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Evidence for an Intermediate in the Methylation of CB₁₁H₁₂⁻ with Methyl Triflate: Comparison of Electrophilic Substitution in Cage Boranes and in Arenes

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In memory of Detlef Schröder

The trideuteriomethylation of BH vertices in $CB_{11}H_{12}^{-}$ and its derivatives with CD_3OTf (OTf = triflate, trifluoromethanesulfonate) yields a mixture of B–CD₃ and B–CHD₂ substitution products, thus demonstrating the intermediacy of a species with a long enough lifetime for hydrogen scrambling between the boron vertex and the methyl substituent. No such scrambling is observed if CD₃OTf is used to methylate toluene. According to density functional theory calculations, the intermediate in BH vertex methylation is a three-center bonded σ adduct of a methyl cation to the BH bond and the proton scrambling

Introduction

Electrophilic substitution on BH bonds in *closo*-boranes and -carboranes plays an important role in their chemistry,^[1-3] and is comparable with electrophilic substitution on benzene and other π -electron aromatic systems (Scheme 1). The exocyclic bonds in *closo*-boranes and arenes are analogous: the boron cages carry two-electron σ BH bonds, built from *exo*-directed radial sp hybrids on boron, and at the end of the substitution process these bonds are replaced with similar two-electron σ bonds BX. In arenes, two-electron σ CH bonds, built from *exo*-directed sp² hybrids on carbon, are substituted with similar two-electron CX bonds.

The electrophile used in the substitution reaction on BH vertices can be a donor of a proton (X=H),^[4] a halogen cation

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occurs via a transition structure containing a distorted squarepyramidal methane attached axially to a "naked" boron vertex. The subsequent proton or deuteron loss is presently not understood in detail. A general comparison of electrophilic substitution on *closo*-boranes and arenes is provided and similarities as well as differences are discussed. A recalculation of the optimized geometry of the $CB_{11}Me_{12}$ radical produced a second Jahn-Teller distorted minimum and resulted in a somewhat improved agreement between calculated and measured proton hyperfine coupling constants.



Scheme 1. Electrophilic substitution on BH and CH bonds.

(X = halogen),^[5–7] a carbocation (X = alkyl),^[8,9] a metal cation (X = HgR),^[10] and many others. We are particularly interested in electrophilic alkylation.^[8,11–14] In spite of the preparative importance of these substitution reactions, little is known with certainty about their mechanism. It is usually assumed that they proceed via an intermediate adduct of X⁺ to one of the BH vertices, [XBH]⁺, followed by deprotonation, as suggested by calculations.^[15,16]

We now present experimental evidence for the intermediacy of such an adduct in the methylation of the $CB_{11}H_{12}^{-}$ anion and its derivatives with methyl triflate (TfOMe), and computational evidence for its anticipated three-center bonded σ -complex nature. Initial results were collected during a recent preparation^[17] of all 16 symmetrically CH₃/CD₃ substituted derivatives of the anion $CB_{11}(CH_3)_{12}^{-}$. The anions were oxidized to the radicals $CB_{11}(CH_3)_{12}^{-}$ and the relative proton hyperfine coupling constants in their four inequivalent positions were deduced from deuterium-substitution-induced line narrowing. The constants were thought to be in only imperfect agreement with the values calculated by density functional theory (DFT). We have now located an essentially isoergic second minimum in the potential energy surface of the Jahn–Teller distorted ground state of $CB_{11}(CH_3)_{12}$. If DFT is used to calculate the proton hyperfine coupling constants averaged over the two minima, a reasonable agreement with experiment is found.

Results

Our initial intention was to introduce CD₃ groups at the BH vertices of selected derivatives of the CB₁₁H₁₂⁻ anion by reaction with TfOCD₃ in sulfolane.^[17] As usual,^[18] CaH₂ was present to remove the triflic acid byproduct. Unexpectedly, the reactions yielded mixtures of CD₃- and CHD₂-substituted products, although the isotopic purity of TfOCD₃, declared by the supplier and independently verified, was 99 atom % D. The presence of B–CHD₂ groups was revealed in IR spectra by characteristic vibrations at 2872 cm⁻¹ [strong, $\tilde{\nu}$ (C–H)] and 1276 cm⁻¹ [weak, δ (C–H)] and in ²H NMR spectra (broad doublets with *J*_{H,D}= 2.1 Hz). Formation of B–CH₂D and B–CH₃ groups was not observed.

Ten $CB_{11}H_{12}^{-}$ anions variously substituted with CH_{3}^{--} , CD_{3}^{--} , I--, and $iPr_{3}Si-$ groups $[1-CH_{3}$, $1-CD_{3}$, $1-iPr_{3}Si$, $1-CH_{3}$ -12-1, $1-CD_{3}^{--}$, $1-iPr_{3}Si-12-1$, $1,(7-12)-Me_{7}$, $1-CD_{3}^{-}(7-12)-Me_{6}$, $1,(7-11)-Me_{6}$, $1-CD_{3}^{-}(7-11)Me)$] were treated with TfOCD₃ and CaH₂ in sulfolane at room temperature (see Scheme 1 for vertex numbering). The ratio of CHD_{2} to CD_{3} groups in each of the four types of positions of substitution in the product was determined by NMR spectroscopy and mass spectrometry.^[17] The results were

the same within experimental error in all ten cases: in positions 2-6, the CHD₂/CD₃ ratio was 0.6:0.4, and in positions 7-12, it was 0.5:0.5. Once the final substitution product was formed, the content of hydrogen and deuterium atoms in its methyl groups was immutable. It did not change on stirring a solution of the product of 11-fold trideuteriomethylation of Cs[1-CH₃CB₁₁H₁₁] in anhydrous sulfolane for 7 days alone, with CaH₂, or with TfOCD₃ and CaH₂.

