

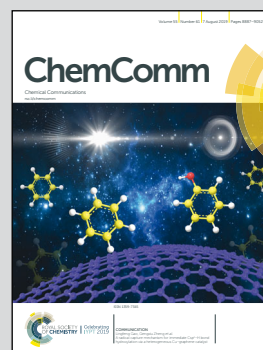


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Icosahedral carboranes as scaffolds for congested regioselective polyaryl compounds: the distinct distance tuning of C–C and its antipodal B–B†

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Four-fold aryl substituted *o*-carborane derivatives with defined patterns of substitution at the antipodal region of the cluster carbon atoms have been achieved. It is proven that this region is congested but lacks steric hindrance. Also, the two antipodal sites C_c–C_c and B9–B12 are affected very distinctly by electron donor substituents.

The *closo* C₂B₁₀H₁₂ icosahedral carboranes, *o*-(1,2), *m*-(1,7), or *p*-(1,12), are the most widely studied boron clusters; they can be functionalized by different reactions,¹ in a regioselective manner, with many possible sites of substitution. *o*-Carborane, 1,2-*closo*-C₂B₁₀H₁₂, acts as a strong electron-withdrawing molecule through the substitution on the carbon, C_c,² and as an electron-donating moiety through the boron vertices with a gradation depending on the distance to the carbon atoms.³ On the other hand, it is well known that the C_c–C_c bond length in *o*-carborane and metalla-*o*-carborane strongly depends on the electronic nature of the immediate C_c-substituents;⁴ π -donor substituents bonded to the C_c, as well as atoms with lone pairs, donate electron density to the $\sigma^*(\text{C}_c\text{--C}_c)$ antibonding orbital (negative hyperconjugation) of *o*-carborane, which lies in the C_c–C_c bond, increasing significantly the C_c–C_c bond distance.⁵ In the case of aryl substituents, the orientation of the substituents has a significant impact on the electron donation.⁶ The longest C_c–C_c distance ever reported is 2.156(4) Å for the 1,2-(CR₂F_c)₂-1,2-*closo*-C₂B₁₀H₁₀, {R = pentamethylene; F_c = (η^5 -C₅H₄)Fe(η^5 -C₅H₅)} *o*-carborane cluster derivative.⁷ While the plasticity of the C_c–C_c bond has been investigated, the possibility of a similar behaviour at the B–B bonds located antipodal to the cluster carbon atoms remained unexplored.

In addition, if π -aromaticity and tridimensional aromaticity of the icosahedral boranes are two sides of the same coin,⁸

could it be possible to obtain hybrid polyaryl compounds by merging the 2D organic aromatic groups at the dense antipodal region of the cluster carbon atoms with 3D inorganic icosahedral clusters?

To produce B–C substitutions, a useful and general method is by electrophilic iodination of *o*-carborane followed by Kumada cross-coupling reaction.⁹ This implies that one should start from the appropriate iodocarborane derivatives. A less regioselective B(8)/B(9)-aryl-*o*-carborane Pd-catalysed monoarylation with aryl iodides *via* B–H activation was reported,¹⁰ as well as a palladium-catalysed regioselective diarylation on B(4,5) of *o*-carborane directly from B–H with aryl halides, with the help of the traceless directing carboxylic group.¹¹ With hindered substitutions on the neighbouring C/B atoms, 3-Ph-1,2-Ph₂-1,2-*closo*-C₂B₁₀H₉ and 3,6-Ph₂-1,2-Ph₂-1,2-*closo*-C₂B₁₀H₉¹² derivatives were obtained in low yield by using the sequential nucleophilic-capping reactions of BPhCl₂ in the precursors [7,8-Ph₂-7,8-*nido*-C₂B₉H₉]^{2–} and [6-Ph-7,8-Ph₂-7,8-*nido*-C₂B₉H₈]^{2–}. It should be noted that disubstituted 9,12-Ph₂-1,2-*closo*-C₂B₁₀H₁₀,¹³ 1,9- and 1,12-(*p*-MeC₆H₄)₂-1,2-*closo*-C₂B₁₀H₁₀ were also reported.¹⁴ We interpret that the presence of the four phenyl groups in the crowded area adjacent to the C_c vertices is accessible because of the different behaviour of all the atoms connected to the C₂B₂ region where the strong electron-withdrawing (C_c) and electron-donating moieties (B) of the *o*-carboranyl group co-exist. As mentioned, it was our main target to elucidate if the four iodo groups in the compact and electron-rich region of the *o*-carborane cluster (Chart 1) could be fully or only partially replaced by the organic aryl (sp²) groups such as phenyl to produce a “four phenyl congested site”. Furthermore, it could provide a good picture of the B–B tuning possibility to the antipodal C_c–C_c unit. This would be a potentially useful heavily congested electron-rich region due to the regioselective formation of B–C(sp²), B–C(sp) and B–C(sp³). To achieve so, the cross-coupling reaction on the B-iodinated *o*-carboranes with Grignard reagents in the presence of the Pd(II) and Cu(I) catalysts was studied. Two were the starting iodinated derivatives, 9,12-I₂-1,2-*closo*-C₂B₁₀H₁₀ (1) and 8,10,9,12-I₄-1,2-*closo*-C₂B₁₀H₈ (2). In 2, the four iodo groups occupy a highly dense region antipodal to the

