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How to Protect *ortho*-Carborane from Decapitation—Practical Synthesis of 3,6-Dihalogen Derivatives 3,6-X_2-1,2-$C_2B_{10}H_{10}$ (X = Cl, Br, I)

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Abstract: The 3-halogen and 3,6-dihalogen derivatives of *ortho*-carborane 3-X-1,2-$C_2B_{10}H_{11}$ and 3,6-X_2-1,2-$C_2B_{10}H_{10}$ (X = Cl, Br, I) were prepared by Cu-assisted halodeboronation of the corresponding pinacolborate derivatives 3-Bpin-1,2-$C_2B_{10}H_{11}$ and 3,6-$(Bpin)_2$-1,2-$C_2B_{10}H_{10}$. It was shown that decapitation of 3-Cl-1,2-$C_2B_{10}H_{11}$, similarly to the corresponding bromo and iodo derivatives, proceeds regioselectively with the retention of the B-Cl bond. Crystal structures of 3,6-Cl_2-1,2-$C_2B_{10}H_{10}$ and Cs [3-Cl-7,8-$C_2B_9H_{11}$] were determined by single crystal X-ray diffraction.

Keywords: *ortho*-carborane; halogen derivatives; synthesis; NMR spectra; single crystal X-ray diffraction

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1. Introduction

The discovery of the decapitation of *ortho*-carborane under the action of strong nucleophiles with the formation of *nido*-carborane in the 1960s [1,2] initiated the development of at least two main directions in the development of carborane chemistry. The first one was the use of dicarbollide ligands, which are formed upon the deprotonation of *nido*-carboranes with strong bases, for the synthesis of π-complexes of transition metals analogous to complexes with cyclopentadiene ligands, the so-called metallacarboranes [3–11]. Another direction was the transformation of *closo*-carborane derivatives into the corresponding *nido*-carboranes in order to increase their water solubility for use in boron neutron capture therapy for cancer [12–19], radio-immunodiagnostics and radio-immunotherapy [20–22], as well as some other medical applications [23–27]. Later, the use of *nido*-carboranes in the design of carborane-containing luminescent materials was reported [28–34]. However, the transformation of the *closo*-carborane cage into the *nido*-carborane one leads to the appearance of an anionic charge, which implies the presence of a counterion, and also results in a significant decrease in the thermal and chemical stability of the carborane cage. In addition, during decapitation, the strong electron-withdrawing effect of the *C*-carboranyl group changes to an electron-donating one [30,31,35–38]. Therefore, for many important applications of carboranes in material chemistry [39–52], their decapitation is highly undesirable. Therefore, the protection of the *ortho*-carborane cage from decapitation is one of the urgent problems in the design of new carborane-based materials.

It was earlier demonstrated that the substitution of hydrogen atoms in positions 3 and 6 of *ortho*-carborane with phenyl groups successfully protects the carborane cage from decapitation [53]. However, the rather large size of the phenyl groups precludes substitution at adjacent carborane carbons and obstructs the rational design of *ortho*-carborane-based materials. Therefore, the goal of this study was to develop convenient methods for the synthesis of 3,6-dihalogen-substituted derivatives of *ortho*-carborane 3,6-X_2-1,2-$C_2B_{10}H_{10}$, the substituents in which have the smallest size that do not prevent further modification.

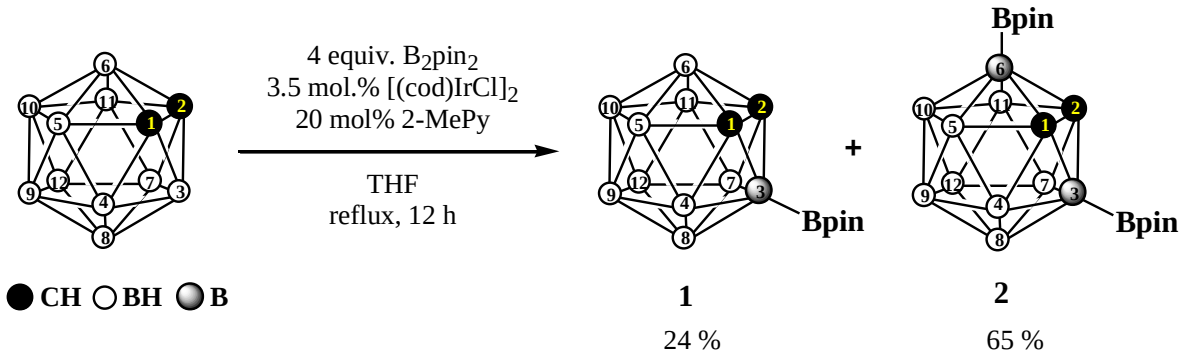
2. Results and Discussion

The introduction of substituents into positions 3 and 6 of the *ortho*-carborane cage by a direct route is impossible and usually involves several steps. The simplest approach involves two consecutive decapitations of *ortho*-carborane to *nido*-carborane followed by the insertion of the "missing" boron vertex with the corresponding substituent BX. It is this approach that was first used for the synthesis of 3,6-diiodo-*ortho*-carborane [54,55].

An important issue here is the retention of the substituent during the decapitation of 3-substituted *ortho*-carboranes, which in general can go through both the free position 6 and the substituted position 3. Earlier, it was shown that the decapitation of 3-bromo- and 3-iodo-*ortho*-carboranes proceeds with the retention of the substituent [56]. The retention of a substituent is also characteristic of 3-alkyl-, 3-aryl-, and 3-alkynyl-*ortho*-carboranes [53,57–60], as well as of 3-amino-*ortho*-carborane and other derivatives with a B-N bond [61–65]. At the same time, decapitation of 3-fluoro [66] and 3-hydroxy [67] derivatives of *ortho*-carborane leads to mixtures of the parent *nido*-carborane and the corresponding substituted *nido*-carboranes, i.e., is not selective. Thus, both the fluorine and the hydroxy group cannot be used to protect *ortho*-carborane from decapitation.

Alternatively, the first decapitation-insertion sequence can be replaced by diazotization of the 3-amino derivative formed by the reduction of *ortho*-carborane with sodium metal in liquid ammonia, followed by oxidation of the resulting product with $KMnO_4$ or $CuCl_2$, followed by replacement of the diazo group with various nucleophiles [68–71]. Recently, the direct way to the synthesis of the 3-amino derivative by the Ir-catalysed reaction of the parent *ortho*-carborane with ammonia in tetrahydrofuran has been proposed [72]. This approach is also applicable to various derivatives of *ortho*-carborane, including 3-substituted derivatives, which makes it possible to avoid the use of highly aggressive boron trihalides and liquid ammonia.

