B–H Activation

International Edition: DOI: 10.1002/anie.201605880
German Edition: DOI: 10.1002/ange.201605880

Rhodium-Catalyzed Regioselective Hydroxylation of Cage B–H Bonds of *o*-Carboranes with O_2 or Air

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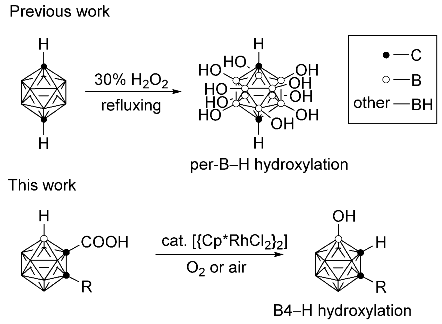
Dedicated to Prof. Thomas C. W. Mak on the occasion of his 80th birthday

Abstract: *A rhodium-catalyzed hydroxylation of a cage B4–H bond in o-carboranes with either O_2 or air as the oxygen source is described, and serves as a new methodology for the regioselective generation of a series of 4-OH-o-carboranes in a one-pot process. The use of either O_2 or air as both the oxidant and the oxygen source makes this protocol very environmentally friendly and practical.*

Carboranes are a class of boron hydride clusters in which one or more of the BH vertices are replaced by CH units, and can be viewed as three-dimensional analogues to benzene.[1] They are finding many applications in medicine as boron neutron capture therapy agents,[2] in supramolecular design as building blocks,[3] and in coordination/organometallic chemistry as versatile ligands.[4] As a class of electronically useful molecules, carboranes have recently been incorporated into π-conjugated systems for applications in optoelectronic functional materials.[5] As a result, considerable attention has been directed towards the functionalization of carborane molecules. However, the unique structures of carboranes make the derivatization difficult, thereby limiting their application scope. Thus it is eagerly desired to develop new methodologies for the selective functionalization of carboranes.

It has been well-documented that B–H bonds in organoboranes are generally sensitive toward water,[6] thus leading to the formation of a large class of boronic/borinic acids which are finding broad applications in materials science, organic synthesis, and medicine.[7] In sharp contrast, those in carboranes are much less reactive.[1,8] They can, however, be activated by transition metals[9] or subjected to electrophilic substitution reactions,[10] similar to the C–H bonds in benzenes. For example, perhydroxylation of B–H bonds in $B_{12}H_{12}^{2-}$, $CB_{11}H_{12}^{-}$, and *p*-$C_2B_{10}H_{12}$ has been achieved by refluxing a 30 % hydrogen peroxide solution of these clusters (Scheme 1),[11] though regioselective hydroxylation of cage B–H bonds of these icosahedron boron clusters still remains elusive.[12] In contrast, transition-metal-catalyzed direct cage B–H hydroxylation of carboranes has not been reported thus far.[1,8]



Scheme 1. Cage B–H hydroxylation of carboranes.

Inspired by transition-metal catalyzed C–H hydroxylation of benzenes[13] and recent works on catalytic regioselective alkenylation,[14] arylation,[15] and alkynylation[16] of cage B–H bonds in *o*-carboranes from our group and others,[17,18] we are interested in developing catalytic and regioselective hydroxylation of cage B–H bond in *o*-carboranes using environmentally benign molecular oxygen as a reagent.

We accidently discovered a rhodium(III)-catalyzed B4-hydroxylation reaction by refluxing a toluene solution of 1-COOH-2-CH_3-*o*-$C_2B_{10}H_{10}$ (**1a**) in the presence of 5 mol % [{Cp*RhCl$_2$}$_2$] and 2 equivalents of KOAc open to the air. The significance of the present work is threefold: 1) O_2 or air is employed as a reagent and the sole oxidant, thus making this method very environmentally benign and practical; 2) to the best of our knowledge, this is the first example of rhodium-catalyzed hydroxylation with molecular oxygen, although rhodium-promoted cage B–H[18a,b,g] or organic C–H[19] functionalization has been extensively investigated; and 3) this also represents the first example of catalytic cage B–H hydroxylation of *o*-carboranes.

