

# Electrochemical Oxidation of [1-X-12-I-CB<sub>11</sub>Me<sub>10</sub><sup>−</sup>] Anions: Formation of Borenium Ylides [12-Dehydro-1-X-CB<sub>11</sub>Me<sub>10</sub>] and Iodonium Ylide Anions [{12-(1-X-CB<sub>11</sub>Me<sub>10</sub><sup>−</sup>)}<sub>2</sub>I<sup>+</sup>]

Abdul Wahab,<sup>†,‡,§,||</sup> Jiří Kaleta,<sup>‡</sup> Jin Wen,<sup>‡,§</sup> Michal Valášek,<sup>‡</sup> Miroslav Polášek,<sup>†</sup> Josef Michl,<sup>\*,‡,§,||</sup> and Jiří Ludvík<sup>\*,†</sup>

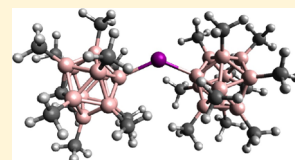
<sup>†</sup>J. Heyrovský Institute of Physical Chemistry, Academy of Sciences of the Czech Republic, Dolejškova 3, 182 23 Prague 8, Czech Republic

<sup>‡</sup>Institute of Organic Chemistry and Biochemistry, Academy of Sciences of the Czech Republic, Flemingovo nám. 2, 166 10 Prague 6, Czech Republic

<sup>§</sup>Department of Chemistry and Biochemistry, University of Colorado, Boulder, Colorado 80309-0215, United States

## S Supporting Information

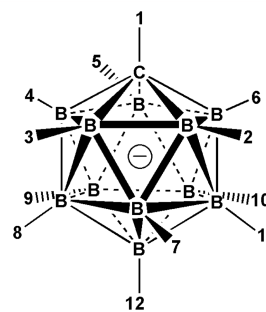
**ABSTRACT:** Cyclic voltammograms of 12-iodinated icosahedral carborane anions [1-X-12-I-CB<sub>11</sub>Me<sub>10</sub><sup>−</sup>] (X = H, CH<sub>3</sub>, C<sub>2</sub>H<sub>5</sub>, C<sub>3</sub>H<sub>7</sub>, C<sub>4</sub>H<sub>9</sub>, C<sub>6</sub>H<sub>13</sub>, and COOCH<sub>3</sub>) show two one-electron anodic oxidation peaks at the Pt electrode in liquid SO<sub>2</sub>. Oddly, the first is irreversible and the second partially reversible. Mass spectrometry of the principal anionic product of preparative anodic oxidation of [1-H-12-I-CB<sub>11</sub>Me<sub>10</sub><sup>−</sup>], identical with the anionic product of its reaction with [Et<sub>3</sub>Si-H-SiEt<sub>3</sub>]<sup>+</sup> and/or Et<sub>3</sub>Si<sup>+</sup>, allows it to be identified as the iodonium ylide anion [{12-(1-H-CB<sub>11</sub>Me<sub>10</sub><sup>−</sup>)}<sub>2</sub>I<sup>+</sup>]. Its reversible oxidation to a neutral ylide radical [{12-(1-H-CB<sub>11</sub>Me<sub>10</sub><sup>−</sup>)}<sub>2</sub>I<sup>•</sup>] is responsible for the second peak. A DFT geometry optimization suggests that both the ylide anion and the ylide radical are very crowded and have an unusually large C–I–C valence angle of ~132°; they are the first compounds with two bulky highly methylated CB<sub>11</sub> cages attached to the same atom. Molecular iodine is another product of the electrolysis. We propose an electrode mechanism in which initial one-electron oxidation of [1-X-12-I-CB<sub>11</sub>Me<sub>10</sub><sup>−</sup>] is followed by a transfer of an iodine atom from the B–I bond to SO<sub>2</sub> to yield a weakly bound radical ISO<sub>2</sub><sup>•</sup> which disproportionates into SO<sub>2</sub> and I<sub>2</sub>. The other product is the borenium ylide [12-dehydro-1-X-CB<sub>11</sub>Me<sub>10</sub>], which has a strongly Lewis acidic naked vertex in position 12 that rapidly adds to another [1-X-12-I-CB<sub>11</sub>Me<sub>10</sub><sup>−</sup>] anion to form the observed stable ylide anion [{12-(1-X-CB<sub>11</sub>Me<sub>10</sub><sup>−</sup>)}<sub>2</sub>I<sup>+</sup>]. In acetonitrile, where it presumably exists as a solvent adduct, [12-dehydro-1-X-CB<sub>11</sub>Me<sub>10</sub>] has been trapped with H<sub>2</sub>O and, to a small extent, with MeOH, but not with several other potential trapping agents.



