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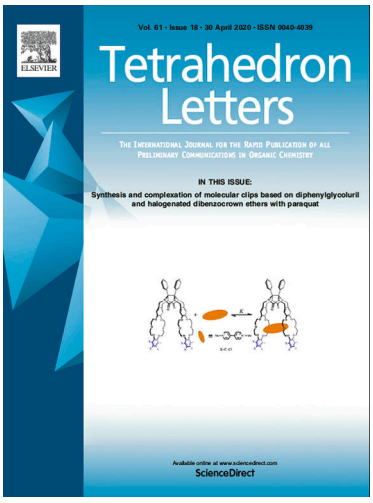

Phosphine Oxide-Directed Palladium-Catalyzed B(3)–H Arylation of o-Carboranes

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Graphical Abstract

Phosphine Oxide-Directed Palladium-Catalyzed B(3)–H Arylation of *o*-Carboranes

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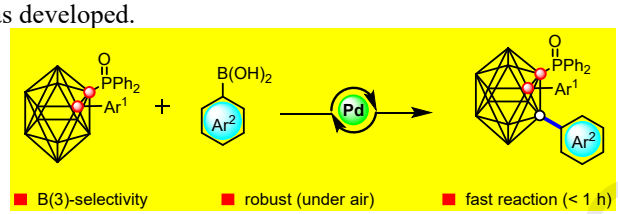
Lingxiang Lian, Caixiang Lin*, Yi Yu, Yaofeng Yuan and Ke-Yin Ye*

A highly selective, robust and efficient phosphine oxide-directed palladium-catalyzed B(3)–H arylation of *o*-carborane with a variety of arylboronic aicds was developed.



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Phosphine Oxide-Directed Palladium-Catalyzed B(3)–H Arylation of *o*-Carboranes

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ABSTRACT

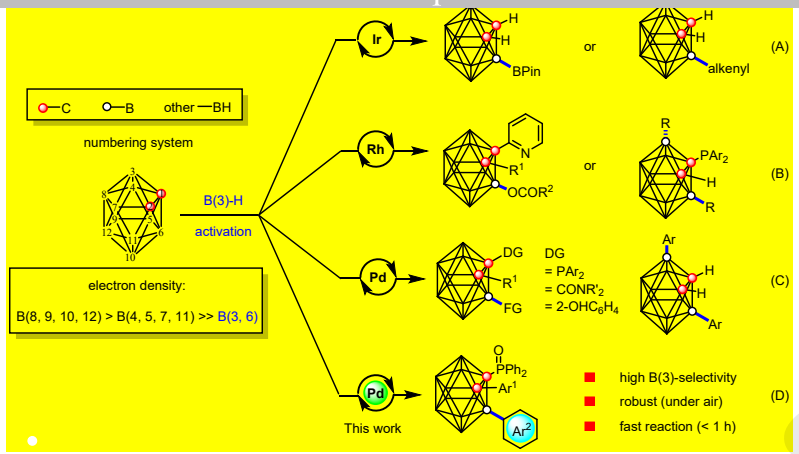
The selective functionalization of carboranes has received increasing research interests due to their wild applications in chemistry, life, and material sciences. Among various structurally diverse carboranes, the development of selective functionalization of the commercially available *o*-carborane (1,2-$C_2B_{10}H_{12}$) has largely focused on the two acidic C–H bonds. By contrast, research on the activation of the other ten hydridic cage B–H vertices is relatively less explored. Of particularly challenging, the most electron-deficient nature of B(3,6)-H bonds render very few synthetic methods available for their functionalization. Herein, we develop a phosphine oxide-directed palladium-catalyzed highly B(3)–H selective arylation of *o*-carboranes under very mild reaction conditions in short reaction time.

