

Synthesis, Structure, and Reactivity of Zirconacyclopentene Incorporating a Carboranyl Unit

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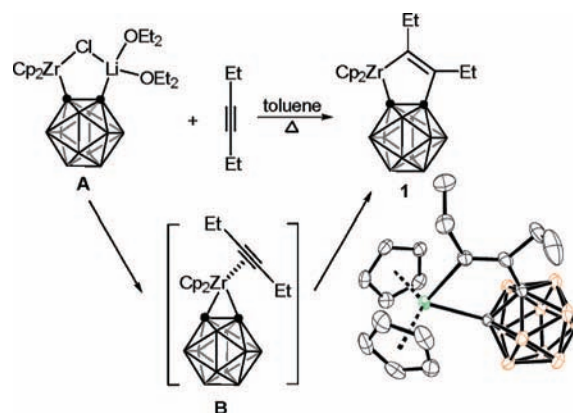
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Transition metal mediated cycloadditions of alkynes and/or alkenes serve as a powerful strategy to construct a wide range of compounds since complexation of the metal center to an olefin or alkyne significantly modifies the reactivity of this moiety.¹ In view of the similar reactivity pattern between carboryne (1,2-dehydro-*o*-carborane) and alkyne,² we have developed the nickel-mediated two-component [2+2+2] cycloaddition of carboryne with alkynes to afford benzocarboranes,³ cross-coupling reaction of carboryne with alkenes to generate alkenylcarboranes,⁴ and three-component [2+2+2] cycloaddition of carboryne with alkene and alkyne to give dihydrobenzocarboranes.⁵ Many attempts to isolate the proposed intermediate nickelacyclopentene in Ni-mediated cycloaddition of carboryne with alkynes failed due to the high reactive nature of this intermediate.³ On the other hand, we learned from literature that zirconacyclopentadienes are in general much more stable than their nickel analogues⁶ and often serve as very important versatile intermediates for construction of a carbon–carbon bond.⁷ In view of the unique features of zirconacyclopentadienes, we became interested in developing a carborane version of these reagents. Our previous work showed that Cp₂Zr(μ-Cl)(μ-C₂B₁₀H₁₀)Li(OEt)₂ (**A**) is the precursor of Cp₂Zr(η²-C₂B₁₀H₁₀) as evidenced by reactions with polar unsaturated molecules.⁸ Complex **A** does not show any activity toward alkynes at temperatures below 60 °C. However, we found, after many attempts, that **A** can react well with EtC≡CEt in reflux toluene to generate the corresponding zirconacyclopentene **1** which provides a valuable entry point to the synthesis of carborane derivatives that can not be prepared by conventional methods.

Treatment of **A** with 2 equiv of EtC≡CEt in reflux toluene gave 1,2-[Cp₂ZrC(Et)=C(Et)]-1,2-C₂B₁₀H₁₀ (**1**) as yellow crystals in 93% isolated yield (Scheme 1).⁹ It is noted that both solvents and temperatures are crucial to this reaction. Complex **1** was not observed if the donor solvents such as Et₂O and THF were used instead of toluene, suggesting that the coordination of alkyne to the Zr atom is essential for the subsequent insertion. High temperatures not only promote the dissociation of LiCl from **A** forming the zirconocene-carboryne intermediate³ but also facilitate the coupling reaction between carboryne and the coordinated alkyne via the intermediate **B**. The characteristic vinyl carbons were observed at 195.1 and 144.1 ppm in the ¹³C NMR spectrum. The Zr–C_{vinyl}/C=C distances of 2.277(2)/1.346(3) Å in the five-membered metallacycle are close to the corresponding values found in zirconacyclopentadienes.¹⁰

Significantly different from the nickelacyclopentene,³ **1** does not react with another equivalent of alkyne even in the presence of CuCl and is stable in air for a few minutes in the solid state. It hydrolyzed under acidic media to afford alkenylcarborane 1-[CH(Et)=C(Et)]-1,2-C₂B₁₀H₁₁ (**2**) (Scheme 2). The unique cage C–H and vinyl =C–H protons were found at 3.74 ppm as a broad singlet and 5.70 ppm as a triplet, respectively, in the ¹H NMR spectrum of **2**. Interaction of **1** with I₂ in the presence of CuCl

