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A facile approach for the synthesis of *nido*-carborane fused oxazoles *via* one pot deboronation/cyclization of 9-amide-*o*-carboranes†

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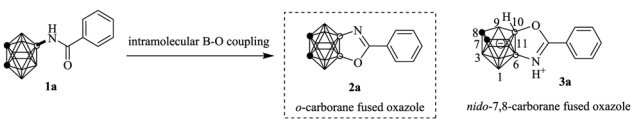
A one pot deboronation/cyclization of 9-amide-*o*-carboranes for the synthesis of *nido*-7,8-carborane fused oxazole by cooperation of $Pd(OAc)_2$, AgOAc and K_2CO_3 has been developed. A plausible mechanism involving an amide directed electrophilic palladation of the B–H bond and deboronation/cyclization process was proposed based on the successful isolation and structural characterization of the key deboronated intermediate.

Carboranes are a class of boron hydride clusters and have extensive applications in functional materials,[1] supramolecular chemistry,[2] coordination chemistry[3] and boron neutron capture therapy (BNCT).[4] Therefore, synthesis of carborane derivatives with diverse functional groups anchored to the cage carbon and boron is an important topic, which would offer a platform to explore the uncovered properties and applications of carborane derivatives with novel structures. In recent years, the transition metal catalyzed B–H activation for regioselective boron functionalization of carboranes has gained much advancement.[5] This succinct synthetic strategy for direct functionalization of B–H bonds offers an efficient protocol for the synthesis of various kinds of carborane derivatives, which are difficult to synthesize by classic synthetic methods.

Benzoxazole is a key structural feature of a large number of biologically active natural products and pharmaceutical compounds. Besides the traditional condensation of 2-aminophenol with carboxylic acid or aldehyde, the copper-catalyzed intramolecular *o*-arylation or intermolecular domino annulation of *o*-arylhalides[6] for the synthesis of benzoxazoles has been developed as a more efficient and economical approach. Inspired by the promising application of carborane derivatives in BNCT, we envisioned introduction of the oxazole unit into carborane *via* intramolecular cyclization of amide *via* oxidative B–O coupling, which would lead to a class of previously unavailable three dimensional carborane fused oxazoles[7] (Scheme 1).

To initiate our work, 9-benzamide-*o*-carborane (**1a**), which was synthesized according to Hawthorne's procedure,[8] was selected as the model substrate to screen the conditions. After many efforts, we could not obtain the desired *o*-carborane fused oxazole (**2a**) under oxidative conditions. However, when 1 equivalent of K_2CO_3 was loaded with 10 mol% $Pd(OAc)_2$ and 2 equivalents of AgOAc in CH_3CN at 80 °C for 24 h, we found that such cyclization could occur along with deboronation of B(3), and gave the *nido*-7,8-carborane fused oxazole (**3a**) with 52% yield. Its exact structure was fully characterized using ^1H, ^{13}C and ^{11}B NMR spectroscopy as well as X-ray crystallographic analysis,[9] and the B–O bond was formed on B(10) (Fig. 1).

Due to the significant applications of *nido*-7,8-carboranes in the synthesis of diverse metallacarboranes as novel catalysts,[10] and for use in nuclear medicine and diagnosis of cancer,[11] we decided to further optimize the conditions and the results are summarized in Table 1. As we can see dioxane was more favorable for this transformation (entries 1–7), and the desired



Scheme 1 Strategy for synthesis of carborane fused oxazoles.

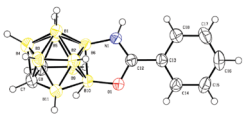


Fig. 1 Crystal structure of *nido*-7,8-carborane fused oxazole (**3a**).

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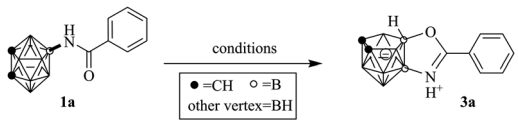
† Electronic supplementary information (ESI) available: ^1H, $^1H\{^{11}B\}$, ^{13}C, $^{11}B\{^1H\}$ and ^{11}B NMR spectra, crystallographic data for **3a**, **3s-10**, **3s-11**, **4**(Cs^+) and **3q**. CCDC 1852797, 1852820, 1852840, 1852837 and 1852798. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c8cc07728b

Table 1 Optimized conditions for deboronation/cyclization of 9-benzamide-*o*-carborane[a]



