10}$] (Cp″ = η^5-C_5Me_5, η^5-C_5H_5 or η^6-4-isopropyltoluene, E = S, Se, M = Co, Rh, Ir, Ru or Os) with alkynes systematically and found that the M−E (E = S, Se) bond in these complexes is very reactive and it is easy to insert a C≡C bond.[10,13] Second, Nomura and co-workers[8a,29] found that imido-bridged complexes easily undergo ring-opening and imido group transfer reactions. Additionally, DFT calculations show that the contributions of Highest Occupied Molecular Orbital (HOMO) and Lowest Unoccupied Molecular Orbital (LUMO) in complexes **2a** and **2b** are mainly from the S atom and the Co atom, respetively, which suggest that the S atom can act as nucleophile while the Co center acts as electron acceptor for further reaction (Figure 3).

A terminal alkyne was chosen, methyl propiolate, which acts as a very reactive alkyne in the reaction with Cp″M-[$E_2C_2(B_{10}H_{10})$],[10a,d,e,13b] reacting with **2a** and **2b** at room temperature. The color of the mixture changed immediately from green to brownish black. The reaction was complete within one hour. After workup with chromatography, brownish black pastes **5a** and **5b** were obtained in the yields of 75.2% and 69.0%, respectively. Both **5a** and **5b** are soluble in common organic solvents and somewhat thermally unstable, slowly decomposing at ambient temperature even in the solid state.

Complex **5a** was characterized by X-ray crystallography, and the ORTEP drawing is shown in Figure 4 with selected bond distances and angles. The structure of **5a** shows the expected four-membered ring formed by insertion of the alkyne into one Co−S bond followed by the cleavage of the other Co−S bond to form a distorted Co−S−C−C−S−N six-membered ring. It is well-known that asymmetric alkyne insertion into a metal−heteroatom bond shows two possible isomers with regard to

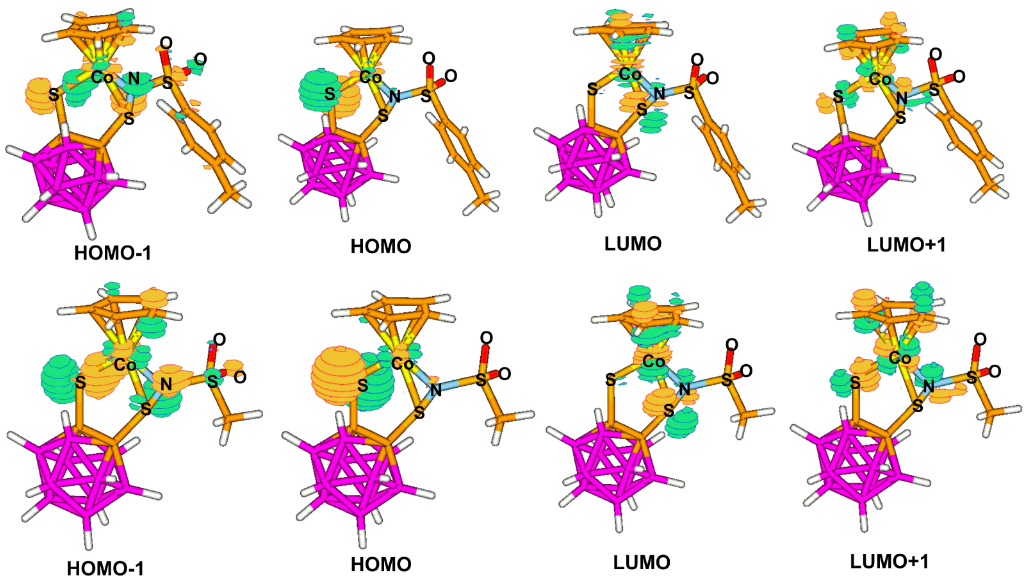


Figure 3. The orbital distribution of complexes **2a** (top) and **2b** (bottom).

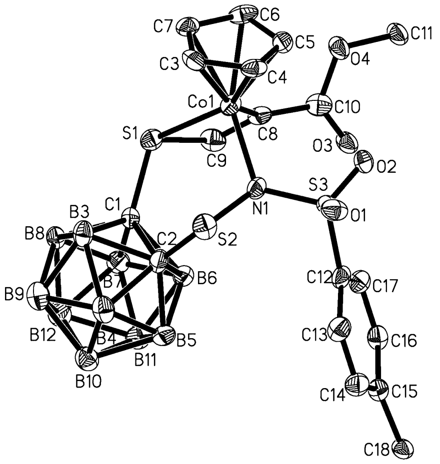


Figure 4. Molecular structure of **5a** with 30% displacement ellipsoids. All H atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): Co1−S1 = 2.3068(10), Co1−N1 = 1.976(3), Co1−C8 = 1.931(3), N1−S2 = 1.681(3), S1−C9 = 1.761(4), C8−C9 = 1.329(5); S1−Co1−N1 = 93.29(9), S1−Co1−C8 = 71.05(10), N1−Co1−C8 = 91.91(13), Co1−S1−C1 = 116.76(10), Co1−S1−C9 = 78.20(14), C1−S1−C9 = 105.27(15), N1−S2−C2 = 102.78(15), Co1−N1−S2 = 113.90(14), Co1−N1−S3 = 122.38(16), S2−N1−S3 = 114.22(17), S1−C1−C2 = 120.8(2), S2−C2−C1 = 120.1(2), Co1−C8−C9 = 104.3(2), S1−C9−C8 = 106.0(3).

the position of the substituent group compared to the metal center. In the case of **5a**, the structure confirms that only one regioisomer has formed with the CO_2Me group on the carbon attached to the metal and with the hydrogen next to the carborane cage. This regioselectivity is also reported in cyclometalated oxazoline, pyrazole, and imine complexes[23a,30] and the reaction of **1** with N-1-naphthylpropargylamide.[31a] Compared to the structure of **1**, an organic ligand is inserted into each Co−S bond located at the two sides of the original Co−S−C−C−S plane.[31b,c] The Co−C−C−S four-membered ring is almost planar within 0.04° mean deviation. Very interestingly, our previous detailed study of the reaction of **1** with methyl propiolate could not obtain a product with one alkyne inserted into one Co−S bond, although we assumed that it is an important intermediate for further transformation as evidenced by dimethyl acetylenedicarboxylate insertion analogues.[10d,13c] In the present case, the determination of the structure of **5a** provides direct evidence for the key intermediate and further confirms our mechanistic proposal on metal-induced B−H activation and B−H functionalization of the *o*-carborane cage.[10a,d,e] ^1H NMR spectroscopic resonances appearing at δ = 6.75 ppm in both compounds are ascribed to C═C*H* and correspond to ^{13}C NMR signals at δ = 127.57 and 127.82 ppm, respectively. The ^{13}C data of carborane (67.11 and 85.04 ppm in **5a** and 67.54 and 80.30 ppm in **5b**) shift to higher field than the corresponding starting complexes (87.64 and 90.45 ppm in **2a** and 88.35 and 90.31 ppm in **2b**). The $^{11}B\{^1H\}$ NMR spectra of **5a** and **5b** exhibit five signals approximately between δ = 2.6 and −10.5 ppm with an intensity ratio of 1:1:2:4:2.

Similar to methyl propiolate, the reaction of **2a** or **2b** with dimethyl acetylenedicarboxylate (DMAD) rapidly gave a color change of the solution from green to brownish red and was complete within 2 h to afford **6a** or **6b** in good yield. The structure of **6a** has been confirmed by X-ray crystallography and is shown in Figure S3 in the Supporting Information. It reveals that the alkyne has inserted into the Co−S bond rather than the Co−N bond to give a four-membered ring, as found in the same alkyne insertion into Cp^*MS_2 (M = Rh, Ir), (*p*-cymene)MS_2 (M = Ru, Os), and $CpCoE_2$ (E = S, Se) half-sandwich complexes.[10a,d,13c] Similar to **5a**, **6a** also contains a distorted Co−S−C−C−S−N six-membered ring which shares one Co−S bond of the existing four-membered metallacyclic ring (Co−S−C−C). The ^1H NMR spectra of **6a** and **6b** show the expected signals for Cp and two methoxy signals for the nonequivalent CO_2Me groups of the alkyne. Similar to **5a** and **5b**, signals of carborane in ^{13}C NMR spectra appear at approximately 67 and 86 ppm for both compounds which are 10−20 ppm upfield from the corresponding signals of starting complexes. The same phenomenon was observed in the addition products of complex **1** and its selenium analogue with DMAD.[13c] The chemical shifts of the two olefinic carbon atoms are similar in both compounds which appear at approximately 123 and 155 ppm. In contrast to **5a** and **5b**, which are unstable both in the solution and in solid form, **6a** and **6b** are stable in solution and solid state for at least several months.

