



Palladium catalyzed/counter ion tuned selective methylation of *o*-carboranes

Ke Cao^{a,*}, Cai-Yan Zhang^a, Tao-Tao Xu^a, Ji Wu^a, Li-Fang Ding^a, Linhai Jiang^b, Junxiao Yang^a

^a State Key Laboratory of Environment-friendly Energy Materials & School of Material Science and Engineering, Southwest University of Science and Technology, 59 Qinglong Road, Mianyang, Sichuan, PR China

^b Instrumental Analysis Center, Shenzhen University, Xili Campus, PR China

ARTICLE INFO

Article history:

Received 6 July 2019

Received in revised form

20 September 2019

Accepted 25 September 2019

Available online 26 September 2019

Keywords:

o-carborane

B–H activation

Methylation

Selectivity

ABSTRACT

The palladium catalyzed/counter ion tuned selective methylation of 9-amide-*o*-carboranes on B(4) and B(12) has been developed, and a series of *o*-carborane derivatives decorated with various groups have been synthesized with moderate yields. The in situ formed palladium species via counter ion exchange was proposed for the tunable B–H activation.

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1. Introduction

Carboranes are a class of carbon-boron molecular clusters with three dimensional aromaticity analogues to benzene, which have proved to be important building blocks in functional materials [1–5], coordination chemistry [6–13] as well as pharmaceuticals [14–21]. Therefore, developing methodologies for selective functionalization of cage carbon and cage boron has attracting much interest from chemists. However, as the 10 B–H bonds of *o*-carborane are not fully equal and have slight difference in reactivity [22,23], which makes the selective boron functionalization more difficult and complicated. In recent years, by utilizing the transition metal catalyzed B–H activation for regioselective boron functionalization of *o*-carborane, especially for arylation, has achieved much advancement [24–46]. This succinct synthetic strategy has proved to be a powerful tool in controlling the selectivity in B–H functionalization. However, the selective alkylation of *o*-carborane via B–H activation is still an intricate subject as the alkyl halides are liable to β -H elimination prior to oxidative addition to transition metal, especially for palladium catalysts.

For direct alkylation of B–H bonds in *o*-carborane, the AlCl_3 promoted Friedel-Crafts reaction has been the well known transformation for decades [47–49]. However, the insurmountable drawback is the uncontrollable selectivity and multiple alkylation. Recently, Xie and coworkers have developed a selective nucleophilic alkylation of B–H bond with Grignard reagents by adjusting the electron density and steric effect of B–H vertex via introducing electron-withdrawing groups on cage carbon, which has proved to be an effective strategy for regioselective alkylation of *o*-carboranes on B(4), B(3,6) and B(9) [50,51] (Scheme 1). In connection with our recent work on amide reversed/directed selective arylation on B(4) based on the polarized B(4)-H and B(5)-H bonds [42], we envisioned to exploring a selective alkylation of *o*-carboranes via B–H activation.

2. Material and methods

2.1. Generals

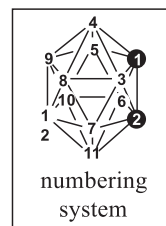
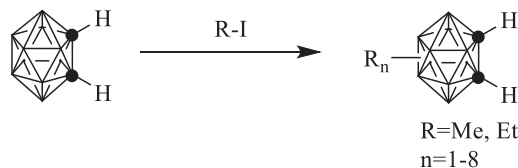
1a–1n were synthesized according to literature methods [52–56]. Other materials were purchased from Acros, J&K and Aladdin, and used as received unless otherwise specified. All reactions under standard conditions were monitored by thin-layer chromatography (TLC) on gel F254 plates. The silica gel (200–300

* Corresponding author.

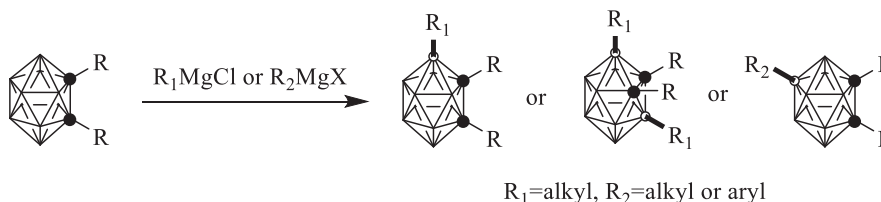
E-mail address: caoke@swust.edu.cn (K. Cao).

