

Chemistry of the three-dimensionally aromatic CB_{11} cage*

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Abstract: After a brief introduction to the electronic structure of the three-dimensionally aromatic icosahedral *closo*-monocarbododecaborate anion $\text{CB}_{11}\text{H}_{12}^-$, some recent results for its permethylated version, $\text{CB}_{11}\text{Me}_{12}^-$ and three highly reactive electroneutral analogs are presented and discussed. These are the radical $\text{CB}_{11}\text{Me}_{12}^\bullet$, the boronium ylide $\text{CB}_{11}\text{Me}_{11}$ with a naked boron vertex, and the isomeric carbonium ylide with a naked carbon vertex. These ylides are probably better viewed as unusual types of singlet borylene and carbene, respectively.

Keywords: carboranes; carborate anions; reactive intermediates; aromatic substitution; Grob fragmentation; molecular orbitals.

INTRODUCTION

Polyhedral cage boranes and heteroboranes do not possess a single dominant valence structure and are characterized by strong electron delocalization. They also satisfy most and possibly all other common criteria for aromaticity [1]. They are frequently referred to as three-dimensionally aromatic, and thus fit well within the scope of the International Symposium on Novel Aromatic Compounds (ISNA) conference series.

Even though they have been known for many decades, cage boranes and carboranes offer much novelty. Most carborane reaction mechanisms have never been investigated in the kind of detail that is taken for granted in their organic aromatic cousins, and many of their reaction intermediates have been characterized only poorly or not at all. The detailed investigation of reaction mechanisms and intermediates that occurred in organic chemistry a long time ago has only begun to take place in carborane chemistry in recent times, in the era of reliable quantum chemical calculations. Therefore, quantum theory plays a very different and much more predictive role than it played in the development of mechanistic concepts in organic chemistry in the heyday of Hückel theory. The feeling that surprises are to be found around every corner, and that the mysteries encountered can be solved efficiently with modern tools, including computations, makes the field of carborane chemistry attractive to me and others.

This curiosity-driven motivation is complemented by more pragmatic incentives. It has already been richly demonstrated that the remarkably weak nucleophilicity of halogenated carborane anions can be utilized to stabilize highly reactive cations, and more developments in this direction can surely be expected. This theme is developed in Prof. Reed's lecture at the ISNA-12 meeting and will not be addressed here. Furthermore, it seems quite probable that practical applications of carboranes are forthcoming, perhaps in the area of boron neutron capture therapy [2] or in the catalysis of radical polymer-

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ization of alkenes [3], and perhaps even in materials science. Once a motivation for a large-scale production of these materials is established, their presently considerable cost will diminish greatly, and one can anticipate a flowering of academic and industrial research in this presently still rather esoteric sub-discipline.

Presently, we shall deal with the icosahedral CB_{11} cage, the most common and probably the most stable of all monocarbaborane structures. Several laboratories have been contributing recently to the development of its chemistry, and a recent exhaustive review is available [4]. The following text provides a description of some of the salient new results recently obtained in my laboratory for the 12 or 11 times methylated CB_{11} cages **1–5**.

Extensive alkylation modifies the properties of the boron cluster in at least four important ways: (i) It makes it highly lipophilic and solubilizes it in nonpolar solvents. This is true even of ionic compounds, such as salts of the highly methylated derivatives of the parent anion $CB_{11}H_{12}^-$ (**1**), the most stable form of the cage. (ii) It introduces a high degree of steric protection that blocks many of the dimerization processes that take place in reactive intermediates derived from the unsubstituted parent, such as **1** itself. (iii) It strongly reduces the otherwise quite high oxidation potential of the anions, making the neutral radical **3** readily accessible from the anion **2**. (iv) It greatly diminishes the acidity of the proton attached at the carbon vertex and thus prevents the use of some synthetic steps that are useful in the parent species, such as **1**.

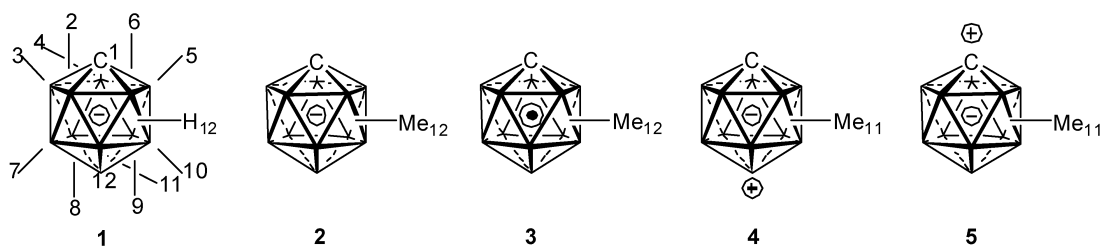
We start with a brief general introduction, which does not assume any knowledge of cage borane and carborane chemistry on the part of the reader. The subsequent sections address first, the properties and reactions of the very stable $CB_{11}Me_{12}^-$ anion (**2**) [5]. Then, three highly reactive electroneutral analogs of this stable structure are considered in sequence. The first one, the isolable but reactive radical $CB_{11}Me_{12}^\bullet$ (**3**) [6], is obtained from **2** by one-electron oxidation. The second and third electroneutral species are obtained from **2** by abstraction of a methide anion. The boronium ylide $CB_{11}Me_{11}$ (**4**) [7] with an empty radial orbital in position 12 results when the abstraction occurs at the boron vertex 12, antipodal to the cage carbon atom. This highly reactive reaction intermediate has been observed as a solid precipitate in alkane solvents, stable only at low temperatures [8]. A formal abstraction of a methide anion from the cage carbon yields the isomeric carbonium ylide $CB_{11}Me_{11}$ (**5**), with an empty radial orbital on the carbon vertex 1. This species has never been directly observed and has only been postulated as a reaction intermediate [9,10].

THE CB_{11} ICOSAHEDRON AND ITS MOLECULAR ORBITALS

The starting material for the chemistry of the CB_{11} cage are the salts of the parent anion **1**, which was first prepared by Knoth in 1967 [11], and whose first efficient synthesis was devised in the group of Plešek and Heřmánek in 1984 [12]. In my laboratory, we use a more recent synthesis [13] that yields the material in only two steps from bulk chemicals, albeit in an only 10–15 % overall yield when performed on a multigram scale.

The usual representation of the structure of the C_{5v} -symmetric CB_{11} cage is shown in formula **1**, along with the standard vertex numbering, which starts with the carbon vertex 1 and proceeds through 2–6 in the pentagonal belt of boron atoms proximate to the carbon. Then, it continues through 7–11 in the distal pentagon of borons (vertex 7 is a neighbor of vertices 2 and 3), and finally ends with the boron B(12), antipodal to the carbon. The usual representation adopted in **1** is somewhat confusing to an organic chemist in that the lines shown do not represent two-electron bonds, but merely indicate adjacency. A very large number of valence structures can be drawn for the anion **1**, and in the important ones there are two-electron three-center bonds in 13 of the 20 triangular faces of the icosahedron, while the remaining 7 are empty. This bonding scheme accounts for all those valence electrons on each vertex atom that are used for cluster bonding. It leaves one electron in a radial hybrid orbital on each vertex, and these are used to form 12 ordinary two-electron radial bonds to the substituents, H in **1** and CH_3 in **2**.

The $2n + 2$ count of cluster bonding electrons, where n is the number of vertices, is characteristic of closo carboranes (and closo boranes). Their adjacency pattern is deltahedral (i.e., it corresponds to a polyhedron consisting exclusively of triangles). There are additional classes of more reduced boranes and carboranes (nido, arachno, and hypho), with more complicated polyhedral structures, but we will have no opportunity to deal with them here. There also is a less reduced class, usually called hypercloso, with only $2n$ cluster electrons. The boronium (4) and carbonium (5) ylides belong to it in a formal sense, because they can be derived on paper by the deprotonation of CB₁₁H₁₂⁺ on a boron or a carbon, respectively, and subsequent replacement of hydrogens by methyls. We shall see below that it is more useful to think of 4 and 5 as members of the closo series in which a radial two-electron bond to a substituent at one of the vertices has been replaced with an empty radial orbital.



