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Microwave-Assisted Kumada-Type Cross-Coupling Reactions of Iodinated Carba-*closo*-dodecaborate Anions

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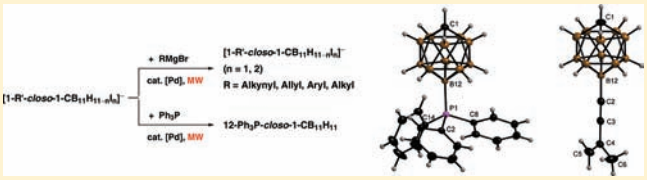
Supporting Information

ABSTRACT: The microwave-assisted Pd-catalyzed Kumada-type cross-coupling reaction of iodinated carba-*closo*-dodecaborate anions requires smaller amounts of Grignard reagent and catalyst and results in higher yields in much shorter reaction times in comparison to a reaction with conventional heat transfer. 12-Ph_3P-*closo*-1-$CB_{11}H_{11}$ was identified as the side product of the cross-coupling reactions that use $[PdCl_2(PPh_3)_2]$. The inner salt, which is the first example for a {*closo*-1-CB_{11}} cluster with a B−P bond, was selectively synthesized via a related microwave-assisted cross-coupling protocol and characterized by NMR spectroscopy, elemental analysis, and single-crystal X-ray diffraction. In addition, the crystal structures of the tetraethyl ammonium salts of [12-Ph-*closo*-1-$CB_{11}H_{11}]^-$, [12-(4-$MeOC_6H_4$)-*closo*-1-$CB_{11}H_{11}]^-$, and [12-(H_2C═(Me)CC≡C)-*closo*-1-$CB_{11}H_{11}]^-$ are described.



INTRODUCTION

Carba-*closo*-dodecaborate anions are of growing interest because they are used in various applications,[1] for example, as weakly coordinating anions,[2−6] in catalysis,[7−10] in ionic liquids,[11,12] and in supramolecular chemistry.[13,14] {*closo*-1-CB_{11}} clusters with substituents that can be easily modified are especially useful because they may allow easy incorporation of boron clusters into more complex structures. A number of syntheses of derivatives with an easy-to-modify functional group that is bonded to the cluster carbon atom have been reported,[1] e.g., [1-R-*closo*-1-$CB_{11}H_{11}]^-$ (R = CO_2H, NH_2, CN).[15,16] In contrast, only a very limited number of regioselective syntheses for carba-*closo*-dodecaborate anions with a functional group that is bonded to one of the boron atoms has been described. The Pd-catalyzed cross-coupling reaction of Grignard reagents with mono- and diiodinated {*closo*-1-CB_{11}} clusters represents one of these rare examples.[17−22] Its usefulness stems from (i) the availability of the iodinated precursors, e.g., [12-I-*closo*-1-$CB_{11}H_{11}]^-$,[15,18] [7-I-12-X-*closo*-1-$CB_{11}H_{10}]^-$ (X = F, Cl, Br, OH),[23] and [7,12-I_2-*closo*-1-$CB_{11}H_{10}]^-$,[15] and (ii) the broad range of Grignard reagents that can be used as starting materials. However, the reactions often require a large excess of the Grignard reagent, high catalyst loadings, and long reaction times, and in most cases the yields do not exceed 60%. Thus, development of the further chemistry and application of the functionalized carba-*closo*-dodecaborate anions, which so far are accessible solely via a Kumada-type cross-coupling reaction, is often hampered because salts of the anions are available in small quantities only.

In this contribution we report on the microwave-assisted Kumada-type cross-coupling reaction of mono- and diiodinated carba-*closo*-dodecaborate anions. Application of microwave irradiation resulted in higher yields and improved reaction conditions as reported earlier for related transition-metal-catalyzed cross-coupling reactions of organic substrates[24−27] including Kumada-type cross-coupling reactions.[28] In the field of boron cluster chemistry only a few examples of microwave-assisted reactions have been described so far, e.g., preparation of methylated carba-*closo*-dodecaborate anions[29,30] and metallacarboranes.[31] The inner salt 12-Ph_3P-*closo*-1-$CB_{11}H_{11}$ (**2**) was identified as a side product of the cross-coupling reactions for the first time. Its selective synthesis is described as well. The crystal structure of the zwitterion **2** was obtained, and a comparison of the experimental bond distances to those of $[Ph_3P$-*closo*-$B_{12}H_{11}]^-$ and to values derived from theoretical calculations is given. Furthermore, crystal structures of the $[Et_4N]^+$ salts of the anions [12-Ph-*closo*-1-$CB_{11}H_{11}]^-$ (**1h**), [12-(4-MeO-C_6H_4)-*closo*-1-$CB_{11}H_{11}]^-$ (**1j**), and [12-(H_2C═(Me)-CC≡C)-*closo*-1-$CB_{11}H_{11}]^-$ (**1g**) are reported.

RESULTS AND DISCUSSION

Microwave-Assisted Kumada-Type Cross-Coupling Reactions. The microwave-assisted Pd-catalyzed cross-coupling reaction of [12-I-*closo*-1-$CB_{11}H_{11}]^-$ (**1**) with Me_3SiC≡$CMgBr$ results in the trimethylsilylalkynyl derivative [12-Me_3SiC≡C-*closo*-1-$CB_{11}H_{11}]^-$ (**1a**) in a yield of 85% (Scheme 1). The yield of this reaction amounts to only 55% when it is performed under conventional heating instead of microwave irradiation as reported earlier.[22]

In addition to the improved yield of the microwave-assisted synthesis, the reaction time is reduced from 10 days to 1−3 h,

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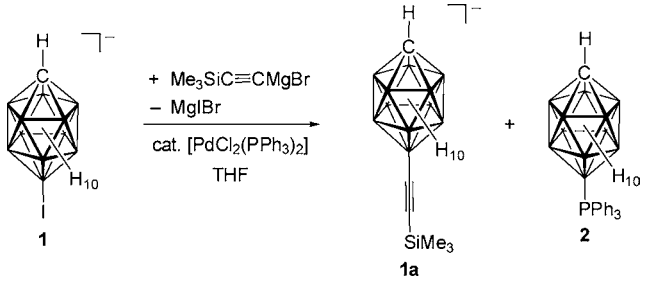
Scheme 1. Kumada-Type Cross-Coupling Reaction of 1 To Result in 1a as the Main Product and the Inner Salt 2 as a Side Product



depending on the amount of precatalyst $[PdCl_2(PPh_3)_2]$. The amount of the Pd complex is lowered from 30 mol % to 2−3 mol %. Furthermore, 2 equiv of the Grignard reagent $Me_3SiC{\equiv}CMgBr$ is sufficient, whereas as much as 14 equiv are required to achieve complete conversion of the conventional reaction. A comparison of the parameters of the microwave-assisted and conventional reactions is given in Table 1.

Table 1. Comparison of the Conventional and the Microwave-Assisted Pd-Catalyzed Cross-Coupling Reaction of 1 with $Me_3SiC{\equiv}CMgBr$ To Result in $[Et_4N]$1a

conditions	$Me_3SiC{\equiv}CMgBr$ (equiv)	$[PdCl_2(PPh_3)_2]$ [mol %]	t [h]	yield **1a** [%]	yield **2** [%]
conventional heating[22]	14	30	240	55	10
microwave	2	2	3	85	(<1)[a]
microwave	2	3	1	85	(<1)[a]

[a]Determined by $^{11}B\{^1H\}$ NMR spectroscopy.

The zwitterion 12-Ph_3P-*closo*-1-$CB_{11}H_{11}$ (**2**) was identified as a side product of the Kumada-type cross-coupling reaction performed with $[PdCl_2(PPh_3)_2]$ for the first time, and it was isolated in yields of 10% from product mixtures of conventional reactions. Its spectroscopic and structural characterization is presented in the successive section. The amount formed of **2** drops to less than 1% by applying microwave irradiation and optimized conditions as evident from NMR spectroscopic analyses of the reaction mixtures (Table 1).

Addition of CuI to the reaction mixture, which is used as a reagent in some related Pd-catalyzed cross-coupling reactions of iodinated boron clusters,[32] did not result in a further improvement of the reaction but leads to a strong decrease of the reaction rate. An attempted synthesis of **1a** with conditions comparable to those of the microwave-assisted reactions listed in Table 1 but with 10 mol % of CuI resulted in a conversion of only 20% after 3 h.

Synthesis can easily be scaled up as demonstrated by preparation of almost 3 g of Cs[12-HC≡C-*closo*-1-$CB_{11}H_{11}$] (Cs**1b**) in a one-step synthesis starting from 5 g of Cs[12-I-*closo*-1-$CB_{11}H_{11}$] (Cs**1**) in a yield of 78%. This synthesis involves the reaction depicted in Scheme 1 followed by cleavage of the trimethylsilyl group. Preparation of Cs**1b** starting from Cs**1** with $[Et_4N]$**1a**, which was synthesized as shown in Scheme 1, as intermediate was reported earlier with an overall yield of 49%.[22,33]

The protocol of the microwave-promoted Kumada-type cross-coupling reaction was adopted for preparation of a variety of other derivatives of the carba-*closo*-dodecaborate anion with a functional group that is bonded via a carbon atom to the antipodal boron atom in yields of up to 90%. The study includes preparation of alkynyl, aryl, alkyl, and allyl substituents, and the results are summarized in Table 2. In general, significantly increased yields, shorter reaction times, lower catalyst loadings, and a reduction of the amount of the respective Grignard reagent were achieved in comparison to the conventional reactions that were reported for some of the compounds by other groups or us. For example, yields of 52% and 54% were reported for $[Me_4N]$[12-Et-*closo*-1-$CB_{11}H_{11}$] ($[Me_4N]$**1l**)[18] and $[Et_4N]$[12-PhC≡C-*closo*-1-$CB_{11}H_{11}$] ($[Et_4N]$**1f**),[22] respectively, whereas the microwave-assisted syntheses gave yields of 84% for $[Et_4N]$**1l** and Cs**1f**.

The tetraethylammonium salts of [12-Ph-*closo*-1-$CB_{11}H_{11}$]$^-$ (**1h**), [12-(4-MeO-C_6H_4)-*closo*-1-$CB_{11}H_{11}$]$^-$ (**1j**), and [12-(H_2C═(Me)CC≡C)-*closo*-1-$CB_{11}H_{11}$]$^-$ (**1g**) were characterized by single-crystal X-ray diffraction (Figure 1). $[Et_4N]$**1j** crystallizes as solvate with one acetone molecule per formula unit of the $[Et_4N]^+$ salt, and the carba-*closo*-dodecaborate anion has crystallographic mirror symmetry. In contrast, neither anion **1h** nor anion **1j** shows any symmetry in the crystal.

