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Dicarba-*closo*-dodecaboranes with One and Two Ethynyl Groups Bonded to Boron

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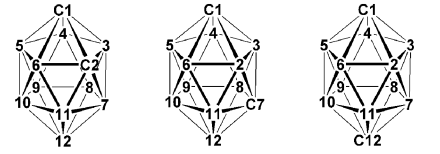
The diethynyldicarba-*closo*-dodecaboranes 1,2-R_2-9,12-$(HCC)_2$-*closo*-1,2-$C_2B_{10}H_8$ [R = H (**1a**), Me (**2a**)] and 9,10-$(HCC)_2$-*closo*-1,7-$C_2B_{10}H_{10}$ (**3a**) were obtained by Pd-catalyzed Kumada-type cross-coupling reactions of the corresponding diiodinated dicarba-*closo*-dodecaboranes with $Me_3SiCCMgBr$ followed by desilylation of the trimethylsilylalkynyl-substituted clusters. In addition, the related {*closo*-C_2B_{10}} derivatives with one ethynyl group 1,2-R-9-HCC-*closo*-1,2-$C_2B_{10}H_9$ [R = H (**4a**), Me (**5a**)], 9-HCC-*closo*-1,7-$C_2B_{10}H_{11}$ (**6a**), and 2-HCC-*closo*-1,12-$C_2B_{10}H_{11}$ (**7a**) were synthesized and their spectroscopic properties were compared to those of the diethynyl-substituted {*closo*-C_2B_{10}} clusters. The ethynyl- and trimethylsilylalkynyl-functionalized dicarba-*closo*-dodecaboranes were characterized by elemental analysis, mass spectrometry, as well as by multinuclear NMR, IR, and Raman spectroscopy. The assignment of the NMR spectroscopic chemical shifts and the IR and Raman bands is supported by theoretical values derived from density functional calculations. The crystal structures of 9,12-$(HCC)_2$-*closo*-1,2-$C_2B_{10}H_{10}$ (**1a**), 9,10-$(HCC)_2$-*closo*-1,7-$C_2B_{10}H_{10}$ (**3a**), and 1,2-Me-9,12-$(Me_3SiCC)_2$-*closo*-1,2-$C_2B_{10}H_8$ (**2b**) were determined by single-crystal X-ray diffraction. Selected experimental bond properties are compared to bond lengths and angles calculated at the B3LYP/6-311++G(d,p) level of theory.

Introduction

On account of their potential uses as building blocks for a wide range of applications, for example, in supramolecular chemistry,[1,2] pharmaceuticals,[3,4] and dendrimers[5] or polymers,[6] the functionalization of the three isomeric icosahedral dicarba-*closo*-dodecaboranes (Scheme 1) has been studied extensively.[7,8] This includes the incorporation of functional groups at the carbon vertices that may be achieved by deprotonation and subsequent reaction with an electrophile, as well as the modification of the substituents at the boron vertices (e.g., by electrophilic halogenation or alkylation).

A versatile synthetic strategy for the preparation of {*closo*-C_2B_{10}} derivatives with one or more functional groups bonded to boron is the partial iodination[4,9–14] of the cluster followed by transition-metal-catalyzed cross-coupling reactions.[7] The first report on cross-coupling reactions using iodinated dicarba-*closo*-dodecaboranes as starting materials was published in 1981,[15] and 9-Me_3-SiCC-*closo*-1,2-$C_2B_{10}H_{11}$ and 9-Me_3SiCC-*closo*-1,7-$C_2B_{10}H_{11}$ were obtained from the corresponding iodinated clusters and $Me_3SiCCMgBr$ in Pd-catalyzed Kumada-type[16] coupling reactions. The desilylation of the protected alkynes under basic conditions yielded the respective ethynyl-substituted clusters.[15] Thereafter, other dicarba-*closo*-dodecaboranes with alkynyl substituents bonded to boron have been described that were either synthesized following a Kumada-type reaction protocol or a related coupling procedure.[17–20] Furthermore, cross-coupling reactions were employed for the preparation of other {*closo*-C_2B_{10}} derivatives with various substituents bonded to boron, for example, by means of a carbon[9,11,15,17–22] or a nitrogen[23] atom.



Scheme 1. Labeling of the vertices of the clusters of the three isomers of the dicarba-*closo*-dodecaborane *closo*-1,2-$C_2B_{10}H_{12}$ (*ortho*-carborane), *closo*-1,7-$C_2B_{10}H_{12}$ (*meta*-carborane), and *closo*-1,12-$C_2B_{10}H_{12}$ (*para*-carborane).

In this contribution, the syntheses of the diethynyldicarba-*closo*-dodecaboranes 1,2-R_2-9,12-$(HCC)_2$-*closo*-1,2-$C_2B_{10}H_8$ [R = H (**1a**), Me (**2a**)] and 9,10-$(HCC)_2$-*closo*-1,7-$C_2B_{10}H_{10}$ (**3a**) and their NMR and vibrational spectroscopic data are presented. Furthermore, the crystal structures of 9,12-$(HCC)_2$-*closo*-1,2-$C_2B_{10}H_{10}$ (**1a**), 9,10-

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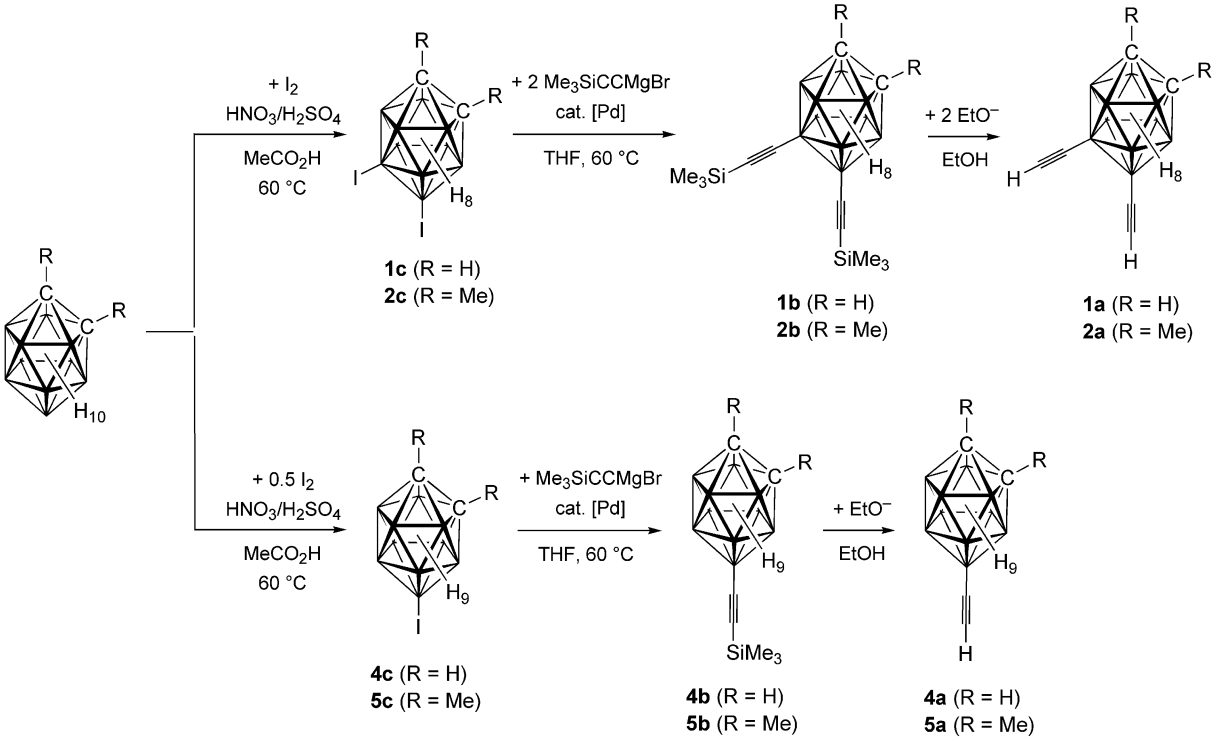
(HCC)$_2$-*closo*-1,7-$C_2B_{10}H_{10}$ (**3a**), and 1,2-Me_2-9,12-(Me_3SiCC)$_2$-*closo*-1,2-$C_2B_{10}H_8$ (**2b**) are reported. In addition, selected monoethynyldicarba-*closo*-dodecaboranes were prepared and the synthetic procedures are described in this contribution, because they differ from synthetic protocols reported previously.[15,17–19]

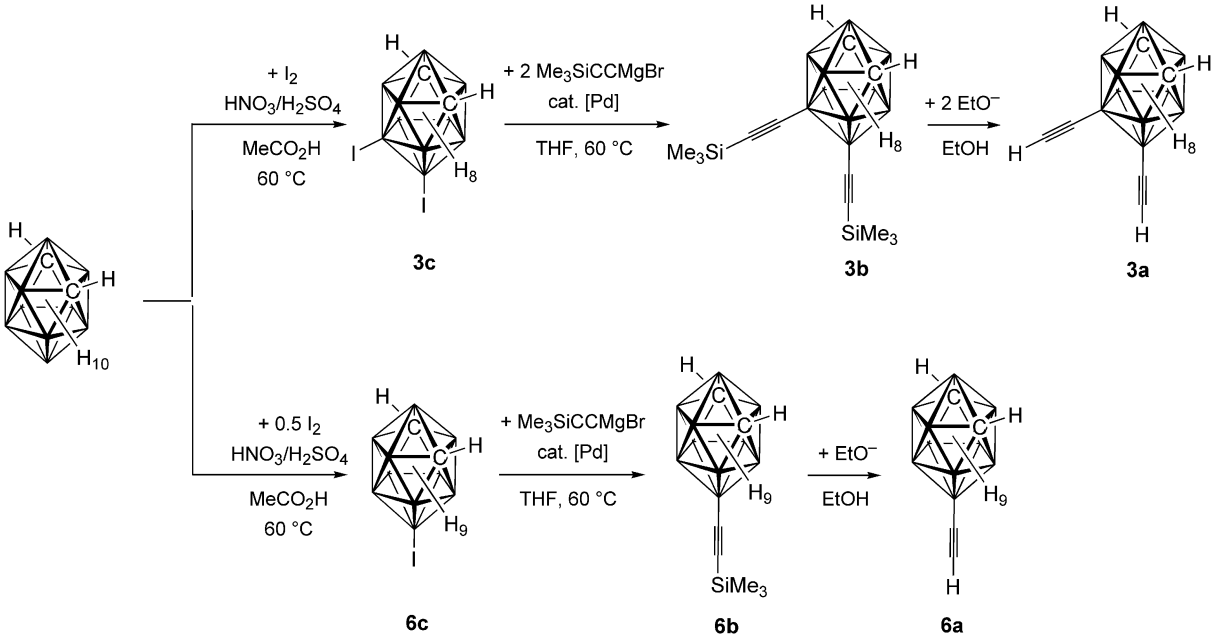
Results and Discussion

Iodination Reactions of Dicarba-*closo*-dodecaboranes

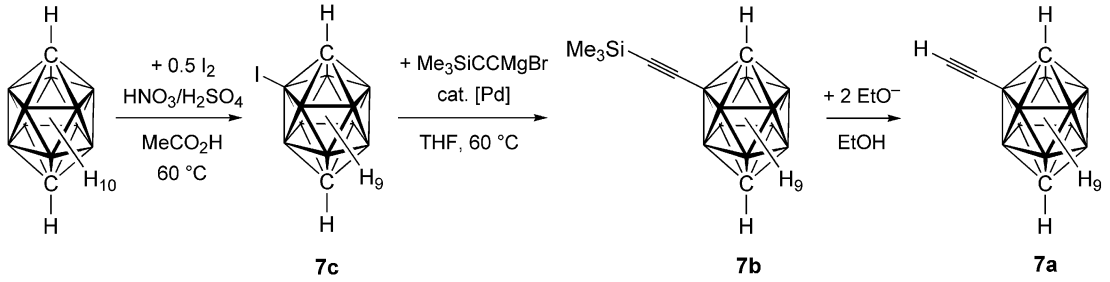
The starting materials for the palladium-catalyzed cross-coupling reactions used in this study are mono- and diio-



Scheme 2. Three-step synthesis of 1,2-R-9,12-(HCC)$_2$-*closo*-1,2-$C_2B_{10}H_8$ [R = H (**1a**), Me (**2a**)] and 1,2-R-9-HCC-*closo*-1,2-$C_2B_{10}H_9$ [R = H (**4a**), Me (**5a**)] starting from *closo*-1,2-$C_2B_{10}H_{12}$.



Scheme 3. Three-step synthesis of 9,10-(HCC)$_2$-*closo*-1,7-$C_2B_{10}H_{10}$ (**3a**) and 9-HCC-*closo*-1,7-$C_2B_{10}H_{11}$ (**6a**) starting from *closo*-1,7-$C_2B_{10}H_{12}$.



Scheme 4. Synthesis of 2-HCC-*closo*-1,12-$C_2B_{10}H_{11}$ in three steps starting from *closo*-1,12-$C_2B_{10}H_{12}$.

dinated 1,2-dicarba-*closo*-dodecaboranes[4,9–12] and 1,7-dicarba-*closo*-dodecaboranes[4,11,12] as well as 2-I-*closo*-1,12-$C_2B_{10}H_{11}$,[4,13,14] which are accessible by iodination of the respective {*closo*-C_2B_{10}} cluster either with elemental iodine or iodine monochloride; in most reactions reported, $AlCl_3$ is used as Lewis acid.[4,9–14]

A different synthetic protocol was described for the preparation of mono- and diiodinated *ortho*-carboranes 1,2-R_2-9-I-*closo*-1,2-$C_2B_{10}H_9$ and 1,2-R_2-9,12-I_2-*closo*-1,2-$C_2B_{10}H_9$ (R = H, aryl), which employs elemental iodine in combination with a mixture of concentrated H_2SO_4 and concentrated HNO_3 (1:1 v/v) in glacial acetic acid.[24,25] This method was used for the preparation of the mono- and diiodinated 1,2-dicarba-*closo*-dodecaboranes **1c**, **2c**, **4c**, and **5c** in yields of 80 to 95% as shown in Scheme 2.

