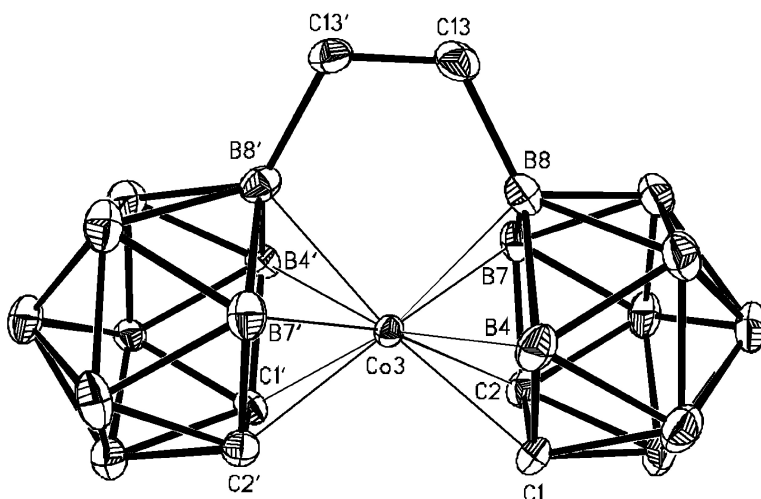## Communication

# Formation of Bridging Alkene and Conjugated Dialkenes Exclusively Generated from Alkynes on the [3,3'-Co(1,2-CBH)] Platform. The Unique Hydroboration Role of [3,3'-Co(1,2-CBH)]

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# Formation of Bridging Alkene and Conjugated Dialkenes Exclusively Generated from Alkynes on the [3,3′-Co(1,2-C₂B₉H₁₁)₂]⁻ Platform. The Unique Hydroboration Role of [3,3′-Co(1,2-C₂B₉H₁₁)₂]⁻

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The cobaltabis(dicarbollide) anion, [3,3′-Co(1,2-C₂B₉H₁₁)₂]⁻, [1]⁻, first synthesized by Hawthorne and co-workers,[1] has proven to be very valuable in many areas of applied research.[2] Our group has focused on the synthesis of carbon-substituted derivatives[3] of [1]⁻ and recently has begun to explore its B-substituted derivatives.[4] In this paper, we report on the unprecedented metal-mediated transformation of an alkyne into an alkene unit that bridges the two subclusters.

The alkene formation can be associated with the cooperative effect of a B−I and a B−H geometrically placed on an appropriate platform, and to their electronic properties. In addition, the synthesis of a conjugated dialkene derivative of [1]⁻ is described. The novelty reported in this paper is that it was generated from an alkyne (trimethylsilylacetylene) only, in addition to being the first B-alkene-bridged metallacarborane cluster. Contrary to the usual conjugated dialkene formation that requires both one alkyne and one alkene moietie,[5] in the case reported here, the alkyne is also the source of the alkene due to the hydroboration originated in one B−H cluster unit.

The 8-monoiodinated derivative, Cs[3,3′-Co(8-I-1,2-C₂B₉H₁₀) (1′,2′-C₂B₉H₁₁)], Cs[2],[4,6] is obtained from Cs[1] and is used as the starting material for the preparation of the alkene-linked cobaltabis(dicarbollide). Reaction of Cs[2] with trimethylsilylacetylene in the presence of [PdCl₂(PPh₃)₂]/CuI and diisopropylamine in refluxing THF, followed by removal of solvent and precipitation in CH₂Cl₂ with constant stirring, produced an insoluble red solid, identified as Cs[3] (Scheme 1). ¹H NMR spectra of Cs[3] indicate the absence of the −SiMe₃ group. This was unexpected as removal of −SiMe₃ requires the use of specific reagents, for example, Bu₄-NF.[7] The ¹¹B-NMR spectrum displays a pattern 1:3:2:2:1 ranging from +26.0 to −25.4 ppm, which suggests that in Cs[3] both dicarbollide moieties are symmetry related if the resonance of intensity 3 is due to the coincidental overlap of two resonances (1 + 2). The two moieties would have been equivalent if two alkynyl groups, one in each moiety, had been introduced. It is important to note the recent work of Grimes and co-workers, in which the reaction of [Cp*Co(5-I-1,2-Et₂-1,2-C₂B₃H₄)][8] with trimethylsilyl-acetylene using a catalyst set similar to the one used for Cs[3] and diethylamine as solvent led to a mixture of trimethylsilylalkynyl mono- and disubstituted metallacarboranes, the latter being produced in 58% yield. In this example, the disubstitution had taken place in contiguous boron atoms at the same carborane ligand moiety. Relevant information about the structure of [3]⁻ was obtained from the matrix assisted laser desorption ionization mass spectrum (MALDI-TOF) in the negative mode. An envelope was observed