The B12−C_{aryl} distances in anions **1h** and **1j** are similar to those reported for related {*closo*-1-CB_{11}} clusters with aryl groups bonded to the antipodal boron atom, e.g., 1.591(4) Å in [1-(4-Me-C_6H_4-4-C_6H_4)-12-(4-Me-C_6H_4)-*closo*-$CB_{11}H_{10}$]$^{2-}$.[20,21] The corresponding B12−C distance and d(C≡C) in the alkynyl derivative **1g** are close to values derived for other {12-RC≡C-*closo*-1-CB_{11}} clusters, for example, in [12-PhC≡C-*closo*-1-$CB_{11}H_{11}$]$^-$ (**1f**) (d(B12−C) = 1.548(2) Å, d(C≡C) = 1.202(2) Å).[34] The bond distances of the B−C≡CC(Me)═CH_2 fragment in **1g** are similar to those described for (H_2C═(Me)-CC≡C)(C_6F_5)$_2$B(C_2H_4PHMes$_2$) (d(B−C) = 1.587(3) Å, d(C≡C) = 1.203(3) Å, d(C−C) = 1.435(3) Å, d(C═CH_2) = 1.322(4) Å, d(C−CH_3) = 1.473(4) Å).[35]

The Kumada-type Pd-catalyzed cross-coupling reaction of H_2C═$CHCH_2MgBr$ with Cs**1** solely resulted in [12-H_2C═$CHCH_2$-*closo*-1-$CB_{11}H_{11}$]$^-$ (**1n**) as shown by NMR spectroscopy (Table 2, entries 12 and 13). During aqueous workup the allyl group partially isomerizes to a vinyl group to selectively give [12-(*trans*-CH_3CH═CH)-*closo*-1-$CB_{11}H_{11}$]$^-$ (**1o**). Hence, mixtures of both $[Et_4N]^+$ salts were obtained with a total yield of 77−79%. The extent of isomerization depends on the temperature during and the time of the aqueous workup procedure. Thus, one of the reactions described in the Experimental Section yielded a mixture of salts that consisted of 94% of $[Et_4N]$**1o** and 6% of $[Et_4N]$**1n** (entry 12) and the other of 16% of $[Et_4N]$**1o** and 84% of $[Et_4N]$**1n** (entry 13). However, the workup conditions were not fully optimized to exclusively yield either the allyl (**1n**) or the vinyl (**1o**) derivative. In contrast to the cross-coupling reaction with $Me_3SiC{\equiv}CMgBr$ to result in **1a** (Scheme 1), CuI lead to a strong acceleration of the reaction with a change of the reaction time from 30 (entry 12) to 2.5 h (entry 13).

An analogous isomerization as observed for anions **1n** and **1o** was reported for preparation of $[Et_4N]$[1-Ph-12-(*trans*-CH_3CH═CH)-*closo*-1-$CB_{11}H_{10}$] during aqueous workup under acidic conditions.[21] The conventional Kumada-type cross-coupling reaction yielded after isomerization the tetraethylammonium salt of the carba-*closo*-dodecaborate anion in a yield of 42%. No isomerization was found for the neutral allyl derivative 1-Me_3N-2-Ph-8-(H_2C═$CHCH_2$)-*closo*-1-$CB_{11}H_9$, which was obtained also via a cross-coupling reaction using an allyl Grignard reagent in a yield of 82%.[17]

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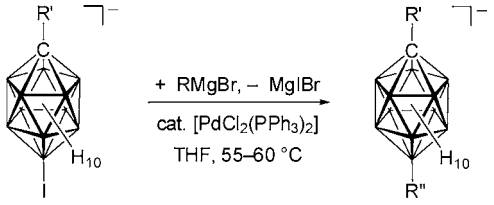
Table 2. Microwave-Assisted Kumada-Type Cross-Coupling Reaction of 1, 3, and 4



R' = H (**1**), Me (**3**), Ph (**4**) **1b–m**, **3a**, **4a**

entry	–R"	Grignard reagent (equiv)	$[PdCl_2(PPh_3)_2]$ [mol%]	*t* [h]	product[a]	yield [%]
1	–≡–$SiEt_3$	2	3	2	**1c**	70
2	–≡–Si^iPr_3	2	3	3	**1d**	61
3	–≡–nC_4H_9	2	3	5	**1e**	70
4	–≡–Ph	3	3	3	**1f**	84
5	–≡–C(Me)=CH_2	3	11[b]	5	**1g**	65[b]
6	–Ph	3	3	0.25	**1h**	75
7	–Ph–$SiMe_3$	3	5	2	**1i**	73
8	–Ph–OMe	2	3	1	**1j**	74
9	–Ph–≡–$SiMe_3$	2	3	1	**1k**[c]	90
10	$-C_2H_5$	4	5	3	**1l**	84
11	$-CH_2SiMe_3$	3[d]	3	0.25	**1m**	80
12	–CH=CH–CH=CH_2 / –CH_2–CH=CH–CH_2–	7[e]	8[e]	30[e]	**1n/1o**[f]	77
13	–CH=CH–CH=CH_2 / –CH_2–CH=CH–CH_2–	6[g]	12[g]	2.5[g]	**1n/1o**[f]	79
14	–≡–$SiMe_3$	3	3	3	**3a**[c]	80
15	–≡–$SiMe_3$	3	3	6	**4a**[c]	58[b]

[a]Isolated as either Cs^+ or $[Et_4N]^+$ salt. [b]Not a fully optimized reaction. [c]The Me_3Si group was removed during workup under basic aqueous conditions to result in the terminal alkyne. [d]Me_3SiCH_2MgCl. [e]Three mole percent of catalyst and 2 equiv of $H_2C{=}CHCH_2MgBr$ were added at the beginning of the reaction, and after 24 h further 4 mol % $[PdCl_2(PPh_3)_2]$ and 5 equiv of $H_2C{=}CHCH_2MgBr$ were added. [f]The allyl derivative **1o** partially isomerizes to the vinyl derivative [12-(*trans*-$CH_3CH{=}CH$)-*closo*-1-$CB_{11}H_{11}]^-$ (**1p**). The extent depends on the conditions of the workup procedure as described in the Experimental Section. [g]$H_2C{=}CHCH_2MgBr$, $[PdCl_2(PPh_3)_2]$, and CuI were added in three equal batches.

The versatility of the novel microwave-assisted protocol is furthermore demonstrated by preparation of a series of carba-*closo*-dodecaborate anions with a functional group that is bonded via carbon to the boron atom at the 7 position of the cluster. The yields and conditions of these reactions that are collected in Table 3 are similar to those described for the analogous cross-coupling reactions starting from [12-I-*closo*-1-$CB_{11}H_{11}]^-$ (**1**) in Tables 1 and 2.

In Table 3 one example for a microwave-assisted cross-coupling reaction of the diiodinated precursor [7,12-I_2-*closo*-1-$CB_{11}H_{10}]^-$ (**8**) is presented as well. The conditions for preparation of $[Et_4N]$[7,12-$(HC{\equiv}C)_2$-*closo*-1-$CB_{11}H_{10}]$ ($[Et_4N]$**8a**) via [7,12-$(Me_3SiC{\equiv}C)_2$-*closo*-1-$CB_{11}H_{10}]^-$ are also highly improved in comparison to the conventional method similar to preparation of [12-$Me_3SiC{\equiv}C$-*closo*-1-$CB_{11}H_{11}]^-$ (**1a**) (Table 1).[22] The yield was improved from 38% for Cs**8a** (41% for the cross-coupling procedure[22] and 93% for the desilylation reaction[33]) to 63%.

Synthesis and Characterization of 12-Ph_3P-*closo*-1-$CB_{11}H_{11}$ (2). The inner salt 12-Ph_3P-*closo*-1-$CB_{11}H_{11}$ (**2**), which is the side product of all Kumada-type cross-coupling reactions presented in Tables 1 and 2, was selectively synthesized in a yield of 88% via a microwave-assisted Pd-catalyzed cross-coupling reaction as shown in Scheme 2. The precatalyst of the synthesis is $[Pd(PPh_3)_4]$. Similar to preparation of the isoelectronic anionic triphenylphosphane derivative [Ph_3P-*closo*-$B_{12}H_{11}]^-$, which was described earlier,[36] addition of a carbonate salt was necessary. Without either K_2CO_3 or $[Pd(PPh_3)_4]$ no conversion of **1** to result in **2** was observed. However, the function of K_2CO_3 remains unclear. Attempted synthesis of **2** using the same reaction conditions but with conventional heating instead of microwave irradiation resulted in a much slower reaction, and thus, the reaction was aborted after a few percent of conversion.

Zwitterion **2** was characterized by multi-NMR spectroscopy and elemental analysis. The ^{31}P NMR signal of **2** is shifted

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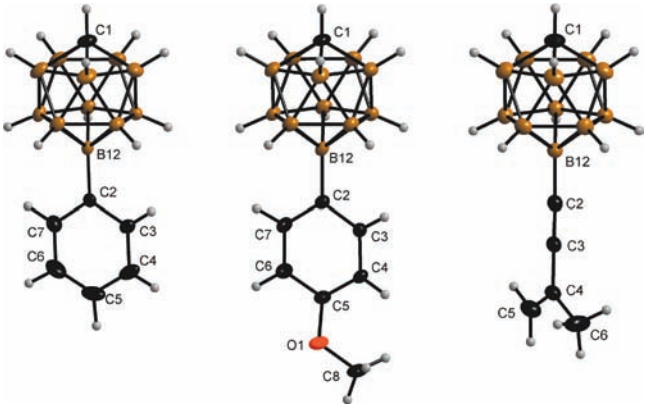

Figure 1. Anions [12-Ph-*closo*-1-$CB_{11}H_{11}$]$^-$ (**1h**, left), [12-(4-MeO-C_6H_4)-*closo*-1-$CB_{11}H_{11}$]$^-$ (**1j**, middle), and [12-(H_2C═(Me)CC≡C)-*closo*-1-$CB_{11}H_{11}$]$^-$ (**1g**, right) in the crystals of their [Et_4N]$^+$ salts. Selected bond lengths [Angstroms] and angles [degrees]: **1h** B12−C2 1.583(2); **1j** B12−C2 1.582(4), C5−O1 1.372(4), O1−C8 1.420(4), C5−O1−C8 117.0(2); **1g** B12−C2 1.545(2), C2≡C3 1.197(2), C3−C4 1.431(2), C4═C5 1.322(3), C4−C6 1.494(3), B12−C2≡C3 177.9(2), C2≡C3−C4 179.0(2), C3−C4═C5 121.0(2), C3−C4−C6 116.1(2), C5═C4−C6 123.0(2).

to a lower resonance frequency than the signal of [Ph_3P-*closo*-$B_{12}H_{11}$]$^-$ (Table 4). The $^{31}P-^{13}C$ coupling constant of **2** (147 Hz) is slightly larger compared to $^1J(^{31}P,^{13}C)$ of [Ph_3P-*closo*-$B_{12}H_{11}$]$^-$ (134 Hz).

A single crystal of the neutral inner salt **2** was studied by X-ray diffraction, and a molecule in the crystal is depicted in Figure 2. In Table 4 selected bond distances of **2** are compared to values of [Ph_3P-*closo*-$B_{12}H_{11}$]$^-$ and values derived from DFT and ab initio calculations for both of them. The experimental bond properties of the *closo*-boron species are well reproduced by the DFT and (RI)-MP2 calculations, which confirms the differences between both cluster derivatives as suggested by the experimental data. The B−P distance in **2** of 1.944(3) Å is slightly longer than *d*(B−P) in [nBu_4N][Ph_3P-*closo*-$B_{12}H_{11}$] of 1.928(2) Å. The mean value of the three phosphorus carbon distances is slightly shorter for **2** compared to the anion, which contrasts the trend in *d*(B−P). The longer B−P distance in **2** is accompanied by a smaller B−P−C angle. The inner cluster bond distances of **2** are close to values derived for other {*closo*-1-CB_{11}} clusters from single-crystal X-ray diffraction and theoretical calculations, e.g., for [12-PhC≡C-*closo*-1-$CB_{11}H_{11}$]$^-$ (**1f**).[22,34]

SUMMARY AND CONCLUSION

Microwave irradiation instead of conventional heat transfer results in a tremendous improvement of the Pd-catalyzed Kumada-type cross-coupling reaction of mono- and diiodinated carba-*closo*-dodecaborate anions. The enhancement of the reactions includes higher yields, shorter reaction times, lower catalyst loadings, and a reduction of the Grignard reagent. Probably, application of microwave irradiation to other cross-coupling reactions in the field of boron cluster chemistry will lead to similar improvements. A first example is preparation of the inner salt 12-Ph_3P-*closo*-1-$CB_{11}H_{11}$ (**2**) that can be prepared in 4 h in high yield from Ph_3P and [12-I-*closo*-1-$CB_{11}H_{11}$]$^-$ (**1**), whereas the reaction is very slow when conventional heat transfer is used.