## ■ INTRODUCTION

The icosahedral carborane anion [CB<sub>11</sub>H<sub>12</sub><sup>−</sup>] and its derivatives<sup>1,2</sup> are known for being among the least coordinating anions.<sup>3–5</sup> Over the years, they also attracted considerable interest because of their diverse applications, as counterions for reactive cationic organometallic catalysts,<sup>6</sup> including “naked” Li<sup>+</sup>, which catalyzes the radical polymerization of simple alkenes,<sup>7</sup> as electrolytes for nonaqueous solvents<sup>8,9</sup> and lithium ion batteries,<sup>10–12</sup> as solubilizers of cations in organic solvents<sup>13</sup> for applications such as solvent extraction of radionuclides,<sup>14</sup> as components of ionic liquids<sup>15,16</sup> and nonlinear optical materials,<sup>17</sup> etc. Most of these applications were based on their great stability, low nucleophilicity, lipophilicity, and high redox potentials.

The permethylated anion [CB<sub>11</sub>Me<sub>12</sub><sup>−</sup>] (Figure 1) oxidizes reversibly to the isolable and stable neutral radical [CB<sub>11</sub>Me<sub>12</sub><sup>•</sup>],<sup>18,19</sup> which has seen use as an oxidant to prepare salts of highly electrophilic cations.<sup>20,21</sup> This radical can also act as methyl radical transfer agent to C=C double bonds<sup>7</sup> and to Si–Si bonds,<sup>22</sup> especially from position 12, thus transforming itself into an internally charge-compensated borenium ylide [12-dehydro-CB<sub>11</sub>Me<sub>11</sub>] with a delocalized negative charge and



**Figure 1.** Vertex numbering in the CB<sub>11</sub> icosahedron. In this study, vertices 2–11 are always occupied with methyl groups.

a positively charged naked boron vertex in position 12. This highly reactive hypovalent species is analogous to a carbene. In pentane solution, 2 equiv of [CB<sub>11</sub>Me<sub>12</sub><sup>•</sup>] react with hexaalkyldisilanes to form 2 equiv of methyltrialkylsilanes and [12-dehydro-CB<sub>11</sub>Me<sub>11</sub>], which precipitates and is stable at −60

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°C.<sup>22</sup> EXAFS and computational studies suggest that in the  $\text{Me}_3\text{M}^+$  salts of main group<sup>21,22</sup> and transition<sup>23</sup> metal cations with  $[\text{CB}_{11}\text{Me}_{12}]^-$ , the cation is coordinated to the carbon of one or more methyl groups of the anion, which have considerable methide anion character. Proceeding from  $\text{M} = \text{Pb}$  to  $\text{M} = \text{Sn}$  and  $\text{M} = \text{Ge}$  reveals increasing metal cation-12-methyl carbon interaction along a reaction path that corresponds to classical backside  $\text{S}_{\text{E}}2$  substitution and thus converts the anion to the ylide. The preferential electrophilic substitution ( $\text{S}_{\text{E}}2$ ) reaction in position 12 by  $\text{Li}^+$ -induced  $\sigma$ -bond metathesis has also been suggested to occur through the formation of a borenium ylide,  $[\text{12-dehydro-1-(C}_6\text{H}_{12}\text{O}_2\text{)B-CB}_{11}\text{Me}_{10}]$ , as an intermediate.<sup>24</sup>

Our specific interest is the possible utility of anions of the  $\text{CB}_{11}^-$  type as reversible redox shuttles in solar cell applications. Several electrochemical studies of numerous substituted anions of this type have been reported,<sup>25–28</sup> mostly in liquid  $\text{SO}_2$  but also in other solvents. We have determined the relative susceptibility of various positions in the anion to substituent effects on the redox potential and discovered that anions carrying an iodine substituent differed from most by showing a completely irreversible oxidation behavior.<sup>26</sup> We speculated that the oxidized form loses an iodine atom to form a highly reactive borenium ylide, which then reacts with available nucleophiles.

