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Cobalt-Promoted B−H and C−H Activation: Facile B−C Coupling of Carboranedithiolate and Cyclopentadienyl

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Supporting Information

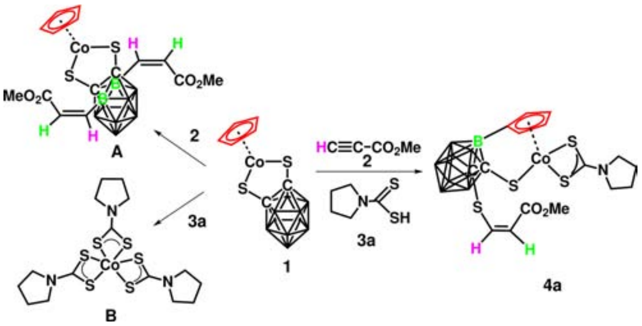
ABSTRACT: We report the one-pot reactions of the 16e$^-$ half-sandwich complex $CpCoS_2C_2B_{10}H_{10}$ (**1**), methyl propiolate, and 3e$^-$-donor ligands, which lead to selective B-functionalization at carborane with cyclopentadienyl as a functional group at ambient temperature in good yields. Metal-promoted activations of both a B−H bond of the carborane and a C−H bond of the Cp unit take place sequentially in the cooperation of organic ligands. The reaction requires a 3e$^-$-donor ligand and an activated alkyne and is therefore suitable for a broad range of substrates. This investigation provides a simple and efficient synthetic route to B-functionalized carborane derivatives.

For decades, considerable effort has been devoted to developing new synthetic methods to functionalize polyhedral boranes because of the important applications[1−3](actual and potential) of their derivatives in medicine, catalysis, and materials. In the functionalization of polyhedral boranes, however, selective and straightforward boron substitution has been proven difficult,[4] although significant advances in metal-promoted or -catalyzed hydroboration of polyhedral boranes have been achieved.[5−8] Metal-catalyzed carborane−alkyne hydroboration reactions that provide alkenylcarborane derivatives have been developed,[6a] and metal-promoted stepwise and selective hydroboration of *o*-carborane with selected substrates has also been reported.[7,8] Of course, in the absence of a metal, an alternative route to selective B-substituted *o*-carborane derivatives could be obtained from carborane cage reconstruction by an insertion reaction, but this way is limited by the availability of borane reagents with suitable functional groups.[9]

Metal-promoted C(sp^2)−H activation,[10] including that of cyclopentadienyl (Cp)[11] and its subsequent functionalization, has been extensively investigated. Compounds with Cp and a carborane conjugated through either a bridging atom (i.e., C, Si, P, B)[12] or even a direct C−C bond[13] have been described, but the direct coupling of the two units through a B−C bond is rare because of the bulkiness of the carborane cage.[14] Here we report how carboranedithiolate and metal-bound Cp interact at a metal in the presence of a range of ligands and how the metal facilitates elaborate steric and electronic arrangements to realize the coupling of the two units via a stable B−C bond.

In this study, a third reagent was introduced to the reaction of the cobalt-centered *o*-carboranedithiolato compound $CpCoS_2C_2B_{10}H_{10}$ (**1**) with methyl propiolate (**2**), and as a result, an unexpected product containing B−C coupling between the carborane cage and the Cp ligand was generated at ambient temperature (Schemes 1 and 2). As an example, the addition of **3a** to a mixture of **1** and **2** in diclorомethane led to adduct **4a** in a good yield. In sharp contrast, the reaction of **1** with either **2** or **3a** alone gave rise to the hydroborated product **A**[8a] or **B**, respectively (Scheme 1).

Scheme 1. Reaction of 1, 2, and 3a at Ambient Temperature Leading to 4a, in Contrast to the Reactions of 1 with 2 or 3a Leading to A or B, Respectively



The solid-state structure of **4a** demonstrates that the carborane cage is linked to the Cp ring through a covalent B−C bond with a length of 1.569(6) Å (Figure 1). The substituted Cp ring remains coordinated to cobalt in an η^5-mode. Compound **3a** has lost one hydrogen atom and contributes 3e$^-$ to metal, while the alkyne has been reduced to an olefinic unit in a *Z* configuration and is connected to one S atom rather than to a

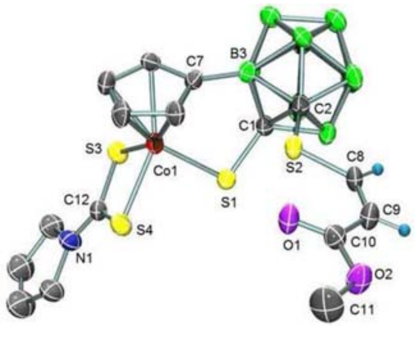


Figure 1. Molecular structure of **4a**.

