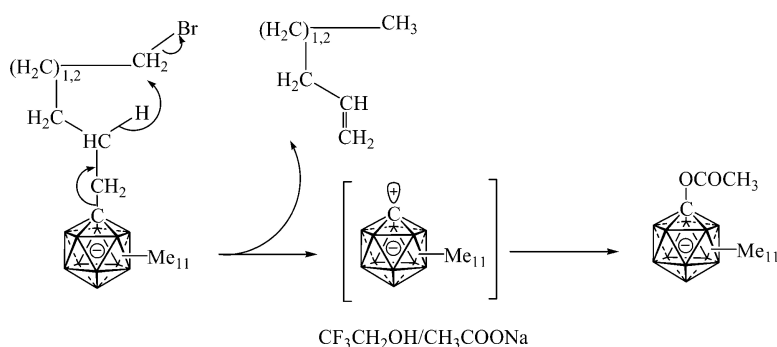


A New Type of Intermediate, C(BCH) \rightarrow C(BCH), in a Grob Fragmentation Coupled with Intramolecular Hydride Transfer. A Nonclassical Carbocation Ylide or a Carbenoid?

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A New Type of Intermediate, $C^+(BCH_3)_{11}^- \leftrightarrow C(BCH_3)_{11}$, in a Grob Fragmentation Coupled with Intramolecular Hydride Transfer. A Nonclassical Carbocation Ylide or a Carbenoid?

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Abstract: In solvolysis of alkyl halides $Hal-(CH_2)_n-C(BCH_3)_{11}^-$ ($n = 2, 5, 6$, but not 3, 4, or 7) and protonation of alkenes $CH_2=CH-(CH_2)_{n-2}-C(BCH_3)_{11}^-$ ($n = 3, 6, 7$, but not 4 or 5) carrying the icosahedral electrofuge $-C(BCH_3)_{11}^-$ attached through its cage carbon atom, generation of incipient positive charge on C_α (as shown in Scheme 1 in the article) leads to simultaneous cleavage of the $C_\beta-C(BCH_3)_{11}^-$ bond. The products are a $C_\alpha=C_\beta$ alkene and a postulated intermediate $C^+(BCH_3)_{11}^- \leftrightarrow C(BCH_3)_{11}$, trapped as the adduct $Nu-C(BCH_3)_{11}^-$ by one of the nucleophiles (Nu^-) present. The reaction kinetics is E1, first order in the haloalkylcarborane and zero order in $[Nu^-]$, and the elimination appears to be concerted, as in the usual E2 mechanism. The process is best viewed as a Grob fragmentation. The loss of the longer chains involves intrachain hydride transfer from the $C_\alpha-H$ bond to an incipient carbocation on C_δ or C_ϵ via a five- or six-membered cyclic transition state, respectively. The electronic structure of the postulated intermediate is believed to lie between those of a nonclassical carbonium ylide $C^+(BCH_3)_{11}^-$ and a carbenoid $C(BCH_3)_{11}$ whose electronic ground state resembles the S_2 state of ordinary carbenes.

We report the results of a study in which an observation of an unexpected C–C bond cleavage in the course of a seemingly innocuous synthetic manipulation of organic derivatives of the carba-*closo*-dodecaborate(–) anion¹ $HC(BH)_{11}^-$ (**1**) led us to postulate the intervention of a new kind of highly reactive species whose electronic structure appears to be intermediate between that of an internally charge-compensated nonclassical carbocation $C^+(BCH_3)_{11}^-$ and that of a singlet carbenoid $C(BCH_3)_{11}$.

For a project in polymer chemistry we needed to prepare linear terminal alkenes $CH_2=CH-(CH_2)_{n-2}-C(BCH_3)_{11}^-$, $n = 2-7$ (**2a–2f**), whose saturated terminus carries a permethylated version of **1** attached through C_1 , the carbon atom in position 1 of the icosahedral cage. The synthesis appeared to be a laborious but straightforward task, since the readily accessible² anion **1** was already known to be easily alkylated on carbon after deprotonation with a strong base,³ and both the C-methyl⁴ and the C-hexyl⁵ derivatives were known to be readily undecamethylated on boron with methyl triflate.⁶ The only slight concern was the anticipated need to protect the double bond during the methylation reaction. We thought this could be done by starting with the terminal chlorides or bromides

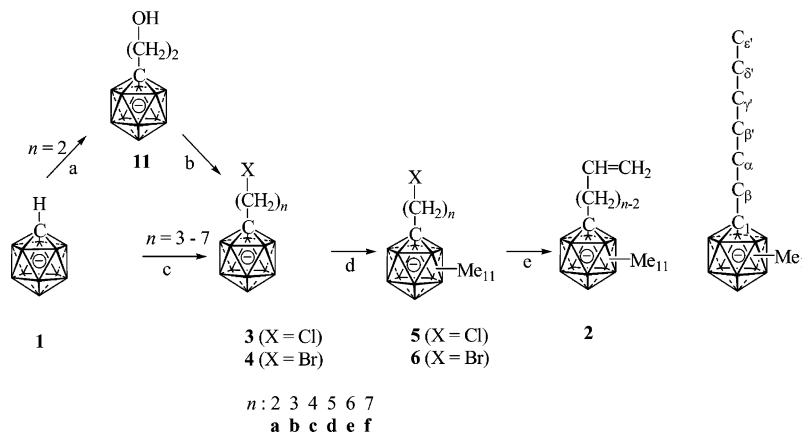
$X-(CH_2)_n-C(BH)_{11}^-$, where $n = 2-7$ (**3a–3f**, $X = Cl$, and **4a–4f**, $X = Br$), undecamethylating to obtain **5a–5f** or **6a–6f**, and subsequently dehydrohalogenating to form **2a–2f** (Scheme 1).