These results indicated that the source of the hydrogen atom in the CHD_2 group is the starting carborate anion itself; therefore, we prepared the $1-CH_3CB_{11}D_{11}^{-}$ anion as shown in Scheme 2 and repeated the trideuteriomethylation experiment. The first step in the synthesis followed a published procedure



Scheme 2. Stepwise preparation of B-CHD₂-free Cs[1-CH₃CB₁₁(CD₃)₁₁].

with slight modifications that simplified the isolation and purification of the product, and proceeded smoothly. The second step was disappointing. Although the dehalogenation using Birch reduction in liquid $[D_3]$ ammonia at -78° C was complete in less than 5 min at -78 °C (ESI-MS) and 1-CH₃CB₁₁D₁₁⁻ was the major ionic component of the crude reaction mixture (charged boron-containing impurities formed less than 15% of the total negative ESI-MS signal), its yield was very small, barely sufficient for subsequent use without any purification. The identity of the product was beyond doubt, but no attempt was made to prepare an analytically pure sample. Upon treatment with TfOCD₃ in sulfolane in the presence of CaH₂, 1-CH₃CB₁₁(CD₃)₁₁⁻ was formed and a comparison of ¹H and ²H NMR spectra (Figure 1) showed clearly that only B–CD₃ and no B–CHD₂ groups were now present. Infrared and high-resolution mass spectra confirmed this conclusion.



Figure 1. Comparison of ¹H NMR (A) and ²H NMR spectra (B) of Cs[1-CH₃CB₁₁(CD₃)₁₁] with ¹H NMR (C) and ²H NMR spectra (D) of the product of its methylation with TfOCD₃. The peak at 2.05 ppm is a result of the acetone solvent.

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Attempts to convert all BH bonds in $CB_{11}H_{12}^{-}$ into BD bonds by treatment with D_2SO_4 , either concentrated or diluted with D_2O , or with DCl in D_2O , produced mixtures of partially (mostly six times) deuterated carborane anions with products carrying an OSO₃D or OD substituent on the anionic carborane cage, and were abandoned as unpromising.

A similar trideuteriomethylation reaction was run on toluene, known^[19] to be methylated with methyl triflate. The xylenes formed contained only CH_3 and CD_3 groups and there was no indication of any hydrogen scrambling.

The observations described above demonstrate that the BH methylation reaction proceeds through an intermediate with a lifetime sufficient for proton scrambling. To identify a possible mechanism for the scrambling, we performed DFT (B3LYP/SVP) calculations on the anticipated $[CD_3BH]^+$ intermediate at all three inequivalent boron vertices in $CB_{11}H_{12}^-$ (Figure 2 and Table 1). We used the conductor-like polarizable continuum



Figure 2. DFT optimized structures of the methylation intermediate **i** and of the transition state **t** for hydrogen scrambling. See Table 2.

Table 1. Energies ^[a] [kcalmol ⁻¹] of optimized structures of intermediates i'			
and \mathbf{i}'' in the methylation of $CB_{11}H_{12}^{-}$ with TfOMe in positions 2, 7, and			
12, and of the hydrogen scrambling transition state t.			

Compound	ΔE	$\Delta E + ZPE$	ΔH°	ΔG°	
$CB_{11}H_{12}^{-}+TfOMe$	0.00	149.52	161.54	107.44	
2i' + TfO-	23.55	166.36	178.93	124.30	
2t + TfO ⁻	42.31	183.20	195.34	141.57	
2i'' + TfO-	23.55	166.41	178.97	124.37	
7i' + TfO-	17.90	160.92	173.52	118.68	
7t + TfO ⁻	40.16	181.28	193.36	139.80	
7i'' + TfO-	17.90	160.97	173.57	118.76	
12i' + TfO-	15.54	158.41	171.16	115.47	
12t + TfO ⁻	39.32	180.12	191.79	139.13	
$12i'' + TfO^-$	15.54	158.47	171.22	115.55	
[a] At 298.15 K, relative to the potential energy ΔE of the starting materials (CB ₁₁ H ₁₂ ⁻ + TfOMe, $\Delta E = -1319.573650$ Hartree).					

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model (CPCM)^[20] to take into account solvation in sulfolane ($\varepsilon = 46$) and assumed that there is no association with the triflate counterion. The force constant matrix was evaluated and contributions from zero-point energy (ZPE), heat capacity, and entropy were included in the free energies ΔG° reported.

The species $[CD_3BH]^+$ and $[CHD_2BD]^+$ were found to correspond to a minimum on the potential energy (ΔE) surface, and had the expected^[21] triangular structure. The bond lengths and valence angles are given in Table 2. The transition state con-

Table 2. Selected bond lengths [Å] and valence angles [°] calculated (B3LYP/SVP) for intermediates (i) in the methylation of CB₁₁H₁₂⁻ in positions 2, 7, and 12, and for transition states (t) of their proton scrambling reactions (see Figure 2).