Carba-*closo*-dodecaborate anions with different functional groups that are bonded via carbon to the antipodal boron atom or to one of the boron atoms of the lower belt or to both of them are now much more easily accessible. This will facilitate the study of their reactions and properties, for example, the coordination chemistry of carba-*closo*-dodecaboranylethynido ligands in coordination chemistry as in [{12-($Me_3PAu)_2$C≡C-*closo*-1-$CB_{11}H_{11}$}$_2$].[14]

EXPERIMENTAL SECTION

General Methods. ^1H, ^{11}B, ^{13}C, ^{19}F, and ^{31}P NMR spectra were recorded at 25 °C either in CD_3CN, $(CD_3)_2CO$, or toluene-d_8 on a Bruker Avance III 400 spectrometer operating at 400.17 (^1H), 128.39 (^{11}B), 100.62 MHz (^{13}C), 376.45 MHz (^{19}F), and 128.39 MHz (^{31}P). The NMR signals were referenced against TMS (^1H, ^{13}C), $BF_3{\cdot}OEt_2$ in CD_3CN (^{11}B), $CFCl_3$ (^{19}F), and H_3PO_4 (85%) in H_2O (^{31}P) as external standards. Assignments of the ^1H and ^{11}B NMR signals are supported by $^{11}B\{^1H\}-^1H\{^{11}B\}$ 2D[37,38] and $^{11}B\{^1H\}-^{11}B\{^1H\}$ COSY[39,40] experiments. Infrared and Raman spectra were recorded at room temperature on an Excalibur FTS 3500 spectrometer (Digilab, Germany) with an apodized resolution of 2 (IR) and 4 cm^{-1} (Raman), respectively. IR spectra were measured in the attenuated total reflection (ATR) mode in the region of 4000−530 cm^{-1}. Raman spectra were measured using the 1064 nm excitation line of a Nd/YAG laser on crystalline samples contained in melting point capillaries in the region of 3500−80 cm^{-1}. Elemental analyses (C, H, N) were performed with a Euro EA3000 instrument (HEKA-Tech, Germany).

Chemicals. All standard chemicals were obtained from commercial sources. Tetrahydrofuran was distilled from K/Na alloy under a nitrogen atmosphere and stored in a flask equipped with a valve with a PTFE stem (Young, London) over molecular sieves (4 Å) under an argon atmosphere. The following alkynes were obtained from commercial sources: $Me_3SiC{\equiv}CH$, Apollo Scientific; $Et_3SiC{\equiv}CH$, ABCR; $iPr_3SiC{\equiv}CH$, Sigma-Aldrich; $nC_4H_9C{\equiv}CH$, ACROS; 1-Br-4-($Me_3SiC{\equiv}C$)-C_6H_4, Sigma-Aldrich. Solutions of $Me_3SiC{\equiv}CMgBr$, $Et_3SiC{\equiv}CMgBr$, $iPr_3SiC{\equiv}CMgBr$, and $nC_4H_9C{\equiv}CMgBr$ in THF (0.75 mol L^{-1}) were prepared from the corresponding ethyne and EtMgBr (1 mol L^{-1} in THF) and kept in round-bottom flasks with a valve with a PTFE stem (Young, London) at 4 °C. The aryl Grignard reagents were synthesized from the corresponding aryl bromide and Mg in THF (1 mol L^{-1}). EtMgBr (1 mol L^{-1} in THF), PhC≡CMgBr (1 mol L^{-1} in THF), Me_3SiCH_2MgCl (1 mol L^{-1} in Et_2O), and H_2C═$CHCH_2MgBr$ (1 mol L^{-1} in Et_2O) were obtained from Sigma-Aldrich. H_2C═(Me)CC≡CMgBr (0.5 mol L^{-1} in THF) was prepared from (Me_3SiO)$Me_2CC{\equiv}CH$ and EtMgBr. Cs[12-I-*closo*-1-$CB_{11}H_{11}$][15,18] and Cs[7,12-I_2-*closo*-1-$CB_{11}H_{10}$],[15] were synthesized according to modified literature procedures. The monoiodinated carborates Cs[7-I-12-Hal-*closo*-1-$CB_{11}H_{10}$] (Hal = F, Cl, Br) were prepared as described elsewhere.[23] Cs[1-Ph-*closo*-1-$CB_{11}H_{11}$] was prepared from *nido*-$B_{10}H_{14}$ via [Et_4N][6-Ph-*nido*-6-CB_9H_{11}].[41−44] Iodination resulting in Cs[1-Ph-12-I-*closo*-1-$CB_{11}H_{10}$] followed a known protocol.[19,21] Cs[1-Me-12-I-*closo*-1-$CB_{11}H_{10}$] was synthesized as described in the literature.[18] Cesium carba-*closo*-1-dodecaborate was obtained from Katchem spol. sro (Praha, Czech Republic) or synthesized from [Me_3NH][*nido*-$B_{11}H_{14}$][45] according to a literature procedure.[46]

Single-Crystal X-ray Diffraction. Colorless crystals of **2** suitable for a X-ray diffraction study were grown from toluene by slow evaporation of the solvents. Slow uptake of diethyl ether into solutions of [Et_4N]**1h**, [Et_4N]**1j**·Me_2CO, and [Et_4N]**1g** in acetone resulted in colorless crystals. A crystal of **2** was investigated with a Stoe STADI CCD diffractometer, and crystals of the other three substances were studied with an Oxford Xcalibur diffractometer equipped with an EOS detector using Mo Kα radiation (λ = 0.71073 Å). All structures were solved by direct methods,[47,48] and refinement is based on full-matrix least-squares calculations on F^2.[48,49]

The positions of most of the hydrogen atoms in the crystal structures were located via ΔF syntheses. The only exceptions are those of the hydrogen atoms of the disordered acetone molecule in [Et_4N]**1j**·Me_2CO. All non-hydrogen atoms were refined anisotropically.

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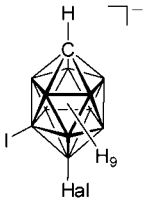
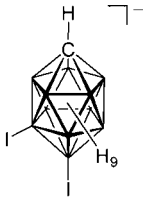
Table 3. Microwave-Assisted Kumada-Type Cross-Coupling Reaction of 5−8



Hal = F (**5**), Cl (**6**), Br (**7**)

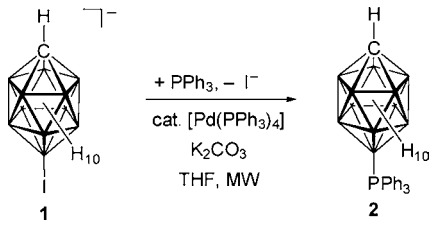


8

entry	−R"	Grignard reagent (equiv)	$[PdCl_2(PPh_3)_2]$ [mol%]	*t* [h]	product[a]	yield [%]
1	−C≡C−SiMe$_3$	2	3	3	**5a**[b]	73
2	−C≡C−SiMe$_3$	2	3	3	**6a**[b]	86
3	−C≡C−SiMe$_3$	3	3	3	**7a**[b]	66[c]
4	−C≡C−SiMe$_3$	6[d]	6[d]	9[d]	**8a**[b]	63
5	−C$_6$H$_4$−C≡C−SiMe$_3$	2	3	6	**6b**[b]	70

[a]Isolated either as Cs^+ or $[Et_4N]^+$ salt. [b]The Me_3Si group was removed during workup under basic aqueous conditions to result in the terminal alkyne. [c]Not a fully optimized reaction. [d]Three mole percent of catalyst and 3 equiv of $Me_3SiC{\equiv}CMgBr$ were added at the beginning of the reaction, and after 5 h additional 3 mol % $[PdCl_2(PPh_3)_2]$ and 3 equiv of $Me_3SiC{\equiv}CMgBr$ were added.

Scheme 2. Microwave-Assisted Pd-Catalyzed Synthesis of 2 (yield 88%)



1 **2**

Most of the hydrogen atoms were refined using idealized bond lengths as well as angles.

Calculations were carried out using the WinGX program package.[50] Molecular structure diagrams were drawn with the program Diamond 3.2 g.[51] Experimental details, crystal data, and CCDC numbers are collected in Table 5. Supplementary crystallographic data for this publication are deposited in the Supporting Information or can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Quantum Chemical Calculations. Density functional calculations (DFT)[52] were carried out using Becke's three-parameter hybrid functional and the Lee−Yang−Parr correlation functional (B3LYP)[53−55] using the Gaussian03 program suite.[56] Geometries were optimized, and energies were calculated with the 6-311++G(d,p) basis sets. Diffuse functions were incorporated because improved energies are obtained for anions.[57] Structures represent true minima with no imaginary frequency on the respective hypersurface. Geometries were optimized at the second-order Møller−Plesset perturbation (MP2) level of theory also using the resolution-of-the-identity approximation [(RI)-CC2 module][58] in combination with the def2-TZVPP basis sets and auxiliary bases.[59]

General Procedure for the Microwave-Assisted Cross-Coupling Reactions. The iodinated carba-*closo*-dodecaborate and $[PdCl_2(PPh_3)_2]$ was dissolved in dry THF (2−10 mL per mmol cluster) under an Ar atmosphere in a glass finger (70 mL) equipped with a valve with a PTFE stem (Young, London) and fitted with a magnetic stirring bar. A solution of the respective Grignard reagent in THF (0.75−1.0 mmol mL^{-1}) was added via syringe. The reaction mixture was heated to 55 °C by microwave irradiation (CEM Discover S-Klasse Plus (SP)), and the progress of the reaction was periodically checked by $^{11}B\{^1H\}$ NMR spectroscopy. The reaction mixture was poured into deionized water (2−10 mL per mmol cluster) after complete conversion, and most of the THF was removed under reduced pressure. The black residue was filtered off, and the water was stored separately. The black residue was dissolved in a minimum amount of CH_2Cl_2 and extracted twice with deionized water (2 × ∼20 mL per mmol cluster). All water layers were combined, and the Cs^+ or $[Et_4N]^+$ salt of the respective carba-*closo*-dodecaborate anion was precipitated by addition of a concentrated aqueous solution of CsCl or $[Et_4N]Br$ (2 mmol per mmol cluster), respectively. The resulting white precipitate was collected by filtration and dried in a vacuum.

