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Iridium Catalyzed Regioselective Cage Boron Alkenylation of *o*-Carboranes via Direct Cage B−H Activation

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Supporting Information

ABSTRACT: Iridium catalyzed alkyne hydroboration with *o*-carborane cage B−H has been achieved, leading to the formation of a series of 4-B-alkenylated-*o*-carborane derivatives in high yields with excellent regioselectivity via direct B−H bond activation. In this reaction the carboxy group is used as a traceless directing group, which is removed during a one-pot process. After the confirmation of a key intermediate, a possible mechanism is proposed, involving a tandem sequence of Ir-mediated B−H activation, alkyne insertion, protonation, and decarboxylation.

Carboranes have proved as useful basic units in boron neutron capture therapy agents,[1] in supramolecular design/materials,[2] and in coordination/organometallic chemistry,[3] which has drawn increasing interest in the selective functionalization of carboranes.[4] Although the methods of producing cage B−X (X = C, P, N, S, I, etc.) bond via cage B−H activation of boranes,[5] heteroboranes,[6] and metallacarboranes[7] are known, selective and straightforward boron substitution of *o*-carboranes is much less studied.[8] In contrast to the substitution at the cage-(3,6)boron (capitation reaction of nido-$C_2B_9H_{11}^{2-}$ with boron halides)[9] and cage-(8,9,10,12)boron (electrophilic substitution),[10] selective and direct cage-(4,5,7,11) boron substitutions are much more challenging, and the corresponding methodology is waiting for development.[11] In view of recent advances in transition metal catalyzed C−H functionalization,[12] transition metal catalyzed cage B−H functionalization of *o*-carboranes is very rare and only two examples have been reported to the best of our knowledge (Scheme 1),[13] though several stoichiometric reactions of transition metal mediated B−H derivatization of *o*-carboranes have been documented.[10,14]

To this end, we are interested in developing transition metal catalyzed selective cage B−H activation, in particular at B(4,5,7,11) positions, for the direct functionalization of *o*-carboranes. In general, low-valent transition metals preferentially activate cage B(3,6)-H bonds via oxidative addition,[13a,15] whereas the cage B(8,9,10,12)-H bonds favor electrophilic reactions.[10] To activate other cage B positions, a directing group is necessary. We selected carboxyl group as it can be easily introduced to the cage carbon and removed after reactions.

The initial reaction of 1-COOH-*o*-$C_2B_{10}H_{11}$ (**1a**) with diphenylacetylene (**2a**) in the presence of 5 mol % $[Cp^*RhCl_2]_2$ and 2 equiv of $Cu(OAc)_2$ in refluxing toluene gave the product 4-[PhCH═C(Ph)]-*o*-$C_2B_{10}H_{11}$ (**3a**) in 74% GC yield. We then screened various reaction conditions for such reaction using different catalysts and additives. The results were summarized in Table 1. Both Rh(III) and Ir(III) complexes showed catalytic activity. Polar solvent DMF only gave the decarboxylation product, *o*-carborane, and *o*-xylene (OX) resulted in lower yield (entries 2 and 3, Table 1). In the absence of −COOH, no reaction was observed (entry 4, Table 1). Lower catalyst loading or reaction temperature led to decreased yields (entries 1 vs 5, 9 vs 11, and 9 vs 12, Table 1). The additives played an important role in the formation of **3a**. The use of $Cu(OAc)_2$ and AgOAc as united additives offered much higher yields than the sole additive $Cu(OAc)_2$ or AgOAc (entries 8−10 vs 6−7, Table 1) due probably to the differences in the solubility. In view of **3a**'s yield, entry 9 in Table 1 was chosen as the optimal reaction condition.

