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Carba-*closo*-dodecaborates with One or Two Alkynyl Substituents Bonded to Boron

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Salts of the carba-*closo*-dodecaborate anion with one or two phenyl- or trimethylsilylalkynyl substituents were synthesized by Pd-catalyzed Kumada-type cross-coupling reactions of the corresponding iodinated clusters with alkynyl Grignard reagents. Selective monofunctionalization in the 7- and 12-position of the {*closo*-CB_{11}} cluster was achieved, resulting in salts of the anions: [1-R-12-R′C≡C-*closo*-$CB_{11}H_{10}]^-$ (R = H, Ph; R′ = Ph, Me_3Si (**1**−**4**)), [12-Hal-7-PhC≡C-*closo*-$CB_{11}H_{10}]^-$ (Hal = F (**5**), Cl (**6**), Br (**7**)), and [12-F-7-Me_3SiC≡C-*closo*-$CB_{11}H_{10}]^-$ (**8**). Furthermore, the disubstituted derivatives [7,12-$(RC≡C)_2$-*closo*-$CB_{11}H_{10}]^-$ (R = Ph (**9**), Me_3Si (**10**)) are described. All salts were characterized by multi-NMR, IR, and Raman spectroscopy as well as by mass spectrometry (MALDI). The crystal structures of Cs^+**1** and $[Et_4N]^+$**6** were determined by single-crystal X-ray diffraction. The spectroscopic and structural properties are compared to values derived from DFT calculations and to data of related boron species with alkynyl groups.

Introduction

In the past 20 years, the development of the chemistry of the carba-*closo*-dodecaborate anion[1,2] [*closo*-$CB_{11}H_{12}]^-$ was mostly stimulated by the increasing demand for new weakly coordinating anions[3] that were used to stabilize highly reactive cations like $[Rh(CO)_4]^+$,[4] $[Me_2Al]^+$,[5] and $[R_3Si]^+$ (R = alkyl, aryl).[6] However, selective mono- and multiple-substitution of the carba-*closo*-dodecaborate anion with functional groups is of growing interest because they may serve as building blocks for substances with applications in medicine (pharmaceuticals, contrast agents, and boron neutron capture therapy),[7] as ligands in transition metal chemistry (catalysis),[8] and for material sciences (ionic liquids, materials with nonlinear optical properties, coordination networks, and self-assembly).[9,10]

In a recent review, the derivatives of the [*closo*-$CB_{11}H_{12}]^-$ anion, that have been prepared so far, are summarized.[2] While substitution of the hydrogen atom of the CH vertex is straightforward in most cases, deprotonation followed by reactions with electrophiles; selective

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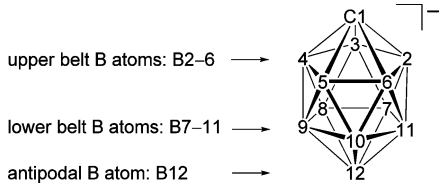
Scheme 1. Numbering of the Vertices of the Monocarba-*closo*-dodecaborate Anion



modification of the BH vertices is more complex because of side reactions and missing site selectivity (the numbering of the vertices of the $[closo\text{-}CB_{11}H_{12}]^-$ anion is shown in Scheme 1). Different strategies for substitution reactions of the $[closo\text{-}CB_{11}H_{12}]^-$ anion have been developed, and a few reactions resulting in boron vertices with substituents bonded via carbon to boron have been published. Direct transformation of a BH vertex into a BC vertex was achieved by treatment of carba-*closo*-dodecaborates with methyl- or ethyltriflate,[2,11,12] for example, M[1-H-*closo*-$CB_{11}(CH_3)_{11}$].[11] The application of this method is limited, because most functional groups are not tolerated. In addition, selective monoalkylation is hardly achievable and multiple-substitution occurs in general.[11,12] In a single contribution, peralkylation of all 11 BH vertices was also reported by treatment of $[closo\text{-}CB_{11}H_{12}]^-$ with alkylbromides at elevated temperatures.[13] A different approach to {*closo*-CB_{11}} clusters with boron−carbon bonds is the transition-metal-initiated conversion of BH into BC units,[14,15] as demonstrated for the preparation of [Rh(Ph_3P)$_2$-(norbornadiene)][(C_2H_5)$_5$-*closo*-$CB_{11}H_7$].[14] So far, these reactions are not selective, do not proceed with catalytic amounts of Rh(I), and are not compatible with many functional groups.[15] An alternative to the aforementioned methods is the conversion of BI vertices of {*closo*-CB_{11}} clusters into BC units by Pd-catalyzed cross-coupling reactions using Grignard reagents. Alkyl,[10] aryl,[10,16,17] and allyl[18,19] groups were transferred using Kumada-type cross-coupling conditions[20] and single as well as multiple substitutions were reported.[2,19]

Cross-coupling reactions, using Kumada,[21−26] Sonogashira,[27] Suzuki,[28] or related protocols,[26,29] are well-studied for partially iodinated 1,2-, 1,7-, and 1,12-dicarba-*closo*-dodecaboranes, with the first examples dating back to the early 1980s.[23] These reactions have emerged to standard synthetic tools, giving access to a variety of carboranes with BC vertices.[25,30] For iodinated derivatives of the isoelectronic $[closo\text{-}B_{12}H_{12}]^{2-}$ dianion, Kumada-type cross-coupling reactions have been reported as well.[31,32] For both classes of boron clusters, iodinated dicarba-*closo*-dodecaboranes and *closo*-dodecaborates, the attachment of alkynyl substituents through cross-coupling reactions was reported.[22,24,26,27,32] In contrast, for BI vertices in {*closo*-CB_{11}} clusters, these reactions are not known, and no report on derivatives of the $[closo\text{-}CB_{11}H_{12}]^-$ anion with B−C≡CR vertices has been published so far, to the best of our knowledge.[2]

In this contribution, Pd-catalyzed cross-coupling reactions of mono- and diiodinated carba-*closo*-dodecaborate anions with alkynyl Grignard reagents are reported. Selective introduction of the RC≡C group at different positions of the cluster was achieved: Selective monofunctionalization with an alkynyl substituent at the antipodal boron atom (B12) and at one boron atom of the lower belt (B7), as well as disubstitution at B7 and B12, was accomplished (Scheme 1). The novel alkynyl-substituted derivatives of the $[closo\text{-}CB_{11}H_{12}]^-$ anion were characterized by multi-NMR, IR, and Raman spectroscopy; elemental analysis; and mass spectrometry. The solid-state structures of the salts Cs[12-PhCC-*closo*-$CB_{11}H_{11}$] (Cs^+**1**) and [Et_4N][7-PhCC-12-Cl-*closo*-

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$CB_{11}H_{10}]$ ($[Et_4N]^+$**6**) determined by single-crystal X-ray diffraction are reported.

Experimental Section

General Procedures and Reagents. Apparatus. Reactions involving air-sensitive compounds were performed in 50, 100, or 250 mL round-bottom flasks equipped with valves with PTFE stems (Young, London) under argon using standard Schlenk line techniques. ^{1}H, ^{11}B, ^{13}C, and ^{19}F NMR spectra were recorded at room temperature either in $(CD_3)_2CO$ or in CD_3CN on a Bruker Avance DRX-500 spectrometer operating at 500.13, 125.76, 470.59, or 160.46 MHz for ^{1}H, ^{13}C, ^{19}F, or ^{11}B nuclei, respectively. NMR signals were referenced against TMS (^{1}H, ^{13}C), $CFCl_3$ (^{19}F), and $BF_3\cdot OEt_2$ in CD_3CN (^{11}B) as external standards. Infrared and Raman spectra were recorded at room temperature on an Excalibur FTS 3500 spectrometer (Digilab, Germany) with an apodized resolution of 2 cm^{-1} (IR) and 4 cm^{-1} (Raman), respectively. IR spectra were measured in the attenuated total reflection 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}. Matrix-assisted laser desorption/ionization (MALDI) mass spectra in the negative-ion mode were recorded on a Bruker Ultraflex TOF spectrometer. Elemental analyses (C, H, N) were performed with a Euro EA3000 instrument (HEKA-Tech, Germany). The values of the elemental analyses for some of the compounds are slightly beyond the commonly accepted differences from theory. These deviations are mainly attributed to the general problem in obtaining correct elemental analyses of boron-rich compounds.[33]

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) in an argon atmosphere. A solution of $Me_3SiCCMgBr$ in THF (0.75 mol L^{-1}) was prepared from trimethylsilylacetylene and EtMgBr (1 mol L^{-1} in THF) and kept in a 250 mL round-bottom flask with a valve with a PTFE stem (Young, London) at 4 °C. PhCCMgBr dissolved in THF (1.0 mol L^{-1}) was obtained from Sigma-Aldrich. Cs[12-I-*closo*-$CB_{11}H_{11}$],[10,34] Cs[7,12-I_2-*closo*-$CB_{11}H_{10}$],[34] and Cs[7,8,9,10,11,12-I-*closo*-$CB_{11}H_6$][35] were synthesized according to modified literature procedures. The monoiodinated carborates Cs[7-I-12-X-*closo*-$CB_{11}H_{10}$] (X = F, Cl, Br, I) were prepared as described elsewhere.[36] Cs[1-Ph-*closo*-$CB_{11}H_{11}$] was prepared from *nido*-$B_{10}H_{14}$ via $[Et_4N]$[6-Ph-*nido*-6-CB_9H_{11}].[37,38] Iodination resulting in Cs[1-Ph-12-I-*closo*-$CB_{11}H_{10}$] followed a known protocol.[16,19] Cesium carba-*closo*-dodecaborate was synthesized from $[Me_3NH]$[*nido*-$B_{11}H_{14}$][39] according to a literature procedure.[40] Decaborane(14) was obtained from Katchem spol. sro (Praha, Czech Republic) or synthesized from $Na[BH_4]$ and $BF_3\cdot OEt_2$.[39]