$[Et_4N][12\text{-}Me_3SiC{\equiv}C\text{-}closo\text{-}1\text{-}CB_{11}H_{11}]$ ($[Et_4N]$1a). $[Et_4N]$**1a** was prepared from Cs[12-I-*closo*-1-$CB_{11}H_{11}$] (200 mg, 0.50 mmol) and $Me_3SiC{\equiv}CMgBr$ (1.3 mL, 1 mmol) with $[PdCl_2(PPh_3)_2]$ (10 mg, 0.015 mmol) as precatalyst. Yield: 157 mg (0.43 mmol, 85%). Spectroscopic data and results of elemental analysis have been reported earlier.[22]

Cs[12-HC≡C-*closo*-1-$CB_{11}H_{11}$] (Cs1b). Cs[12-I-*closo*-1-$CB_{11}H_{11}$] (5.00 g, 12.44 mmol), $Me_3SiC{\equiv}CMgBr$ (33 mL, 25 mmol), and $[PdCl_2(PPh_3)_2]$ (262 mg, 0.375 mmol) were used. $[Et_4N]$**1a** was not dried after precipitation but immediately treated with hydrochloric acid (50 mL, 2 mol L^{-1}) and diethyl ether (200 mL). The ethereal layer was separated after complete dissolution of the tetraethylammonium salt, and the aqueous phase was extracted three times with diethyl ether (3 × 100 mL). The combined organic phases were dried with $MgSO_4$. The magnesium sulfate was filtered off, and a saturated aqueous solution of cesium carbonate (5 g, 15.3 mmol) was added to the solution. Ether was removed using a rotary evaporator, and acetone (200 mL) was added to the remaining solid. The solution was dried with Cs_2CO_3 and filtered, and most of the solvent was removed with a rotary evaporator to result in a concentrated solution of Cs**1b** (5 mL). The cesium salt was precipitated by addition of chloroform (300 mL), filtered, and dried in a vacuum. Yield: 2.91 g (9.67 mmol, 78%). Spectroscopic data and results of the elemental analysis for Cs**1b** have been reported earlier.[33]

Attempted Synthesis of the Salt of $[12\text{-}Me_3SiC{\equiv}C\text{-}closo\text{-}1\text{-}CB_{11}H_{11}]^-$ (1a) in the Presence of CuI. The reaction was performed as described for the general procedure with Cs[12-I-*closo*-1-$CB_{11}H_{11}$] (200 mg, 0.50 mmol) and $Me_3SiC{\equiv}CMgBr$ (1.3 mL, 1 mmol) with $[PdCl_2(PPh_3)_2]$ (10 mg, 0.015 mmol), but CuI (10 mg, 0.050 mmol) was added. After 3 h only 20% of the starting material had reacted to **1a** and small amounts of **2**. Because of the very slow conversion the reaction was discontinued.

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Table 4. Comparison of Selected Experimental and Calculated[a] Data of 12-Ph_3P-*closo*-1-$CB_{11}H_{11}$ (2) and [Ph_3P-*closo*-$B_{12}H_{11}$]$^-$ [b,c]

12-Ph_3P-*closo*-1-$CB_{11}H_{11}$ (2)										
method	$\delta(^{31}P)$	$^1J(^{31}P,^{11}B)$	d(B12−P)	d(P−C_{ipso})[d]	∠(B12−P−C)	d($C_{cluster}$−B 2/3/4/5/6)	d(B2/3/4/5/6 −B2/3/4/5/6)	d(B2/3/4/5/6− B7/8/9/10/11)	d(B7/8/9/10/11 −B7/8/9/10/11)	d(B7/8/9/10/11 −B12)
exptl	2.3	147	1.944(3)	1.808(2)	112.58(11)	1.696(4)	1.766(5)	1.765(5)	1.786(4)	1.771(4)
B3LYP			1.971	1.837	113.04	1.705	1.782	1.770	1.798	1.779
MP2			1.904	1.791	112.93	1.699	1.778	1.766	1.794	1.768
[Ph_3P-*closo*-$B_{12}H_{11}$]$^-$										
method	$\delta(^{31}P)$	$^1J(^{31}P,^{11}B)$	d(B1−P)	d(P−C_{ipso})[d]	∠(B1−P−C)	d(B 7/8/9/10/11 −B12)	d(B7/8/9/10/11− B7/8/9/10/11)	d(B2/3/4/5/6−B 7/8/9/10/11)	d(B2/3/4/5/6− B2/3/4/5/6)	d(B1−B2/ 3/4/5/6)
exptl[e]	6.8	134	1.928(2)	1.816(2)	113.48(9)	1.787(4)	1.787(4)	1.778(3)	1.796(3)	1.780(3)
B3LYP			1.949	1.845	114.38	1.784	1.788	1.779	1.799	1.775
MP2			1.869	1.795	114.27	1.761	1.786	1.775	1.796	1.761

[a]Methods: B3LYP/6-311++G(d,p) and (RI)-MP2/def2-TZVPP. [b]Distances in Angstroms, angles in degrees, chemical shifts in parts per million, and coupling constants in Hertz. [c]Mean values for C_{5v} symmetry of the clusters. [d]Mean value. [nBu_4N][Ph_3P-*closo*-$B_{12}H_{11}$].[36]

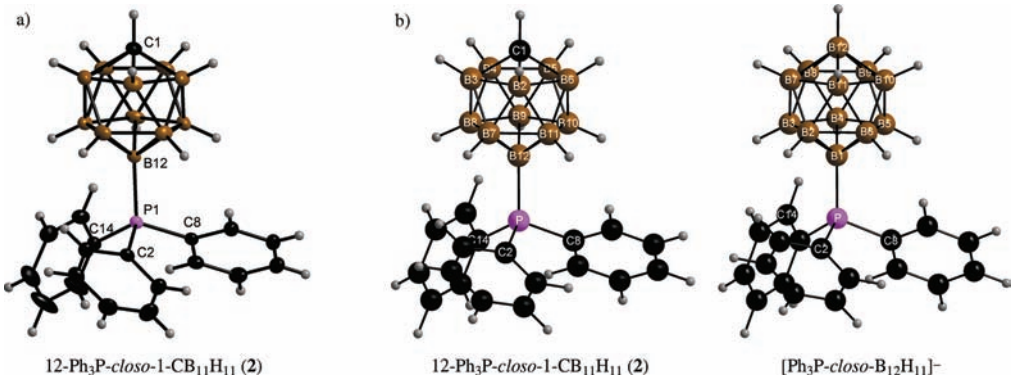

Figure 2. (a) Molecule of 12-Ph_3P-*closo*-1-$CB_{11}H_{11}$ (2) in the crystal (displacement ellipsoids at the 35% probability level). (b) Calculated structures at the B3LYP/6-311++G(d,p) level of theory, and labeling schemes for the cluster atoms of 2 and [Ph_3P-*closo*-$B_{12}H_{11}$]$^-$.

[Et_4N][12-$Et_3SiC{\equiv}C$-*closo*-1-$CB_{11}H_{11}$] ([Et_4N]1c). [Et_4N]**1c** was synthesized from Cs[12-I-*closo*-1-$CB_{11}H_{11}$] (200 mg, 0.50 mmol) and $Et_3SiC{\equiv}CMgBr$ (1.3 mL, 1 mmol) with [$PdCl_2(PPh_3)_2$] (10 mg, 0.015 mmol). Yield: 145 mg (0.35 mmol, 70%). NMR data for anion **1c**: $^1H\{^{11}B\}$ NMR ($(CD_3)_2CO$, δ ppm): 2.14 (sextet, 1H, $^3J(^1H,^1H)$ = 3.3 Hz, $CH_{cluster}$), 1.71 (s, 5H, BH7−11), 1.61 (s, 5H, BH2−6), 0.92 (t, 9H, $^3J(^1H,^1H)$ = 7.9 Hz, $^1J(^{13}C,^1H)$ = 125.8 Hz, CH_3), 0.45 (q, 6H, $^3J(^1H,^1H)$ = 7.9 Hz, $^1J(^{13}C,^1H)$ = 118.4 Hz, $SiCH_2$). $^{13}C\{^1H\}$ NMR ($(CD_3)_2CO$, δ ppm): 124.59 (q, 1C, $^1J(^{13}C,^{11}B)$ = 98.9 Hz, B12−$^{13}C{\equiv}$C), 94.01 (q, 1C, $^2J(^{13}C,^{11}B)$ = 15.7 Hz, B12−C$\equiv^{13}$C), 48.75 (s, 1C, $C_{cluster}$), 7.82 (s, 3C, CH_3), 5.44 (s, 3C, $^1J(^{29}Si,^{13}C)$ = 55.8 Hz, $^1J(^{13}C,^{13}C)$ = 31.6 Hz, $Si^{13}CH_2$). ^{11}B NMR ($(CD_3)_2CO$, δ ppm): −7.4 (s, 1B, B12), −12.2 (d, 5B, $^1J(^{11}B,^1H)$ = 139, B7−11), −16.7 (d, 5B, $^1J(^{11}B,^1H)$ = 151 Hz, B2−6). IR/Raman (cm^{-1}): 2114 cm^{-1} (ν(C≡C)). MALDI-MS *m*/*z* (isotopic abundance > 60) calcd for **1c** ([$C_9H_{26}B_{11}Si$]$^-$): 280 (75%), 281 (100%), 282 (80%). Found: 280 (80%), 281 (100%), 282 (93%). Anal. Calcd for $C_{17}H_{46}B_{11}NSi$: C, 49.61; H, 11.27; N, 3.40. Found: C, 48.65; H, 11.27; N, 3.36.

Cs[12-iPr$_3$SiC≡C-*closo*-1-$CB_{11}H_{11}$] (Cs1d). Cs[12-I-*closo*-1-$CB_{11}H_{11}$] (1 g, 2.49 mmol), [$PdCl_2(PPh_3)_2$] (50 mg, 0.075 mmol), and iPr$_3$SiC≡CMgBr (6.5 mL, 5 mmol) were used. Yield: 700 mg (1.54 mmol, 61%). $^1H\{^{11}B\}$ NMR ($(CD_3)_2CO$, δ ppm): 1.59 (s, 10H, BH2−11), 2.26 (s, 1H, $CH_{cluster}$), 1.02 (d, 18H, $^1J(^{13}C,^1H)$ = 125 Hz, $^3J(^1H,^1H)$ = 6.6 Hz, CH_3), 0.95 (heptet, 3H, $^3J(^1H,^1H)$ = 6.6 Hz, SiCH). $^{13}C\{^1H\}$ NMR ($(CD_3)_2CO$, δ ppm): 125.82 (q, 1C, $^1J(^{13}C,^{11}B)$ = 98 Hz, B12−$^{13}C{\equiv}$C), 92.95 (q, 1C, $^2J(^{13}C,^{11}B)$ = 15 Hz, B12−C$\equiv^{13}$C), 48.70 (s, 1C, $C_{cluster}$), 19.18 (s, 6C, $^2J(^{13}C,^{13}C)$ = 31 Hz, CH_3), 12.32 (s, 3C, $^1J(^{29}Si,^{13}C)$ = 56 Hz, $^2J(^{13}C,^{13}C)$ = 31 Hz, SiC). ^{11}B NMR ($(CD_3)_2CO$, δ ppm): −7.6 (s, 1B, B12), −12.3 (d, 5B, $^1J(^{11}B,^1H)$ = 139 Hz, B7−11), −16.7 (d, 5B, $^1J(^{11}B,^1H)$ = 152 Hz, B2−6). IR/Raman (cm^{-1}): 2116 cm^{-1} (ν(C≡C)). MALDI-MS *m*/*z* (isotopic abundance > 60) calcd for **1d** ([$C_{12}H_{32}B_{11}Si$]$^-$): 322 (67%), 323 (100%), 324 (70%). Found: 322 (74%), 323 (100%), 324 (79%). Anal. Calcd for $C_{12}H_{32}B_{11}CsSi$: C, 31.59; H, 7.07. Found: C, 31.76; H, 7.26.

