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Carba-*Closo*-Dodecaborates – Synthesis, Structure and Energetics

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Abstract: A full set of analytical data of salts (e.g. Me_3NH^+ , Cs^+ , Ag^+) bearing the *nido*- $B_{11}H_{14}$, *closo*- $[CHB_{11}H_{11}]^-$ anion and its chlorinated congener $[CHB_{11}CI_{11}]^-$ is reported. Structures and energetics of $[CHB_{11}H_{11-n}X_n]^-$ and $[B_{12}X_mH_{m-12}]^{2-}$ (n = 5, 11; m = 0, 12; X = halogen, CH₃, CF₃) and their protonated and silylated forms are studied. A direct correlation between theoretical calculated NICS values, gas phase acidities and experimentally detected ¹³C NMR shifts are discussed.

Introduction

Closo-borates and carba-closo-borates have been known for more than hundred years. The development of boron cage chemistry started in the early 20th century with Alfred Stock who was one of the pioneers in borane chemistry.^[1] In 1976 William N. Lipscom was honored with the Nobel prize for his investigations on the stereochemistry of boron cages.^[2] In the course of the discovery of carba-closo-boranes they and their corresponding anions were classified as a spherical and expensive obscurity.^[3] In recent years a lot of work was carried out with such cage molecules which are now appreciated for their low basicity, low nucleophilicity, as well as their (electro)chemical and thermal robustness.[4-6] Borane based cage molecules found a wide range of applications in medicine, [7,8] catalysis^[9,10] or even as weakly coordinating anion (WCA) for the stabilization of highly reactive cations in solution and the solid state if none of the well-known WCAs work (e.g. stable [Cat][CHB₁₁Cl₁₁] versus unstable [Cat][A]; [Cat]⁺ = H⁺, [Alk₃E]⁺; Alk = Me, Et, t-Bu; E = Group 14, $[A]^- = [BF_4]^-$, $[PF_6]^-$, $[B(C_6F_5)_4]^-$ [AI(OR^f)₄]⁻.^[11–16] Josef Michl summarized in his review articles of carba-closo-dodecaboranes the development of such chemistry in the last decades.^[17,18] Halogenated, arylated and alkylated derivatives of carba-closo-boranes and -borates (e.g. p-CH₂B₁₀H₁₀, [B₁₂F₁₁X]⁻, [CHB₁₁H₅Cl₆]⁻, X = NR₃) are useful irreplaceable building blocks in nowadays chemistry.[3,7,8,19-21]

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Carborane anions have been studied both experimentally and analytically, as they offer an almost inexhaustible variety with regard to feasible substitution- and constitution pattern. For example, a direct correlation between computed aromaticity (NICS values, NICS = nucleus independent chemical shift) and stability depending on the size, symmetry and substitution pattern of carborane species was reported.^[22]

It was our intention to investigate in particular halogenated carborate ions with regard to physical properties/correlations such as a correlation between theoretically determined NICS values, experimentally measured ^{13}C NMR shifts and gas phase acidities as well as [Me_3Si]^+ affinities. Moreover, we report here an optimized and detailed synthesis procedure for perchlorinated carba-*closo*-dodecaborates.

Results and Discussion

Synthesis and characterization of perchlorinated carbacloso-dodecaborates. A common precursor for the synthesis of salts containing carba-*closo*-dodecaborates are salts of the *nido*- $[B_{11}H_{14}]^-$ ion (1). There are different ways of synthesizing $[B_{11}H_{14}]^-$ salts using simple starting materials like BF₃·OEt₂ and Na[BH₄] (Scheme 1, eq. 1) or neutral higher borane-clusters like decaborane(10) or pentaborane(9) in combination with appropriate hydride sources (Scheme 1, eq. 2 and 3).^[23–25] Utilizing the first reaction path (eq. 1) with a subsequent cation metathesis reaction, we were able to isolate salts of 1 as analytically pure [Me₃NH]⁺-salt, [Me₃NH]1, in yields up to 32 %.^[24,26] With regard to the atom economy, which plays an essential role in borate syntheses, this constitutes a rather excellent yield.

17 Na[BH] 20 BEat OFta -	diglyme, 105°C	- 2 Na[B ₁₁ H ₁₄]		20 H ₂	(1)
	-Et ₂ O -Na[BF ₄]				
	dioxane, 90°C			2 11	(2)

 $M[BH_4] + B_{10}H_{10} \longrightarrow M[B_{11}H_{14}] + 2 H_2$ (2) DME, 85°C

 $MH + 2.2 B_5 H_9 \longrightarrow M[B_{11}H_{14}] + 3.4 H_2 (3)$ Scheme 1. Synthesis routes for salts containing nido-[B_{11}H_{14}]^- with M = Na, K.

Closing the *nido*-boron vertex in $[B_{11}H_{14}]^-$ (Figure 1, left) by carbene insertion utilizing the well-known dichlorocarbene led to the formation of the carba-*closo*-dodecaborane anion $[CHB_{11}H_{11}]^-$ (2) (Figure 1, middle) in rather poor yields of 9 % in a laboratory scale (Scheme 2, eq. 4). This procedure was initially introduced by the group of Michl.^[27] Other possible (known) routes include the use of decaborane(14) and alkali cyanides or *iso*-cyanides (Scheme 2, eq. 5 and 6).^[28–31] For safety and handling reasons (e.g. solvent mixtures of decaborane(14) are able to explode instantaneously, acidic work up procedures for cyanide containing borates, carcinogenic activity of methanal), we chose the more comfortable but low

yield synthesis of the carba-*closo*-dodecaborane anion (2) employing the *in situ* generated dichlorocarbene (Scheme 2, eq. 4).



Scheme 2. Selected common synthesis routes for closo-[CHB11H11] (2).

The carbon capped icosahedron of **2** offers now a new electronic situation, e.g. a three-dimensional σ -aromaticity was discussed in this diatropic closed shell inorganic cage molecule.^[22,32] The electronic situation can be changed by replacing the hydrogen atoms directly bonded to the cage boron atoms by proper atoms/groups like halogens or alkyl groups (Figure 2).



