Cage Compounds

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Photoarylation of Iodocarboranes with Unactivated (Hetero)Arenes: Facile Synthesis of 1,2-[(Hetero)Aryl]$_n$-*o*-Carboranes ($n = 1,2$) and *o*-Carborane-Fused Cyclics

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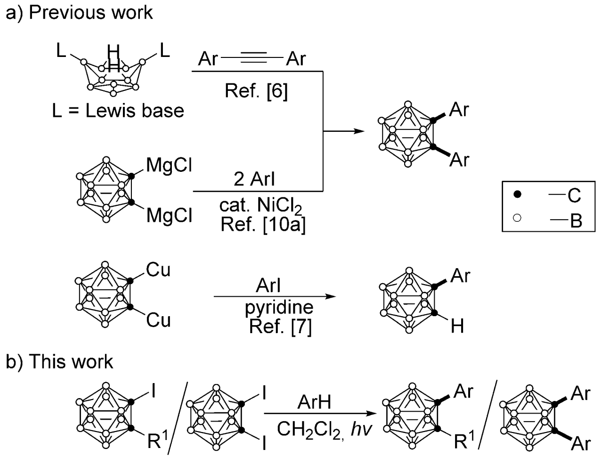
Abstract: *Photoarylation of iodocarboranes with unactivated arenes/heteroarenes at room temperature has been achieved, for the first time, thus leading to the facile synthesis of a large variety of cage carbon mono(hetero)arylated and di-(hetero)arylated o-carboranes. This work represents a clean, efficient, transition-metal-free, and cheap synthesis of functionalized carboranes, which has significant advantages over the known methods.*



Scheme 1. Cage carbon arylation of *o*-carboranes.

Icosahedral carboranes are carbon-boron molecular clusters which can be viewed as three-dimensional analogues to benzene.[1] Their unique characteristics such as thermal and chemical stabilities as well as three-dimensional structures make them attractive building blocks for boron neuron capture therapy agents in medicine,[2] functional units in supramolecular design/materials,[3] and versatile ligands in organometallic/coordination chemistry.[4] Recent results have also demonstrated that cage carbon-arylated *o*-carboranes are a class of AIE (aggregation induced emission) active and stimuli-responsive luminescent materials, thus exhibiting very interesting photophysical properties, where the carborane moiety plays a unique role.[5] These arylated *o*-carboranes are generally prepared from the condensation reaction of decaborane with the corresponding aryl or diaryl acetylenes,[6] and the yields of the desired products are variable.[5,6] The hypertoxicity of decaborane also complicates this method. To tackle this problem, two cross-coupling reactions have been developed using commercially available *o*-carborane as a coupling partner (Scheme 1 a). One is the Ullmann-type coupling reaction of 1-copper-*o*-$C_2B_{10}H_{11}$ or 1,2-dicopper-*o*-$C_2B_{10}H_{10}$ with aryl iodides to give 1-aryl-*o*-carboranes in moderate yields.[7] No 1,2-diaryl-*o*-carboranes are produced,[8] probably because of steric reasons and the homocoupling of *o*-carboranyls.[9] Another one is the transition metal catalyzed Kumada-type cross-coupling of 1-magnesium chloride-*o*-carboranes or 1-lithium-*o*-carboranes or 1,2-di-magnesium chloride-*o*-carboranes with aryl iodides for the preparation of 1,2-(aryl)$_n$-*o*-carboranes ($n = 1,2$).[10] However, the strong basic conditions used in the coupling reactions result in limited substrate scope and poor functional-group tolerance. Thus, it is important to develop new methodologies for cage carbon-arylated *o*-carboranes.

In recent years, photocatalysis has been recognized as an increasingly viable tool to realize one-electron transfer cross-coupling reactions.[11] Among these, photoarylation of aryl iodides with unactivated arenes is particularly attractive because of its mild reaction conditions and broad substrate scope.[12] Inspired by these results, we studied a UV light promoted photoarylation of iodocarboranes with unactivated (hetero)arenes at room temperature. The findings are reported herein (Scheme 1 b).