A more efficient route in which the undecamethylation would be performed on **1** to obtain $HC(BCH_3)_{11}^-$ (**7**), which would then be deprotonated and alkylated with the various halides $CH_2=CH-(CH_2)_{n-2}Br$, was blocked by our inability to find a base strong enough to deprotonate **7**, which appears to be much less kinetically acidic than **1** (and undoubtedly is less acidic thermodynamically as well). Since previous attempts to undecamethylate $1-I-C(BH)_{11}^-$ only produced mixtures of partially methylated derivatives,⁷ the lithium–iodine exchange route to deprotonated **7** did not look promising, either.

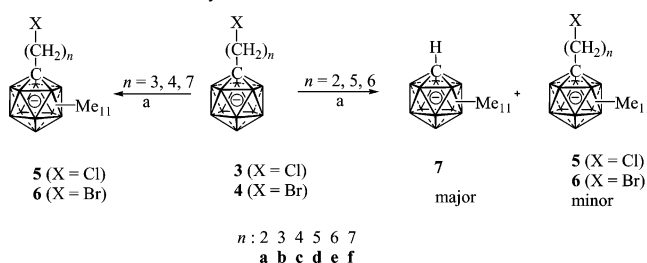
The preparation and undecamethylation of **3** and **4** proceeded smoothly and in high yield. To our initial amazement, however, only half of these ω -haloalkyl compounds, those with $n = 3, 4$, and 7 (**3** or **4 b, c**, and **f**), afforded the expected products **5** or **6 b, c**, and **f** (Scheme 2). Those with $n = 2, 5$, and 6 (**3** or **4 a, d**, and **e**) suffered a cleavage of the exocyclic C_1-C_β bond (Scheme 1) in the course of undecamethylation, and these three yielded the same anion **7** as the chief boron-containing product. Although, to our knowledge, the exocyclic C_1-C bond in carboranes and carborate anions has always been viewed as a perfectly normal carbon–carbon bond of ordinary strength, in this instance not only the halogen atom but also the $-C(BCH_3)_{11}^-$ substituent behaved as a leaving group. In the product structure the C_1-C_β bond was lost and the original ω -haloalkyl side chain

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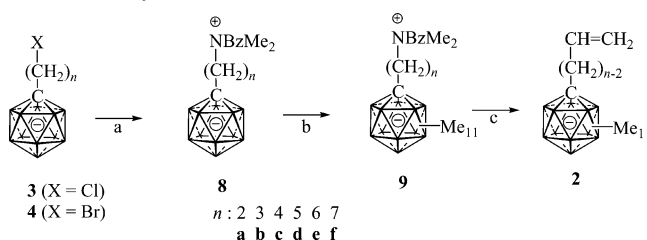
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Scheme 1. Original Plan for the Synthesis of **2a–2f**^a

^a Reagents and conditions: (a) *n*-BuLi, THF, 0 °C, oxirane; (b) NBS, PPh₃; (c) *n*-BuLi, 0 °C, X-(CH₂)_n-X; (d) MeOTf, CaH₂, sulfolane; (e) base. The labeling of the side-chain carbon atoms shown on the right anticipates the mechanistic discussion below.

Scheme 2. Permethylation of **3a–3f** or **4a–4f**^a

^a Reagents: (a) MeOTf, CaH₂, sulfolane.

Scheme 3. Synthesis of **2a–2f**^a

^a Reagents and conditions: (a) C₆H₅CH₂NMe₂, methanol, reflux; (b) MeOTf, CaH₂, sulfolane; (c) MeLi, -10 °C, ether.

on the cage was replaced by a hydrogen. In these three cases, the reaction was thus of limited utility for our purposes. Moreover, unlike the dehydrohalogenation of **4**, that of **6** turned out to be surprisingly difficult.

Both obstacles were overcome as shown in Scheme 3: the 1-(*ω*-haloalkyl)carborate salts **3** or **4** were converted into the ammonium zwitterions **8**, which were permethylated to **9** without problems. Hofmann elimination afforded all of the desired alkene salts **2**. These exhibit some remarkable properties that are currently under scrutiny. In particular, while under ambient conditions all the Cs salts are perfectly stable, some of the solid dry Li salts oligomerize to low molecular weight oligoalkenes in less than a day.

