ChemPubSoc Europe
DOI: 10.1002/chem.201603967
CHEMISTRY
A European Journal
Communication

Cross-Coupling

Palladium-Catalyzed Direct Cross-Coupling of Carboranyllithium with (Hetero)Aryl Halides

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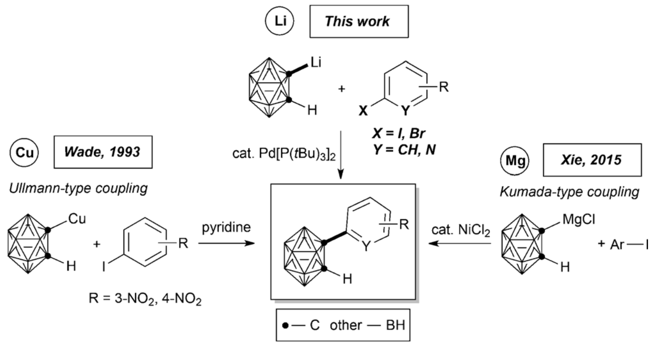
Abstract: A palladium-catalyzed direct C-arylation reaction of readily available cage carboranyllithium reagents with aryl halides has been developed for the first time. This method is applicable to a wide range of aryl halide substrates including aryl iodides, aryl bromides, and heteroaromatic halides.

Owing to the unique physical and chemical properties, *o*-carboranes are finding many applications in materials science as building blocks,[1] in medicinal chemistry as boron neutron capture therapy agents,[2] and in coordination chemistry as ligands.[3] Recently, a growing interest has been directed toward the synthesis of aryl-*o*-carboranes for their potential applications in luminescent materials[4] and phosphorescent probes.[2d,5] In general, arylated *o*-carboranes are prepared through the condensation reaction of aryl acetylenes with decaborane.[6] However, the hypertoxicity of decaborane complicates this methodology. It is therefore highly desirable to develop an efficient synthetic method for the direct C-arylation of *o*-carboranes. Obviously, a direct cross-coupling of carboranyl organometallic reagents and aryl halides is an attractive strategy (Scheme 1). This approach has been successfully implemented in Cu-mediated Ullmann-type coupling reactions in a number of pioneering examples.[7,8] Wade et al. reported a C-arylation reaction of carboranylcopper(I) derivatives with aryl iodides.[7] The strategy of using a C-copper derivative of *o*-carborane has also been employed by Endo et al. for the synthesis of 1-(*o*-carboranyl)naphthalene.[8] For these protocols, an additional transformation step must be added to the synthetic sequence for preparing the carboranylcopper(I) reagents, frequently starting from the corresponding carboranyllithium reagents. Moreover, stoichiometric amounts of copper salts and an activating group (such as a nitro group) are required. Very recently, using carboranylmagnesium reagents as nucleophilic partners, Xie and co-workers developed a direct Ni-catalyzed C-arylation by Kumada-type coupling of aryl iodides.[9] However, the direct cross-coupling of carboranyllithium reagents with aryl halides still represents a very challenging project, despite extensive research on the reactions with alkyl halides.[10] Here, we report the first transition-metal-catalyzed direct C-arylation of carboranyllithium for the synthesis of aryl-*o*-carboranes. With palladium complexes as catalyst, the cross-coupling of carboranyllithium and (hetero)aryl halides proceeds readily to provide the corresponding (hetero)arylated *o*-carborane derivatives in good yields.



Scheme 1. Direct C-arylation of carboranyl organometallic reagents.

