Inorganic Chemistry
Article
pubs.acs.org/IC

Anodic Oxidation of 18 Halogenated and/or Methylated Derivatives of $CB_{11}H_{12}^-$

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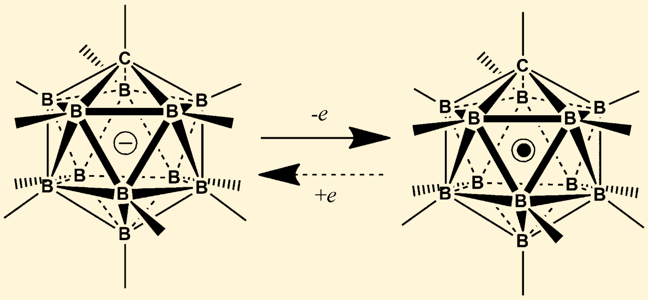
S *Supporting Information*

ABSTRACT: Anodic oxidation of $[CB_{11}H_{12}]^-$ and 18 of its halogenated and/or methylated derivatives was examined. Reversible oxidation was found for four of the anions in liquid SO_2 and for four more in 1,1,1,3,3,3-hexafluoroisopropyl alcohol. The oxidation occurred at ~1 V (for $[CB_{11}Me_{12}]^-$) up to more than 4 V (for $[1\text{-H-}(2{-}6)\text{-}F_5\text{-}(7{-}12)\text{-}(CF_3)_6\text{-}CB_{11}]^-$) relative to ferrocene/ferricinium. The anodic peak potentials are reproduced by a set of additive position-sensitive substituent increments.



INTRODUCTION

We are interested in finding electrochemically reversible anion−radical redox couples with highly positive potentials and both partners stable and interconvertible. Although many anions with very positive oxidation potentials are known and are commonly used by electrochemists as constituents of supporting electrolytes (e.g., ClO_4^-, BF_4^-, PF_6^-, AsF_6^-, and SbF_6^-), few if any of their oxidations are reversible, and the oxidized electroneutral forms cannot be isolated. Such neutral radicals cannot be used to store charge in high-voltage batteries, nor can they be used as oxidizing reagents.

Substituted derivatives of the icosahedral carborane anion $[CB_{11}H_{12}]^-$ (**1**,[1] Figure 1) are of considerable interest in this regard, because of their remarkably high redox potentials, unusually low nucleophilicity, and general inertness and stability (however, the salts of very highly trifluoromethylated ones, although unreactive, are explosive[2,3]). These properties have been well reviewed[4−10] and suggest many possible applications in research and practice.

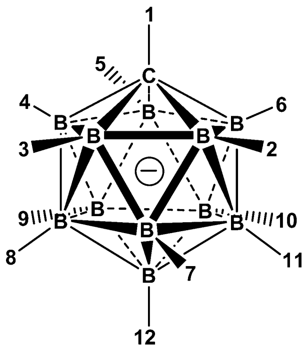


Figure 1. Vertex numbering in the CB_{11} cluster. In the parent anion $[CB_{11}H_{12}]^-$ (**1**), all 12 substituents are H.

Many derivatives of **1** have already been examined in a series of electrochemical studies mostly focused on oxidation in liquid SO_2 (lSO_2) and often combined with density functional theory (DFT) computations.[11−18] Even the electron-rich methyl substituted $[CB_{11}(CH_3)_{12}]^-$ anion[11,19]/$[CB_{11}(CH_3)_{12}]^\bullet$ radical[20] couple already has a relatively high redox potential (1.15 V in CH_3CN[11] against ferrocene/ferricinium, $Fc^{0/+}$), permitting the radical to oxidize metal−metal and carbon−metal bonds,[21,22] and both members of the couple are perfectly stable at room temperature. Both have been analyzed by X-ray diffraction as single crystals,[11,20] and the electron paramagnetic resonance (EPR) spectra of the radical have been examined in considerable detail[23] and interpreted in terms of DFT calculations.[23,24] Anions with fewer than 12 methyl groups have even higher redox potentials, yet their oxidized radical forms are sufficiently stable for electrochemical reversibility, as long as sufficient steric hindrance to dimerization is provided by the steric bulk of substituents in positions 7−12.[14] The increase in the redox potential as the methyl groups are gradually replaced with hydrogens is easily understood as a result of the

Received: September 2, 2016
Published: December 12, 2016

DOI: 10.1021/acs.inorgchem.6b02126

Table 1. Cyclic Voltammetry of Anions 1−19 in lSO$_2$ and HFIPA[a]

	anion		lSO$_2$			HFIPA		
No.	formula[b]	$E_{1/2}$	E_{pa}	ΔE_p	$E_{1/2}$	E_{pa}	ΔE_p	E_{pa}(second)
1	$CB_{11}H_{12}^{-}$[1]		2.03[c]			2.05		
2	$(1-12)\text{-}Me_{12}$[11]	1.16	1.19	0.060	0.95	0.98	0.070	
3	$(2-6,8-11)\text{-}Me_9$	1.34	1.37	0.056	1.20	1.26	0.130	
4	$(2-12)\text{-}F_{11}$[34]		2.71[d]		2.42	2.49	0.137	
5	$1\text{-}Me\text{-}(2-12)\text{-}F_{11}$[34]		2.69		2.39	2.47	0.150	
6	$(2-12)\text{-}Cl_{11}$[35]		2.86[e]			2.76		3.14
7	$(2-6)\text{-}Me_5\text{-}(7-12)\text{-}Cl_6$[36]		2.42			2.24		
8	$(7-12)\text{-}Cl_6$[35]		2.56			2.33		
9	$(2-12)\text{-}Br_{11}$[35]		2.79[f]			2.72		2.94
10	$(2-6)\text{-}Me_5\text{-}(7-12)\text{-}Br_6$[36]		2.35[g]			2.21		
11	$(2-6,8-11)\text{-}Me_9\text{-}7,12\text{-}Br_2$	1.60	1.63	0.060	1.51	1.57	0.114	
12	$(2-12)\text{-}I_{11}$[35]		1.81[h]			1.95		2.22
13	$1\text{-}Me\text{-}(2-12)\text{-}I_{11}$[35]		1.80			2.10		
14	$(2-6)\text{-}Me_5\text{-}(7-12)\text{-}I_6$[36]		1.80		1.39	1.44	0.094	1.93
15	$(2-6,12)\text{-}Me_6\text{-}(7-11)\text{-}I_5$[14]		1.66		1.36	1.40	0.083	1.81
16	$1\text{-}Me\text{-}(7-12)\text{-}I_6$[37]		1.84			1.45		1.87
17	$(7-12)\text{-}I_6$[38]		1.88			1.49		
18	$(2-6,8-11)\text{-}Me_9\text{-}7,12\text{-}I_2$	1.37	1.43	0.116	1.04	1.17	0.240	
19	$(2-6)\text{-}F_5\text{-}(7-12)\text{-}(CF_3)_6$[3]	>4			>4			

[a] Versus $Fe^{0/+}$, potentials in volts. Reversible half-wave potential $E_{1/2}$ is the average of the anodic (E_{pa}) and cathodic (E_{pc}) peak potentials. [b] Footnotes refer to the original synthetic procedures. [c] Reference 16 2.35 V. [d] Reference 16 2.72 V. [e] Reference 16 2.85 V. [f] Reference 16 2.76 V. [g] Reference 16 2.29 V. [h] Reference 16 2.15 V.

hyperconjugative π-electron donating nature of methyl relative to hydrogen (the σ effect of methyl on the CB_{11} cage is negligible[14]). Note that we are using the standard definition of a substituent effect, that is, difference relative to hydrogen. Although the methyl group on a boron vertex is not an electron donor in an absolute sense because carbon is much more electronegative than boron, and it has even been referred to as an electron acceptor,[25] it is more electron-donating than the parent hydrogen reference, and therefore by standard convention needs to be called a donor substituent.

