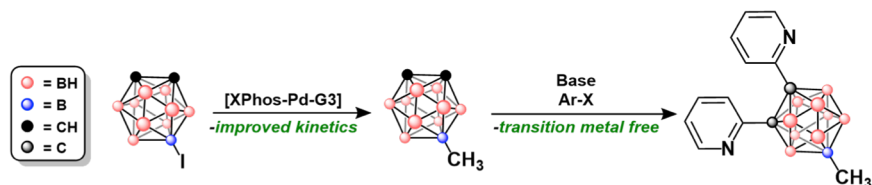


Improved synthesis of icosahedral carboranes containing exohedral B–C and C–C bonds.

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Improved synthesis of icosahedral carboranes containing exohedral B–C and C–C bonds

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ABSTRACT

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Carboranes are boron-rich molecular clusters that possess electronic characteristics allowing for orthogonal approaches to vertex selective modification. We report improved methods utilizing orthogonal chemistry to achieve efficient substitution at electron-rich B-vertices and electron-poor C-vertices of carborane. Functionalization of B-vertices with alkyl and (hetero)aryl groups using corresponding Grignard reagents has been improved by the use of a Pd-based precatalyst featuring an electron-rich biaryl phosphine ligand. Using the developed catalytic conditions lead to cross-coupling transformations achieved within several hours. Importantly, this method is applicable towards alkyl-based Grignard reagents containing β -hydrogens. Additionally, transition metal-free substitution of (hetero)aryl substrates on C-vertices was developed under S_NAr conditions. The selective substitution of carboranes afforded by these methods holds potential for the rational synthesis of heterofunctionalized boron clusters with substituents on both boron and carbon-based vertices.

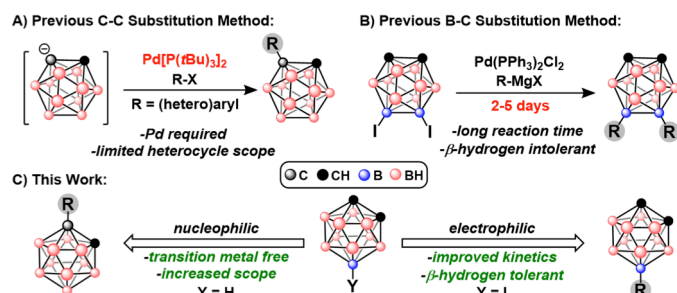


Figure 1: A) Previous substitution method for C-(hetero)arylation. B) Previous B-substitution method via Kumada coupling. C) Improved C- and B-vertex functionalization procedures.

1. Introduction

Since the discovery of neutral carboranes ($C_2B_{10}H_{12}$) more than 50 years ago, these icosahedral clusters have emerged as diverse building blocks for a variety of applications, including organic light emitting diodes,¹ biomedicine,² batteries,³ catalysis⁴, self-assembled materials⁵ and medicinal drug design.⁶ These compounds feature several unique properties, such as three dimensional aromaticity, large HOMO-LUMO gap, tunable dipole moment as a function of cluster symmetry, and thermal stability.^{7a} The diversity of carborane applications, however, requires synthetic methods that can provide access to vertex-selective modification. Selectivity can be achieved, to a certain extent, by utilizing the inherent electron delocalization of the cluster cage where certain B-H vertices are more reactive than others towards electrophilic^{7a} or organometallic reagents.^{7b-g} Furthermore, under basic conditions the acidic protons bound to