Species	Bond or angle	Position		
	5	2	7	12
i	B–C	1.982	2.030	2.064
	C–H1	1.166	1.161	1.158
	C–H2	1.104	1.103	1.102
	C—H3	1.091	1.091	1.091
	C-H4	1.091	1.091	1.091
	H1–C–H2	88.46	90.36	91.67
	H1–C–H3	116.41	112.95	112.16
	H1–C–H4	114.33	116.25	115.91
	H2–C–H3	109.29	110.63	110.99
	H2–C–H4	110.18	109.52	109.73
	H3-C-H4	114.83	114.48	114.16
t	B-C	1.609	1.614	1.615
	B-C-H1	112.14	113.09	112.53
	B–C–H2	113.11	112.29	112.54
	BCH3	119.25	118.60	118.65
	B-C-H4	117.50	118.75	118.64
	H1–C–H2	48.53	48.60	48.39
	H1–C–H3	119.32	118.62	118.81
	H1–C–H4	81.68	81.05	81.46
	H2–C–H3	81.88	81.73	81.48
	H2–C–H4	119.10	119.00	118.80
	H3-C-H4	100.29	100.25	100.47

necting the minima had a structure similar to one of those known from CH_5^{+} ,^[22, 23] with methane shaped as a distorted square pyramid that is attached axially to the "naked" boron vertex. The simplest description of the transition-state geometry is to say that it contains an H₂ molecule complexed with a carboranylmethyl cation. The calculated isotope effects on the equilibrium and the activation energy of the scrambling reaction were small and very similar at all boron vertices at $CB_{11}H_{12}^{-}$ (Table 1). For this anion, the calculated free energies of the intermediate relative to the starting materials were 23.55, 17.90, and 15.54 kcalmol⁻¹ in positions 2, 7, and 12, respectively.

Finally, we complement the previously published^[17] calculated properties of the radical $CB_{11}Me_{12}$. In addition to the reported optimized geometry of C_1 symmetry with a ground-state electronic wave function of A' symmetry, we now describe an isomeric C_1 geometry with an A'' electronic ground state (Figure 3). Both were found by DFT [M06-2X/6-311G(d,p)] geometry optimization and neither has any imaginary vibrational



Figure 3. Geometries of the A' (left) and A'' (right) forms of Jahn–Teller distorted $CB_{11}(CH_{3})_{12}$.

frequencies (Figure 3). The A' ground-state isomer is slightly more distorted from the C_s symmetry (the methyl groups in A' are less overlapped than in A"). In the A' ground-state isomer the B-B neighbor distances in the proximate pentagon (B2-B6) range from 1.754 to 1.783 Å and in the A" ground-state isomer they lie between 1.753 and 1.820 Å. Neighbor distances in the B7-B11 pentagon are between 1.776 and 1.811 Å for the A' isomer and between 1.761 and 1.836 Å for the A" isomer. The variation is smaller than in the parent $CB_{11}H_{12}$ radical at the B3LYP/6-31G* level of calculation.^[24] The differences observed for the A' isomer are smaller than those obtained for the A" isomer, similarly to the parent $CB_{11}H_{12}$. The potential energy ΔE value for the A' minimum is 0.45 kcal mol⁻¹ below that of the A" minimum, but the order of the free energy ΔG° values, which include the ZPE, thermal corrections, and entropy, is the opposite: the A" minimum lies below the A' minimum, by $0.38 \text{ kcal mol}^{-1}$ at 77 K and by $0.51 \text{ kcal mol}^{-1}$ at 298 K. Spin density distributions at both geometries are presented in Figure 4.



Figure 4. Spin density distribution in A' (left) and A'' (right) minimum geometry of $CB_{11}(CH_3)_{12}$.

The relative proton hyperfine coupling constants for both geometries and their averages are compared with experimental values in Table 3.

Table 3. Proton hyperfine coupling constants (G) in the A' and A'' form	s
of $CB_{11}(CH_3)_{12}$ in positions 1, 2, 7, and 12.	

α	$a_{H}(lpha)$ calcd. ^[a]			$a_{\rm H}(lpha)/a_{\rm H}(7)$ calcd. ^[a]			$a_{\rm H}(\alpha)/a_{\rm H}(7)$ obsd. ^[b]
	A′	Α″	ave.	A'	Α″	ave.	
1	0.21	0.32	0.27	0.04	0.06	0.05	0.18±0.09
2	2.61	3.60	3.10	0.55	0.72	0.64	0.71 ± 0.02
7	4.75	4.97	4.86	1	1	1	1.00 ± 0.03
12	2.48	0.49	1.48	0.52	0.10	0.31	0.52 ± 0.05
[a] Ca	lculated	usina	the B3LY	P/FPRIII	method ^{[25}	^{,26]} at	an M06-2X/6-

 $311G(d,p)^{[27]}$ optimized geometry, assuming an equal mixture of the two forms of the radical. [b] Ref. [17].

Discussion

An intermediate in BH methylation

The results described above provide firm experimental evidence that the methylation of BH vertices in $CB_{11}H_{12}^{-}$ and its derivatives is not a one-step process but proceeds through an intermediate, the lifetime of which is sufficient for hydrogen exchange between the incoming methyl group and the reacting vertex. It is reasonable to accept the computational result and take this intermediate to be a triangular σ complex in which a methyl cation has been added to the BH bond. The computed relative energies of the intermediates formed in the three inequivalent positions in $CB_{11}H_{12}^{-}$ follow the well-established order of their reactivity in electrophilic substitution, 12 > 7 > 2.

The nature of the hydrogen scrambling process suggested by the DFT results also appears plausible, and the transition state can be viewed as a complex of a methane molecule with a naked boron vertex or, even better, as a complex of a hydrogen molecule (atoms H1 and H2, which are only 0.98 Å apart) with a carboranylmethyl cation. The calculated isotope effects on the rate and equilibrium in the hydrogen scrambling reaction are small and nearly the same in all three positions. The proposed mechanism for the methylation reaction is summarized in Scheme 3.

