catalysts

MDPI

Article

One-Pot Synthesis of *B*-Aryl Carboranes with Sensitive Functional Groups Using Sequential Cobalt- and Palladium-Catalyzed Reactions

Sergey A. Anufriev [1], Akim V. Shmal'ko [1], Kyrill Yu. Suponitsky [1,2] and Igor B. Sivaev [1,3,*]

[1] A.N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, 28 Vavilov Str., 119991 Moscow, Russia; trueMan476@mail.ru (S.A.A.); akimbend@yandex.ru (A.V.S.); kirshik@yahoo.com (K.Y.S.)

[2] N.S. Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences, 31 Leninskii Av., 119991 Moscow, Russia

[3] Basic Department of Chemistry of Innovative Materials and Technologies, G.V. Plekhanov Russian University of Economics, 36 Stremyannyi Line, 117997 Moscow, Russia

* Correspondence: sivaev@ineos.ac.ru; Tel.: +7-916-590-2025

Received: 30 October 2020; Accepted: 17 November 2020; Published: 19 November 2020

Abstract: The simple and efficient method was developed for the one-pot synthesis of *B*-substituted aryl derivatives of *ortho*-carborane with functional groups sensitive to organolithium and organomagnesium reagents using 9-iodo-*ortho*-carborane and generated in situ organozinc compounds. The method proposed was used to prepare a series of 9-aryl-*ortho*-carboranes, including those containing nitrile and ester groups, 9-RC_6H_4-1,2-$C_2B_{10}H_{11}$ (R = *p*-Me, *p*-NMe_2, *p*-OCH_2OMe, *o*-OMe, *p*-OMe, *o*-CN, *p*-CN, *o*-COOEt, *m*-COOEt, and *p*-COOEt). It was demonstrated that the same approach can be used for synthesis of diaryl derivatives of *ortho*-carborane 9,12-$(RC_6H_4)_2$-1,2-$C_2B_{10}H_{10}$ (R = H, *p*-Me). The solid-state structures of 9-RC_6H_4-1,2-$C_2B_{10}H_{11}$ (R = *p*-NMe_2, *p*-OCH_2OMe, *o*-OMe, *o*-CN, *p*-CN, *m*-COOEt, and *p*-COOEt) and 9,12-(*p*-$MeC_6H_4)_2$-1,2-$C_2B_{10}H_{10}$ were determined by single crystal X-ray diffraction.

Keywords: *ortho*-carborane; *B*-aryl derivatives; synthesis; Co/Pd catalysis; X-ray diffraction

1. Introduction

Aryl derivatives of icosahedral carboranes $C_2B_{10}H_{12}$ (Figure 1) are of interest for a wide variety of applications, starting with medical chemistry [1–4] and ending with the development of new materials [5–12]. This necessitates the development of new convenient methods for their synthesis. Since the properties of the CH and BH groups in carboranes differ significantly, different methods are used to synthesize their *C*- and *B*-aryl derivatives.

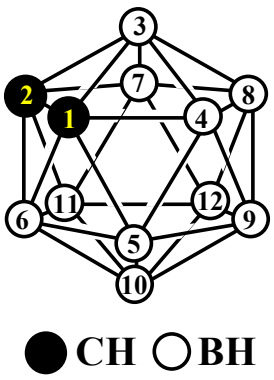


Figure 1. Atom numeration in *ortho*-carborane 1,2-$C_2B_{10}H_{12}$.

There are several methods for synthesis of *C*-arylcarboranes, where an aryl group is directly bonded to the cage carbon [13]. A general method involves the use of decaborane *nido*-$B_{10}H_{14}$ and reacting it with Lewis bases, such as dialkyl sulfides, acetonitrile or alkylamines. This leads to the formation of compounds with a general formula of 6,9-*arachno*-$B_{10}H_{12}L_2$. On reacting this species with alkynes with aromatic substituents, the corresponding C-aryl-*ortho*-carboranes are formed [14]. However, this reaction gives very low yields for some alkynes, especially those containing two aromatic units [15,16]. This reaction cannot be used when the aryl groups have acidic or readily reduced substituents. This method is also unsuitable for synthesis of aryl derivatives of *meta*- and *para*-carboranes. Therefore, for the synthesis of aryl derivatives of *meta*- and *para*-carboranes an Ullmann-type copper-coupling reaction is used. In this way, mono- and diaryl derivatives of *meta*- and *para*-carboranes can be obtained, as well as monoaryl derivatives of *ortho*-carborane [15,17–20]. An alternative method includes Ni-catalyzed cross-coupling reactions of aryl iodides with carboranyl Grignard reagents. In such way both monoaryl- and diaryl derivatives of *ortho*-carborane can be prepared [21,22]. Another approach is based on S_NAr reactions of carborane-derived carbanions with fluorinated aromatics [23–25]. This approach is widely used for synthesis of asymmetrically substituted diaryl derivatives of carboranes [19,26].

Unlike *C*-aryl derivatives, the synthesis of *B*-aryl derivatives of carboranes is mainly based on Pd-catalyzed cross-coupling reactions of their iodo derivatives with aryl Grignard reagents (Kumada cross-coupling) [27–36]. However, available substituents on the aromatic ring in these reactions are strictly limited because of the high reactivity of Grignard reagents. Mild *B*-arylation of carboranes via Suzuki cross-coupling reactions of aryl boronic acids with 9-iodo-*meta*-, 2-iodo-*para*-, and 3-iodo-*ortho*-carboranes were reported [37–39]. It is important that these cross-coupling reactions can be used for direct introduction of functionalized aryl substituents that are not compatible with the previously mentioned Kumada reaction conditions. However, this approach was found to be ineffective for 9-iodo-*ortho*-carborane. Moreover, Suzuki cross-coupling reactions normally employ inorganic bases such as F^- or OH^- to facilitate the transmetallation step, but these bases are strong nucleophiles that can result in deboronation of the *ortho*-carborane cage during the cross-coupling. The possibility of *B*-arylation of *ortho*- and *meta*-carboranes using organozinc reagents (Negishi cross-coupling) has been demonstrated as well [40,41], however the arylzinc reagents were obtained by transmetallation of the corresponding Grignard reagents that decreases the synthetic utility of this method.

Direct arylation of *ortho*-carborane derivatives via Pd-catalyzed B-H activation has been recently reported [42]. This reaction is tolerant to various functional groups including acyl and ester; however, it is not selective leading to mixtures of 8- and 9-aryl derivatives and is not applicable to the parent *ortho*-carborane. A series of aryl derivatives of *ortho*-carborane were prepared by Pd-catalyzed B-H activation reactions with aryl iodides under functional group assistance or by intramolecular cyclization via Pd-catalyzed B-H activation involving pendant *ortho*-bromoaryl groups [43]; however, these reactions are currently of academic interest rather than real synthetic methods. Of greater interest is the direct arylation of 1,2-bis(dimethylphenylsilyl)-*ortho*-carborane 1,2-$(PhMe_2Si)_2$-1,2-$C_2B_{10}H_{10}$ with arylmagnesium chlorides in diethyl ether, followed by the removal of the silyl protective groups with K_2CO_3 in acetone [44]; however, this approach gives only moderate yields of 9-aryl-*ortho*-carboranes and is not tolerant to many functional groups.

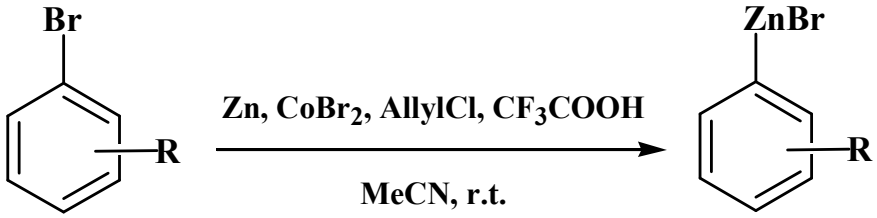
In this contribution we describe convenient and mild synthesis of *B*-aryl derivatives of *ortho*-carborane containing various functional groups including ester and nitrile ones.

2. Results and Discussion

The possibility of synthesis of *B*-aryl derivatives of *ortho*-carborane using organozinc reagents has been demonstrated earlier [40,41]. However, the preparation of these organozinc compounds was achieved by a transmetallation reaction of preformed organolithium or magnesium counterparts with zinc halide. Later, various methods were elaborated for preparation of zinc organometallics bearing highly sensitive functional groups [45,46]. However, most of these methods are based on the use of

bimetallic zinc-lithium or zinc-magnesium reagents and, despite their indisputable synthetic utility, the use of such activated zinc reagents requires specific conditions together with careful handling. Therefore, such methods for the synthesis of organozinc compounds that do not require the use of organolithium and organomagnesium reagents are of particular interest. We chose the method based on Co-catalyzed preparation of arylzinc organics starting from readily available aryl bromides and zinc dust [47–49]. Thus, the obtained organozinc species can be easily coupled with various aryl iodides in the presence of a catalytic amount of $(Ph_3P)_2PdCl_2$ [49]. In addition to the formation of the C–C bond, this approach can be used to form the C–B bond in the reaction of aryl bromides with haloboronic esters, leading to the formation of the corresponding arylboronates [50]. The reaction was found to be tolerate to many functional groups including nitriles and esters. Earlier this approach was used for synthesis of 1,4-bis(*ortho*-carboran-8′-yl)benzene staring from 8-iodo-*ortho*-carborane [51].