Figure 1. ORTEP representation of the molecular structures of the anions of [Me₃NH]**1**, Cs**2** and Cs**3** in the crystal. Thermal ellipsoids correspond to 50% probability at 173 K. Cations and solvents are omitted for clarity.

Depending time, solvent, pressure, halogenation, on respectively, alkylation reagent it is feasible to get selectively six- and elevenfold substitution. Even a mixed substitution pattern with regard to ortho- and meta-belt substituents is possible (Figure 2).^[5,14,33–40]Moreover, substitution on the carbon atom is also feasible. Eleven-fold chlorination $[CHB_{11}CI_{11}]^{-}$ (3) can be achieved by different routes. Ozerov et al. reported of a complete chlorination under reflux conditions, which only worked with a special batch of SO₂Cl₂ under atmospheric conditions.^[38] H. Poleschner and co-workers optimized a synthesis also reported by Ozerov taking SbCl₅ as chlorination reagent.^[41] Unfortunately, we were not able to reproduce their results, when taking a prechlorinated carborane anion as starting material. Only recently, new attempts using SO₂Cl₂ as (single) chlorination agent under pressurized or photochemical conditions were reported.^[42-44] We found it necessary for safety and handling purposes (see Supporting Information) to use SO₂Cl₂ as prechlorination agent and treated afterwards the partly halogenated vertex ([CHB₁₁H_nCl_{11-n}]⁻ with n = 2-5) with ICI and triflic acid in an autoclave (V4A) equipped with a teflon beaker at 200 °C (Scheme 3, eq. 7). Splitting up the reaction procedure led to analytically pure Cs3 (Figure 1, right) in reproducible yields of 40 %. Six-fold chlorination of 2 can be achieved by a more comfortable reaction pathway when using glacial acetic acid and chlorine gas as halogenation agent leading to $[CHB_{11}H_5Cl_6]^-$ (4) (Scheme 3, eq 8).^[5]



Scheme 3. Synthesis routes for *closo*-[CHB₁₁Cl₁₁]⁻ (3) and *closo*-[CHB₁₁H₅Cl₆]⁻ (4), with n = 2-5).

Carba-closo-borates are well known for their (electro)-chemical and thermal robustness,^[44,45] e.g. the truncated icosahedral species [Me₃NH]1 decomposes at a temperature of 237 °C. Closing the cage by carbene-insertion as in [Me₃NH]2 raises the decomposition temperature by more than 100 °C up to 357 °C. A cation exchange to the alkali metal Cs (Cs2: 517 °C) and the chlorination of the boron vertex led to a remarkable melting/decomposition point of >600 °C for Cs3. With regard to vBH stretching modes it was observed that a closed cage displays a slight blue-shift of 30 cm⁻¹ which even can be extended by the introduction of electron withdrawing halogens to more than 40 cm⁻¹ (cf. vBH 1: 2554 cm⁻¹, 2: 2580⁻¹ cm⁻¹, 4: 2593 cm⁻¹, Table 1).



Figure 2. Numbering scheme of closo-[CHB₁₁XnY_{11-n}]- (n = 6, 11; X, Y = H, F, Cl. Br. I. CH₃. CF₃).

Forming *closo*-cage anions **2**, **3** or **4** from *nido*-species **1** led to a contraction of all B-B bond lengths within the cage, especially the distances between the *antipodal* boron atom and the upper *ortho*-belt were affected (cf. Table S80, Σr_{cov} (B-B) = 1.76 Å, (C-B) = 1.61 Å, see also Figure 2).^[46] However, in comparison with the calculated gas phase structures, these structural changes were less pronounced or not observed. Hence, it can be assumed that anion-cation interactions or packaging effects might be the origin of these structure differences.

Gas phase DFT (Density Functional Theory) calculations (pbe0/aug-cc-pwCVDZ, see below) agree well with data obtained from solid state X-ray structure elucidations. The solid state structural data of all investigated anions **1-4** have already been reported, however, in combination with other cations e.g. [Ph₃PH]**1**,^[47] [Bpy-H]**2**,^[48] [Ph₃C]**3**^[49] and [Ph₃C]**4**,^[49] therefore we abstain here from a detailed structural discussion.

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Table 1: Physical properties and spectroscopic details of selected carbacloso-borates.

	mp. [°C]	vCH [cm ⁻¹]	vBH [cm⁻¹]	δ ¹³ C exp.
[Me₃NH]1	237 ^[c]	-	2518/2554	-
[Me ₃ NH] 2	350 ^[c]	3027	2519/2549	51.5
Cs 2	517	3048/3059	2580	51.4
Cs 3	>600°C ^[d]	3022	-	47.6
Ag 3 ^[a]	196 ^[c]	3022	-	47.6
[Ph ₃ C] 3 ^[b]	207 ^[c]	3022/3043 ^[e]	-	47.4
[Ph ₃ C] 4 ^[b]	230 ^[c]	3058 ^[e]	2593	32.8

[a] ¹/₃ · CH₃CN solvate adduct; [b] taken from ref. ^[49]; [c] decomposition; [d] no changes during DSC measurement until 635 °C; [e] superimposed by CHphenyl stretching mode.

Computational details. Gas phase DFT calculations at the pbe0/aug-cc-pwCVDZ level of theory were carried to elucidate structural and electronic effects of differently substituted halo*closo*-carborates ([Cat][CHB₁₁H_{11-n}X_n]; n = 6, 11; X = H, F, Cl, Br, I; Me, and CF₃; [Cat]_m[B₁₂X₁₂]^{m-2} X = H, halogen, m = 1, 2; Cat = H^+ , $[Me_3Si]^+$). To study the electronic situation of substituted halo-closo-carborates in detail we computed ¹³C NMR shifts, NICS values (Nucleus-independent chemical shift), and trimethylsilyl and proton affinities.[50-56] Additionally, the partial charges (NBO = natural bond orbital) and a NLMO calculation (Natural Localized Molecular Orbital) were calculated.[57-59]

Structural effects. I. Koppel et al. and C. Jenne et al. already investigated different protonation sites for fluorinated and chlorinated B12-closo-borates, as well as some other carbacloso-dodecaborates.[60-62]

mp.	VCH	vВН	δ ¹³ C	eleven-fold halog
[°C]	[cm ⁻¹]	[cm ⁻¹]	exp.	closo-borates. F
237 ^[c]	-	2518/2554	-	Each of the mo
350 ^[c]	3027	2519/2549	51.5	supporting inform
517	3048/3059	2580	51.4	H I
>600°C ^[d]	3022	-	47.6	Y B ₆
196 ^[c]	3022	-	47.6	X-B

Table 2: Selected values of halogenated closo-borates.