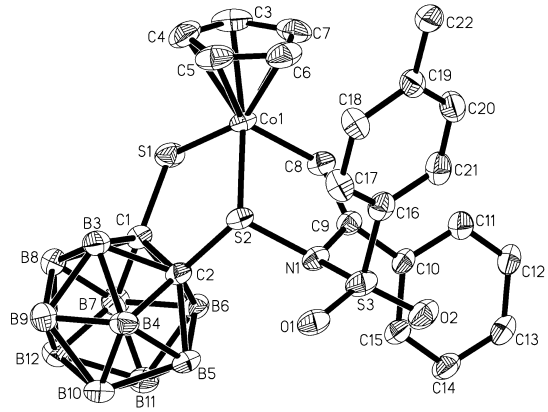


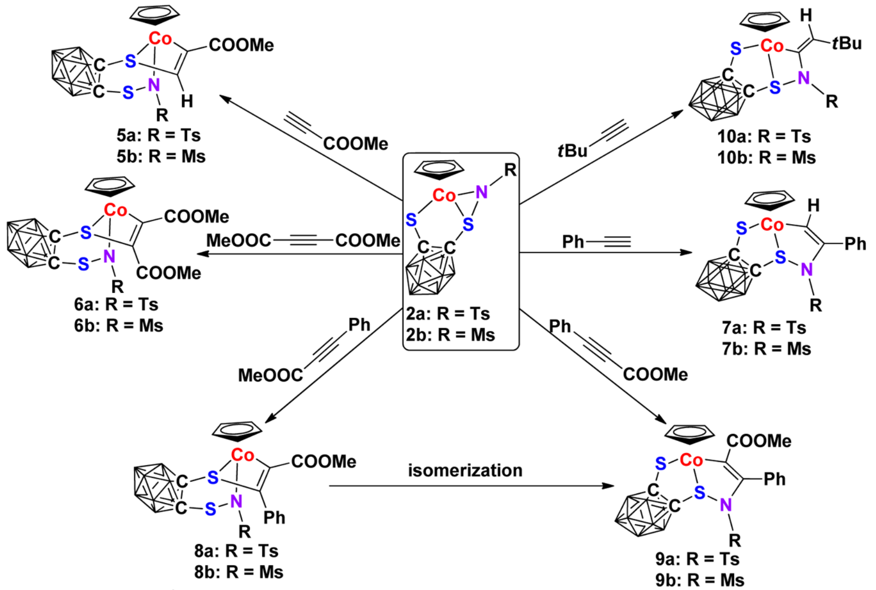
Figure 5. Molecular structure of **7a** with 30% displacement ellipsoids. All H atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): Co1−S1 = 2.2520(9), Co1−S2 = 2.1442(8), Co1−C8 = 1.927(3), N1−S2 = 1.707(2), N1−C9 = 1.454(3), C8−C9 = 1.331(4); S1−Co1−S2 = 95.26(3), S1−Co1−C8 = 92.23(8), S2−Co1−C8 = 83.50(8), Co1−S1−C1 = 104.02(9), Co1−S2−N1 = 104.09(7), Co1−S2−C2 = 107.12(8), N1−S2−C2 = 100.23(10), S2−N1−S3 = 111.45(12), S2−N1−C9 = 111.19(16), S3−N1−C9 = 121.36(17), S1−C1−C2 = 117.62(17), S2−C2−C1 = 115.02(16), Co1−C8−C9 = 122.4(2), N1−C9−C8 = 117.2(2).

The reactions of phenylacetylene with **2a** and **2b** were also examined and gave yellowish brown solid **7a** and **7b** with 60% isolated yield. Suitable crystals of both **7a** and **7b** were successfully obtained by slow diffusion of petroleum ether into a concentrated dichloromethane solution of the complex and were determined by X-ray crystallography. ORTEP drawings of **7a** and **7b** and selected bonds and angles are shown in Figure 5 and Figure S4 in the Supporting Information, respectively. Differing from the alkyne insertion into the M−S bond in **5a**−**6b**, the structures of **7a** and **7b** reveal that the alkyne has inserted into the M−N bond to form a Co−C−C−N−S five-membered ring. Furthermore, the structures of **7a** and **7b** show that the hydrogen atom is located on the carbon attached to the metal while the phenyl group is next to the original sulfonyl group, which is consistent with that ^{1}H NMR spectroscopic signal of C═C*H* group at downfield with δ = 7.47 and 7.53 ppm, respectively. Clearly, the different insertion mode of phenylacetylene is determined by the electronic property of the phenyl group.

Thus reactions of **2a** and **2b** with methyl phenylpropiolate were investigated in order to gain a mixed type of products. As expected, the reactions gave two types of products **8a**, **9a** or **8b**, **9b** respectively. Further detailed studies revealed that the formation of **8a** and **9a** or **8b** and **9b** occurs not by two competitive processes but by subsequent transformations. This conclusion is supported by the observations below: (a) performing the reaction of **2a** or **2b** with methyl phenylpropiolate around half hour gave an incomplete reaction only affording **8a** or **8b**; (b) stirring the dichloromethane solution of **8a** or **8b** at room temperature for 24 h proceeded to generate **9a** or **9b** in good yield (Scheme 2). These results indicate that the formation of **8a** and **8b** takes place by kinetically controlled processes while **9a** and **9b** are likely thermodynamic products, which is further supported by DFT calculations (Figure S8 in the Supporting Information). It should be noted that attempts to obtain the analogues of **9a** and **9b** from **5a** and **5b** at room temperature over several days or from **6a** and **6b** refluxing in toluene for 24 h just led to decomposition. This anomaly is possibly attributed to different alkynes in these insertion reactions undergoing different reaction pathways, which lead to different kinetic or thermodynamic products (Figures S6−S8 in the Supporting Information).

Although **8a**, **9a** and **8b**, **9b** are configurational isomers, they can be readily isolated by chromatography. Furthermore, the structures of **8a**, **9a**, and **9b** have been determined by X-ray

Scheme 2. The Insertion Reactions of 2a and 2b with Alkynes[a]



Ts = *p*-toluenesulfonyl
Ms = methanesulfonyl

---

[a] Conditions: excess alkynes, dichloromethane, room temperature, 1−12 h.

crystallography and are shown in Figures 6 and 7 and Figure S5 in the Supporting Information. The structure of **8a** is analogous to **5a** and **6a** discussed above, with regioselectivity of the CO$_2$Me group on the carbon attached to the metal and with the phenyl group next to the carborane cage. Addtionally, **9a** and **9b** have the same structure pattern as **7a** and **7b** except for a CO$_2$Me group replacing a hydrogen atom on the carbon attached to the metal. The ^{1}H NMR spectra of **8a** and **8b** are similar to those of their isomers **9a** and **9b** except that the signal for methoxy is shifted ~0.5 ppm upfield of the latter. The ^{13}C NMR data have shown some differences between the two isomers. Signals of carborane appear at approximately 66 and 86 ppm in **8a** and **8b** but 96 and 103 ppm in **9a** and **9b**. Additionally, the chemical shifts of the two olefinic carbon atoms appear at approximately 135 and 154 ppm in **8a** and **8b** but 136 and 144 ppm in **9a** and **9b**. Similarly, in contrast to all the signals of ^{11}B NMR spectra in negative values in **9a** and **9b**, **8a** and **8b** show two additional positive signals at δ = 2.60 and 0.13 ppm on average. Such difference in NMR data between the two isomers might be explained by the exogenous ligand falling in a different chemical environment, where **8a** and **8b** possess a Co−C−C−S four-membered ring and **9a** and **9b** contain a Co−C−C−N−S five-membered ring.

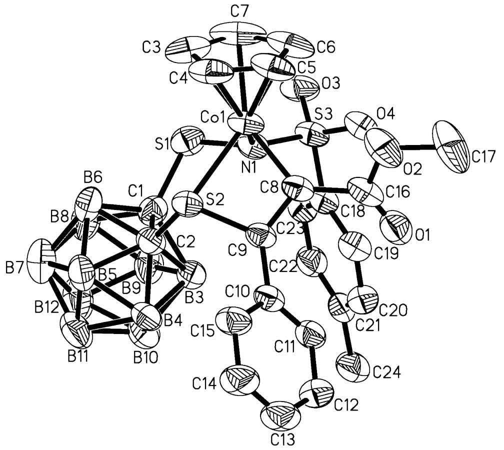


Figure 6. Molecular structure of **8a** with 30% displacement ellipsoids. All H atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): Co1−S2 = 2.3022(16), Co1−N1 = 1.960(4), Co1−C8 = 1.952(5), N1−S1 = 1.681(4), S2−C9 = 1.802(5), C8−C9 = 1.358(6); S2−Co1−N1 = 93.67(12), S2−Co1−C8 = 71.24(14), N1−Co1−C8 = 91.28(19), N1−S1−C1 = 104.0(2), Co1−S2−C2 = 116.44(16), Co1−S2−C9 = 79.61(15), C2−S2−C9 = 107.9(2), Co1−N1−S3 = 125.1(2), S1−N1−S3 = 114.1(3), Co1−N1−S1 = 112.7(2), S1−C1−C2 = 121.1(3), S2−C2−C1 = 120.2(3), Co1−C8−C9 = 105.3(3), S2−C9−C8 = 103.3(4).

