

Noncatalyzed Intramolecular B–N and B–O Cross-Coupling of “Inert” Carboranes Lead to the Formation of an Unusual Oxoborane, via Reversible Cluster C–B Bond Scission

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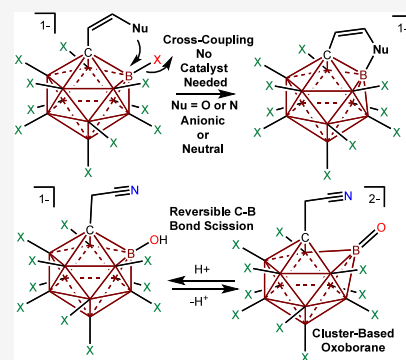
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ABSTRACT: Polyhalogenated *closo*-12-vertex carborane anions are thought to be inert species incapable of participating in direct B–X substitution reactions. Here, we show that this is not true and that such species can be easily coaxed into intramolecular cross-coupling cyclizations without the need for a catalyst. When cage C-tethered O and N-heteroallylic anions are generated, a variety of cyclized products can be formed in high yield under mild conditions. Additionally, we show that even C-tethered neutral nucleophiles, such as the pyridine moiety, undergo facile B–X substitution chemistry and these reactions are not dependent on the counteranion. Serendipitously, we also found that when these cyclizations are attempted with acetamide derivatives, an unprecedented cluster C–B bond scission reaction occurs, producing an unprecedented oxoborane stabilized by multicentered bonding. Amazingly this molecule can be protonated, leading to reformation of the C–B bond and cluster reorganization, and this process is reversible.



INTRODUCTION

Carboranes and related boron cluster compounds make up a diverse family of intriguing molecules that display fascinating multicenter bonding. These species are not only curiosities as they have found applications in medicine,^{1–3} electrochemical energy storage,^{4–10} catalyst design,^{11–13} polymeric materials,¹⁴ nuclear waste remediation, and as weakly coordinating anions.^{15–17} There is a dogma that exists for the most thermodynamically stable variants, such as *closo*-12 and 10-vertex clusters,¹⁸ that they are inert. In the literature, this term is used rather loosely and used as a basis to justify publication of various catalytic methods to functionalize these cages B–H or B–X vertices. But are carboranes truly inert? The reality is they undergo various reactions akin to electrophilic aromatic substitution and can also be easily functionalized at C with a base/electrophile sequence.^{19,20} Additionally, like all molecules, they will atomize at high enough temperatures. They are inert in the sense that the B–H bonds are not very hydridic at all as evidenced by the fact that they are compatible with any protic acid and when perhalogenated form the strongest now acids and methylating agents.^{21,22} At first glance, it is odd that the B–H and B–X bonds in these molecules are so unreactive. With respect to the B–H bonds, calculations show that these bonds are nearly nonpolar and thus have exceedingly weak hydridic characters.²³ This weak hydricity can also be explained qualitatively because of the high s-character in the sp-hybridized boron vertices, which in the simplest sense increases the boron's effective electronegativity. These bonds are also strong and very electrochemically stable (E_{ox} up to +6

V vs Li, and reductively stable),¹⁸ which retards radical-based functionalization strategies. With respect to B–X bonds, they are anomalously strong preventing straightforward S_N1 chemistry and S_N2 reactions do not occur because a backside attack through the cage atoms is not possible. Most cages appear to be susceptible to Pd-catalyzed cross-coupling when they are monohalogenated but not poly halogenated.²⁴ Another very common strategy to functionalize these cages is via a directed B–H activation followed by cross-coupling, basically analogous to the plethora of examples of organic reactions mediated by $Pd(OAc)_2$.^{25–32} Herein, we disclose that perhalogenated *closo*-carborane anions can be easily coaxed into intramolecular cross-coupling of B–X bonds with O and N nucleophiles without a catalyst, providing evidence that these clusters are more reactive than previously thought and suggesting that a variety of possible reactions may have been overlooked because of the false dogma of inertness surrounding such clusters. Additionally, this new reactivity pattern has unexpectedly afforded a truly unprecedented reversible C–B bond scission reaction that yields an unusual oxoborane^{33–40} stabilized via multicenter cluster bonding.

