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An alternative and quick way to *closo* boron clusters.

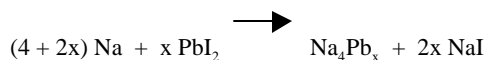
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The type of bonding in boron clusters is seen as a curiosity for the vast majority of synthetic chemists. Unfortunately most of them associate this chemistry with the words singularity and scarcity. Therefore, the use of boron clusters is very much restricted to boron chemists, or to situations where the boron itself is mandatory, as in Boron Neutron Capture Therapy (BNCT).¹ It is true that the synthesis process leading to the different clusters requires in the vast majority of cases to start from B₂H₆, and that after many steps and careful separations, usually low yields are encountered.² Finding a rapid way to generate these clusters in good yield would certainly stimulate their use and benefit from their unique properties. With this aim we undertook a research leading to explore the possibilities to generate cluster borate anions in a fast way. For that purpose we aimed at synthesizing [B_nX_n]²⁻ (X= I, Br, F), halogenoderivatives of [B_nH_n]²⁻, that with the current procedures require a sequential synthesis. If we restrict our discussion to n=6 that correspond to the smallest *closo*-borate, the number of reactions required for [B₆I₆]²⁻ is cumbersome,^{3,4,5} with an overall yield near 15%.^{3,4} Efforts to get relevant products in few steps from available chemicals,⁶ or in solvent free procedures⁷ are of current great interest. Concerning boron compounds the synthesis of B₃H₉ from B(OH)₃ is noteworthy.⁶

Our strategy basically consists in emulating the syntheses of Zintl anions,⁸ e.g. [Sn_n]⁴⁻,⁹ [Pb_n]⁴⁻,¹⁰ [Ge_n]⁴⁻.¹¹ According to the Polyhedral Skeleton Electron Pair Theory (PSEPT)¹² a BX group (X= H, F, Br, I) is equivalent to a Sn, Pb or Ge.¹³ In the Zintl anion generation only the metal and the reducing agent are present. The reaction we will follow maintains a close similarity with the very initial discovery of the Zintl anions, to say the titration of sodium solutions in liquid ammonia by salts of post-transition elements.¹⁴ For lead, the titration refers to

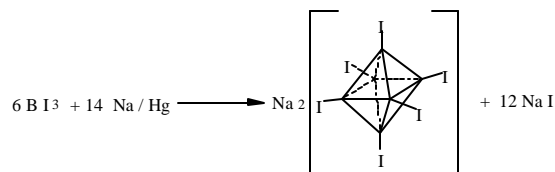


Thus, a similar strategy seems reasonable. Naked metal clusters benefited from boron cluster chemistry,¹⁵ and the opposite could also be true. Although our strategy, in agreement with the Zintl anions, is based in avoiding any coordinating solvent at the moment of their generation, the results obtained by Shore and coworkers¹⁶ for the successful synthesis of M[B₃H₈] (M= K, Rb, Cs), in which the adduct BH₃←THF was reacted with M/Hg (M= K, Rb, Cs), motivated us to try to synthesize [B_nF_n]²⁻ from the readily available BF₃·Et₂O. For this purpose the BF₃ adduct was reacted with sodium amalgam Na/Hg (1.2% w/w).¹⁷ The experiments were followed by ¹¹B-NMR and MALDI-TOF techniques, and evidenced that no reaction had taken place. As Shore and co-workers had not used Na/Hg, we attempted to synthesize Na[B₃H₈] using BH₃←THF with Na/Hg. The reaction can be considered a modification of this reported by Hough et al. using B₂H₆.¹⁸ Basically BH₃←THF (1M) was added to frozen

Na/Hg in a flask flushed with N₂ at -63.6°C. Full conversion was achieved after a total of three hours at room temperature.