Introduction

Carboranes, featured as a class of σ-aromatic boron hydride clusters mixed with one or more CH unit(s), have received much attention of chemists[1] due to their wild applications in coordination chemistry,[2] material sciences,[3] and arguably most prominent in medicinal chemistry as boron neutron capture therapy agents or pharmacophores.[4] The functionalization of carboranes, therefore, is a very significant research topic to construct novel carborane-containing scaffolds for diverse applications.[5] Among them, the functionalization of the commercially available, most extensively investigated *o*-carborane (1,2-$C_2B_{10}H_{12}$) has largely focused on the weakly acidic C—H bonds.[6] By contrast, the selective functionalization of the other ten similar B—H bonds of *o*-carboranes are very challenging and thus much less developed.[7,8]

Typically, the reactivity of ten hydridic cage B—H vertices of *o*-carborane towards electrophilic substitution are mainly limited by their relative electron density, therefore, the B(3,6)—H bonds are not prone to such an electrophilic transformation as they fall into the most electron-deficient subunits (Scheme 1).[9] Therefore, the indirect methods via capitation reaction of dicarbollides with boron halides are historically dominant in the preparation of the B(3)–functionalized *o*-carboranes.[10] Along with the development of stoichiometric protocols,[11] transition-metal catalyzed cage B(3,6)—H derivatization have been developed recently. However, these methods generally suffered from harsh reaction conditions including high temperature and/or long reaction time. For instance, iridium has been shown to be capable to catalyze the B(3)-propenylation by Sneddon at 100 °C for 48 h (Scheme 1A). [12] Notably, Xie and co-workers have developed an elegant iridium-catalyzed selective cage B(3,6)-functionalization including the monoborylation/diborylation,[13] and monoalkenylation/dialkenylation of *o*-carboranes.[14] Unlike iridium, the rhodium-catalyzed highly selective B(3,6)-functionalization only proceeded in the presence of an appropriate directing group. While *o*-carboranes tethered a pyridine has been demonstrated by Yan and co-workers to undergo a facile B(3)-acyloxylation,[15] Che, Yu and their co-worker employed the monophosphino-*o*-carboranes in their B(3,6)-diarylation and dialkylation reactions (Scheme 1B).[16] Moreover, the directed[17] and undirected[18] palladium catalyzed B(3)-functionalization of *o*-carboranes have also been reported recently (Scheme 1C). Despite these impressive advances, the development of a highly selective, catalytic B(3)-functionalization under mild reaction conditions is still challenging yet demanding.

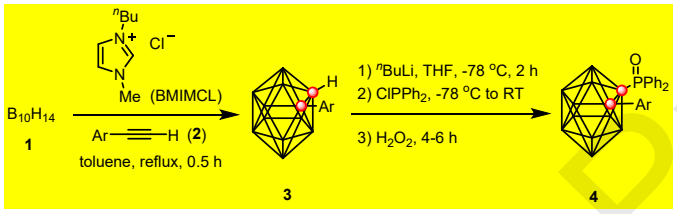
Phosphine oxides are easy to prepare, air and moisture stable moieties, which have been demonstrated to be very competent directing groups in the diverse transition-metal-catalyzed C—H activation.[19] Herein, we demonstrate the phosphine oxide could be introduced as a readily available and efficient directing group in the palladium-catalyzed highly selective B(3)—H arylation of *o*-carboranes with arylboronic acids under very mild reaction conditions (Scheme 1D). Using hydrogen peroxide (H_2O_2) as the oxidant, a wild array of the B(3)-arylated *o*-carboranes could be readily obtained in short reaction time. The robustness of this protocol was further substantiated by the high reaction efficiency even when reactions were run under air.



Scheme 1 Transition-metal-catalyzed B(3)-functionalization of *o*-carboranes.

Results and Discussion

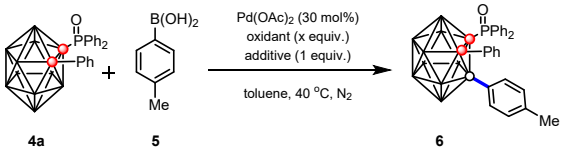
Our phosphine oxide-tethered *o*-carboranes could be conveniently prepared following the reported synthetic procedures (Scheme 2). The dehydrogenative alkyne-insertion products **3** of decarborane were easily synthesized according to Sneddon's protocol using biphasic ionic-liquid/toluene mixtures.[20] The sequential lithiation-phosphinylation-oxidation then delivered the anticipated functionalized *o*-carboranes **4** tethered with a desired phosphine oxide directing group.[21]



Scheme 2 Synthetic route towards the phosphine oxide-tethered *o*-carboranes.