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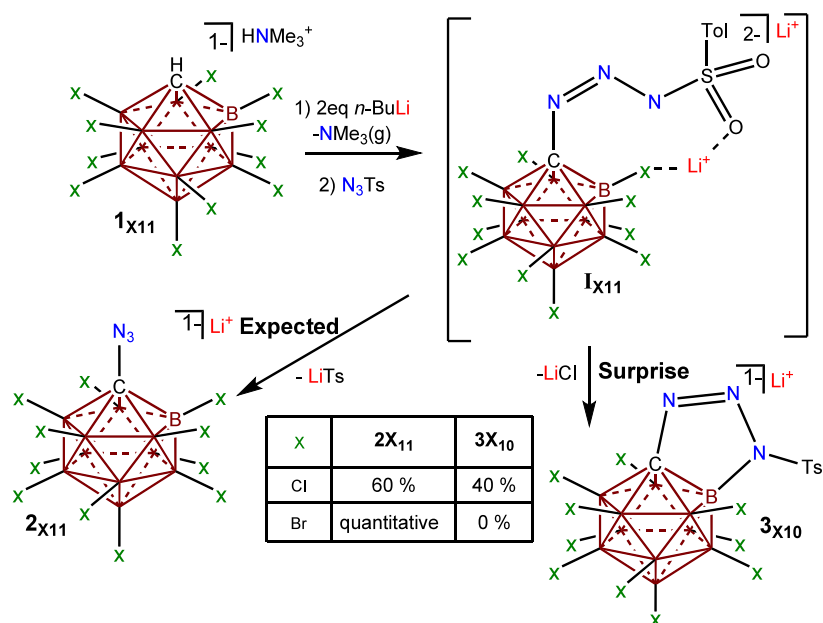


Figure 1. An observation of an unusual side reaction resulting in the formation of the B–Cl substitution at the cage of 1Cl₁₁. The same cyclization is not observed using brominated analogue 1Br₁₁. Unlabeled vertices = B.

