Photocatalysis

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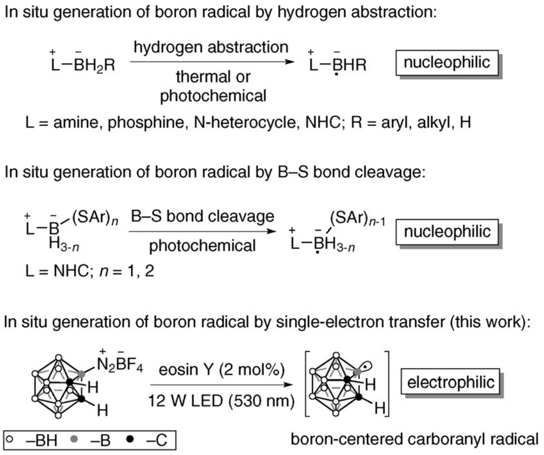
Visible-Light-Promoted Photocatalytic B−C Coupling via a Boron-Centered Carboranyl Radical: Facile Synthesis of B(3)-Arylated *o*-Carboranes

*Da Zhao and Zuowei Xie**

Abstract: *A visible-light-mediated in situ generation of a boron-centered carboranyl radical (o-$C_2B_{10}H_{11}^{\bullet}$) has been described. With eosin Y as a photoredox catalyst, 3-diazonium-o-carborane tetrafluoroborate [3-N_2-o-$C_2B_{10}H_{11}$][BF_4] was converted into the corresponding boron-centered carboranyl radical intermediate, which can undergo efficient electrophilic substitution reaction with a wide range of (hetero)arenes. This general and simple procedure provides a metal-free alternative for the synthesis of 3-(hetero)arylated-o-carboranes.*

Boron-centered radical species (boryl radicals) have recently attracted considerable attention.[1] The major work in this area focuses on the isolation and characterization of such reactive species by overcoming daunting synthetic difficulties.[2,3] In contrast, a growing interest has been directed towards the reactivities and applications of in situ generated boryl radicals.[2f,4] For instance, N-heterocyclic carbene (NHC) stabilized boryl radicals have been used in various organic radical reactions, such as radical deoxygenation of xanthates,[2f,4c,5] radical reductions of alkyl halides,[6] radical chain homolytic substitution reactions,[7] and reductive decyanation of organic nitriles.[8] However, their applications are far less developed compared with other main group element based radicals, such as carbon-, tin-, silicon-, nitrogen-, or oxygen-centered radical species. This gap may be attributed to limited number of available methods for generating transient boryl radicals. The established methods rely on hydrogen abstraction from the parent boranes or the homolysis of B−S bonds in NHC–boryl sulfides (Scheme 1).[2f,4,9] Meanwhile, it has been documented that the photolysis of bis(*m*-carboran-9-yl)mercury [(*m*-$C_2B_{10}H_{11})_2$Hg] leads to the formation of a boron-centered carboranyl radical,[10] a nonclassical boron-centered radical. However, its synthetic utility has been limited because of the harsh reaction conditions required and the use of toxic reagents.



Scheme 1. In situ generation of boryl radicals.

Owing to their unique steric/electronic properties, carboranes are finding many applications in drug design,[11] as well as in materials[12] and organometallic/coordination chemistry.[13] A growing interest has been in the design and synthesis of compounds which combine *o*-carborane (*o*-$C_2B_{10}H_{12}$) clusters and aromatic units.[14] Despite the remarkable progress in carborane chemistry, straightforward and general syntheses of 3-aryl-*o*-carboranes, in particular 3-heteroaryl-*o*-carboranes, still represents a very challenging task.[15] They are generally prepared either by the reaction of [*nido*-7,8-$C_2B_9H_{11}$]$^{2-}$ with ArBX_2 (X = Cl, Br, I),[16] or the palladium-catalyzed cross-coupling reaction of 3-iodo-*o*-carboranes with either aryl Grignard/organozinc reagents or boronic acids.[17] Recently, we reported another approach to 3-aryl-*o*-carboranes by using an aromatic ene reaction of 1,3-dehydro-*o*-carborane.[18] However, the substrate scope is limited to arenes bearing benzylic C−H bonds. Relatively lower yields coupled with competitive side reactions (Diels–Alder reactions) further restrict its synthetic application. In addition, such an aromatic ene reaction is not compatible with heteroarenes. To the best of our knowledge, there has been no example on the synthesis of 3-heteroaryl-*o*-carboranes in the literature.[19]