The synthesis of Na[B₃H₈] represents an example of the formation of a boron cluster by a reduction process in a very mild conditions, one pot reaction, high yield process, from a readily available monoboron starting reagent. [B₃H₈] is a small cluster, and it is our thought that it can't grow further in this reaction media because of the competition of the coordinating solvent. If this is removed the cluster necessarily has to grow. To avoid the ether influence present in the starting reagents BF₃←Et₂O and BH₃←THF, and in order to use innocent solvents, BBr₃ and BI₃ which are available neat were considered adequate starting precursors. With this aim and, in a typical experiment BBr₃ (0.25 ml, 2.6 mmols) in dry hexane (20.0 ml) were deposited on 12 g of Na/Hg in a flask flushed with N₂ at -63.6°C. The reaction was continued for 1h at room temperature. Then, the solvent was evaporated to dryness and the residue was extracted with dry THF (30.0 ml). After filtration, the ¹¹B-NMR of the solution in a concentric tube containing d₆-acetone in the inner tube indicated that only one resonance, at -18.5 ppm, was present in solution. The MALDI-TOF analysis of the solid result of evaporating the solution displayed only one envelope of peaks near 545 m/z that matches the simulation for [B₆Br₆H]⁻, as a result of [B₆Br₆]²⁻ getting a proton or to the m/z for [B₁₂Br₁₂]²⁻. To assist in the interpretation, two dianionic boron clusters, [NH₄]₂[B₁₀Cl₁₀]²⁻ and [NH₄]₂[B₁₂Cl₁₂]²⁻, were studied with MALDI-TOF using the same experimental conditions. In both cases the peaks corresponding to the monoanionic species [B₁₀Cl₁₀H]⁻ and [B₁₂Cl₁₂H]⁻ were observed as the highest m/z peaks. Further evidence is provided by the neighboring m/z values in the envelope that are separated by 1.0 m/z units and not by 0.5 m/z units. Upon comparison with literature data, the ¹¹B-NMR chemical shift resonances unambiguously indicated that the generated species was [B₆Br₆]²⁻.⁴ The ¹¹B-NMR of a sample of [B₆Br₆]²⁻ in which a crystal structure¹⁹ had been obtained has been reported to be at -18.5 ppm.⁴ The reported chemical shift for [B₁₂Br₁₂]²⁻ is at -12.4 ppm.²⁰ A large cluster had been obtained in 92 % yield in only one step reaction in mild conditions.

Scheme 3



The reaction with BI₃ was done as for BBr₃ and is represented in Scheme 3. The ¹¹B-NMR spectrum of the reaction crude displayed only one resonance at -24.8 ppm. The MALDI-TOF

analysis presented only one envelop of peaks near 827 m/z that matches the simulation for $[B_6I_6H]^-$ (Figure 1). In agreement with the results from BBr_3 , this corresponds to the m/z for $[B_6I_6H]^-$, or to the m/z for $[B_{12}I_{12}]^{2-}$. The reported chemical shift for $[B_{12}I_{12}]^{2-}$ and $[B_6I_6]^{2-}$ are at -16.1 and -24.7 ppm respectively.^{20,21} The ^{11}B -NMR spectrum indicated that the generated species was $[B_6I_6]^{2-}$.²¹ As it is evidenced from these results we did not have any hint before hand of which species would be generated. We believe that given the right conditions and reagents different species can be generated, and that the concept may be of quite general applicability.

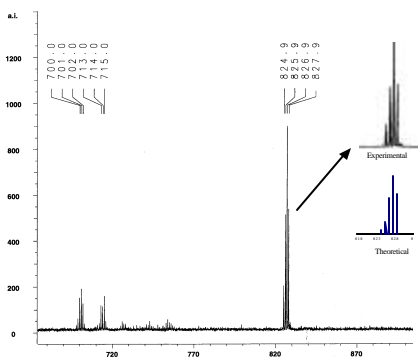


Figure 1. MALDI-TOF mass spectrum obtained for the species $[B_6I_6H]^-$. A comparison of the theoretical and experimental distribution for the molecular peak is shown at the right.

Nido^{9b,c,10c,11} and *closo*²² Zintl ions, mostly with nine atoms, were generated. In our case we have not yet found any example of *nido* species, as the number of examples studied is small, but the synthesis of *arachno* compounds, $[B_3H_8]^-$, and *closo* $[B_6I_6]^{2-}$ and $[B_6Br_6]^{2-}$ have been proven. Therefore, considering that the formation of *nido* structures in the Zintl anions is possible, it seems that the possibilities of the method are very large.

To explore if the similarities between Zintl anions and the $BX_3 + Na/Hg$ reaction could go further, we have studied the reaction with mixed halides $BX_{3-n}Y_n$ ($X = I, Y = Br, n = 1, 2$).

It has been reported that starting from ternary phases of composition $NaSnPb$, the whole series $[Sn_{9-x}Pb_x]^{4-}$ were obtained.²³ To emulate this reaction BI_3 and BBr_3 (1:1) were deposited on Na/Hg maintaining the ratio $Na:BX_3$ as is described above. If the system had totally matched the syntheses of the Zintl anions, the series $[B_6I_{6-x}Br_x]^{2-}$ ($x=0-6$) would have been obtained. However, only $[B_6I_5Br]^{2-}$, and $[B_6I_4Br_2]^{2-}$ have been observed by MALDI-TOF. None of the end compounds $[B_6I_6]^{2-}$ and $[B_6Br_6]^{2-}$ were detected in this experiment. This absence and the non-parallel behavior to the Zintl anions can be partly explained since BX_3 undergo rapid scrambling reactions producing the mixed halides $BIBr_2$ and BI_2Br .² Interestingly to notice is the fact that the mixed clusters obtained are these with the higher number of BI units. Considering that the bond enthalpies $E(B-X)$ follow the sequence $B-Br > B-I^2$ and that I is a better leaving group, we shall conclude that the lattice energy U_L is very relevant in this reaction. Therefore even the species $[B_6F_6]^{2-}$ should be generated following this procedure, although for the moment the right conditions have not been found.

