ORGANOMETALLICS

Article

pubs.acs.org/Organometallics

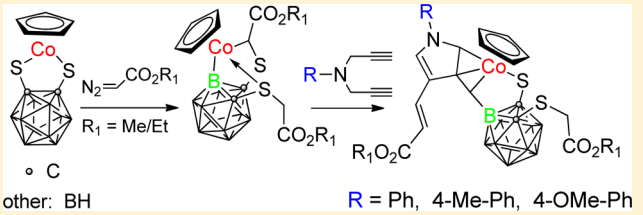
Pyrrolylmethyl Functionalized *o*-Carborane Derivatives

Huimin Dai, Guifeng Liu, Xiaolei Zhang, Hong Yan,* and Changsheng Lu*

State Key Laboratory of Coordination Chemistry, School of Chemistry and Chemical Engineering, Nanjing University, Nanjing, Jiangsu 210023, People's Republic of China

Supporting Information

ABSTRACT: The reactions of the 16e half-sandwich complex $CpCoS_2C_2B_{10}H_{10}$ (**1**), diazo esters, and various 1,6-diynes (**3a–i**; $PhN(CH_2C{\equiv}CH)_2$, 4-Me-$PhN(CH_2C{\equiv}CH)_2$, 4-OMe-$PhN(CH_2C{\equiv}CH)_2$, 4-F-$PhN(CH_2C{\equiv}CH)_2$, $BzN(CH_2C{\equiv}CH)_2$, $O(CH_2C{\equiv}CH)_2$, $C(Ac)_2(CH_2C{\equiv}CH)_2$, $N(CH_2C{\equiv}CH)_3$, $NH(CH_2C{\equiv}CH)N(CH_2C{\equiv}CH)_2$) were investigated, in which two novel types of B–H activated products $CpCoS_2B_{10}H_9(CH_2CO_2Et)C_5H_3N(R)(CH{=}CHCO_2Et)$ (**4a–c**; R = Ph, 4-Me-Ph, 4-OMe-Ph) and the key intermediate $CpCoS_2B_{10}H_9(CHCO_2Me)(CH_2CO_2Me)$ (**9**) were isolated. **9** features a reactive Co–B bond, which triggers insertion of various 1,6-diynes to further lead to different final products. Substrates **3a–c** are activated by the Co–B bond to produce *o*-carborane derivatives **4a–c** which are functionalized by a cobalt-complexed η^3-pyrrolylmethyl group. The pyrrole ring is formed by in situ ring closure of 1,6-diynes. Control experiments and isolation of the intermediate $CpCoS_2B_{10}H_9(CHCO_2Me)(CH_2CO_2Me)HC{=}CCH_2N(4\text{-Me-Ph})(CH_2C{\equiv}CH)$ (**10**) support the proposed mechanism concerning the formation of **4a–c** analogues by oxidation. All of the new complexes were characterized by NMR, IR, elemental analysis, and mass spectrometry. The structures of **4a–6a** and **9** were determined by single-crystal X-ray diffraction analysis as well.

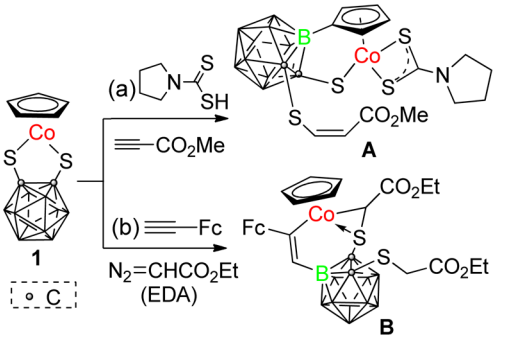


INTRODUCTION

Due to their unique structural rigidity, chemical stability, and three-dimensional aromaticity, icosahedral carboranes and their derivatives have attracted much attention to expand their applications in versatile fields such as supramolecular chemistry, functional materials, catalysis, and pharmaceutical research.[1−5] In terms of chemical functionalization of carboranes, selective and straightforward B–H activation[6] has been proved challenging in comparison with the facile modification of the C–H vertexes of carborane cages.[7] Fortunately, significant advances have been achieved by using transition-metal-catalyzed or -promoted B–H activation and sequential modification to form boron–heteroatom bonds.[8] During the past decade, our group has focused on the stoichiometric B–H activation of the type of half-sandwich transition-metal complexes $Cp'ME_2C_2B_{10}H_{10}$ (Cp′ = Cp, Cp*, M = Co, Rh, Ir, E = S, Se). Various boron-substituted carboranyl species have been isolated and fully characterized. Moreover, mechanisms behind the transformations have been investigated as well.[9−13]

Recently three-component reactions, in which a third reagent is introduced into the reaction of the *o*-carboranyl dithiolato half-sandwich compound $CpCoS_2C_2B_{10}H_{10}$ (**1**) with an alkyne, have led to unusual B–H functionalized carboranyl species which cannot be obtained by conventional methods. For example, the presence of an organic $3e^-$ donor (e.g., dithioic acid) in the reaction of **1** with methyl propiolate has induced facile B–C coupling between the carboranyl unit and the cyclopentadienyl ring (Scheme 1a).[14] By introduction of a diazo compound into the reaction mixture of **1** and an alkyne, a species resulting from alkyne insertion into a Co–B bond could be isolated (Scheme 1b).[15] Inspired by the interesting chemistry observed in this approach, we are curious about the probability of intramolecular domino transformations as well as B–H functionalization by incorporating a substrate with multiple functional groups. Diynes have been taken into consideration, as they have shown differing reactivity in macromolecule synthesis and ring-backbone formation.[16] The introduction of diynes into our three-component reactions

Scheme 1. Three-Component Reactions of (a) 1, Dithioic Acid, and Methyl Propiolate Leading to A and (b) 1, Ethyl Diazoacetate (EDA), and Ethynylferrocene Leading to B



Special Issue: Organometallics in Asia

Received: January 31, 2016

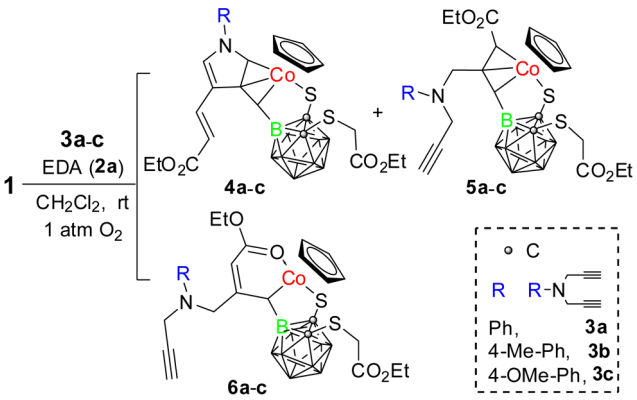
DOI: 10.1021/acs.organomet.6b00082
Organometallics XXXX, XXX, XXX–XXX

might produce more versatile functionalization at the boron sites of *o*-carborane cage and realize domino ring formation. Herein, we report a three-component reaction among **1**, a diazo compound, and a 1,6-diyne, which led to the isolation of an unprecedented carborane species. This carborane species is B(3) functionalized by a cobalt-complexed η^3-pyrrolylmethyl group. In addition, isolation and characterization of the key intermediate **9** bearing a reactive Co−B bond support the alkyne insertion step in B−C bond formation. Finally, a plausible oxidation mechanism concerning the formation of those pyrrolylmethyl functionalized *o*-carborane derivatives has also been proposed on the basis of control experiments.

RESULTS AND DISCUSSION

Three-Component Reactions of 1, EDA (2a), and Aryldipropargylamines 3a−c. In our previous studies, reactions of **1** with an alkyne and another small organic molecule such as a thiol, allene, or diazo compound have been investigated, where cyclopentadienyl or alkenyl functionalization at the B(3/6) position of the *o*-carborane cage were achieved. Evidently, this is a feasible method to selectively activate a B−H bond and construct a B−C linkage in carborane chemistry. However, it remains unknown whether or not this approach could lead to any new functionalization of B−H bonds. Thus, the 1,6-diyne **3a**, which features two propargyl groups fixed at one phenyl nitrogen, was selected for the three-component reaction. Compounds **3a** and **2a** were added sequentially to a CH_2Cl_2 solution of **1** at room temperature, and the reaction mixture was stirred for 5 h under oxygen, which led to the isolation of the new complexes **4a** (27%), **5a** (25%), and **6a** (30%) (Scheme 2). The last two were

Scheme 2. Three-Component Reactions of 1, EDA (2a), and Aryldipropargylamines 3a−c Leading to B−H Functionalized Carboranyl Complexes 4a−c, 5a−c, and 6a−c



characterized as structural analogues generated from the three-component reaction of **1**, **2a**, and monoalkynes.[13] All of these complexes (**4a−6a**) have been characterized by a combination of X-ray diffraction analysis and spectroscopic methods.

The crystal structure of **4a** (Figure 1) demonstrates that a five-membered pyrrole ring was generated, which binds with the cobalt center via allylic coordination (4e donor) to furnish 18e, as indicated by electron-counting rules. In fact, the Co-coordinated double bond (C8−C9, 1.425(3) Å) in the pyrrole ring is 0.05 Å longer than that of the noncoordinated bond (C10−C11, 1.373(4) Å). Therefore, the coordination has

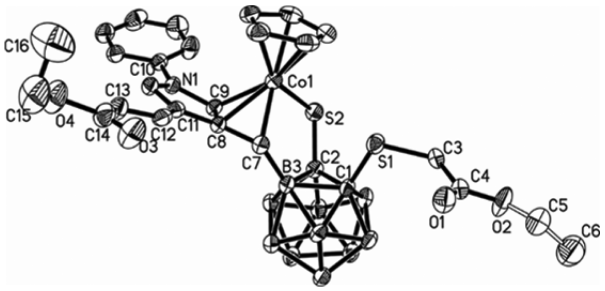


Figure 1. Crystal structure of **4a**. Ellipsoids are shown at the 30% probability level, and the hydrogen atoms have been omitted for clarity. Selected bond lengths (Å): Co(1)−C(7) 2.053(3), Co(1)−C(8) 2.071(3), Co(1)−C(9) 2.149(3), C(1)−C(2) 1.833(4), B(3)−C(7) 1.563(5), C(7)−C(8) 1.426(4), N(1)−C(9) 1.399(3), N(1)−C(10) 1.352(3), C(8)−C(9) 1.425(3), C(8)−C(11) 1.453(4), C(10)−C(11) 1.373(4).