C. Reed and co-workers were able to determine the X-ray crystallographic structure for H[CHB₁₁Cl₁₁].^[12] With these results in hand, we calculated the minimum structures for all six- and genated carborates, as well as the dianionic urthermore, the minimum structures of the trimethylsilylated congeners were computed. ore than 200 structures were determined as ecked for zero imaginary frequencies (see ation Tables S14-S16, S64-S113).



Figure 3. Optimized gas phase structures of different proton binding modes, A: X = Y = H, B: H[CHB₁₁XY]: X = halogen / Y = H; X = Y = halogen and $H[B_{12}X_{12}]^{-}X = Y = CI, Br, I, C: X = CH_3 / Y = H; X = Y = CH_3, CF_3, D: X = CF_3,$ Y = H, E: X = H, F: X = F, G: X = Cl, Br, I, protons highlighted by arrows.

As expected, all halogenated carba-closo-borates of the type $[CHB_{11}H_5X_6]^-$ and $[CHB_{11}X_{11}]^-$ feature a $C_{5\nu}$ symmetric structure as global minimum in the gas phase, while only C_1 symmetry is found for the minima of $[CHB_{11}H_5R_6]^-$ and $[CHB_{11}R_{11}]^-$ (R = CH₃, CF₃). Dianionic borates of the type [B₁₂X₁₂]²⁻ display the expected ideal Ih symmetry. All optimized structures can be found in the supporting information (see S64-S113).

For the mono and diprotonated species, the situation is rather complex (Table S15/S16) since in most cases different isomers with similar energy are found displaying different binding modes as depicted in Figure 3. There are six (Figure 3 A - G) major

compound	δ(¹³ C) calc.	qC [<i>e</i>] ^[a]	NICS ^[b]	C-B ¹² -X ¹² [°] E [kcal·mol ⁻¹] ^[c]	compound	δ(¹³ C) calc.	qC [e] ^[a]	NICS ^[b]	C-B ¹² -X ¹² [°] E [kcal·mol ⁻¹] ^[c]
[CHB ₁₁ H ₅ F ₆] [−]	7.8	-0.779	-34.8	177.6 / 39.5 ^[d]	[CHB11H5Br6]⁻	37.6	-0.806	-30.6	171.5 / 112.9
[CHB11F11] ⁻	19.9	-0.936	-33.3	177.6 / 42.8	[CHB ₁₁ Br ₁₁] [−]	54.4	-0.978	-32.0	171.8 / 131.7
[B ₁₂ F ₁₂] ²⁻	-	-	-35.7	-	[B ₁₂ Br ₁₂] ²⁻	-	-	-34.3	-
[CHB ₁₁ H₅Cl ₆] [−]	32.2	-0.801	-32.2	172.3 / 71.6	[CHB ₁₁ H ₅ I ₆] [−]	49.6	-0.816	-28.0	171.7 / 106.9
[CHB11CI11] [−]	51.3	-0.947	-34.4	171.6 / 73.5	[CHB ₁₁ I ₁₁] [−]	59.6	-1.028	-28.5	172.1 / 133.5
[B ₁₂ Cl ₁₂] ²⁻	-		-37.2	-	[B ₁₂ I ₁₂] ²⁻	-	-	-30.9	-
[CHB11H11] [−]	52.8	-0.812	-27.7	-	[B ₁₂ H ₁₂] ²⁻	-	-	-27.8	-

[a] NBO charge; [b] GIAO magnetic shield tensor at the boron cage center; [c] C-B¹²-X¹² angle of distortion by coordination of [Me₃Si]⁺ for [Me₃Si][CHB₁₁H_{11-n}Y_n] / Gain of energy (E) for building a hydrogen bridge (X-H-X) determined by a NLMO calculation for H[CHB₁₁H_{11-n}Y_n]; [d] sum of three equivalent hydrogen bridges.

different binding modes for the singly and doubly protonated (car)borate anions (Figure 3). However, it should be noted that 13 different structures are located (see Table S15) for the monoprotonated species while 38 structures are found for the doubly protonated species (see Table S16).

H[CHB₁₁H₁₁] displays a rather interesting binding mode, which is best described as a side-on coordination of a H₂ molecule to boron atom B¹² (H–H 0.846 Å, vide supra). As depicted in Figure 3A, for H[CHB₁₁H₁₁] protonation is favored at the antipodal B¹² atom, in contrast to the situation found for H[CHB₁₁H₅X₆], H[CHB₁₁X₁₁] and H[B₁₂X'₁₂]⁻ (X' = Cl, Br, and I) for which the proton is observed between X¹² (attached to B¹²) and X⁸ (attached to B⁸) with two distinct different X···H distances (Tables S13). By this intramolecular hydrogen bonding, C_{5v} symmetry of the deprotonated species is decreased to C_1 . Interestingly, in case of H[CHB₁₁I₁₂] identical d(H···I) distances are computed. According to NBO analysis data, the donoracceptor energies for LP(X) $\rightarrow \sigma^*$ (X-H) interactions (LP = lone pair) lie in the range between 40 – 134 kcal/mol (Table 2).