To summarize, we have proven that a certain parallel exists between the formation of Zintl anions and cluster borates, and that the reduction process leading to the first can also be applied to monoborane compounds in order to get boron clusters. The process is one pot reaction, fast, high yield, opened to a variety of synthetic conditions, and reagents and brings an excellent opportunity to make borane clusters less esoteric and closer to the

synthetic chemists. In this report we have presented the synthesis of $[B_6Br_6]^{2-}$ and $[B_6I_6]^{2-}$ as two examples of interesting *closo* compounds that did require extensive work for their syntheses, and that as most of $[B_6H_6]^{2-}$ derivatives they were scarcely studied due to their unavailability.^{4b} Work must be done to further explore the possibilities of the method. We have just briefly shown that alternative methods can be found to produce boron clusters from readily available monoborane compounds.

[NMe₄][B₆I₆]: BI_3 (1.0 g, 2.6 mmols) in dry hexane (20.0 ml) was deposited on 12 g of Na/Hg (0.14 g Na/ 12.0 g Hg; 1.2% w/w) in a flask flushed with N_2 at $-63.6^\circ C$ ($CHCl_3$ /liquid N_2). The bath was removed and the reaction was continued for 1h at room temperature. Then, the solvent was evaporated to dryness and dry THF (30.0 ml) was added to the residue. After filtration the solvent was removed and water (10.0 ml) was added. $[B_6I_6]^{2-}$ was precipitated with $[NMe_4]Cl$ to yield $[NMe_4]_2[B_6I_6]$. (0.40 g, 95%)

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Sequential nucleophilic –electrophilic reactions to selectively produce isomerically pure nona boron substituted *o*-carborane derivatives

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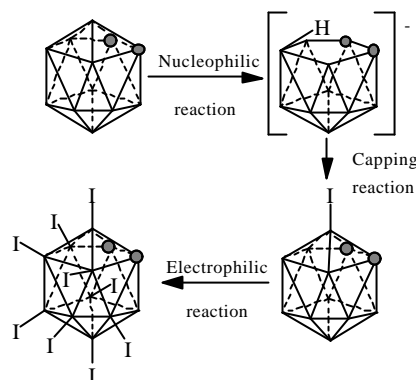
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Nine equal substituents on the intensively studied *o*-carborane have been obtained for the first time combining nucleophilic and electrophilic sequential processes. Iodine and methyl groups have been introduced to prove the generality of the method.

In the last decade great interest in introducing a large number of substituents on boron in icosahedral borates, and heteroboranes has been experienced.^{1,2,3,4,5,6} The possibility to generate weakly coordinating anions,^{6,7,3} X-ray contrast agents,⁸ camouflaged boron clusters,⁵ or to attain the size of C₆₀⁹ in addition to generate stable radicals⁴ have been some of the reasons to stimulate this research. Substitutions have been achieved with good success with the cluster anions, but there are few examples on the dicarboranes. This is surprising considering that the chemistry of the latter has become one of the most intensively investigated in the field of boranes and heteroboranes.¹⁰ The paucity of reported examples is in agreement with the relative rates of halogenation which decrease in the order [B₁₂H₁₂]²⁻ > [CB₁₁H₁₂]⁻ > C₂B₁₀H₁₂.¹¹ Therefore methods to introduce substituents on the largely studied *o*-carborane need to be investigated. The *o*-carborane, 1,2-dicarba-*closo*-dodecaborane, contains four distinct type of boron atoms that can be ordered according to their distance to the C atoms, B(9,12), B(8,10), B(4,5,7,11), and the borons B(3,6) that are adjacent to both carbon atoms. The farthest to the carbon atoms are, the more electron-rich are the boron atoms, the closest being the electron-poorest. As it is generally accepted the icosahedral carboranes are aromatic¹² and undergo electrophilic substitution reactions, making this method attractive for introducing iodine into the cage molecules.¹⁰ While perfluorination¹³ and perchlorination¹⁴ of dicarboranes have been obtained, perbromination has not been accomplished. Indeed only a maximum of 4 bromine atoms had been incorporated in dicarboranes until now. Periodination of *o*-carborane has neither been achieved. Before 1996 the maximum number of iodines in *o*-carborane was 2 which were occupying the 9,12 positions.^{1,15} Little information exists on higher substitution, although reference has been made on iodo *o*-carboranes in 9,12,8,10.¹⁶ A major progress was recently achieved upon the synthesis of the eight iodine 4,5,7,8,9,10,11,12-octa-B-iodo-1,2-dicarba-*closo*-dodecaborane.⁸ Therefore the carbons adjacent B(3,6) are resistant to electrophilic methods. All methods described above are based on electrophilic substitutions. With the extremely powerful electrophiles, F⁺, Cl⁺, full substitution has been achieved. However, with the milder electrophiles, Br⁺, I⁺, this has not been possible. Our hypothesis is that the first introduced group in the cluster determines the subsequent reactivity of the cluster towards further substitution causing, in some cases such as *o*-carborane with mild electrophiles, persubstitution to be impossible. Therefore, to attain such substitution more than one type of reaction is necessary: an electrophilic reaction for the electron-rich boron atoms and a nucleophilic for the electron-poor B(3,6). With this aim we devised the sequence of reactions shown in scheme 1.