Because there is such a vast number of applicable valence structures in 1, they are not very useful for discussions of bonding, substituent effects, or reaction mechanisms, and arrow-pushing has not seen much use in reactions involving polyhedral borane cages. The molecular orbital (MO) description is more helpful, and we find Stone's simple model [14] based on tensorial harmonics especially instructive. The basis set that it uses (Fig. 1) organizes the four valence orbitals of each vertex atom into a set of two tangential p atomic orbitals and a set of two radial approximately sp² hybridized orbitals. It is analogous to the standard basis set used in planar conjugated systems, in which the four valence orbitals are organized into three approximately sp² and one pure p orbital.

It is useful to transform the MOs resulting from a standard calculation for a CB₁₁ cluster compound, which are normally initially expressed in the usual basis set of Cartesian atomic orbitals, into this natural cluster basis set. We have written the necessary computer code to accomplish this [15,16], using the natural atomic orbital concept of Weinhold [17]. The two tangential orbitals and the inward-pointing radial orbital on each of the n vertices combine into $n + 1$ bonding MOs that are occupied and bring about cluster bonding, and $2n - 1$ high-energy antibonding MOs that remain empty in the ground electronic state. The n outward-pointing radial orbitals, along with n substituent orbitals, are used to make the n radial bonds to substituents. In the equatorial positions 2–11, the axis of one of the tangential p orbitals (the "horizontal" orbital) is parallel to the planes of the two pentagonal boron belts and the axis of the other (the "vertical" orbital) lies in a plane perpendicular to the boron pentagon planes. In the axial positions 1 and 12, the axes of both tangential p orbitals are parallel to the boron pentagon planes.

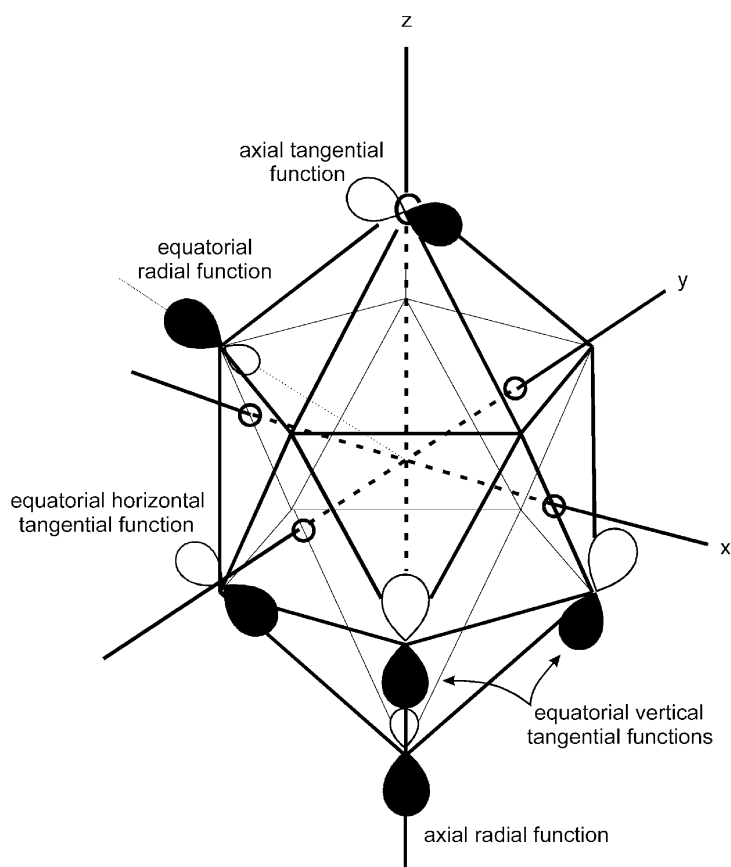


Fig. 1 Definition of the cluster basis functions in the CB_{11} icosahedron. Reproduced by permission from ref. [16].

Figure 2 shows the highest few cluster MOs of **1** occupied in the ground state, arranged by their energies, expressed in terms of the natural cluster basis set. The contributions provided to these orbitals by the substituents are small and are not shown. The orbitals used by the atoms of the cluster for attaching their substituents are low in energy and do not appear on the list. The highest occupied molecular orbital (HOMO) and the HOMO-1, both of which are doubly degenerate, jointly correlate with the quadruply degenerate HOMO of the parent $B_{12}H_{12}^{2-}$ borane cluster. This parentage is undoubtedly responsible for the fact they both need to be considered when one attempts to use frontier MO theory to understand the reactivity of **1**. It is likely that in derivatives of **1** carrying strong π donors in the axial positions, the order of these two degenerate sets of frontier orbitals is actually reversed.

Each component of the HOMO has zero amplitude on the axial positions C(1) and B(12) in the minimum basis set representation used, since it has three nodal planes sharing the fivefold symmetry axis. Therefore, it cannot interact with s, p, and d orbitals on substituents in these axial positions, but it would interact with a substituent f orbital. The largest HOMO amplitude is found on the horizontal tangential orbitals at the two equatorial boron belts, and the interaction with p orbitals on substituents that are locally of π symmetry and are located in the 10 equatorial positions is indeed strong. The HOMO has no s character on any of the vertices, and a substituent can interact with it only by π conjugation or hyperconjugation. In that sense, the HOMO is like the π orbitals of planar aromatic systems. The interaction is the strongest when the axis of the interacting substituent's p orbital is lined up parallel to the equatorial plane of the cluster. For instance, this result predicts that the interaction of the HOMO with the p-type lone pair on a hydroxyl group attached in one of the equatorial positions will be maxi-

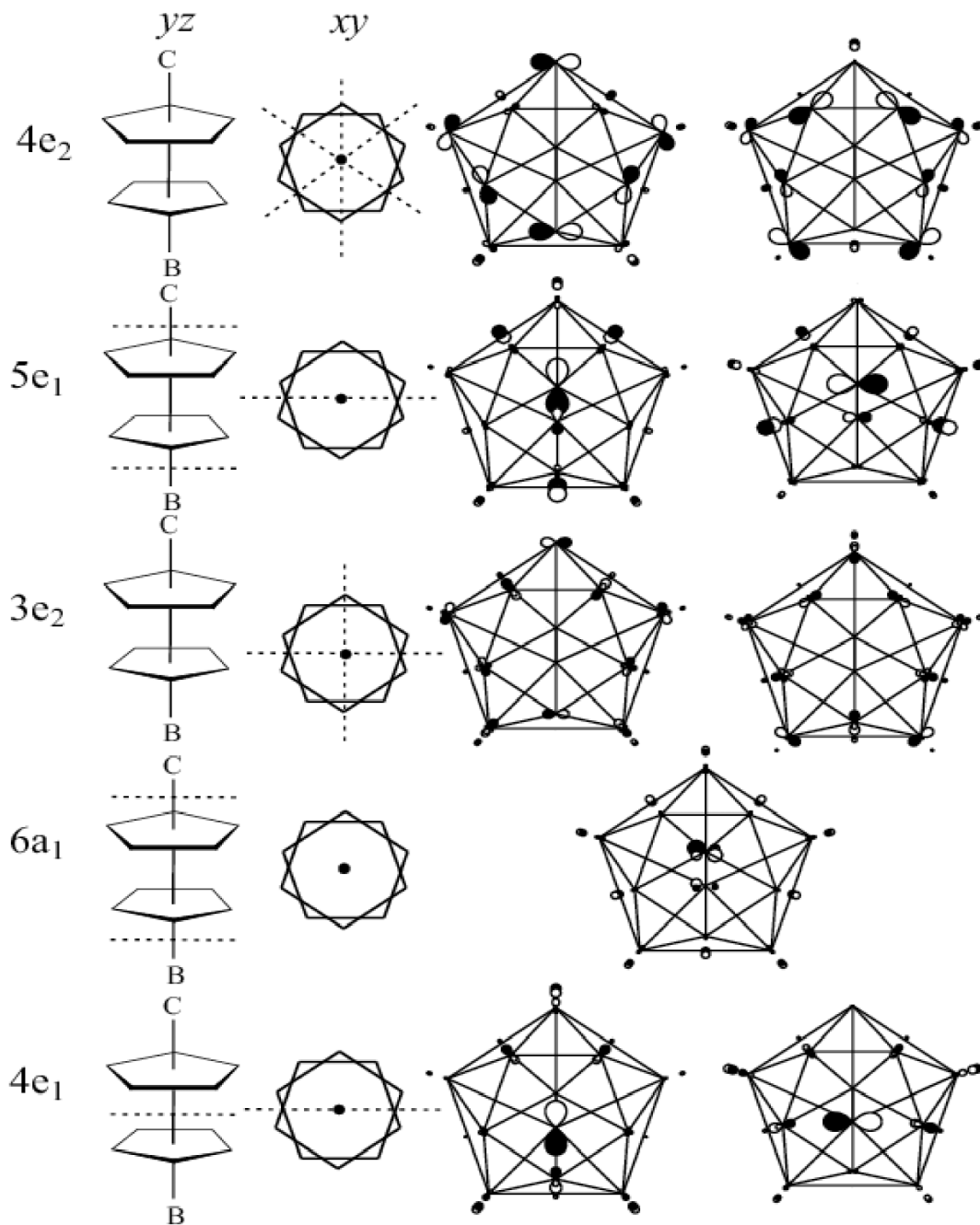


Fig. 2 Occupied frontier MOs of **1**. The left column gives the orbital label. The next two columns show the nearly horizontal and nearly vertical nodal surfaces of the MOs shown immediately to the right. Dashed lines represent the intersection of the nodal surfaces with the yz plane and xy plane (see Fig. 1 for axis labels). The next two columns are diagrams of the MOs, viewed from C(1) to B(12). The larger pentagon is formed by the boron atoms adjacent to the carbon vertex. Reproduced by permission from ref. [16].