With the diphenylphosphine oxide *o*-carboranes in hand, we then began to evaluate the palladium-catalyzed direct B—H arylation reaction (**Table 1**). Initial trial of the phosphine oxide-directed palladium-catalyzed cross-coupling reaction between **4a** and *p*-tolylboronic acid **5** [reaction conditions: 30 mol% of $Pd(OAc)_2$ as catalyst, 2 equiv. of $Cu(OAc)_2$ as oxidant, 1 equiv. of HOAc as additive in toluene at 40 °C, 24 h] afforded the desired B(3)-arylated *o*-carborane **6** in 15% yield (entry 1). X-ray diffraction analysis of the arylated product **6** (CCDC number: 1924703) unambiguously confirmed the B(3)—H bond being site-selectively functionalized (Figure 1). We then found the replacement of HOAc by TFA as the additive afforded a slightly higher yield (entry 2). Screening of various inorganic oxidants (entries 3-5) revealed that the aqueous hydrogen peroxide (H_2O_2) turned out to be the optimal oxidant giving the arylated product **6** in 50% yield. Notably, the adoption of 4 equiv. of both the *p*-tolylboronic acid **5** and hydrogen peroxide could promote the reaction yield to 84% in less than 1 h (entry 6). The robustness of this reaction further allowed the decreasing the catalyst loading as low as to 10 mol% and running under air without affecting the reaction efficiency (entries 7, 8).

Table 1. Reaction condition optimization.[a]



4a 5 6

entry	oxidant	X (equiv.)	additive	time (h)	yield[b] (%)
1	$Cu(OAc)_2$	2	HOAc	24	15
2	$Cu(OAc)_2$	2	TFA	24	25
3	AgOAc	2	TFA	24	5
4	$K_2S_2O_8$	2	TFA	24	40
5	H_2O_2	2	TFA	24	50
6[c]	H_2O_2	4	TFA	24	84
7[c,d]	H_2O_2	4	TFA	0.5	83
8[c,d,e]	**H_2O_2**	**4**	**TFA**	**0.5**	**85 (78)[f]**

[a] 0.05 mmol of **4a**, 0.1 mmol of **5**, 30 mol% of $Pd(OAc)_2$, 1 equiv. of additive, 2 equiv. of oxidant, and 1 mL of solvent for 24 h under an argon atmosphere.
[b] ^{31}P NMR yield.
[c] 4 equiv. of **5** and 4 equiv. of H_2O_2.
[d] 10 mol% of $Pd(OAc)_2$.
[e] Reaction under air.
[f] Isolated yield.

