Iridium-catalysed regioselective borylation of carboranes via direct B–H activation

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Carboranes are carbon–boron molecular clusters, which can be viewed as three-dimensional analogues to benzene. They are finding many applications in medicine, materials and organometallic chemistry. On the other hand, their exceptional thermal and chemical stabilities, as well as 3D structures, make them very difficult to be functionalized, in particular the regioselective functionalization of BH vertex among ten similar B–H bonds. Here we report a very efficient iridium-catalysed borylation of cage B(3,6)–H bonds of o-carboranes with excellent yields and regioselectivity using bis(pinacolato)diboron (B2pin2) as a reagent. Selective cage B(4)–H borylation has also been achieved by introducing a bulky TBDMS (tert-butyldimethylsilyl) group to one cage carbon vertex. The resultant 3,6-(Bpin)2-o-carboranes are useful synthons for the synthesis of a wide variety of B(3,6)-difunctionalized o-carboranes bearing cage B–X (X = O, N, C, I and Br) bonds.
osahedral carboranes are carbon–boron molecular clusters, sharing many features with benzene such as aromaticity, high thermal and chemical stability1,2. On the other hand, carboranes have their own unique characteristics such as spherical geometry and hydrophobic molecular surface1,2, which make them attractive building blocks for boron neutron capture therapy agents in medicine3–6, functional units in supramolecular design/materials7–17 and versatile ligands in coordination/organometallic chemistry18–23. These research activities have drawn growing interests in the selective functionalization of carboranes1,24–26.

Classic routes to functionalized carboranes rely on the polarized cage C–H/B–H bonds: the weakly acidic C–H proton (pKa ~ 23) and basic B–H hydride1. Accordingly, cage C–H bonds can be deprotonated by strong bases, followed by reactions with electrophiles to give carbon-substituted carboranes1,2, and cage B–H bonds are subjected to electrophilic substitution reactions, leading to the formation of cage boron-substituted carborane derivatives with the reaction rate B(9,12)–H > B(8,10)–H > B(4,5,7,11)–H (refs 1,2,7,28). However, the B(3,6)-disubstituted o-carboranes cannot be prepared by electrophilic substitution reactions. They are generally achieved via multistep reaction of deboration–capping–deboration–capping (Fig. 1)1,28,29

Very recently, we have developed −COOH guided transition metal-catalysed regioselective B(4)-alkenylation30, -alkynylation31, -amination32 and -hydroxylation33, as well as B(4,5)-dialkenylation34 and -diarylation35 of o-carboranes. In contrast, transition metal-catalysed B(3,6)-difunctionalization of o-carboranes is much less studied36–37, although transition metal promoted B(3)–H activation in o-carboranes has been well documented38–44

Encouraged by transition metal-catalysed C–H borylation and application of the resultant boronate esters/boronic acids in C–C/C–O/C–N/C–halogen bond forming process45–47, we initiated a research program to study transition metal-catalysed direct cage B–H borylation of o-carboranes and the results are reported in this study (Fig. 1).

Results

B(3,6)-diborylation of o-carboranes. The optimization of reaction conditions for the following reactions was summarized in Supplementary Tables 1 and 2. The initial reaction of o-carborane (1a) with B2pin2 ([B(OCMe2CMe2O)]2) in the presence of 3.5 mol% [(cod)IrCl2] (cod = 1,5-cyclooctadiene) in tetrahydrofuran (THF) gave 3-Bpin-1,2-C2B10H11 (2a) in 60% gas chromatography (GC) yield. It was later found that the ligands played an important role in the reaction48,49. Addition of 0.21 equiv. of pyridine (Py) significantly increased the reaction efficiency, leading to the formation of 2a and 3,6-(Bpin)1,2-C2B10H11 (3a) in 23% and 67% GC yields, respectively. Replacement of Py by 2-Me- and 4-Me-Py resulted in 98% and 95% GC yields of 3a. Increasing the steric hindrance of Py derivatives led to much lower yields of 3a. It was noted that bipyrindil ligands commonly used in C–H borylation led to the formation of inseparable geometrical isomers of mono-, di- and tri-borylated products (see Supplementary Table 2). Other Ir(I) complexes such as [(cod)Ir(OMe)]2, (cod)Ir(acac), (cod)2IrBF4 and (cod)2IrB[3,5-(CF3)2C6H3]4 also worked well, giving very good to excellent yields of 3a, whereas the Ir(III) complexes such as [Cp*IrCl2]2 and IrCl3, as well as [(cod)RhCl]2 and Pd(OAc)2 showed poor or no catalytic activity. On the other hand, HBpin did not give any borylation product. Extensive screening of solvents, catalyst loadings, reaction temperatures and molar ratios of ligand/B2pin2 led to the optimal reaction conditions shown entry 6 of Supplementary Table 1.

