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B–N, B–O, and B–CN Bond Formation via Palladium-Catalyzed Cross-Coupling of B-Bromo-Carboranes

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Supporting Information

ABSTRACT: Carboranes are boron-rich molecules that can be functionalized through metal-catalyzed cross-coupling. Here, for the first time, we report the use of bromo-carboranes in palladium-catalyzed cross-coupling for efficient B–N, B–O, and unprecedented B–CN bond formation. In many cases bromo-carboranes outperform the traditionally utilized iodo-carborane species. This marked difference in reactivity is leveraged to circumvent multistep functionalization by directly coupling small nucleophiles (-OH, -NH_2, and -CN) and multiple functional groups onto the boron-rich clusters.

Icosahedral carboranes are boron-rich molecular clusters that are often described as three-dimensional (3D) analogs to benzene.[1] Their unique delocalized 3D aromatic bonding, high stability, and potential for site-selective functionalization make them attractive building blocks for tunable pharmacophores, unique ligand scaffolds, and building blocks for materials applications.[2] Further development of these and other applications with carboranes requires efficient methods for cluster synthesis and functionalization, where ultimately each individual vertex can be specifically addressed.[1]

Over the past 50 years, palladium-catalyzed cross-coupling has emerged as a powerful synthetic method for creating new molecules.[3] In particular, the emergence of designer ligands (beyond PPh_3) for Pd-catalyzed cross-coupling dramatically expanded the scope of electrophile substrates beyond aryl iodides.[4a] These new catalyst systems demonstrated a clear ability to cross-couple aryl-bromides and aryl-chlorides, thereby facilitating transformations of synthetically challenging substrates. Among existing ligand platforms, biaryl phosphine ligands significantly increased the efficacy of Pd-catalyzed C–C, C–N, and C–O bond formation.[4]

Despite these advances in catalyst design for aromatic substrates, effective methodologies for metal-catalyzed B–N, B–O and B–C cross-coupling in carboranes are lacking. In fact, only B-iodo-carboranes have been used in Pd-catalyzed cross-coupling thus far.[5] Yet, analogy between carboranes and arenes provides a clear hypothesis that other B-functionalized electrophiles, beyond B-iodo-carboranes, may be competent cross-coupling partners. Here we report our discovery validating this hypothesis by demonstrating for the first time that B-bromo-carboranes can be efficient electrophiles for B–N, B–O, and B–CN bond formation in Pd-catalyzed cross-coupling. Furthermore, we show conditions where these B-bromo-carboranes are superior to the iodinated congeners enabling the synthesis of previously inaccessible B-substituted carboranes. This chemistry is furthermore attractive given the greater synthetic accessibility of B-bromo-carboranes compared to their iodo-based congeners (see SI).[1]

Hawthorne and co-workers recently reported Pd-catalyzed amidation of 9-I-*m*-carborane (**I-mCB**) utilizing the biaryl phosphine ligand DavePhos (**L1**, Figure 1).[5h] To test our hypothesis, we replaced **I-mCB** with the bromo-carborane congener, 9-Br-*m*-carborane (**Br-mCB**), as a substrate under the reported cross-coupling conditions. However, our initial attempts at cross-coupling trifluoroacetamide with **Br-mCB** proved unsuccessful. Rapid formation of Pd metal was observed without any consumption of **Br-mCB**. We postulated that the Pd(0) precursor (Pd_2dba_3, dba = dibenzylideneacetone) was not efficiently forming the catalytically active species [**L1**Pd^0]. To resolve this issue, we employed a commercially available Pd(II) precatalyst (Figure 1B inset), which has been previously shown to dramatically improve catalytic activity across a large pool of aryl-based substrates and catalytic conditions.[6] Importantly, this change tremendously improved the catalytic conversion of **Br-mCB** producing **1a** in nearly quantitative conversion within 2 h (Figure 1A). This discovery demonstrates for the first time that one can efficiently activate a relatively inert B–Br bond in a carborane with electron-rich Pd-based species supported by a biaryl phosphine ligand (Figure 1B).