The four different kinds of vertices in **1** (1, 2−6, 7−11, and 12) have been characterized by additive increments that an introduction of a methyl group provides toward lowering the value of the redox potential,[14,15] permitting the redox potentials of additional anion-radical couples to be easily predicted with reasonable accuracy. Anions carrying substituents other than methyl in positions 1 and 12 have also been examined, and several of the oxidations were found to be reversible.[15,17] DFT calculations without[16] and with[14,15] inclusion of solvent effects were used to account for the observed reversible redox potentials.

In a search for redox couples with still higher redox potentials, a logical next step is to use halogen substituents instead of methyls. They are weak π-donors and strong σ-acceptors. The smaller halogens however provide little or no steric hindrance, and the radicals are likely to be unstable with respect to dimerization or other forms of decay, similarly as the unsubstituted parent radical **1**$^{\bullet}$. The iodine substituent is bulky, but its lone pairs are at relatively high energy. Depending on cage substitution, they may be more readily oxidized than the CB_{11}^{-} cage itself. The neutral radical loses an iodine atom from its B−I bond, and it has been suggested that this possibly occurs by transfer to an SO_2 solvent molecule.[26] Similar irreversible anodic behavior is known for the related dianion $[B_{12}I_{12}]^{2-}$.[27] Substitution with bromine might thus appear to offer the best compromise, but as already reported[16] in lSO$_2$ and presently found also in 1,1,1,3,3,3-hexafluoroisopropyl alcohol (HFIPA), the oxidation of $[1\text{-}H{-}CB_{11}Br_{11}]^{-}$ is irreversible, and the undecabrominated radical $[1\text{-}H{-}CB_{11}Br_{11}]^{\bullet}$ clearly does not have sufficient stability, either.

Trifluoromethyl groups, with their large steric bulk and strong π- as well as σ-electron-withdrawing ability, appealed to us more than halogens, and we were thrilled by the calculated redox potential of $[CB_{11}(CF_3)_{12}]^{-}$, an incredible ~5 V above $Fc^{0/+}$, until we discovered the explosive properties of its Cs^{+} salt, which decomposes violently with formation of C and BF_3.[2] We then examined how many of the 12 CF_3 groups would have to be replaced with F substituents before the salt could be handled safely and found that $Cs[1\text{-}H\text{-}(CF_3)_{11}\text{-}CB_{11}]$, with an anion calculated to be about as hard to oxidize as $[CB_{11}(CF_3)_{12}]^{-}$, can still be brought to explosion easily. We were uncertain about $Cs[1\text{-}H\text{-}12\text{-}F\text{-}(2-11)\text{-}(CF_3)_{10}\text{-}CB_{11}]$, but we were unable to make $Cs[1\text{-}H\text{-}(2-6)\text{-}F_5\text{-}(7-12)\text{-}(CF_3)_6\text{-}CB_{11}]^{-}$ explode, and it appears safe (its other salts and the radical need not be).[3] Inevitably, the replacement of five CF_3 groups with five F substituents is associated with a lowering of the calculated redox potential. The calculated decrease is a little over 1 V, and indeed while we were unable to oxidize the $[CB_{11}(CF_3)_{12}]^{-}$ anion to the radical with NiF_4/BF_3 in liquid HF, $[1\text{-}H\text{-}(2-6)\text{-}F_5\text{-}(7-12)\text{-}(CF_3)_6\text{-}CB_{11}]^{-}$ was oxidized to $[1\text{-}H\text{-}(2-6)\text{-}F_5\text{-}(7-12)\text{-}(CF_3)_6\text{-}CB_{11}]^{\bullet}$ under the same conditions.[3] The resulting gain in safety was deemed worth this sacrifice in the oxidizing power. The blue solution of the $[1\text{-}H\text{-}(2-6)\text{-}F_5\text{-}(7-12)\text{-}(CF_3)_6\text{-}CB_{11}]^{\bullet}$ radical in C_6F_{14} is stable up to −60 to −40 °C, but at higher temperatures it appears to oxidize the solvent in both Teflon and quartz vessels, regenerating the $[1\text{-}H\text{-}(2-6)\text{-}F_5\text{-}(7-12)\text{-}(CF_3)_6\text{-}CB_{11}]^{-}$ anion.[3]

This observation highlights a complicating factor: the search for the strongest possible neutral oxidant is coupled to a search for a suitable solvent. An ideal solvent would be one that resists oxidation and dissolves not only neutral compounds but also salts, allowing electrochemical studies, yet at the same time is

DOI: 10.1021/acs.inorgchem.6b02126
Inorg. Chem. 2017, 56, 269−276

non-nucleophilic, non-electrophilic, inert, and not aggressive (in contrast to liquid HF). We have been using liquid SO_2,[14,15,17,26] introduced into electrochemistry by Bard[28,29] and found useful in investigations of oxidation-resistant anions by others[16,27] as well, but the potential oxidation of tetravalent to hexavalent sulfur catalyzed by the substrate or the products of its oxidation is always a concern at the very positive potentials of interest to us.

Presently, we address the anodic oxidation of the parent $[CB_{11}H_{12}]^-$ anion and 18 of its derivatives carrying halogen and/or methyl substituents, both in lSO_2 and in an additional solvent that appears promising for the study of carborane anions with highly positive redox potentials, HFIPA. Although the results with HFIPA reported here are highly encouraging, this solvent has its own set of potential weaknesses, such as an ability to act as a proton donor or as a nucleophile, as well as a potential oxidizability to form hexafluoroacetone. However, it speaks in its favor that it allows reversible oxidation of eight of the presently examined anions as opposed to only four whose oxidation is reversible in lSO_2.

Recently, a report of irreversible electrochemical oxidation of $[CB_{11}H_{12}]^-$ and six of its halogenated and mixed halogenated/methylated derivatives in lSO_2 and acetonitrile appeared,[16] with at least partial reversibility only in the case of $[1\text{-H-}(2{-}6)\text{-Me}_5\text{-}(7{-}12)\text{-Br}_6{-}CB_{11}]^-$. Our results are in agreement, and we find that two of the anions are oxidized reversibly in HFIPA. For most of the anions that were examined in lSO_2, both laboratories find essentially identical redox potentials, but for $[CB_{11}H_{12}]^-$ and $[1\text{-H}{-}CB_{11}I_{11}]^-$ our oxidation potential is much less positive than reported.[16]

■ RESULTS

Synthesis. All the carborane salts except for those of the new anions **3** and **11** were prepared and purified by published procedures. References to the original syntheses are provided in Table 1. The syntheses of **3** and **11** used conventional steps (Experimental Section). In case of **4** we followed a more recent procedure.[30] The synthesis of **6** was improved relative to that reported[31] (Experimental Section). In our hands, the chlorination with SO_2Cl_2 described[31] for **8** produced only incompletely converted mixtures, but introduction of Cl_2 into the reaction mixture forced the reaction to completion. Anion **18** was synthesized from **1** using a literature procedure,[32,33] except that we found it necessary to monitor the reaction by ^{11}B NMR spectroscopy.