Inspired by the photocatalytic transformations of aryl diazonium salts into the corresponding aryl radicals,[20] we wondered whether a boron-centered carboranyl radical (*o*-$C_2B_{10}H_{11}^{\bullet}$) could be generated by visible-light-induced photoredox catalysis from 3-diazonium-*o*-carborane tetrafluoroborate ([3-N_2-*o*-$C_2B_{10}H_{11}$][BF_4], **1**;[18] Scheme 1). Herein, we describe the generation of such a carboranyl radical by photoredox catalysis and its reactions with (hetero)arenes for high-yielding syntheses of 3-(hetero)aryl-*o*-carboranes.

To test our hypothesis, direct carboranylation of thiophene (**2a**) with the diazonium salt **1** in the presence of the commercially available organic dye eosin Y (2 mol %), as the photoredox catalyst,[21] was conducted to establish the optimal

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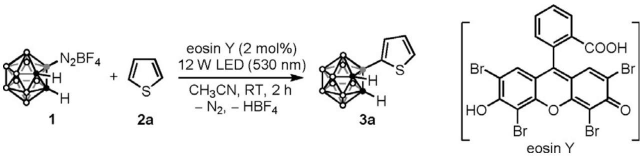
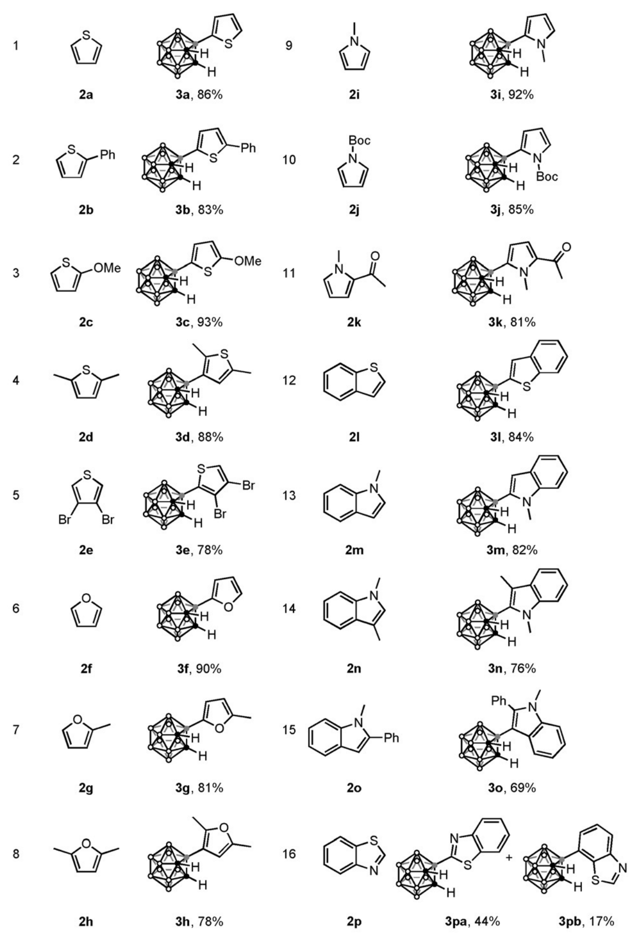
Table 1: Optimization of reaction conditions.[a]



Entry	Reaction conditions	Yield [%][b]
1	**2a** (10 equiv)	83
2	**2a** (5 equiv)	89
3	**2a** (2 equiv)	86
4	**2a** (5 equiv), no eosin Y, no light	n.r.
5[c]	**2a** (5 equiv), no eosin Y, 12 h	35
6[d]	**2a** (5 equiv), no light, 12 h	trace

[a] Reaction conditions: **1** (0.1 mmol), **2a** (0.2, 0.5 or 1.0 mmol), eosin Y (2 mol %), CH_3CN (2 mL), 12 W LED (530 nm), room temperature for 2 h. n.r. = no reaction. [b] Yield of isolated product. [c] Main products were 3-fluoro-*o*-carborane and 3-$NHCOCH_3$-*o*-carborane. [d] The starting material **1** was recovered.