Carboranyllithium reagents, directly accessible by metalation of the cage C−H bonds, have witnessed rapid development in the past two decades.[11] We chose cross-coupling of carboranyllithium ($1\text{-Li-}1,2\text{-}C_2B_{10}H_{11}$) with 4-iodotoluene **2a** as the model reaction for optimization. The $1\text{-Li-}1,2\text{-}C_2B_{10}H_{11}$ was conveniently prepared in situ from an equimolar reaction of *o*-carborane ($1,2\text{-}C_2B_{10}H_{12}$, **1**) with *n*-butyllithium (*n*BuLi) in THF. Inspired by the transition-metal-catalyzed cross-coupling of organolithium reagents with aryl halides,[12] we initially used P(*t*Bu)$_3$ as the ligand and toluene as the solvent because these conditions may suppress undesirable side reactions such as lithium–halogen exchange and homo-coupling reactions. $Pd_2(dba)_3$ (dba = dibenzylideneacetone) was used as the catalyst according to the previous work.[12a] Unfortunately, the yield of the desired product **3a** was very low (Table 1, entry 1). Screening different palladium complexes, we found that the use of $Pd(acac)_2$ (acac = acetylacetonate) did not significantly improve the reaction (entry 2), but we were delighted to find that $PdCl_2$, $Pd(OAc)_2$ and Pd[P(*t*Bu)$_3$]$_2$ provided moderate yields (entries 3–5). To enhance reactivity, we examined in situ prepared

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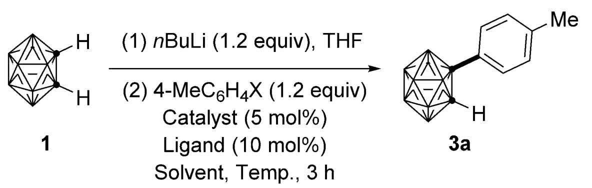
Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.201603967.

Table 1. Optimization of reaction conditions.[a,b]



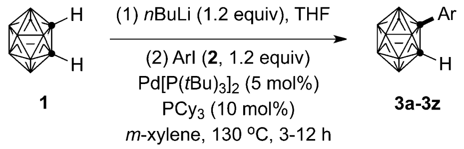
Entry	X	Catalyst (5 mol %)	Ligand (10 mol %)	Temp. [°C]	Yield [%]
1	I	$Pd_2(dba)_3$	$P(tBu)_3$	100	29
2	I	$Pd(acac)_2$	$P(tBu)_3$	100	24
3	I	$PdCl_2$	$P(tBu)_3$	100	49
4	I	$Pd(OAc)_2$	$P(tBu)_3$	100	56
5	I	$Pd[P(tBu)_3]_2$	$P(tBu)_3$	100	63
6	I	$Pd[P(tBu)_3]_2$	PCy_3	100	77
7	I	$Pd[P(tBu)_3]_2$	JohnPhos	100	44
8	I	$Pd[P(tBu)_3]_2$	XPhos	100	62
9	I	$Pd[P(tBu)_3]_2$	DavePhos	100	63
10	I	$Pd[P(tBu)_3]_2$	BrettPhos	100	68
11	I	$Pd[P(tBu)_3]_2$	PPh_3	100	55
12	I	$Pd[P(tBu)_3]_2$	(*R*)-BINAP	100	52
13	I	$Pd[P(tBu)_3]_2$	XantPhos	100	67
14	I	$Pd[P(tBu)_3]_2$	–	100	61
15	I	$Pd[P(tBu)_3]_2$	PCy_3	80	50
16[c]	I	$Pd[P(tBu)_3]_2$	PCy_3	110	81
17[c]	I	$Pd[P(tBu)_3]_2$	PCy_3	120	83
18[c]	*I*	$Pd[P(tBu)_3]_2$	PCy_3	*130*	*91*
19[c]	Br	$Pd[P(tBu)_3]_2$	PCy_3	130	71
20[c]	Cl	$Pd[P(tBu)_3]_2$	PCy_3	130	15
21[c]	OTs	$Pd[P(tBu)_3]_2$	PCy_3	130	Trace
22[c]	OTf	$Pd[P(tBu)_3]_2$	PCy_3	130	Trace
23[c]	I	–	PCy_3	130	Trace

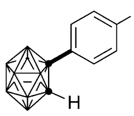
[a] Reaction conditions: 1,2-$C_2B_{10}H_{12}$ (0.25 mmol), *n*BuLi (0.3 mmol), THF (1 mL), at 0 °C for 1 h; 4-MeC_6H_4X (0.3 mmol), catalyst (0.0125 mmol), ligand (0.025 mmol), toluene (1 mL); [b] yield of isolated product; [c] *m*-xylene (1 mL) as solvent.