The present experimental and computational study is limited to establishing the existence of an intermediate in the methylation of a BH vertex in a *closo-carborane* and proposing a mechanism for proton scrambling between the boron vertex and the methyl substituent. It is likely that the nature of the intermediate in the methylation reaction is prototypical of other electrophilic substitution reactions on BH vertices of cage boranes and carboranes and that the main features of the results are generally applicable.

Additional experimental and computational studies will be needed to establish the nature of the transition states that lead from the starting materials to the intermediate by transfer of a methyl cation from methyl triflate, and from the intermediate to the products by transfer of a proton to a base. The latter should be subject to a large primary isotope effect.^[28,29] As indicated in Scheme 3, it is not clear whether the bridging

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Scheme 3. Proposed mechanism for the methylation of BH vertices. Both possibilities for the loss of H^+ or D^+ to a base are indicated, from the bridge position or from the methyl group.

proton or one of the other three protons on the methyl substituent is transferred from the intermediate to a base, which of the three methyl protons is most easily removed, and whether their positions can be interchanged by methyl rotation. Until these factors are determined, the significance of the observed isotope effects will remain ambiguous.

An examination of the kinetics of the methylation reaction, including isotope effects, would go a long way toward elucidating the situation and establishing the nature of the rate-determining step in the overall process. This would be best done on a presently unknown highly substituted derivative of $CB_{11}H_{12}^{-}$ that has only three free BH vertices, one in each of the three inequivalent positions, or on a series of derivatives with a single free BH vertex in one of the positions.

Analogies in electrophilic substitution on *closo*-boranes and on arenes

Closo-boranes and -carboranes are frequently referred to as aromatic, one of the reasons being their preference for substitution over addition reactions. The present acquisition of experimental evidence for the mechanism of electrophilic methylation of the $CB_{11}H_{12}^{-}$ cage provides an opportunity for a comprehensive comparison of the presumably analogous electrophilic substitution processes on *closo*-boranes and on arenes.

The basic similarity is shown in Scheme 1, but how much farther does it really extend? In an arene two sp² orbitals on carbon make two two-electron σ bonds to their carbon perimeter neighbors, its *exo*-directed sp² hybrid is used to attach a substituent, and its p orbital becomes a part of the delocalized π system (Figure 5). In a species such as CB₁₁H₁₂⁻ the delocalized orbitals are not of π character and instead are formed from the inward-pointing sp hybrid and the two tangential p valence electrons of boron that are of local σ symmetry. Unlike the electron-rich delocalized π system of neutral arenes, which contain one electron per atomic orbital, the delocalized system of *closo*-boranes contains only about two-thirds of an electron per atomic orbital and is electron-poor.



Figure 5. Hybridization of a vertex atom in a *closo*-borane (A) and in an arene (B). In red, orbitals used to form the delocalized system; in blue, orbitals used to attach a substituent; and in black, orbitals used to form the σ perimeter.

This difference has far-reaching consequences for electrophilic substitution. In an arene, an attacking electrophile can recruit two electrons from the electron-rich delocalized π system and use them to make a new two-electron σ bond (Wheland intermediate, e.g., protonated benzene^[30]), thus taking one vertex out of the delocalized system. In a closo-borane, recruiting electrons from the electron-poor delocalized system is not an option, and electrons for a new bond need to be taken from the radial two-electron σ BH bonds. For example, protonation of a borane cage may occur on a single vertex, on an edge, or on a triangular face,^[2,31] but in none of these cases does it suppress the participation of any vertices in the delocalized electronic system. On evaluating relative reactivities of different vertices in an arene, it is reasonable to examine first the energetic cost of taking a vertex out of π conjugation. In closo-boranes and -carboranes, such a consideration is largely irrelevant and one needs to examine first the Lewis basicity of the BH bonds available.

Before concluding that the commonly invoked analogy between electrophilic substitution on arenes and on *closo*-boranes is entirely spurious, one needs to recognize that there is more than one mechanism for electrophilic substitution on an arene. It has just been noted that a reaction via the classical Wheland intermediate, in which one vertex is taken out of conjugation (Scheme 4, mechanism (i)), is without a counterpart in *closo*-borane chemistry. However, there are at least three other fundamentally distinct mechanisms for electrophilic aromatic substitution in the ground electronic state, and two of them are analogous in arenes and in boranes. As in all of these processes an initial π complex^(32, 33) between the reaction partners



Scheme 4. Mechanisms of electrophilic substitution on an arene.

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may be an intermediate or a side diversion,^[34,35] certain steps may be reversible, and one or another can be rate-determining, the actual number of possible detailed mechanisms is even higher.

The four most important possibilities for attack by an electrophile on an arene are summarized in Scheme 4. (i) The most common^[36, 37] attack at one of the vertices in which its CH bond is a bystander and two π electrons are recruited to form a new bond in a Wheland intermediate^[38] or, in some cases, a Wheland transition state,^[39] followed by deprotonation. (ii) Electron transfer from the arene to the electrophile (E) forming an arene radical cation, which then reacts with a nucleophile (Nu), usually with the radical produced from the original electrophile by electron transfer,^[40-42] but possibly with another one. There is little doubt that the electronic structure of the classical transition state of the path that leads to the Wheland intermediate will often have significant charge-transfer character,^[43-46] but here one considers cases in which a radical-cation/ radical-anion pair is a true intermediate.[47-50] The CH bond is again a bystander until deprotonation takes place. (iii) Simultaneous attack at two vertices (usually ortho or para to each other) by a species that not only accepts two π electrons but also donates two electrons, forming two new bonds. The CH bonds at both vertices again initially act as bystanders. This initial step can be followed by a variety of events, only some of which (deprotonation with a loss of one of the newly formed bonds^[51]) lead directly to a monosubstituted product, whereas others first lead to monocyclic or bicyclic addition products. (iv) Insertion into a CH bond through a three-center interaction, in which the π -electron system is a bystander, as in the activation of aromatic C-H bonds by metal complexes^[52-56] and activation of aromatic C-H bonds for addition to CC multiple bonds.[57]

Little is known with certainty about the substitution mechanisms on deltahedral boranes and carboranes, since no mechanistic studies seem to have been performed. As noted above, π electrons are absent and cannot be recruited for the formation of a new bond, excluding the above mechanisms (i) and (iii). However, a distant analogy to mechanism (ii) and an essentially exact analogy to mechanism (iv) could exist (see Scheme 5).

