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Carba-*closo*-dodecaborate Anions with Two Functional Groups: [1-R-12-HC$\equiv$C-*closo*-1-$CB_{11}H_{10}$]$^-$ (R = CN, NC, CO_2H, $C(O)NH_2$, NHC(O)H)

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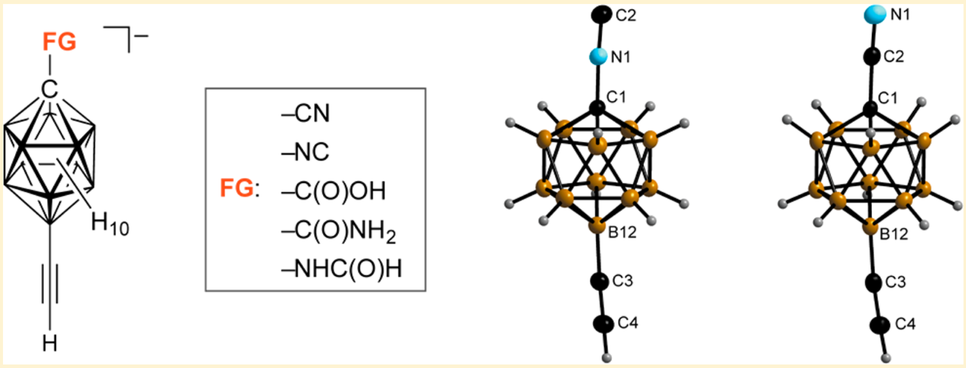
Supporting Information



ABSTRACT: Disubstituted carba-*closo*-dodecaborate anions with one functional group bonded to the cluster carbon atom and one ethynyl group bonded to the antipodal boron atom were synthesized from easily accessible {*closo*-1-CB_{11}} clusters. $[Et_4N]$[1-NC-12-HC$\equiv$C-*closo*-1-$CB_{11}H_{10}$] ($[Et_4N]$**4b**) was prepared starting from Cs[12-Et_3SiC$\equiv$C-*closo*-1-$CB_{11}H_{11}$] (Cs**1c**) via salts of the anions [1-HO(O)C-12-HC$\equiv$C-*closo*-1-$CB_{11}H_{10}$]$^-$ (**2b**) and [1-H_2N(O)C-12-HC$\equiv$C-*closo*-1-$CB_{11}H_{10}$]$^-$ (**3b**). In a similar reaction sequence $[Et_4N]$[1-CN-12-HC$\equiv$C-*closo*-1-$CB_{11}H_{10}$] ($[Et_4N]$**7b**) was obtained from Cs[1-H_2N-12-HC$\equiv$C-*closo*-1-$CB_{11}H_{10}$] (Cs**5b**) by formamidation to yield $[Et_4N]$[1-H(O)CHN-12-HC$\equiv$C-*closo*-1-$CB_{11}H_{10}$] ($[Et_4N]$**6b**) and successive dehydration. In addition, the synthesis of the isonitrile $[Et_4N]$[1-CN-*closo*-1-$CB_{11}H_{11}$] ($[Et_4N]$**7a**) is presented. The {*closo*-1-CB_{11}} derivatives were characterized by multinuclear NMR as well as vibrational spectroscopy, mass spectrometry, and elemental analysis. The crystal structures of $[Et_4N]$[1-HO(O)C-12-HC$\equiv$C-*closo*-1-$CB_{11}H_{10}$] ($[Et_4N]$**2b**), $[Et_4N]$[1-H_2N(O)C-12-HC$\equiv$C-*closo*-1-$CB_{11}H_{10}$] ($[Et_4N]$**3b**), $[Et_4N]$[1-NC-12-HC$\equiv$C-*closo*-1-$CB_{11}H_{10}$] ($[Et_4N]$**4b**), $[Et_4N]$[1-H(O)CHN-12-HC$\equiv$C-*closo*-1-$CB_{11}H_{10}$] ($[Et_4N]$**6b**), $[Et_4N]$[1-CN-12-HC$\equiv$C-*closo*-1-$CB_{11}H_{10}$] ($[Et_4N]$**7b**), and K[1-H(O)CHN-*closo*-1-$CB_{11}H_{11}$] ($[Et_4N]$**6a**) were determined. The transmission of electronic effects through the carba-*closo*-dodecaboron cage was studied based on ^{13}C NMR spectroscopic data, by results derived from density functional theory calculations, and by a comparison to the data of related benzene and bicyclo[2.2.2]octane derivatives.

INTRODUCTION

Carba-*closo*-dodecaborate anions have attracted considerable interest because of their unique chemical and physical properties.[1−3] Derivatives of the carborate anion are thermally and chemically highly stable, in general. Especially, salts of per- and polyhalogenated or trifluormethylated {*closo*-1-CB_{11}} anions often exhibit an extraordinary high chemical resistance and low nucleophilicity.[4−6] Therefore, these negatively charged clusters have been applied as very weakly coordinating anions and a number of highly reactive cations have been stabilized in their presence.[6−9] A variety of applications with these weakly interacting anions have been reported or suggested, for example, in catalysis,[8,10] ionic liquids,[9,11] and as strong oxidizing reagents.[5,12]

A further unusual property of boron clusters in general and of the carborate cage in particular is three-dimensional σ-aromaticity,[13] which leads to compounds and materials with unusual electronic properties. Furthermore, the icosahedral {*closo*-1-CB_{11}} cluster that has local C_{5v} symmetry offers the possibility to realize unusual geometrical arrangements. Recently, {*closo*-1-CB_{11}} clusters with one or more functional substituents have gained increasing interest, which is due to the aforementioned unusual properties of the anionic carba-*closo*-dodecaboron cage.[1,2] Examples for {*closo*-1-CB_{11}} anions with one or two functional groups include clusters with carboxyl groups,[14−18] cyano substituents,[19,20] amino groups,[14,17,21−23]

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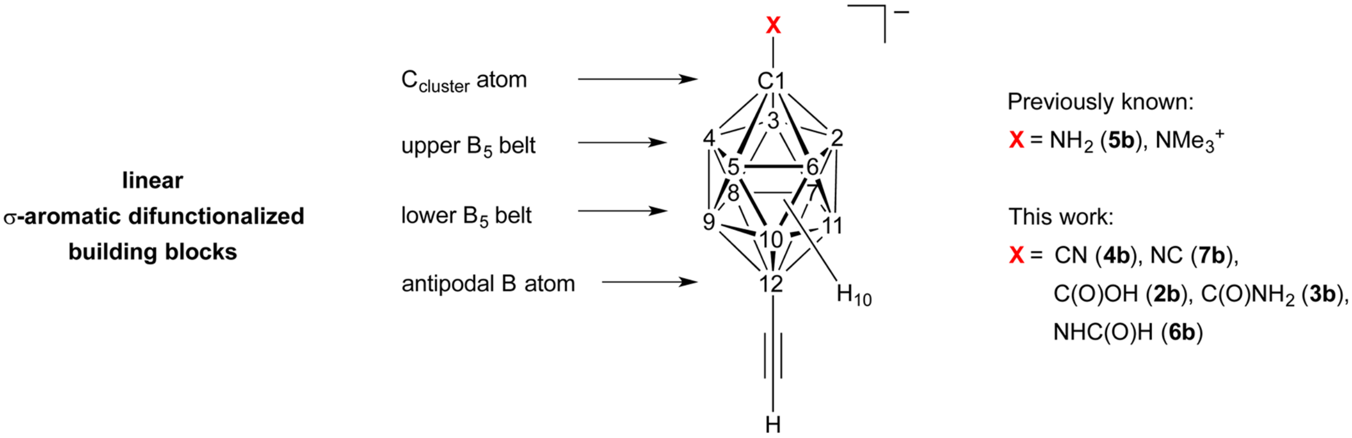
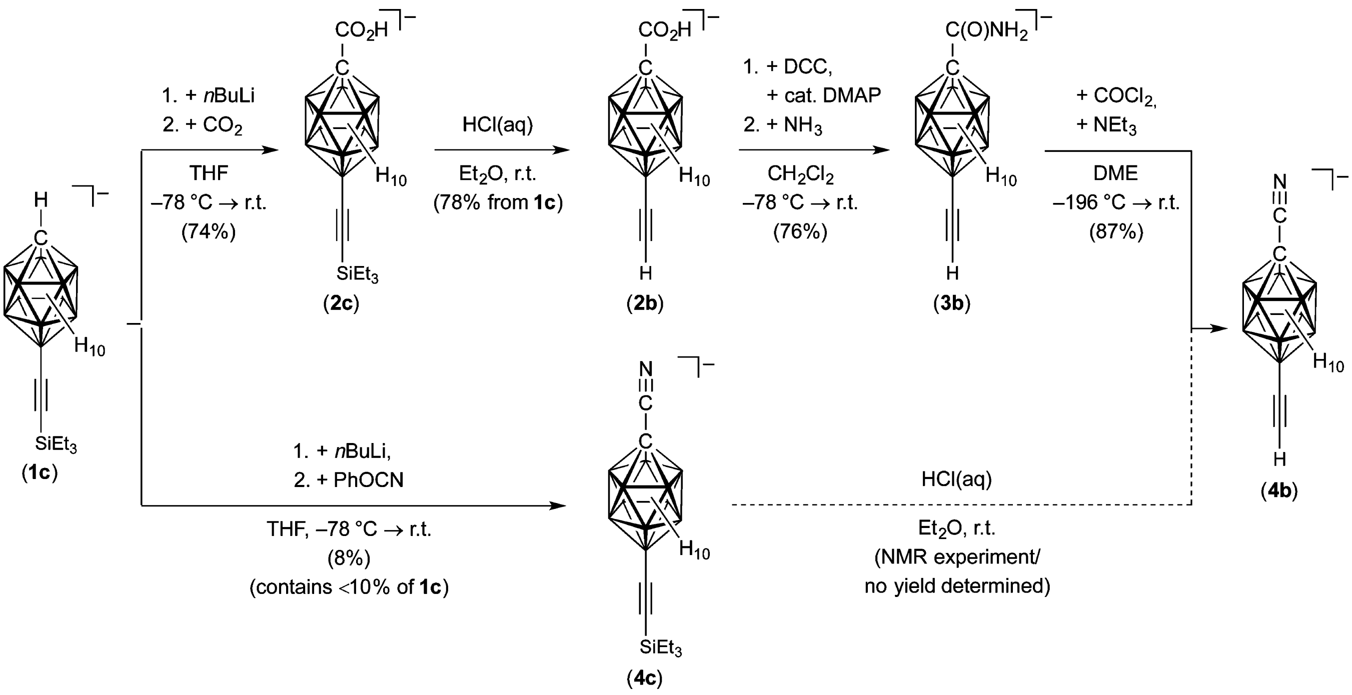
Scheme 1. Labeling Scheme for the {*closo*-1-CB_{11}} Cluster and Denotation of the Previously Known 1,12-Difunctionalized {1-X-12-HC≡C-*closo*-1-$CB_{11}H_{10}$} Derivatives[23] and the Ones That Are Described in This Contribution



Scheme 2. Syntheses of the [1-NC-12-HC≡C-*closo*-1-$CB_{11}H_{10}$]$^-$ Anion (4b)[a]



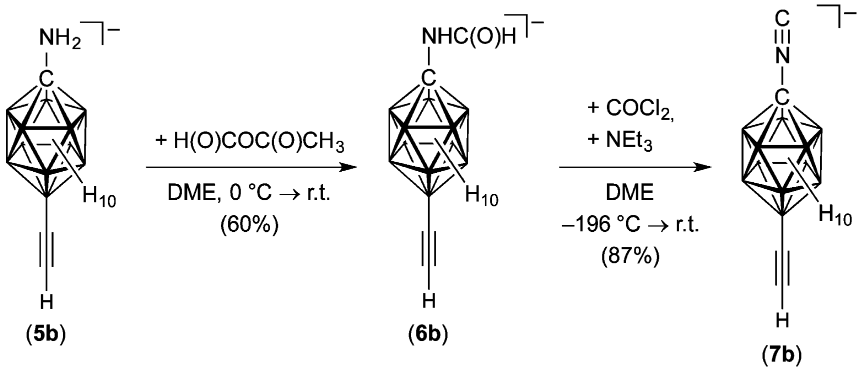
[a]Yields are reported for the respective $[Et_4N]^+$ salts; DCC = *N*,*N*′-dicyclohexylcarbodiimide; DMAP = 4-(dimethylamino)pyridine.

phospanyl moieties,[24,25] and ethynyl groups,[23,26,27] as well as *N*-heterocyclic carbenes with {*closo*-1-$CB_{11}H_{11}$} moieties connected via the $C_{cluster}$ atom to the nitrogen atoms[28] and {*closo*-1-CB_{11}} derivatives with aryl and related groups that have functional substituents.[29,30] Some of these functionalized carba-*closo*-dodecaboron derivatives have been used for applications, e.g. in medicine and biochemistry,[30,31] for the preparation of ionic liquid crystals,[16,18,30,32] in catalysis,[25] and as novel ligands in coordination chemistry.[33]

Recently, we reported on difunctionalized {*closo*-1-CB_{11}} clusters that have an ethynyl group bonded to the antipodal B atom and an amino group that is attached either to the $C_{cluster}$ atom or to one of the B atoms of the upper B_5 belt (Scheme 1).[23] Especially salts of the linearly difunctionalized [1-H_2N-12-HC≡C-closo-1-$CB_{11}H_{10}$]$^-$ anion are easily accessible and have therefore a high potential to serve as versatile linear building blocks. So far only one reaction of a salt of the [1-H_2N-12-HC≡C-closo-1-$CB_{11}H_{10}$]$^-$ anion to yield the inner salt 1-Me_3N-12-HC≡C-*closo*-1-$CB_{11}H_{10}$ was reported.[23]

Here, we report on salts of novel 1,12-difunctionalized carba-*closo*-dodecaborate anions of the type [1-X-12-HC≡C-*closo*-1-$CB_{11}H_{10}$]$^-$ (X = CN (**4b**), NC (**7b**), C(O)OH (**2b**), C(O)NH_2 (**3b**), NHC(O)H (**6b**)) (Scheme 1). In addition, a new synthetic route to salts of the anion [1-NC-*closo*-1-$CB_{11}H_{11}$]$^-$ (**4a**) as well as first syntheses of salts of the isoelectronic [1-CN-*closo*-1-$CB_{11}H_{11}$]$^-$ anion (**7a**) are described. The functional group that is bonded to the $C_{cluster}$ atom significantly influences the properties of the ethynyl moiety that is bonded to the antipodal atom as evident from ^{13}C NMR spectroscopic data. The experimental results are supported by data derived from density functional theory (DFT) calculations. These combined experimental and theoretical results provide an insight on the transmittance of electronic effects through the {*closo*-1-CB_{11}} cage. In addition,

Scheme 3. Syntheses of the [1-CN-12-HC≡C-*closo*-1-CB$_{11}$H$_{10}$]$^-$ Anion (7b)^a



^{a}Yields are reported for the respective [Et$_4$N]$^+$ salts.

structural and bonding properties of the doubly substituted clusters are described.