mized when the BOH plane is perpendicular to the equatorial plane of the cluster, and minimized when they are parallel. Similarly, interaction with a planar amino group is predicted to be the strongest when the H_2NC plane is perpendicular to the equatorial plane. The expected effects of substituent rotation thus are somewhat reminiscent of those observed when the same substituents are located on a π system, such as benzene.

The two components of HOMO-1 are similar in that each also contains only tangential p orbitals and can also interact only with π -symmetry orbitals of substituents. However, the distribution the amplitudes of the HOMO-1 over the icosahedral cage is very different than was the case in the HOMO. Two of the nodal planes of each component of the HOMO-1 are horizontal, and only one is vertical and contains the fivefold symmetry axis. This MO can therefore interact with p orbitals on π -conjugating or hyperconjugating substituents located in the axial positions 1 and, especially, 12, where it has a very large amplitude. The HOMO-1 has only a quite small amplitude on the equatorial boron atoms. It is especially small on borons 2–6 in the proximate pentagonal belt, and somewhat larger on borons 7–11 in the distal pentagon. This amplitude is concentrated in the vertical tangential orbitals of the vertices. Conjugating or hyperconjugating substituents with high symmetry, such as ethynyl and methyl, thus have the ability to interact with both HOMO and HOMO-1 when they are located in positions 2–11, but only with the HOMO-1 when they are in positions 1 or 12. This is illustrated by Fig. 3, which shows the MO energies of all symmetrically methylated derivatives of **1**.

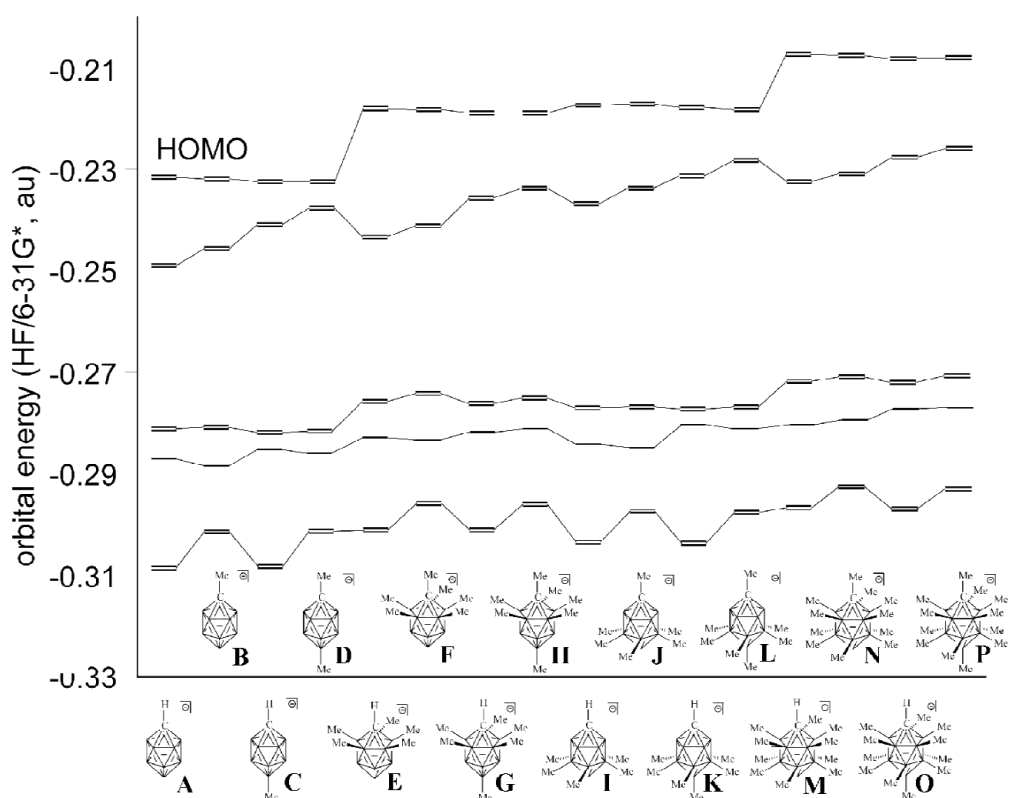


Fig. 3 Calculated (HF/6-31G*) energies of the nine topmost occupied MOs of the anion **1** and its 15 symmetrically methylated derivatives (the e_1 and e_2 orbitals are doubly degenerate or approximately so). Adapted by permission from ref. [16].

Four of the next five more bonding MOs are also primarily composed of tangential p orbitals on the vertices, and together with the HOMO and HOMO-1 pairs constitute an orbital set that is strongly reminiscent of the π -electron set of planar aromatics. The fifth MO has a large radial character in position 12. The π character of eight of the nine highest lying occupied MOs is probably partly responsible for the striking similarity of the chemistry of the two classes of compounds, which look so different at first sight. In both cases, the MOs that are weakly bound only interact with π orbitals of substituents.

Only the remaining four most strongly bonding cage MOs contain large contributions of the inward directed radial hybrids. They lie below the substituent-carrying MOs, composed of the outward-directed-hybrids and of substituent orbitals, but mix somewhat with them. The radial bond orbitals are normally strongly polarized toward the substituents, which are typically attached through atoms that are more electronegative than boron, such as hydrogen or carbon, not to mention nitrogen, oxygen, or the halogens. All these MOs can interact with the σ orbitals on the substituents and are thus analogous to the MOs of the σ framework of planar aromatics. The σ - π separation, enforced by overall symmetry of planar aromatics in a very obvious manner, is only approximate in cage boranes and carboranes, where it results from more subtle local symmetry, but it is still strongly reflected in their properties.

THE CB₁₁Me₁₂⁻ ANION (2)

The calculated charge distribution in the anions **1** and **2** (natural atomic charges) is shown in Fig. 4. Not surprisingly, most of the negative charge in the cage (0.71 in **1** and 0.55 in **2**) resides on the most electronegative atom, the vertex carbon. The hydrogen attached to this carbon in **1** carries a large positive charge (0.31) and is significantly acidic, about as strongly as the CH₂ hydrogens in indene or fluorene (the pK_a value in DMSO is 21.8 [18]). Deprotonation followed by methylation with a reagent such as methyl iodide permits an easy introduction of a methyl group into position 1 in **1**. In **2**, this methyl group again carries considerable positive charge. As a result, in both **1** and **2**, the electrostatic potential just outside the cluster calculated for the vicinity of vertex 1 is quite high [7] and a positively charged counterion is not likely to be found in this region, in spite of the concentration of negative charge on the carbon atom on vertex 1 that is buried inside. Indeed, in crystal structures of the salts, the cation is never located near this vertex.