Cs[12-nC$_4$H$_9$C≡C-*closo*-1-$CB_{11}H_{11}$] (Cs1e). Cs1e was prepared from Cs[12-I-*closo*-1-$CB_{11}H_{11}$] (500 mg, 1.25 mmol) and nC$_4$H$_9$C≡CMgBr (5 mL, 3.75 mmol) with [$PdCl_2(PPh_3)_2$] (25 mg, 0.035 mmol). Yield: 460 mg (1.41 mmol, 70%). $^1H\{^{11}B\}$ NMR ($(CD_3)_2CO$, δ ppm): 2.10 (sextet, 1H, $^3J(^1H,^1H)$ = 3.4 Hz, $CH_{cluster}$), 1.99 (tm, 2H, $^3J(^1H,^1H)$ = 6.9 Hz, C≡C−CH_2), 1.67 (s, 5H, BH7−11), 1.60 (s, 5H, BH2−6), 1.32 (m, 4H, CH_2CH_2), 0.83 (tm, 3H, $^3J(^1H,^1H)$ = 7.1 Hz, CH_3). $^{13}C\{^1H\}$ NMR ($(CD_3)_2CO$, δ ppm): 93.54 (q, 1C, $^2J(^{13}C,^{11}B)$ = 18.6 Hz, B12−C$\equiv^{13}$C), 91.42 (q, 1C, $^1J(^{13}C,^{11}B)$ = 104.2 Hz, B12−$^{13}C{\equiv}$C), 47.92 (s, 1C, $C_{cluster}$), 32.36 (s, 1C, CH_2), 22.51 (s, 1C, CH_2), 20.14 (s, 1C, CH_2), 13.90 (s, 1C, CH_3). ^{11}B NMR ($(CD_3)_2CO$, δ ppm): −6.7 (s, 1B, B12), −12.34 (d, 5B, $^1J(^{11}B,^1H)$ = 138 Hz B7−11), −16.9 (d, 5B, $^1J(^{11}B,^1H)$ = 151 Hz, B2−6). IR/Raman (cm^{-1}): 2188 cm^{-1} (ν(C≡C)). MALDI-MS *m*/*z* (isotopic abundance > 60) calcd for **1e** ([$C_7H_{20}B_{11}$]$^-$): 222 (75%), 223 (100%), 224 (80%). Found: 222 (81%), 223 (100%), 224 (88%). Anal. Calcd for $C_7H_{20}B_{11}Cs$: C, 23.61; H, 5.66. Found: C, 23.58; H, 5.51.

Cs[12-PhC≡C-*closo*-1-$CB_{11}H_{11}$] (Cs1f). Cs1f was synthesized from Cs[12-I-*closo*-1-$CB_{11}H_{11}$] (200 mg, 0.50 mmol) and PhC≡CMgBr (1.3 mL, 1 mmol) with [$PdCl_2(PPh_3)_2$] (10 mg, 0.015 mmol). Yield: 158 g (0.42 mmol, 84%). Spectroscopic data and results of elemental analysis have been published elsewhere.[22]

[Et_4N][12-(H_2C=(Me)CC≡C)-*closo*-1-$CB_{11}H_{11}$] ([Et_4N]1g). Cs-[12-I-*closo*-1-$CB_{11}H_{11}$] (500 mg, 1.25 mmol), [$PdCl_2(PPh_3)_2$] (75 mg, 0.110 mmol), and H_2C=(Me)CC≡CMgBr (7.6 mL, 3.8 mmol) were

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Table 5. Selected Crystal Data and Details of the Refinement of the Crystal Structures of 12-Ph_3P-*closo*-1-$CB_{11}H_{11}$ (2), $[Et_4N][$12-Ph-*closo*-1-$CB_{11}H_{11}]$ ($[Et_4N]$1h**), $[Et_4N][$12-(4-MeO-C_6H_4)-*closo*-1-$CB_{11}H_{11}]\cdot Me_2CO$ ($[Et_4N]$**1j**$\cdot Me_2CO$), and $[Et_4N][$12-($H_2C{=}(Me)CC{\equiv}C$)-*closo*-1-$CB_{11}H_{11}]$ ($[Et_4N]$**1g**)**

	2	$[Et_4N]$**1h**	$[Et_4N]$**1j**$\cdot Me_2CO$	$[Et_4N]$**1g**
empirical formula	$C_{19}H_{26}B_{11}P$	$C_{15}H_{36}B_{11}N$	$C_{19}H_{44}B_{11}NO_2$	$C_{14}H_{36}B_{11}N$
fw	404.28	349.36	437.46	337.35
T/K	290	290	290	290
cryst syst	triclinic	orthorhombic	orthorhombic	orthorhombic
space group	$P\bar{1}$	*Pbca*	*Cmca*	*Pbca*
a/Å	7.979(3)	10.2163(3)	16.739(3)	10.7180(7)
b/Å	10.106(4)	17.0365(6)	32.500(7)	16.8947(9)
c/Å	14.852(6)	26.2239(10)	10.328(2)	24.9893(14)
α/deg	85.88(3)			
β/deg	86.36(3)			
γ/deg	75.45(3)			
volume/Å^3	1154.9(8)	4564.3(3)	5618.6(19)	4525.0(5)
Z	2	8	8	8
D_{calcd}/Mg m^{-3}	1.163	1.017	1.034	0.990
μ/mm^{-1}	0.124	0.050	0.057	0.049
F(000)	420	1504	1888	1456
no. of collected reflns	15883	56490	23820	19119
no. of unique reflns, R(int)	4048, 0.070	3986, 0.065	2569, 0.063	3942, 0.045
no. of params/restraints	291/0	344/0	299/0	303/1
$R1$ ($I > 2\sigma(I)$)	0.055	0.058	0.073	0.050
$wR2$ (all)	0.130	0.110	0.146	0.094
GOF on F^2	1.008	1.036	1.915	1.063
largest diff. peak/hole/e Å^{-3}	0.311/−0.420	0.198/−0.179	0.377/−0.349	0.155/−0.172
CCDC no.	790764	851853	851854	851852

used. Yield: 274 mg (0.81 mmol, 65%). NMR data for anion **1g**. $^1H\{^{11}B\}$ NMR ($(CD_3)_2CO$, δ ppm): 4.91 (m, 2H, C=CH_2), 2.17 (sextet, 1H, $^3J(^1H,^1H)$ = 3.1 Hz, $CH_{cluster}$), 1.74 (s, 5H, BH7−11), 1.73 (pseudo triplet, 3H, $^4J(^1H,^1H) \approx$ 1.2 Hz, CH_3), 1.64 (s, 5H, BH2−6). $^{13}C\{^1H\}$ NMR ($(CD_3)_2CO$, δ ppm): 130.26 (s, 1C, ^{13}C=CH_2), 118.03 (s, 1C, CH_2), 102.35 (q, 1C, $^1J(^{13}C,^{11}B)$ = 103.3 Hz, B12−$^{13}C{\equiv}C$), 94.87 (q, 1C, $^2J(^{13}C,^{11}B)$ = 19.1 Hz, B12−C$\equiv{}^{13}$C), 48.80 (s, 1C, $CH_{cluster}$), 24.39 (s, 1C, CH_3). ^{11}B NMR ($(CD_3)_2CO$, δ ppm): −6.9 (s, 1B, B12), −12.3 (d, 5B, $^1J(^{11}B,^1H)$ = 138 Hz, B7−11), −16.7 (d, 5B, $^1J(^{11}B,^1H)$ = 151 Hz, B2−6). IR/Raman (cm^{-1}): 2170 cm^{-1} (ν(C≡C)), 1601 (ν(C=C)). MALDI-MS m/z (isotopic abundance > 60) calcd for **1g** ($[C_6H_{16}B_{11}]^-$): 206 (75%), 207 (100%), 208 (80%). Found: 206 (96%), 207 (100%), 208 (99%). Anal. Calcd for $C_{14}H_{36}B_{11}N$: C, 49.84; H, 10.75; N, 4.15. Found: C, 46.61; H, 10.38; N, 4.39.

$[Et_4N][$12-Ph-*closo*-1-$CB_{11}H_{11}]$ ($[Et_4N]$1h). $[Et_4N]$**1h** was prepared from Cs[12-I-*closo*-1-$CB_{11}H_{11}$] (100 mg, 0.25 mmol) and PhMgBr (0.8 mL, 0.8 mmol) with $[PdCl_2(PPh_3)_2]$ (5 mg, 0.007 mmol). Yield: 66 mg (0.19 mmol, 75%). NMR data for anion **1h**. $^1H\{^{11}B\}$ NMR ($(CD_3)_2CO$, δ ppm): 7.41−7.39 (m, 2H, Ph), 7.02−6.90 (m, 3H, Ph), 2.22 (sextet, 1H, $^3J(^1H,^1H)$ = 3.3 Hz, $CH_{cluster}$), 1.79 (s, 5H, BH7−11), 1.73 (s, 5H, BH2−6). $^{13}C\{^1H\}$ NMR ($(CD_3)_2CO$, δ ppm): 148.28 (q, 1C, $^1J(^{13}C,^{11}B)$ = 74.9 Hz, C_{ipso}), 133.65 (s, 2C, Ph), 126.82 (s, 2C, Ph), 125.20 (s, 1C, C_{para}), 47.10 (s, 1C, $C_{cluster}$). ^{11}B NMR ($(CD_3)_2CO$, δ ppm): 2.70 (s, 1B, B12), −12.51 (d, 5B, $^1J(^{11}B,^1H)$ = 136 Hz, B7−11), −16.6 (d, 5B, $^1J(^{11}B,^1H)$ = 150 Hz, B2−6). MALDI-MS m/z (isotopic abundance > 60) calcd for **1h** ($[C_7H_{16}B_{11}]^-$): 218 (75%), 219 (100%), 220 (80%). Found: 218 (89%), 219 (100%), 220 (94%). Anal. Calcd for $C_{15}H_{36}B_{11}N$: C, 51.57; H, 10.39; N, 4.01. Found: C, 48.83; H, 10.43; N, 4.01.

Cs[12-(4-Me_3Si−C_6H_4)-*closo*-1-$CB_{11}H_{11}$] (Cs1i). The starting materials were Cs[12-I-*closo*-1-$CB_{11}H_{11}$] (200 mg, 0.50 mmol), $[PdCl_2(PPh_3)_2]$ (10 mg, 0.015 mmol), and 4-Me_3Si−C_6H_4MgBr (1 mL, 1 mmol). Yield: 155 mg (0.36 mmol, 73%). $^1H\{^{11}B\}$ NMR ($(CD_3)_2CO$, δ ppm): 7.40−7.18 (m, 4H, Ph), 2.22 (sextet, 1H, $^3J(^1H,^1H)$ = 3.6 Hz, $CH_{cluster}$), 1.80 (s, 5H, B7−11), 1.73 (s, 5H, B2−6), 0.18 (s, 9H, $^1J(^{13}C,^1H)$ = 118.7 Hz, CH_3). $^{13}C\{^1H\}$ NMR ($(CD_3)_2CO$, δ ppm): 149.06 (q, $^1J(^{13}C,^{11}B) \approx$ 75 Hz, 1C, C_{ipso}), 135.18 (s, 1C, C_{para}), 133.27 (s, 2C, Ph), 131.90 (s, 2C, Ph), 47.18 (s, 1C, $C_{cluster}$), −0.85 (s, 3C, CH_3). ^{11}B NMR ($(CD_3)_2CO$, δ ppm): 2.5 (s, 1B, B12), −12.49 (d, 5B, $^1J(^{11}B,^1H)$ = 138 Hz, B7−11), −16.5 (d, 5B, $^1J(^{11}B,^1H)$ = 151 Hz, B2−6). MALDI-MS m/z (isotopic abundance > 60) calcd for **1i** ($[C_{10}H_{24}B_{11}Si]^-$): 290 (75%), 291 (100%), 292 (80%). Found: 290 (78%), 291 (100%), 292 (83%). Anal. Calcd for $C_{10}H_{24}B_{11}SiCs$: C, 28.31; H, 5.70. Found: C, 29.02; H, 5.73.