Pd catalysts from $Pd[P(tBu)_3]_2$ with various phosphine ligands for this C(cage)–C(sp^2) bond formation. Because sterically hindered trialkylphosphines are frequently used as attractive ligands in cross-coupling to enhance reductive elimination and avoid *beta*-hydrogen elimination,[12d] the ligand PCy_3 was also tested. The use of the in situ formed complex from $Pd[P(tBu)_3]_2$ and PCy_3 led to **3a** in 77% yield at 100 °C (entry 6). As dialkylbiaryl phosphine ligands have proved to be useful in effecting the cross-coupling with organometallic reagents,[12c] different dialkylbiaryl phosphines were screened. Utilizing JohnPhos as the ligand dramatically reduced the yield, implying that the nature of the phosphine ligand is a crucial parameter (entry 7). Other dialkylbiaryl phosphines besides JohnPhos, including XPhos, DavePhos, and BrettPhos, could also promote the reaction but gave lower yields (entries 8–10). Further optimization could not increase the yields when triaryl phosphine ligands were used (entries 11–13). When the commercially available preformed complex $Pd[P(tBu)_3]_2$ was used instead of the in situ formed catalyst, cross-coupled product **3a** was obtained only in modest yield, meaning that the use of ligands is essential for this reaction (entry 14). On the other hand, the reaction temperature also played an important role in this reaction. A dramatic drop in yield was observed when the temperature was changed from 100 to 80 °C (entry 15). High temperatures could facilitate the reaction using *m*-xylene as the solvent (entries 16–18), and the reaction conditions of entry 18 were identified as the optimal reaction conditions. An aryl bromide was also a good substrate (entry 19), but the present conditions were not effective for the coupling of an aryl chloride, tosylate, or triflate (entries 20–22). Finally, the reaction did not occur in the absence of catalyst (entry 23).

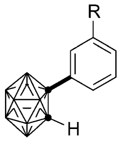
Under optimal conditions, we next examined the scope of the direct C-arylation reaction (Table 2). The cross-coupling of carboranyllithium reagent **1a** proceeded with a wide range of aryl iodides in good yields. The reaction can accommodate various functional groups, including halides (F and Cl), ethers, thioethers, trifluoromethyl, trifluoromethoxyl, and even benzyl-protected phenol groups. Both electron-donating (**3a**–**e** and **3j**–**l**) and electron-withdrawing (**3g**–**i** and **3m**–**o**) substituents were well-tolerated at either the *para* or *meta* positions of the

Table 2. Palladium-catalyzed cross-coupling of carboranyllithium with aryl iodides.[a,b]

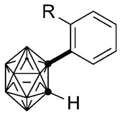




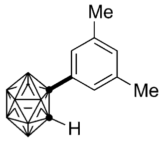
3a, R = Me, 91%
3b, R = OMe, 77%
3c, R = SMe, 49%
3d, R = *t*Bu, 87%
3e, R = OCF_3, 54%
3f, R = H, 85%
3g, R = Cl, 73%
3h, R = F, 67%
3i, R = CF_3, 50%



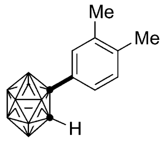
3j, R = Me, 69%
3k, R = OMe, 53%
3l, R = OCF_3, 50%
3m, R = Cl, 55%
3n, R = F, 63%
3o, R = CF_3, 54%



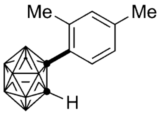
3p, R = Me, 66%
3q, R = OMe, 51%
3r, R = *i*Pr, 63%



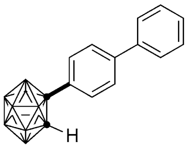
3s, 90%



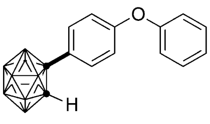
3t, 83%



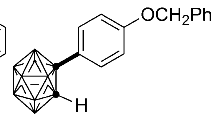
3u, 80%



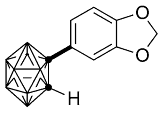
3v, 84%



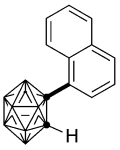
3w, 68%



3x, 80%



3y, 64%



3z, 77%

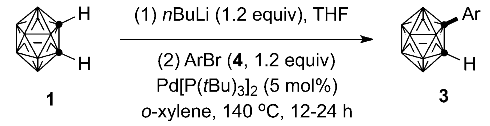
[a] Reactions were conducted at 0.25 mmol scale in 1 mL of *m*-xylene in a closed flask at 130 °C for 3–12 h; [b] yield of isolated product.