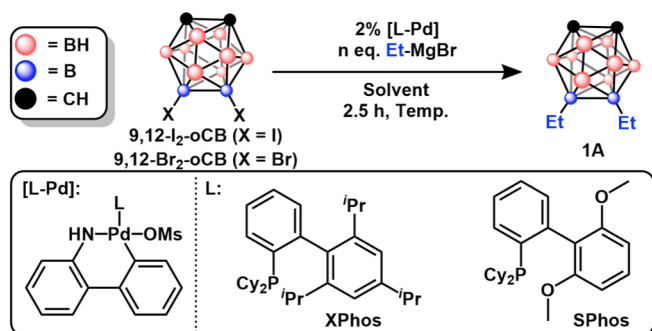
the carbon vertices can undergo facile deprotonation and subsequent selective functionalization with electrophiles. Nevertheless, current synthetic methods are still limited in their ability to achieve efficient substitution of carboranes. For example, current C-vertex substitution methods can install (hetero)aryl groups, but require the use of transition metal reagents (Figure 1A).⁸ Similarly, metal-catalyzed cross-coupling can be used to achieve B-vertex functionalization. However, the substitution of carbon-based nucleophiles is limited by substrate tolerance, long reaction times, and even poor reproducibility (Figure 1B).^{9a-d} To improve on these procedures, we report a fast, high yielding B-vertex substitution method for B-substituted carboranes as well as a transition metal-free C-vertex substitution of (hetero)aryl substrates (Figure 1C). Importantly, these two methods can be combined into a synthetic sequence, producing a strategy to form B- and C-functionalized carboranes.

2. B-Vertex Substitution

The boron vertices of carborane have been especially difficult to substitute relative to traditional organic molecules. This is largely due to their hindered steric environment, variable electronic character, and strong non-hydridic B-H bonds.^{7a} Friedel-Crafts halogenation, however, has been a vital tool for harnessing electrophilic reactivity at the electron-rich boron vertices of carborane. The resulting B-halogenated carborane electrophiles provide access to B-C, B-O, or B-N substitution through metal-catalyzed cross-coupling. Zakharkin *et al.* was the first to report a Pd-mediated cross-coupling process with $Pd(PPh_3)_2Cl_2$ between 9-I-*o*-carborane (**9-I-oCB**) or 9-I-*m*-carborane (**9-I-mCB**) and several organomagnesium reagents, claiming to produce B-substituted clusters in a manner

reminiscent to classical Kumada cross-coupling chemistry used for aryl halides.^{9a,b} Subsequently, Li *et al.* reported a similar protocol for transformations between 9,12-I₂-*o*-carborane (**9,12-I₂-oCB**) and alkylmagnesium reagents.^{9c} In both cases, authors claimed 60-99% yields for reactions that required 24-30 h to complete the coupling. Notably, a later report by Zheng *et al.* called the obtained yields and reaction times by the original authors into question, claiming that: "In our hands, the product yields of these reactions are not as high as been reported, and in most cases we have studied the yields are extremely low."^{9d} Additionally, Zheng *et al.* determined that reproducible cross-coupling could be obtained in 20-75% yield only after the introduction of a catalytic amount of CuI. While the method by Zheng *et al.* has improved the overall cross-coupling chemistry, several limitations, including long reaction times (2-5 days) and restricted tolerance for Grignard reagents containing β -hydrogens, persisted. We hypothesize that these drawbacks can be further mitigated by replacing the Pd(PPh₃)₂Cl₂ precatalyst with a system containing a biaryl phosphine ligand as was observed previously for B-O, B-N, and B-CN metal-catalyzed cross-coupling chemistry.^{9e-g}

Initially, we explored the use of XPhos-Pd-G3¹⁰ precatalyst with **9,12-I₂-oCB** under the coupling conditions previously reported by Zheng *et al.*, and targeted Et-MgBr due to the presence of β -hydrogens. Under these conditions, we observed very low conversion (<5%) to 9,12-diethyl-*o*-carborane (**1A**) after 2.5 h (Entry 1, see SI for experimental details) with the inclusion of a catalytic amount of CuI as an additive. Notably, CuI has previously been found to improve the yield when Pd(PPh₃)₂Cl₂ was used as a precatalyst.^{9d} Screening solvent at a decreased temperature, we identified 1,4-dioxane as a promising candidate (Entry 2). Further optimization of the temperature allowed nearly full conversion (89%) for this transformation within 2.5 hours (Entry 3). To determine whether or not this reactivity was a function of the use of the biaryl phosphine-based precatalyst, we tested SPhos-Pd-G3 (Entry 4), which presented a comparable result to XPhos-Pd-G3. Furthermore, these conditions are