In the presence of 5 mol % [{Cp*RhCl$_2$}$_2$] and 2 equivalents of KOAc, a toluene solution of 1-COOH-2-CH_3-*o*-$C_2B_{10}H_{10}$ (**1a**) was heated at 95 °C in the open air for 36 hours to afford the B4-hydroxylated product **2a** in 50 % yield (entry 1, Table 1). The use of O_2 in place of air led to the isolation of **2a** in 82 % yield (entry 2). Shortening the reaction time to 24 hours resulted in a decreased yield (entry 3). Replacement of toluene by chlorobenzene or 1,2-dichloroethane gave **2a** in much lower yields (entries 4 and 5). Screening for base additives proved that 2 equivalents of KOAc was the optimal choice (see Table S1 in the Supporting Information). Higher or lower reaction temperatures did not enhance the yield of **2a** (entries 6 and 7). Control experiments showed that no reaction was observed in the absence of either

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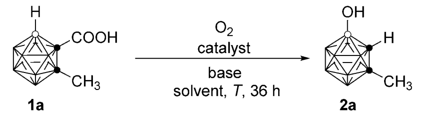
Supporting information for this article can be found under:
http://dx.doi.org/10.1002/anie.201605880.

Table 1: Optimization of reaction conditions.[a]



1a **2a**

Entry	Catalyst (mol%)	Base (equiv)	Solvent	T [°C]	Yield [%][b]
1[c]	[{Cp*RhCl$_2$}$_2$] (5)	KOAc (2)	toluene	95	50
2	[{Cp*RhCl$_2$}$_2$] (5)	KOAc (2)	toluene	95	82
3[d]	[{Cp*RhCl$_2$}$_2$] (5)	KOAc (2)	toluene	95	76
4	[{Cp*RhCl$_2$}$_2$] (5)	KOAc (2)	PhCl	95	46
5	[{Cp*RhCl$_2$}$_2$] (5)	KOAc (2)	DCE	95	12
6	[{Cp*RhCl$_2$}$_2$] (5)	KOAc (2)	toluene	85	70
7	[{Cp*RhCl$_2$}$_2$] (5)	KOAc (2)	toluene	105	71
8	[{Cp*RhCl$_2$}$_2$] (2.5)	KOAc (2)	toluene	95	80
9[e]	[{Cp*RhCl$_2$}$_2$] (2.5)	KOAc (2)	toluene	95	N.R.
10	–	KOAc (2)	toluene	95	N.R.
11	[{Cp*IrCl$_2$}$_2$] (5)	KOAc (2)	toluene	95	28
12	Pd(OAc)$_2$ (10)	KOAc (2)	toluene	95	trace

[a] Reactions were conducted on 0.05 mmol scale in 2 mL of solvents in a closed flask. [b] Yield of isolated product. [c] The reaction was carried out in the open air. [d] Reaction time was 24 h. [e] **1a** was replaced with 1-methyl-*o*-carborane. Cp* = C_5Me_5.

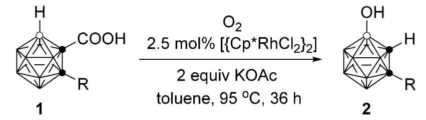
the directing group COOH or rhodium catalyst (entries 9 and 10). Lowering the catalyst loading to 2.5 mol% just slightly affected the yield of **2a** (entry 8). Other transition metals offered poor results (entries 11 and 12). Thus, the parameters in entry 8 in Table 1 were chosen as the optimal reaction conditions.

Under such optimized reaction conditions, the scope of this reaction was investigated. Alkyl substituents at the cage C2 gave the B4-hydroxylated products **2** in 70–80% yields upon isolation, whereas benzyl groups at the same position afforded only 40–45% yields of **2** (**2a–e** and **2q–s** vs. **2g–i**; Table 2). Electron-donating groups on the phenyl ring of styryl groups generally offered slightly higher yields of **2** than those with electron-withdrawing substituents (**2k–n** vs. **2o,p**). This reaction was tolerant of chloro, fluoro, and methoxy groups, which could be utilized for further synthetic elaboration (**2n–p**). Oxygen-containing substituents, **1n** and **1s**, reacted smoothly to the corresponding give **2n** and **2s** in 72 and 73% yields, respectively. For R = TMS, the desilylation product **2f** was isolated in 30% yield. The cage boron substituted substrate 1-COOH-2-Me-9,12-Me$_2$-*o*-$C_2B_{10}H_8$ (**1t**) was also examined, thus resulting in the formation of 2-Me-4-OH-9,12-Me$_2$-*o*-$C_2B_{10}H_8$ (**2t**) in 49% yield (see page S15).

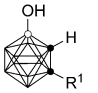
To illustrate the synthetic utility of the resultant B4-hydroxylated carborane derivatives, several transformations of **2a** are illustrated in Scheme 2. The OH group in **2a** was conveniently converted into OTf for further derivatization. In contrast, several carborane incorporated esters and ethers were also easily prepared from **2a**.