Recently, the simultaneous introduction of substituents at positions 3 and 6 of the *ortho*-carborane cage was reported using the Ir-catalysed reaction of the parent *ortho*-carborane with bis(pinacolato)diboron B_2pin_2 followed by the replacement of the pinacolborane groups in 3,6-$(Bpin)_2$-1,2-$C_2B_{10}H_{10}$. In particular, the authors used this approach to obtain 3,6-dibromo- and 3,6-diiodo-derivatives of *ortho*-carborane [73]. Wishing to use this approach, we prepared 3-pinacolborane (**1**) and 3,6-di(pinacolborane) (**2**) derivatives by reaction of the parent *ortho*-carborane with B_2pin_2 in the presence of a $[(cod)Ir(\mu\text{-}Cl)]_2$ iridium catalyst according to the previously described procedure modified by us at the product separation stage (Scheme 1). However, in our hands, the further Pd-catalysed substitution reactions described by them did not give the desired result.

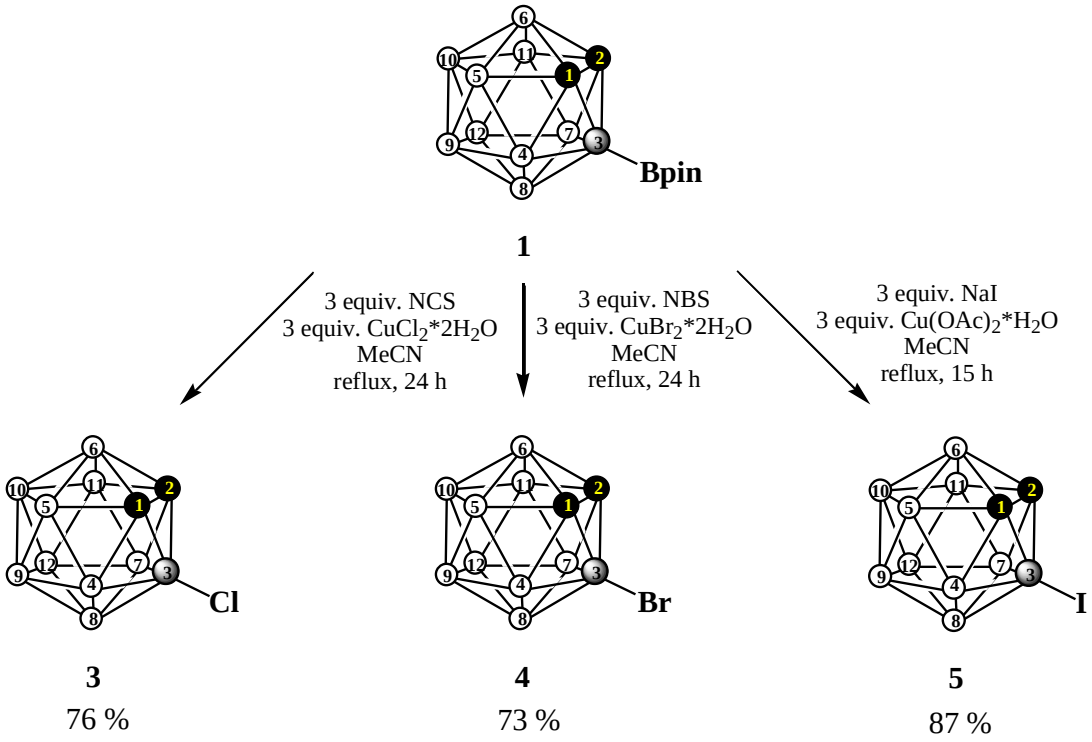


Scheme 1. Synthesis of 3-Bpin-1,2-$C_2B_{10}H_{11}$ (**1**) and 3,6-$(Bpin)_2$-1,2-$C_2B_{10}H_{10}$ (**2**).

To solve the problem, we have developed a method for the Cu-catalysed halodeboronation of pinacolborane derivatives of *ortho*-carborane, similar to that used in organic chemistry for halodeboronation of aryl boronic acids [74–79].

The reactions of 3-Bpin-1,2-$C_2B_{10}H_{11}$ (**1**) with three equivalents of *N*-chloro- and *N*-bromosuccinimides in the presence of three equivalents of $CuX_2 \cdot 2H_2O$ in boiling ace-

tonitrile for 24 h gave the corresponding 3-chloro (**3**) and 3-bromo (**4**) derivatives of *ortho*-carborane in high yields (Scheme 2). The 3-iodo derivative 3-I-1,2-$C_2B_{10}H_{11}$ (**5**) was prepared using I2 and $Cu(OAc)_2 \cdot H_2O$ instead of the corresponding *N*-halogen-succinimide and copper(II) halogenide (Scheme 2). It should be noted that in the absence of an iodine source, the latter reaction leads to the formation of the corresponding acetoxy derivative 3-AcO-1,2-$C_2B_{10}H_{11}$ (**6**).

