Carborane Functionalization

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Palladium-Catalyzed Regioselective Diarylation of *o*-Carboranes By Direct Cage B–H Activation

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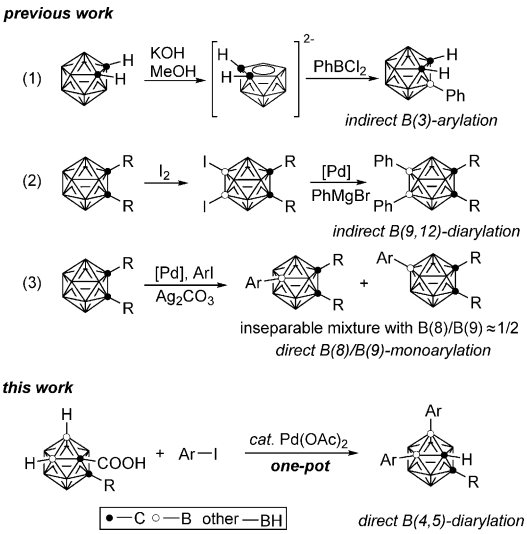
Abstract: *Palladium-catalyzed intermolecular coupling of o-carborane with aromatics by direct cage B–H bond activation has been achieved, leading to the synthesis of a series of cage B(4,5)-diarylated-o-carboranes in high yields with excellent regioselectivity. Traceless directing group -COOH plays a crucial role for site- and di-selectivity of such intermolecular coupling reaction. A Pd^{II}–Pd^{IV}–Pd^{II} catalytic cycle is proposed to be responsible for the stepwise arylation.*

Carboranes are a class of boron hydride clusters in which one or more of the BH vertices are replaced by CH units, which can be viewed as three-dimensional relatives of benzene.[1] They are finding many applications in medicine as boron neutron capture therapy agents,[2] in supramolecular design as building blocks,[3] and in coordination/organometallic chemistry as versatile ligands.[4] As a class of electronically useful molecules, carboranes have recently been incorporated into π-conjugated systems for applications in light-emitting materials.[5] This report focuses on cage carbon arylated carboranes, 1-aryl-*o*-carboranes, and 1,2-diaryl-*o*-carboranes. They are generally prepared from the condensation reaction of decarborane with the corresponding aryl or diaryl acetylenes,[6] or more recently by a nickel-catalyzed cross-coupling of 1-MgCl-*o*-carborane or 1,2-$(MgCl)_2$-*o*-carborane with aryl iodides.[7] For cage boron arylated *o*-carboranes, indirect methods are often used.[8] For example, capitation reaction of *nido*-$C_2B_9H_{11}^{2-}$ with $PhBCl_2$ gives 3-Ph-*o*-carborane,[9] or Pd^0-catalyzed cross-coupling reaction of 9,12-I_2-*o*-carborane with PhMgBr affords 9,12-Ph_2-*o*-carborane, in which the installation of iodo groups into the specific boron positions is required (Scheme 1).[10] However, selective iodination of cage B(4,5,7,11)–H bonds is rather challenging, if not impossible.[1,8]

We have recently disclosed Pd^0 or Ni^0-catalyzed intramolecular coupling of *o*-carborane with aromatics by direct cage B–H activation, selectively generating cage B(3)-, B(4)-, or B(7)-monoarylated *o*-carboranes.[11] A Pd-catalyzed monoarylation of *o*-carborane with aryl iodides was very recently reported, yielding an inseparable mixture of cage B(8)/B(9)-aryl-*o*-carboranes with a ratio of about 1:2.[12] In view of recent work on transition metal-catalyzed, carboxylic acid directed cage B–H alkenylation of *o*-carboranes,[13] catalytic cage B–H functionalization of *o*-carboranes,[14] and transition metal catalyzed cross-coupling of aryls by benzene C–H activation,[15] we wondered whether regioselective coupling of *o*-carborane with aryl halides could be achieved by cage B–H activation. Herein, we report a Pd-catalyzed regioselective and direct cage-(4,5) boron diarylation of *o*-carboranes by intermolecular cross-coupling of *o*-carborane with aryl iodides (Scheme 1).



Scheme 1. Synthesis of aryl-substituted *o*-carboranes.