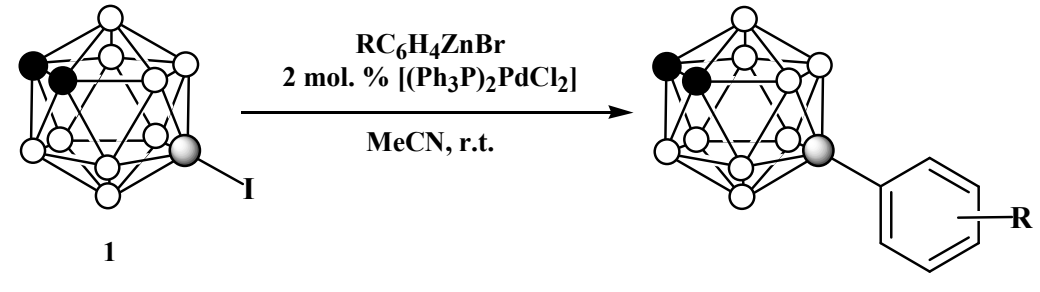
Arylzinc bromides containing various substituents including sensitive functional groups (-CN, -COOEt) were prepared by the reaction of the corresponding aryl bromides with allyl zinc chloride/bromide generated from allyl chloride and zinc metal in the presence of 25 mol % of $CoBr_2$ and catalytic amount of trifluoroacetic acid in acetonitrile at ambient temperature (Scheme 1).



R = H, *p*-Me, *p*-NMe_2, *p*-OCH_2OMe, *o*-OMe, *p*-OMe, *o*-CN, *p*-CN, *o*-COOEt, *m*-COOEt, *p*-COOEt

Scheme 1. Synthesis of arylzinc bromides.

The reactions of the prepared arylzinc bromides with 9-iodo-*ortho*-carborane in the presence of 2 mol.% of $[(Ph_3P)_2PdCl_2]$ in acetonitrile at room temperature lead to its nearly quantitative conversion to the corresponding 9-aryl-*ortho*-carboranes with isolated yields varying from 60 to 91% (Schemes 2 and 3).

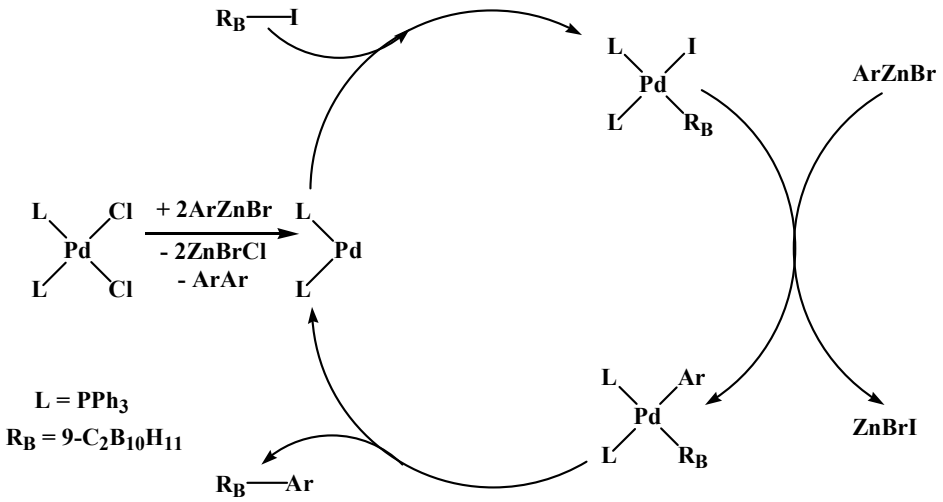


R = *p*-Me (2)	88 %	*o*-CN (7)	75 %
p-NMe_2 (3)	65 %	*p*-CN (8)	90 %
p-OCH_2OMe (4)	67 %	*o*-COOEt (9)	60 %
o-OMe (5)	71 %	*m*-COOEt (10)	70 %
p-OMe (6)	91 %	*p*-COOEt (11)	86 %

Scheme 2. Synthesis of 9-aryl-*ortho*-carboranes.

The synthesized 9-aryl-*ortho*-carboranes were characterized by the methods of ^1H, ^{13}C and ^{11}B NMR and IR spectroscopy. The ^1H and ^{13}C NMR spectra of all compounds contain signals of the corresponding aryl substituents as well as the signals of two non-equivalent carborane *CH* groups in the

range of 3.3–3.7 ppm and 48–53 ppm, respectively. The ^{11}B NMR spectra of the 9-aryl-*ortho*-carboranes contain singlet of the *C*-substituted boron atom at ~ 6–8 ppm and five doublets with a total integral ratio of 1:1:2:2:2:2 (except for the spectra of 9-cyanophenyl and 9-ethoxycarbonylphenyl derivatives with a ratio of 1:1:2:4:2 ratio). The solid-state structures of all new 9-aryl-*ortho*-carboranes (except for **6**, which is liquid) were determined by single crystal X-ray diffraction (Figures 2 and 3).



Scheme 3. Proposed mechanism of Pd-catalyzed arylation of 9-iodo-*ortho*-carboranes.

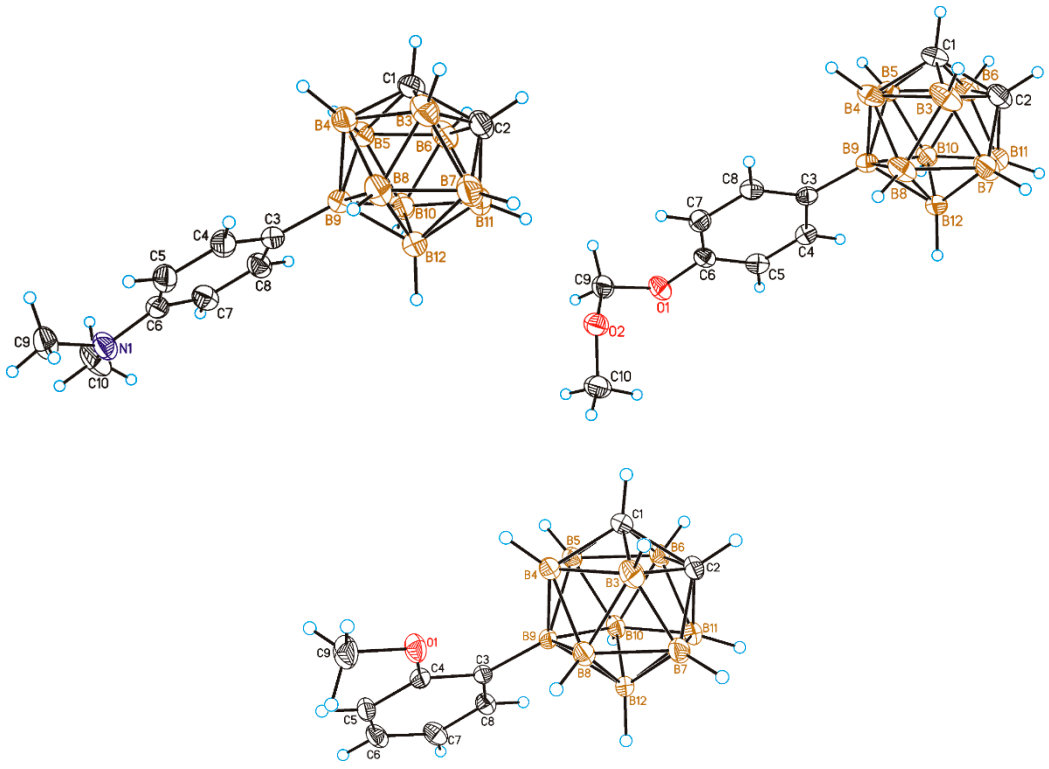


Figure 2. General views of 9-(*p*-$Me_2NC_6H_4$)-1,2-$C_2B_{10}H_{11}$ (**3**, topleft), 9-(*p*-$MeOCH_2OC_6H_4$)-1,2-$C_2B_{10}H_{11}$ (**4**, top right), and 9-(*o*-$MeOC_6H_4$)-1,2-$C_2B_{10}H_{11}$ (**5**, bottom) showing atomic numbering. Thermal ellipsoids are drawn at 50% probability level.