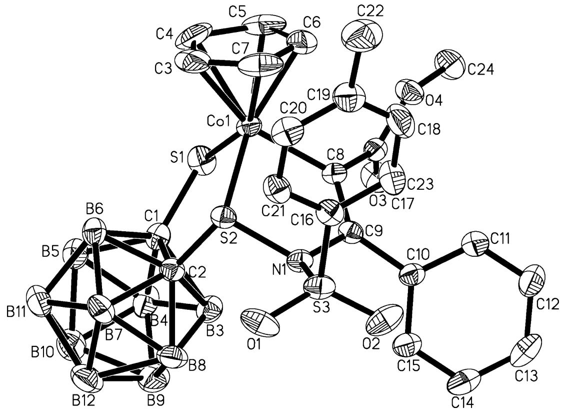


Figure 7. Molecular structure of **9a** with 30% displacement ellipsoids. All H atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): Co1−S1 = 2.2558(10), Co1−S2 = 2.1416(9), Co1−C8 = 1.940(3), N1−S2 = 1.712(2), N1−C9 = 1.458(4), C8−C9 = 1.337(4); S1−Co1−S2 = 95.85(4), S1−Co1−C8 = 91.70(10), S2−Co1−C8 = 84.79(9), Co1−S1−C1 = 103.07(14), Co1−S2−N1 = 102.80(9), Co1−S2−C2 = 107.11(11), N1−S2−C2 = 101.88(14), S2−N1−S3 = 111.06(14), S2−N1−C9 = 112.8(2), S3−N1−C9 = 123.0(2), S1−C1−C2 = 118.5(3), S2−C2−C1 = 114.5(2), Co1−C8−C9 = 121.2(2), N1−C9−C8 = 116.9(3).

Surprisingly, the corresponding reaction of **2a** and **2b** with *tert*-butylacetylene affords a new type of product, **10a** and **10b**, within 4 h with an isolated yield over 85%. Unlike other complexes we present in this paper with good solubility in dichloromethane, chloroform, or tetrahydrofuran, **10a** and **10b** are only partially soluble in these solvents. Additionally, **10a** and **10b** are not stable in solution or in the solid state, and can easily decompose in solution within several hours.

The structure of **10b** has been determined by X-ray crystallography and is shown in Figure 8 with selected bond lengths and angles. Unlike carbon−carbon triple bond insertion into metal−heteroatom in the reported literature[13c,g,23a,24a] and other compounds in the present text, the structure of **10b** shows that the terminal carbon of *tert*-butylacetylene inserts into a Co−N bond to form a Co−C−N−S four-membered ring accompanied by a 1,2-hydrogen shift to an internal carbon. Similar proton transfer occurrs commonly in many vinylidene complexes.[32] Here the insertion pattern in **10b** is rare and the nature of the alkyne perhaps plays an important role in the formation of the final product. ^{1}H NMR spectra of **10a** and **10b** show the characteristic resonances for the groups of Ts, Ms, *t*Bu, and Cp. In particular, the singlet signals at δ = 6.00 and 5.51 ppm are ascribed to C═C*H* in both compounds, which correspond to ^{13}C NMR signals at δ = 120.41 and 125.85 ppm, respectively.

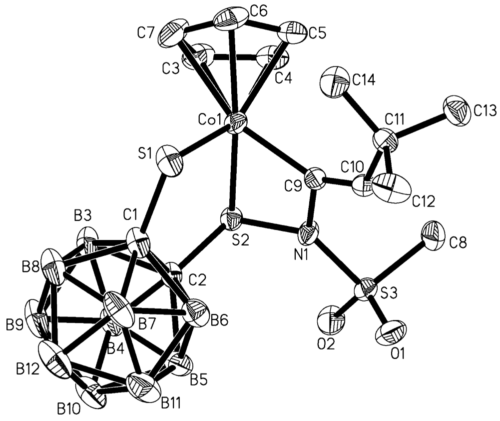
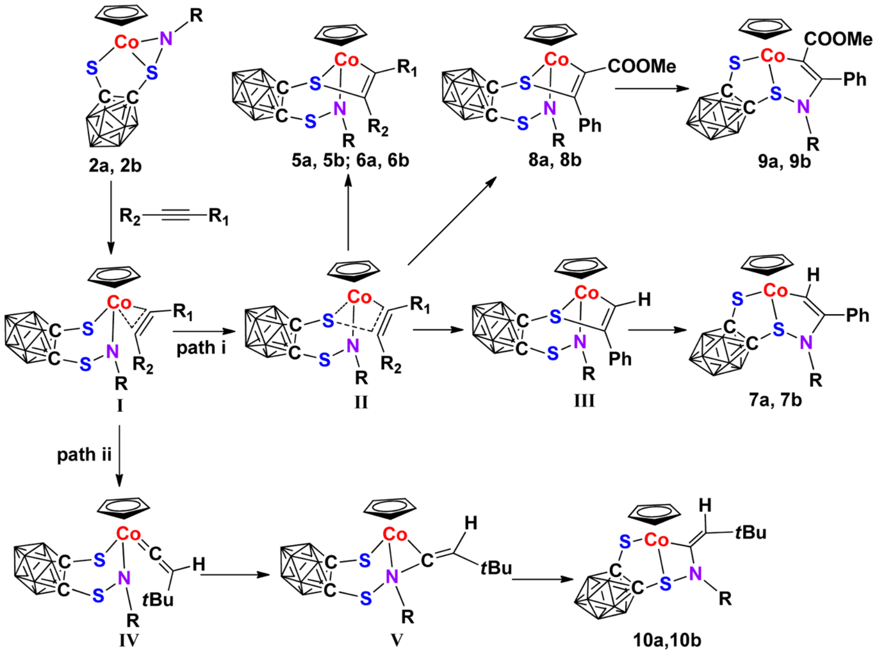


Figure 8. Molecular structure of **10b** with 30% displacement ellipsoids. All H atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): Co1−S1 = 2.2417(8), Co1−S2 = 2.1851(7), Co1−C9 = 1.962(2), N1−S2 = 1.673(2), N1−C9 = 1.469(3); S1−Co1−S2 = 96.16(3), S1−Co1−C9 = 92.17(8), S2−Co1−C9 = 74.32(7), Co1−S1−C1 = 103.88(10), Co1−S2−N1 = 82.42(7), Co1−S2−C2 = 105.38(8), N1−S2−C2 = 104.77(11), S2−N1−S3 = 121.65(13), S2−N1−C9 = 105.94(15), S3−N1−C9 = 131.41(16), S1−C1−C2 = 118.06(18), S2−C2−C1 = 115.76(16), Co1−C9−N1 = 95.95(14).

Scheme 3. Proposed Mechanisms for the Formation of **5a**−**10b**



Mechanistic Considerations. The different behavior of alkyne insertion into complexes **2a** and **2b** suggests that the insertion process may undergo different reaction pathways. Alkyne insertion into a Co−S or Co−N bond can be considered as a process of S or N atom nucleophilic addition to the incoming alkyne. Thus, comparison of the nucleophilicity of the S and N atoms in **2a** and **2b** is very important to these insertion reactions. As we can see from Figure 3, the contribution of HOMO orbital is mainly from the S atom, although partial contribution of the HOMO−1 orbital derives from the N atom. We can conclude from the orbital calculations that the S atom has higher nucleophilicity than the N atom in complexes **2a** and **2b**, and the S atom preferentially acts as the nucleophile. The experimental results show that different kinds of products were obtained where the S or N atom acts as nucleophile. We speculate that it may be attributed to the thermodynamically vs kinetically controlled process, i.e., the S atom has the higher nucleophilicity, whereas products resulting from N attack are stable under some conditions. To gain full insight into the mechanism of the alkyne insertion reactions, related calculations were conducted and fit the experimental results (Figures S6−S8 in the Supporting Information).

Thus, the experimental results and computational studies allow us to assume the mechanistic suggestions for the generation of **5a**−**10b**, which is depicted in Scheme 3. Initial alkyne coordination to metal center gives species **I**, which is well-known as the first step of the interaction between alkyne and the metal fragment. Alkyne species **I** has two isomers with the different direction of the subsitutent groups according the nature of the alkyne, but only one isomer is preferred to form thermodynamically stable product (see Figures S6−S8 in the Supporting Information). From alkyne species **I**, there are two reaction pathways to generate final products. One pathway is that alkyne species **I** can be easily intramolecular attacked by one S atom due to its high nucleophilicity to form a four-membered transition state **II**, which is similar to alkyne addition to the 16-electron complexes previously reported.[10,13] The transition state **II** yields **5a**−**6b** directly due to the kinetically preferred processes or **8a**, **8b** for their considerably kinetical stability. Complexes **8a** and **8b** can easily isomerize to **9a** and **9b** as a result of the thermodynamically preferred processes (Figure S8 in the Supporting Information). For phenylacetylene, the transition state **II** may also afford intermediate **III**, which is analogous to **5a**−**6b** and **8a**, **8b** but cannot be isolated experimentally. In this case, intermediate **III** readily rearranges to thermodynamically stable products **7a** and **7b**. These subsequent processes are driven by the formation of the lowest energy product among all the possible products due to its being a thermodynamically controlled reaction (Figure S7 in the Supporting Information). Alternatively, for *tert*-butylacetylene, its pathway to form **10a** or **10b** might be quite different from the former examples. From alkyne species **I**, the system can eventually convert into vinylidene derivatives **IV** via a hydride alkynyl or direct 1,2-hydrogen shift of the terminal C−H of the alkyne, which was proposed or even evidenced in the formation of many other vinylidene complexes.[32,33] A nucleophilic addition attacked by nitrogen at the terminal carbon of the alkyne (close to metal center) affords a three-membered transition state **V**, which could give rise to **10a** or **10b** after further rearrangement.