Table 2: Synthesis of 3-heteroaryl-*o*-carboranes.[a]



Entry	2	3	Entry	2	3
1	2a	3a, 86%	9	2i	3i, 92%
2	2b	3b, 83%	10	2j	3j, 85%
3	2c	3c, 93%	11	2k	3k, 81%
4	2d	3d, 88%	12	2l	3l, 84%
5	2e	3e, 78%	13	2m	3m, 82%
6	2f	3f, 90%	14	2n	3n, 76%
7	2g	3g, 81%	15	2o	3o, 69%
8	2h	3h, 78%	16	2p	3pa, 44% + 3pb, 17%

[a] Reaction conditions: **1** (0.1 mmol), heteroarene **2a** (0.5 mmol for thiophene derivatives, 0.2 mmol for other heteroarenes), eosin Y (2 mol %), CH_3CN (2 mL), 12 W LED (530 nm), room temperature for 2 h. Yield is that of the isolated product. Boc = *tert*-butyloxycarbonyl.

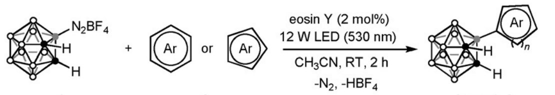
reaction conditions (Table 1). The desired 3-thienyl-*o*-carborane **3a** was obtained in very good yields in the presence of 2–10 equivalents of **2a** (entries 1–3). Control experiments confirmed that both light and eosin Y were required for significant conversion into the product (entries 4–6).[22] It was noted that this reaction proceeded with excellent regioselectivity as only substitution at the C2-position of the thiophene was observed.

Under the optimal reaction conditions (Table 1, entry 2), various thiophene substrates underwent C–H carboranylation with the precursor **1** (Table 2, entries 1–5). In addition to thiophene derivatives, this method was also compatible with a variety of heterocycles (entries 6–16). Different substituents such as alkyl, halogen, alkoxy, carbonyl, phenyl, and ester groups were well-tolerated and the desired B(3)-(hetero)-arylated products **3** were produced in very good to excellent yields. The Boc group in **3j** was easily removed to afford 3-pyrrolyl-*o*-carborane.[22] It was noted that this reaction proceeded with excellent regioselectivity as the carboranylation occurred only at the C2-position of the heteroarenes. If the C2-position was unavailable, substitution at the C3-position would take place instead (entries 4, 8, and 15). It is noteworthy that for both **2b** and **2o**, which feature a phenyl substituent, substitution at the phenyl ring was not observed (entries 2 and 15). These results may indicate that electron-rich arenes are more favored compared to the less-electron-rich ones, thus suggesting the electrophilic nature of the boron-centered carboranyl radical. For benzothiazole (**2p**), a mixture of C2- and C7-carboranylated products was formed with a molar ratio of 5:2 (entry 16).

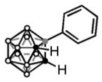
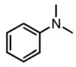
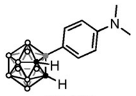
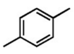
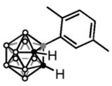
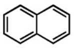
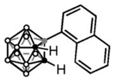
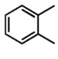
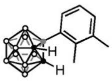
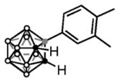
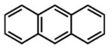
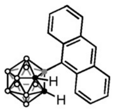
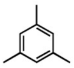
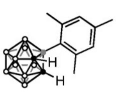
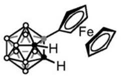
To further explore the efficiency of this light-mediated coupling reaction, simple benzene derivatives were also examined and the results are compiled in Table 3. In general, compared to those electron-rich heterocycles depicted in Table 2, the reaction efficiency of these simple arenes was lower as 10 equivalents of the arene were needed to achieve a high conversion (Table 3, entries 1–5). Notably, for *N*,*N*-dimethyl aniline (**2u**) the C–H carboranylation occurred only at the *para*-position (entry 5). The reactions of naphthalene (**2v**) and anthracene (**2w**) worked well to give the corresponding carboranylated products **3v** and **3w** in 75 and 62 % yields, respectively, upon isolation (entries 6 and 7). Moreover, for ferrocene (**2x**), which can also serve as an one-electron reductant,[23] the desired product was obtained quantitatively after 5 minutes with only 1 equivalent of ferrocene (entry 8).