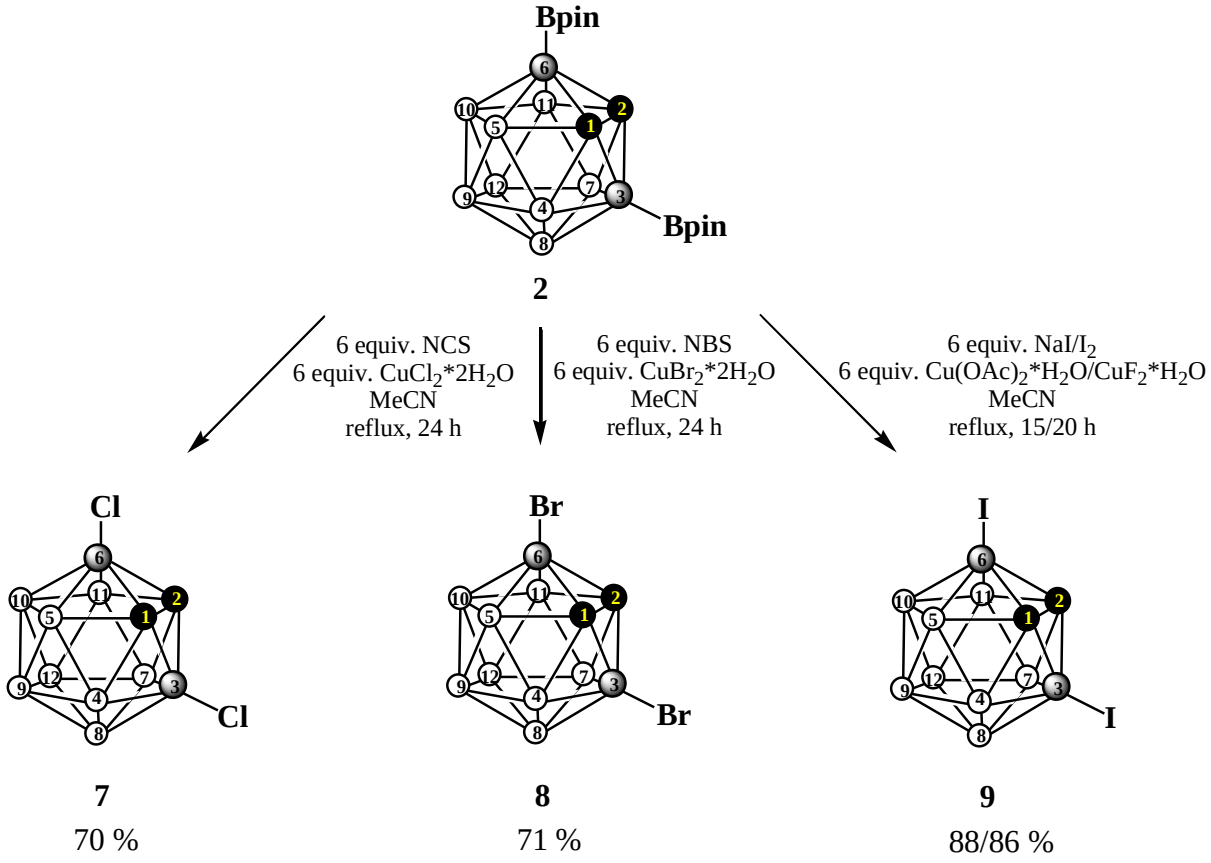


Scheme 2. Synthesis of 3-halogen derivatives 3-X-1,2-$C_2B_{10}H_{11}$ (X = Cl (**3**), Br (**4**), I (**5**)).

Similarly, the reactions of 3,6-$(Bpin)_2$-1,2-$C_2B_{10}H_{10}$ (**2**) with six equivalents of *N*-chloro- and *N*-bromosuccinimides in the presence of six equivalents of $CuX_2 \cdot 2H_2O$ in boiling acetonitrile for 24 h result in the corresponding 3,6-dichloro (**7**) and 3,6-dibromo (**8**) derivatives of *ortho*-carborane. The 3,6-diiodo derivative 3,6-I_2-1,2-$C_2B_{10}H_{10}$ (**9**) was prepared by the treatment of the 3,6-di(pinacolborate) derivative **2** with six equivalents of sodium iodide NaI and copper acetate $Cu(OAc)_2 \cdot H_2O$ or iodine I_2 and copper fluoride $CuF_2 \cdot H_2O$ in refluxing acetonitrile (Scheme 3). The reaction with copper acetate in the absence of NaI results in the known 3,6-di(acetoxy) derivative 3,6-$(AcO)_2$-1,2-$C_2B_{10}H_{10}$ (**10**). It should be noted that the reaction of the 3,6-di(pinacolborate) derivative **2** with copper acetate in the presence of NaBr also led to the 3,6-di(acetoxy) derivative **10**, while the reactions with *N*-bromosuccinimide or $(Bu_4N)Br$ and Br_2 gave mixtures of 3,6-dibromo **8** and 3,6-(diacetoxy) **10** derivatives. The reactions of the 3,6-di(pinacolborate) derivative **2** with $CuF_2 \cdot 2H_2O$ in the presence of CsF, KHF_2, or MeI were found to result in the parent *ortho*-carborane 1,2-$C_2B_{10}H_{12}$ in 7 h.

The structure of 3,6-dichloro derivative 3,6-Cl_2-1,2-$C_2B_{10}H_{10}$ (**7**) was determined by single crystal X-ray diffraction. The general view of **7** is presented in Figure 1. In the crystal, the molecule occupies special positions located at the two-fold symmetry axis. The B3-Cl1 bond (1.757(5) Å) is noticeable shorter than the B-Cl bonds in the 9,12-isomer 9,12-Cl_2-1,2-$C_2B_{10}H_{10}$ (1.798(2) Å) [80]. In contrast to the crystal structure of the 3,6-diiodo derivative, which is characterized by the presence of the I···I dihalogen bonds of type II (I···I distance 4.067 Å, B-I···I angle is 91.19°) [81], there was not any strong intermolecular interactions in the crystal structure of the titled compound. Weak Cl···Cl dihalogen bonds of type I with a distance of 3.768(3) Å (that is longer than the sum of Van der Waals radii

(3.65 Å) [82]) linked molecules into chains along the (101) direction while all the other interactions were Van der Waals (Figure 2).



Scheme 3. Synthesis of 3,6-dihalogen derivatives 3,6-X_2-1,2-$C_2B_{10}H_{10}$ (X = Cl (**7**), Br (**8**), I (**9**)).

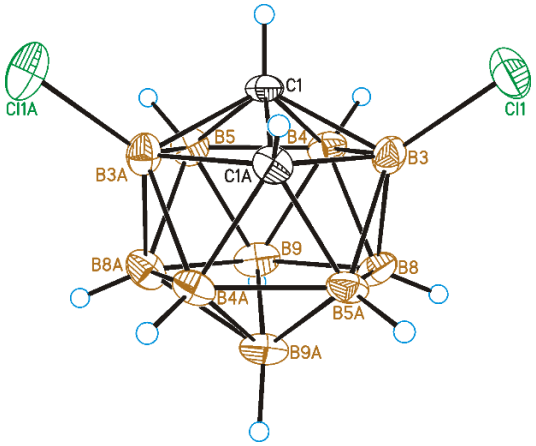


Figure 1. General view of 3,6-Cl_2-1,2-$C_2B_{10}H_{10}$ along with atomic numbering. Thermal ellipsoids are shown at 50% probability level.

