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Nickel-Mediated Regioselective [2 + 2 + 2] Cycloaddition of Carboryne with Alkynes

Liang Deng, Hoi-Shan Chan, and Zuowei Xie*

Department of Chemistry, The Chinese University of Hong Kong, Shatin, New Territory, Hong Kong, China

Received March 8, 2006; E-mail: zxie@cuhk.edu.hk

Benzyne (and its transition metal complexes) has found many applications in organic synthesis, mechanistic studies, and the synthesis of functional materials since it was reported as an active intermediate in the 1950s.[1,2] In sharp contrast, carboryne (1,2-dehydro-*o*-carborane), a three-dimensional relative of benzyne, came to the scene at a much later stage, which was first reported in 1990 as a very reactive intermediate.[3] Similar to benzyne, the in situ generated carboryne can react with alkenes, dienes, and alkynes in [2 + 2] cycloaddition and ene reaction patterns.[3,4] On the other hand, the chemistry of metal−carboryne complexes is largely unexplored, although the first example of (η^2-$C_2B_{10}H_{10}$)$Ni(PPh_3)_2$ was reported in 1973,[5] even earlier than the parent carboryne intermediate.

Recently, we prepared an early transition metal−carboryne complex, [{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] and investigated the reactivity of $Cp_2Zr(\mu$-$Cl)(\mu$-$C_2B_{10}H_{10})$-$Li(OEt_2)_2$, a precursor of $Cp_2Zr(\eta^2$-$C_2B_{10}H_{10})$.[7] Our work revealed that $Cp_2Zr(\eta^2$-$C_2B_{10}H_{10})$ produced in situ has a similar reactivity pattern to that of $Cp_2Zr(\eta^2$-$C_6H_4)$ in reactions with polar unsaturated organic substrates, such as isonitrile, nitrile, and azide. However, significantly different from Zr−benzyne species, Zr−carboryne is inert toward internal alkynes because of steric hindrance of the carborane moiety and the π coordination requirement of alkynes.[7] To overcome these problems, we thought about (η^2-$C_2B_{10}H_{10}$)$Ni(PPh_3)_2$ since the coordinated phosphines, which can create vacant sites for incoming substrates, are often labile during the reactions. With this in mind and in view of the reactions of nickel−benzynes with alkynes to generate substituted naphthalenes[8] and the analogy between nickel−benzyne and nickel−carboryne complexes (Chart 1), we then examined the reactivity of (η^2-$C_2B_{10}H_{10}$)$Ni(PPh_3)_2$ (**2**) toward alkynes. Herein, we report our preliminary results on the reactions of **2** with 2 equiv of alkynes to afford [2 + 2 + 2] cycloaddition product, benzocarborane **3**, as shown in Table 1.

A typical procedure is as follows.[9] To a THF solution (30 mL) of $Li_2C_2B_{10}H_{10}$ (10 mmol), prepared in situ from the reaction of ^{n}BuLi (20 mmol) with *o*-carborane (10 mmol), was added $(PPh_3)_2$-$NiCl_2$ (10 mmol) at room temperature. The reaction mixture was further stirred for 0.5 h giving the Ni−carboryne intermediate **2**.[5] 3-Hexyne (30 mmol) was then added, and the closed reaction vessel was heated at 90 °C for 4 days. The reaction mixture was then cooled to room temperature and quenched with $NaHCO_3$ solution. Normal workup afforded the coupling product **3a** ($R_1 = R_2 =$ Et) in 67% isolated yield with a small amount of hexaethylbenzene as the byproduct (8% based on 3-hexyne). The reaction temperature is crucial for this reaction. Lower temperatures often gave lower yields, and the reaction did not proceed at $T < 60$ °C. On the other hand, higher reaction temperatures (>90 °C) led to the decomposition of **2** as indicated by the ^{11}B NMR. The use of excess alkynes was also necessary because of the side reaction of the trimerization of alkynes by the extruded nickel(0) species.[10] More than 3 equiv of alkyne was not necessary, as it did not offer higher yield of **3**. It is noteworthy that other nickel−carboryne complexes, (η^2-$C_2B_{10}H_{10}$)NiL_n (L = PEt_3, $P(OEt)_3$, $n = 2$; L = dppe, $n = 1$), gave very similar results.