The present paper describes the syntheses of the alkenes **2** and focuses on a rationalization for the unexpected side-chain loss. We propose a reaction mechanism that invokes the unusual electrophile C⁺(BCH₃)₁₁⁻ (**10**) as a leaving group (electrofuge). Although this species is formally a member of the hypercloso family of carboranes, it is perhaps best viewed as an icosahedral carba-*closo*-dodecaborate anion whose delocalized negative

charge is compensated by a positive charge of a “naked” cage carbon atom. Unlike the 11 boron atoms at the other vertices of the icosahedron, the carbon atom has no ligand and can be viewed as a carbocationic center with a low-lying empty orbital. Alternatively, since according to density functional theory (DFT) calculations^{8,9} the C atom carries much of the negative charge even in the cage of the parent anion **1**, it can be viewed as carrying both a positive and a negative charge in **10**, as in C⁺-(BCH₃)₁₁⁻, and more simply, C(BCH₃)₁₁, and hence as somewhat analogous to a carbon in a singlet carbene. This is discussed in more detail below.

The calculations^{8,9} suggested that **10** is 37 kcal/mol destabilized relative to the most stable of its “boronium ylide” isomers, in which a ligand is missing on the antipodal boron atom 12 instead of the carbon atom, and we did not at first expect **10** to be an easily accessible reaction intermediate. Note that carbocations derived from uncharged 12-vertex carboranes are extremely difficult if not impossible to generate.¹⁰ In the case of **10** this initial expectation was wrong, and this intermediate appears to be accessible readily. The present results thus support the view¹¹ that the much more stable boronium ylide isomers CH₃CB(BCH₃)₁₀ represent easily accessible reaction intermediates. We consider it likely that they play a role in Heřmánek’s¹² “electrophilically assisted nucleophilic substitution” mechanism for deltahedral carboranes.

Results

Preparation of the Hal-(CH₂)_n-C(BH)₁₁⁻ Salts (3** and **4**, Scheme 1).** The conversion of the trimethylammonium or cesium salt of the starting anion **1** to salts of X-(CH₂)_n-C(BH)₁₁⁻ (*n* = 3–7, X = Cl, **3a–3f**, or X = Br, **4a–4f**) by deprotonation on carbon with *n*-butyllithium and treatment with a 1,*ω*-dihaloalkane proceeded smoothly. The dichloroalkanes are less reactive than the dibromoalkanes and tend to give somewhat lower conversions in the first round of alkylation. However, unlike the bromides, they do not readily react with *n*-butyllithium, and therefore either deprotonation and alkylation

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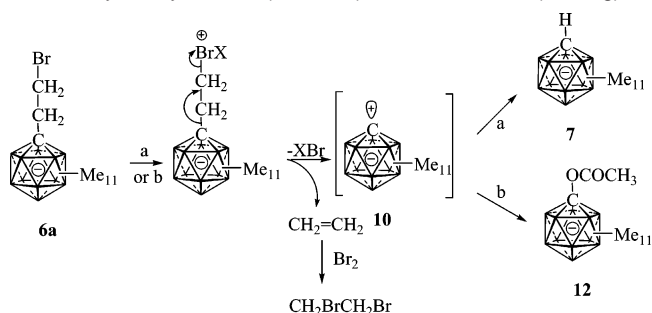
can be repeated two or more times in the crude reaction mixture, or excess *n*-butyllithium can be used to start with, ultimately providing higher yields. In case of the anions **4a–4f**, the best results were achieved by the transfer of the dilithium salt of **1** into the solution of 1, ω -dibromoalkane. The poorest results were obtained for *n* = 3, both with X = Cl (71%) and Br (66%), and purification by reverse-phase chromatography using a MeOH/water buffer was necessary. The lower yields were attributed to the formation of side products.¹³ For the longer haloalkyl chains, the reactions produced cleaner products in higher yields (78–94%).

The procedure was unsatisfactory when *n* = 2, even with X = I, which led to cage iodination (this type of behavior has been observed before¹⁴). In this instance, we used a two-step sequence in which deprotonated **1** was treated with oxirane and the resulting 1-(2-hydroxyethyl)carborate anion **11**, formed in a 67% yield, was converted into the bromide **4a** in a 73% yield by reaction with *N*-bromosuccinimide and triphenylphosphine.¹⁵ The reaction of lithiated uncharged carboranes with oxirane was described long ago,¹⁶ and the anion **11** had been prepared from **1** before in two steps in an overall yield of 45%.¹⁷

Methylation of the Hal-(CH₂)_n-C(BH)₁₁⁻ Salts (3 and 4, Scheme 2). Methylation with methyl triflate under standard conditions,⁶ in sulfolane as solvent and with CaH₂ as the base for the removal of the triflic acid byproduct, replaced all boron-bound hydrogen atoms with methyl groups. With *n* = 3, 4, or 7, the main products from the chloroalkyl or bromoalkyl starting material were the desired anions **5b**, **5c**, and **5f** or **6b**, **6c**, and **6f**, respectively. With *n* = 2, 5, or 6, the major product was the undecamethylated anion **7**. The haloalkyl chain was lost in the form of a terminal alkene, and the desired compounds were formed only as minor byproducts. In the case of **4a**, ethylene bubbled from the solution, was trapped in a solution of bromine, and was identified as ethylene dibromide by NMR spectroscopy and gas chromatography. In the case of **4d** and **4e**, 1-pentene and 1-hexene, respectively, were identified by GC–MS and NMR as the major side products in ~90% spectroscopic yield.