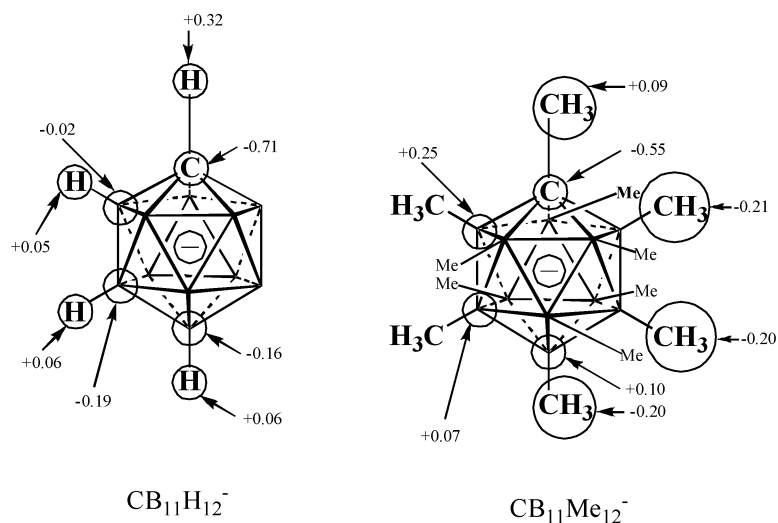


Fig. 4 Calculated (B3LYP/6-31+G(d)) natural charges in **1** (left) and **2** (right). Data from ref. [7].

A second region of significant negative charge is the hemisphere antipodal to the cage carbon, the positions 7–12. The charge resides primarily on the boron atoms in **1** and on the methyl groups in **2**. This suggests that the methyl substituents withdraw considerably more electron density from the cage by their σ inductive effect than hydrogens do, presumably primarily due to the somewhat higher electronegativity of carbon.

Just outside the antipodal hemisphere, the electrostatic potential is computed to be low [7], and this indeed is the usual location of the positive counterion in the crystal structures of the salts of **1** and **2**. At the same time, the occupied locally π -symmetry combinations of CH bond orbitals of the methyl substituents interact strongly with the HOMO and other high-lying occupied MOs of the cage by their hyperconjugative effect, and raise their energy. One might be tempted to call this a latent substituent π -donor effect, since this orbital interaction is of the occupied-occupied type and does not cause a net donation of electron density to the anionic cage. Such donation would result from a hyperconjugative interaction of the methyl CH bonds with the unoccupied orbitals of the cage. However, the latter type of donation appears to be weak due to the large energy separation of these orbitals in the anion, and perhaps also to the opposing effect of the interaction with the vacant orbitals of the methyl CH antibonds. The π donation from methyl substituents is strong in the electroneutral radical **3**, which is relatively easily produced from the anion **2** by chemical or electrochemical removal of one electron from the HOMO. Thus, while the methyl groups of **2** can be thought of as masked methide anions, those of **3** can be thought of as masked methyl radicals, and this is reflected in their chemistry.

The relatively electron-rich nature of the boron vertices in **1**, particularly in position 12 and a little less in positions 7–11, is reflected in their facile reaction with electrophilic reagents. Strong electrophiles are capable of replacing all boron-bound hydrogen atoms with substituents. Thus, methylation of the 1-methylated anion **6** with excess methyl triflate in the presence of a base [5], best done in sulfolane solution [16], smoothly introduces 11 additional methyl groups and yields **2** in an essentially quantitative yield (Fig. 5). The base is needed to neutralize the triflic acid byproduct, which would otherwise tend to protonate one of the methyl groups of **2** to produce methane, placing a triflyloxy substituent on the cage. Other anhydrous strong acids induce similar substitution, and the mechanism is believed to proceed via an intermediate ylide such as **4**. For instance, treatment of **2** with anhydrous HF produces a mixture of monofluoroundecamethylated anions, with fluorine mostly in position 12 [5]. This is in keeping with the view of the methyl substituent in **2** as a masked methide anion. We shall return to this subject when we deal with the chemistry of **4**. Otherwise, **2** has remarkable stability, and withstands treatment with strong aqueous acids and reflux with 20 % KOH in ethanol.

The permethylated anion **2** is very lipophilic, and its salts with organic [19] and inorganic [20] cations tend to be soluble in solvents of low polarity. A 30 % solution of the lithium salt of **2** in benzene conducts electricity [20], and its high Lewis acidity catalyzes pericyclic reactions [21] and radical polymerization of terminal alkenes [3]. Anions carrying longer alkyl groups that are now being examined are even more strongly lipophilic.

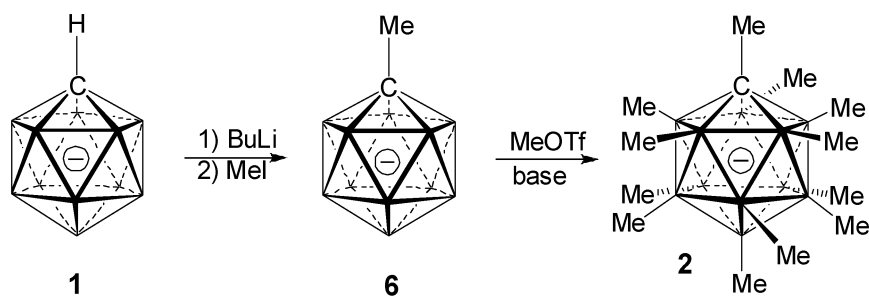


Fig. 5 Conversion of **1** into **2**.

Unlike the carbon vertex in **1**, those in highly methylated derivatives of **1** are not noticeably acidic. For instance, the (7-12)-hexamethyl and (2-12)-undecamethyl (**7**) derivatives of **1** cannot be deprotonated with *t*-butyllithium. This peculiar sensitivity of the acidity of vertex 1 to substituent effects is theoretically interesting and presently under examination. Its immediate practical consequence was that undecamethylated 1-substituted derivatives of **1** had to be prepared by undecamethylation of the 1-substituted anion **1**. Such exhaustive methylation is restricted to anions carrying substituents that survive prolonged treatment with methyl triflate, especially alkyls, but is impractical with many others, such as those containing multiple bonds or aromatic rings. Only after it was discovered that 1-iodo and 1-bromo derivatives of **1** [22] can be undecamethylated in good yield [23], and that the resulting 1-haloundecamethylated anions **8** and **9** undergo halogen-lithium exchange, did the 1-lithio-(2-12)-undecamethyl derivative **10** become available as a useful and versatile nucleophilic reaction intermediate for the introduction of the $-\text{C}(\text{BMe})_{11}$ substituent into organic molecules (Fig. 6) [24]. We shall see below that in some respects, this substituent behaves as an oversized and sterically very demanding proton capable of departing without assistance by a base, and this behavior could conceivably have some interesting applications in organic synthesis.

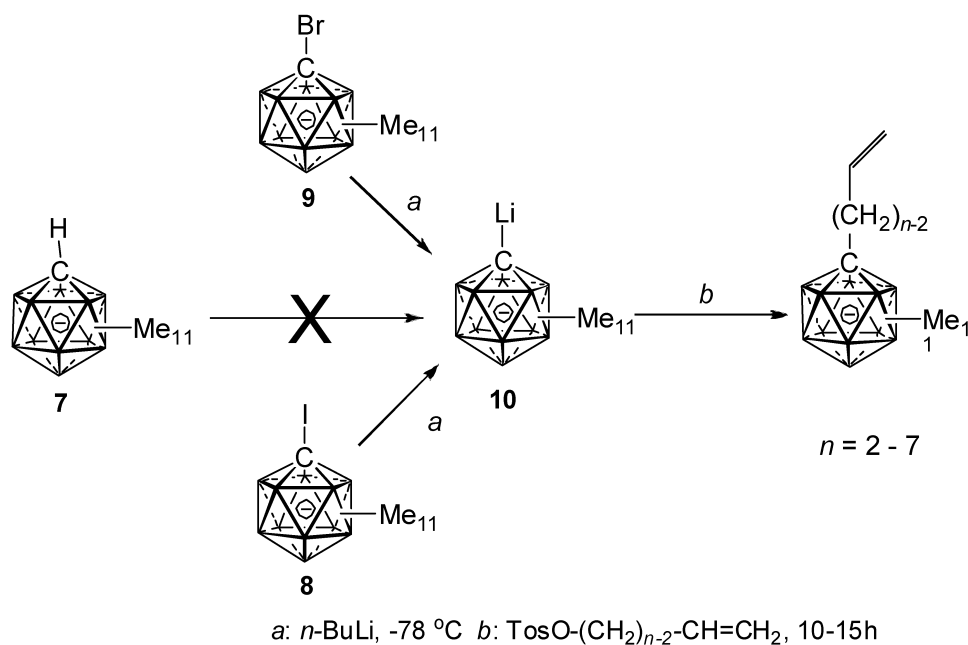


Fig. 6 Introduction of the $-\text{C}(\text{BMe})_{11}^-$ substituent into organic structures.