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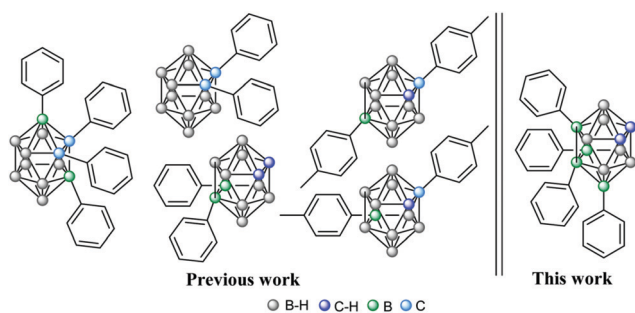
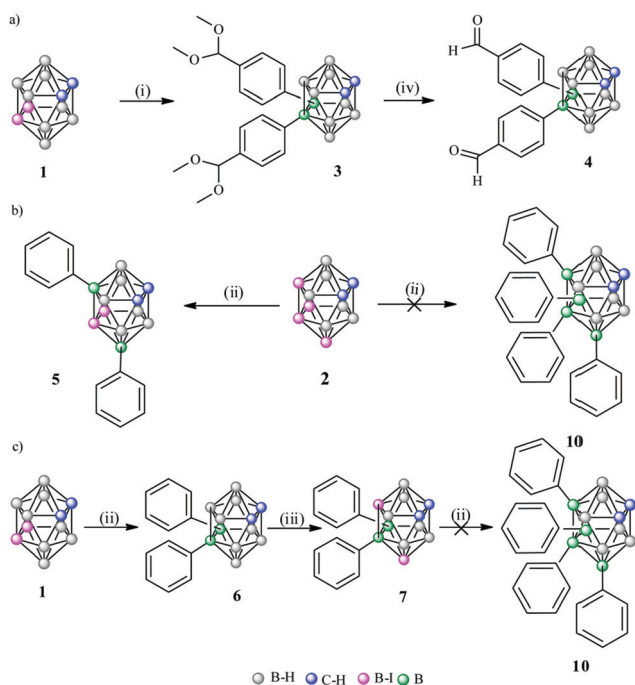


Chart 1 Different polyaryl-*o*-carboranes.

C_c–C_c atoms. In **1**, only two adjacent iodo groups are present, again antipodal to the C_c–C_c unit. Four Grignard reagents were used, phenylethynyl magnesium, phenyl magnesium and allyl magnesium chlorides, and 4-benzaldehyde dimethyl acetal magnesium bromide. The first, the second and the fourth would produce a highly electron dense and congested region in *o*-carborane derivatives, whereas the third would produce a more relaxed space. In a typical experiment, **1** and *cis*-[PdCl₂(PPh₃)₂] and CuI as catalysts were dispersed in anhydrous THF and treated with the appropriate Grignard reagent at low temperatures (Scheme 1). After refluxing overnight, the corresponding crude compounds were purified (see ESI[†]). The cross-coupling reaction of **1** with 4-benzaldehyde dimethyl acetal magnesium bromide proceeded to give 9,12-(C₆H₄CH(OCH₃)₂)₂-1,2-*closo*-C₂B₁₀H₁₀, **3**, in 71% yield (Scheme 1a), which was confirmed by multinuclear NMR, FTIR, mass spectrometry and elemental analysis.



Scheme 1 Kumada cross coupling reactions on **1** (a) and **2** (b) using *cis*-[Pd(PPh₃)₂Cl₂] and CuI as catalysts, in THF refluxing overnight. (i) 4-Benzaldehyde dimethyl acetal magnesium bromide, (ii) PhMgCl,¹³ (iii) solvent free electrophilic iodination with I₂ (10 eq.) at 210 °C during 4 h. (iv) Extraction with Et₂O in 3 M aqueous solution HCl.