A further complexation mode of the proton is shown in Figure 3C displaying a 3-coordinated H⁺ between X⁸, X⁹ and X¹². Besides four other, less favored, minimum structures (Figure S45-S47, Table S15) such a 3-coordinated H⁺ species are found for H[CHB₁₁H₅Me₆], H[CHB₁₁Me₁₁], H[CHB₁₁(CF₃)₁₁], H[B₁₂X'₁₂]⁻ (X' = H, F). This intramolecular hydrogen bonding situation arises from the fact that the alkyl groups form a pocket which provides enough space for the proton, leading to rather short H-B distances (1.387 - 1.431; cf. $\sum r_{cov}(B-H) = 1.17$ Å)^[63] and significantly longer H–CR₃ distances (2.189 – 2.254 Å). While for H[CHB₁₁X'₁₂] all three H–B distances are identical, for the alkyl substituted species one short and two longer distances are found (Table S13). The origin of the unusual trigonal prismatic coordination is reasoned by an increased steric demand of the alkyl groups. Interestingly, the carbon atoms of the methyl groups possess a large negative charges (-0.95 - -1.00e) while the carbon atoms in the perfluorinated species are positively charged (+0.91 - +0.95e). Hence a complex situation of van der Waals interactions with all atoms forming the "pocket" for the proton can be expected.^[64]

The six-fold (trifluoro)methylated carborate shows an exception probably due to an increased sterical stress between the trifluoromethyl groups (Figure 3 D). Here structure type A with a side-on bonded dihydrogen at one boron atom of the meta-belt (d(H-H) = 0.87 Å, $4(H-B-H) = 37.5^{\circ}$, Σr_{cov} (H-H) = 0.64 Å) is found to be favored by 11.1 kcal·mol⁻¹ over isomer **C** (see Table S15). H[CHB₁₁H₅(CF₃)₆] favors protonation at one of the *meta*-belt boron atoms (Figure 3 D) with one distinct H-B bond (d(H-B) = 1.33/1.36 Å, d(H-F) = 1.86, d(H-H) = 0.866 Å).

Upon double protonation as in H₂[B₁₂H₁₂] the second proton is directly attached to the H–B¹² unit (Figure 3 E) again in a side-on H₂ coordination mode with H–H distances of 0.848 Å (*cf.* $\sum r_{cov}$ (H-H) = 0.64 Å), while the first proton as in H[B₁₂H₁₂]⁻ (see above) is 3-coordinated by one B₃H₃ moiety (Figure 3 E, *d*(H^{...}H) = 1.82-1.85 Å). Such H₂-side-on binding mode is also discussed for CH₅⁺ for which calculations hinted at a very high degree of fluxionality owing to the unusual two-electron–three-center bonding.^[65,66] A completely different situation was found for

 $H_2[B_{12}F_{12}]$ (Figure 3 F) displaying two doubly coordinated protons (by F⁸, F⁹ / F¹, F⁴). A similar situation is found for all $H_2[B_{12}X_{12}]$ species (X = Cl,^[67] Br,^[67] I), however, here the second doubly coordinated proton sits between X⁸ and X¹² (Figure 3 G).



Figure 4. Optimized gas phase structures of different [Me3Si]+ binding modes, **A**: [Me₃Si][CHB₁₁XY]: X = halogen / Y = H; X = Y = halogen and [Me₃Si][B₁₂X₁₂]⁻ X = Y = H, halogen; **B**: [Me₃Si]₂[B₁₂X₁₂] X = Y = H, halogen; **C**: X = CH₃, CF₃, Y = H; **D**: X = Y = CH₃, CF₃, R = F, H; [Me₃Si]-groups highlighted by arrows.

In a second series of computations, the proton is formally substituted by the Me₃Si moiety which can be regarded as a "big proton".[68-72] Interestingly, stable isomers for the monosilylated are only found for those species which provide B-X (X = halogen, H) bonds. In all other cases $[Me_3Si][CHB_{11}R_{11}]$ (R = CH₃, CF₃), contrary to the H⁺ species, decomposition into Me₃Si-H/F and (H/F)₂C=R are observed (Figure 4 D). As long as there are B-X and B-H bonds present, the highly reactive Me₃Si group forms Me₃Si···X···B 4-electron-3-center bonds ([Me₃Si][B₁₂F₁₂]⁻: e.g. d(Si–F) = 1.78 Å, cf. ∑r_{cov}(Si–F) = 1.8 Å, d(Si–F) = 1.753(9) Å in $[Me_3Si-F-SiMe_3]^+)$.^[69] For all $[Me_3Si][CHB_{11}X_{11}]$ and [Me₃Si][B₁₂X₁₂]⁻ species silylation is always favored at the antipodal boron atom (Figure 4 A, Table S14). This phenomena is not known in literature. Published solid state X-ray structures revealed a trimethylsilylation at the ortho-belt (Figure 2, cf. $[Me_3Si][CHB_{11}F_{11}]^{[14]}.$ For those species with an alkylated lower boron belt (as in $[Me_3Si][CHB_{11}H_5R_6]$ R = CH₃, CF₃), stable isomers are only computed with Me₃Si^{...}H^{...}B (attached to a meta belt boron atom, Figure 2) bonds. Again silylation at the alkyl groups results in decomposition yielding Me₃Si-X and X₂C=R (X = H, F). Double silulation for all $[B_{12}X_{12}]^{2-}$ species, which gives [Me₃Si]₂[B₁₂X₁₂], affords para-silylated species as the most favorable species (Figure 4 B, Table S14) displaying Si...X...B 4electron-3-center bonds. This is also in contrast to literature

known structures of borates. The attachment of two Et_3Si groups were found in 1,7 position (*meta*-silylation, Figure 2) in the case of $[B_{12}CI_{12}]^{2\cdot[73]}$ and $[Me_3NB_{12}CI_{11}]^{\cdot[74]}$