In addition to analogs of **2** in which position 1 carries a group other than a methyl, we have prepared and studied many others. In particular, in addition to **2**, all 14 partially methylated derivatives of **1** that preserve fivefold substitution symmetry (Fig. 3) are now known. They were prepared using various combinations of selective substitution, Pd-catalyzed coupling, and protecting/deprotecting reactions developed for the purpose (Fig. 7) [16].

Although **2** has many appealing properties, especially lipophilicity, we have seen that it is not stable to strong oxidizing agents and to very strong acids. This anion is therefore not suitable for use as a stable counterion for very aggressive cations. Oxidizing agents such as Pb(IV) perform a one-electron oxidation [6]. Reactive cations such as *t*-butyl abstract a methide anion, and less reactive cations such as trimethylgermyl, trimethylstannyl, and trimethylplumbyl form weak adducts to the negatively

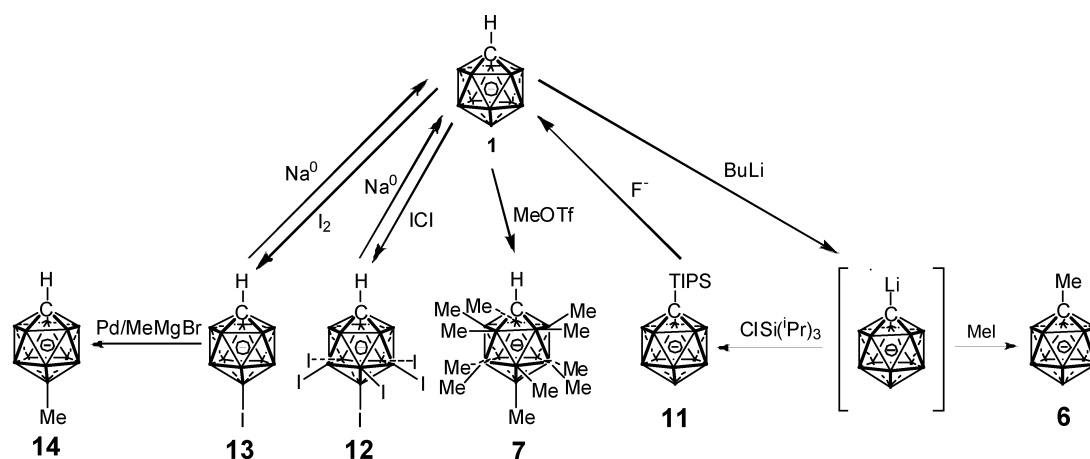


Fig. 7 Synthetic tools for regioselective derivatization of **1**. Adapted by permission from ref. [16].

charged methyl group in position 12 [7]. These actual or attempted (virtual) electrophilic substitution reactions on the methyl carbon will be discussed below.

In an attempt to prepare an anion that could coexist even with the most strongly oxidizing and Lewis acidic cations, we have replaced all 36 hydrogen atoms in **2** with fluorines. This yielded the anion $\text{CB}_{11}(\text{CF}_3)_{12}^-$ that indeed resisted all oxidizing agents, including O_2^+ , AsF_6^- , and was inert to concentrated triflic acid, anhydrous HF/BF_3 , concentrated H_2SO_4 at 150 °C, and 20 % KOH . Unfortunately, its salts were treacherously and unpredictably explosive. The main decomposition products were identified as soot and BF_3 . A calculation for the cesium salt predicted a heat of explosion per gram that was substantially higher than that of TNT [25]. We have refrained from pursuing the chemistry of this anion further and instead have looked for a less energy-rich analog. Since the instability is primarily due to the B–F bond energy being ~40 kcal/mol higher than the C–F bond energy, with steric crowding also adding considerable strain, it appeared likely that the replacement of a sufficient number of CF_3 groups by F substituents will solve the problem. Indeed, while a salt of the much less crowded anion with 11 CF_3 groups on boron atoms is still explosive, those of anions whose boron atoms carry 6 or fewer CF_3 groups, with the rest occupied with F substituents, no longer appear to be. The price paid for safety is considerable, as now the anions can be oxidized to the neutral radical with cationic “ NiF_3^+ ” in liquid HF at low temperature, whereas those with a larger number of CF_3 groups could not, and they will undoubtedly also associate with cationic Lewis acids more easily [26]. Nevertheless, they appear worth investigating.

THE $\text{CB}_{11}\text{Me}_{12}^\bullet$ RADICAL (3)

The anion **2** and many of its analogs undergo a one-electron oxidation to deeply colored neutral radicals. The most strongly hindered radicals are isolable. The crystal structure of **3**, which sublimates at 150 °C, has been determined. This radical is perfectly stable, for a few hours even in air [6]. It is very soluble in nonpolar solvents.

Electrochemical oxidation of **1** and all 15 of its C_{5v} symmetrically methylated derivatives in liquid SO_2 solvent is possible for all but three of the least substituted anions, and is fully reversible for five of them (Fig. 8) [16]. The oxidation potential depends on substitution as suggested by the HOMO energies in Fig. 3, and even the relatively weakly interacting methyl groups are capable of changing it by as much as a volt. The redox potentials of the reversibly oxidized anions correlate qualitatively with the HOMO energies and very well with higher-level quantum chemical calculations when solvent effects are included explicitly. The irreversible potentials also follow the calculated trends and lie within ~0.2 V

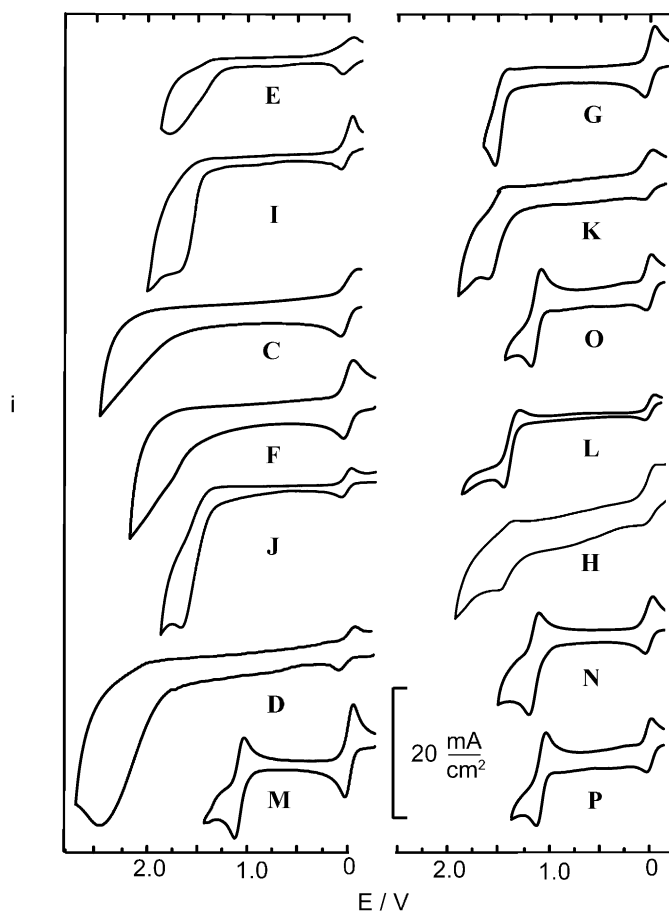


Fig. 8 Cyclic voltammograms (first scans) in liquid SO₂ at 0 °C and 0.5 V/s, against 3 mM Fc/Fc⁺ (10–20 mM cesium carborate, 0.1 M Bu₄NPF₆). See Fig. 3 for anion labels. Adapted by permission from ref. [16].

of the calculated reversible values. The potentials of reversible oxidation can also be fitted to empirical increments chosen to describe the effect of a methyl in each of the four nonequivalent positions of substitution in **1**, and the magnitudes of the increments can be understood qualitatively in terms of the HOMO amplitudes shown in Fig. 2: a single methyl group facilitates the reduction by 50, 70, 70, and 10 mV in positions 1, 2, 7, and 12, respectively. Only the first of these numbers is unexpectedly large, and this may be related to the Jahn–Teller distortion of the radical, discussed briefly next.