■ RESULTS AND DISCUSSION

Synthetic Aspects. M[1-NC-12-HC≡C-*closo*-1-CB$_{11}$H$_{10}$] (M = [Et$_4$N]$^+$ ([Et$_4$N]4b), Cs (Cs4b)). The deprotonation of Cs[12-Et$_3$SiC≡C-*closo*-1-CB$_{11}$H$_{11}$] (Cs**1c**) with *n*BuLi and subsequent reaction with carbon dioxide followed by aqueous workup yielded the carboxylic acid derivative [1-HO$_2$C-12-Et$_3$SiC≡C-*closo*-1-CB$_{11}$H$_{10}$]$^-$ (**2c**) that was isolated as [Et$_4$N]$^+$ salt (Scheme 2). Similar syntheses have been described for salts of the anions [1-HO$_2$C-12-R-*closo*-1-CB$_{11}$H$_{10}$]$^-$ (R = H (**2a**), I), earlier.[14−16] Cleavage of the Et$_3$Si protecting group led to [1-HO$_2$C-12-HC≡C-*closo*-1-CB$_{11}$H$_{10}$]$^-$ (**2b**), which was isolated as [Et$_4$N]$^+$ salt. The carboxylic acid derivative was converted to the acid amide compound [Et$_4$N][1-H$_2$N(O)C-12-HC≡C-*closo*-1-CB$_{11}$H$_{10}$] ([Et$_4$N]**3b**) with *N*,*N*′-dicyclohexylcarbodiimide (DCC), ammonia, and catalytic amounts of 4-(dimethylamino)pyridine (DMAP). Dehydration of the amide **3b** with phosgene and Et$_3$N gave the nitrile [Et$_4$N][1-NC-12-HC≡C-*closo*-1-CB$_{11}$H$_{10}$] ([Et$_4$N]**4b**). The overall yield of the four-step synthesis starting from Cs**1c** was 52%.

The parent nitrile [Et$_4$N][1-NC-*closo*-1-CB$_{11}$H$_{11}$] ([Et$_4$N]**4a**) was obtained via an analogous four-step procedure with Cs[*closo*-1-CB$_{11}$H$_{12}$] as the starting material. Earlier, we reported on an alternative synthesis for salts of anion **4a** that employs Cs[*closo*-1-CB$_{11}$H$_{12}$] as starting material, as well.[20] Deprotonation of the cluster with *n*BuLi followed by the reaction with PhOCN yielded a mixture of salts of the anions [1-NC-*closo*-1-CB$_{11}$H$_{11}$]$^-$ and [*closo*-1-CB$_{11}$H$_{12}$]$^-$. Only the repeated deprotonation followed by electrophilic cyanation gave [Et$_4$N]**4a** with a purity of more than 95%. Hence, the method described herein is (i) more convenient and (ii) gives the cyano substituted {*closo*-1-CB$_{11}$} in higher purity.

In analogy to the electrophilic cyanation to yield [Et$_4$N]**4a**,[20] Cs[12-Et$_3$SiC≡C-*closo*-1-CB$_{11}$H$_{11}$] (Cs**1c**) was deprotonated with ^{n}BuLi and cyanated with phenyl cyanate. Similar to the reaction of the parent carba-*closo*-dodecaborate anion, a mixture of the [Et$_4$N]$^+$ salts **1c** and **4c** was obtained. Recrystallization of the tetraethylammonium salts gave [Et$_4$N]**4c** in a yield of 8% with less than 10% of [Et$_4$N]**1c** (Scheme 2). Desilylation of **1c** with hydrochloric acid was achieved, but the procedure was not optimized.

The carboxylic acid and the cyano derivative [Et$_4$N]**2b** and [Et$_4$N]**4b** were converted to the cesium salts Cs**2b** and Cs**4b**. In the first step, the tetraethylammonium salts were taken up into diethyl ether and hydrochloric acid. The ethereal layer that contained the carba-*closo*-dodecaborate anions was treated with aqueous Cs$_2$CO$_3$ to yield the respective cesium salt.

Cs**2b** is a weak acid in aqueous solution. Its pK_a of 3.3 ± 0.2 was determined by potentiometric titration. This value is in good agreement to the pH dependent NMR spectra that have been measured for Cs**2b** in water at different pH values. For example, the ^{13}C NMR signals of the C$_{\text{cluster}}$ atom and the C atom of the carboxylic acid group are both shifted to smaller resonance frequencies with decreasing pH in the range from 4.4 to ∼1. A smaller effect is found for the signals of the C atoms of the ethynyl group. The signal of the C atom that is bonded to the B12 atom is shifted to a slightly smaller resonance frequency whereas for the signal of the terminal C atom a reverse trend is observed (Figure S6 in the Supporting Information). For the related parent acid derivative K[1-HO(O)C-*closo*-1-CB$_{11}$H$_{11}$] a pK_a of 3.3 ± 0.1 was determined, as well. [Et$_4$N][1-HO(O)C-*closo*-1-CB$_{11}$H$_{11}$] in a water ethanol mixture (1/1, v/v) was reported to be significantly less acidic (pK_a = 6.17 ± 0.02).[17]

[Et$_4$N][1-CN-12-HC≡C-*closo*-1-CB$_{11}$H$_{10}$] ([Et$_4$N]7b). The formamidation of the primary amine K[1-H$_2$N-12-HC≡C-*closo*-1-CB$_{11}$H$_{10}$] (K**5b**)[23] was achieved with acetic formic anhydride. The mixed anhydride[34] was either used as pure compound[35] or it was prepared from an excess of formic acid and acetic acid anhydride prior to the formamidation reaction.[36] [Et$_4$N][1-H(O)CHN-12-HC≡C-*closo*-1-CB$_{11}$H$_{10}$] ([Et$_4$N]**6b**) was dehydrated with COCl$_2$ and triethylamine as base[37] to yield [Et$_4$N][1-CN-12-HC≡C-*closo*-1-CB$_{11}$H$_{10}$] ([Et$_4$N]**7b**) in an overall yield of 52% for the two-step procedure (Scheme 3).

The tetraethylammonium salt of the previously unknown, monofunctionalized cluster [1-CN-*closo*-1-CB$_{11}$H$_{11}$]$^-$ (**7a**) was obtained from K[1-H$_2$N-*closo*-1-CB$_{11}$H$_{11}$] (K**5a**)[14,21] following the two-step procedure outlined for the synthesis of [Et$_4$N]**7b** in Scheme 3. A number of other dehydration procedures were tested for K[1-H(O)CHN-*closo*-1-CB$_{11}$H$_{11}$], e.g. POCl$_3$/Et$_3$N. However, all other attempts failed, so far. Dehydration of related 1-H(O)CHN-*closo*-1,12-C$_2$B$_{10}$H$_{11}$ to give 1-CN-*closo*-1,12-C$_2$B$_{10}$H$_{11}$ remained unsuccessful, at all.[38] In contrast, the successful preparation of a first complex with this isocyanide [Re(1-CN-*closo*-1,12-C$_2$B$_{10}$H$_{11}$)$_6$]$^+$ was reported.[39]

In contrast to [1-NC-12-HC≡C-*closo*-1-CB$_{11}$H$_{10}$]$^-$ (**4b**) and [1-NC-*closo*-1-CB$_{11}$H$_{11}$]$^-$ (**4a**),[20] the isocyano derivatives [1-CN-12-HC≡C-*closo*-1-CB$_{11}$H$_{10}$]$^-$ (**7b**) and [1-CN-*closo*-1-CB$_{11}$H$_{11}$]$^-$ (**7a**) are sensitive toward dilute aqueous acids.

Table 1. Selected Experimental and Calculated[a] Bond Properties[b]

						d(B–B)[c]				
anion	d(C≡C)	d(B12–C)	d(N≡C)	$d(C_{cluster}–X)$	$d(C_{cluster}–B)$	upper belt	inter belt	lower belt	antipodal	ref
4b[d]	118.9(3)	155.5(3)	114.6(2)	145.0(2)	171.8(2)	179.5(3)	176.8(2)	179.3(3)	178.6(3)	*e,f*
	121.0	154.3	115.5	143.8	172.5	179.3	176.8	179.2	179.2	*e*
[1-NC-*closo*-1-$CB_{11}H_{11}]^-$ (**4a**)			115.5	143.9	172.6	179.3	177.0	178.8	178.5	20,*g*
7b[h]	117.0(3)	154.3(3)	114.6(3)	141.6(2)	170.7(3)	178.7(4)	176.3(3)	178.9(4)	178.6(3)	*e,f*
	121.0	154.3	117.0	140.1	172.2	179.1	176.8	179.2	179.2	*e*
[1-CN-*closo*-1-$CB_{11}H_{11}]^-$ (**7a**)			117.0	140.2	172.2	179.1	177.0	178.8	178.5	*e*
2b[i]	114.6(5)	156.3(5)		149.9(3)	171.7(4)	178.3(3)	177.1(5)	179.0(3)	178.7(4)	*e,f*
	121.1	154.4		150.4	172.3	178.8	176.9	179.1	179.2	*e*
3b[j]	119.2(3)	155.5(3)		152.2(2)	172.1(3)	178.2(3)	177.2(3)	178.1(3)	179.1(3)	*e,f*
	121.1	154.4		152.6	172.3	178.3	176.9	179.0	179.1	*e*
6b[k]	115.8(3)	155.1(3)		143.7(2)	170.3(3)	176.6(4)	175.9(4)	177.3(4)	177.4(3)	*e,f*
	121.0	154.3		144.0	172.0	178.2	176.8	179.1	179.2	*e*
6a[l]				143.6(5)	172.3(5)	178.8(3)	177.6(4)	178.9(3)	178.4(5)	*e,m*
				144.2	172.0	178.2	177.1	178.8	178.6	*e*
[12-HC≡C-*closo*-1-$CB_{11}H_{11}]^-$	117.2(10)	156.8(8)		100(4)	170.6(6)	176.9(7)	176.8(6)	178.7(6)	178.2(6)	27,*n*
	121.1	154.5		119.0	170.7	178.0	177.1	179.2	179.2	27
[*closo*-1-$CB_{11}H_{12}]^-$				112	172.8(5)	175.6(5)	176.0(4)	178.1(4)	177.6(4)	41,*o*
				119.0	170.7	178.0	177.4	178.9	178.6	42

[a] B3LYP/6-311++G(d,p); calculated values are given below the respective experimental values in italics. [b] Bond lengths in pm. [c] Mean values. [d] [1-NC-12-HC≡C-*closo*-1-$CB_{11}H_{10}]^-$ (**4b**). [e] This work. [f] Cation: $[Et_4N]^+$. [g] Anion 4a is disordered in the crystal of its $[Et_4N]^+$ salt. Therefore, no reliable experimental data are available.[20] [h] [1-CN-12-HC≡C-*closo*-1-$CB_{11}H_{10}]^-$ (**7b**). [i] [1-HO(O)C-12-HC≡C-*closo*-1-$CB_{11}H_{10}]^-$ (**2b**). [j] [1-H_2N(O)C-12-HC≡C-*closo*-1-$CB_{11}H_{10}]^-$ (**3b**). [k] [1-H(O)CHN-12-HC≡C-*closo*-1-$CB_{11}H_{10}]^-$ (**6b**). [l] [1-H(O)CHN-*closo*-1-$CB_{11}H_{11}]^-$ (**6a**). [m] Cation: K^+. [n] Cation: Cs^+. [o] Cation: $[Ag(PPh_3)_2]^+$.

Table 2. Selected Experimental and Calculated[a] Spectroscopic Data[b,c]

	4b[d]		**7b**[e]		**2b**[f]		**3b**[g]		**6b**[h]	
	exptl	calcd	exptl	calcd	exptl	calcd	exptl	calcd	exptl	calcd
δ (^{11}B) B2–B6	−14.9	−15.5	−14.6	−15.2	−15.4	−16.4	−15.6	−16.8	−15.3	−16.4
δ (^{11}B) B7–B11	−12.5	−13.0	−13.7	−14.2	−13.2	−13.4	−13.2	−13.6	−13.9	−14.3
δ (^{11}B) B12	−6.1	−6.8	−10.1	−10.8	−8.0	−7.8	−8.5	−9.0	−12.0	$^{-}$12.7
δ (^{13}C) $C_{cluster}$	43.95	48.87	65.74	70.11	65.97	68.54	68.87	73.06	74.65	78.36
δ (^{13}C) ^{13}C≡C	94.54	102.58	94.42	102.40	95.93	103.39	95.88	103.29	95.31	102.34
δ (^{13}C) C≡^{13}C	83.95	78.10	83.95	78.05	83.02	77.40	82.99	77.09	83.09	77.48
δ (^{1}H) BH2–BH6	1.90	2.12	2.01	2.23	1.93	2.15	1.90	2.07	1.94	2.07
δ (^{1}H) BH7–BH11	1.81	2.09	1.74	2.02	1.74	2.07	1.74	2.06	1.72	2.04
δ (^{1}H) CC–^{1}H	2.12	1.17	2.05	1.12	2.04	1.15	2.02	1.11	2.01	1.09
$^{1}J(^{13}C,^{13}C)$ C≡C	n.o.[i]	169.02	n.o.	169.00	n.o.	168.44	n.o.	168.42	n.o.	168.59
$^{1}J(^{13}C,^{11}B)$ B–CC	103.8	106.41	103.7	106.86	101.8	105.91	102.4	105.96	101.7	106.92
$^{2}J(^{13}C,^{11}B)$ B–CC	19.4	22.00	19.6	22.07	17.2	21.88	18.2	21.90	18.2	22.09
$^{1}J(^{13}C,^{1}H)$ CC–H	236.0	229.79	235.3	229.73	235.1	229.07	234.7	229.05	n.o.	229.54
$^{2}J(^{13}C,^{1}H)$ CC–H	45.0	44.17	45.5	44.20	44.7	44.00	42.8	43.99	n.o.	44.18
$\tilde{\nu}$(C≡C)	2061[j]	2149	2064[j]	2149	2060[j]	2147	2061[j]	2147	2063[j]	2148
$\tilde{\nu}$(CC–H)	3262[j,k]	3475	3261[j,l]	3475	3257[j]	3475	3259[j]	3475	3281[j]	3475

[a] B3LYP/6-311++G(d,p); NMR spectroscopic data calculated at the GIAO/B3LYP/6-311++G(2d,p) level of theory. [b] δ in ppm; J in Hz; $\tilde{\nu}$ in cm^{-1}. [c] Solvent for the NMR spectroscopic studies: $(CD_3)_2CO$. [d] [1-NC-12-HC≡C-*closo*-1-$CB_{11}H_{10}]^-$ (**4b**). [e] [1-CN-12-HC≡C-*closo*-1-$CB_{11}H_{10}]^-$ (**7b**). [f] [1-HO(O)C-12-HC≡C-*closo*-1-$CB_{11}H_{10}]^-$ (**2b**). [g] [1-H_2N(O)C-12-HC≡C-*closo*-1-$CB_{11}H_{10}]^-$ (**3b**). [h] [1-H(O)CHN-12-HC≡C-*closo*-1-$CB_{11}H_{10}]^-$ (**6b**). [i] n.o. = not observed. [j] $[Et_4N]^+$ salt. [k] A second band is observed at 3287 cm^{-1}. [l] A second band is observed at 3286 cm^{-1}.

According to NMR spectroscopic data, the main products of the decomposition in aqueous acids are the formamides **6b** and **6a**. However, the stability of the isonitriles is high enough to allow the isolation of trialkylammonium salts as exemplified by the synthesis of $[Me_3NH]$[1-CN-*closo*-1-$CB_{11}H_{11}$] ($[Me_3NH]$ **7a**).