■ CONCLUSIONS

In summary, we have established the reactivity of the 16-electron half-sandwich complex **1** toward different types of organic azides, and three different coordination modes of the products were captured. Compared to previous work which showed that complex **1** presents a range of reactivities toward alkynes and diazo compounds,[10,13,14] the results presented here suggest that complex **1** is not a good precursor to react with organic azides for further functionalization. The insertion reaction of imido-bridged adducts **2a** and **2b** with alkynes under mild conditions was also investigated. These insertion reactions give three types of products via alkyne addition to Co−S or Co−N bond according to the nature of alkynes. The mechanism of such insertion reactions is proposed and supported by DFT calculations. The coordination modes of the insertion products reported in the present study may provide evidence for the existence of some intermediates in some metal-induced catalytic cycles involving insertion of carbon−carbon multiple bonds and be a useful method to construct new carbon−heteroatom (C−E) bonds of the existing organometallic compounds.

■ EXPERIMENTAL SECTION

General Procedures. *n*BuLi (2.0 M in hexanes, Aldrich) was used as supplied. CpCo(CO)I_2,[34] CpCo($S_2C_2B_{10}H_{10}$),[11a] and azides[35] 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 ^{1}H = 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, H, and N microanalyses were carried out with an Elementar Vario EL III elemental analyzer. Mass data were determined with the LCQ (ESI-MS, Thermo Finnigan) mass spectrometer.

Reaction of 1 with Sulfonyl Azides. Complex **1** (265 mg, 0.8 mmol) was treated with *p*-toluenesulfonyl azide (790 mg, 4 mmol) or methanesulfonyl azide (485 mg, 4 mmol) under reflux in dichloromethane (40 mL) under Ar for 18 h. The red-brown mixture turned to dark-green. The solvent was then removed, and the residue was chromatographed on silica (dichloromethane/ethyl ether, 20:1) to give **2a** or **2b** as a green solid. If the reactions were heated at 80 °C in toluene for 8 h, **3a** or **3b** was obtained as a yellow solid.

2a (340.5 mg, 85.1%): green solid. Mp: 188−189 °C. ^{1}H NMR ($CDCl_3$, ppm): 7.87 (d, *J* = 7.5 Hz, 2H, Ar*H*), 7.38 (d, *J* = 7.5 Hz, 2H, Ar*H*), 5.62 (s, 5H, C_5H_5), 2.47 (s, 3H, CH_3). ^{11}B{^{1}H} NMR ($CDCl_3$, ppm): −2.1 (2B), −4.0 (1B), −4.9 (2B), −7.2 (4B), −8.9 (1B). ^{13}C NMR ($CDCl_3$, ppm): 21.76 (CH_3), 83.92 (Cp), 87.64 (carborane), 90.45 (carborane), 127.77 (CH, Ph), 129.73 (CH, Ph), 136.41 (C, Ph), 144.88 (C, Ph). ESI-MS (*m*/*z*): 501.17 (100%) [M + H]$^+$. IR (KBr, cm^{-1}): 2583.5 (ν_{B-H}). Elemental analysis calcd (%) for $C_{14}H_{22}B_{10}NO_2S_3Co$: C 33.66, H 4.44, N 2.80. Found: C 33.32, H 4.59, N 2.92.

2b (245.2 mg, 72.4%): green solid. Mp: 176−178 °C. ^{1}H NMR ($CDCl_3$, ppm): 5.55 (s, 5H, C_5H_5), 3.29 (s, 3H, CH_3). ^{11}B{^{1}H} NMR($CDCl_3$, ppm): −1.8 (2B), −4.2 (3B), −6.9 (4B), −8.6 (1B). ^{13}C NMR ($CDCl_3$, ppm): 42.19 (CH_3), 84.06 (Cp), 88.35 (carborane), 90.31 (carborane). ESI-MS (*m*/*z*): 423.50 (10%) [M]$^+$. IR (KBr, cm^{-1}): 2588.5 (ν_{B-H}). Elemental analysis calcd (%) for $C_8H_{18}B_{10}NO_2S_3Co$: C 22.69, H 4.28, N 3.31. Found: C 22.35, H 4.19, N 3.44.

3a (33.5 mg, 45.6%): yellow solid. Mp: 180−182 °C. ^{1}H NMR ($CDCl_3$, ppm): 7.97 (d, *J* = 8 Hz, 2 × 2H, Ar*H*), 7.29 (d, *J* = 8 Hz, 2 × 2H, Ar*H*), 5.94 (s, 5H, C_5H_5), 2.40 (s, 2 × 3H, CH_3). ^{13}C NMR ($CDCl_3$, ppm): 21.61 (CH_3), 81.88 (Cp), 128.94 (CH, Ph), 129.71 (CH, Ph), 135.14 (C, Ph), 144.69 (C, Ph). ESI-MS (*m*/*z*): 490.75 (31%) [M + H]$^+$, 512.75 (100%) [M + Na]$^+$. IR (KBr, cm^{-1}): 1598.5 ($\nu_{N=N}$). Elemental analysis calcd (%) for $C_{19}H_{19}N_4O_4S_2Co$: C 46.53, H 3.90, N 11.42. Found: C 46.28, H 4.09, N 11.23.

3b (24.5 mg, 48.2%): yellow solid. Mp: 173−174 °C. ^{1}H NMR ($CDCl_3$, ppm): 5.93 (s, 5H, C_5H_5), 3.46 (s, 2 × 3H, CH_3). ^{13}C NMR ($CDCl_3$, ppm): 40.61 (CH_3), 81.89 (Cp). ESI-MS (*m*/*z*): 338.08 (34%) [M]$^+$. IR (KBr, cm^{-1}): 1620.6 ($\nu_{N=N}$). Elemental analysis calcd (%) for $C_7H_{11}N_4O_4S_2Co$: C 24.86, H 3.28, N 16.56. Found: C 24.62, H 3.42, N 16.33.

Reaction of 1 with Methyl Azidoformate or Benzoyl Azide. A mixture of complex **1** (330 mg, 1 mmol) and methyl azidoformate (506 mg, 5 mmol) or benzoyl azide (735 mg, 5 mmol) was heated at 80 °C in toluene for 24 h. The red-brown mixture turned to green. The solvent was removed, and the crude product was purified by flash chromatography using silica gel (dichloromethane/ethyl ether = 10/1, v/v) to give complex **4a** or **4b**.

4a (245.6 mg, 60.7%); green solid. Mp: 268−269 °C. ^{1}H NMR ($CDCl_3$, ppm): 5.55 (s, 5H, C_5H_5), 3.83 (s, 3H, OC*H*$_3$). ^{11}B{^{1}H} NMR($CDCl_3$, ppm): −1.6 (2B), −2.5 (1B), −4.5 (1B), −6.0 (4B), −7.8 (1B), −8.8 (1B). ^{13}C NMR ($CDCl_3$, ppm): 58.52 (OCH_3), 86.08 (Cp), 96.24 (carborane), 103.50 (carborane), 184.23 (C═O). ESI-MS (*m*/*z*): 404.17 (77%) [M]$^+$. IR (KBr, cm^{-1}): 2593.5 (ν_{B-H}), 1736.6 (ν_{CO}). Elemental analysis calcd (%) for $C_9H_{18}B_{10}NO_2S_2Co$: C 26.80, H 4.50, N 3.47. Found: C 26.46, H 4.61, N 3.29.

4b (22.2 mg, 4.9%): yellow-green solid. Mp: 282−284 °C. ^{1}H NMR ($CDCl_3$, ppm): 8.02 (d, *J* = 7.5 Hz, 2H, Ar*H*), 7.48 (t, *J* = 7.5 Hz, 1H, Ar*H*), 7.37 (t, *J* = 7.5 Hz, 2H, Ar*H*), 5.57 (s, 5H, C_5H_5). ^{11}B{^{1}H} NMR($CDCl_3$, ppm): −1.2 (2B), −2.3 (1B), −4.4 (1B), −5.9 (4B), −7.8 (1B), −8.7 (1B). ^{13}C NMR ($CDCl_3$, ppm): 86.50 (Cp), 95.93 (carborane), 104.37 (carborane), 128.13 (CH, Ph), 130.03 (CH, Ph), 131.66 (C, Ph), 131.90 (CH, Ph), 186.50 (C═O). ESI-MS (*m*/*z*): 449.17 (21%) [M]$^+$, 450.25 (37%) [M + H]$^+$. IR (KBr, cm^{-1}): 2588.2 (ν_{B-H}), 1740.2 (ν_{CO}). Elemental analysis calcd (%) for $C_{14}H_{20}B_{10}NOS_2Co$: C 37.41, H 4.48, N 3.12. Found: C 36.99, H 4.66, N 3.27.

Reactions of 2a or 2b with Alkynes. General Procedures. To a solution of **2a** (75 mg, 0.15 mmol) or **2b** (64 mg, 0.15 mmol) in dichloromethane (15 mL) was added the corresponding alkyne (1.5 mmol). The mixture was stirred at room temperature for 1−12 h. The solvent was then removed under reduced pressure, and the residue obtained was dissolved in the minimum amount of dichloromethane for flash chromatographic separation on silica gel in a gradient eluting manner (petroleum ether/dichloromethane, 2:1, 1:1, 1:3 and then dichloromethane/ethyl ether, 10:1) to give the target compounds.