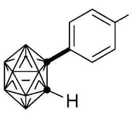
aryl iodides (49–91 % yield). The cross-coupling of *p*-MeO or *m*-MeO-substituted substrates, as reluctant coupling partners, proceeded well to afford the arylated products **3 b** and **3 k** in 77 and 53 % yields, respectively. A *para*-thioether substituent was also compatible with this protocol (**3 c**). As expected, with *p*-chloro-iodobenzene **2 g** or *m*-chloro-iodobenzene **2 m**, coupling reactions occurred exclusively at the iodine-substituted carbon, but with no detectable chloride displacement (**3 g** and **3 m**). Notably, the presence of MeO or Cl substituents in products (**3 b**, **3 g**, **3 k**, **3 m**, and **3 q**) allows for further functionalization of the aromatic ring. Fluorinated iodides also underwent clean coupling without any traces of side products (**3 h** and **3 n**). The electron-deficient 4-iodobenzotrifluoride **2 i** and 3-iodobenzotrifluoride **2 o** also underwent clean coupling with carboranyllithium, and the trifluoromethylated aryl-*o*-carborane scaffolds **3 i** and **3 o** were isolated in moderate yields. The use of trifluoromethoxyl-substituted aryl iodides led to reduced yields (**3 e** and **3 l**). A challenging problem in cross-coupling processes is the combination of carboranyllithium with sterically hindered coupling partners bearing large *ortho*-substituents. To our delight, the coupling with 2-iodotoluene **2 p** proceeded smoothly, and aryl-substituted product **3 p** was obtained in good yield. Remarkably, the highly hindered 2-iodoisopropylbenzene **2 r** could be coupled under these optimal conditions, affording the corresponding product **3 r** in 63 % yield. It is important to note that carboranylation of 4-iodo-1,1′-biphenyl to form **3 v** was achieved in high yield. The biaryl-*o*-carborane compound **3 v** is a precursor for a variety of carborane-based biphenyl derivates with application in optoelectronic materials.[4a,g–k] More importantly, 4-benzyloxy-iodobenzene **2 x** could be carboranylated (**3 x**) using the carboranyllithium reagent, despite the acidity of the benzylic protons. The reactions employing other electron-rich aryl iodides also proceeded in good yields (**3 s**–**u**, **3 w**, and **3 y**). The polyaromatic compound 1-iodonaphthalene **2 z** was regioselectively carboranylated at position 1 (**3 z**), indicating that the benzyne intermediate through 1,2-elimination was not formed. However, aryl iodides with electron-withdrawing substituents, such as NO_2, CN, $COOCH_3$, or COOH, are not suitable substrates because competing reaction pathways lead to the decomposition of the starting material under current conditions.

We next investigated whether the same strategy could be applied to aryl bromide substrates, which are versatile and widely used synthetic intermediates, although carboranylation of aryl bromides has only been studied by using carboranylmagnesium as nucleophilic reagent, giving one example in 50 % yield.[9] We were aware that direct cross-coupling of carboranyllithium with aryl bromides would pose an inevitable challenge: Aryl bromides are generally less reactive than iodides under these C-arylation conditions. The reactivity trend of organic halides is inversely proportional to their bond-dissociation energy, and C–Br bonds arguably possess shorter bond lengths than C–I bonds. With this consideration in mind, we further optimized the reaction conditions for the coupling of aryl bromides. Although an initial investigation with 4-bromotoluene (**4 a**) only provided 60 % yield of the desired product **3 a** under the optimal conditions for aryl iodides (Table S1, entry 1 in the Supporting Information), we found that by using 5 mol % commercially available $Pd[P(tBu)_3]_2$ as the catalyst and phosphine ligand-free conditions, the yield of aryl product **3 a** could be substantially improved to 90 % (Table S1, entry 6 in the Supporting Information). However, a variety of dialkylbiaryl phosphines proved inferior and led to diminished yields (Table S1, entries 7–10 in the Supporting Information).