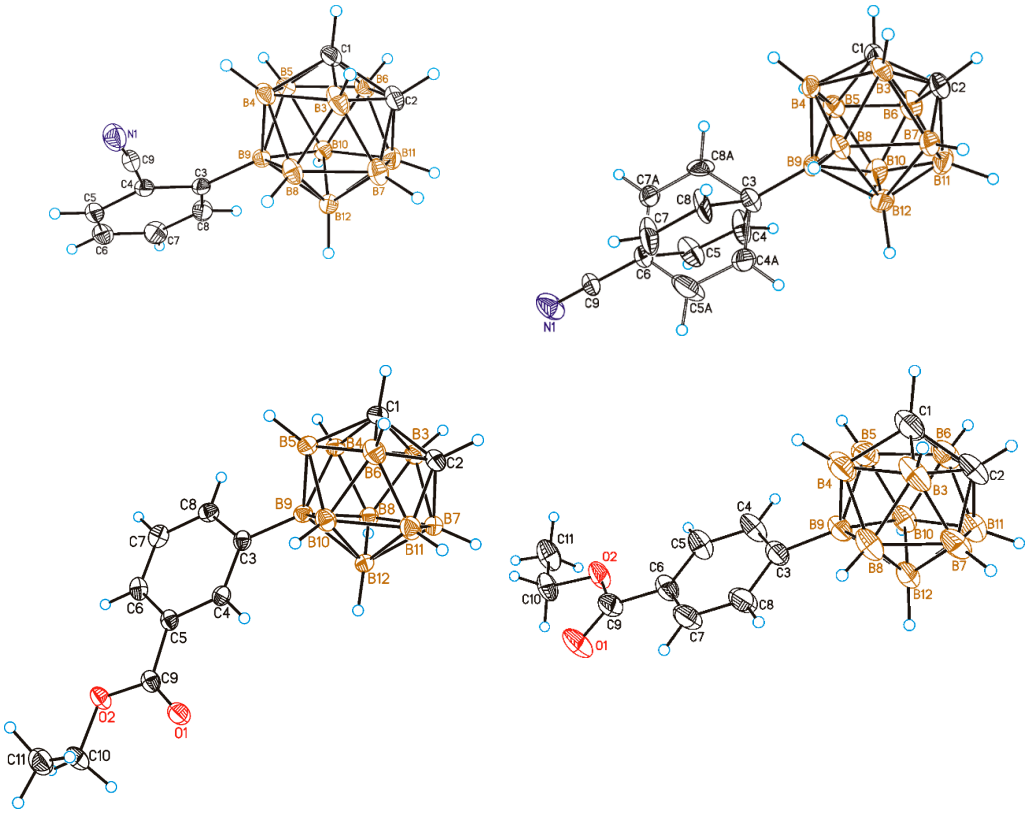
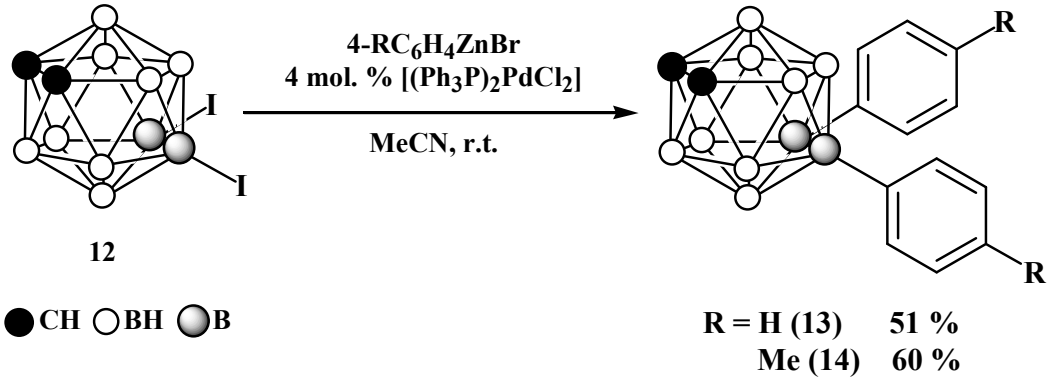


Figure 3. General views of 9-(*o*-NCC_6H_4)-1,2-$C_2B_{10}H_{11}$ (**7**, top left), 9-(*p*-NCC_6H_4)-1,2-$C_2B_{10}H_{11}$ (**8**, top right), 9-(*m*-$EtOOCC_6H_4$)-1,2-$C_2B_{10}H_{11}$ (**10**, bottom left), and 9-(*p*-$EtOOCC_6H_4$)-1,2-$C_2B_{10}H_{11}$ (**11**, bottom right) showing atomic numbering. Thermal ellipsoids are drawn at 50% probability level.

The same approach can be used for synthesis of disubstituted aryl derivatives: the reactions of phenyl- and *p*-tolylzinc bromides with 9,12-diiodo-*ortho*-carborane in the presence of 4 mol. % of $[(Ph_3P)_2PdCl_2]$ in acetonitrile at room temperature lead to the corresponding 9,12-diaryl-*ortho*-carboranes (Scheme 4).



Scheme 4. Synthesis of 9,12-diaryl-*ortho*-carboranes.

The solid-state structures of 9,12-di(*p*-tolyl)-*ortho*-carborane **14** was determined by single crystal X-ray diffraction (Figure 4).

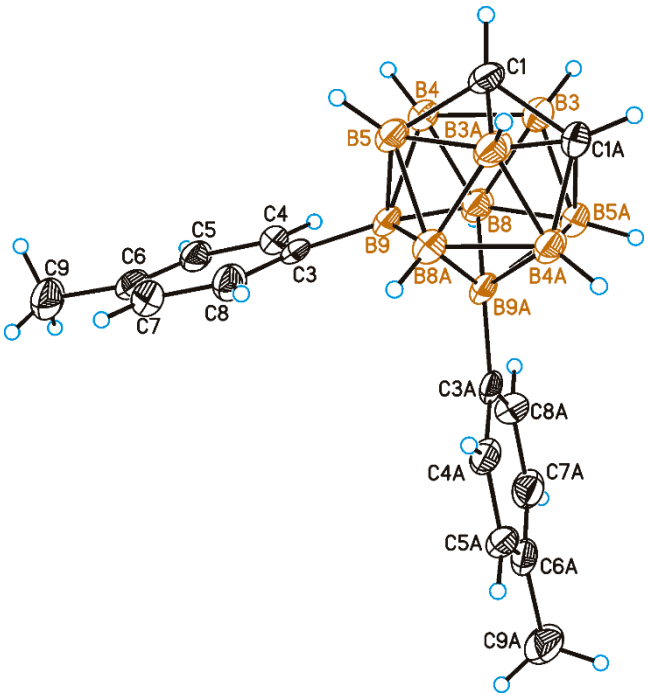


Figure 4. General view of 9,12-(p-MeC_6H_4)$_2$-1,2-$C_2B_{10}H_{11}$ (**14**) showing atomic numbering. Thermal ellipsoids are drawn at 50% probability level. The molecule occupies special position. Numbering of symmetrically dependent part are marked with letter "A".

3. Materials and Methods

3.1. General Methods

9-Iodo-*ortho*-carborane (**1**) [52], 9,12-diiodo-*ortho*-carborane (**12**) [28] and bis(triphenylphosphine) palladium dichloride [53] were prepared according to the literature procedures. Anhydrous cobalt dibromide was prepared from cobalt bromide hexahydrate by heating at 160 °C under vacuum for 3 h and stored under argon atmosphere. Acetonitrile was dried using standard procedures [54]. All other chemical reagents were purchased from Sigma Aldrich, Acros Organics and ABCR and used without purification. All reactions were carried out at argon atmosphere. The reaction progress was monitored by thin layer chromatography (Merck F254 silica gel on aluminum plates) and visualized using 0.5 % $PdCl_2$ in 1% HCl in aq. MeOH (1:10). Acros Organics silica gel (0.060–0.200 mm) was used for column chromatography. The NMR spectra at 400 MHz (^{1}H), 128 MHz (^{11}B) and 100 MHz (^{13}C) were recorded with Varian Inova 400 spectrometer. The residual signal of the NMR solvent relative to tetramethylsilane was taken as the internal reference for ^{1}H and ^{13}C NMR spectra. ^{11}B NMR spectra were referenced using BF_3•Et_2O as external standard. Infrared spectra were recorded on an IR Prestige-21 (SHIMADZU) instrument.

Single crystal X-ray diffraction experiments for compounds **3**–**5**, **7**, **8**, **10**, **11**, and **14** were carried out using 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 [55]. 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 [56]. The CCDC numbers (2041390, 2041385, 2041386, 2041387, 2041388, 2041389, 2044200, and 2044199 for **3**, **4**, **5**, **7**, **8**, **10**, **11**, and **14**, respectively) 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.