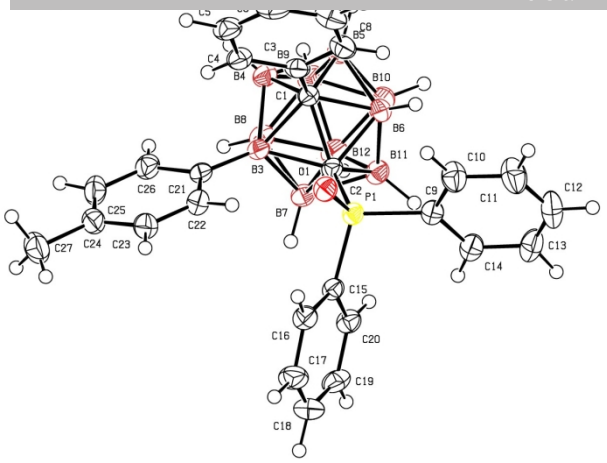
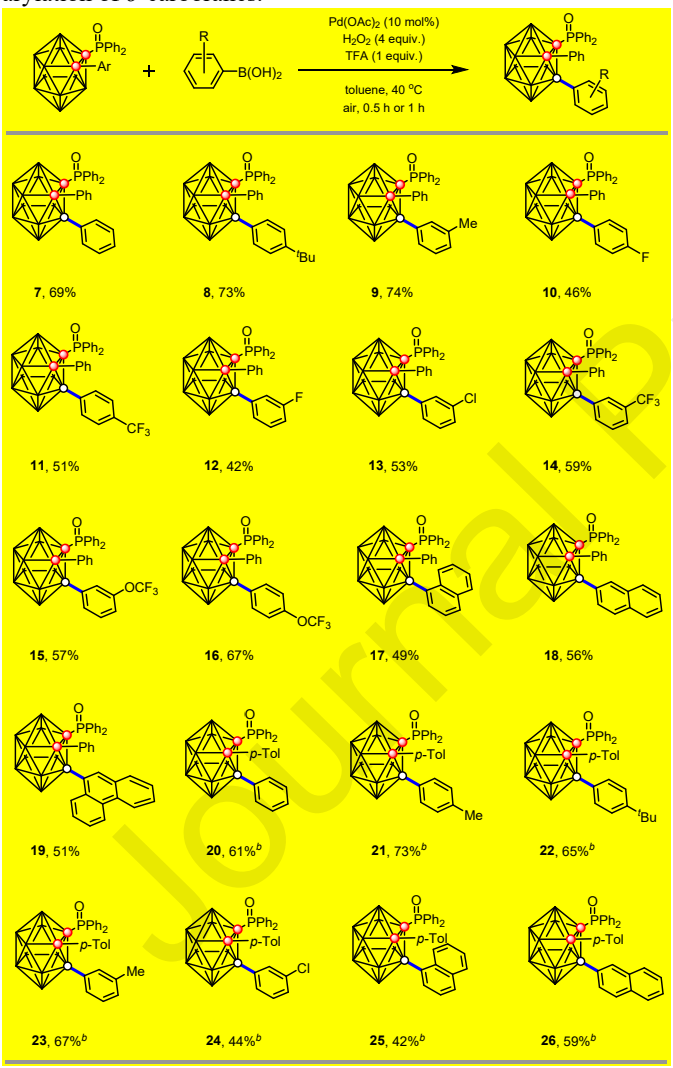


Figure 1. X-ray diffraction analysis of B(3)-arylated *o*-carborane **6**.

Table 2 Substrate scope of the palladium-catalyzed B(3)-arylation of *o*-carboranes.[a]



[a] 0.05 mmol of *o*-carborane, 0.2 mmol of boronic acid, 10 mol% of $Pd(OAc)_2$, 1 equiv. of TFA, 4 equiv. of H_2O_2, and 1 mL of solvent for 0.5 h or 1 h under air.

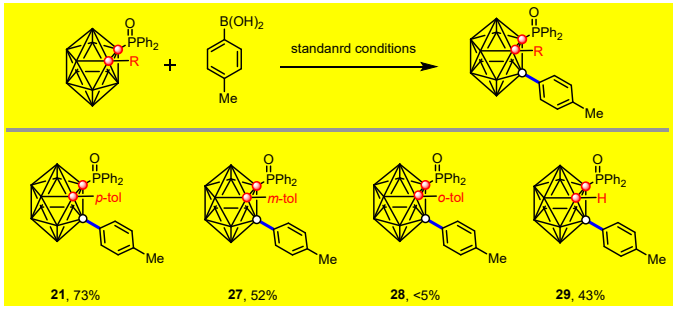
[b] 0.65 mmol scale reaction.

The scope and limitation of this highly selective B(3)-H arylation of *o*-carboranes were then further evaluated (**Table 2**). Specifically, phenyl and arylboronic acid derivatives bearing electron-donating groups (4-Me, 4-^{t}Bu, 3-Me) were generally well tolerated under current reaction conditions to afford the desired arylation products in good yields (**6-9**, 69-78%). On the contrary, the reactions with arylboronic acid derivatives bearing

ill proceeded smoothly albeit with slightly lower yields (**10-14**, 42-59%). It is noteworthy the trifluoromethoxy substituted arylboronic acids were also well survived (**15** and **16**). Other fused aromatic moieties including 1-naphthalene (**17**), 2-naphthalene (**18**), and 1-phenanthrene (**19**) could also be efficiently incorporated into the *o*-carborane scaffold by using their corresponding boronic acids. Following the preparative procedure shown in Scheme 2, a diverse array of phosphine oxide-tethered *o*-carboranes could be potentially assembled from readily available starting materials. To demonstrate such a modularity, we synthesized *p*-tolyl substituted phosphine oxide-tethered *o*-carboranes, which could also be well applied in current B(3)-arylation protocol even in preparative scale (**20-26**). However, boronic acids bearing potentially competing coordination site versus phosphine oxide such as pyridine, indole, tetrahydrothiophene *etc*. were not reactive under current reaction setting (see *Supplementary Material* for more details).