Single-Crystal X-Ray Diffraction. Colorless crystals of Cs[12-PhCC-*closo*-$CB_{11}H_{11}$] (Cs^+**1**) suitable for X-ray diffraction studies were grown from acetone by slow evaporation of the solvent. The slow uptake of diethyl ether into a solution of $[Et_4N]$[7-PhCC-12-Cl-*closo*-$CB_{11}H_{10}$] ($[Et_4N]^+$**6**) in acetone resulted in colorless crystals. A crystal of $[Et_4N]^+$**6** was investigated with an imaging plate diffraction system (IPDS, Stoe & Cie) at 123 K, and a crystal of Cs^+**1** was studied using a Stoe STADI CCD diffractometer at 293 K using Mo Kα radiation (λ = 0.71073 Å). Numerical absorption corrections[41] based on indexed crystal faces were applied to the data of Cs^+**1** after optimization of the crystal shape.[42] Both structures were solved by direct methods,[43] and refinement is based on full-matrix least-squares calculations on F^2.[44]

The structure of Cs^+**1** was solved in the noncentrosymmetric orthorhombic space group *Pna*2$_1$ (no. 33) with Z = 8 and two independent formula units in the unit cell. Attempted transformation of the structure into the centrosymmetric space group *Pnam* (nonstandard setting of *Pnma* (no. 62)) resulted in disordering of the aryl and carboranyl subunits of each [12-PhCC-*closo*-$CB_{11}H_{11}$]$^-$ anion (**1**). Both independent formula units are related by pseudosymmetry. Related crystal structures with the space group *Pna*2$_1$ and similar pseudosymmetry relations are well-known.[45] The Flack parameter[46] calculated for Cs^+**1** using the "hole-in-one" method implemented in SHELXL97 indicated twinning by inversion.[44] Therefore, the inversion twin matrix (−100, 0−10, 00−1) was introduced, and a batch scale factor (BASF) was refined (∼0.85). The refinement converged to slightly lower residuals and improved standard deviations.

$[Et_4N]^+$**6** crystallizes in the triclinic space group $P\bar{1}$ with Z = 2.

The positions of all hydrogen atoms in both crystal structures Cs^+**1** and $[Et_4N]^+$**6** were located via ΔF syntheses. All nonhydrogen atoms were refined anisotropically. Due to the pseudosymmetry in Cs^+**1**, it was necessary to use equal atomic displacement parameters for the respective atoms related by the pseudoinversion center. The hydrogen atoms were refined using idealized bond lengths as well as angles, and their isotropic displacement parameters were kept equal to 130% for the aromatic H atoms and for the hydrogen atoms bonded to boron and to 150% for the aliphatic H atoms of the respective parent carbon or boron atom.

Molecular structure diagrams were drawn with the program Diamond 3.1.[47] Experimental details and crystal data are collected in Table 1. CCDC-699230 (Cs^+**1**) and CCDC-699231 ($[Et_4N]^+$**6**) contain the supplementary crystallographic data for this publication. These data 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)[48] were carried out using Becke's three-parameter hybrid functional and the Lee−Yang−Parr correlation functional

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Table 1. Crystal Data and Structure Refinement Parameters for Cs[12-PhCC-*closo*-$CB_{11}H_{11}$] (Cs^+**1**) and [Et_4N][7-PhCC-12-Cl-*closo*-$CB_{11}H_{10}$] ([Et_4N]$^+$**6**)

compound	Cs^+**1**	[Et_4N]$^+$**6**
empirical formula	$C_9H_{16}B_{11}Cs$	$C_{17}H_{35}B_{11}ClN$
fw (g mol^{-1})	376.048	407.848
color	colorless	colorless
T (K)	293	123
cryst. syst.	orthorhombic	triclinic
space group	$Pna2_1$ (no.33)	$P\bar{1}$ (no.2)
a (Å)	13.737(3)	8.8249(7)
b (Å)	10.231(3)	11.9360(11)
c (Å)	23.435(4)	12.3526(10)
α (deg)		84.22(1)
β (deg)		77.99(1)
γ (deg)		72.26(1)
V (Å^3)	3293.7(13)	1211.2(2)
Z	8	2
ρ_{calcd} (Mg m^{-3})	1.517	1.118
μ (mm^{-1})	2.226	0.163
F(000) (e)	1440	432
θ range(deg)	4.25−25.00	2.31−25.00
R1 indicies [$I > 2\sigma(I)$][a]	5.03	4.08
wR2(all data) (%)[b]	13.43	7.23
GOF on F^2 [c]	1.065	1.059
larg. diff. peak/hole (e Å^{-3})	1.696/−1.140	0.231/−0.173

[a] $R1 = (\sum||F_o| - |F_c||)/\sum|F_o|$. [b] $wR2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{0.5}$. Weight scheme: $w = [\sigma^2F_o + (aP)^2 + bP]^{-1}$; $P = [\max(0,F_o^2) + 2F_c^2]/3$. Cs^+**1**: $a = 0.0721$, $b = 4.653$. [Et_4N]$^+$**6**: $a = 0.011$, $b = 0$. [c] GOF: $S = \sum w(F_o^2 - F_c^2)^2/(m - n)$; ($m$ = reflections, n = variables).

(B3LYP).[49] Geometries were optimized, and energies were calculated with the 6-311++G(d,p) basis set. Diffuse functions were incorporated because improved energies are obtained for anions.[50] For the calculations, no symmetry constraints were applied. All structures represent true minima with no imaginary frequency on the respective hypersurface. DFT-GIAO[51] NMR shielding constants $\sigma(^{11}B)$ and $\sigma(^{13}C)$ as well as spin−spin coupling constants[52] were calculated at the B3LYP/6-311++G(2d,p) level of theory using the geometries computed at the B3LYP/6-311++G(d,p) level of theory. The ^{11}B and ^{13}C NMR shielding constants were calibrated to the respective chemical shift scales, $\delta(^{11}B)$ and $\delta(^{13}C)$, using predictions on diborane(6) and Me_4Si with chemical shifts of −16.6 ppm for B_2H_6[53] and 0 ppm for Me_4Si.[54] All calculations were carried out using the Gaussian 03 program suite.[55]

Synthetic Reactions. [Et_4N][12-PhCC-*closo*-$CB_{11}H_{11}$] ([Et_4N]$^+$1). The iodinated carba-*closo*-dodecaborate Cs[12-I-*closo*-$CB_{11}H_{11}$] (502 mg, 2.49 mmol) was dissolved in 15 mL of dry tetrahydrofuran under an argon atmosphere in a round-bottom flask equipped with a valve with a PTFE stem (Young, London) and fitted with a magnetic stirring bar. A solution of 6 mL of PhCCMgBr in THF (6 mmol) was added at room temperature. The resulting suspension was transferred via cannula into a second round-bottom flask equipped with a valve with a PTFE stem (Young, London) and fitted with a magnetic stirring bar that contained 90 mg of [$PdCl_2(Ph_3P)_2$] (0.13 mmol). The reaction mixture was stirred at 55−60 °C, and the progress of the reaction was periodically checked by $^{11}B\{^1H\}$ NMR spectroscopy. The reaction was complete after 20 h. The mixture was cooled to room temperature, and then it was poured into water (150 mL) while stirring. The THF was removed using a rotary evaporator, and subsequently the reaction mixture was filtered through a fine glass frit packed with diatomaceous earth (Celite) to yield a clear colorless solution. Addition of an aqueous solution of [Et_4N]Br (2 g dissolved in 50 mL of H_2O) resulted in a precipitate that was isolated by filtration. After drying in a vacuum, white [Et_4N]$^+$**1** was obtained. The tetraethylammonium salt was further purified by two different methods: (i) The salt was dissolved in a small amount of acetone, and the dropwise addition of water resulted in a white precipitate. (ii) Recrystallization from acetone by the slow uptake of diethyl ether vapor resulted in colorless crystals. Yield: 326 mg (1.34 mmol, 54%). $^1H\{^{11}B\}$ NMR (500 MHz, CD_3CN, δ ppm): 7.2−7.3 (m, 5H, phenyl), 2.37 (s, 1H, br, cluster CH), 1.70 (s, 5H, BH2−6), 1.68 (s, 5H, BH7−11). $^{13}C\{^1H\}$ NMR (126 MHz, $(CD_3)_2CO$, δ ppm): 131.8 (s, 2C, phenyl), 129.0 (s, 2C, phenyl), 127.3 (s, 1C, phenyl), 127.2 (s, 1C, phenyl), 103.2 (q, 1C, $^1J(^{13}C,^{11}B)$ = ∼100 Hz, B***C***≡C), 93.6 (q, 1C, $^2J(^{13}C,^{11}B)$ = <20 Hz, BC≡***C***), 49.0 (s, br, 1C, cluster). ^{11}B NMR (160 MHz, CD_3CN, δ ppm): −7.2 (s, 1B, B12), −12.3 (d, 5B, $^1J(^{11}B,^1H)$ = 135 Hz, B7−11), −16.5 (d, 5B, $^1J(^{11}B,^1H)$ = 149 Hz, B2−6). Raman (cm^{-1}): 2176 (ν(C≡C)). MALDI-MS *m*/*z* (isotopic abundance) calcd for **1** ([$C_9H_{16}B_{11}$]$^-$): 238(1), 239(3), 240(12), 241(36), 242(73), 243(100), 244(85), 245(35), 246(3). Found: 238(<1), 239(4), 240(15), 241(37), 242(75), 243(100), 244(87), 245(37), 246(4). Elem anal. calcd (%) for $C_{17}H_{36}B_{11}N$: C, 54.68; H, 9.72; N, 3.75. Found: C, 53.61; H, 10.04; N, 3.81.

Syntheses of [Et_4N][7-PhCC-12-Hal-*closo*-$CB_{11}H_{10}$] (Hal = F ([Et_4N]$^+$5), Cl ([Et_4N]$^+$6), Br ([Et_4N]$^+$7)). [Et_4N]$^+$**5**, [Et_4N]$^+$**6**, and [Et_4N]$^+$**7** were synthesized and isolated similarly to [Et_4N]$^+$**1**.