This example demonstrates the potential competence of **Br-mCB** toward cross-coupling (Figure 1B), which does not have any literature precedent. This advance was also appealing given that **Br-mCB** can be synthesized in a fraction of the time (1 h) that is required for the synthesis of **I-mCB** (1 day). We therefore investigated the scope of Pd-catalyzed cross-coupling

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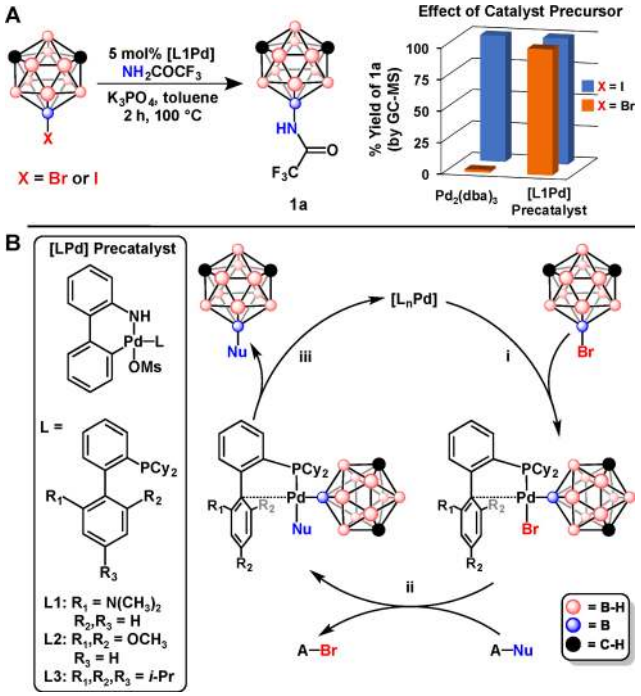

Figure 1. (A) General amidation conditions (inset, GC-MS yield of **1a** from **Br-mCB** and **I-mCB** using different palladium precursors). (B) Proposed catalytic cycle employing biaryl phosphine ligands (step i, oxidative addition; step ii, transmetalation; step iii, reductive elimination).