Anodic Oxidation. Electrochemical oxidation of the Cs salts of the parent and substituted CB_{11} carborane anions **1**−**19** (the structures are defined in Table 1) was examined by voltammetry in lSO_2 at −70 °C and in HFIPA at room temperature (~23 °C). They provide a wide anodic potential window. We used a Pt electrode and scan rates from 0.08 to 5.0 V/s. A glassy carbon electrode was also used for moderately soluble salts. Both solvents dissolve the salts well, except for the salt of **17**, which is poorly soluble in lSO_2, and the salts of **8** and **17**, which have limited solubility in HFIPA. A Ag wire served as a quasireference electrode in lSO_2, and a saturated calomel electrode (SCE) separated by a salt bridge was employed as reference electrode in HFIPA. The $Fc^{0/+}$ couple was used as an internal/external reference, and all potentials are expressed relative to it.

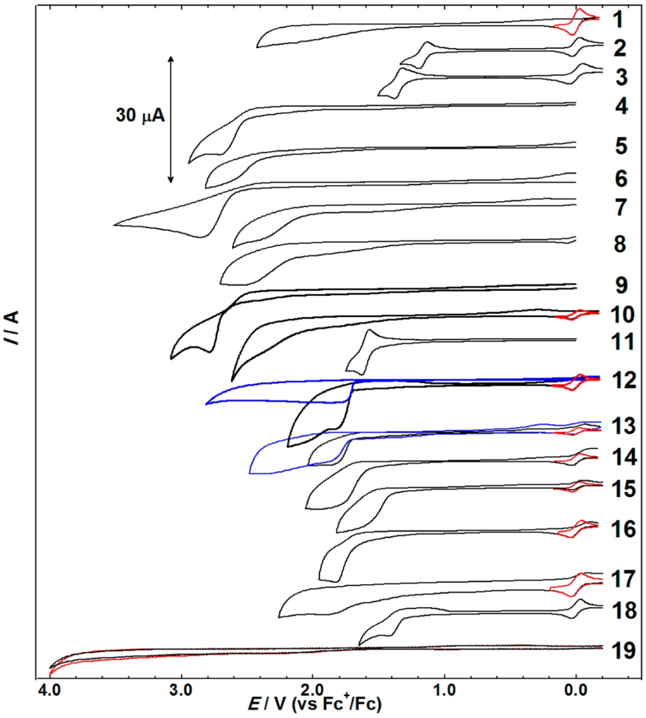


Figure 2. Cyclic voltammograms of anions **1**−**19** in lSO_2 at −70 °C: Pt electrode, 0.2 V/s, 0.1 M $[Bu_4N][PF_6]$, vs $Fc^{0/+}$ (the first redox couple). Blue curves for **12** and **13** show absence of other peaks. For poorly soluble salt of **17** a glassy carbon electrode was used. **19**: CV, red; blank, black.

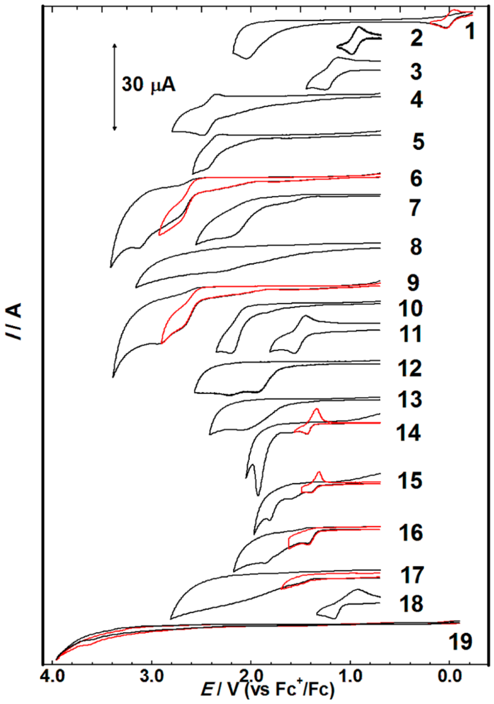


Figure 3. Cyclic voltammograms of anions **1**−**19** in HFIPA at 23 °C: Pt electrode, 0.2 V/s, 0.1 M $[Bu_4N][PF_6]$, vs $Fc^{0/+}$, shown in red for **1**. Anions **3**, **11**, **17**, and **18**, at a glassy carbon electrode. **19**: CV, red; blank, black.

Figures 2 and 3 present the cyclic voltammograms (CVs) measured at 0.2 V/s in lSO_2 and in HFIPA, respectively (the first redox couples from the right are due to $Fc^{0/+}$). The measured potentials are listed in Table 1. All the anions show at least one anodic oxidation peak, except for **19**, which yielded no peak up to 4 V above $Fc^{0/+}$, the end of the available potential window. Figure 4 exemplifies the dependence of the CV on the scan rate v. Plots of the anodic peak currents I_{pa} against the square root of the scan rate $v^{1/2}$ and against concentration c are linear (examples are given in Supporting Information, Figures S1−S5). Normalized peak heights relative to that of the anion **2** show that all the oxidations are one-electron, except for the iodinated anions **12**, **13**, **14**, **15**, and **16**, in *l*SO_2 and **13** in HFIPA, which are two-electron. In HFIPA, some of the heavily halogenated anions (especially iodinated and brominated) show another peak at higher potentials.

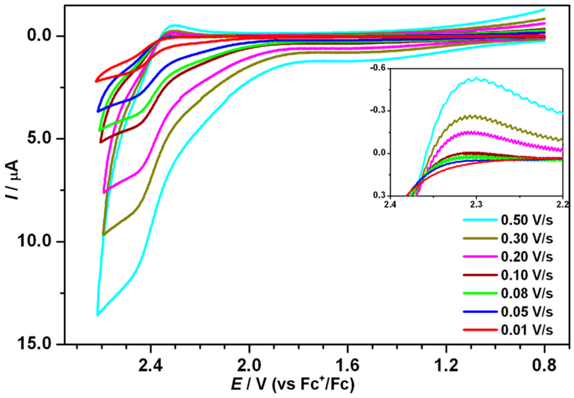


Figure 4. Cyclic voltammograms of **5** in HFIPA at different scan rates (1.10 mM, 0.1 M $[Bu_4N][PF_6]$, vs Fc^+/Fc). (inset) Enlarged return peaks.

In *l*SO_2, the observed anodic oxidation peaks lie between 1.16 and 2.86 V, and all but four are irreversible. The parent anion **1** shows a very poorly defined oxidation wave with a maximum at 2.03 V. After **19**, the undecachlorinated anion **6** with an oxidation potential of 2.86 V is the next hardest to oxidize, noticeably more difficult than the fluorinated anions **4** and **5** whose potentials are at 2.71 and 2.69 V, respectively. Anions differing only in the H or Me group in position 1 show little difference in oxidation potentials. The highly iodinated anions **12**, **13**, **14**, **16**, and **17** are all oxidized at 1.80 ± 0.08 V, ~1 V more easily than the other highly halogenated anions. These anions do not show any other peaks at higher potentials, as illustrated by the blue curves for **12** and **13** in Figure 1. The anion **18** shows a chemically reversible behavior with a ΔE_p of 116 mV. The most easily oxidized anions are the highly methylated **3** and **11**, which oxidize reversibly with ΔE_p of 56 and 60 mV, respectively, and the previously examined[11,14,15] permethylated anion **2** with a ΔE_p of 60 mV, all very close to the ideal theoretical value.