Since the HOMO of **1** is doubly degenerate, the radical obtained from it by electron detachment is subject to first-order Jahn–Teller distortion. Moreover, the first electronically excited state is remarkably low in energy, and second-order Jahn–Teller distortion is important as well. This results in additional crossings, and the final picture of the potential energy surface is exceedingly complicated, with five pairs of nonequivalent minima surrounding the principal intersection, and most likely with five subsidiary conical intersections also present [16]. It is very probable that the structure of the radicals is fluxional, and this is probably responsible for our failure to saturate the broad featureless electron paramagnetic resonance (EPR) signal of **3** in an unsuccessful attempt to determine its hyperfine coupling constants from the electron–nuclear double resonance (ENDOR) spectrum [6].

The radical **3** is stable but highly reactive. The simplest reaction is electron transfer from an oxidizable substrate such as an aromatic hydrocarbon or amine [6], tetrathiafulvalene [27], or an

organometallic compound with a metal–metal [6,7] or metal–carbon [7] bond. Some interesting oxidized products have been produced in this way, and the byproduct is the fairly inert anion **2**. In some cases, such as the oxidation of Sn–Sn or Ge–Ge bonds, two equivalents of **3** are needed and two metal cations result. As already mentioned above, in certain cases, the metal cations produced coexist happily with the anionic byproduct **2** in the form of a weak complex.

The chemistry of **3** has not yet been investigated in as much detail as it deserves, but it is already clear that it can undergo reactions other than simple electron transfer. We suspect that it is capable of acting as a methyl radical transfer agent, in keeping with its description above as a masked methyl radical. Thus, in its reaction with hexa-*t*-butyldisilane, **3** transfers a methyl group to one of the silicon atoms to form methyltri-*t*-butylsilane, which has been isolated, and presumably tri-*t*-butylsilyl radical, which subsequently abstracts a methyl radical from another molecule of **3**. After the loss of a methyl in either methyl radical transfer step, **3** is transformed into **4**, possibly mixed with its isomers if the methyl group is lost from a boron other than B(12). When the reaction is performed in pentane at temperatures below $-60\text{ }^{\circ}\text{C}$, **4** precipitates and can be examined (Fig. 9) [8].

Another way to account for the observed products, **4** and methyltri-*t*-butylsilane, would be to postulate the formation of two equivalents of the tri-*t*-butylsilyl cation, which then abstracts a methide substituent from the byproduct, **2**. The initial steps of this mechanism would be analogous to those observed for hexaalkylated digermene and distannane. However, it seems much less likely than the methyl radical transfer mechanism, since all attempts to trap the silyl cation failed. The chemistry of **4** will be taken up below.

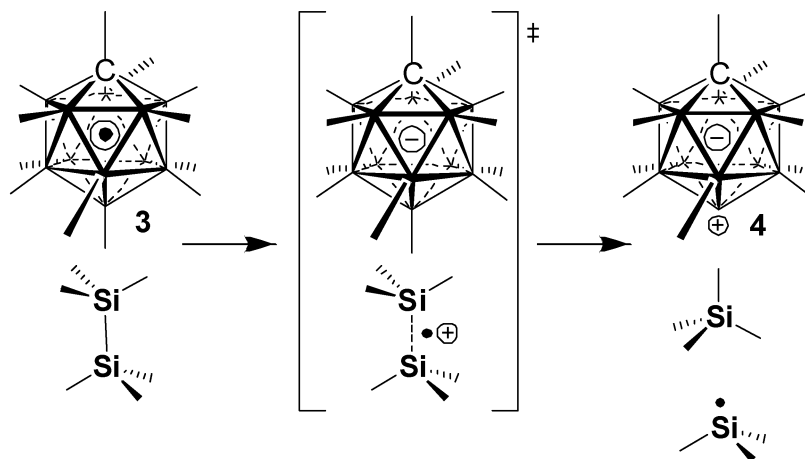


Fig. 9 Proposed methyl transfer from **3** to a disilane. Reproduced by permission from ref. [8].

The stability of **3** and several of its analogs, the wide tunability of their redox potential by choice of the methyl substitution pattern, and the possibility that these radicals might participate in conjugation in all three dimensions invite the thought that it would be interesting to use **3** as a basic building block for a three-dimensionally conducting polymer. As an initial step in the investigation of this possibility, we prepared a dimeric dianion and a dimeric biradical in which two units of **2** were connected through a two-carbon unit, either triply or doubly bonded (Fig. 10) [28]. It was reassuring to see that the first and the second oxidation potential of the dianion differ by about $1/4\text{ V}$, suggesting that there is good communication between the two cages and that the rate of hole hopping from one to the other may be sufficient to assure reasonable conductivity. The ability to tune the redox potential of the cage by substitution represents another attractive feature of this hypothetical polymer.

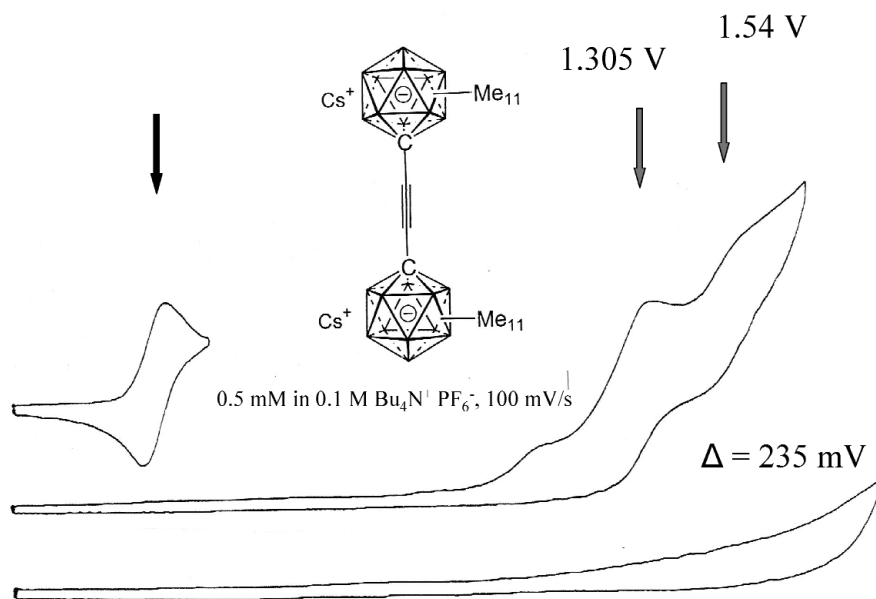


Fig. 10 Cyclic voltammetry in acetonitrile (SCE ref. el.). Top: ferrocene, bottom: blank solution. The small unmarked wave has been attributed to adsorption phenomena. Adapted by permission from ref. [28].

Finally, before leaving the subject of radicals, we recall that unlike the anion CB₁₁(CF₃)₁₂⁻, which resisted all attempts at chemical oxidation, the anion 1-H-(2-6)-F₅CB₁₁(CF₃)₆⁻ is oxidized to the neutral radical with cationic “NiF₃⁺” in liquid HF at low temperature. This reflects the strong π -electron withdrawing power of the CF₃ group, and contrasts it with the π -donor nature of the fluorine substituent. Both groups are strong σ withdrawers, but as we noted above, the HOMO of **1** is uniquely sensitive to the π effect.

The greenish blue EPR-active solution of the radical in perfluorohexane is stable in a Teflon container below about -60 °C, but at higher temperatures its color fades and the NMR spectrum of the intact original anion again becomes observable. It appears that the radical has performed a one-electron oxidation of the perfluorohexane solvent or perhaps of the Teflon walls, demonstrating its still quite formidable oxidizing power [26]. This observation needs to be followed up.

THE CB₁₁Me₁₁ BORONIUM YLIDE (**4**)

Structures with an empty radial orbital on one of the boron vertices, such as **4**, have been long postulated as intermediates in the so called electrophile-induced nucleophilic substitution reaction (EINS) characteristic of cage boranes [29], which are often performed with a proton as the electrophile. When the boron cage carries a delocalized negative charge, the overall species is electroneutral and can be viewed at least formally as an ylide. However, since the positive and negative charges can also be drawn on the same boron atom, there is some similarity to a singlet borylene, a hypovalent species analogous to a carbene.

Two simple ways in which **4** can be generated are (i) radical substitution (S_R2) on the methyl carbon in position 12 in the radical **3**, in which the methyl group behaves as a masked methyl radical, and (ii) electrophilic substitution (S_E2) on the same carbon of the anion **2**, in which the methyl group behaves as a masked methide anion.