The substrate scope was then examined under the optimized reaction conditions and the results were compiled in Table 1. The borylation efficiency was generally very high regardless of the nature of substituents on cage B(9,12) of o-carboranes (3a–3m).

It was noted that the double bond in 9-vinyl-o-carborane (1k) underwent hydroboration with HBpin, a byproduct of B–H borylation (vide infra), to afford 3k in 91% isolated yield with excellent regioselectivity, probably owing to steric effect of o-carboranyl moiety. The B(3,6)-diborylation efficiency of 4-I-o-C2B10H11 (1n) was lower than other substrates likely to be due to steric effect of vicinal iodo group. In fact, both the mono- and diborylation products 2n and 3n were observed by GC–mass spectrometry with a molar ratio of 25:75. The bulkier substituents at the B(4) position such as 4-Ph and 4-(Ph)CH = (Ph)C or at B(4,7) positions such as 4,7-I did not block the B(3)-borylation, giving 2o, 2p and 2q in 76–89% isolated yields, respectively. For 3-Ph-o-C2B10H11, the expected monoborylation product 2r was isolated in 89% yield. It was noteworthy that substituents on cage C had a significant impact on the borylation...
reaction. For example, 1-Me-o-C₂B₁₀H₁₁ gave an inseparable mixture of geometrical isomers and no borylation with 1,2-Me₂-o-C₂B₁₀H₁₀ was observed.

We also examined the gram-scale borylation reaction. Under the optimal reaction conditions, treatment of 1a (1.44 g, 10 mmol) with B₂pin₂ (10.16 g, 40 mmol) in THF (50 ml) afforded 3.75 g of 3a (95% isolated yield).

In a similar manner, reaction of m-C₂B₁₀H₁₂ (4) with 1.5 equiv. of B₂pin₂ in the presence of 3.5 mol% [(cod)IrCl]₂ and 21 mol% 2-MePy in THF at 80 °C for 5 h gave 2-Bpin-m-carborane (5) in 74% isolated yield (see Supplementary Table 3 and Supplementary Fig. 6). On the other hand, under the same reaction conditions, p-carborane afforded an inseparable mixture of mono-, di- and triborylated products.

B(4)-borylation of o-carboranes. The aforementioned results clearly show that bulky substituents such as Ph (2o in Table 1) and C(Ph) = CH(Ph) (2p in Table 1) can completely block the borylation of ortho-BH vertices, suggesting the importance of steric factors. We wondered whether Ir-catalysed regioselective cage B(4)–H borylation in o-carboranes could be achieved by introducing a bulky substituent at the cage C position. Accordingly, 1-trimethylsilyl-o-carborane was chosen as the model substrate for initial screening and the results were compiled in Supplementary Table 4. It was found that 2,2₀-bipyridine (2,2₀-bipy) derivatives were better ligands than monodentate Pys as the latters caused partial desilylation of 1-trimethylsilyl-o-carborane. The screening results indicated clearly that substrates with bulkier silyl groups can efficiently block the ortho-B–H activation, resulting in higher regioselectivity. If 2-TBDMS-o-carboranes 6 (TBDMS = tert-butyldimethylsilyl) were used as starting materials and 2,2₀-bipy as the ligand, the desired product 4-Bpin-2-TBDMS-o-carboranes 7a–c were isolated in 89–92% yields. Subsequently, the TBDMS group can be easily removed by caesium fluoride (CsF) under very mild condition to give the corresponding compound 8 in ca. 94% isolated yield (Fig. 2).

**Table 1 | Substrate scope for selective cage B–H borylation of o-carboranes.**

| R       | Product            | Yield  |
|---------|--------------------|--------|
| H       | Bpin              | 83%    |
| o-Me    | Bpin              | 95%    |
| p-Me    | Bpin              | 88%    |
| p-F     | Bpin              | 84%    |
| p-Cl    | Bpin              | 89%    |
| p-CF₃   | Bpin              | 89%    |
| R = Ph  | Bpin              | 76%    |
| 3.5 mol% [(cod)IrCl]₂ | 4 equiv. B₂pin₂ |        |
| THF, 110 °C, 5 h |                    |        |

*Reactions were conducted on 0.5 mmol scale in a closed flask at 110 °C (bath temperature) for 5 h.