Since the decapitations of 3-bromo and 3-iodo derivatives of *ortho*-carborane occur selectively with the retention of the substituent, and in the case of the 3-fluoro derivative non-selectively, it was important to understand how the decapitation of the 3-chloro derivative **3** occurs. We found that heating **3** with CsF in ethanol led to selective decapitation of the unsubstituted vertex to form *nido*-carborane Cs [3-Cl-7,8-$C_2B_9H_{11}$] (**11**) (Scheme 4). Thus, unlike fluorine, the chlorine atom protects the boron atom bound to two carbon atoms from nucleophilic attack.

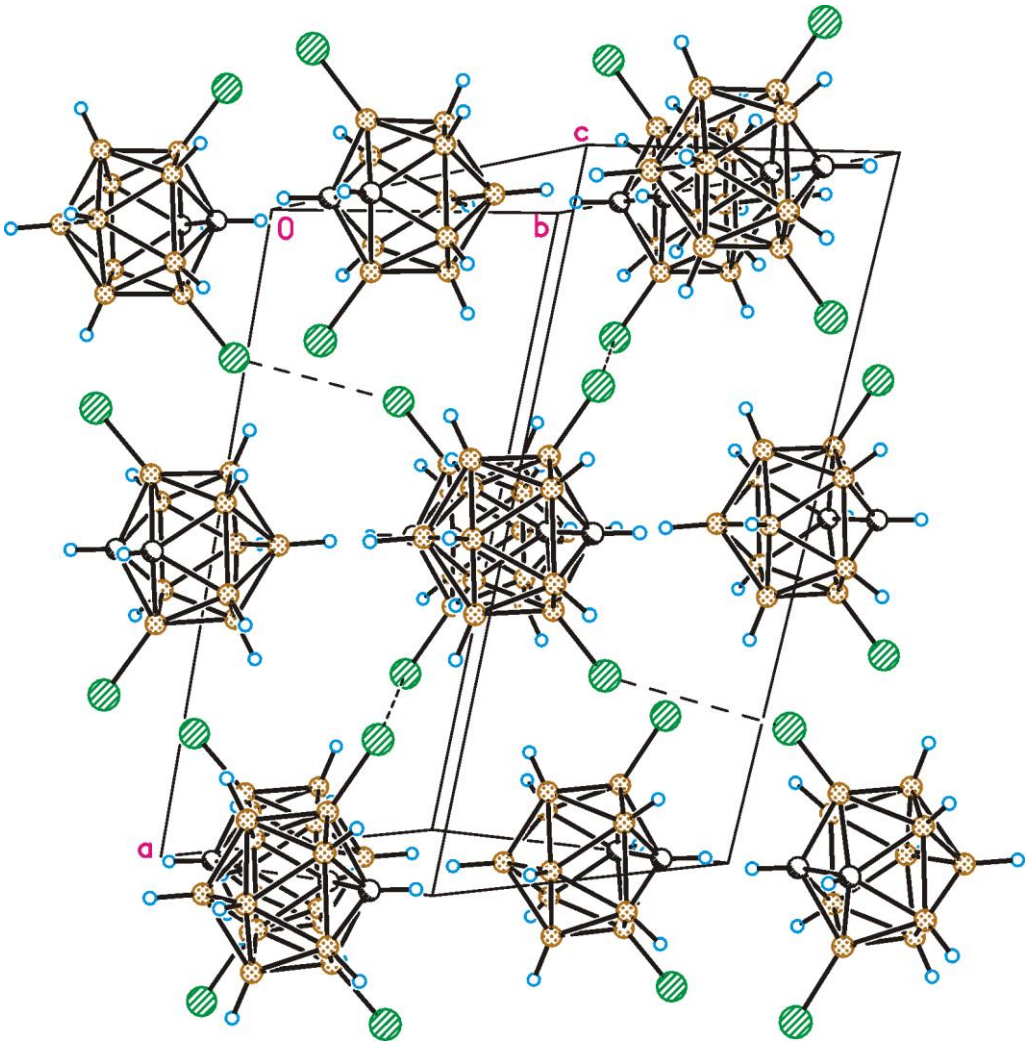
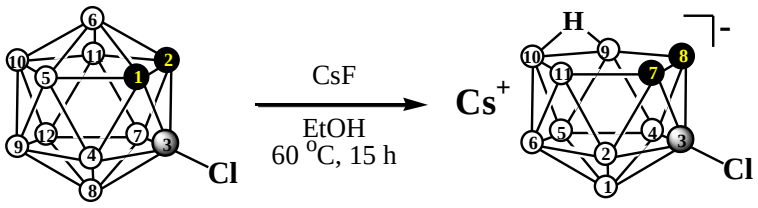


Figure 2. Crystal packing fragment of 3,6-Cl_2-1,2-$C_2B_{10}H_{10}$. The Cl···Cl contacts are shown by dashed lines.



3 **11**

88 %

Scheme 4. Decapitation of 3,6-Cl_2-1,2-$C_2B_{10}H_{10}$ (**7**).

The crystal structure of Cs [3-Cl-7,8-$C_2B_9H_{11}$] (**11**) was determined by single crystal X-ray diffraction. The general view of 3-chloro-*nido*-carborane with Cs counterion is given in Figure 3. The B3-Cl1 bond length was somewhat longer than that in **7** (1.790 (10) Å). In the crystal there was not even any weak Cl···Cl and Cl···H contacts that was probably due to the presence of the Cs cation which governs crystal packing motifs by the formation of numerous Cs···H and Cs···Cl contacts. Through those contacts, each Cs cation simultaneously binds six carborane cages (Figure 4).