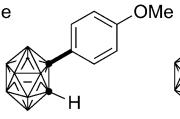
We then explored the scope of aryl bromides and carboranyllithium reagent under new conditions. As illustrated in Table 3, a wide range of aryl bromides with electron-donating, -neutral, or -withdrawing substituents were well tolerated (**3 a**, **3 b**, **3 f**, and **3 h**). Remarkably, highly deactivated dimethylamine- or morpholine-substituted aryl bromides **4 e** and **4 f** were also converted under the optimized reaction conditions to the desired products in excellent yields (**3 aa** and **3 ab**). Furthermore, the cross-coupling of the functionalized aryl bromide (4-bromophenyl)trimethylsilane **4 e** proceeded with good yield (**3 ac**). Moderate to good yields were achieved after conducting the reaction with polyaromatic compounds (**3 ad** and **3 z**). The use of sterically hindered *ortho*-substituted aryl bromides led to a reduced yield (**3 p**, 52 %).

Table 3. Palladium-catalyzed cross-coupling of carboranyllithium with aryl bromides.[a,b]

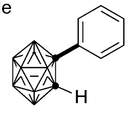




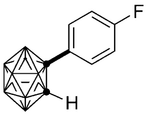
3a, 90%



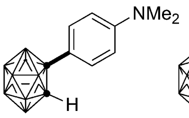
3b, 68%



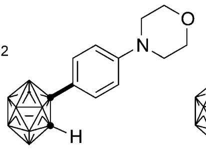
3f, 71%



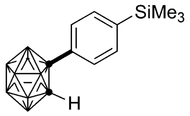
3h, 60%



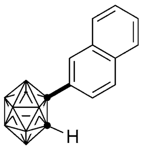
3aa, 83%



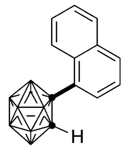
3ab, 84%



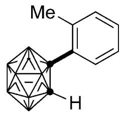
3ac, 64%



3ad, 76%



3z, 53%

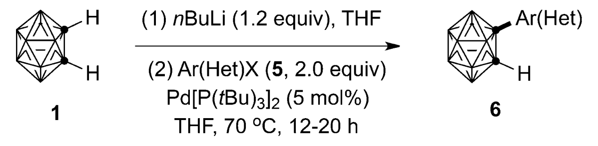


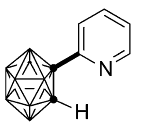
3p, 52%

[a] Reactions were conducted at 0.25 mmol scale in 1 mL of *o*-xylene in a closed flask at 140 °C for 12–24 h; [b] yield of isolated product.

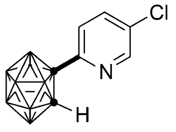
Finally, we examined whether this approach for C-arylation could be adapted to achieve C-heteroarylation, thereby providing a method for the synthesis of heteroarylated compounds (Table 4). In remarkable contrast to diheteroarylation of a carboranylcopper(I) reagent with 2-bromopyridine **5 a′**,[7] direct cross-coupling of carboranyllithium with 2-iodopyridine **5 a** proceeded smoothly to afford the monopyridyl product **6 a** in

Table 4. Palladium-catalyzed cross-coupling of carboranyllithium with heteroaromatic halides.[a,b]

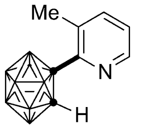




X = I, **6a**, 60%
X = Br, **6a**, 70%
X = Cl, **6a**, 21%



6b, 44%



6c, 50%

[a] Reactions were conducted at 0.25 mmol scale in 1 mL of THF in a closed flask at 70 °C for 12–20 h; [b] yield of isolated product.