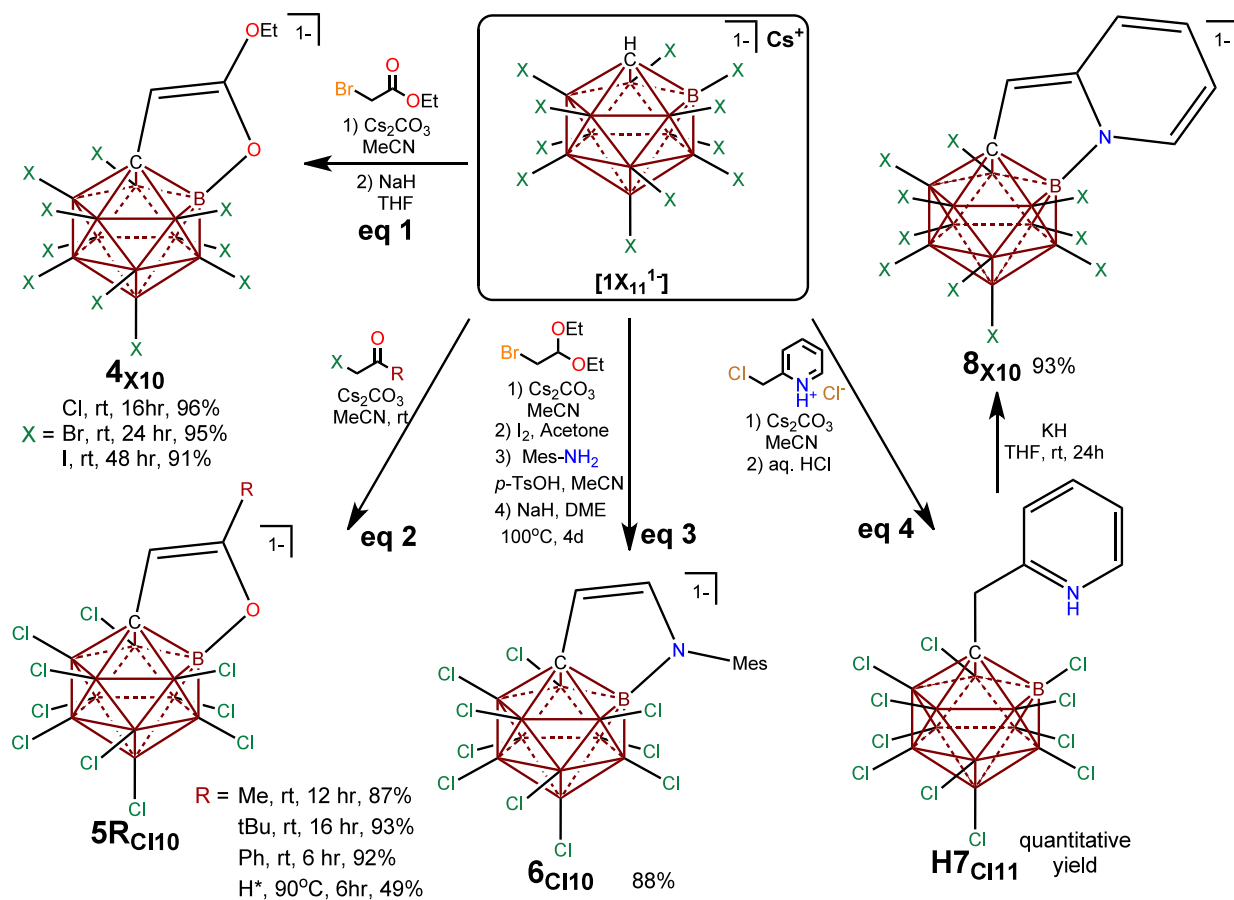


Figure 2. Intramolecular cross-coupling of “inert” carborane anions without a catalyst.

RESULTS AND DISCUSSION

In 2013, we reported the synthesis of a polychlorinated carboranyl azide from the $\text{HCB}_{11}\text{Cl}_{11}^{1-}$ anion **1Cl₁₁** with a base/tosylazide sequence (Figure 1). However, the reaction resulted in two products: the expected azide **2Cl₁₁** and the

unexpected heterocycle **3Cl₁₁**.⁴¹ Calculations suggested that this reaction occurs via a Li^+ -assisted cage $\text{S}_{\text{N}}1$ -like reaction via an intermediate species **IX₁₁**, although the B–X cleavage and B–N formation are concerted with concomitant elimination of LiCl. However, this is not the dominant pathway and the

intermediate \mathbf{I}_{Cl11} predominantly eliminates $\text{LiSO}_2\text{tolyl}$ giving the expected azide substitution product. The observed cross-coupling chemistry of \mathbf{I}_{Cl11} is particularly striking given the fact that the $\text{HCB}_{11}\text{Cl}_{11}^{1-}$ anion is supposed to be one of the least reactive molecules that exist. Subsequently, we showed that if alkyl or aryl azides are used in place of tosyl azide, the azide formation pathway can be blocked,⁴² giving unusual species that lead to the first isolable triazole radical anion.⁴³ It should be noted that in a separate report, we showed that the brominated analogue \mathbf{I}_{Br11} affords the corresponding azide $\mathbf{2}_{\text{Br11}}$ as the sole product with no trace of the cyclized product.⁴⁴ Additionally, alkyl or aryl azides are ineffective in this cyclization chemistry with \mathbf{I}_{Br11} . Most recently, and in collaboration with the Nelson group,²⁰ we established a facile and mild C–H functionalization protocol using Cs_2CO_3 to attach various electrophiles to the C-vertex of \mathbf{I}_{Cl11} . We also showed that Cs_2CO_3 is highly efficient at generating not only the nucleophilic dianion $[\text{2Cs}^+][\text{CB}_{11}\text{Cl}_{11}^{2-}]$ but also the brominated and iodinated $[\text{2Cs}^+][\text{CB}_{11}\text{X}_{11}^{2-}]$ species, which can be readily C-functionalized with various electrophiles. With this new convenient synthetic protocol developed, we sought to investigate what would happen if we accessed intermediates similar to \mathbf{I}_{X11} ? We hypothesized that if we accessed such intermediates, reactions may occur that would lead to a new valuable synthetic method to form carborane-fused heterocycles, via cross-coupling chemistry that does not require a catalyst.