Dehydrohalogenation. Attempts to dehydrohalogenate **6e** under several sets of standard conditions (*t*-BuOK/*t*-BuOH, EtOK/EtOH, KOCH₂CH₂OH/HOCH₂CH₂OH, and CsF/dimethylformamide) failed, with a few percent yield of **2e** at best. Either there was essentially no reaction or substitution took place. The desired elimination proceeded very slowly with Schwesinger's phosphazene base^{18,19} P₂-*t*-Bu in tetrahydrofuran (THF) (14% yield after 24 h at room temperature) and somewhat better with 1,8-diazobicyclo[5.4.0]undec-7-ene (DBU) in refluxing benzene (55% isolated yield after 48 h). In contrast, either *t*-BuOK/*t*-BuOH or Schwesinger's phosphazene base P₂-*t*-Bu/THF converted the parent bromohexyl anion **4e** to the alkene CH₂=CH(CH₂)₄C(BH)₁₁⁻ rapidly and in good yields.

Scheme 4. Proposed Mechanism for the Fragmentation of **6a** Induced by Methyl Triflate (X = CH₃) or Silver Acetate (X = Ag)^a



^a Reagents and conditions: (a) MeOTf, CaH₂, sulfolane, room temperature; (b) CH₃COOAg, sulfolane, 120 °C.

Conversion of the Haloalkyl Anion Salts (3 and 4) to the Anions 2 via the Quaternary Ammonium Zwitterions 8 and 9 (Scheme 3). To prevent chain cleavage during permethylation, the haloalkyl anions **3** or **4** were converted to the dimethylbenzylammonium zwitterions **8** by reaction with dimethylbenzylamine. Room-temperature permethylation with methyl triflate in sulfolane in the presence of CaH₂ required one (*n* = 7) to four (*n* = 2) weeks for full conversion to **9**, but the yields were good. The best results were obtained when the first portion of the triflate was added slowly over a period of 20 h, and the second and third portions were added later, all at once. Attempts to accelerate the reaction by raising the temperature yielded unwanted and unisolated side products, mainly triflyloxy substituted on the carboranyl cage according to ESI-MS measurements. The ammonium zwitterions **9** were converted into the alkenes **2** with methylolithium in ether in 2–3 h. Since the dehydrohalogenation of **6** was difficult, the route via ammonium zwitterions **8** and **9** (Scheme 3) was in the end used for all chain lengths *n* = 2–7, even those for which permethylation at the ω -haloalkyl stage did not cause side-chain loss.

Solvolysis of the Bromoalkyl Anions 6. To test the hypothesis that we formulated for the mechanism of the fragmentation observed during the methylation of **3** or **4** for certain values of *n*, we performed several additional reactions (Schemes 4–7).

Reflux of a solution of **6a** in acetic acid caused a slow but clean decomposition. After 45 h, the only detected products were 1-AcO-C(BCH₃)₁₁⁻ (**12**) and ethylene, trapped as ethylene dibromide (Scheme 4). Under these conditions, **6e** yielded **12** and 1-hexene, identified by GC–MS and NMR (Scheme 5), whereas **6c** did not undergo any detectable reaction. Results in formic acid were similar.

Heating of a sulfolane solution of **6d** with silver acetate to 120 °C for 20 h also resulted in chain cleavage. The main products were **12** and 1-pentene, identified by GC–MS and NMR (Scheme 5). The disappearance of **6e** in a DMSO-*d*₆ solution containing a 100-fold molar excess of silver acetate at 120 °C was first order. The rate constant, *k* = (1.37 ± 0.25) × 10⁻¹ s⁻¹, was not affected significantly when the concentration of acetate ions was doubled or tripled by addition of sodium acetate.

Rates of unassisted solvolysis of **6** for *n* = 2–7 were measured in CF₃CH₂OH at 60 ± 1 °C (Table 1). Clean chain cleavage

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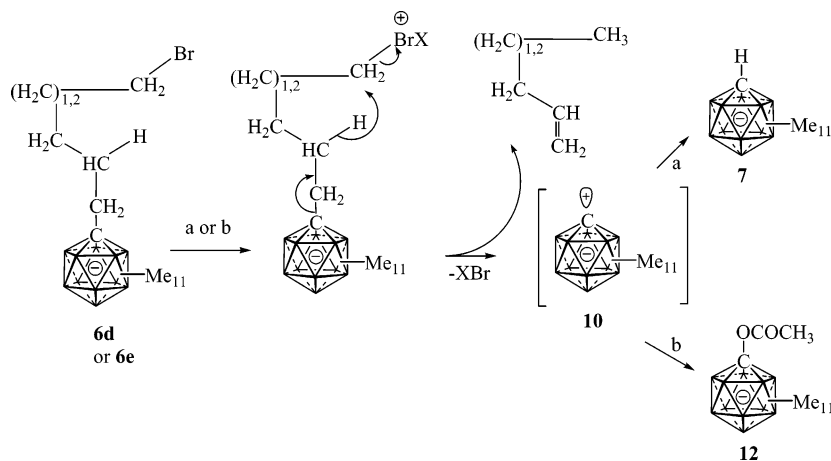
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Scheme 5. Proposed Mechanism for the Fragmentation of **6d** and **6e** Induced by Methyl Triflate (X = CH₃) or Silver Acetate (X = Ag)^a

^a Reagents and conditions: (a) MeOTf, CaH₂, sulfolane, room temperature; (b) CH₃COOAg, sulfolane, 120 °C.