We initiated our study by screening for a suitable amount of acetic acid for intermolecular cross-coupling of 1-COOH-2-CH_3-*o*-$C_2B_{10}H_{10}$ (**1a**) with iodobenzene in the presence of 10 mol% $Pd(OAc)_2$ and 3 equiv of AgOAc in toluene. In the absence of any additive, no reaction proceeded at 100 °C after 12 h (entry 1, Table 1). However, addition of 5 equiv of AcOH to the reaction mixture could effectively promote the reaction to give the corresponding cross-coupling products 2-CH_3-4,5-Ph_2-*o*-$C_2B_{10}H_9$ (**3a**) and 2-CH_3-4-Ph-*o*-$C_2B_{10}H_{10}$ (**4a**) in 40% and 30% GC yields, respectively (entry 2, Table 1). Lowering the reaction temperature resulted in higher molar ratios of **3a**/**4a**, probably owing to the decarboxylation of 1-COOH-2-CH_3-4-Ph-*o*-carborane at higher temperatures (see below, entries 2–6, Table 1). Increasing the amount of AcOH to 10 equiv, or decreasing it to 2 equiv, led to lower reaction efficiency (entries 7 and 8, Table 1). Lower catalyst loading (5 mol%) gave a decreased yield of **3a** (entry 9, Table 1). In view of the reaction efficiency and molar ratio of **3a**/**4a**, entry 5 (Table 1) was chosen as the optimal reaction condition.

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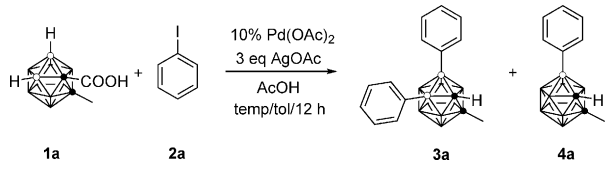
Table 1: Optimization of reaction conditions.[a]

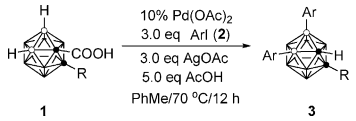


1a 2a 3a 4a

entry	AcOH (equiv)	Temp (°C)	**3a**/**4a** (%)[b]
1	–	100	–
2	5	100	40/30
3	5	90	70/15
4	5	80	85/8
5	5	70	91/5
6	5	60	80/2
7	2	70	82/10
8	10	70	85/3
9[c]	5	70	80/5

[a] Reactions were conducted on 0.05 mmol scale in 0.5 mL of toluene in a closed flask. [b] GC yields. [c] 5 mol% of $Pd(OAc)_2$ was used.

Table 2: Synthesis of cage B(4,5)-diarylated *o*-carboranes.[a]



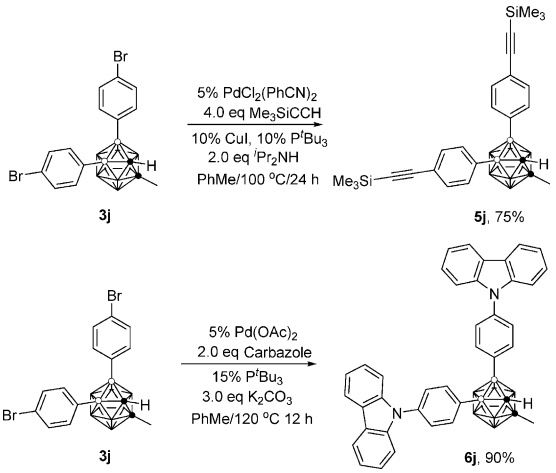
1 3

entry	R	Ar	Isolated Yield (%)
1	Me	Ph	73 (**3a**)
2	Me	4-$CH_3C_6H_4$	76 (**3b**)
3	Me	3-$CH_3C_6H_4$	72 (**3c**)
4	Me	2-$CH_3C_6H_4$	–
5	Me	3,5-$(CH_3)_2C_6H_3$	75 (**3e**)
6	Me	4-*t*BuC_6H_4	75 (**3f**)
7	Me	4-PhC_6H_4	82 (**3g**)
8	Me	4-ClC_6H_4	67 (**3h**)
9	Me	3-ClC_6H_4	64 (**3i**)
10	Me	4-BrC_6H_4	65 (**3j**)
11	Me	3-BrC_6H_4	60 (**3k**)
12	Me	4-FC_6H_4	66 (**3l**)
13	Me	4-MeOC_6H_4	65 (**3m**)
14	Me	3-$CH_3CO_2C_6H_4$	52 (**3n**)
15	Me	4-$CH_3COC_6H_4$	50 (**3o**)
16	Me	2-naphthalyl	71 (**3p**)
17	Ph	Ph	55 (**3q**)
18	CH_2Ph	Ph	78 (**3r**)
19	H	Ph	41 (**3s**)
20	Me_3Si	Ph	9 (**3t**) + 69 (**3s**)[b]

[a] Reactions were conducted at 0.2 mmol scale in a sealed flask.
[b] Me_3Si was removed after work up.