Crystal Structures and Bond Properties. The $[Et_4N]^+$ salts of [1-NC-12-HC≡C-*closo*-1-$CB_{11}H_{10}]^-$ (**4b**) and [1-CN-12-HC≡C-*closo*-1-$CB_{11}H_{10}]^-$ (**7b**) crystallize in the orthorhombic space group *Pbcm* ($Z = 4$) and the monoclinic space group $P2_1/c$ ($Z = 4$), respectively (Table 4). The experimental bond properties of the ethynyl group and the {*closo*-1-CB_{11}} cage of both anions are very similar, which is in good agreement to results of DFT calculations (Table 1). Within the accuracy of the experiment no difference for d(C≡N) of the isoelectronic anions is found (114.6(2) pm for **4b**; 114.6(3) pm for **7b**) (Figure 1). However, a slightly longer C≡N bond is predicted for the isocyanide **7b** (117.0 pm) than for the cyanide **4b** (115.5 pm) by DFT calculations, which is in agreement to (i) the lower $\tilde{\nu}$(C≡N) of **7b** (Table 3) and (ii) the general trend of longer d(C≡N) of isocyanides compared to cyanides.[40] The carba-*closo*-dodecaborate anions [1-NC-*closo*-1-$CB_{11}H_{11}]^-$ (**4a**)

Table 3. Selected Experimental and Calculated[a] Spectroscopic Data[b,c]

	4a[d]		**4b**[e]		**7a**[f]		**7b**[g]	
	exptl	calcd	exptl	calcd	exptl	calcd	exptl	calcd
δ (^{13}C) $C_{cluster}$	46.74	51.13	43.95	48.87	67.79[h]	71.51	65.74	70.11
δ (^{13}C) C_{CN}	120.14	126.89	120.28	127.15	150.88[h]	158.43	152.09	160.32
δ (^{15}N) N_{CN}	−152.7	−126.9	−150.9	−124.36	−201.1	−172.2	n.o.[i]	−172.9
$^{1}J(^{13}C,^{15}N)$ C≡N	16	11.5	17.1	11.5	6.6[h]	6.5	n.o.	6.5
$^{1}J(^{13}C,^{13}C)$ $C_{cluster}$−CN	n.o.	85.9	n.o.	86.6				
$^{2}J(^{13}C,^{15}N)$ $C_{cluster}$−CN	n.o.	−2.3	n.o.	−2.3				
$^{1}J(^{13}C,^{15}N)$ $C_{cluster}$−NC					n.o.	11.6	n.o.	12.0
$^{2}J(^{13}C,^{13}C)$ $C_{cluster}$−NC					7[h]	−9.3	n.o.	−9.3
$\tilde{\nu}$(C≡N)	2252[j]	2333	2245[k]	2335	2144[k]	2214	2136[k]	2212

[a] B3LYP/6-311++G(d,p); NMR spectroscopic data calculated at the GIAO/B3LYP/6-311++G(2d,p) level of theory. [b] δ in ppm; J in Hz; $\tilde{\nu}$ in cm^{-1}. [c] Solvent for the NMR spectroscopic studies: $(CD_3)_2CO$. [d] $[1\text{-NC-}closo\text{-}1\text{-}CB_{11}H_{11}]^-$ (**4a**). [e] $[1\text{-NC-}12\text{-HC}{\equiv}\text{C-}closo\text{-}1\text{-}CB_{11}H_{10}]^-$ (**4b**). [f] $[1\text{-CN-}closo\text{-}1\text{-}CB_{11}H_{11}]^-$ (**7a**). [g] $[1\text{-CN-}12\text{-HC}{\equiv}\text{C-}closo\text{-}1\text{-}CB_{11}H_{10}]^-$ (**7b**). [h] Solvent: CD_3CN. [i] n.o. = not observed. [j] Cs^+ salt.[20] [k] $[Et_4N]^+$ salt.

Table 4. Selected Crystal Data and Details of the Refinement of the Crystal Structures

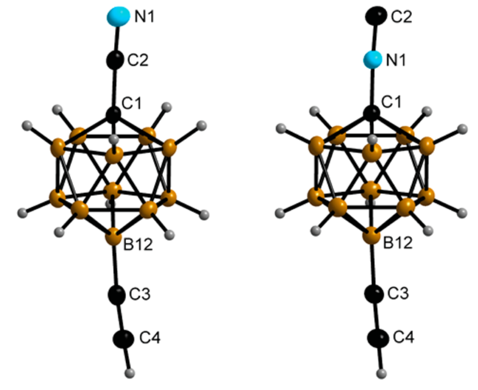
	$[Et_4N]$**2b**[a]	$[Et_4N]$**3b**[b]	$[Et_4N]$**4b**[c]	K**6a**[d]	$[Et_4N]$**6b**[e]	$[Et_4N]$**7b**[f]
empirical formula	$C_{11.96}H_{31.98}B_{11}I_{0.02}NO_2$	$C_{12}H_{33}B_{11}N_2O$	$C_{12}H_{31}B_{11}N_2$	$C_2H_{13}B_{11}KNO$	$C_{12}H_{33}B_{11}N_2O$	$C_{12}H_{31}B_{11}N_2$
formula wt	343.36	340.31	322.30	225.14	340.31	322.30
T/K	100	100	100	173	290	290
cryst syst	tetragonal	monoclinic	orthorhombic	monoclinic	orthorhombic	monoclinic
space group	$I4_1/a$	$P2_1/c$	$Pbcm$	$C2/m$	$Pbca$	$P2_1/c$
a/Å	17.3207(9)	10.5828(10)	12.7742(5)	10.7739(7)	13.4171(4)	9.2605(4)
b/Å		7.2500(6)	11.6626(5)	9.2520(6)	13.8162(3)	10.0555(4)
c/Å	26.9149(14)	26.907(3)	13.5228(5)	11.7942(7)	23.3326(6)	22.8852(12)
β/deg		90.570(4)		101.670(7)		97.200(4)
volume/Å^3	8074.6(9)	2064.4(3)	2014.63(14)	1151.35(13)	4325.2(2)	2114.2(2)
Z	16	4	4	4	8	4
D_{calcd}/Mg m^{-3}	1.130	1.095	1.063	1.299	1.045	1.013
μ/mm^{-1}	0.093	0.059	0.053	0.419	0.056	0.051
F(000)	2924.8	728	688	456	1456	688
no. of collected rflns	46 362	12 149	20 051	7497	24 183	34 152
no. of unique rflns, R(int)	3555, 0.032	4028, 0.025	2070, 0.012	1024, 0.051	3795, 0.030	4153/0.031
no. of parameters/restraints	274/24	287/0	191/0	116/0	247/0	230/0
$R1$ ($I > 2\sigma(I)$)	0.065	0.048	0.043	0.037	0.057	0.061
$wR2$ (all)	0.129	0.127	0.129	0.076	0.107	0.136
GOF on F^2	1.224	1.042	1.081	1.056	1.078	1.028
largest diff. peak/hole/e Å^{-3}	0.612/−0.667	0.296/−0.268	0.363/−0.205	0.243/−0.283	0.163/−0.233	0.310/−0.214
CCDC No.	1004 611	1004 610	1004 613	1004 614	1004 612	1004 609

[a] Crystalline $[Et_4N][1\text{-HO(O)C-}12\text{-HC}{\equiv}\text{C-}closo\text{-}1\text{-}CB_{11}H_{10}]$ ($[Et_4N]$**2b**) contained 2% of $[Et_4N][1\text{-HO(O)C-}12\text{-I-}closo\text{-}1\text{-}CB_{11}H_{10}]$ ($[Et_4N]$**2d**). [b] $[Et_4N][1\text{-}H_2N\text{(O)C-}12\text{-HC}{\equiv}\text{C-}closo\text{-}1\text{-}CB_{11}H_{10}]$ ($[Et_4N]$**3b**). [c] $[Et_4N][1\text{-NC-}12\text{-HC}{\equiv}\text{C-}closo\text{-}1\text{-}CB_{11}H_{10}]$ ($[Et_4N]$**4b**). [d] $K[1\text{-H(O)CHN-}closo\text{-}1\text{-}CB_{11}H_{11}]$ (K**6a**). [e] $[Et_4N][1\text{-H(O)CHN-}12\text{-HC}{\equiv}\text{C-}closo\text{-}1\text{-}CB_{11}H_{10}]$ ($[Et_4N]$**6b**). [f] $[Et_4N][1\text{-CN-}12\text{-HC}{\equiv}\text{C-}closo\text{-}1\text{-}CB_{11}H_{10}]$ ($[Et_4N]$**7b**).

and $[1\text{-CN-}closo\text{-}1\text{-}CB_{11}H_{11}]^-$ (**7a**) exhibit very similar bond properties compared to **4b** and **7b**, respectively (Table 1). The only minor differences are slightly longer interatomic distances for the lower part of the boron clusters that reflect the influence of the ethynyl group in **4b** and **7b**, which is bonded to the antipodal B atom. An analogous effect is found for $[closo\text{-}1\text{-}CB_{11}H_{12}]^-$ and $[12\text{-HC}{\equiv}\text{C-}closo\text{-}1\text{-}CB_{11}H_{11}]^-$, as well. Furthermore, the introduction of a cyano or isocyano group at the $C_{cluster}$ atom leads to slightly longer interatomic cluster distances compared to those of $[closo\text{-}1\text{-}CB_{11}H_{12}]^-$ and $[12\text{-HC}{\equiv}\text{C-}closo\text{-}1\text{-}CB_{11}H_{11}]^-$. However, all differences are rather small.

The bond properties of the $C_{cluster}$−CN fragment of the anion $[1\text{-NC-}12\text{-HC}{\equiv}\text{C-}closo\text{-}1\text{-}CB_{11}H_{10}]^-$ (**4b**) are similar to those reported for related boron clusters with $C_{cluster}$−CN vertices: $1,12\text{-(NC)}_2\text{-}closo\text{-}1,12\text{-}C_2B_{10}H_{10}$ (d(C≡N) = 114.3(2) pm; $d(C_{cluster}$−C) = 145.3(2) pm),[43] $1,10\text{-(NC)}_2\text{-}closo\text{-}1,12\text{-}C_2B_8H_8$ (d(C≡N) = 114.6(2) pm; $d(C_{cluster}$−C) = 143.8(2) pm),[44] and $PPN[8\text{-NC-}arachno\text{-}7,8\text{-}C_2B_{10}H_{14}]$ (d(C≡N) = 114.4(7) pm; $d(C_{cluster}$−C) = 145.5(7) pm; PPN^+ = bis(triphenylphosphine)iminium) cation).[45]

The formamide derivatives $[Et_4N][1\text{-H(O)CHN-}12\text{-HC}{\equiv}\text{C-}closo\text{-}1\text{-}CB_{11}H_{10}]$ ($[Et_4N]$**6b**) and $K[1\text{-H(O)CHN-}closo\text{-}1\text{-}CB_{11}H_{11}]$ (K**6a**) crystallize in the orthorhombic space group $Pbca$ (Z = 8) and in the monoclinic space group $C2/m$ (Z = 4), respectively. The tetraethylammonium salt of the acid amide derivative $[1\text{-}H_2N\text{(O)C-}12\text{-HC}{\equiv}\text{C-}closo\text{-}1\text{-}CB_{11}H_{10}]^-$ (**3b**) crystallizes in the monoclinic space group $P2_1/c$ (Z = 4). Each of the three anions **6a**, **6b**, and **3b** forms hydrogen-bonded dimers in the solid state with the inversion center located in their center. The dimers are composed of two hydrogen bonds with the formamide N−H or the acid amide NH−H moieties as donors and the respective O atoms as acceptors. This structural motif is typical for acid amides[46] and



4b **7b**

Figure 1. Anions [1-NC-12-HC≡C-*closo*-1-$CB_{11}H_{10}$]$^-$ (**4b**) and [1-CN-12-HC≡C-*closo*-1-$CB_{11}H_{10}$]$^-$ (**7b**) in the crystals of their $[Et_4N]^+$ salts [ellipsoids are drawn at the 50% ($[Et_4N]$**4b**) and 25% probability level ($[Et_4N]$**7b**) except for H atoms, which are depicted with arbitrary radii]. Selected interatomic distances [Å] and angles [deg] of **4b**: C1−C2 145.0(2), C2−N1 114.6(2), C1−C2−N1 177.5(2); **7b**: C1−N1 141.6(2), N1−C2 114.6(3), C1−N1−C2 176.4(2).

it is classified with the graph set descriptor $R^2_2(8)$.[47] In Figure 2 these dimers are depicted, and selected interatomic distances and angles of the hydrogen-bond motifs are summarized in the caption. The molecular self-assembly of the ethynyl-substituted anions **3b** and **6b** through hydrogen bonds results in almost linear rods with lengths of 2.10 nm (**3b**) and 2.00 nm (**6b**) and with functional groups at both ends.

$[Et_4N]$[1-HO(O)C-12-HC≡C-*closo*-1-$CB_{11}H_{10}$] ($[Et_4N]$**2b**) crystallizes in the tetragonal space group $I4_1/a$ with Z = 16. Four adjacent anions form an almost planar C_4-symmetric hydrogen-bond motif via O−H···O hydrogen bonds (Figure 3). The rare hydrogen-bond motif of this cyclic tetramer can be described with the graph set descriptor $[R^4_4(16)]$.[47] The maximal size of the tetraethynyl-functionalized macrocycle, which corresponds to the distance of the H atoms of two opposite boron clusters, is 2.24 nm. In contrast to the tetrameric hydrogen-bond motif found for anion **2b**, dimeric hydrogen-bond motifs are often observed for carboxylic acids.[46]

The experimental as well as calculated bond parameters of the {*closo*-1-CB_{11}} cage and the ethynyl group of the formamide, acid amide, and carboxylic acid derivatives **6a**, **6b**, **3b**, and **2b** are collected in Table 1. They are similar to those of [1-NC-12-HC≡C-*closo*-1-$CB_{11}H_{10}$]$^-$ (**4b**) and [1-CN-12-HC≡C-*closo*-1-$CB_{11}H_{10}$]$^-$ (**7b**) and to values reported for other {12-HC≡C-*closo*-1-CB_{11}} anions, earlier.[23,27]

NMR Spectroscopy. The new [1-X-12-HC≡C-*closo*-1-$CB_{11}H_{10}$]$^-$ derivatives were characterized by multinuclear NMR spectroscopy and selected experimental NMR spectroscopic data are compared to calculated ones in Tables 2 and 3. Because of the local C_{5v} symmetry of the {*closo*-1-CB_{11}} cage three signals are observed in the ^{11}B NMR spectra. One signal for the antipodal B atom, a second one with a relative intensity

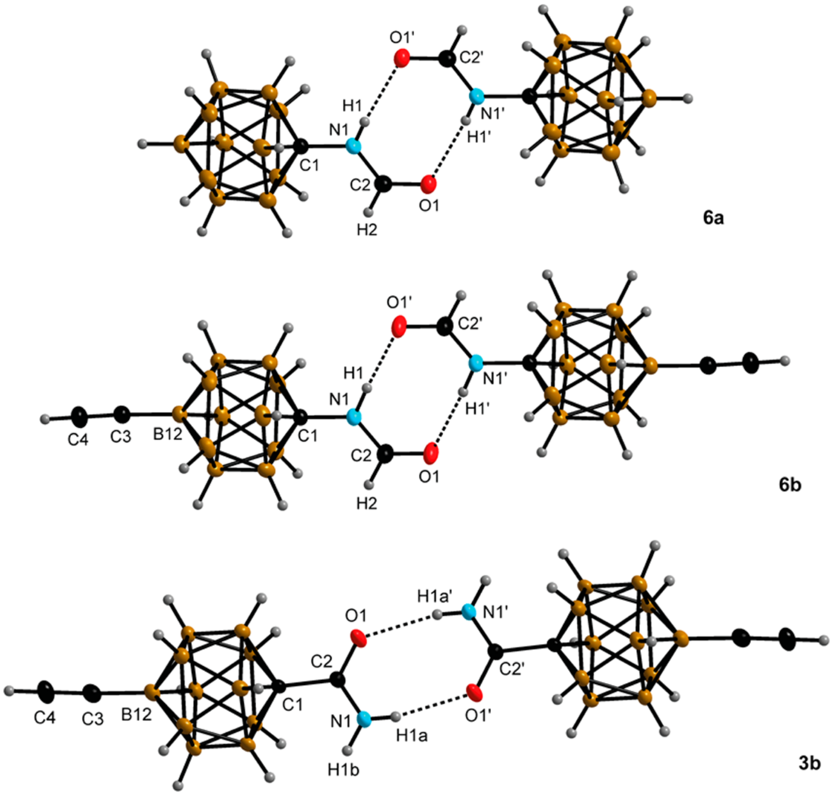


Figure 2. Hydrogen-bond dimers of the anions [1-H(O)CHN-*closo*-1-$CB_{11}H_{11}$]$^-$ (**6a**), [1-H(O)CHN-12-HC≡C-*closo*-1-$CB_{11}H_{10}$]$^-$ (**6b**), and [1-H_2N(O)C-12-HC≡C-*closo*-1-$CB_{11}H_{10}$]$^-$ (**3b**) in the crystals of their K^+ (**6a**) or $[Et_4N]^+$ salt (**6b**, **3b**) [ellipsoids are drawn at the 50% (K**6a**, $[Et_4N]$**3b**) and 25% probability level ($[Et_4N]$**6b**) except for H atoms, which are depicted with arbitrary radii]. Selected interatomic distances [Å] and angles [deg] of **6a**: C1−N1 143.7(5), N1−C2 131.4(4), C2−O1 123.2(4), C2−H2 100(3), N1···O1′ 290.5(4), O1′···H1 214(3), N1−H1 77(3), N1−H1−O1′ 175(3); **6b**: C1−N1 143.7(2), N1−C2 132.2(3), C2−O1 122.6(3), C2−H2 103(2), N1···O1′ 290.8(3), O1′···H1 199(2), N1−H1 92(2), N1−H1−O1′ 176(2); **3b**: C1−C2 152.2(2), C2−O1 122.6(2), C2−N1 132.7(2), N1···O1′ 292.5(2), O1′···H1a 213(2), N1−H1a 81(2), N1−H1b 92(2), N1−H1a−O1′ 167(2), H1a−N1−H1b 121(2).