In HFIPA, the positions of the anodic peaks range from 0.95 to 2.76 V above $Fc^{0/+}$. Eight are reversible (**2**, **3**, **4**, **5**, **11**, **14**, **15**, and **18**, with ΔE_p of 70−240 mV at 0.2 V/s), and three more (**6**, **9**, and **16**) show at least vague return peaks. At 0.2 V/s, the peak separation potentials ΔE_p of **4** and **5** are 137 and 150 mV, respectively, and the cathodic return peak potentials shift to slightly less positive potentials with increasing scan rates. The anion **4** shows a slightly better reversibility (at 0.2 V/s scan, its cathodic-to-anodic peak current ratio is 0.75, and for **5** it is 0.70; the ratios decrease at slower scan rates). Attempts to prepare and isolate neutral radicals by preparative electrolytic oxidation of the fluorinated or iodinated anions **4**, **5**, **12**, and **13** in *l*SO_2/0.1 M Me_4NPF_6 and **4** in HFIPA/0.1 M KPF_6 were unsuccessful. Attempts to measure an in situ EPR signal or absorption spectrum of electrochemically produced radicals of **4** also failed.

The parent anion **1** has a well-developed irreversible oxidation peak at 2.05 V. The anion **19** is again unoxidizable up to the 4 V limit, and the anion **6** again has the highest oxidation potential of those that can be oxidized. The fluorinated anions **4** and **5** show the next highest reversible potentials. Anions **6**, **9**, **12**, **14**, **15**, and **16** show a second peak at higher potentials (1.81 to 3.14 V). In the case of **13**, the two peaks overlap at 2.10 V (the peak height suggests a two-electron process). The iodinated anion **8** shows a broad oxidation wave that starts at 1.70 V and has a maximum at 2.33 V. The lower-belt iodinated anions **14**, **15**, **16**, and **17** are again almost 1 V easier to oxidize than other highly halogenated anions (**4**, **5**, **6**, and **9**).

■ DISCUSSION

The results collected in Table 1 meet the standard tests for diffusion-controlled anodic oxidation. Plots of the anodic peak currents I_{pa} against the square root of the scan rate $v^{1/2}$ (Figures 4, S1, and S2; cf. Figure S5) and against concentration c (Figures S3 and S4) are linear. For reversible oxidations, the repeatability of our results is ca. ±10 mV, but for some of the irreversible oxidations, the peak values cannot be read off the CV curves with an accuracy better than 20 mV, and this needs to be kept in mind in the following discussion.

We start with a comparison of the present results in *l*SO_2 with those reported earlier for several of the anions. A value of $E_{1/2}$ = 1.16 V (at −65 °C) for the perfectly reversible oxidation of **2** was measured in our laboratory at least 10 times independently and reported repeatedly[15,17] and agrees with the present result. However, the oldest reported value, $E_{1/2}$ = 1.08 V,[14] is 80 mV lower. This might be due to the much higher temperature used (0 °C as opposed to the present −70 °C), to the earlier use of ferrocene internal standard, or to a systematic error in the conversion of potentials measured against a silver wire pseudoreference electrode to values against $Fc^{0/+}$. We shall see below that a statistical evaluation of the difference between the oldest value set for methylated anions and all others suggests that the old values are best raised by 43 mV to become compatible with the newer ones.

Among the halogenated anions for which earlier reports of E_{pa} values exist,[16] we find good agreement with the results in Table 1 for **4** and **6**, a difference of 60 mV for **10**, and very large discrepancies for **1** (320 mV) and **12** (340 mV). Since these oxidations are irreversible, the kinetics of processes that follow the initial electron transfer may affect the observed anodic peak positions substantially, and the differences in the temperature used in the three studies (0 °C,[14] −33 to −23 °C,[16] and −70 °C presently) may well be responsible for the difference in the observed peak potentials. It is likely that they also account for the differing findings concerning the oxidizability of the parent anion **1**. No peak for anodic oxidation was observed at 0 °C,[14] but such a peak was observed from −33 to −23 °C,[16] and also in the present work at −70 °C, albeit at a very different potential.

For a discussion of the values of the oxidation potentials collected in Table 1, the anions will be separated into two groups, those that do not carry iodine substituents (group A) and those that do (group B). The oxidation potentials of anions of group A respond to the nature, location, and number of the substituents present and can be treated similarly as those of the methylated anions were earlier.[14,15] We believe that in these,

Table 2. Values of Increments for Shifts of the Oxidation Potential of 1 by Substitution (mV)

i	$Me^{(i)}$	$[Me^{(i)}]$	$\{Me^{(i)}\}$	$F^{(i)}$	$[F^{(i)}]$	$\{F^{(i)}\}$	$Cl^{(i)}$	$[Cl^{(i)}]$	$\{Cl^{(i)}\}$	$Br^{(i)}$	$[Br^{(i)}]$	$\{Br^{(i)}\}$
1	−23	10	−6	156	200	207				96	140	147
2	−30	−63	−65	116[a]	119[b]	120[c]	59	43	41	58	25	23
7	−120	−88	−84				73	89	92	60	92	97
12	−63	−106	−123	89	74	72	173	174	164	173	174	164

[a] The entry is the sum of $F^{(2)}$ and $F^{(7)}$. [b] The entry is the sum of $[F^{(2)}]$ and $[F^{(7)}]$. [c] The entry is the sum of $\{F^{(2)}\}$ and $\{F^{(7)}\}$.

the carborane cage is being oxidized. In most of the anions of group B, oxidation occurs near 1.8 V regardless of the location and number of iodine and other substituents, and we believe that in this case lone pairs on iodines are being oxidized. A few exceptions exist and are rationalized below.

Anions of Group A. As described in more detail elsewhere,[14] the substitution of the parent anion **1** can be viewed as a relatively weak perturbation, and it is sensible to assume that the substituent effects can be described by a set of additive increments. The size of each increment is determined by the nature of the substituent and its location on the cage (1, 2, 7, or 12, Figure 1). Once the increments have been determined, they can be used for predictive purposes. This procedure should work best for cases in which the oxidation is reversible and true redox potentials $E_{1/2}$ have been measured, although even there, the assumption of additivity represents an approximation. The procedure was tested some time ago on derivatives of **1** that carried only methyl groups and was found to work quite well even for E_p values of anions that were oxidized irreversibly.[14] Two of the four resulting increment values (for positions 1 and 12) were subsequently refined when the oxidation potentials of additional derivatives of **1** became available,[15] and the resulting values for methyl increments were $Me^{(1)} = -30$ mV for position 1 and $Me^{(2)} = Me^{(7)} = Me^{(12)} = -70$ mV for positions 2, 7, and 12. The negative sign indicates that the introduction of the substituent causes a decrease of the redox potential of the cage.

When the same least-squares procedure is applied to the presently reported E_p values (Table 1) alone (group I), increments $X^{(i)}$ result (Table 2). When literature[16] data for **4**, **6**, **9**, **10**, $[1\text{-Me-Br}_{11}CB_{11}]^-$, and $[(7-12)\text{-Br}_6CB_{11}]^-$, group II, are included, the increments $[X^{(i)}]$ are obtained ($E_{1/2}$ values were converted to E_p values by adding 30 mV; the theoretical value for a fully reversible system is 29 mV). When the E_p values of the anions used earlier[14,15] to obtain the original $Me^{(i)}$ increments (group III) are increased by 43 mV to correct for the shift mentioned above and included as well, the increments $\{X^{(i)}\}$ result. The magnitude of the constant shift of the old E_p values[14] was obtained by including it as one of the unknown quantities in the overdetermined least-squares search for the values of the increments $\{X^{(i)}\}$.

Figure 5 compares the observed E_p values relative to that of the parent anion **1** (2 030 mV vs $Fc^{0/+}$) with those obtained by addition of the increments $\{X^{(i)}\}$ that are based on the largest number of data, and suggests that the values listed in Table 2 permit an approximate estimation of the anodic potentials. Although useful as an empirical guide, the result is not entirely satisfactory, for two reasons.