$[Et_4N][$12-(4-MeO−C_6H_4)-*closo*-1-$CB_{11}H_{11}]$ ($[Et_4N]$1j). Cs[12-I-*closo*-1-$CB_{11}H_{11}$] (200 mg, 0.50 mmol), $[PdCl_2(PPh_3)_2]$ (10 mg, 0.015 mmol), 4-MeO-C_6H_4MgBr (1 mL, 1 mmol) were used. Yield: 141 mg (0.37 mmol, 74%). NMR data for anion **1j**. $^1H\{^{11}B\}$ NMR ($(CD_3)_2CO$, δ ppm): 7.30−7.26 (m, 2H, Ph), 6.63−6.59 (m, 2H, Ph), 3.68 (s, 3H, $^1J(^{13}C,^1H)$ = 143.0 Hz, OCH_3), 2.21 (sextet, 1H, $^3J(^1H,^1H)$ = 3.2 Hz, $CH_{cluster}$), 1.76 (s, 5H, BH7−11), 1.72 (s, 5H, BH2−6). $^{13}C\{^1H\}$ NMR ($(CD_3)_2CO$, δ ppm): 158.51 (s, 1C, C_{para}), 139.67 (q, 1C, $^1J(^{13}C,^{11}B) \approx$ 72 Hz, C_{ipso}), 134.43 (s, 2C, Ph), 112.59 (s, 2C, Ph), 55.08 (s, 1C, OCH_3), 46.65 (s, 1C, $C_{cluster}$). ^{11}B NMR ($(CD_3)_2CO$, δ ppm): 2.6 (s, 1B, B12), −12.5 (d, 5B, $^1J(^{11}B,^1H)$ = 136 Hz, B7−11), −16.6 (d, 5B, $^1J(^{11}B,^1H)$ = 150 Hz, B2−6). MALDI-MS m/z (isotopic abundance > 60) calcd for **1j** ($[C_8H_{18}B_{11}O]^-$): 248 (75%), 249 (100%), 250 (80%). Found: 248 (84%), 249 (100%), 250 (95%). Anal. Calcd for $C_{16}H_{38}B_{11}NO$: C, 50.65; H, 10.10; N, 3.69. Found: C, 50.45; H, 10.34; N, 3.68.

$[Et_4N][$12-(4-HC≡C−C_6H_4)-*closo*-1-$CB_{11}H_{11}]$ ($[Et_4N]$1k). Cs[12-I-*closo*-1-$CB_{11}H_{11}$] (1 g, 2.5 mmol), $[PdCl_2(PPh_3)_2]$ (50 mg, 0.075 mmol), and 4-$Me_3SiC{\equiv}C-C_6H_4MgBr$ (5 mL, 5 mmol) were used. The trimethylsilyl group was removed under basic aqueous conditions during workup. Yield: 837 mg (2.24 mmol, 90%). NMR data for anion **1k**. $^1H\{^{11}B\}$ NMR (CD_3CN, δ ppm): 7.40−7.35 (m, 2H, Ph), 7.15−7.08 (m, 2H, Ph), 3.42 (s, 1H, C≡CH), 2.24 (sextet, 1H, $^3J(^1H,^1H) \approx$ 3.5 Hz, $CH_{cluster}$), 1.78 (s, 5H, BH7−11), 1.74 (s, 5H, BH2−6). $^{13}C\{^1H\}$ NMR (CD_3CN, δ ppm): 150.10 (q, 1C, $^1J(^{13}C,^{11}B)$ = 73.4 Hz, C_{ipso}), 133.56 (s, 2C, Ph), 130.42 (s, 2C, Ph), 118.92 (s, 1C, C_{para}), 85.48 (s, 1C, Ph−$^{13}C{\equiv}CH$), 77.37 (d, 1C, Ph−C≡^{13}CH),

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47.52 (s, 1C, $C_{cluster}$). ^{11}B NMR (CD_3CN, δ ppm): 2.0 (s, 1B, B12), −12.5 (d, 5B, $^1J(^{11}B,^1H)$ = 137 Hz, B7−11), −16.5 (d, 5B, $^1J(^{11}B,^1H)$ = 150 Hz, B2−6). IR/Raman (cm^{-1}): 2105 cm^{-1} (ν(C≡C)). MALDI-MS m/z (isotopic abundance > 60) calcd for **1k** ($[C_9H_{16}B_{11}]^-$): 242 (75%), 243 (100%), 244 (80%). Found: 242 (62%), 243 (100%), 244 (70%). Anal. Calcd for $C_9H_{16}B_{11}Cs$: C, 28.75; H, 4.29. Found: C, 28.85; H, 4.05.

[Et$_4$N][12-Et-*closo*-1-CB$_{11}$H$_{11}$] ([Et$_4$N]1l). The starting materials were Cs[12-I-*closo*-1-$CB_{11}H_{11}$] (200 mg, 0.50 mmol), [$PdCl_2(PPh_3)_2$] (30 mg, 0.045 mmol), and EtMgBr (1 mL, 1 mmol). Yield: 126 mg (0.42 mmol, 84%). NMR data for anion **1l**. $^1H\{^{11}B\}$ NMR ($(CD_3)_2CO$, δ ppm): 2.07 (s, 1H, $CH_{cluster}$), 1.59 (s, 5H, BH7−11), 1.53 (s, 5H, BH2−6), 0.75 (t, 3H, $^3J(^1H,^1H)$ = 7.8 Hz, $^1J(^{13}C,^1H)$ = 124.0 Hz, CH_3), 0.49 (q, 2H, $^3J(^1H,^1H)$ = 7.8 Hz, $^1J(^{13}C,^1H)$ = 117.4 Hz, CH_2). $^{13}C\{^1H\}$ NMR ($(CD_3)_2CO$, δ ppm): 45.28 (d, 1C, $C_{cluster}$), 14.66 (s, 1C, CH_3), 12.95 (q, 1C, $^1J(^{13}C,^{11}B)$ = 62.0 Hz, BCH_2). ^{11}B NMR ($(CD_3)_2CO$, δ ppm): 4.0 (s, 1B, B12), −12.71 (d, 5B, $^1J(^{11}B,^1H)$ = 135 Hz, B2−6), −16.9 (d, 5B, $^1J(^{11}B,^1H)$ = 149 Hz, B7−11). MALDI-MS m/z (isotopic abundance > 60) calcd for **1l** ($[C_3H_{16}B_{11}]^-$): 170 (75%), 171 (100%), 172 (80%). Found: 170 (88%), 171 (100%), 172 (92%). Anal. Calcd for $C_{11}H_{36}B_{11}N$: C, 43.85; H, 12.04; N, 4.65. Found: C, 43.43; H, 12.30; N, 4.61.

[Et$_4$N][12-Me$_3$SiCH$_2$-*closo*-1-CB$_{11}$H$_{11}$] ([Et$_4$N]1m). Cs[12-I-*closo*-1-$CB_{11}H_{11}$] (200 mg, 0.50 mmol), [$PdCl_2(PPh_3)_2$] (10 mg, 0.015 mmol), and $Me_3SiC{\equiv}CMgBr$ (1.3 mL, 1 mmol) were used. Yield: 144 mg (0.40 mmol, 80%). NMR data for anion **1m**. $^1H\{^{11}B\}$ NMR ($(CD_3)_2CO$, δ ppm): 2.02 (s, 1H, $CH_{cluster}$), 1.58 (s, 10H, BH2−11), 0.02 (s, 2H, CH_2), −0.23 (s, 9H, CH_3). $^{13}C\{^1H\}$ NMR ($(CD_3)_2CO$, δ ppm): 44.88 (s, 1C, $C_{cluster}$), 8.63 (q, 1C, $^1J(^{13}C,^{11}B)$ = 58.3 Hz, CH_2), 1.05 (s, 3C, $^1J(^{29}Si,^{13}C)$ = 49.0 Hz, CH_3). ^{11}B NMR ($(CD_3)_2CO$, δ ppm): 2.3 (s, 1B, B12), −12.0 (d, 5B, $^1J(^{11}B,^1H)$ = 134 Hz, B2−6), −16.82 (d, 5B, $^1J(^{11}B,^1H)$ = 149 Hz, B7−11). MALDI-MS m/z (isotopic abundance > 60) calcd for **1m** ($[C_5H_{22}B_{11}Si]^-$): 228 (71%), 229 (100%), 230 (89%). Found: 228 (64%), 229 (100%), 230 (90%). Anal. Calcd for $C_{13}H_{42}B_{11}NSi$: C, 43.43; H, 11.78; N, 3.89. Found: C, 42.93; H, 12.26; N, 3.77.

[Et$_4$N][1-Me-12-HC≡C-*closo*-1-CB$_{11}$H$_{10}$] ([Et$_4$N]3a). Prepared from Cs[1-Me-12-I-*closo*-1-$CB_{11}H_{10}$] (400 g, 0.96 mmol) and $Me_3SiC{\equiv}CMgBr$ (4 mL, 3 mmol) with [$PdCl_2(PPh_3)_2$] (35 mg, 0.050 mmol). The trimethylsilyl group was removed under basic aqueous conditions during workup. Yield: 240 mg (0.75 mmol, 80%). NMR data for anion **3a**: $^1H\{^{11}B\}$ NMR ($(CD_3)_2CO$, δ ppm): 1.89 (s, 1H, C≡CH), 1.71 (s, 10H, BH2−11), 1.48 (s, 3H, CH_3). $^{13}C\{^1H\}$ NMR ($(CD_3)_2CO$, δ ppm): 96.63 (q, 1C, $^1J(^{13}C,^{11}B)$ = 96.0 Hz, B12−$^{13}C{\equiv}$C), 81.85 (q, 1C, $^2J(^{13}C,^{11}B)$ = 16.8 Hz, B12−C≡^{13}C), 62.72 (s, 1C, $C_{cluster}$), 27.27 (s, 1C, CH_3). ^{11}B NMR ($(CD_3)_2CO$, δ ppm): −11.3 (s, 1B, B12), −11.9 (d, 5B, $^1J(^{11}B,^1H)$ = 147 Hz, B7−11), −13.1 (d, 5B, $^1J(^{11}B,^1H)$ = 152 Hz, B2−6). IR/Raman (cm^{-1}): 2066 cm^{-1} (ν(C≡C)). MALDI-MS m/z (isotopic abundance > 60) calcd for **3a** ($[C_4H_{14}B_{11}]^-$): 180 (75%), 181 (100%), 182 (85%). Found: 180 (77%), 181 (100%), 182 (84%). Anal. Calcd for $C_{12}H_{34}B_{11}N$: C, 46.29; H, 11.01; N, 4.50. Found: C, 45.72; H, 11.22; N, 3.69.