A variety of aryl iodides were examined under the chosen reaction conditions (Table 2). Electron-donating groups on the phenyl ring generally offered higher yields of **3** than did electron-withdrawing substituents (entries 2–3 and 5–6 vs 8–12, Table 2). Sterically hindered 2-methyl iodobenzene did not give desired product (entry 4, Table 2). On the other hand, 2-iodonaphthalene afforded **3p** in 71% isolated yield (entry 16, Table 2). Notably, this reaction was tolerant of many functional groups, such as -OMe, -COMe, and $-CO_2Me$, though the desired products **3m**, **3n**, and **3o** were isolated in relatively lower yields, probably owing to the interactions of the heteroatom with the metal center (entries 13–15, Table 2). Furthermore, this reaction was well compatible with fluoro, chloro, and bromo groups, which could be utilized for further synthetic elaborations (entries 8–12, Table 2). The effects of substituents R of the second cage carbon atom on the reaction results were also examined. For R = Ph and CH_2Ph, products **3q** and **3r** were obtained in 55% and 78% isolated yields (entries 17 and 18), whereas 1-COOH-*o*-$C_2B_{10}H_{11}$ afforded the corresponding compound **3s** in 41% yield (entry 19, Table 2). When R = Me_3Si, the expected product **3t** was isolated in 9% yield together with the desilylation species **3s** in 69% isolated yield (entry 20, Table 2).

Compound **3j** can be further functionalized through its C–Br bonds (Scheme 2). Sonogashira coupling of **3j** with



Scheme 2. Transformations of **3j**.

$Me_3SiC{\equiv}CH$ generated **5j** in 75% isolated yield. The coupling reaction of **3j** with carbazole also afforded the corresponding product **6j** in 90% isolated yield, which offers a new route to cage B-substituted carborane-based host materials for possible application in light-emitting diodes.[5a,b]

Compounds **3**, **5j**, and **6j** were fully characterized by ^1H, ^{13}C, and ^{11}B NMR spectroscopy, as well as high-resolution mass spectrometry. The molecular structures of **3a**, **3b**, and **3q** were further confirmed by single-crystal X-ray analyses. Figure 1 shows the representative structures of **3a** and **3q**.

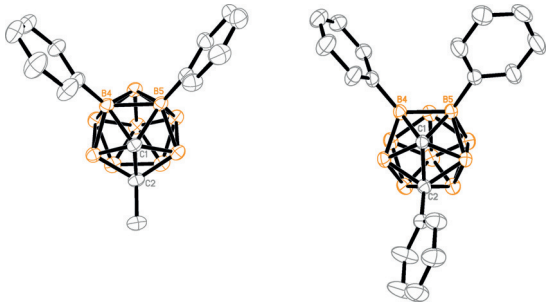
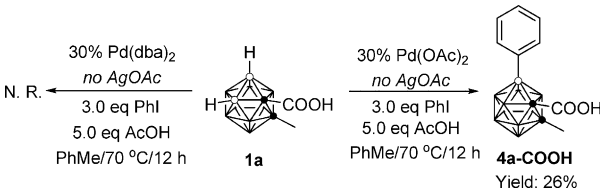


Figure 1. Molecular structures of **3a** (left) and **3q** (right).

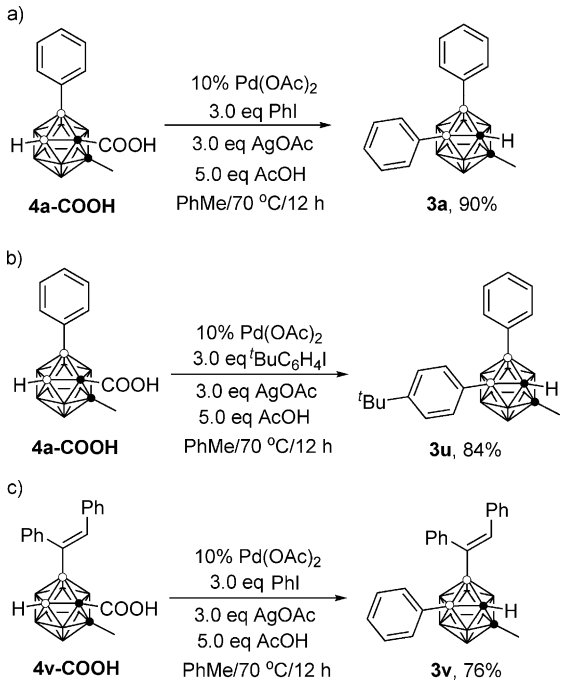
Mechanistically, either a Pd^0–Pd^{II}—Pd^0 or Pd^{II}–Pd^{IV}–Pd^{II} catalytic cycle might be responsible for this reaction. To distinguish between these two possibilities, the following control experiments were carried out. No reaction was observed if 1-COOH-2-CH_3-*o*-$C_2B_{10}H_{10}$ (**1a**) was treated with 3 equiv of iodobenzene in the presence of 30 mol% $Pd(dba)_2$ (dba = dibenzylideneacetone) in toluene at 70 °C for 12 h in the absence of AgOAc (Scheme 3). On the other hand,



Scheme 3. Control experiments.