Scheme 1. Synthesis of 3,4,5,7,8,9,10,11,12-nona-B-iodo-1,2-dicarba-*closo*-dodecaborane (*closo*-1) from *o*-carborane.

First step consists in producing 3-I-1,2-C₂B₁₀H₁₁.¹ This is achieved after a nucleophilic reaction to remove one boron adjacent to both carbon atoms. Next, a capping reaction with BI₃ leads to 3-I-1,2-C₂B₁₀H₁₁. Next step consists in producing the electrophilic reaction. The existence of already one B(3)-I will inform on the lability of the second boron adjacent to both carbons to electrophilic attack.

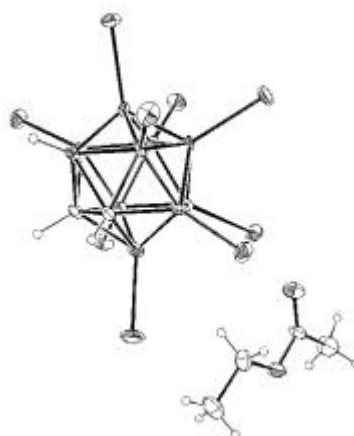


Fig. 1. Perspective view of *closo*-1 AcOEt with 30% ellipsoids. H atoms are omitted for clarity. Selected bond lengths (Å): C(1)-C(2) 1.637(14), B-I 2.113(6) – 2.166(11).

In a typical experiment 3-I-1,2-C₂B₁₀H₁₁ (3.7 mmol) was mixed with triflic acid¹⁷ (66.5 mmol) and ICl (6 mL, 111 mmol). Following heating at 90°C for 3 days, and after working up a 94% yield of 3,4,5,7,8,9,10,11,12-nona-B-iodo-1,2-dicarba-*closo*-dodecaborane (*closo*-1) was obtained. The ¹¹B{¹H}-NMR shows a pattern 2:1:1:1:2:2:1 spanning from -4.2 to -22.1 ppm. Only the resonance at -11.1 ppm of intensity 1 splits in the ¹¹B-NMR confirming that all but one, the B(6), of the boron atoms have one *exo*-cluster iodine.

The structure was definitely supported by X-ray diffraction analysis of *closo*-1·AcOEt.¹⁸ Therefore it is proven that the pre-introduced B(3)-I does not labilize B(6)-H, being therefore, a method adequate to introduce selected substituents.

Therefore, the method is successful for mild electron-withdrawing elements, but could it be applicable to introduce Me substituents?

A good target could be with the long sought 3,4,5,7,8,9,10,11,12-nona-B-methyl-1,2-dicarba-*closo*-dodecaborane (*closo*-2). The strategy for its synthesis was also a combination of nucleophilic and electrophilic attacks, first producing 3-CH₃-1,2-C₂B₁₀H₁₁,¹⁹ then producing *closo*-2 through reaction with AlCl₃ and CH₃I. The ¹¹B{¹H}-NMR shows a pattern 2:1:1:5:1 indicating the geometrical similarity of *closo*-1 and *closo*-2. The B(6) resonance is observed at -17.16 ppm. Again, the pre-introduced B(3)-CH₃ does not labilize B(6)-H permitting to maintain the *closo* structure in this case adequate to introduce selected substituent.

To summarize, a combined nucleophilic and electrophilic sequential process has permitted to get for the first time nine equal substituents on the well studied *o*-carborane. Iodine and methyl groups have been introduced to prove the generality of the method.