A variety of alkynes were examined under the chosen optimal reaction conditions, and the results were compiled in Table 2. Electron-withdrawing groups on phenyl ring generally offered faster reaction rate and higher yields of **3** than those of electron-donating substituents (entries 2−6 vs 7−11, Table 2). Steric factors also played a crucial role in the formation of **3**. When the

Scheme 1. Transition-Metal Catalyzed Cage B−H Activation/Functionalization

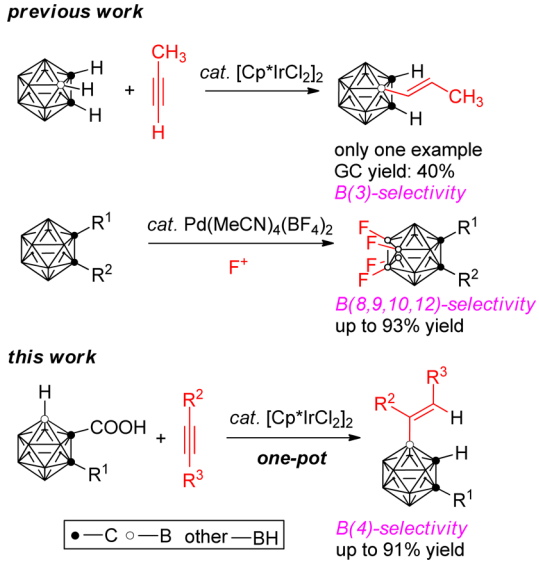

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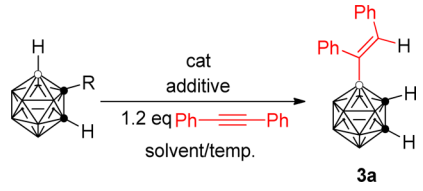
Table 1. Optimization of Reaction Conditions[a]

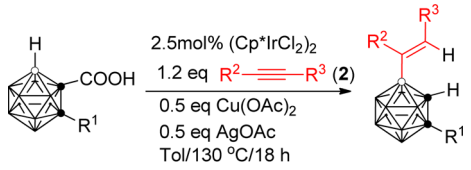


3a

entry	R	cat[b]	solvent	T (°C)	additive[c]	**3a** yield (%)[d]
1	CO_2H	5% [Rh]	PhMe	130	2 eq [Cu]	74
2	CO_2H	5% [Rh]	OX	140	2 eq [Cu]	46
3	CO_2H	5% [Rh]	DMF	130	2 eq [Cu]	*e*
4	H	5% [Rh]	PhMe	130	2 eq [Cu]	N.R.
5	CO_2H	2.5%[Rh]	PhMe	130	2 eq [Cu]	70
6	CO_2H	2.5% [Ir]	PhMe	130	2 eq [Cu]	81
7	CO_2H	2.5% [Ir]	PhMe	130	2 eq [Ag]	75
8	CO_2H	2.5% [Ir]	PhMe	130	1 eq [Cu] 1 eq [Ag]	93
9	CO_2H	2.5% [Ir]	PhMe	130	0.5 eq [Cu] 0.5 eq [Ag]	99
10	CO_2H	2.5% [Ir]	PhMe	130	0.25 eq [Cu] 0.25 eq [Ag]	93
11	CO_2H	1.5% [Ir]	PhMe	130	0.5 eq [Cu] 0.5 eq [Ag]	80
12	CO_2H	2.5% [Ir]	PhMe	110	0.5 eq [Cu] 0.5 eq [Ag]	90
13	CO_2H	2.5% [Ir]	PhMe	130	none	N.R.

[a]Reactions were conducted at 0.05 mmol scale in 0.5 mL of solvent in a sealed flask; OX = *o*-xylene. [b][Rh] = $[Cp^*RhCl_2]_2$; [Ir] = $[Cp^*IrCl_2]_2$. [c][Cu] = $Cu(OAc)_2$; [Ag] = AgOAc. [d]GC yield. [e]*o*-Carborane was the major product as confirmed by ^{11}B NMR spectra.