[Et$_4$N][1-Ph-12-Me$_3$SiC≡C-*closo*-1-CB$_{11}$H$_{10}$] ([Et$_4$N]4a). [Et_4N] **4a** was synthesized from Cs[1-Ph-12-I-*closo*-1-$CB_{11}H_{11}$] (220 mg, 0.46 mmol) and $Me_3SiC{\equiv}CMgBr$ (1.84 mL, 1.38 mmol) with [$PdCl_2(PPh_3)_2$] (16 mg, 0.023 mmol). Yield: 120 mg (0.27 mmol, 58%). Spectroscopic data and results of elemental analysis have been reported earlier.[22]

[Et$_4$N][7-HC≡C-12-F-*closo*-1-CB$_{11}$H$_{10}$] ([Et$_4$N]5a). [Et_4N]**5a** was prepared from Cs[12-I-*closo*-1-$CB_{11}H_{11}$] (420 mg, 0.68 mmol) and $Me_3SiC{\equiv}CMgBr$ (1.3 mL, 1 mmol) with [$PdCl_2(PPh_3)_2$] (10 mg, 0.015 mmol). The trimethylsilyl group was removed under basic aqueous conditions during workup. Yield: 110 mg (0.35 mmol, 73%). NMR data for anion **5a**. $^1H\{^{11}B\}$ NMR ($(CD_3)_2CO$, δ ppm): 2.04 (s, 1H, $CH_{cluster}$), 2.02 (s, 1H, B7−C≡CH), 1.78 (s, 2H, BH8 + 11), 1.67 (s, 4H, BH2 + 3+9 + 10), 1.44 (s, 3H, BH4−5). $^{13}C\{^1H\}$ NMR ($(CD_3)_2CO$, δ ppm): 93.12 (q, 1C, $^1J(^{13}C,^{11}B)$ = 101.9 Hz, B7−^{13}C≡CH), 82.19 (q, 1C, $^2J(^{13}C,^{11}B)$ = 19.1 Hz, B7−C≡^{13}CH), 36.28 (s, 1C, $C_{cluster}$). ^{11}B NMR ($(CD_3)_2CO$, δ ppm): 13.4 (s, 1B, B12), −13.8 (d, 2B, $^1J(^{11}B,^1H)$ = 131 Hz, B8 + 11), ∼−15 (s, 1B, B7), −15.2 (d, 2B, $^1J(^{11}B,^1H)$ = 162 Hz, B9 + 10), −18.4 (d, 2B, $^1J(^{11}B,^1H)$ = 159 Hz, B2 + 3), −20.1 (d, 3B, $^1J(^{11}B,^1H)$ = 157 Hz, B4−6). ^{19}F NMR ($(CD_3)_2CO$, δ ppm): −191.44 (q, $^1J(^{19}F,^{11}B)$ = 59 Hz). IR/Raman (cm^{-1}): 2066 cm^{-1} (ν(C≡C)). MALDI-MS m/z (isotopic abundance > 60) calcd for **7a** ($[C_3H_{11}B_{11}F]^-$): 184 (74%), 185 (100%), 186 (80%). Found: 184 (68%), 185 (100%), 186 (72%). Anal. Calcd for $C_{11}H_{31}B_{11}NF$: C, 41.91; H, 9.91; N, 4.44. Found: C, 41.211; H, 9.88; N, 4.45.

[Et$_4$N][7-HC≡C-12-Cl-*closo*-1-CB$_{11}$H$_{10}$] ([Et$_4$N]6a). Cs[12-I-*closo*-1-$CB_{11}H_{11}$] (200 mg, 0.46 mmol), [$PdCl_2(PPh_3)_2$] (10 mg, 0.015 mmol), and $Me_3SiC{\equiv}CMgBr$ (1.3 mL, 1 mmol) were used. The trimethylsilyl group was removed under basic aqueous conditions during workup. Yield: 270 mg (0.81 mmol, 70%). NMR data for anion **6a**. $^1H\{^{11}B\}$ NMR ($(CD_3)_2CO$, δ ppm): 2.18 (sextet, 1H, $^1J(^1H,^1H)$ = 3.6 Hz, $CH_{cluster}$), 2.01 (s, 1H, B7−C≡CH), 1.87 (s, 2H, BH8 + 11), 1.80 (s, 4H, BH2 + 3+9 + 10), 1.57 (s, 3H, BH4 + 6), 1.53 (s, 1H, BH5). $^{13}C\{^1H\}$ NMR ($(CD_3)_2CO$, δ ppm): 93.00 (q, 1C, $^1J(^{13}C,^{11}B)$ = 105.1 Hz, B7−^{13}C≡CH), 82.28 (q, 1C, $^2J(^{13}C,^{11}B)$ = 19.3 Hz, B7−C≡^{13}CH), 42.55 (s, 1C, $C_{cluster}$). ^{11}B NMR ($(CD_3)_2CO$, δ ppm): 4.0 (s, 1B, B12), −11.7 (d, 2B, $^1J(^{11}B,^1H)$ = 148 Hz, B8 + 11), −12.7 (d, 2B, B9 + 10), ∼−12.7 (s, 1B, B7), −16.7 (d, 2B, $^1J(^{11}B,^1H)$ = 160 Hz, B2 + 3), ∼−17 (d, $^1J(^{11}B,^1H)$ = overlapped, 1B, B5), −18.1 (d, 2B, $^1J(^{11}B,^1H)$ = 145 Hz, B4−6). IR/Raman (cm^{-1}): 2065 cm^{-1} (ν(C≡C)). MALDI-MS m/z (isotopic abundance > 60) calcd for **6a** ($[C_3H_{11}B_{11}Cl]^-$): 200 (75%), 201 (100%), 202 (80%). Found: 200 (76%), 201 (100%), 202 (86%). Anal. Calcd for $C_{11}H_{31}B_{11}ClN$: C, 39.83; H, 9.42; N, 4.22. Found: C, 40.44; H, 9.99; N, 3.69.

[Et$_4$N][7-(4-HC≡C−C$_6$H$_4$)-12-Cl-*closo*-1-CB$_{11}$H$_{10}$] ([Et$_4$N]6b). Cs[12-I-*closo*-1-$CB_{11}H_{11}$] (200 mg, 0.46 mmol), [$PdCl_2(PPh_3)_2$] (10 mg, 0.015 mmol), and 4-$Me_3SiC{\equiv}C{-}C_6H_4MgBr$ (0.7 mL, 0.7 mmol) were used as starting materials. The trimethylsilyl group was removed under basic aqueous conditions during workup. Yield: 130 mg (0.32 mmol, 70%). NMR data for anion **6b**. $^1H\{^{11}B\}$ NMR ($(CD_3)_2CO$, δ ppm): 7.65−7.55 (m, 2H, Ph), 7.30−7.20 (m, 2H, Ph), 3.46 (s, 1H, Ph−C≡CH), 2.31 (sextet, 1H, $^3J(^1H,^1H)$ = 3.4 Hz, $CH_{cluster}$), 2.00 (s, 2B, BH9 + 10), 1.91 (s, 2B, BH8 + 11), 1.85 (s, 2B, BH2 + 3), 1.67 (s, 2B, BH4 + 6), 1.62 (s, 1B, BH5). $^{13}C\{^1H\}$ NMR ($(CD_3)_2CO$, δ ppm): 145.76 (q, 1C, $^1J(^{13}C,^{11}B)$ = 73.0 Hz, C_{ipso}), 134.82 (s, 2C, Ph), 130.64 (s, 2C, Ph), 119.75 (s, 1C, C_{para}), 85.33 (s, 1C, Ph−^{13}C≡CH), 77.76 (s, 1C, Ph−C≡^{13}CH), 43.83 (s, 1C, $C_{cluster}$). ^{11}B NMR ($(CD_3)_2CO$, δ ppm): δ = 4.1 (s, 1B, B12), −4.4 (s, 1B, B7), −12.4 (d, 4B, $^1J(^{11}B,^1H)$ = 138 Hz, B8−11), −16.9 (d, 2B, $^1J(^{11}B,^1H)$ = 157, B2 + 3), −18.2 (d, 2B, $^1J(^{11}B,^1H)$ = 133, B4 + 6), −19.0 (d, 1B, $^1J(^{11}B,^1H)$ = 154 Hz, B5). IR/Raman (cm^{-1}): 2104 cm^{-1} (ν(C≡C)). MALDI-MS m/z (isotopic abundance > 60) calcd for **6b** ($[C_9H_{15}B_{11}Cl]^-$): 276 (75%), 277 (100%), 278 (80%). Found: 276 (74%), 277 (100%), 278 (93%), 279 (75%). Anal. Calcd for $C_{17}H_{35}NB_{11}Cl$: C, 50.07; H, 8.65; N, 3.43. Found: C, 44.95; H, 8.65; N, 3.51.

[Et$_4$N][7-HC≡C-12-Br-*closo*-1-CB$_{11}$H$_{10}$] ([Et$_4$N]7a). Cs[12-I-*closo*-1-$CB_{11}H_{11}$] (50 mg, 0.1 mmol), [$PdCl_2(PPh_3)_2$] (3 mg, 0.004 mmol), and $Me_3SiC{\equiv}CMgBr$ (0.5 mL, 0.38 mmol) were used. The trimethylsilyl group was removed under basic aqueous conditions during workup. Yield: 25 mg (0.07 mmol, 66%). NMR data for anion **7a**. $^1H\{^{11}B\}$ NMR ($(CD_3)_2CO$, δ ppm): 2.34 (sextet, 1H, $^3J(^1H,^1H)$ = 3.4 Hz, $CH_{cluster}$), 2.02 (s, 1H, C≡CH), 1.94 (s, 2H, BH8 + 11), 1.89 (s, 2H, BH9 + 10), 1.85 (s, 2H, BH4 + 6), 1.68 (s, 1B, BH5), 1.62 (s, 2H, BH2 + 3). $^{13}C\{^1H\}$ NMR ($(CD_3)_2CO$, δ ppm): 93.45 (q, 1C, $^1J(^{13}C,^{11}B)$ = 105.4 Hz, B7−^{13}C≡CH), 82.13 (q, 1C, 2$J(^{13}C,^{11}B)$ = 19.3 Hz, B7−C≡^{13}CH), 44.59 (d, 1C, $C_{cluster}$). ^{11}B NMR ($(CD_3)_2CO$, δ ppm): −2.5 (s, 1B, B12), −11.3 (d, 2B, $^1J(^{11}B,^1H)$ = 141 Hz, B8 + 11), −12.7 (d, 3B, $^1J(^{11}B,^1H)$ ≈ 142 Hz, B9 + 10), ∼−12.7 (s, 1B, B7), −16.3 (d, 2B, $^1J(^{11}B,^1H)$ = 156 Hz, B2 + 3), ∼−17.0 (d, 1B, $^1J(^{11}B,^1H)$ ≈ 145 Hz, B5), −17.7 (d, 2B, $^1J(^{11}B,^1H)$ = 150 Hz, B4 + 6). IR/Raman (cm^{-1}): 2065 cm^{-1} (ν(C≡C)). MALDI-MS m/z (isotopic abundance > 60) calcd for **7a** ($[C_3H_{11}B_{11}Br]^-$): 244 (74%), 245 (100%), 246 (80%), 247 (97%), 248 (78%). Found: 243 (66%), 244 (88%), 245 (100%), 246 (92%), 247 (78%), 248 (62%). Anal. Calcd for $C_{11}H_{31}B_{11}BrN$: C, 35.12; H, 8.31; N, 3.72. Found: C, 33.09; H, 8.31; N, 3.74.