[Et_4N][7-PhCC-12-F-*closo*-$CB_{11}H_{10}$] ([Et_4N]$^+$5). Yield: 28 mg (0.11 mmol, 31%). $^1H\{^{11}B\}$ NMR (500 MHz, CD_3CN, δ ppm): 7.5−7.2 (m, 5H, phenyl), 2.23 (s, 1H, br, cluster CH), 1.78 (s, 2H, BH8 + 11), 1.72 (s, 2H, BH2 + 3), 1.67 (s, 2H, BH9 + 10), 1.49 (s, 2H, BH4 + 6), 1.45 (s, 1H, BH5). $^{13}C\{^1H\}$ NMR (126 MHz, CD_3CN, δ ppm): 132.0 (s, 2C, phenyl), 129.1 (s, 2C, phenyl), 128.0 (s, 1C, phenyl), 125.9 (s, 1C, phenyl), 94.6 (s, vbr, 1C, BC≡***C***), 36.7 (s, br, 1C, cluster), the signal of B^{13}***C***≡C was not detected. ^{11}B NMR (160 MHz, CD_3CN, δ ppm): 13.4 (s, 1B, B12), −13.9 (d, 2B, $^1J(^{11}B,^1H)$ = overlapped, B8 + 11), −14.6 (s, 1B, B7),

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−15.2 (d, 2B, $^1J(^{11}B,^1H)$ = overlapped, B9 + 10), −18.3 (d, 2B, $^1J(^{11}B,^1H)$ = ∼160 Hz, B2 + 3), −19.9 (d, 3B, $^1J(^{11}B,^1H)$ = ∼154 Hz, B4−6). ^{19}F NMR (471 MHz, $(CD_3)_2CO$, δ ppm): −192.7 (q, 1F, $^1J(^{19}F,^{11}B)$ = 60 Hz, BF12). Raman (cm^{-1}): 2184 (ν(C≡C)). MALDI-MS *m*/*z* (isotopic abundance) calcd for **5** ($[C_9H_{15}B_{11}F]^-$): 256(1), 257(3), 258(12), 259(36), 260(73), 261(100), 262(84), 263(35), 264(3). Found: 256(1), 257(2), 258(14), 259(35), 260(71), 261(100), 262(80), 263(30), 264(4). Elem anal. calcd (%) for $C_{17}H_{35}B_{11}FN$: C, 52.17; H, 9.01; N, 3.58. Found: C, 51.98; H, 9.18; N, 3.94.

[Et$_4$N][7-PhCC-12-Cl-*closo*-CB$_{11}$H$_{10}$] ([Et$_4$N]$^+$6). Yield: 115 mg (0.41 mmol, 51%). $^1H\{^{11}B\}$ NMR (500 MHz, $(CD_3)_2CO$, δ ppm): 7.5−7.2 (m, 5H, phenyl), 2.25 (s, 1H, br, cluster CH), 1.96 (s, 2H, BH8 + 11), 1.89 (s, 2H, BH2 + 3), 1.86 (s, 2H, BH9 + 10), 1.63 (s, 2H, BH4 + 6), 1.59 (s, 1H, BH5). $^{13}C\{^1H\}$ NMR (126 MHz, $(CD_3)_2CO$, δ ppm): 132.1 (s, 2C, phenyl), 128.9 (s, 2C, phenyl), 127.5 (s, 1C, phenyl), 126.8 (s, 1C, phenyl), ∼100 (q, 1C, $^1J(^{13}C,^{11}B)$ = ∼100 Hz, B***C***≡C), 94.1 (q, 1C, $^2J(^{13}C,^{11}B)$ = ∼17 Hz, BC≡***C***), 42.6 (s, br, 1C, cluster). ^{11}B NMR (160 MHz, $(CD_3)_2CO$, δ ppm): 4.1 (s, 1B, B12), −11.6 (d, 2B, $^1J(^{11}B,^1H)$ = overlapped, B8 + 11), −12.5 (s, 1B, B7), −12.9 (d, 2B, $^1J(^{11}B,^1H)$ = overlapped, B9 + 10), −16.7 (d, 2B, $^1J(^{11}B,^1H)$ = ∼151 Hz, B2 + 3), −18.1 (d, 3B, $^1J(^{11}B,^1H)$ = ∼157 Hz, B4−6). Raman (cm^{-1}): 2183 (ν(C≡C)). MALDI-MS *m*/*z* (isotopic abundance) calcd for **6** ($[C_9H_{15}B_{11}Cl]^-$): 273(3), 274(11), 275(33), 276(69), 277(100), 278(97), 279(61), 280(27), 281(10), 282(1). Found: 273(3), 274(12), 275(35), 276(67), 277(100), 278(95), 279(65), 280(30), 281(11), 282(<1). Elem anal. calcd (%) for $C_{17}H_{35}B_{11}ClN$: C, 50.06; H, 8.65; N, 3.43. Found: C, 49.89; H, 8.59; N, 3.77.

[Et$_4$N][7-PhCC-12-Br-*closo*-CB$_{11}$H$_{10}$] ([Et$_4$N]$^+$7). Yield: 140 mg (0.43 mmol, 54%). $^1H\{^{11}B\}$ NMR (500 MHz, CD_3CN, δ ppm): 7.5−7.2 (m, 5H, phenyl), 2.41 (s, 1H, br, cluster CH), 2.03 (s, 2H, BH8 + 11), 1.95 (s, 4H, BH2 + 3+9 + 10), 1.67 (s, 2H, BH4 + 6), 1.62 (s, 1H, BH5). $^{13}C\{^1H\}$ NMR (126 MHz, CD_3CN, δ ppm): 132.1 (s, 2C, phenyl), 128.9 (s, 2C, phenyl), 127.5 (s, 1C, phenyl), 126.9 (s, 1C, phenyl), ∼100 (q, 1C, $^1J(^{13}C,^{11}B)$ = ∼100 Hz, B***C***≡C), 94.2 (q, 1C, $^2J(^{13}C,^{11}B)$ = <20 Hz, BC≡***C***), 44.5 (s, br, 1C, cluster). ^{11}B NMR (160 MHz, CD_3CN, δ ppm): −2.3 (s, 1B, B12), −11.2 (d, 2B, $^1J(^{11}B,^1H)$ = overlapped, B8 + 11), −12.4 (s, 1B, B7), −12.5 (d, 2B, $^1J(^{11}B,^1H)$ = overlapped, B9 + 10), −16.3 (d, 2B, $^1J(^{11}B,^1H)$ = overlapped, B2 + 3), −17.0 (d, 1B, $^1J(^{11}B,^1H)$ = overlapped, B5), −17.6 (d, 2B, $^1J(^{11}B,^1H)$ = overlapped, B4 + 6). Raman (cm^{-1}): 2183 (ν(C≡C)). MALDI-MS *m*/*z* (isotopic abundance) calcd for **7** ($[C_9H_{15}B_{11}Br]^-$): 317(2), 318(8), 319(25), 320(55), 321(87), 322(100), 323(85), 324(55), 325(22), 326(2). Found: 317(1), 318(9), 319(27), 320(60), 321(90), 322(100), 323(88), 324(52), 325(25), 326(3). Elem anal. calcd (%) for $C_{17}H_{35}B_{11}BrN$: C, 45.14; H, 7.80; N, 3.10. Found: C, 44.11; H, 7.90; N, 3.52.

[Et$_4$N][1-Ph-12-PhCC-*closo*-CB$_{11}$H$_{10}$] ([Et$_4$N]$^+$2). The synthesis of $[Et_4N]^+$**2** was performed analogously to the preparation of $[Et_4N]^+$**1** with one exception: the black tar adsorbed on the diatomaceous earth (Celite), which was left after filtration of the reaction mixture, was extracted with diethyl ether. To this ethereal solution was added a large amount of water. The ether was removed under reduced pressure; the resulting suspension was filtered, and a second crop of $[Et_4N]^+$**2** was precipitated by the addition of an aqueous solution of [Et$_4$N]Br. Yield of the combined fractions: 87 mg (0.27 mmol, 34%). $^1H\{^{11}B\}$ NMR (500 MHz, CD_3CN, δ ppm): 7.55−7.50 (m, 2H, phenyl group bonded to C1 of the cluster), 7.31−7.28 (m, 5H, phenyl group bonded to the alkynyl group), 7.20−7.15 (m, 3H, phenyl group attached to C1 of the cluster), 2.05 (s, 5H, BH2−6), 1.83 (s, 5H, BH7−11). $^{13}C\{^1H\}$ NMR (126 MHz, CD_3CN, δ ppm): 141.9 (s, 1C, phenyl), 131.7 (s, 2C, phenyl), 129.0 (s, 2C, phenyl), 128.9 (s, 2C, phenyl), 128.3 (s, 2C, phenyl), 127.7 (s, 1C, phenyl), 127.5 (s, 1C, phenyl), 126.2 (s, 1C, phenyl), 95.7 (s, vbr, 1C, BC≡***C***), 71.0 (s, br, 1C, cluster); the signal of B^{13}***C***≡C was not detected. ^{11}B NMR (160 MHz, CD_3CN, δ ppm): −8.1 (s, 1B, B12), −11.9 (d, 5B, $^1J(^{11}B,^1H)$ = 143 Hz, B7−11), −13.4 (d, 5B, $^1J(^{11}B,^1H)$ = 154 Hz, B2−6). Raman (cm^{-1}): 2181 (ν(C≡C)). MALDI-MS *m*/*z* (isotopic abundance) calcd for **2** ($[C_{15}H_{20}B_{11}]^-$): 314(1), 315(3), 316(12), 317(35), 318(72), 319(100), 320(87), 321(39), 322(5). Found: 314(<1), 315(3), 316(13), 317(34), 318(78), 319(100), 320(91), 321(41), 322(4). Elem anal. calcd (%) for $C_{23}H_{40}B_{11}N$: C, 61.46; H, 8.97; N, 3.12. Found: C, 60.06; H, 8.75; N, 3.28.