Table 1. First-Order Solvolytic Rate Constants for the Alkyl Bromides **6** (10⁵ k/s⁻¹, CF₃CH₂OH, 60 ± 1 °C)^a

n	[AcO ⁻]			n	[AcO ⁻]		
	0	0.20 M	0.40 M		0	0.20 M	0.40 M
2	12.8	13.2	14.2	5-d ₁	4.3	4.2	4.6
	12.0	13.8	15.3	6	1.8	2.5	2.7
	12.5	13.9	14.6		2.2	3.0	2.5
3	<0.1	<0.1	<0.1		2.1	2.7	2.9
	<0.1	<0.1	<0.1	7	<0.1	<0.1	<0.1
4	<0.1	<0.1	<0.1				
	4.2	5.3	4.8				
	4.7	5.0	5.8				
5	4.3	5.5	5.0				

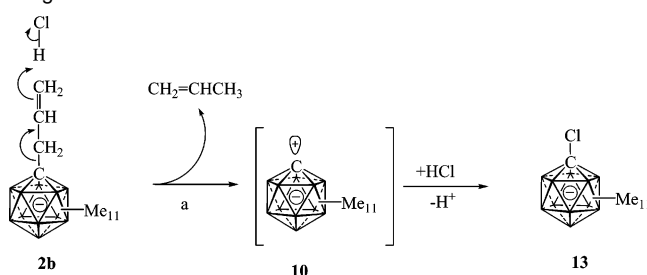
^a In first-order plots, $\sigma = 0.8 \times 10^{-5} \text{ s}^{-1}$.

reactions were observed for $n = 2, 5,$ and 6 . Addition of acetate as a nucleophile changed the product from $\text{CF}_3\text{CH}_2\text{OC}(\text{BCH}_3)_{11}^-$ to $\text{CH}_3\text{COOC}(\text{BCH}_3)_{11}^-$, but had practically no effect on the reaction rate. Under the same conditions, **4a** did not react detectably in 48 h.

To establish the position of the double bond in the terminal alkenes formed in the solvolysis, $\text{Br}-\text{CH}_2-\text{CHD}-(\text{CH}_2)_3-\text{C}(\text{BMe})_{11}^-$ (**6d-d₁**) was synthesized. The alkene **2d** was deuterioborated with $\text{BD}_3 \cdot \text{THF}$ and then treated with excess Br_2 in NaOMe ²⁰ to give **6d-d₁** in 88% isolated yield. Heating its sulfolane solution with silver acetate to 120 °C for 20 h resulted in chain cleavage. The main products were **12** and $\text{CH}_3-\text{CHD}-\text{CH}_2-\text{CH}=\text{CH}_2$,²¹ identified by comparison with reported GC-MS²² and NMR²³ data.

Protonation of the Terminal Alkenes 2. Treatment of a solution of **2b**, **2e**, or **2f** in hot sulfolane with dry HCl for 16 h produced 1-Cl-C(BCH₃)₁₁⁻ (**13**) and 1-propene (Scheme 6), 1-hexene, or 1-heptene (Scheme 7), respectively (identified by GC-MS and NMR). Under these conditions, **2c** and **2d** did not react.

Calculations. We show the B3LYP/6-31G(d)²⁴ optimized geometry of **10** in Figure 1, important interatomic distances in Table 2, and the natural atomic charges²⁵ in Table 3 (the three-

Scheme 6. Proposed Mechanism for the Acid-Induced Fragmentation of **2b**^a

^a Reagents and conditions: (a) sulfolane, 120 °C.

center bond option was used). The calculated dipole moment is 2.32 D, with C(1) at the positive and B(12) at the negative end. More detailed results of calculations on all four CB₁₁(CH₃)₁₁ isomers will appear elsewhere.⁹

Discussion

Synthesis of Alkenes 2. Although the syntheses of the desired alkenylcarborate anions **2** from the starting carborate anion **1** (Scheme 3) require four steps, they all proceed in good yields and we have had no difficulty producing gram quantities of these materials for studies of polymerization, which will be reported elsewhere. In contrast, only some of the haloalkylcarborate anions **3** and **4** are conveniently accessible by the presently developed procedures ($n = 3, 4,$ and 7). Since they promise to provide access to additional interesting polymers, alternative synthetic approaches to those with $n = 2, 5,$ and 6 still need to be developed.