Proton and TMS affinities. The gas phase proton affinity (PA) for the reaction $A^n{}_{(g)}$ + $H^+{}_{(g)} \rightarrow [AH]^{n+1}{}_{(g)}$ (n = –1, –2; A^n = borate ion) is defined as the negative of the reaction enthalpy at 298.15 K.^[75] Trimethylsilyl affinity (TMSA) can be defined in similar way as the negative of the reaction enthalpy at 298.15 K for the reaction $A^{n}_{(g)}$ + $[Me_{3}Si]^{+}_{(g)} \rightarrow [A(Me_{3}Si)]^{n+1}_{(g)}$.^[69,76] These PA values are usually discussed for $[AH]^{n+1}_{(g)}$ and $[A(Me_3Si)]^{n+1}_{(g)}$ species that is for the reverse reaction. The proton and trimethylsilyl affinities of all considered species are listed in Table S12. The proton affinities lie in the range between 366.9 kcal/mol (formation of $H[B_{12}H_{12}]^{-})$ and 184.9 kcal/mol (formation of $H[CB_{11}(CF_3)_{11}]$, (cf. PA [kcal·mol⁻¹]: A = F⁻ 368.5, OH⁻ 390.1, [ClO₄]⁻ 301.1, [CF₃SO₃]⁻ 299.7). The calculated data are in agreement with already known literature data. An exchange of the computational method HF, DFT (PBEO, B3LYP) or the perturbation theory MP2 in combination with different basis sets aug-cc-pwCVDZ, def2-TZVPP, 6-31+G*, 6-311+G** partly displays a large influences on the the absolute PA values. Deviations of up to 14.2 kcal mol-1 were found (see H[CHB₁₁H₅F₆]). Moreover, depend on the utilized method/basis set different global minima were found on the PES in some cases (see $H_2[B_{12}F_{12}]$ Isomer 22 (Figure S56). For a detailed comparison see supporting information (Tables S81-S84).

A proton transfer reaction is best possible with $H[CHB_{11}(CF_3)_{11}]$, which represents the strongest acid amongst all considered species. However, also all other species represent very strong acids compared to common acids (cf. PA [kcal-mol⁻¹]: A = [HSO₄]⁻ 311.1, H₂O 164.3, [NO₃]⁻ 322.6, Et₂O 196.9). Within the series $[CHB_{11}H_5X_6]^-$ ions the smallest PA value was found for H[CHB₁₁H₅F₆] (241.6 kcal·mol⁻¹) and the largest value for H[CHB₁₁H₅I₆] (257.7 kcal·mol⁻¹, Figure 5). The same trend is found for all [CHB₁₁X₁₁]⁻ species with the largest PA determined for H[CHB₁₁I₁₁] (250.5 kcal·mol⁻¹) and the smallest for the fluorine species H[CHB₁₁F₁₁] (226.4 kcal·mol⁻¹, Figure 6). For all these species protonation is favored between BX12 and BX8 (Figure 3 B). Comparison of the PAs between H[CHB₁₁X₁₁] and $H[CHB_{11}H_5X_6]$ displays that the PAs of $H[CHB_{11}H_5X_6]$ are larger by 7-15 kcal·mol⁻¹. With increasing degree of alkylation, the PA values increase (e.g. H[CHB₁₁(Me)₁₁]: 271.4 kcal·mol⁻¹), while in case of the H[CHB₁₁(R^{F})₁₁] (R^{F} = fluorinated alkyl group) the opposite is observed (cf. PA H[CHB₁₁(CF₃)₁₁] = 184.9 kcal·mol⁻¹). Usually, protonation is favored between B12X12 and B8X8/B9X9 with the exception of $[CHB_{11}H_5(CF_3)_6]^-$ for which H₂ formation is found upon protonation at the meta-belt B atom (Figures 3 C/D). The proton affinities of $H[B_{12}X_{12}]^-$ (formation of the dianions [B₁₂X₁₂]²⁻) are significantly larger and follow the trend as observed above F (318.6) > CI (314.2) ≈ Br (314.5) ≈ I (314.6 kcal·mol⁻¹), while the PA of $[B_{12}H_{12}]^{2-}$ is largest of all considered species with 366.9 kcal·mol⁻¹. The PA values for the second protonation drop into the range 230.4 (F) to 268.7 kcal·mol⁻¹ (H). The TMSA values lie all within the range 71.5 [Me₃Si][CHB₁₁H₅(CF₃)₆] and 109.8 kcal-mol⁻¹ [Me₃Si][CHB₁₁H₁₁] (cf. [Me₃Si-F-SiMe₃]⁺ 34.8 kcal·mol⁻¹).^[69]

Hence, [Me₃Si][CHB₁₁H₅(CF₃)₆] represents the best silvlation species and most "naked" Me₃Si⁺ species within the considered species. Nevertheless within [Me₃Si-F-SiMe₃]+ "[Me₃Si]+" is less strong bound. Silvlation at the para position is favored for $[CHBH_5X_6]^-$ and $[CHB_{11}X_{11}]^-$ while silvlation in $[CHB_{11}H_5Alk_6]^$ only occurs at the meta protons otherwise in case of a para or ortho silulation the formation of Me₃Si-H and Me₃Si-F is predicted (vide supra, Figure 4 D). In all other case silulation at the ortho belt is less favored by 1 - 5 kcal·mol⁻¹. The small energy differences might indicate a moveable TMS group on the carborane surface known for the protonated species (vide supra). As discussed before solid state structures revealed a silylation in ortho-position, which might be favored due to crystal packing.[14] The TMSA difference between [CHBH₅X₆]⁻ and [CHB₁₁X₁₁]⁻ is roughly 10 kcal-mol⁻¹. A similar situation is found for the silvlation of the dianions. The TMSA values decreases along the series H (193.6) > F (167.0) > Cl (151.5) > Br (149.4) > I (146.7 kcal-mol⁻¹) for the first step, while for the second silvlation step much smaller TMSA values are computed (H (119.1) > F (108.2) > CI (99.2) > Br (98.9) > I (98.6 kcal·mol⁻¹), which is within the range of the TMSA values of the [Me₃Si][carborate] series (vide supra, Figure 5).



Figure 5. NICS values (blue triangles) and gas phase acidity (green diamonds) / trimethylsilyl affinity (red crosses) each in dependency to the ¹³C NMR shift of closo-[CHB₁₁H₅X₆]⁻ with X = F, Cl, Br, I.