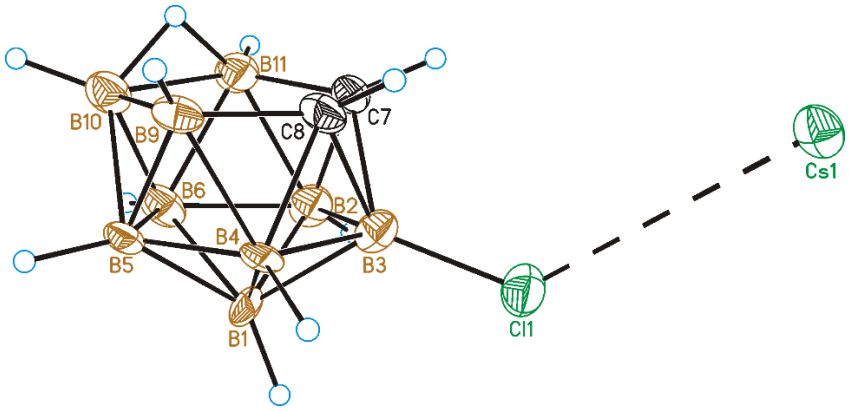


Figure 3. General view of Cs [3-Cl-7,8-$C_2B_9H_{11}$] along with atomic numbering. Thermal ellipsoids are shown at 50% probability level.

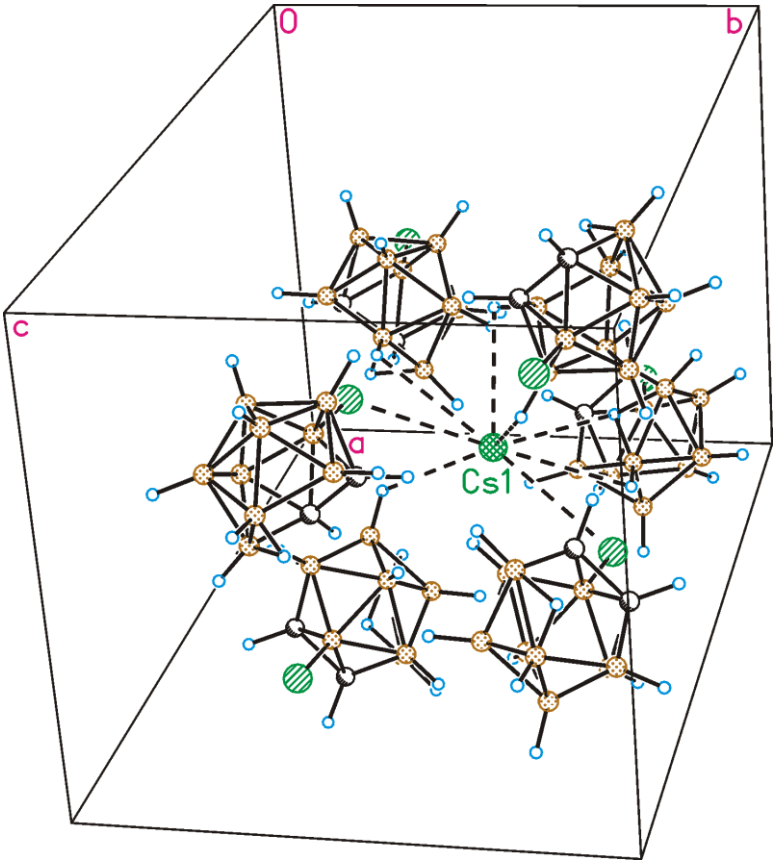


Figure 4. Crystal packing fragment of Cs [3-Cl-7,8-$C_2B_9H_{11}$]. The closest environment of the Cs cation is shown by solid dashed lines. The Cs1···Cl1 distances are 3.762 (2) Å and 3.776 (2) Å, the Cs-H distances are in the range of 3.15–3.35 Å.

The 3,6-dihalogen derivatives 3,6-X_2-1,2-$C_2B_{10}H_{10}$ (X = Cl, Br, I) were found to resist decapitation under the conditions which were used for decapitation of the 3-chloro derivative of *ortho*-carborane (refluxing with CsF in ethanol).

3. Materials and Methods

3.1. General Methods

Acetonitrile and tetrahydrofuran were dried using standard procedures [83]. All other chemical reagents were purchased from Sigma Aldrich (Burlington, MA, USA), Acros

Organics (Geel, Belgium), and ABCR (Karlsruhe, Germany) and used without purification. The reaction progress was monitored by thin-layer chromatography (Merck F254 silica gel on aluminium plates and Macherey-Nagel ALUGRAM Xtra SIL G UV254) and visualized using 0.5 % $PdCl_2$ in 1% HCl in aq. MeOH (1:10). Acros Organics (0.060–0.200 mm) silica gel was used for column chromatography. The NMR spectra at 400 MHz (^{1}H), 128 MHz (^{11}B) and 100 MHz (^{13}C) (See Supplementary Materials) were recorded with a Varian Inova 400 spectrometer (Palo Alto, CA, USA). The residual signal of the NMR solvent relative to Me_4Si was taken as the internal reference for the ^{1}H and ^{13}C NMR spectra. The ^{11}B NMR spectra were referenced using $BF_3{\cdot}Et_2O$ as external standard. Mass spectra (MS) were measured using the Shimadzu LCMS-2020 instrument (Kyoto, Japan) with DUIS ionization (ESI—electrospray ionization and APCI—atmospheric pressure chemical ionization). The measurements were performed in a negative ion mode with a mass range from *m/z* 50 to *m/z* 2000.

3.2. Synthesis of 3-Bpin-1,2-$C_2B_{10}H_{11}$ (**1**) *and 3,6-(Bpin)$_2$-1,2-$C_2B_{10}H_{10}$* (**2**)

Under an argon atmosphere, *ortho*-carborane (1.440 g, 10.00 mmol), bis(pinacolato)-diboron B_2pin_2 (1.016 g, 40.00 mmol), and bis(1,5-cyclooctadiene)diiridium (I) dichloride $[(cod)Ir(\mu\text{-}Cl)]_2$ (235 mg, 0.35 mmol) were placed in a 50 mL two-neck flask and dry THF (10 mL) was added. Then, 2-methylpyridine (196 mg, 207 µL, 2.10 mmol) was added and heated under reflux for 12 h, monitoring the progress of the reaction by thin-layer chromatography (dichloromethane) and ^{11}B NMR spectroscopy. After cooling the reaction mixture to ambient temperature, silica gel was added, and all volatiles were removed on a rotary evaporator. The resulting solid residue was subjected to column chromatography using dichloromethane as the eluent. The first and second fractions were collected and concentrated on a rotary evaporator to obtain white compounds **1** (648 mg, 24%) and **2** (2574 mg, 65%), respectively.