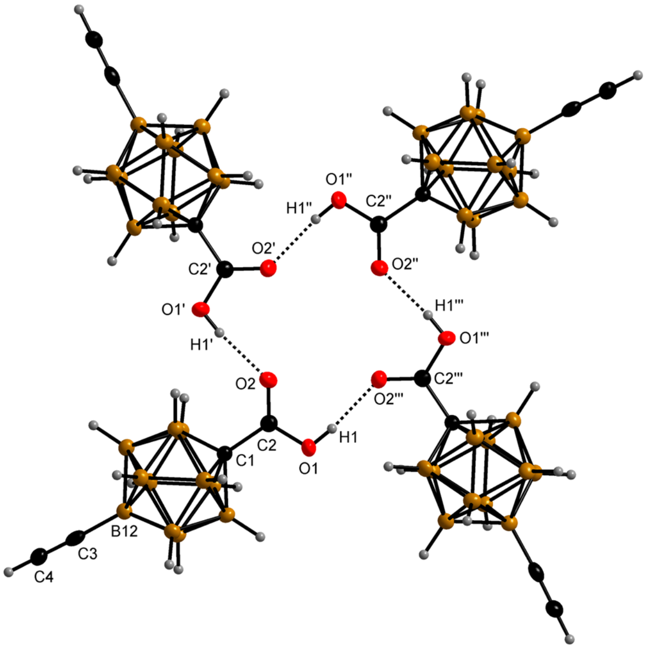


Figure 3. Hydrogen-bond motif of the [1-HO(O)C-12-HC≡C-*closo*-1-$CB_{11}H_{10}$]$^-$ anions (**2b**) in the crystal of [Et_4N]**2b** [50% probability ellipsoids except for H atoms, which are depicted with arbitrary radii]. Selected interatomic distances [Å] and angles [deg]: C1−C2 149.9(3), C2−O1 131.1(3), C2−O2 122.0(3), O1′···O2 274.2(3), O2···H1′ 192(3), O1−H1 83(3), O1′−H1′−O2 175(3).

of 5 for the upper B_5 belt, and a third signal that has a relative intensity of 5, as well, for the lower B_5 belt. In Figure 4 the ^{11}B and ^{11}B{^{1}H} NMR spectra of the anions [1-NC-12-HC≡C-*closo*-1-$CB_{11}H_{10}$]$^-$ (**4b**) and [1-CN-12-HC≡C-*closo*-1-$CB_{11}H_{10}$]$^-$ (**7b**) are depicted. The assignment of the signals with equal intensities is based on ^{11}B{^{1}H}−^{11}B{^{1}H} correlation spectroscopy (COSY) experiments.[48]

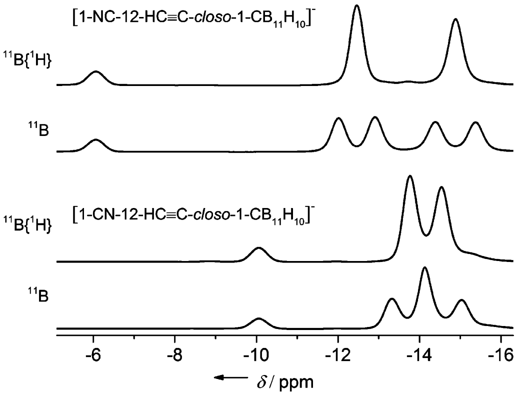


Figure 4. ^{11}B and ^{11}B{^{1}H} NMR spectra of [1-NC-12-HC≡C-*closo*-1-$CB_{11}H_{10}$]$^-$ (**4b**) and [1-CN-12-HC≡C-*closo*-1-$CB_{11}H_{10}$]$^-$ (**7b**).

In the ^{1}H{^{11}B} NMR spectra for the {12-HC≡C-*closo*-1-$CB_{11}H_{10}$} units of **4b** and **7b** two signals are observed for the BH vertices (upper and lower B_5 belt) and one signal for the ethynyl H atom. The assignment of the ^{1}H NMR signals of the H atoms that are bonded to the B atoms is aided by ^{11}B{^{1}H}−^{1}H{^{11}B} two-dimensional (2D)[49] and ^{1}H{^{11}B$_{\text{selective}}$} experiments.

In the ^{13}C NMR spectra of the [1-X-12-HC≡C-*closo*-1-$CB_{11}H_{10}$]$^-$ anions, two signals are observed for the ^{13}C nuclei of the C≡C units. The signal of the C atom that is bonded to the antipodal B atom is split into a quartet with a coupling constant of about 100 Hz, whereas the $^2J(^{13}C,^{11}B)$ coupling constant of the terminal C nucleus is approximately 17−20 Hz (Table 2). In the proton coupled spectra the $^1J(^{13}C,^1H)$ and the $^2J(^{13}C,^1H)$ are observed. In Figure 5 the ^{13}C, ^{13}C{^{1}H}, and ^{13}C{^{11}B,^{1}H} NMR spectra of the anions [1-NC-12-HC≡C-*closo*-1-$CB_{11}H_{10}$]$^-$ (**4b**) and [1-CN-12-HC≡C-*closo*-1-$CB_{11}H_{10}$]$^-$ (**7b**) are plotted.

The most relevant NMR spectroscopic data of the C_{cluster}−CN/NC fragments of the anions [1-NC-12-HC≡C-*closo*-1-$CB_{11}H_{10}$]$^-$ (**4b**) and [1-CN-12-HC≡C-*closo*-1-$CB_{11}H_{10}$]$^-$ (**7b**) are opposed to values of the anions [1-NC-*closo*-1-$CB_{11}H_{11}$]$^-$ (**4a**) and [1-CN-*closo*-1-$CB_{11}H_{11}$]$^-$ (**7a**) in Table 3. In general, chemical shifts and coupling constants of both cyano derivatives **4a** and **4b** are very similar and the data of the isocyano-functionalized clusters **7a** and **7b** are similar, as well. In contrast, the comparison of the NMR spectroscopic data of the cyano versus the isocyano derivatives reveals strong differences. The ^{13}C NMR signals of the C_{cluster} as well as of the C atoms of the CN groups are shifted to higher resonance frequencies for the isocyano derivatives, whereas for $\delta(^{15}N)$ a reverse trend is predicted based upon DFT calculations. $^1J(^{13}C,^{15}N)$ of the CN group is significantly larger for the cyano derivatives **4a** and **4b** compared to the isocyano derivatives **7a** and **7b**. These larger values for **4a** and **4b** indicate stronger C≡N bonds for the cyano groups, which is in agreement to larger $\tilde{\nu}$(C≡N) (Table 3). The differences observed for **4a/b** versus **7a/b** are typical for cyano and isocyano derivatives.[40]

Vibrational Spectroscopy. In Figure 6 the IR and Raman spectra of [Et_4N][1-NC-12-HC≡C-*closo*-1-$CB_{11}H_{10}$] ([Et_4N]**4b**) and [Et_4N][1-CN-12-HC≡C-*closo*-1-$CB_{11}H_{10}$] ([Et_4N]**7b**) are depicted. The most intense bands in the spectra are assigned to ν(B−H) in the region of 2450−2650 cm^{-1}, which is typical for {*closo*-1-CB_{11}} and related boron clusters. The C≡C stretch of **4b** and **7b** is observed as a strong band in the Raman spectrum at 2062 and 2061 cm^{-1}, respectively (Table 2). The intensities of these bands are almost zero in the corresponding IR spectra. Similarly, the IR intensities of the C≡C stretch of **2b**, **3b**, as well as **6b**, and further 7- and 12-ethynyl-substituted {*closo*-1-CB_{11}} derivatives,[23,50] and [1-HC≡C-*closo*-$B_{12}H_{11}$]$^-$[51] are almost zero. In contrast, for ν(C≡C) of dicarba-*closo*-dodecaboranes with the ethynyl group bonded to a B atom, a band of significantly higher intensity (weak to medium) is found in the IR spectra.[50,52] Such different intensities account for different electron distributions (polarizations) in the C≡C moieties.[53,54]

In contrast to ν(C≡C), the $C_{C\equiv C}$−H band of ethynyl-functionalized carba-*closo*-dodecaboron derivatives is medium strong in the respective IR spectrum and only very weak in the Raman spectrum. For **4b** and **7b** the $C_{C\equiv C}$−H bands are split in the IR spectra (Figure 6, Table 2). Presumably, only one of the two bands has to be assigned to ν($C_{C\equiv C}$−H) because only one band is observed for the C≡C stretch, which is in agreement with the results of the crystal structure analyses of only one position of the anions in [Et_4N]**4b** and [Et_4N]**7b** (Z' = 1). Hence, the second band is most likely a combination or an overtone band. Because of Fermi resonance the intensity of a combination or an overtone band is enhanced and a doubtless assignment of ν($C_{C\equiv C}$−H) is not straightforward. Furthermore, if significant Fermi resonance has to be considered the

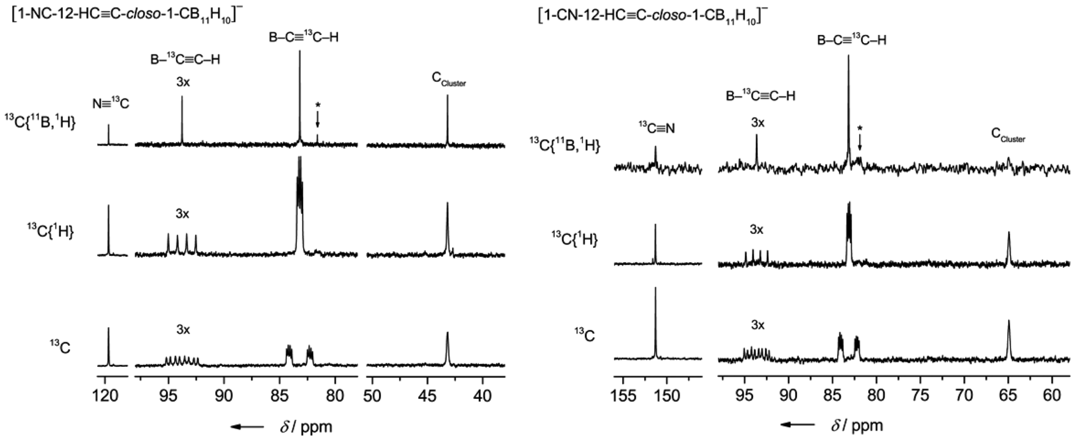


Figure 5. ^{13}C, ^{13}C{^{1}H}, and ^{13}C{^{11}B,^{1}H} NMR spectra of [1-NC-12-HC≡C-*closo*-1-CB$_{11}$H$_{10}$]$^-$ (**4b**) and [1-CN-12-HC≡C-*closo*-1-CB$_{11}$H$_{10}$]$^-$ (**7b**).

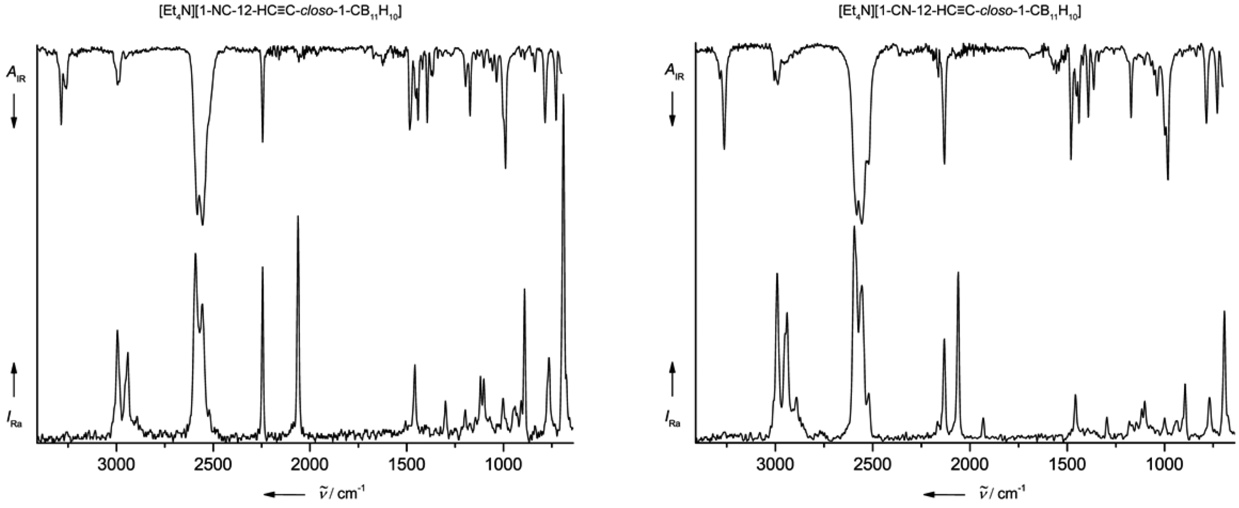


Figure 6. IR and Raman spectra of [Et$_4$N][1-NC-12-HC≡C-*closo*-1-CB$_{11}$H$_{10}$] ([Et$_4$N]**4b**) and [Et$_4$N][1-CN-12-HC≡C-*closo*-1-CB$_{11}$H$_{10}$] ([Et$_4$N]**7b**).