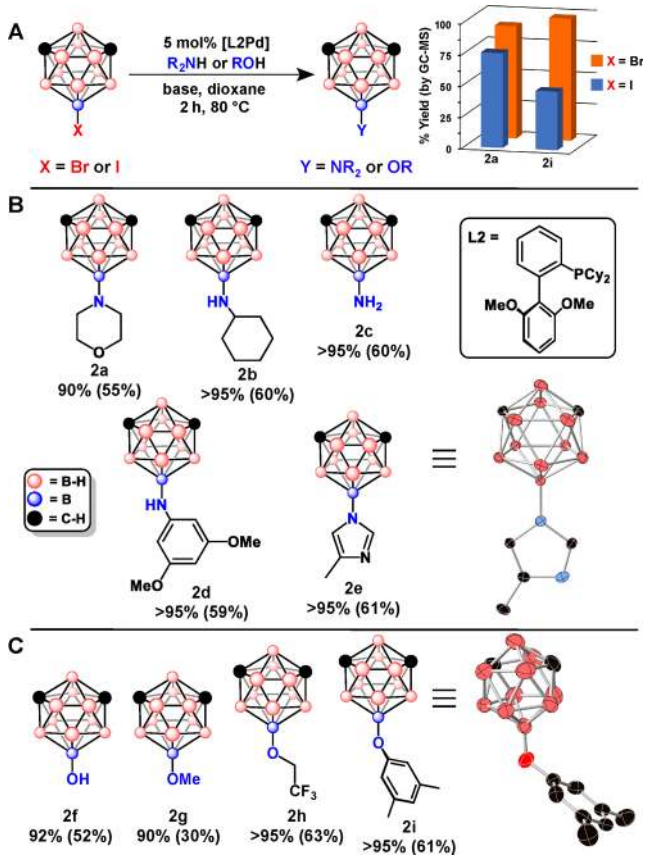

Figure 2. (A) General amination and alkoxylation conditions (inset, GC-MS yield of **2a** obtained from **Br-mCB** and **I-mCB**). (B) Amination scope using **Br-mCB** and X-ray crystal structure confirming B–N bond formation. (C) Alkoxylation scope using **Br-mCB** and X-ray crystal structure confirming B–O bond formation (ellipsoids at 50% probability and H atoms omitted for clarity). GC-MS yields, and isolated yields in parentheses. *K^{t}BuO used as a base except for: **2e**, anhydrous K_3PO_4; **2f**, 1 M aqueous K_3PO_4; **2g**, $NaOCH_3$.

of **Br-mCB** with other nucleophiles utilizing biaryl-ligand containing precatalysts.

To further probe the scope of B–N bond formation using **Br-mCB**, we evaluated several conditions and substrates for Pd-catalyzed amination. Using morpholine as a substrate (**2a**, Figure 2), we evaluated the cross-coupling efficiency of three precatalysts featuring **L1**, SPhos (**L2**), and XPhos (**L3**) ligands (see SI). For this transformation, **L2** afforded complete consumption of **Br-mCB** and a high amount of B–N coupling product **2a** as determined by GC-MS analysis. Evaluation of various bases indicated the superior performance of K^{t}BuO for forming **2a**. Importantly, **Br-mCB** showed superior cross-coupling efficiency compared to **I-mCB** for the formation of **2a** (Figure 2A). Using these optimized conditions, cross-coupling of **Br-mCB** proceeds with primary, secondary, aromatic, and heterocyclic amines in nearly quantitative conversion affording the corresponding B–N compounds (**2b–2e**, Figure 2B and SI).

In general, cross-coupling using unprotected nitrogen-rich heterocyclic substrates is known to be challenging.[6c] Amination of halocarboranes has only been shown on the 2-I-*p*-carborane, which is a significantly more reactive substrate than **Br-mCB**.[7] The cross-coupling methodology we developed addresses this issue for the first time in the context of *m*-carborane chemistry since, to the best of our knowledge, **2e** represents the first product resulting from the direct cross-coupling of an unprotected five-membered heterocycle with a B-halo-*m*-carborane.

The versatility of **Br-mCB** as a cross-coupling partner can be further seen from its efficient reaction with challenging nucleophiles. For example, **Br-mCB** cross-couples with ammonia producing **2c** (Figure 2B), whereas previously **2c** could only be prepared by lengthy hydrolysis of **1a**.[5h]

Importantly, our method represents the first example of a direct cross-coupling leading to **2c** and is enabled by the previously unrecognized reactivity of **Br-mCB** when using biaryl phosphine supported Pd-based catalysts.

During the course of our amination studies, we observed B–OH coupling with **Br-mCB** (**2f**, see SI) when nonanhydrous bases were used. This is remarkable, given that the only example of a Pd-catalyzed carborane B–O bond formation was reported on 2-I-*p*-carborane. Importantly, the **I-mCB** congener was previously deemed too unreactive.[8a]

Based on these observations, we developed a new cross-coupling protocol enabling the direct coupling of water, methanol, trifluoroethanol, and 3,5-dimethylphenol with **Br-mCB** (**2f–2i**, Figure 2C).

This constitutes the first reported Pd-catalyzed cross-coupling leading to a B–O bond formation with *m*-carborane substrates. Significantly, a control reaction where **I-mCB** was used as a substrate led to a significantly lower conversion to **2i** (Figure 2A). This Pd-catalyzed route is also superior to the exisiting method for forming related B–O compounds utilizing carborane B-halonium salts.[8b] Additionally, **2f** can be readily converted to **2g** by deprotonation with NaH and followed by treatment with MeI, demonstrating the added synthetic utility of **2f**.