1a 3a

Entry	$Pd(OAc)_2$	AgOAc	Base	Solvent	Yield[b]
1	10 mol%	2 eq.	K_2CO_3	CH_3CN[c]	52
2	10 mol%	2 eq.	K_2CO_3	Toluene	16
3	10 mol%	2 eq.	K_2CO_3	THF[c]	29
4	10 mol%	2 eq.	K_2CO_3	Dioxane	93
5	10 mol%	2 eq.	K_2CO_3	DCE[c]	12
6	10 mol%	2 eq.	Cs_2CO_3	Dioxane	67
7	10 mol%	2 eq.	Na_2CO_3	Dioxane	10
8	—	2 eq.	K_2CO_3	Dioxane[d]	44
9	10 mol%	—	K_2CO_3	Dioxane[e]	20
10	10 mol%	1 eq.	K_2CO_3	Dioxane	85
11	5 mol%	2 eq.	K_2CO_3	Dioxane	70

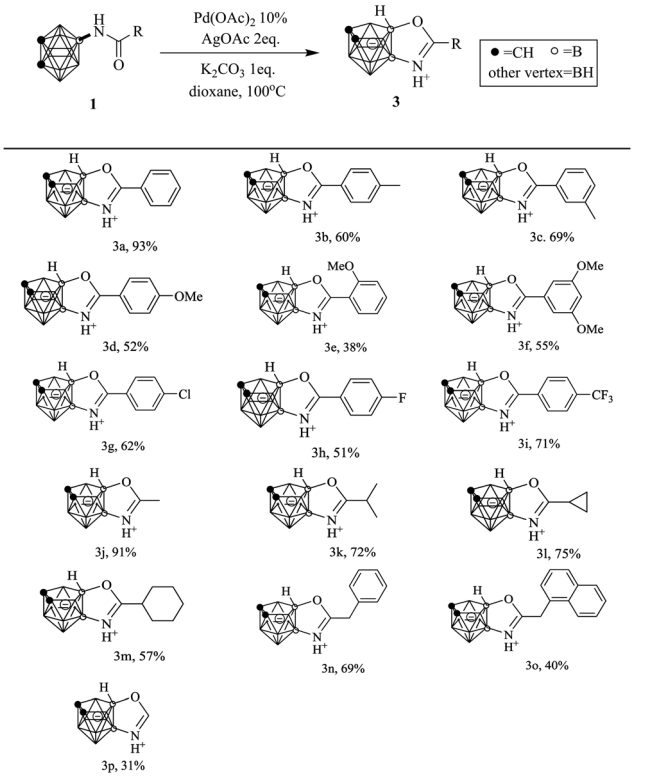
[a] Unless noted otherwise, all reactions were carried out using 0.1 mmol of **1a** and 1 equivalent of base in 1 mL solvent at 100 °C for 24 h under an argon atmosphere. [b] Isolated yields. [c] Reacted at 80 °C. [d] Reacted for 48 h. [e] Reacted for 36 h.

product could be obtained in 93% yield (entry 4). Control experiments demonstrated that when the reaction was carried out without $Pd(OAc)_2$ or AgOAc, the transformation proceeded sluggishly and gave the expected product with 44% and 20% yields, respectively (entries 8 and 9). Additionally, the yields decreased slightly upon lowering the loading amount of $Pd(OAc)_2$ or AgOAc (entries 10 and 11).

Under the optimized conditions (Table 1, entry 4), the scope of 9-amide-*o*-carboranes was then examined. As can be seen from Table 2, the benzamides substituted with electron-donating or electron-withdrawing groups were all compatible with this transformation, and gave the corresponding products with moderate to good yields (**3a–3d**, **3f–3i**). However, when 9-(2-methoxy-benzamide)-*o*-carborane was subjected to the standard conditions, the desired product was only afforded with 38% yield (**3e**). These results indicated that the steric effect of phenyl has a distinct influence on the cyclization event. Subsequently, 9-alkylamide-*o*-carboranes substituted with acyclic or cyclic groups were also examined, and the expected products were obtained in moderate to good yields (**3j–3o**). Additionally, 9-formamide-*o*-carborane was also compatible with this transformation, and gave the desired product in a slightly lower yield (**3p**).