Deprotection of the carbonyl group was achieved with diethyl-ether in aqueous HCl 3 M solution to produce 9,12-(C₆H₄CHO)₂-1,2-*closo*-C₂B₁₀H₁₀, **4**, in 96% yield (Scheme 1a). Suitable crystals for X-ray diffraction of **3** and **4**, which were grown in chloroform (Fig. 1) unambiguously and unequivocally confirmed that **3** and **4** were obtained. Furthermore, tetrasubstitution on **2** to yield 8,9,10,12-Ph₄-1,2-*closo*-C₂B₁₀H₈ (**10**) was expected by reaction of **2** with phenyl magnesium chloride but 8,10-Ph₂-9,12-I₂-1,2-*closo*-C₂B₁₀H₈ (**5**) was obtained with only two substitutions (Scheme 1b).^{9d} To get more insight into the reason for this atypical or at least unexpected result, we investigated ¹¹B{¹H}-NMR chemical shifts (Fig. 2) and performed DFT calculations. The ¹¹B{¹H}-NMR chemical shifts of **2** were unambiguously assigned^{9d} with the aid of a 2D ¹¹B{¹H}-¹¹B{¹H}-NMR COSY experiment.¹⁵ The B(9,12) resonances of these B–I vertices at **2** appear at –7.1 ppm that are not so different from the B–H resonances of the unreactive B(9,12) vertices in the pristine 1,2-*closo*-C₂B₁₀H₁₂ (–3.1 ppm); on the contrary, the B(8,10) vertex resonances of **2** appear close to –16 ppm being very similar to the B–I reactive B(9,12) vertices in **1** that resonate at –14.9 ppm (Fig. 2). It can be seen in the ¹¹B{¹H}-NMR of 1,2-*closo*-C₂B₁₀H₁₂, 9,12-I₂-*closo*-1,2-C₂B₁₀H₁₀ (**1**) and 8,10,9,12-I₄-1,2-*closo*-C₂B₁₀H₈ (**2**) that the four iodo groups in the congested area of **2** are not electronically identical. Electronically, the B(8,10) vertices in **2** are strongly affected upon I substitution shifting 12 ppm upfield from B(8,10)–H to B(8,10)–I. These B(8,10)–I vertices are highly reactive and lead readily to disubstitution to obtain B–Ph in **5**. The calculated Mulliken charges (Table S1 in ESI[†]) are in good agreement with the chemical shifts; the charge of the reactive B(8,10)–I vertices in **2** is +0.66, while the charge of the B(8,10)–I vertices is +0.31 in **5**.

Clearly, the B(9,12) vertices in **5** are not only less reactive electronically, but less accessible for the reactant (steric hindrance) due to the phenyl substituents at the B(8,10) vertices. Since the four-fold phenylation of **2** was unsuccessful, a new synthetic strategy aiming at 8,9,10,12-Ph₄-1,2-*closo*-C₂B₁₀H₈ was designed. The positional isomer of **5**, 8,10-I₂-9,12-Ph₂-1,2-*closo*-C₂B₁₀H₈ (**7**) was synthesised starting from **6**. In **7** the two iodo substituents would be ready for substitution at less crowded positions than in **5**; moreover, DFT calculations suggest a more reactive B–I vertex. This led us to perform the cross coupling reaction of **2** with PhMgCl to obtain 9,12-Ph₂-1,2-*closo*-C₂B₁₀H₁₀, **6**.¹³ This was

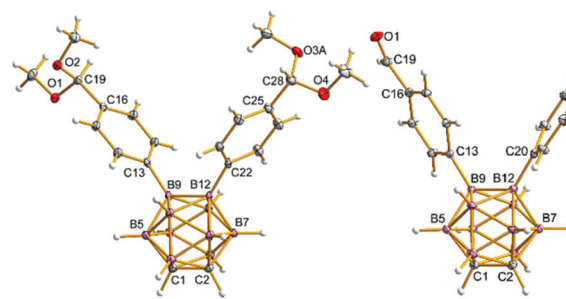


Fig. 1 Crystal structures of **3** (left) and **4** (right). Thermal ellipsoids have been drawn with 20% probability. The B9–B12 distances are 1.804(4) and 1.798(3) Å for **3** and **4**.