This iodination reaction using elemental iodine and a 1:1 mixture of concentrated sulfuric acid and nitric acid in $MeCO_2H$ was applied for the selective preparations of 9,10-I_2-*closo*-1,7-$C_2B_{10}H_{10}$ (**3c**), 9-I-*closo*-1,7-$C_2B_{10}H_{11}$ (**6c**), and 2-I-*closo*-1,12-$C_2B_{10}H_{11}$ (**7c**) for the first time (see Schemes 3 and 4). This procedure enables the fast and simple preparation of **3c**, **6c**, and **7c** in yields of up to 95% and does not require inert reaction conditions. Diiodination of 1,12-dicarba-*closo*-dodecaboranes was also achieved, thereby resulting in a mixture of regioisomers similar to the reaction of *closo*-1,12-$C_2B_{10}H_{12}$ with ICl in the presence of $AlCl_3$.[13]

Synthesis of Alkynyl-Substituted {*closo*-C_2B_{10}} Derivatives

Mono- and diiodinated dicarba-*closo*-dodecaboranes were converted into the corresponding trimethylsilylalkynyl-functionalized clusters with $Me_3SiCCMgBr$ and $[PdCl_2(Ph_3P)_2]$ as a catalyst (see Schemes 2, 3, and 4). For the first examples of Pd-catalyzed Kumada-type cross-coupling reactions of monoiodinated dicarba-*closo*-dodecaboranes that were described in the early 1980s, similar reaction conditions were reported.[15,17,21,26] The yields of the {*closo*-C_2B_{10}} clusters with one and two trimethylsilylalkynyl substituents depicted in Schemes 2, 3, and 4 are in the range of 73 to 83%. The only exception is the synthesis of 9,12-(Me_3SiCC)$_2$-*closo*-1,2-$C_2B_{10}H_{10}$ (**1b**) starting from 9,12-I_2-*closo*-1,2-$C_2B_{10}H_{10}$ (**1c**) and $Me_3SiCCMgBr$ that resulted in a significantly lower yield of 40%. A yellow side-product was obtained that slowly decomposes. In the ^{11}B NMR spectrum of this yellow substance, six signals are observed. These are listed in the Exp. Section and assigned to nine boron atoms indicative of a {*nido*-C_2B_9} cluster with local C_s symmetry.

The (trimethylsilyl)alkynyl-substituted dicarba-*closo*-dodecaboranes were desilylated in ethanol with 1–2 equiv. of KOH per (trimethylsilyl)alkynyl group at room temperature, thereby resulting in the respective mono- and diethynyl-substituted dicarba-*closo*-dodecaboranes in approximately 95% yield (see Schemes 2, 3, and 4). In the case of the desilylation reactions of the {*closo*-1,2-C_2B_{10}} derivatives, small amounts of {*nido*-7,8-C_2B_9} species (<5%) were formed as determined by $^{11}B\{^1H\}$ NMR spectroscopy.

Single-Crystal Structures of 1a, 3a, and 2b

9,12-(HCC)$_2$-*closo*-1,2-$C_2B_{10}H_{10}$ (**1a**) crystallizes in the monoclinic space group *C*2/*c* with 16 formula units in the unit cell. The deviations of the bond parameters of the two independent molecules in the structure of **1a** are insignificant. 9,10-(HCC)$_2$-*closo*-1,7-$C_2B_{10}H_{10}$ (**3a**) crystallizes in the orthorhombic space group *Pnma* with $Z = 4$. Details of the structural determinations are given in the Exp. Section.

9,12-(HCC)$_2$-*closo*-1,2-$C_2B_{10}H_{10}$ (**1a**) and 9,10-(HCC)$_2$-*closo*-1,7-$C_2B_{10}H_{10}$ (**3a**) are the first structurally characterized dicarba-*closo*-dodecaboranes with ethynyl groups bonded to boron. Only two structures of related {*closo*-C_2B_{10}} clusters with alkynyl groups bonded to boron have been previously reported: 2,9-(Me_3SiCC)$_2$-*closo*-1,12-$C_2B_{10}H_{10}$ and 1,4-(*closo*-1′,12′-$C_2B_{10}H_{11}$-2′-yl)$_2$-1,3-butadiyne.[19] In contrast, a number of dicarba-*closo*-dodecaboranes with ethynyl groups or other alkynyl substituents bonded to carbon were structurally characterized.[2,27–32] In Figure 1 the diethynyl-substituted clusters **1a** and **3a** are depicted. The C≡C and B–C bond lengths of **1a** and **3a** are similar (Table 1) and they are also similar to bond lengths determined for ethynyl groups bonded to boron of different clusters, for example, in the anion [12-HCC-*closo*-1-$CB_{11}H_{11}$]$^-$ [d(C≡C) = 1.172(10) Å; d(B–C) = 1.568(8) Å][33] (Table 1) and in [1-(η^5-C_5H_5)-2-Ph-6-(HCC)-*closo*-1,2,3,4-$FeC_3B_7H_8$] [d(C≡C) = 1.188(3) Å; d(B–C) = 1.542(3) Å].[34] The differences of the experimentally determined d(C≡C) of the ethynyl-functionalized boron clusters listed in Table 1 are small and not significant (<3σ). Bond lengths derived from density functional theory (DFT) calculations are more reliable for comparisons: d(C≡C) and d(B–C) of **1a**, **3a**, and

Table 1. Selected experimental and calculated[a] bond parameters and vibrational spectroscopic data of ethynyl and trimethylsilylalkynyl substituents bonded to boron or carbon in dicarba-*closo*-dodecaboranes or carba-*closo*-dodecaborate anions.

Compound/anion		*d*(C≡C) [Å]	*d*(B–CC)/*d*(C–CC) [Å]	*d*(CC–Si) [Å]	∠(B–C≡C)/∠(C–C≡C) [°]	ṽ(C≡C) [cm^{-1}]	ṽ(C–H) [cm^{-1}]	Ref.
9,12-(HCC)$_2$-*closo*-1,2-$C_2B_{10}H_{10}$ (**1a**)	exp.	1.161(7)[b]	1.557(7)[b]	–	177.7(4)[b]	2074	3287/3269	[c]
	calcd.	1.207	1.529	–	179.7	2175/2174	3469	[c]
1,2-Me$_2$-9,12-(Me$_3$SiCC)$_2$-*closo*-1,2-$C_2B_{10}H_8$ (**2b**)[d,e]	exp.	1.193(5)[b]	1.536(5)[b]	1.831(4)[b]	178.1(3)[b]	2137	–	[c]
	calcd.	1.217	1.529	1.842	179.4	2232/2231	–	[c]
9,10-(HCC)$_2$-*closo*-1,7-$C_2B_{10}H_{10}$ (**3a**)	exp.	1.180(3)	1.542(3)	–	178.7(2)	2072	3276	[c]
	calcd.	1.207	1.528	–	179.8	2177/2176	3469	[c]
2,9-(Me$_3$SiCC)$_2$-*closo*-1,12-$C_2B_{10}H_{10}$	exp.	1.206(7)	1.532(7)	1.837(5)	178.5(3)	n.r.[f]	n.r.	[19]
1-HCC-*closo*-1,2-$C_2B_{10}H_{11}$	exp.	1.185(2)	1.441	–	178.3	2140	3297	[35,28]
	calcd.	1.200	1.433	–	179.7	2231	3473	[c]
1,12-(HCC)$_2$-*closo*-1,12-$C_2B_{10}H_{10}$	exp.	1.180(3)	1.451(2)	–	179.2	n.r.	3305/3294	[32]
	calcd.	1.201	1.438	–	180.0	2227/2229	3476	[c]
1,12-(Me$_3$SiCC)$_2$-*closo*-1,12-$C_2B_{10}H_{10}$	exp.	1.193(3)	1.452(2)	1.857(2)	179.1(2)	2178	–	[32,30]
[12-HCC-*closo*-1-$CB_{11}H_{11}$]$^-$	exp.	1.172(10)	1.568(8)	–	178.7(7)	2055	3272	[33]
	calcd.	1.211	1.545	–	180.0	2145	3474	[33]
[7,12-(HCC)$_2$-*closo*-1-$CB_{11}H_{10}$]$^-$	exp.[f]	1.01(2)[b,g]	1.62(3)[b,g]	–	177.3(1)[b,g]	2064	3278/3264	[33]
	calcd.	1.210/1.210	1.541/1.542	–	179.7	2150/2152	3475/3475	[33]

[a] B3LYP/6-311++G(d,p). [b] Averaged value. [c] This work. [d] Only the bond lengths of the molecule that is not disordered were considered. [e] $d(C_{cluster}–CH_3)_{exp.}$ = 1.529(5) Å; $d(C_{cluster}–CH_3)_{calcd.}$ = 1.520 Å. [f] n.r. = not reported. [g] The anion is disordered over two positions, thereby resulting in relatively imprecise bond parameters.[33]

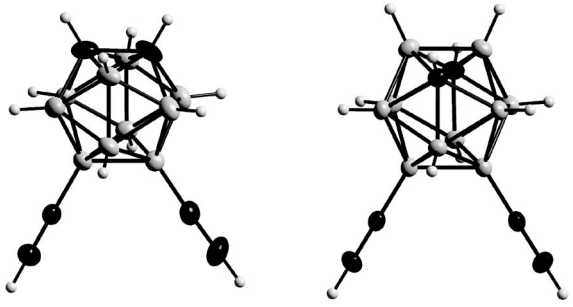


Figure 1. One of the two independent molecules of 9,12-(HCC)$_2$-*closo*-1,2-$C_2B_{10}H_{10}$ (**1a**) in the crystal (left) and the molecule of 9,10-(HCC)$_2$-*closo*-1,7-$C_2B_{10}H_{10}$ (**3a**) in the crystal (right) (displacement ellipsoids at the 40% probability level).

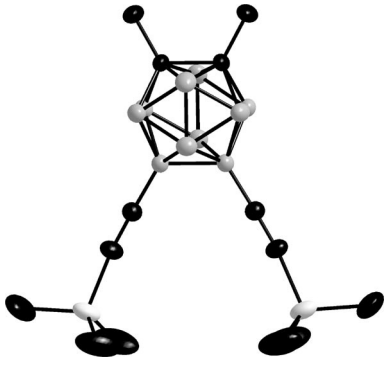


Figure 2. One of the two independent molecules of 1,2-Me$_2$-9,12-(Me$_3$SiCC)$_2$-*closo*-1,2-$C_2B_{10}H_8$ (**2b**) in the crystal (displacement ellipsoids at the 30% probability level).

monoethynyldicarba-*closo*-dodecaboranes with the CCH group bonded to boron are very similar (Table S1 in the Supporting Information). In contrast, calculated *d*(C≡C) as well as *d*(B–C) of the anions [12-HCC-*closo*-1-$CB_{11}H_{11}$]$^-$ and [7,12-(HCC)$_2$-*closo*-1-$CB_{11}H_{10}$]$^-$ are slightly longer,[33] whereas *d*(C≡C) of ethynyl groups bonded to carbon of {*closo*-C_2B_{10}} clusters are shorter (Table 1).

The bis[(trimethylsilyl)alkynyl]-functionalized molecule 1,2-Me$_2$-9,12-(Me$_3$SiCC)$_2$-*closo*-1,2-$C_2B_{10}H_8$ (**2b**) crystallizes in the orthorhombic space group *Pnma* with Z = 8. Experimental details of the structure determination are presented in the Experimental Section. In Figure 2 one of the two independent molecules of **2b** is depicted. The Me$_3$SiCC groups of the second independent molecule in the crystal of **2b** are disordered. The bond lengths of the alkynyl groups in **2b** are similar to values reported for 2,9-(Me$_3$SiCC)$_2$-*closo*-1,12-$C_2B_{10}H_8$[19] (Table 1).

The experimentally determined bond lengths of the {*closo*-C_2B_{10}} clusters of **1a**, **2b**, and **3a** are in good agreement with values calculated at the B3LYP/6-311++G(d,p) level of theory. In Table S2 in the Supporting Information, the C–C, C–B, and B–B bond lengths of **1a** and **2b** are compared to those of the parent carba-*closo*-dodecaboranes *closo*-1,2-$C_2B_{10}H_{12}$[36] and 1,2-Me$_2$-*closo*-1,2-$C_2B_{10}H_{10}$,[37] and in Table S3 in the Supporting Information, the cluster bond lengths of **3a** are compared to *d*(C–B) and *d*(B–B) of *closo*-1,7-$C_2B_{10}H_{12}$.[38,39] The substitution of the 1,2- as well as 1,7-dicarba-*closo*-dodecaboranes with two alkynyl groups results in slightly longer bonds between the functionalized boron atoms, *d*(B9–B12) in **1a** and **2b** and *d*(B9–B10) in **3a**, in comparison to the parent clusters, respectively. The bonds of the alkynyl-substituted boron atoms to their nonfunctionalized neighbor boron atoms are slightly longer as well. The differences of the remaining cluster

bonds in the dialkynyldicarba-*closo*-dodecaboranes compared to the respective parent clusters are small (Tables S2 and S3).

