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Synthesis, Structure, and Reactivity of a Zirconocene−Carboryne Precursor

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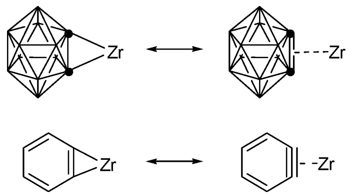
Benzyne and its transition metal complexes have found many applications in organic synthesis, mechanistic studies, and the synthesis of functional materials.[1] Carboryne (1,2-dehydro-*o*-carborane), as a three-dimensional relative of benzyne, came to the scene at a much later stage, which was first reported as a reactive intermediate in 1990.[2] The theoretical calculations indicated that the formations of carboryne (1,2-$C_2B_{10}H_{10}$) and benzyne are very energetically comparable.[3] Reactivity studies also showed that they are quite similar in reactions with dienes.[3,4] Like benzyne, carboryne can be trapped and stabilized by transition metals. Two examples of this sort have been reported and structurally characterized, (η^2-$C_2B_{10}H_{10}$)$Ni(PPh_3)_2$[5] and [{η^5:σ-$Me_2C(C_9H_6)(C_2B_{10}H_{10})$}ZrCl($\eta^3$-$C_2B_{10}H_{10}$)][$Li(THF)_4$].[6] Molecular orbital calculations on the latter suggested that the bonding interactions between Zr and carboryne are best described as a resonance hybrid of both Zr−C σ and Zr−C π bonding forms which is similar to that observed in the Zr−benzyne complex shown in Chart 1.[6] However, the reaction chemistry of transition metal−carboryne complexes is virtually unknown. In view of the very rich and exciting chemistry of zirconocene−benzyne complexes,[1e] we are interested in exploring the totally undeveloped reaction chemistry of zirconocene−carboryne complexes. Herein we report the synthesis, structure, and reactivity of an unprecedented zirconocene−carboranyl complex $Cp_2Zr(\mu\text{-}Cl)(\mu\text{-}C_2B_{10}H_{10})Li(OEt_2)_2$ (**1**) as an efficient precursor of the zirconocene−carboryne species.

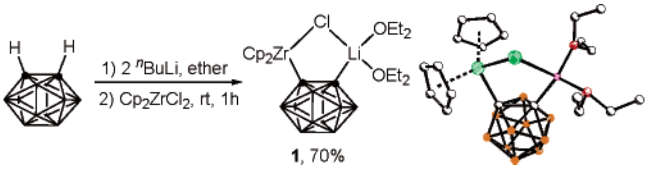
Treatment of Cp_2ZrCl_2 with 1 equiv of $Li_2C_2B_{10}H_{10}$ in Et_2O at room temperature for 1 h gave **1** in 70% isolated yield, rather than the expected zirconocene−carboryne complex (Scheme 1). Complex **1** was stable at −30 °C for weeks but slowly decomposed at room temperature. It was fully characterized by various spectroscopic techniques, elemental analyses, and single-crystal X-ray diffraction studies.[7] This unique molecule could be viewed as an intermediate to the zirconocene−carboryne. Attempts to isolate $Cp_2Zr(\eta^2\text{-}C_2B_{10}H_{10})(L)$, an analogue of $Cp_2Zr(\eta^2\text{-}C_6H_4)(L)$, in the presence of PMe_3, TMEDA, or 12-crown-4 ether via a complete salt metathesis reaction failed. One possible reason may be attributed to the instability of the resultant zirconocene−carboryne complex. If so, this reactive species could be trapped by unsaturated organic molecules.

In fact, **1** was very active toward Cy−N=C=N−Cy (DCC; Cy = C_6H_{11}), PhN_3, ^{t}BuNC, and PhCN, leading to the isolation of $Cp_2Zr[\sigma\text{:}\sigma\text{-}CyNC(=NCy)(C_2B_{10}H_{10})]$ (**2**), $Cp_2Zr[\eta^2\text{:}\sigma\text{-}(PhNN=N)(C_2B_{10}H_{10})]$ (**3**), $Cp_2Zr[\eta^2\text{-}{}^tBuNC(C_2B_{10}H_{10})=CN^tBu](CN^tBu)$ (**4**) and $Cp_2Zr[\sigma\text{:}\sigma\text{-}N=C(Ph)(C_2B_{10}H_{10})](PhCN)$ (**5**), respectively, in moderate to high yields (Scheme 2). All of these complexes were fully characterized by ^{1}H, ^{13}C, and ^{11}B NMR spectroscopy and elemental analyses as well as single-crystal X-ray analyses.[7]