somehow activated the C8−C9 double bond but still keeps this bond shorter than single bonds such as C8−C11 (1.453(4) Å) and C15−C16 (1.471(7) Å). The C7−C8 (1.426(4) Å) bond is almost as long as C8−C9 due to the allylic coordination. As indicated by the largest deviation of atoms to the plane (0.0138 Å), the five-membered ring C8C9N1C10C11 was found to remain planar. Moreover, the N-linked carbon atom of the phenyl ring is also in the same plane. The bonds N1−C10 (1.352(3) Å) and N1−C9 (1.399(3) Å) are shorter than those in diyne reactants (around 1.45 Å). Those further support the pyrrolyl property of the five-membered ring C8C9N1C10C11. Two molecules of the diazo ester are involved in the formation of **4a**: one is used to generate a pyrrole-conjugated *E*-type alkene, and the other is connected to one sulfur atom to give rise to a sulfide. B−H bond activation has occurred at the B(3) position of the carboranyl unit to generate the five-membered ring Co1S2C2B3C7 in **4a** with a B−C bond length of 1.563(5) Å, which is comparable to the usual B−C bond length (1.55−1.58 Å) in B-functionalized complexes.[17] The five atoms B3, C2, S2, Co1, and C7 are almost in the same plane with the largest deviation of 0.0578 Å. The C−C bond of the carborane cage is lengthened to 1.833(4) Å, longer than that in **1** (1.64 Å).[17]

The NMR data of complex **4a** are consistent with the X-ray structural analysis. ^{13}C NMR signals of C8 and C9 are located at 99.16 and 89.38 ppm, respectively, shifted to high field in comparison to C10 and C11 (131.18 and 122.79 ppm), but still at much lower field than C7 (a broad peak at 37.57 ppm). In the ^{1}H NMR spectrum, signals of the two hydrogens at C9 and C10 appear at 6.70 and 7.91 ppm, respectively, whereas the hydrogen at C7 appears at 5.84 ppm. All of the NMR data above suggest that the group C8C9N1C10C11 features a five-membered pyrrole ring and C7C8C9 adopts an allylic model to coordinate to the cobalt center. Two doublets with a 16 Hz coupling constant indicate the *E*-type configuration of the alkenyl unit linked to the pyrrole ring. The ^{11}B signal of B(3) (7.0 ppm) is shifted ca. 4 ppm to low field in comparison with that in **1**, indicating the activation of the B(3)−H bond.

Complex **4a** is unique. Both the ring closure and B(3) functionalization are interesting. Most likely, the pyrrole ring and B(3)−H functionalization in **4a** are generated by domino reactions with the assistance of the cobalt center. In order not only to explore the possible mechanism behind the formation of **4a** but also to extend the scope of this ring closure chemistry in selective functionalization of the carborane cage, 1,6-diynes

DOI: 10.1021/acs.organomet.6b00082
Organometallics XXXX, XXX, XXX−XXX

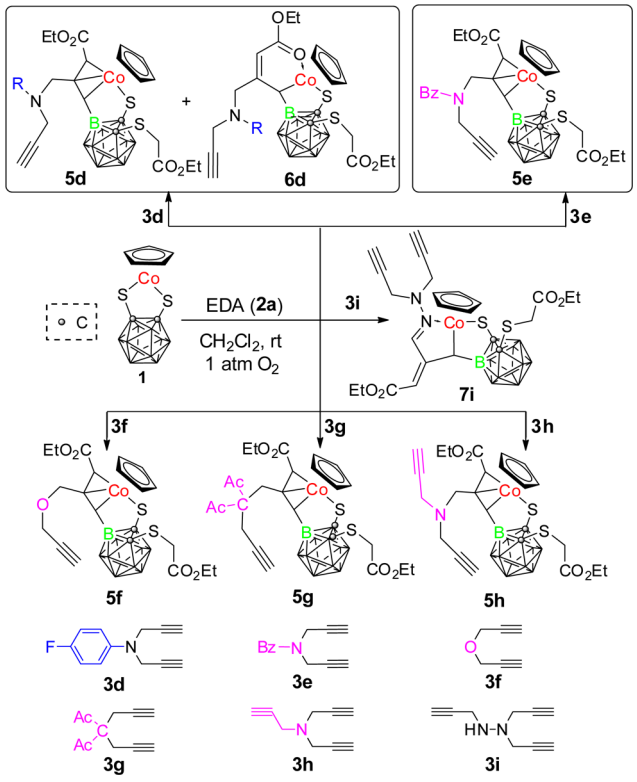
3b–i have been introduced to the three-component reactions with the consideration of electronic and steric effects as well as the bridging atoms. When **3b,c** were used, each of which contains an electron-donating group at the para position of the arylamine, complexes **4b,c** were isolated and characterized as the structural analogues of **4a** in similar yields (32% and 35%, respectively) (Scheme 2). Note that 1,6-diynes with an electron-donating group at the phenyl ring favor the ring formation. NMR data of the core frameworks of complexes **4a–c** are parallel, as shown in Table 1, from which a rational conclusion could be drawn that **4b,c** are the analogues of **4a**.

Table 1. Selected NMR Data (in ppm) for 4a–c

	^{1}H NMR		^{13}C NMR		
	B–C*H*	Co–C*H*–N	B–CH	Co–CH–N	Co–*C*–CH
4a	5.84	6.70	37.73	89.38	99.08
4b	5.86	6.69	37.54	89.56	98.71
4c	5.86	6.66	37.35	90.02	98.79

However, except for **3b,c**, all the other examined 1,6-diynes (**3d–i**) failed to form **4a** analogues (Scheme 3). Substrate **3d**,

Scheme 3. Three-Component Reactions of 1, EDA (2a), and Alkynes 3d–i Leading to Complexes 5d–h, 6d, and 7i



which bears a fluoro group at the phenyl ring, gave rise to **5d** and **6d** in moderate yields. Substrate **3e**, with a benzoyl group at the bridging nitrogen, could only generate **5e** in good yield (72%). In addition, the reactivity of **3f–h**, which possess different bridging atoms in connecting to the two propargyl groups, is similar to that of **3e**. However, the triyne **3i** has shown reactivity totally different from that of the above substrates. Despite the existence of three alkynyl groups in **3i**, the reaction does not lead to the expected ring closure of any two of the alkynyl groups as seen in **4a–c**. However, a different type of ring closure takes place at the less sterically hindered alkynyl group. The crystal structure of **7i** features a B-functionalized product by B(3)–H activation as well, and the generated B–C bond length is 1.578(4) Å, within the normal range (1.55–1.58 Å) for B-functionalized complexes. As illustrated in Figure 2, an imine group has formed between

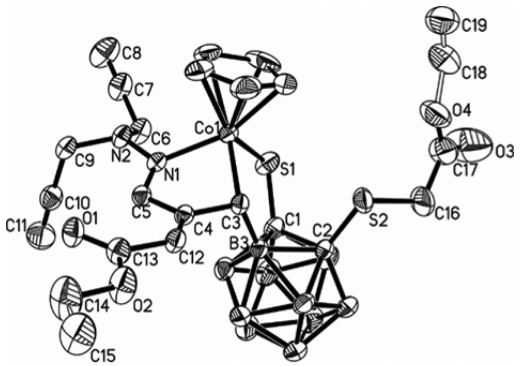


Figure 2. Crystal structure of **7i**. Ellipsoids are shown at the 30% probability level, and the hydrogen atoms have been omitted for clarity. Selected bond lengths (Å): Co(1)–N(1) 1.972(2), Co(1)–C(3) 2.026(3), C(1)–C(2) 1.798(5), C(3)–B(3) 1.578(4), C(5)–N(1) 1.291(4).

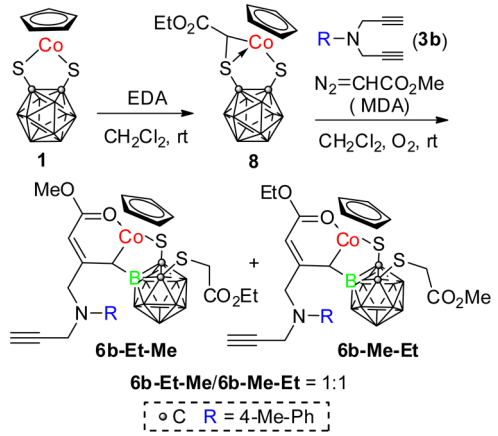
C5 and N1 (C5–N1 1.291(4) Å, shorter than a C–N single bond of around 1.45 Å). The imine group strongly favors coordinating complexation with the cobalt center to form a five-membered metallacycle. The NMR data of **7i** support the crystal structure. Signals of the imine group appear at 8.40 ppm in ^{1}H NMR and 152.34 ppm in ^{13}C NMR, respectively. The signal of C3 exhibits a broad peak at 28.60 ppm in ^{13}C NMR due to its connection to the boron atom. The signal of B3 is shifted to lower field to 11.5 ppm in comparison with that in **1**. Even though all of the introduced substrates containing either two or three alkynyl groups have led to functionalization of the *o*-carborane cage, their reactivities are different. Only **3a–c** reveal the transformation of both alkynyl groups; the others exhibit the reactivity of monoalkynes. The reactivity differences of the tested alkynes as well as the in situ ring formation of **4a–c** inspired us to investigate the formation mechanism.

In an attempt to elucidate the mechanism behind the generation of **4a**, control experiments have been performed. The intermediate **8**,[11,18] generated from the stoichiometric reaction between **1** and **2a**, was found not able to react with **3b** even in boiling toluene. This demonstrates the necessity of a second diazo acetate to drive the three-component reaction. This was further experimentally confirmed by the fact that the addition of methyl diazoacetate (MDA) to a mixture of **8** and **3b** led to a hypo dispersion (1:1 by ^{1}H NMR, Figure S1 in the Supporting Information) of the **6b** analogues **6b-Et-Me** and **6b-Me-Et**, as shown in Scheme 4. Afterward, B–H activation at the B(3) site of the *o*-carboranyl unit takes place upon the Co–S insertion of both diazo esters to generate a Co–B bond.