In the crystal of **3a** the molecules form layers parallel to the *a*–*c* plane with weak hydrogen contacts between the hydrogen atoms of the cluster carbon atoms and the C≡C bonds as depicted in Figure 3. For the structure of 1,4-(*closo*-1′,12′-$C_2B_{10}H_{11}$-2′-yl)$_2$-1,3-butadiyne, similar $C_{cluster}$–H···C≡C have been discussed.[38] The layers in the crystal of **3a** are interconnected by further weak C–H···C≡C interactions of the acetylenic hydrogen atoms of one layer and the C≡C bonds of the molecules of the neighboring layer, thereby resulting in a three-dimensional network. Related $C_{ethynyl}$–H···π hydrogen contacts are well known from crystal structures of terminal alkynes.[40]

In the structure of **1a**, similar weak hydrogen contacts are observed as discussed for **3a**; the shortest distance for a hydrogen contact is d(H–M) = 2.73(3) Å for $C_{cluster}$–H···C≡C. Although molecules **1a** and **3a** are very similar, their crystal structures are different (see Figures 3 and S1, the latter is available in the Supporting Information). This can probably be attributed to the different positions of the cluster carbon atoms in **1a** and **3a**, which result in differences in the weak hydrogen bridges formed between the acidic

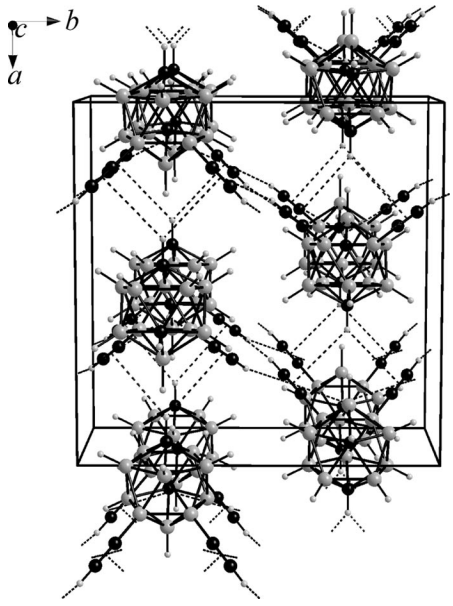


Figure 3. Partial packing diagram and unit cell of the crystal structure of 9,10-(HCC)$_2$-*closo*-1,7-$C_2B_{10}H_{10}$ (**8**) and weak hydrogen contacts: $C_{ethynyl}$–H···C≡C: d(H–M) = 3.118(13) Å, d($C_{ethynyl}$–M) = 4.020(2) Å, ∠(C≡C–M) = 171.7(2)°; $C_{cluster}$–H···C≡C: d(H–M) = 2.91(2) and 3.10(2) Å (M = center of the carbon C≡C bond).

Table 2. Selected experimental[a] and calculated[b] NMR spectroscopic data of ethynyl and trimethylsilylalkynyl-substituted dicarba-*closo*-dodecaboranes and carba-*closo*-dodecaborate anions.

Compound/anion		δ(^{13}C) B–^{13}C≡C [ppm]	δ(^{13}C) B–C≡^{13}C [ppm]	δ(^{11}B) ^{11}B–C≡C [ppm]	δ(^{1}H) C≡C–^{1}H [ppm]	^{1}J(^{13}C,^{11}B) ^{11}B–^{13}C≡C [Hz]	^{2}J(^{13}C,^{11}B) ^{11}B–C≡^{13}C [Hz]	^{1}J(^{13}C,^{1}H) C≡^{13}C–^{1}H [Hz]	^{2}J(^{13}C,^{1}H) ^{13}C≡C–^{1}H [Hz]	^{3}J(^{11}B,^{1}H) ^{11}B–C≡C–^{1}H [Hz]	Ref.
9-HCC-*closo*-1,2-$C_2B_{10}H_{11}$ (**4a**)	exp.	88.0	88.1	–3.3	2.58	107	19	240.2	45.2	n.o.[c]	[d]
	calcd.	91.0	91.0	–3.2	1.96	113.9	23.6	238.6	46.1	3.9	[d]
9,12-(HCC)$_2$-*closo*-1,2-$C_2B_{10}H_{10}$ (**1a**)	exp.	87.0	89.1	–2.9	2.68	111	20	240.5	45.5	n.o.	[d]
	calcd.	89.6	92.5	–2.8	2.07	115.2	23.5	239.1	46.1	4.0	[d]
9-HCC-*closo*-1,7-$C_2B_{10}H_{11}$ (**6a**)	exp.	85.7	86.2	–10.0	2.56	110	20	243.7	46	n.o.	[d]
	calcd.	89.8	88.5	–11.2	1.74	114.8	23.7	239.0	46.3	4.0	[d]
9,10-(HCC)$_2$-*closo*-1,7-$C_2B_{10}H_{10}$ (**3a**)	exp.	85.5	87.9	–9.5	2.65	110	19–20	241.1	45.9	n.o.	[d]
	calcd.	88.3	89.7	–10.8	1.87	116.1	23.7	239.4	46.3	4.0	[d]
2-HCC-*closo*-1,12-$C_2B_{10}H_{11}$ (**7a**)	exp.	83.3	86.5	–14.3	2.69	110	≈19	242	47	n.o.	[d]
	calcd.	88.0	89.7	–10.8	1.87	121.8	24.9	240.5	46.6	4.2	[d]
[12-HCC-*closo*-1-$CB_{11}H_{11}$]$^-$	exp.	96.0	80.9	–7.5	1.87	101.5	19.1	234.3	45.4	4	[33]
	calcd.	104.2	74.5	–9.5	0.97	105.4	21.8	228.6	43.8	3.5	[33]
[7,12-(HCC)$_2$-*closo*-1-$CB_{11}H_{10}$]$^-$[e]	exp.	94.6/93.4	82.1/80.9	–6.7/–12.6	1.97/1.95	103.1/104.1	19.0/18.8	234.0/235.7	46.0/43.5	4/4	[33]
	calcd.	102.3/101.3	76.8/75.1	–7.4/–14.0	1.13/1.04	107.3/108.4	21.9/22.0	229.6/230.0	44.1/44.3	3.6/3.6	[33]
9,12-(Me_3SiCC)$_2$-*closo*-1,2-$C_2B_{10}H_{10}$ (**1b**)	exp.	111.0	106.9	–4.9	–	104	14–20	–	–	–	[d]
	calcd.	115.7	113.8	–1.5	–	110.4	19.8	–	–	–	[d]
9,10-(Me_3SiCC)$_2$-*closo*-1,7-$C_2B_{10}H_{10}$ (**3b**)	exp.	109.7	105.4	–9.5	–	≈105	15–20	–	–	–	[d]
	calcd.	114.4	111.0	–10.1	–	111.3	20.0	–	–	–	[d]
[12-Me_3SiCC-*closo*-1-$CB_{11}H_{11}$]$^-$	exp.	122.4	97.1	–7.9[f]	–	≈100	≈18	–	–	–	[43]
	calcd.	138.3	91.0	–10.1	–	110.0	21.8	–	–	–	[43]

[a] Solvent: $(CD_3)_2CO$. [b] GIAO/B3LYP/6-311++G(2d,p)//6-311++G(d,p). [c] n.o. = not observed. [d] This work. [e] The first value listed for the chemical shifts and coupling constants corresponds to the B12–C≡C–H group, and the second value to the B7–C≡C–H group. [f] Solvent: CD_3CN.

hydrogen atoms of the cluster carbon atoms and the acetylenic hydrogen atoms with the electron-rich triple bonds of the ethynyl groups.

NMR Spectroscopy

The mono- and dialkynyl-substituted dicarba-*closo*-dodecaboranes were characterized by ^{11}B, ^{1}H, and ^{13}C NMR spectroscopy. The assignment of the ^{11}B and ^{1}H NMR signals presented in the Experimental Section and in Table 2 is aided by $^{11}B\{^{1}H\}$-$^{1}H\{^{11}B\}$ 2D[41] and $^{11}B\{^{1}H\}$-$^{11}B\{^{1}H\}$ COSY[42] experiments. The experimental chemical shifts and coupling constants are well reproduced by theoretical studies at the gauge-including atomic orbital (GIAO)/B3LYP-6-311++G(2d,p) level of theory (Table 2). The ^{11}B and $^{11}B\{^{1}H\}$ NMR spectra of **1a** and **3a** depicted in Figure 4 are in agreement with disubstitution at the positions 9 and 12 for **1a** and 9 and 10 for **3a**, respectively, and C_{2v} symmetry of the clusters.

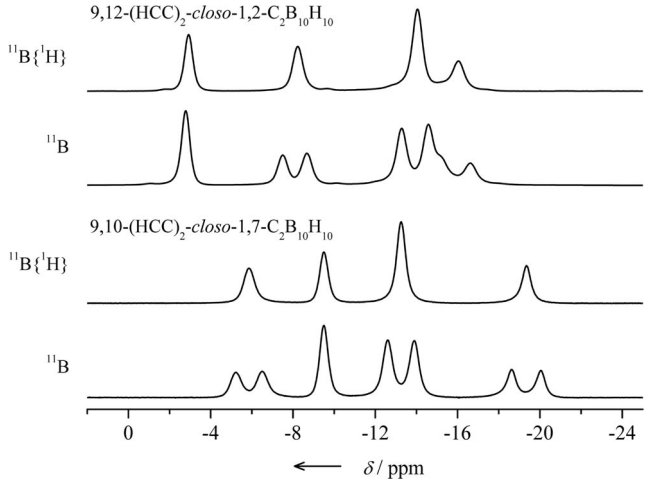


Figure 4. ^{11}B NMR spectra of 9,12-$(HCC)_2$-*closo*-1,2-$C_2B_{10}H_{10}$ (**1a**) and 9,10-$(HCC)_2$-*closo*-1,7-$C_2B_{10}H_{10}$ (**3a**).

In Figure 5 the ^{13}C and $^{13}C\{^{1}H\}$ NMR spectra of the diethynyldicarba-*closo*-dodecaboranes **1a** and **3a** are shown. The signals of the cluster carbon atoms are singlets in the ^{13}C NMR spectra and they are split into doublets in the proton-coupled spectra. Both ^{13}C signals that correspond to the ethynyl groups are split into quartets due to the coupling to ^{11}B (I = 3/2), and the coupling to the acetylenic proton results in a further splitting into doublets. The signals assigned to the carbon atoms bonded to boron exhibit larger coupling constants with ^{11}B [$^{1}J(^{13}C,^{11}B) \approx 110$ Hz] and smaller coupling constants with ^{1}H [$^{2}J(^{13}C,^{1}H) \approx 46$ Hz], compared to the signals of the terminal carbon atoms [$^{2}J(^{13}C,^{11}B) \approx 21$ Hz, $^{1}J(^{13}C,^{1}H) \approx 241$ Hz]. The distortion of the quartets of the ^{13}C signals of the terminal carbon atoms, as exemplified by the spectra in Figure 5, is typical of signals of nuclei that couple to ^{11}B and it is an indication that the respective coupling constant $^{2}J(^{13}C,^{11}B)$ is similar to the inverse spin-lattice relaxation rate σ^{1} of the ^{11}B nucleus.[33,44]

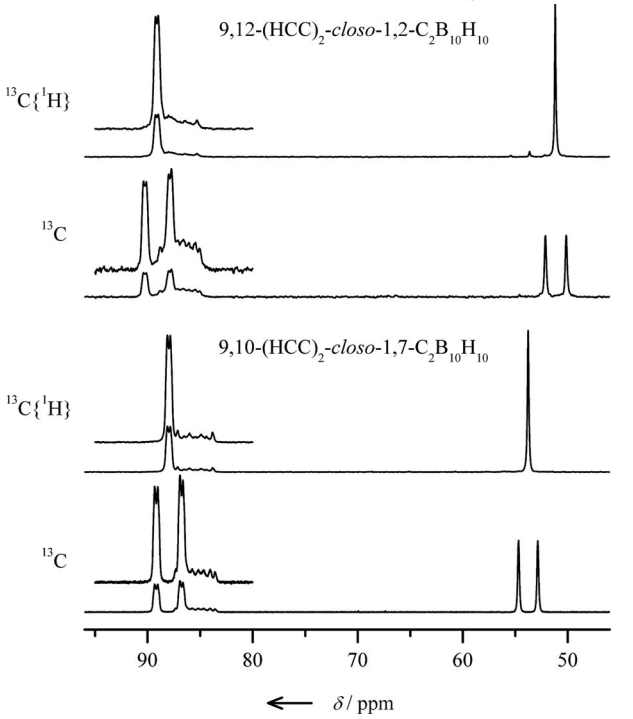


Figure 5. ^{13}C and $^{13}C\{^{1}H\}$ NMR spectra of 9,12-$(HCC)_2$-*closo*-1,2-$C_2B_{10}H_{10}$ (**1a**) and 9,10-$(HCC)_2$-*closo*-1,7-$C_2B_{10}H_{10}$ (**3a**).

