Journal of Organometallic Chemistry 902 (2019) 120956

Contents lists available at ScienceDirect

Journal of Organometallic Chemistry

journal homepage: www.elsevier.com/locate/jorganchem

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

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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.

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

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https://doi.org/10.1016/j.jorganchem.2019.120956
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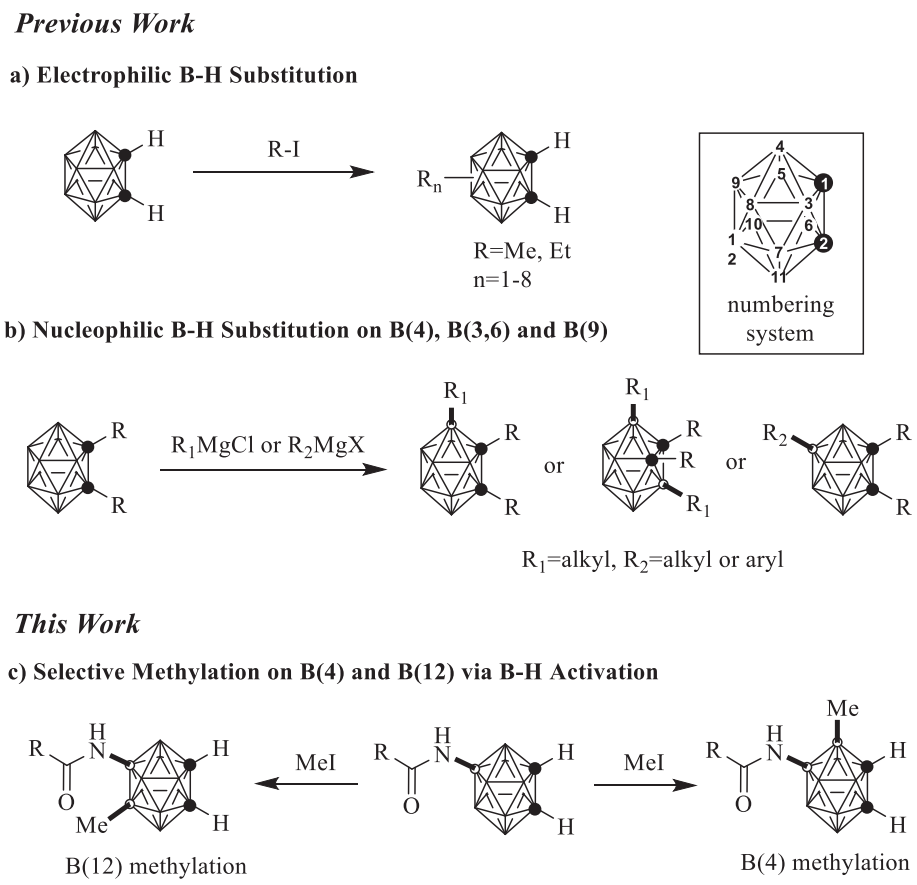


Scheme 1. Strategies for selective alkylation of *o*-carboranes.

meshes) was used for column chromatography, and the distillation range of petroleum ether was 60–90 °C. ^{1}H, $^{13}C\{^{1}H\}$, $^{11}B\{^{1}H\}$ and ^{11}B NMR spectra were recorded on the Bruker 600 MHz instruments. All ^{1}H NMR and $^{13}C\{^{1}H\}$ NMR spectral data were reported in *ppm* relative to tetramethylsilane (TMS) as internal standard, ^{11}B NMR and $^{11}B\{^{1}H\}$ NMR spectra data were referenced to external $BF_3 \cdot Et_2O$. 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), $Pd(MeCN)_2Cl_2$ (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 ^{1}H, $^{13}C\{^{1}H\}$, $^{11}B\{^{1}H\}$ and ^{11}B NMR spectra (refer to electronic supporting information).

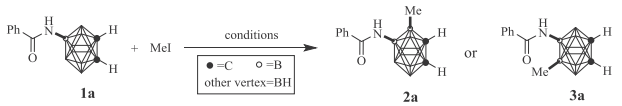
2.3. General procedure for synthesis of 3a-3l

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), $Pd(MeCN)_2Cl_2$ (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 ^{1}H, $^{13}C\{^{1}H\}$, $^{11}B\{^{1}H\}$ and ^{11}B NMR spectra (refer to electronic supporting information).