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[Et$_4$N][7,12-(HC≡C)$_2$-*closo*-1-CB$_{11}$H$_{10}$] ([Et$_4$N]8a). For preparation of the dialkynyl-functionalized anion a slightly modified synthesis was applied. Me$_3$SiC≡CMgBr (2.5 mL, 1.9 mmol) and [PdCl$_2$(PPh$_3$)$_2$] (16 mg, 0.023 mmol) were added in two equal portions to Cs**8** (200 mg, 0.38 mmol). The first one was added at the beginning of the reaction and the second after 5 h. The reaction was complete after microwave irradiation for further 4 h. The trimethylsilyl groups were removed under basic aqueous conditions during workup. Yield: 77 mg (0.24 mmol, 63%). Spectroscopic data and results of elemental analysis have been reported earlier.[33]

Preparation of [Et$_4$N][12-(CH$_2$=CHCH$_2$)-*closo*-1-CB$_{11}$H$_{11}$]/[Et$_4$N][12-(*trans*-CH$_3$CH=CH)-*closo*-1-CB$_{11}$H$_{11}$] ([Et$_4$N]1n/[Et$_4$N]1o): Method A (Table 2, entry 12). Cs**1** (200 mg, 0.50 mmol), [PdCl$_2$(PPh$_3$)$_2$] (28 mg, 0.040 mmol), and H$_2$C=CHCH$_2$MgBr (3.5 mL, 3.5 mmol) were used in a slightly modified general procedure. Catalyst and Grignard reagent were added in two portions: the first one of [PdCl$_2$(PPh$_3$)$_2$] (10 mg, 0.015 mmol) and H$_2$C=CHCH$_2$MgBr (1.0 mL, 1.0 mmol) at the start of the synthesis and the second of [PdCl$_2$(PPh$_3$)$_2$] (15 mg, 0.020 mmol) and H$_2$C=CHCH$_2$MgBr (2.5 mL, 2.5 mmol) after 24 h. The reaction was complete after further 6 h. According to ^{11}B{^{1}H} NMR spectra the mixture contains the allyl derivative [12-(CH$_2$=CHCH$_2$)-*closo*-1-CB$_{11}$H$_{11}$]$^-$ (**1n**) and approximately 12% of **2**. The black reaction mixture was poured into 50 mL of distilled water. The mixture was stirred at 40 °C for 1 h, and then THF was removed at a rotary evaporator. The clear aqueous phase was separated by filtration from the black residue. For a further extraction, the black residue was dissolved in 20 mL of dichloromethane and 30 mL of distilled water were added. Dichloromethane was removed in a rotary evaporator, and the aqueous phase was filtered. Product was precipitated as [Et$_4$N]$^+$ salt from the combined aqueous solutions by addition of [Et$_4$N]Br (500 mg, 2.4 mmol) dissolved in water (10 mL). Yield 120 mg (77%) of [Et$_4$N][12-(*trans*-CH$_3$CH=CH)-*closo*-1-CB$_{11}$H$_{11}$] ([Et$_4$N]**1o**, 94%) and [Et$_4$N][12-(CH$_2$=CHCH$_2$)-*closo*-1-CB$_{11}$H$_{11}$] ([Et$_4$N]**1n**, 6%). Spectroscopic data of the anion **1n**. ^{1}H{^{11}B} NMR ((CD$_3$)$_2$CO, δ ppm): 5.77 (ddt, 1H, $^3J(^1H,^1H)_{trans}$ = 17.0 Hz, $^3J(^1H,^1H)_{cis}$ = 9.9 Hz, $^3J(^1H,^1H)$ = 7.7 Hz, B12−CH$_2$−C^{1}H=CH$_2$), 4.50 (dm, 1H, $^3J(^1H,^1H)_{trans}$ = 17.0 Hz, B12−CH$_2$−CH=C(H^{1}H$_{trans}$)), 4.44 (dm, 1H, $^3J(^1H,^1H)_{cis}$ = 9.9 Hz, B12−CH$_2$−CH=C(H^{1}H$_{cis}$)), 2.08 (sextet, 1H, $^3J(^1H,^1H)$ = 3.1 Hz, CH$_{cluster}$), 1.61 (s, 5H, BH), 1.56 (s, 5H, BH), 1.44 (m, 2H, B12−CH$_2$). ^{13}C{^{1}H} NMR ((CD$_3$)$_2$CO, δ ppm): 145.16 (s, 1C, B12−CH$_2$−^{13}CH=CH$_2$), 108.36 (s, 1C, B12−CH$_2$−CH=^{13}CH$_2$), 45.88 (s, 1C, C$_{cluster}$), 26.16 (q, 1C, $^1J(^{13}C,^{11}B)$ = 59.2 Hz, B12−CH$_2$−CH=CH$_2$). ^{11}B NMR ((CD$_3$)$_2$CO, δ ppm): 2.3 (s, 1B, B12), −12.5 (d, 5B, $^1J(^{11}B,^1H)$ = 135 Hz, B7−11), −16.6 (d, 5B, $^1J(^{11}B,^1H)$ = 150 Hz, B2−6). IR/Raman (cm^{-1}): 1628 cm^{-1} (ν(C=C)). Spectroscopic data of the anion **1o**. ^{1}H{^{11}B} NMR ((CD$_3$)$_2$CO, δ ppm): 5.48 (d, 1H, $^3J(^1H,^1H)$ = 16.9 Hz, B12−C^{1}H=CH−CH$_3$), 5.40 (dq, 1H, $^3J(^1H,^1H)$ = 16.9 Hz, $^3J(^1H,^1H)$ = 5.6 Hz, B12−CH=C^{1}H−CH$_3$), 1.51 (d, 3H, $^3J(^1H,^1H)$ = 5.6 Hz, CH$_3$), 1.60 (s, 10H, BH2−11), 2.09 (s, 1H, CH$_{cluster}$). ^{13}C{^{1}H} NMR ((CD$_3$)$_2$CO, δ ppm): 138.96 (q, 1C, $^1J(^{13}C,^{11}B)$ = 75.5 Hz, B12−^{13}CH=CH−CH$_3$), 129.37 (s, 1C, B12−CH=^{13}CH−CH$_3$), 46.22 (s, 1C, C$_{cluster}$), 21.45 (s, 1C, CH$_3$). ^{11}B NMR ((CD$_3$)$_2$CO, δ ppm): 0.9 (s, 1B, B12), −12.7 (d, 5B, $^1J(^{11}B,^1H)$ = 134 Hz, B7−11), −16.8 (d, 5B, $^1J(^{11}B,^1H)$ = 149 Hz, B2−6). IR/Raman (cm^{-1}): 1634 cm^{-1} (ν(C=C)). Identical data for [Et$_4$N]**1o** and [Et$_4$N]**1n**. MALDI-MS m/z (isotopic abundance > 60) calcd for **1o** and **1n** ([C$_4$H$_{16}$B$_{11}$]$^-$): 182 (75%), 183 (100%), 184 (80%). Found: 182 (80%), 183 (100%), 184 (84%). Anal. Calcd for C$_{12}$H$_{36}$B$_{11}$N: C, 45.99; H, 11.58; N, 4.47. Found: C, 45.16; H, 11.51; N, 4.23.

Preparation of [Et$_4$N][12-(CH$_2$=CHCH$_2$)-*closo*-1-CB$_{11}$H$_{11}$]/[Et$_4$N][12-(*trans*-CH$_3$CH=CH)-*closo*-1-CB$_{11}$H$_{11}$] ([Et$_4$N]1n/[Et$_4$N]1o): Method B (Table 2, entry 13). Synthesis was performed similar to method A described for [Et$_4$N]**1n** and [Et$_4$N]**1o** starting with Cs**1** (200 mg, 0.50 mmol). However, the amount of [PdCl$_2$(PPh$_3$)$_2$] (42 mg, 0.060 mmol) and H$_2$C=CHCH$_2$MgBr (3.0 mL, 3.0 mmol) was slightly different and CuI (10 mg, 0.050 mmol) was added. The reagents were added in three equal portions: the first at the beginning of the reaction, the second after 50 min, and the third after further 50 min of microwave irradiation. Workup was performed analogously to the procedure described for method A, except for stirring in THF at 40 °C for 1 h that was omitted, and thus, only a minor amount of the allyl derivative **1n** was isomerized to the vinyl species **1o**. Yield 123 mg (79%) of [Et$_4$N][12-(CH$_2$=CHCH$_2$)-*closo*-1-CB$_{11}$H$_{11}$] ([Et$_4$N]**1n**, 84%) and [Et$_4$N][12-(*trans*-CH$_3$CH=CH)-*closo*-1-CB$_{11}$H$_{11}$] ([Et$_4$N]**1o**, 16%).

12-Ph$_3$P-*closo*-1-CB$_{11}$H$_{11}$ (2). Under an Ar atmosphere Cs[12-I-*closo*-CB$_{11}$H$_{11}$] (Cs**1**) (100 mg, 0.25 mmol), [Pd(PPh$_3$)$_4$] (16.8 mg, 0.0145 mmol), PPh$_3$ (130 mg, 0.5 mmol), and K$_2$CO$_3$ (35 mg, 0.25 mmol) were dissolved in dry THF (10 mL) in a glass finger (70 mL) equipped with a valve with a PTFE stem (Young, London) and fitted with a magnetic stirring bar. While stirring, the reaction mixture was heated to 66 °C for 4 h by microwave irradiation. The black reaction mixture was filtered, and all volatiles were removed under reduced pressure. The solid residue was dissolved in a small amount of chloroform, and pure **2** was precipitated by addition of hexane. Yield: 89 mg (0.22 mmol, 88%). ^{1}H{^{11}B} NMR (toluene-d_8, δ ppm): 7.53−7.44 (m, 6H, Ph), 7.03−6.98 (m, 3H, Ph), 6.94−6.88 (m, 6H, Ph), 2.67 (s, 1H, CH$_{cluster}$), 2.55 (s, 5H, BH7−11), 2.37 (d, 5H, $^3J(^{31}P,^1H)$ = 5.3 Hz, BH2−6). ^{13}C{^{1}H} NMR (toluene-d_8, δ ppm): 134.70 (d, 6C, $^2J(^{31}P,^{13}C)$ = 9.0 Hz, C$_{ortho}$), 132.52 (d, 3C, $^4J(^{31}P,^{13}C)$ = 2.8 Hz, C$_{para}$), 128.84 (d, 6C, $^3J(^{31}P,^{13}C)$ = 11.4 Hz, C$_{meta}$), 123.47 (d, 3C, $^1J(^{31}P,^{13}C)$ = 70.7 Hz, C$_{ipso}$), 58.78 (s, 1C, C$_{cluster}$). ^{11}B NMR (toluene-d_8, δ ppm): −9.6 (d, 1B, $^1J(^{31}P,^{11}B)$ = 147 Hz, B12), −12.2 (d, 5B, $^1J(^{11}B,^1H)$ = 144 Hz, B7−11), −14.1 (d, 5B, $^1J(^{11}B,^1H)$ = 160, B2−6). ^{31}P{^{11}B} NMR (toluene-d_8, δ ppm): 2.3 (q, $^1J(^{31}P,^{11}B)$ = 146.8 Hz). Anal. Calcd for C$_{19}$H$_{26}$B$_{11}$P: C, 56.44; H, 6.48. Found: C, 56.63; H, 6.42.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

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Notes

The authors declare no competing financial interest.

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