Vibrational Spectroscopy

The ethynyl- and (trimethylsilyl)alkynyl-functionalized dicarba-*closo*-dodecaboranes were studied by IR and Raman spectroscopy and the experimental band positions of the most characteristic vibrations [$\tilde{\nu}$(C≡C), $\tilde{\nu}$(CC–H), $\tilde{\nu}(C_{cluster}–H)$, $\tilde{\nu}$(B–H)] are compared to wavenumbers derived from DFT calculations in Table S4 in the Supporting Information. The wavenumbers of the C≡C and CC–H stretches of the ethynyl groups bonded to a boron atom of dicarba-*closo*-dodecaboranes exhibit only small differences in agreement with earlier reports.[45] For ethynyl groups bonded to cluster carbon atoms, $\tilde{\nu}$(C≡C) is shifted to higher wavenumbers by approximately 70 cm^{-1} (Table 1).[45] In contrast, for the ethynyl groups that are bonded to boron in the anions [12-HCC-*closo*-1-$CB_{11}H_{11}]^-$ and [7,12-$(HCC)_2$-*closo*-1-$CB_{11}H_{10}]^-$, slightly smaller wavenumbers are observed and predicted by DFT calculations as well (ca. 10–20 cm^{-1}).[33] These differences in experimental as well as theoretical $\tilde{\nu}$(C≡C) display the trend in calculated d(C≡C) discussed in this contribution and they can be interpreted in terms of decreasing triple bond strengths in the following order: ethynyl groups bonded to cluster carbon atoms of {*closo*-C_2B_{10}} clusters > ethynyl groups bonded to boron atoms in {*closo*-C_2B_{10}} clusters > ethynyl groups bonded to boron atoms of anionic {*closo*-CB_{11}} clusters.

In Figure 6 the vibrational spectra of **1a** and **3a** are depicted. $\tilde{\nu}$(CC–H) and $\tilde{\nu}(C_{cluster}–H)$ in the IR and Raman spectrum of **1a** are split in contrast to single bands that are found in the respective spectra of **3a**. This difference reflects the different arrangement of the isoelectronic molecules **1a** and **3a** that is presumably a result of the different intermo-

lecular hydrogen bridges in the solid state, as evident from the crystal structures (see Figures 3 and S1, S: Supporting Information).

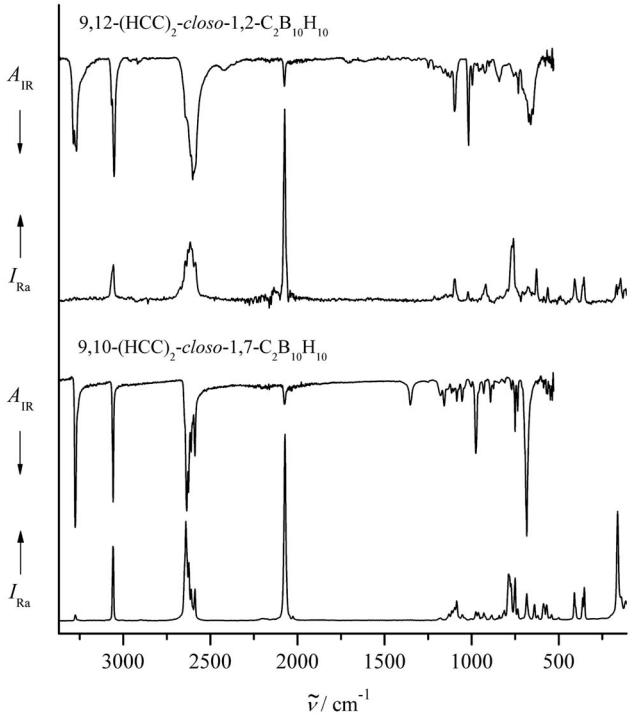


Figure 6. IR and Raman spectra of 9,12-$(HCC)_2$-*closo*-1,2-$C_2B_{10}H_{10}$ (**1a**) and 9,10-$(HCC)_2$-*closo*-1,7-$C_2B_{10}H_{10}$ (**3a**).

Conclusion

The 1,2- and 1,7-dicarba-*closo*-dodecaboranes with two and one ethynyl substituents bonded to boron that are comprehensively characterized by structural and spectroscopic methods in this study are attractive starting materials for the further derivatization of the {*closo*-C_2B_{10}} cage and potential ligands for coordination chemistry. Their application in coordination chemistry is especially promising, as suggested by a comparison to related compounds: (i) dicarba-*closo*-dodecaboranes with ethynyl groups bonded to the cluster carbon atoms have been successfully used as ligands,[2,25,27,29,46] for example, in [{Ru(dppe)Cp*}$_2${μ-1,12-$(C{\equiv}C)_2$-*closo*-1,12-$C_2B_{10}H_{10}$}][27] (dppe = 1,2-bis(diphenylphosphanyl)ethane) and (ii) 9,12-$(HCC)_2$-*closo*-1,2-$C_2B_{10}H_{10}$ (**1a**) as well as 9,10-$(HCC)_2$-*closo*-1,7-$C_2B_{10}H_{10}$ (**3a**) reveal structural similarities to 1,2-diethynylbenzene that has proven to be a versatile bridging ligand, for example, in metallamacrocycles.[47] Furthermore, with the ethynyl-functionalized carba-*closo*-dodecaborate anions [12-HCC-*closo*-1-$CB_{11}H_{11}$]$^-$ and [7,12-$(HCC)_2$-*closo*-1-$CB_{11}H_{10}$]$^-$, isoelectronic anionic counterparts[33,48] are available for comparative studies.

Experimental Section

General Remarks: ^{1}H, ^{11}B, and ^{13}C NMR spectra were recorded at 25 °C either in $(CD_3)_2CO$ or [D_8]THF with a Bruker Avance III 400 spectrometer operating at 400.17 (^{1}H), 128.39 (^{11}B), and 100.62 MHz (^{13}C). The NMR spectroscopic signals were referenced against TMS (^{1}H, ^{13}C) and $BF_3{\cdot}OEt_2$ in CD_3CN (^{11}B) as external standards. Infrared and Raman spectra were recorded at room temperature with 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 (ATR) mode in the region of 4000–530 cm^{-1}. Raman spectra were measured using the 1064 nm excitation line of a Nd/YAG laser on crystalline samples contained in melting point capillaries in the region of 3500–80 cm^{-1}. EI mass spectra were recorded with a Finnigan MAT 8200 spectrometer. Elemental analyses (C, H, N) were performed with a Euro EA3000 instrument (HEKA-Tech, Germany).

Chemicals: All standard chemicals were obtained from commercial sources. Tetrahydrofuran was distilled from K/Na alloy under a nitrogen atmosphere and stored in a flask equipped with a valve with a polytetrafluoroethylene (PTFE) stem (Young, London) over molecular sieves (4 Å) under 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-bottomed flask with a valve with a PTFE stem (Young, London) at 4 °C. 1,2-, 1,7-, and 1,12-Dicarba-*closo*-dodecaborane were obtained from Katchem spol. s.r.o. (Prague, Czech Republic) and used as received. 1,2-Me_2-*closo*-1,2-$C_2B_{10}H_{10}$ was prepared by a modified literature procedure.[49] The partially iodinated {*closo*-1,2-C_2B_{10}} derivatives 9-I-*closo*-1,2-$C_2B_{10}H_{11}$ (**4c**) and 9,12-I_2-*closo*-1,2-$C_2B_{10}H_{10}$ (**1c**) were synthesized from *closo*-1,2-$C_2B_{10}H_{12}$ and elemental iodine in glacial acetic acid by slow addition of a mixture of concentrated H_2SO_4 and concentrated HNO_3 (50:50 v/v) according to a literature procedure in yields of 80–95%.[24,25]

General Protocol for the Iodination Reactions: The iodination reactions were performed similar to the syntheses described for some mono- and diiodinated 1,2-dicarba-*closo*-dodecaboranes in the literature.[24,25]

In a typical diiodination experiment, a 50 mL round-bottomed flask equipped with a dropping funnel was charged with the respective dicarba-*closo*-dodecaborane (2.1 mmol), elemental iodine (270 mg, 2.1 mmol), and glacial acetic acid (16 mL). The solution was warmed to 60 °C and then a mixture of concentrated H_2SO_4 and concentrated HNO_3 (6 mL; 50:50 v/v) was added dropwise in 40 min. After complete addition, the reaction mixture was stirred at 80 °C for 1 h. The mixture was cooled to room tempertaure and ice-cold water (200 mL) was added. During this addition, a colorless precipitate formed that was isolated by filtration through a glass frit. The crude product was washed with water (100 mL) and dissolved in diethyl ether (100 mL). The solution was treated with a dilute aqueous solution of sodium sulfite (10 mL, 0.1 mol L^{-1}). The solution was dried with $MgSO_4$, filtered, and the solvent was removed using a rotary evaporator to result in a colorless solid.

1,2-Me_2-9-I-*closo*-1,2-$C_2B_{10}H_9$ (5c): Yield 2.92 g (9.8 mmol, 84%). $C_4H_{15}B_{10}I$ (298.17): calcd. C 16.11, H 5.07; found C 16.22, H 4.97. $^1H\{^{11}B\}$ NMR [$(CD_3)_2CO$]: δ = 2.71 (s, 2 H, BH, 7-H and 11-H), 2.55 (s, 1 H, BH, 12-H), 2.48 (s, 2 H, BH, 4-H and 5-H), 2.34 (s, 2 H, BH, 3-H and 6-H), 2.30 (s, 2 H, BH, 8-H and 10-H), 2.22 (s, 3 H, CH_3), 2.06 (s, 3 H, CH_3) ppm. $^{13}C\{^1H\}$ NMR [$(CD_3)_2CO$]: δ = 74.4 (s, 1 C, $C_{cluster}$), 69.8 (s, 1 C, $C_{cluster}$), 21.1 (s, 1 C, CH_3), 20.9 (s, 1 C, CH_3) ppm. ^{11}B NMR [$(CD_3)_2CO$]: δ = –4.1 [d, $^1J(^{11}B,^1H)$ = 152.1 Hz, 1 B, B-12], –7.9 [d, $^1J(^{11}B,^1H)$ = overlapped, 2 B, B-8 and B-9], –8.7 [d, $^1J(^{11}B,^1H)$ = overlapped, 2 B, B-7 and B-11], –8.9 [d, $^1J(^{11}B,^1H)$ = overlapped, 2 B, B-3 and B-6], –9.2 [d, $^1J(^{11}B,^1H)$

= overlapped, 2 B, B-4 and B-5], –18.3 (s, 1 B, B-9) ppm. MS (EI): *m*/*z* (isotopic abundance) calcd. for **6** ($C_4H_{15}B_{10}I$): 294 (2), 295 (8), 296 (28), 297 (66), 298 (100), 299 (91), 300 (39), 301 (2); found 294 (11), 295 (18), 296 (35), 297 (78), 298 (100), 299 (87), 300 (40), 301 (<1).

1,2-Me_2-9,12-I_2-*closo*-1,2-$C_2B_{10}H_8$ (2c): Yield 4.28 g (10.1 mmol, 86%). $C_4H_{14}B_{10}I_2$ (424.07): calcd. C 11.33, H 3.33; found C 11.46, H 3.34. $^1H\{^{11}B\}$ NMR ([D$_8$]THF): δ = 2.79 (s, 4 H, BH, 4-H, 5-H, 7-H, and 11-H), 2.69 (s, 2 H, BH, 8-H and 10-H), 2.29 (s, 2 H, BH, 3-H and 6-H), 2.03 (s, 6 H, CH_3) ppm. $^{13}C\{^1H\}$ NMR ([D$_8$]-THF): δ = 72.2 (s, 2 C, $C_{cluster}$), 21.8 (s, 2 C, CH_3) ppm. ^{11}B NMR ([D$_8$]THF): δ = –8.9 [d, $^1J(^{11}B,^1H)$ = 153.6 Hz, 2 B, B-8 and B-10], –9.5 [d, $^1J(^{11}B,^1H)$ ≈ 173 Hz, 2 B, B-3 and B-6], –10.5 [d, $^1J(^{11}B,^1H)$ ≈ 167 Hz, 4 B, B-4, B-5, B-7, and B-11], –17.8 (s, 2 B, B-9 and B-12) ppm. MS (EI): *m*/*z* (isotopic abundance) calcd. for **7** ($C_4H_{14}B_{10}I_2$): 420 (2), 421 (8), 422 (28), 423 (66), 424 (100), 425 (91), 426 (39), 427 (2); found 420 (7), 421 (15), 422 (34), 423 (75), 424 (100), 425 (85), 426 (34), 427 (1).

9-I-*closo*-1,7-$C_2B_{10}H_{11}$ (6c): Yield 540 mg (2.0 mmol, 95%). $C_2H_{11}B_{10}I$ (270.12): calcd. C 8.89, H 4.10; found C 9.27, H 3.97. $^1H\{^{11}B\}$ NMR [$(CD_3)_2CO$]: δ = 3.86 (s, 2 H, $C_{cluster}H$), 3.08 (s, 1 H, BH, 2-H), 2.71 (s, 1 H, BH, 3-H), 2.68 (s, 2 H, BH, 5-H and 12-H), 2.58 (s, 2 H, BH, 4-H and 8-H), 2.45 (s, 1 H, BH, 10-H), 2.24 (s, 2 H, BH-6 and BH-11) ppm. $^{13}C\{^1H\}$ NMR [$(CD_3)_2CO$]: δ = 58.3 (s, 2 C, $C_{cluster}$) ppm. ^{11}B NMR [$(CD_3)_2CO$]: δ = –5.7 [d, $^1J(^{11}B,^1H)$ = 165.4 Hz, 2 B, B-5 and B-12], –8.6 [d, $^1J(^{11}B,^1H)$ = 152.4 Hz, 1 B, B-10], –11.8 [d, $^1J(^{11}B,^1H)$ ≈ 161 Hz, 2 B, B-4 and B-8], –13.0 [d, $^1J(^{11}B,^1H)$ ≈ 161 Hz, 2 B, B-6 and B-11], –16.5 [d, $^1J(^{11}B,^1H)$ = 183.2 Hz, 1 B, B-3], –18.6 [d, $^1J(^{11}B,^1H)$ = 182.9 Hz, 1 B, B-2], –23.6 (s, 1 B, B-9) ppm. MS (EI): *m*/*z* (isotopic abundance) calcd. for **6** ($C_2H_{11}B_{10}I$): 266 (2), 267 (8), 268 (29), 269 (66), 270 (100), 271 (90), 272 (38), 273 (1); found 266 (5), 267 (13), 268 (30), 269 (72), 270 (100), 271 (87), 272 (36), 273 (<1).