The first disturbing observation is the differences between the three sets of increments for any one substituent. Given that the accuracy with which the E_p values for irreversible oxidations are determined is ca. ±20 mV, they can be considered generally similar, but for the methyl and bromine substituents, the difference between the increments $X^{(i)}$ on the one hand and the two very similar sets $[X^{(i)}]$ and $\{X^{(i)}\}$ on the other hand is disturbing. A second and possibly related vexing observation is the huge values of the increments for positions 1 (with the exception of methyl substitution) and particularly 12. In both of these positions, three nodal planes intersect in the highest occupied molecular orbital (HOMO) of **1**, and to first order, the substituent effect should vanish.[14] True, Jahn−Teller distortion may make the first-order approximation particularly poor, but it seems likely to us that the halogen substituents and possibly even the weaker methyl substituents have the ability to reorder the MOs and change the nature of the HOMO, or even worse, that a proper description of the electron removal process involves more than one MO. In that case, the very notions on which the increment concept is based may become invalid. We are planning a detailed computational investigation of the matter and for the moment accept the results displayed in Table 2 and Figure 5 as an empirical result.

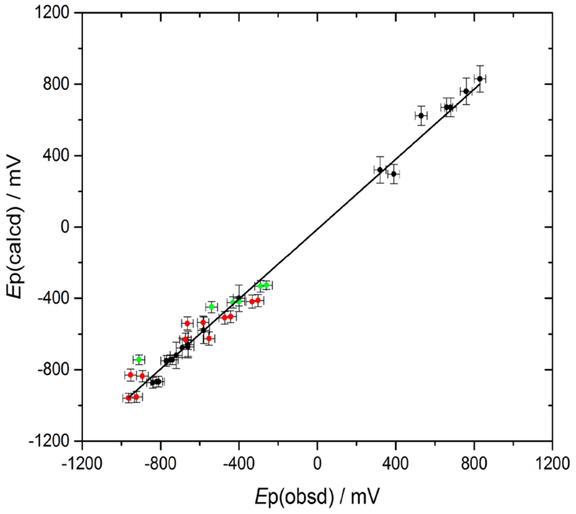


Figure 5. E_p values relative to **1** (E_p = 2 030 mV). Vertical axis, computed; horizontal axis, observed from the increments $\{X^{(i)}\}$ listed in Table 2. Anions of group I (black), group II (green), and group III (red).

Not surprisingly, in all positions methyl acts as a net donor relative to hydrogen. In position 1, its effect is essentially negligible, and it generally increases with the distance of the substituent from the carbon vertex 1, in the order 2 < 7 < 12. All three halogens act as net acceptors. In position 1, fluorine has the largest effect of all three halogens by a factor of 1.5, whereas in position 12, it has the smallest effect by a factor of 2, and the effects of chlorine and bromine are nearly identical and much larger than in any other position. The sum of the increments in positions 2 and 7 is almost the same for all three halogens, ∼120 mV for fluorine and bromine and ∼130 for chlorine, and the order of increment size tends to be 2 < 7. A more detailed consideration of the nature of substituent effects will have to await the completion of our computational study and will need to reflect the interplay between their σ-withdrawing and π-donating effects, with both the former and the latter decreasing in the order F > Cl > Br.

In lSO$_2$, only the highly methylated radicals with relatively low redox potentials are sufficiently stable to make the anodic oxidation of the anions reversible. This probably reflects the effects of steric hindrance to dimerization and is in line with earlier observations.[14] These radicals could most likely be isolated and stored. In HFIPA, even the anions that carry fewer methyls and many halogens are oxidized reversibly, and this suggests that the instability of such anions in lSO$_2$ is not caused by dimerization, but by reaction with the solvent. A possible process is a transfer of a halogen atom to SO$_2$ with ultimate production of S(VI). An oxidation of species such as $ISO_2^•$ to ISO_2^+ could then be responsible for the two-electron nature of the oxidation process in the iodinated anions. The nature of the second oxidation peak observed in these anions in HFIPA is not clear. For the time being, we base our discussion on the more numerous results obtained in lSO$_2$, but it is possible that in the future HFIPA will turn out the be the solvent of choice for similar studies.

Anions of Group B. As proposed recently for the analogous $[B_{12}I_{12}]^{2-}$ dianion,[27] we believe that the nearly constant position of the anodic peak that appears in the CV of the iodinated anions **12**−**17** at 1.8 ± 0.08 V is attributable to the oxidation of iodine lone pairs and not the carborane cages. The lone pairs apparently interact among themselves only weakly, and as a result it does not matter much how many of them are present. When a sufficient number of methyl groups is present to displace the oxidation potential of the cage below 1.8 V, as in **18** (reversible, $E_{1/2}$ = 1.37 V) and in [12-I-(2−11)-Me$_{10}$-HCB$_{11}$] and [12-I-(1−11)-Me$_{11}$-CB$_{11}$] (irreversible, E_p = 1.43 and 1.39, respectively[15,26]), it is the cage that is oxidized, even if an iodine is present. In these exceptional instances, one may attempt to extend the increment concept to the iodine substituent and compare the E_p values of anions carrying a methyl with those of anions carrying an iodine in position 12. One then arrives at the enormous value $\{I^{(12)}\}$ = 333 mV, nearly twice that obtained for chlorine or bromine. This suggests that the electron removed in the oxidative process is removed from an orbital in which cage and iodine lone pair contributions are mixed. Once again, the issue will require computational attention.

■ CONCLUSIONS

The oxidation peak potentials of about three dozen methylated and/or halogenated anions containing an icosaedral CB$_{11}$ cage in lSO$_2$ can be fitted by a set of position- and substituent-dependent increments. Only a few of the anodic oxidations are reversible in this solvent, but many more are reversible in HFIPA, suggesting that the instability of the corresponding halogenated neutral radicals in lSO$_2$ is due to reaction with solvent rather than to dimerization. We suggest that HFIPA may be a superior solvent for the study of anions of this class. Except for those that are particularly easily oxidized, iodinated anions are not oxidized in the cage but on iodine lone pairs.

■ EXPERIMENTAL SECTION

Materials. The synthesis, purification, and identification of all the carborane salts followed the references given in Table 1, except for **3**, **6**, **11**, and **18**, whose preparation is described below. Tetra-*n*-butylammonium hexafluorophosphate obtained from Fluka AG (99.0%) was recrystallized twice from ethanol and dried in a vacuum desiccator over P$_2$O$_5$. HFIPA purchased from Apollo Scientific (99.0%) was freshly distilled from KMnO$_4$, CaH$_2$, and NaHCO$_3$ before use. Tetrahydrofuran (THF) was dried and distilled from LiAlH$_4$. Benzene was dried and distilled over sodium benzophenone. Dichloromethane was dried and distilled over calcium hydride. Anhydrous SO$_2$ gas (99.98%) obtained from Linde Technoplyn, Prague, Czech Republic, was condensed at −70 °C with an ethanol/ice bath and purified by stirring magnetically for 30 min in a dried flask with highly activated alumina (basic type 5016A, Fluka AG). [Me$_3$NH][CB$_{11}$H$_{12}$] (Katchem Ltd., Elišky Krásnohorské, Prague 1, 11000, Czech Republic), potassium graphite (Strem), methyl triflate (Matrix) and sulfolane (Aldrich) were used as purchased. All synthetic manipulations were performed under an inert atmosphere.