3-Bpin-1,2-$C_2B_{10}H_{11}$ (**1**): ^{1}H NMR ($CDCl_3$, ppm): 3.56 (2H, br.s, CH_{carb}), 1.25 (12H, s, CH_3). ^{11}B NMR ($CDCl_3$), δ: 33.3 (1B, s, Bpin), −1.6 (2B, d, *J* = 145 Hz), −7.7 (1B, d, *J* = 155 Hz), −8.3 (1B, d, *J* = 146 Hz), −12.8 (5B, d + s, *J* = 163 Hz), −14.3 (1B, d, *J* = 177 Hz).

3,6-(Bpin)$_2$-1,2-$C_2B_{10}H_{10}$ (**2**): ^{1}H NMR ($CDCl_3$, ppm): 3.55 (2H, br.s, CH_{carb}), 1.26 (24H, s, CH_3). ^{11}B NMR ($CDCl_3$), δ: 33.7 (2B, s, Bpin), −0.7 (2B, d, *J* = 145 Hz), −6.4 (2B, d, *J* = 155 Hz), −11.7 (6B, d + s, J = 146 Hz).

3.3. General Procedure for the Synthesis of 3-Halogen-ortho-carboranes 3-X-1,2-$C_2B_{10}H_{11}$ (X = Cl (**3**)*, Br*(**4**)*)*

3-Bpin-1,2-$C_2B_{10}H_{11}$ (**1**) (50.0 mg, 0.185 mmol), *N*-X-succinimide (0.555 mmol) and CuX_2 (0.555 mmol) were placed in a 25 mL round bottom flask and acetonitrile (5 mL) was added. The reaction mixture was heated under reflux for ~ 24 h until complete conversion according to ^{11}B NMR and allowed to cool to room temperature. The solvent was removed in vacuo and the resulting solid residue was subjected to column chromatography on silica using a mixture of chloroform and petroleum ether (2:1, *v/v*) as the eluent.

3-Cl-1,2-$C_2B_{10}H_{11}$ (**3**): According to the general procedure using *N*-chlorosuccinimide (74.0 mg) and $CuCl_2{\cdot}2H_2O$ (75.0 mg), 25.8 mg (76% yield) of a white crystalline compound **3** was obtained. ^{1}H NMR ($CDCl_3$, ppm): 3.81 (2H, br.s, CH_{carb}). ^{11}B NMR ($CDCl_3$, ppm): −2.7 (2B, d, *J* = 151 Hz), −5.5 (1B, s), −8.9 (1B, d, *J* = 152 Hz), −12.4 (2B, d, *J* = 184 Hz), −13.9 (3B, d, *J* = 174 Hz), −14.8 (1B, d, *J* = 115 Hz).

3-Br-1,2-$C_2B_{10}H_{11}$ (**4**): According to the general procedure using *N*-bromosuccinimide (98.8 mg) and $CuBr_2{\cdot}2H_2O$ (144.0 mg), 30.1 mg (73% yield) of a white crystalline compound **4** was obtained. ^{1}H NMR ($CDCl_3$, ppm): 3.84 (2H, br.s, CH_{carb}). ^{11}B NMR ($CDCl_3$, ppm): −2.2 (2B, d, *J* = 151 Hz), −8.3 (1B, d, *J* = 155 Hz), −11.9 (2B, d, *J* = 175 Hz), −12.4 (1B, s), −13.4 (4B, d, *J* = 174 Hz).

3.4. Synthesis of 3-Iodo-ortho-Carborane 3-I-1,2-$C_2B_{10}H_{11}$ (**5**)

3-Bpin-1,2-$C_2B_{10}H_{11}$ (**1**) (50.0 mg, 0.185 mmol), NaI (83.2 mg, 0.555 mmol) and $Cu(OAc)_2 \cdot H_2O$ (110.8 mg, 0.555 mmol) were placed in a 25 mL round bottom flask and acetonitrile (5 mL) was added. The reaction mixture was heated under reflux for 15 h until complete conversion according to ^{11}B NMR and allowed to cool to room temperature. The solvent was removed in vacuo and the resulting solid residue was subjected to column chromatography on silica using a mixture of chloroform and petroleum ether (2:1, *v/v*) as the eluent. The first boron-containing fraction was collected and concentrated on a rotary evaporator under reduced pressure to obtain a white crystalline compound **5** (43.4 mg, 87% yield). ^1H NMR ($CDCl_3$, ppm): 3.84 (2H, br.s, CH_{carb}). ^{11}B NMR ($CDCl_3$, ppm): −1.3 (2B, d, *J* = 151 Hz), −7.1 (1B, d, *J* = 156 Hz), −11.0 (3B, d, *J* = 174 Hz), −12.4 (2B, d, *J* = 174 Hz), −13.1 (1B, d, *J* = 188 Hz), −29.3 (1B, s).

3.5. Synthesis of 3-Acetoxy-ortho-Carborane 3-AcO-1,2-$C_2B_{10}H_{11}$ (**6**)

3-Bpin-1,2-$C_2B_{10}H_{11}$ (**1**) (50.0 mg, 0.185 mmol) and $Cu(OAc)_2 \cdot H_2O$ (110.8 mg, 0.555 mmol) were placed in a 25 mL round bottom flask and acetonitrile (5 mL) was added. The reaction mixture was heated under reflux for 30 h until complete conversion according to ^{11}B NMR and allowed to cool to room temperature. The solvent was removed in vacuo and the resulting solid residue was subjected to column chromatography on silica using a mixture of chloroform and petroleum ether (2:1, *v/v*) as the eluent. The first boron-containing fraction was collected and concentrated on a rotary evaporator under reduced pressure to obtain a white crystalline compound **6** (33.2 mg, 89% yield). ^1H NMR (acetone-d_6, ppm): 4.86 (2H, br.s, CH_{carb}), 2.12 (3H, s, CH_3). ^{11}B NMR (acetone-d_6, ppm): −4.0 (1B, s), −5.5 (2B, d, *J* = 153 Hz), −11.2 (1B, d, *J* = 178 Hz), −13.9 (2B, d, *J* = 174 Hz), −14.8 (1B, d), −15.6 (2B, d, *J* = 188 Hz), −17.0 (1B, d, *J* = 162 Hz).