We tested our hypothesis via the C-alkylative esterification of \mathbf{I}_{Cl11} with subsequent deprotonation with NaH to generate the corresponding ester enolate (Figure 2, eq 1). After stirring overnight and analyzing the ^{11}B NMR of the crude mixture, we observed a sole new product with the local C_{5v} symmetry of the cluster broken. The compound could be isolated in 96% yield, and all spectroscopic data (mass-spec, ^{13}C , ^1H , and ^{11}B NMR) (Figures S1–S5) are consistent with the predicted carborane-fused heterocycle $\mathbf{4}_{\text{Cl10}}$. We next attempted the same reaction with the perbrominated and iodinated clusters \mathbf{I}_{X11} (Figure 2, eq 1), and gratifyingly, the reactions afforded the corresponding cyclized compounds in excellent yields. To further corroborate the structures of $\mathbf{4}_{\text{X10}}$, we unambiguously demonstrated the 3D structure of the iodinated derivative $\mathbf{4}_{\text{I10}}$ via a single-crystal X-ray diffraction study (Table S1).

Encouraged by these initial results, we next sought to explore the reactivity of other covalently tethered heteroallylic anions. As higher yields were observed in the ester enolate cyclizations with the chlorinated cage \mathbf{I}_{Cl11} , we used this compound as a probe to attempt one-pot alkylative carbonylative enolate cyclizations of ketone derivatives (Figure 2, eq 2). These reactions work very well, affording the cyclized products $\mathbf{5R}_{\text{Cl10}}$ in excellent yields (Figure 2, eq 2), even with sterically demanding R-groups such as *t*-Bu. The reaction is also effective with the analogous aldehyde derivative, but heat is required and the yield drops significantly (Figure 2, eq 2), likely as a result of the more promiscuous reactivity of aldehyde enolates. We next formed the aldehyde and subsequently condensed it with mesityl amine to afford the corresponding imine. To our delight, the generation of the aza-enolate with NaH in DME at 100 °C produced the desired carborane-fused aza-heterocycle $\mathbf{6}_{\text{Cl10}}$ in 88% yield. Lastly, we formed the pyridyl derivative $\mathbf{7}_{\text{Cl11}}$, which upon deprotonation of its methylene linker with KH forms the corresponding azaallyl anion, which spontaneously cyclizes at room temperature to afford $\mathbf{8}_{\text{Cl10}}$ (Figure 2, eq 4).

Since the formation of five-membered rings seemed facile, we also attempted applying a similar strategy to forming six-membered rings. To test this hypothesis, we first synthesized ethylene-linked carboranyl *tert*-butyl esters via the reaction of $\text{Cs}[1\text{-Cl}_{11}]$ and $\text{Cs}[1\text{-I}_{11}]$ with *tert*-butyl acrylate in $\text{Cs}_2\text{CO}_3/\text{MeCN}$ media (Figure S67). The ensuing nucleophilic carborane dianions are indeed capable of 1,4 addition to α,β -unsaturated esters, and ester enolate oligomerizations are disfavored under these weakly basic conditions. These two substrates represent the two extremes of reactivity with Cl_{11} being the most acidic and least sterically encumbering and the opposite for I_{11} . Treatment of the HNMe_3^+ salts of these species with NaH does not yield heterocyclic species but instead cause E1 elimination with extrusion of the nucleophilic carborane dianion as evidenced by ^{11}B NMR spectroscopy. Productive cyclization is further hindered in these systems due to the absence of acidic protons in the solution, causing the persistence of generated ester enolates consuming *tert*-butyl acrylate presumably creating oligomeric acrylates seen in the breadth of peaks in the ^1H NMR spectrum. Interestingly, such carborane dianions have not been reported to act as leaving groups until this study.²⁰ While not exhaustive, these results discouraged further attempts to form six-membered rings in this initial report, but a comprehensive investigation of other substrates is planned in the near future.