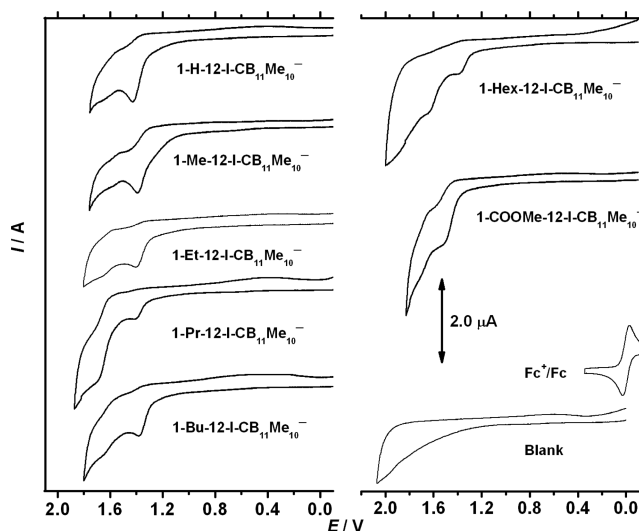
In this paper, we investigate the cause of the irreversibility of electrochemical oxidations of seven 12-iodo carborane anions  $[\text{1-X-12-I-CB}_{11}\text{Me}_{10}]^-$  ( $\text{X} = \text{H}, \text{CH}_3, \text{C}_2\text{H}_5, \text{C}_3\text{H}_7, \text{C}_4\text{H}_9, \text{C}_6\text{H}_{13}$ , and  $\text{COOCH}_3$ ). They show no sign of reversibility even at 5.0 V/s scan rate, indicating that fast follow-up reactions intervene. We discuss the mechanism and use spectral analysis of mixtures obtained from preparative electrolysis and of a sample formed by an independent chemical route to identify the ultimate product of the first one-electron oxidation in liquid  $\text{SO}_2$  as the crowded iodonium ylide anion  $[\{\text{12-(1-H-CB}_{11}\text{Me}_{10})\}_2\text{I}^+]^-$ . Its stability suggests that it may be isolable and could serve as a useful source of the highly reactive borenium ylide  $[\text{12-dehydro-1-H-CB}_{11}\text{Me}_{10}]$ , but the development of its synthesis lies beyond the scope of the present study of electrochemical mechanisms. Reversible oxidation of the ylide anion to an ylide radical accounts for the second observed peak in the CV of  $[\text{1-X-12-I-CB}_{11}\text{Me}_{10}]^-$  anions. Supporting evidence is obtained from DFT calculations and from trapping of the borenium ylide with  $\text{H}_2\text{O}$ .

## RESULTS

A cyclic voltammetric (CV) oxidation at a Pt electrode of a series of cesium salts of icosahedral carborane anions  $[\text{1-X-12-I-CB}_{11}\text{Me}_{10}]^-$  ( $\text{X} = \text{H}, \text{CH}_3, \text{C}_2\text{H}_5, \text{C}_3\text{H}_7, \text{C}_4\text{H}_9, \text{C}_6\text{H}_{13}$ , and  $\text{COOCH}_3$ ) in liquid  $\text{SO}_2$  at  $-65^\circ\text{C}$  showed two one-electron anodic oxidation peaks. The potentials of the first ( $E_{\text{pa}}^1$ ) and second ( $E_{\text{pa}}^2$ ) peak are summarized in Table 1. The  $E_{\text{pa}}^1$  values agree well with those reported earlier for a few of the anions.<sup>26–28</sup> Liquid  $\text{SO}_2$  dissolves all the carborane anion salts well and has a wide electrochemical window, permitting the observation of two oxidation processes, which acetonitrile does not. A Ag wire was used as a quasireference electrode, and ferrocene ( $\text{Fc}^{0/+}$ ) was used as an external reference. Figure 2 shows the CV curves at 0.2 V/s scan rate, with potentials referenced to the  $\text{Fc}^{0/+}$  couple. The first peak for all the anions is sharp but exhibits no sign of reversibility over the scan rates examined (0.08–5.0 V/s). Linear variation of the anodic peak current with concentration and with square root of scan rate

**Table 1.** Anodic Oxidation Potentials ( $E_{\text{pa}}^1$  and  $E_{\text{pa}}^2$ , V vs  $\text{Fc}^{0/+}$ ) of  $\text{Cs}^+[\text{1-X-12-I-Me}_{10}\text{-CB}_{11}]^-$  in Liquid  $\text{SO}_2$  Containing 0.1 M  $(n\text{-C}_4\text{H}_9)_4\text{N}^+\text{PF}_6^-$  at 0.2 V/s

anion	X	$E_{\text{pa}}^1$	$E_{\text{pa}}^2$
1	H	1.43	1.65
2	$\text{CH}_3$	1.39	1.59
3	$\text{C}_2\text{H}_5$	1.40	1.65
4	$\text{C}_3\text{H}_7$	1.41	1.72
5	$\text{C}_4\text{H}_9$	1.38	1.66
6	$\text{C}_6\text{H}_{13}$	1.39	1.64
7	$\text{COOCH}_3$	1.52	1.72