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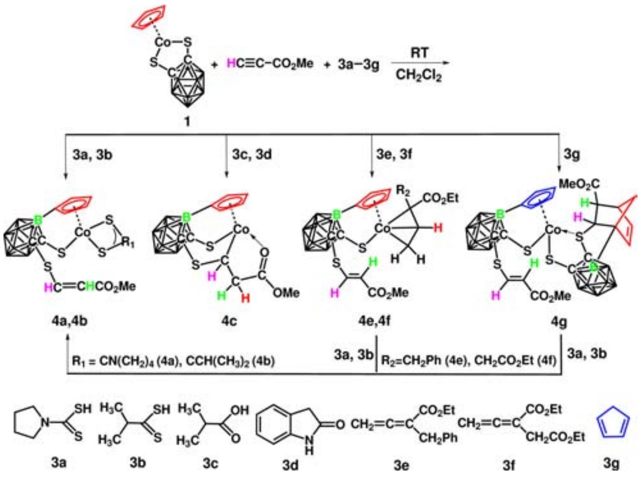
B atom as in **A**.[8a] Clearly, the breakage of the rigid S-chelating binding in **1** is essential for constructing the intramolecular coupling of the carboranedithiolate and cyclopentadienyl moieties. Consistent with the solid-state structure, the ^{1}H NMR spectrum displays four well-separated singlets at 6.01, 5.92, 5.24, and 4.97 ppm for the substituted Cp group, in contrast to one singlet at 5.26 ppm in **1**.[15] The ^{13}C resonances of the Cp ring appear at 91.0, 84.7, 84.3, and 83.8 ppm for the four C–H bonds compared with 81.8 ppm in **1**,[15] but the characteristic broad C resonance of the B–C bond is remarkably low-field-shifted to 127.0 ppm. The ^{11}B signal of the B–C bond (2.1 ppm) is low-field-shifted by 7–11 ppm in comparison with those in **1**,[15] further supporting the formation of a B–C bond.

4a is unique. The small ligand **3a** plays a vital role in the formation of adduct **4a**. To provide a better understanding of the role of the organic ligand, other small molecules were examined (Scheme 2). As expected, the similar **3b** was able to lead to **4b** containing a B–C bond. However, the sodium salts of **3a** and **3b** did not react, indicating the importance of an acidic hydrogen atom. The weakly coordinating **3c** and **3d** also gave rise to a product with the B–C bond formation (**4c**), but the ligand did not appear in the structure. Instead, the newly generated olefinic unit was utilized to donate 3e$^-$ to metal and yield the stable five-membered ring Co1–C3–C4–C5–O1 (Figure 2). Here, **3c** and **3d** might be considered as Brønsted acid catalysts. The 4e$^-$-donor chelating ligands such as 2,2-bipyridine and 1,10-phenanthroline did not lead to similar products, reflecting the requirement of electron accounting of the metal center. Interestingly, allenes such as **3e** and **3f** could also lead to the analogous products **4e** and **4f** with an allyl unit (3e$^-$ donor) [SI-Figure 4 in the Supporting Information (SI)], parallel to the chelating mode of **3a** and **3b**. To our surprise, cyclopentadiene (**3g**) also produced a B–C-coupled complex (**4g**) containing an unusual in situ-generated 3e$^-$-donor *o*-carboranedithio ligand that bears a moiety formed by a [4 + 2] Diels–Alder cycloaddition (Figure 3). The chelating ability of the newly generated bulky dimercapto ligand is weaker because of the electron-deficiency of the adjacent carborane cage, allowing it to be replaced by the stronger chelating ligands **3a** and **3b** to yield **4a** and **4b** quantitatively. Similarly, **4e** and **4f** can be readily converted to **4a** or **4b** upon addition of **3a** or **3b**, but **4c** remains intact, demonstrating the binding ability of these organic ligands (see Scheme 2 and section III in the SI). It should be noted that in control experiments substrates **3c–g** did not react with **1**. Furthermore, the reaction should be applicable to many other 3e$^-$-donor ligands and activated alkynes containing an electron-withdrawing group to yield analogous products.

Scheme 2. Three-Component Reactions of 1, 2, and 3a–3g and the Ligand Substitution Reactions Leading to 4a or 4b from 4e–g upon Addition of 3a or 3b, Respectively



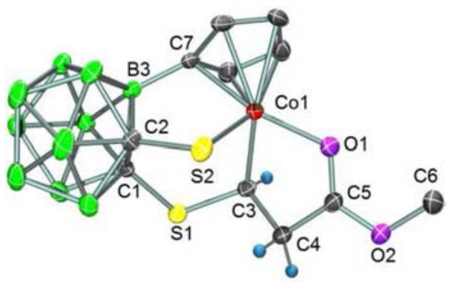


Figure 2. Molecular structure of **4c**.