good yield and with excellent selectivity at a decreased temperature (70 °C). Both electron-donating and electron-withdrawing substituents of the heterocyclic halide coupling partners were tolerated, and we were able to provide the C-heteroarylated products in moderate yields (**6b** and **6c**). Similarly, with 5-chloro-2-iodopyridine **5b**, cross-coupling occurred exclusively at the iodine-substituted carbon, with no detectable chloride displacement (**6b**). Remarkably, the sterically hindered 2-iodo-3-methylpyridine **5c** could be coupled under the standard conditions, affording the desired product **6c** in 50% yield. It is noteworthy that the use of less reactive 2-bromopyridine **5a′** led to an enhanced yield (**6a**, 70%). These experiments suggest that this reaction is compatible with heteroaromatic halides as coupling partners, overriding the strong coordination of heteroatoms to the metal catalyst. This feature renders the reaction particularly useful for the synthesis of biologically active compounds bearing icosahedral *o*-carboranes and heterocycles.

In conclusion, we have demonstrated the Pd-catalyzed direct cross-coupling of carboranyllithium with (hetero)aryl halides for the selective formation of C(cage)–C(sp^2) bonds, providing a new route for the preparation of (hetero)aryl-*o*-carboranes. This method does not involve transmetalation of the carboranyllithium reagent. As a consequence, we expect that this methodology will be rapidly adopted to prepare diverse (hetero)aryl-substituted *o*-carboranes for use in materials science, medicinal, and coordination chemistry. Additionally, this transformation is a valuable addition to the tool box for making icosahedral functionalized carboranes.

Experimental Section

General procedure for the Pd-catalyzed cross-coupling of carboranyllithium with aryl halides

In a dry Schlenk flask, *n*BuLi (1.6 M in *n*-hexane, 0.3 mmol, 0.18 mL) was added slowly to a THF solution (1 mL) of 1,2-$C_2B_{10}H_{12}$ (0.25 mmol, 36 mg) at 0 °C. The solution was kept at low temperature with stirring for 1 h, and was allowed to reach room temperature. Subsequently, Pd[P(*t*Bu)$_3$]$_2$ (5 mol%, 0.0125 mmol, 6.4 mg), PCy$_3$ (10 mol%, 0.025 mmol, 7.0 mg), *m*-xylene (1 mL), and the substrate aryl halides (0.3 mmol) were added under an inert nitrogen atmosphere, and the mixture was heated at 130 °C under stirring in a closed flask. After the reaction was completed, a saturated solution of aqueous NH$_4$Cl was added and the mixture was extracted three times with diethyl ether. The organic phases were collected, and solvent evaporation under reduced pressure afforded the crude product, which was then purified by column chromatography to remove the catalyst and ancillary ligand and provide the product, by using silica gel as stationary phase and *n*-hexane as eluent.

Acknowledgements

We thank the National Natural Science Foundation of China (21403163, 21327011, 21376146) and the Natural Science Basic Research Plan in Shaanxi Province of China (2014JQ2062) for financial support.

Keywords: C(cage)–C(sp^2) formation · carboranyllithium · cross-coupling · direct C-arylation · palladium

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Received: August 20, 2016

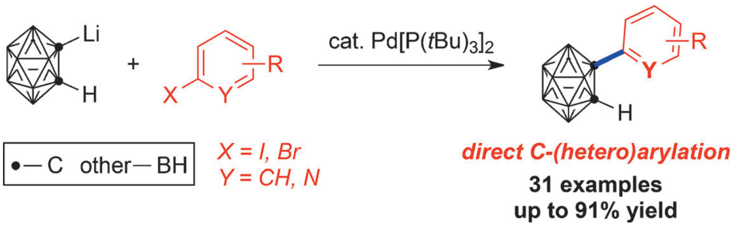
COMMUNICATION

Cross-Coupling

J.-Y. Lu, H. Wan, J. Zhang, Z. Wang, Y. Li, Y. Du, C. Li, Z.-T. Liu, Z.-W. Liu, J. Lu**

■■ – ■■

Palladium-Catalyzed Direct Cross-Coupling of Carboranyllithium with (Hetero)Aryl Halides



Palladium-catalyzed direct C-arylation of readily available cage carboranyllithium reagents with aryl halides has been developed for the first time. This method is applicable to a wide range of aryl halide substrates including aryl iodides, aryl bromides, and heteroaromatic halides.