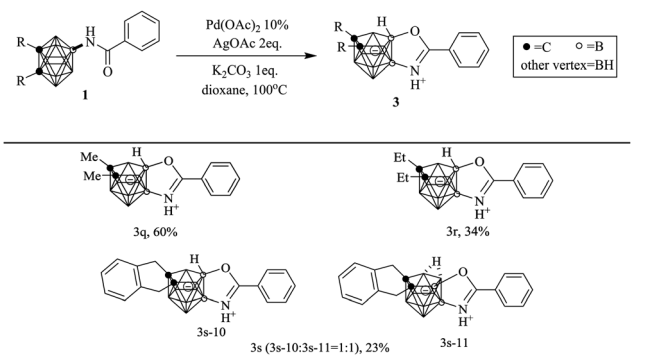
Subsequently, C_{cage}-substituted 9-benzamide-*o*-carboranes were further explored (Table 3). For 1,2-Me_2-9-benzamide-*o*-carborane (**1q**), the corresponding product could be formed in 60% yield (**3q**). However, when ethyl was introduced into substrate **1r**, the transformation proceeded very sluggishly and only gave the desired **3r** in 34% yield. Surprisingly, in the ^1H NMR spectrum, there was a bridging hydrogen signal at about −2.4 ppm, which indicated that except for the expected **3r**, an isomer was also afforded by formation of a B(11)–O or B(9)–O bond, and the isomer ratio was about 10 : 1 as determined by GC analysis. From these results, we concluded that

Table 2 Synthesis of *nido*-7,8-carborane fused oxazoles[a,b]



[a] All reactions were carried out on a 0.1 mmol scale in 1 mL dioxane at 100 °C for 24–48 h under an argon atmosphere. [b] Isolated yields.

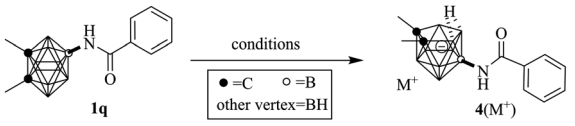
Table 3 Synthesis of *nido*-7,8-carborane fused oxazoles[ab]



[a] All reactions were carried out on a 0.1 mmol scale in 1 mL dioxane at 100 °C for 48 h under an argon atmosphere. [b] Isolated yields.

this might be caused by the electron-donating effect of alkyls as well as their steric effect. To validate our assumption, **1s** with a stronger electron-donating and bulky group was further examined. Just as we expected, **3s-10** and **3s-11** were isolated in a 1 : 1 (**3s**) ratio, and X-ray crystallographic analysis further confirmed that the B–O bond was formed at B(10) and B(11), respectively (ESI,† Fig. S1 and S2).

To understand the mechanism of the deboronation/cyclization reaction, some control experiments have been carried out.



a: $Pd(OAc)_2$ 10%, Cs_2CO_3 1eq., dioxane, 100°C, 12h, **4**(Cs^+) 65% yield
b: Cs_2CO_3 1eq., dioxane, 100°C, 48h, **4**(Cs^+) 11% yield (22% conversion of 1q)
c: K_2CO_3 1eq., dioxane, 100°C, 48h, **4**(K^+) trace
d: $Pd(OAc)_2$ 10%, KOAc 2eq., dioxane, 100°C, 6h, **4**(K^+) 92% yield

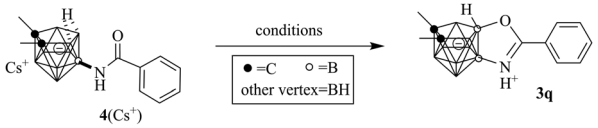
Scheme 2 Conditions for deboronation of **1q**.

As shown in Scheme 2, the deboronation reaction of **1q** was completed with Cs_2CO_3 within 12 hours and gave the intermediate **4**(Cs^+) in 65% yield (a), and its exact structure was confirmed by X-ray crystallographic analysis (ESI,† Fig. S3), meanwhile, the product **3q** was also formed in about 5% yield. However, the deboronation reaction proceeded very sluggishly in the absence of $Pd(OAc)_2$ (b). These results indicated the coordination effect of $Pd(OAc)_2$ with amide played an important role in promoting the deboronation. Interestingly, when K_2CO_3 was used, the deboronation hardly occurred (c), however, the intermediate **4**(K^+) could be detected by GC analysis under standard conditions (Table 1, entry 4). Furthermore, the deboronation could proceed effectively when KOAc was loaded (d). These results demonstrated that K_2CO_3 with weak basicity could not achieve the complete deboronation of B(3), and the AcO^- of AgOAc plays an important role in promoting the deboronation reaction.[12]

Subsequently, the cyclization of intermediate **4**(Cs^+) was performed with 2 equivalents of AgOAc in dioxane. As shown in Scheme 3, the desired product **3q** could be obtained in 84% yield after 5 h (a). However, when $Pd(OAc)_2$ was loaded, the yield slightly decreased (b). Combining the results of these control experimental and the results in Table 1 (entries 4, 8 and 9), we consider that this one pot deboronation/cyclization reaction should be promoted by the cooperative effect of $Pd(OAc)_2$, AgOAc and K_2CO_3, and either is indispensable to facilitate this one pot transformation.