Compounds **2** and **3a–6a** were fully characterized by ^{1}H, ^{13}C, and ^{11}B NMR spectroscopy as well as high-resolution mass spectrometry. The molecular structures of **2b** and **2e** were further confirmed by single-crystal X-ray analyses (see Figures S1 and S2).

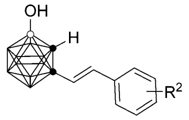
Table 2: Synthesis of cage B4-hydroxylated-*o*-carboranes.[a]



1 **2**

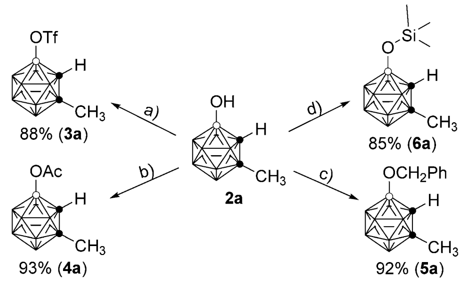


R^1 = Me, 80% (61%)[b] (**2a**)
Et, 71% (**2b**)
*n*Pr, 73% (**2c**)
*n*Bu, 74% (**2d**)
*i*Pr, 74% (**2e**)
TMS, 30% (**2f**)[c,d]
benzyl, 40% (**2g**)[c]
4-CH$_3$-benzyl, 44%(**2h**)[c]
4-Cl-benzyl, 45% (**2i**)[c]
cyclopentyl, 73% (**2q**)
cyclohexyl, 70% (**2r**)
2-methoxy ethyl, 73% (**2s**)



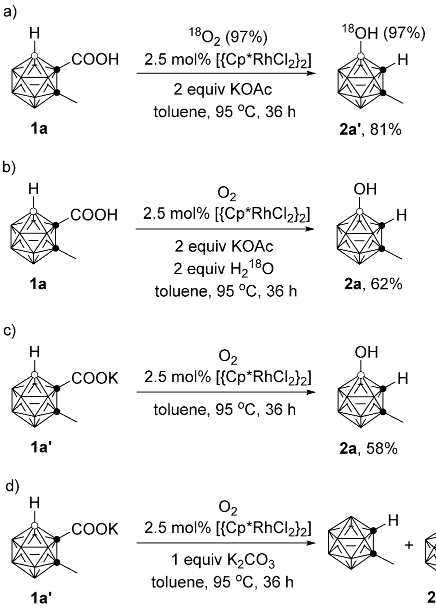
R^2 = H, 66% (**2j**)[c]
o-Me, 65% (**2k**)[c]
m-Me, 70% (**2l**)[c]
p-Me, 70% (**2m**)[c]
p-OMe, 72% (**2n**)[c]
p-Cl, 64% (**2o**)[c]
p-F, 64% (**2p**)[c]

[a] Reactions were conducted on 0.2 mmol scale in 5 mL of toluene at 95 °C in a closed flask for 36 h (yield is that of isolated product). [b] Air instead of O_2. [c] 5 mol% [{Cp*RhCl$_2$}$_2$] was loaded. [d] TMS was removed after work up.



Scheme 2. Transformations of **2a**: a) Tf$_2$O, pyridine, DCM, RT, 1 h; b) Ac$_2$O, DMAP, toluene, RT, 12 h; c) PhCH$_2$Br, K$_2$CO$_3$, CH$_3$CN, 90 °C, 12 h; d) TMSCl, Et$_3$N, DCM, RT, 12 h. DCM = dichloromethane, DMAP = 4-dimethylaminopyridine, TMS = trimethylsilyl.