[Et$_4$N][7,12-(PhCC)$_2$-*closo*-CB$_{11}$H$_{10}$] ([Et$_4$N]$^+$9). The synthetic procedure described for the preparation of $[Et_4N]^+$**1** was followed, but the addition of a second crop of PhCCMgBr (6 equiv) and $[PdCl_2(Ph_3P)_2]$ (0.1 equiv) was necessary to ensure completion of the reaction. The isolation of $[Et_4N]^+$**9** was performed similarly to the method described for $[Et_4N]^+$**2**. Yield: 102 mg (0.30 mmol, 39%). $^1H\{^{11}B\}$ NMR (500 MHz, CD_3CN, δ ppm): 7.4−7.2 (m, 10H, phenyl), 2.46 (s, 1H, br, cluster CH), 1.90 (s, 2H, BH2 + 3), 1.85 (s, 2H, BH8 + 11), 1.73 (s, 2H, BH9 + 10), 1.69 (s, 2H, BH4 + 6), 1.63 (s, 1H, BH5). $^{13}C\{^1H\}$ NMR (126 MHz, CD_3CN, δ ppm): 132.0 (s, 2C, phenyl), 131.8 (s, 2C, phenyl), 129.1 (s, 4C, phenyl), 127.9 (s, 1C, phenyl), 127.7 (s, 1C, phenyl), 126.2 (s, 1C, phenyl), 126.1 (s, 1C, phenyl), 95.6 (vbr, 1C, BC≡***C***), 94.4 (vbr, 1C, BC≡***C***), 49.0 (s, br, 1C, cluster); the signals of the different B^{13}***C***≡C were not detected. ^{11}B NMR (160 MHz, CD_3CN, δ ppm): −6.2 (s, 1B, B12), −11.3 (d, 2B, $^1J(^{11}B,^1H)$ = overlapped, B8 + 11), −12.1 (s, 1B, B7), −12.7 (d, 2B, $^1J(^{11}B,^1H)$ = overlapped, B9 + 10), −15.8 (d, 2B, $^1J(^{11}B,^1H)$ = overlapped, B2 + 3), −17.0 (d, 2B, $^1J(^{11}B,^1H)$ = overlapped, B4 + 6), −17.6 (d, 1B, $^1J(^{11}B,^1H)$ = overlapped, B5). Raman (cm^{-1}): 2185 (ν(C≡C)). MALDI-MS *m*/*z* (isotopic abundance) calcd. for **9** ($[C_{17}H_{20}B_{11}]^-$): 339(3), 340(12), 341(34), 342(71), 343(100), 344(88), 345(41), 346(6), 347(1). Found: 339(3), 340(15), 341(35), 342(74), 343(100), 344(93), 345(40), 346(5), 347(1). Elem anal. calcd (%) for $C_{25}H_{40}B_{11}N$: C, 63.41; H, 8.51; N, 2.96. Found: C, 62.05; H, 8.64; N, 3.05.

[Et$_4$N][12-Me$_3$SiCC-*closo*-CB$_{11}$H$_{11}$] ([Et$_4$N]$^+$3). The synthesis and isolation of $[Et_4N]^+$**3** was performed similarly to the procedure described for $[Et_4N]^+$**1**. But two additional amounts of $Me_3SiCCMgBr$ (2 × 6 equiv) and of $[PdCl_2(Ph_3P)_2]$ (2 × 0.1 equiv) were added to the reaction mixture after 2 and 4 days of stirring at 55−60 °C, respectively. Yield: 810 mg (3.39 mmol, 55%). $^1H\{^{11}B\}$ NMR (500 MHz, CD_3CN, δ ppm): 2.32 (s, 1H, br, cluster CH), 1.62 (s, 5H, BH2−6), 1.59 (s, 5H, BH7−11), 0.08 (s, 9H, $^1J(^{13}C,^1H)$ = 119.6 Hz, $^2J(^{29}Si,^1H)$ = 7.0 Hz, $Si(CH_3)_3$). $^{13}C\{^1H\}$ NMR (126 MHz, $(CD_3)_2CO$, δ ppm): 122.4 (q, 1C, $^1J(^{13}C,^{11}B)$ = ∼100 Hz, B***C***≡C), 97.1 (q, 1C, $^2J(^{13}C,^{11}B)$ = ∼18 Hz, BC≡***C***), 48.9 (s, br, 1C, cluster), 0.7 (s, 3C, $^1J(^{29}Si,^{13}C)$ = 53 Hz, $Si(CH_3)_3$). ^{11}B NMR (160 MHz, CD_3CN, δ ppm): −7.9 (s, 1B, B12), −12.4 (d, 5B, $^1J(^{11}B,^1H)$ = 139 Hz, B7−11), −16.6 (d, 5B, $^1J(^{11}B,^1H)$ = 149 Hz, B2−6). Raman (cm^{-1}): 2121 (ν(C≡C)). MALDI-MS *m*/*z* (isotopic abundance) calcd. for **3** ($[C_6H_{20}B_{11}Si]^-$): 234(1), 235(3), 236(12), 237(35), 238(72), 239(100), 240(87), 241(39), 242(6), 241(1). Found: 234(<1), 235(3), 236(16), 237(38), 238(75), 239(100), 240(90), 241(37), 242(5), 241(1). Elem anal. calcd (%) for $C_{14}H_{39}B_{11}NSi$: C, 45.41; H, 10.91; N, 3.79. Found: C, 44.93; H, 11.14; N, 3.81.

[Et$_4$N][1-Ph-12-Me$_3$SiCC-*closo*-CB$_{11}$H$_{10}$] ([Et$_4$N]$^+$4). The preparation was performed similarly to the procedures described for $[Et_4N]^+$**1** and $[Et_4N]^+$**3**. The product was isolated in two steps as

discussed for $[Et_4N]^+$**2**. Yield: 146 mg (0.46 mmol, 38%). $^1H\{^{11}B\}$ NMR (500 MHz, $(CD_3)_2CO$, δ ppm): 7.55−7.40 (m, 2H, phenyl), 7.15−7.05 (m, 3H, phenyl), 2.01 (s, 5H, BH2−6), 1.84 (s, 5H, BH7−11), 0.00 (s, 9H, $Si(CH_3)_3$). $^{13}C\{^1H\}$ NMR (126 MHz, $(CD_3)_2CO$, δ ppm): 142.5 (s, 1C, phenyl), 129.0 (s, 2C, phenyl), 127.8 (s, 2C, phenyl), 127.0 (s, 1C, phenyl), 98.5 (s, vbr, 1C, BC≡***C***), 70.7 (s, br, 1C, cluster), 0.7 (s, 3C, $Si(CH_3)_3$); the signal of B^{13}***C***≡C was not detected. ^{11}B NMR (160 MHz, $(CD_3)_2CO$, δ ppm): −8.2 (s, 1B, B12), −11.7 (d, 5B, $^1J(^{11}B,^1H)$ = 137 Hz, B7−11), −13.5 (d, 5B, $^1J(^{11}B,^1H)$ = 150 Hz, B2−6). Raman (cm^{-1}): 2115 (ν(C≡C)). MALDI-MS *m*/*z* (isotopic abundance) calcd for **4** ($[C_{12}H_{24}B_{11}Si]^-$): 311(3), 312(12), 313(34), 314(71), 315(100), 316(89), 317(43), 318(9), 319(2). Found: 311(3), 312(15), 313(35), 314(77), 315(100), 316(90), 317(45), 318(11), 319(1). Elem anal. calcd (%) for $C_{20}H_{44}B_{11}NSi$: C, 53.91; H, 9.95; N, 3.14. Found: C, 53.43; H, 10.35; N, 3.30.

$[Et_4N][7,12\text{-}(Me_3SiCC)_2\text{-}closo\text{-}CB_{11}H_{10}]$ ($[Et_4N]^+$10). $[Et_4N]^+$**10** was prepared similarly to $[Et_4N]^+$**3**. Yield: 164 mg (0.51 mmol, 41%). $^1H\{^{11}B\}$ NMR (500 MHz, CD_3CN, δ ppm): 2.35 (s, 1H, br, cluster CH), 1.75 (s, 2H, BH2 + 3), 1.64 (s, 2H, BH8 + 11), 1.58 (s, 4H, BH4 + 6 + 9 + 10), 1.53 (s, 1H, BH5), 0.13 (s, 9H, $^1J(^{13}C,^1H)$ = 119.6 Hz, $^2J(^{29}Si,^1H)$ = 6.7 Hz, $Si(CH_3)_3$), 0.10 (s, 9H, $^1J(^{13}C,^1H)$ = 119.3 Hz, $^2J(^{29}Si,^1H)$ = 7.0 Hz, $Si(CH_3)_3$). $^{13}C\{^1H\}$ NMR (126 MHz, $(CD_3)_2CO$, δ ppm): 121.1 (q, 1C, $^1J(^{13}C,^{11}B)$ = ∼100 Hz, B***C***≡C), 120.6 (q, 1C, $^1J(^{13}C,^{11}B)$ = ∼100 Hz, B***C***≡C), 98.2 (s, vbr, 1C, BC≡***C***), 97.5 (s, vbr, 1C, BC≡***C***), 48.2 (s, br, 1C, cluster), 0.7 (s, 6C, $Si(CH_3)_3$). ^{11}B NMR (160 MHz, CD_3CN, δ ppm): −7.0 (s, 1B, B12), −11.5 (d, 2B, $^1J(^{11}B,^1H)$ = ∼160 Hz, B8 + 11), −12.8 (d, 2B, $^1J(^{11}B,^1H)$ = ∼140 Hz, B9 + 10), −12.8 (s, 1B, B7), −15.9 (d, 2B, $^1J(^{11}B,^1H)$ = overlapped, B2 + 3), −17.1 (d, 2B, $^1J(^{11}B,^1H)$ = overlapped, B4 + 6), −17.5 (d, 1B, $^1J(^{11}B,^1H)$ = overlapped, B5). Raman (cm^{-1}): 2124 (ν(C≡C)). MALDI-MS *m*/*z* (isotopic abundance) calcd for **10** ($[C_{11}H_{28}B_{11}Si_2]^-$): 331(3), 332(11), 333(33), 334(70), 335(100), 336(92), 337(48), 338(13), 339(4), 340(1). Found: 331(4), 332(13), 333(34), 334(70), 335(100), 336(95), 337(45), 338(11), 339(5), 340(3). Elem anal. calcd (%) for $C_{19}H_{48}B_{11}NSi_2$: C, 49.00; H, 10.39; N, 3.01. Found: C, 48.76; H, 10.45; N, 3.22.