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Notes and references

Preparation of *closo*-1:

To 3-iodo-1,2-dicarba-*closo*-dodecaborane (1.0 g, 3.7 mmol) were added under nitrogen flow first (10.0 g, 66.5 mmol) of triflic acid and then ICl (6 mL). The mixture was heated at 90°C during three days and after that was allowed to cool to room temperature. Cold water (10 mL) and then aqueous NaHSO₃ were added to the mixture. The precipitate was filtered and was immediately dissolved in 125 mL of hot AcOEt and Zn was added until the solution become colourless. The colourless solution was filtered and then the solvent evaporated at the water pump. The solid obtained was recrystallized from AcOEt. (4.45g, R: 94%). Anal. Calcd. for C₂B₁₀I₉H₃: C, 1.89; H, 0.24. Found: C, 1.97; H, 0.20. IR: ν [cm⁻¹] = 3012.2 (C_{cluster}-H), 2650 (B-H). ¹H NMR: CD₃COCD₃, δ = 6.98 (br s, C_{cluster}-H, B-H). ¹³C{¹H} NMR: CD₃COCD₃, δ = 72.5 (s, C_{cluster}). ¹¹B NMR: δ = -4.2 (s, 2B), -9.7 (s, 1B), -11.1 (1B, B(6)), -12.6 (s, 1B), -17.2 (s, 2B), -20.3 (s, 2B), -22.1 (s, 1B). MS: 1277.0. The ¹H{¹¹B} NMR of the crystals *closo*-1·AcOEt. was run in CD₃COCD₃, δ = 6.98 (d, ³J(H, H) = 3.8 Hz, 2H, C_{cluster}-H), 6.98 (br s, 1H, B-H), 4.06 (q, ²J(H, H) = 7.1 Hz, 2H, CH₂), 3.54 (s, 3H, CH₃), 1.2 (t, ³J(H, H) = 7.1 Hz, 3H, CH₃).

Preparation of *closo*-2:

To a mixture of 3-methyl-1,2-dicarba-*closo*-dodecaborane (700 mg, 4.4 mmol) and AlCl₃ (1.17 g, 8.8 mmol), MeI (6.4 mL) was added. The mixture was refluxed for 2 days and at the end the unreacted MeI was distilled off. The residue was hydrolyzed and extracted with pentane. The combined organic phases were treated with Na₂S₂O₃ and dried over MgSO₄. The final compound was purified by flash silica gel chromatography using pentane as the eluting solvent to give 3,4,5,7,8,9,10,11,12-nona-B-methyl-1,2-dicarba-*closo*-dodecaborane. (1.17 g, R: 98 %). Anal. Calcd. for C₁₁B₁₀H₃₀: C, 48.85; H, 11.18. Found: C, 48.98; H, 11.25. IR: ν [cm⁻¹] = 3056.0 (C_{cluster}-H), 2945.2, 2904.6, 2833.2 (C-H), 2590.2 (B-H). ¹H{¹¹B} NMR: CDCl₃, δ = 0.32 (br s, 3H, CH₃), 0.13 (br s, 6H, CH₃), 0.05 (br s, 6H, CH₃), 0.01 (br s, 3H, CH₃), -0.12 (br s, 3H, CH₃), -0.23 (br s, 6H, CH₃), 2.89 (d, ³J(H, H) = 43

Hz, 2H, C_{cluster}-H), 1.86 (br s, 1H, B-H). ¹³C{¹H} NMR: CDCl₃, δ = -3.02 (br, CH₃), 54.25 (s, C_{cluster}). ¹¹B NMR: CDCl₃, δ = 5.44 (s, 2B), -2.10 (s, 1B), -4.23 (s, 1B), -8.84 (s, 5B), -17.16 (d, ¹J(B, H) = 161 Hz, 1B). MS: 270.1

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“The role of methyl substituent groups on boron clusters, are electron donating or electron withdrawing?. A description of the B-methylation of *o*-carborane through the crystal structure of 9-I_{0.707}H_{0.293}-12-Cl_{0.566}H_{0.434}-3,4,5,6,7,8,10,11-Me₈-1,2-C₂B₁₀H₂”

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That methyl groups attached to carbon atoms, heteroatoms or π -electron systems are electron donors is widely accepted in organic chemistry. This, and the many reactions in organic chemistry and boron cluster chemistry that are shared,¹ has led the assumption that methyl groups on boron are also donating groups. Contrarily to this view, it will be shown in this report that, in respect of *o*-carborane, methyl groups are in fact electron-withdrawing. This statement may be controversial as conflicts with common opinion but the data presented here fully support this unexpected effect, and considering the difference in electronegativity between C (2.5) and B (2.0), the transfer of electron density to carbon rather than the reverse should not be unexpected.