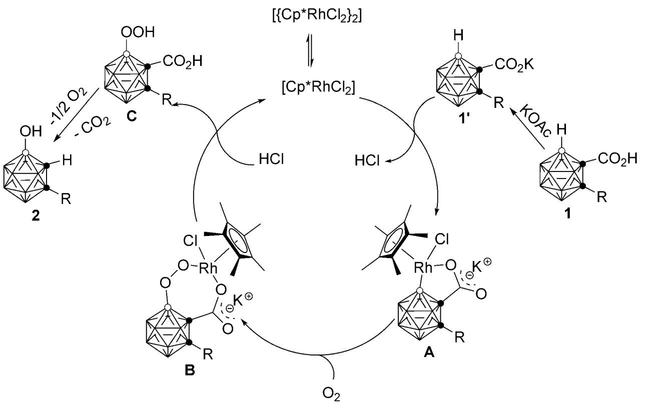
Preliminary mechanistic studies were carried out to shed some light on this hydroxylation pathway. Under the optimal reaction conditions, reaction of **1a** with $^{18}O_2$ resulted in the formation of the ^{18}O-labled product **2a′** in 81% yield with high fidelity, and proved that the oxygen atom in the hydroxy group originates from molecular oxygen (Scheme 3a; determined by HRMS. See the Supporting Information). Meanwhile, the experimental results in the presence of 2 equivalents of $H_2{}^{18}O$ ruled out oxygen incorporation from H_2O (Scheme 3b). In contrast, using 1-COOK-2-CH$_3$-*o*-$C_2B_{10}H_{10}$ (**1a′**) as the substrate, the yield of **2a** significantly dropped to 58% (Scheme 3c). If 1 equivalent of K_2CO_3 was added to the reaction shown in Scheme 3d to remove the in situ generated acid in the reaction system, only trace amounts of **2a** were observed by GC-MS with decarboxylated species 1-CH$_3$-*o*-$C_2B_{10}H_{11}$ as the major product (Scheme 3d). These control experiments suggested the importance of acid in this reaction.



Scheme 3. Control experiments.

On the basis of the aforementioned experimental results and our previous work of iridium-catalyzed alkenylation of *o*-carboranes,[14a] a possible mechanism is proposed for the present catalytic reaction (Scheme 4). Acid-base reaction of **1** with KOAc gives the potassium salt **1′**.[20] Coordination of the oxygen atom of **1′** to the rhodium(III) center, followed by regioselective electrophilic attack at the more electron-rich cage B4 site generates the intermediate **A**.[14,10f] It is proposed that oxygen insertion into the Rh−B bond proceeds to produce the seven-membered rhodocycle **B**.[21] Protonation of **B** affords the peroxy species **C** and regenerates the rhodium(III) catalyst. **C** undergoes decomposition and decarboxylation to give the final product **2**. The formation of **B** was observed by MALDI-TOF MS (see the Supporting Information), and verified by control experiments using $^{18}O_2$.

In summary, a regioselective and efficient rhodium(III)-catalyzed hydroxylation of cage B4−H of *o*-carboranes by direct B−H activation has been achieved for the first time, and molecular oxygen is employed as a reagent and the sole oxidant. This reaction serves as a new methodology for the selective preparation of a series of 4-hydroxy-*o*-carborane derivatives in an environmentally benign and simple one-pot process. This work can also offer useful references for selective hydroxylation of B−H bonds with O_2 in other boron clusters.



Scheme 4. Proposed reaction mechanism.

Experimental Section

o-Carboranyl monocarboxylic acid **1** (0.20 mmol), [{Cp*RhCl$_2$}$_2$] (2.5 mol%, 0.005 mmol), and KOAc (2 equiv, 0.40 mmol) were mixed in toluene (5 mL). After the reaction mixture was cooled to −78 °C, the reaction tube was evacuated and back-filled with O_2 (3 times, balloon). The tube was closed when the temperature was warmed up to room temperature. The resulting mixture was stirred at 95 °C for 36 h. After hydrolysis with water (10 mL) and extraction with diethyl ether (10 mL × 3), the organic solutions were combined and concentrated to dryness in vacuo. The residue was subjected to flash column chromatography on silica gel (230–400 mesh) using *n*-hexane and ethyl acetate (10:1) as the eluent to give the product **2**.

Acknowledgments

This work was supported by grants from the Research Grants Council of The Hong Kong Special Administration Region (Project No. 14304115) and the Vice-Chancellor's (CUHK) Discretionary Fund.

Keywords: B−H activation · carboranes · homogeneous catalysis · hydroxylation · rhodium

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Received: June 17, 2016
Revised: August 8, 2016

Communications

B−H Activation

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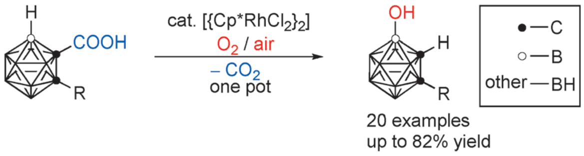
Rhodium-Catalyzed Regioselective Hydroxylation of Cage B−H Bonds of *o*-Carboranes with O_2 or Air



Cage decorations: The title reaction of a cage B4−H bond in *o*-carboranes with either O_2 or air as the oxygen source serves as a new method for the regioselective generation of a series of 4-OH-*o*-carboranes in a one-pot process. The use of either O_2 or air as both the oxidant and the oxygen source makes this protocol environmentally friendly and practical. $Cp^* = C_5Me_5$.