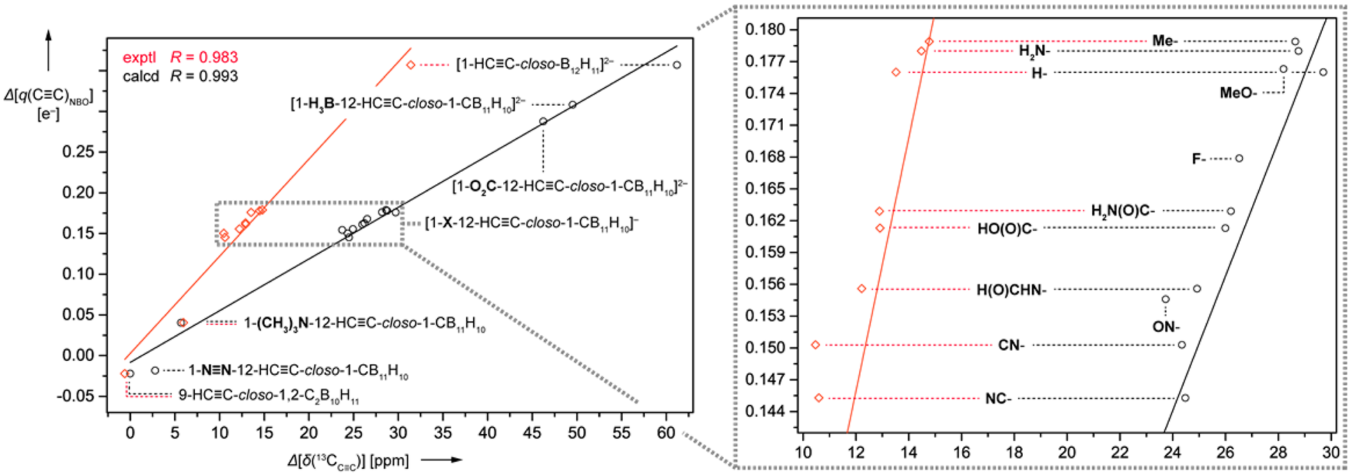


Figure 7. Plot of experimental (red) and calculated (black) Δ[δ(^{13}C$_{C≡C}$)] vs Δ[*q*(C≡C)$_{NBO}$].

band positions are shifted. So, a comparison of the wavenumbers of ν(C$_{C≡C}$−H) of **4b** and **7b** to those of other ethynyl derivatives is arbitrary.

In the IR and Raman spectra of [Et$_4$N]**4b** and [Et$_4$N]**7b** the C≡N stretch is observed at 2245 cm^{-1} for **4b** and at 2212 cm^{-1} for **7b** (Figure 6). These wavenumbers are close to the values observed for Cs[1-NC-*closo*-1-CB$_{11}$H$_{11}$] (Cs**4a**)[20] and [Et$_4$N][1-CN-*closo*-1-CB$_{11}$H$_{11}$] ([Et$_4$N]**7a**), respectively (Table 3). In addition, similar $\tilde{\nu}$(C≡N) have been reported for other carba-*closo*-boron clusters with C$_{cluster}$−CN vertices, for

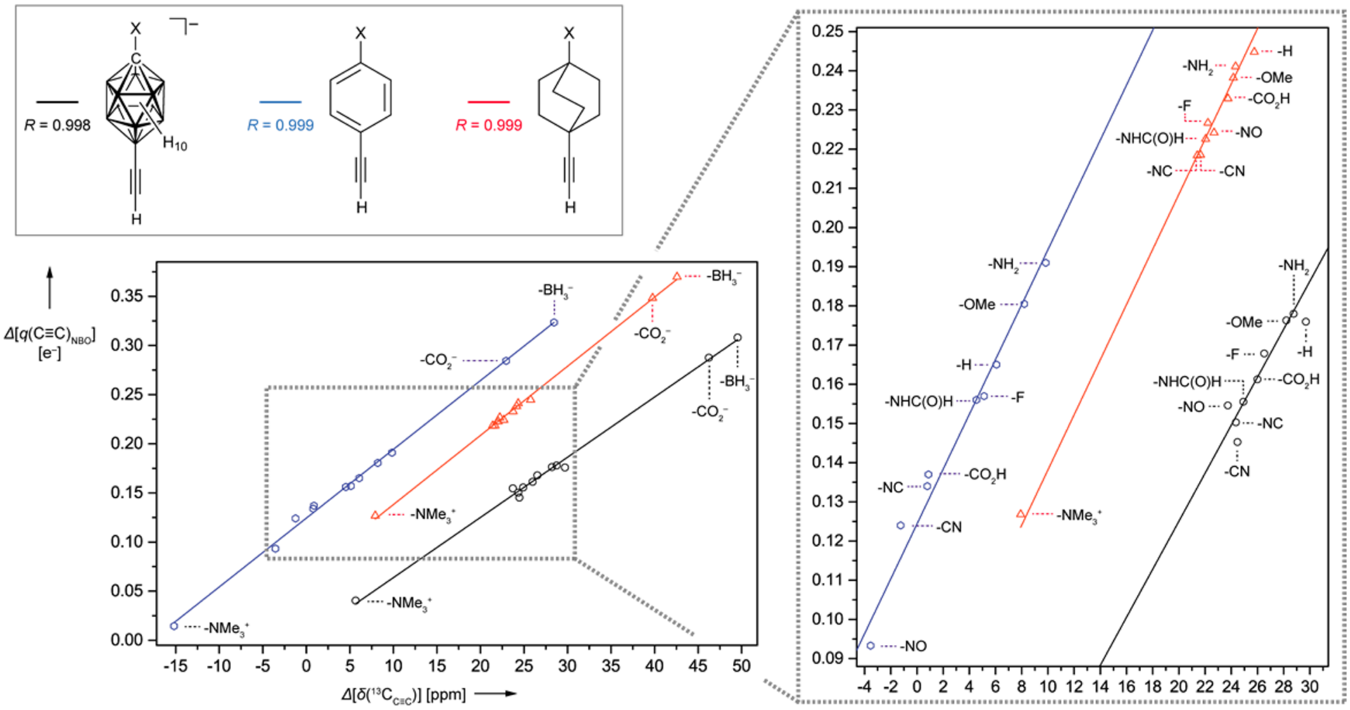


Figure 8. Plots of calculated Δ[δ(^{13}C$_{C≡C}$)] versus Δ[q(C≡C)$_{NBO}$] for [1-X-12-HC≡C-*closo*-1-CB$_{11}$H$_{10}$]$^-$ and related 1-X-4-HC≡C-benzene and 1-X-4-HC≡C-bicyclo[2.2.2]octane derivatives.

example, for [1-NC-*closo*-1-CB$_{11}$Hal$_{11}$]$^-$ (Hal = F, Cl, Br, I) (2246–2262 cm^{-1}),[20] 1-NC-2-Me-*closo*-1,2-C$_2$B$_{10}$H$_{10}$ (2260 cm^{-1}),[55] 1,10-(NC)$_2$-*closo*-1,10-C$_2$B$_8$H$_8$ (2255 cm^{-1}),[44] and 1-NC-10-Ph-*closo*-1,10-C$_2$B$_8$H$_8$ (2260 cm^{-1}).[56]

Trends of Spectroscopic, Electronic, and Bond Properties of Ethynyl Groups of *closo*-Boron Clusters. The difference of the chemical shifts of the C$_{C≡C}$ atoms Δ[δ(^{13}C$_{C≡C}$)] is known to be a measure for the polarization of the electron density of the C≡C units of alkynyl groups.[53,57,58] This explains the linear relationship between Δ[δ(^{13}C$_{C≡C}$)] and the difference of the partial charges of the ethynyl C atoms Δ[q(C≡C)] that was already described for some {1-X-12-HC≡C-*closo*-1-CB$_{11}$H$_{10}$} derivatives, 9-HC≡C-*closo*-1,2-C$_2$B$_{10}$H$_{11}$, and [1-HC≡C-*closo*-B$_{12}$H$_{11}$]$^{2-}$.[23] The anions [1-X-12-HC≡C-*closo*-1-CB$_{11}$H$_{10}$]$^-$ (X = NC (**4b**), CN (**7b**), C(O)OH (**2b**), C(O)NH$_2$ (**3b**), NHC(O)H (**6b**)) and further [1-X-12-HC≡C-*closo*-1-CB$_{11}$H$_{10}$]$^-$ derivatives (X = BH$_3^-$, CO$_2^-$, OMe, F, NO, N≡N$^+$) that were investigated by DFT calculations fit into this series (Tables S2–S4 in the Supporting Information). The calculated Δ[δ(^{13}C$_{C≡C}$)] is approximately twice as large as the respective experimental difference in δ(^{13}C$_{C≡C}$), which is evident from the plots of the experimental as well as the calculated Δ[δ(^{13}C$_{C≡C}$)] against Δ[q(C≡C)$_{NBO}$] (Figure 7) and Δ[q(C≡C)$_{APT}$] (Supporting Information, Figure S2).

The smallest Δ[δ(^{13}C$_{C≡C}$)] and Δ[q(C≡C)$_{NBO}$] are found for the dicarba-*closo*-dodecaborane 9-HC≡C-*closo*-1,2-C$_2$B$_{10}$H$_{11}$, the largest for the dianion [1-HC≡C-*closo*-B$_{12}$H$_{11}$]$^{2-}$, and those of {1-X-12-HC≡C-*closo*-1-CB$_{11}$H$_{10}$} are in between. The differences in Δ[δ(^{13}C$_{C≡C}$)] as well as in Δ[q(C≡C)$_{NBO}$] of the single negatively charged [1-X-12-HC≡C-*closo*-1-CB$_{11}$H$_{10}$]$^-$ derivatives are relatively small compared to the maximum differences. However, the general trend is observed, which is shown by the enlarged section of the correlation diagram in Figure 7. The introduction of a positively charged group at the anionic {*closo*-1-CB$_{11}$} cluster as exemplified by 1-N$_2$-12-HC≡C-*closo*-1-CB$_{11}$H$_{10}$ and 1-Me$_3$N-12-HC≡C-*closo*-1-CB$_{11}$H$_{10}$[23] renders the properties of the ethynyl group to become more similar to those of 9-HC≡C-*closo*-1,2-C$_2$B$_{10}$H$_{11}$. Increasing the overall negative charge as in [1-H$_3$B-12-HC≡C-*closo*-1-CB$_{11}$H$_{10}$]$^{2-}$ and [1-O$_2$C-12-HC≡C-*closo*-1-CB$_{11}$H$_{10}$]$^{2-}$ results in a reverse effect and the properties of the ethynyl group are changed toward those of [1-HC≡C-*closo*-B$_{12}$H$_{11}$]$^{2-}$. The experimental values for [1-O$_2$C-12-HC≡C-*closo*-1-CB$_{11}$H$_{10}$]$^{2-}$ have been omitted in the analysis in Figure 7 because the deprotonation of **2b** was investigated in aqueous solution, only. Hence, the data are not comparable to the other ^{13}C NMR spectroscopic data that were measured in (CD$_3$)$_2$CO or CD$_3$CN. However, as predicted from the calculated chemical shifts an increase of Δ[δ(^{13}C$_{C≡C}$)] for [1-O$_2$C-12-HC≡C-*closo*-1-CB$_{11}$H$_{10}$]$^{2-}$ compared to **2b** was observed in aqueous solution (Figure S1 in the Supporting Information). Selected other experimental and calculated spectroscopic as well as bonding properties of {1-X-12-HC≡C-*closo*-1-CB$_{11}$H$_{10}$} derivatives, 9-HC≡C-*closo*-1,2-C$_2$B$_{10}$H$_{11}$, and [1-HC≡C-*closo*-B$_{12}$H$_{11}$]$^{2-}$ have been related to Δ[q(C≡C)$_{NBO}$] and the respective plots are depicted in Figures S3–S13 in the Supporting Information.

Transfer of Electronic Effects Through the {*closo*-1-CB$_{11}$} Cluster. The dependence of a variety of spectroscopic and bonding properties of the C≡C group of {1-X-12-HC≡C-*closo*-1-CB$_{11}$H$_{10}$} derivatives as described in the previous section provides evidence for the transfer of electronic effects through the {*closo*-1-CB$_{11}$} cage. On the basis of a comparison of the substituent effects on {1-X-12-HC≡C-*closo*-1-CB$_{11}$H$_{10}$} clusters to those of a few related 1-X-4-HC≡C-benzene derivatives, we have presumed that resonance effects are more important for the transfer of electronic effects through the π-aromatic benzene framework than through the σ-aromatic[13] carborate cluster.[23] This assumption is in accord with results of a study on acidity constants of a number of {1-HO(O)C-12-X-*closo*-1-$CB_{11}H_{10}$}, 1-HO(O)C-4-X-benzene, and 1-HO(O)C-4-X-bicyclo[2.2.2]octane derivatives.[17]

Similar to the functionalized {1-X-12-HC$\equiv$C-*closo*-1-$CB_{11}H_{10}$} clusters, excellent linear correlations of $\Delta[\delta(^{13}C_{C\equiv C})]$ versus $\Delta[q(C\equiv C)_{NBO}]$ (Figure 8) and $\Delta[q(C\equiv C)_{APT}]$ (Figure S14 in the Supporting Information) are predicted for related 1-X-4-HC$\equiv$C-benzenes and 1-X-4-HC$\equiv$C-bicyclo[2.2.2]octanes by DFT calculations. The value of such correlations was demonstrated for ethynyl-substituted benzenes[58] and bicyclo[2.2.2]octanes,[53] earlier. It was shown that resonance and inductive effects are important for benzenes whereas for bicyclo[2.2.2]octanes inductive effects are dominant and resonance effects negligible.[53]

The study includes substituents that are either pure σ-donors or σ-acceptors and substituents that display a strong π-effect.[59] Especially informative is the comparison of {*closo*-1-CB_{11}}, benzene, and bicyclo[2.2.2]octane derivatives with neutral uncharged substituents in the expanded section of Figure 8. Compared to the parent 4-HC$\equiv$C$-C_6H_5$, for 1-H_2N-4-HC$\equiv$C$-C_6H_4$ and 1-MeO-4-HC$\equiv$C$-C_6H_4$ $\Delta[\delta(^{13}C_{C\equiv C})]$ and $\Delta[q(C\equiv C)_{NBO}]$ are significantly shifted toward the anionic derivatives $[1\text{-}O_2C\text{-}4\text{-}HC\equiv C-C_6H_4]^-$ and $[1\text{-}H_3B\text{-}4\text{-}HC\equiv C-C_6H_4]^-$. In case of the three respective 4-HC$\equiv$C-bicyclo[2.2.2]octane derivatives a contrary but smaller effect is found while for the [1-X-12-HC$\equiv$C-*closo*-1-$CB_{11}H_{10}$]$^-$ (X = H, NH_2, OMe) anions $\Delta[\delta(^{13}C_{C\equiv C})]$ and $\Delta[q(C\equiv C)_{NBO}]$ are very similar. The amino and the methoxy group are both π-donors. Since resonance effects are negligible for the bicyclo[2.2.2]octane fragment whereas they are strong for benzene derivatives the finding of an intermediate behavior for the {*closo*-1-CB_{11}} cage is an indication for some resonance participation on the transmission of electronic effects. Further examples that support this interpretation are the relative effects of cyano and isocyano substituents on $\Delta[\delta(^{13}C_{C\equiv C})]$ and $\Delta[q(C\equiv C)_{NBO}]$. Similar trends are found for the respective benzene and {*closo*-1-CB_{11}} derivatives whereas the bicyclo[2.2.2]octane molecules reveal a slightly different trend. The nitrosyl group that is a strong π- and σ-acceptor leads to a strong shift toward smaller $\Delta[\delta(^{13}C_{C\equiv C})]$ and $\Delta[q(C\equiv C)_{NBO}]$ for 1-ON-4-HC$\equiv$C$-C_6H_4$. For 1-ON-4-HC$\equiv$C-bicyclo[2.2.2]octane the effect is smallest and for [1-ON-12-HC$\equiv$C-*closo*-1-$CB_{11}H_{10}$]$^-$ a bit more pronounced.