Dehydrohalogenation of 4e and 6e. There is nothing unusual about the easy dehydrohalogenation of the alkyl bromide **4e**. However, the suppression of the reaction by the permethylation of the carborane cage (**6e**) is remarkable. Intramolecular salt effects on chemical reactivity have been observed before^{27,28} but are not well understood, and it appears worthwhile to

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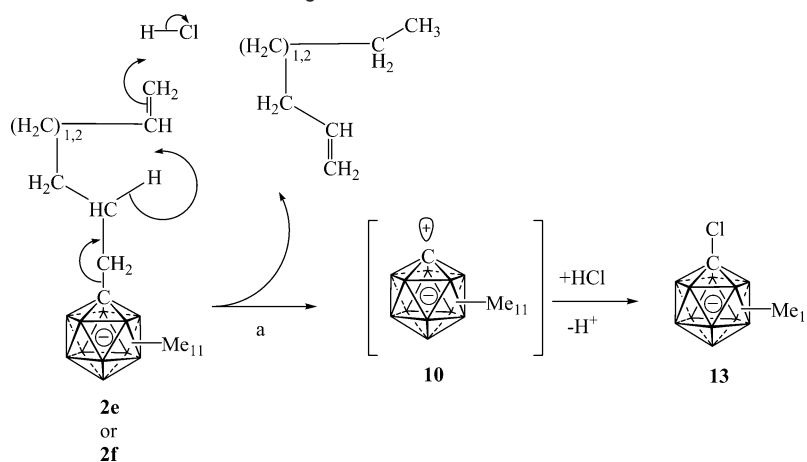
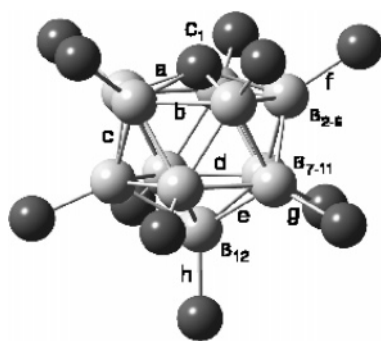
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Scheme 7. Proposed Mechanism for the Acid-Induced Fragmentation of **2e** and **2f**^a^a Reagents and conditions: (a) sulfolane, 120 °C.**Figure 1.** Structure of **10**.**Table 2.** Computed-Optimized Internuclear Distances in C(BCH₃)₁₁ (**10**) and CB₁₁(CH₃)₁₂^{-a}

internuclear distance (Å)	C(BCH ₃) ₁₁	CB ₁₁ (CH ₃) ₁₂ ⁻
a (C–B)	1.641	1.728
b (B–B)	1.823	1.790
c (B–B)	1.803	1.784
d (B–B)	1.820	1.799
e (B–B)	1.785	1.796
f (B–C)	1.597	1.605
g (B–C)	1.601	1.612
h (B–C)	1.620	1.613
C(1)–B(12) diameter	2.954	3.272

^a B3LYP/6-31G(d); averaged assuming five-fold cage symmetry.**Table 3.** Natural Atomic Charges^a in C(BCH₃)₁₁ (**10**) and CB₁₁(CH₃)₁₂^{-b}

position	C(BCH ₃) ₁₁		CB ₁₁ (CH ₃) ₁₂ ^{-c}	
	B (C) charge	CH ₃ charge	B (C) charge	CH ₃ charge
1	-0.22 ^d		-0.55	0.09
2–6	0.26	-0.16	0.25	-0.21
7–11	0.13	-0.18	0.07	-0.20
12	0.04	-0.13	0.10	-0.20

^a Reference 25. ^b In elementary charge units. B3LYP/6-31G(d); averaged assuming five-fold cage symmetry and three-fold methyl symmetry. CH₃ charges represent sums over all four atoms of a methyl group. ^c From reference 26. ^d +0.39 in the radial 2p orbital and -0.62 in the other three valence orbitals; the discrepancy in the last digit is due to round-off error.

examine the effect of remote -C(BCH₃)₁₁⁻ substitution on organic reactivity more closely in the future.

Side-Chain Loss Mechanism. The initially puzzling results observed in the methylation of **3** and **4** (Scheme 2) become

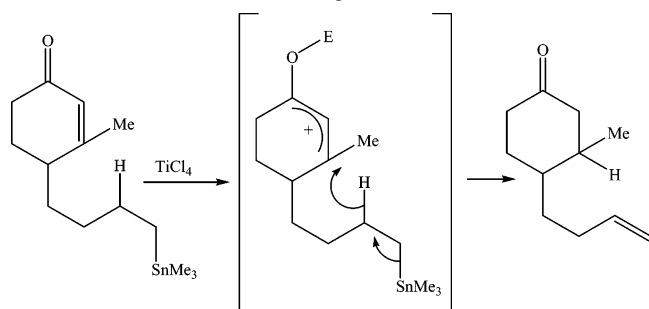
understandable in terms of the standard carbocation chemistry of half a century ago, once it is postulated that **10** (but not its unmethylated analogue) is a good electrofuge capable of departing without the two electrons of the C₁–C_β bond in the absence of nucleophilic assistance whenever there is a good opportunity to develop a positive charge on the neighboring carbon C_α (Scheme 1 shows the Greek labels; the cationic carbon is labeled α). The loss of the side chain in **6a** under solvolytic conditions (Scheme 4) then becomes another case of Grob fragmentation^{29,30} if the cage carbon C₁ is considered a part of the carbon chain, and a case of elimination if the -C(BCH₃)₁₁⁻ group is viewed as a substituent. The failure of **4a** to solvolyze under the same conditions suggests that the unmethylated -C(BH)₁₁⁻ group is a much poorer electrofuge. There is independent evidence that the permethylated anion MeC(BCH₃)₁₁⁻ is far more electron-rich than the parent HC-(BH)₁₁⁻: in acetonitrile, the reversible oxidation potential of the former is at least 0.4 V lower than those of the latter and of MeC(BH)₁₁⁻.⁴