In the last decade enormous efforts have been dedicated to the alkylation or peralkylation of *closo*-borates, the monocarborane anion, and the dicarbaboranes.^{2,3} Good success has been obtained with anionic clusters, but there has been much less success with the dicarba-*closo*-dodecaboranes, even though the chemistry of the latter is the most intensively studied.¹ This lack of methylated dicarbaboranes parallels the relative rates of cluster halogenation which decrease in the order [B₁₂H₁₂]²⁻ > [CB₁₁H₁₂]⁻ > C₂B₁₀H₁₂.⁴ Our interpretation of this fact is that the halogenation rate decreases with the decreasing amount of negative charge on the cluster. Zakharkin *et al.*⁵ and Plesek *et al.*⁶ demonstrated that alkylation of *o*-carborane (**1**) is possible under electrophilic conditions. However, the authors obtained complex mixtures of compounds. It was suggested that the substituents enter sequentially according to the decreasing electron density of the boron atoms. In **1** the BH vertexes bearing the greatest amount of electron density are boron atoms B(9,12) and B(8,10) while these with the least are B(3,6). In this sense, positions B(8,9,10,12) should be among the first to be attacked by electrophiles.⁷ Of the three possible dicarba-*closo*-dodecaborane isomers, the *p*-carborane which has no C,C connectivity has been the most successfully methylated and decakis-B-methyl-*p*-carborane and dodecamethyl-*p*-carborane have been obtained.^{3h} No B permethylation has been possible at the boron vertexes adjacent to both carbon cluster moieties, a situation present in 1,2-C₂B₁₀H₁₂ and 1,7-C₂B₁₀H₁₂.^{3g}

Hawthorne *et al.* have achieved maximum methylation starting from **1** and the compound 4,5,7,8,9,10,11,12-Me₈-1,2-C₂B₁₀H₄ (**2**) has been obtained.^{3g} Therefore, the expected sequence of methylation should begin with one of the electron rich B(8,9,10,12) vertexes and successively until it was the turn for B(3,6) for which methylation was not found. However, if methyl groups are electron donating then electrophilic attack would be enhanced as electronic charge on the cage would be building up

and B(3,6) would be methylated. The no methylation of B(3,6) induced us to believe that the role of Me groups in boron clusters may not be electron-donating. We decided to alter the sequential order of methyl incorporation in the cluster and check if boron permethylation or again octa boron methylation, now with different substituted boron atoms, would be obtained. Our approach was first to methylate B(3,6) which are the boron atoms not substituted on **2**, then perform maximum substitution on the remaining boron atoms. Our starting species was therefore 3,6-Me₂-1,2-C₂B₁₀H₁₀ (**3**). To aid our synthetic strategy, we performed *ab initio* calculations at the Hartree-Fork 3-21G level⁸ on **1**, **3** and 3-Me-1,2-C₂B₁₀H₁₁ (**4**), and this indicated that no noticeable changes were observed in the HOMO, HOMO-1 and HOMO-2 molecular orbitals of these molecules. Surprisingly, in all three cases the HOMO was pinned on the B(3,6) antipodal boron atoms which are B(8,10), and the charges on B(9,12) were practically unaltered. Based on local charges and frontier orbitals not much difference in the most susceptible sites for electrophilic attack was then expected. However a major difference had appeared; the cluster total charge⁹ was increasing parallel to the increasing number of Me groups on boron atoms with each Me group approximately increasing the cluster total charge in 0.5 units, as computed from **3** and **4**. If the original cluster total charge on **1** was -0.9, addition of eight Me groups would alter the cluster's total charge to approximately +3.1 (computed HF 3-21G on **2** is 3.374). The situation was the opposite to the one expected if the Me group had been electron donating. Our explanation, therefore, to the difficulty of generating ten B-Me vertexes on the cluster by electrophilic methods is the repulsion originated between the positive cluster total charge and the electrophile, and not the point charges. To perform a better comparison, 1,2-Me₂-1,2-C₂B₁₀H₁₀ was also calculated, and the effect of Me groups on their connected carbon atoms also computed. This also increases the positive charge of the C, but the effect is much smaller, +0.1 in C-Me vs. +0.5 in B-Me. The electron-withdrawing character in C-Me can be either an artifact of Mulliken's charges or a consequence of the pseudoaromatic character of the cluster. Hoffmann and Libit pointed out that the substituent effect of Me groups in π -electron systems are due not to electron donation by the methyl substituent but to a polarization caused by the π -system.¹⁰ These conclusions are fully confirmed with the synthesis of 9-X-12-Y-3,4,5,6,7,8,10,11-Me₈-1,2-C₂B₁₀H₂ (X, Y = I, Cl; I, H; H, H; and H, Cl) and the solid state structure of 9-I_{0.707}H_{0.293}-12-Cl_{0.566}H_{0.434}-3,4,5,6,7,8,10,11-Me₈-1,2-C₂B₁₀H₂ (**5**). If the 9,12 positions are not considered, **5** is the complementary compound of **2**. Both have methyl substituents at B(4,5,7,8,10,11) vertexes. The compound **2** has Me groups in B(9,12) but not in B(3,6), **5** has Me