Entry #	X	L	n	Solvent	T	% Conv. (% Yield)
1 ^a	I	XPhos	5	THF	75	2
2	I	XPhos	4.2	1,4-dioxane	65	30
3	I	XPhos	4.2	1,4-dioxane	75	89 ^b (77)
4	I	SPhos	4.2	1,4-dioxane	75	90 ^b (66)
5	Br	XPhos	4.2	1,4-dioxane	75	0

Table 1: Optimization table for Kumada coupling with 9,12-I₂-oCB or 9,12-Br₂-oCB and Et-MgBr. % Conv. indicates the % of 9,12-Et₂-oCB present in the crude reaction mixture as determined by GC-MS.

^a Included 2 mol% CuI additive.

^b Reaction mixture contained 5-10% dehalogenated product by GC-MS.

selective for B-I bonds, with no desired product observed when using B-Br electrophiles (Entry 5). Under these optimized conditions, the issue of β -hydride elimination has been mitigated.

With optimized conditions established, we assessed the scope of this method with *o*-carboranyl electrophiles (Figure 2). Starting with **9,12-I₂-oCB**, we observed near full conversions (>90%) to the disubstituted products in the presence of alkyl or arylmagnesium reagents. These compounds were purified *via* silica gel column chromatography providing products **1A**, **1B**, and **1C** in 57-72% isolated yields. While these conditions allow for the isolation of disubstituted products (**1A-C**), we note that approximately 5-10% of the partially dehalogenated products (**1D-E**) are present in the reaction mixture of **1A-B**. Interestingly, no observable dehalogenation is encountered when **9-I-oCB** is

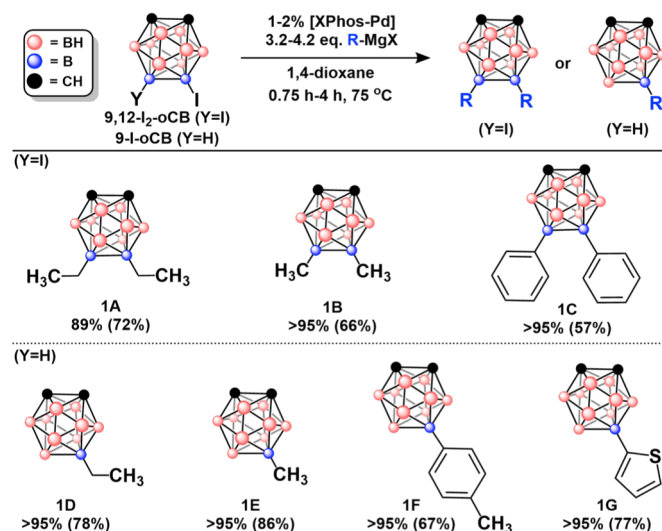


Figure 2: Reaction scheme for mono- and disubstitution of *o*-carborane. *O*-carborane coupling products with GC-MS conversion and percent isolated yields in parentheses. See Table S2 in SI for exact reaction conditions.

used as a substrate and >95% conversions to the monosubstituted products **1D**, **1E**, and **1F** are observed within 2 hours. Notably, a heterocycle compatible with magnesium reagents afforded >95% conversion to **1G**, although slightly longer reaction time was needed (4 h).