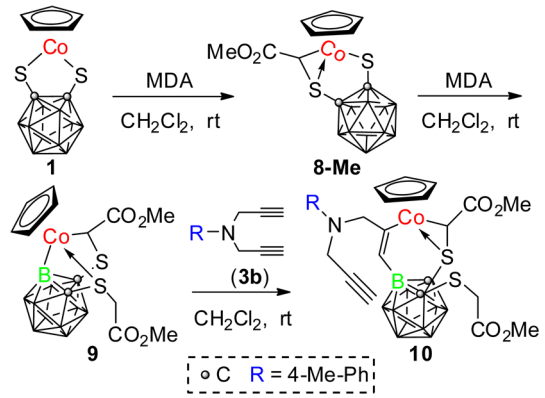
To our delight, intermediate **9** (Scheme 5) was isolated and fully characterized by a combination of NMR spectroscopy and single crystal X-ray analysis. The crystal structure indicates a Co–B bond length (1.944(2) Å) (Figure 3) comparable to the reported data (1.91–2.01 Å).[11,19] ^{11}B{^{1}H} NMR and ^{11}B NMR indicate the signal of Co–B to be at −3.7 ppm, which is significantly shifted to high field in comparison with B(3)–H

DOI: 10.1021/acs.organomet.6b00082
Organometallics XXXX, XXX, XXX–XXX

Scheme 4. Preparation of 6b Analogues by 8, Methyl Diazoacetate (MDA), and 3b



Scheme 5. Isolation of Intermediates 9 and 10 from the Three-Component Reaction of 1, MDA, and 3b



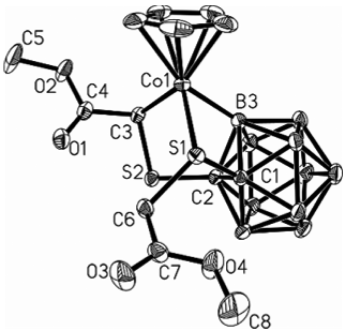
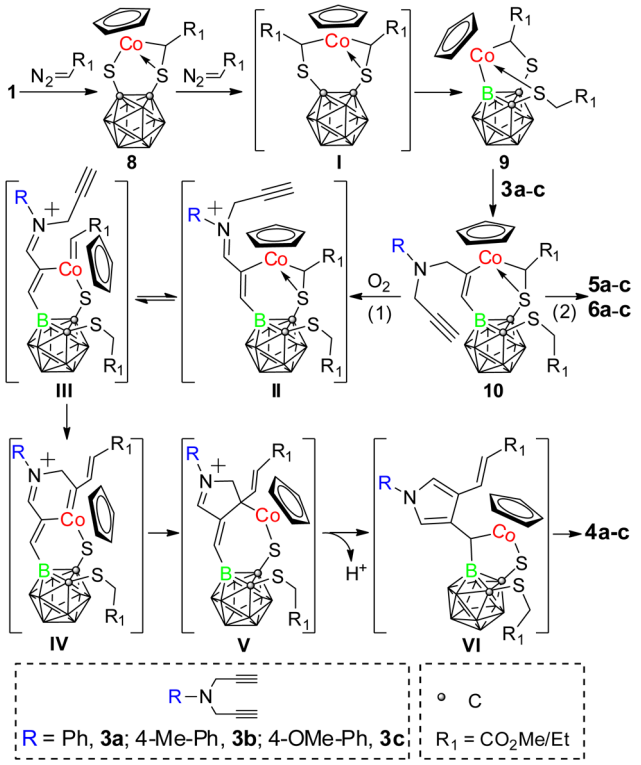


Figure 3. Crystal structure of intermediate **9**. Ellipsoids are shown at the 30% probability level, and the hydrogen atoms have been omitted for clarity. Selected bond lengths (Å): Co(1)−B(3) 1.944(2), Co(1)−C(3) 2.007(2), Co(1)−S(1) 2.240(6), C(1)−C(2) 1.691(3).

and B(3)−C bonds. Complex **9** is thermodynamically stable. However, the green intermediate **10** was immediately observed upon the addition of **3b** to a CH_2Cl_2 solution of **9** at 0 °C. A quick detection of the reaction mixture by ^1H NMR (Figure S2 in the Supporting Information) and HRMS-ESI (positive charge mode, m/z 682.2279) led to the identification of compound **10** as a product of alkyne insertion into the Co−B bond (Scheme 5). Compound **10** is kinetically stable and is readily converted to thermodynamically stable products (the analogues of **5b** and **6b**) at room temperature even under argon. In addition, analogues of **4a−c** were generated in the presence of an oxygen atmosphere at room temperature, indicating the importance of oxygen oxidation in pyrrole ring construction.

On the basis of the above experimental results, a plausible mechanism for the formation of **4a** analogues is summarized in Scheme 6. After two diazo compounds insert into the Co−S

Scheme 6. Proposed Mechanism for the Generation of Complexes 4a−c



bond of **1**, intermediate **I** is generated prior to B−H bond activation and subsequent Co−B bond formation affords **9**. Then alkyne insertion into the Co−B bond gives rise to **10** with the terminal alkynyl carbon selectively bonding with the boron atom. The formation of **10** is followed by two probable pathways of kinetic transformations dependent on the presence of oxygen: (1) oxidization to the imine-type intermediate **II** under oxygen[20] and (2) direct conversion to form the analogues of **5a** and **6a** in a nonoxidation procedure. Oxidation species **II** is proposed, and it is in equilibrium with species **III**, where the cobalt center bears a Fisher carbene and a thiolato ligand.[21] By metal carbene−alkyne metathesis,[22] the intermediate **IV** having one metallic six-membered ring is generated. Then subsequent carbon nucleophile insertion into the metal carbene gives rise to **V**.[23] Driven by the macrocycle tension release and conjugation stabilization in **V**, the pyrrole group is formed in **VI** by the release of H^+ and a double bond shift. Finally, one double bond in the pyrrole ring coordinates to cobalt to produce analogues **4a−c**.

CONCLUSION

The three-component reactions of *o*-carboranyl dichalcogen complexes **1**, diazo esters, and various diynes **3a−i** were investigated. All of the selected alkynes can lead to B(3)−H activation and functionalization, but the type of products depends on the alkynes. In particular, the bridging atom

DOI: 10.1021/acs.organomet.6b00082
Organometallics XXXX, XXX, XXX−XXX

between the two alkynyl groups of the diynes plays a key role in determining the structure of the products. Diynes **3a−c** without electron-withdrawing groups in aniline could give rise to the new-type carborane species **4a−c** in which B(3) functionalization by a cobalt-complexed η^3-pyrrolylmethyl group was achieved. Other diynes **3d−i** functionalize as monoalkynes. The intermediate **9** containing a reactive Co−B bond and the intermediate **10** showing alkyne insertion into a Co−B bond provide key evidence for mechanistic studies of the generation of novel products **4a−c** containing ring closure. Here these results provide a new pathway to the generation of complicated carborane functionalized products.

EXPERIMENTAL SECTION

All reactions were performed without moisture using standard Schlenk techniques. Solvents were dehadrated by refluxing over calcium hydride (dichloromethane) under nitrogen and then distilled prior to use. All of the reactants were prepared according to the literature methods. NMR data were recorded on Bruker 400, 500, and 600 MHz spectrometers. ^{1}H NMR and ^{13}C NMR spectra were reported in ppm with respect to residual chloroform ($\delta(^1$H) 7.27 ppm and $\delta(^{13}$C) 77.00 ppm), and ^{11}B NMR spectra were reported in ppm with respect to external $Et_2O{\cdot}BF_3$ ($\delta(^{11}$B) 0.0 ppm). The MS-ESI mass spectra were recorded on a Finnigan MAT TSQ7000 instrument, and HRMS-ESI high-resolution mass spectra were measured on an Agilent-G6540 UHD Accurate-MassQ-TOF instrument. IR spectra were measured with KBr pellets on a Bruker Vector 22 spectrophotometer in the region 4000−400 cm^{-1}. Elemental analyses were performed with an Elementar Vario EL III elemental analyzer.

General Procedure for the Preparation of B(3)-Functionalized Carborane Complexes 4a−7i. Compounds **3a−i** (1.2 mmol) and EDA (**2a**; about 1 mol/L in dichloromethane, 0.21 mL) were placed dropwise into a Schlenk flask which was charged with 5 mL of a dichloromethane solution of $CpCoS_2C_2B_{10}H_{10}$ (**1**; 330 mg, 1 mmol) at room temperature under an oxygen atmosphere. The mixture was stirred for 5 h and then concentrated. The residue was purified by column chromatography (dichloromethane/ethyl acetate 40/1) to give **4a−c**, **5a−h**, **6a−d**, and **7i**.

4a: yield 27%, brown solid. Mp: 170.5−171.9 °C. ^{1}H NMR ($CDCl_3$): δ 1.39 (t, 3H, J = 7.1 Hz, CH_2-CH_3); 1.40 (t, 3H, J = 7.1 Hz, CH_2-CH_3); 1.48−3.35 (9H, B−*H*); 4.02 (s, 2H, S−CH_2); 4.32 (q, 2H, J = 7.1 Hz, CH_2-CH_3); 4.34 (q, 2H, J = 7.1 Hz, CH_2-CH_3); 4.52 (s, 5H, Cp); 5.84 (s, 1H, B−*CH*−Co); 6.39 (d, 1H, J = 16.0 Hz, CH═*CH*−C═O); 6.70 (s, 1H, N−*CH*−Co); 7.41 (t, 1H, J = 7.7 Hz, Ph); 7.64 (t, 2H, J = 7.7 Hz, Ph); 7.72 (d, 1H, J = 16.0 Hz, *CH*═CH−C═O); 7.83 (d, J = 7.7 Hz, 2H, Ph); 7.91 (s, 1H, N−*CH*═C). ^{13}C NMR ($CDCl_3$): 14.17, 14.38 (CH_2-CH_3); 37.73 (br, B−CH−Co); 39.60 (S−CH_2), 60.57, 62.22 (CH_2-CH_3); 85.95 (Cp); 89.38 (N−*C*H−Co); 99.08 (Co−*C*−CH); 91.16, 108.56 (carborane *C*); 116.16 (C═*C*H−C═O); 122.79 (*C*−CH═CH); 131.18 (N−*C*H═C); 134.84 (CH═*C*H−C═O); 118.89, 126.39, 130.43, 138.99 (Ph); 167.35, 168.23 (*C*═O). ^{11}B{^{1}H} NMR ($CDCl_3$): 7.0 (B−CH, 1B), 1.6 (1B), −4.9 (2B), −7.3 (3B), −9.4 (1B), −12.1 (2B). IR (KBr): ν (cm^{-1}) 1689, 1733 (C═O); 2572 (B−H). MS-ESI for (M + Na$^+$): 692.15. Anal. Calcd for $C_{27}H_{36}B_{10}CoNO_4S_2$: C, 48.42; H, 5.42. Found: C, 48.04; H, 5.23.