3. Results and discussion

To initiate our research, 9-benzamide-*o*-carborane and iodomethane 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% $Pd(OAc)_2$ and 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 $Pd(MeCN)_2Cl_2$ (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 took place in the absence of $Pd(MeCN)_2Cl_2$ (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	MeI (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	$Pd(PPh_3)_2Cl_2$	AgOAc	12	–	–
6	3	$Pd(MeCN)_2Cl_2$	AgOAc	3	54	–
7	2	$Pd(MeCN)_2Cl_2$	AgOAc	3	64	–
8	2	$Pd(MeCN)_2Cl_2$	AgOAc	3	43[e]	–
9	2	$Pd(MeCN)_2Cl_2$	AgOAc	12	60[f]	–
10	2	$Pd(MeCN)_2Cl_2$	$AgBF_4$	3	4[g]	21
11	2	$Pd(MeCN)_2Cl_2$	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 CH_2Cl_2.
[d] Reacted in Et_2O. [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).

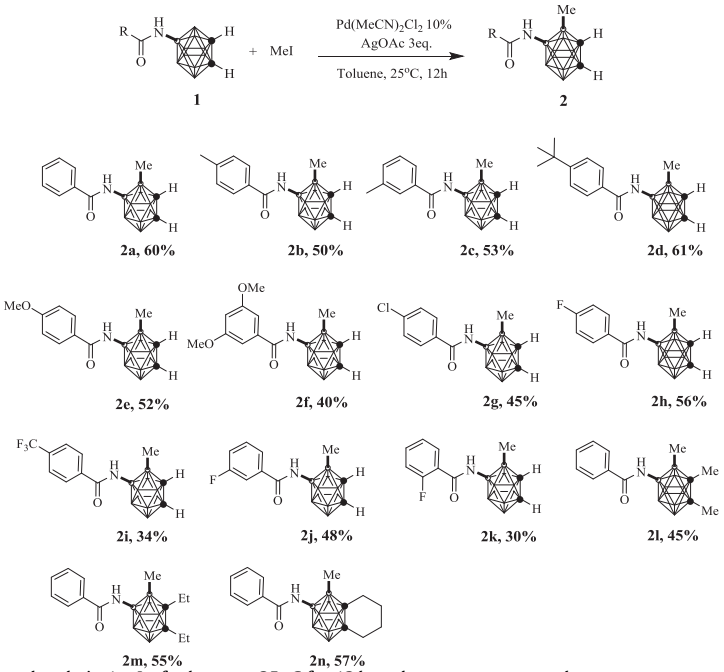
Subsequently, the scope of 9-amide-*o*-carboranes was explored for B(12) methylation. As shown in Table 3, we can see that the methylation could proceed smoothly for amides substituted with kinds of groups, and generated the corresponding products with moderate yields (3a-3j), the exact structure of 3 g 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 $PdL_2(OAc)_2$, 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 $PdL_2(OTf)_2$, 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.

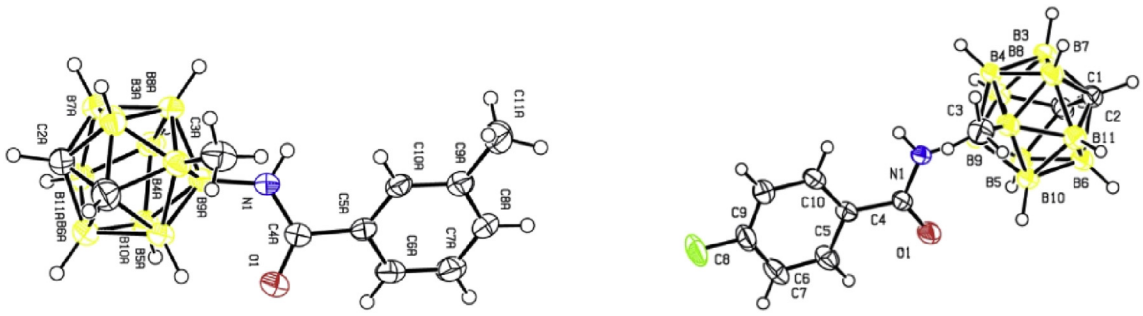
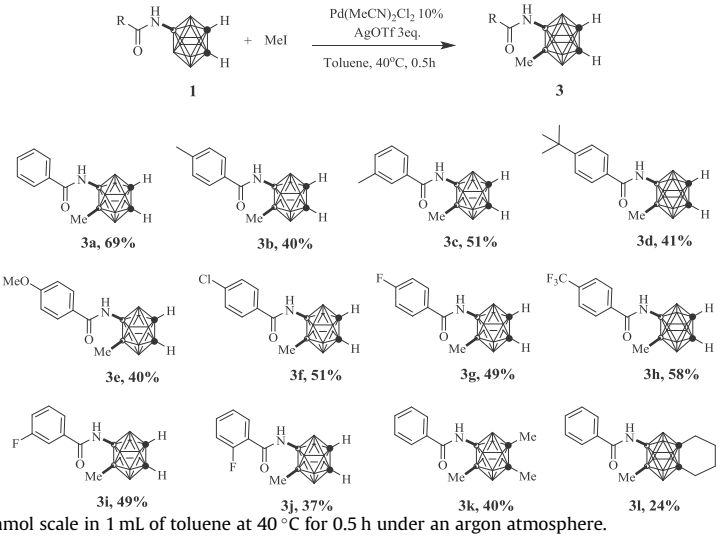
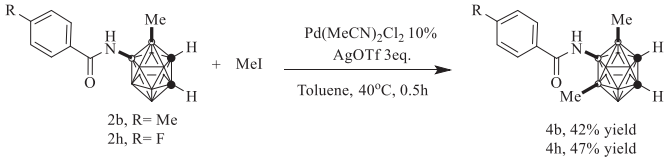