**Transformation of 3a.** Although it has been well documented that Bpin can be replaced by a wide variety of functional groups,⁴⁵–⁴⁷ the chemical properties of cage B–Bpin bonds have
not been explored thus far. To illustrate the synthetic applications of B-borylated-α-carboranes, various transformations of 3 in an example of 3a were studied and the results were outlined in Fig. 3. Suzuki–Miyaura cross-coupling of 3a with PhBr in the presence of 20 mol% Pd(PPh3)4 and 3 equiv. of Cs2CO3 gave 3,6-diphenyl-α-carborane (9) in 81% isolated yield. Treatment of 3a with CH2=CHCH2Cl in the presence of Pd(dba)2 (dba, dibenzyldieneacetone) at room temperature afforded 10 in 87% yield. Surprisingly, replacement of Cs2CO3 by tBuOK, reaction of 3a with PhBr in the presence of Pd(PPh3)4 produced 3,6-Br2-C2B10H10 (11a) in 73% yield. Similarly, 3,6-I2-o-C2B10H10 (11b) was prepared in 78% isolated yield if PhI was used as coupling agent. It is not clear at this stage why tBuOK can alter the coupling partner in these cross-coupling reactions. The two Bpin moieties in 3a were readily replaced by acetoxy groups using Cu(OAc)2/KF in CH3CN under 1 atm of O2. 3,6-(NH2)2-α-carborane (3l) was also synthesized from 3a in 90% isolated yield by treatment of 3a with in situ generated MeONH+ in THF. Reaction of 3a with TMSN3 in the presence of KF and CuCl gave 3,6-(N3)2-α-C2B10H10 (14) in 83% yield. Double click reaction of 14 with Et2O,CC≡CO2Et afforded 3,6-dinitroaryl-α-carborane (15) in 83% yield. In addition, carbornylboronic acid 3,6-[B(OH)2]2-α-C2B10H10 (16) was also synthesized from 3a in 85% isolated yield. Compounds 2, 3, 5 and 7–16 were fully characterized by 1H, 13C and 11B nuclear magnetic resonance (NMR) spectroscopy, as well as elemental analyses. The molecular structures of 2a, 2p, 2q, 3a, 3l, 5, 7c, 8a and 15 were further confirmed by single-crystal X-ray analyses.

Mechanistic study. To shed some light on the reaction mechanism of the first Ir-catalysed regioselective cage B–H borylation, NMR reactions (Fig. 4) were carried out in d8-THF, which were monitored by 1H and 11B NMR spectra (see Supplementary Figs 12–16 for detail). The following results were observed: (1) dissociation of [(cod)IrCl]2 in the presence of 2-MePy generated a monomeric species (cod)IrCl(2-MePy) (A) (Fig. 4, eq. a). (2) Bpin2 underwent rapid oxidative addition reaction on Ir(I) species in the presence of 2-MePy to generate a Ir(III) species50,51 and release ClBpin that was trapped by THF to form ROBpin (see Supplementary Fig. 14)52,53. However, no reaction was observed by treatment of [(cod)IrCl]2 with 1a or HBpin under the same reaction conditions (Fig. 4, eq. b and d). (3) Under the optimal reaction conditions, both 2a and HBpin were observed by 1H and 11B NMR at the initial stage. As the reaction proceeded, 3a gradually appeared at the expense of 2a. These results suggested that the borylation proceeded stepwise (Fig. 4, eq. e). (4) The Ir(III) complex (η5-MesH)Ir(Bpin)3 (ref. 54) was found to catalyse the diborylation of 1a equally well as [(cod)IrCl]2 did to give 3a in 98% GC yield (Fig. 4, eq. f). (5) B(3,6)–H bonds were more reactive than B(4,5,7,11)–H ones in the above borylation, suggesting that the activation of cage B–H bond may proceed via oxidative addition pathway13,36–39,55–57, instead of electrophilic substitution mechanism30–35 as the electron density in α-carborane follows the trend: B(3,6) < B(4,5,7,11) < B(8,10) < B(9,12)127.

Figure 3 | Chemical transformations of 3a. Reaction conditions: (a) PhBr (3 equiv.), Pd(PPh3)4 (20 mol%), Cs2CO3 (3 equiv.), cyclohexane, 150 °C (bath), 8 h. (b) Allyl chloride (6 equiv.), Pd(dba)2 (20 mol%), Cs2CO3 (3 equiv.), toluene, room temperature, 24 h. (c) PhX (3 equiv.), Pd(PPh3)4 (10 mol%), tBuOK (3 equiv.), THF, 80 °C, 24 h. (d) Cu(OAc)2 (6 equiv.), KF (6 equiv.), CH3CN, 80 °C, 12 h, under 1 atm of O2. (e) MeONH-Li, THF, 80 °C, 8 h. (f) TMSN3 (2.4 equiv.), CuCl (2.1 equiv.), KF (2.4 equiv.), THF, 60 °C, 24 h. (g) Diethyl acetylenedicarboxylate (2.4 equiv.), toluene, 95 °C. (h) 1) DEA (diethanolamine, 2.5 equiv.), Et2O, room temperature, 18 h, 2) HCl aq. (0.5 M, excess).
On the basis of the aforementioned experimental results and literature work\(^1\), a proposed mechanism for the borylation reaction is shown in Fig. 5. Dissociation of \((\text{cod})\text{IrCl}_2\) in the presence of 2-MePy ligand generates a monomeric active species \((\text{cod})\text{IrCl}(2\text{-MePy})\) (A), which undergoes oxidative addition with B\(_2\)pin\(_2\), followed by reductive elimination to form Ir(I)-Bpin B and release ClBpin\(^{20,28,39}\), entering the catalytic cycle. Oxidative addition of B\(_2\)pin\(_2\) on B gives the Ir(III) intermediate C\(^{48}\), followed by another oxidative addition of the most electron-deficient cage B(3)-H bond\(^{1,36,37}\) to afford D (path a). Reductive elimination yields the intermediate E and HBpin.