Chart 1. Isolobal Analogue

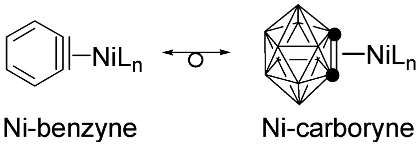
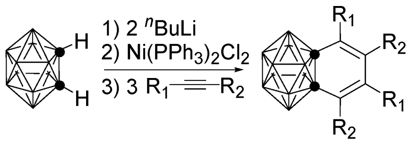


Table 1. Ni-Mediated Coupling Reaction of Carboryne with Alkynes



1 **3**

entry	R_1/R_2	product	yield (%)[a,b]
1	Et/Et	**3a**	67 (8)
2	^{n}Pr/^{n}Pr	**3b**	65 (7)
3	^{n}Bu/^{n}Bu	**3c**	65 (7)
4	Ph/Ph	**3d**	33 (0)
5	Me/Ph	**3e**	54 (0)
6	^{n}Bu/CCBu^n	**3f**	57 (4)
7	^{t}Bu/^{n}Bu	NR	
8	COOMe/COOMe	NR	

[a] Isolated yields. [b] Yields in parentheses are corresponding to those of benzene derivatives.

Listed in Table 1 are representative results obtained from the nickel-mediated coupling reactions of carboryne with alkynes. All products were fully characterized by ^1H, ^{13}C, and ^{11}B NMR as well as high-resolution mass spectrometry.[9] The molecular structures of **3a** ($R_1 = R_2 =$ Et), **3b** ($R_1 = R_2 = {}^n$Pr), **3d** ($R_1 = R_2 =$ Ph), and **3e** ($R_1 =$ Ph, $R_2 =$ Me) were further confirmed by single-crystal X-ray analyses (see Supporting Information).[9] Figure 1 shows the representative structure of **3e**. The localized double bonds C(3)−C(4)/C(5)−C(6) suggest there is no substantial π-delocalization in the six-membered ring. As indicated in Table 1, both aliphatic and aromatic alkynes underwent [2 + 2 + 2] cycloaddition reactions. The electron-rich alkynes were more favorable as indicated by the relatively high yields in entries 1−3. No reaction was observed for the electron-deficient alkyne (entry 8). Steric factors also played an important role in the reactions. Sterically less demanding linear dialkylalkynes offered the best results in comparison to the phenyl and *tert*-butyl-substituted ones. No reaction proceeded for ^{t}BuC≡CBu^n (entry 7). Such a large steric effect made the reactions highly regioselective. As a result, only head-to-tail addition product was observed (entries 5 and 6). It is noted that terminal alkynes are not suitable for the reactions because they can protonate **2** to give *o*-carborane as monitored by the ^{11}B NMR.