Charge transfer, ²⁹Si / ¹³C NMR shifts and NICS values. To get insight into the electronic situation of the protonated and silvtated species, the charge transfer ($Q_{CT}(H^+)$ and $Q_{CT}(Me_3Si^+)$, Table S13) is calculated by NBO analysis describing the amount of electrons transferred from the borate anion to the H⁺ and Me₃Si⁺ ion upon protonation and silylation, respectively. The monoprotonated species display a charge transfer between 0.96 e, which means the formation of a formal "H⁰" as in [CHB₁₁I₁₁]⁻, and 0.37 e in the fluorine species [CHB₁₁F₁₁]⁻, $[CHB_{11}H_5F_{11}]^-$ or $[B_{12}F_{12}]^{2-}$. As expected the observed trends follow the electronegativities of the substituents. Interestingly, there are almost no differences between the charge transfers of the $[CHB_{11}X_{11}]^{-}$, $[CHB_{11}H_5X_{11}]^{-}$ and $[B_{12}X_{12}]^{2-}$ species. The methylated species are in the range of the chlorine species (0.71-0.75 e). It should be noted that also the charge transfer of the CF_3 substituted species lies in the same range (0.71-0.74 e). A much smaller charge transfer is found for the silylated compared to the protonated species ranging between 0.17 e $([CHB_{11}F_{11}])^{-}$ and 0.63 e $([B_{12}I_{12}]^{2-})$. Again the trends agree with those of the protonated species. It is noteworthy to mention that bond-dissociation energies (BDE) of H-X and Si-X^[77] following

the same trend, the more electronegative the substituent the larger the BDE ($\Delta H_{H/Si-X}$ F > Cl > Br > l).



Figure 6. NICS values (blue triangles) and gas phase acidity (green diamonds) / trimethylsilyl affinity (red crosses) each in dependency to the ¹³C NMR shift of closo-[CHB₁₁X₁₁]⁻ with X = F, Cl, Br, I.

The computed NICS values are all negative ranging between -25 ([CHB₁₁H₅(CF₃)₆]⁻) - -37 ([B₁₂Cl₁₂]²⁻) indicating aromaticity for all considered species. The computed ²⁹Si NMR shifts are found between +52.3 ($[B_{12}H_{12}]^{2-}$) and +135.4 ppm ($[CHB_{11}F_{11}]^{-}$). In accord with the above ²⁹Si NMR data, the charge transfer is smaller and the TMSA values are larger the higher the ²⁹Si NMR shift. Hence, [Me₃Si][CHB₁₁F₁₁] contains the most less stabilized [Me₃Si]⁺ ion amongst the considered species. Experimental evidence for a three-coordinate silyl cation was first provided by the crystal structure of [(Mes)₃Si][CHB₁₁Me₅Br₆] (where Mes is 2,4,6-trimethyl-phenyl).^[78] Here ortho-methyl groups of the mesityl substituents shield the silicon atom. The downfield ²⁹Si shift in the solid state (226.7 ppm) was found to be almost identical to that in "gas phase" calculations, indicating that threecoordination can be preserved in all phases. The resonance of naked [Me₃Si]⁺ is computed at 385 ppm, indicating for our species still significantly stabilized [Me₃Si]⁺ species in accord with the computed TMSA values.

Until now there are only four X-ray crystallographic structures of *nido*-cage compounds (1) known. The authors of these structural reports assumed bridging H atoms on the upper *meta*-boron-belt in highly disordered anions (Figure 1, left).^[47,48] In the liquid phase a dynamic behavior of the protons is observed. ¹H NMR analysis (Figure 7, Figures S1/S2, S6-S9) show a broad signal strongly highfield shifted for three chemically equal protons attached to the *meta* belt at -3.60 ppm ($\Delta v_{1/2} = 100$ Hz).

Calculations by Crabtree revealed a small energy gap for a free rotation of the capping H atoms with an activation barrier of only 1.2 kcal·mol⁻¹.^[79] We calculated ¹J(¹H-¹¹B) coupling constants for this proton which are rather small and lie within the range of 40 Hz (Table S11). Crabtree determined the coalescence temperature of **1** at 140 K which is rather low and does not allow any resolution for further investigations. Furthermore, in the range of 0.4-2.8 ppm a complex pattern with ¹J(¹H-¹¹B) = 120-140 Hz was detected. Decoupling of ¹¹B nucleus led to the collapse of this complex pattern with the ¹⁰B nuclei (Figure 7, Figure S9). A closer look at the ¹³C NMR shifts of the capping carbon atom shows a highfield shift (*cf.* δ^{13} C Cs**2** = 51.4, Cs**3** = 47.6, [Ph₃C]**4** = 32.8 ppm, Table 1) upon chlorine substitution.



Interestingly, a six fold substitution of the carborate vertex

reveals a greater highfield shift than full chlorination with a shift

Figure 7. ¹H NMR spectra (top) and ¹H{¹¹B} NMR spectra (bottom) of [Me₃NH]1 both in THF-[D₈]. **A** = N*H*, **B** = NC*H*₃, **C** = B¹²*H*, **D** = B²⁻⁶*H*, **E** = B⁷⁻¹¹*H*, **F** = H^{12-14} .

All computed ¹³C NMR shifts lie between 7.8 ([CHB₁₁H₅F₆]⁻) and 67.9 ppm ([CHB₁₁(CH₃)₁₁]⁻). With respect to the accuracy of the computed ¹³C NMR shifts, the average deviation between experiment and theory amounts to 3.4 ppm, while the largest deviation is found for the [CHB₁₁(CH₃)₁₁]⁻ anion with –7.4 ppm. The full set of both the experimental and theoretical NMR data are listed in Table S12.