The electron-transfer mechanism (ii)

Like many arenes, boranes and carboranes can be converted by one-electron oxidation to delocalized radicals,^[17, 58, 59] some of which are actually isolable (Scheme 5). In arenes, the lost electron is taken from the π system, and in cage boranes, it is taken in part from the delocalized system of cluster orbitals and in part from the radial BH bonds. Unlike arene radical cations, the CH and other peripheral CX bonds of which are only weakly perturbed relative to the original arene, peripheral BX bonds of cage borane radicals therefore have considerable one-electron character and are capable of transferring the group X as a radical to a suitable substrate (such as a disilane^[60] or an alkene^[61]). This leaves behind a naked vertex with an empty radial orbital on a B atom, which is analogous to the



Scheme 5. Mechanisms of electrophilic substitution on a *closo*-borane.

phenyl cation in the arene series but much more accessible energetically, and readily adds a nucleophile to yield a substitution product.

The σ -bond insertion mechanism (iv)

Unlike the electron-transfer mechanism of substitution on boron cages, which bears only a limited resemblance to its counterpart in arene chemistry, the σ -bond insertion mechanism is nearly identical in the two realms. In deltahedral boranes and carboranes, it is believed to proceed by the addition of an incoming electrophile (X⁺) to a BH bond under the formation of an intermediate with a positively charged threemembered ring [XBH]⁺, and above we have provided support for this notion (Scheme 5).

The three-center bonded intermediate [XBH]⁺ is believed to be capable of losing any one of its three vertices to a Lewis base and forming an ordinary two-electron bond between the remaining two vertices. If X⁺ is lost, no net reaction results. If H⁺ is lost, the substitution product with a BX bond is formed. These two possibilities are exactly analogous to the options available in arene chemistry. A third possibility, loss of the boron vertex with the formation of HX, does not normally occur in an arene, since aryl cations have very high energy. In polyhedral borane chemistry it is, however, fairly common and produces a cage with a naked vertex of the type discussed above. Addition of a nucleophile Nu⁻ then completes a substitution reaction in which BH has been converted into BNu. In cage borane chemistry, this mechanism is traditionally referred to as EINS (electrophile-induced nucleophilic substitution).^[2,4,62] As noted above, there are other possibilities, in that a proton loss could occur from a substituent X, such as a methyl, accompanied by a shift of the bridging proton to X.

Although this picture of electrophilic substitution on boranes and carboranes seems fairly appealing, it is mostly based on speculation and some calculations, and not on hard experi-

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mental data, which still remain to be collected. The presently obtained evidence for the intervention of an intermediate represents a step in this direction.

Comment on the Birch reduction of $1-CH_3CB_{11}I_{11}^{-1}$

The disappointing yield in the attempted reduction of this anion to 1-CH₃CB₁₁D₁₁⁻ demonstrates the limits of the Birch reduction procedure for the conversion of BI to BH substituents. This process is a mainstay of preparative manipulations on the CB₁₁ cage.^[2,14] Anions with up to six iodine substituents were reduced efficiently in reaction sequences that used the iodine substituent as a protection of a boron vertex or for acidification of the CH vertex, but 11 iodine atoms apparently make the cage excessively susceptible to over-reduction. Most of the undecaiodinated carborane anion clearly decomposed during the reaction to form uncharged volatiles (probably $B_2 D_6 \mbox{ and }$ other low-molecular-weight boranes). This result is somewhat reminiscent of the rapid and nearly complete decomposition of $HCB_{11}I_{11}^{-}$ into BF_3 and BF_4^{-} upon attempted fluorination with 20% F_2/N_2 in anhydrous HF at -78 °C, in which only traces of the desired $HCB_{11}F_{11}^{-}$ were detected.^[63] The undecaiodinated cage is not as robust as we initially assumed.

It is unfortunate that the simple process of D for H exchange in CB₁₁H₁₂⁻ by electrophilic substitution with a donor of D⁺ cations yields only mixtures of partly deuterated with monohydroxylated anions, since the EINS mechanism apparently interferes. An efficient preparation of 1-CH₃CB₁₁D₁₁⁻ and similar anions remains to be developed.

Conclusion

Experimental evidence has been found for the intervention of an intermediate in the mechanism of BH vertex methylation with methyl triflate, and DFT calculations strongly suggest that its structure is characterized by a protonated CB bond. In this species, hydrogen atoms scramble between the bridging position and a position on the methyl group, and DFT results indicate that the transition state for this process has the structure of a distorted square-pyramidal methane attached to a naked boron vertex, perhaps best viewed as a complex of H_2 with a carboranylmethyl cation. We have provided a general overview of the similarities and differences between electrophilic substitution at a BH vertex of a *closo*-borane and a CH vertex of an arene.

We have also noted the instability of the $HCB_{11}I_{11}^{-}$ anion to Birch reduction conditions and have improved the description of the $CB_{11}Me_{12}$ radical by finding a second isomeric structure for its Jahn–Teller distorted ground state. Averaged over both nearly isoenergetic structures, the computed relative proton hyperfine coupling constants agree fairly closely with those observed.