$[Et_4N][7\text{-}Me_3SiCC\text{-}12\text{-}F\text{-}closo\text{-}CB_{11}H_{10}]$ ($[Et_4N]^+$8). The synthesis and isolation of $[Et_4N]^+$**8** was performed similarly to those described for $[Et_4N]^+$**1** and $[Et_4N]^+$**3**. Yield: 187 mg (0.73 mmol, 44%). $^1H\{^{11}B\}$ NMR (500 MHz, $CD_3)_2CO$, δ ppm): 2.04 (s, 1H, br, cluster CH), 1.82 (s, 2H, BH8 + 11), 1.70 (s, 4H, BH2 + 3 + 9 + 10), 1.46 (s, 2H, BH4 + 6); the signal of the ^1H nucleus of BH5 is covered by the signal of the CH_2 groups of the $[Et_4N]^+$ cation at ∼1.4 ppm, 0.08 (s, 9H, $^1J(^{13}C,^1H)$ = 119.0 Hz, $^2J(^{29}Si,^1H)$ = 7.0 Hz, $Si(CH_3)_3$). $^{13}C\{^1H\}$ NMR (126 MHz, $(CD_3)_2CO$, δ ppm): 118.4 (q, 1C, $^1J(^{13}C,^{11}B)$ = 95 ± 8 Hz, B***C***≡C), 98.4 (q, 1C, $^2J(^{13}C,^{11}B)$ = ∼17 Hz, BC≡***C***), 36.3 (s, br, 1C, cluster), 0.7 (s, 3C, $Si(CH_3)_3$). ^{11}B NMR (160 MHz, $CD_3)_2CO$, δ ppm): 13.5 (s, 1B, B12), −13.8 (d, 2B, $^1J(^{11}B,^1H)$ = ∼150, B8 + 11), −15.1 (s, 1B, B7), −15.1 (d, 2B, $^1J(^{11}B,^1H)$ = overlapped, B9 + 10), −18.3 (d, 2B, $^1J(^{11}B,^1H)$ = ∼152 Hz, B2 + 3), −20.0 (d, 3B, $^1J(^{11}B,^1H)$ = ∼153 Hz, B4−6). ^{19}F NMR (471 MHz, $CD_3)_2CO$, δ ppm): −191.8 (q, 1F, $^1J(^{19}F,^{11}B)$ = 60 Hz, BF12). Raman (cm^{-1}): 2121 (ν(C≡C)). MALDI-MS *m*/*z* (isotopic abundance) calcd. for **8** ($[C_6H_{19}B_{11}FSi]^-$): 252(1), 253(3), 254(12), 255(35), 256(72), 257(100), 258(87), 259(39), 260(6), 261(1). Found: 252(<1), 253(4), 254(14), 255(36), 256(79), 257(100), 258(91), 259(33), 260(5), 261(<1). Elem anal. calcd (%) for $C_{14}H_{39}B_{11}FNSi$: C, 43.40; H, 10.15; N, 3.61. Found: C, 42.24; H, 9.77; N, 3.57.

$Cs[12\text{-}PhCC\text{-}closo\text{-}CB_{11}H_{11}]$ (Cs^+1). In a 250 mL Erlenmeyer flask, $[Et_4N]^+$**1** (960 mg, 2.57 mmol) was suspended in 30 mL of aqueous hydrochloric acid (10% v/v), and 150 mL of diethyl ether was added. The mixture was stirred until all solid material dissolved. The ether layer was separated, and the aqueous phase was extracted two more times with Et_2O (2 × 50 mL). The combined ether solutions were dried with $MgSO_4$ and filtered, and the volume of the solution was reduced to approximately 20 mL. The resulting mixture was treated with a solution of 800 mg of CsCl in 15 mL of water. Ether and water were removed under reduced pressure, and the colorless solid residue was extracted with a total of 100 mL of acetone. The acetone was evaporated, and the semi-solid residue was treated with 300 mL of $CHCl_3$. The mixture was stored in a refrigerator for 2 h. The white solid was isolated by filtration. Yield: 870 mg (2.31 mmol, 90%). Raman (cm^{-1}): 2171 (ν(C≡C)). Elem anal. calcd (%) for $C_9H_{16}B_{11}Cs$: C, 28.75; H, 4.29. Found: C, 29.10; H, 4.36.

Results and Discussion

Synthetic Aspects. The mono- and diiodinated *closo*-carborate anions $[12\text{-I-}closo\text{-}CB_{11}H_{11}]^-$,[10,34] $[1\text{-Ph-12-I-}closo\text{-}CB_{11}H_{10}]^-$,[16,19] and $[7,12\text{-}I_2\text{-}closo\text{-}CB_{11}H_{10}]^-$[34] used in this study as starting materials are accessible in high yields by direct iodination of the anions $[closo\text{-}CB_{11}H_{12}]^-$ and $[1\text{-Ph-}closo\text{-}CB_{11}H_{11}]^-$ with elemental iodine in glacial acetic acid, respectively. Salts of the anions $[7\text{-I-12-X-}closo\text{-}CB_{11}H_{10}]^-$ (X = F, Cl, Br) with one iodine substituent bonded to the lower belt boron atom B7 were synthesized in two steps from the parent anion $[closo\text{-}CB_{11}H_{12}]^-$:[36] Introduction of the halogen atom at the antipodal boron vertex was accomplished by reacting salts of the $[closo\text{-}CB_{11}H_{12}]^-$ anion with either anhydrous hydrogen fluoride,[56] *N*-chlorosuccinimide,[57] or *N*-bromosuccinimide.[57] Treatment of the resulting monohalogeno *closo*-carborate anions with elemental I_2 in glacial acetic acid resulted in $[7\text{-I-12-X-}closo\text{-}CB_{11}H_{10}]^-$ (X = F, Cl, Br).[36]

In Schemes 2 and 3, the Pd-catalyzed cross-coupling reactions resulting in phenyl- and trimethylsilylalkynyl-substituted derivatives of the $[closo\text{-}CB_{11}H_{12}]^-$ anion presented in this contribution as well as the preparations of the iodinated starting materials are shown.

The monoiodinated *closo*-carborate anions $[12\text{-I-}closo\text{-}CB_{11}H_{11}]^-$, $[7\text{-I-12-X-}closo\text{-}CB_{11}H_{10}]^-$ (X = F, Cl, Br), and $[1\text{-Ph-12-I-}closo\text{-}CB_{11}H_{10}]^-$ were transformed into the corresponding phenylacetylene-substituted anions with PhCC-MgBr in tetrahydrofuran and $[PdCl_2(Ph_3P)_2]$ as a catalyst at 55−60 °C. The reactions were complete within 20 h, as deduced from $^{11}B\{^1H\}$ NMR spectroscopy. The synthesis of salts of the anion $[7,12\text{-}(PhCC)_2\text{-}closo\text{-}CB_{11}H_{10}]^-$ (**9**) afforded longer reaction times, and it was necessary to add additional PhCCMgBr as well as catalyst.

In contrast to the preparations of $\{CB_{11}\}$ clusters with phenylalkynyl substituents, the respective reactions using $Me_3SiCCMgBr$ as starting material required prolonged reaction times. Moreover, further amounts of the catalyst and Grignard reagent had to be added, even for syntheses of monoalkynyl derivatives. The MALDI mass spectra of the

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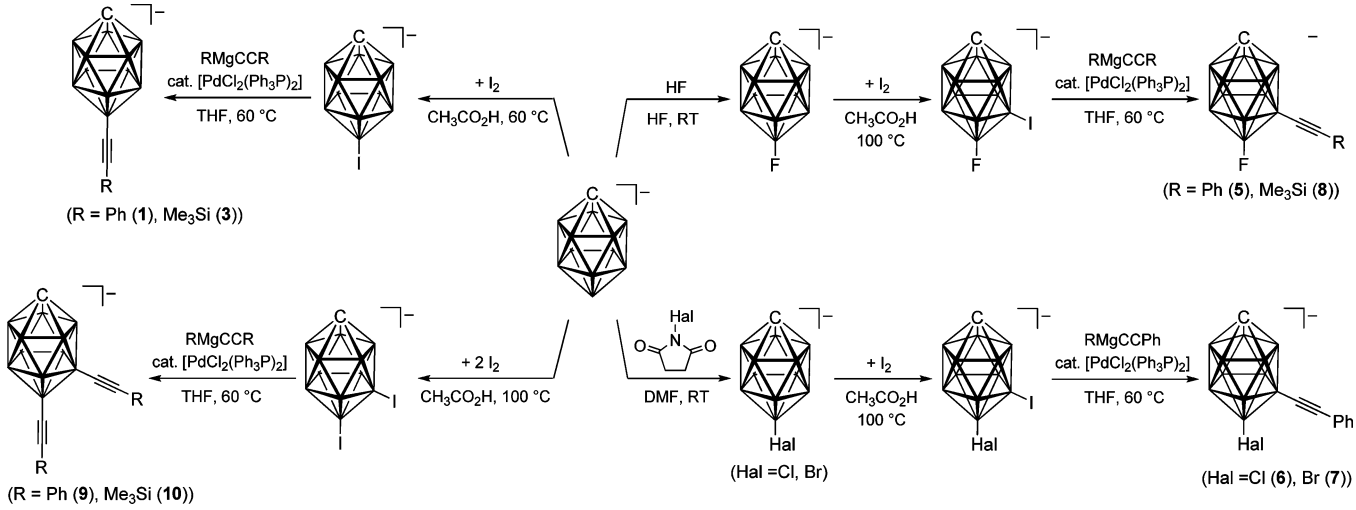
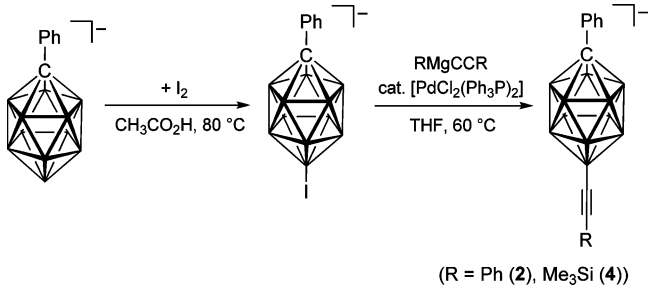
Scheme 2. Syntheses of Alkynyl Substituted Carba-*closo*-dodecaborate Anions Starting from the [*closo*-$CB_{11}H_{12}]^-$ Anion by Halogenation and Followed by Pd-Catalyzed Cross-Coupling Reactions