3.2. General Synthetic Procedure and Characterization of Monosubstituted B-Aryl Derivatives of Ortho-Carborane

Allyl chloride (82 μL, 77 mg, 1.00 mmol) and trifluoroacetic acid (25 μL, catalytic amount) were added to a blue mixture of zinc powder (490 mg, 7.50 mmol) and anhydrous cobalt dibromide (55 mg, 0.25 mmol) in 2.5 mL of fresh distilled acetonitrile. The resulting dark orange mixture was stirred at room temperature for 15 min. Then corresponding aryl bromide (2.50 mmol) was added, and reaction was stirred at room temperature for another 1 h. Then 9-iodo-*ortho*-carborane (270 mg, 1.00 mmol) with bis(triphenylphosphine)palladium dichloride (14 mg, 0.02 mmol, catalytic amount) were added. The reaction was stirred at room temperature overnight. After removal of volatiles under reduced pressure, the residue was washed with water (25 mL), dichloromethane (3 × 25 mL) and acetone (until no trace of carborane appeared on TLC). The organic phases were combined, dried over Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by column chromatography on silica to give the corresponding B-aryl derivative of *ortho*-carborane.

9-(4-Methylphenyl)-*ortho*-carborane (**2**): 4-Methylphenyl bromide (315 μL, 435 mg, 2.50 mmol) was used; diethyl ether was used as eluent for column chromatography; a pale-yellow crystalline solid was obtained (207 mg, yield 88%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34 (2H, d, J = 7.7 Hz, CH_{Ar}), 7.12 (2H, d, J = 7.7 Hz, CH_{Ar}), 3.41 (1H, br s, CH_{Carb}), 3.31 (1H, br s, CH_{Carb}), 2.37 (3H, s, CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.8 (C_{Ar}-B), 137.0 (C_{Ar}-CH_3), 132.5 (C_{Ar}H), 128.4 (C_{Ar}H), 53.3 (C_{Carb}H), 48.9 (C_{Carb}H), 21.3 (CH_3) ppm; ^{11}B NMR (128 MHz, $CDCl_3$): δ 7.6 (1B, s, *B*-C), −2.2 (1B, d, J = 148 Hz), −8.7 (2B, d, J = 150 Hz), −13.8 (2B, d, J = 194 Hz), −14.2 (2B, d, J = 156 Hz), −15.3 (2B, d, J = 174 Hz) ppm. The spectral data correspond to those described in the literature [36].

9-(4-*N*,*N*-Dimethylaminophenyl)-ortho-carborane (**3**): 4-*N*,*N*-Dimethylaminophenyl bromide (500 mg, 2.50 mmol) was used; a mixture of chloroform and hexane (3:1, *v*/*v*) was used as eluent for column chromatography; a pale-pink crystalline solid was obtained (170 mg, yield 65%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.26 (2H, d, J = 8.4 Hz, CH_{Ar}), 6.66 (2H, d, J = 8.4 Hz, CH_{Ar}), 3.50 (1H, br s, CH_{Carb}), 3.39 (1H, br s, CH_{Carb}), 2.92 (6H, s, N(CH_3)$_2$) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.1 (C_{Ar}-N), 133.3 (C_{Ar}H), 126.1 (C_{Ar}-B), 112.2 (C_{Ar}H), 53.0 (C_{Carb}H), 48.0 (C_{Carb}H), 40.7 (N(CH_3)$_2$) ppm; ^{11}B NMR (128 MHz, $CDCl_3$): δ 8.1 (1B, s, *B*-C), −2.3 (1B, d, J = 147 Hz), −8.7 (2B, d, J = 149 Hz), −13.9 (2B, d, J = 148 Hz), −14.4 (2B, d, J = 150 Hz), −15.4 (2B, d, J = 190 Hz) ppm; IR (film): υ_{max} 3047 (C_{Carb}-H, C_{Ar}-H), 3028 (C_{Carb}-H, C_{Ar}-H), 2816-2941 (C_{Alkyl}-H), 2625 (B-H), 2590 (B-H), 2563 (B-H), 1601 (C_{Ar}-C_{Ar}), 1516 (C_{Ar}-C_{Ar}) cm^{-1}. Crystallographic data: $C_{10}H_{21}B_{10}N$ are monoclinic, space group $P2_1/c$: a = 7.5405(2) Å, b = 13.0917(3) Å, c = 16.2594(4) Å, β = 102.3370(10)°, V = 1568.03(7) Å^3, Z = 4, M = 263.38, d_{cryst} = 1.116 g cm^{-3}. $wR2$ = 0.1238 calculated on F^2_{hkl} for all 3094 independent reflections with 2θ < 52.2°, (GOF = 1.056, R = 0.0442 calculated on F_{hkl} for 2667 reflections with $I > 2\sigma(I)$).

9-(4-Methoxymethoxyphenyl)-*ortho*-carborane (**4**): 4-Methoxymethoxy bromide (381 μL, 543 mg, 2.50 mmol) was used; a mixture of diethyl ether and hexane (1:2, *v*/*v*) was used as eluent for column chromatography; a pale-yellow solid was obtained (189 mg, yield 67%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.30 (2H, d, J = 8.4 Hz, CH_{Ar}), 6.92 (2H, d, J = 8.4 Hz, CH_{Ar}), 5.16 (2H, s, OCH_2O), 3.55 (1H, br s, CH_{Carb}), 3.47 (3H, s, OCH_3), 3.44 (1H, br s, CH_{Carb}) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.9 (C_{Ar}-O), 133.6 (C_{Ar}H), 115.4 (C_{Ar}H), 94.4 (OCH_2O), 56.1 (OCH_3), 53.2 (C_{Carb}H), 48.7 (C_{Carb}H) ppm; ^{11}B NMR (128 MHz, $CDCl_3$): δ 7.7 (1B, s, *B*-C), −2.2 (1B, d, J = 149 Hz), −8.7 (2B, d, J = 149 Hz), −13.8 (2B, d, J = 156 Hz), −14.3 (2B, d, J = 139 Hz), −15.4 (2B, d, J = 170 Hz) ppm; IR (film): υ_{max} 3066 (C_{Carb}-H, C_{Ar}-H), 3027 (C_{Carb}-H, C_{Ar}-H), 2785-3002 (C_{Alkyl}-H), 2633 (B-H), 2603 (B-H), 2589 (B-H), 2570 (B-H), 1600 (C_{Ar}-C_{Ar}), 1507 (C_{Ar}-C_{Ar}) cm^{-1}. *Crystallographic data:* $C_{10}H_{20}B_{10}O_2$ are monoclinic, space group $P2_1/c$: a = 7.9988(2) Å, b = 12.7477(3) Å, c = 15.4187(4) Å, β = 91.4090(10)°, V = 1571.71(7) Å^3, Z = 4, M = 280.36, d_{cryst} = 1.185 g cm^{-3}. $wR2$ = 0.1203 calculated on F^2_{hkl} for all 3830 independent reflections with 2θ < 56.2°, (GOF = 1.050, R = 0.0520 calculated on F_{hkl} for 2839 reflections with $I > 2\sigma(I)$).

9-(2-Methoxyphenyl)-*ortho*-carborane (**5**): 2-Methoxyphenyl bromide (310 μL, 468 mg, 2.50 mmol) was used; a mixture of diethyl ether and hexane (1:2, *v*/*v*) was used as eluent for column chromatography; a pale-yellow crystalline solid was obtained (177 mg, yield 71%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37

(1H, d, J = 7.1 Hz, CH_{Ar}), 7.21 (1H, dd, J_1 = 8.3 Hz, J_2 = 7.2 Hz, CH_{Ar}), 6.87 (1H, dd, J_1 = 7.2 Hz, J_2 = 7.1 Hz, CH_{Ar}), 6.78 (1H, d, J = 8.3 Hz, CH_{Ar}), 3.76 (3H, s, OCH_3), 3.55 (1H, br s, CH_{Carb}), 3.51 (1H, br s, CH_{Carb}) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.6 (C_{Ar}-O), 136.1 (C_{Ar}H), 129.1 (C_{Ar}H), 120.3 (C_{Ar}H), 110.5 (C_{Ar}H), 55.2 (OCH_3), 53.1 (C_{Carb}H), 50.1 (C_{Carb}H) ppm; ^{11}B NMR (128 MHz, $CDCl_3$): δ 6.1 (1B, s, *B*-C), −1.9 (1B, d, J = 146 Hz), −8.6 (2B, d, J = 151 Hz), −13.5 (2B, d, J = 182 Hz), −14.6 (2B, d, J = 148 Hz), −15.6 (2B, d, J = 188 Hz) ppm; IR (film): υ_{max} 3065 (C_{Carb}-H, C_{Ar}-H), 2832-3003 (C_{Alkyl}-H), 2600 (B-H), 2571 (B-H), 1589 (C_{Ar}-C_{Ar}), 1570 (C_{Ar}-C_{Ar}), 1483 (C_{Ar}-C_{Ar}), 1460 (C_{Ar}-C_{Ar}) cm^{-1}. *Crystallographic data:* $C_9H_{18}B_{10}O$ are monoclinic, space group $P2_1/n$: a = 7.6038(2) Å, b = 12.5827(3) Å, c = 14.9903(4) Å, β = 91.5740(10)°, V = 1433.68(6) Å^3, Z = 4, M = 250.33, d_{cryst} = 1.160 g cm^{-3}. $wR2$ = 0.1077 calculated on F^2_{hkl} for all 3502 independent reflections with 2θ < 56.3°, (*GOF* = 1.081, R = 0.0408 calculated on F_{hkl} for 3132 reflections with $I > 2\sigma(I)$).