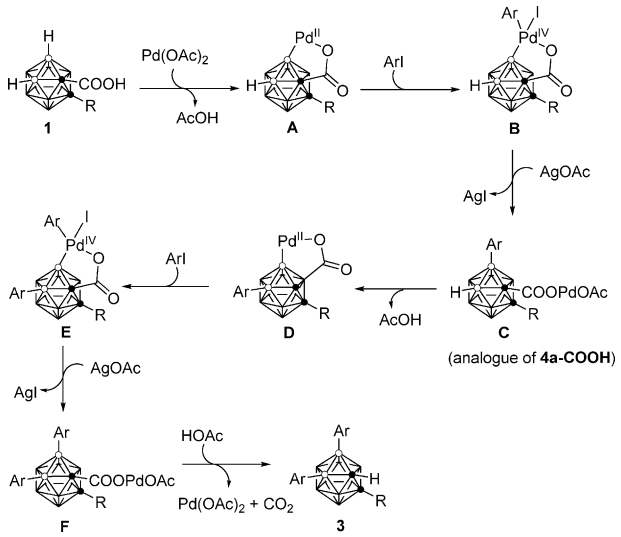
under the same reaction conditions, replacement of $Pd(dba)_2$ with $Pd(OAc)_2$ gave the monoarylation product 1-COOH-2-CH_3-4-Ph-1,2-$C_2B_{10}H_9$ (**4a**-COOH) in 26% isolated yield (Scheme 3). These results suggest that Pd^0 cannot initiate such cross-coupling reactions, while Pd^{II} does promote cage B–H activation/arylation reactions. However, in the absence of AgOAc, Pd^{II} cannot catalyze such reaction.

Furthermore, treatment of **4a**-COOH with 3 equiv of PhI under optimal reaction conditions gave **3a** in 90% GC yield (Scheme 4a). Similarly, reaction of **4a**-COOH with 3 equiv of 4-*t*BuC_6H_4I generated unsymmetrical 2-Me-4-Ph-5-(*p*-*t*BuC_6H_4)-1,2-$C_2B_{10}H_9$ (**3u**) in 84% isolated yield (Scheme 4b). When **4v**-COOH was used as reagent, unsymmetrical 2-Me-4-[*cis*-(Ph)CH=C(Ph)]-5-Ph-1,2-$C_2B_{10}H_9$ (**3v**) was isolated in 76% yield (Scheme 4c). These results imply that AgOAc is essential to realize the catalytic cycle, and decarboxylation proceeds after the installation of the second aryl group on the cage B(5) position.



Scheme 4. Stepwise cage B–H functionalization.

Based on these data, a Pd^{II}–Pd^{IV}–Pd^{II} catalytic cycle is proposed (Scheme 5). Exchange reaction of **1** with $Pd(OAc)_2$



Scheme 5. Proposed catalytic cycle.

followed by regioselective electrophilic attack at the more electron-rich cage B(4) site[13] yields the intermediate **A** as the charge distribution on the cage follows the trend B(9,12) > B(8,10) > B(4,5,7,11) > B(3,6).[16] Oxidative addition of ArI affords a Pd^{IV} intermediate **B**.[17] Reductive elimination and salt metathesis reactions produce the cage B(4)-arylated palladium(II) carboxylate **C**, an analogue of **4a**-COOH. Further regioselective electrophilic attack at the cage B(5) site generates the intermediate **D**, which undergoes a similar tandem sequence of oxidative addition, reductive elimination, and salt metathesis to generate cage B(4,5)-diarylated Pd^{II} carboxylate **F**. Protonation and decarboxylation give the final product **3** and regenerate the catalyst $Pd(OAc)_2$.

In summary, a regioselective and efficient Pd^{II}-catalyzed diarylation of cage B(4,5)-H bonds in *o*-carboranes by direct B–H activation has been achieved with the help of a traceless directing group -COOH. This serves as a methodology for transition metal catalyzed, intermolecular cross-coupling of carborane with aromatics, leading to the preparation of a series of B(4,5) diarylated-*o*-carborane derivatives for possible application in materials science.[18] This work can also offer useful references for selective aromatic C–H activation/functionalization in organic synthesis.

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