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The versatility of **Br-mCB** cross-coupling with small nucleophiles led us to investigate B−CN bond formation. Cyanide is known to be a difficult cross-coupling partner in metal catalysis due to its propensity toward binding to catalytically active species, resulting in their deactivation.[9] Recently several groups reported efficient protocols for cyanation of aromatic substrates using $K_4[Fe(CN)_6]$ as a mild cyanide source.[9b,d] Pd-catalyzed cyanation of **Br-mCB** using $K_4[Fe(CN)_6]$ with an **L3**-based precatalyst led to the formation of 9-CN-*m*-carborane in a nearly quantitive conversion (**3a**, Figure 3A). This example represents the first

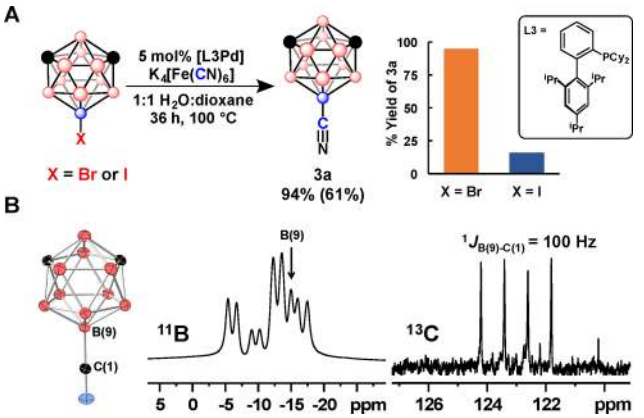

Figure 3. (A) Cyanation protocol; GC-MS yield of **3a** obtained from **Br-mCB** and **I-mCB** (isolated yield in parentheses). (B) X-ray crystal structure, ^{11}B and $^{13}C\{^1H\}$ NMR spectra of **3a** (ellipsoids at 50% probability and H atoms omitted for clarity).

direct cyanation of a halogenated derivative of dicarba-*closo*-dodecaborane. Importantly, cross-coupling activity of the **I-mCB** species under these conditions is dramatically diminished compared to **Br-mCB** (Figure 3A).

The ability to append multiple functional groups is crucial to developing carboranes for new and existing materials.[2,10,11] While polyfunctionalization of arene-based electrophiles via cross-coupling is well-established, similar methods for carboranes are rare.[5,10] Our methodology can be applied toward disubstitution cross-coupling chemistry. Specifically, 9,10-Br_2-*m*-carborane (**4a**) can be functionalized with two bulky 3,5-dimethylphenolate substituents (**4c**, Figure 4). Interestingly, under B−OH cross-coupling conditions (*vide supra*), **4a** undergoes exclusive monosubstitution to produce **4d**.

In addition, given the pronounced orthogonal reactivity of B−Br versus B−I bonds in cross-coupling, our methodology can be used to heterofunctionalize mixed halo-carborane substrates. We leveraged the selectivity of $PdCl_2(PPh_3)_2$ for B−I bond functionalization to produce 9-Br-10-Et-*m*-carborane (**4e**) from 9-Br-10-I-*m*-carborane (**4b**, Figure 4 and SI).

Selective Pd-catalyzed cross-coupling of the B−Br moiety in **4e** with **L2**-containing precatalyst yields the heterofunctionalized 9-O-(3,5-$Me_2C_6H_3$)-10-Et-*m*-carborane (**4f**). This transformation represents the first metal-catalyzed B-heterofunctionalization of dicarba-*closo*-dodecaborane via cross-coupling demonstrating that B-Br-carboranes offer an additional pathway for multifunctionalization. These experiments also suggest that our methodology is amenable to sterically encumbered carborane-based electrophiles.