9,10-I_2-*closo*-1,7-$C_2B_{10}H_{10}$ (3c): Yield 810 mg (2.0 mmol, 90%). $C_2H_{10}B_{10}I_2$ (396.01): calcd. C 6.07, H 2.55; found C 6.04, H 2.54. $^1H\{^{11}B\}$ NMR [$(CD_3)_2CO$]: δ = 4.08 (s, 2 H, $C_{cluster}H$), 3.17 (s, 2 H, BH, 2-H and 3-H), 2.85 (s, 2 H, BH, 5-H and 12-H), 2.70 (s, 4 H, BH, 4-H, 6-H, 8-H, and 11-H) ppm. $^{13}C\{^1H\}$ NMR [$(CD_3)_2$-CO]: δ = 59.1 (s, 2 C, $C_{cluster}$) ppm. ^{11}B NMR [$(CD_3)_2CO$]: δ = –4.5 [d, $^1J(^{11}B,^1H)$ = 168.3 Hz, 2 B, B-5 and B-12], –11.8 [d, $^1J(^{11}B,^1H)$ = 168.9 Hz, 4 B, B-4, B-6, B-8, and B-11], –18.4 [d, $^1J(^{11}B,^1H)$ = 185.1 Hz, 2 B, B-2 and B-3], –20.8 (s, 2 B, B-9 and B-10) ppm. MS (EI): *m*/*z* (isotopic abundance) calcd. for **7** ($C_2H_{10}B_{10}I_2$): 293 (2), 393 (8), 394 (29), 395 (66), 396 (100), 397 (90), 398 (38), 399 (1); found 293 (9), 393 (17), 394 (38), 395 (79), 396 (100), 397 (91), 398 (41), 399 (4).

2-I-*closo*-1,12-$C_2B_{10}H_{11}$ (7c): Yield 300 mg (1.1 mmol, 90%). $C_2H_{11}B_{10}I$ (270.12): calcd. C 8.89, H 4.10; found C 8.88, H 3.97. $^1H\{^{11}B\}$ NMR [$(CD_3)_2CO$]: δ = 3.92 [pseudoquintet, $^3J(^1H,^1H)$ = 4.0 Hz, 1 H, $C_{cluster}H$, 1-H], 3.62 [pseudosextet, $^3J(^1H,^1H)$ = 3.9 Hz, 1 H, $C_{cluster}H$, 12-H], 2.61 (s, 1 H, BH, 9-H), 2.59 (s, 2 H, BH), 2.55 (s, 2 H, BH), 2.30 (s, 2 H, BH), 2.26 (s, 2 H, BH) ppm. $^{13}C\{^1H\}$ NMR [$(CD_3)_2CO$]: δ = 66.9 (s, 1 C, $C_{cluster}$), 64.9 (s, 1 C, $C_{cluster}$) ppm. ^{11}B NMR [$(CD_3)_2CO$]: δ = –11.8 [d, $^1J(^{11}B,^1H)$ = overlapped, 2 B], –13.2 [d, $^1J(^{11}B,^1H)$ = overlapped, 2 B], –13.5 [d, $^1J(^{11}B,^1H)$ = overlapped, 2 B], –14.1 [d, $^1J(^{11}B,^1H)$ = overlapped, 2 B], –16.4 [d, $^1J(^{11}B,^1H)$ = 168.0 Hz, 1 B, B-9], –28.4 (s, 1 B, B-2) ppm. MS (EI): *m*/*z* (isotopic abundance) calcd. for **8** ($C_2H_{11}B_{10}I$): 266 (2), 267 (8), 268 (29), 269 (66), 270 (100), 271 (90), 272 (38), 273 (1); found 266 (4), 267 (13), 268 (41), 269 (80), 270 (100), 271 (85), 272 (36), 273 (1).

General Procedure for the Kumada-Type Cross-Coupling Reactions: The iodinated dicarba-*closo*-dodecaboranes were weighed in a round-bottomed flask equipped with a valve with a PTFE stem (Young, London) and fitted with a magnetic stirring bar. Dry tetrahydrofuran was added under an argon atmosphere to result in a clear colorless solution with a concentration of approximately 2 mol L^{-1} of the respective dicarba-*closo*-dodecaborane. A solution of $Me_3SiCCMgBr$ in THF (2.5 equiv. per iodine atom) was added at room temperature. The resulting suspension was transferred by means of a cannula into a second round-bottomed flask equipped with a valve with a PTFE stem (Young, London) and fitted with a magnetic stirring bar that contained [$PdCl_2(Ph_3P)_2$] (5 mol% per iodine atom). The reaction mixture was stirred at 40–50 °C. (The reactions of the monoiodinated dicarba-*closo*-dodecaboranes were complete within 12 h; in contrast, the diiodinated molecules required reaction times of 48–72 h.) The progress of the reaction was checked by $^{11}B\{^1H\}$ NMR spectroscopy. The resulting reaction mixture was poured into ice-cold hydrochloric acid (10% v/v; 10 mL per mmol of cluster) while stirring. The organic layer was separated and the aqueous phase was extracted two times with diethyl ether. The combined organic fractions were dried with $MgSO_4$, filtered, and the solvents were removed using a rotary evaporator. The crude product was purified by column chromatography on silica gel (Kieselgel 60, Merck KGaA, Germany) as stationary phase and a mixture of hexane and benzene (70:30 v/v) as mobile phase.

9-Me_3SiCC-*closo*-1,2-$C_2B_{10}H_{11}$ (4b): Yield 2.13 g (8.9 mmol, 73%). $C_7H_{20}B_{10}Si$ (240.43): calcd. C 34.97, H 8.38; found C 33.61, H 8.35. $^1H\{^{11}B\}$ NMR [$(CD_3)_2CO$]: δ = 4.52 [pseudosextet, $^3J(^1H,^1H)$ = 3.4 Hz, 1 H, $C_{cluster}H$], 4.43 [pseudosextet, $^3J(^1H,^1H)$ = 3.5 Hz, 1 H, $C_{cluster}H$], 2.36 (s, 1 H, BH, 12-H), 2.31 (s, 2 H, BH, 3-H and 6-H), 2.25 (s, 2 H, BH, 8-H and 10-H), 2.22 (s, 2 H, BH, 4-H and 5-H), 2.05 (s, 2 H, BH, 7-H and 11-H), 0.10 [s, $^1J(^{13}C,^1H)$ = 119.7 Hz, $^2J(^{29}Si,^1H)$ = 7.1 Hz, 9 H, Me_3Si] ppm. ^{13}C NMR [$(CD_3)_2CO$]: δ = 112.3 [q, $^1J(^{13}C,^{11}B)$ = 101 Hz, 1 C, B^{13}C≡C], 105.2 [q, $^2J(^{13}C,^{11}B)$ ≈ 15–21 Hz, 1 C, BC≡^{13}C], 55.4 [d, $^1J(^{13}C,^1H)$ = 196.0 Hz, 1 C, $C_{cluster}$], 52.2 [d, $^1J(^{13}C,^1H)$ = 198.2 Hz, 1 C, $C_{cluster}$], 0.1 [q of septets, $^1J(^{29}Si,^{13}C)$ = 56.1 Hz, $^1J(^{13}C,^1H)$ = 119.7 Hz, $^3J(^{13}C,^1H)$ = 2.0 Hz, 3 C, Me_3Si] ppm. ^{11}B NMR [$(CD_3)_2CO$]: δ = –2.6 [d, $^1J(^{11}B,^1H)$ ≈ 158 Hz, 1 B, B-12], –3.2 (s, 1 B, B-9), –8.9 [d, $^1J(^{11}B,^1H)$ = 151 Hz, 2 B, B-8 and B-10], –13.4 [d, $^1J(^{11}B,^1H)$ = overlapped, 2 B, B-4 and B-5], –14.5 [d, $^1J(^{11}B,^1H)$ = overlapped, 2 B, B-7 and B-11], –15.2 [d, $^1J(^{11}B,^1H)$ = 185 Hz, 2 B, B-3 and B-6] ppm. IR (ATR): $\tilde{\nu}$ = 3070 (m, $C_{cluster}$–H), 3042 (w, sh, $C_{cluster}$–H), 2635–2584 (vs, B–H), 2132 (w, C≡C) cm^{-1}. Raman: $\tilde{\nu}$ = 3069 (m, $C_{cluster}$–H), 3043 (w, $C_{cluster}$–H), 2638–2573 (vs, B–H), 2132 (vs, C≡C) cm^{-1}. MS (EI): *m*/*z* (isotopic abundance) calcd. for **7** ($C_7H_{20}B_{10}Si$): 236 (2), 237 (8), 238 (27), 239 (64), 240 (100), 241 (96), 242 (47), 243 (8), 244 (2); found 236 (1), 237 (9), 238 (27), 239 (65), 240 (100), 241 (95), 242 (49), 243 (10), 244 (2).

1,2-Me_2-9-Me_3SiCC-*closo*-1,2-$C_2B_{10}H_9$ (5b): Yield 1.51 g (5.6 mmol, 83%). $C_9H_{24}B_{10}Si$ (268.49): calcd. C 40.26, H 9.01; found C 40.55, H 8.94. $^1H\{^{11}B\}$ NMR [$(CD_3)_2CO$]: δ = 2.40 (s, 2 H, BH), 2.26 (s, 2 H, BH), 2.22 (s, 3 H, BH), 2.18 (s, 2 H, BH), 2.17 [s, $^1J(^{13}C,^1H)$ = 133.3 Hz, 3 H, Me$C_{cluster}$], 2.16 [s, $^1J(^{13}C,^1H)$ = 133.4 Hz, 3 H, Me$C_{cluster}$], 0.10 [s, $^1J(^{13}C,^1H)$ = 119.6 Hz, $^2J(^{29}Si,^1H)$ = 7.0 Hz, 9 H, Me_3Si] ppm. $^{13}C\{^1H\}$ NMR [$(CD_3)_2$-CO]: δ = 111.9 [q, $^1J(^{13}C,^{11}B)$ ≈ 103 Hz, 1 C, B^{13}C≡C], 105.8 [q, $^2J(^{13}C,^{11}B)$ ≈ 17–21 Hz, 1 C, BC≡^{13}C], 74.0 (s, 1 C, $C_{cluster}$), 70.8 (s, 1 C, $C_{cluster}$), 23.4 (s, 1 C, Me$C_{cluster}$), 22.7 (s, 1 C, Me$C_{cluster}$), 0.1 [s, $^1J(^{29}Si,^{13}C)$ = 55.7 Hz, 3 C, Me_3Si] ppm. ^{11}B NMR [$(CD_3)_2CO$]: δ = –4.7 [d, $^1J(^{11}B,^1H)$ = overlapped, 1 B, B-12], –3.2 (s, 1 B, B-9), –5.1 (s, 1 B, B-9), –8.8 [d, $^1J(^{11}B,^1H)$ = overlapped, 2

B] –9.2 [d, $^1J(^{11}B,^1H)$ = overlapped, 2 B], –10.1 [d, $^1J(^{11}B,^1H)$ = overlapped, 2 B], –10.2 [d, $^1J(^{11}B,^1H)$ = overlapped, 2 B] ppm. IR (ATR): $\tilde{\nu}$ = 2612–2574 (vs, B–H), 2136 (w, C≡C) cm^{-1}. Raman: $\tilde{\nu}$ = 2615–2580 (vs, B–H), 2137 (vs, C≡C) cm^{-1}. MS (EI): *m*/*z* (isotopic abundance) calcd. for **7** ($C_9H_{24}B_{10}Si$): 264 (2), 265 (8), 266 (27), 267 (64), 268 (100), 269 (97), 270 (49), 271 (9), 272 (2); found 264 (5), 265 (15), 266 (30), 267 (66), 268 (100), 269 (94), 270 (45), 271 (8), 272 (1).