Fig. 1. Crystal structure of 2c (left) and 3 g (right).

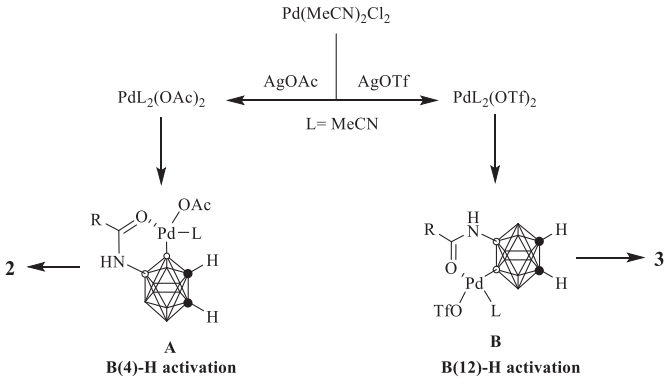
Table 3
Selective B(12) methylation of 9-amide-*o*-carboranes[a,b].



[a]All reactions were carried out on a 0.1 mmol scale in 1 mL of toluene at 40 °C for 0.5 h under an argon atmosphere.
[b]Isolated yields.



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



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

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, 18LZXT02) 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.

References

[1] N.S. Hosmane, Boron Science: New Technologies and Applications, Taylor & Francis Group, 2012.
[2] A.M. Prokhorov, T. Hofbeck, R. Czerwieniec, A.F. Suleymanova, D.N. Kozhevnikov, H. Yersin, Brightly luminescent Pt(II) pincer complexes with a sterically demanding carboranyl-phenylpyridine ligand: a new material class for diverse optoelectronic applications, J. Am. Chem. Soc. 136 (2014) 9637–9642.
[3] K.O. Kirlikovali, J.C. Axtell, A. Gonzalez, A.C. Phung, S.I. Khan, A.M. Spokoyny, Luminescent metal complexes featuring photophysically innocent boron cluster ligands, Chem. Sci. 7 (2016) 5132–5138.
[4] S. Mukherjee, P. Thilagar, Boron clusters in luminescent materials, Chem. Commun. 52 (2016) 1070–1093.
[5] X. Wu, J. Guo, Y. Cao, J. Zhao, W. Jia, Y. Chen, D. Jia, Mechanically triggered reversible stepwise tricolor switching and thermochromism of anthracene-*o*-carborane dyad, Chem. Sci. 9 (2018) 5270–5277.
[6] Z. Xie, Cyclopentadienyl-carboranyl hybrid compounds: a new class of versatile ligands for organometallic chemistry, Acc. Chem. Res. 36 (2003) 1–9.
[7] L. Deng, Z. Xie, Advances in the chemistry of carboranes and metallacarboranes with more than 12 vertices, Coord. Chem. Rev. 251 (2007) 2452–2476.
[8] A.M. Spokoyny, M.G. Reuter, C.L. Stern, M.A. Ratner, T. Seideman, C.A. Mirkin, Carborane-based pincers: synthesis and structure of SeBSe and SBS Pd(II) complexes, J. Am. Chem. Soc. 131 (2009) 9482–9483.
[9] A.M. Spokoyny, C.W. Machan, D.J. Clingerman, M.S. Rosen, M.J. Wiester, R.D. Kennedy, C.L. Stern, A.A. Sarjeant, C.A. Mirkin, A coordination chemistry dichotomy for icosahedral carborane-based ligands, Nat. Chem. 3 (2011) 590–596.
[10] Z.-J. Yao, G.-X. Jin, Transition metal complexes based on carboranyl ligands containing N, P, and S donors: synthesis, reactivity and applications, Coord. Chem. Rev. 257 (2013) 2522–2535.
[11] A.M. Spokoyny, New ligand platforms featuring boron-rich clusters as organomimetic substituents, Pure Appl. Chem. 85 (2013) 903–919.
[12] Y. Zhang, Z.-X. Zhang, Y. Wang, H. Li, F.-Q. Bai, H.-X. Zhang, The effect of the embedded *o*-carborane ligand on the photophysical properties of a cyclometalated Pt(II) complex: a theoretical investigation, Inorg. Chem. Front. 5 (2018) 1016–1025.
[13] N.S. Hosmane, J.A. Maguire, Comprehensive Organometallic Chemistry III, vol. 3, Elsevier, Oxford, 2007 (Chapter 5).