Direct irradiation of a benzene solution of 1-iodo-2-methyl-*o*-caborane (**1a**) under 36 W UV lamp ($\lambda = 365$ nm) at room temperature for 24 hours gave the coupling product 1-phenyl-2-methyl-*o*-caborane (**3a**) in 51 % yield (GC; Table 1, entry 1). Addition of 1.2 equivalents of Na_2CO_3 afforded **3a** in 92 % yield (entry 2). The same yield was obtained with 40 equivalents of benzene in dichloromethane (DCM), while the yield of **3a** was decreased if 20 equivalents of benzene was used (entries 3–6). Other solvents and bases did not improve the yield of **3a** (entries 8–14). Though an 18 W UV lamp worked as well as a 36 W one, thus producing **3a** in 92 % yield (entry 15), no reaction was observed without UV irradiation (entry 18).

Under the optimal reaction conditions (entry 15, Table 1), the substrate scope was examined and the results are compiled in Table 2. In general, the photoarylation reaction proceeded well to give the desired products in very high yields

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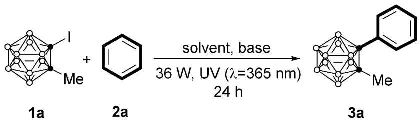
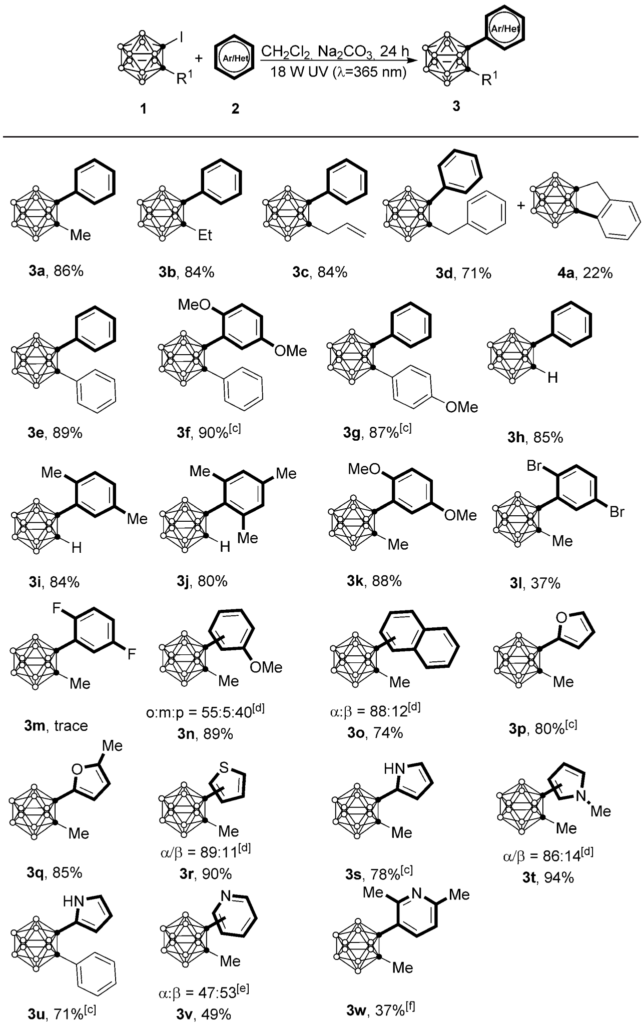
Table 1: Optimization of reaction conditions.[a]



Entry	Base (equiv)	Benzene (equiv)	Solvent	Yield [%][b]
1	–	–	benzene	51
2	Na_2CO_3 (1.2)	–	benzene	92
3	Na_2CO_3 (1.2)	20	CH_2Cl_2	82
4	Na_2CO_3 (1.2)	30	CH_2Cl_2	86
5	Na_2CO_3 (1.2)	40	CH_2Cl_2	92
6	Na_2CO_3 (1.2)	60	CH_2Cl_2	92
7	Na_2CO_3 (0.6)	40	CH_2Cl_2	81
8	Et_3N (1.2)	40	CH_2Cl_2	25
9	pyridine (1.2)	40	CH_2Cl_2	55
10	K_2CO_3 (1.2)	40	CH_2Cl_2	91
11	Na_2CO_3 (1.2)	40	cyclohexane	16
12	Na_2CO_3 (1.2)	40	THF	8
13	Na_2CO_3 (1.2)	40	CH_3CN	81
14	Na_2CO_3 (1.2)	40	DMSO	24
15[c]	Na_2CO_3 (1.2)	40	CH_2Cl_2	92
16[d]	Na_2CO_3 (1.2)	40	CH_2Cl_2	55
17[e]	Na_2CO_3 (1.2)	40	CH_2Cl_2	58
18[f]	Na_2CO_3 (1.2)	40	CH_2Cl_2	n.r.