Ortho-carboranes are the most challenging substrates in cross-coupling methodologies, since these species undergo

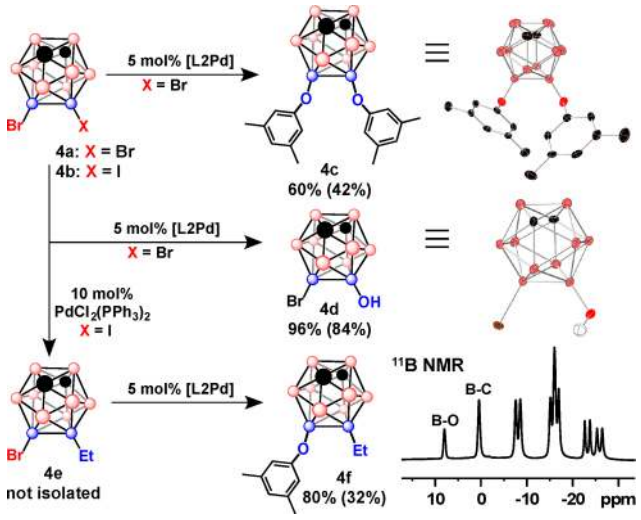

Figure 4. Difunctionalization conditions and X-ray crystal structure confirming B−O bond formation. X-ray crystal structure (ellipsoids at 50% probability and H atoms omitted for clarity); see SI for detailed conditions. GC-MS yields, and isolated yields in parentheses.

facile deboronation in the presence of nucleophiles.[12] Our conditions are sufficiently mild and enable the cross-coupling of 3-Br-*o*-carborane (**Br-oCB**, see SI for details) with amine and alcohol substrates that are not strongly nucleophilic (**5a**−**5b**, Figure 5). Using 3-Br-*o*-carborane in this case is preferred, given its higher conversion efficiency and ease of preparation compared to the 3-I-*o*-carborane analogue.

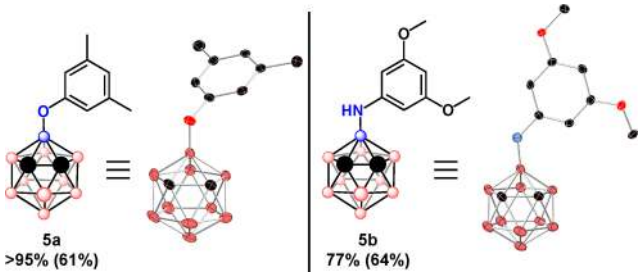

Figure 5. Alkoxylation and amination of *ortho*-carboranes using **Br-oCB** (ellipsoids at 50% probability and H atoms omitted for clarity). GC-MS yields, and isolated yields in parentheses.

In summary, we discovered that B-bromo-*m*-carboranes undergo efficient Pd-catalyzed B−N, B−O, and B−CN cross-coupling enabled by precatalysts featuring electron-rich biaryl phosphine ligands. The higher reactivity of **Br-mCB** likely stems from faster transmetalation (Figure 1B, step II) due to a weaker Pd−Br bond compared to Pd−I congener. This is consistent with previously observed trends in palladium-catalyzed transformations using aryl halide electrophiles and Pd-based catalysts supported by bulky electron-rich phosphine ligands.[13,14] The use of B-bromo-carboranes allows direct access to previously unknown B-functionalizations of these clusters. In addition, judicious use of Pd-catalyst systems with either iodo- or bromo-functionalized carborane was used to access unprecedented heterofunctionalized species. This approach is also amenable to *o*-carborane, which is the most challenging carborane substrate. Notably, this cross-coupling chemistry is complementary to the recently developed efforts in directed B−H functionalization strategies[15] and, if successfully

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combined, may provide unprecedented densely functionalized carborane species.[16] Further expansion of this methodology to other cross-coupling chemistry[17] along with a full mechanistic investigation[18] is currently underway in our laboratory.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.6b05505.

Full procedures and other characterization data (PDF)
Crystallographic data (CIF)

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Notes

The authors declare no competing financial interest.

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