The fragmentations of **6d** and **6e** are similar to the fragmentation of **6a**, except that a concurrent intrachain hydride transfer with a five-membered or six-membered cyclic transition state, respectively, needs to be invoked as well (Scheme 5). Intramolecular hydride transfers in an alkane chain with transition states of these ring sizes are well documented.^{31,32} Other ring sizes would be strained and higher in energy, accounting for the absence of the fragmentation process in **3** and **4 b, c, and f**. Indeed, the reaction pathway presently proposed for our carboranes is quite analogous to that suggested³³ some time ago to account for the results of protonation of certain cyclic enones carrying a trialkylstannylated side chain (Scheme 8), except that the departure of the stannyl substituent probably requires nucleophilic assistance.

The observation that the departure of a halide anion from the terminus of the ω-haloalkyl chain can be induced by boiling in acetic or formic acid and can be assisted by the Ag⁺ cation as well as by methyl triflate (presumably via an incipient or

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Scheme 8. A Previously Reported³³ Intramolecular Hydride Transfer Combined with Grob Fragmentation



discrete methylhalonium cation) supports the proposed mechanism. The alternative access to incipient or discrete carbocations that is provided by alkene protonation provides additional evidence for the proposed interpretation. As shown in Schemes 6 and 7, now the side chain needs to have one more carbon, $n = 3, 6, \text{ or } 7$, for the fragmentation to proceed. These reactions provide access to derivatives of the undecamethylated carborate anion **7** halogenated or oxygenated in position 1.

Detailed mechanistic studies of the chain loss process have not been undertaken. However, the observation that added acetate anion does not accelerate the Ag^+ -assisted transformation of **4e** to **7** in dimethyl sulfoxide nor the unassisted solvolysis of **6a, d, and e** in 2,2,2-trifluoroethanol (Table 1) is significant. It suggests that unlike most other electrofuges, such as a trialkylsilyl group or a proton, **10** is able to leave without assistance from a nucleophile. At any rate, a nucleophile would have difficult access to the sterically very hindered cage carbon. The complete stability of **4a** under solvolytic conditions that induce rapid elimination in **6a**, and the absence of products substituted on the primary carbon of **6a–6f** even in the presence of excess nucleophile, suggest very strongly that the cleavage of the $\text{C}_\beta\text{--C}(\text{BCH}_3)_{11}^-$ bond is concurrent with the departure of the leaving group from C_α . In this regard, the elimination resembles common concerted E2 eliminations, although its rate follows E1 kinetics. This type of behavior has precedent in other fragmentations of the Grob type.^{34,35}

Free **10** thus appears to be the initial product in the solvolytic fragmentation reaction when $n = 2, 5, \text{ or } 6$ (Scheme 2) and is only subsequently trapped by one of the nucleophiles present. Under the methylation conditions, this is a hydride either from CaH_2 or possibly from an as yet unmethylated BH bond in a molecule of the reactant **3** or **4**. When **10** is generated during solvolysis in acetic acid, the trapping nucleophile is acetic acid or the acetate anion. During CH_3COOAg -assisted solvolysis in sulfolane, it is the acetate anion, and in the reaction of the alkenes with HCl, it is HCl, HCl_2^- , or Cl^- . The results of the isotopic labeling experiment demonstrate that the double bond in the terminal alkene formed is located at the chain terminus that was originally attached to the carborane cage and eliminate other plausible mechanisms. It is probable that free **10** is formed in the protonation reactions ($n = 3, 6, 7$) as well.

The Nature of the Proposed Intermediate 10. We believe that the information reported presently established the existence of **10** as an electrophilic reaction intermediate of an intriguing

and not well preceded structure. Formally, $\text{C}(\text{BCH}_3)_{11}$ (**10**) belongs to the hypercloso series and is derived by the deprotonation of the cage carbon in $\text{HC}(\text{BCH}_3)_{11}^+$, whose parents are $\text{HC}(\text{BH})_{11}^+$ and, ultimately, $(\text{BH})_{12}$. This description does not relate simply to the observed reactivity, in that the cage carbon is acting as an electrophile and not a nucleophile. Perhaps **10** is best placed in a category of its own, but as we indicate in the title, it may be possible to classify it using already established labels.