**Scheme 1.** Preparation of the Alkene-Linked Cobaltabisdicarbollide, [3]⁻
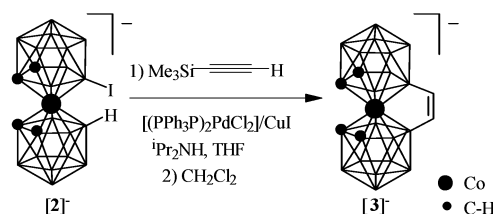


near 348.6 *m/z* which precisely corresponds to the calculated envelope for [*μ*-8,8′-C₂H₂-3,3′-Co(1,2-C₂B₉H₁₀)₂]⁻, [3]⁻. This formula is in agreement with the NMR spectroscopic data. The formation of Cs[3] can be described in terms of an ethenylidene group, generated from an alkyne, that bridges the two equivalent sites of the precursor. A single-crystal X-ray diffraction study of Cs[3] confirmed the formulation (Figure 1).[9] The CH═CH bridge with a C13−C13′ distance of 1.325(5) Å dictates the mutual orientation of the carborane moieties: the C₂B₃ faces coordinated to Co are tilted by 7.1(2)° from parallel orientation, bringing B8 and B8′ closer and deviating 11° from an ideal eclipsed conformation.

In an attempt to investigate the requirements for the bridging to occur, two reactions were conducted: (i) Cs[3,3′-Co(8-I-1,2-C₂B₉H₁₀)₂], Cs[4] having two B(8)−I units, was reacted with trimethylsilylacetylene, and (ii) Cs[1] with two B(8)−H was also reacted with the alkyne. In both cases, the reaction conditions were the same as those for the synthesis of Cs[3]. No reaction was observed in either case. This implies that both of the two nonequivalent groups B(8)−I and B(8′)−H are complementary and necessary for the alkyne insertion. The role of the trimethylsilyl group was also assessed by performing the reaction of [2]⁻ with acetylene, phenylacetylene, methyl propargyl ether, and propar-gyltrimethylsilane. Again, no reaction was observed. Why and how does this reaction then take place? We currently interpret the pathway as shown in Figure 2. Initially a reversible B−C coupling reaction would take place, which is shifted to the reagents side (step i). This could explain the absence of dicarbollide alkyne derivatives with any of the alkynes tested. For the particular case of trimethylsilylacetylene, the polarizable C−Si bond should facilitate hydroboration by the B(8)−H (step ii).[10] Upon the formation of the alkene, the ═*C*BSi carbon becomes electron-rich and susceptible to electrophilic attack. This plus the bulkiness of the −SiMe₃ groups and the electropositive character of Si provide a pathway for a hydrodesilylation process leading to the bridging alkene (step iii).

This reaction finds no parallel in alkyne organic or organometallic chemistry, but some similarities can be found in the enyne

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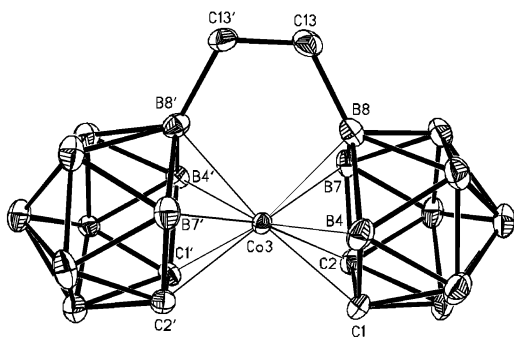‡ University of Helsinki.
§ University of Jyväskylä.