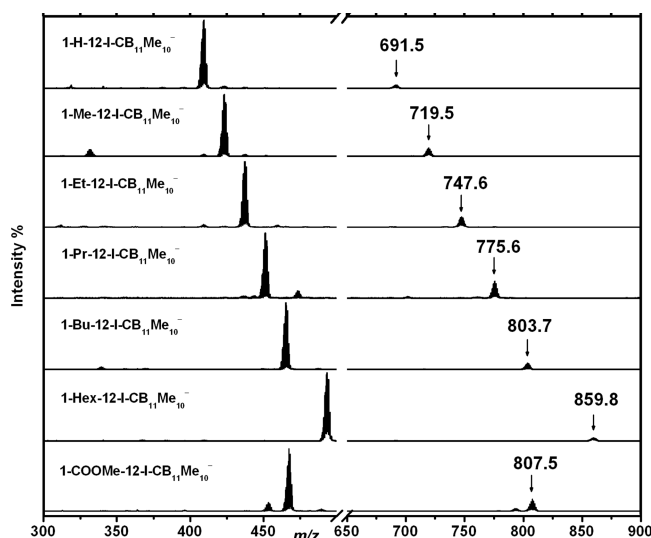


**Figure 2.** Cyclic voltammograms of carborane anions in liquid  $\text{SO}_2$  and 0.1 M  $(n\text{-C}_4\text{H}_9)_4\text{NPF}_6$  vs  $\text{Fc}/\text{Fc}^+$  at 0.2 V/s.

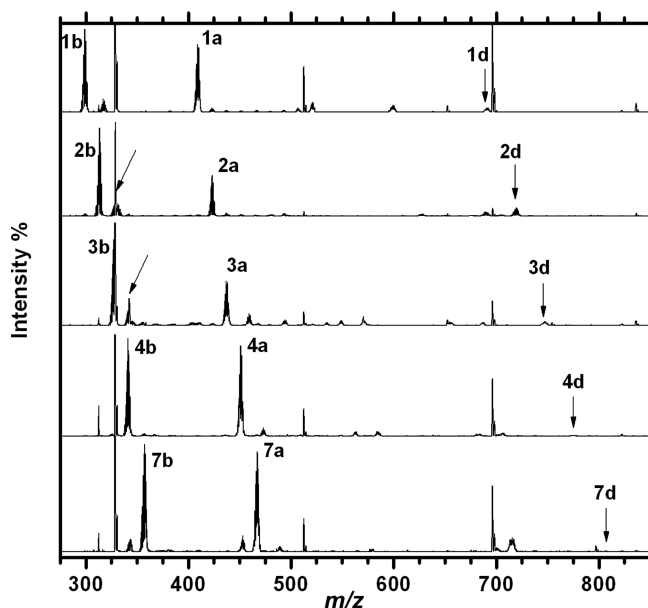
shows that the oxidation processes corresponding to the first peak are diffusion controlled. The second peaks generally have much smaller oxidation current heights than the first peaks, but unlike the first peaks, they are chemically reversible as clear hints of return peaks are apparent.

On average, the second peak is only 0.24 V above the first one, and this seems to be too small a difference to correspond to the removal of a second electron from the oxidized neutral radicals  $[\text{1-X-12-I-CB}_{11}\text{Me}_{10}]^\bullet$ . To identify the products of the first one-electron oxidation, suspected of being responsible for the second oxidation process, preparative electrolysis was carried out with all the anions in a two-compartment cell at a potential slightly higher than that of the first peak (Table 1) under the experimental conditions of the CV measurements in liquid  $\text{SO}_2$ , using 0.08 M  $(\text{CH}_3)_4\text{N}^+\text{PF}_6^-$  as the supporting electrolyte. The solutions were stirred magnetically, and CVs were checked occasionally to monitor any shift in potentials. After evaporation of liquid  $\text{SO}_2$ , the electrolyzed products were extracted into methanol for mass spectrometric analysis. Methanol is a suitable choice of extraction solvent because it dissolves all the carborane anion salts well but the supporting electrolyte only poorly.

The same preparative electrolysis experiments were also conducted in acetonitrile at room temperature, using 0.1 M  $\text{K}^+\text{PF}_6^-$  as the supporting electrolyte, and the electrolyzed products were analyzed directly by mass spectrometry. Mass spectral data of the electrolyzed products obtained in liquid  $\text{SO}_2$  and acetonitrile are collected in Figures 3 and 4, respectively.



**Figure 3.** Negative ion ESI<sup>−</sup> mass spectra of electrolyzed products from the carborane anions 1–7 ( $10^{-3}$  M) in liquid  $\text{SO}_2$  and 0.08 M  $(\text{CH}_3)_4\text{N}^+\text{PF}_6^-$ , extracted into methanol.



