Carboranes

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Palladium-Catalyzed Direct Dialkenylation of Cage B–H Bonds in *o*-Carboranes through Cross-Coupling Reactions

*Hairong Lyu, Yangjian Quan, and Zuowei Xie**

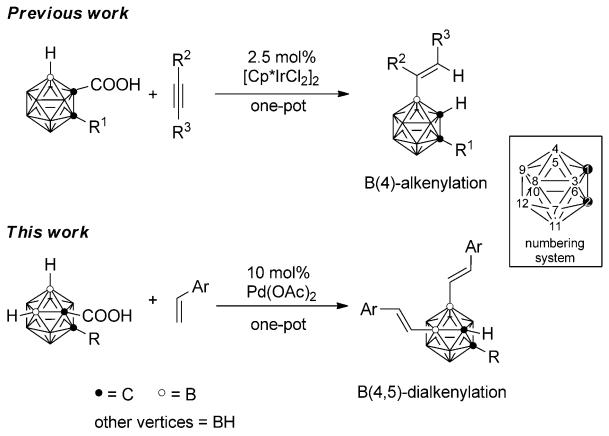
Abstract: *Palladium-catalyzed direct dialkenylation of cage B(4,5)–H bonds in o-carboranes has been achieved with the help of a carboxylic acid directing group, leading to the preparation of a series of 4,5-[trans-(ArCH=CH)]$_2$-o-carboranes in high yields with excellent regioselectivity. The traceless directing group, eliminated during the course of the reaction, is responsible for controlling regioselectivity and dialkenylation. A possible catalytic cycle is proposed, involving a tandem sequence of Pd^{II}-initiated cage B–H activation, alkene insertion, β-H elimination, reductive elimination, and decarboxylation.*

Carboranes, a three-dimensional class of compounds related to benzene, have been shown to be useful basic units in boron neutron capture therapy agents,[1] in supramolecular design/materials,[2] and in coordination/organometallic chemistry.[3] Their unique electronic and cage structures result in different chemical properties of cage hydrogen atoms: hydrogens bonded to cage carbon atoms are acidic, whereas those on cage boron atoms are basic.[4] Accordingly, cage C–H bonds can be readily activated by bases, followed by reaction with electrophiles to give cage carbon-substituted *o*-carborane derivatives.[5] In contrast, cage B–H bonds prefer to undergo electrophilic substitution reactions with strong electrophiles, such as halogens and methyl cations, resulting in the formation of cage boron-substituted *o*-carboranes.[6] Such reactions proceed stepwise in the order B(9,12) > B(8,10) > B(4,5,7,11) > B(3,6), which corresponds to the calculated charge distribution on the cage (see Scheme 1 for the numbering scheme).[7] As charge differences are very small, regioselectivity in these substitution reactions is usually problematic. On the other hand, several stoichiometric transition-metal-mediated cage B(3,6)–H derivatization reactions of *o*-carboranes have been documented.[8] Transition-metal-catalyzed monoarylation of B–H bonds involving B(3), B(4), B(7), B(8), or B(9) centers in *o*-carboranes has recently been reported.[9]

We have recently achieved Ir-catalyzed carboxylic acid directed formal alkyne hydroboration with the B(4)–H bond in a *o*-carborane cage, affording monoalkenylation products 4-(*cis*-CR^1=CR^{2}H)-*o*-carborane, in which the alkenyl moiety is always in *cis* configuration (Scheme 1).[10] In view of the achievements in transition-metal-catalyzed alkenylation of aromatic C–H bonds,[11] and inspired by the aforementioned Ir chemistry,[10,12] we wondered whether an alkene could insert into the M–B bond, in a similar way to the Heck reaction,[13] for developing a new method of cage B–H alkenylation. Herein, we report the first Pd-catalyzed carboxylic acid directed regioselective dialkenylation of *o*-carboranes by direct cage B–H activation (Scheme 1).