In any event, **10** is quite different from known *closo*-carboranes containing a carbon vertex without a ligand, in which this vertex has been deprotonated and carries a negative charge. Ordinarily, these species carry an overall negative charge, such as $\text{C}_2\text{B}_{10}\text{H}_{11}^-$ or $\text{CB}_{11}\text{H}_{11}^{2-}$, but neutral $\text{C}_3\text{B}_5\text{H}_7$ is also known.³⁶ The deprotonated carbon in these structures is not “naked” in that it carries a lone pair and resembles a localized carbanion.

Although in itself the DFT optimized geometry of **10** shown in Figure 1 and Table 2 cannot answer the question formulated in the title, it is informative. Like $\text{CB}_{11}(\text{CH}_3)_{12}^-$, **10** is icosahedral, but it is considerably flattened at the carbon vertex, with the $\text{C}(1)\text{--B}(12)$ diameter shortened by $\sim 0.3 \text{ \AA}$ as a result. The distances from the cage carbon to its boron neighbors are $\sim 0.1 \text{ \AA}$ shorter than in $\text{CB}_{11}(\text{CH}_3)_{12}^-$ and the pentagon of boron atoms adjacent to the carbon atom is slightly expanded, with B–B distances increased by $\sim 0.03 \text{ \AA}$. The structure of the remainder of the icosahedron is nearly the same as that of $\text{CB}_{11}(\text{CH}_3)_{12}^-$, with B–B distances in the two species equal within $\sim 0.02 \text{ \AA}$. These geometrical parameters are compatible with the notion that the cage carbon carries an empty radial orbital as it would in a carbocation, and this indeed is exactly what the calculated lowest unoccupied molecular orbital looks like. At first sight, then, one is inclined to consider **10** to be a delocalized icosahedral carba-*closo*-dodecaborate anion whose cage carbon atom is naked (has no ligand and no lone pair) and can be viewed as a localized carbocation that compensates the delocalized negative charge of the cage. Then, **10** is simply a carbocation ylide with a delocalized negative charge, $\text{C}^+(\text{BCH}_3)_{11}^-$. One way of thinking of this ylide structure for **10** is to derive it by the formal capping of the undecaborate- $(2-)$ dianion with the carbene-like dication C^{2+} ; this bears a formal resemblance to the mechanism proposed³⁷ for the formation of the $\text{HC}(\text{BH})_{11}^-$ anion from $\text{B}_{11}\text{H}_{13}^{2-}$ and dichlorocarbene with loss of HCl.

However, because of the delocalized electronic structure of the carborane cage, the positive and the negative charges of the ylide can be drawn on the same atom. Even in the dodecamethylated anion $\text{CB}_{11}(\text{CH}_3)_{12}^-$, half of the delocalized negative charge of the cage is calculated²⁶ to be carried by its carbon atom. After the loss of the 1-methyl ligand, the proportion can be expected to be even higher. The calculated charges are listed in Table 3. Although the radial 2p orbital on the cage carbon C(1) only has an electron population of 0.61, and thus contributes $+0.39$ to the net atomic charge, the total population of 3.62 in the other three valence orbitals on C(1) contributes -0.62 , overwhelming the positive charge easily and making the net charge on C(1) actually negative. Much positive charge is, however, carried by the neighboring boron atoms B(2)–B(6), and the calculated dipole moment of 2.32 D is still

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directed from B(12) (negative end) to C(1) (positive end). A comparison of atomic charges in **10** and in $\text{CB}_{11}(\text{CH}_3)_{12}^-$ suggests that the negative charge on C(1), which more than compensates the positive charge of this “carbocation” center, has been taken mostly from the borons B(7)–B(11) and from the methyl substituents. The best simple representation of the structure apparently is not $\text{C}^+(\text{BCH}_3)_{11}^-$, but perhaps $\text{C}^+-(\text{BCH}_3)_{11}$ or simply $\text{C}(\text{BCH}_3)_{11}$.

The presence of both an empty and a doubly filled orbital on an atom in a dominant resonance structure is the hallmark of a singlet carbene. In the case of **10**, the similarity would be to the S_2 state of ordinary carbenes, with unoccupied σ -type and doubly occupied π -type orbitals on the carbon atom. In singlet carbenes, the lone pair on the divalent carbon is carried by a single nonbonding atomic (hybrid) orbital, whereas in **10**, it is distributed among the 2s and the two tangential 2p orbitals that are simultaneously used for cluster bonding, but otherwise the similarity is considerable. Even though in products obtained from **10** only one stable new bond to the cage carbon is established, whereas in carbene reactions two new bonds to the divalent carbon can be formed, it may be reasonable to think of **10** as a singlet electrophilic carbenoid.

Although the ground-state electronic structure may be better represented as $\text{C}(\text{BCH}_3)_{11}$, it is still legitimate to ask which representation gives a more useful prediction of the reactivity, carbocation ylide, $\text{C}^+(\text{BCH}_3)_{11}^-$, or electrophilic singlet carbenoid, $\text{C}(\text{BCH}_3)_{11}$? The experimental evidence available presently shows that **10** is a good nucleophile, but does not allow us to answer this question, and we are performing additional trapping experiments to resolve the issue experimentally.

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Supporting Information Available: Experimental details. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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