Previous Work

a) Electrophilic B-H Substitution

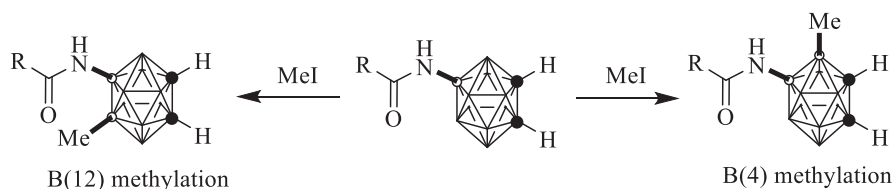


b) Nucleophilic B-H Substitution on B(4), B(3,6) and B(9)



This Work

c) Selective Methylation on B(4) and B(12) via B-H Activation



Scheme 1. Strategies for selective alkylation of *o*-carboranes.

meshes) was used for column chromatography, and the distillation range of petroleum ether was 60–90 °C. ^1H , $^{13}\text{C}\{^1\text{H}\}$, $^{11}\text{B}\{^1\text{H}\}$ and ^{11}B NMR spectra were recorded on the Bruker 600 MHz instruments. All ^1H NMR and $^{13}\text{C}\{^1\text{H}\}$ NMR spectral data were reported in *ppm* relative to tetramethylsilane (TMS) as internal standard, ^{11}B NMR and $^{11}\text{B}\{^1\text{H}\}$ NMR spectra data were referenced to external $\text{BF}_3 \cdot \text{Et}_2\text{O}$. HRMS data were measured with ESI techniques.

2.2. General procedure for synthesis of 2a-2n

To a 10 mL dried flask was sequentially added 9-amide-*o*-carborane (0.1 mmol), toluene (1 mL), iodomethane (12.5 μL , 0.2 mmol), $\text{Pd}(\text{MeCN})_2\text{Cl}_2$ (2.6 mg, 0.01 mmol) and AgOAc (50.1 mg, 0.3 mmol) under an argon atmosphere. After the reaction mixture was stirred at 25 °C for 12 h, the reaction mixture was filtered through a short silica gel column using ethyl acetate as eluent. After evaporation of the solvent, the residue was purified by column chromatography on 200–300 mesh silica gel with petroleum ether/EtOAc = 4:1 as eluent. All products were characterized by ^1H , $^{13}\text{C}\{^1\text{H}\}$, $^{11}\text{B}\{^1\text{H}\}$ and ^{11}B NMR spectra (refer to electronic supporting information).

2.3. General procedure for synthesis of 3a-3l

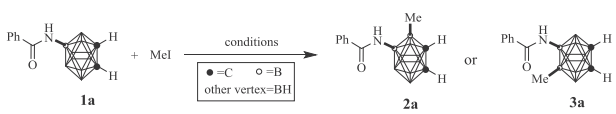
To a 10 mL dried flask was sequentially added 9-amide-*o*-carborane (0.1 mmol), toluene (1 mL), iodomethane (12.5 μL , 0.2 mmol), $\text{Pd}(\text{MeCN})_2\text{Cl}_2$ (2.6 mg, 0.01 mmol) and AgOTf (77.1 mg, 0.3 mmol) under an argon atmosphere. After the reaction mixture was stirred at 40 °C for 0.5 h, the reaction mixture was cooled to room temperature and filtered through a short silica gel column using ethyl acetate as eluent. After evaporation of the solvent, the

residue was purified by column chromatography on 200–300 mesh silica gel with petroleum ether/EtOAc = 4:1 as eluent. All products were characterized by ^1H , $^{13}\text{C}\{^1\text{H}\}$, $^{11}\text{B}\{^1\text{H}\}$ and ^{11}B NMR spectra (refer to electronic supporting information).