SUMMARY AND CONCLUSION

Salts of carba-*closo*-dodecaborate anions with two functional groups have been prepared and fully characterized by spectroscopic and structural methods. In addition, first 1-isocyanocarba-*closo*-dodecaborates are described.[1] The isoelectronic anions [1-NC-12-HC$\equiv$C-*closo*-1-$CB_{11}H_{10}$]$^-$ (**4b**) and [1-CN-12-HC$\equiv$C-*closo*-1-$CB_{11}H_{10}$]$^-$ (**7b**) are promising ligands for coordination chemistry as they may serve as linear bridging linkers between two metal centers. The [1-X-12-HC$\equiv$C-*closo*-1-$CB_{11}H_{10}$]$^-$ anions with a carboxylic acid (**2b**), acid amide (**3b**), or formamide (**6b**) substituent are of interest for coordination chemistry, as well. Furthermore, they reveal a great potential for supramolecular chemistry because of the ability to form aggregates (dimers or tetramers) via hydrogen bonds. Related dicarba-*closo*-dodecaboranes that have two functional substituents, e.g. carboxylic acid groups,[60] have been successfully used as building blocks in supramolecular coordination chemistry.[2,61] Currently, we are studying the coordination chemistry of the corresponding carboranylethynyl ligands with a special focus on complexes of the coinage metals.

Furthermore, a detailed evaluation of the spectroscopic data of selected {1-X-12-HC$\equiv$C-*closo*-1-$CB_{11}H_{10}$} derivatives in combination with data from DFT calculations and a comparison to the respective properties of related 1-X-4-HC$\equiv$C-benzene and 1-X-4-HC$\equiv$C-bicyclo[2.2.2]octane derivatives provided some insight into the transmission of electronic effects through the {*closo*-1-CB_{11}} cage.[17,23] Resonance-type effects are less important for the {*closo*-1-CB_{11}} derivatives than for the related benzenes but more important than for the corresponding bicyclo[2.2.2]octanes.

EXPERIMENTAL SECTION

General Methods. ^1H, ^{11}B, ^{13}C, and ^{15}N NMR spectra were recorded at 25 °C in $(CD_3)_2CO$, CD_3CN, or H_2O on a Bruker Avance 500 NMR spectrometer, a Bruker Avance III 400 NMR spectrometer, or on a Bruker Avance III HD 300 NMR spectrometer. A glass capillary filled with $(CD_3)_2CO$ was placed inside the NMR tubes for measurements in H_2O. The NMR signals were referenced against TMS (^1H and ^{13}C), $BF_3\cdot OEt_2$ in $CDCl_3$ with $\Xi(^{11}B)$ = 32.083974 MHz and $MeNO_2$ with $\Xi(^{15}N)$ = 10.136 767 MHz as external standards. ^1H and ^{13}C chemical shifts were calibrated against the residual solvent signal and the solvent signal, respectively ($\delta(^1H)$: $(CD_3)(CD_2H)CO$ 2.05 ppm, CD_2HCN 1.94 ppm; $\delta(^{13}C)$: $(CD_3)_2CO$ 206.26 and 29.84 ppm, CD_3CN 118.26 and 1.32 ppm).[62] The assignment of the ^{11}B and ^1H NMR signals is aided by $^{11}B\{^1H\}-^1H\{^{11}B\}$ 2D,[49] $^{11}B\{^1H\}-^{11}B\{^1H\}$ COSY,[48] and $^1H\{^{11}B_{selective}\}$ experiments. The assignment of some of the ^{15}N NMR signals is based on $^1H-^{15}N$ heteronuclear single quantum correlation (HSQC) experiments or on direct measurements of ^{15}N labeled compounds. $^1H-^{13}C$ heteronuclear multiple-bond correlation (HMBC) and HSQC studies as well as $^{13}C\{^{11}B,^1H\}$ triple resonance experiments were performed to support the interpretation of the ^{13}C NMR spectroscopic data. $^nJ(^{13}C,^1H)$ coupling constants derived from $^1H-^{13}C$ HMBC or ^{13}C experiments are listed with the $^{13}C\{^1H\}$ NMR spectroscopic data. The NMR spectroscopic data of the $[Et_4N]^+$ cation are omitted for clarity where applicable. IR spectra were recorded at room temperature with a Bruker Alpha spectrometer with an apodized resolution of 2 cm^{-1} in the attenuated total reflection (ATR) mode in the region of 4000−500 cm^{-1} using either a setup with a diamond or a Ge crystal. Raman spectra were recorded at room temperature on a Bruker IFS-120 spectrometer with an apodized resolution of 2 cm^{-1} using the 1064 nm excitation line of a Nd/YAG laser on crystalline samples contained in melting point capillaries in the region of 3500−100 cm^{-1}. Matrix-assisted laser desorption ionization (MALDI) mass spectra were acquired on an Autoflex II LRF (Bruker Daltonics). 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 (THF) was distilled from K/Na alloy under an argon atmosphere and stored in a flask equipped with a valve with a poly(tetrafluoroethylene) (PTFE) stem (Young, London) over molecular sieves (4 Å) under an argon atmosphere. Anhydrous CH_2Cl_2 was taken from a SPS solvent purification system (Innovative Technology) and stored under an Ar atmosphere. Solutions of $Me_3SiC\equiv CMgBr$ and $Et_3SiC\equiv CMgBr$ in THF (0.75 mol L^{-1}) were prepared from $Me_3SiC\equiv CH$ (Apollo Scientific) and $Et_3SiC\equiv CH$ (ABCR), respectively, by the reaction with 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. Acetic formic anhydride was prepared from $CH_3C(O)Cl$ and sodium formate[35] and PhOCN was obtained from phenol, Et_3N, and BrCN.[63] Cs[12-I-*closo*-1-$CB_{11}H_{11}$] (Cs**1d**),[14,64] Cs[12-$Et_3SiC\equiv C$-*closo*-1-$CB_{11}H_{11}$] (Cs**1c**),[26] K[1-H_2N-*closo*-1-$CB_{11}H_{11}$] (K**5a**),[14,21] K[1-H_2N-12-HC$\equiv$C-*closo*-1-$CB_{11}H_{10}$] (K**5b**),[23] and Cs[1-HO(O)C-*closo*-1-$CB_{11}H_{11}$] (Cs**2a**)[14] were prepared as described elsewhere. Cesium carba-*closo*-dodecaborate (Cs**1a**) and decaborane(14) were obtained either from Katchem spol. s.r.o.

(Prague, Czech Republic) or were synthesized from [Me_3NH][*nido*-$B_{11}H_{14}$][65] according to literature procedures.[65,66]

Single-Crystal X-ray Diffraction. Colorless crystals of [Et_4N]**2b** and K**6a** suitable for a X-ray diffraction study were grown from acetone by slow evaporation of the solvent. Slow uptake of diethyl ether into solutions of [Et_4N]**3b** and [Et_4N]**4b** in dichloromethane as well as of [Et_4N]**6b** and [Et_4N]**7b** in acetone resulted in colorless crystals. Crystals of the tetraethylammonium salts were investigated with CCD diffractometers using Mo Kα radiation (λ = 0.710 73 Å) (Bruker X8-Apex II for [Et_4N]**2b**, [Et_4N]**3b**, and [Et_4N]**4b**; Oxford Xcalibur equipped with an EOS detector for [Et_4N]**6b** and [Et_4N]**7b**). A crystal of K**6a** was studied with a Stoe IPDS I diffractometer using Mo Kα radiation, as well. All structures were solved by direct methods,[67,68] and refinement is based on full-matrix least-squares calculations on F^2.[68,69]

The positions of the hydrogen atoms in the crystal structures were located via ΔF syntheses. All non-hydrogen atoms were refined anisotropically with the iodine atom of the [1-HO(O)C-12-I-*closo*-1-$CB_{11}H_{10}$]$^-$ anion (**2d**), which is present in the crystal of [Et_4N]**2b** as a very minor impurity (2%), being the only exception. Most of the hydrogen atoms were refined using idealized bond lengths as well as angles. The H atoms that are part of the hydrogen-bond motifs were refined without any restraints. Calculations were carried out using the ShelXle graphical interface.[70] Molecular structure diagrams were drawn with the program Diamond 3.2i.[71] Experimental details, crystal data, and CCDC numbers are collected in Table 4. Supplementary crystallographic data for this publication are deposited in the Supporting Information.

Quantum Chemical Calculations. DFT[72] calculations were carried out using Becke's three-parameter hybrid functional and the Lee–Yang–Parr correlation functional (B3LYP)[73] using the Gaussian09 program suite.[74] 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.[75] Structures represent true minima with no imaginary frequency on the respective hypersurface. DFT-gauge-independent atomic orbital (GIAO)[76] NMR shielding constants $\sigma(^{11}B)$, $\sigma(^{13}C)$, $\sigma(^{15}N)$, and $\sigma(^{1}H)$ were calculated at the B3LYP/6-311++G(2d,p) level of theory using the geometries computed as described. The ^{11}B, ^{13}C, ^{15}N, and ^{1}H NMR shielding constants were calibrated to the respective chemical shift scale $\delta(^{11}B)$, $\delta(^{13}C)$, $\delta(^{15}N)$, and $\delta(^{1}H)$ using predictions on diborane(6), ammonia, and Me_4Si with chemical shifts of 16.6 ppm for B_2H_6,[77] −380.3 ppm for liquid NH_3,[78] and 0 ppm for Me_4Si. Spin–spin coupling constants were calculated at the same level as the NMR shielding constants. Calculations of all NMR parameters were performed with the Gaussian09 program suite.[74] Atomic charges were derived from atomic polar tensor (ATP)[79] and natural bond orbital (NBO, version 3.1)[80] populations analyses as implemented in the Gaussian09 program suite.[74]

*Experimental Determination of the pK_a Values Cs[1-HO(O)C-12-HC≡C-closo-1-$CB_{11}H_{10}$] (Cs**2b**) and K[1-HO(O)C-closo-1-$CB_{11}H_{11}$] (K**2a**).* Potentiometric titrations on aqueous solutions of Cs**2b** and K**2a** (ca. 0.2 mol L^{-1}) were performed with a pH meter Lab860 and a BlueLine 14 pH electrode (Schott Instruments GmbH, Germany).

*NMR Spectroscopic Study of the Deprotonation of Cs[1-HO(O)C-12-HC≡C-closo-1-$CB_{11}H_{10}$] (Cs**2b**) in H_2O.* A small amount of Cs**2b** (350 mg, 1.0 mmol) was dissolved in deionized water (5 mL) and the pH was adjusted to 11 by addition of aqueous CsOH. This solution was titrated with hydrochloric acid (12 mol L^{-1}) and the pH value was measured with a pH meter Lab860 and a BlueLine 14 pH electrode (Schott Instruments GmbH, Germany). Aliquots of the solution were taken at different pH values and were transferred into NMR tubes, containing a capillary with $(CD_3)_2CO$ as an internal standard. The samples of Cs**2b** were investigated by ^1H, $^1H\{^{11}B\}$, ^{11}B, $^{11}B\{^1H\}$, and $^{13}C\{^{11}B,^1H\}$ NMR spectroscopy. $^{13}C\{^{11}B,^1H\}$ NMR spectra at different pH values are collected in Figure S1 in the Supporting Information.

[Et_4N][1-HO(O)C-12-HC≡C-*closo*-1-$CB_{11}H_{10}$] ([Et_4N]2b). A glass finger (70 mL) equipped with a valve with a PTFE stem (Young, London) and fitted with a magnetic stirring bar was charged with Cs[12-Et_3SiC≡C-*closo*-1-$CB_{11}H_{11}$] (Cs**1c**) (2.00 g, 4.83 mmol) and THF (20 mL). ^{n}BuLi in hexanes (2.1 mL, 2.5 mol L^{-1}, 5.1 mmol) was added to the solution at −78 °C. The reaction mixture was allowed to warm to room temperature and was stirred for further 15 min. The mixture was cooled to −78 °C, and gaseous CO_2 (440 mg, 10 mmol) was added. Subsequently, the reaction mixture was allowed to warm to room temperature and was stirred overnight. The suspension was transferred into a round-bottom flask containing hydrochloric acid (50 mL, 3 mol L^{-1}). The THF was removed under reduced pressure. Diethyl ether (200 mL) was added, and the mixture was stirred overnight. The ethereal layer was separated, and the aqueous solution was extracted with additional Et_2O (2 × 100 mL). The combined organic layers were dried over $MgSO_4$. A concentrated aqueous solution of Cs_2CO_3 (1.60 g, 4.91 mmol) was added, and after removal of the ether at a rotary evaporator the solid residue was dissolved in H_2O (150 mL). The pH value was adjusted to 11 by the addition of KOH pellets. Slow addition of an aqueous solution of [Et_4N]OH (8.1 mL, 35% w/w, 19 mmol) resulted in the formation of a precipitate that mainly consisted of [Et_4N]**1c**. The solid material was removed via filtration through a fine glass frit packed with diatomaceous earth (Celite). Aqueous HCl (20 mL, 3 mol L^{-1}) was added until the pH value reached 2. A colorless precipitate formed that was collected by filtration and dried in a vacuum. Yield: 1.29 g (3.78 mmol, 78%). $^1H\{^{11}B\}$ NMR ($(CD_3)_2CO$, δ ppm): 2.04 (s, 1H, C≡CH, [^1H NMR: $^3J(^{11}B,^1H)$ = coupling not resolved]), 1.93 (s, 5H, BH2−6), 1.74 (s, 5H, BH7−11), the signal of the C(O)OH group was not observed. $^{13}C\{^1H\}$ NMR ($(CD_3)_2CO$, δ ppm): 168.31 (s, 1C, COOH), 95.93 (q, 1C, $^1J(^{13}C,^{11}B)$ = 101.8 Hz, $^2J(^{13}C,^1H)$ = 44.7 Hz, $B^{13}C{\equiv}CH$), 83.02 (q, 1C, $^2J(^{13}C,^{11}B)$ = 17.2 Hz, $^1J(^{13}C,^1H)$ = 235.1 Hz, $BC{\equiv}^{13}CH$), 65.97 (s, 1C, $C_{cluster}$). ^{11}B NMR ($(CD_3)_2CO$, δ ppm): −8.0 (d, 1B, $^1J(^{11}B,^1H)$ = 136 Hz, B12), −13.2 (d, 5B, $^1J(^{11}B,^1H)$ = 141 Hz, B7−11), −15.4 (d, 5B, $^1J(^{11}B,^1H)$ = 155 Hz, B2−6). IR/Raman (cm^{-1}): 3257 (ν(CC−H)), 3050 (vbr, ν(O−H)), 2668−2464 (ν(B−H)), 2060 (ν(C≡C)), 1664 (ν(C=O)). MALDI-MS *m*/*z* (isotopic abundance > 60) calcd for **2b** ([$C_4H_{12}B_{11}O_2$]$^-$): 210(74), 211(100), 212(83). Found: 210(69), 211(100), 212(88). Anal. Calcd for $C_{12}H_{32}B_{11}NO_2$: C, 42.23; H, 9.45; N, 4.10. Found: C, 42.72; H, 9.38; N, 4.10%.

Cs[1-HO(O)C-12-HC≡C-*closo*-1-$CB_{11}H_{10}$] (Cs2b). [Et_4N]**2b** (100 mg, 0.293 mmol) was treated with hydrochloric acid (20 mL, 2 mol L^{-1}) and diethyl ether (100 mL). The ethereal layer was separated after complete dissolution of the tetraethylammonium salt, and the aqueous phase was extracted two times with diethyl ether (2 × 50 mL). The combined organic phases were dried with $MgSO_4$. The magnesium sulfate was filtered off, and a saturated aqueous solution of cesium chloride (98.7 mg, 0.586 mmol) was added to the solution. Ether was removed using a rotary evaporator, and acetone (50 mL) was added to the remaining solid. The solution was dried with Cs_2CO_3 and filtered. Most of the solvent was removed with a rotary evaporator to result in a concentrated solution of Cs**2b** (5 mL). The cesium salt was precipitated by addition of chloroform (50 mL) and *n*-hexane (50 mL), filtered, and dried in a vacuum. Yield: 85 mg (0.247 mmol, 84%). The NMR spectroscopic data of anion **2b** observed for Cs**2b** are identical to those described for [Et_4N]**2b**. IR/Raman (cm^{-1}): 3386 (vbr, ν(O−H)), 3226 (ν(CC−H)), 2628−2478 (ν(B−H)), 2055 (ν(C≡C)), 1595 (ν(C=O)). Anal. Calcd for $C_4H_{12}B_{11}CsO_2$: C, 13.97; H, 3.52. Found: C, 13.90; H, 3.56%.

