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Cobalt-Mediated $B-H$ Activation and Cyclopentadienyl-Participated Diels−Alder Addition in the Reaction of a 16e CpCo Complex Containing an *o*-Carborane-1,2-dithiolato Ligand with $HC\equiv C-C(O)Ph$

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The reaction of the 16e half-sandwich complex CpCo($S_2C_2B_{10}H_{10}$) (**1**) with $HC\equiv C-C(O)Ph$ leads to a 17e complex **2** containing a bicyclo[2.2.1]heptene unit at the B3/B6 site of carborane. In the presence of air, water and silica **2** converts to two 16e complexes, **3** and **4**, bearing new types of functionalized groups.

Transition-metal-induced $B-H$ activation in organic and organometallic chemistry has been a subject of interest. $B-H$ activation has led to the formation of transition-metal borane, boryl, and borylene complexes.[1,2] Transition-metal-catalyzed borylation of hydrocarbons could generate alkylborane and arylboron compounds,[3] which are useful synthetic intermediates in organic chemistry. In the polyhedral borane chemistry, $B-H$ activation has also played a key role in the synthesis of highly substituted carboranes, such as polyalkylated carboranes,[4] polyhydroxylated icosahedral boranes,[5] and highly halogenated carborane anions.[6] These substituted products of $B-H$ vertices have received much attention for applications in metathesis, stabilization of unusual cations, catalysis, oxidation chemistry, etc.[7] In this chemistry, however, the selective boron substitution or hydroboration has proven rather difficult, although some examples have been reported.[8−10] Additionally, it has been described that cyclopentadienyl (Cp) and indenyl ligands

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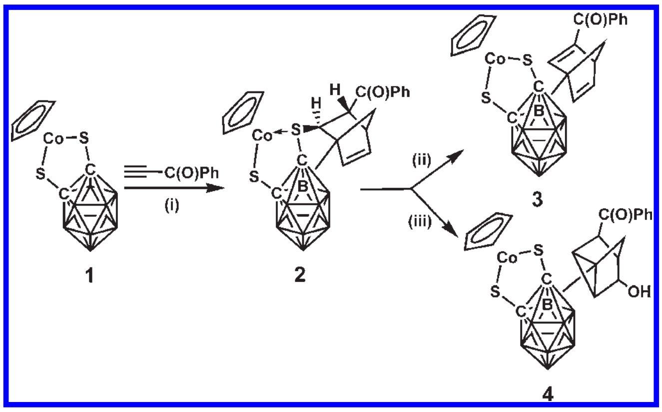
Scheme 1.[a]



[a] Steps: (i) ambient temperature, 12 h, CH_2Cl_2; (ii) air, silica, CH_2Cl_2; (iii) air, H_2O, silica, CH_2Cl_2.

could convert coordination from η^5-mode to η^3- or η^1-mode and take part in further reactions.[11,12] We report herein how the B−H bond and the unusual η^1-Cp-participated Diels−Alder reaction simultaneously play in a cobalt center to generate novel type functionalized carboranes.

The reaction of the 16e half-sandwich complex CpCo($S_2C_2B_{10}H_{10}$) (**1**) with HC≡C−C(O)Ph at ambient temperature leads to **2** (Scheme 1). Its solid-state structure contains a substituted bicyclo[2.2.1]heptene unit that is bound to **1** through both a C−S bond and a C−B bond in the B3/B6 position of the carborane cage (Figure 1). The presence of a S → Co coordinative bond leads to **2** as a 17e species. This is confirmed by its broad signals in a range from −5 to 12 ppm in the ^{1}H NMR spectrum.

2 is novel; we are unaware of any previous characterization of compounds containing a norbornenyl unit at *o*-carborane, although a substituted norbornene is quite common[13] and selective hydroboration at *o*-carborane has been reported.[10] Obviously, the origin of the norbornenyl unit arises from a Cp-involved Diels−Alder reaction. To confirm this, two experiments were designed. The first was to use a pentamethylcyclopentadienyl (Cp*) ligand to replace Cp; no similar 17e cobalt complex was observed. Instead, in the Cp* analogues,[14] two alkyne molecules were inserted into one of the Co−S bonds, emphasizing the necessity of a Cp ligand in the Diels−Alder reaction. The second was to use an excess of alkyne, which led to boron disubstitution in the B3 and B6 positions of carborane[15] rather than **2**. This demonstrates that the generation of **2** requires excessive **1** to supply the Cp ligand. The proposed mechanistic pathway in the formation of **2** is outlined in Scheme S1 (Supporting Information). The processes may involve metal-induced B−H activation at carborane, the conversion of a η^5-Cp binding mode to a η^1-Cp type[12] as well as a η^1-Cp-participated Diels−Alder reaction with in situ vinyl ketone.[16,17]

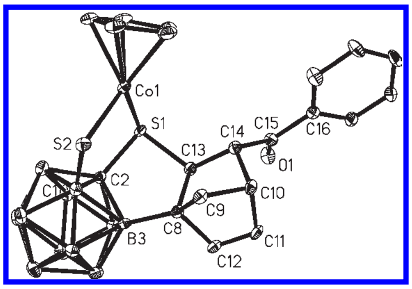


Figure 1. Molecular structure of **2**. Selected bond lengths (Å): Co1−S1 2.1835(14), Co1−S2 2.1699(15), S1−C2 1.801(4), S2−C1 1.795(5), C1−C2 1.655(6), S1−C13 1.860(4), B3−C8 1.565(7), C8−C9 1.540(6), C8−C12 1.528(6), C8−C13 1.579(6), C9−C10 1.535(6), C10−C11 1.501(6), C10−C14 1.578(6), C11−C12 1.319(7), C13−C14 1.541(6).