A reaction of **3** with hexaalkyldisilanes that produces **4** has been discussed in the preceding section (Fig. 9). We believe that its mechanism is S_R2 substitution on the methyl carbon. Since the byprod-

ucts are not nucleophilic, the process is ideal for direct observation of the highly reactive boronium ylide **4**, but the low-temperature characterization of the material is not yet fully satisfactory [8].

We have already noted above that certain Lewis acids have the ability to associate with a methyl group on **2** as if they were attempting to perform an S_E2 substitution on the methyl carbon, in keeping with its nature as a masked methide anion. A combined extended X-ray absorption fine structure (EXAFS) and computational examination [7] of the salts of **2** with Me_3M^+ cations from Me_3Pb^+ to Me_3Ge^+ revealed a gradually increasing interaction between the metal cation and the 12-methyl group of the anion, reflected in a gradual decrease of the metal–carbon distance well below the sum of van der Waals radii, increase of the carbon–boron length, and pyramidalization at the metal atom. An attempt to generate *t*-butyl cations in the presence of **2** yielded neopentane and products expected from **4** in the presence of nucleophiles. This result was reproduced computationally; the transition state for the S_E2 substitution is approached gradually as the thermodynamic driving force for the reaction increases upon going up column 14 in the periodic table, until for Si and C there is no potential energy minimum for the reactant cation–anion combination, and the substitution takes place immediately. Although we consider it very likely that the Me_3Si^+ cation would abstract a methide anion from **2** just as the Me_3C^+ cation does, the former reaction has not yet been attempted.

The usual fate of **4** when formed as an intermediate in solution is combination with a nucleophile. This reaction can be utilized in synthesis. As an example, we quote the heating of a lithium salt of a derivative of **2** carrying a pinacol boronate substituent in position 1 (**15**) in solutions in aromatic solvents. At elevated temperatures, the Li^+ cation appears to perform an S_E2 substitution on one of the methyl groups of the anion, and the resulting boronium ylide, analogous to **4**, then reacts with the aromatic ring. The end result is a substitution of a methyl for an aryl substituent on the cage. When the aromatic ring carries a trimethylsilyl substituent, ipso substitution yields **16** (Fig. 11) [30]. The simplest mechanism that one could write for the reaction is electrophilic aromatic substitution by the empty orbital of the boronium ylide. However, the low regioselectivity of the reaction with monosubstituted benzenes, both on the benzene ring and on the carborane cage, makes us suspect that the mechanism of this aromatic substitution is unusual. This type of substitution has been investigated in far greater detail on the carboronium ylide **5**, to which we turn our attention next.

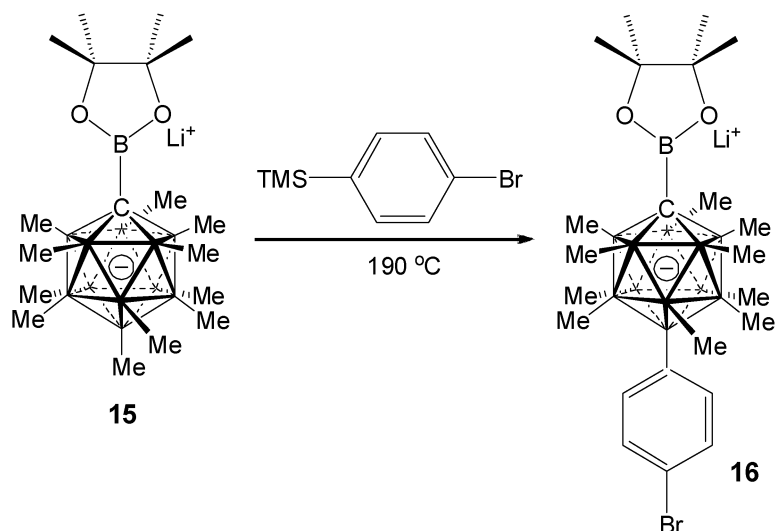


Fig. 11 Replacement of methyl by an aryl under Li^+ catalysis [30].

THE CB₁₁Me₁₁ CARBONIUM YLIDE (5)

This isomer of **4** carries an empty radial orbital on the carbon in position 1 instead of the boron in position 12. It is thus formally an ylide composed of a delocalized boron cage anion and a localized carbocation. In view of the electronegativity of carbon relative to boron, it is understandable that **5** is by far the least stable of the four isomeric ylides, with an empty orbital and formal positive charge in the nonequivalent positions 1, 2, 7, and 12 [7]. However, it is not clear that **5** in fact should be called an ylide, since the negative and positive charges are probably best drawn on the same carbon atom, in a structure reminiscent of a singlet carbene. After all, even in **2** half of the nominally delocalized negative charge actually resides on the carbon (Fig. 4), and in **5** it is likely to be still more.

The reaction that initially yielded **5** is quite interesting (Fig. 12) [9]. The positively charged C-methyl group in position 1 of **2** seems rather different from the negatively charged B-methyl groups on the other vertices, and it came as a surprise to us that an alkyl group can depart “spontaneously” from position 1 with the two electrons of the cage substituent C–C bond, much like the methyl group leaves from other positions when attacked by an electrophile. All that is required is the formation of an incipient carbenium center on the adjacent carbon in position β to the cage. This can be accomplished by the solvolytic departure of a leaving group in **17**, by protonation of a double bond, or by hydride abstraction. The process that ensues is like a Grob fragmentation: the cage provides additional negative charge to its carbon at vertex 1, and the two electrons of the C–C bond connecting vertex 1 to the substituent are used to convert the single bond between the departing carbon and its neighbor into a double bond. One of the nucleophiles present traps **5** and converts it to a stable product, such as **18**.

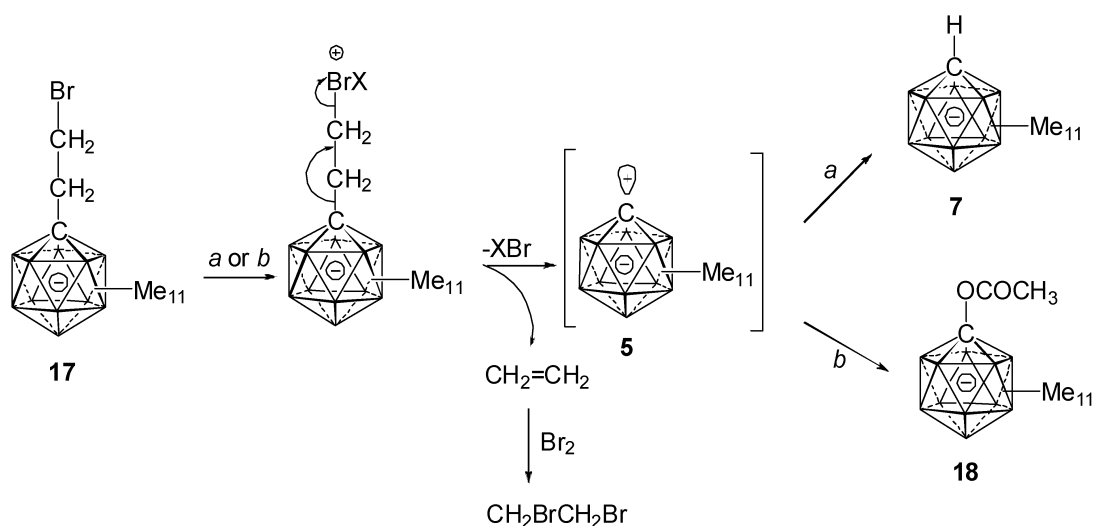


Fig. 12 Solvolytic generation of the carbonium ylide **5**. Reagents and conditions: (a) MeOTf, CaH₂, sulfolane, room temperature; (b) CH₃COOAg, sulfolane, 120 °C. Reproduced by permission from ref. [9].

The hydride transfer that has been observed to trigger the fragmentation reaction occurs intramolecularly, via a cyclic transition state with a five- or six-membered ring (Fig. 13) [9].