5a (65.7 mg, 75.2%): brownish-black solid. Mp: 86 °C (dec).^{1}H NMR ($CDCl_3$, ppm): 7.66 (d, *J* = 8 Hz, 2H, Ar*H*), 7.23 (d, *J* = 8 Hz, 2H, Ar*H*), 6.75 (s, 1H, C═C*H*), 5.46 (s, 5H, C_5H_5), 3.96 (s, 3H, OC*H*$_3$), 2.39 (s, 3H, C*H*$_3$). ^{11}B{^{1}H} NMR($CDCl_3$, ppm): 2.6 (1B), 0.1 (1B), −4.3 (2B), −8.3 (4B), −10.5 (2B). ^{13}C NMR ($CDCl_3$, ppm): 21.45 (CH_3), 52.42 (OCH_3), 67.11 (carborane), 85.04 (carborane), 85.35 (Cp), 127.57 (C═*C*H), 128.53 (CH, Ph), 128.89 (CH, Ph), 136.28 (C, Ph), 142.84 (C, Ph), 159.00 (*C*═CH), 167.46 (C═O). ESI-MS (*m*/*z*): 584.25 (43%) [M + H]$^+$. IR (KBr, cm^{-1}): 2586 (ν_{B-H}), 1713 (ν_{CO}). Elemental analysis calcd (%) for $C_{18}H_{26}B_{10}NO_4S_3Co$: C 37.04, H 4.49, N 2.40. Found: C 37.22, H 4.38, N 2.55.

5b (52.5 mg, 69.0%): brownish-black solid. Mp: 78 °C (dec). ^{1}H NMR ($CDCl_3$, ppm): 6.75 (s, 1H, C═C*H*), 5.51 (s, 5H, C_5H_5), 3.87 (s, 3H, OC*H*$_3$), 2.82 (s, 3H, C*H*$_3$). ^{11}B{^{1}H} NMR($CDCl_3$, ppm): 2.9 (1B), 0.8 (1B), −4.0 (2B), −8.1 (4B), −10.6 (2B). ^{13}C NMR ($CDCl_3$, ppm): 38.56 (CH_3), 52.46 (OCH_3), 67.54 (carborane), 80.30 (carborane), 85.44 (Cp), 127.82 (C═*C*H), 159.00 (*C*═CH), 167.68 (C═O). ESI-MS (*m*/*z*): 509.33 (100%) [M + H]$^+$. IR (KBr, cm^{-1}): 2589.1 (ν_{B-H}), 1715.2 (ν_{CO}). Elemental analysis calcd (%) for $C_{12}H_{22}B_{10}NO_4S_3Co$: C 28.40, H 4.37, N 2.76. Found: C 28.62, H 4.54, N 2.57.

6a (84.1 mg, 87.3%): brownish-red solid. Mp: 117−119 °C. ^{1}H NMR ($CDCl_3$, ppm): 7.72 (d, *J* = 8 Hz, 2H, Ar*H*), 7.23 (d, *J* = 8 Hz, 2H, Ar*H*), 5.61 (s, 5H, C_5H_5), 4.03 (s, 3H, OC*H*$_3$), 3.80 (s, 3H, OC*H*$_3$), 2.38 (s, 3H, C*H*$_3$). ^{11}B{^{1}H} NMR($CDCl_3$, ppm): 3.1 (1B), 0.3 (1B), −4.9 (2B), −8.4 (4B), −10.7 (2B). ^{13}C NMR ($CDCl_3$, ppm): 21.52 (CH_3), 52.61 (OCH_3), 52.87 (OCH_3), 67.01 (carborane), 86.35 (carborane), 86.72 (Cp), 123.10 (C═C), 128.94 (CH, Ph), 129.12 (CH, Ph), 135.21 (C, Ph), 143.24 (C, Ph), 155.60 (C═C), 171.06 (C═O), 187.26 (C═O). ESI-MS (*m*/*z*): 641.33 (6%) [M]$^+$, 665.17 (100%) [M + Na]$^+$. IR (KBr, cm^{-1}): 2583.3 (ν_{B-H}), 1714.8 (ν_{CO}). Elemental analysis calcd (%) for $C_{20}H_{28}B_{10}NO_6S_3Co$: C 37.44, H 4.40, N 2.18. Found: C 37.53, H 4.56, N 1.97.

6b (59.0 mg, 69.5%): brownish-red solid. Mp: 112−113 °C. ^{1}H NMR ($CDCl_3$, ppm): 5.54 (s, 5H, C_5H_5), 3.93 (s, 3H, OC*H*$_3$), 3.82 (s, 3H, OC*H*$_3$), 2.82 (s, 3H, C*H*$_3$). ^{11}B{^{1}H} NMR($CDCl_3$, ppm): 3.3 (1B), 0.6 (1B), −4.6 (2B), −7.9 (4B), −10.3 (1B), −12.3 (1B). ^{13}C NMR ($CDCl_3$, ppm): 39.15 (CH_3), 52.60 (OCH_3), 52.98 (OCH_3), 67.33 (carborane), 86.75 (Cp), 86.93 (carborane), 123.12 (C═C), 155.52 (C═C), 170.84 (C═O), 186.63 (C═O). ESI-MS (*m*/*z*): 567.25 (18%) [M + H]$^+$, 589.17 (100%) [M + Na]$^+$. IR (KBr, cm^{-1}): 2584.7 ($\nu_{\mathrm{B-H}}$), 1715.9 (ν_{CO}). Elemental analysis calcd (%) for $C_{14}H_{24}B_{10}NO_6S_3Co$: C 29.73, H 4.28, N 2.48. Found: C 29.48, H 4.55, N 2.67.

7a (52.8 mg, 58.6%): yellowish-brown solid. Mp: 208−209 °C. ^{1}H NMR (CDCl$_3$, ppm): 7.72 (d, *J* = 8 Hz, 2H, Ar*H*), 7.49 (d, *J* = 7 Hz, 2H, Ar*H*), 7.47 (s, 1H, C═C*H*), 7.41 (d, *J* = 8 Hz, 2H, Ar*H*), 7.35 (t, *J* = 7 Hz, 2H, Ar*H*), 7.29 (t, *J* = 7 Hz, 1H, Ar*H*), 4.83 (s, 5H, C_5H_5), 2.48 (s, 3H, C*H*$_3$). ^{11}B{^{1}H} NMR(CDCl$_3$, ppm): −0.8 (3B), −3.9 (2B), −5.0 (2B), −6.8 (3B). ^{13}C NMR (CDCl$_3$, ppm): 21.70 (CH$_3$), 88.35 (Cp), 94.97 (carborane), 103.49 (carborane), 126.80 (CH, Ph), 127.80 (CH, Ph), 127.91 (CH, Ph), 128.72 (CH, Ph), 129.73 (CH, Ph), 133.76 (C, Ph), 136.30 (C═CH), 139.70 (C═CH), 145.87 (C, Ph), 146.80 (C, Ph). ESI-MS (*m*/*z*): 602.17 (3%) [M]$^+$, 1267.17 (100%) [2M + Na + MeCN]$^+$. IR (KBr, cm^{-1}): 2567.2 ($\nu_{\mathrm{B-H}}$). Elemental analysis calcd (%) for $C_{22}H_{28}B_{10}NO_2S_3Co$: C 43.91, H 4.69, N 2.33. Found: C 43.63, H 4.53, N 2.17.

7b (42.0 mg, 53.3%): yellowish-brown solid. Mp: 168−170 °C. ^{1}H NMR (CDCl$_3$, ppm): 7.53 (s, 1H, C═C*H*), 7.47 (d, *J* = 8 Hz, 2H, Ar*H*), 7.37 (t, *J* = 7.5 Hz, 2H, Ar*H*), 7.30 (t, *J* = 7.5 Hz, 1H, Ar*H*), 5.31 (s, 5H, C_5H_5), 3.12 (s, 3H, OC*H*$_3$). ^{11}B{^{1}H} NMR(CDCl$_3$, ppm): −0.8 (3B), −3.9 (1B), −4.7 (2B), −6.8 (3B), −9.3 (1B). ^{13}C NMR (CDCl$_3$, ppm): 41.87 (CH$_3$), 88.76 (Cp), 95.82 (carborane), 102.58 (carborane), 126.78 (CH, Ph), 128.13 (CH, Ph), 128.35 (CH, Ph), 135.75 (C═CH), 139.80 (C═CH), 145.71 (C, Ph). ESI-MS (*m*/*z*): 527.08 (22%) [M + H]$^+$. IR (KBr, cm^{-1}): 2571.0 ($\nu_{\mathrm{B-H}}$). Elemental analysis calcd (%) for $C_{16}H_{24}B_{10}NO_2S_3Co$: C 36.56, H 4.60, N 2.66. Found: C 36.33, H 4.85, N 2.49.

8a (72 mg, 72.7%): brownish-black solid. Mp: 175−176 °C. ^{1}H NMR (CDCl$_3$, ppm): 7.84 (d, *J* = 8 Hz, 2H, Ar*H*), 7.49 (d, *J* = 7 Hz, 2H, Ar*H*), 7.37 (m, 3H, Ar*H*), 7.27 (d, J = 8 Hz, 2H, Ar*H*), 5.57 (s, 5H, C_5H_5), 3.93 (s, 3H, OC*H*$_3$), 2.41 (s, 3H, C*H*$_3$). ^{11}B{^{1}H} NMR(CDCl$_3$, ppm): 2.5 (1B), 0.1 (1B), −3.9 (2B), −8.6 (4B), −10.9 (2B). ^{13}C NMR (CDCl$_3$, ppm): 21.42 (CH$_3$), 52.12 (OCH$_3$), 66.33 (carborane), 85.51 (carborane), 86.28 (Cp), 128.21 (CH, Ph), 128.27 (CH, Ph), 128.46 (CH, Ph), 128.84 (CH, Ph), 129.06 (CH, Ph), 135.39 (C═C), 136.68 (C, Ph), 138.54 (C, Ph), 142.76 (C, Ph), 154.06 (C═C), 168.74 (C═O). ESI-MS (*m*/*z*): 659.17 (7%) [M]$^+$, 682.17 (21%) [M + Na]$^+$, 1342.08 (100%) [2M + Na]$^+$. IR (KBr, cm^{-1}): 2580.7 ($\nu_{\mathrm{B-H}}$), 1702.4 (ν_{CO}). Elemental analysis calcd (%) for $C_{24}H_{30}B_{10}NO_4S_3Co$: C 43.69, H 4.58, N 2.12. Found: C 43.91, H 4.65, N 2.03.