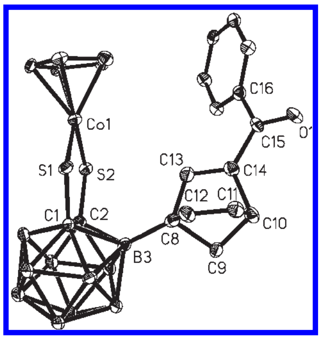


Figure 2. Molecular structure of **3**. Selected bond lengths (Å): Co1−S1 2.1281(8), Co1−S2 2.1425(9), S1−C1 1.780(3), S2−C2 1.779(3), C1−C2 1.640(4), B3−C8 1.571(5), C8−C9 1.558(4), C8−C12 1.556(5), C8−C13 1.513(4), C9−C10 1.505(4), C10−C11 1.499(5), C10−C14 1.516(5), C11−C12 1.302(5), C13−C14 1.308(5).

As a Co^{II} species, **2** can be readily oxidized by air in the presence of silica. This leads to **3**, where C−S bond cleavage and then dehydrogenation may take place (Figure 2). The resultant substituted norbornadienyl unit at the B3/B6 site of carborane is analogous to the compound bicycl[2.2.1]hepta-2,5-dien-2-ylphenylmethanone generated directly from the Diels−Alder addition of cyclopentadiene and phenyl ethynyl ketone.[18] This provides evidence that the Diels−Alder reaction occurs in the generation of **2**. If moisture is copresent,

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(14) Cp*Co($S_2C_2B_{10}H_{10}$)(C_9H_6O)$_2$ (Cp* = η^5-C_5Me_5), monoclinic, space group $P2_1/c$, a = 16.3162(16) Å, b = 11.1712(10) Å, c = 19.0888(18) Å, β = 107.930(2)°, V = 3310.4(5) Å^3, Z = 4, ρ_{calc} = 1.326 g·cm^{-3}, GOF = 1.009, R1 = 0.0562 [$I > 2\sigma(I)$], wR2 = 0.1342 (all unique reflections). CCDC 738008.

(15) CpCo($S_2C_2B_{10}H_8$)(C_9H_7O)$_2$ (Cp = η^5-C_5H_5), orthorhombic, space group $P2_12_12_1$, a = 7.9575(8) Å, b = 15.6813(14) Å, c = 22.837(2) Å, V = 2849.7(5) Å^3, Z = 4, ρ_{calc} = 1.377 g·cm^{-3}, GOF = 0.992, R1 = 0.0420 [$I > 2\sigma(I)$], wR2 = 0.0934 (all unique reflections). CCDC 738002.

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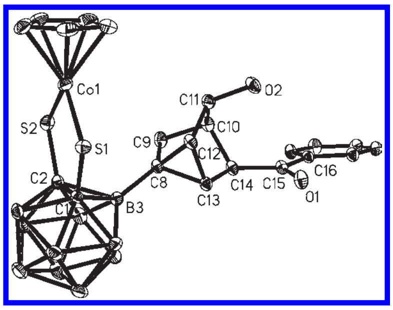

Figure 3. Molecular structure of **4**. Selected bond lengths (Å): Co1−S1 2.1341(10), Co1−S2 2.1243(10), S1−C1 1.782(3), S2−C2 1.786(3), C1−C2 1.620(4), B3−C8 1.546(5), C8−C9 1.537(4), C8−C12 1.522(4), C8−C13 1.538(4), C9−C10 1.531(4), C10−C11 1.524(4), C10−C14 1.546(5), C11−C12 1.508(4), C12−C13 1.485(4), C13−C14 1.512(4).

2 immediately converts to **4** (Figure 3). Here oxidation at the metal center initiates cleavage of the C−S bond followed by attack of H_2O at the C═C bond. The newly generated organic tricyclic (one three-membered and two five-membered rings) unit is of interest, and related structures were scarcely described.[19] **3** cannot convert to **4** in the presence of water. They are generated independently. Both are air-stable 16e Co^{III} complexes containing unprecedented B substitution at carborane.

This work demonstrates an unexpected reactivity of complex **1** with HC≡C−C(O)Ph that leads to novel substitution in the B3/B6 position of *o*-carborane via cobalt-mediated B−H activation and Cp-participated Diels−Alder reaction in one step. This finding offers a facile route to selective B−H functionalization at carborane and novel compounds. Detailed investigations are continuing to define the scope of the reaction reported here with respect to other alkynes.

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Supporting Information Available: Crystallographic data in CIF format, experimental details, and crystallographic data. This material is available free of charge via the Internet at http://pubs.acs.org.

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