Experimental Section

Calculations

Density functional calculations for the intermediates of the reaction of CB₁₁H₁₂⁻ with TfOCH₃ were performed by using the B3LYP functional with the SVP basis set as defined in the Gaussian 09 program package.^[64] Solvent effects were approximated using the CPCM.^[20] Minima in ΔE were characterized by all positive second derivatives and transition states by a single negative second derivative. DFT computations for the radical CB₁₁Me₁₂⁻ used the B3LYP/EPRIII^[25,26] method at an M06-2X/6-311G(d,p)^[27] optimized geometry.

General information and materials

All reactions were performed under an argon atmosphere with dry solvents, freshly distilled under anhydrous conditions, unless otherwise noted. Standard Schlenk and vacuum line techniques were employed for all manipulations of air- or moisture-sensitive compounds. Yields refer to isolated, chromatographically and spectroscopically homogeneous materials, unless otherwise stated.

 $\rm Me_3NH[CB_{11}H_{12}]$ was purchased from Katchem Ltd. (Prague, Czech Republic). [D₃]Ammonia (99 atom % D) and [D₃]methyl trifluoromethanesulfonate (99 atom % D) were purchased from Sigma–Aldrich. *n*-Butyllithium (solution in hexane), calcium hydride, cesium chloride, iodine monochloride, anhydrous sulfolane, and 1,1,2,2-tetra-chloroethane were purchased and used without further purification. Cs[CB₁₁H₁₂] and Cs[1-CH₃CB₁₁H₁₁] were prepared from Me₃NH-[CB₁₁H₁₂] according to published procedures,^[17,65] and all reactions were performed on cesium salts.

Equipment and measurements

The NMR spectra were measured in [D₆]acetone and [H₆]acetone, and the following referencing was used: ¹H, residual signal of $[D_6]$ acetone (δ = 2.05 ppm); ²H, signal of $[D_6]$ acetone (δ = 2.05 ppm) as an internal standard (a few drops of [D₆]acetone added to $[H_6]$ acetone); ¹³C, signal of a $[D_6]$ acetone deuteriomethyl group $(\delta = 29.80 \text{ ppm})$; ¹¹B, signal of BF₃·Et₂O as an external standard in a coaxial capillary ($\delta\!=\!0.00$ ppm). ^1H and ^{13}C NMR spectra were recorded with Bruker Avance 400, 500, and 600 spectrometers working at 400.1, 499.8, and 600.1 MHz for ¹H NMR spectroscopy and 100.6, 125.7, and 150.9 MHz for ¹³C NMR spectroscopy, respectively. ²H NMR spectra were recorded with a Bruker Avance 600 spectrometer working at 92.1 MHz. ¹H {¹¹B}, ¹¹B, and ¹¹B {¹H} NMR spectra were accumulated with Bruker Avance 400 and 500 spectrometers working at 400.1 and 499.8 MHz for ¹H NMR spectroscopy and 128.3 and 160.4 MHz for ¹¹B NMR spectroscopy, respectively. Carbon signals of methyl groups on carborane and the C(1) carborane vertex are usually not easily detectable directly because of ¹³C–¹¹B coupling and therefore HSQC and HMBC were used for the assignment of ¹³C NMR resonances. Carbon signals of CD₃ and CHD₂ groups on carborane were not detected in some cases because of strong ¹³C-²H and ¹³C-¹¹B coupling. Assignments of boron signals were done by ¹¹B,¹¹B COSY NMR spectroscopy.

The content of ²H was determined by elemental analysis as ¹H, since this method is not able to recognize the difference between ²H and ¹H (both of these species were converted to water during the analysis and its amount was finally determined by thermal conductometry; the thermal conductivity of ¹H₂O and ²H₂O is the same).

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General procedure for iodination of all BH vertices (GP 1)

A procedure previously published by Wilbur et al.^[7] was adapted as follows. A flame-dried and argon-filled high-pressure Schlenk flask was charged with dry Cs[1-RCB₁₁H₁₁] (R=H or CH₃; 4.000 mmol) and 1,1,2,2-tetrachloroethane (25 mL). Subsequently, ICI (7.02 mL, 140.000 mmol) was added slowly by syringe. An exothermic iodination caused massive evolution of gases (according to ESI-MS, the $[1-RCB_{11}H_5I_6]$ anion (R = H or CH₃) was formed quantitatively during that time). The Schlenk flask was sealed tightly and the dark reaction mixture was stirred vigorously for 3 days at 150 °C. A brown solid precipitated during that time. The reaction mixture was diluted with 1,1,2,2-tetrachloroethane (15 mL) and transferred to a 50 mL round-bottom flask. The temperature of the oil bath was increased to 190°C and all volatiles were thoroughly removed by distillation at atmospheric pressure. The brown solid residue was dissolved in methanol (40 mL), all volatiles were evaporated using rotary evaporator, and the brownish solid was then triturated with ice-cold ether (2×15 mL). The resulting gray solid was suspended in boiling deionized water (30 mL) and dissolved by careful addition of methanol. The volume of the solution was reduced to approximately 25%. The precipitated solid was isolated by filtration, washed with deionized water $(3 \times 15 \text{ mL})$, ether $(1 \times 5 \text{ mL})$, and hexane (3×15 mL), and finally dried thoroughly by using Kugelrohr distillation apparatus (4 h, 160 °C, 500 mTorr) to afford Cs[1- $RCB_{11}I_{11}$] as snow-white solids.