5a: yield 25%, brown solid. Mp: 172.8−174.1 °C. ^{1}H NMR ($CDCl_3$): δ 1.37 (t, 3H, J = 7.0 Hz, CH_2-CH_3); 1.38 (t, 3H, J = 7.0 Hz, CH_2-CH_3); 2.37 (t, 1H, J = 2.1 Hz, CC*H*); 1.30−3.20 (9H, B−*H*); 3.71 (s, 1H, Co−*CH*−C═O); 3.97 (d, 1H, J = 15.5 Hz, S−CH_2); 4.02 (d, 1H, J = 15.5 Hz, S−CH_2); 3.93 (d, 1H, J = 13.6 Hz, CH_2−C−Co); 5.37 (d, 1H, J = 13.6 Hz, CH_2−C−Co); 4.22−4.34 (4H, CH_2-CH_3); 4.18 (d, 1H, J = 2.1, 18.0 Hz, CH_2−CCH); 4.34 (d, 1H, J = 2.1, 18.0 Hz, CH_2−CCH); 4.88 (s, 1H, B−*CH*−Co); 5.11 (s, 5H, Cp); 6.94 (t, 1H, J = 7.8 Hz, Ph); 7.16 (d, 2H, J = 7.8 Hz, Ph), 7.31 (t, 2H, J = 7.8 Hz, Ph). ^{13}C NMR ($CDCl_3$): 14.12, 14.31 (CH_2-CH_3); 39.56 (S−CH_2); 39.83 (CH_2−CCH); 56.79 (CH_2−C−Co); 56.82 (Co−CH−C═O); 61.00, 62.31 (CH_2-CH_3); 61.22 (br, B−CH−Co); 73.86 (CCH); 79.30 (CCH); 88.63 (Cp); 92.68, 110.05 (carborane *C*); 113.50 (Co−*C*−CH_2); 117.80, 120.60, 129.08, 148.35 (Ph); 168.22, 174.30 (*C*═O). ^{11}B{^{1}H} NMR ($CDCl_3$): 5.6 (B−CH, 1B), 2.2 (1B), −3.4 (2B), −6.8 (3B), −9.4 (1B), −11.3 (2B). IR (KBr): ν (cm^{-1}) 1700, 1734 (C═O); 2562 (B−H). MS-ESI for (M + Na$^+$): 694.10. Anal. Calcd for $C_{27}H_{38}B_{10}CoNO_4S_2$: C, 48.27; H, 5.70. Found: C, 48.02; H, 5.89. The molecular structure is given in Figure 4.

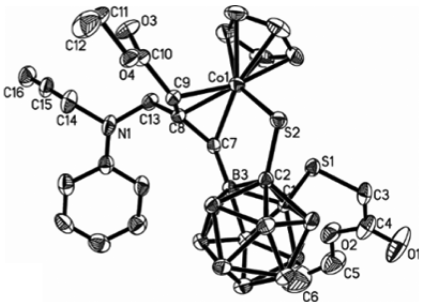


Figure 4. Molecular structure of **5a**. Ellipsoids are shown at the 30% probability level, and hydrogen atoms have been omitted for clarity. Selected bond lengths (Å): C(7)−B(3) 1.570(4), Co(1)−C(7) 2.085(3), Co(1)−C(8) 2.029(3), Co(1)−C(9) 2.059(3), C(1)−C(2) 1.825(3).

6a: yield 30%, purple solid. Mp: 161.4−162.3 °C. ^{1}H NMR ($CDCl_3$): δ 1.29 (t, 3H, J = 7.1 Hz, CH_2-CH_3); 1.34 (t, 3H, J = 7.1 Hz, CH_2-CH_3); 2.33 (s, 1H, CC*H*); 1.81−3.20 (9H, B−*H*); 3.90 (d, 1H, J = 15.5 Hz, S−CH_2); 3.98 (d, 1H, J = 15.5 Hz, S−CH_2); 4.10−4.30 (6H, CH_2−CCH, CO−CH_2); 4.52 (d, 1H, J = 19.0 Hz, CH_2−C═CH); 4.60 (d, 1H, J = 19.0 Hz, CH_2−C═CH); 4.93 (s, 5H, Cp); 5.04 (s, 1H, B−*CH*−Co); 5.96 (s, 1H, C═*CH*); 6.89 (t, J = 7.8 Hz, 1H, Ph); 6.98 (d, J = 7.8 Hz, 2H, Ph); 7.35 (t, J = 7.8 Hz, 2H, Ph). ^{13}C NMR ($CDCl_3$): 9.13 (br, B−*C*H−Co); 13.84, 14.08 (CH_2-CH_3); 38.73 (S−CH_2); 41.06 (CH_2−CCH); 57.64 (CH_2−C═CH); 62.03, 63.44 (CH_2-CH_3); 72.72 (*C*CH); 79.36 (*C*CH); 83.13 (Cp); 89.33, 111.47 (carborane *C*); 112.19 (C═*C*H); 113.49, 118.55, 129.31, 147.70 (Ph); 174.48, 168.21 (*C*═O), 180.86 (CH═*C*). ^{11}B{^{1}H} NMR ($CDCl_3$): δ 13.6 (B−CH, 1B), 0.7 (1B), −4.2 (3B), −7.1 (4B), −12.4 (1B). IR (KBr): ν (cm^{-1}) 1632, 1734 (C═O), 2552 (B−H). MS-ESI for (M + Na$^+$): 694.30. Anal. Calcd for $C_{27}H_{38}B_{10}CoNO_4S_2$: C, 48.27; H, 5.70. Found: C, 47.94; H, 5.58. The molecular structure is given in Figure 5.

4b: yield 32%, brown solid. Mp: 178.1−179.5 °C. ^{1}H NMR ($CDCl_3$): δ: 1.39 (t, J = 7.0 Hz, 3H, CH_2-CH_3), 1.40 (t, J = 7.0 Hz, 3H, CH_2-CH_3); 2.47 (s, 3H, Ph−CH_3); 1.48−3.35 (9H, B−*H*); 4.02 (s, 2H, S−CH_2); 4.32 (q, J = 7.0 Hz, 2H, CH_2-CH_3), 4.34 (q, J = 7.0 Hz, 2H, CH_2-CH_3); 4.50 (s, 5H, Cp); 5.86 (s, 1H, B−*CH*−Co); 6.37

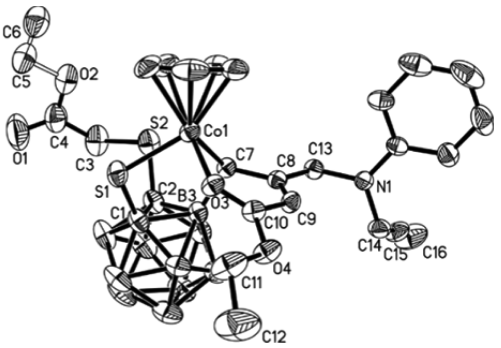


Figure 5. Molecular structure of **6a**. Ellipsoids are shown at the 30% probability level, and hydrogen atoms have been omitted for clarity. Selected bond lengths (Å): Co(1)−O(3) 1.979(2), Co(1)−C(7) 2.025(3), C(1)−C(2) 1.808(5), B(3)−C(7) 1.571(4).

DOI: 10.1021/acs.organomet.6b00082
Organometallics XXXX, XXX, XXX−XXX

(d, 1H, J = 16.0 Hz, C*H*−C═O); 6.69 (s, 1H, Co−C*H*−N); 7.72 (d, 1H, J = 16.0 Hz, C*H*═CH−CO); 7.43 (d, 2H, J = 8.1 Hz, Ph); 7.71 (d, 2H, J = 8.1 Hz, Ph); 7.89 (s, 1H, N−C*H*═C). ^{13}C NMR ($CDCl_3$): 14.21, 14.42 (CH_2−CH_3); 20.99 (Ph−CH_3); 37.54 (br, B−CH−Co); 39.64 (S−CH_2); 60.62, 62.27 (CH_2−CH_3); 85.93 (Cp); 89.56 (N−CH−Co); 98.71 (Co−*C*−CH); 91.10, 108.56 (carborane *C*); 115.85 (C═*C*H−C═O); 122.52 (*C*−CH═CH); 131.41 (N−CH═C); 134.99 (*C*H═CH−C═O); 118.88, 130.95, 136.74, 136.47 (*Ph*); 167.51, 168.34 (*C*═O). ^{11}B{^{1}H} NMR ($CDCl_3$): 7.4 (B−CH, 1B), 1.9 (1B), −3.3 (2B), −7.3 (3B), −9.4 (1B), −12.0 (2B). IR (KBr): ν (cm^{-1}) 1701, 1732 (C═O); 2574 (B−H). MS-ESI for (M + Na^+): 706.01. Anal. Calcd for $C_{28}H_{38}B_{10}NO_4S_2Co$: C, 49.18; H, 5.60. Found: C, 49.01; H, 5.72.

5b: yield 24%, brown solid. Mp: 182.3−183.2 °C. ^{1}H NMR ($CDCl_3$): δ 1.36 (t, J = 7.1 Hz, 3H, CH_2−CH_3); 1.38 (t, J = 7.1 Hz, 3H, CH_2−CH_3); 2.30 (s, 3H, Ph−CH_3); 2.36 (t, J = 2.3 Hz, 1H, CC*H*); 1.30−3.20 (9H, B−*H*); 3.70 (s, 1H, Co−C*H*−C═O); 3.85 (d, J = 13.4 Hz, 1H, CH_2−C−Co); 5.30 (d, J = 13.4 Hz, 1H, CH_2−C−Co); 3.98 (d, J = 15.5 Hz, 1H, S−CH_2); 4.03 (d, J = 15.5 Hz, 1H, S−CH_2); 4.12 (dd, J = 2.3, 18.0 Hz, 1H, CH_2−CCH); 4.32 (dd, J = 2.3, 18.0 Hz, 1H, CH_2−CCH); 4.20−4.28 (m, 2H, CO−CH_2); 4.31 (q, J = 7.1 Hz, 2H, CO−CH_2); 4.86 (s, 1H, B−C*H*−Co); 5.10 (s, 5H, Cp); 7.07 (d, J = 8.6 Hz, 2H, Ph); 7.12 (d, J = 8.6 Hz, 2H, Ph). ^{13}C NMR ($CDCl_3$): δ 14.15, 14.30 (CH_2−CH_3); 20.49 (Ph−CH_3); 39.60 (S−CH_2); 40.05 (CH_2−CCH); 57.06 (CH_2−C−Co); 57.27 (Co−CH−C═O); 61.69 (br, B−CH−Co); 60.98, 62.32 (CO−CH_2); 73.79 (CH_2−CCH); 79.41 (CH_2−CCH); 88.63 (Cp); 92.72, 110.17 (carborane *C*); 113.45 (Co−*C*−CH_2); 118.66, 129.60, 130.42, 146.36 (Ph); 168.23, 174.16 (*C*═O). ^{11}B{^{1}H} NMR ($CDCl_3$): 6.1 (B−CH, 1B); 2.6 (1B); −2.9 (2B); −6.6 (3B); −9.2 (1B); −11.1 (2B). IR (KBr): ν (cm^{-1}) 1730, 1734 (C═O); 2573 (B−H). MS-ESI for (M + Na^+): 707.98. Anal. Calcd for $C_{28}H_{40}B_{10}NO_4S_2Co$: C, 49.04; H, 5.88. Found: C, 48.77; H, 5.99.