9-(4-Methoxyphenyl)-*ortho*-carborane (**6**): 4-Methoxyphenyl bromide (312 μL, 468 mg, 2.50 mmol) was used; a mixture of diethyl ether and hexane (1:2, *v*/*v*) was used as eluent for column chromatography; a pale-yellow crystalline solid was obtained (228 mg, yield 91%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.30 (2H, d, J = 8.6 Hz, CH_{Ar}), 6.79 (2H, d, J = 8.6 Hz, CH_{Ar}), 3.77 (3H, s, OCH_3), 3.61 (1H, br s, CH_{Carb}), 3.51 (1H, br s, CH_{Carb}) ppm; ^{11}B NMR (128 MHz, $CDCl_3$): δ 7.7 (s, 1B, *B*-C), −2.2 (1B, d, J = 151 Hz), −8.7 (2B, d, J = 145 Hz), −13.9 (2B, d, J = 160 Hz), −14.3 (2B, d, J = 138 Hz), −15.4 (2B, d, J = 182 Hz) ppm. The spectral data correspond to those described in the literature [34].

9-(2-Cyanophenyl)-*ortho*-carborane (**7**): 2-Cyanophenyl bromide (455 mg, 2.50 mmol) was used; mixture of chloroform and hexane (1:1, *v*/*v*) was used as eluent for column chromatography; a pale-yellow crystalline solid was obtained (184 mg, yield 75%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.58 (2H, m, CH_{Ar}), 7.42 (1H, dd, J_1 = 7.7 Hz, J_2 = 7.5 Hz, CH_{Ar}), 7.29 (1H, dd, J_1 = 7.7 Hz, J_2 = 9.6 Hz, CH_{Ar}), 3.72 (1H, br s, CH_{Carb}), 3.65 (1H, br s, CH_{Carb}) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 135.3 (C_{Ar}H), 134.3 (C_{Ar}H), 131.5 (C_{Ar}H), 127.7 (C_{Ar}H), 118.0 (C_{Ar}-CN), 114.6 (CN), 53.6 (C_{Carb}H), 51.4 (C_{Carb}H) ppm; ^{11}B NMR (128 MHz, $CDCl_3$): δ 5.5 (1B, s, *B*-C), −1.9 (1B, d, J = 151 Hz), −8.5 (2B, d, J = 155 Hz), −13.7 (2B, d, J = 148 Hz), −14.0 (2B, d, J = 140 Hz), −15.2 (2B, d, J = 184 Hz) ppm; IR (film): υ_{max} 3053 (C_{Carb}-H, C_{Ar}-H), 3034 (C_{Carb}-H, C_{Ar}-H), 2634 (B-H), 2613 (B-H), 2598 (B-H), 2565 (B-H), 2224 (C≡N), 1591 (C_{Ar}-C_{Ar}), 1558 (C_{Ar}-C_{Ar}), 1476 (C_{Ar}-C_{Ar}), 1456 (C_{Ar}-C_{Ar}) cm^{-1}. *Crystallographic data:* $C_9H_{15}B_{10}N$ are monoclinic, space group *C*2*c*: a = 20.6075(5) Å, b = 12.2065(3) Å, c = 13.9109(6) Å, β = 129.0580(10)°, V = 2717.17(15) Å^3, Z = 8, M = 245.32, d_{cryst} = 1.199 g cm^{-3}. $wR2$ = 0.1201 calculated on F^2_{hkl} for all 3308 independent reflections with 2θ < 56.1°, (*GOF* = 1.066, R = 0.0445 calculated on F_{hkl} for 2835 reflections with $I > 2\sigma(I)$).

9-(4-Cyanophenyl)-*ortho*-carborane (**8**): 4-Cyanophenyl bromide (455 mg, 2.50 mmol) was used; a mixture of chloroform and hexane (3:1, *v*/*v*) was used as eluent for column chromatography; a pale-yellow crystalline solid was obtained (221 mg, yield 90%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.47 (4H, m, CH_{Ar}), 3.69 (1H, br s, CH_{Carb}), 3.60 (1H, br s, CH_{Carb}) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): 133.0 (C_{Ar}H), 131.0 (C_{Ar}H), 119.6 (C_{Ar}-CN), 110.9 (CN), 53.6 (C_{Carb}H), 50.1 (C_{Carb}H) ppm; ^{11}B NMR (128 MHz, $CDCl_3$): δ 6.4 (1B, s, *B*-C), −2.1 (1B, d, J = 154 Hz), −8.7 (2B, d, J = 148 Hz), −14.0 (4B, d, J = 157 Hz), −15.2 (2B, d, J = 176 Hz) ppm; IR (film): υ_{max} 3075 (C_{Carb}-H, C_{Ar}-H), 3049 (C_{Carb}-H, C_{Ar}-H), 2598 (B-H), 2577 (B-H), 2226 (C≡N), 1603 (C_{Ar}-C_{Ar}), 1495 (C_{Ar}-C_{Ar}) cm^{-1}. *Crystallographic data:* $C_9H_{15}B_{10}N$ are orthorhombic, space group $Pca2_1$: a = 10.2431(6) Å, b = 13.4908(5) Å, c = 10.1576(4) Å, V = 1403.65(11) Å^3, Z = 4, M = 245.32, d_{cryst} = 1.161 g cm^{-3}. $wR2$ = 0.1283 calculated on F^2_{hkl} for all 3253 independent reflections with 2θ < 56.0°, (*GOF* = 1.038, R = 0.0520 calculated on F_{hkl} for 2243 reflections with $I > 2\sigma(I)$).

9-(2-Ethoxycarbonylphenyl)-*ortho*-carborane (**9**): 2-Ethoxycarbonyl bromide (398 μL, 573 mg, 2.50 mmol)was used; a mixture of diethyl ether and hexane (1:2, *v*/*v*) was used as eluent for column chromatography; a colorless liquid was obtained (176 mg, yield 60%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.50 (1H, d, J = 7.5 Hz, CH_{Ar}), 7.28 (1H, m, CH_{Ar}), 7.23 (2H, m, CH_{Ar}), 4.29 (2H, q, J = 7.2 Hz, OCH_2CH$_3$), 3.54 (1H, br s, CH_{Carb}), 3.49 (1H, br s, CH_{Carb}), 1.36 (3H, t, J = 7.2 Hz, OCH_2CH$_3$) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.5 (*C*O), 137.9 (C_{Ar}-CO), 136.1 (C_{Ar}H), 128.8 (C_{Ar}H), 127.2 (C_{Ar}H),

126.8 (C_{Ar}H), 61.1 (OCH_2CH_3), 53.4 (C_{Carb}H), 50.8 (C_{Carb}H), 14.2 (OCH_2CH_3) ppm; ^{11}B NMR (128 MHz, $CDCl_3$): δ 6.1 (1B, s, *B*-C), −2.0 (1B, d, J = 148 Hz), −8.7 (2B, d, J = 150 Hz), −13.8 (2B, d), −14.3 (2B, d), −15.3 (2B, d, J = 178 Hz) ppm; IR (film): υ_{max} 3065 (C_{Carb}-H, C_{Ar}-H), 2855-2982 (C_{Alkyl}-H), 2596 (B-H), 1713 (C=O), 1558 (C_{Ar}-C_{Ar}), 1474 (C_{Ar}-C_{Ar}) cm^{-1}.

