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Pyridyl-Directed Cp*Rh(III)-Catalyzed B(3)−H Acyloxylation of *o*-Carborane

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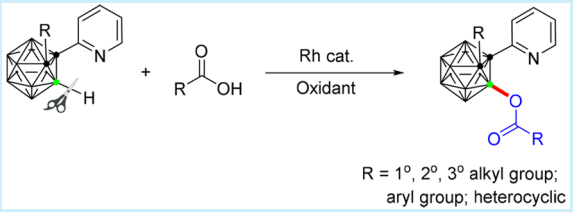
Supporting Information

ABSTRACT: An efficient pyridyl-directed Rh(III)-catalyzed *o*-carborane B(3)−H acyloxylation is reported. The B(3)−H bond is the most electron-deficient vertex on *o*-carborane whose functionalization is challenging. The combination of $Cu(OH)_2$ and diverse carboxylic acids provides low cost and abundant acyloxyl sources which could lead to moderate to excellent yields.



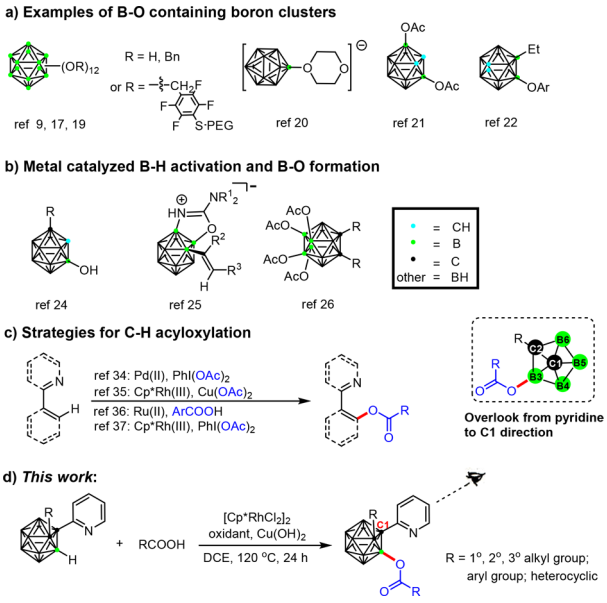
Since its discovery over 60 years ago, boron chemists have studied the family of 12-vertex icosahedral $[C_nB_{12-n}H_{12}]^{n-2}$ (n = 0, 1, 2) clusters and their derivatives owing to their unique three-dimensional benzene-analogue physicochemical properties.[1,2] Although their emergence was mainly spurred by the prosperity of theoretical chemistry and imperative military programs, boron clusters have, to date, exhibited applications in fields such as boron neutron capture therapy,[3] medicinal chemistry,[4,5] single molecule magnets,[6] optoelectronic functional materials,[7−9] weakly coordinating anions,[10] polymer materials,[11] MOFs, and catalysis.[9a,12−14] As stable structures, icosahedral boron clusters have been assembled in nanocars,[15] *o*-CB@CNTs,[16] and organomimetic cluster nanomolecules.[17] Very recently, our group found $[Cp^*Ir(PPh_3)S_2C_2B_{10}H_{10}]$ as a case in point that includes a novel B−H···π hydrogen bond.[18]

B−O bonds exist in borates, boron esters, and boric acids. However, O-substituted icosahedral boron clusters have not been well investigated. Traditionally, perhydroxylation of BH vertices was acquired by mingling hydrogen peroxide solution with boron clusters.[19] B_{cage}−O bonds were formed with the help of Lewis acids as well.[20] A streak of B_{cage}−O products were prepared by cross-coupling between prefunctionalized carboranes and related oxygen sources.[21,22] Since transition metals can locate specific positions precisely on organic backbones, chemists consider metal catalysts as vital tools to functionalize C−H bonds.[23] Enlightened by C−H activation efforts, oxygen was guided to polyhedron borane derivatives by employing a suitable directing group.[24,25] A 4-fold acetoxylation of *o*-carboranes on B(8,9,10,12) in the absence of a directing group was also disclosed.[26]