To expand the utility of this method, we tested our conditions with **9-I-mCB** and **9-Br-10-I-mCB** to determine the tolerance of *m*-carboranyl electrophiles and B-Br bonds (Figure 3). Slightly longer reaction times were required to reach >95% conversion for products **1H**, **1I**, and **1J**. Despite >95% conversion observed for **1H**, the low isolated yield (34%) likely resulted from the high volatility of the compound, as evidenced by observed sublimation *in vacuo* at room temperature when removing solvent. For products **1I** and **1J**, no substitution and/or reduction at the brominated vertex was observed, lending further evidence to the selectivity of this method for B-I bonds over B-Br bonds.

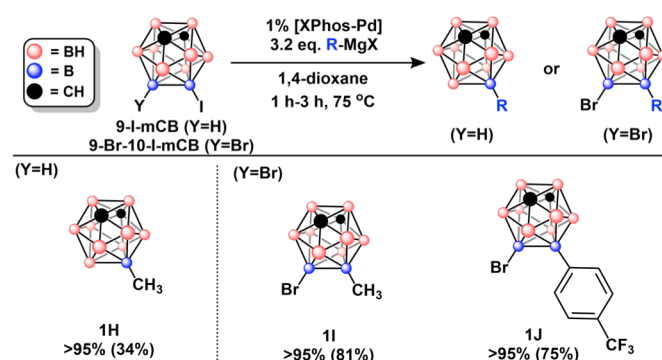
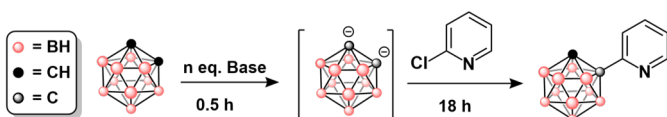


Figure 3: Reaction scheme for monocoupling of *m*-carborane in the presence of B-Br bonds. *M*-carborane coupling products with GC-MS conversion and percent isolated yields in parentheses. See Table S2 in SI for exact reaction conditions.

This stands in contrast to the previously developed B-N and B-O cross-coupling methods using Pd-based catalysts with biaryl ligands that showed preferential functionalization of B-Br bonds over B-I congeners.^{9f}

3. C-vertex substitution

C-vertex substitution methods are perceived as more straightforward than the B-vertex functionalization. Due to the acidic nature of the C-H bond, C-vertices can be deprotonated and reacted with electrophiles or used as nucleophiles.⁸ While the metalation of carborane and subsequent reactions with alkyl halides has produced a library of alkyl carboranes,¹¹ C-vertex (hetero)arylation has been achieved through less straightforward procedures, such as metal-catalyzed cross-coupling that requires either stoichiometric or catalytic amounts of transition-metal reagents.⁸ For example, Cu-mediated coupling with (hetero)aryl iodides or bromides can yield C-pyridyl- and C-aryl-carboranes, but requires 25-90 h reaction times and can tolerate only a select group of functionalized (hetero)aryl substrates.^{8b} More recent methods, such as Ni- and Pd-catalyzed cross coupling, demonstrate improved functional group tolerance for C-arylation, but are limited to attaching chloro- and methyl-pyridine.^{8a,c} Transition metal-free C-substitution methods have been investigated, but require the reaction between a C-monosubstituted *o*-carborane and a fluoroarene possessing a strong electron withdrawing group.¹² This selectively produces 1,2-diaryl-*o*-carboranes, but this methodology was not applied to heterocyclic substrates. Overall, procedures for C-(hetero)arylation are currently limited by their use of transition metal reagents and small substrate scopes. Previous reports have demonstrated the possibility of the C-vertex substitution under S_NAr conditions,^{1a,13} prompting us to expand the number and type of substrates that can be appended to carborane using this approach.



Entry #	Base	Base eq.	Solvent	% Conv.
1	ⁿ BuLi	2	THF	0
2	KHMDS	2	THF	92
3	KHMDS	1	THF	80
4	KHMDS	3	THF	99
5	LiHMDS	3	THF	45
6	NaHMDS	3	THF	90
7	KHMDS	3	MTBE ^a	86
8	KHMDS	3	Ether ^b	90
9	KHMDS	3	DME ^c	98

Table 2: Optimization table of S_NAr reaction between 2-chloropyridine and *o*-carborane. % Conv. indicates the % of 1-(2-pyridine)-*o*-CB present in the crude reaction mixture as determined by GC-MS.