6b: yield 34%, purple solid. Mp: 165.4−167.0 °C. ^{1}H NMR ($CDCl_3$): δ 1.27 (t, J = 7.1 Hz, 3H, CH_2−CH_3), 1.34 (t, J = 7.1 Hz, 3H, CH_2−CH_3); 2.32 (t, J = 2.2 Hz, 1H, CC*H*); 2.30 (s, 3H, PhCH_3); 1.81−3.20 (9H, B−*H*); 3.89 (d, J = 15.5 Hz, 1H, S−CH_2); 3.97 (d, J = 15.5 Hz, 1H, S−CH_2); 4.10−4.30 (6H, CH_2−CCH, CO−CH_2); 4.46 (d, J = 18.7 Hz, 1H, CH═CCH_2); 4.55 (d, J = 18.7 Hz, 1H, CH═CCH_2); 4.92 (s, 5H, Cp); 5.04 (s, 1H, B−C*H*−Co); 5.98 (s, 1H, C*H*−C═O); 6.90 (d, J = 8.4 Hz, 2H, Ph); 7.16 (d, J = 8.4 Hz, 2H, Ph). ^{13}C NMR ($CDCl_3$): δ 13.90, 14.14 (CH_2−CH_3); 9.20 (br, Co−CH−B); 20.31 (Ph−CH_3); 38.82 (S−CH_2); 41.29 (CH_2−CCH); 57.89 (CH_2−C═CH); 62.13, 63.49 (CO−CH_2); 72.66 (CCH); 79.49 (CCH); 83.19 (Cp); 89.26, 111.32 (carborane *C*); 112.26 (CH═*C*); 113.77, 129.88, 127.96, 145.58 (Ph); 174.58, 168.34 (*C*═O); 181.14 (*C*═CH). ^{11}B{^{1}H} NMR ($CDCl_3$): δ 13.7 (B−CH, 1B); 0.6 (1B); −4.4 (3B); −7.4 (4B); −12.5 (1B). IR (KBr): ν (cm^{-1}) 1699, 1733 (C═O), 2559 (B−H). MS-ESI for (M + Na^+): 708.12. Anal. Calcd for $C_{28}H_{40}B_{10}NO_4S_2Co$: C, 49.04; H, 5.88. Found: C, 48.85; H, 5.63.

4c: yield 35%, brown solid. Mp: 181.3−182.2 °C. ^{1}H NMR ($CDCl_3$): δ 1.38 (t, J = 7.0 Hz, 3H, CH_2−CH_3), 1.39 (t, J = 7.0 Hz, 3H, CH_2−CH_3); 1.48−3.35 (9H, B−*H*); 3.92 (s, 3H, Ph−OCH_3); 4.02 (s, 2H, S−CH_2); 4.31 (q, J = 7.0 Hz, 2H, CH_2−CH_3), 4.33 (q, J = 7.0 Hz, 2H, CH_2−CH_3); 4.50 (s, 5H, Cp); 5.87 (s, 1H, B−C*H*−Co); 6.36 (d, 1H, J = 16.0 Hz, C*H*−C═O); 6.67 (s, 1H, Co−C*H*−N); 7.71 (d, 1H, J = 16.0 Hz, C*H*═CH−CO); 7.15 (d, 2H, J = 8.7 Hz, Ph); 7.75 (d, 2H, J = 8.7 Hz, Ph); 7.84 (s, 1H, N−C*H*═C). ^{13}C NMR ($CDCl_3$): 14.20, 14.42 (CH_2−CH_3); 37.35 (br, B−CH−Co); 39.63 (S−CH_2); 55.73 (Ph−OCH_3), 60.60, 62.27 (CH_2−CH_3); 85.87 (Cp); 90.02 (N−CH−Co); 98.79 (Co−*C*−CH); 91.10, 108.54 (carborane *C*); 115.58 (C═*C*H−C═O); 122.32 (*C*−CH═CH); 131.67 (N−CH═C); 135.01 (CH═CH−C═O); 120.44, 115.58, 132.66, 158.26 (*Ph*); 167.52, 168.32 (*C*═O). ^{11}B{^{1}H} NMR ($CDCl_3$): 7.5 (B−CH, 1B), 2.1 (1B), −4.0 (2B), −6.9 (3B), −9.3 (1B), −11.5 (2B). IR (KBr): ν (cm^{-1}) 1689, 1733 (C═O); 2572 (B−H). MS-ESI for (M + Na^+): 722.09. Anal. Calcd for $C_{28}H_{38}B_{10}NO_5S_2Co$: C, 48.06; H, 5.47. Found: C, 47.81; H, 5.39.

5c: yield 27%, brown solid. Mp: 184.2−185.3 °C. ^{1}H NMR ($CDCl_3$): δ 1.35 (t, J = 7.0 Hz, 3H, CH_2−CH_3); 1.38 (t, 7.0 Hz, 3H, CH_2−CH_3); 2.38 (t, J = 2.3 Hz, 1H, CC*H*); 1.50−3.20 (9H, B−*H*); 3.67 (s, 1H, Co−C*H*−C═O); 3.79 (s, 3H, OCH_3); 3.78 (d, J = 13.1 Hz, 1H, CH_2−C−Co); 5.30 (d, J = 13.1 Hz, 1H, CH_2−C−Co); 3.98 (d, J = 15.5 Hz, 1H, S−CH_2); 4.03 (d, J = 15.5 Hz, 1H, S−CH_2); 4.06 (dd, J = 2.3, 17.5 Hz, 1H, CH_2−CCH); 4.29 (dd, J = 2.3, 17.5 Hz, 1H, CH_2−CCH); 4.21 (q, J = 7.0 Hz, 2H, CO−CH_2); 4.32 (q, J = 7.0 Hz, 2H, CO−CH_2); 4.83 (s, 1H, B−C*H*−Co); 5.09 (s, 5H, Cp); 6.87 (d, J = 9.0 Hz, 2H, Ph); 7.14 (d, J = 9.0 Hz, 2H, Ph). ^{13}C NMR ($CDCl_3$): δ 14.18, 14.30 (CH_2−CH_3); 39.66 (S−CH_2); 40.88 (CH_2−CCH); 55.56 (Ph−OCH_3); 57.25 (Co−CH−C═O); 58.06 (CH_2−C−Co); 61.40 (br, B−CH−Co); 61.00, 62.36 (CH_2−C═O); 73.89 (CCH); 79.57 (CCH); 88.64 (Cp); 92.77, 110.27 (carborane *C*); 113.08 (Co−*C*−CH_2); 114.39, 121.44, 142.71, 154.87 (Ph); 168.29, 174.12 (*C*═O). ^{11}B{^{1}H} NMR ($CDCl_3$): δ 6.0 (B−CH, 1B); 2.6 (1B); −3.0 (2B); −6.6 (3B); −9.2 (1B); −11.1 (2B). IR (KBr): ν (cm^{-1}) 1730, 1750 (C═O); 2582 (B−H). MS-ESI for (M + Na^+): 724.01. Anal. Calcd for $C_{28}H_{40}B_{10}NO_5S_2Co$: C, 47.92; H, 5.74. Found: C, 47.79; H, 5.96.

6c: yield 32%, purple solid. Mp: 171.2−172.4 °C. ^{1}H NMR ($CDCl_3$): δ 1.28 (t, J = 7.1 Hz, 3H, CH_2−CH_3); 1.34 (t, J = 7.1 Hz, 3H, CH_2−CH_3); 2.33 (t, J = 2.3 Hz, 1H, CC*H*); 1.81−3.20 (9H, B−*H*); 3.80 (s, 3H, OCH_3); 3.89 (d, J = 15.5 Hz, 1H, S−CH_2); 3.97 (d, J = 15.5 Hz, 1H, S−CH_2); 4.10−4.29 (6H, CH_2−CCH, CO−CH_2); 4.41 (d, J = 19.1 Hz, 1H, CH═C−CH_2); 4.51 (d, J = 19.1 Hz, 1H, CH═C−CH_2); 4.90 (s, 5H, Cp); 5.07 (s, 1H, B−C*H*−Co); 6.01 (s, 1H, C*H*−C═O); 6.93 (d, J = 9.2 Hz, 2H, Ph); 6.98 (d, J = 9.2 Hz, 2H, Ph). ^{13}C NMR ($CDCl_3$): δ 9.44 (br, Co−CH−B); 13.95, 14.17 (CH_2−CH_3); 38.86 (S−CH_2); 42.00 (CH_2−CCH); 55.74 (OCH_3); 62.32 (CH_2−C═CH); 62.15, 63.53 (CO−CH_2); 72.90 (CCH); 79.56 (CCH); 83.23 (Cp); 89.34, 111.43 (carborane *C*); 112.47 (CH═C); 114.85, 115.95, 142.46, 153.17 (Ph); 168.37, 174.61 (*C*═O); 181.51 (*C*═CH). ^{11}B{^{1}H} NMR ($CDCl_3$): δ 14.6 (B−CH, 1B), 0.8 (1B), −4.1 (3B), −7.1 (4B), −12.6 (1B). IR (KBr): ν (cm^{-1}) 1730, 1730 (C═O); 2577 (B−H). MS-ESI for (M + Na^+): 724.19. Anal. Calcd for $C_{28}H_{40}B_{10}NO_5S_2Co$: C, 47.92; H, 5.74. Found: C, 47.67; H, 5.95.

5d: yield 63%, brown solid. Mp: 176.4−177.1 °C. ^{1}H NMR ($CDCl_3$): δ 1.37 (t, J = 7.1 Hz, 3H, CH_2−CH_3), 1.38 (t, J = 7.1 Hz, 3H, CH_2−CH_3); 2.39 (t, J = 2.2 Hz, 1H, CC*H*); 1.50−3.20 (9H, B−*H*); 3.69 (s, 1H, Co−C*H*−C═O); 3.80 (d, J = 13.2 Hz, 1H, CH_2−C−Co); 5.30 (d, J = 13.2 Hz, 1H, CH_2−C−Co); 3.98 (d, J = 15.5 Hz, 1H, S−CH_2); 4.03 (d, J = 15.5 Hz, 1H, S−CH_2); 4.08 (dd, J = 17.9, 2.2 Hz, 1H, CH_2−CCH); 4.20−4.35 (5H, CH_2−CCH, CO−CH_2); 4.82 (s, 1H, B−C*H*−Co); 5.10 (s, 5H, Cp); 7.00 (t, J = 8.7 Hz, 2H, Ph); 7.14 (dd, J = 4.6, 9.1 Hz, 2H, Ph). ^{13}C NMR ($CDCl_3$): δ 14.13, 14.28 (CH_2−CH_3); 39.59 (S−CH_2); 40.48 (CH_2−CCH); 56.94 (Co−CH−C═O); 57.73 (CH_2−C−Co); 61.37 (br, B−CH−Co); 61.02, 62.33 (CO−CH_2); 79.10 (CCH); 74.11 (CCH); 88.64 (Cp); 92.79, 110.20 (carborane *C*); 112.87 (Co−*C*−CH_2); 115.52 (J_{C-F} = 22.2 Hz, Ph); 120.51 (J_{C-F} = 7.7 Hz, Ph); 145.03 (Ph); 157.35 (J_{C-F} = 240.3 Hz, Ph); 168.20, 174.22 (C═O). ^{11}B{^{1}H} NMR ($CDCl_3$): δ 6.1 (B−CH, 1B); 2.5 (1B); −3.2 (2B); −6.6 (3B); −9.2 (1B); −11.0 (2B). IR (KBr): ν (cm^{-1}) 1730, 1742 (C═O); 2567 (B−H). MS-ESI for (M + Na^+): 711.93. Anal. Calcd for $C_{27}H_{37}B_{10}NO_4FS_2Co$: C, 47.01; H, 5.41. Found: C, 46.83; H, 5.32.