According to calculated charge distribution at the *o*-carborane cage, the order of electron enrichment at boron sites is B(9,12) > B(8,10) > B(4,5,7,11) > B(3,6).[27] Therefore, B(8,9,10,12)−H can be activated even without auxiliary of heteroatom.[26] In recent years, metal-catalyzed carboxylic[24,28] or aldehyde group[29] directed B(4) functionalization was well developed, whereas catalytic B(3) functionalization appears to be inevitably more challenging, despite the fact that metal-promoted B(3)−H activation has been described.[30−32]

Pyridyl is such a useful substructure that pyridyl-embedded carboranes have been applied in fluorescent Ir complexes[7d,8f,9b] and Pd-pincer catalysts.[13a] Over the past few years, N-directed oxygenations were identified as an enticing step-economical equipment.[33] The first pyridyl-directed palladium-catalyzed acetoxylation was reported as shown in Scheme 1c.[34] Very recently, C(sp^2)−O formation was disclosed by several groups.[35−37] With our persistent endeavors devoted to

Scheme 1. Several B−O-Containing Clusters and C−H Acyloxylation Strategies



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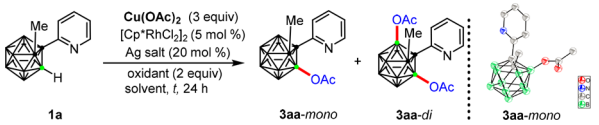
exploration of B(3)−H activation[32a−c] and our ongoing interest in synthesis of nitrogen-containing organic compounds,[28b,29,38] we herein report the first pyridyl-directed B(3)−H acyloxylation of *o*-carborane.

We initiated our investigation on coupling of 1-pyridyl-2-methylcarborane (**1a**) with copper acetate using $[Cp^*RhCl_2]_2$ as the catalyst (Table 1). The use of 5 mol % of catalyst and 20 mol % of $AgSbF_6$ led to a 17% total yield of **3aa** (entry 1, mono/di = 14:3). Employing AgOAc improved the yield to 23% (entry 2, 18:5). The yield of **3aa** was drastically lifted with the addition of 2 equiv of $K_2S_2O_8$ (entry 3). Trace product was obtained when $AgNTf_2$ was used (entry 4). To our delight, the use of 2 equiv of Oxone gave **3aa** in 85% (55:30) yield (entry 5). The change of either solvents (entries 6 and 7) or catalyst (entries 8 and 9) led to no **3aa**. A sharp decline of yield resulted from the decrease of rhodium catalyst (entry 10). A temperature of 120 °C turned out to be the best reaction temperature according to the control experiment (entries 11 and 12). We postponed or shortened the reaction time, which brought about a slight drop of the yield (entries 13 and 14). Air atmosphere has no significant effect on yield (entry 15).

Table 1. Condition Optimization for Acetoxylation[a]