The kinetics of the solvolytic process are first order in the carborane substrate and zero order in the nucleophile, showing that **5** is a bona fide intermediate in the reaction. Thus, from the point of view of the organic part of the molecule, the –CB₁₁Me₁₁[–] substituent behaves as a proton or a trialkylsilyl substituent in position β to an incipient carbenium center. There are two obvious differences: it is huge (roughly the size of C₆₀), and its departure is spontaneous and does not need to be promoted by a base

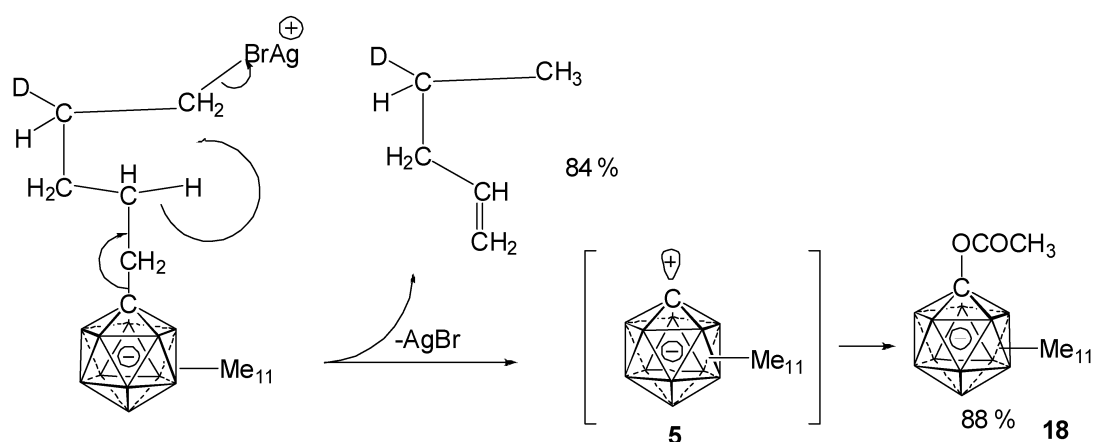
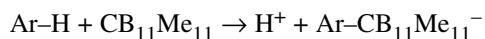


Fig. 13 Solvolysis in sulfolane, promoted with AgOCOCH₃. Reproduced by permission from ref. [9].

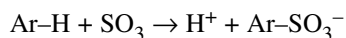
or a fluoride anion, since it is obviously promoted internally, by the negative charge of the cluster anion. These features might find use in organic synthesis.

Another pathway to **5** is provided by the solvolysis of a derivative of **2** that carries a good leaving group in position 1. We found that in the presence of a small amount of triflic acid in a fluorinated alcohol solvent, fluorinated alkoxy substituents are suitable [10]. In line with the existence of **5** as a distinct species, product ratios obtained from this source of **5** agree with those obtained from the Grob fragmentation.

The trapping of **5** with the usual lone-pair nucleophiles, such as azide, pyridine, acetate, alcohols, and formic acid is very efficient and gives the expected products [9,10]. In contrast, the equally efficient trapping with aromatics has some remarkable features [10]. It results in an aromatic substitution according to the equation



and is thus formally analogous to aromatic sulfonation



but the similarity ends there. None of the standard rules for substituent effects on the rates and regioselectivity in electrophilic aromatic substitution are followed. The observation that substitution with CB₁₁Me₁₁ never takes place in an ortho position to a substituent or to another ring can be readily attributed to steric hindrance by the five methyl groups in the proximate pentagon. Thus, in naphthalene and biphenylene substitution only occurs in position 2, in *o*-xylene it only occurs in position 4, and in *p*-xylene it does not occur at all. Judging by the relative yields of the product of substitution and solvent trapping, all these reactions occur at similar rates. Some relative rates were determined from competition experiments. The fact that biphenylene reacts about four times faster than naphthalene is not striking, but the observation that anisole and nitrobenzene react at similar rates makes it very clear that the reaction does not proceed by the expected electrophilic aromatic substitution mechanism. This is further confirmed by a curious lack of regioselectivity in monosubstituted benzenes. The meta/para ratios for nitrobenzene and dimethylaniline are the same within a factor of five, and they are similar in all other derivatives. Isotope effects on the reaction rate are small, and C₆H₆ reacts only about 10 % faster than C₆D₆. Effects on regioselectivity are larger, and in 1,3,5-trideuteriobenzene H is replaced about 1.4 times faster than D. These results exclude insertion into a CH bond in the rate-determining step and seem to be pointing in the direction of a radical mechanism. This might be rationalized by assuming that the Wheland complex is a biradical instead of a zwitterion. However, such a proposal would fail to

account for several key observations: The reaction fails to occur in *m*-xylene, acenaphthylene, pyrene, and pleiadiene, although it proceeds well in toluene and naphthalene.

Instead, we have proposed that the substitution does not occur by attack on a single vertex but by a 2 + 1 addition to an aromatic CC bond to give a norcaradiene-like intermediate that is subsequently deprotonated with a simultaneous loss of one of the newly formed bonds (path A in Fig. 14; path B is also possible but less compatible with the observed isotope effects) [10]. Neither position adjacent to the attacked bond is allowed to carry a substituent. Interestingly, an ipso trimethylsilyl substituent is allowed. This mechanism would predict higher reactivity for aromatic bonds with a higher bond order, and it thus automatically accounts for the higher reactivity of biphenylene compared with naphthalene, and for the lack of reactivity of pleiadiene, whose only sterically qualified bond has a very low π bond order.

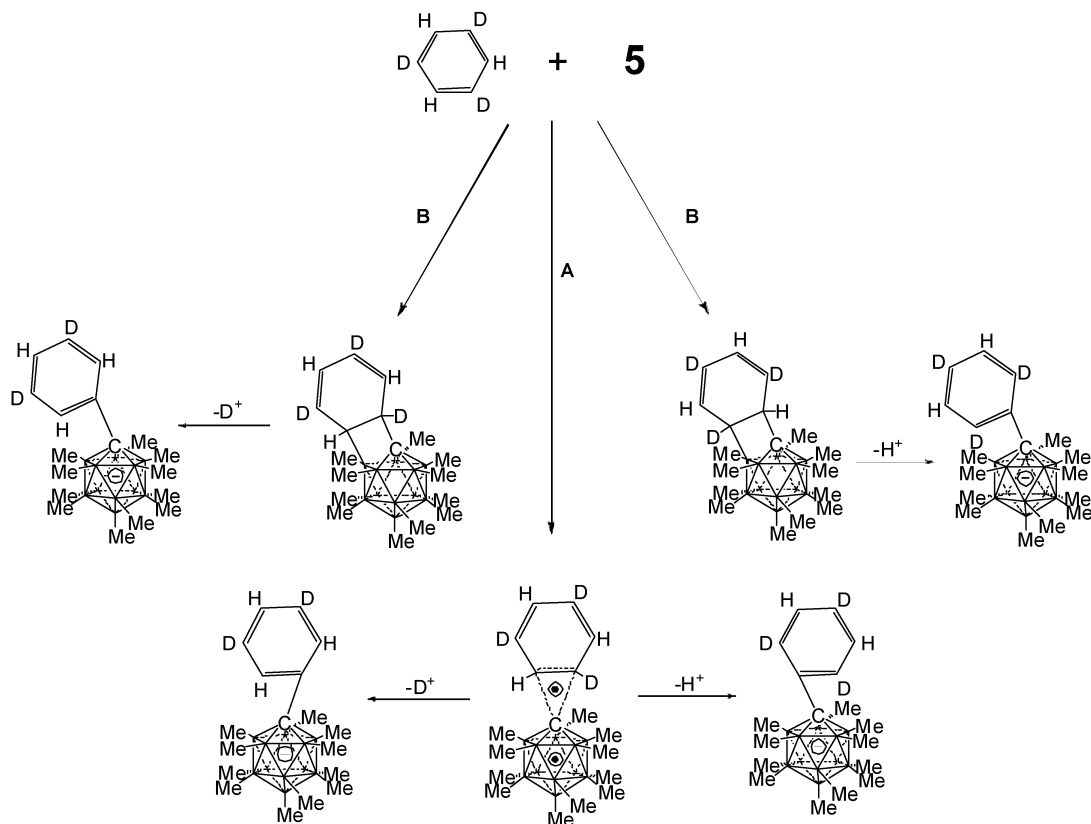


Fig. 14 Aromatic substitution with **5**: cluster participation through a vertex (A) and through an edge (B). Adapted with permission from ref. [10].

This proposal represents an unprecedented new mechanism for aromatic substitution but is in keeping with the proposed singlet carbene-like electronic structure of **5**.

SUMMARY

The chemistry of the three-dimensionally aromatic carboranes **1–5** is curiously reminiscent of aromatic chemistry, yet is distinctly different. It offers many intriguing puzzles, some of which we believe to have solved at least in part, and it promises many applications for mainstream organic chemistry.

ACKNOWLEDGMENT

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