3. Results and discussion

To initiate our research, 9-benzamide-*o*-carborane and iodo-methane were selected as model substrates to screen conditions, and the results were summarized in Table 1. Just as we expected, the B(4) methylation could take place in the presence of 10 mol% $\text{Pd}(\text{OAc})_2$ with 3 equivalents of AgOAc in CH_2Cl_2 for 12 h (entry 1). Further studies indicated that toluene is more favorable for this transformation (entries 2–3), and the methylation could be completed in 3 h with $\text{Pd}(\text{MeCN})_2\text{Cl}_2$ (entries 4–6). Moreover, we found that 2 equivalents of MeI are enough to fulfill this selective methylation and generated the expected 2a with 64% yield (entry 7). On the other hand, the yield was reduced distinctly along with decreasing the loading amount of AgOAc (entry 8). Furthermore, we found that this transformation could proceed smoothly at 25 °C, and gave the 2a with 60% yield after 12 h (entry 9). To our surprise, when AgBF_4 and AgOTf were examined, the regioselectivity was reversed, the B(4) methylation was almost inhibited and the B(12) with more electrophilicity was methylated with 21% and 69% yields, respectively (entries 10–11). It is worth noting that the electrophilic multi-methylation was not found even with excess amount of MeI , and the methylation could not take place in the absence of $\text{Pd}(\text{MeCN})_2\text{Cl}_2$ (entry 12). These results indicated the selective methylation would not be a AgOTf promoted Friedel-Crafts reaction.

Table 1
Optimized conditions for the selective methylation of 9-benzamide-*o*-carborane.^{a,b}



Entry	Mel (eq.)	Catalyst	Oxidant	t/h	Yield/2a	Yield/3a
1	3	Pd(OAc) ₂	AgOAc	12	22 ^c	—
2	3	Pd(OAc) ₂	AgOAc	12	40 ^d	—
3	3	Pd(OAc) ₂	AgOAc	12	63	—
4	3	Pd(TFA) ₂	AgOAc	12	38	—
5	3	Pd(PPh ₃) ₂ Cl ₂	AgOAc	12	—	—
6	3	Pd(MeCN) ₂ Cl ₂	AgOAc	3	54	—
7	2	Pd(MeCN) ₂ Cl ₂	AgOAc	3	64	—
8	2	Pd(MeCN) ₂ Cl ₂	AgOAc	3	43 ^e	—
9	2	Pd(MeCN) ₂ Cl ₂	AgOAc	12	60 ^f	—
10	2	Pd(MeCN) ₂ Cl ₂	AgBF ₄	3	4 ^g	21
11	2	Pd(MeCN) ₂ Cl ₂	AgOTf	0.5	5 ^g	69
12	2	—	AgOTf	12	—	—

^a All reactions were carried out using 0.1 mmol 1a, 10 mol% catalyst, 3 equivalents of oxidant and 1 mL toluene at 40 °C under an argon atmosphere.

^b Isolated yields. ^c Reacted in CH₂Cl₂.

^d Reacted in Et₂O. ^e 2 equivalents of AgOAc.

^f Reaction conducted at 25 °C.

^g The yield is determined by GC analysis.

Based on the optimized conditions for selective B(4) methylation (Table 1, entry 9), the scope of 9-amide-*o*-carboranes was then examined. As can be seen from Table 2, either the amides substituted with electron donating groups or electron withdrawing groups were all compatible with this selective methylation, and gave the corresponding products with moderate yields (2a-2k), meanwhile, the exact structure of 2c was further confirmed by X-ray crystallographic analysis [57] (Fig. 1). Additionally, when the cage carbon substituted 9-benzamide-*o*-carboranes were subjected to the standard conditions, the expected products were afforded

with moderate yields (2l-2n).