Cesium 2,3,4,5,6,7,8,9,10,11,12-undecaiodocarba-*closo*-dodecaborate:^[7] Prepared from Cs[CB₁₁H₁₂] (1.100 g, 3.987 mmol) and ICl (7.02 mL, 140.000 mmol) in 1,1,2,2-tetrachloroethane (25 mL) according to GP 1 as a snow-white solid (6.490 g, 3.908 mmol, 98%). ¹H NMR (400 MHz, [D₆]acetone): δ = 4.21 ppm [s, 1 H; C-*H*]; ¹¹B NMR (128 MHz, [D₆]acetone): δ = -19.74 [br s, 5B; *B*-I(2–6)], -12.86 [br s, 5B; *B*-I(7–11)], -8.45 ppm [br s, 1B; *B*-I(12)]; ¹³C NMR (151 MHz, [D₆]acetone): δ = 62.1 ppm [C-H]; IR (KBr): $\tilde{\nu}$ = 3012 (m) and 3002 (w, v(C-H)), 1098 (m, δ (C-H)), 1037 (s), 919 (vs), 542 cm⁻¹ (vw, v(B-I)); MS (ESI-): *m/z* (%): 1529.4 (center of isotope cluster); HRMS (ESI-) for (HCB₁₁I₁₁⁻¹): *m/z* calcd: 1530.05988; found: 1530.05608; elemental analysis calcd (%) for CsCHB₁₁I₁₁: C 0.72, H 0.06, I 84.05; found: C 0.81, H 0.19, I 84.07.

Cesium 1-[H₃]methyl-2,3,4,5,6,7,8,9,10,11,12-undecaiodo-carba*closo*-**dodecaborate**: Prepared from Cs[1-CH₃CB₁₁H₁₁] (700 mg, 2.414 mmol) and ICI (4.26 mL, 85.000 mmol) in 1,1,2,2-tetrachloro-ethane (15 mL) according to GP 1 as a snow-white solid (3.013 g, 1.799 mmol, 75%). ¹H NMR (400 MHz, [D₆]acetone): δ = 2.17 ppm [s, 3H; C-CH₃]; ¹¹B NMR (128 MHz, [D₆]acetone): δ = -15.49 [br s, 5B; *B*-I(2–6)], -12.17 [br s, 5B; *B*-I(7–11)], -8.73 ppm [br s, 1B; *B*-I(12)]; ¹³C NMR (125.7 MHz, [D₆]acetone): δ = 35.4 [C-CH₃], 62.4 ppm [C-CH₃]; IR (KBr): $\tilde{\nu}$ = 2997 (vvw, v_{as}(CH₃), C-CH₃), 1430 (vw, δ _{as}(CH₃), C-CH₃), 1382 (w, δ _s(CH₃), C-CH₃), 1125 (w), 1094 (vw), 976 (w), 948 (s), 933 (vs), 532 cm⁻¹ (w, v(B-I)); MS (ESI-): *m/z* (%): 1542.1 (center of isotope cluster); HRMS (ESI-) for (C₂H₃B₁₁H₁₁⁻): *m/z* calcd: 1544.07553; found: 1544.07424; elemental analysis calcd (%) for CsC₂H₃B₁₁H₁₁: C 1.43, H 0.18, I 83.35; found: C 1.42, H 0.21, I 83.61.

Cesium 1-[H₃]methylcarba-*closo*-[D₁₁]dodecaborate: Sodium (1.241 g, 54.000 mmol) freshly cut into small pieces was carefully dissolved in liquid [D₃]ammonia (\approx 15 mL) in a high-pressure Schlenk flask at -78 °C. The deep blue solution was stirred vigorously at this temperature for 10 min with a glass stirrer. Subsequently, a solution of Cs[1-CH₃CB₁₁I₁₁] (4.523 g, 2.701 mmol) in dry [D₈]THF (6 mL) was added dropwise to the reaction mixture under vigorous stirring, which was continued for an additional 10 min. Progress of the reduction was checked by ESI-MS. On completion

of the reduction, excess sodium was carefully quenched by slow addition of $[D_4]$ MeOH (\approx 5 mL) until the dark blue color disappeared. Cooling was interrupted and the ammonia was carefully allowed to evaporate through a bubbler filled with mineral oil. Volatiles were then removed under reduced pressure. The yellow oily residue was washed with ether (4×25 mL) and the yellowish ethereal phase was washed with 20% aqueous CsCl (2×8 mL). The combined CsCl wash was extracted with ether (2×30 mL). All ethereal phases were combined and solvent was removed under reduced pressure. The residue was dried thoroughly using a Kugelrohr distillation apparatus (2 h, 160 °C, 500 mTorr). The crude product (190 mg) was used in the following reaction without further purification. MS (ESI-): m/z (%): 167.3 (center of isotope cluster); HRMS (ESI-) for $(C_2^{-1}H_3^{-2}H_{11}^{-1}B_{11}^{--})$: m/z calcd: 170.28150; found: 170.28160.