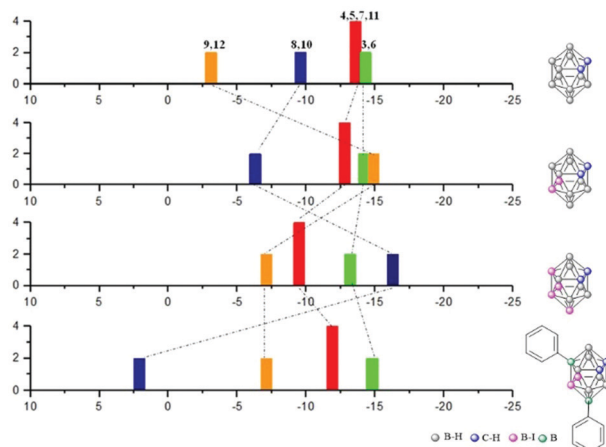
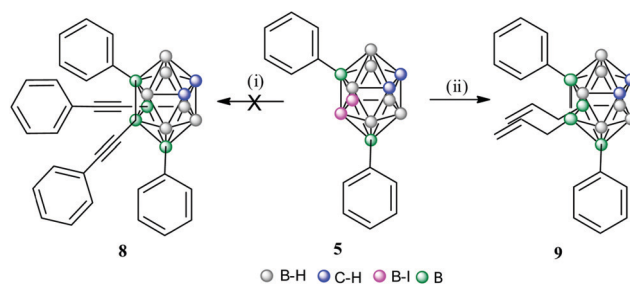


Fig. 2 Diagram $^{11}\text{B}\{^1\text{H}\}$ -NMR spectra with the peak assignments for the *o*-carborane, **1**, **2** and **5** derivatives.

treated with I_2 in a sealed tube at 210°C for 4 h (73% yield, Scheme 1c).

The ^{11}B NMR spectra of **7** verified the more reactive B-I vertices (they resonate at -20.1 ppm), in agreement with the DFT calculations. Furthermore, as it was mentioned earlier, the different allocation of the four substituents in **7** with respect to **5** could decrease the steric effect of the two bulky phenyl groups since they are sited at the neighbouring vertices B(9,12), and the two remaining iodo substituents are placed one far from the other and at the lateral position, so the B-I substitutions by the phenyl groups are sterically feasible. However, the cross-coupling reaction of **7** with PhMgCl did not lead to the sought four-fold phenylation, only to unreacted **7** (Scheme 1c).

To check the possibility of further substitution on the **5** congested electron-rich region of the *o*-carborane cluster, we decided to combine the pre-existing sp^2 (Ph) in **5**, with the sp ($\text{PhC}\equiv\text{C}$) and sp^3 (allyl) units, respectively. The reaction of **5** with phenylethynyl magnesium chloride to produce **8** was unsuccessful as no iodo was exchanged (Scheme 2). Instead, when using a less crowded allyl magnesium chloride, the coupling reaction of **5** with allyl magnesium chloride leads to the four-fold substitution by the formation of 8,10- Ph_2 -9,12- $(\text{CH}_2\text{CHCH}_2)_2$ -1,2-*closo*- $\text{C}_2\text{B}_{10}\text{H}_8$, **9**, in 75% yield (Scheme 2). ^{11}B and ^1H NMR spectroscopy, MALDI-TOF-MS and EA data along with its X-ray structure from the crystals grown from a chloroform solution (Fig. 3 and ESI†) confirmed the allylation of B(9,12) vertices on **5**. Since the sp and sp^2 four-fold substitution is possible, the steric hindrance in the proposed tetra-substituted 8,10,9,12- Ph_4 -1,2-*closo*- $\text{C}_2\text{B}_{10}\text{H}_8$ (**10**, Scheme 3) compound was investigated by using different hypothetical isodesmic reactions (see more details in ESI†). The DFT calculations indicated that there is not enough steric hindrance in **10** to prevent four-fold phenyl substitution, therefore **10** should be thermodynamically available and so its synthesis should be restricted only by kinetic reasons. To prove this hypothesis, we have modified the reaction conditions by using 1,4-dioxane instead of THF, which increases the reaction temperature up to 101°C (Scheme 3). After 16 hours of refluxing, the ^1H -NMR spectra of the crude mixture displayed new broad



Scheme 2 Kumada cross coupling reactions on **2** by using (i) $\text{PhC}\equiv\text{CMgCl}$, (ii) $\text{CH}_2=\text{CHCH}_2\text{MgCl}$, in the presence of *cis*- $[\text{PdCl}_2(\text{PPh}_3)_2]$ and CuI as catalysts, in refluxing THF overnight.