8b (61.5 mg, 70.3%): brownish-black solid. Mp: 161−163 °C. ^{1}H NMR (CDCl$_3$, ppm): 7.49 (d, *J* = 7 Hz, 2H, Ar*H*), 7.38 (m, 3H, Ar*H*), 5.54 (s, 5H, C_5H_5), 3.87 (s, 3H, OC*H*$_3$), 2.90 (s, 3H, C*H*$_3$). ^{11}B{^{1}H} NMR(CDCl$_3$, ppm): 2.7 (1B), 0.2 (1B), −3.8 (1B), −5.7 (1B), −8.4 (4B), −10.7 (1B), −12.2 (1B). ^{13}C NMR (CDCl$_3$, ppm): 39.67 (CH$_3$), 52.23 (OCH$_3$), 66.64 (carborane), 85.96 (carborane), 86.37 (Cp), 127.82 (CH, Ph), 128.53 (CH, Ph), 129.25 (CH, Ph), 135.20 (C═C), 137.30 (C, Ph), 153.84 (C═C), 169.20 (C═O). ESI-MS (*m*/*z*): 585.17 (20%) [M + H]$^+$, 607.08 (78%) [M + Na]$^+$, 1189.92 (100%) [2M + Na]$^+$. IR (KBr, cm^{-1}): 2583.8 ($\nu_{\mathrm{B-H}}$), 1703.9 (ν_{CO}). Elemental analysis calcd (%) for $C_{18}H_{26}B_{10}NO_4S_3Co$: C 37.04, H 4.49, N 2.40. Found: C 37.26, H 4.69, N 2.23.

9a (15.1 mg, 15.2%): brownish-red solid. Mp: 235−237 °C. ^{1}H NMR (CDCl$_3$, ppm): 7.64 (d, *J* = 8 Hz, 2H, Ar*H*), 7.38 (d, *J* = 8 Hz, 2H, Ar*H*), 7.32 (m, 5H, Ar*H*), 5.09 (s, 5H, C_5H_5), 3.36 (s, 3H, OC*H*$_3$), 2.48 (s, 3H, C*H*$_3$). ^{11}B{^{1}H} NMR(CDCl$_3$, ppm): −0.9 (3B), −4.3 (4B), −6.8 (3B). ^{13}C NMR (CDCl$_3$, ppm): 21.74 (CH$_3$), 51.69 (OCH$_3$), 89.39 (Cp), 95.87 (carborane), 102.98 (carborane), 127.94 (3 × CH, Ph), 128.60 (CH, Ph), 129.91 (CH, Ph), 134.19 (C, Ph), 135.34 (C, Ph), 136.25 (C═C), 144.30 (C═C), 146.11(C, Ph), 173.51 (C═O). ESI-MS (*m*/*z*): 661.00 (30%) [M + H]$^+$, 683.08 (100%) [M + Na]$^+$. IR (KBr, cm^{-1}): 2597.9 ($\nu_{\mathrm{B-H}}$), 1692.6 (ν_{CO}). Elemental analysis calcd (%) for $C_{24}H_{30}B_{10}NO_4S_3Co$: C 43.69, H 4.58, N 2.12. Found: C 43.38, H 4.46, N 1.97.

9b (14.5 mg, 16.5%): brownish-red solid. Mp: 216−217 °C. ^{1}H NMR (CDCl$_3$, ppm): 7.39 (m, 5H, Ar*H*), 5.47 (s, 5H, C_5H_5), 3.39 (s, 3H, OC*H*$_3$), 2.97 (s, 3H, C*H*$_3$). ^{11}B{^{1}H} NMR(CDCl$_3$, ppm): −1.0 (3B), −4.3 (3B), −7.0 (3B), −9.1 (1B). ^{13}C NMR (CDCl$_3$, ppm): 43.01 (CH$_3$), 51.68 (OCH$_3$), 89.63 (Cp), 96.50 (carborane), 102.52 (carborane), 128.44 (CH, Ph), 129.13 (CH, Ph), 134.65 (C, Ph), 136.56 (C═C), 143.51 (C═C), 172.96 (C═O). ESI-MS (*m*/*z*): 585.00 (15%) [M + H]$^+$, 607.08 (100%) [M + Na]$^+$. IR (KBr, cm^{-1}): 2591.1 ($\nu_{\mathrm{B-H}}$), 1698.1 (ν_{CO}). Elemental analysis calcd (%) for $C_{18}H_{26}B_{10}NO_4S_3Co$: C 37.04, H 4.49, N 2.40. Found: C 36.79, H 4.33, N 2.55.

10a (75.7 mg, 86.8%): brownish-red solid. Mp: 142−143 °C. ^{1}H NMR (CDCl$_3$, ppm): 7.90 (d, *J* = 8 Hz, 2H, Ar*H*), 7.48 (d, *J* = 8 Hz, 2H, Ar*H*), 6.00 (s, 1H, C═C*H*), 4.69 (s, 5H, C_5H_5), 2.54 (s, 3H, C*H*$_3$), 1.08 (s, 9H, 3 × C*H*$_3$). ^{11}B{^{1}H} NMR(CDCl$_3$, ppm): −1.1 (2B), −3.5 (1B), −6.0 (4B), −7.1 (3B). ^{13}C NMR (CDCl$_3$, ppm): 21.77 (CH$_3$), 31.13 (CH$_3$, ^{t}Bu), 38.43 (C, ^{t}Bu), 87.56 (Cp), 98.57 (carborane), 99.69 (carborane), 120.41 (C═CH), 128.12 (CH, Ph), 129.77 (CH, Ph), 134.83 (C, Ph), 139.12 (C═CH), 145.89 (C, Ph). ESI-MS (*m*/*z*): 583.08 (28%) [M + H]$^+$, 620.92 (100%) [M + K]$^+$. IR (KBr, cm^{-1}): 2565.3 ($\nu_{\mathrm{B-H}}$). Elemental analysis calcd (%) for $C_{20}H_{32}B_{10}NO_2S_3Co$: C 41.29, H 5.54, N 2.41. Found: C 41.57, H 5.66, N 2.30.

10b (67.7 mg, 89.3%): brownish-red solid. Mp: 133−134 °C. ^{1}H NMR (CDCl$_3$, ppm): 5.51 (s, 1H, C═C*H*), 5.24 (s, 5H, C_5H_5), 3.24 (s, 3H, C*H*$_3$), 1.13 (s, 9H, 3 × C*H*$_3$) . ^{11}B{^{1}H} NMR(CDCl$_3$, ppm): −1.1 (2B), −3.5 (1B), −5.8 (4B), −7.1 (2B), −8.6 (1B). ^{13}C NMR (CDCl$_3$, ppm): 31.29 (CH$_3$, ^{t}Bu), 39.89 38.43 (C, ^{t}Bu), 41.38 (CH$_3$), 87.97 (Cp), 99.03 (carborane), 99.42 (carborane), 125.85 (C═CH), 138.99 (C═CH). ESI-MS (*m*/*z*): 507.00 (27%) [M + H]$^+$, 544.00 (100%) [M + K]$^+$. IR (KBr, cm^{-1}): 2568.6 ($\nu_{\mathrm{B-H}}$). Elemental analysis calcd (%) for $C_{14}H_{28}B_{10}NO_2S_3Co$: C 33.26, H 5.58, N 2.77. Found: C 33.53, H 5.39, N 2.91.

Transformations of 8a and 8b to 9a and 9b. A solution of **8a** or **8b** (0.05 mmol) in CH$_2$Cl$_2$ (10 mL) was stirred for 24 h at room temperature. After removal of the solvent, the residue was chromatographed on silica, and elution with dichloromethane gave **9a** (25.3 mg, 76.7%) or **9b** (20.2 mg, 69.2%).

Computational Details. Molecular geometries of model complexes were optimized using the M06[36] functional. The M06 functional is a new hybrid meta exchange-correlation functional, which has been shown to accurately describe transition metal catalyzed organic transformations in recent reports.[37] The 6-31G(d) basis set was used for C, N, O, and S atoms, and the 6-31G basis set was used for the B and H atoms. The effective core potentials (ECPs) of Hay and Wadt with a double-ξ basis set (LanL2DZ)[38] were used for Co. Frequency calculations at the same level of theory have also been performed to identify all of the stationary points as minima (zero imaginary frequency) or transition states (one imaginary frequency). Intrinsic reaction coordinates (IRC)[39] were calculated for the transition states to confirm that such structures indeed connect two relevant minima. All calculations were performed with the Gaussian 09[40] software package.