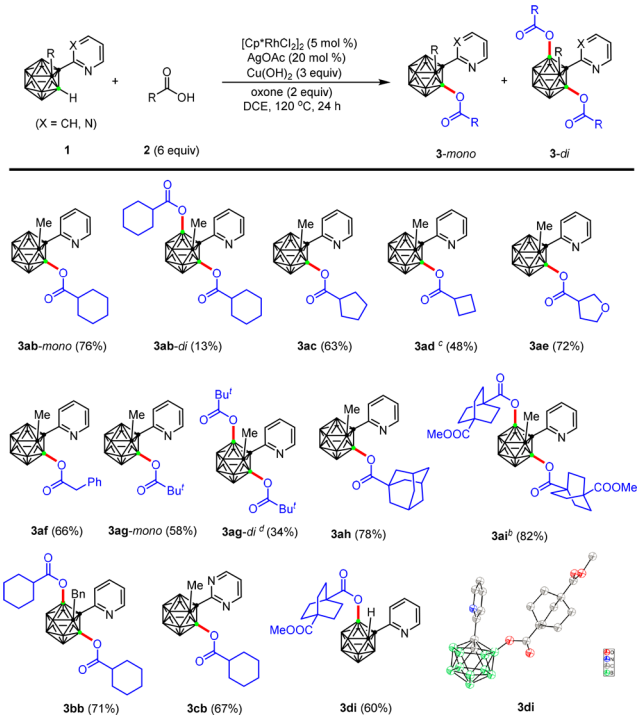


entry	solvent	temp (°C)	Ag salt	oxidant	yield[b] (%)
1	DCE	120	$AgSbF_6$		17 (14:3)
2	DCE	120	AgOAc		23 (18:5)
3	DCE	120	AgOAc	$K_2S_2O_8$	62 (49:13)
4	DCE	120	$AgNTf_2$	$K_2S_2O_8$	trace
5	DCE	120	AgOAc	Oxone	85 (55:30)
6	1,4-dioxane	120	AgOAc	Oxone	ND
7	PhCl	120	AgOAc	Oxone	ND
8[c]	DCE	120	AgOAc	Oxone	ND
9[d]	DCE	120	AgOAc	Oxone	ND
10[e]	DCE	120	AgOAc	Oxone	44 (32:12)
11	DCE	140	AgOAc	Oxone	69 (61:8)
12	DCE	100	AgOAc	Oxone	72 (55:17)
13[f]	DCE	120	AgOAc	Oxone	62 (42:20)
14[g]	DCE	120	AgOAc	Oxone	83 (52:31)
15[h]	DCE	120	AgOAc	Oxone	80 (51:29)

[a]Reaction conditions: **1a** (0.1 mmol), $Cu(OAc)_2{\cdot}H_2O$ (0.3 mmol), $[Cp^*RhCl_2]_2$ (5 mol %), Ag salt (20 mol %), oxidant (2 equiv), solvent 1 mL under argon for 24 h. [b]GC yield. Ratio of mono-/disubstitution in parentheses. [c]$[RuCl_2(p\text{-cymene})]_2$ instead of $[Cp^*RhCl_2]_2$. [d]$[Cp^*IrCl_2]_2$ instead of $[Cp^*RhCl_2]_2$. [e]2.5 mol % of $[Cp^*RhCl_2]_2$, 10 mol % of AgOAc. [f]12 h. [g]48 h. [h]Under air.

With the optimized conditions in hand, we then surveyed the generality of B(3)−H acyloxylation (Scheme 2). Taking cognizance of sparse commercially available copper carboxylates, we decided to utilize the combination of carboxylic acids with $Cu(OH)_2$ in replace of copper carboxylates. In the series of secondary acids, **2b** led to separable **3ab**-mono (76%) and **3ab**-di in a total yield of 89%. Fortunately, all of the coupled monosubstituted and disubstituted products in the context could be separated as a pure substance rather than a mixture. Good to moderate yields were acquired when other secondary acids **2c−f** were used. The reactions were not influenced by the use of tertiary acids (**3ag**, **3ah**). Noteworthy, 82% disubstituted **3ai** was isolated if the amounts of **2i** and $Cu(OH)_2$ were doubled. Good yields could also be obtained when a benzyl group, pyrimidyl, or hydrogen atom was connected to the cage carbon (**3bb**, **3cb**, **3di**). Notably, the doubled dosage of **2d** resulted in an increased yield (65%) of **3ad**. Meanwhile, the disubstituted product **3ag**-di is predominantly generated (from 34% to 87%) when the dosage of **2g** is doubled.

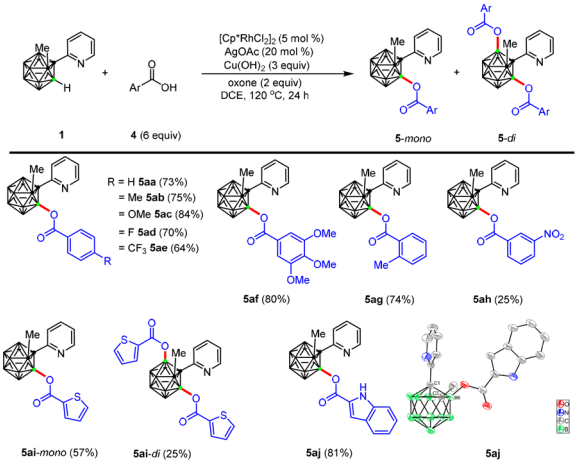
Scheme 2. Scope of Alkyl Carboxylic Acids[a]



[a]Isolated yields. [b]12 equiv of **2i** and 6 equiv of $Cu(OH)_2$. [c]When 12 equiv of **2d** was used, the yield of **3ad** increased to 65%. [d]When 12 equiv of **2g** was used, 87% of **3ag**-di was isolated.