The initial reaction of 1-COOH-2-TMS-$C_2B_{10}H_{10}$ (**1a**; TMS = trimethylsilyl) with styrene (**2a**) in the presence of 10 mol% $Pd(OAc)_2$ and 2 equiv of AgOAc in dichloroethane (DCE) at 90 °C for 12 h gave 4-[*trans*-(PhCH=CH)]-*o*-$C_2B_{10}H_{11}$ (**3a**) and 4,5-[*trans*-(PhCH=CH)]$_2$-*o*-$C_2B_{10}H_{10}$ (**4a**) in 49% and 37% yields (as determined by gas chromatography) after treatment with Na_2CO_3 (entry 1, Table 1). The use of 4 equiv of AgOAc resulted in higher reaction efficiency and much better yield of **4a** (entry 2, Table 1). Lowering reaction temperature to 50 °C afforded a sole product **4a**, probably owing to higher stability of the carboxylic acid directing group at low temperatures (see below; entries 3,4, Table 1). On the other hand, lowering the catalyst loading to 5 mol% led to the decreased selectivity of **4a** though the reaction efficiency remained very high (entry 5, Table 1). Toluene resulted in a low selectivity for **4a**, whereas THF led to very poor reaction efficiency (entries 6 and 7, Table 1). Considering the reaction efficiency and selectivity of **4a**, entry 3 in Table 1 was chosen as the optimal set of reaction conditions.

A variety of styrenes were examined under the chosen optimal reaction conditions and the results were compiled in Table 2. Both electron-withdrawing and electron-donating groups on phenyl ring afforded the corresponding products



Scheme 1. Transition-metal-catalyzed cage B–H alkenylation.[10]

[*] H. Lyu, Y. Quan, Prof. Dr. Z. Xie
Department of Chemistry and State Key Laboratory of Synthetic Chemistry, The Chinese University of Hong Kong
Shatin, N.T., Hong Kong (China)
E-mail: zxie@cuhk.edu.hk

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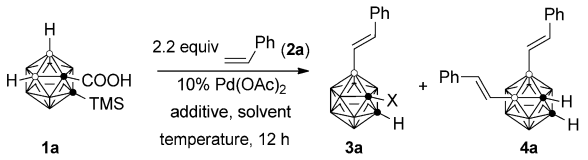
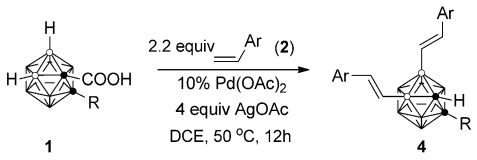
Table 1: Optimization of reaction conditions.[a]



entry	additive	solvent	*T* [°C]	**3a**/**4a** [%][b]
1	2 equiv AgOAc	DCE	90	49/37
2	4 equiv AgOAc	DCE	90	9/91
3	4 equiv AgOAc	DCE	50	1/99
4	4 equiv AgOAc	DCE	70	3/97
5[c]	4 equiv AgOAc	DCE	50	52/47
6	4 equiv AgOAc	toluene	50	28/72
7	4 equiv AgOAc	THF	50	14/0
8	4 equiv $Cu(OAc)_2$	DCE	50	nd[d]
9	–	DCE	50	9/0

[a] Reactions were conducted on a 0.1 mmol scale in 2 mL of solvent in a closed flask. DCE = dichloroethane. X = H at 90 °C; X = COOH at < 70 °C. [b] Yield determined using gas chromatography after treatment with Na_2CO_3. [c] 5 mol% $Pd(OAc)_2$ was used. [d] Not determined, difficult to isolate the product.

Table 2: Synthesis of 4,5-[*trans*-(ArCH=CH)]$_2$-2-R-*o*-$C_2B_{10}H_9$.[a]



Entry	R	Ar	Yield [%][b]
1	TMS	Ph	89 (**4a**)
2	TMS	4-MeC_6H_4	91 (**4b**)
3	TMS	3-MeC_6H_4	90 (**4c**)
4	TMS	2-MeC_6H_4	–
5	TMS	4-$CF_3C_6H_4$	95 (**4d**)
6	TMS	3-$CF_3C_6H_4$	74 (**4e**)
7	TMS	4-ClC_6H_4	88 (**4f**)
8	TMS	3-ClC_6H_4	93 (**4g**)
9	TMS	4-FC_6H_4	72 (**4h**)
10	TMS	4-PhC_6H_4	70 (**4i**)
11	TMS	2-naphthyl	93 (**4j**)
12	TMS	4-$MeOC_6H_4$	39 (**4k**)
13[c]	Me	Ph	79 (**4l**)
14[c]	Et	Ph	80 (**4m**)
15[c]	*i*Pr	Ph	74 (**4n**)
16[c]	Ph	Ph	84 (**4o**)
17[c]	CH_2Ph	Ph	80 (**4p**)
18[c]	3,5-$(CH_3)_2C_6H_3$	Ph	89 (**4q**)
19[c]	4-ClC_6H_4	Ph	74 (**4r**)
20[c]	H	Ph	66 (**4a**)