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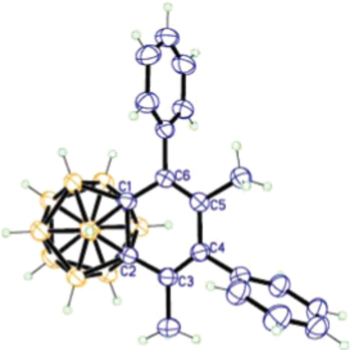
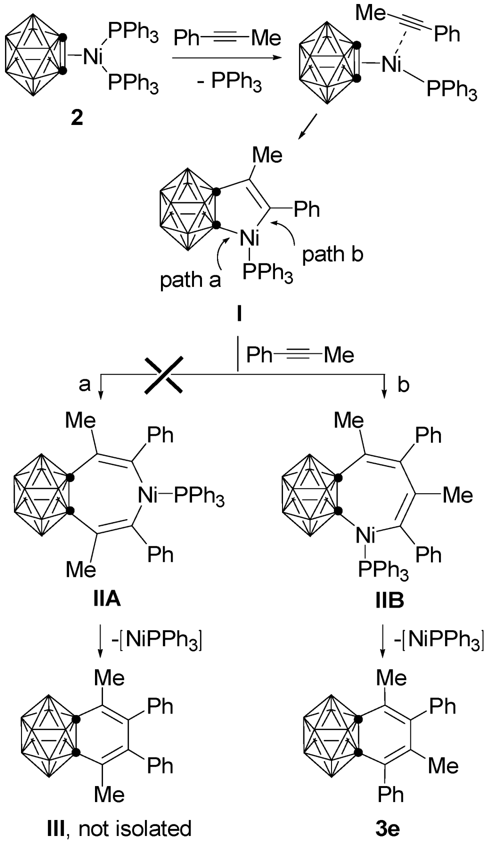


Figure 1. Molecular structure of **3e**. Selected bond lengths (Å): C1−C2 1.648(3), C1−C6 1.486(3), C2−C3 1.493(3), C3−C4 1.338(3), C4−C5 1.476(3), C5−C6 1.351(3).

Scheme 1. Proposed Mechanism for the Formation of **3e**



The formation of products **3** can be rationalized by the sequential insertion of alkynes into the Ni−C bond, as illustrated in Scheme 1. The first insertion gives a nickelacyclopentene intermediate (**I**). The second equivalent of alkyne can possibly insert into either the nickel−C(cage) bond giving a nickelacycloheptadiene (**IIA**) or the nickel−C(vinyl) bond giving **IIB**. Both of them could undergo reductive elimination to form the same product **3** and highly reactive Ni(0) species that is capable of catalyzing the cyclotrimerization of alkynes.[10] The insertion of unsymmetrical alkynes in the two consecutive steps clearly determines the substitution pattern in the final product. The exclusive formation of the head-to-tail products **3e** and **3f** suggests that path b is preferred over the path a. As shown in Scheme 1, the sterically controlled insertion of phenylpropyne into the Ni−C(vinyl) bond of the intermediate **I** is supported by the absence of **III**.[11] In addition, the control experiments indicated that (σ-MeC$_2$B$_{10}$H$_{10}$)$_2$Ni(PPh$_3$)$_2$ was inert toward 3-hexyne under various reaction conditions.[12] Many attempts to isolate the intermediate **I** failed. NMR experiments were not able to detect it, suggesting that the second insertion was very fast.

In conclusion, we have shown for the first time that a nickel−carboryne complex can regioselectively react with internal alkynes in a [2 + 2 + 2] cycloaddition manner to give highly substituted benzocarboranes. The presence of the very bulky carborane moiety dominates the regioselectivity.

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

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(9) Detailed experimental procedures and complete characterization data including X-ray data for complexes **3a**,**b**,**d**,**e** are provided in the Supporting Information.

(10) Ni(0) species catalyzed coupling reactions of alkynes have been well documented. For examples, see ref 8 and (a) Alphonse, P.; Moyen, F.; Mazerolles, P. *J. Organomet. Chem.* **1988**, *345*, 209−216. (b) Sambaiah, T.; Cheng, C.-H. *Bull. Inst. Chem., Acad. Sin.* **1999**, *46*, 41−51.

(11) The regioselectivity of the first insertion was similar to that observed in the sterically controlled insertion of unsymmetrical alkyne into Ni(η^2-4,5-X$_2$-C$_6$H$_2$)(PEt$_3$)$_2$; see ref 8c.

(12) The (σ-MeC$_2$B$_{10}$H$_{10}$)$_2$Ni(PPh$_3$)$_2$ was prepared according to literature method. See: Bresadola, S.; Cecchin, G.; Turco, A. *Gazz. Chim. Ital.* **1970**, *100*, 682−683.

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