^a Methyl-*tert*-butyl ether

^b Diethyl ether

^c 1,2-Dimethoxyethane

For the initial optimization studies we tested 2-chloropyridine, estimating that it would be less reactive than fluoroheterocycles and more reactive than fluoroarenes. Typically, C-H deprotonation and successive metalation of carborane have been achieved with ⁿBuLi in either ether or THF.^{7a} Nevertheless, we found that ⁿBuLi was unable to facilitate the heteroarylation of carborane to 1-(2-pyridine)-*o*-carborane (**2A**) under these conditions (Entry 1). We previously observed that KHMDS deprotonates 1,1'-bis(*o*-carborane),¹⁴ indicating that it could potentially be applicable to our system. While 2 and 1 equivalents of KHMDS yielded sub-quantitative conversions (Entries 2 and 3, respectively), 3 equivalents of this base produced 99% conversion to the desired product (Entry 4). Testing the effect of the base cation on the reaction, we observed 45% and 90% conversion with LiHMDS and NaHMDS,

respectively (Entries 5 and 6), suggesting the cation has influence on the reaction progression. High conversion efficiency with KHMDS led us to continue its use throughout the optimization studies. Next, we examined other etheral solvents to see if there was any significant effect of solvent on the outcome of the reaction. With conversions ranging from 86%-98% (Entries 7-9), we selected THF as our primary solvent.

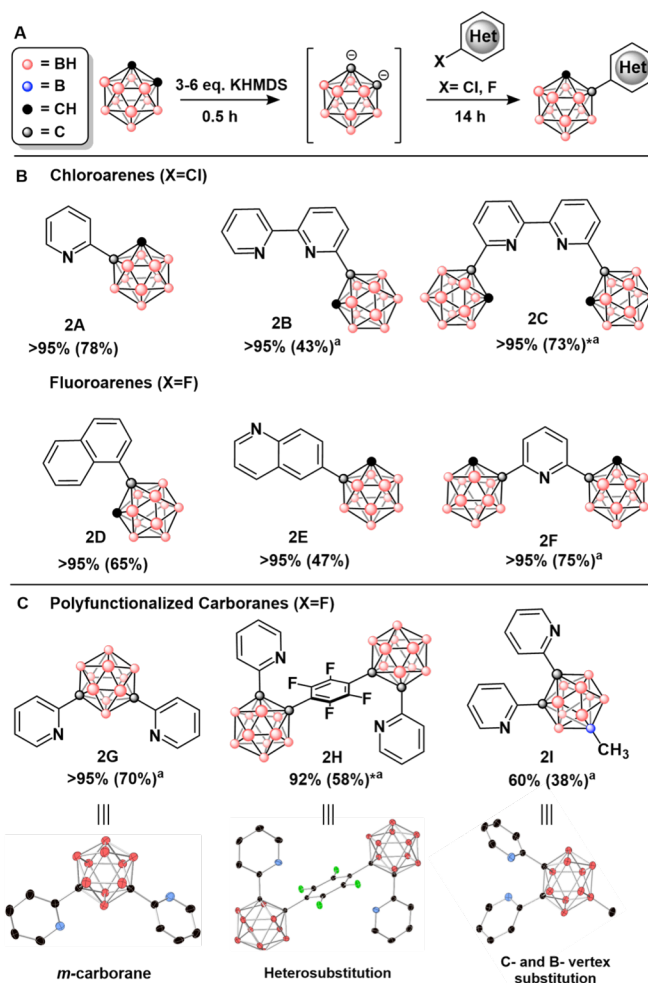


Figure 4: A) C-functionalization reaction scheme B) Products with GC-MS conversions and isolated yields in parentheses. C) Polyfunctionalized carboranes with associated single crystal X-ray structures obtained by extrapolating the general method in A. (*) indicates that conversion was determined through ¹H NMR instead of GC-MS. See Table S4 in SI for exact reaction conditions.