3.6. General Procedure for the Synthesis of 3,6-Dihalogen-ortho-carboranes 3,6-X_2-1,2-$C_2B_{10}H_{10}$ (X = Cl (**7**)*, Br*(**8**)*)*

3,6-$(Bpin)_2$-1,2-$C_2B_{10}H_{10}$ (**2**) (1 equiv.), *N*-X-succinimide (6 equiv.) and CuX_2 (6 equiv.) were placed in a 25 mL round bottom flask and acetonitrile (5 mL) was added. The reaction mixture was heated under reflux for ~24 h until complete conversion according to ^{11}B NMR and allowed to cool to room temperature. The solvent was removed in vacuo and the resulting solid residue was subjected to column chromatography on silica using a mixture of chloroform and petroleum ether (2:1, *v/v*) as the eluent.

3,6-Cl_2-1,2-$C_2B_{10}H_{10}$ (**7**): According to the general procedure using 3,6-$(Bpin)_2$-1,2-$C_2B_{10}H_{10}$ (396.0 mg, 1.000 mmol), *N*-chlorosuccinimide (801.0 mg, 6.000 mmol) and $CuCl_2 \cdot 2H_2O$ (1022.7 mg, 6.000 mmol), 168.3 mg (79% yield) of a white crystalline compound **7** was obtained. ^1H NMR ($CDCl_3$, ppm): 4.07 (2H, br.s, CH_{carb}). ^1H NMR (acetone-d_6, ppm): 5.40 (2H, br.s, CH_{carb}). ^{11}B NMR ($CDCl_3$, ppm): −3.2 (2B, d, *J* = 153 Hz, B(9) + B(12)), −4.4 (2B, s, B(3) + B(6)), −12.6 (4B, d, *J* = 169 Hz, B(4) + B(5) + B(7) + B(11)), −14.6 (2B, d, *J* = 159 Hz, B(8) + B(10)). ^{11}B NMR (acetone-d_6, ppm): −4.2 (4B, d + s, *J* = 147 Hz, B(3) + B(6)+ B(9) + B(12)), −12.6 (4B, d, *J* = 167 Hz, B(4) + B(5) + B(7) + B(11)), −14.7 (2B, d, *J* = 150 Hz, B(8) + B(10)). ^{13}C NMR (acetone-d_6, ppm): 63.5 (CH_{carb}). MS (DUIS), m/z: found: 212.2 $(M–H)^-$; calculated for $C_2H_9B_{10}Cl_2$ $(M–H)^-$: 212.1.

3,6-Br_2-1,2-$C_2B_{10}H_{10}$ (**8**): According to the general procedure using 3,6-$(Bpin)_2$-1,2-$C_2B_{10}H_{10}$ (50.0 mg, 0.126 mmol), *N*-bromosuccinimide (133.50 mg, 0.756 mmol) and $CuBr_2 \cdot 2H_2O$ (194.5 mg, 0.756 mmol), 27.0 mg (71% yield) of a white crystalline compound **8** was obtained. ^1H NMR ($CDCl_3$, ppm): 4.14 (2H, br.s, CH_{carb}). ^1H NMR (acetone-d_6, ppm): 5.47 (2H, br.s, CH_{carb}). ^{11}B NMR ($CDCl_3$, ppm): −1.9 (2B, d, *J* = 151 Hz), −11.6 (8B, m). ^{11}B NMR (acetone-d_6, ppm), δ: −2.8 (4B, d, *J* = 151 Hz), −10.9 (2B, d + s, *J* = 156 Hz), −11.5 (4B, d, *J* = 156 Hz), −12.5 (2B, d, *J* = 127 Hz).

*3.7. Synthesis of 3,6-Diiodo-ortho-Carborane 3,6-I_2-1,2-$C_2B_{10}H_{11}$ (**9**)*

(a) 3,6-$(Bpin)_2$-1,2-$C_2B_{10}H_{10}$ (**2**) (50.0 mg, 0.126 mmol), NaI (112.0 mg, 0.756 mmol) and $Cu(OAc)_2 \cdot H_2O$ (150.0 mg, 0.756 mmol) were placed in a 25 mL round bottom flask and acetonitrile (5 mL) was added. The reaction mixture was heated under reflux for 15 h until complete conversion according to ^{11}B NMR and allowed to cool to room temperature. The solvent was removed in vacuo and the resulting solid residue was subjected to column chromatography on silica using a mixture of chloroform and petroleum ether (2:1, *v/v*) as the eluent. The first boron-containing fraction was collected and concentrated on a rotary evaporator under reduced pressure to obtain a white crystalline compound **9** (43.8 mg, 88% yield).

(b) 3,6-$(Bpin)_2$-1,2-$C_2B_{10}H_{10}$ (**1**) (50.0 mg, 0.126 mmol), I_2 (192.0 mg, 0.756 mmol), and $CuF_2 \cdot H_2O$ (104.0 mg, 0.756 mmol) were placed in a 25 mL round bottom flask and acetonitrile (5 mL) was added. The reaction mixture was heated under reflux for 20 h until complete conversion according to ^{11}B NMR and allowed to cool to room temperature. The solvent was removed in vacuo and the resulting solid residue was subjected to column chromatography on silica using a mixture of chloroform and petroleum ether (2:1, *v/v*) as the eluent. The first boron-containing fraction was collected and concentrated on a rotary evaporator under reduced pressure to obtain a white crystalline compound **9** (42.8 mg, 86% yield).

^{1}H NMR ($CDCl_3$, ppm): 4.13 (2H, br.s, CH_{carb}). ^{11}B NMR ($CDCl_3$, ppm): −0.2 (2B, d, J = 144 Hz), −8.9 (2B, d, J = 182 Hz), −9.9 (4B, d, J = 151 Hz), −27.9 (2B, s).

3.8. Synthesis of 3,6-Diacetoxy-ortho-Carborane 3,6-$(AcO)_2$-1,2-$C_2B_{10}H_{10}$ (**10**)

3,6-$(Bpin)_2$-1,2-$C_2B_{10}H_{10}$ (**2**) (50.0 mg, 0.126 mmol) and $Cu(OAc)_2 \cdot H_2O$ (150.0 mg, 0.756 mmol) were placed in a 25 mL round bottom flask and acetonitrile (5 mL) was added. The reaction mixture was heated under reflux for 25 h until complete conversion according to ^{11}B NMR and allowed to cool to room temperature. The solvent was removed in vacuo and the resulting solid residue was subjected to column chromatography on silica using a mixture of chloroform and petroleum ether (2:1, *v/v*) as the eluent. The first boron-containing fraction was collected and concentrated on a rotary evaporator under reduced pressure to obtain a white crystalline compound **10** (28.2 mg, 86% yield). ^{1}H NMR (acetone-d_6, ppm): 5.21 (2H, br.s, CH_{carb}), 2.12 (6H, s, CH_3). ^{11}B NMR (acetone-d_6, ppm): −4.3 (2B, s), −8.1 (2B, d, J = 150 Hz), −15.8 (4B, d, J = 164 Hz), −18.6 (2B, d, J = 152 Hz).