9-(3-Ethoxycarbonylphenyl)-*ortho*-carborane (**10**): 3-Ethoxycarbonyl bromide (401 μL, 573 mg, 2.50 mmol) was used; diethyl ether was used as eluent for column chromatography; a pale-yellow crystalline solid was obtained (226 mg, yield 70%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.04 (1H, s, CH_{Ar}), 7.89 (1H, d, J = 7.8 Hz, CH_{Ar}), 7.56 (1H, d, J = 7.4 Hz, CH_{Ar}), 7.29 (1H, dd, J_1 = 7.8 Hz, J_2 = 7.4 Hz, CH_{Ar}), 4.36 (2H, q, J = 7.1 Hz, OCH_2CH$_3$), 3.65 (1H, br s, CH_{Carb}), 3.55 (1H, br s, CH_{Carb}), 1.39 (3H, t, J = 7.1 Hz, OCH_2CH$_3$) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.3 (CO), 137.1 (C_{Ar}H), 133.4 (C_{Ar}H), 129.5 (C_{Ar}-CO), 128.5 (C_{Ar}H), 127.5 (C_{Ar}H), 60.9 (OCH_2CH_3), 53.5 (C_{Carb}H), 49.4 (C_{Carb}H), 14.5 (OCH_2CH_3) ppm; ^{11}B NMR (128 MHz, $CDCl_3$): δ 7.1 (1B, s, *B*-C), –2.1 (1B, d, J = 143 Hz), −8.6 (2B, d, J = 151 Hz), –13.8 (2B, d, J = 148 Hz), −14.1 (2B, d, J = 154 Hz), −15.3 (2B, d, J = 186 Hz) ppm; IR (film): υ_{max} 3070 (C_{Carb}-H, C_{Ar}-H), 2854-2982 (C_{Alkyl}-H), 2598 (B-H), 2574 (B-H), 1707 (C=O), 1597 (C_{Ar}-C_{Ar}), 1577 (C_{Ar}-C_{Ar}), 1477 (C_{Ar}-C_{Ar}), 1465 (C_{Ar}-C_{Ar}) cm^{-1}. *Crystallographic data:* $C_{11}H_{20}B_{10}O_2$ are orthorhombic, space group $Pna2_1$: a = 18.4106(4) Å, b = 12.2532(3) Å, c = 7.2177(2) Å, V = 1628.23(7) Å^3, Z = 4, M = 292.37, d_{cryst} = 1.193 g cm^{-3}. $wR2$ = 0.0951 calculated on F^2_{hkl} for all 3929 independent reflections with $2\theta < 56.1°$, (*GOF* = 1.080, R = 0.0452 calculated on F_{hkl} for 3543 reflections with $I > 2\sigma(I)$).

9-(4-Ethoxycarbonylphenyl)-*ortho*-carborane (**11**): 4-Ethoxycarbonyl bromide (408 μL, 573 mg, 2.50 mmol) was used; diethyl ether was used as eluent for column chromatography; a pale-yellow crystalline solid was obtained (252 mg, yield 86%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.88 (2H, d, J = 8.2 Hz, CH_{Ar}), 7.44 (2H, d, J = 8.2 Hz, CH_{Ar}), 4.35 (2H, q, J = 7.1 Hz, OCH_2CH$_3$), 3.66 (1H, br s, CH_{Carb}), 3.56 (1H, br s, CH_{Carb}), 1.37 (3H, t, J = 7.1 Hz, OCH_2CH$_3$) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.1 (CO), 144.9 (C_{Ar}-B), 132.5 (C_{Ar}H), 129.4 (C_{Ar}-CO), 128.5 (C_{Ar}H), 60.8 (OCH_2CH_3), 53.5 (C_{Carb}H), 49.7 (C_{Carb}H), 14.5 (OCH_2CH_3) ppm; ^{11}B NMR (128 MHz, $CDCl_3$): δ 7.0 (1B, s, *B*-C), −2.1 (1B, d, J = 152 Hz), −8.7 (2B, d, J = 149 Hz), −14.0 (4B, d, J = 150 Hz), −15.2 (2B, d, J = 176 Hz) ppm; IR (film): υ_{max} 3057 (C_{Carb}-H, C_{Ar}-H), 2851-2994 (C_{Alkyl}-H), 2602 (B-H), 2579 (B-H), 1694 (C=O), 1605 (C_{Ar}-C_{Ar}), 1558 (C_{Ar}-C_{Ar}), 1474 (C_{Ar}-C_{Ar}), 1445 (C_{Ar}-C_{Ar}) cm^{-1}. *Crystallographic data:* $C_{11}H_{20}B_{10}O_2$ are monoclinic, space group $P2_1/n$: a = 10.701(3) Å, b = 7.0121(18) Å, c = 21.715(5) Å, β = 91.609(7)°, V = 1628.7(7) Å^3, Z = 4, M = 292.37, d_{cryst} = 1.192 g cm^{-3}. $wR2$ = 0.2004 calculated on F^2_{hkl} for all 3089 independent reflections with $2\theta < 52.0°$, (*GOF* = 0.998, R = 0.0705 calculated on F_{hkl} for 1636 reflections with $I > 2\sigma(I)$).

3.3. General Synthetic Procedure and Characterization of Disubstituted B-Aryl Derivatives of Ortho-Carborane

Allyl chloride (82 μL, 77 mg, 1.00 mmol) and trifluoroacetic acid (25 μL, catalytic amount) were added to a blue mixture of zinc powder (490 mg, 7.50 mmol) and anhydrous cobalt dibromide (55 mg, 0.25 mmol) in 2.5 mL of freshly distilled acetonitrile. The resulting dark orange mixture was stirred at room temperature for 15 min. Then corresponding aryl bromide (2.50 mmol) was added, and reaction was stirred at room temperature for another 1 h. Then 9,12-diiodo-*ortho*-carborane (198 mg, 0.50 mmol) with bis(triphenylphosphine)palladium dichloride (14 mg, 0.02 mmol, catalytic amount) were added. The reaction mixture was stirred at room temperature overnight and filtered, the solid was washed with hot acetonitrile (until no trace of carborane appeared on TLC). The organic phases were combined and concentrated under reduced pressure. The crude product was washed by 5% HCl and water to remove inorganic solids and by Et_2O and acetone to remove starting materials to give the corresponding diaryl derivatives of *ortho*-carborane.

9,12-Diphenyl-*ortho*-carborane (**13**): Phenyl bromide (262 μL, 393 mg, 2.50 mmol) was used. White powder was obtained (76 mg, yield 51%). ^{1}H NMR (400 MHz, CD_3COCD_3): δ 7.19 (4H, m, CH_{Ar}), 7.07 (6H, m, CH_{Ar}), 4.69 (2H, br s, CH_{Carb}) ppm; ^{11}B NMR (128 MHz, $CDCl_3$): δ 7.3 (2B, s, *B*-C), −9.7 (2B, d, J = 144 Hz), −13.9 (4B, d, J = 161 Hz), −16.1 (,2B d, J = 174 Hz) ppm. The spectral data correspond to those described in the literature [32,35].

9,12-Di(4-Methylphenyl)-*ortho*-carborane (**14**): 4-Methylphenyl bromide (315 μL, 435 mg, 2.50 mmol) was used; a white powder was obtained (98 mg, yield 60%). ^{1}H NMR (400 MHz, CD_3COCD_3): δ 7.09 (4H, d, J = 6.7 Hz, CH_{Ar}), 6.89 (4H, d, J = 6.7 Hz, CH_{Ar}), 4.63 (2H, br s, CH_{Carb}), 2.18 (6H, s, CH_3) ppm; ^{13}C NMR (100 MHz, CD_3COCD_3): δ 148.8 (C_{Ar}-B), 137.0 (C_{Ar}-CH_3), 132.5 (C_{Ar}H), 128.4 (C_{Ar}H), 53.3 (C_{Carb}H), 48.9 (C_{Carb}H), 21.3 (CH_3) ppm; ^{11}B NMR (128 MHz, CD_3COCD_3): δ 7.4 (2B, s, *B*-C), −9.4 (2B, d, J = 152 Hz), −14.0 (4B, d, J = 156 Hz), −16.3 (2B, d, J = 193 Hz) ppm. The spectral data correspond to those described in the literature [32,35]. Crystallographic data: $C_{16}H_{24}B_{10}$ are monoclinic, space group *C*2/*c*: a = 21.421(6) Å, b = 7.7182(18) Å, c = 14.405(4) Å, β = 127.139(14)°, V = 1898.6(9) Å^3, Z = 4, M = 324.45, d_{cryst} = 1.135 g cm^{-3}. $wR2$ = 0.1983 calculated on F^2_{hkl} for all 1886 independent reflections with $2\theta < 52.4°$, (GOF = 1.034, R = 0.0801 calculated on F_{hkl} for 1034 reflections with $I > 2\sigma(I)$).

4. Conclusions

In conclusion, the simple and efficient method was developed for the one-pot synthesis of *B*-substituted aryl derivatives of *ortho*-carborane with functional groups sensitive to organolithium and organomagnesium reagents using 9-iodo-*ortho*-carborane and generated in situ organozinc compounds. The method proposed provides near quantitative conversion of the starting 9-iodo-*ortho*-carborane to the corresponding aryl derivativs. A series of 9-aryl-*ortho*-carboranes, including those containing nitrile and ester groups, 9-RC_6H_4-1,2-$C_2B_{10}H_{11}$ (R = *p*-Me, *p*-NMe_2, *p*-OCH_2OMe, *o*-OMe, *p*-OMe, *o*-CN, *p*-CN, *o*-COOEt, *m*-COOEt, *p*-COOEt) was synthesized. The same approach was used for synthesis of the diaryl derivatives of *ortho*-carborane 9,12-(RC_6H_4)$_2$-1,2-$C_2B_{10}H_{10}$ (R = H, *p*-Me). The study of the applicability of this approach for the synthesis of aryl derivatives using other iodo derivatives of carboranes and metallacarboranes is in progress.