The C–H carboranylation of heteroarenes with **1** using eosin Y is expected to proceed through a radical mechanism,[24] and preliminary mechanistic investigations support this assumption. Addition of 1.2 equivalents of 2,2,6,6-tetramethylpiperdinoxyl (TEMPO) to the reaction mixture completely suppressed this carboranylation process and the TEMPO-trapped adduct **4** was isolated in 89 % yield,[22] thus suggesting that a radical pathway is involved in this photoreaction [Eq. (1)].

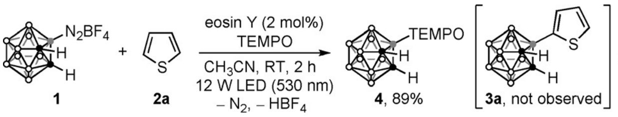
Table 3: Scope with respect to the simple arenes.[a]



1 + 2 → 3, *n* = 1, 2

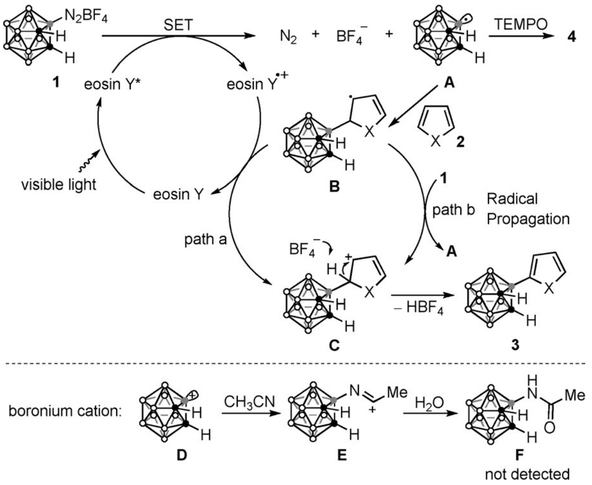
Entry	2	3	Entry	2	3
1	 **2q**	 **3q**, 33%	5	 **2u**	 **3u**, 77%
2	 **2r**	 **3r**, 47%	6[b]	 **2v**	 **3v**, 75%
3	 **2s**	 **3sa**, 17% +  **3sb**, 35%	7[b]	 **2w**	 **3w**, 62%
4	 **2t**	 **3t**, 51%	8[c]	 **2x**	 **3x**, quant

[a] Reaction conditions: **1** (0.1 mmol), arene **2a** (1.0 mmol), eosin Y (2 mol%), CH_3CN (2 mL), 12 W LED (530 nm), room temperature for 2 h. Yield is that of the isolated product. [b] 5 equiv (0.5 mmol) of **2** was used. [c] 1 equiv (0.1 mmol) of **2x** was used, 5 min.



(1)

On the basis of the above experimental results, a plausible reaction mechanism is proposed in Scheme 2. Irradiation of eosin Y by visible light generates a photoexcited species, eosin Y*, which can undergo single-electron transfer (SET) with **1** ($E_{1/2}^{red} = -0.23$ V vs. SCE in CH_3CN; see the Supporting Information) to afford the boron-centered carboranyl radical **A**. Addition of **A** to the arene **2** gives the intermediate **B**. Oxidation of **B** by either the eosin Y radical cation (path a) or the diazonium salt **1** through a radical-chain transfer (path b) generates the carbocation intermediate **C**. Deprotonation of **C** leads to the final rearomatized product **3**.



Scheme 2. Proposed reaction pathways.

The possibility that **3** is produced from the Friedel–Crafts reaction via the carboranyl boronium cation[25] **D** can be ruled out by the following observations. First, for the indole **2m**, which can easily undergo Friedel–Crafts reaction at the C3-position, carboranylation occurred only at the C2-position (Table 2, entry 13), which is consistent with the fact that radicals preferentially tend to add at C2 of the indole nucleus.[26] Secondly, if **D** was formed in the reaction, it would be trapped by the solvent CH_3CN to generate the corresponding solvated adduct.[25] However, no such species was detected.

In summary, this work shows that boron-centered carboranyl radical can be generated in situ by photoredox catalysis and it can undergo electrophilic substitution with a broad range of (hetero)arenes to efficiently produce 3-(hetero)aryl-*o*-carboranes. More importantly, this general and convenient procedure provides a metal-free approach to 3-heteroaryl-*o*-carboranes, and may find applications in medicine and materials science.[27] Efforts to utilize such carborane boryl radicals for other synthetically useful transformations are underway in our laboratory.

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