X-ray Crystal 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 = 0.71073 Å) radiation. 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.[41] The structures were solved by direct methods with the SHELXS-97 program[42] and were refined on F^2 with SHELXTL (version 6.14).[43] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in calculated positions and were refined using a riding model. A summary of crystal data, data collection parameters, and structure refinement details is given in Tables S1 and S2 in the Supporting Information. CCDC 869405−869417 for the complexes **2a**, **3a**, **3b**, **4a**, **4b**, **5a**, **6a**, **7a**, **7b**, **8a**, **9a**, **9b**, and **10b** contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The structural views of complexes **3a**, **3b**, **4b**, **6a**, **7b**, and **9b**, potential energy profiles and corresponding optimized structures calculated for the insertion reactions, X-ray crystallographic data and the details of data collection and structural refinements, and CIF and checkcif files giving X-ray crystallographic data for the structural determinations of **2a**, **3a**, **3b**, **4a**, **4b**, **5a**, **6a**, **7a**, **7b**, **8a**, **9a**, **9b**, and **10b**. 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; htzhao@tju.edu.cn.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was supported by the National Natural Science Foundation of China (20925104, 21021062, 20872109, 20702037 and 20834002), the National Basic Research Program of China (2010CB923303), the Natural Science Foundation of Jiangsu Province (BK2010052), the Ministry of Education of China (20090091110015), the Scientific Research Foudation of Graduate School of Nanjing University (2010CL04) and Innovation Foundation of Tianjin University.

■ REFERENCES

(1) (a) Wang, K. *Prog. Inorg. Chem.* **2004**, *52*, 267. (b) Cummings, S. D.; Eisenberg, R. *Prog. Inorg. Chem.* **2004**, *52*, 315. (c) Nomura, M. *Dalton Trans.* **2011**, *40*, 2112.

(2) Fourmigué, M. *Coord. Chem. Rev.* **1998**, *178–180*, 823.

(3) (a) Cummings, S. D.; Cheng, L. T.; Eisenberg, R. *Chem. Mater.* **1997**, *9*, 440. (b) Faulmann, C.; Cassoux, P. *Prog. Inorg. Chem.* **2004**, *52*, 399. (c) Fourmigué, M. *Acc. Chem. Res.* **2004**, *37*, 179. (d) Kato, R. *Chem. Rev.* **2004**, *104*, 5319. (e) Kobayashi, A.; Fujiwara, E.; Kobayashi, H. *Chem. Rev.* **2004**, *104*, 5243. (f) Deplano, P.; Pilia, L.; Espa, D.; Mercuri, M. L.; Serpe, A. *Coord. Chem. Rev.* **2010**, *254*, 1434.

(4) (a) Holm, R. H. *Coord. Chem. Rev.* **1990**, *100*, 183. (b) Burgmayer, S. J. N. *Prog. Inorg. Chem.* **2004**, *52*, 491. (c) McMaster, J.; Tunney, J. M.; Garner, C. D. *Prog. Inorg. Chem.* **2004**, *52*, 539.

(5) (a) Sakurada, M.; Kajitani, M.; Dohki, K.; Akiyama, T.; Sugimori, A. *J. Organomet. Chem.* **1992**, *423*, 141. (b) Kajitani, M.; Sakurada, M.; Dohki, K.; Suetsugu, T.; Akiyama, T.; Sugimori, A. *J. Chem. Soc., Chem. Commun.* **1990**, 19.

(6) Kajitani, M.; Suetsugu, T.; Wakabayashi, R.; Igarashi, A.; Akiyama, T.; Sugimori, A. *J. Organomet. Chem.* **1985**, *293*, C15.

(7) (a) Kajitani, M.; Hatano, H.; Fujita, T.; Okumachi, T.; Nagao, H.; Akiyama, T.; Sugimori, A. *J. Organomet. Chem.* **1992**, *430*, C64. (b) Nomura, M.; Hatano, H.; Fujita, T.; Eguchi, Y.; Abe, R.; Yokoyama, M.; Takayama, C.; Akiyama, T.; Sugimori, A.; Kajitani, M. *J. Organomet. Chem.* **2004**, *689*, 997.

(8) (a) Nomura, M.; Yagisawa, T.; Takayama, C.; Sugiyama, T.; Yokoyama, Y.; Shimizu, K.; Sugimori, A.; Kajitani, M. *J. Organomet. Chem.* **2000**, *611*, 376. (b) Katsuta, N. N. H.; Inomata, Y.; Kajitani, M.; Akiyama, T.; Sugimori, A. *Chem. Lett.* **1994**, 1165. (c) Nomura, M.; Kawakita, A.; Katsuta, H.; Takayama, C.; Sugiyama, T.; Yokoyama, Y.; Kajitani, M. *J. Organomet. Chem.* **2003**, *681*, 180.

(9) (a) Kajitani, M.; Hagino, G.; Tamada, M.; Fujita, T.; Sakurada, M.; Akiyama, T.; Sugimori, A. *J. Am. Chem. Soc.* **1996**, *118*, 489. (b) Sugimori, A.; Tachiya, N.; Kajitani, M.; Akiyama, T. *Organometallics* **1996**, *15*, 5664. (c) Sugimori, A.; Akiyama, T.; Kajitani, M.; Sugiyama, T. *Bull. Chem. Soc. Jpn.* **1999**, *72*, 879.

(10) (a) Herberhold, M.; Yan, H.; Milius, W.; Wrackmeyer, B. *Angew. Chem., Int. Ed.* **1999**, *38*, 3689. (b) Wrackmeyer, B.; Yan, H.; Milius, W.; Herberhold, M. *Russ. Chem. Bull.* **2001**, *50*, 1518. (c) Herberhold, M.; Yan, H.; Milius, W.; Wrackmeyer, B. *Chem.—Eur. J.* **2002**, *8*, 388. (d) Herberhold, M.; Yan, H.; Milius, W.; Wrackmeyer, B. *Chem.—Eur. J.* **2000**, *6*, 3026. (e) Herberhold, M.; Yan, H.; Milius, W.; Wrackmeyer, B. *J. Chem. Soc., Dalton Trans.* **2001**, 1782. (f) Herberhold, M.; Yan, H.; Milius, W.; Wrackmeyer, B. *J. Organomet. Chem.* **2000**, *604*, 170. (g) Herberhold, M.; Yan, H.; Milius, W.; Wrackmeyer, B. *Z. Anorg. Allg. Chem.* **2000**, *626*, 1627.

(11) (a) Kim, D. H.; Ko, J.; Park, K.; Cho, S.; Kang, S. O. *Organometallics* **1999**, *18*, 2738. (b) Bae, J. Y.; Lee, Y. J.; Kim, S. J.; Ko, J.; Cho, S.; Kang, S. O. *Organometallics* **2000**, *19*, 1514. (c) Bae, J. Y.; Park, Y. I.; Ko, J.; Park, K. I.; Cho, S. I.; Kang, S. O. *Inorg. Chim. Acta* **1999**, *289*, 141. (d) Won, J. H.; Lim, H. G.; Kim, B. Y.; Lee, J. D.; Lee, C.; Lee, Y. J.; Cho, S.; Ko, J.; Kang, S. O. *Organometallics* **2002**, *21*, 5703. (e) Won, J. H.; Kim, D. H.; Lee, C.; Cho, S.; Kang, S. O. *Organometallics* **2002**, *21*, 1443.

(12) (a) Jin, G. X. *Coord. Chem. Rev.* **2004**, *248*, 587. (b) Jin, G. X.; Wang, J. Q.; Zhang, C.; Weng, L. H.; Herberhold, M. *Angew. Chem., Int. Ed.* **2005**, *44*, 259. (c) Wang, J. Q.; Cai, S. Y.; Jin, G. X.; Weng, L. H.; Herberhold, M. *Chem.—Eur. J.* **2005**, *11*, 7342. (d) Cai, S. Y.; Lin, Y. J.; Jin, G. X. *Dalton Trans.* **2006**, 912. (e) Liu, S.; Han, Y. F.; Jin, G. X. *Chem. Soc. Rev.* **2007**, *36*, 1543. (f) Meng, X.; Wang, F. S.; Jin, G. X. *Coord. Chem. Rev.* **2010**, *254*, 1260.

(13) (a) Xu, B. H.; Wu, D. H.; Li, Y. Z.; Yan, H. *Organometallics* **2007**, *26*, 4344. (b) Xu, B. H.; Tao, J. C.; Li, Y. Z.; Li, S. H.; Yan, H. *Organometallics* **2008**, *27*, 334. (c) Xu, B. H.; Peng, X. Q.; Li, Y. Z.; Yan, H. *Chem.—Eur. J.* **2008**, *14*, 9347. (d) Li, Y. G.; Jiang, Q. B.; Li, Y. Z.; Yan, H.; Bregadze, V. I. *Inorg. Chem.* **2010**, *49*, 4. (e) Li, Y. G.; Jiang, Q. B.; Zhang, X. L.; Li, Y. Z.; Yan, H.; Bregadze, V. I. *Inorg. Chem.* **2010**, *49*, 3911. (f) Li, Y. G.; Ye, H. D.; Guoyiqibayi, G.; Jiang, Q. B.; Li, Y. Z.; Yan, H. *Sci. China: Chem.* **2010**, *53*, 2129. (g) Ye, H. D.; Ding, G. Y.; Xie, M. S.; Li, Y. Z.; Yan, H. *Dalton Trans.* **2011**, *40*, 2306.