As negative NICS values are found for all carborates, lying between -25.1 ([CHB₁₁(CH₃)₁₁]⁻) and -34.8 [CHB₁₁H₅F₆]⁻, a three-dimensional aromaticity^[51,80,81] can be assumed (e.g. 1: -25.7, 2: -27.2, 3: -34.4, 4: -32.2, [B₁₂H₁₂]²⁻: -27.7, [B₁₂Cl₁₂]²⁻: -37.2). Already Paul Ragué von Schleyer, investigated the stability and established three-dimensional aromaticity for unsubstituted mono/di-carba-closo-borates.[22] With increasing symmetry and an increasing number of halogen atoms, the more negative NICS values are found displaying a better delocalization upon halogen substitution (Table 2, Table S12), an effect also known for planar perchlorinated Hückel aromatic heterocycles (see Table S18). The aromaticity of closo-borane hydride clusters was also studied by other methods such as ECSA method (ECSA = electronic confined space analogy).^[82,83] A lower electronegativity of the halogen atom and an unsymmetrical substitution (six-fold halogenation) results in a polarization of the boron cage which is indicated by a high-field shift of the cage carbon atom resonance by more than 10 ppm compared to eleven- and six-fold substituted derivatives (cf. δ [¹³C_{calc.}] (δ [¹³C_{exp.}]) of [CHB₁₁H_{11-n}X_n]⁻ X = F,^[84] Cl, Br, I, Me; n = 6: 7.8, 32.2 (32.8),^[49] 37.6 (41.5),^[85] 49.6 (55.8),^[86] 42.1^[84]; n = 11: 19.9, 51.3 (Cs3: 47.6), 54.4 (54.1),^[35] 49.6 (55.5),^[35] (60.5);^[37] **2** = 52.8 (51.4) ppm, Table 2, Table S12) Interestingly, the fully methylated carborane anion exhibits the largest low-field ¹³C shift, thus featuring the largest Lewis acidic carbon center compared to the halogenated congeners.

Fluorinated carborates feature the smallest NICS values while their ^{13}C NMR shifts are most high field shifted. Comparing sixfold and fully-halogenated carborates, the six-fold species show a slightly smaller ^{13}C NMR shift and smallest negative NICS values. A similar trend is also found for halogenated benzene derivatives (see supporting information, Table S18), with the hexachlorobenzene featuring the largest negative NICS value. Moreover, the fluorine derivatives display also larger negative NICS values compared to the less electronegative species (e.g. Cl, Br, I or H substituted species). A glance at the literature reveals that the outstanding formal $[R_3Si]^{t+1,86,88,89]}$ are already being used unconsciously.

Conclusions

Herein, we report an optimized laboratory scaled reaction procedure for the preparation of [CHB₁₁Cl₁₁]⁻ starting from easy to handle building blocks. To summarize, upon protonation the proton becomes bound in either mono/di or even tri-coordinated fashion: (i) The proton is attached to one of the boron or carbon atoms, (ii) the proton sits between halogen atoms with one short and one longer HX distance, and (iii) the proton interacts with one B₃X₃ unit which forms kind of a pocket with different H···B/H···X interactions. In the latter case of tri-coordination, the proton is located inside a distorted trigonal $B_3^{8,9,12}X_3^{8,9,12}$ (see Figure 3C) prism slightly above the boron triangle which is formed of two ortho-belt and one antipodal boron atoms. While the B-H distances are rather short (1.38 - 1.43 Å), the distance to the (trifluoro)methyl-carbon atoms ($d(H-CR_3) = 2.19 - 2.25 \text{ Å}$) are rather long. Obviously, the alkyl-substituted species are unable to form classic hydrogen bonds on the surface of the borate ion. For all species a highly dynamic behavior of the proton at the cage surface can expected since the energy difference between the lowest lying isomers is rather small (< 10 kcal mol⁻¹).

Stable isomers of the monosilylated species are only found for those species which provide B-X (X = halogen, H) bonds. In all other cases ([Me₃Si][CHB₁₁Alk₁₁]) decomposition into Me₃Si-H and H₂C=R is predicted (Figure 4 D).

The computed proton affinities, ranging between 366.9 and 184.9 kcal·mol⁻¹, are characteristic for very strong acids such as (PA [SO₃CF₃]⁻ = 299.7 kcal·mol⁻¹). The TMSA values are all within the range 58.2 and 109.8 kcal·mol⁻¹ therefore displaying very good silylating reagents. [Me₃Si][CHB₁₁H₅(CF₃)₆] is the best silylation reagent and most "naked" Me₃Si⁺ species within the considered species.

¹³C NMR shifts and NICS values might be used as indicators to classify the reactivity of the considered borate towards (Lewis) acids. While a large ¹³C NMR shift can be seen as an indicator for an increased acidic character of the anion, a larger NICS value might hint on a perturbed possibility of charge delocalization inside the boron cage. This already favors an electrophilic attack for instance by a [Me₃Si]⁺ - ion with its empty p_z-orbital abstracting an exposed atom (with regard to disturbed aromaticity) from an terminal alkyl group. The abstraction of an

H or F atoms from the alkyl group results in the formation of a neutral charged trimethylsilane and a carborane bearing a formal $X_2C=B^N$ group (X = H, F, N = 2, 8, 12, for positions see Figure 2). In general, with an increase of the ¹³C NMR shift of *closo*-carborates there is also an increase of the basicity of the anion (Figures 5-6) while a decrease of the corresponding NICS values occurs.

Experimental Section

Detailed information for the syntheses of $[Me_3NH]1$ and $[Me_3NH]2$ can be found in the Supporting information.

Cs2. Cesium carba-closo-undecahydrododecaborate: To a clear and colorless water boiling solution of [Me₃NH]2 (1.75 g, 8.6 mmol) CsOH·H₂O (2.88 g, 17.2 mmol) was added. After stirring for 0.5 h the solvent was removed and the product dried in vacuo for 2 h. The product was redissolved in water (50 mL) and four times extracted with diethylether (50 mL). The combined organic phases were dried in vacuo for 6 h at 100 °C yielding in colorless Cs2 (0.93 g, 3.37 mmol, 39 %). Elemental analysis for CH12B11Cs (275.93 g/mol) calc. (found), %: C, 4.35 (4.56); H, 4.38 (4.14). mp. 517 °C. ¹H NMR (25 °C, [D₆]-acetone, 300.13 MHz): $\delta = 0.59-2.59$ (m, 12H, CH/BH). ¹¹B NMR (25 °C, [D₆]acetone, 96.29 MHz): $\delta = -16.18$ (d, $B^{2-6}H$, ${}^{1}J({}^{11}B-{}^{1}H) = 150$ Hz), -13.11(d, B^{7-11} H, ${}^{1}J({}^{11}$ B- 1 H) = 140 Hz), -6.69 (d, B^{12} H, ${}^{1}J({}^{11}$ B- 1 H) = 140 Hz). ¹³C{¹H} NMR (25 °C, [D₆]-acetone, 75.47 MHz): δ = 51.4 (b, CH). IR (ATR, 16 scans, 25 °C, cm⁻¹): 3058 (w), 2927 (w), 2856 (w), 2510 (s), 2352 (w), 1309 (w), 1214 (w), 1145 (w), 1089 (m), 1064 (w), 1024 (s), 972 (w), 891 (w), 854 (w), 757 (w), 715 (s), 588 (w). Raman (473 nm, 6 mW, 40 s, 8 acc., 25 °C, cm⁻¹): 3059 (1), 3048 (1), 2580 (5), 1144 (1), 1091 (1), 1025 (1), 986 (1), 945 (1), 926 (1), 890 (1), 860 (1), 761 (10), 715 (1), 676 (1), 632 (1), 586 (2), 570 (2), 547 (1), 497 (1), 338 (1), 190 (1). MS (Cl⁻, m/z (%)): 128 (85), 133 (17), 143 (6) [CHB₁₁H₁₁]⁻, 149 (25), 215 (100). MS (CI+, m/z (%)): 69 (23), 75 (100), 81 (12). 85 (24).