Chart 1. Bonding Description



Scheme 1. Synthesis of **1**



The most interesting feature in the observation of complexes **2**−**5** is the mechanism by which they are formed. One may attribute these to the results of direct nucleophilic reactions of the cage carbon with these unsaturated molecules. This hypothesis was, however, not supported by the control experiments. Except for DCC, all PhN_3, ^{t}BuNC, and PhCN were confirmed to be totally inert toward $Li_2C_2B_{10}H_{10}$ in ether. Furthermore, PhCN showed no reactivity toward $Li_2C_2B_{10}H_{10}$ in the presence of $Cp_2ZrCl(Me)$ or Cp_2ZrMe_2.[8] These results ruled out the possibility of direct nucleophilic attack by the carboanion of the C(cage)−Li unit. The question subsequently arises as to whether the zirconocene−carboryne ($Cp_2Zr(\eta^2\text{-}C_2B_{10}H_{10})$) was involved in these reactions. Complexes **2** and **3** could be produced via the insertion and followed by the elimination of LiCl, which might not be necessary to go through the carboryne intermediate.[9] For ^{t}BuNC, if ^{t}BuNC is inserted into the Zr−C(cage) bond in **1** first, a three-membered azazirconacycle $Cp_2ZrCl(\eta^2\text{-}{}^tBuN=C)C_2B_{10}H_{10}Li(OEt_2)_2$ would be favored due to the hard−hard interactions between the N atom and Zr(IV) center,[9c] which might preclude the possibility for the formation of a four-membered metallacycle via the elimination of LiCl. Consequently, the insertion of the second ^{t}BuNC molecule would not be possible. Therefore, the formation of **4** is likely via a zirconocene−carboryne intermediate (Scheme 3) although other pathways cannot be ruled out at this moment. The first insertion of ^{t}BuNC into the Zr−C(cage) bond gives a four-membered metallacycle, followed by the further insertion of the second molecule of ^{t}BuNC to afford a five-membered metallacycle. The coordination of the imine nitrogen and the cleavage of one Zr−C(imine) bond lead to the production of **4**. Back-donation of the carboanion to the cage carbon leading to the formation of *exo* C(cage)=C double bond and the subsequent cleavage of the cage C−C bond have been reported in the literature.[10] On the other hand, PhCN was reported not to insert into the Zr−C bond in alkyl- and alkenylzirconocenes,[8] but it can insert into the Zr−C bond in $Cp_2Zr(\eta^2\text{-}C_6H_4)$.[11] The formation of **5** further supports zirconocene−carboryne to be the intermediate in this reaction, since PhCN does not insert into the Zr−C(cage) bond in zirconocene−carboranyl complexes,[12] which was also discussed previously. Otherwise, further insertion of the coordinated PhCN should be observed in the present reaction. The proposed reaction pathway is shown in Scheme 3.