[14] M.F. Hawthorne, The role of chemistry in the development of boron neutron capture therapy of cancer, Angew. Chem. Int. Ed. Engl. 32 (1993) 950–984.
[15] A.H. Soloway, W. Tjarks, B.A. Barnum, F.G. Rong, R.F. Barth, I.M. Codogni, J.G. Wilson, The chemistry of neutron capture therapy, Chem. Rev. 98 (1998) 1515–1562.
[16] J.F. Valliant, K.J. Guenther, A.S. King, P. Morel, P. Schaffer, O.O. Sogbein, K.A. Stephenson, The medicinal chemistry of carboranes, Coord. Chem. Rev. 232 (2002) 173–230.
[17] A.F. Armstrong, J.F. Valliant, The bioinorganic and medicinal chemistry of carboranes: from new drug discovery to molecular imaging and therapy, Dalton Trans. (2007) 4240–4251.
[18] F. Issa, M. Kassiou, L.M. Rendina, Boron in drug discovery: carboranes as unique pharmacophores in biologically active compounds, Chem. Rev. 111 (2011) 5701–5722.
[19] A.N. Ay, H. Akar, A. Zaulet, C. Viñas, F. Teixidor, B. Zumreoglu-Karan, Carborane-layered double hydroxide nanohybrids for potential targeted- and magnetically targeted-BNCT applications, Dalton Trans. 46 (2017) 3303–3310.
[20] N. Kuthala, R. Vankayala, Y.-N. Li, C.S. Chiang, K.C. Hwang, Engineering novel targeted boron-10-enriched theranostic nanomedicine to combat against murine brain tumors via MR imaging-guided boron neutron capture therapy, Adv. Mater. 29 (2017) 1700850.
[21] G. Calabrese, A. Daou, E. Barbu, J. Tsibouklis, Towards carborane-functionalised structures for the treatment of brain cancer, Drug Discov. Today 23 (2018) 63–75.
[22] J.A. Potenza, W.N. Lipscomb, G.D. Vickers, H. Schroeder, Order of electrophilic substitution in 1,2-dicarbaclovododecaborane(12) and nuclear magnetic resonance assignment, J. Am. Chem. Soc. 88 (1966) 628–629.
[23] T.F. Koetzle, W.N. Lipscomb, Approximate wave functions for carboranes parametrized from self-consistent field model calculations, Inorg. Chem. 9 (1970) 2743–2748.
[24] Z. Qiu, Y. Quan, Z. Xie, Palladium-catalyzed selective fluorination of *o*-carboranes, J. Am. Chem. Soc. 135 (2013) 12192–12195.
[25] Y. Quan, Z. Xie, Iridium catalyzed regioselective cage boron alkenylation of *o*-carboranes via direct cage B-H activation, J. Am. Chem. Soc. 136 (2014) 15513–15516.
[26] H. Lyu, Y. Quan, Z. Xie, Palladium-catalyzed direct dialkenylation of cage B-H bonds in *o*-carboranes through cross-coupling reactions, Angew. Chem. Int. Ed. 54 (2015) 10623–10626.
[27] Y. Quan, Z. Xie, Palladium-catalyzed direct dialkenylation of cage B-H Bonds in *o*-carboranes through cross-coupling reactions, Angew. Chem. Int. Ed. 55 (2016) 1295–1298.
[28] H. Lyu, Y. Quan, Z. Xie, Rhodium-catalyzed regioselective hydroxylation of cage B-H bonds of *o*-carboranes with O_2 or air, Angew. Chem. Int. Ed. 55 (2016) 11840–11844.
[29] H. Lyu, Y. Quan, Z. Xie, Transition metal catalyzed direct amination of the cage B(4)-H bond in *o*-carboranes: synthesis of tertiary, secondary, and primary *o*-carboranyl amines, J. Am. Chem. Soc. 138 (2016) 12727–12730.