groups in B(3,6) but not in B(9,12). Interestingly, a maximum of eight methyl groups were incorporated following a complete different strategy and a different starting material. HF/ 3-21G calculations gives a cluster total charge of +3.309 on **5** that is very similar to +3.374 obtained with **2**.

Treatment of **3** with MeI/AICl₃ at reflux for 2 days gives, after work up, a solid whose ¹¹B-NMR spectrum indicates a mixture of species. The ¹¹B{¹H}-NMR spectrum was identical suggesting that there were no remaining BH moieties. Attempts to improve the purity of the solid by chromatography and re-crystallization techniques were unsuccessful suggesting that the components had very similar physical properties. The ¹H-NMR spectrum confirmed this observation. The carborane C-H region between 2.6 and 4.6 ppm was very informative. Resonances due to C-H (in ppm with relative areas in parentheses) were observed at 4.47 (2.97); 3.16 (1); 2.99 (1); 3.04 (5); 2.94 (5), 2.77 (2.65) and 2.74 (2.65). This implies that four dominant species, only one being symmetrical, are formed in this reaction. The most abundant compound displays its cluster C-H's at 3.04 and 2.94 ppm, the second in importance at 2.77 and 2.74 ppm, the third at 4.47 ppm, this being most probably symmetrical, and the less abundant at 3.16 ppm and 2.99 ppm. The abundances would be 49%, 26%, 15% and 10% approximately.

Although we were unable to purify this mixture, suitable colourless crystals were obtained from hexane. The crystal structure of **5** confirms the octa boron methyl substitution of the C₂B₁₀ icosahedron. X-ray analysis¹¹ confirmed that the *exo*-cluster substituent positions at B(9) and B(12) are each partially occupied by halogen and hydrogen atoms. Site occupation parameters for I and H(9), connected to B(9), are 0.707(3) and 0.293(3), respectively, while the position at B(12) is partially occupied by Cl (SOP = 0.566(5)) and H(12) (SOP = 0.434(5)). The crystal's components are concordant to the average composition of the solid studied by NMR. It is made of four compounds that can be named **5**(X,Y), for 9-X-12-Y-3,4,5,6,7,8,10,11-Me₈-1,2-C₂B₁₀H₂ being **5**(I,Cl), **5**(I,H), **5**(H,H), and **5**(H,Cl). The X-ray structural analysis has permitted to identify the species in solution, that in order of abundance are **5**(I,Cl)>**5**(I,H)>**5**(H,H)>**5**(H,Cl).(Figure 1)

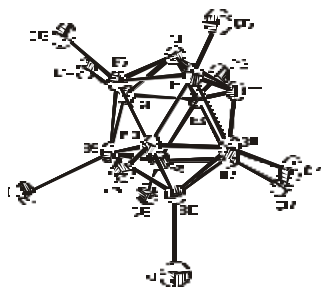


Figure 1. Perspective view of 9-X-12-Y-3,4,5,6,7,8,10,11-(CH₃)₈-1,2-C₂B₁₀H₂ (X,Y = I,Cl) with 30% ellipsoids. H atoms are omitted for clarity. Selected bond lengths (Å): C(1)-C(2) 1.632(4), B(9)-I2.159(4), B(12)-Cl 1.816(4), B-C_{Me} 1.561(5)-1.649(5).

The fact that these four species have been identified in solution and in solid state brings new information on the alkylation process for the *o*-carborane cluster. The existence of three species with H in the 9,12 positions, **5**(I,H), **5**(H,H) and **5**(H,Cl) while all other B positions are methyl substituted indicate that positions 9,12 are not the first to suffer electrophilic attack. Furthermore the fact that 9,12 positions are the only ones with no methyl substituents suggests that the type of reaction (electrophilic/ nucleophilic) to produce alkylation shall not be the same for B(4,5,6,8,10,11) and