(14) Liu, G. F.; Hu, J. R.; Wen, J. L.; Dai, H. M.; Li, Y. Z.; Yan, H. *Inorg. Chem.* **2011**, *50*, 4187.

(15) Zhong, W.; Xie, M. S.; Jiang, Q. B.; Li, Y. Z.; Yan, H. *Chem. Commun.* **2012**, *48*, 2152.

(16) (a) Cenini, S.; La Monica, G. *Inorg. Chim. Acta* **1976**, *18*, 279. (b) Cenini, S.; Gallo, E.; Caselli, A.; Ragaini, F.; Fantauzzi, S.; Piangiolino, C. *Coord. Chem. Rev.* **2006**, *250*, 1234.

(17) (a) Montilla, F.; Clara, E.; Aviles, T.; Casimiro, T.; Ricardo, A. A.; da Ponte, M. N. *J. Organomet. Chem.* **2001**, *626*, 227. (b) Martinez, R.; Jimenez-Vazquez, H. A.; Delgado, F.; Tamariz, J. *Tetrahedron* **2003**, *59*, 481.

(18) (a) Pfeiffer, J.; Maringgele, W.; Noltemeyer, M.; Meller, A. *Chem. Ber.* **1989**, *122*, 245. (b) Leung, W. H.; Chim, J. L. C.; Hou, H. W.; Hun, T. S. M.; Williams, I. D.; Wong, W. T. *Inorg. Chem.* **1997**, *36*, 4432. (c) Albertin, G.; Antoniutti, S.; Bacchi, A.; Celebrin, A.; Pelizzi, G.; Zanardo, G. *Dalton Trans.* **2007**, 661.

(19) (a) Lee, S. W.; Miller, G. A.; Campana, C. F.; Trogler, W. C. *Inorg. Chem.* **1988**, *27*, 1215. (b) Lee, S. W.; Trogler, W. C. *Organometallics* **1990**, *9*, 1470.

(20) Gross, M. E.; Trogler, W. C.; Ibers, J. A. *J. Am. Chem. Soc.* **1981**, *103*, 192.

(21) (a) Kondo, T.; Mitsudo, T. *Chem. Rev.* **2000**, *100*, 3205. (b) Suginome, M.; Ito, Y. *J. Organomet. Chem.* **2003**, *685*, 218. (c) Suginome, M.; Ito, Y. *J. Organomet. Chem.* **2003**, *680*, 43. (d) Alonso, F.; Beletskaya, I. P.; Yus, M. *Chem. Rev.* **2004**, *104*, 3079. (e) Beller, M.; Seayad, J.; Tillack, A.; Jiao, H. *Angew. Chem., Int. Ed.* **2004**, *43*, 3368. (f) Beletskaya, I.; Moberg, C. *Chem. Rev.* **2006**, *106*, 2320.

(22) (a) Pandey, K. K. *Coord. Chem. Rev.* **1995**, *140*, 37. (b) Bai, T.; Ma, S. M.; Jia, G. C. *Coord. Chem. Rev.* **2009**, *253*, 423.

(23) (a) Boutadla, Y.; Davies, D. L.; Al-Duaij, O.; Fawcett, J.; Jones, R. C.; Singh, K. *Dalton Trans.* **2010**, *39*, 10447. (b) Evans, W. J.; Walensky, J. R.; Ziller, J. W. *Organometallics* **2010**, *29*, 945. (c) Leshinski, S.; Shalumova, T.; Tanski, J. M.; Waterman, R. *Dalton Trans.* **2010**, *39*, 9073.

(24) (a) Bouwkamp, M. W.; Batinas, A. A.; Witte, P. T.; Hubregtse, T.; Dam, J.; Meetsma, A.; Teuben, J. H.; Hessen, B. *Organometallics* **2008**, *27*, 4071. (b) Panda, T. K.; Tsurugi, H.; Pal, K.; Kaneko, H.; Mashima, K. *Organometallics* **2010**, *29*, 34. (c) Zhang, J.; Zhou, X. G. *C. R. Chim.* **2010**, *13*, 633.

(25) Chen, Y. H.; Peng, Y.; Chen, P. P.; Zhao, J. F.; Liu, L. T.; Li, Y.; Chen, S. Y.; Qu, J. P. *Dalton Trans.* **2010**, *39*, 3020.

(26) Hartwig, J. F.; Bergman, R. G.; Andersen, R. A. *J. Am. Chem. Soc.* **1991**, *113*, 6499.

(27) Martins, A. M.; Ascenso, J. R.; de Azevedo, C. G.; Dias, A. R.; Duarte, M. T.; da Silva, J. F.; Veiros, L. F.; Rodrigues, S. S. *Organometallics* **2003**, *22*, 4218.

(28) Cano, J.; Sudupe, M.; Royo, P.; Mosquera, M. E. G. *Organometallics* **2005**, *24*, 2424.

(29) (a) Nomura, M.; Takayama, C.; Janairo, G. C.; Sugiyama, T.; Yokoyama, Y.; Kajitani, M. *Organometallics* **2003**, *22*, 195. (b) Nomura, M.; Takayama, C.; Sugiyama, T.; Yokoyama, Y.; Kajitani, M. *Organometallics* **2004**, *23*, 1305.

(30) Davies, D. L.; Al-Duaij, O.; Fawcett, J.; Singh, K. *Organometallics* **2010**, *29*, 1413.

(31) (a) Ye, H. D.; Ding, G. Y.; Xie, M. S.; Li, Y. Z.; Yan, H. *Dalton Trans.* **2011**, *40*, 2306. (b) Teixidor, F.; Ayllón, J. A.; Viñas, C.; Kivekäs, R.; Sillanpää, R.; Casabó, J. *Inorg. Chem.* **1994**, *33*, 4815. (c) Teixidor, F.; Ayllón, J. A.; Viñas, C.; Kivekäs, R.; Sillanpää, R.; Casabó, J. *Organometallics* **1994**, *13*, 2751.

(32) (a) Esteruelas, M. A.; López, A. M.; Oliván, M. *Coord. Chem. Rev.* **2007**, *251*, 795. (b) Lynam, J. M.; Welby, C. E.; Whitwood, A. C. *Organometallics* **2009**, *28*, 1320. (c) Wakatsuki, Y.; Koga, N.; Werner, H.; Morokuma, K. *J. Am. Chem. Soc.* **1997**, *119*, 360.

(33) (a) Blanchini, C.; Peruzzini, M.; Vacca, A.; Zanobini, F. *Organometallics* **1991**, *10*, 3697. (b) Wakatsuki, Y. *J. Organomet. Chem.* **2004**, *689*, 4092. (c) Grotjahn, D. B.; Zeng, X.; Cooksy, A. L.; Kassel, W. S.; DiPasquale, A. G.; Zakharov, L. N.; Rheingold, A. L. *Organometallics* **2007**, *26*, 3385.

(34) King, R. B. *Inorg. Chem.* **1966**, *5*, 82.

(35) (a) McElwee-White, L.; Dougherty, D. A. *J. Am. Chem. Soc.* **1984**, *106*, 3466. (b) Alvarez, S. G.; Alvarez, M. T. *Synthesis* **1997**, 413. (c) Cwiklicki, A.; Rehse, K. *Arch. Pharm.* **2004**, *337*, 156. (d) Dyke, J. M.; Levita, G.; Morris, A.; Ogden, J. S.; Dias, A. A.; Algarra, M.; Santos, J. P.; Costa, M. L.; Rodrigues, P.; Andrade, M. M.; Barros, M. T. *Chem.—Eur. J.* **2005**, *11*, 1665. (e) Davis, M. C. *Synth. Commun.* **2007**, *37*, 2079.

(36) Zhao, Y.; Truhlar, D. G. *Theor. Chem. Acc.* **2008**, *120*, 215.

(37) (a) Fedorov, A.; Couzijn, E. P. A.; Nagornova, N. S.; Boyarkin, O. V.; Rizzo, T. R.; Chen, P. *J. Am. Chem. Soc.* **2010**, *132*, 13789. (b) Benitez, D.; Shapiro, N. D.; Tkatchouk, E.; Wang, Y.; Goddard, W. A.; Toste, F. D. *Nat. Chem.* **2009**, *1*, 482. (c) Torker, S.; Merki, D.; Chen, P. *J. Am. Chem. Soc.* **2008**, *130*, 4808.

(38) (a) Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**, *82*, 270. (b) Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**, *82*, 299. (c) Wadt, W. R.; Hay, P. J. *J. Chem. Phys.* **1985**, *82*, 284.

(39) (a) Fukui, K. *J. Phys. Chem.* **1970**, *74*, 4161. (b) Fukui, K. *Acc. Chem. Res.* **1981**, *14*, 363.

(40) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A., Jr., Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, O.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. *Gaussian 09, Revision A.02*; Gaussian, Inc.: Wallingford, CT, 2009

(41) Sheldrick, G. M. *SADABS, A Program for Empirical Absorption Correction*; University of Göttingen: Göttingen, Germany, 1998.

(42) Sheldrick, G. M. *SHELXL-97, Program for the Refinement of Crystal Structures*; University of Göttingen: Göttingen, Germany, 1997.

(43) Sheldrick, G. M. *Acta Crystallogr., Sect. A: Found. Crystallogr.* **2008**, *64*, 112.