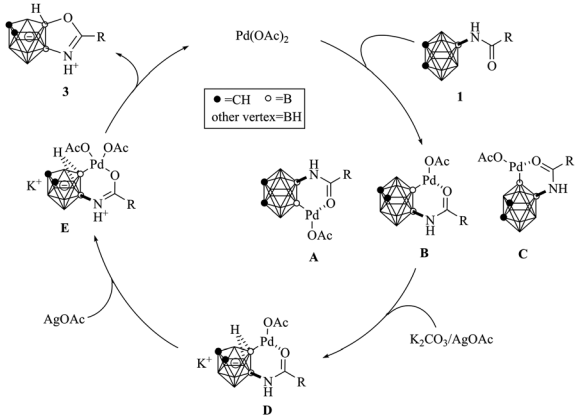
In the course of preparing our work, Duttwyler and coworkers disclosed an oxidative cyclization of *closo*-dodecaborate amides for synthesis of *closo*-dodecaborate dianion fused oxazoles mediated by iodobenzene diacetate (PIDA).[7i] Therefore, the effect of PIDA was then examined in our work (ESI,† Schemes S1 and S2). Experimental results demonstrated that PIDA displayed poor activity for this deboronation/cyclization transformation, which indicated a different cyclization mechanism.

Pioneering works demonstrated that the base induced deboronation of B-substituted *o*-carboranes is different from



a: AgOAc 2eq., dioxane, 100°C, 5h, 84% yield
b: $Pd(OAc)_2$ 10%, AgOAc 2eq., dioxane, 100°C, 5h, 75 % yield

Scheme 3 Conditions for cyclization of intermediate **4**(Cs^+).



Scheme 4 Plausible mechanism for synthesis *nido*-7,8-carborane fused oxazole by a one pot deboronation/cyclization process.

the C_{cage}-substituted ones, which is largely affected by the electron withdrawing capacity and location of the substituent.[13] For 9-amide-*o*-carboranes, we consider that the amide with electron withdrawing effect decorated on B(9) would change the charge distribution of the adjacent B(12), B(8,10) and B(4,5). Therefore, the Mulliken charge analysis of 9-benzamide-*o*-carborane was performed using Dmol3 in the Materials Studio (ESI,† Table S1). The calculated results demonstrate that the charge of B(8,10,12) was much more negative than that in *o*-carborane, and indicated that these B–H bonds were more favorable for electrophilic palladation to form intermediates **A** and **B** guided by the amide (Scheme 4). Based on the experimental results, it seems that intermediate **B** formed with B(8)–H would be the more favorable intermediate, which could facilitate subsequent deboronation of B(3) to form intermediate **D** by cooperation of AgOAc and K_2CO_3.[12] These results might be ascribed to the more electron positive nature of B(3) induced in intermediate **B**. Then, Pd(IV) intermediate **E** would be formed by oxidation and tautomerization of amide. Subsequently, the desired *nido*-7,8-carborane fused oxazole would be generated after reductive elimination and release Pd(II) for the next catalytic cycle. Additionally, for the C_{cage}-substituted products (**3r** and **3s**), the formation of B(11)–O bond indicates that B(4)-Pd intermediate **C** might also be formed depending on the electron and steric effect of substituents on C_{cage}, which might arise from activation of the more polarized B(4)–H bond (ESI,† Table S1).[5s]

In conclusion, a facile approach for synthesis of *nido*-7,8-carborane fused oxazole by cooperation of $Pd(OAc)_2$, AgOAc and K_2CO_3 from 9-amide-*o*-carborane was developed for the first time. A series of *nido*-7,8-carborane fused oxazoles anchored with diverse active groups have been synthesized in moderate to good yields, which opened a window for the synthesis of novel kinds of metallacarboranes and BNCT reagents. A plausible mechanism involving amide directed electrophilic palladation of the B–H bond and a deboronation/cyclization process was proposed. This work represents a novel strategy for construction of carborane fused heterocycles, which has important value in the design and synthesis of heterocycles in carborane chemistry.

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Conflicts of interest

There are no conflicts to declare.

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