Table 2. Synthesis of Cage B(4)-Alkenylated *o*-Carboranes[a]



1 **3**

entry	R^1	R^2	R^3	yield (%)[b]
1	H	Ph	Ph	80 (**3a**)
2	H	4-$CH_3C_6H_4$	4-$CH_3C_6H_4$	82 (**3b**)
3	H	3-$CH_3C_6H_4$	3-$CH_3C_6H_4$	69[c] (**3c**)
4	H	2-$CH_3C_6H_4$	2-$CH_3C_6H_4$	45[c] (**3d**)
5	H	4-^{t}BuC_6H_4	4-^{t}BuC_6H_4	83[c] (**3e**)
6	H	4-^{i}PrC_6H_4	4-^{i}PrC_6H_4	78[c] (**3f**)
7	H	4-ClC_6H_4	4-ClC_6H_4	89 (**3g**)
8	H	3-ClC_6H_4	3-ClC_6H_4	86 (**3h**)
9	H	4-FC_6H_4	4-FC_6H_4	83 (**3i**)
10	H	4-$CF_3C_6H_4$	4-$CF_3C_6H_4$	91 (**3j**)
11	H	4-BrC_6H_4	4-BrC_6H_4	70 (**3k**)
12	H	4-$MeOC_6H_4$	4-$MeOC_6H_4$	80[c] (**3l**)
13	H	4-$MeSC_6H_4$	4-$MeSC_6H_4$	72[c] (**3m**)
14	H	4-MeO_2C $CH_2C_6H_4$	4-MeO_2C $CH_2C_6H_4$	65 (**3n**)
15	H	4-$MeO_2CC_6H_4$	4-$MeO_2CC_6H_4$	72 (**3o**)
16	H	thiophenyl	thiophenyl	65 (**3p**)
17	H	CH_3CH_2	Ph	9 (**3q**)[d]
18	H	CH_3CH_2	CH_3CH_2	trace[e]
19	Me	Ph	Ph	75 (**3s**)
20	$PhCH_2$	Ph	Ph	71 (**3t**)

[a]Reactions were conducted at 0.5 mmol scale in 10 mL of toluene at 130 °C in a sealed flask. [b]Isolated yield. [c]Heated for 48 h. [d]Another product, 1,4-[COOC(Ph)=C(Et)]-*o*-$C_2B_{10}H_{10}$ (**3′q**), was isolated in 12% yield. [e]A trace amount of target product was observed by GC.

methyl group on the phenyl ring was changed from ortho- to meta- to para-position, the isolated yield of **3** was increased from 45% to 69% to 82% (entries 2–4, Table 2). For heteroatom containing *p*-substituents such as −OMe, −SMe, $-CO_2Me$, and $-CH_2CO_2Me$, the products **3l**, **3m**, **3n**, and **3o** were isolated in relatively lower yields, probably owing to the interactions of the heteroatom with the metal center (entries 12–15, Table 2). This reaction was compatible with thiophenyl (**2p**), affording **3p** in 65% yield (entry 16, Table 2). Alkyne PhC≡CEt (**2q**) gave two products **3q** and 1,4-[COOC(Ph)=C(Et)]-*o*-$C_2B_{10}H_{10}$ (**3′q**) in only 9% and 12% isolated yields, respectively (entry 17, Table 2). For alkyl alkyne EtC≡CEt (**2r**), only trace product was observed from GC–MS, owing to its low reactivity (entry 18, Table 2). Effects of R^1 on reaction results were also examined. For $R^1 = CH_3$ and CH_2Ph, the corresponding products **3s** and **3t** were obtained in 75% and 71% isolated yields (entries 19 and 20, Table 2).

Compounds **3** were fully characterized by ^1H, ^{13}C, and ^{11}B NMR spectroscopy as well as high-resolution mass spectrometry. The molecular structures of **3a**, **3n**, and **3′q** were further confirmed by single-crystal X-ray analyses. Figure 1 shows the representative structures of **3a** and **3′q**.

To gain some insight into the reaction intermediate, an equimolar reaction of **1b** with $Cp^*Ir(OAc)_2$(DMSO) in toluene at room temperature was carried out, giving the iridacycle **B**(DMSO) in 80% yield (Scheme 2). It was noted that the complex was not isolable in the absence of DMSO. Single-crystal X-ray analyses clearly indicate that the cage B(4)-H bond has been activated with the Ir–B(4) distance of 2.129(7) Å.

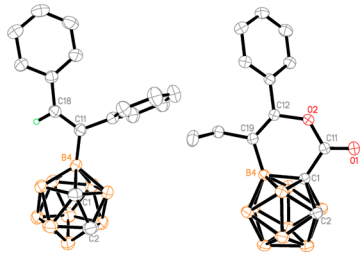


Figure 1. Molecular structures of **3a** (left) and **3′q** (right).