[30] Y. Quan, C. Tang, Z. Xie, Palladium catalyzed regioselective B-C(sp) coupling via direct cage B-H activation: synthesis of B(4)-alkynylated *o*-carboranes, Chem. Sci. 7 (2016) 5838–5845.
[31] H. Lyu, Y. Quan, Z. Xie, Transition metal catalyzed regioselective B(4)-halogenation and B(4,5)-diiodination of cage B-H bonds in *o*-carboranes, Chem. Eur J. 23 (2017) 14866–14871.
[32] R. Cheng, Z. Qiu, Z. Xie, Iridium-catalysed regioselective borylation of carboranes via direct B-H activation, Nat. Commun. 8 (2017) 14827.
[33] H. Lyu, J. Zhang, J. Yang, Y. Quan, Z. Xie, Catalytic regioselective cage B(8)-H arylation of *o*-carboranes via "Cage-Walking" strategy, J. Am. Chem. Soc. 141 (2019) 4219–4224.
[34] Y. Quan, Z. Xie, Controlled functionalization of *o*-carborane via transition metal catalyzed B-H activation, Chem. Soc. Rev. 48 (2019) 3660–3673.
[35] X. Zhang, H. Zheng, J. Li, F. Xu, J. Zhao, H. Yan, Selective catalytic B-H arylation of *o*-carboranyl aldehydes by a transient directing strategy, J. Am. Chem. Soc. 139 (2017) 14511–14517.
[36] X. Zhang, H. Yan, Pd(II)-catalyzed synthesis of bifunctionalized carboranes via cage B-H activation of 1-CH_2NH_2-*o*-carboranes, Chem. Sci. 9 (2018) 3964–3969.
[37] K. Cao, Y. Huang, J. Yang, J. Wu, Palladium catalyzed selective mono-arylation of *o*-carboranes via B-H activation, Chem. Commun. 51 (2015) 7257–7260.
[38] J. Wu, K. Cao, T.-T. Xu, X.-J. Zhang, L. Jiang, J. Yang, Y. Huang, Palladium catalyzed regioselective mono-alkenylation of *o*-carboranes via Heck type coupling reaction of a cage B-H bond, RSC Adv. 5 (2015) 91683–91685.
[39] K. Cao, T.-T. Xu, J. Wu, L. Jiang, J. Yang, Palladium catalyzed/silver tuned selective mono-/tetra-acetoxylation of *o*-carboranes via B-H activation, Chem. Commun. 52 (2016) 11446–11449.
[40] T.-T. Xu, C.-Y. Zhang, K. Cao, J. Wu, L. Jiang, J. Li, B. Li, J. Yang, Palladium-catalyzed selective mono-chlorination of mono-chlorination of *o*-carboranes: changing the concept of $FeCl_3$ from Lewis acid to chlorine source in carboranes, ChemistrySelect 2 (2017) 3396–3399.
[41] T.-T. Xu, K. Cao, J. Wu, C.-Y. Zhang, J. Yang, Palladium-catalyzed selective mono-/tetraacetoxylation of *o*-carboranes with acetic acid via cross dehydrogenative coupling of cage B-H/O-H bonds, Inorg. Chem. 57 (2018) 2925–2932.
[42] T.-T. Xu, K. Cao, C.-Y. Zhang, J. Wu, L. Jiang, J. Yang, Palladium catalyzed selective arylation of *o*-carboranes via B(4)-H activation: amide induced regioselectivity reversal, Chem. Commun. 54 (2018) 13603–13606.
[43] C.-Y. Zhang, K. Cao, T.-T. Xu, J. Wu, L. Jiang, J. Yang, A facile approach for the synthesis of *nido*-carborane fused oxazoles via one pot deboronation/cyclization of 9-amide-*o*-carboranes, Chem. Commun. 55 (2019) 830–833.