Cs3. Cesium carba-closo-undecachlorododecaborate: SO₂Cl₂ (100 mL) was condensed in vacuo on cooled (-196 °C) Cs2 (1.6 g, 5.8 mmol). The reaction mixture was allowed to warm up in a pressure equalized flask and refluxed additionally for 2 h. The prechlorinated carborate was dried in vacuo for 1 h at 60 °C. The resulting crude product was dissolved in water (50 mL) and four times extracted with diethyl ether (50 mL). The combined ether phases were dried in vacuo for 1 h at 60 °C. This product was transferred into a V4A stainless steel autoclave under a steam of argon. ICI (48.7 g, 0.3 mol) and HOTf (67 g, 0.45 mol) were added quickly and the autoclave was heated 5 d at 200 °C. The reaction mixture was transferred into a flask and the product was dried in vacuo, by removing excess ICI, I2 and HOTf. The resulting powder was dissolved in boiling water filtered G3 through kieselguhr. After an extraction with diethylether the combined organic layers were dried in vacuo resulting in colorless Cs3 (1.52 g, 2.32 mmol, 40%). Elemental analysis for CHB11Cl11Cs (654.83 g/mol) calc. (found), %: C, 1.83 (2.23); H, 0.15 (0.69). mp./dec. >600 °C. ¹H NMR (25 °C, [D₆]-acetone, 300.13 MHz): δ = 4.33 (b, 1H, CH). ¹¹B NMR (25 °C, [D₆]-acetone, 96.29 MHz): δ = -12.94 (s, B²⁻⁶Cl), -9.84 (s, B⁷⁻¹¹Cl), -2.41 (s, B¹²Cl). ¹³C{¹H} NMR (25 °C, [D₆]-acetone, 75.47 MHz): δ = 47.6 (s, CH). IR (ATR, 64 scans, 25 °C, cm⁻¹): 3646 (w, v_{H2O}), 3569 (w, vH2O), 3023 (m), 1608 (w), 1253 (w), 1116 (s), 1008 (s), 952 (s), 898 (m), 715 (m), 671 (m), 582 (m), 530 (s). Raman (473 nm, 6 mW, 10 s, 10 acc., 25 °C, cm⁻¹): 3024 (2), 1081 (1), 898 (1), 490 (1), 319 (4), 305 (10), 164 (1), 132 (2). MS (CI⁻, m/z (%)): 127 (59), 148 (34), 286 (100), 324 (11), 380 (12). MS (Cl+, m/z (%)): 75 (21), 173 (6), 276 (11), 520 (100) [CB₁₁Cl₁₁]⁺.

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FULL PAPER

Ag3. Silver(I) carba-closo-undecachlordodecdecaborate: Cs3 (0.267 g, 0.41 mmol) was dissolved in hot (60 °C) water (40 mL). After addition of a few drops HNO3 a solution of AgNO3 (0.16 g, 0.82 mmol) was added. 3 mL CH₃CN was needed to precipitate the silver salt. After stirring in the dark for 0.25 h the salt was extracted four times with toluene by extensively shaking. The combined toluene layers were dried in vacuo at 70 °C for 12 h. The product was washed with a small amount of cold toluene and dried again yielding in Ag3.1/3 CH3CN (0.1 g, 0.16 mmol, 40%). Elemental analysis for CHB11AgCl11 · ¹/₃ CH3CN (641.35 g/mol) calc. (found), %: C, 3.11 (3.25); H, 0.31 (0.67); N, 0.73 (0.74). mp. 196 °C. ¹H NMR (25 °C, [D₆]-acetone, 300.13 MHz): δ = 2.01 (m, CH₃CN) 4.21 (b, 1H, CH). ¹¹B NMR (25 °C, [D₆]-acetone, 96.29 MHz): δ = -12.94 (s, B²⁻⁶Cl), -9.83 (s, B⁷⁻¹¹Cl), -2.44 (s, B¹²Cl). ¹³C{¹H} NMR (25 °C, [D₆]acetone, 75.47 MHz): δ = 47.61 (b, CH). IR (ATR, 8 scans, 25 °C, cm⁻¹): 3022 (m), 2308 (w, v(C-N_{CH3CN})), 2279 (w, v(C-N_{CH3CN})), 1025 (sh, v(C-C_{CH3CN}), 1118 (s), 1006 (s), 954 (m), 898 (m), 709 (m), 671 (m), 582 (m), 528 (s). Raman (784 nm, 17 mW, 15 s, 6 acc., 25 °C, cm⁻¹): 320 (2), 306 (4), 294 (2), 128 (4), 71 (10). MS (CI-, m/z (%)): 106 (12), 128 (80), 245 (80), 350 (80), 450 (38), 828 (100). MS (Cl+, m/z (%)): 77 (8), 160 (6), 260 (23), 520 (100) $[CB_{11}CI_{11}]^+$.

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Full check up. An optimized synthesis procedure for perchlorinated carba-*closo*borates starting from inexpensive building blocks is shown. Next to this a detailed overview of different quantum chemical information is given.



Carba-closo-borates

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