[a] Reactions were conducted on a 0.2 mmol scale in 5 mL of DCE in a closed flask. [b] Yield of isolated product, TMS was removed after work up. [c] Reactions were heated for 18 h.

which were isolated in very good to excellent yields (entries 1–3, 5–11, Table 2). 2-Vinylnaphthalene also worked well, giving **4j** in 93% yield (entry 11, Table 2). Sterically hindered 2-methylstyrene did not give any product (entry 4, Table 2). For heteroatom-containing substrate *p*-methoxystyrene, the product **4k** was isolated in a decreased yield of 39%, probably owing to the interaction of the heteroatom with the metal center (entry 12, Table 2). Effects of cage carbon substituents R on the reaction results were also examined. Both alkyl and aryl substituents gave the corresponding dialkenylated product **4** which in both cases were isolated in more than 74% yield (entries 13–19, Table 2). If R = H, the corresponding product **4a** was isolated in 66% yield (entry 20, Table 2), and no other structural isomers were isolated. It was noted that the TMS group was removed in all products after work up.

Compounds **4** were fully characterized by ^1H, ^{13}C, and ^{11}B NMR spectroscopy as well as high-resolution mass spectrometry. The molecular structures of **4e**, **4g**, and **4r** were further confirmed by single-crystal X-ray analyses.[14] Figure 1 shows the representative structures of **4e** and **4r**.

To gain some insight into the reaction mechanism, monoalkenylated compound 1-COOH-2-Me-4-[*trans*-(PhCH=CH)]-1,2-$C_2B_{10}H_9$ (**3l**-COOH) was isolated in 35% yield from the reaction of 1-COOH-2-Me-1,2-$C_2B_{10}H_{10}$ with $PhCH{=}CH_2$ under the conditions shown in entry 5, Table 1. Under the optimal reaction conditions (entry 3, Table 1), reaction of **3l**-COOH with $PhCH{=}CH_2$ (**2a**) afforded **4l** in 89% yield (Scheme 2a). As **3l**-COOH was stable at 50 °C, it was suggested that the decarboxylation proceeded after the installation of the second alkenyl unit onto the B(5) position.

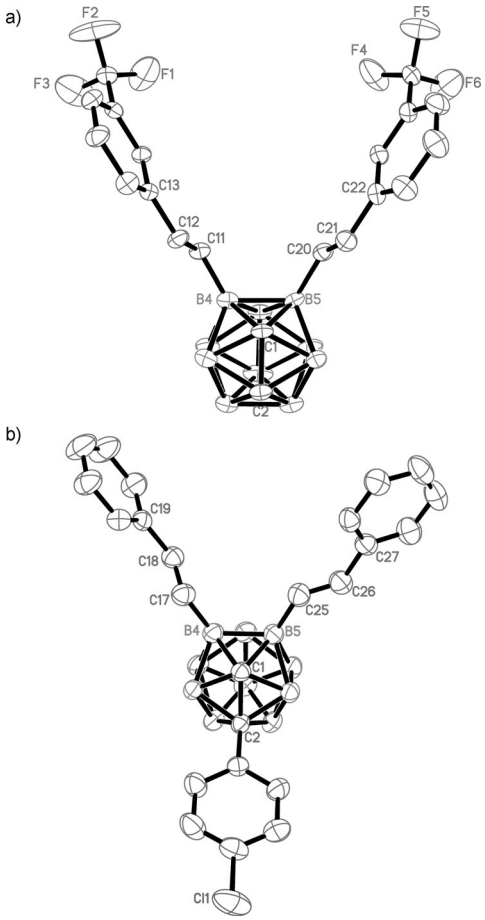
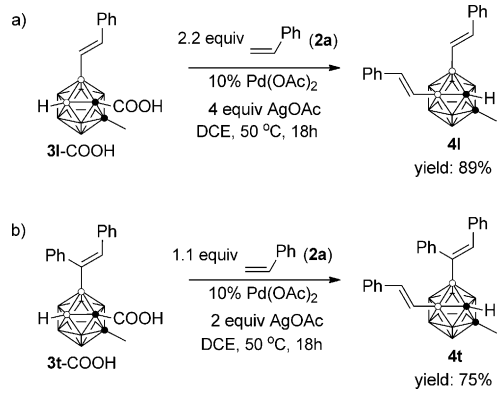