[a] Reaction conditions: **1a** (0.2 mmol), solvent (2.0 mL), 36 W UV ($\lambda = 365$ nm), room temperature for 24 h. [b] GC yield. [c] 18 W UV lamp as the irradiation source. [d] 9 W UV lamp as the irradiation source. [e] Reaction time was 12 h. [f] Without irradiation. DMSO = dimethylsulfoxide, THF = tetrahydrofuran.

Table 2: Synthesis of 1-(hetero)aryl-*o*-carboranes.[a,b]



[a] All reactions were conducted on a 0.5 mmol scale of **1** in 5.0 mL of DCM in a closed flask for 24 h at room temperature under the irradiation of an 18 W UV lamp. [b] Yield of isolated product. [c] Irradiation for 48 h. [d] Ratio determined by ^{1}H NMR spectroscopy. [e] Reaction was carried out in 5 mL of pyridine. [f] 1-Me-*o*-carborane was observed in 49% GC yield.

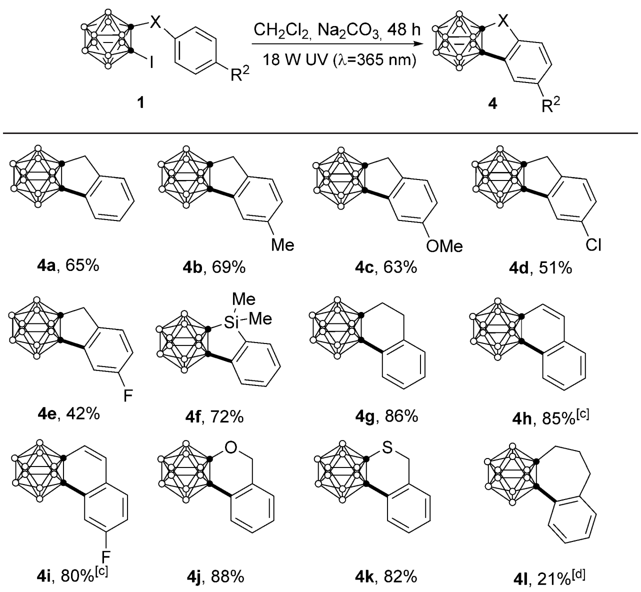
upon isolation. The nature of cage substitutents (R^1) did not affect the yields (**3a–h**). In contrast, the electron-rich arenes worked much better than the electron-poor ones, and 1,4-$F_2C_6H_4$ only gave a trace amount of product (**3k–m**). For unsymmetrical arenes, regioisomers were obtained. Anisole gave the arylated product **3n** in a total yield of 89% with a ratio of *o*/*m*/*p* = 55:5:40. Naphthalene afforded two regioisomers of **3o** in 74% yield with a ratio of α/β = 88:12.

This method was compatible with a variety of heteroarenes. Furan, 2-methyl-furan, and pyrrole generated the corresponding α-carboranylation products **3p**, **3q**, **3s**, and **3u** in very high yields (Table 2). Thiophene and *N*-methyl pyrrole gave both regioisomers in excellent yields with a molar ratio of α/β = 89:11 for **3r** or 86:14 for **3t**, respectively. In contrast, pyridine derivatives were not good arylation agents. Pyridine led to the isolation of **3v** in 49% yield with a molar ratio of α/β = 47:53, whereas 2,6-lutidine afforded a single isomer, **3w**, in only 37% yield.