[44] Y. Zhang, Y. Sun, F. Lin, J. Liu, S. Duttwyler, Rhodium(III)-catalyzed alkenylation-annulation of *closo*-dodecaborate anions through double B-H activation at room temperature, Angew. Chem. Int. Ed. 55 (2016) 15609–15614.
[45] F. Lin, J.-L. Yu, Y. Shen, S.-Q. Zhang, B. Spingler, J. Liu, X. Hong, S. Duttwyler, Palladium-catalyzed selective five-fold cascade arylation of the 12-vertex monocarborane anion by B-H activation, J. Am. Chem. Soc. 140 (2018) 13798–13807.
[46] J. Wu, K. Cao, C.-Y. Zhang, T.-T. Xu, L.-F. Ding, B. Li, J. Yang, Catalytic oxidative dehydrogenative coupling of cage B-H/B-H bonds for synthesis of bis(*o*-carborane)s, Org. Lett. 21 (2019) 5986–5989.
[47] J. Plešek, Z. Plzàk, J. Stuchlík, S. Heřmánek, Synthesis of B-alkyl derivatives of *o*-carborane by alkylation under electrophilic conditions; Scope and limitation, Collect. Czechoslov. Chem. Commun. 46 (1981) 1748–1763.
[48] L.L. Zakharkin, V.A. Ol'shevskaya, E.V. Vorontsov, P.V. Petrovsky, Synthesis of mono-, di-, tri-, and tetraethyl-*o*-carboranes by electrophilic alkylation of *o*-carborane with ethyl bromide in the presence of $AlCl_3$ and their transformations, Russ. Chem. Bull. 45 (1996) 2614–2622.
[49] A. Herzog, A. Maderna, G.N. Harakas, C.B. Knobler, M.F. Hawthorne, A camouflaged *nido*-carborane anion: facile synthesis of octa-B-methyl-1,2-dicarba-*closo*-dodecaborane(12) and its deboration reaction, Chem. Eur J. 5 (1999) 1212–1217.
[50] C. Tang, J. Zhang, Z. Xie, Angew. Chem. Int. Ed. 129 (2017) 8768–8772.
[51] C. Tang, J. Zhang, J. Zhang, Z. Xie, Regioselective nucleophilic alkylation/arylation of B-H bonds in *o*-carboranes: an alternative method for selective cage boron functionalization, J. Am. Chem. Soc. 140 (2018) 16423–16427.
[52] S.N. Mukhin, K.Z. Kabytaev, G.G. Zhigareva, I.V. Glukhov, Z.A. Starikova, V.I. Bregadze, I.P. Beletskaya, Catalytic amidation of 9-Iodo-*m*-carborane and 2-Iodo-*p*-carborane at a boron atom, Organometallics 27 (2008) 5937–5942.
[53] Y. Sevryugina, R.L. Julius, M.F. Hawthorne, Novel approach to amino-carboranes by mild amidation of selected iodo-carboranes, Inorg. Chem. 49 (2010) 10627–10634.
[54] T.L. Heying, J.W. Ager Jr., S.L. Clark, R.P. Alexander, S. Papetti, J.A. Reid, S.I. Trotz, A new series of organoboranes. III. Some reactions of 1,2-dicarbaclovododecaborane(12) and its derivatives, Inorg. Chem. 2 (1963) 1097–1105.
[55] T.E. Paxson, M.K. Kaloustian, G.M. Tom, R.J. Wiersema, M.F. Hawthorne, Metallocene compounds derived from .mu.-1,2-trimethylene-1,2-dicarba-*closo*-dodecaborane(10), J. Am. Chem. Soc. 94 (1972) 4882–4888.
[56] A.F. Armstrong, J.F. Valliant, Microwave-assisted synthesis of tricarbonyl Rhenacarboranes: steric and electronic effects on the 1,2→1,7 carborane cage isomerization, Inorg. Chem. 46 (2007) 2148–2158.
[57] CCDC Numbers of 2c and 3g Are 1910640 and 1910639, Respectively.
[58] S.J. Tremont, H.U. Rahman, *Ortho*-alkylation of acetanilides using alkyl halides and palladium acetate, J. Am. Chem. Soc. 106 (1984) 5759–5760.