Scheme 3. Syntheses of Alkynyl Substituted 1-Phenylcarba-*closo*-dodecaborate Anions by Halogenation and Pd-Catalyzed Cross-Coupling Reactions



crude products of most of the reactions revealed the formation of traces of *closo*-carborate anions containing one chlorine atom. This observation is explained by the exchange of iodine against chlorine, which is introduced into the reaction via the catalyst $[PdCl_2(Ph_3P)_2]$.

Attempted conversion of [7,8,9,10,11,12-I_6-*closo*-$CB_{11}H_6]^-$[35] into [7,8,9,10,11,12-$(PhCC)_6$-*closo*-$CB_{11}H_6]^-$ failed, although additional amounts of Pd catalyst and PhCCMgBr were added. According to MALDI mass spectrometry, no hexaalkynylated product was formed, and tetra- as well as pentasubstituted anions were only formed in small amounts. The main anions detected were those with one, two, and three PhCC groups. This finding is not surprising, because multiple Kumada-type coupling reactions of alkyl Grignard reagents with iodinated *closo*-carborate anions are known to proceed slowly and to give only low yields.[12] However, the [1-Ph-7,8,9,10,11,12-I_6-*closo*-$CB_{11}H_5]^-$ anion reacts with *p*-toloylMgBr to produce [1-Ph-7,8,9,10,11-(*p*-toloyl)$_5$-12-I-*closo*-$CB_{11}H_5]^-$; replacement of all six iodine substituents was not observed.[19]

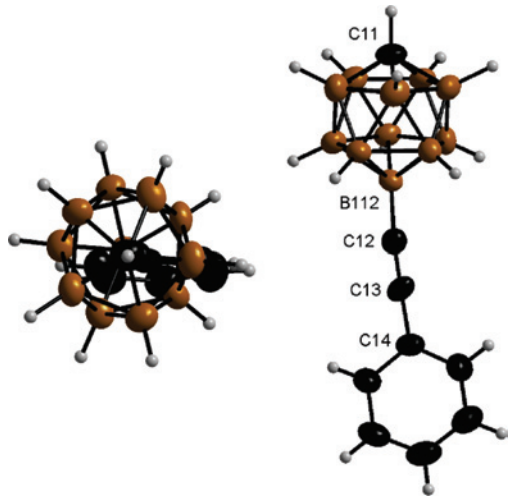


Figure 1. Two different views of the [12-PhCC-*closo*-$CB_{11}H_{11}]^-$ anion in the crystal structure of Cs^+**1** (displacement ellipsoids at the 50% probability level).

The alkynyl *closo*-carborate anions were isolated as tetraethylammonium salts from aqueous solutions in approximately 30−55% yield. This yield is similar to those reported in earlier studies on related coupling reactions of [12-I-*closo*-$CB_{11}H_{11}]^-$ with alkyl and aryl Grignard reagents.[10]

The $[Et_4N]^+$ cation of the tetraethylammonium alkynylcarba-*closo*-dodecaborates can be exchanged against alkali metal cations: The $[Et_4N]^+$ salt is treated with dilute hydrochloric acid and diethyl ether. The ethereal layer contains the H^+ salt of the carborate anion, which is easily transformed into other salts, as demonstrated for the preparation of Cs[12-PhCC-*closo*-$CB_{11}H_{11}]$ (Cs^+**1**).

Crystal Structures of Cs[12-PhCC-*closo*-$CB_{11}H_{11}$] (Cs^+1) and [Et_4N][7-PhCC-12-Cl-*closo*-$CB_{11}H_{10}$] ([$Et_4N]^+$6). Cs^+**1** crstallizes in the orthorhombic space group $Pna2_1$ (no. 33) with two independent formula units and $Z = 8$ in the unit cell. The structure of $[Et_4N]^+$**6** was solved and refined in the triclinic space group $P\bar{1}$ with $Z = 2$. Experimental details of the structure determinations are summarized in Table 1 and discussed in the Experimental Section. In Figures 1 and 2, models of the carba-*closo*-dodecaborate anions **1** and **6** are depicted, and in Table 2, selected bond lengths and angles are collected. The experimental data are in good agreement with values derived from DFT calculations (B3LYP/6-311++G(d,p)).

The carbon−carbon triple bond lengths in both closely related phenylethynyl-substituted *closo*-carborate anions are

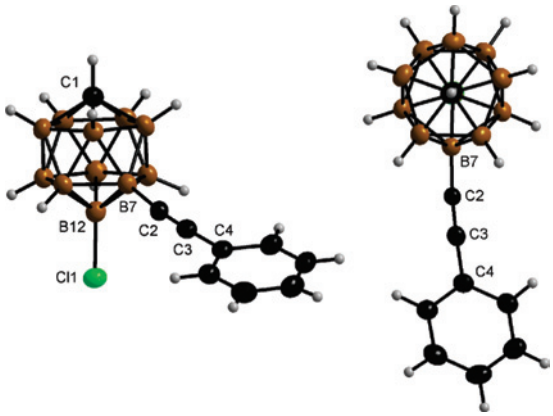


Figure 2. Two different views of the [7-PhCC-12-Cl-*closo*-$CB_{11}H_{10}$]$^-$ anion in the crystal structure of $[Et_4N]^+$**6** (displacement ellipsoids at the 50% probability level).

Table 2. Selected Experimental and Calculated[a] Bond Lengths and Angles of the Anions [12-PhCC-*closo*-$CB_{11}H_{11}$]$^-$ (**1**) and [7-PhCC-12-Cl-*closo*-$CB_{11}H_{10}$]$^-$ (**6**)[b]

	1		**6**	
	Cs^+[c]	calcd	$[Et_4N]^+$	calcd
	Bond Lengths[d] (Å)			
C−B2/3/4/5/6	1.704(14)	1.706	1.697(4)	1.705
B−B (upper belt)	1.765(13)	1.780	1.766(4)	1.780
B−B (inter belt)	1.771(14)	1.772	1.768(4)	1.774
B−B (lower belt)	1.778(13)	1.793	1.788(4)	1.795
B12−B7/8/9/10/11	1.777(13)	1.792	1.776(4)	1.786
B−C	1.572(15)	1.542	1.556(3)	1.537
C≡C	1.184(13)	1.215	1.195(3)	1.214
CC−C	1.453(15)	1.423	1.451(3)	1.423
B12−Cl			1.849(3)	1.843
	Bond Angles (deg)			
B−C≡C	172.2(10)	179.7	174.4(2)	179.6
C≡C−C	176.4(10)	179.8	177.0(2)	178.8

[a] B3LYP/6-311++G(d,p). [b] Bond parameters are mean values for local C_{5v} and C_s symmetry of the {*closo*-CB_{11}} cluster in anions **1** and **6**, respectively. [c] Mean value for both independent anions in the solid-state structure. [d] Average value.

comparable: 1.184(13) (**1**) and 1.195(3) Å (**6**). This observation is in agreement with results of DFT calculations which predict nearly identical *d*(C≡C) values (Table 2). The B−CC and CC−C bond lengths of the alkynyl substituents in anions **1** and **6** are similar, too, as evident from experimental as well as theoretical data. The B−C≡C−C units in the solid-state structures of **1** and **6** are slightly bent, whereas the calculated bond angles for B−C≡C and C≡C−C in **1** and **6** are nearly 180 ° (Table 2). However, DFT calculations indicate negligible changes in energy for small distortions of the B−C≡C−C units.

Comparable values for *d*(C≡C) and *d*(B−CC) as observed for **1** and **6** have been reported for a variety of other boranes, borates, and carboranes with alkynyl groups bonded to boron, for example, for the $[B(CCPh)_4]^-$ anion,[58] for 2,9-$(Me_3SiCC)_2$-*closo*-1,12-$C_2B_{10}H_{10}$,[27] and for the *ortho*-catecholato borane $(C_6H_4O_2)$BCCPh[59] (Table 3).