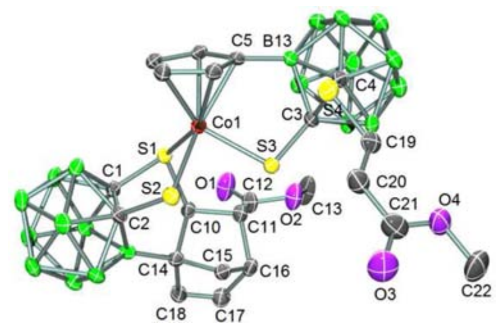


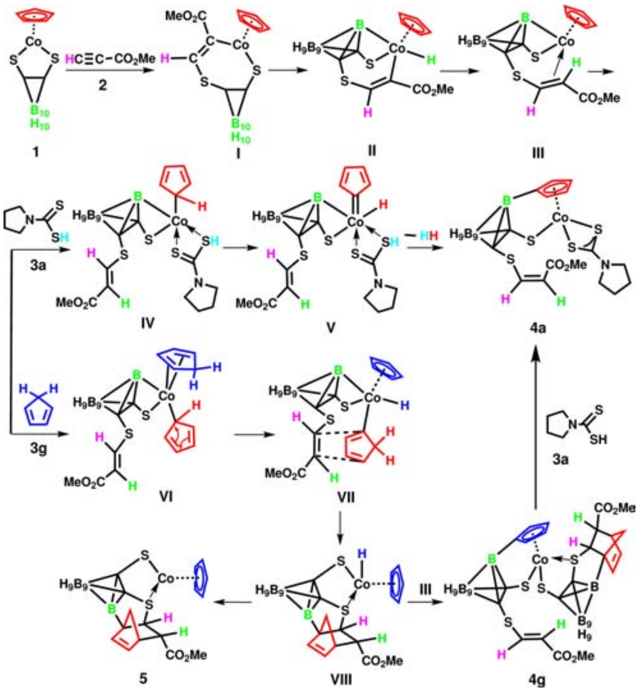
Figure 3. Molecular structure of **4g**.

Both B–H and C–H activation as well as hydrogen transfer play key roles in the formation of the B–C-coupled products. Therefore, a series of deuterium-labeling experiments were performed with the deuterated reagents **d5-1** [(d_5-Cp)-$CoS_2C_2B_{10}H_{10}$], **d1-2** [$DC{\equiv}C{-}CO_2Me$], **d1-3a** [$(CH_2)_4NCS_2D$], and **d1-3c** [$(CH_3)_2CHCO_2D$] to find out the origin and destination of the hydrogen transfer (see reactions 14–21 in the SI). As an example, the reaction of **d5-1**, **d1-2**, and **d1-3a** led to **d5-4a**, demonstrating that the ^{1}H NMR signal at 7.64 ppm for C8–H arises from the terminal alkyne and that the signal at 6.12 ppm for C9–H of the olefinic unit migrates from the activated B3–H of the carborane (see Figure 1 and reaction 16 in the SI). Those two hydrogen atoms from **3a** and the Cp ligand that were not detected by NMR spectroscopy formed H_2, as confirmed by GC analysis (see section V in the SI).

On the basis of these experimental results, a plausible mechanism for the generation of **4a** is summarized in Scheme 3. The B–H activation at B3 of the carborane and hydrogen transfer to the alkyne should occur as the earlier steps (**I–III**) after alkyne insertion into one Co–S bond, as previously reported[7,8] and revealed by the capture experiments (see section V in the SI). It should noted that the iridium analogue of intermediate **III** is rather stable,[7g] suggesting that the proposed cobalt complex is reasonable. The chelating coordination of **3a** would induce a change in the binding mode of Cp from η^5 to η^1 (**IV**),[16] and subsequent α-H elimination (**V**),[11a,17] H_2 release, Co–B and Co–C cleavage, B–C bond formation, and Cp switching back to η^5 coordination[16] would lead to **4a**.

Concerning the formation of **4g** (Scheme 3), as for **3a**, the coordination of CpH to the metal could lead to ring slippage of

Scheme 3. Proposed Mechanisms for the Formation of 4a and 4g



the existing η^5-Cp unit to form **VI** (see reaction 21 in the SI). Subsequent oxidative addition of the bound CpH to the metal might occur,[11,17] and the resulting η^1-Cp might undergo hydrogen 1,5-sigmatropic rearrangement[18] over the ring (**VII**), driven by the intramolecular [4 + 2] cycloaddition[19] with the in situ-generated olefinic unit. As a result, the hydride species (**VIII**) is produced after cleavage of the Co−B and Co−C bonds and generation of the B−C bond. Intermediate **VIII** is involved in two competitive pathways. One proceeds by reductive elimination to yield the isolatable 17e$^-$ species **5** (see reaction 6 in the SI), and such an analogous species has been previously described by our group.[8b] The other is to repeat the role of **3a** to react further with the active intermediate **III** to finally give rise to **4g**. Monitoring experiments showed that the formation of **5** started earlier and is more competitive (see section VIII in the SI). Other experiments supporting the formation mechanism of **4g** are discussed in sections VII−IX in the SI.

In conclusion, we have demonstrated facile B−C coupling between carboranedithiolate and Cp through the cooperation of cobalt and two organic compounds in a one-pot reaction at ambient temperature. Here both metal-promoted B−H and C−H activation occur, leading to selective B-functionalization of the carborane by a metal-bound η^5-Cp group in good yield. The introduction of an additional 3e$^-$-donating species has led to interesting prospects for the development of new types of functional groups at a boron site of carborane. This reaction appears to be suitable for a broad range of substrates, and we are continuing to explore the scope of the reaction.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental details, spectroscopic data, crystallographic data (CIF), and detailed mechanisms. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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