We noted that an unexpected intramolecular cyclization product **4a** was isolated in 22% yield in addition to **3d** from the reaction of 1-iodo-2-benzyl-*o*-carborane (**1d**) with benzene (Table 2). This finding prompted us to study the photomediated intramolecular cyclization for the synthesis of *o*-carborane-fused cyclics. The results are outlined in Table 3. Irradiation of **1d** in DCM at room temperature for 48 hours generated **4a** in 65% yield. It was found that the reaction efficiency was dependent upon the substituents on the phenyl ring. Electron-rich substituents offered the corresponding cyclization product **4** in higher yields than those of electron-poor ones (**4a**, **4b**, **4c** versus **4d**, **4e**). In contrast, the efficiency of the construction of six-membered ring systems was much higher than those of five-membered ones (**4e** verrsus **4i**; **4a** versus **4g**). In addition, *o*-carborane-fused heterocyclics were also prepared in the same manner in very high yields (**4f**, **4j**, and **4k**). Following this motif, a seven-membered ring (**4l**) was constructed in 21% yield.

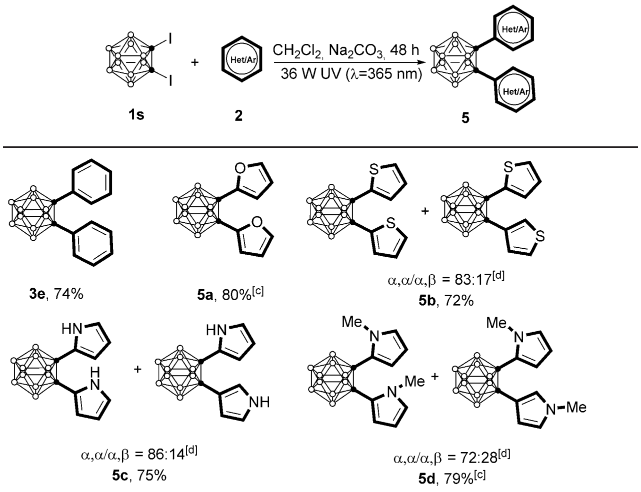
Having achieved the intramolecular and intermolecular photoarylation/photoheteroarylation of 1-iodo-*o*-carborane, we then explored the photodi(hetero)arylation of 1,2-diiodo-*o*-carborane (**1s**) with (hetero)arenes and the results are summarized in Table 4. Under the standard reaction conditions, irradiation of **1s** with benzene in DCM at room temperature for 48 hours gave 1,2-diphenyl-*o*-carborane (**3t**) in 74% yield. Heteroarenes worked equally well, thus affording the desired 1,2-diheteroarene-*o*-carboranes in 72–80% yields. For furan, a single α,α-isomer, **5a**, was produced,

Table 3: Synthesis of *o*-carborane-fused (hetero)cyclics.[a,b]



[a] All reactions were conducted on 0.5 mmol scale of **1** in 5.0 mL of DCM in a closed flask for 48 h at room temperature under the irradiation of an 18 W UV lamp. [b] Yield of isolated product. [c] *cis*-Alkene was used as the starting material. [d] 1-Cinnamyl-*o*-carborane was isolated in 54% yield.

Table 4: Synthesis of 1,2-di(hetero)aryl-*o*-carboranes.[a,b]

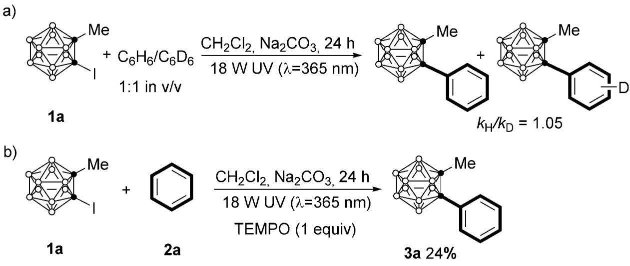


[a] All reactions were conducted on 0.5 mmol scale of **1s**, 2.4 equiv of Na$_2$CO$_3$ under the irradiation of an 36 W UV lamp in 5.0 mL of DCM in a closed flask at room temperature for 48 h. [b] Yield of isolated product. [c] Reaction for 72 h. [d] Ratio determined by ^{1}H NMR spectroscopy.

while thiophene, pyrrole, and *N*-methylpyrrole generated both α,α and α,β-isomers with the α,α-isomer as a major product (**5b–d**). It was noted that such a diarylation reaction was very sensitive to steric factors. For example, only the monoarylation product was isolated from the reaction of **1s** with *p*-xylene, even after prolonged reaction time.