6d: yield 21%, purple solid. Mp: 159.6−160.6 °C. ^{1}H NMR ($CDCl_3$): δ 1.28 (t, J = 7.1 Hz, 3H, CH_2−CH_3), 1.34 (t, J = 7.1 Hz, 3H, CH_2−CH_3); 2.35 (t, J = 2.3 Hz, 1H, CC*H*); 1.51−3.20 (9H, B−*H*); 3.89 (d, J = 15.5 Hz, 1H, S−CH_2); 3.97 (d, J = 15.5 Hz, 1H, S−CH_2); 4.13−4.29 (6H, CH_2−CCH, CO−CH_2); 4.44 (d, J = 19.6 Hz, 1H, CH═CCH_2); 4.54 (d, J = 19.6 Hz, 1H, CH═CCH_2); 4.92 (s, 5H, Cp); 5.03 (s, 1H, B−C*H*−Co); 5.96 (s, 1H, C*H*−C═O); 6.93 (dd, J = 4.3, 9.2 Hz, 2H, Ph), 7.05 (t, J = 8.8 Hz, 2H, Ph). ^{13}C NMR ($CDCl_3$): 9.29 (br, Co−CH−B); 13.89, 14.13 (CH_2−CH_3); 38.82 (S−CH_2); 41.63 (CH_2−CCH); 58.23 (CH_2−C−Co); 62.14, 63.58 (CO−CH_2); 73.01 (CCH); 79.14 (CCH); 83.16 (Cp); 89.30, 110.40 (carborane *C*); 112.25 (CH═C); 115.10 (J_{C-F} = 7.7 Hz, Ph); 115.88 (J_{C-F} = 22.2 Hz, Ph); 144.47 (Ph); 157.53 (J_{C-F} = 240.3, Ph); 168.31, 174.48 (*C*═O); 180.88 (*C*═CH). ^{11}B{^{1}H} NMR ($CDCl_3$): δ 13.9 (B−CH, 1B), 0.7 (2B), −4.4 (3B), −7.3 (3B), −12.5 (2B). IR (KBr): ν (cm^{-1}) 1733, 1635 (C═O); 2582 (B−H). MS-ESI for (M + Na^+):

DOI: 10.1021/acs.organomet.6b00082
Organometallics XXXX, XXX, XXX−XXX

712.08. Anal. Calcd for $C_{27}H_{37}B_{10}NO_4FS_2Co$: C, 47.01; H, 5.41. Found: C, 46.77; H, 5.63.

5e: yield 72%, brown solid. Mp: 204.7−205.3 °C. ^{1}H NMR ($CDCl_3$): δ 1.37 (t, J = 7.0 Hz, 3H, CH_2-CH_3); 1.42 (t, J = 7.0 Hz, 3H, CH_2-CH_3); 2.40 (s, J = 1H, CCH); 1.50−3.20 (9H, B−H); 3.90 (1H, CH_2−C−Co); 3.97 (d, J = 15.5 Hz, 1H, S−CH_2); 4.02 (d, J = 15.5 Hz, 1H, S−CH_2); 4.19 (2H, CH_2−CCH); 4.26−4.44 (4H, CO−CH_2); 5.17 (5H, Cp); 4.84−5.27 (3H, B−CH−Co, CH_2−C−Co); 7.47 (3H, Ph); 7.56 (m, 2H, Ph); ^{13}C NMR ($CDCl_3$): δ 14.16, 14.44 (CH_2-CH_3); 39.33 (CH_2−CCH); 39.58 (S−CH_2); 56.76 (CH_2−C−Co); 60.44 (br, B−CH−Co); 61.11, 62.33 (CO−CH_2); 73.85 (CCH), 78.37 (CCH); 88.93 (Cp); 93.08, 110.11 (carborane C); 113.99 (CH=C); 126.72, 128.72, 130.19, 135.10 (Ph); 171.71 (CO−Ph); 168.14, 174.39 ($CO-CH_2$). ^{11}B{^{1}H} NMR ($CDCl_3$): δ 6.1 (B−CH, 1B), 2.3 (1B), −3.0 (2B), −6.8 (3B), −9.2 (1B), −11.3 (2B). IR (KBr): ν (cm^{-1}) 1699, 1640 (C=O); 2559 (B−H). MS-ESI for (M + Na^+): 722.10. Anal. Calcd for $C_{28}H_{38}B_{10}NO_5S_2Co$: C, 48.06; H, 5.47. Found: C, 47.66; H, 5.69.

5f: yield 94%, brown solid. Mp: 224.1−224.9 °C. ^{1}H NMR-($CDCl_3$): δ 1.37 (t, J = 7.1 Hz, 3H, CH_2-CH_3) 1.41 (t, J = 7.1 Hz, 3H, CH_2-CH_3); 2.52 (s, 1H, CCH); 1.30−3.20 (9H, B−H); 3.78 (s, 1H, Co−CH−C=O); 3.98 (d, J = 15.4 Hz, 1H, S−CH_2); 4.03 (d, J = 15.4 Hz, 1H, S−CH_2); 4.25−4.35 (5H, CH_2−CCH, CO−CH_2); 4.43 (d, J = 16.1 Hz, 1H, CH_2−CCH); 4.80 (d, J = 13.3 Hz, 1H, CH_2−C−Co); 5.07 (d, J = 13.3 Hz, 1H, CH_2−C−Co); 5.08 (s, 5H, Cp); 5.12 (s, 1H, B−CH−Co); ^{13}C NMR ($CDCl_3$): δ 14.16, 14.44 (CH_2-CH_3); 39.61 (S−CH_2); 54.74 (Co−CH−C=O); 55.90 (br, B−CH−Co); 57.98 (CH_2−CCH); 60.94, 62.31 (CO−CH_2); 69.17 (CH_2−C−Co); 75.55 (CCH), 79.06 (CCH); 88.59 (Cp); 92.62, 110.08 (carborane C); 114.99 (Co−C−CH_2); 168.25, 174.47 (C=O). ^{11}B{^{1}H} NMR ($CDCl_3$): δ 6.2 (B−CH, 1B), 2.4 (1B), −3.1(2B), −6.7 (3B), −9.2 (1B), −11.2 (2B). IR (KBr): ν (cm^{-1}) 1728, 1661 (C=O); 2562 (B−H). MS-ESI for (M + Na^+): 619.01. Anal. Calcd for $C_{21}H_{33}B_{10}CoO_5S_2$: C, 42.27; H, 5.57. Found: C, 42.01; H, 5.69.

5g: yield 79%, brown solid. Mp: 203.5−204.2 °C. ^{1}H NMR ($CDCl_3$): δ 1.37 (t, J = 7.1 Hz, 3H, CH_2-CH_3); 1.40 (t, J = 7.1 Hz, 3H, CH_2-CH_3); 2.19 (t, J = 2.3 Hz, 1H, CCH); 2.21 (s, 3H, CO−CH_3); 2.30 (s, 3H, CO−CH_3); 1.50−3.20 (9H, B−H); 2.66 (d, J = 13.5 Hz, 1H, CH_2−C−Co); 2.90 (d, J = 18.2 Hz, 1H, CH_2−CCH); 3.33 (d, J = 18.2 Hz, 1H, CH_2−CCH); 3.59 (s, 1H, Co−CH−C=O); 3.98 (d, J = 15.5 Hz, 1H, S−CH_2); 4.03 (d, J = 15.5 Hz, 1H, S−CH_2); 4.25−4.35 (5H, CH_2−C−Co, CO−CH_2); 4.85 (s, 1H, B−CH−Co); 5.10 (s, 5H, Cp); ^{13}C NMR ($CDCl_3$): δ 14.06, 14.38 (CH_2-CH_3); 21.23 (CH_2−CCH); 27.45, 27.80 (CO−CH_3); 38.89 (S−CH_2, CH_2−C−CO); 60.93, 61.98 (CO−CH_2); 63.30 (Co−CH−C=O); 65.26 (br, B−CH−Co); 71.02 (CO−C−CO); 73.38 (CCH); 79.12 (CCH); 87.95 (Cp); 97.21, 118.26 (carborane C); 113.94 (Co−C−CH_2); 167.26, 174.09 (CH_2−C=O); 203.57, 204.00 (CH_3−C=O). ^{11}B{^{1}H} NMR ($CDCl_3$): δ 6.8 (B−CH, 1B), 1.8 (1B), −0.3(1B), −1.6 (1B), −4.6 (3B), −7.6 (1B), −9.4 (2B). IR (KBr): ν (cm^{-1}) 1789, 1740, 1670 (C=O); 2557 (B−H). MS-ESI for (M + Na^+): 701.00. Anal. Calcd for $C_{26}H_{39}B_{10}CoO_6S_2$: C, 46.01; H, 5.79. Found: C, 45.78; H, 5.61.