Electrochemistry. All the voltammetric measurements were performed using an AUTOLAB potentiostat (PGSTAT30) controlled by a personal computer with GPES software. The supporting electrolyte was 0.1 M [NBu$_4$][PF$_6$]. Cyclic voltammetric (CV) measurements were performed in a single compartment glass cell using a Pt disk (1.0 mm diameter) working electrode, a Pt plate counter electrode, and a Ag rod as quasireference electrode. Ferrocene (Fc$^{0/+}$) was used (0.3−0.5 mM) as both an internal and external reference. The volume of the five-neck conical electrochemical cell was ∼10 mL. In HFIPA, millimolar carborane solutions were prepared by dissolution of solid sample in the solvent, and the measurements were performed under argon atmosphere after several minutes of deaeration with argon. For measurements in lSO$_2$, the cell containing the carborane salt and electrolyte along with a magnetic stirrer was placed on a vacuum line (7.0 mbar) and then filled with argon and evacuated several times. Purified SO$_2$ was distilled into the cell at −70 °C to prepare a millimolar solution (∼4 mL), and the measurements were performed at the same temperature under argon atmosphere. After each experiment ferrocene was added to the solution carefully from a capped-glass tip (kept above the solution level) without exposure to moisture to check the reference potentials. The scan rates of CVs were varied from 0.01 to 5.0 V/s. Normalized peak heights relative to that of **2** were used to determine whether the oxidations are one- or two-electron. The reproducibility of potential measurements under these conditions was ±10 mV.

Synthesis. All synthetic procedures used Schlenk inert-atmosphere techniques, and the reaction mixtures were worked up in air. NMR was measured with Bruker Avance-III 300 NMR and Varian Inova 500 NMR spectrometers. ^{1}H chemical shifts were measured relative to residual protons from acetonitrile-d_3. ^{11}B chemical shifts were measured relative to BF$_3$·OEt$_2$. Mass spectra were recorded with an electrospray triple quadrupole/time-of-flight mass spectrometer (ESI-qTOF-MS) from Applied Biosystems, PE SCIEX/AB/AP/QSTAR Pulsar Hybrid LC/MS/MS. Elemental analysis was performed by Columbia Analytical Services, Inc., for the trimethylammonium salts of the carboranes.

Cesium 1-H-(2−12)-Undecachloromonocarba-closo-dodecaborate (6). This compound was prepared by a modification of a published procedure.[31] Cs$^+$ salt of **1** (1.60 g, 5.80 mmol) was placed into a 250 mL three-neck round-bottom flask with a stirring bar. A reflux condenser was fitted to the central neck of the flask, and the end of the condenser was connected using a hose adapter and Tygon tube to a 1000 mL beaker containing a 500 mL aqueous solution of NaOH (10 g) and Na$_2$SO$_3$ (10 g). To prevent the scavenging solution from being sucked back, the Tygon tube was connected to an inverted funnel only slightly submerged into the solution. Both side necks of the flask were closed with septa and used for additions and monitoring. SO$_2$Cl$_2$ (50 mL) was added, and the suspension was carefully heated to reflux and stirred overnight. The day after, a mixture of products containing between 4 and 11 times chlorinated carborane was detected by MS ESI(−) analysis. Further additions of SO$_2$Cl$_2$ to a volume of ca. 120 mL and reflux for a total of 36 h afforded a product containing a mixture of 9, 10, and 11 times chlorinated carborane anion. After the suspension cooled to room temperature, chlorine was bubbled in at moderate rate. A trap was installed between the reaction vessel and the chlorine cylinder to prevent the reaction mixture from entering the cylinder. While the gas bubbled into the suspension, the temperature was slowly increased to 80 °C until most (ca. 95%) of the product detected by MS ESI(−) was the desired 11 times chlorinated anion, and the suspension turned into a yellow solution. After the bubbling was terminated and the solution cooled to room temperature, the system was flushed with argon for 30 min to remove excess chlorine. Workup followed the published procedure, and spectroscopic properties of the product agreed with those published.[31] Yield 2.51g (66%).

*Cesium 7,12-Bromo-(2–6, 8–11)-nonamethylcarba-closo-dodecaborate, Cs[7,12-Br$_2$-(2–6,8–11)-Me$_9$-CB$_{11}$] (**11**).* Dried (100 °C, 0.01 torr, 5 h), Cs[7,12-Br$_2$−CB$_{11}$H$_{10}$][32] (0.5 g, 1.45 mmol) and CaH$_2$ (1 g, 23.75 mmol) were placed in a two-neck Schlenk round-bottom flask equipped with a stir bar and a septum. The flask was connected to a vacuum line and evacuated. It was then filled with argon, and sulfolane (10 mL) was syringed in through the septum. The mixture was stirred for 10 min before MeOTf (2 g, 12.18 mmol) was syringed in through the septum. The solution was stirred for 24 h at room temperature and was subsequently heated to 60 °C for 72 h. After this time, ^{11}B NMR and MS/ESI(−) analysis of an aliquot of the reaction mixture showed complete conversion to product. The flask was allowed to reach room temperature and was opened to air. Dry CH$_2$Cl$_2$ (50 mL) was added, and the solution was filtered through a coarse frit funnel. The CaH$_2$ residue was carefully quenched with isopropyl alcohol and water. Isopropyl alcohol (10 mL) and then water (50 mL) were also added to the filtrate. Finally, excess NH$_4$OH (30 mL) was added, and the solution was stirred for 1 h. Afterward, all volatiles but sulfolane were removed under reduced pressure. Water (50 mL) was added to the sulfolane solution, and a white precipitate formed. CsCl (0.8 g, 4.75 mmol) was added, the solution was filtered, and the white solid was washed with water and dried at 170 °C/0.01 torr to remove all sulfolane. Recrystallization, first from boiling water and then from benzene, gave analytically pure product as a white solid (0.5 g, 73% yield). ^{1}H{^{11}B} NMR (499.8 MHz, CD$_3$CN): δ −0.25 (s, 6H, B(8,11)−CH$_3$), −0.17 (s, 15H, B(2−6)−CH$_3$), −0.09 (s, 6H, B(9,10)−CH$_3$), 1.53 (s, 1H, CH). ^{11}B{^{1}H} NMR (96.2 MHz, CD$_3$CN): δ −0.34 (s, 1B, B(12)), −7.49 (s, 1B, B(7), −9.54 (s, 4B, B(8−11)), −12.8 (s, 5B, B(2−6)). IR (KBr pellet): 2972, 2929, 1356, 1219, 1028 cm^{-1}. ESIMS(−): m/z 427, expected isotope distribution. High-resolution (HR) ESI MS(−): m/z 427.1637, calcd 427.1640. Anal. Calcd for NMe$_3$HCHB$_{11}$Me$_9$Br$_2$: C, 32.05; H, 7.86. Found: C, 31.91; H, 7.60%.

*Cesium (2–6, 8–11)-Nonamethylcarba-closo-dodecaborate, Cs-[(2–6,8–11)-Me$_9$CB$_{11}$] (**3**).* Inside a glovebox, dried (100 °C, 0.01 torr, 5 h) Cs[7,12-Br$_2$-(2–6,8–11)-CB$_{11}$] (0.3 g, 0.54 mmol) was placed in a Schlenk flask equipped with a stir bar, and dry THF (20 mL) was added. The mixture was stirred for 5 min, and then KC$_8$ (0.73 g, 5.4 mmol) was added in five portions over 1 h with stirring. The mixture was subsequently stirred for 24 h. After this time, ^{11}B NMR and MS/ESI(−) analysis of an aliquot of the reaction mixture showed complete conversion to product. The reaction mixture was filtered inside the glovebox, and the filtrate was taken out of the box and connected to a vacuum line. All volatiles were removed under reduced pressure, and the off-white precipitate was recrystallized from benzene to give an analytically pure product as a white solid (0.13 g, 59% yield). ^{1}H{^{11}B} NMR (499.8 MHz, CD$_3$CN): δ −0.32 (s, 6H, B(8,11)−CH$_3$), −0.17 (s, 15H, B(2−6)−CH$_3$), 0.00 (s, 6H, B(9,10)−CH$_3$), 1.29 (s, 1H, CH). ^{11}B{^{1}H} NMR (96.2 MHz, CD$_3$CN): δ −3.47 (s, 1B, B(12)), −4.79 (s, 1B, B(7), −8.23 (s, 4B, B(8−11)), −11.47 (s, 5B, B(2−6)). IR (KBr pellet): 2950, 2921, 1357, 1234, 1087, 1064 cm^{-1}. ESI MS(−): m/z 269, expected isotope distribution. HR ESI MS(−): m/z 269.3448, calcd 269.3454. Anal. Calcd for N(CH)$_3$HCB$_{11}$(CH$_3$)$_9$H$_3$: C, 47.40; H, 12.24. Found: C, 47.81; H, 12.38%.