The compounds **3–5** were fully characterized by ^{1}H, ^{13}C, and ^{11}B NMR spectroscopy, as well as high-resolution mass spectrometry. The molecular structures of **3j**, **3n**, **3p**, **3t**, **3v**, **4f**, **4j**, and **4l** were further confirmed by single-crystal X-ray analyses.[13]

To gain some insight into the reaction mechanism, an intermolecular primary kinetic isotope effect (KIE) experiment was performed under the standard reaction conditions. The low KIE value ($k_H/k_D = 1.05$) implied that an aromatic C–H bond cleavage is not involved in the rate-determining step (Scheme 2a). In contrast, the addition of the radical scavenger 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) led to a significant decrease in the yield of **3a** (from 86 to 24%; Scheme 2b), thus suggesting that a radical process is involved in the reaction.[14] In addition, control experiments indicated that the arylation of **1a** with benzene gave **3a** in 51% yield in the absence of any base, while such arylation did not proceed without UV irradiation (Table 1, entries 1 and 18). These experimental data suggest that both a base-promoted homolytic aromatic substitution (BHAS) mechanism[15] and a photoinduced carboranyl radical process involving the homolytic cleavage of the cage C–I bond[12g,16] may be operative in the above photoarylation/photoheteroarylation reactions (see Scheme S1 in the Supporting Information for details).



Scheme 2. Kinetic isotopic effect and radical trapping experiments.

In summary, a photoarylation/photoheteroarylation of either 1-iodo-*o*-carborane or 1,2-diiodo-*o*-carborane with a wide variety of arenes and heteroarenes under very mild reaction conditions has been developed for the first time, and is a very promising approach for clean, efficient, transition-metal-free, and cheap synthesis of a large class of 1,2-[(hetero)aryl]$_n$-*o*-carboranes ($n = 1,2$). As this photoarylation reaction does not require strong bases, photocatalysts, and high temperatures, it is tolerant of many types of functional groups. This work represents significant advances over the known methods for the synthesis of cage C-arylated *o*-carboranes,[6,7,10] and also sets a good example for the functionalization of boron clusters using photochemistry approach.

Experimental Section

Typical procedure for the preparation of 1-(hetero)aryl-*o*-carboranes (**3**): Iodocarborane **1** (0.5 mmol), (hetero)arene (20 mmol), and Na$_2$CO$_3$ (0.6 mmol) were mixed in dry CH$_2$Cl$_2$ (5 mL) in a 25 mL Schlenk flask equipped with a magnetic stirring bar. Under an atmosphere of dry nitrogen, the reaction mixture was irradiated using an 18 W UV lamp ($\lambda = 365$ nm) at room temperature for 24 h with stirring. After removal of the solvent in vacuo, the residue was subjected to flash column chromatography on silica gel (230–400 mesh) using *n*-hexane as the eluent to give the products **3**.

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Keywords: arenes · carboranes · cross-coupling · photochemistry · radicals

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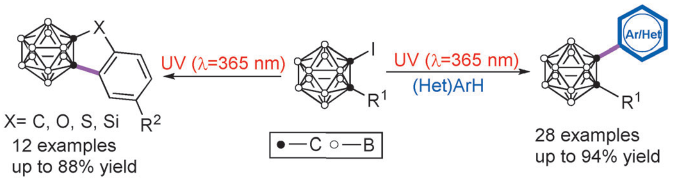
Communications

Cage Compounds

H. Ni, Z. Qiu, Z. Xie* ______ ▮▮▮▮–▮▮▮▮

Photoarylation of Iodocarboranes with Unactivated (Hetero)Arenes: Facile Synthesis of 1,2-[(Hetero)Aryl]$_n$-*o*-Carboranes ($n=1,2$) and *o*-Carborane-Fused Cyclics



Caught in a cage: Photoarylation of iodocarboranes with unactivated arenes and heteroarenes at room temperature represents a facile approach to a large variety of mono(hetero)arylated and di-(hetero)arylated functionalized *o*-carboranes. The procedure is clean, efficient, transition-metal-free, and cheap.