Supplementary Materials: The following are available online at http://www.mdpi.com/2073-4344/10/11/1348/s1: ^{1}H, ^{13}C and ^{11}B NMR spectra of compounds **2**–**11**, **13**, and **14**.

Author Contributions: Experiment design, synthesis, and NMR spectroscopy studies, S.A.A.; synthesis, A.V.S.; single crystal X-ray diffraction experiments, K.Y.S.; supervision and manuscript concept, I.B.S. All authors have read and agreed to the published version of the manuscript.

Funding: This work was supported by the Russian Science Foundation (Grant No. 19-73-00353).

Acknowledgments: The NMR spectral data were obtained by using equipment from the Center for Molecular Structure Studies at A.N. Nesmeyanov Institute of Organoelement Compounds, operating with support from the Ministry of Science and Higher Education of the Russian Federation.

Conflicts of Interest: The authors declare no conflict of interest. The funders had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript, or in the decision to publish the results.

References

1. Yamamoto, K.; Endo, Y. Utility of boron clusters for drug design. Hansch-Fujita hydrophobic parameters π of dicarba-*closo*-dodecaboranyl groups. *Bioorg. Med. Chem. Lett.* **2001**, *11*, 2389–2392. [CrossRef]
2. Issa, F.; Kassiou, M.; Rendina, L.M. Boron in drug discovery: Carboranes as unique pharmacophores in biologically active compounds. *Chem. Rev.* **2011**, *111*, 5701–5722. [CrossRef] [PubMed]
3. Scholz, M.; Hey-Hawkins, E. Carbaboranes as pharmacophores: Properties, synthesis, and application strategies. *Chem. Rev.* **2011**, *111*, 7035–7062. [CrossRef] [PubMed]
4. Endo, Y. Carboranes as hydrophobic pharmacophores: Applications for design of nuclear receptor ligands. In *Boron-Based Compounds: Potential and Emerging Applications in Medicine*; Hey-Hawkins, E., Viñas Teixidor, C., Eds.; John Wiley & Sons Ltd.: Oxford, UK, 2018; pp. 3–19. [CrossRef]
5. Spokoyny, A.M.; Farha, O.K.; Mulfort, K.L.; Hupp, J.T.; Mirkin, C.A. Porosity tuning of carborane-based metal–organic frameworks (MOFs) via coordination chemistry and ligand design. *Inorg. Chim. Acta* **2010**, *364*, 266–271. [CrossRef]

6. Kennedy, R.D.; Krungleviciute, V.; Clingerman, D.J.; Mondloch, J.E.; Peng, Y.; Wilmer, C.E.; Sarjeant, A.A.; Snurr, R.Q.; Hupp, J.T.; Yildirim, T.; et al. A carborane-based metal-organic framework with high methane and hydrogen storage capacities. *Chem. Mater.* **2013**, *25*, 3539–3543. [CrossRef]
7. Qi, S.-C.; Han, G.; Wang, H.-R.; Li, N.; Zhang, X.; Jiang, S.-L.; Lu, Y.-F. Synthesis and characterization of carborane bisphenol resol phenolic resins with ultrahigh char yield. *Chin. J. Polym. Sci.* **2015**, *33*, 1606–1617. [CrossRef]
8. Wu, Y.; Chen, G.; Feng, C.; Yang, J. High Tg and thermo-oxidatively stable thermosetting polyimides derived from a carborane-containing diamine. *Macromol. Rapid Commun.* **2018**, *39*, 1800484. [CrossRef]
9. Cui, M.; Zhang, L.; Lou, P.; Zhang, X.; Han, X.; Zhang, Z.; Zhu, S. Study on thermal degradation mechanism of heat-resistant epoxy resin modified with carboranes. *Polym. Degrad. Stabil.* **2020**, 109143. [CrossRef]
10. So, H.; Kim, J.H.; Lee, J.H.; Hwang, H.; An, D.K.; Lee, K.M. Planarity of terphenyl rings possessing *o*-carborane cages: Turning on intramolecular-charge-transfer-based emission. *Chem. Commun.* **2019**, *55*, 14518–14521. [CrossRef]
11. Ochi, J.; Tanaka, K.; Chujo, Y. Recent progress in the development of solid-state luminescent *o*-carboranes with stimuli responsivity. *Angew. Chem. Int. Ed.* **2020**, *59*. [CrossRef]
12. Wu, X.; Guo, J.; Lv, Y.; Jia, D.; Zhao, J.; Shan, H.; Jin, X.; Ma, Y. Aggregation-induced emission characteristics of *o*-carborane-functionalized fluorene and its heteroanalogs: The influence of heteroatoms on photoluminescence. *Mater. Chem. Front.* **2020**, *4*, 257–267. [CrossRef]
13. Grimes, R.N. *Carboranes*, 3rd ed.; Academic Press: London, UK, 2016; pp. 283–502. [CrossRef]
14. Heying, T.L.; Ager, J.W.; Clark, S.L.; Mangold, D.J.; Goldstein, H.L.; Hillman, M.; Polak, R.J.; Szymanski, J.W. A new series of organoboranes. I. Carboranes from the reaction of decaborane with acetylenic compounds. *Inorg. Chem.* **1963**, *2*, 1089–1092. [CrossRef]
15. Ohta, K.; Goto, T.; Endo, Y. 1,2-Dicarba-*closo*-dodecaboran-1-yl naphthalene derivatives. *Inorg. Chem.* **2005**, *44*, 8569–8573. [CrossRef] [PubMed]
16. Naito, H.; Morisaki, Y.; Chujo, Y. *o*-Carborane-based anthracene: A variety of emission behaviors. *Angew. Chem. Int. Ed.* **2015**, *54*, 5084–5087. [CrossRef] [PubMed]
17. Coult, R.; Fox, M.A.; Gill, W.R.; Herbertson, P.L.; MacBride, J.A.H.; Wade, K. *C*-arylation and *C*-heteroarylation of icosahedral carboranes via their copper(I) derivatives. *J. Organomet. Chem.* **1993**, *462*, 19–29. [CrossRef]
18. Colquhoun, H.M.; Herbertson, P.L.; Wade, K.; Baxter, I.; Williams, D.J. A carborane-based analogue of poly(*p*-phenylene). *Macromolecules* **1998**, *31*, 1694–1696. [CrossRef]
19. Fujii, S.; Yamada, A.; Nakano, E.; Takeuchi, Y.; Mori, S.; Masuno, H.; Kagechika, H. Design and synthesis of nonsteroidal progesterone receptor antagonists based on *C*,*C*′-diphenylcarborane scaffold as a hydrophobic pharmacophore. *Eur. J. Med. Chem.* **2014**, *84*, 264–277. [CrossRef]
20. Naito, H.; Nishino, K.; Morisaki, Y.; Tanaka, K.; Chujo, Y. Solid-state emission of the anthracene-*o*-carborane dyad from the twisted-intramolecular charge transfer in the crystalline state. *Angew. Chem. Int. Ed.* **2017**, *56*, 254–259. [CrossRef]
21. Tang, C.; Xie, Z. Nickel-catalyzed cross-coupling reactions of *o*-carboranyl with aryl iodides: Facile synthesis of 1-aryl-*o*-carboranes and 1,2-diaryl-*o*-carboranes. *Angew. Chem. Int. Ed.* **2015**, *54*, 7662–7665. [CrossRef]
22. Wu, X.; Guo, J.; Cao, Y.; Zhao, J.; Jia, W.; Chen, Y.; Jia, D. Mechanically triggered reversible stepwise tricolor switching and thermochromism of anthracene-*o*-carborane dyad. *Chem. Sci.* **2018**, *9*, 5270–5277. [CrossRef]
23. Zakharkin, L.I.; Lebedev, V.N. Reaction of lithium 1-methyl-*o*-carborane and lithium 1-methyl-*m*-carborane with hexafluorobenzene and pentafluorochlorobenzene. *Bull. Acad. Sci. USSR Div. Chem. Sci.* **1972**, *21*, 2273–2275. [CrossRef]
24. Thomas, R.L.; Welch, A.J. Haloaryl carbaboranes: 2. Synthesis and characterisation of haloaryl-*closo*-carbaboranes. Crystal structures of 1-(4-BrC_6F_4)-2-R-1,2-*closo*-$C_2B_{10}H_{10}$ (R = Me, Ph, Bu^t). *Polyhedron* **1999**, *18*, 1961–1968. [CrossRef]
25. Batsanov, A.S.; Fox, M.A.; Howard, J.A.K.; Wade, K. Syntheses and reactions of some new *C*-pentafluorophenyl and tetrafluorophenylene carborane systems. *J. Organomet. Chem.* **2000**, *597*, 157–163. [CrossRef]
26. Ohta, K.; Goto, T.; Endo, Y. New synthetic method of 1,2-diaryl-1,2-dicarba-*closo*-dodecaboranes employing aromatic nucleophilic substitution (S_NAr) reaction. *Tetrahedron Lett.* **2005**, *46*, 483–485. [CrossRef]
27. Zakharkin, L.I.; Koveredov, A.I.; Ol'shevskaya, V.A.; Shaugumbekova, S. Synthesis of *B*-organo-substituted 1,2-, 1,7-, and 1,12-Dicarba-*closo*-dodecarboranes(12). *J. Organomet. Chem.* **1982**, *226*, 217–226. [CrossRef]