3.9. Synthesis of Cesium 3-chloro-7,8-Dicarba-Nido-Undecaborate Cs [3-Cl-7,8-$C_2B_9H_{11}$] (**11**)

3-Cl-1,2-$C_2B_{10}H_{11}$ (**3**) (25.0 mg, 0.140 mmol) and CsF (64.0 mg, 0.420 mmol) were placed in a 25 mL round bottom flask and ethanol (5 mL) was added. The reaction mixture was heated at 60 °C for 15 h until complete conversion according to ^{11}B NMR and allowed to cool to room temperature. The solvent was removed in vacuo, to the residue dichloromethane (15 mL) was added and resulting solution was washed with water (3 × 15 mL). The organic fraction was collected and dried over Na_2SO_4, filtered and concentrated in vacuo to obtain a white crystalline compound **11** (43.8 mg, 88% yield). ^{1}H NMR (acetone-d_6, ppm): 1.90 (2H, br.s, CH_{carb}), −2.68 (BHB, br.m). ^{11}B NMR (acetone-d_6, ppm), δ: −8.5 (1B, s, B(3)), −10.7 (2B, d, J = 138 Hz, B(9) + B(11)), −16.8 (2B, d, J = 138 Hz, B(5) + B(6)), −21.4 (2B, d, J = 152 Hz, B(2) + B(4)), −37.6 (2B, d, J = 139 Hz, B(1) + B(10)). ^{13}C NMR (acetone-d_6, ppm): 63.5 (CH_{carb}). MS (DUIS), *m/z*: found: 168.2 $(M)^-$; calculated for $C_2H_{11}B_9Cl$ $(M)^-$: 168.1.

3.10. Single Crystal X-ray Diffraction Study

The single crystals of 3,6-Cl_2-1,2-$C_2B_{10}H_{10}$ (**3**) and Cs [3-Cl-7,8-$C_2B_9H_{11}$] (**11**) were grown by slow evaporation of a solution in chloroform and acetone, respectively, at room temperature. Single crystal X-ray diffraction experiments were carried out using a SMART APEX2 CCD diffractometer (λ(Mo-Kα) = 0.71073 Å, graphite monochromator, ω-scans) at 120 K. Collected data were processed by the SAINT and SADABS programs incorporated

into the APEX2 program package [84]. The structures were solved by the direct methods and refined by the full-matrix least-squares procedure against F^2 in anisotropic approximation. The refinement was carried out with the SHELXTL program [85]. Details of the refinement are provided in Table 1. The CCDC numbers (221,3255 for **3**, and 221,3256 for **11**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif.

Table 1. Crystallographic data for compounds 3,6-Cl_2-1,2-$C_2B_{10}H_{10}$ (**3**) and Cs [3-Cl-7,8-$C_2B_9H_{11}$] (**11**).

	3,6-Cl_2-1,2-$C_2B_{10}H_{10}$ (3)	**Cs [3-Cl-7,8-$C_2B_9H_{11}$] (11)**
Formula	$C_2H_{10}B_{10}Cl_2$	$Cs^+C_2B_9H_{11}Cl^-$
FW	213.10	300.76
Crystal system	Monoclinic	Orthorhombic
Space group	*C*2/*c*	*Pbca*
a, Å	14.746(7)	10.693(2)
b, Å	6.805(4)	11.149(2)
c, Å	11.485(6)	18.174(4)
β, deg	115.259(14)	90
V, Å^3	1042.4(9)	2166.6(8)
Z	4	8
ρ_{calc}, g·cm^{-3}	1.358	1.844
F(000)	424	1120
μ, mm^{-1}	0.557	3.599
θ range, deg	3.06–26.08	2.24–26.15
Independent reflections	1030	2141
Completeness to theta *θ*, %	99.0	98.8
Refined parameters	85	122
GOF (F^2)	0.984	1.037
Reflections with $I > 2\sigma(I)$	587	1549
$R_1(F)$ ($I > 2\sigma(I)$) [a]	0.0592	0.0579
$wR_2(F^2)$ (all data) [b]	0.1473	0.1382
Largest diff. peak/hole, *e*·Å^{-3}	0.400/−0.478	0.977/−1.299

[a] $R_1 = \sum | |F_o| - |F_c| | / \sum(F_o)$; [b] $wR_2 = (\sum[w(F_o^2 - F_c^2)^2] / \sum[w(F_o^2)^2])^{\frac{1}{2}}$.

4. Conclusions

A convenient two-stage method for the preparation of 3-halogen and 3,6-dihalogen *ortho*-carborane derivatives 3-X-1,2-$C_2B_{10}H_{11}$ and 3,6-X_2-1,2-$C_2B_{10}H_{10}$ (X = Cl, Br, I) through Cu-assisted halodeboronation of the corresponding pinacolborate derivatives has been proposed. This approach allows to avoid the use of highly aggressive boron trihalides and liquid ammonia. It was demonstrated that a chlorine atom effectively protects the boron atom bound to two carbon atoms from nucleophilic attack. Crystal structures of 3,6-Cl_2-1,2-$C_2B_{10}H_{10}$ and Cs [3-Cl-7,8-$C_2B_9H_{11}$] were determined by single crystal X-ray diffraction.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/inorganics10110207/s1, Crystallographic data for compounds **3** and **11**, NMR and MS spectra of compounds **1**–**11**.

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Data Availability Statement: Crystallographic data for the structures of 3,6-Cl_2-1,2-$C_2B_{10}H_{10}$ (**3**) and Cs [3-Cl-7,8-$C_2B_9H_{11}$] (**11**) were deposited with the Cambridge Crystallographic Data Centre as supplementary publications CCDC 2213255 (for **3**) and 2213256 (for **11**). The Supplementary Information contains crystallographic data for compounds **3** and **11**, and NMR and MS spectra of compounds **1**–**11**.

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