[Et_4N][1-HO(O)C-12-Et_3SiC≡C-*closo*-1-$CB_{11}H_{10}$] ([Et_4N]2c). The triethylsilyl-substituted alkyne was obtained as described for the preparation of [Et_4N]**2b** but without stirring with hydrochloric acid (50 mL, 3 mol L^{-1}) overnight. [Et_4N]**2c** was characterized by NMR spectroscopy, only. Yield: 1.36 g (2.99 mmol, 74%). $^1H\{^{11}B\}$ NMR ($(CD_3)_2CO$, δ ppm): 1.94 (s, 5H, BH2−6), 1.77 (s, 5H, BH7−11), 0.92 (t, 9H, $^3J(^1H,^1H)$ = 7.9 Hz, $^1J(^{13}C,^1H)$ = 125.9 Hz, CH_3), 0.46 (q, 6H, $^3J(^1H,^1H)$ = 7.9 Hz, $^1J(^{13}C,^1H)$ = 118.2 Hz, $SiCH_2$), the signal of the C(O)OH group was not observed. $^{13}C\{^1H\}$ NMR ($(CD_3)_2CO$, δ ppm): 168.5 (s, 1C, C(O)OH), 123.9 (q, 1C, $^1J(^{13}C,^{11}B)$ = 97 Hz, $B^{13}C{\equiv}CSi$), 95.8 (q, 1C, $^2J(^{13}C,^{11}B) \approx$ 17 Hz, $BC{\equiv}^{13}CSi$), 66.3 (s, 1C, $C_{cluster}$), 7.7 (s, 9C, CH_3), 5.4 (s, 6C, $^1J(^{29}Si,^{13}C)$ = 55 Hz, $SiCH_2$). ^{11}B NMR ($(CD_3)_2CO$, δ ppm): −7.9 (d, 1B, $^1J(^{11}B,^1H)$ = 140 Hz, B12), −13.1 (d, 5B, $^{1}J(^{11}B,^{1}H)$ = 140 Hz, B7−11), −15.4 (d, 5B, $^{1}J(^{11}B,^{1}H)$ = 154 Hz, B2−6).

$[Et_4N][1\text{-}H_2{}^{15}N(O)C$-*closo*-$1\text{-}CB_{11}H_{11}]$ ($[Et_4N]$3a). A glass finger (70 mL) equipped with a valve with a PTFE stem (Young, London) and fitted with a magnetic stirring bar was charged with $[Et_4N][1\text{-}HO(O)C$-*closo*-$1\text{-}CB_{11}H_{11}]$ ($[Et_4N]$**2a**) (500 mg, 1.58 mmol), *N,N′*-dicyclohexylcarbodiimide (DCC) (325 mg, 1.58 mmol), and 4-(dimethylamino)pyridine (DMAP) (19.3 mg, 0.158 mmol). The mixture of solids was dissolved in CH_2Cl_2 (10 mL) and stirred for 30 min. $^{15}NH_3$ (85 mg, 4.7 mmol) was added under reduced pressure at −78 °C, and the mixture was stirred for one additional hour at room temperature. All volatiles were removed under reduced pressure. The solid residue was taken up into hydrochloric acid (30 mL, 3 mol L^{-1}), and the mixture was extracted with Et_2O (3 × 100 mL). The combined ethereal layers were dried over $MgSO_4$. A solution of Cs_2CO_3 (1.03 g, 3.15 mmol) in a minimum amount of water was added, and subsequently all volatiles were removed under reduced pressure. The solid residue was dissolved in a mixture of H_2O (30 mL) and acetone (10 mL). Most of the acetone was removed under reduced pressure, and the resulting suspension was filtered to give a clear solution. An aqueous solution of $[Et_4N]OH$ (2.7 mL, 35% w/w, 6.32 mmol) was added. The white precipitate that had formed was filtered off and dried in a vacuum. Yield: 280 mg (0.88 mmol, 56%). $^{1}H\{^{11}B\}$ NMR ($(CD_3)_2CO$, *δ* ppm): 6.18 (dd, 1H, $^{1}J(^{15}N,^{1}H)$ = 89.3 Hz, $^{2}J(^{1}H,^{1}H)$ = 2.5 Hz, NH), 6.05 (dd, 1H, $^{1}J(^{15}N,^{1}H)$ = 89.3 Hz, $^{2}J(^{1}H,^{1}H)$ = 2.5 Hz, NH), 1.93 (s, 5H, BH2−6), 1.74 (s, 1H, BH12), 1.61 (s, 5H, BH7−11). $^{13}C\{^{1}H\}$ NMR ($(CD_3)_2CO$, *δ* ppm): 168.09 (s, 1C, $^{1}J(^{15}N,^{13}C)$ = 17 Hz, $C(O)NH_2$), 71.61 (s, 1C, $C_{cluster}$). ^{11}B NMR ($(CD_3)_2CO$, *δ* ppm): −7.9 (d, 1B, $^{1}J(^{11}B,^{1}H)$ = 136 Hz, B12), −14.0 (d, 5B, $^{1}J(^{11}B,^{1}H)$ = 152 Hz, B7−11), −15.1 (d, 5B, $^{1}J(^{11}B,^{1}H)$ = 167 Hz, B2−6). ^{15}N NMR ($(CD_3)_2CO$, *δ* ppm): −282.5 (dd, 1N, $^{1}J(^{15}N,^{1}H)$ = 89.3 Hz, NH_2). IR/Raman (cm^{-1}): 3485 ($\nu_{as}(^{15}N{-}H)$), 3451 ($\nu_{s}(^{15}N{-}H)$), 2631−2466 (ν(B−H)), 1669 (ν(C═O)). MALDI-MS *m/z* (isotopic abundance > 60) calcd for **3a** ($[C_2H_{13}{}^{15}NB_{11}O]^-$): 186(75), 187(100), 188(83). Found: 186(71), 187(100), 188(88). Anal. Calcd for $C_{10}H_{33}B_{11}N_2O$: C, 37.85; H, 10.48; N, 9.14. Found: C, 39.74; H, 10.09, N, 7.93%.

$[Et_4N][1\text{-}H_2N(O)C\text{-}12\text{-}HC{\equiv}C$-*closo*-$1\text{-}CB_{11}H_{10}]$ ($[Et_4N]$3b). $[Et_4N]$**3b** was synthesized from $[Et_4N]$**2b** (300 mg, 0.879 mmol), DCC (181 mg, 0.879 mmol), DMAP (10.7 mg, 0.0879 mmol), and NH_3 (48 mg, 2.66 mmol) as described for the preparation of $[Et_4N]$**3a**. Yield: 229 mg (0.673 mmol, 76%). $^{1}H\{^{11}B\}$ NMR ($(CD_3)_2CO$, *δ* ppm): 6.29 (s, 1H, NH_2), 6.23 (s, 1H, NH_2), 2.02 (s, 1H, C≡CH, [^{1}H NMR: $^{3}J(^{11}B,^{1}H)$ = coupling not resolved]), 1.90 (s, 5H, BH2−6), 1.74 (s, 5H, BH7−11). $^{13}C\{^{1}H\}$ NMR ($(CD_3)_2CO$, *δ* ppm): 196.12 (s, 1C, $^{1}J(^{15}N,^{13}C)$ = 17.1 Hz, $C(O)NH_2$), 95.88 (q, 1C, $^{1}J(^{13}C,^{11}B)$ = 102.4 Hz, $^{2}J(^{13}C,^{1}H)$ = 42.8 Hz, $B^{13}C{\equiv}CH$), 82.99 (q, 1C, $^{2}J(^{13}C,^{11}B)$ = 18.2 Hz, $^{1}J(^{13}C,^{1}H)$ = 234.7 Hz, $BC{\equiv}^{13}CH$), 68.87 (s, 1C, $C_{cluster}$). ^{11}B NMR ($(CD_3)_2CO$, *δ* ppm): −8.5 (s, 1B, B12), −13.2 (d, 5B, $^{1}J(^{11}B,^{1}H)$ = 142 Hz, B7−11), −15.6 (d, 5B, $^{1}J(^{11}B,^{1}H)$ = 155 Hz, B2−6). $^{15}N\{^{1}H\}$ NMR ($(CD_3)_2CO$, *δ* ppm): −281.8 (s, 1N, NH_2). IR/Raman (cm^{-1}): 3500 (ν_{as}(N−H)), 3393 (ν_{s}(N−H)), 3259 (ν(CC−H)), 2633−2474 (ν(B−H)), 2061 (ν(C≡C)), 1673 (ν(C═O)). MALDI-MS *m/z* (isotopic abundance > 60) calcd for **3b** ($[C_4H_{13}NB_{11}O]^-$): 209(74), 210(100), 211(83). Found: 209 (67), 210 (100), 211 (79). Anal. Calcd for $C_{12}H_{33}B_{11}N_2O$: C, 42.35; H, 9.77; N, 8.23. Found: C, 42.64; H, 9.89, N, 8.20%.

$[Et_4N][1\text{-}^{15}NC$-*closo*-$1\text{-}CB_{11}H_{11}]$ ($[Et_4N]$4a). A glass finger (70 mL) equipped with a valve with a PTFE stem (Young, London) and fitted with a magnetic stirring bar was charged with ^{15}N-labeled $[Et_4N]$**3a** (150 mg, 0.473 mmol) and Et_3N (3 mL). $COCl_2$ (1.5 g, 15.2 mmol) was added at −78 °C, and the reaction mixture was stirred overnight. All volatiles were removed in a vacuum, the solid residue was taken up into hydrochloric acid (30 mL, 3 mol L^{-1}) and Et_2O (100 mL), and the mixture was stirred for 20 min. The ethereal phase was separated, and the aqueous solution was extracted with Et_2O (2 × 50 mL). The combined organic layers were dried over $MgSO_4$. Cs_2CO_3 (231 mg, 0.710 mmol) dissolved in a minimum amount of H_2O was added, and the ether was removed at a rotary evaporator. The semisolid residue was dissolved in H_2O, and the addition of $[Et_4N]OH$ (0.79 mL, 35% w/w, 1.89 mmol) resulted in the formation of a white precipitate. The solid was collected by filtration and dried in a vacuum overnight. Yield: 108 mg (0.361 mmol, 76%). $^{1}H\{^{11}B\}$ NMR ($(CD_3)_2CO$, *δ* ppm): 1.93 (s, 5H, BH2−6), 1.82 (quintet, $^{3}J(^{1}H,^{1}H)$ = 3.4 Hz, 1H, BH12), 1.66 ppm (s, 5H, BH7−11). $^{13}C\{^{1}H\}$ NMR ($(CD_3)_2CO$, *δ* ppm): 120.14 (s, 1C, $^{1}J(^{15}N,^{13}C)$ = 16 Hz, C≡N), 46.74 (s, 1C, $C_{cluster}$). ^{11}B NMR ($(CD_3)_2CO$, *δ* ppm): −5.2 (d, 1B, $^{1}J(^{11}B,^{1}H)$ = 140 Hz, B12), −13.2 (d, 5B, $^{1}J(^{11}B,^{1}H)$ = 153 Hz, B7−11), −14.3 (d, 5B, $^{1}J(^{11}B,^{1}H)$ = 165 Hz, B2−6). ^{15}N NMR ($(CD_3)_2CO$, *δ* ppm): −152.7 (s, 1N, C≡N). IR/Raman (cm^{-1}): 2623−2472 (ν(B−H)), 2215 ($\nu(C{\equiv}^{15}N)$). MALDI-MS *m/z* (isotopic abundance > 60) calcd for **4a** ($[C_2H_{11}{}^{15}NB_{11}]^-$): 168(75), 169(100), 170(83). Found: 168(69), 169(100), 170(85). Anal. Calcd for $C_{10}H_{31}B_{11}N_2$: C, 40.13; H, 10.44; N, 9.69. Found: C, 39.74; H, 10.03; N, 8.55%.

$[Et_4N][1\text{-}NC\text{-}12\text{-}HC{\equiv}C$-*closo*-$1\text{-}CB_{11}H_{10}]$ ($[Et_4N]$4b). $[Et_4N]$**4b** was synthesized starting from $[NEt_4]$**3b** (100 mg, 0.294 mmol), Et_3N (3 mL), and $COCl_2$ (1.5 g, 15.2 mmol). Yield: 82 mg (0.254 mmol, 87%). $^{1}H\{^{11}B\}$ NMR ($(CD_3)_2CO$, *δ* ppm): 2.12 (s, 1H, C≡CH, [^{1}H NMR: $^{3}J(^{11}B,^{1}H)$ ≈ 3.3 Hz]), 1.90 (s, 5H, BH2−6), 1.81 (s, 5H, BH7−11). $^{13}C\{^{1}H\}$ NMR ($(CD_3)_2CO$, *δ* ppm): 120.28 (s, 1C, $^{1}J(^{15}N,^{13}C)$ = 17.1 Hz, C≡N), 94.54 (q, 1C, $^{1}J(^{13}C,^{11}B)$ = 103.8 Hz, $^{2}J(^{13}C,^{1}H)$ = 45.0 Hz, $B^{13}C{\equiv}CH$)), 83.95 (q, 1C, $^{2}J(^{13}C,^{11}B)$ = 19.4 Hz, $^{1}J(^{13}C,^{1}H)$ = 236.0 Hz, $BC{\equiv}^{13}CH$), 43.95 (s, 1C, $C_{cluster}$). ^{11}B NMR ($(CD_3)_2CO$, *δ* ppm): −6.1 (s, 1B, B12), −12.5 (d, 5B, $^{1}J(^{11}B,^{1}H)$ = 143 Hz, B7−11), −14.9 (d, 5B, $^{1}J(^{11}B,^{1}H)$ = 158 Hz, B2−6). ^{15}N NMR ($(CD_3)_2CO$, *δ* ppm): −150.9 (s, 1N, C≡N). IR/Raman (cm^{-1}): 3287 (not assigned), 3262 (ν(CC−H)), 2615−2488 (ν(B−H)), 2245 (ν(C≡N)), 2061 (ν(C≡C)). MALDI-MS *m/z* (isotopic abundance > 60) calcd for **4b** ($[C_4H_{11}NB_{11}]^-$): 191(74), 192(100), 193(82). Found: 191(95), 192(100), 193(85). Anal. Calcd for $C_{12}H_{31}B_{11}N_2$: C, 44.72; H, 9.69; N, 8.69. Found: C, 44.00; H, 9.72; N, 8.37%.

$Cs[1\text{-}NC\text{-}12\text{-}HC{\equiv}C$-*closo*-$1\text{-}CB_{11}H_{10}]$ (Cs4b). Cs**4b** was synthesized from $[Et_4N]$**4b** (50 mg, 0.155 mmol) as described for the preparation of Cs**2b**. Yield: 35 mg (0.107 mmol, 69%). The NMR spectroscopic data of the anion **4b** found for Cs**4b** are identical to those reported for $[Et_4N]$**4b**. IR/Raman (cm^{-1}): 3278 (ν(CC−H)), 2647−2483 (ν(B−H)), 2240/2220 (ν(C≡N)), 2060 (ν(C≡C)). Anal. Calcd for $C_4H_{11}B_{11}CsN$: C, 14.74; H, 3.40; N, 4.60. Found: C, 15.83; H, 3.47; N, 4.10%.