9,12-$(Me_3SiCC)_2$-*closo*-1,2-$C_2B_{10}H_{10}$ (1b): Yield 1.01 g (3.0 mmol, 40%). $C_{12}H_{28}B_{10}Si_2$ (336.64): calcd. C 42.82, H 8.38; found C 41.44, H 8.14. $^1H\{^{11}B\}$ NMR [$(CD_3)_2CO$]: δ = 4.46 [s, $^1J(^{13}C,^1H)$ = 199.7 Hz, 2 H, $C_{cluster}H$], 2.30 (s, 2 H, BH, 8-H and 10-H), 2.25 (s, 2 H, BH, 3-H and 6-H), 2.16 (s, 4 H, BH, 4-H, 5-H, 7-H, and 11-H), 0.12 [s, $^1J(^{13}C,^1H)$ = 119.7 Hz, $^2J(^{29}Si,^1H)$ = 7.2 Hz, 18 H, Me_3Si] ppm. $^{13}C\{^1H\}$ NMR [$(CD_3)_2CO$]: δ = 111.3 [q, $^1J(^{13}C,^{11}B)$ ≈ 100 Hz, 2 C, $B^{13}C{\equiv}C$], 106.3 [q, $^2J(^{13}C,^{11}B)$ ≈ 15–20 Hz, 2 C, $BC{\equiv}^{13}C$], 50.9 (s, 2 C, $C_{cluster}$), 0.1 [s, $^1J(^{29}Si,^{13}C)$ = 56.0 Hz, 6 C, Me_3Si] ppm. ^{11}B NMR [$(CD_3)_2CO$]: δ = –2.9 (s, 2 B, B-9 and B-12), –8.2 [d, $^1J(^{11}B,^1H)$ = 148 Hz, 2 B, B-8 and B-10], –14.2 [d, $^1J(^{11}B,^1H)$ = 167 Hz, 4 B, B-4, B-5, B-7, and B-11], –16.1 [d, $^1J(^{11}B,^1H)$ = overlapped, 2 B, B-3 and B-6] ppm. IR (ATR): $\tilde{\nu}$ = 3064 (w, sh, $C_{cluster}$–H), 3039 (m, $C_{cluster}$–H), 2639–2589 (vs, B–H), 2131 (vw, C≡C) cm^{-1}. Raman: $\tilde{\nu}$ = 3063 (w, sh, $C_{cluster}$–H), 3038 (w, $C_{cluster}$–H), 2651–2590 (s, B–H), 2133 (vs, C≡C) cm^{-1}. MS (EI): *m*/*z* (isotopic abundance) calcd. for **7** ($C_{12}H_{28}B_{10}Si_2$): 332 (2), 333 (8), 334 (26), 335 (62), 336 (99), 337 (100), 338 (57), 339 (16), 340 (4), 341 (1); found 332 (4), 333 (7), 334 (28), 335 (65), 336 (95), 337 (100), 338 (56), 339 (16), 340 (10), 341 (2). ^{11}B NMR spectroscopic data of the side product of the cross-coupling reaction: [$(CD_3)_2CO$]: δ = –9.8 [d, $^1J(^{11}B,^1H)$ = 141 Hz, 2 B], –13.5 (s, 2 B, B–C≡CR), –16.5 [d, $^1J(^{11}B,^1H)$ = 166 Hz, 1 B], –21.6 [d, $^1J(^{11}B,^1H)$ = 157 Hz, 2 B], –31.3 [dd, $^1J(^{11}B,^1H)$ = 138 Hz; $^nJ(^{11}B,^1H)$ = 60 Hz, 1 B], –36.4 [d, $^1J(^{11}B,^1H)$ = 144 Hz, 1 B] ppm.

1,2-Me_2-9,12-$(Me_3SiCC)_2$-*closo*-1,2-$C_2B_{10}H_8$ (2b): Yield 1.42 g (3.9 mmol, 80%). $C_{14}H_{32}B_{10}Si_2$ (364.69): calcd. C 46.11, H 8.84; found C 46.99, H 8.81. $^1H\{^{11}B\}$ NMR [$(CD_3)_2CO$]: δ = 2.36 (s, 4 H, BH), 2.24 (s, 2 H, BH), ca. 2.2 (s, 2 H, BH), 2.17 [s, $^1J(^{13}C,^1H)$ = 133.6 Hz, 6 H, $MeC_{cluster}$], 0.12 [s, $^1J(^{13}C,^1H)$ = 119.7 Hz, $^2J(^{29}Si,^1H)$ = 7.1 Hz, 18 H, Me_3Si] ppm. $^{13}C\{^1H\}$ NMR [$(CD_3)_2CO$]: δ = 111.0 [q, $^1J(^{13}C,^{11}B)$ = 104 Hz, 2 C, $B^{13}C{\equiv}C$], 106.9 [q, $^2J(^{13}C,^{11}B)$ = 14–20 Hz, 2 C, $BC{\equiv}^{13}C$], 69.6 (s, 2 C, $C_{cluster}$), 22.8 (s, 2 C, $MeC_{cluster}$), 0.2 [s, $^1J(^{29}Si,^{13}C)$ = 55.9 Hz, 6 C, Me_3Si] ppm. ^{11}B NMR [$(CD_3)_2CO$]: δ = –4.9 (s, 2 B, B-9 and B-12), –9.3—10.0 (m, 8 B) ppm. IR (ATR): $\tilde{\nu}$ = 2613–2582 (vs, B–H), 2139 (w, C≡C) cm^{-1}. Raman: $\tilde{\nu}$ = 2622–2582 (s, B–H), 2137 (vs, C≡C) cm^{-1}. MS (EI): *m*/*z* (isotopic abundance) calcd. for **7** ($C_{14}H_{32}B_{10}Si_2$): 360 (2), 361 (7), 362 (25), 363 (61), 364 (98), 365 (100), 366 (58), 367 (17), 368 (5), 369 (1); found 360 (4), 361 (15), 362 (38), 363 (55), 364 (95), 365 (100), 366 (62), 367 (19), 368 (5), 369 (3).

9-Me_3SiCC-*closo*-1,7-$C_2B_{10}H_{11}$ (6b): Yield 1.99 g (8.3 mmol, 75%). $C_7H_{20}B_{10}Si$ (240.43): calcd. C 34.97, H 8.38; found C 35.48, H 8.28. $^1H\{^{11}B\}$ NMR [$(CD_3)_2CO$]: δ = 3.64 [s, $^1J(^{13}C,^1H)$ = 181.7 Hz, 2 H, $C_{cluster}H$], 2.60 (s, 1 H, BH, 3-H), 2.53 (s, 1 H, BH, 2-H), 2.39 (s, 2 H, BH, 5-H and 12-H), 2.29 (s, 2 H, BH, 4-H and 8-H), 2.16 (s, 1 H, BH, 10-H), 2.12 (s, 2 H, BH, 6-H and 11-H), 0.13 [s, $^1J(^{13}C,^1H)$ = 119.8 Hz, $^2J(^{29}Si,^1H)$ = 7.0 Hz, 9 H, Me_3Si] ppm. $^{13}C\{^1H\}$ NMR [$(CD_3)_2CO$]: δ = 110.6 [q, $^1J(^{13}C,^{11}B)$ = 104 Hz, 1 C, $B^{13}C{\equiv}C$], 104.2 [q, $^2J(^{13}C,^{11}B)$ ≈ 16–20 Hz, 1 C, $BC{\equiv}^{13}C$], 55.6 (s, 2 C, $C_{cluster}$), 0.1 [s, $^1J(^{29}Si,^{13}C)$ = 56.1 Hz, 3 C, Me_3Si] ppm. ^{11}B NMR [$(CD_3)_2CO$]: δ = –6.5 [d, $^1J(^{11}B,^1H)$ = 162 Hz, 2 B, B-5 and B-12], –9.8 [d, $^1J(^{11}B,^1H)$ = overlapped, 1 B, B-10], –9.9 (s, 1 B, B-9), –12.8 [d, $^1J(^{11}B,^1H)$ = 161 Hz, 2 B, B-4 and B-8], –14.0 [d, $^1J(^{11}B,^1H)$ = 162 Hz, 2 B, B-6 and B-11], –17.4 [d, $^1J(^{11}B,^1H)$ = 184 Hz, 1 B, B-3], –19.0 [d, $^1J(^{11}B,^1H)$ = 185 Hz, 1 B, B-2] ppm. IR (ATR): $\tilde{\nu}$ = 3056 (w, $C_{cluster}$–H), 3037 (m, $C_{cluster}$–H), 2628–2606 (vs, B–H), 2135 (w, C≡C) cm^{-1}. Raman: $\tilde{\nu}$ = 3065 (m, $C_{cluster}$–H), 2637–2612 (s, B–H), 2137 (vs, C≡C) cm^{-1}. MS (EI): *m*/*z* (isotopic abundance) calcd. for **7** ($C_7H_{20}B_{10}Si$): 236 (2), 237 (8), 238 (27), 239 (64), 240 (100), 241 (96), 242 (47), 243 (8), 244 (2); found 236 (6), 237 (10), 238 (25), 239 (65), 240 (100), 241 (96), 242 (50), 243 (12), 244 (3).

9,10-$(Me_3SiCC)_2$-*closo*-1,7-$C_2B_{10}H_{10}$ (3b): Yield 456 mg (1.9 mmol, 75%). $C_{12}H_{28}B_{10}Si_2$ (336.64): calcd. C 42.82, H 8.38; found C 41.89, H 8.29. $^1H\{^{11}B\}$ NMR [$(CD_3)_2CO$]: δ = 3.65 [s, $^1J(^{13}C,^1H)$ = 183.2 Hz, 2 H, $C_{cluster}H$], 2.50 (s, 2 H, BH, 2-H and 3-H), 2.48 (s, 2 H, BH, 5-H and 12-H), 2.24 (s, 4 H, BH, 4-H, 6-H, 8-H, and 11-H), 0.16 [s, $^1J(^{13}C,^1H)$ = 119.8 Hz, $^2J(^{29}Si,^1H)$ = 7.1 Hz, 18 H, Me_3Si] ppm. $^{13}C\{^1H\}$ NMR [$(CD_3)_2CO$]: δ = 109.7 [q, $^1J(^{13}C,^{11}B)$ ≈ 105 Hz, 2 C, $B^{13}C{\equiv}C$], 105.4 [q, $^2J(^{13}C,^{11}B)$ ≈ 15–20 Hz, 2 C, $BC{\equiv}^{13}C$], 53.6 (s, 2 C, $C_{cluster}$), 0.2 [s, $^1J(^{29}Si,^{13}C)$ = 55.9 Hz, 6 C, Me_3Si] ppm. ^{11}B NMR [$(CD_3)_2CO$]: δ = –6.0 [d, $^1J(^{11}B,^1H)$ = 160 Hz, 2 B, B-5 and B-12], –9.5 (s, 2 B, B-9 and B-10), –13.6 [d, $^1J(^{11}B,^1H)$ = 162 Hz, 4 B, B-4, B-6, B-8, and B-11], –19.7 [d, $^1J(^{11}B,^1H)$ = 177 Hz, 2 B, B-2 and B-3] ppm. IR (ATR): $\tilde{\nu}$ = 3057 (w, $C_{cluster}$–H), 3038 (m, $C_{cluster}$–H), 2653–2607 (vs, B–H), 2133 (w, C≡C) cm^{-1}. Raman: $\tilde{\nu}$ = 3056 (w, $C_{cluster}$–H), 3036 (w, $C_{cluster}$–H), 2641–2606 (s, B–H), 2130 (vs, C≡C) cm^{-1}. MS (EI): *m*/*z* (isotopic abundance) calcd. for **7** ($C_{12}H_{28}B_{10}Si_2$): 332 (2), 333 (8), 334 (26), 335 (62), 336 (99), 337 (100), 338 (57), 339 (16), 340 (4), 341 (1); found 332 (2), 333 (9), 334 (28), 335 (70), 336 (98), 337 (100), 338 (61), 339 (21), 340 (8), 341 (2).

2-Me_3SiCC-*closo*-1,12-$C_2B_{10}H_{11}$ (7b): Yield 2.12 g (8.8 mmol, 80%). $C_7H_{20}B_{10}Si$ (240.43): calcd. C 34.97, H 8.38; found C 35.79, H 8.10. $^1H\{^{11}B\}$ NMR [$(CD_3)_2CO$]: δ = 3.58 [pseudoquintet, $^3J(^1H,^1H)$ = 3.8 Hz, 1 H, $C_{cluster}H$, 1-H], 3.43 [pseudosextet, $^3J(^1H,^1H)$ = 3.7 Hz, 1 H, $C_{cluster}H$, 12-H], 2.31 (s, 2 H, BH), 2.26 (s, 2 H, BH), 2.18 (s, 2 H, BH), 2.13 (s, 2 H, BH), 2.02 (s, 1 H, BH, 9-H), 0.16 [s, $^1J(^{13}C,^1H)$ = 119.9 Hz, $^2J(^{29}Si,^1H)$ = 6.5 Hz, 9 H, Me_3Si] ppm. $^{13}C\{^1H\}$ NMR [$(CD_3)_2CO$]: δ = 107.3 (very br. q, 1 C, $B^{13}C{\equiv}C$), 105.0 [q, $^2J(^{13}C,^{11}B)$ ≈ 18 Hz, 1 C, $BC{\equiv}^{13}C$], 67.4 (s, 1 C, $C_{cluster}$), 64.4 (s, 1 C, $C_{cluster}$), –0.2 [s, $^1J(^{29}Si,^{13}C)$ = 56.3 Hz, 3 C, Me_3Si] ppm. ^{11}B NMR [$(CD_3)_2CO$]: δ = –13.2 [d, $^1J(^{11}B,^1H)$ = overlapped, 2 B], –14.2 (s, 1 B, B-2), –14.2 [d, $^1J(^{11}B,^1H)$ = overlapped, 2 B], –14.7 [d, $^1J(^{11}B,^1H)$ = overlapped, 2 B], –14.9 [d, $^1J(^{11}B,^1H)$ = overlapped, 2 B], –16.7 [d, $^1J(^{11}B,^1H)$ = overlapped, 1 B] ppm. IR (ATR): $\tilde{\nu}$ = 3059 (w, $C_{cluster}$–H), 2606 (vs, B–H), 2141 (vvw, C≡C) cm^{-1}. Raman: $\tilde{\nu}$ = 3059 (m, $C_{cluster}$–H), 2625–2614 (s, B–H), 2140 (vs, C≡C) cm^{-1}. MS (EI): *m*/*z* (isotopic abundance) calcd. for **7** ($C_7H_{20}B_{10}Si$): 236 (2), 237 (8), 238 (27), 239 (64), 240 (100), 241 (96), 242 (47), 243 (8), 244 (2); found 236 (5), 237 (11), 238 (32), 239 (68), 240 (100), 241 (98), 242 (52), 243 (12), 244 (1).

Desilylation Reactions: The trimethylsilylalkynyl-substituted dicarba-*closo*-dodecaborane was placed in a round-bottomed flask. A solution of KOH (1–2 equiv. per Me_3Si group) in a mixture of water and methanol (1:4 v/v, 10 mL per mmol of the cluster) was added and the resulting solution was stirred for 2 h. Water was added to the reaction mixture (30 mL per mmol of the cluster) to result in a colorless suspension. The precipitate was filtered off and the aqueous solution was extracted with diethyl ether. The ether solution was dried with $MgSO_4$, filtered, and the solvent was removed under reduced pressure. The solid residue and the filtered precipitate were combined. In general, a further purification of the primary alkynes was not necessary. Some substances were recrystallized or sublimed.