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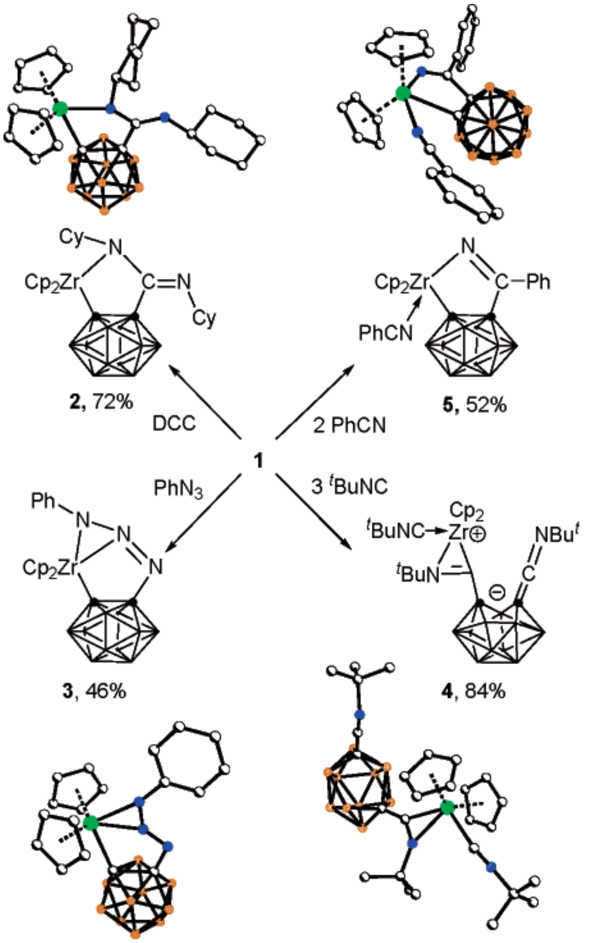
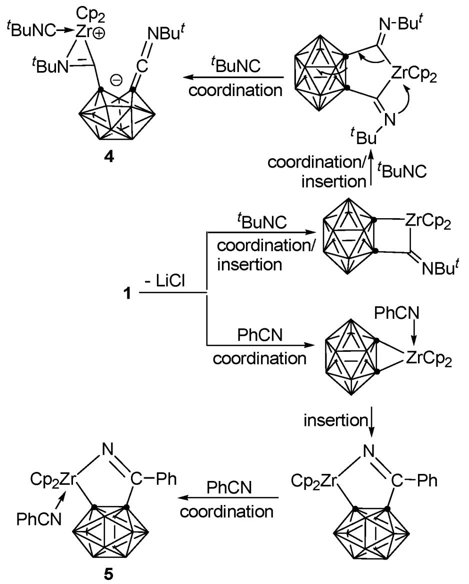
Scheme 2. Reactivity of **1**



Scheme 3. Proposed Reaction Mechanism for the Formation of **4** and **5**



Unlike the zirconocene−benzyne complexes,[1e] **1** showed no reactivity toward alkynes and alkenes even under forced reaction conditions. The reason is probably due to the steric demanding of the carboryne cage[4c] which prevents the π coordination of alkynes or alkenes to the Zr metal center.

In conclusion, we synthesized a novel zirconocene−carboranyl complex **1**, a very efficient precursor of the zirconocene−carboryne, and studied its reactivity pattern for the first time. The results clearly showed that **1** and the zirconocene−benzyne complexes have a very similar reactivity in the reactions with polar unsaturated organic molecules that can coordinate to the Zr center via their lone-pair electrons. On the other hand, **1** and zirconocene−benzyne complexes showed very different properties toward alkynes and alkenes due to the very large size of the carborane cage. This work also furnished a novel method for the preparation of functional *o*-carboranes and their metal complexes which cannot be synthesized by other methods presently known.

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Supporting Information Available: Detailed experimental procedures, complete characterization data, and X-ray data in cif format for **1**−**5**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(7) Detailed experimental procedures and complete characterization data including X-ray data for complexes **1**−**5** are provided in the Supporting Information.

(8) Nitriles are inert toward the Zr−C σ bond of Cp_2ZrR_2 and Cp_2ZrRX; see: (a) Neigishi, E.; Montchamp, J. In *Metallocenes*; Togni, A., Halterman, R. L., Eds.; Wiley: Chichester, 1998; Vol. 1, pp 264−266. (b) Bercaw, J. E.; Davies, D. L.; Wolczanski, P. T. *Organometallics* **1986**, *5*, 443−450. (c) Jordan, R. F.; Dasher, W. E.; Echols, S. F. *J. Am. Chem. Soc.* **1986**, *108*, 1718−1719.

(9) It is documented that DCC, PhN_3, and ^{t}BuNC can insert into the Zr−C bond of Cp_2ZrR_2. (a) For DCC, see: Gambarotta, S.; Strologo, S.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *Inorg. Chem.* **1985**, *24*, 654−660. (b) For PhN_3, see: Chiu, K. W.; Wilkinson, G.; Thornton-Pett, M.; Hursthouse, M. B. *Polyhedron* **1984**, *3*, 79−85. (c) For ^{t}BuNC, see: Guram, A. S.; Jordan, R. F. *J. Org. Chem.* **1993**, *58*, 5595−5597.

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