**Figure 4.** Negative ion ESI<sup>−</sup> mass spectra of electrolyzed products from the carborane anions 1–4 and 7 ( $10^{-3}$  M) in acetonitrile containing 0.1 M  $\text{K}^+\text{PF}_6^-$ .

Negative ion electrospray ionization (ESI<sup>−</sup>) mass spectra of the electrolysis products obtained from 1–7 in liquid  $\text{SO}_2$  show a major peak at  $m/z$  400–500 and another peak at  $m/z$  650–900 (Figure 3). The major peaks correspond to the remaining original parent carborate anions, and the peaks at higher mass fit expectations for the iodonium ylide anions  $[\{12-(1-X\text{-CB}_{11}\text{Me}_{10})\}_2\text{I}^+]$ . Additional minor peaks are also observed and correspond to methylated carborane anions with H or OH substituents, presumably located in position 12. Although we performed the preparative electrolysis under argon, the amounts of iodonium ylide products always remained small, and this is attributed to the presence of another electrolytic product, molecular iodine, which undergoes two-step one-electron oxidation at lower potentials than the carborate anions. The amount of  $[\{12-(1-X\text{-CB}_{11}\text{Me}_{10})\}_2\text{I}^+]$  produced was

increased when a little mercury was added to trap the iodine in the main electrolysis compartment. The percent height of the iodonium ylide product peak relative to the parent anion peak is listed in Table 2, but the detection sensitivities are unknown and the numbers provide only a qualitative indication of relative amounts.

**Table 2.** Mass Spectral Results from Preparative Electrolysis Products in Liquid  $\text{SO}_2$  and 0.08 M  $(\text{CH}_3)_4\text{N}^+\text{PF}_6^-$

anion	X	product $m/z^a$	rel product peak int <sup>b</sup>
1	H	691.5	5
2	Me	719.5	14
3	Et	747.6	14
4	Pr	775.6	26
5	Bu	803.7	9
6	Hex	859.8	6
7	COOMe	807.5	19

<sup>a</sup>For the most abundant  $^{11}\text{B}$  isotopologue. <sup>b</sup>Product peak intensity relative to the peak of the starting anion (%).

The electrochemical behavior was similar in acetonitrile. UV–vis absorption measurements on the electrolyzed solutions exhibited the absorption bands of molecular iodine (Figure S1 in Supporting Information). Preparative electrolysis of anions 1–4 and 7 was performed, and the small amount of water present acted as a nucleophilic trapping agent for the borenium ylides, presumably present as their acetonitrile adducts. In addition to the parent anion peak (1a, 2a, 3a, 4a, and 7a in Figure 4), the ESI<sup>−</sup> mass spectra of the anionic products showed an additional peak (1b, 2b, 3b, 4b, and 7b) attributed to 12-OH substituted carborane anions. Weak peaks of iodonium ylide anions (1d, 2d, and 3d) were also present. Other trapping agents were tried at 1.0 mM to 1.5 M concentrations (MeOH, benzene, toluene, pyridine, *o*-xylene, nitrobenzene, benzonitrile, acetonitrile, and LiF), but only weak trapping product peaks of 12-OMe substituted anions were observed (Figure 4, slanted lines for 2 and 3).

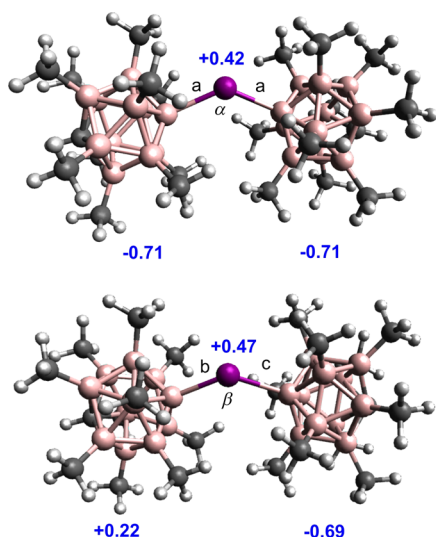
An alternative purely chemical partial conversion of 1 into the iodonium ylide  $[\{12-(1\text{-H-CB}_{11}\text{Me}_{10})\}_2\text{I}^+]$  was performed to provide an additional confirmation of its mode of formation and chemical structure. The reaction used was a treatment of 1 with  $[\text{Et}_3\text{Si-H-SiEt}_3]^+$  or  $\text{Et}_3\text{Si}^+$ ,<sup>29</sup> expected to abstract an iodide anion from position 12 to yield a borenium ylide, which should add to anion 1 to yield  $[\{12-(1\text{-H-CB}_{11}\text{Me}_{10})\}_2\text{I}^+]$ , similarly as proposed for the electrochemically generated species. The cation associated with 1 was first exchanged from  $\text{Cs}^+$  to  $\text{Ti}^+$  nearly quantitatively by exchange with  $\text{Ti}_2\text{SO}_4$ ; the product was converted in solution to the deep yellow  $\text{Ph}_3\text{C}^+$  salt with trityl bromide, and finally colorless  $[\text{Et}_3\text{Si-H-SiEt}_3]^+$  and/or  $\text{Et}_3\text{Si}^+$  were produced by treatment with various amounts of  $\text{Et}_3\text{SiH}$ .