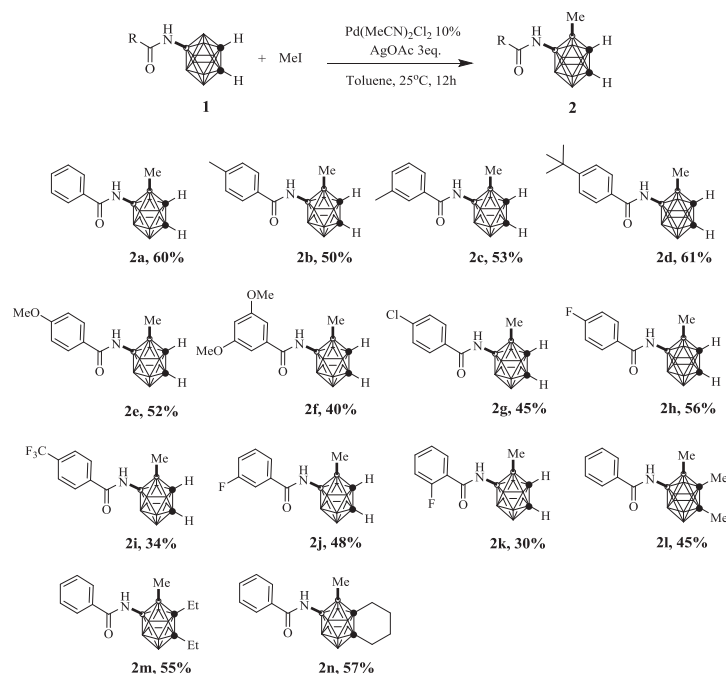
Subsequently, the scope of 9-amide-*o*-carboranes was explored for B(12) methylation. As shown in Table 3, we can see that the methylation could proceed smoothly for amides substituted with kinds of groups, and generated the corresponding products with moderate yields (3a-3j), the exact structure of 3g was also confirmed by X-ray crystallographic analysis [57] (Fig. 1). On the other hand, the cage carbon substituted 9-benzamide-*o*-carboranes were also compatible with this transformation despite with slight lower yields (3k-3l).

To further expanding the scope of alkyl iodide, the iodoethane, 2-iodopropane and *n*-iodobutane were subjected to the standard conditions for B(4) and B(12) methylation, respectively. However, the expected products were not found due to the β-H elimination of alkyl iodide in the presence of palladium. This result further proved that the selective methylation is arise from the palladium catalyzed B-H activation other than a Friedel-Crafts reaction.

Additionally, the B(4) methylated products could be further methylated on B(12), and gave the 4,12-dimethyl-9-amide-*o*-carboranes with moderate yields (Scheme 2). This stepwise transformation offers an efficient approach for selective methylation of B-H bonds with different reactivity.

Based on the Mulliken charge calculation and the selective B(4) arylation of 9-amide-*o*-carboranes [42], a plausible mechanism for tuned selective methylation on B(4) and B(12) was proposed (Scheme 3). For B(4) methylation, the reaction is most likely initiated by the ion exchange to form catalytic active species PdL₂(OAc)₂, which would activate the more polarized B(4)-H bond by forming intermediate A, after oxidative addition/reductive elimination would generate the B(4) methylated products 2 [58]. On the other hand, the stronger electron withdrawing effect of TfO⁻ would increase the electrophilicity of the in situ formed PdL₂(OTf)₂, which would favorable to activate the B(12)-H bond with much more negative charge via intermediate B, after oxidative addition/reductive elimination would gave the B(12) methylated products 3.

Table 2
Selective B(4) methylation of 9-amide-*o*-carboranes^{a,b}.



^a All reactions were carried out on a 0.1 mmol scale in 1 mL of toluene at 25 °C for 12 h under an argon atmosphere.

^b Isolated yields.