*Cesium 7,12-Iodo-(2–6, 8–11)-nonamethylcarba-closo-dodecaborate, Cs[7,12-I$_2$-(2–6, 8–11)-Me$_9$CB$_{11}$] (**18**).* A reaction of dried (100 °C, 0.01 torr, 5 h) Cs[7,12-I$_2$−CB$_{11}$H$_{10}$][33] (0.5 g, 0.95 mmol), CaH$_2$ (1 g, 23.75 mmol), sulfolane (10 mL), and MeOTf (2 g, 12.18 mmol) was performed and worked up in the way described above for **11**. The Cs salt of **18** is a white solid (0.42 g, 67% yield). ^{1}H{^{11}B} NMR (499.8 MHz, CD$_3$CN): δ −0.20 (s, 6H, B(8,11)−CH$_3$),-0.07 (s, 15H, B(2−6)−CH$_3$), 0.04 (s, 6H, B(9,10)−CH$_3$), 1.81 (s, 1H, CH). ^{11}B{^{1}H} NMR (96.2 MHz, CD$_3$CN): δ −7.05 (s, 1B, B(12)), −8.86 (s, 1B, B(7), −12.03 (s, 4B, B(8−11)), −14.74 (s, 5B, B(2−6)). IR (KBr pellet): 2924, 2919, 1399, 1256, 1011 cm^{-1}. ESI MS(−): m/z 521, expected isotope distribution. HR ESI MS(−): m/z 521.1392, calcd 521.1387. Anal. Calcd for NMe$_3$HCHB$_{11}$Me$_9$I$_2$: C, 26.87; H, 6.59. Found: C, 27.24; H, 6.09%.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.6b02126.

Electrochemical characteristics (PDF)

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was supported by the Czech Science Foundation, Grant No. P206/11/0727, by the Institute of Organic Chemistry and Biochemistry AS CR, v.v.i., RVO 61388963, and by the U.S. National Science Foundation (CHE-1566435). We are grateful to Dr. T. F. Magnera for least-squares evaluation of the substituent increments.

■ REFERENCES

(1) Knoth, W. H. 1-B$_9$H$_9$CH$^-$ and B$_{11}$H$_{11}$CH$^-$. *J. Am. Chem. Soc.* **1967**, *89*, 1274−1275.

(2) King, B. T.; Michl, J. The Explosive "Inert" Anion CB$_{11}$(CF$_3$)$_{12}$$^-$. *J. Am. Chem. Soc.* **2000**, *122*, 10255−10256.

(3) Fete, M. G.; Havlas, Z.; Michl, J. HCB$_{11}$(CF$_3$)$_n$F$_{11-n}$$^-$: Inert Anions with High Anodic Oxidation Potentials. *J. Am. Chem. Soc.* **2011**, *133*, 4123−4131.

(4) Strauss, S. H. The Search for Larger and More Weakly Coordinating Anions. *Chem. Rev.* **1993**, *93*, 927−942.

(5) Reed, C. A. Carboranes: A New Class of Weakly Coordinating Anions for Strong Electrophiles, Oxidants, and Superacids. *Acc. Chem. Res.* **1998**, *31*, 133−139.

(6) Krossing, I.; Raabe, I. Noncoordinating Anions—Fact or Fiction? A Survey of. *Angew. Chem., Int. Ed.* **2004**, *43*, 2066−2090.

(7) Körbe, S.; Schreiber, P. J.; Michl, J. Chemistry of the Carba-*closo*-Dodecaborate(−) Anion, CB$_{11}$H$_{12}$$^-$. *Chem. Rev.* **2006**, *106*, 5208−5249.

(8) Reed, C. A. H$^+$, CH3$^+$, and R$_3$Si$^+$ Carborane Reagents: When Triflates Fail. *Acc. Chem. Res.* **2010**, *43*, 121−128.

(9) Grimes, R. N.*Carboranes*, 2nd ed.; Elsevier: Amsterdam, The Netherlands, 2011.

(10) Douvris, C.; Michl, J. Update 1 of: Chemistry of the Carba-*closo*-Dodecaborate(−) Anion, $CB_{11}H_{12}^{-}$. *Chem. Rev.* **2013**, *113*, PR179−PR233.

(11) King, B. T.; Janoušek, Z.; Grüner, B.; Trammell, M.; Noll, B. C.; Michl, J. Dodecamethylcarba-*closo*-dodecaborate(−) Anion, $CB_{11}Me_{12}^{-}$. *J. Am. Chem. Soc.* **1996**, *118*, 3313−3314.

(12) McKee, M. L. Computed Properties of the CB_9H_{10} and $CB_{11}H_{12}$ Free Radicals. *J. Am. Chem. Soc.* **1997**, *119*, 4220−4223.

(13) Pospíšil, L.; King, B. T.; Michl, J. Voltammetry in Benzene Using Lithium Dodecamethylcarba-*closo*-dodecaborate, $LiCB_{11}Me_{12}$, as a Supporting Electrolyte: Reduction of Ag^{+}. *Electrochim. Acta* **1998**, *44*, 103−108.

(14) King, B. T.; Körbe, S.; Schreiber, P. J.; Clayton, J.; Němcová, A.; Havlas, Z.; Vyakaranam, K.; Fete, M. G.; Zharov, I.; Ceremuga, J.; Michl, J. The Sixteen $CB_{11}H_{n}Me_{12-n}^{-}$ Anions with Five-fold Substitution Symmetry: Anodic Oxidation and Electronic Structure. *J. Am. Chem. Soc.* **2007**, *129*, 12960−12980.

(15) Wahab, A.; Stepp, B. R.; Douvris, C.; Valášek, M.; Štursa, J.; Klíma, J.; Piqueras, M.-C.; Crespo, R.; Ludvík, J.; Michl, J. Measured and Calculated Oxidation Potentials of 1-X-12-Y-$CB_{11}Me_{10}^{-}$ Anions. *Inorg. Chem.* **2012**, *51*, 5128−5137.

(16) Boeré, R. T.; Bolli, C.; Finze, M.; Himmelspach, A.; Knapp, C.; Roemmele, T. L. Quantum-Chemical and Electrochemical Investigation of the Electrochemical Windows of Halogenated Carborate Anions. *Chem. - Eur. J.* **2013**, *19*, 1784−1795.

(17) Wahab, A.; Kvapilová, H.; Klíma, J.; Michl, J.; Ludvík, J. Isoflurane as a Solvent for Electrochemistry. Electrooxidation Study of Icosahedral Carborane Anions in Four Different Solvents. *J. Electroanal. Chem.* **2013**, *689*, 257−261.

(18) Pospíšil, L.; Kaleta, J.; Michl, J. Electrochemical Hydrogen Oxidation in Toluene/$LiCB_{11}Me_{12}$: H_2 as a Surrogate for Lithium Metal? *ChemElectroChem* **2016**, *3*, 332−336.