Given the ease of the synthesis of the pyridyl substituted species $\mathbf{7}_{\text{Cl11}}$, we created the analogous brominated and iodinated derivatives to complete series $\mathbf{7}_{\text{X11}}$ (Figure 3). The rationale for this is that we wanted to probe whether an anionic nucleophile is really required to do such substitution chemistry. To our surprise, all of the compounds $\mathbf{7}_{\text{X11}}$ spontaneously cyclized at elevated temperature to afford neutral pyridyl cyclized product $\mathbf{9}_{\text{X10}}$ with the methylene linker intact. A single-crystal X-ray diffraction study of $\mathbf{9}_{\text{Cl10}}$

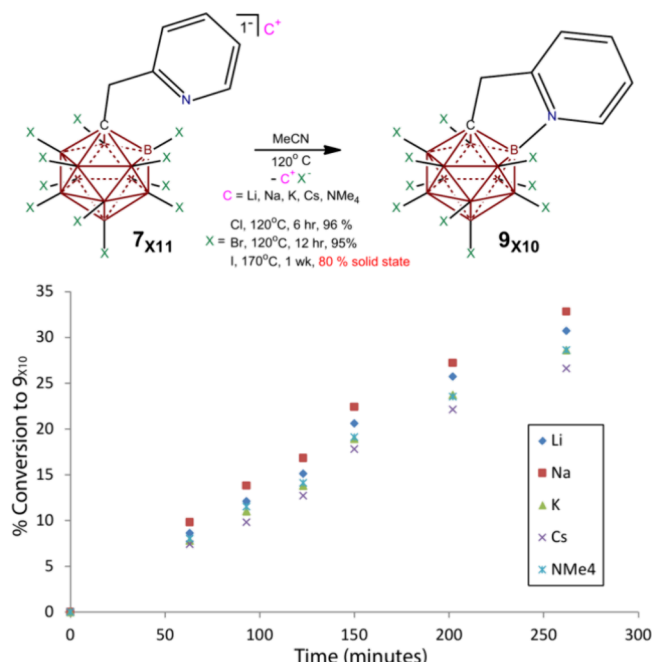


Figure 3. Coupling reactions with a neutral nucleophile (top). Graph showing that these reactions are not dependent on the nature of the counterion (bottom).

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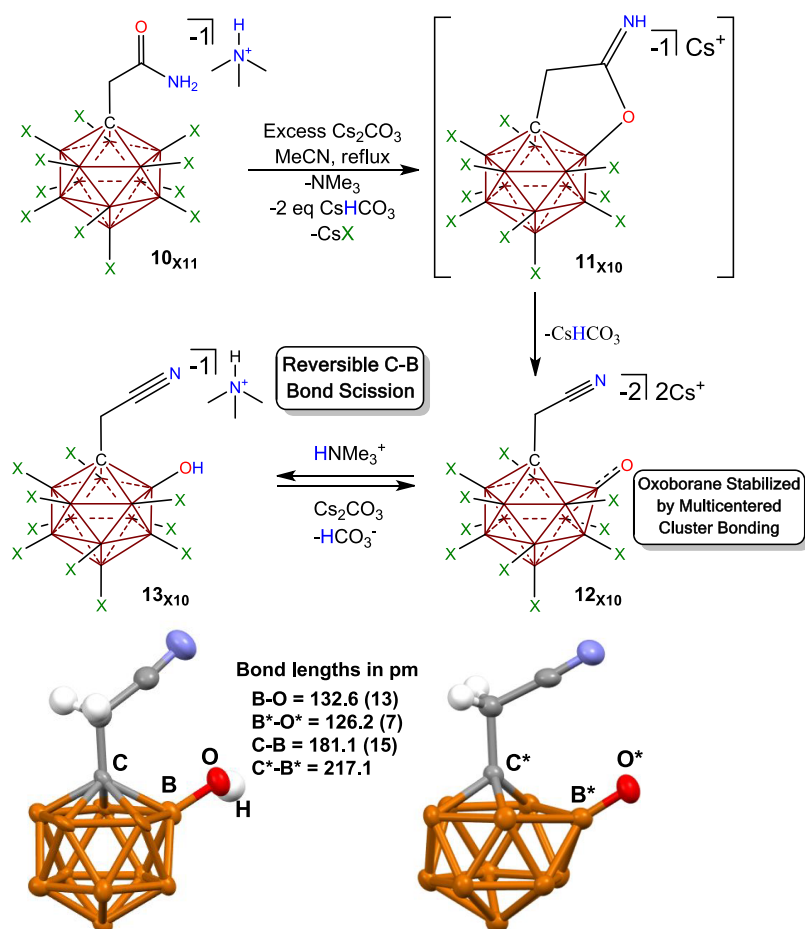