$[Et_4N][1\text{-}NC\text{-}12\text{-}Et_3SiC{\equiv}C$-*closo*-$1\text{-}CB_{11}H_{10}]$ ($[Et_4N]$4c). A glass finger (70 mL) equipped with a valve with a PTFE stem (Young, London) and fitted with a magnetic stirring bar was charged with Cs**1c** (1.00 g, 2.41 mmol) and THF (20 mL). The solution was cooled to −78 °C, and ^{n}BuLi in hexanes (1.0 mL, 2.5 mol L^{-1}, 2.53 mmol) was added, slowly. The reaction mixture was warmed to room temperature and stirred for additional 30 min. The colorless suspension was cooled to −78 °C, and PhOCN (0.6 mL, 5.5 mmol) was added. The mixture was warmed to room temperature and stirred for further 30 min. The solvent was removed in a vacuum. The solid residue was dissolved in water (100 mL) and filtered through a plug of diatomaceous earth (Celite). Addition of an aqueous solution of $[Et_4N]OH$ (3.0 mL, 35% w/w, 7.23 mmol) while stirring resulted in the formation of a white precipitate that was subsequently isolated by filtration. According to a ^{11}B NMR spectroscopic analysis the white precipitate contained a mixture of 60% of $[Et_4N]$**4c** and 40% of $[Et_4N]$**1c**.

The mixture of $[Et_4N]^+$ salts was dissolved in a minimum amount of CH_2Cl_2, and the clear solution was extracted with an aqueous solution of Cs_2CO_3 (5 × 10 mL, 0.1 mol L^{-1}). After the organic layer was dried with Cs_2CO_3 and filtered, all volatiles were removed under reduced pressure. Yield: 80 mg of $[Et_4N]$**4c** that contained <10% of $[Et_4N]$**1c** (0.184 mmol, ~8%). $^{1}H\{^{11}B\}$ NMR ($(CD_3)_2CO$, *δ* ppm): 1.92 (s, 5H, BH2−6), 1.83 (s, 5H, BH7−11), 0.92 (t, 9H, $^{3}J(^{1}H,^{1}H)$ = 7.9 Hz, $^{1}J(^{13}C,^{1}H)$ = 126.4 Hz, CH_3), 0.46 (q, 6H, $^{3}J(^{1}H,^{1}H)$ = 7.9 Hz, $SiCH_2$). $^{13}C\{^{1}H\}$ NMR ($(CD_3)_2CO$, *δ* ppm): 120.5 (s, 1C, CN), 97.0 (q, 1C, $BC{\equiv}^{13}CSi$), 44.0 (s, 1C, $C_{cluster}$), 7.7 (s, 9C, CH_3), 5.4 (s, 6C, $SiCH_2$), the signal of $B^{13}C{\equiv}CSi$ was not observed. ^{11}B NMR

((CD$_3$)$_2$CO, δ ppm): −6.0 (s, 1B, B12), −12.4 (d, 5B, $^1J(^{11}B,^1H)$ = 139 Hz, B7−11), −14.9 (d, 5B, $^1J(^{11}B,^1H)$ = 157 Hz, B2−6). IR/Raman (cm^{-1}): 2654−2474 (ν(B−H)), 2244 (ν(C≡N)), 2118 (ν(C≡C)). MALDI-MS *m*/*z* (isotopic abundance > 60) calcd for **4c** ([C$_{10}$H$_{25}$NB$_{11}$Si]$^-$): 305(68), 306(100), 307(76). Found: 305(69), 306(100), 307(89).

K[1-H(O)CHN-*closo*-1-CB$_{11}$H$_{11}$] (K6a). K**5a** (400 mg, 1.78 mmol) was dissolved in 1,2-dimethoxyethane (DME) (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. HC(O)OC(O)CH$_3$ (1.57 g, 17.8 mmol) was added at 0 °C, and the reaction mixture was stirred overnight at room temperature. After removing the solvent in a vacuum the semisolid residue was taken up into a concentrated aqueous solution of KOH (5 mL) and (THF 200 mL). The THF layer was separated, and the aqueous phase was extracted with THF (2 × 50 mL). The combined THF phases were dried with K$_2$CO$_3$, filtered, and most of the solvent was removed under reduced pressure. Chloroform (300 mL) was added, and the residual THF was removed at a rotary evaporator. The solution was cooled to 6 °C, and solid K**6a** formed. The potassium salt was filtered and dried in a vacuum. Yield: 2.01 g (8.95 mmol, 90%). ^{1}H{^{11}B} NMR (CD$_3$CN, δ ppm): 8.14 (d, 1H, $^3J(^1H,^1H)$ = 11.3 Hz, $^2J(^{15}N,^1H)$ = 14.3 Hz, $^1J(^{13}C,^1H)$ = 196.0 Hz, C(O)H), 6.79 (s, br, 1H, NH), 1.91 (s, 5H, BH2−6 or BH7−11), 1.48 (s, 5H, BH2−6 or BH7−11), 1.43 (s, 1H, BH12). ^{13}C{^{1}H} NMR (CD$_3$CN, δ ppm): 163.95 (s, 1C, $^2J(^{13}C,^{13}C)$ = 3 Hz, $^1J(^{15}N,^{13}C)$ = 13 Hz, C(O)H), 76.44 (s, 1C, C$_{\text{cluster}}$). ^{11}B NMR (CD$_3$CN, δ ppm): −12.2 (d, 1B, $^1J(^{11}B,^1H)$ = 137 Hz, B12), −14.9 (d, 5B, $^1J(^{11}B,^1H)$ = 146 Hz, B2−6 or B7−11), −15.0 (d, 5B, $^1J(^{11}B,^1H)$ = 146 Hz, B2−6 or B7−11). ^{15}N NMR (CD$_3$CN, δ ppm): 132.1 (dd, 1N, $^1J(^{15}N,^1H)$ = 91.9 Hz, $^3J(^{15}N,^1H)$ = 14.3 Hz, NH). IR/Raman (cm^{-1}): 3186−3060 (ν(N−H)), 2932 (ν(C(O)−H)), 2590−2500 (ν(B−H)), 1681 (ν(C═O)). MALDI-MS *m*/*z* (isotopic abundance > 60) calcd for ([C$_2$B$_{11}$H$_{13}$NO]$^-$): 185(75), 186(100), 187(81). Found: 185(86), 186(100), 187(92). Anal. Calcd for C$_2$H$_{13}$B$_{11}$KNO: C, 10.67; H, 5.82; N, 6.22. Found: C, 11.03; H, 5.70; N, 5.84%.

[Et$_4$N][1-H(O)CHN-12-HC≡C-*closo*-1-CB$_{11}$H$_{10}$] ([Et$_4$N]6b). Formic acid (1.0 mL, 27 mmol) and acetic anhydride (600 mg, 2.7 mmol) were stirred at 55 °C for 2 h.[36] The mixture was cooled to 0 °C and transferred to a solution of K**5b** (600 mg, 2.7 mmol) in DME (30 mL) at 0 °C. The reaction mixture was stirred overnight at room temperature. All volatiles were removed under reduced pressure, and the semisolid residue was taken up into a concentrated aqueous solution of KOH (5 mL) and THF (200 mL). The THF layer was separated, and the aqueous phase was extracted with THF (2 × 50 mL). The combined THF phases were dried with K$_2$CO$_3$ and filtered. Water (100 mL) was added to the combined organic phases, and subsequently the THF was removed at a rotary evaporator. Slowly, a solution of [Et$_4$N]Br (2.27 g, 10.8 mmol) in water (20 mL) was added. The colorless precipitate was isolated by filtration and dried in a vacuum. Yield: 554 mg (1.63 mmol, 60%). ^{1}H{^{11}B} NMR ((CD$_3$)$_2$CO, δ ppm): 8.11 (s, 1H, C(O)H), 7.69 (s, vbr, 1H, NH), 2.01 (s, 1H, C≡CH, [^{1}H NMR: $^3J(^{11}B,^1H)$ ≈ 3 Hz]), 1.94 (s, 5H, BH2−6), 1.72 (s, 5H, BH7−11). ^{13}C{^{1}H} NMR ((CD$_3$)$_2$CO, δ ppm): 163.72 (s, 1C, C(O)H), 95.31 (q, 1C, $^1J(^{11}B,^{13}C)$ = 101.7 Hz, B^{13}C≡CH), 83.09 (q, 1C, $^2J(^{11}B,^{13}C)$ = 18.2 Hz, BC≡^{13}CH), 74.65 (s, 1C, C$_{\text{cluster}}$). ^{11}B NMR ((CD$_3$)$_2$CO, δ ppm): −12.0 (s, 1B, B12), −13.9 (d, 5B, $^1J(^{11}B,^1H)$ = 147 Hz, B7−11), −15.3 (d, 5B, $^1J(^{11}B,^1H)$ = 164 Hz, B2−6). IR/Raman (cm^{-1}): 3281 (ν(CC−H)), 2583−2549 (ν(B−H)), 2063 (ν(C≡C)), 1686 (ν(C═O)). MALDI-MS *m*/*z* (isotopic abundance > 60) calcd for **6b** ([C$_4$B$_{11}$H$_{13}$NO]$^-$): 209(75), 210(100), 211(81). Found: 209(79), 210(100), 211(85). Anal. Calcd for C$_{12}$H$_{33}$B$_{11}$N$_2$O: C, 42.35; H, 9.77; N, 8.23. Found: C, 41.97; H, 10.06; N, 8.16%.

[Et$_4$N][1-CN-*closo*-1-CB$_{11}$H$_{11}$] ([Et$_4$N]7a). K**6a** (400 mg, 1.78 mmol) was dissolved in DME (10 mL), and Et$_3$N (2 mL) was added. The solution was cooled to −196 °C, and COCl$_2$ (200 mg, 2.02 mmol) was vacuum-transferred into the reaction vessel. The mixture was allowed to warm to room temperature and was stirred for 3 h. All volatiles were removed under reduced pressure, and the residue was taken up into a concentrated aqueous solution of KOH (5 mL). The solution was extracted with THF (3 × 50 mL). The combined THF phases were dried with K$_2$CO$_3$, filtered, and the volume of the solution was reduced to 20 mL. Water (100 mL) was added, and most of the remaining THF was removed at a rotary evaporator. An aqueous solution of [Et$_4$N]OH (3.0 mL, 35% w/w, 7.23 mmol) was added. The resulting white precipitate was filtered and dried in a vacuum. Yield: 450 mg (1.51 mmol, 85%). ^{1}H{^{11}B} NMR (CD$_3$CN, δ ppm): 1.99 (s, 5H, BH2−6), 1.51 (s, 6H, BH12 and BH7−11). ^{13}C{^{1}H} NMR (CD$_3$CN, δ ppm): 150.88 (s, 1C, $^2J(^{13}C,^{13}C)$ = 7 Hz, $^1J(^{15}N,^{13}C)$ = 6.6 Hz, CN), 67.79 (s, 1C, C$_{\text{cluster}}$). ^{11}B NMR (CD$_3$CN, δ ppm): −10.1 (d, 1B, $^1J(^{11}B,^1H)$ = 139.2 Hz, B12), −14.1 (d, 5B, $^1J(^{11}B,^1H)$: overlapped signal, B2−6), −14.8 (d, 5B, $^1J(^{11}B,^1H)$: overlapped signal, B7−11). ^{15}N NMR (CD$_3$CN, δ ppm): −201.1 (s, 1N, N≡C). IR/Raman (cm^{-1}): 2582−2545 (ν(B−H)), 2144 (ν(N≡C)). MALDI-MS *m*/*z* (isotopic abundance > 60) calcd for **7a** ([C$_2$B$_{11}$H$_{11}$N]$^-$): 167(74), 168(100), 169(80). Found: 167(83), 168(100), 169(80). Anal. Calcd for C$_{10}$H$_{21}$B$_{11}$N$_2$: C, 40.27; H, 10.48; N, 9.39. Found: C, 40.86; H, 11.28; N, 9.30%.

[Me$_3$NH][1-CN-*closo*-1-CB$_{11}$H$_{11}$] ([Me$_3$NH]7a). [Me$_3$NH]**7a** was synthesized from K**6a** (1.00 g, 4.44 mmol) as described for [Et$_4$N]**7a**. Yield: 600 mg (0.26 mmol, 59%). The NMR spectroscopic data of anion **7a** are consistent with those described for the [Et$_4$N]$^+$ salt. IR/Raman (cm^{-1}): 2585−2546 (ν(B−H)), 2148 (ν(N≡C)). Anal. Calcd for C$_5$H$_{21}$B$_{11}$N$_2$: C, 26.34; H, 9.28; N, 12.28. Found: C, 27.24; H, 9.14; N, 11.70%.

[Et$_4$N][1-CN-12-HC≡C-*closo*-1-CB$_{11}$H$_{10}$] ([Et$_4$N]7b). [Et$_4$N]**7b** was prepared from [Et$_4$N]**6b** (120 mg, 0.37 mmol), Et$_3$N (0.4 mL, 2.82 mmol), and COCl$_2$ (40 g, 0.41 mmol) as described for the preparation of [Et$_4$N]**7a**. Yield: 101 mg (0.33 mmol, 89%). ^{1}H{^{11}B} NMR ((CD$_3$)$_2$CO, δ ppm): 2.05 (s, 1H, C≡CH, [^{1}H NMR: $^3J(^{11}B,^1H)$ ≈ 3.4 Hz]), 2.01 (s, 5H, BH2−6), 1.74 (s, 5H, BH7−11). ^{13}C{^{1}H} NMR ((CD$_3$)$_2$CO, δ ppm): 152.09 (s, 1C, CN), 94.42 (q, 1C, $^1J(^{13}C,^{11}B)$ = 103.7 Hz, $^2J(^{13}C,^1H)$ = 45.5 Hz, B^{13}C≡CH), 83.95 (q, 1C, $^2J(^{13}C,^{11}B)$ = 19.6 Hz, $^1J(^{13}C,^1H)$ = 235.3 Hz, BC≡^{13}CH), 65.74 (s, 1C, C$_{\text{cluster}}$). ^{11}B NMR ((CD$_3$)$_2$CO, δ ppm): −10.1 (s, 1B, B12), −13.7 (d, 5B, $^1J(^{11}B,^1H)$: overlapped signal, B7−11), −14.6 (d, B5, $^1J(^{11}B,^1H)$: overlapped signal, B2−6). IR/Raman (cm^{-1}): 3286 (not assigned), 3261 (ν(CC-H)), 2594−2518 (ν(B−H)), 2136 (ν(N≡C)), 2064 (ν(C≡C)). MALDI-MS *m*/*z* (isotopic abundance > 60) calcd for **7b** ([C$_4$B$_{11}$H$_{11}$N]$^-$): 191(75), 192(100), 193(80). Found: 191(87), 192(100), 193(95). Anal. Calcd for C$_{12}$H$_{31}$B$_{11}$N$_2$: C, 44.72; H, 9.70; N, 8.69. Found: C, 44.61; H, 10.17; N, 8.20%.

■ ASSOCIATED CONTENT

Supporting Information

Tables of experimental as well as calculated spectroscopic data, bond lengths, and atomic charges; ^{13}C{^{11}B,^{1}H} NMR spectra of Cs[1-HO(O)C-12-HC≡C-*closo*-1-CB$_{11}$H$_{10}$] (Cs**2b**) at different pH values; correlation diagrams of selected experimental as well as calculated spectroscopic data and bond lengths versus Δ[*q*(C≡C)]; and crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org. Additional crystallographic information is available free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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Notes

The authors declare no competing financial interest.

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