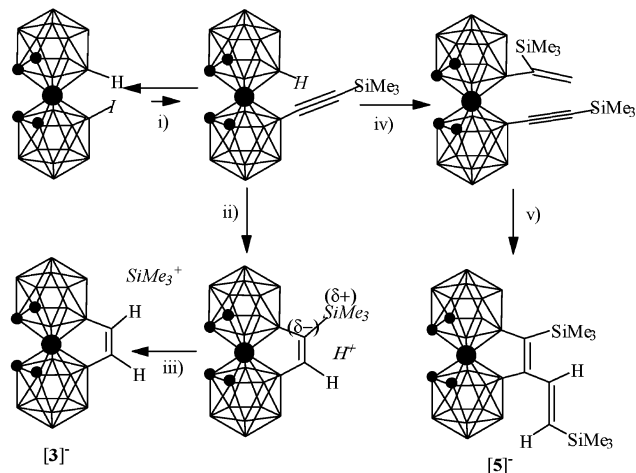**Figure 1.** Structure of the anion in Cs[**3**]. Thermal ellipsoids are drawn at the 50% probability level.



**Figure 2.** Possible paths of the reaction between [**2**]⁻ and trimethylsilyl-acetylene.

metatheses first described by Katz.[11] Katz's original example generates a conjugated dialkene in which one of the two ene groups bridges the 2,2′ positions in biphenyl to yield 9-vinylphenanthrene. Conceptually, phenanthrene and [**3**]⁻ are similar. They are formally generated from biphenyl and [**1**]⁻, respectively, upon the addition of a C≡C moiety. This could have been just a geometrical curiosity, but it provided some hints about the reactivity of iodocosane, [**2**]⁻, as we describe next.

The reaction leading to the bridged species Cs[**3**] was not quantitative. After removal of Cs[**3**] and evaporation of H₂CCl₂, MALDI-TOF mass spectrometric analysis of the solid exhibited several peak envelopes, indicating that its composition was complex. The two largest envelopes correspond to unreacted [**2**]⁻ and to a derivative of [**1**]⁻, so-called [**5**]⁻ that would result from the fusion of two trimethylsilyl moieties (Figure 2). Optimization of the reaction conditions to improve the yield of [**5**]⁻ has been carried out. Proton sponge, triethylamine, diethylamine, diisopropylamine, and butyllithium have been used as base, and diisopropylamine and THF have been used as solvent. Room temperature and refluxing conditions or a combination of both have also been tested. Additionally, different ratios of the alkyne versus the anion [**2**]⁻ have been studied. The nature of the final products does not vary much with the different conditions, but the reaction at room temperature in which diisopropylamine is used both as a base and as solvent produces [**5**]⁻ in largest quantity. We currently consider

that the initial step of the pathway proposed for [**3**]⁻ could also be valid for the formation of [**5**]⁻. Once the boron–carbon bond formation has taken place [step (i) in Figure 2], an alternative route to step (ii) is possible. This is indicated as step (iv). Both steps (ii) and (iv) are based on a hydroboration. For (ii), the hydroboration on the triple bond is intramolecular, whereas for (iv) the hydroboration is intermolecular. It has been known that hydroboration of alkynylsilanes proceeds with a regiochemistry that places the boron atom on the carbon atom bonded to silicon.[12] This also applies here: both steps (ii) and (iv) would be in agreement with this observation. According to step (iv), an alkene group would be generated in the molecule which adds to the alkyne unit that is already present. In the presence of the palladium-based catalyst, an enyne-metathesis catalytic cycle,[13] reasonably[14] leading to the formation of the cobaltabis(dicarbollide) conjugated dialkene, then takes place, step (v). The spectroscopic data are in agreement with the formulation for [**5**]⁻. The simulation of the MALDI-TOF peak corresponding to [**5**]⁻ matches the experimental one observed at 518.5 $m/z$. The ¹H NMR spectrum of [**5**]⁻ shows in addition to other resonances two doublets at +6.68 and +5.95 ppm with $J(H,H)$ = 21 Hz, consistent with alkene protons in a trans disposition. The nonequivalency of the two dicarbollide moieties in [**5**]⁻ is clear from the 1:1:1:1:4:2:2:4:2 ¹¹B-NMR pattern spectra.

**Supporting Information Available:** Synthetic and characterization details for Cs[**3**] and Cs[**5**]; X-ray structure details (PDF) and crystallographic data (CIF) for Cs[**3**]. This material is available free of charge via the Internet at http://pubs.acs.org.

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