These reactions were performed in dried THF and acetonitrile at several temperatures between  $-78$  and  $25$  °C. From ESI<sup>−</sup> mass spectral results, the iodide abstraction proceeded in both solvents, and  $[\{12-(1\text{-H-CB}_{11}\text{Me}_{10})\}_2\text{I}^+]$  was formed as the only new anionic product. Its elemental composition was confirmed by a high-resolution mass spectrum (Figure S2). The conversion was about 10%, and the concentrations of the iodonium ylide were similar to those observed in samples obtained after preparative electrolysis. In both cases, once formed,  $[\{12-(1\text{-H-CB}_{11}\text{Me}_{10})\}_2\text{I}^+]$  seemed to be stable indefinitely in solution. The addition reactions of the silyl cations and the borenium ylide to the solvent under



formation of neutral ylides such as  $[1\text{-H-}12\text{-(C}_4\text{H}_8\text{O}^+)\text{-CB}_{11}\text{Me}_{10}]^-$  are the likely competing processes, but the course of these reactions was not examined in any detail once our objective of establishing the formation of the  $[\{12\text{-(1-H-CB}_{11}\text{Me}_{10})\}_2\text{I}^+]$  ylide anion was achieved.

Since the ylide anion and its neutral ylide radical oxidation product  $[\{12\text{-(1-H-CB}_{11}\text{Me}_{10})\}_2\text{I}^+]$  are relatively unusual and to our knowledge are the first species known to contain two highly methylated bulky  $\text{CB}_{11}$  anions connected to a single atom, we calculated their electronic structure by the DFT method. The calculated structures and charge distributions are shown in Figure 5, and the optimized



**Figure 5.** DFT (RI-BP86/TZVP/COSMO) optimized geometries of the iodonium ylide in its anion (top) and radical (bottom) forms with the total NBO charges on the iodine atom and carborane cages indicated: bond lengths in Å,  $a = 2.36$ ,  $b = 2.31$ ,  $c = 2.41$ ; bond angles in deg,  $\alpha = 132.8^\circ$ ,  $\beta = 131.7^\circ$ .

geometries and energies are listed in the Supporting Information. The anion form has  $C_2$  symmetry with a charge of  $-0.71$  on each carborane cage ( $-0.53$  on the cage carbon C1 and  $+0.20$  on the antipodal boron B12). It is well described as containing a dicoordinated positively charged iodine atom carrying two carborane anion substituents. All bond lengths and valence angles are unexceptional except for the B–I–B valence angle, which is  $132.8^\circ$  instead of the usual  $\sim 97^\circ$ .<sup>30,31</sup>

In contrast, the calculated geometry of the ylide radical is unsymmetrical, with one of the carborane cages best described as a radical (total cage charge  $+0.22$ , with  $-0.67$  on C1 and  $-0.01$  on B12) and the other as an anion (total cage charge  $-0.69$ , with  $-0.54$  on C1 and  $+0.19$  on B12). The B–I–B valence angle is again unusually large ( $131.7^\circ$ ). The B–I bond pointing to the radical cage is shorter ( $2.31$  Å), and that pointing to the anion cage is longer ( $2.41$  Å) than the B–I bonds in the ylide anion ( $2.36$  Å).

The expected reversible oxidation potential of the iodonium ylide anion/radical redox couple was estimated from the adiabatic electron detachment energy of  $6.16$  eV calculated from the energy difference of the anion and the neutral radical of the iodonium ylide in acetone, whose dielectric properties resemble those of liquid  $\text{SO}_2$ . For  $[\text{CB}_{11}\text{Me}_{12}]^-$ , a similar calculation yielded an adiabatic electron detachment energy of  $5.83$  V, and its reversible anodic oxidation potential against

$\text{Fc}^{0/+}$  is  $1.16$  V.<sup>26</sup> Using this anion as a standard and ignoring solvation energy differences, we expect the oxidation potential of the ylide anion to be roughly  $1.5$  V, and this can be compared with the observed value of  $1.65$  V (Table 1). Since the first oxidation step of the anion **1** is irreversible, it is difficult to compare it with any calculated absolute value.