Figure 4. Intramolecular cross-coupling followed by spontaneous cage C–B bond rupture and formation of oxoborane 12×10 (top). Treating 12×10 with HNMe_3Cl protonates the oxygen of the B=O bond leading to B–OH, which reforms the C–B bond to afford 13×10 . Subsequent treatment of 13×10 with Cs_2CO_3 reforms 12×10 . Unlabeled cluster vertices in the scheme above are boron. Solid-state structures of $12\text{I}10$ and $13\text{I}10$, thermal ellipsoids drawn at the 50% probability level (bottom). Color code: C = gray, H = white, B = brown, N = blue, and O = red. I, Cs, and MeCN are omitted for clarity.

unambiguously confirms the connectivity in these molecules (Table S3). Here, we see a similar trend in that the reaction of the chlorinated cage affords the highest yield and fastest rate out of the halogenated derivatives $9_{\text{X}10}$ (Cl = 96%, Br = 95%), but the iodinated cage $9_{\text{I}10}$ resulted in an unclear reaction with mostly uncyclized starting material even after heating in the solution for 2 weeks at elevated temperatures. However, serendipitously, we found that heating the iodinated pyridine derivative in the solid state in the dry oven (170°C , open air, 1 week) afforded clean conversion (80% conversion) to the cyclized product $9_{\text{I}10}$. The reluctance of the iodinated derivative to cyclize is likely attributed to steric congestion in the molecule relative to its brominated and chlorinated homologues. Given that calculations showed that Li^+ was intimately involved in the mechanism of the reported azide cyclization in Figure 1, we sought to probe cation effects for these cross-coupling reactions. We prepared the Li^+ , Na^+ , K^+ , Cs^+ , and NMe_4^+ $7_{\text{Cl}11}$ and subjected them all to the optimized cyclization conditions and monitored the reactions over time. As can be seen in the bottom of Figure 3, there is no major deviation from the reaction rates of the various salts, and they all result in $9_{\text{Cl}11}$, proving there is no cation effect at play in these reactions. Additionally, refluxing the parent compound $1_{\text{Cl}11}$ in neat pyridine for 1 week shows no sign of substitution chemistry, indicating that the entropic advantage of the

intramolecular cyclization is required for such reactions to occur.

Something very interesting happens when carboranyl acetamide $10_{\text{X}11}$, which is made via our Cs_2CO_3 C–H functionalization protocol (Figures S53–S57), is subsequently heated with more cesium carbonate (Figure 4). We postulate that the expected ring closure occurs, but compound $11_{\text{X}10}$ is not stable under the reaction conditions. Amazingly the sole product observed is $12_{\text{X}10}$, which is a unique oxoborane that is stabilized by multicenter cluster bonding. The overall reaction is similar to amide dehydration to create a nitrile, but in this case, the oxygen is sequestered by a cage B atom.⁴⁰ Simultaneously, as the B=O double bond forms, the cage C–B bond of the carborane anion ruptures. The reaction is also effective using nonoxygen containing bases, confirming that the BO bond is not formed by transfer of an oxygen atom from Cs_2CO_3 , but multiple unidentified side products are observed. Reversible C–C bond cleavage in neutral *o*-carborane is well known to occur in the presence of reductants and has cleverly been applied by Menard and Peryshkov to create catch-and-release systems for UO_2 ^{45–47} and small-molecule activation,^{48–52} respectively. However, C–B bond scission of this sort has never been observed for any *closo*-carborane anions, but a couple of examples of irreversible C–B bond scission with *o*-carborane.^{53,54}