5h: yield 84%, brown solid. Mp: 176.3−177.2 °C. ^{1}H NMR ($CDCl_3$): δ 1.37 (t, J = 7.1 Hz, 3H, CH_2-CH_3) 1.42 (t, J = 7.1 Hz, 3H, CH_2-CH_3); 2.32 (t, J = 2.3 Hz, 2H, CCH); 1.50−3.20 (9H, B−H); 3.12 (d, J = 12.4 Hz, 1H, CH_2−C−Co); 4.61 (d, J = 12.4 Hz, 1H, CH_2−C−Co); 3.70 (d, J = 2.3 Hz, 4H, CH_2−CCH); 3.77 (s, 1H, Co−CH−C=O); 3.98 (d, J = 15.5 Hz, 1H, S−CH_2); 4.03 (d, J = 15.5 Hz, 1H, S−CH_2); 4.25−4.35 (4H, CO−CH_2); 4.82 (s, 1H, B−CH−Co); 5.08 (s, 5H, Cp). ^{13}C NMR ($CDCl_3$): δ 14.16, 14.39 (CH_2-CH_3); 39.63 (S−CH_2); 42.00 (CH_2−CCH); 57.32 (Co−CH−C=O); 58.32 (CH_2−C−Co); 61.69 (br, B−CH−Co); 60.93, 62.34 (CO−CH_2); 73.82 (CCH); 78.70 (CCH); 88.55 (Cp); 92.78, 110.25 (carborane C); 113.92 (Co−C−CH_2); 168.25, 174.18 (C=O). ^{11}B{^{1}H} NMR ($CDCl_3$): δ 5.9 (B−CH, 1B), 2.5 (1B), −3.1 (2B), −6.6 (3B), −9.2 (1B), −11.0 (2B). IR (KBr): ν (cm^{-1}) 1730, 1665 (C=O); 2562 (B−H). MS-ESI for (M + Na^+): 655.98. Anal. Calcd for $C_{24}H_{36}B_{10}CoNO_4S_2$: C, 45.49; H, 5.73. Found: C, 45.12; H, 5.87.

7i: yield 62%, brown solid. Mp: 169−170.1 °C. ^{1}H NMR ($CDCl_3$): δ 1.33 (t, 3H, J = 7.1 Hz, CH_2-CH_3); 1.34 (t, 3H, J = 7.1 Hz, CH_2-CH_3); 2.45 (t, 2H, J = 2.2 Hz, CCH); 1.31−3.10 (9H, B−H); 3.87 (s, 2H, S−CH_2); 4.19 (q, 2H, J = 7.1 Hz, CH_2−CH_3); 4.27 (q, 2H, J = 7.1 Hz, CH_2−CH_3); 4.43 (dd, 2H, J = 17.9, 2.2 Hz,CH_2−CCH); 5.32 (dd, 2H, J = 17.9, 2.2 Hz,CH_2−CCH); 4.95 (s, 5H, Cp); 5.22 (s, 1H, B−CH−Co); 6.16 (s, 1H, C=CH); 8.40 (s, 1H, N=CH). ^{13}C NMR ($CDCl_3$): δ 14.09, 14.26 (CH_2-CH_3); 28.60 (br, B−CH−Co); 38.78 (S−CH_2); 42.85 (CH_2−CCH); 60.15, 62.02 (CH_2-CH_3); 75.37 (CCH); 76.14 (CCH); 85.51 (Cp); 83.10, 109.42 (carborane C); 89.43 (C=CH); 111.48 (C=CH); 152.34 (N=CH); 166.30, 168.21 (C=O). ^{11}B{^{1}H} NMR ($CDCl_3$): δ 11.5 (B−CH, 1B), 0.2 (1B), −4.9 (3B), −7.0 (4B), −12.5 (1B). IR (KBr): ν (cm^{-1}) 1689, 1735 (C=O), 2555 (B−H). MS-ESI for (M + Na^+): 669.15. Anal. Calcd for $C_{24}H_{35}B_{10}CoN_2O_4S_2$: C, 44.57; H, 5.45. Found: C, 44.22; H, 5.67.

Isolation of Intermediate 9. MDA (about 1 mol/L in dichloromethane, 0.2 mL) was added dropwise to a dichloromethane solution of **1** (33.0 mg, 0.1 mmol) at room temperature under an oxygen atmosphere. The mixture was stirred for 1 h and separated by chromatography (dichloromethane/ethyl acetate 40/1) to give **9** in 89% yield. **9** could be recrystallized from dichloromethane and petroleum ether. Yellow solid. Mp: 157.3−157.9 °C. ^{1}H NMR ($CDCl_3$): δ 1.56−3.27 (9H, BH); 3.74 (d, J = 16.2 Hz, 1H, S−CH_2); 4.63 (d, J = 16.2 Hz, 1H, S−CH_2); 3.75 (s, 3H, OCH_3); 3.78 (s, 3H, OCH_3); 4.87 (s, 5H, Cp); 5.28 (s, 1H, S−CH−Co). ^{13}C NMR ($CDCl_3$): δ 32.90 (S−C−Co); 36.61 (S−CH_2); 51.45, 52.99 (O−CH_3); 85.13 (Cp); 93.15, 96.41 (carborane C); 166.46, 181.56 (C=O). ^{11}B{^{1}H} NMR ($CDCl_3$): δ −0.4 (1B), −3.7 (1B, Co−B), −5.0 (2B), −6.0 (2B), −8.7 (2B), −10.9 (1B), −12.6 (1B). IR (KBr): ν (cm^{-1}) 1739, 1682 (C=O); 2558 (B−H). **HRMS-ESI** for $C_{13}H_{23}B_{10}CoNaO_4S_2$ (M + Na^+): calculated, 497.1198; found, 497.1273.

Isolation of Intermediate 10. **3b** (36.8 mg, 0.2 mmol) was added to 5 mL of a dichloromethane solution of intermediate **9** (95.0 mg, 0.2 mmol) under the protection of Ar, and the mixture was stirred at −0 °C for 0.5 h. A green complex was then separated in 91% yield using preparative TLC. ^{1}H NMR ($CDCl_3$): δ 2.25 (t, 1H, J = 2.2 Hz, CCH); 1.51−3.10 (9H, B−H); 2.28 (s, 3H, Ph−CH_3); 3.53 (s, 1H, CH−Co); 3.76 (d, 1H, J = 16.0 Hz, CH_2−S); 4.11 (d, 1H, J = 16.0 Hz, CH_2−S); 3.82 (s, 3H, O−CH_3); 3.87 (s, 3H, O−CH_3); 4.05−4.11 (m, 2H, CH_2−CCH); 4.72 (d, 1H, J = 18.0 Hz, CH_2−C−Co); 4.83 (d, 1H, J = 18.0 Hz, CH_2−C−Co); 4.98 (s, 5H, Cp); 5.66 (s, 1H, C=CH−B); 6.73 (d, 2H, J = 8.3 Hz, Ph); 7.09 (d, 2H, J = 8.3 Hz, Ph). HRMS-ESI for $C_{26}H_{36}B_{10}CoNNaO_4S_2$ (M + Na^+): calculated, 682.2245, found, 682.2279.

X-ray Crystallography. Crystals suitable for X-ray analysis were obtained by slow evaporation of a solution in petroleum ether/dichloromethane. Diffraction data were collected on a Bruker SMART Apex II CCD diffractometer 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.[24] The structures were solved by direct methods with the SHELXL-97 program.[25] All non-hydrogen atoms were found from the difference Fourier syntheses. The H atoms were included in calculated positions with isotropic thermal parameters related to those of the supporting carbon atoms but were not included in the refinement. All calculations were performed by using the Bruker Smart program. CCDC files 1444668−1444672 contain supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/datarequest/cif.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.6b00082.

DOI: 10.1021/acs.organomet.6b00082
Organometallics XXXX, XXX, XXX−XXX

Synthesis of **3a−i**, details of control experiments, NMR spectra, and crystallographic data (PDF)
Crystallographic data (CIF)

AUTHOR INFORMATION

Corresponding Authors

*E-mail for H.Y.: hyan1965@nju.edu.cn.
*E-mail for C.L.: luchsh@nju.edu.cn.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work was supported by the National Natural Science Foundation of China (21271102, 21472086, and 21531004), the National Basic Research Program of China (2013CB922101), the Natural Science Foundation of Jiangsu Province (BK20130054), and the High Performance Computing Center of Nanjing University.

REFERENCES

(1) For reviews, see: (a) Yinghuai, Z.; Hosmane, N. S. *J. Organomet. Chem.* **2013**, *747*, 25−29. (b) Grimes, R. N. *Dalton Trans.* **2015**, *44*, 5939−5956. (c) Barry, N. P. E.; Sadler, P. J. *Chem. Soc. Rev.* **2012**, *41*, 3264−3279. (d) Han, Y.-F.; Jin, G.-X. *Acc. Chem. Res.* **2014**, *47*, 3571−3579. (e) Williams, E. *Chem. Rev.* **1992**, *92*, 177−207. (f) Bregadze, V. I. *Chem. Rev.* **1992**, *92*, 209−223. (g) Hawthorne, M. F.; Maderna, A. *Chem. Rev.* **1999**, *99*, 3421−3434. (h) Valliant, J. F.; Guenther, K. J.; King, A. S.; Morel, P.; Schaffer, P.; Sogbein, O. O.; Stephenson, K. A. *Coord. Chem. Rev.* **2002**, *232*, 173−230. (i) Scholz, M.; Hey-Hawkins, E. *Chem. Rev.* **2011**, *111*, 7035−7062.

(2) (a) Spokoyny, A. M.; Machan, C. W.; Clingerman, D. J.; Rosen, M. S.; Wiester, M. J.; Kennedy, R. D.; Stem, C. L.; Sarieant, A. A.; Mirkin, C. A. *Nat. Chem.* **2011**, *3*, 590−596. (b) Liu, S.; Wang, G.-L.; Jin, G.-X. *Dalton Trans.* **2008**, 425−432.

(3) (a) Lee, Y.-H.; Park, J.-H.; Lee, J.-S.; Lee, S.-U.; Lee, M.-H. *J. Am. Chem. Soc.* **2015**, *137*, 8018−8021. (b) Naito, H.; Morisaki, Y.; Chujo, Y. *Angew. Chem., Int. Ed.* **2015**, *54*, 5084−5087. (c) Wee, K.-R.; Han, W.-S.; Cho, D.-W.; Kwon, S.; Pac, C.; Kang, S.-O. *Angew. Chem., Int. Ed.* **2012**, *51*, 2677−2680. (d) Shi, C.; Sun, H.-B.; Tang, X.; Lv, W.; Yan, H.; Zhao, Q.; Wang, J.-X.; Huang, W. *Angew. Chem., Int. Ed.* **2013**, *52*, 13434−13438. (e) Ferrer-Ugalde, A.; Juárez-Pérez, E. J.; Teixidor, F.; Viñas, C.; Núñez, R. *Chem. - Eur. J.* **2013**, *19*, 17021−17030.

(4) (a) Douvris, C.; Ozerov, O. V. *Science* **2008**, *321*, 1188−1190. (b) Wang, X.; Jin, G.-X. *Chem. - Eur. J.* **2005**, *11*, 5758−5764. (c) Teixidor, F.; Flores, M. A.; Viñas, C.; Sillanpää, R.; Kivekas, R. *J. Am. Chem. Soc.* **2000**, *122*, 1963−1973.