The C−B and B−B bond lengths of anions **1** and **6** as listed in Table 2 are averaged to local C_{5v} symmetry of the {*closo*-CB_{11}} clusters. For the [7-PhCC-12-Cl-*closo*-$CB_{11}H_{10}$]$^-$ anion (**6**), a more detailed summary of experimental and theoretical bond lengths of the cluster is given in Table S1 in the Supporting Information. The respective bond lengths are close to those found for related derivatives of the carba-*closo*-dodecaborate anion.[2,19,38,64,65] The experimental B−Cl bond length of 1.848(3) Å compares well to the calculated value of 1.843 Å and to a *d*(B−Cl) of 1.836(4) Å of the related [12-Cl-*closo*-$CB_{11}H_{11}$]$^-$ anion in $[Pd(dppe)_2][12\text{-Cl-}closo\text{-}CB_{11}H_{11}]_2\cdot 3CH_2Cl_2$.[64]

In the crystal of Cs[12-PhCC-*closo*-$CB_{11}H_{11}$] (Cs^+**1**), the cesium cations are coordinated to the alkynyl groups, resulting in infinite chains along the crystallographic *a* axis, as depicted in Figure 3. The Cs···C contacts are in the range of 3.497(10)−3.567(8) Å. An inquiry to the Cambridge Crystallographic Database resulted in only one other example for a similar π complexation of Cs^+ toward alkynes. In $Cs[(C_5HMe_4)_2Ti(C{\equiv}CSiMe_3)_2]$, the trimethylsilylethynyl ligands are σ-bonded to the Ti atom, and their triple bonds are coordinated to the Cs^+ cation.[66] The Cs−C distances of 3.423(6)−3.379(5) Å are similar to those observed for Cs^+**1**.

NMR Spectroscopy. The phenylethynyl and trimethylsilylethynyl carba-*closo*-dodecaborates were characterized by ^{1}H, ^{11}B, ^{19}F, and ^{13}C NMR spectroscopy. Assignments of the ^{1}H and ^{11}B NMR signals are supported by $^{11}B\{^1H\}-^1H\{^{11}B\}$ 2D[67] and $^{11}B\{^1H\}-^{11}B\{^1H\}$ correlation spectroscopy[68] experiments. The ^{11}B and the ^{13}C NMR spectroscopic data of the {*closo*-CB_{11}} clusters and the ethynyl carbon atoms are collected in Table S2 (Supporting Information). Theoretical ^{11}B and ^{13}C chemical shifts derived from DFT-GIAO calculations are in good agreement with the experimental values (Table S2, Supporting Information). Selected examples for $^{11}B\{^1H\}$ and ^{11}B NMR spectra of PhCC substituted derivatives of the [*closo*-$CB_{11}H_{12}$]$^-$ anion are depicted in Figure 4.

The signal corresponding to the antipodal boron atom has the highest resonance frequency for all anions described in this contribution. However, large differences in $\delta(^{11}B)$ are observed for B12 of the anions depending on the substituent bonded to this boron atom. Two further signals are observed for the {*closo*-CB_{11}} clusters with local C_{5v} symmetry, for example, for the [12-PhCC-*closo*-$CB_{11}H_{11}$]$^-$ anion (**1**; see Figure 4). The signal with the higher ^{11}B chemical shift is assigned to the boron nuclei of the lower-belt atoms and the second signal with a lower chemical shift to the ^{11}B nuclei of the upper-belt boron atoms (Table S2, Supporting Information; Scheme 1). In the 7,12-disubstituted carba-*closo*-dodecaborate anions, the local sym-

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Table 3. Selected Structural and Spectroscopic Properties of Phenyl- and Trimethylsilylalkynyl Substituted Carba-*closo*-dodecaborates and Related Species[a,b]

	d(B−C), [Å]	*d*(C≡C), [Å]	$\delta(^{13}C)$ B−***C***, [ppm]	$\delta(^{13}C)$ BC≡***C***, [ppm]	$\delta(^{11}B)$ ***B***−C, [ppm]	$^1J(^{13}C,^{11}B)$, [Hz]	$^2J(^{13}C,^{11}B)$, [Hz]	ν(C≡C), [cm^{-1}]	ref
[12-PhCC-*closo*-$CB_{11}H_{11}$]$^-$ (**1**)	1.54(2)[c]	1.20(2)[c]	103.2	93.6	−7.2	∼100	<20	2171[c]	*d*
	1.542	*1.215*	*122.5*	*94.7*	*−9.3*	*105.7*	*21.3*	*2265*	*d*
[7-PhCC-12-Cl-*closo*-$CB_{11}H_{10}$]$^-$ (**6**)	1.558(3)[e]	1.195(3)[e]	∼100	94.1	−12.5	∼100	∼17	2183[e]	*d*
	1.537	*1.214*	*117.6*	*94.9*	*−15.5*	*110.0*	*21.8*	*2273*	*d*
[12-Me_3SiCC-*closo*-$CB_{11}H_{11}$]$^-$ (**3**)	n.o.[f]	n.o.	122.4	97.1	−7.9	∼100	∼18	2121[e]	*d*
	1.545	*1.221*	*138.3*	*91.0*	*−10.1*	*110.0*	*21.8*	*2206*	*d*
2,9-$(Me_3SiCC)_2$-*closo*-1,12-$C_2B_{10}H_{10}$	1.532(7)	1.206(7)	105.7	93.8	−15.5	n.o.	n.o.	n.o.	27
9-PhCC-1,2-$C_2B_{10}H_{11}$	n.o.	n.o.	n.o.	n.o.	−2.8	n.o.	n.o.	2180	24,62
9-Me_3SiCC-1,2-$C_2B_{10}H_{11}$	n.o.	n.o.	112.3	105.2	−3.2	∼100	∼15	2135	24,62
$[(C_2F_5)_3BCCPh]^-$	n.o.	n.o.	97.8	97.5	−18.9	75.0	13.8	2183[c]	61
$[(C_2F_5)_3BCCSi(CHMe_2)_3]^-$	n.o.	n.o.	118.7	98.0	−19.5	70.2	11.5	2133[c]	61
$[B(CCPh)_4]^-$	1.609(8)[g,h]	1.200(7)[g,h]	102.8	94.2	−31.0	70.0	14.0	n.o.	58,60
$(C_6H_4O_2)BCCPh$[i]	1.513(5)	1.196(5)	n.o.	105.1	25.0	n.o.	n.o.	n.o.	59
pinBCCSiMe_3[j]	n.o.	n.o.	104.4	110.3	23.8	137	n.o.	n.o.	63

[a] Calculated values in italics. [b] B3LYP/6-311++G(d,p) (GIAO/B3LYP//6-311++G(2d,p)//6-311++G(d,p)). [c] Cs^+ salt. [d] This work. [e] $[Et_4N]^+$ salt. [f] n.o. = not observed. [g] (*N*,*N*′-Dimethyl)dimethylindocarbocyanine tetrakis(phenylethynyl)borate. [h] Averaged value. [i] 2-Phenylethynyl-1,3,2-benzodioxaborole. [j] 2-Trimethylsilylethynyl-4,4,5,5-tetramethyl-1,3,2-dioxaborole.

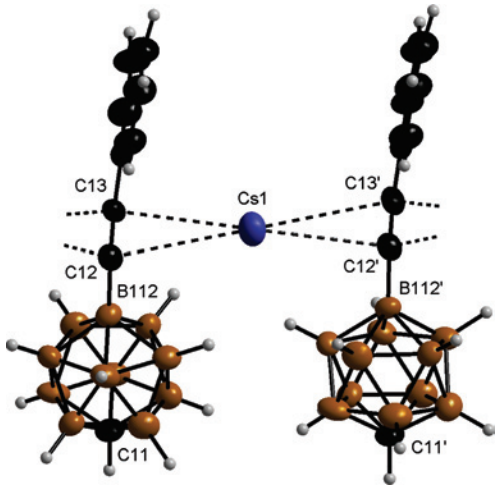

Figure 3. Coordination of the Cs^+ cation in Cs^+**1** (displacement ellipsoids at the 50% probability level).

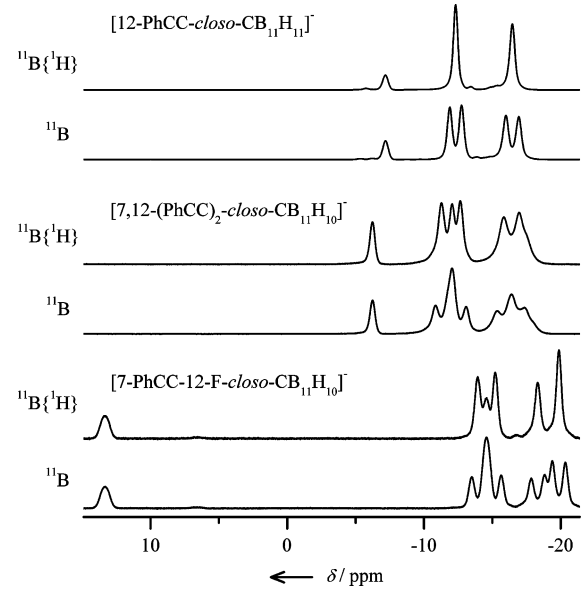

Figure 4. $^{11}B\{^1H\}$ and ^{11}B NMR spectra of the carba-*closo*-dodecaborate anions [12-PhCC-*closo*-$CB_{11}H_{11}$]$^-$ (**1**), [7,12-$(PhCC)_2$-*closo*-$CB_{11}H_{10}$]$^-$ (**9**), and [7-PhCC-12-F-*closo*-$CB_{11}H_{10}$]$^-$ (**5**).

metry of the cluster is reduced to C_s, resulting in seven signals in the ^{11}B NMR spectra. In these spectra, the order of chemical shifts of the three regions of the cluster as found for the {*closo*-CB_{11}} clusters with local C_{5v} symmetry is retained: B12 > B7−B11 > B2−B6.