Complex **B**(DMSO) could indeed catalyze the reaction of **1b** with diphenylacetylene under the same condition to afford **3s** in 30% yield. The low activity may be ascribed to the presence of DMSO. However, under the above optimal reaction conditions, 1-COOH-2-CH_3-4-[(Ph)CH=C(Ph)]-$C_2B_{10}H_9$ underwent smooth decarboxylation to give **3s** in >99% GC yield (Scheme 3).

On the basis of the aforementioned experimental results, a possible reaction mechanism is proposed in Scheme 4. Acid–base reaction of **1** with in situ generated Ir(III) complex gives the intermediate **A**. Subsequent regioselective electrophilic attack at the more electron-rich cage B(4) site yields the intermediate **B**. Alkyne insertion into the Ir–B bond proceeds to produce the seven-membered iridacycle **C**. Protonation of **C** affords the intermediate **D** that undergoes decarboxylation to give final product **3**.[16c] Alternatively, reductive elimination of **C** generates

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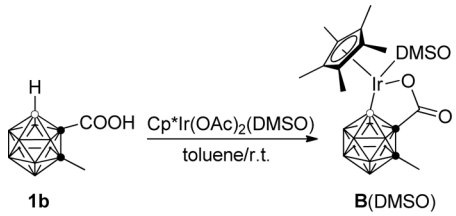
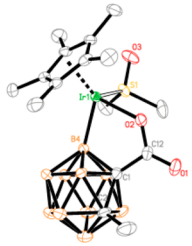
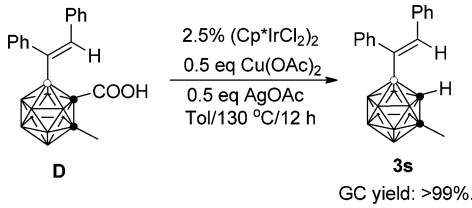
Scheme 2. Preparation of Intermediate B(DMSO)

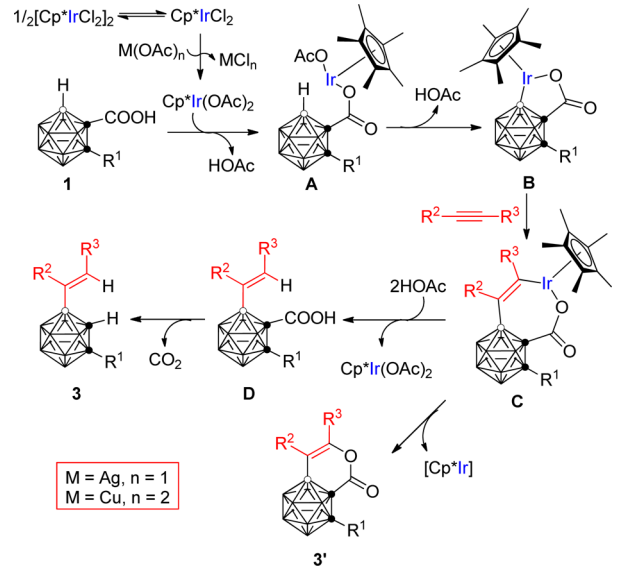




Scheme 3. Decarboxylation Reaction



Scheme 4. Proposed Reaction Mechanism



byproduct **3′** (in the case of **2q**)[16a,b] that is stable under the reaction conditions.

In summary, a regioselective and efficient Ir(III)-catalyzed alkenylation of cage B(4)-H of *o*-carboranes via direct B−H activation has been achieved with the help of a carboxyl group, which is later removed by decarboxylation. This serves as the first methodology for the selective generation of a series of B(4)-alkenylated-*o*-carborane derivatives in a simple one-pot process. This work may also shed some light on developing new methodologies for the functionalization of carboranes at 4,5,7,11-boron positions in a catalytic manner.

■ ASSOCIATED CONTENT

Supporting Information

Detailed experimental procedures, complete characterization data, and X-ray data in CIF format for **3a**, **3n**, **3q′**, and **B**(DMSO). This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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