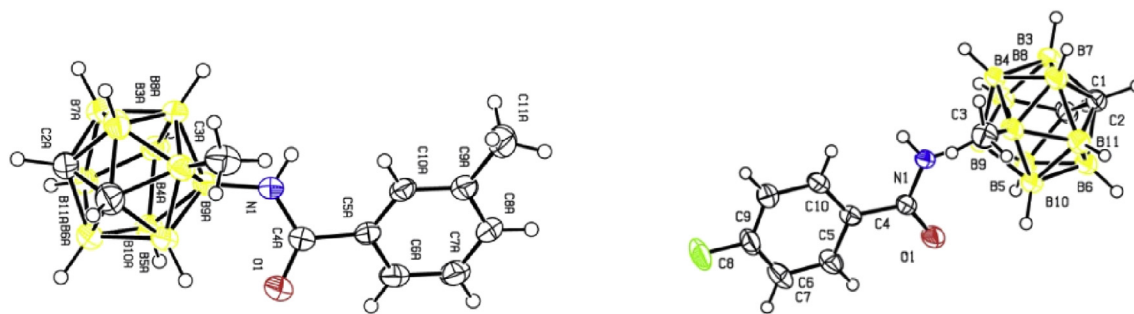
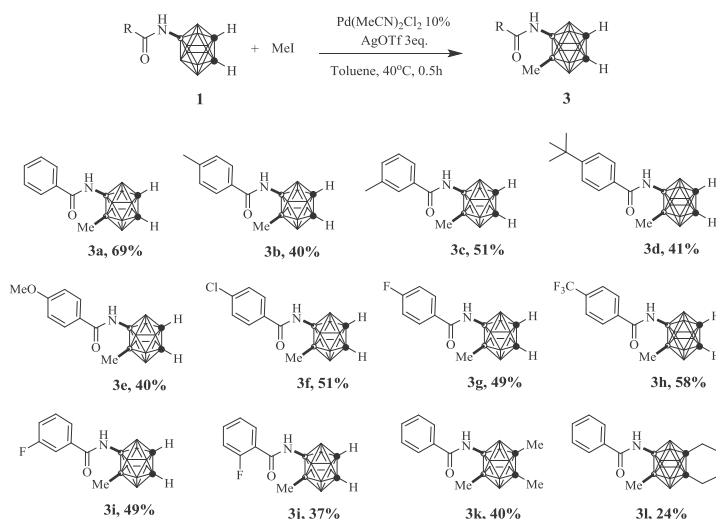


Fig. 1. Crystal structure of 2c (left) and 3g (right).

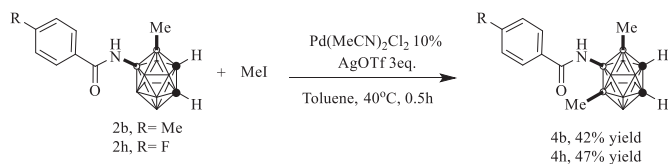
Table 3

Selective B(12) methylation of 9-amide-o-carboranes^{a,b}.



^aAll reactions were carried out on a 0.1 mmol scale in 1 mL of toluene at 40 °C for 0.5 h under an argon atmosphere.

^bIsolated yields.



Scheme 2. Selective B(12) methylation of 2b and 2h.

4. Conclusions

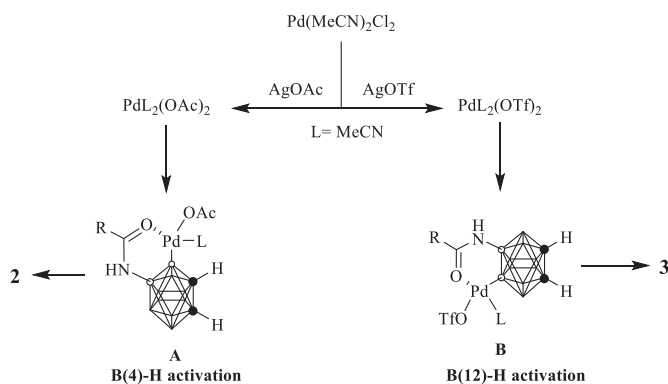
In conclusion, we have developed a tunable selective methylation of 9-amide-o-carboranes on B(4) and B(12) via B–H activation. A series of o-carborane derivatives decorated with various groups have been synthesized with moderate yields. A plausible mechanism involving in situ formed palladium species catalyzed B(4)-H and B(12)-H activation was proposed. This work provides an efficient protocol for the selective methylation of o-carboranes via B–H activation, and has important value in the design and synthesis of o-carborane derivatives with tunable selectivity.

Acknowledgment

This work is supported by National Natural Science Foundation of China (21602182), Longshan academic talent research supporting program of SWUST (17LZX324, 18LZX305, 18LZX02) and the Project of State Key Laboratory of Environment-friendly Energy Materials, SWUST (17fksy0102, 18fksy0206).

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.jorganchem.2019.120956>.



Scheme 3. Proposed mechanism for selective B(4)-H and B(12)-H activation.

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