Alternatively, electrophilic substitution of Ir(III) species C on cage B–H yields the intermediate E and release one equivalent of HBpin (path b)\(^{30}\). Reductive elimination generates cage boron-borylated product 2 (ref. 48). Compound 2 undergoes another catalytic borylation cycle to afford cage B(3,6)- diborylated product 3. As the electron-deficient cage B(3,6)-H bonds preferentially undergo oxidative addition reaction with transition metal species over other more electron-rich cage B–H bonds\(^{1,36,37}\), path a is believed to be more favourable over path b.

In summary, a very efficient and regioselective Ir-catalysed diborylation of cage B(3,6)-H bonds in carboranes has been developed. This serves as a new methodology for the regioselective generation of a series of B(3,6)-diborylated- or B(3)-borylated-o-carboranes. Selective B(4)-borylation of cage B(4)-H bond has also been achieved by introducing a TBDMS group to the cage carbon position. The resultant B-borylated carboranes can be conveniently converted to a variety of functionalized carboranes bearing cage B–X (X = Br, I, B–O, B–C(sp\(^2\)), B–C(sp\(^3\)), B–N\(_2\)H\(_4\) and B–N\(_3\) bonds that otherwise cannot be prepared by other known methods. This work opens up a new way for efficient and regioselective functionalization of carboranes, which may be extended to other boron cluster systems.

**Methods**

**Preparation of B(3,6)-diborylated- or B(3)-borylated-o-carboranes (3 or 2).** An oven-dried Schlenk flask was charged with o-carborane (1) (0.5 mmol), B\(_2\)pin\(_2\) (508 mg, 2.0 mmol), \[(\text{cod})\text{IrCl}_2\] (12 mg, 0.0175 mmol) and 2-MePy (10.3 mg, 0.105 mmol), followed by dry THF (5 ml). The flask was closed under an atmosphere of nitrogen and stirred at 110 °C (bath temperature) for 5 h. After hydrolysis with water (10 ml) and extraction with diethyl ether (10 ml x 3), the ether 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 in v/v) as eluent to give a mixture of product and B\(_2\)pin\(_2\). Removal of B\(_2\)pin\(_2\) via sublimation at 90 °C under vacuum (0.1 torr) gave a pure product 2o or 3a–n.

**B(4)-borylated-carboranes (8).** Compound 7 was prepared from 1-TBDMS-o-carboranes 6 (0.5 mmol), B\(_2\)pin\(_2\) (254 mg, 1.0 mmol), \[(\text{cod})\text{IrCl}_2\] (12 mg, 0.0175 mmol) and 2,2’-bipy (22 mg, 0.07 mmol) in THF (5 ml) at 110 °C (bath temperature) for 3 h, using the same procedure reported for 3. To a solution (2 ml) of 7 (0.3 mmol) (acetone for 7a and 7b; MeOH/DCM (2/1 in v/v) for 7c) was added CsF (182 mg, 1.2 mmol). The mixture was stirred at room temperature (for 1 h for 7a and 7b, and 20 min for 7c). After filtration and removal of the solvent under vacuo, the residue was subjected to flash column chromatography on silica gel (230–400 mesh) using n-hexane/Et\(_3\)N (5/1 in v/v) as eluent to give product 8.

For NMR spectra and single-crystal X-ray structures of the compounds in this study, see Supplementary Figs 1–5, 7–11 and 17–17.

**Data availability.** X-ray crystallographic data for compounds 2a, 2p, 2q, 3a, 3l, 5, 7c, 8a and 15, and complex A have been deposited at the Cambridge Crystallographic Data Centre as CCDC 1500326–1500335, respectively (http://www.ccdc.cam.ac.uk/pages/Home.aspx). The authors declare that the data supporting the findings of this study are available within the article (and Supplementary Information files) and also are available from the corresponding author on request.

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Author contributions
R.C. carried out the experiments and structural determination of the reaction products, and prepared the Supplementary Information. Z.Q. and Z.X. conceived and designed the concepts and experiments, as well as prepared the manuscript.

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