## DISCUSSION

In view of the earlier observations,<sup>26–28</sup> an irreversible one-electron first oxidation peak in **1–7** was expected. The processes responsible for the irreversibility are very fast since there is no reverse peak even at  $5.0$  V/s scan rate. The weakly reversible second redox couple  $\sim 0.24$  V above the first anodic peak is, however, unusual, although not entirely unprecedented.<sup>32–34</sup> A similar CV pattern was also reported<sup>35</sup> previously in acetonitrile for two dianions containing two permethylated carborane cages connected by a doubly or triply bonded two-carbon unit. It thus appeared possible that the second oxidation peak could be due to a structure that contains two carborane anion cages and is formed in the irreversible reactions that take place after one-electron oxidation.

A homolytic dissociation of the B–I bond in the  $[1\text{-X-}12\text{-I-CB}_{11}\text{Me}_{10}]^\bullet$  radical initially formed at the electrode is suggested by the observed formation of elemental iodine. The alternative, a heterolytic dissociation to produce an iodide anion that would be subsequently rapidly oxidized at the potentials used, is unlikely, as it would require the formation of a carborane cation. However, a most likely scenario for the detailed nature of the loss of an iodine atom in liquid  $\text{SO}_2$  is suggested by the well-established<sup>7,22</sup> methyl radical donor character of the parent  $[\text{CB}_{11}\text{Me}_{12}]^\bullet$ . In analogy to the transfer of  $\text{Me}^\bullet$  to a Si–Si or a C=C bond, it is tempting to propose that  $\text{I}^\bullet$  can be similarly transferred to  $\text{SO}_2$  to form  $\text{ISO}_2^\bullet$ , a weakly bound adduct in which the sulfur atom would be half on its way from tetravalency to hexavalency, and which disproportionates into  $\text{SO}_2$  and  $\text{I}_2$ . This would then provide an example of an electrochemical oxidation for which  $\text{SO}_2$  is not an ideally inert solvent and calls for further investigation. Whether the unpaired spin in the initially produced neutral iodinated  $\text{CB}_{11}$  radical resides mostly in the  $\text{CB}_{11}$  cage or mostly on the iodine atom undoubtedly depends on the number and nature of other substituents present, which could make the cage easier or harder to oxidize than an iodine lone pair, but the above analogy makes an iodine atom transfer appear feasible in either case.

A rapid departure of an iodine atom from the neutral radical  $[1\text{-X-}12\text{-I-CB}_{11}\text{Me}_{10}]^\bullet$  leaves behind a borenium ylide  $[12\text{-dehydro-1-X-CB}_{11}\text{Me}_{10}]$  with a naked vertex in position 12. Such species are known<sup>22</sup> and are very strong Lewis acids; hence, an addition to any Lewis base present, even a weak one, would be anticipated. In acetonitrile or THF this would most likely be the solvent, but in liquid  $\text{SO}_2$  the strongest Lewis base available would be the lone pairs on the iodine substituent of another molecule of the starting anion. The addition would be expected to yield the iodonium ylide anion,  $[\{12\text{-(1-X-CB}_{11}\text{Me}_{10})\}_2\text{I}^+]$ . Indeed, the mass spectral analysis of the preparative electrolysis products in liquid  $\text{SO}_2$  (Figure 3) suggests that this is the main anionic trapping product formed. The use of trapping agents in acetonitrile is ineffective because they need to compete with the solvent, but very small peaks of the anionic ylide  $[\{12\text{-(1-X-CB}_{11}\text{Me}_{10})\}_2\text{I}^+]$  were seen; the observation of adducts with water, and to a small degree, with methanol, is reassuring (Figure 4).

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ESI—: capillary voltage, 2.8 kV; cone voltage, 50 V; source temperature, 100 °C; desolvation temperature, 200 °C; desolvation gas, N<sub>2</sub> (200 L h<sup>-1</sup>). Syringe pump flow was typically 5–10 μL min<sup>-1</sup>. UV–vis absorption spectra of ~10<sup>-4</sup> M carborane solutions were recorded in a quartz cell of 1.0 cm path length using a Shimadzu UV-1800 spectrophotometer at room temperature.