Cesium 1-[H₃]methyl-2,3,4,5,6,7,8,9,10,11,12-[D₃₃]undecamethylcarba-closo-dodecaborate: An argon-filled flask was charged with CaH₂ (2.105 g, 50.000 mmol) and dry sulfolane (8 mL) was added by syringe. Subsequently, dry crude Cs[1-CH3-CB11D11] from previous reaction (\approx 0.470 mmol) was added. Finally, TfOCD₃ (1.13 mL, 10.000 mmol) was added slowly by syringe to the vigorously stirred white suspension over a period of 20 min. The grayish reaction mixture was stirred vigorously at room temperature for 5 days. The solution turned brown during that time. Completion of the methylation was checked by ESI-MS. If some less methylated clusters were still present, another portion of TfOCD₃ (2.000 mmol) was added and stirring was continued for an additional 2 days. The dense reaction mixture was then diluted with CH₂Cl₂ (50 mL), and the solids were removed by vacuum filtration and washed with CH_2CI_2 (4×50 mL). The filtrate was neutralized with saturated aqueous NH₃ (30 mL) and volatiles (CH₂Cl₂ and water) were removed under reduced pressure. The brown oily residue was washed with ether (5 \times 50 mL) and the combined ethereal phases were washed with 20% aqueous CsCl (2×20 mL). The brown oil that was left after the first extraction was dissolved in the combined CsCl wash and the solution was extracted again with ether (3×50 mL). All ethereal phases were combined and the solvent was removed under reduced pressure, to leave a brownish oily residue. Most of the sulfolane was distilled from this residue by using a Kugelrohr distillation apparatus (4 h, 165 °C, 500 mTorr). The brown solid residue containing a small amount of sulfolane was then recrystallized from boiling deionized water. The gray crystals were isolated by filtration, subsequently washed with ice-cold deionized water (3 \times 10 mL) and hexane (3×10 mL), and dried thoroughly by using a Kugelrohr distillation apparatus (6 h, 165 °C, 500 mTorr). Final purification was performed by column chromatography on silica gel (CH₂Cl₂). Cs[1-CH₃CB₁₁(CD₃)₁₁] was obtained as a snow-white crystalline solid (28 mg, 0.059 mmol, 2% after two steps). ¹H NMR (499.8 MHz, [D₆]acetone): $\delta = 0.81$ ppm [s, 3H; C-CH₂]; ²H NMR (92.1 MHz, [H₆]acetone): $\delta = -0.54$ [br s, 3D; B-CD₃(12)], -0.44 [br s, 15D; B-CD₃(7-11)], -0.36 ppm [br s, 15D; B-CD₃(2-6)]; ¹¹B NMR (160.4 MHz, $[D_6]$ acetone): $\delta = -10.06$ [br s, 5B; B-CD₃(2-6)], -7.99 [br s, 5B; B-CD₃(7-11)], 0.09 ppm [br s, 1B; B-CD₃(12)]; ¹³C NMR (125.7 MHz, $[D_6]$ acetone): $\delta = 13.3$ [C-CH₃], 56.6 ppm [C-CH₃]; IR (KBr): $\tilde{\nu} = 2938$ (s, ν_{as} (CH₃), C-CH₃), 2182 (vs, ν_{as} (CD₃), B-CD₃), 2120 (s, $\nu_{\rm s}({\rm CD_3}),~{\rm B-CD_3}),~2054~(m),~1376~(w,~\delta_{\rm s}({\rm CH_3}),~{\rm C-CH_3}),~1223~(vs),~1166$ (vs), 1061 (m, $\delta_{as}(CD_3)$, B-CD₃), 1044 (m, $\rho(CH_3)$, C-CH₃), 1011 (w), 980 (w, $\delta_s(CD_3)$, B-CD₃), 786 cm⁻¹ (w, $v(B-CD_3)$, B-CD₃); MS (ESI-): m/z(%): 344.6 (center of isotope cluster); HRMS (ESI-) for (C₁₃¹H₃²H₃₃¹¹B₁₁⁻): *m/z* calcd: 346.59174; found: 346.59163; elemental analysis calcd (%) for CsC₁₃⁻¹H₃⁻²H₃₃B₁₁: C 32.70, H 8.17, Cs 27.84; found: C 32.94, H 8.28, Cs 27.96.

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Three preliminary experiments with Cs[CB₁₁H₁₂], followed by ESI, yielded unpromising results. 1) Dissolved in 96% D₂SO₄, it formed a mixture of CB₁₁H₆D₅OSO₃D⁻, CB₁₁H₆D₆⁻, and less deuterated anions. 2) Dissolved in 80% D₂SO₄, it formed a mixture of CB₁₁H₆D₅OD⁻, CB₁₁H₆D₆⁻, and other anions. 3) Dissolved in 10% DCl in D₂O, it produced mostly CB₁₁H₆D₆ and some CB₁₁H₆D₅OD.

Methylation of toluene with TfOCD₃

Methylation was carried out as described for methylation using TfOCH₃, known to yield *ortho*- and *para*-xylene in 4:3 ratio.^[19] Fresh TfOCD₃ (500 mL, 4.4 mmol) was added to dry toluene (10 mL, 93.9 mmol) at room temperature and the reaction mixture was stirred at 100 °C for 6 h. The initially colorless solution turned brown during that time. GC-HRMS analysis with chemical ionization showed the formation of both xylenes containing CD₃ groups [GC-HRMS (CI) for ($C_8^{1}H_7^2H_3 + {}^{1}H^{+}$): *m/z* calcd: 110.1049; found: 110.1048 for both isomers]. The identity of the *ortho* isomer was verified by addition of an authentic sample of undeuterated material.

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Scrambled protons: Methylation of $HCB_{11}H_{12}^{-}$ and similar anions with deuterated methyl triflate (CD_3OTf) produces a mixture of CD_3^{-} and CHD_2^{-} substituted anions (see scheme), thus demonstrational contract of the scheme) and the scheme of the



strating that the reaction mechanism involves an intermediate in which protons can scramble. A comparison with electrophilic substitution on arenes shows similarities and differences. J. Kaleta, A. Akdag, R. Crespo, M.-C. Piqueras, J. Michl*



Evidence for an Intermediate in the Methylation of $CB_{11}H_{12}^{-}$ with Methyl Triflate: Comparison of Electrophilic Substitution in Cage Boranes and in Arenes