These observations as a whole demonstrate that the claim that CB_{11}^{1-} cages are inert is false dogma, as we show that both surfaces of the cages can be easily modified and the integrity of the cluster core is not absolute. Additionally, when the oxoboranes $\mathbf{12}_{\text{X10}}$ are treated with solutions of HNMe_3Cl , the $\text{B}=\text{O}$ double bond is protonated affording a $\text{B}-\text{OH}$ linkage and the cage simultaneously closes, reorganizing itself back into an icosahedral geometry to produce $\mathbf{13}_{\text{X10}}$. By deprotonation of the $\text{B}-\text{OH}$ in $\mathbf{13}_{\text{X10}}$ with Cs_2CO_3 , the process is reversible and the cage opened oxoboranes $\mathbf{12}_{\text{X10}}$ reform quantitatively. Such reversible cage $\text{C}-\text{B}$ bond scissions have never been observed. Curious about the reactivity of $\mathbf{12}_{\text{X10}}$ with Lewis acids in place of the Brønsted acid HNMe_3^+ , we subjected open cages $\mathbf{12}_{\text{X10}}$ to solutions of tris-(pentafluorophenyl)borane in MeCN. We see a reaction occur based on the changes in the ^{11}B NMR spectrum, and we observe an m/z signal (Figures S45–S47) corresponding to a Lewis base adduct but are unsure if it is simply a Lewis acid–base adduct or reversion to $\mathbf{11}_{\text{X10}}$ type species. All attempts to grow single crystals for X-ray diffraction have been unsuccessful.

As oxoboranes are of great interest to the main group of organometallic community for fundamental reasons, and many efforts have been made to stabilize such species and related triple-bonded variants,³³ we decided to delve deeper into the three-dimensional structures of $\mathbf{12}_{\text{X10}}$ and its corresponding closed-form $\mathbf{13}_{\text{X10}}$ via single-crystal X-ray diffraction studies. Fortunately, we were able to grow crystals of both the iodinated oxoborane $\mathbf{12}_{\text{I10}}(2\text{Cs}^+)$ and its closed-form $\mathbf{13}_{\text{I10}}(\text{HNMe}_3^+)$. For clarity, the counteranions in the crystal structures in Figure 4 have been omitted, but it should be noted that the two Cs^+ counteranions of $\mathbf{12}_{\text{I10}}(2\text{Cs}^+)$ are bound to the nitrile N and the O^- . Likewise, the ammonium cation of $\mathbf{13}_{\text{I10}}(\text{HNMe}_3^+)$ is hydrogen bonded to the nitrile functionality. A double-bond character is clearly demonstrated in $\mathbf{12}_{\text{I10}}(2\text{Cs}^+)$ ($\text{B}=\text{O}$: 126.2 (7) pm), and a significant $\text{B}-\text{O}$ bond elongation is observed in the closed-form $\mathbf{13}_{\text{I10}}(\text{HNMe}_3^+)$ ($\text{B}-\text{O}$: 132.6 (13) pm) consistent with the formation of a $\text{B}-\text{O}-\text{H}$ linkage. Additionally, and consistent with our structural assignments, a $\text{C}-\text{B}$ bond scission is observed for $\mathbf{12}_{\text{I10}}(2\text{Cs}^+)$ ($\text{C}-\text{B}$: 217.1 pm) and a $\text{C}-\text{B}$ bond formation is indicated by the shortened distance between C and B for $\mathbf{13}_{\text{I10}}(\text{HNMe}_3^+)$ ($\text{C}-\text{B}$: 181.1 (15) pm).

To further probe the nature of these unusual $\text{B}-\text{O}$ linkages, we performed infrared spectroscopy in the series of oxoboranes $\mathbf{12}_{\text{X10}}$ and hydroxyboranes $\mathbf{13}_{\text{X10}}$. For context, the few examples of formally triple-bonded species isolated by Braunshweig and Ingleson contain BO stretching frequencies in the range of 1793–1853 cm^{-1} ,^{37,39} while variants with double-bond characters have stretching frequencies that fall in the range of 1462–1667 cm^{-1} .^{38,40,55–57} BO stretching frequencies for chlorinated, brominated, and iodinated $\mathbf{12}_{\text{X10}}$ series are 1501 (Figure S63), 1503 (Figure S79), and 1512 cm^{-1} (Figure S92), respectively, determined by comparative analysis to $\mathbf{13}_{\text{X10}}$ series, which supports our assignment of a BO double bond.