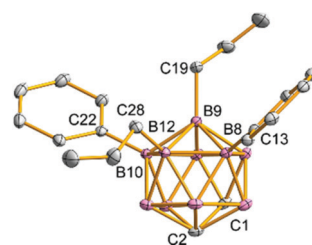
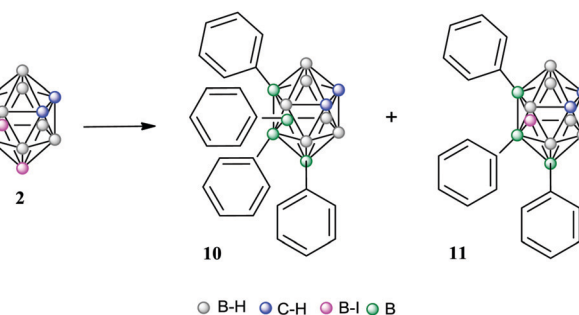


Fig. 3 Crystal structures of **9**. Thermal ellipsoids have been drawn with 20% probability.



Scheme 3 Kumada cross coupling reactions on **2** in refluxing dioxane for 16 h.

peaks in the region 4.5–5.5 ppm, in which the C_c -H resonates, indicating the formation of additional compounds.^{3a} By working up (see ESI†), the isolation of four-fold substituted *o*-carborane derivative **10** as well as the trisubstituted **11** was achieved in 18 and 59% yield, respectively. To further increase the yield of **10**, mesitylene (b.p. 165°C) and diglyme (b.p. 162°C) were used as solvents however, the yield was lower (12% and 16%, respectively) probably due to other side reactions. Finally, the reaction in toluene, slightly increased the yield of **10** to 21 and 34% after 16 h and 5 days' reaction time, respectively. The reaction in toluene was carried out under microwave irradiation (see in ESI†) as well, but a similar ratio of **10** and **11** (comparing the reaction in toluene after 16 h reflux) was observed after 2 h irradiation at 120°C according to the ^1H NMR spectra of the crude product. It is to be emphasized that the by-product of **10** (compound **11**) is suitable for recycling, thus the overall yield can be significantly improved. Crystals of **10** and **11** suitable for X-ray diffraction



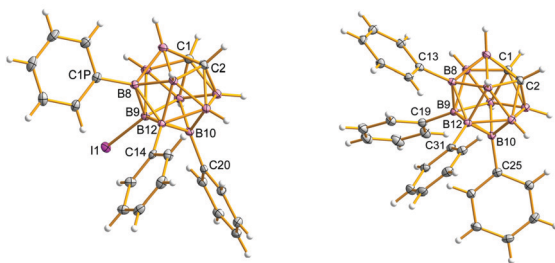


Fig. 4 Crystal structures of **10** (right) and **11** (left). Thermal ellipsoids have been drawn with 20% probability.

(Fig. 4) were obtained using the vapour diffusion technique (pentane/acetone, see ESI†). The four-fold phenyl groups at the dense antipodal region of the cluster carbon atoms of the *closo-o*-carborane in **10** parallels the nanohybrid $[\eta^5\text{-C}_{60}\text{Ph}_5]^-$,^{16a} that made the extremely hydrophobic C₆₀ fullerene soluble in water.^{16b}

A search at the Cambridge Structural Database¹⁷ shows only seven hits for 9,12-(aryl)₂-1,2-*closo*-C₂B₁₀H₁₀, whose B9–B12 distances are in the range 1.781–1.824 Å (Table S1 in ESI†), which are comparable, although a bit longer than that in *o*-carborane (1.776 Å).¹⁸ Although a certain plasticity at the B–B bonds antipodal to the C_c atoms is observed, the effect is considerably smaller than the plasticity found for the adjacent C_c atoms in the *o*-carborane cluster. This is not surprising as the antibonding orbital is mainly located between the adjacent C_c atoms for these derivatives.⁵ Compared to the electron-donation to the $\sigma^*(\text{C}_c\text{--C}_c)$, whose extent in terms of distance has been found experimentally at 2.156(4) Å in 1,2-(CR₂F_c)₂-1,2-*closo*-C₂B₁₀H₁₀⁷ and computed at 2.64 Å for 1,2-(CH₂[−])₂-1,2-C₂B₁₀H₁₀,⁵ the maximum elongation found in the antipodal region of **10** (1.822 Å) or **11** (1.824) indicates a minor effect, near 0.048 Å. In agreement, the second-order perturbation theory analysis on the NBO basis reveals weak interactions (sum of them ~ 12 kcal mol^{−1}) between the aryl π -systems and the antibonding orbitals of the boron atoms, which was in good agreement with enlargement of the B–B distances in the cluster. This enforces the concept of the electron back donation to the $\sigma^*(\text{C}_c\text{--C}_c)$ vs. the very much abused steric hindrance. The proven, although weak, influence of the aryl groups in the plasticity on the B9–B12 bonds and the possibility of substitution at the C_c–H vertices foresee these *o*-carborane derivatives as appropriate synthons for surface functionalization; research in this direction is underway in our laboratories.

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Conflicts of interest

There are no conflicts to declare.

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