(5) (a) Teixidor, F.; Sillanpää, R.; Pepiol, A.; Lupu, M.; Viñas, C. *Chem. - Eur. J.* **2015**, *21*, 12778−12786. (b) Li, S.-H.; Wang, Z.-J.; Wei, Y.-F.; Wu, C.-Y.; Gao, S.-P.; Jiang, H.; Zhao, X.-Q.; Yan, H.; Wang, X.-M. *Biomaterials* **2013**, *34*, 902−911. (c) Cígler, P.; Kožíšek, M.; Řezáčová, P.; Brynda, J.; Otwinowski, Z.; Pokorná, J.; Plešek, J.; Grüner, B.; Dolečková-Marešová, L.; Máša, M.; Sedláček, J.; Bodem, J.; Kräusslich, H.; Král, V.; Konvalinka, J. *Proc. Natl. Acad. Sci. U. S. A.* **2005**, *102*, 15394−15399. (d) Nakamura, H.; Miyajima, Y.; Takei, T.; Kasaoka, S.; Maruyama, K. *Chem. Commun.* **2004**, 1910−1911. (e) Braunschweig, H.; Ghosh, S.; Jimenez-Halla, O. C.; Klein, J. H.; Lambert, C.; Radacki, K.; Steffen, A.; Vargas, A.; Wahler, J. *Chem. - Eur. J.* **2015**, *21*, 210−218.

(6) (a) Olid, D.; Núñez, R.; Viñas, C.; Teixidor, F. *Chem. Soc. Rev.* **2013**, *42*, 3318−3336. (b) Qiu, Z.-Z.; Xie, Z.-W. *Dalton Trans.* **2014**, *43*, 4925−4934. (c) Zhang, J.; Xie, Z.-W. *Acc. Chem. Res.* **2014**, *47*, 1623−1633. (d) Andrews, J. S.; Zayas, J.; Jones, M. *Inorg. Chem.* **1985**, *24*, 3715−3716. (e) Hoel, E. L.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1975**, *97*, 6388−6395. (f) Prokhorov, A. M.; Slepukhin, P. A.; Rusinov, V. L.; Kalinin, V. N.; Kozhevnikov, D. N. *Chem. Commun.* **2011**, *47*, 7713−7715. (g) Yao, Z.-J.; Yu, W.-B.; Lin, Y.-J.; Huang, S.-L.; Li, Z.-H.; Jin, G.-X. *J. Am. Chem. Soc.* **2014**, *136*, 2825−2832.

(7) Zhao, D.; Zhang, J.-J.; Xie, Z.-W. *Angew. Chem., Int. Ed.* **2014**, *53*, 12902−12906. (b) Tang, C.; Xie, Z.-W. *Angew. Chem., Int. Ed.* **2015**, *54*, 7662−7665. (c) Nakamura, H.; Aoyagi, K.; Yamamoto, Y. *J. Am. Chem. Soc.* **1998**, *120*, 1167−1171. (d) Qiu, Z.-Z. *Tetrahedron Lett.* **2015**, *56*, 963−971. (e) Yao, Z.-J.; Jin, G.-X. *Coord. Chem. Rev.* **2013**, *257*, 2522−2535. (f) Kahl, S. B.; Kasar, R. A. *J. Am. Chem. Soc.* **1996**, *118*, 1223−1224. (g) Vinãs, C.; Benakki, R.; Teixidor, F.; Casabo, J. *Inorg. Chem.* **1995**, *34*, 3844−3845.

(8) (a) Mirabelli, M. G. L.; Sneddon, L. G. *J. Am. Chem. Soc.* **1988**, *110*, 449−453. (b) Quan, Y.-J.; Xie, Z.-W. *J. Am. Chem. Soc.* **2014**, *136*, 15513−15516. (c) Quan, Y.-J.; Xie, Z.-W. *J. Am. Chem. Soc.* **2015**, *137*, 3502−3505. (d) Qiu, Z.-Z.; Quan, Y.-J.; Xie, Z.-W. *J. Am. Chem. Soc.* **2013**, *135*, 12192−12195. (e) Cao, K.; Huang, Y.-W.; Yang, J.-X.; Wu, J. *Chem. Commun.* **2015**, *51*, 7257−7260. (f) Herberhold, M.; Yan, H.; Milius, W.; Wrackmeyer, B. *Angew. Chem., Int. Ed.* **1999**, *38*, 3689−3691.

(9) For alkyl ketones, see: (a) Li, Y.-G.; Jiang, Q.-B.; Li, Y.-Z.; Yan, H.; Bregadze, V. I. *Inorg. Chem.* **2010**, *49*, 4−6. (b) Wang, Z.-J.; Ye, H.-D.; Li, Y.-G.; Li, Y.-Z.; Yan, H. *J. Am. Chem. Soc.* **2013**, *135*, 11289−11298. (c) Ye, H.-D.; Bai, W.-J.; Xie, M.-S.; Li, Y.-Z.; Yan, H. *Eur. J. Inorg. Chem.* **2011**, *2011*, 2763−2768. (d) Li, Y.-G.; Jiang, Q.-B.; Zhang, X.-L.; Li, Y.-Z.; Yan, H.; Bregadze, V. I. *Inorg. Chem.* **2010**, *49*, 3911−3917. For alkyl acetate, see: (e) Xu, B.-H.; Tao, J.-C.; Li, Y.-Z.; Li, S.-H.; Yan, H. *Organometallics* **2008**, *27*, 334−340.

(10) For aromatic substituted alkynes, see: (a) Bai, W.-J.; Liu, G.-F.; Guoyiqibayi, G.; Yan, H. *Organometallics* **2011**, *30*, 5188−5195. (b) Xu, B.-H.; Peng, X.-Q.; Li, Y.-Z.; Yan, H. *Chem. - Eur. J.* **2008**, *14*, 9347−9356. (c) Xu, B.-H.; Wu, D.-H.; Li, Y.-Z.; Yan, H. *Organometallics* **2007**, *26*, 4344−4349.

(11) Liu, G.-F.; Hu, J.-R.; Wen, J.-L.; Dai, H.-M.; Li, Y.-Z.; Yan, H. *Inorg. Chem.* **2011**, *50*, 4187−4194.

(12) Xu, Z.-W.; Han, L.; Ji, C.; Zhang, R.; Shen, X.-J.; Yan, H. *Dalton Trans.* **2011**, *40*, 6992−6997.

(13) Zhang, X.-L.; Zhou, Z.-W.; Yan, H. *Chem. Commun.* **2014**, *50*, 13077−13080.

(14) (a) Zhang, R.; Zhu, L.; Liu, G.-F.; Dai, H.-M.; Lu, Z.-Z.; Zhao, J.-B.; Yan, H. *J. Am. Chem. Soc.* **2012**, *134*, 10341−10344. (b) Zhang, R.; Zhu, L.; Lu, Z.-Z.; Yan, H.; Bregadze, V. I. *Dalton Trans.* **2012**, *41*, 12054−12063.

(15) Liu, G.-F.; Yan, H. *Organometallics* **2015**, *34*, 591−598.

(16) (a) Luo, Y.; Pan, X.-L.; Yu, X.-X.; Wu, J. *Chem. Soc. Rev.* **2014**, *43*, 834−846. (b) Zhang, D.-H.; Zhang, Z.; Shi, M. *Chem. Commun.* **2012**, *48*, 10271−10279. (c) Zhang, W.-X.; Zhang, S.-G.; Xi, Z.-F. *Acc. Chem. Res.* **2011**, *44*, 541−551. (d) Abu Sohel, S. M. A.; Liu, R.-S. *Chem. Soc. Rev.* **2009**, *38*, 2269−2281. (e) Tanaka, K.; Saitoh, S.; Hara, H.; Shibata, Y. *Org. Biomol. Chem.* **2009**, *7*, 4817−4820.

(17) Herberhold, M.; Yan, H.; Milius, W.; Wrackmeyer, B. *J. Chem. Soc., Dalton Trans.* **2001**, 1782−1789.

(18) Kim, D. H.; Ko, J. J.; Park, K.; Cho, S.; Kang, S. O. *Organometallics* **1999**, *18*, 2738−2740.

(19) (a) Lin, T.-P.; Peters, J. C. *J. Am. Chem. Soc.* **2013**, *135*, 15310−15313. (b) Adams, C. J.; Baber, R. A.; Batsanov, A. S.; Bramham, G.; Charmant, J. P. H.; Haddow, M. F.; Howard, J. A. K.; Lam, W.-H.; Lin, Z.-Y.; Marder, T. B.; Norman, N. C.; Orpen, A. G. *Dalton Trans.* **2006**, 1370−1373.

(20) (a) Milo, A.; Neel, A. J.; Toste, F. D.; Sigman, M. S. *Science* **2015**, *347*, 737−743. (b) Chen, W.-Q.; Wang, J.-H. *Organometallics* **2013**, *32*, 1958−1963. (c) Zhang, Z.-G.; Tian, Q.; Qian, J.-J.; Liu, Q.-F.; Liu, T.-X.; Shi, L.; Zhang, G.-S. *J. Org. Chem.* **2014**, *79*, 8182−8188.

(21) (a) Glavee, G. N.; Angelici, R. J. *J. Am. Chem. Soc.* **1989**, *111*, 3598−3603. (b) Yuki, M.; Matsuo, T.; Kawaguchi, H. *Angew. Chem., Int. Ed.* **2004**, *43*, 1404−1407. (c) Fukumoto, K.; Sakai, A.; Oya, T.; Nakazawa, H. *Chem. Commun.* **2012**, *48*, 3809−3811.

(22) (a) Fürstner, A.; Davies, P. W.; Lehmann, C. W. *Organometallics* **2005**, *24*, 4065−4071. (b) Mori, M.; Kuriyama, K.; Ochifuji, N.; Watanuki, S. *Chem. Lett.* **1995**, 615−616. (c) Strutz, H.; Dewan, J. C.; Schrock, R. R. *J. Am. Chem. Soc.* **1985**, *107*, 5999−6005.

DOI: 10.1021/acs.organomet.6b00082
Organometallics XXXX, XXX, XXX−XXX

(d) Grotevendt, A. G. D.; Lummiss, J. A. M.; Mastronardi, M. L.; Fogg, D. E. *J. Am. Chem. Soc.* **2011**, *133*, 15918−15921.
(23) Collins, L. R.; Hierlmeier, G.; Mahon, M. F.; Riddlestone, I. M.; Whittlesey, M. K. *Chem. - Eur. J.* **2015**, *21*, 3215−3218.
(24) Sheldrick, G. M. *SADABS, A Program for Empirical Absorption Correction*; University of Göttingen, Göttingen, Germany, 1998.
(25) Sheldrick, G. M. *SHELXL-97, Program for the Refinement of Crystal Structures*; University of Göttingen, Göttingen, Germany, 1997.

DOI: 10.1021/acs.organomet.6b00082
Organometallics XXXX, XXX, XXX−XXX