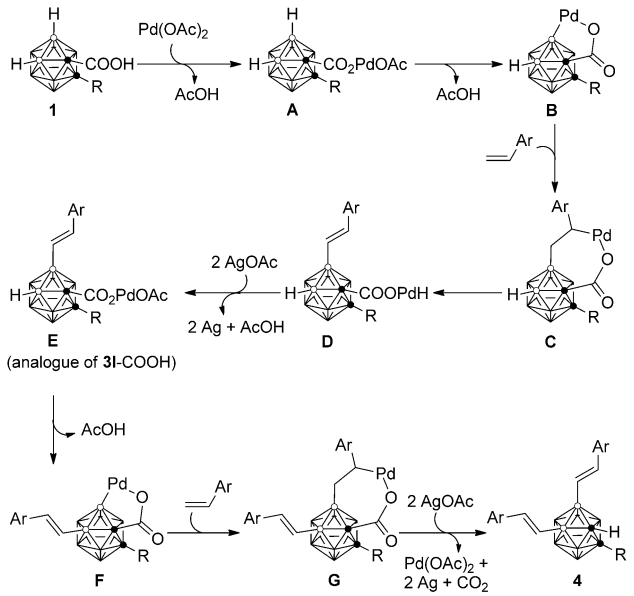
Figure 1. Molecular structures of a) **4e** and b) **4r**.[14]



Scheme 2. Stepwise cage B-alkenylation.

These results indicated that the carboxylic acid directing group is essential for the dialkenylation reaction, and on the other hand, that two different alkenyl units can be introduced at the cage B(4,5) positions by such stepwise reaction. Indeed, treatment of 1-COOH-2-Me-4-[*cis*-(Ph)CH=C(Ph)]-1,2-$C_2B_{10}H_9$ (**3t**-COOH)[10] with $PhCH{=}CH_2$ under similar reaction conditions afforded 2-Me-4-[*cis*-(Ph)CH=C(Ph)]-5-[*trans*-(Ph)CH=CH]-1,2-$C_2B_{10}H_9$ (**4t**) which was isolated in 75% yield (Scheme 2b).

The experimental data (see above) suggests that the catalysis is most likely initiated by a Pd^{II} center. Accordingly, a plausible reaction mechanism is proposed in Scheme 3. The exchange reaction of **1** with $Pd(OAc)_2$ generates the intermediate **A**. Subsequent regioselective electrophilic attack at the more electron-rich cage B(4) site gives the intermediate **B**.[7,10] Steric effects imposed by the substituent R on the second cage carbon atom may also prevent B(3,6) positions from being attacked by Pd^{II}, though only **4a** was isolated if R = H (entry 20, Table 2). Alkene insertion into the Pd–B bond proceeds to produce the seven-membered palladacycle



Scheme 3. Proposed reaction mechanism.

C.[10] β-H Elimination of **C** affords the intermediate **D**. Reductive elimination coupled with oxidation by AgOAc affords the monoalkenylated compound **E** (analogue of **3l**-COOH) and regenerates the active Pd^{II} species. Further regioselective electrophilic attack at the cage B(5) site followed by styrene insertion, β-H elimination, reductive elimination, oxidation, and decarboxylation gives the final dialkenylated product **4** and reproduces the catalyst $Pd(OAc)_2$. It is noted that the carboxylic acid directing group plays a decisive role for the diselectivity of this olefination reaction.

In summary, a regioselective and efficient Pd-catalyzed dialkenylation of cage B(4,5)–H bonds within *o*-carboranes by direct B–H activation has been achieved with the help of a traceless carboxylic acid directing group which is removed during the reaction. This method provides a new procedure for the transition-metal-catalyzed Heck-type reaction of carborane with alkenes, which can be used for the preparation of cage boron dialkenylated carboranes for various purposes.[1–3] It is noted that the two alkenyl units can be the same or different. This work may also prove important for selective borane cage B–H and benzene C–H activation/functionalization.

Experimental Section

o-Carborane monocarboxylic acid **1** (0.20 mmol), alkene **2** (0.44 mmol), $Pd(OAc)_2$ (0.02 mmol), and AgOAc (0.80 mmol) were mixed in 1,2-dichloroethane (5 mL). The resulting mixture was heated in a closed flask at 50 °C for 12 h. After removal of the solvent and addition of Na_2CO_3 (0.20 mmol) and acetone (5 mL), the resulting solution was stirred at room temperature for 3 h to remove the TMS group. Then, the reaction solution was concentrated to dryness in vacuo. The residue was subjected to flash column chromatography on silica gel (230–400 mesh) using *n*-hexane and ethyl acetate (50/1 in v/v) as eluent to give the product **4**.

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[14] CCDC 1401118 (**4e**), 1401119 (**4g**), and 1401120 (**4r**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data request/cif.

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