In most of the ^{13}C NMR spectra of the alkynylcarba-*closo*-dodecaborate anions, two signals are observed for the two ^{13}C nuclei of the C≡C fragments, as exemplified for [Et_4N][12-Me_3SiCC-*closo*-$CB_{11}H_{11}$] ([Et_4N]$^+$**2**) in Figure 5. For some of the anions, the signal of B^{13}***C***≡C is not observed (Table S2, Supporting Information) due to very low intensities. For all anions presented in this contribution, the signal of the carbon nucleus bonded to the boron atom of the cluster is shifted to a higher-resonance frequency compared to the signal of BC≡^{13}***C*** (Table S2, Supporting Information; Figure 5). In general, the $\delta(^{13}C)$ values of either PhC≡C or Me_3SiC≡C groups of the different anions are very similar, while the ^{13}C chemical shifts of the different groups PhC≡C and Me_3SiC≡C are significantly different. Comparable $\delta(^{13}C)$ values were reported for related phenyl- and trimethylsilylalkynyl-substituted borates, whereas for boranes, different values were published; selected examples are listed in Table 3.[27,59−61,63,69,70]

Both ^{13}C nuclei of the alkynyl groups in the carba-*closo*-dodecaborate anions couple to ^{11}B. The signals of the carbon nuclei of the carbon atoms that are bonded to boron are split into quartets with coupling constants of approximately 100 Hz (Table 3, Figure 5). The $^2J(^{13}C,^{11}B)$ coupling constants of the ^{11}***B***C≡^{13}***C*** fragments are in the range of 17−20 Hz. The experimental coupling constants are in good agreement with calculated values (Table 3).

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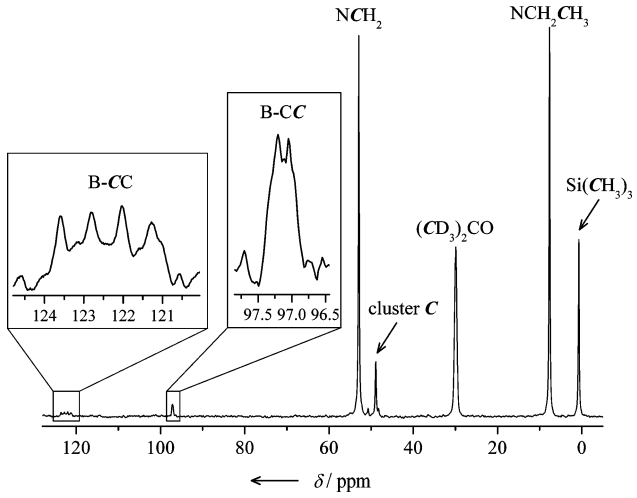

Figure 5. $^{13}C\{^1H\}$ NMR spectrum of $[Et_4N][12\text{-}Me_3SiCC\text{-}closo\text{-}CB_{11}H_{11}]$ ($[Et_4N]^+$**3**).

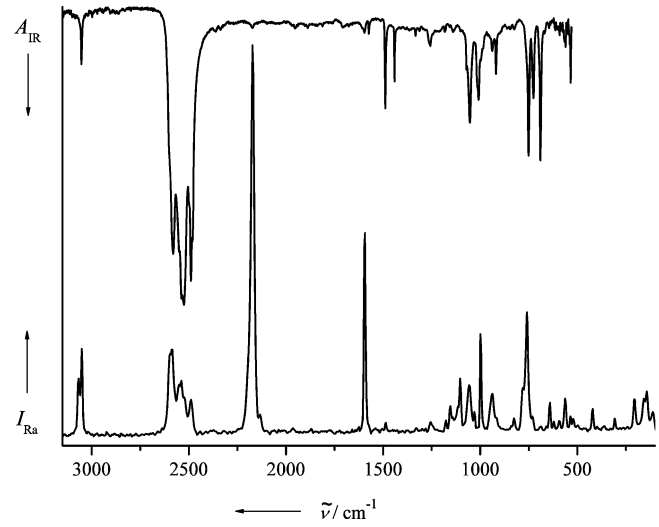

Figure 6. IR and Raman spectrum of $Cs[12\text{-}PhCC\text{-}closo\text{-}CB_{11}H_{11}]$ (Cs^+**1**).

The $^1J(^{13}C,^{11}B)$ coupling constants of the carba-*closo*-dodecaborate anions are between the respective coupling constants found for related tetrahedral borate anions, which exhibit smaller values, for example, in $[B(CCPh)_4]^-$ ($^1J(^{13}C,^{11}B) = 70.0$ Hz),[71] and boranes, for which usually larger coupling constants are observed, for example, $pinBCCSiMe_3$ (pin = pinacolato; $^1J(^{13}C,^{11}B) = 137$ Hz; Table 3).[63,70]

The chemical shift of the ^{13}C nucleus in the {*closo*-CB_{11}} clusters of all new anions described in this study is close to the values reported for the corresponding anions with a hydrogen atom(s) bound to boron instead of an alkynyl substituent(s).[2,36] This result is remarkable since large effects on $\delta(^{13}C_{cluster})$ are often found if one or even more substituent(s) at the cluster is (are) changed.[2]

Vibrational Spectroscopy. All salts described in this contribution were studied by IR as well as by Raman spectroscopy, and in Figure 6, the spectra of Cs[12-PhCC-*closo*-$CB_{11}H_{11}$] (Cs^+**1**) are shown. The characteristic B−H stretching bands are observed in the range of 2650−2450 cm^{-1} for all carborates. In the Raman spectra, the most intense band is assigned to ν(C≡C). The intensities of the respective bands in the IR spectra differ, depending on the substituent bound to the ethynyl subunit: for PhCC groups, a very weak band is observed, whereas for Me_3SiCC fragments, a band with medium intensity is found. The band positions are approximately 2180 cm^{-1} for ν(C≡C) of PhCC and 2120 cm^{-1} for ν(C≡C) of Me_3SiCC. These findings are in agreement to reports on other alkynyl boron compounds, for example, 9-R-1,2-$C_2B_{10}H_{11}$[24] and $[(C_2F_5)_3BCCR]^-$[61] (R = Ph, Me_3SiCC; Table 3).

For the $[1\text{-}PhCC\text{-}closo\text{-}CB_{11}H_{11}]^-$ anion in its cesium salt, a band position of 2250 cm^{-1} for the CC triple-bond stretch was reported,[72] and the calculated value is 2318 cm^{-1} (B3LYP/6-311++G(d,p)). The respective values for its isomer $[12\text{-}PhCC\text{-}closo\text{-}CB_{11}H_{11}]^-$ (**1**) are 2171 and 2265 cm^{-1}. These different behaviors display the different properties of the boron atoms and the carbon atom in the {*closo*-CB_{11}} cluster. In contrast, the differences of the wavenumbers for ν(C≡C) in the phenylethynyl groups bonded to different boron atoms in the anions presented in this study are small and compare well to the ν(C≡C) values of 9-PhCC-1,2-$C_2B_{10}H_{11}$[24] and $Cs[(C_2F_5)_3BCCPh]$[61] (Table 3).

Summary and Conclusions

In this contribution, the first examples of *closo*-carborate anions with alkynyl groups bonded to boron are described. The alkynyl substituent(s) is (are) attached to the 12-, 7-, and 7,12-position(s) of the {CB_{11}} cluster: $[12\text{-}RCC\text{-}closo\text{-}CB_{11}H_{11}]^-$ (R = Ph (**1**), Me_3Si (**3**)), $[1\text{-}Ph\text{-}12\text{-}RCC\text{-}closo\text{-}CB_{11}H_{10}]^-$ (R = Ph (**2**), Me_3Si (**4**)), $[7\text{-}RCC\text{-}12\text{-}Hal\text{-}closo\text{-}CB_{11}H_{10}]^-$ (R = Ph; Hal = F (**5**), Cl (**6**), Br (**7**), R = Me_3Si; Hal = F (**8**)), and $[7,12\text{-}(RCC)_2\text{-}closo\text{-}CB_{11}H_{10}]^-$ (R = Ph (**9**), Me_3Si (**10**)). Preparation of these anions through Pd-catalyzed Kumada-type cross-coupling reactions using salts of the corresponding iodinated clusters as starting materials is straightforward, and isolation of their $[Et_4N]^+$ salts does not require any elaborate purification procedures.

Especially the {CB_{11}} clusters containing trimethylsilylalkynyl groups are attractive ligands for transition-metal complexes, in analogy to the closely related dicarba-*closo*-dodecaboranes: $[M(1\text{-}C{\equiv}C\text{-}1,2\text{-}closo\text{-}C_2B_{10}H_{11})_2(Ph_3P)_2]$ (M = Pd, Pt),[73] $[\{CpFe(CO)_2\}_2\{\mu\text{-}1,12\text{-}(C{\equiv}C)_2\text{-}1,12\text{-}closo\text{-}C_2B_{10}H_{10}\}_2]$,[74] $[\{1,12\text{-}(trans\text{-}Pt(PEt_3)_2\text{-}C{\equiv}C)_2\text{-}1,12\text{-}C_2B_{10}H_{10}\}\{Pt(dppp)(\mu\text{-}4\text{-}C{\equiv}C\text{-}(C_5H_4N))_2\}]_4(CF_3SO_3)_8$,[75] and

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[{Cp*Ru(dppe)$_2$}$_2${μ-1,12-(C≡C)$_2$-1,12-*closo*-$C_2B_{10}H_{10}$}$_2$].[76] Furthermore, the partially alkynylated *closo*-carborate anions are attractive starting materials for the preparation of {CB_{11}} clusters with various other functional groups. This is particularly interesting because derivatives of the [*closo*-$CB_{11}H_{12}]^-$ anion with functional groups bonded to boron, which can be easily and selectively modified, are rare.[2] First studies on the reactivity of the alkynylated carba-*closo*-dodecaborate anions described herein are currently in progress.

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Supporting Information Available: A table containing experimental bond lenghts of the {*closo*-CB_{11}} cluster in the [7-PhCC-12-Cl-*closo*-$CB_{11}H_{10}]^-$ anion in $[Et_4N]^+$**6** (Table S1) and a table containing experimental and calculated ^{11}B as well as ^{13}C NMR spectroscopic data (Table S2). X-ray crystallographic files in CIF format for Cs[12-PhCC-*closo*-$CB_{11}H_{11}$] (Cs^+**1**) and $[Et_4N]$[7-PhCC-12-Cl-*closo*-$CB_{11}H_{10}$] ($[Et_4N]^+$**6**). This material is free of charge via the Internet at http://pubs.acs.org.

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