(19) Clayton, J. R.; King, B. T.; Zharov, I.; Fete, M. G.; Volkis, V.; Douvris, C.; Valášek, M.; Michl, J. Salts of Dodecamethylcarba-*closo*-dodecaborate(−) Anion, $CB_{11}Me_{12}^{-}$, and the Radical Dodecamethylcarba-*closo*-dodecaboranyl, $CB_{11}Me_{12}^{\bullet}$. *Inorg. Synth.* **2010**, *35*, 56−66.

(20) King, B. T.; Noll, B. C.; McKinley, A. J.; Michl, J. Dodecamethylcarba-*closo*-dodecaboranyl ($CB_{11}Me_{12}^{\bullet}$), a Stable Free Radical. *J. Am. Chem. Soc.* **1996**, *118*, 10902−10903.

(21) Zharov, I.; King, B. T.; Havlas, Z.; Pardi, A.; Michl, J. Crystal Structure of *n*-$Bu_3Sn^{+}CB_{11}Me_{12}^{-}$. *J. Am. Chem. Soc.* **2000**, *122*, 10253−10254.

(22) Zharov, I.; Weng, T.; Orendt, A. M.; Barich, D. H.; Penner-Hahn, J.; Grant, D. M.; Havlas, Z.; Michl, J. Metal Cation - Methyl Interactions in $CB_{11}Me_{12}^{-}$ Salts of Me_3Ge^{+}, Me_3Sn^{+}, and Me_3Pb^{+}. *J. Am. Chem. Soc.* **2004**, *126*, 12033−12046.

(23) Kaleta, J.; Tarábek, J.; Akdag, A.; Pohl, R.; Michl, J. Metal Cation - Methyl Interactions in $CB_{11}Me_{12}^{-}$ Salts of Me_3Ge^{+}, Me_3Sn^{+}, and Me_3Pb^{+}. *Inorg. Chem.* **2012**, *51*, 10819−10824.

(24) Kaleta, J.; Akdag, A.; Crespo, R.; Piqueras, M.-C.; Michl, J. Evidence for an Intermediate in the Methylation of $CB_{11}H_{12}^{-}$ with MeOTf. Comparison of Electrophilic Substitution in Cage Boranes and in Arenes. *ChemPlusChem* **2013**, *78*, 1174−1183.

(25) Teixidor, F.; Barbera, G.; Vaca, A.; Kivekas, R.; Sillanpaa, R.; Oliva, J.; Vinas, C. Are Methyl Groups Electron-Donating or Electron-Withdrawing in Boron Clusters? Permethylation of *o*-Carborane. *J. Am. Chem. Soc.* **2005**, *127*, 10158−10159.

(26) Wahab, A.; Kaleta, J.; Wen, J.; Valášek, M.; Polášek, M.; Michl, J.; Ludvík, J. Electrochemical Oxidation of [1-X-12-I-$CB_{11}Me_{10}^{-}$] Anions: Formation of Borenium Ylides [12-Dehydro-1-X-$CB_{11}Me_{10}$] and Iodonium Ylide Anions [{12-(1-X-$CB_{11}Me_{10}^{-}$)}$_2$$I^{+}$]. *Inorg. Chem.* **2016**, DOI: 10.1021/acs.inorgchem.6b02128.

(27) Boeré, R. T.; Derendorf, J.; Jenne, C.; Kacprzak, S.; Keßler, M.; Riebau, R.; Riedel, S.; Roemmele, T. L.; Rühle, M.; Scherer, H.; Vent-Schmidt, T.; Warneke, J.; Weber, S. On the Oxidation of the Three-Dimensional Aromatics $[B_{12}X_{12}]^{2-}$ (X = F, Cl, Br, I). *Chem. - Eur. J.* **2014**, *20*, 4447−4459.

(28) Tinker, L.; Bard, A. J. Electrochemistry in Liquid Sulfur Dioxide. 1. Oxidation of Thianthrene, Phenothiazine, and 9,10-Diphenylanthracene. *J. Am. Chem. Soc.* **1979**, *101*, 2316−2319.

(29) Garcia, E.; Kwak, J.; Bard, A. J. Electrochemistry in Liquid Sulfur Dioxide. 8. Oxidation of Iron, Ruthenium, and Osmium Bipyridine Complexes at Ultramicroelectrodes at Very Positive Potentials. *Inorg. Chem.* **1988**, *27*, 4377−4382.

(30) Valášek, M.; Šembera, F.; Hughes, M. J.; Stibor, I.; Janoušek, Z.; Michl, J. Synthesis of Cs[1-H-$CB_{11}F_{11}$]. In *Efficient Preparation of Fluorine Compounds*, Roesky, H. W., Ed.; John Wiley & Sons: Hoboken, NJ, 2012; p 22.

(31) Gu, W.; McCulloch, B. J.; Reibenspies, J. H.; Ozerov, O. V. Improved Methods for the Halogenation of the $[HCB_{11}H_{11}]^{-}$ anion. *Chem. Commun.* **2010**, *46*, 2820−2822.

(32) Jelinek, T.; Baldwin, P.; Scheidt, W. R.; Reed, C. A. New Weakly Coordinating Anions. 2. Derivatization of the Carborane Anion $CB_{11}H_{12}$. *Inorg. Chem.* **1993**, *32*, 1982−1990.

(33) Finze, M. Carba-*closo*-dodecaborates with One or Two Alkynyl Substituents Bonded to Boron. *Inorg. Chem.* **2008**, *47*, 11857−11867.

(34) Ivanov, S. V.; Rockwell, J. J.; Polyakov, O. G.; Gaudinski, C. M.; Anderson, O. P.; Solntsev, K. A.; Strauss, S. H. Highly Fluorinated Weakly Coordinating Monocarborane Anions. 1-H-$CB_{11}F_{11}^{-}$, 1-CH_3-$CB_{11}F_{11}^{-}$, and the Structure of $[N(n\text{-}Bu)_4]_2[CuCl(CB_{11}F_{11})]$. *J. Am. Chem. Soc.* **1998**, *120*, 4224.

(35) Xie, Z.; Tsang, C.; Sze, E. T.; Yang, Q.; Chan, D. T. W.; Mak, T. C. W. Highly Chlorinated, Brominated, and Iodinated Icosahedral Carborane Anions: 1-H-$CB_{11}X_{11}^{-}$, 1-CH_3-$CB_{11}X_{11}^{-}$ (X = Cl, Br, I); 1-Br-$CB_{11}Br_{11}^{-}$. *Inorg. Chem.* **1998**, *37*, 6444.

(36) Stasko, D.; Reed, C. A. Optimizing the Least Nucleophilic Anion. A New, Strong $Methyl^{+}$ Reagent. *J. Am. Chem. Soc.* **2002**, *124*, 1148.

(37) Grüner, B.; Janoušek, Z.; King, B. T.; Woodford, J. N.; Wang, C. H.; Všetečka, V.; Michl, J. Synthesis of 12-Substituted 1-Carba-*closo*-dodecaborate Anions and First Hyperpolarizability of the 12-$C_7H_6^{+}$−$CB_{11}H_{11}^{-}$ Ylide. *J. Am. Chem. Soc.* **1999**, *121*, 3122; *J. Am. Chem. Soc.* **2000**, *122*, 11274 Erratum.

(38) Xie, Z.; Manning, J.; Reed, R. W.; Mathur, R.; Boyd, P. D. W.; Benesi, A.; Reed, C. A. Approaching the Silylium (R_3Si^{+}) Ion: Trends with Hexahalo (Cl, Br, I) Carboranes as Counterions. *J. Am. Chem. Soc.* **1996**, *118*, 2922.