To gain a deeper understanding of this unusual bonding situation, we performed a full molecular orbital analysis of both the open-form $\mathbf{12}_{\text{Cl10}}$ (Figure 5, right) and the closed-form $\mathbf{13}_{\text{Cl10}}$ (Figure 5, left) (functional: M06-2x-D3; basis set: Def2-tzvpd; acetonitrile PBF implicit solvent) (Figures S132–135). For $\mathbf{13}_{\text{Cl10}}$, oxygen p-orbital contributions are split between 4 MOs (HOMO, HOMO-1, HOMO-2, and HOMO-

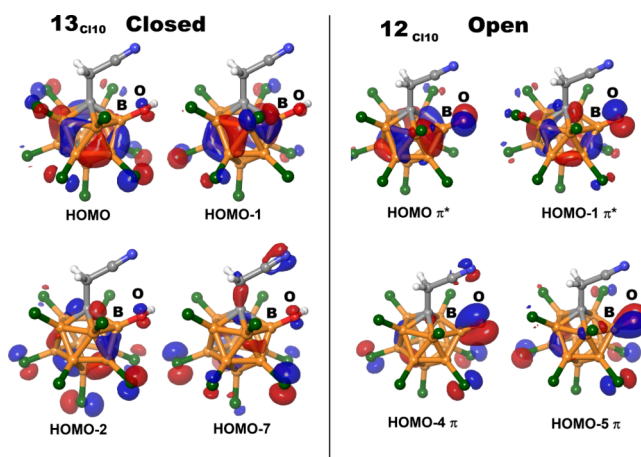


Figure 5. Calculated molecular orbitals of interest for $\mathbf{13}_{\text{Cl10}}$ (left) and $\mathbf{12}_{\text{Cl10}}$ (right). Functional: M06-2x-D3; basis set: Def2-tzvpd; acetonitrile PBF implicit solvent.

7). As depicted in Figure 5, the electrons on the oxygen atoms do not mix at all with the cluster-based orbitals, indicating there is no π -donation into the cage and thus no double-bond character. In contrast, the oxygen p-orbitals of the open-form $\mathbf{12}_{\text{Cl10}}$ are clearly engaged in π -bonding. The HOMO and HOMO-1 both correspond to a doubly occupied $\text{BO } \pi^*$ antibonding orbital. As expected, as we descend deeper into the energetically buried MOs, we find that the HOMO-4 and HOMO-5 both display clear $\text{BO } \pi$ -bonds and a larger probability density on the oxygen side of these lopsided MOs. This bonding situation is reminiscent of the MO diagram for O_2 in that although there are two π -bonds in O_2 , the net bonding is reduced by partial occupation of the O_2 π^* orbitals, reducing the overall bond order. Overall, these calculations are consistent with our assignment of the BO as a double bond.

CONCLUSIONS

The manuscript clearly demonstrated that the legendary inertness of polyhalogenated carborane anions is false if taken out of context. More accurately, these species should be considered to be compatible with all known electrophiles but not immune to nucleophilic attack at $\text{B}-\text{X}$ bonds without a transition metal-based catalyst. Furthermore, by observation of the reversible cluster $\text{C}-\text{B}$ bond cleavage reaction, we demonstrate that the integrity of the cluster core of CB_{11}^{1-} anions can be perturbed and these multicentered architectures are more pliable than once thought. Equally important are the novel methods described in this work, which open up a new paradigm for possible cluster functionalization strategies. Lastly, the facile and reversible formation of the unusual oxoboranes $\mathbf{12}_{\text{X10}}$ opens up new avenues to explore pH-responsive materials and other novel cluster perturbation reactions. We are currently investigating these new directions and working on trying to understand the mechanism of these reactions, which might be related to the so-called $\text{S}_{\text{N}}2$ with retention of configuration pathway.⁵⁸ Lastly, we are also attempting to use this cluster strategy to isolate other reactive intermediates of interest.

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/jacs.5c01106>.

Synthesis and characterization of title compounds and their precursors, kinetic experiments for the conversion of 7_{X11} to 9_{X10} , computational analysis, single-crystal X-ray crystal solution, refinement (PDF)

Accession Codes

Deposition Numbers **2418069–2418072** contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via the joint Cambridge Crystallographic Data Centre (CCDC) and Fachinformationszentrum Karlsruhe [Access Structures service](#).

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Notes

The authors declare no competing financial interest.

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