9-HCC-*closo*-1,2-$C_2B_{10}H_{11}$ (4a): Yield 320 mg (1.9 mmol, 95%). $C_4H_{12}B_{10}$ (168.25): calcd. C 28.56, H 7.19; found C 28.47, H 7.09. $^1H\{^{11}B\}$ NMR [$(CD_3)_2CO$]: δ = 4.53 [pseudosextet, $^3J(^1H,^1H)$ = 3.7 Hz, 1 H, $C_{cluster}H$], 4.44 [pseudosextet, $^3J(^1H,^1H)$ = 3.6 Hz, 1 H, $C_{cluster}H$], 2.58 [s, $^1J(^{13}C,^1H)$ = 240.2 Hz, $^2J(^{13}C,^1H)$ = 45.2 Hz, 1 H, C≡CH], 2.37 (s, 1 H, BH, 12-H), 2.32 (s, 2 H, BH, 3-H and 6-H), 2.26 (s, 2 H, BH, 8-H and 10-H), 2.23 (s, 2 H, BH, 4-H and 5-H), 2.06 (s, 2 H, BH, 7-H and 11-H) ppm. ^{13}C NMR [$(CD_3)_2CO$]: δ = 88.1 [dq, $^1J(^{13}C,^1H)$ = 244 Hz, $^2J(^{13}C,^{11}B)$ = 19 Hz, 1 C, BC≡^{13}C], 88.0 [qd, $^1J(^{13}C,^{11}B)$ = 107 Hz, $^2J(^{13}C,^1H)$ = 51 Hz, 1 C, B^{13}C≡C], 55.6 [d, $^1J(^{13}C,^1H)$ = 198.5 Hz, 1 C, $C_{cluster}$], 52.3 [d, $^1J(^{13}C,^1H)$ = 197.5 Hz, 1 C, $C_{cluster}$] ppm. ^{11}B NMR [$(CD_3)_2CO$]: δ = –2.6 [d, $^1J(^{11}B,^1H)$ = 160 Hz, 1 B, B-12], –3.3 (s, 1 B, B-9), –8.9 [d, $^1J(^{11}B,^1H)$ = 148 Hz, 2 B, B-8 and B-10], –13.4 [d, $^1J(^{11}B,^1H)$ = overlapped, 2 B, B-4 and B-5], –14.4 [d, $^1J(^{11}B,^1H)$ = overlapped, 2 B, B-7 and B-11], –15.2 [d, $^1J(^{11}B,^1H)$ = 182 Hz, 2 B, B-3 and B-6] ppm. IR (ATR): $\tilde{\nu}$ = 3285 (m, CC–H), 3057 (s, $C_{cluster}$–H), 2601–2573 (vs, B–H), 2072 (vw, C≡C) cm^{-1}. Raman: $\tilde{\nu}$ = 3282 (vvw, CC–H), 3060 (s, $C_{cluster}$–H), 2652–2579 (vs, B–H), 2069 (s, C≡C) cm^{-1}. MS (EI): *m*/*z* (isotopic abundance) calcd. for **7** ($C_4H_{12}B_{10}$): 164 (2), 165 (8), 166 (28), 167 (66), 168 (100), 169 (91), 170 (39), 171 (2); found 164 (8), 165 (18), 166 (31), 167 (80), 168 (100), 169 (94), 170 (48), 171 (5).

1,2-Me_2-9-HCC-*closo*-1,2-$C_2B_{10}H_9$ (5a): Yield 627 mg (3.2 mmol, 96%). $C_6H_{16}B_{10}$ (196.30): calcd. C 36.71, H 8.22; found C 36.87, H 8.19. $^1H\{^{11}B\}$ NMR [$(CD_3)_2CO$]: δ = 2.60 [s, $^1J(^{13}C,^1H)$ = 238.2 Hz, $^2J(^{13}C,^1H)$ = 45.7 Hz, 1 H, C≡CH], 2.42 (s, 2 H, BH), 2.26 (s, 2 H, BH), 2.23 (s, 3 H, BH), 2.19 (s, 2 H, BH), 2.18 [s, $^1J(^{13}C,^1H)$ = 133.4 Hz, 3 H, Me$C_{cluster}$], 2.16 [s, $^1J(^{13}C,^1H)$ = 133.3 Hz, 3 H, Me$C_{cluster}$] ppm. ^{13}C NMR [$(CD_3)_2CO$]: δ = 88.7 [dq, $^1J(^{13}C,^1H)$ = 239 Hz, $^2J(^{13}C,^{11}B)$ ≈ 18 Hz, 1 C, BC≡^{13}C], 87.9 [qd, $^1J(^{13}C,^{11}B)$ ≈ 104 Hz, $^2J(^{13}C,^1H)$ ≈ 47 Hz, 1 C, B^{13}C≡C], 74.1 (s, 1 C, $C_{cluster}$), 70.9 (s, 1 C, $C_{cluster}$), 23.4 [q, $^1J(^{13}C,^1H)$ = 133.6 Hz, 1 C, Me$C_{cluster}$], 22.7 [q, $^1J(^{13}C,^1H)$ = 133.2 Hz, 1 C, Me$C_{cluster}$] ppm. ^{11}B NMR [$(CD_3)_2CO$]: δ = –4.9 [d, $^1J(^{11}B,^1H)$ = overlapped, 1 B, B-12], –5.1 (s, 1 B, B-9), –8.7 [d, $^1J(^{11}B,^1H)$ = overlapped, 2 B], –9.3 [d, $^1J(^{11}B,^1H)$ = overlapped, 2 B], –9.9 [d, $^1J(^{11}B,^1H)$ = overlapped, 2 B], –10.2 [d, $^1J(^{11}B,^1H)$ = overlapped, 2 B] ppm. IR (ATR): $\tilde{\nu}$ = 3291 (s, CC–H), 2616–2555 (vs, B–H), 2074 (w, C≡C) cm^{-1}. Raman: $\tilde{\nu}$ = 2616–2567 (vs, B–H), 2072 (s, C≡C) cm^{-1}. MS (EI): *m*/*z* (isotopic abundance) calcd. for **7** ($C_6H_{16}B_{10}$): 192 (2), 193 (8), 194 (28), 195 (65), 196 (100), 197 (92), 198 (41), 199 (3); found 192 (8), 193 (20), 194 (45), 195 (80), 196 (100), 197 (79), 198 (45), 199 (5).

9,12-$(HCC)_2$-*closo*-1,2-$C_2B_{10}H_{10}$ (1a): Yield 250 mg (1.3 mmol, 94%). $C_6H_{12}B_{10}$ (192.27): calcd. C 37.48, H 6.29; found C 37.00, H 6.52. $^1H\{^{11}B\}$ NMR [$(CD_3)_2CO$]: δ = 4.49 [s, $^1J(^{13}C,^1H)$ = 199.7 Hz, 2 H, $C_{cluster}H$], 2.68 [s, $^1J(^{13}C,^1H)$ = 240.5 Hz, $^2J(^{13}C,^1H)$ = 45.5 Hz, 2 H, C≡CH], 2.33 (s, 2 H, BH, 8-H and 10-H), 2.29 (s, 2 H, BH, 3-H and 6-H), 2.21 (s, 4 H, BH, 4-H, 5-H, 7-H, and 11-H) ppm. ^{13}C NMR [$(CD_3)_2CO$]: δ = 89.1 [dq, $^1J(^{13}C,^1H)$ = 240 Hz, $^2J(^{13}C,^{11}B)$ = 20 Hz, 2 C, BC≡^{13}C], 87.0 [qd, $^1J(^{13}C,^{11}B)$ = 111 Hz, $^2J(^{13}C,^1H)$ = 50 Hz, 2 C, B^{13}C≡C], 51.2 [d, $^1J(^{13}C,^1H)$ = 199.2 Hz, 2 C, $C_{cluster}$] ppm. ^{11}B NMR [$(CD_3)_2CO$]: δ = –2.9 (s, 2 B, B-9 and B-12), –8.2 [d, $^1J(^{11}B,^1H)$ = 151 Hz, 2 B, B-8 and B-10], –14.1 [d, $^1J(^{11}B,^1H)$ = 167 Hz, 4 B, B-4, B-5, B-7, and B-11], –16.0 [d, $^1J(^{11}B,^1H)$ = 187 Hz, 2 B, B-3 and B-6] ppm. IR (ATR): $\tilde{\nu}$ = 3287 (s, CC–H), 3269 (s, CC–H), 3067 (w, sh, $C_{cluster}$–H), 3053 (s, $C_{cluster}$–H), 2643–2586 (vs, B–H), 2074 (vw, C≡C) cm^{-1}. Raman: $\tilde{\nu}$ = 3057 (m, $C_{cluster}$–H), 2643–2586 (s, B–H), 2074 (vs, C≡C) cm^{-1}. MS (EI): *m*/*z* (isotopic abundance) calcd. for **7** ($C_6H_{12}B_{10}$): 188 (2), 189 (8), 190 (28), 191 (65), 192 (100), 193 (92), 194 (40), 195 (3); found 188 (8), 189 (19), 190 (45), 191 (72), 192 (100), 193 (90), 194 (38), 195 (<1).

1,2-Me_2-9,12-$(HCC)_2$-*closo*-1,2-$C_2B_{10}H_8$ (2a): Yield 640 mg (2.9 mmol, 91%). $C_8H_{16}B_{10}$ (220.33): calcd. C 43.61, H 7.32; found C 43.93, H 7.43. $^1H\{^{11}B\}$ NMR [$(CD_3)_2CO$]: δ = 2.70 [s, $^1J(^{13}C,^1H)$ = 238.0 Hz, $^2J(^{13}C,^1H)$ = 49.6 Hz, 2 H, C≡CH], 2.38 (s, 4 H, BH, 4-H, 5-H, 7-H, and 11-H), 2.23 (s, 2 H, BH), 2.18 (s, 2 H, BH), 2.17 [s, $^1J(^{13}C,^1H)$ = 133.9 Hz, 6 H, Me$C_{cluster}$] ppm. ^{13}C NMR [$(CD_3)_2CO$]: δ = 89.8 [dq, $^1J(^{13}C,^1H)$ = 242 Hz, $^2J(^{13}C,^{11}B)$ ≈ 17–22 Hz, 1 C, BC≡^{13}C], 86.6 [qd, $^1J(^{13}C,^{11}B)$ = 110 Hz, $^2J(^{13}C,^1H)$ ≈ 50 Hz, 2 C, B^{13}C≡C], 69.9 (s, 2 C, $C_{cluster}$), 22.7 [q, $^1J(^{13}C,^1H)$ = 133.8 Hz, 2 C, Me$C_{cluster}$] ppm. ^{11}B NMR [$(CD_3)_2CO$]: δ = –5.0 (s, 2 B, B-9 and B-12), –9.5 [d, $^1J(^{11}B,^1H)$ = overlapped, 4 B], –9.9 [d, $^1J(^{11}B,^1H)$ = overlapped, 4 B] ppm. IR (ATR): $\tilde{\nu}$ = 3280 (s, CC–H), 2647–2582 (vs, B–H), 2072 (w, C≡C) cm^{-1}. Raman: $\tilde{\nu}$ = 3280 (vw, CC–H), 2658–2581 (vs, B–H), 2069 (s, C≡C) cm^{-1}. MS (EI): *m*/*z* (isotopic abundance) calcd. for **7** ($C_8H_{16}B_{10}$): 216 (2), 217 (8), 218 (28), 219 (65), 220 (100), 221 (93), 222 (42), 223 (3); found 216 (10), 217 (25), 218 (40), 219 (70), 220 (100), 221 (95), 222 (49), 223 (6).

9-HCC-*closo*-1,7-$C_2B_{10}H_{11}$ (6a): Yield 455 mg (2.7 mmol, 95%). $C_4H_{12}B_{10}$ (168.25): calcd. C 28.56, H 7.19; found C 28.92, H 7.21. $^1H\{^{11}B\}$ NMR [$(CD_3)_2CO$]: δ = 3.66 [s, $^1J(^{13}C,^1H)$ = 183.1 Hz, 2 H, $C_{cluster}H$], 2.62 (s, 1 H, BH, 3-H), 2.56 [s, $^1J(^{13}C,^1H)$ = 243.7 Hz, $^2J(^{13}C,^1H)$ = 46 Hz, 1 H, C≡CH], 2.54 (s, 1 H, BH, 2-H), 2.40 (s, 2 H, BH, 5-H and 12-H), 2.30 (s, 2 H, BH, 4-H and 8-H), 2.16 (s, 1 H, BH, 10-H), 2.13 (s, 2 H, BH, 6-H and 11-H) ppm. ^{13}C NMR [$(CD_3)_2CO$]: δ = 86.2 [dq, $^1J(^{13}C,^1H)$ = 241 Hz, $^2J(^{13}C,^{11}B)$ = 20 Hz, 1 C, BC≡^{13}C], 85.7 [qd, $^1J(^{13}C,^{11}B)$ = 110 Hz, $^2J(^{13}C,^1H)$ = 46 Hz, 1 C, B^{13}C≡C], 55.0 [d, $^1J(^{13}C,^1H)$ = 183.6 Hz, 2 C, $C_{cluster}$] ppm. ^{11}B NMR [$(CD_3)_2CO$]: δ = –6.4 [d, $^1J(^{11}B,^1H)$ = 163 Hz, 2 B, B-5 and B-12], –9.8 [d, $^1J(^{11}B,^1H)$ = overlapped, 1 B, B-10], –10.0 (s, 1 B, B-9), –12.7 [d, $^1J(^{11}B,^1H)$ = 161 Hz, 2 B, B-4 and B-8], –14.0 [d, $^1J(^{11}B,^1H)$ = 161 Hz, 2 B, B-6 and B-11], –17.3 [d, $^1J(^{11}B,^1H)$ = 188 Hz, 1 B, B-3], –18.9 [d, $^1J(^{11}B,^1H)$ = 185 Hz, 1 B, B-2] ppm. IR (ATR): $\tilde{\nu}$ = 3280 (s, CC–H), 3068 (w, sh, $C_{cluster}$–H), 3057 (m, $C_{cluster}$–H), 2658–2578 (vs, B–H), 2074 (w, C≡C) cm^{-1}. Raman: $\tilde{\nu}$ = 3269 (vw, CC–H), 3066 (m, $C_{cluster}$–H), 3057 (m, $C_{cluster}$–H), 2657–2577 (vs, B–H), 2073 (s, C≡C) cm^{-1}. MS (EI): *m*/*z* (isotopic abundance) calcd. for **7** ($C_4H_{12}B_{10}$): 164 (2), 165 (8), 166 (28), 167 (66), 168 (100), 169 (91), 170 (39), 171 (2); found 164 (5), 165 (16), 166 (38), 167 (76), 168 (100), 169 (91), 170 (40), 171 (5).