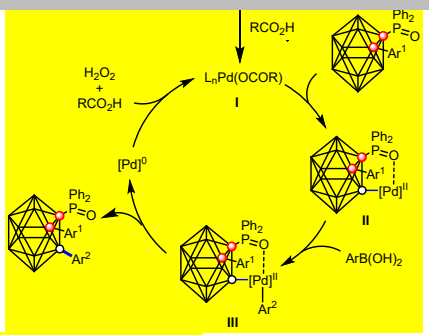
It is important to note that all the reactions were run under very mild reaction conditions. For instance, the robustness nature of current protocol even allowed the reaction proceeding smoothly when open to air. Additionally, the high reaction efficiency of this arylation reaction further rendered most of the reactions to complete within 1 hour. On the contrary to the generally requisite harsh conditions of methods developed in literature, i.e., high temperature (> 100 °C) and long reaction time (>24 h), our method should find broad applications in the diverse functionalization of *o*-carboranes.

Interestingly, it was found that the steric hindrance of aryl substituents vicinal to the phosphine oxide profoundly correlates to the observed reactivity (Scheme 3). While substrate with a *p*-tolyl underwent the cross-coupling reaction smoothly (**21**), the yield of that with a *m*-tolyl substituent decreased to 52% (**27**). Further increasing the steric influence by using a *o*-tolyl substituted carborane, however, led to no desired reactivity but only the recovery of starting material (**28**). Interestingly, the aryl substitution vicinal to the phosphine oxide could also be replaced by a hydrogen atom albeit a slightly lower yield of B(3)-coupling product was obtained (**29**).



Scheme 3 Impact of substituents vicinal to the phosphine oxide on the reactivity.

Based on the experimental observation and literature precedence, a plausible mechanism is proposed (Scheme 4). A ligand exchange event is likely to be involved before the CMD step of the B(3)—H bond. The use of phosphine oxide as the directing group brings the palladium catalyst (**I**) close to carborane moiety and thus determines the putative site selectivity of B—H bond cleavage (**II**). Followed by transmetalation of arylboronic acid and reductive elimination (**III**), the desired B(3)-arylation of *o*-carborane could be readily obtained. The catalytically competent palladium species is then regenerated via an additional oxidation of the resulting Pd(0) in the presence of H_2O_2.



Scheme 4 Proposed mechanism.

In summary, we have developed a phosphine oxide-directed highly regioselective palladium-catalyzed B(3)-arylation of *o*-carboranes with a multitude of arylboronic acids. The mild reaction conditions, short reaction time, and well functional tolerance should render this protocol appealing in the preparation of a diverse array of functionalized *o*-carboranes. The detailed mechanistic investigation as well as the palladium-catalyzed asymmetric functionalization of *o*-carboranes[22] are currently undergoing in our lab.

Acknowledgments

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Supplementary Material

Supplementary data to this article can be found at *https://www.journals.elsevier.com/tetrahedron-letters*.

Crystallographic data (excluding structure factors) for the structure in this paper (compound **6**) have been deposited with the Cambridge Crystallographic Data Centre (CCDC number: 1924703).

Highlights

• P[illegible] arylation of *o*-carboranes.

• Phosphine oxide as the efficient site-selective directing group.

• The reaction is fast, generally less than one hour.

Graphical Abstract

Phosphine Oxide-Directed Palladium-Catalyzed B(3)–H Arylation of *o*-Carboranes

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Lingxiang Lian, Caixiang Lin*, Yi Yu, Yaofeng Yuan and Ke-Yin Ye*

A highly selective, robust and efficient phosphine oxide-directed palladium-catalyzed B(3)–H arylation of *o*-carborane with a variety of arylboronic aicds was developed.