28. Zheng, Z.; Jiang, W.; Zinn, A.A.; Knobler, C.B.; Hawthorne, M.F. Facile electrophilic iodination of icosahedral carboranes. Synthesis of carborane derivatives with boron-carbon bonds via the palladium- catalyzed reaction of diiodocarboranes with Grignard reagents. *Inorg. Chem.* **1995**, *34*, 2095–2100. [CrossRef]
29. Jiang, W.; Knobler, C.B.; Curtis, C.E.; Mortimer, M.D.; Hawthorne, M.F. Iodination reactions of icosahedral *para*-carborane and the synthesis of carborane derivatives with boron-carbon bonds. *Inorg. Chem.* **1995**, *34*, 3491–3498. [CrossRef]
30. Lee, H.; Knobler, C.B.; Hawthorne, M.F. Supramolecular self-assembly directed by carborane C–H ... F interactions. *Chem. Commun.* **2000**, 2485–2486. [CrossRef]
31. Fox, M.A.; Wade, K. Model compounds and monomers for phenylene ether carboranylene ketone (PECK) polymer synthesis: Preparation and characterization of boron-arylated *ortho*-carboranes bearing carboxyphenyl, phenoxyphenyl or benzoylphenyl substituents. *J. Mater. Chem.* **2002**, *12*, 1301–1306. [CrossRef]
32. Bayer, M.J.; Herzog, A.; Diaz, M.; Harakas, G.A.; Lee, H.; Knobler, C.B.; Hawthorne, M.F. The synthesis of carboracycles derived from *B,B′*-bis(aryl) derivatives of icosahedral *ortho*-carborane. *Chem. Eur. J.* **2003**, *9*, 2732–2744. [CrossRef]
33. Viñas, C.; Barbera, G.; Oliva, J.M.; Teixidor, F.; Welch, A.J.; Rosair, G.M. Are halocarboranes suitable for substitution reactions? The case for 3-I-1,2-*closo*-$C_2B_{10}H_{11}$: Molecular orbital calculations, aryldehalogenation reactions, ^{11}B NMR interpretation of *closo*-carboranes, and molecular structures of 1-Ph-3-Br-1,2-*closo*-$C_2B_{10}H_{10}$ and 3-Ph-1,2-*closo*-$C_2B_{10}H_{11}$. *Inorg. Chem.* **2001**, *40*, 6555–6562. [CrossRef] [PubMed]
34. Spokoyny, A.M.; Li, T.C.; Farha, O.K.; Machan, C.W.; She, C.; Stern, C.L.; Marks, T.J.; Hupp, J.T.; Mirkin, C.A. Electronic tuning of nickel-based bis(dicarbollide) redox shuttles in dye-sensitized solar cells. *Angew. Chem. Int. Ed.* **2010**, *49*, 5339–5343. [CrossRef] [PubMed]
35. Anufriev, S.A.; Sivaev, I.B.; Bregadze, V.I. Synthesis of 9,9′,12,12′-substituted cobalt bis(dicarbollide) derivatives. *Russ. Chem. Bull.* **2015**, *64*, 712–717. [CrossRef]
36. Anderson, K.P.; Mills, H.A.; Mao, C.; Kirlikovali, K.O.; Axtell, J.C.; Rheingold, A.L.; Spokoyny, A.M. Improved synthesis of icosahedral carboranes containing exopolyhedral B-C and C-C bonds. *Tetrahedron* **2019**, *75*, 187–191. [CrossRef]
37. Zakharkin, L.I.; Balagurova, E.V.; Lebedev, V.N. Suzuki cross-coupling in the carborane series. *Russ. J. Gen. Chem.* **1998**, *68*, 922–924.
38. Eriksson, L.; Beletskaya, I.P.; Bregadze, V.I.; Sivaev, I.B.; Sjöberg, S. Palladium-catalyzed cross-coupling reactions of arylboronic acids and 2-I-*p*-carborane. *J. Organomet. Chem.* **2002**, *657*, 267–272. [CrossRef]
39. Aizawa, K.; Ohta, K.; Endo, Y. Synthesis of 3-aryl-1,2-dicarba-*closo*-dodecaboranes by Suzuki-Miyaura coupling reaction. *Heterocycles* **2010**, *80*, 369–377. [CrossRef]
40. Zakharkin, L.I.; Ol'shevskaya, V.A. Synthesis of 9-organyl-1,2 and 1,7-dicarba-*closo*-dodecaboranes(12) *via* the cross-coupling reactions between organozinc compounds and 9-iodo-1,2- or 1,7-dicarba-*closo*-dodecaboranes. *Synth. React. Inorg. Met. Org. Chem.* **1991**, *21*, 1041–1046. [CrossRef]
41. Zakharkin, L.I.; Ol'shevskaya, V.A.; Zhigareva, G.G. Synthesis of *B*-organyl-*ortho*-carboranes and *meta*-carboranes *via* cross-correlation reaction of *B*-iodine-*ortho*-carboranes and *meta*-carboranes with organozinc compounds during catalysis by palladium complexes. *Russ. J. Gen. Chem.* **1998**, *68*, 925–927.
42. Cao, K.; Huang, Y.; Yang, J.; Wu, J. Palladium catalyzed selective mono-arylation of *o*-carboranes via B–H activation. *Chem. Commun.* **2015**, *51*, 7257–7260. [CrossRef]
43. Quan, Y.; Xie, Z. Controlled functionalization of *o*-carborane *via* transition metal catalyzed B–H activation. *Chem. Soc. Rev.* **2019**, *48*, 3660–3673. [CrossRef] [PubMed]
44. Tang, C.; Zhang, J.; Zhang, J.; Xie, Z. Regioselective nucleophilic alkylation/arylation of B−H bonds in. o-carboranes: An alternative method for selective cage boron functionalization. *J. Am. Chem. Soc.* **2018**, *140*, 16423–16427. [CrossRef]
45. Klatt, T.; Markiewicz, J.T.; Sämann, C.; Knochel, P. Strategies to prepare and use functionalized organometallic reagents. *J. Org. Chem.* **2014**, *79*, 4253–4269. [CrossRef] [PubMed]
46. Balkenhohl, M.; Knochel, P. Recent advances of the halogen-zinc exchange reactions. *Chem. Eur. J.* **2020**, *26*, 3688–3697. [CrossRef] [PubMed]

47. Fillon, H.; Gosmini, C.; Périchon, J. New chemical synthesis of functionalized arylzinc compounds from aromatic or thienyl bromides under mild conditions using a simple cobalt catalyst and zinc dust. *J. Am. Chem. Soc.* **2003**, *125*, 3867–3870. [CrossRef]
48. Kazmierski, I.; Gosmini, C.; Paris, J.-M.; Périchon, J. New progress in the cobalt-catalysed synthesis of aromatic organozinc compounds by reduction of aromatic halides by zinc dust. *Tetrahedron Lett.* **2003**, *44*, 6417–6420. [CrossRef]
49. Gosmini, C.; Moncomble, A. Cobalt-catalyzed cross-coupling reactions of aryl halides. *Isr. J. Chem.* **2010**, *50*, 568–576. [CrossRef]
50. Claudel, S.; Gosmini, C.; Paris, J.M.; Périchon, J. A novel transmetallation of arylzinc species into arylboronates from aryl halides in a barbier procedure. *Chem. Commun.* **2007**, 3667–3669. [CrossRef]
51. Safronov, A.V.; Sevryugina, Y.V.; Pichaandi, K.R.; Jalisatgi, S.S.; Hawthorne, M.F. Synthesis of *closo*- and *nido*-biscarboranes with rigid unsaturated linkers as precursors to linear metallacarborane-based molecular rods. *Dalton Trans.* **2014**, *43*, 4969–4977. [CrossRef]
52. Andrews, J.S.; Zayas, J.; Jones, M. 9-Iodo-*o*-carborane. *Inorg. Chem.* **1985**, *24*, 3715–3716. [CrossRef]
53. Brauer, G. *Handbuch der Präparativen Anorganischen Chemie*, 3rd ed.; Ferdinand Enke Verlag: Stuttgart, Germany, 1981.
54. Armarego, W.L.F.; Chai, C.L.L. *Purification of Laboratory Chemicals*, 6th ed.; Butterworth-Heinemann: Burlington, NJ, USA, 2009. [CrossRef]
55. *APEX2 and SAINT*; Bruker AXS Inc.: Madison, WI, USA, 2014.
56. Sheldrick, G.M. Crystal structure refinement with SHELXL. *Acta Cryst. C* **2015**, *71*, 3–8. [CrossRef] [PubMed]