^a See SI for corresponding single crystal X-ray structures

Under the optimized conditions, **2A** (Figure 4B) can be isolated in 61% yield after purification *via* silica gel column chromatography. This method tolerates bipyridine-based electrophiles, producing compounds **2B** and **2C** in 43% and 73% isolated yields, respectively. These bipyridine-based compounds are more difficult to produce using metal-catalyzed cross-coupling methods. The ability to generate **2C** suggests that multiple C-C bond forming processes can be achieved at the electrophile under these conditions. Testing this method with (hetero)aryl fluorides resulted in the desired product formation under the optimized conditions (Figure 4, 2D-2I see SI for experimental details). The lower room temperature reactivity of substrates originating from products **2D** and **2E** was circumvented by heating the reaction mixture to 80°C. This initially afforded **2E** in 27% yield, and analysis of the ¹¹B NMR data suggested the presence of deboronated products, which is consistent with previous reports of deboronation of *o*-carborane in the presence fluoride.¹³ To sequester fluoride ions and

potentially prevent cage degradation we used one equivalent of isopropoxytrimethylsilane under otherwise identical conditions, which increased the isolated yield of **2E** to 44%. Similar observations were made with the 2,6-difluoropyridine substrate, but the yield remained nearly identical even with the addition of the fluoride scavenger. However, upon changing the solvent from THF to diethyl ether, the isolated yield for **2F** increased to 75%. We attribute this observation to the likely low solubility of KF byproduct in ether, thereby decreasing its reactivity towards deboronation. Furthermore, under optimized conditions, the disubstituted *m*-carborane **2G** was obtained in 70% isolated yield (Figure 4C). Next, we assessed the viability of conducting sequential C-vertex heterosubstitutions. Deprotonation of **2A** and subsequent treatment with perfluorobenzene selectively produced the para-substituted product **2H** in 29% isolated yield. Upon further optimization, we found that excess perfluorobenzene resulted in higher conversion to desired product. The best results were achieved with DME and 2 equivalents of KHMDS, resulting in 74% isolated product yield. Similar carborane-substituted phenylene molecules have been investigated for their luminescent properties, but are typically synthesized *via* cross coupling procedures that require multiple reagents such as CuI₂ and Pd(PPh₃)₂Cl₂.¹⁵ Overall, we demonstrate that S_NAr methodology can be applied to both chloro- and fluoro(hetero)aryl substrates, however, in the latter case a competing reactivity of the fluoride byproduct needs to be mitigated by the judicious use of the additional reagents and solvents.

Lastly, the described methods for forming B-C and C-C bonds in carboranes prompted us to explore whether these can be used in conjunction with each other to achieve the synthesis of heterofunctionalized clusters. Treatment of methylated carborane (**1E**) with excess 2-fluoropyridine produced product **2I**, demonstrating that both the B- and C- vertex functionalization methods can be used in a sequential manner. This compound was isolated in 38% yield. Single crystals of **2I** were grown with hexanes and analyzed using X-ray crystallography, ultimately proving its structural assignment (Figure 4C).

4. Conclusion

We have developed improved B- and C-vertex functionalization methods that can effectively afford previously inaccessible carborane derivatives. Specifically, by employing biaryl phosphine ligands, we have introduced an improved B-vertex substitution method that increases the rate of Pd-catalyzed cross-coupling. Additionally, we have expanded the scope of C-vertex substitution while circumventing the requirement for transition metal-catalyzed cross-coupling. By utilizing the nucleophilic nature of the C-deprotonated carboranes, mild conditions can be used to achieve substitutions of heterocycles on carboranes. These improved methods represent a robust addition of transformations now available to the practitioners in boron cluster chemistry.

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