**Computations.** The geometries of the ylide anion [ $\{12-(1\text{-H-CB}_{11}\text{Me}_{10}^-)\}_2\text{I}^+$ ] and the ylide neutral radical [ $\{12-(1\text{-H-CB}_{11}\text{Me}_{10}^\bullet)\}_2\text{I}^+$ ] were optimized in the RI-DFT approximation<sup>40</sup> using the BP86 functional,<sup>41,42</sup> the TZVP basis set,<sup>43</sup> the conductor-like screening model (COSMO,<sup>44</sup> dielectric constant 20.7 for acetone solvent, whose dielectric properties resemble those of liquid SO<sub>2</sub>), and the 6.2 version of the TURBOMOLE program package.<sup>45</sup> The atomic charge analysis used the natural bond orbital (NBO) method.<sup>46</sup>

**Synthesis.** All reactions were carried out under argon atmosphere with dry solvents, freshly distilled under anhydrous conditions, unless otherwise noted. Standard Schlenk and vacuum line techniques were employed for all manipulations with air or moisture sensitive compounds. The starting carboranes were prepared according to literature procedures.<sup>37,38</sup> NMR spectra were measured in acetone-*d*<sub>6</sub> and the following referencing was used: <sup>1</sup>H, residual signal of acetone-*d*<sub>6</sub> (δ = 2.05 ppm) as an internal standard; <sup>13</sup>C, signal of an acetone-*d*<sub>6</sub> deuteriomethyl group (δ = 29.80 ppm); <sup>11</sup>B, signal of BF<sub>3</sub>·Et<sub>2</sub>O as an external standard in a coaxial capillary (δ = 0.00 ppm). <sup>1</sup>H and <sup>13</sup>C spectra were recorded with Bruker Avance 400 and 500 spectrometers working at 400.1, 499.8 for <sup>1</sup>H NMR and 100.6 MHz, 125.7 MHz for <sup>13</sup>C NMR, respectively. <sup>11</sup>B NMR spectra were accumulated with Bruker Avance 400 and 500 spectrometers working at 128.3 and 160.4 MHz, respectively.

**Thallium (2-11)-Decamethyl-12-iodocarpa-closo-dodecaborate.** [Caution! Tl<sup>+</sup> salts are highly toxic and should be handled with caution!] The solution of Cs<sup>+</sup>[1-H-12-I-CB<sub>11</sub>Me<sub>10</sub><sup>-</sup>] (200 mg, 0.369 mmol) in ether (20 mL) was washed with 40% aqueous solution of Ti<sub>2</sub>SO<sub>4</sub> (3 × 10 mL). Ether was removed under reduced pressure, and the white solid residue was thoroughly dried using Kugelrohr distillation apparatus (5 h, 140 °C, 600 mTorr). The product was obtained as a white crystalline solid (218 mg, 0.355 mmol, 96%). <sup>1</sup>H NMR (400 MHz, acetone-*d*<sub>6</sub>): δ -0.22 (br s, 15H), -0.12 (br s, 15H), 1.38 (br s, 1H). <sup>11</sup>B NMR (128 MHz, acetone-*d*<sub>6</sub>): δ -12.17 (br s, 5B), -8.99 (br s, 5B), -5.43 (br s, 1B). Anal. Calcd for TlC<sub>13</sub>H<sub>36</sub>B<sub>11</sub>: C, 21.53; H, 5.09. Found: C, 21.89; H, 5.31.

**Generation of the Ylide Anion [ $\{12-(1\text{-H-CB}_{11}\text{Me}_{10}^-)\}_2\text{I}^+$ ].** A flame-dried Schlenk flask was charged with Tl<sup>+</sup>[1-H-12-I-CB<sub>11</sub>Me<sub>10</sub><sup>-</sup>] (50 mg, 0.081 mmol) and Ph<sub>3</sub>CBr (26 mg, 0.081 mmol). After three vacuum/argon cycles dry and degassed THF (3 mL) was added. The color of the reaction mixture turned yellowish brown immediately, and a white precipitate was formed. The reaction mixture was stirred at room temperature for an additional 30 min. Subsequently, solution of Et<sub>3</sub>SiH (13 μL, 0.081 mmol) in THF (500 μL) was added from a syringe during 5 min. The color of the reaction mixture slowly disappeared, and the resulting white suspension was stirred for an additional 60 min. Progress of the reaction was monitored by ESI–MS. When the intensity of the product peak stopped increasing, the solvent was evaporated, the solid residue was dissolved in methanol and filtered. An ESI–HRMS was taken (Figure S2): for C<sub>22</sub>H<sub>62</sub>B<sub>22</sub>I<sup>-</sup> calcd 695.59489, obsd 695.59380.

## ■ ASSOCIATED CONTENT

### ■ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.6b02128.

UV–vis and MS characteristics and computational results (PDF)

## ■ AUTHOR INFORMATION

### Corresponding Authors

\*E-mail: Josef.Michl@colorado.edu.

\*E-mail: jiri.ludvik@jh-inst.cas.cz.

### ORCID

Abdul Wahab: 0000-0003-0055-7004

Josef Michl: 0000-0002-4707-8230

### Present Address

<sup>||</sup>Department of Chemistry, Cotton College State University, Panbazar 781001, Guwahati, India.

### Notes

The authors declare no competing financial interest.

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