9,10-$(HCC)_2$-*closo*-1,7-$C_2B_{10}H_{10}$ (3a): Yield 308 mg (1.6 mmol, 92%). $C_6H_{12}B_{10}$ (192.27): calcd. C 37.48, H 6.29; found C 37.21, H 6.15. $^1H\{^{11}B\}$ NMR [$(CD_3)_2CO$]: δ = 3.67 [s, $^1J(^{13}C,^1H)$ = 184.1 Hz, 2 H, $C_{cluster}H$], 2.65 [s, $^1J(^{13}C,^1H)$ = 241.1 Hz, $^2J(^{13}C,^1H)$ = 45.9 Hz, 2 H, C≡CH], 2.53 (s, 2 H, BH, 2-H and 3-H), 2.51 (s, 2 H, BH, 5-H and 12-H), 2.28 (s, 4 H, BH, 4-H, 6-H, 8-H, and 11-H) ppm. ^{13}C NMR [$(CD_3)_2CO$]: δ = 87.9 [dq, $^1J(^{13}C,^1H)$ = 241 Hz, $^2J(^{13}C,^{11}B)$ ≈ 19–22 Hz, 2 C, BC≡^{13}C], 85.5 [qd, $^1J(^{13}C,^{11}B)$ = 110 Hz, $^2J(^{13}C,^1H)$ = 46 Hz, 2 C, B^{13}C≡C], 53.8 [d, $^1J(^{13}C,^1H)$ = 184.4 Hz, 2 C, $C_{cluster}$] ppm. ^{11}B NMR [$(CD_3)_2CO$]: δ = –5.9 [d, $^1J(^{11}B,^1H)$ = 164 Hz, 2 B, B-5 and B-12], –9.5 (s, 2 B, B-9 and B-10), –13.3 [d, $^1J(^{11}B,^1H)$ = 166 Hz, 4 B, B-4, B-6, B-8, and B-11], –19.4 [d, $^1J(^{11}B,^1H)$ = 181 Hz, 2 B, B-2 and B-3] ppm. IR (ATR): $\tilde{\nu}$ = 3276 (vs, CC–H), 3058 (s, $C_{cluster}$–H), 2636–2588 (vs, B–H), 2074 (w, C≡C) cm^{-1}. Raman: $\tilde{\nu}$ = 3280 (s, CC–H), 3058 (m, $C_{cluster}$–H), 2640–2589 (s, B–H), 2072 (vs, C≡C) cm^{-1}. MS (EI): *m*/*z* (isotopic abundance) calcd. for **7** ($C_6H_{12}B_{10}$): 188 (2), 189 (8), 190 (28), 191 (65), 192 (100), 193 (92), 194 (40), 195 (3); found 188 (10), 189 (20), 190 (50), 191 (82), 192 (100), 193 (90), 194 (40), 195 (5).

2-HCC-*closo*-1,12-$C_2B_{10}H_{11}$ (7a): Yield 538 mg (3.2 mmol, 96%). $C_4H_{12}B_{10}$ (168.25): calcd. C 28.56, H 7.19; found C 29.00, H 7.03. $^1H\{^{11}B\}$ NMR [$(CD_3)_2CO$]: δ = 3.60 [pseudoquintet, $^3J(^1H,^1H)$ = 4.0 Hz, 1 H, $C_{cluster}H$, 1-H], 3.42 [pseudosextet, $^3J(^1H,^1H)$ = 3.9 Hz, 1 H, $C_{cluster}H$, 12-H], 2.69 [s, $^1J(^{13}C,^1H)$ = 242 Hz, $^2J(^{13}C,^1H)$ = 47 Hz, 1 H, C≡CH], 2.32 (s, 2 H, BH), 2.27 (s, 2 H, BH), 2.20 (s, 2 H, BH), 2.15 (s, 2 H, BH), 2.06 (s, 1 H, BH, 9-H) ppm. ^{13}C NMR [$(CD_3)_2CO$]: δ = 86.5 [dq, $^1J(^{13}C,^1H)$ = 243 Hz, $^2J(^{13}C,^{11}B)$ ≈ 19 Hz, 1 C, BC≡^{13}C], 83.3 [br. qd, $^1J(^{13}C,^{11}B)$ = 110 Hz, $^2J(^{13}C,^1H)$ = not resolved, 2 C, B^{13}C≡C], 66.6 [d, $^1J(^{13}C,^1H)$ = 181.7 Hz, 1 C, $C_{cluster}$], 63.7 [d, $^1J(^{13}C,^1H)$ = 181.8 Hz, 1 C, $C_{cluster}$] ppm. ^{11}B NMR [$(CD_3)_2CO$]: δ = –13.4 [d, $^1J(^{11}B,^1H)$ = overlapped, 2 B], –14.3 (s, 1 B, B-2), –14.3 [d, $^1J(^{11}B,^1H)$ = overlapped, 2 B], –14.7 [d, $^1J(^{11}B,^1H)$ = overlapped, 2 B], –15.0 [d, $^1J(^{11}B,^1H)$ = overlapped, 2 B], –16.8 [d, $^1J(^{11}B,^1H)$ = overlapped, 1 B, B-9] ppm. IR (ATR): $\tilde{\nu}$ = 3298 (m, CC–H), 3050 (m, $C_{cluster}$–H), 2615–2601 (vs, B–H), 2086 (w, C≡C) cm^{-1}. Raman: $\tilde{\nu}$ = 3051 (m, $C_{cluster}$–H), 2626–2606 (vs, B–H), 2085 (vs, C≡C) cm^{-1}. MS (EI): *m*/*z* (isotopic abundance) calcd. for **7** ($C_4H_{12}B_{10}$): 164 (2), 165 (8), 166 (28), 167 (66), 168 (100), 169 (91), 170 (39), 171 (2); found 164 (12), 165 (26), 166 (42), 167 (78), 168 (100), 169 (80), 170 (36), 171 (2).

Crystal Structure Determinations: Colorless crystals of 9,12-$(HCC)_2$-*closo*-1,2-$C_2B_{10}H_{10}$ (**1a**) and its isomer 9,10-$(HCC)_2$-*closo*-1,7-$C_2B_{10}H_{10}$ (**3a**) suitable for X-ray diffraction were obtained from solutions in diethyl ether by slow uptake of hexane vapor, and colorless crystals of 1,2-Me_2-9,12-$(Me_3SiCC)_2$-*closo*-1,2-$C_2B_{10}H_8$ (**2b**) were obtained from hexane by slow evaporation of the solvent. A crystal of **1a** and a crystal of **3a** were investigated with an imaging plate diffraction system (IPDS, Stoe & Cie) at 123 K and a crystal of **2b** was studied with a Stoe STADI CCD diffractometer at 293 K using Mo-K_α radiation (λ = 0.71073 Å). All three structures were solved by direct methods,[50,51] and the refinements are based on full-matrix least-squares calculations on F^2.[51,52] 9,12-$(HCC)_2$-*closo*-1,2-$C_2B_{10}H_{10}$ (**1a**) crystallizes in the monoclinic space group *C*2/*c* (no. 15). Both other compounds **3a** and **2b** crystallize in the orthorhombic space group *Pnma* (no. 62). In the crystal structure of **2b** in one of the two independent molecules, the Me_3SiCC group is disordered over two positions with occupancies of 0.25 and 0.75. The positions of almost all hydrogen atoms in the crystal structures of **1a**, **3a**, and **2b** were located by means of ΔF syntheses, with the only exceptions being the hydrogen atoms of the trimethylsilyl groups of **2b**. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms bonded to the boron and carbon cluster atoms were freely refined, except for those in **1a**, which were refined using soft restraints and their isotropic displacement parameters were fixed to U_{eq} of the respective parent atom (130%). For most of the hydrogen atoms of the ethynyl substituents calculated positions were chosen; only *d*(C–H) of the terminal alkynyl group in **3a** was refined freely. The isotropic displacement parameters of all ethynyl hydrogen atoms were kept equal to 140% of the U_{eq} of the respective parent carbon atom. The hydrogen atoms of the methyl groups in **2b** were refined using restraints and their isotropic displacement parameters were kept equal to 140% of the U_{eq} of the respective parent carbon atom.

All calculations were carried out with the WinGX program package.[53] Molecular structure diagrams were drawn with the program Diamond 3.2c.[54] Experimental details and crystal data are collected in Table 3.

CCDC-752151 (for **1a**), -752152 (for **3a**), and -752150 (for **2b**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table 3. Crystal data and structure refinement details for 9,12-$(HCC)_2$-*closo*-1,2-$C_2B_{10}H_{10}$ (**1a**), 9,10-$(HCC)_2$-*closo*-1,7-$C_2B_{10}H_{10}$ (**3a**), and 1,2-Me_2-9,12-$(Me_3SiCC)_2$-*closo*-1,2-$C_2B_{10}H_8$ (**2b**).

	1a	**3a**	**2b**
Chemical formula	$C_6H_{12}B_{10}$	$C_6H_{12}B_{10}$	$C_{14}H_{32}B_{10}Si_2$
M_r [g mol^{-1}]	192.272	192.272	364.692
T [K]	123	123	293
Color	colorless	colorless	colorless
Crystal system	monoclinic	orthorhombic	orthorhombic
Space group	*C*2/*c*	*Pnma*	*Pnma*
a [Å]	25.253(5)	13.1791(10)	17.221(3)
b [Å]	9.577(3)	13.2512(13)	13.763(3)
c [Å]	22.923(4)	6.8310(8)	21.512(4)
β [°]	122.40(3)	–	–
Volume [Å^3]	4281(3)	1193.0(2)	5098.6(17)
Z	16	4	8
$D_{calcd.}$ [Mg m^{-3}]	1.091	1.070	0.950
μ [mm^{-1}]	0.049	0.048	0.136
F(000)	1568	392	1552
θ Range [°]	4.13–25.25	3.07–24.98	4.24–25.00
Reflections collected	15976	6547	41277
Independent reflections	4195	1088	4668
R(int) [%]	4.83	8.65	11.47
Data/restraints/parameters	4195/0/309	1088/0/104	4668/34/312
$R1$ [$I > 2\sigma(I)$][a]	0.0781	0.0488	0.0758
$wR2$ (all)[b]	0.1981	0.0911	0.1596
GOF on F^2[c]	1.112	1.015	1.083
Largest diff. peak/hole [e Å^{-3}]	0.763/–0.230	0.232/–0.124	0.189/–0.204

[a] $R1 = (\Sigma\|\|F_o| - |F_c\|\|)/\Sigma|F_o|$. [b] $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{0.5}$, weight scheme $w = [\sigma^2 F_o + (aP)^2 + bP]^{-1}$; $P = [\max(0,F_o^2) + 2F_c^2]/3$; **1a**: a = 0.0710, b = 9.5; **2b**: a = 0.0278, b = 0; **3a**: a = 0.0308, b = 3.292. [c] GOF: $S = \Sigma w(F_o^2 - F_c^2)^2/(m - n)$; ($m$ = reflections, n = variables).

Quantum Chemical Calculations: Density functional (DF) calculations[55] were carried out using Becke's three-parameter hybrid functional and the Lee–Yang–Parr correlation functional (B3LYP).[56] Geometries were optimized, and energies were calculated with the 6-311++G(d,p) basis sets. Diffuse functions were incorporated because improved energies are obtained for anions.[57] All structures represent true minima with no imaginary frequency on the respective hypersurface. DFT-GIAO[58] NMR spectroscopic shielding constants $\sigma(^{11}B)$, $\sigma(^{13}C)$, and $\sigma(^1H)$ as well as spin–spin coupling constants[59] 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, ^{13}C, and ^1H NMR spectroscopic shielding constants were calibrated to the respective chemical shift scale $\delta(^{11}B)$, $\delta(^{13}C)$, and $\delta(^1H)$ using predictions on diborane(6) and Me_4Si with chemical shifts of –16.6 ppm for B_2H_6[60] and 0 ppm for Me_4Si.[61] All calculations were carried out with the Gaussian 03 program suite.[62]

Supporting Information (see also the footnote on the first page of this article): Tables containing selected experimental and calculated bond lengths and angles and a table containing experimental and calculated IR and Raman spectroscopic data of dicarba-*closo*-dodecaboranes with one and two alkynyl substituents, as well as figures of the projections along the unit cell axes of 9,12-$(HCC)_2$-*closo*-1,2-$C_2B_{10}H_{10}$ (**1a**).

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