Next, substrate groups with respect to aryl carboxylic acids were explored (Scheme 3). Benzoic acid (**4a**) gave a good yield of **5aa**. Neither electron-donating group (EDG) nor electron-withdrawing group (EWG) influenced the yield significantly (**5ab−ag**). A poor yield was gained (25%) when the *m*-nitro-

Scheme 3. Scope of Aryl Carboxylic Acids[a]



[a]Isolated yields.

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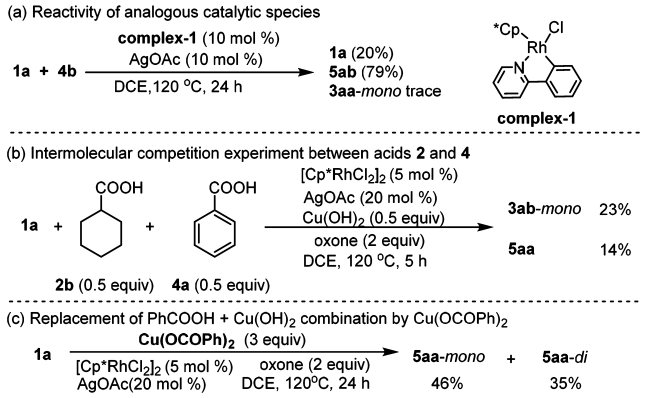
substituted substrate **4h** was used; this may result from partial inactivation of the catalyst. When the electron-rich aromatic heterocyclic rings were screened, good yields were obtained (**5ai**, **5aj**), despite the presence of a free N in indole ring.

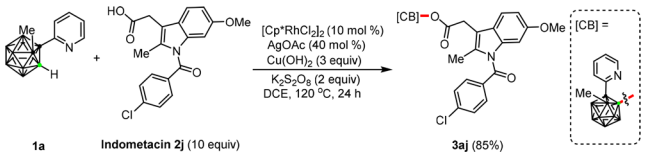
To gain insight into the mechanism of this B(3)−O coupling reaction, some control experiments were performed (Scheme 4). First, if 10 mol % of rhodium **complex-1**[39] was used, a

Scheme 4. Control Experiments



slightly lifted yield was obtained, which suggested that the N−Rh−B(3) complex might exist after ligand exchange between **1a** and 2-phenylpyridine. Next, the competition experiment displayed no significant difference of reactivity between acids **2b** and **4a**. Ultimately, when 3 equiv of $Cu(OH)_2$ and 6 equiv of benzoic acid combination was replaced with 3 equiv of benzoic copper, a higher total yield (81%, including **5aa**-di in 35% yield) was obtained. This demonstrates that $Cu(OCOR)_2$ are likely to be the actual active species. The proposed mechanism is described in the Supporting Information. With the recent advances of numerous C−H activation tactics, the increase of late-stage functionalization strategies for the rapid synthesis of functional substances such as pharmaceutical targets have emerged.[23a,40] We successfully assembled **1a** with indomethacin (**2j**) in a yield of 85% (**3aj**, Scheme 5). It might

Scheme 5. Emerging Synthetic Tools for Potential Carborane-Containing Pharmaceuticals



be concluded that other carboxylic acids in pharmaceuticals should also react under these conditions. Compound **3aj** and other similar products may possess potential bioactivity, which should be deeply developed.

In summary, we have developed efficient construction of a B(3)−O bond by the use of pyridyl-directed rhodium-catalyzed coupling conditions. The combination of inexpensive $Cu(OH)_2$ with commercially available carboxylic acids supplies low cost and abundant oxygen sources for B−H acyloxylation. Utilizing pyridyl as a directing group and Rh(III) as the catalyst, we realized selective and challenging B(3)−H (the most electron-deficient position on *o*-carborane) acyloxylation. With this novel B−O bond formation approach, a series of new-type pyridyl-containing carborane derivatives including potential pharmaceutical targets have been synthesized, and further research of their application in materials and biological tests is ongoing in this laboratory.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.7b02450.

Detailed experimental procedures, NMR spectra, and HRMS data (PDF)

X-ray crystallographic data (CIF)

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Notes

The authors declare no competing financial interest.

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