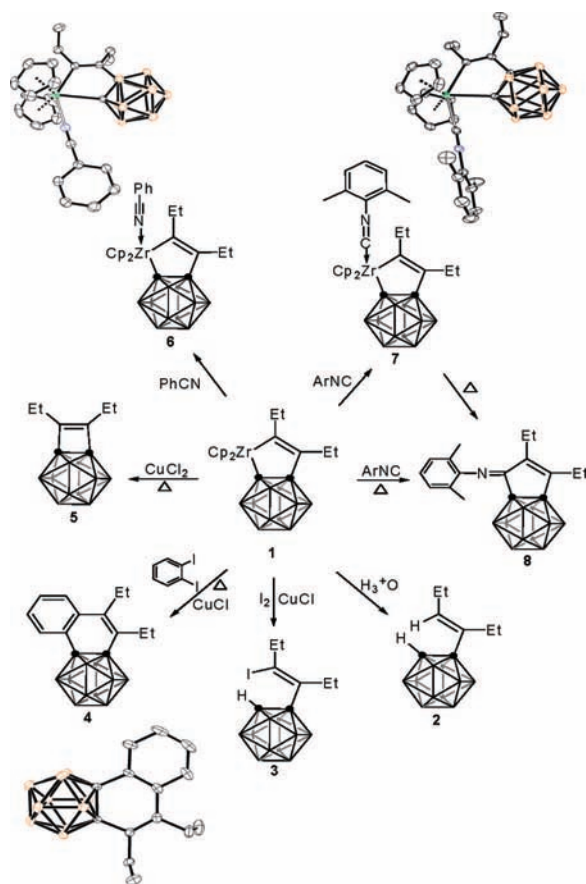
Scheme 1. Preparation of **1**



generated a monosubstituted carborane 1-[Cl(Et)=C(Et)]-1,2-C₂B₁₀H₁₁ (**3**) in 71% isolated yield.⁹ In the absence of CuCl, **3** was isolated in 61%. In both cases, the disubstituted species 1-I-2-[Cl(Et)=C(Et)]-1,2-C₂B₁₀H₁₀ was not observed. This result is very different from that of zirconacyclopentadienes, in which the diiodo species is the major product in the presence of CuCl.¹¹ Therefore, it is rational to suggest that, after transmetalation to Cu(I), only the Cu–C_{vinyl} bond is reactive toward I₂ whereas the Cu–C_{cage} bond is inert probably because of steric reasons.¹² The cage C–H proton in **3** was largely downfield shifted to 5.41 ppm, indicative of an interaction between this acidic proton and iodo group.

Reaction of **1** with *o*-diiodobenzene in the presence of CuCl produced naphthalocarborane **4** in 81% isolated yield.¹³ The transmetalation to Cu is necessary for this reaction. In the absence of CuCl, no reaction was observed. Its structure is confirmed by single-crystal X-ray analyses.⁹ Treatment of **1** with CuCl₂ in toluene at 80 °C gave the C–C coupling product 1,2-[C(Et)=C(Et)]-1,2-C₂B₁₀H₁₀ (**5**) in 46% isolated yield with the formation of copper mirror.¹⁴ If CuCl₂ was replaced by CuCl in the reaction, **5** was isolated in 18%.¹⁵ It is suggested that transmetalation of **1** to Cu(II) gives the intermediate 1,2-[CuC(Et)=C(Et)]-1,2-C₂B₁₀H₁₀. Subsequent reductive elimination affords the coupling product **5** and Cu mirror. It is noteworthy that CuCl₂ is not a common transmetalation agent used in zirconocene chemistry. Both ¹H and ¹³C NMR spectra indicated that **5** is a symmetrical molecule.

Interaction of **1** with PhCN in the presence of CuCl did not yield any insertion product even under forced reaction conditions but rather gave **5** in low yield.¹⁶ In the absence of CuCl, a PhCN-coordinated complex **6** was isolated at room temperature, which is stable at reflux toluene. On the other hand, more reactive 2,6-(CH₃)₂C₆H₃Nc can readily insert into the Zr–C_{vinyl} bond to form an insertion product **8** in reflux toluene in the absence of CuCl. At room temperature, the isocyanide-coordinated complex **7** was isolated, which was converted to **8** upon heating in toluene in the

Scheme 2. Reactivity of **1**

presence of another equivalent of isocyanide.¹⁷ In the presence of CuCl, however, both **5** and **8** were isolated from the reaction mixture under the same reaction conditions. The reaction pathway may be similar to that proposed for the reaction of zirconacyclopentadiene with isocyanides in the presence of CuCl.¹⁸

In summary, zirconacyclopentene **1** resembles its analogue zirconacyclopentadienes $\text{Cp}_2\text{Zr}[\text{C}(\text{R})=\text{C}(\text{R})-\text{C}(\text{R})=\text{C}(\text{R})]$ in some reactions, and on the other hand, **1** has unique properties of its own due to the presence of highly sterically demanding carboranyl unit. This work demonstrates that **1** is an important intermediate for the preparation of a range of functionalized carborane derivatives. In view of the very rich chemistry of zirconacyclopentadienes,^{6,7} synthetic methodologies based on **1** are awaiting exploration.

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Supporting Information Available: Detailed experimental procedures, complete characterization data, and X-ray data in CIF format for **1**, **4**, **6**, and **7**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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