B(9,12) in 3,6-Me₂ modified *o*-carborane, and consequently strategies leading to B-permethylation in *o*-carborane shall account for more than one reaction, contrarily to *p*-carborane, [CB₁₁H₁₂], [B₁₂H₁₂]²⁻, etc. Substitution at positions B(9,12) by I, Cl, H can be interpreted as a substitution by negative species, especially favored due to the high positive cluster total charge. Substitutions of the kind have already been reported in methylated species and fully support our explanation. In this sense it had been observed that replacement of at least one methyl group by a triflate substituent was observed at the antipodal boron atom B(9).^{3g}

To summarize, this work reports that the electron donating capacity of the Me group must not be generally assumed and in boron clusters it has the opposite effect. Care must be taken when the heteroatom connected to Me group is less electronegative than carbon. As a consequence of this, permethylation of the *o*-carborane cluster with electrophiles is not allowed due to positive charge built-up as the number of methyl substituents increases. With this we do not say that permethylation is impossible but simply that a combination of nucleophilic and electrophilic reactions is necessary.

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"Supporting Information Available:" Table containing Mulliken charges on related boron methylated *o*-carborane derivatives, crystallographic data and experimental preparation of **5**. This material is available free of charge at <http://pubs.acs.org/>

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Synthesis of the boron periodinated *o*-carborane and the water stability of its monoprotic salt.

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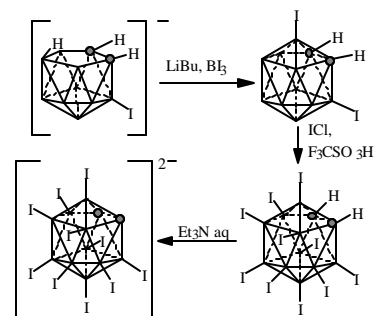
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In the last decade great interest in introducing a large number of substituents on boron in icosahedral borates, and heteroboranes has been experienced.^{1,2,3} Substitutions have been achieved with good success with the cluster anions, but there are few examples on the dicarbaboranes. This is surprising considering that the chemistry of the latter has become one of the most intensively investigated in the field of boranes and heteroboranes.^{4,5} The paucity of reported examples is in agreement with the relative rates of halogenation which decrease in the order $[B_{12}H_{12}]^{2-} > [CB_{11}H_{12}] > C_2B_{10}H_{12}$.⁶ While perfluorination⁷ and perchlorination^{8,9} of dicarbaboranes has been obtained, perbromination has not been accomplished. Indeed only a maximum of 4 bromine atoms had been incorporated in dicarbaboranes until now. Periodination of *o*-carborane has neither been achieved. Before 1996 the maximum number of iodines in *o*-carborane was 2 which were occupying the 9,12 positions.^{1,10} Little information existed on higher substitution, although reference to tetrasubstitution at 8,9,10,12 had been made on *o*-carboranes.¹¹ A major progress was recently achieved upon the synthesis of the eight iodine 4,5,7,8,9,10,11,12-octa-B-iodo-1,2-dicarbaborane.³ The carbons adjacent positions B(3,6) did not iodinate because they are the most electron deficient. Therefore the strongest halogenating agents F^+ and Cl^+ are capable to substitute all boron atoms, the weakest not. Calculations on 1,2- $C_2B_{10}H_{12}$, at HF 3-21G* level, have shown that Mulliken charges are considerably more positive at B(3,6) than at B(8,9,10,12) (0.27 vs 0.00). Surprisingly the HOMO orbital is not located on B(9,12) which, as said,^{1,10} are the first positions to be attacked.¹² This is in agreement with earlier observations¹³ that electrophilic attack takes place in these positions with higher negative charges. Consequently with Br and I it would be difficult to get substitution on B(3,6). Therefore we considered that to get B-I persubstitution it was necessary to treat the highly positive B(3,6) separately from the rest. In this paper we report on the first all boron iodine substituted *o*-carborane, its unprecedented acid properties, and the stability of the monoanionic species in water. Starting from $[3-I-7,8-C_2B_9H_{11}]^-$, first step consists in producing 3,6-I₂-1,2- $C_2B_{10}H_{10}$. This is achieved after removal of the open face proton atom with *n*-BuLi. The unblocked “ C_2B_3 ” open face is now ready to react with BI_3 leading to 3,6-I₂-1,2- $C_2B_{10}H_{10}$. Further reaction with BI_3 in CF_3SO_3H ^{3,14} leads to 1,2-H₂-1,2- $C_2B_{10}I_{10}$, the first total boron periodinated *o*-carborane species. (Scheme 1) In a typical experiment $[HNMe_3][3-I-7,8-C_2B_9H_{11}]$ (1.30 g, 4.0 mmol) was dissolved in anhydrous diethylether (20 mL), and *n*-BuLi (5.0 mL, 8.0 mmol) were added at 0°C. The solvent was evaporated and hexane (20 mL) was added. Slow addition of BI_3 (2.35g, 6.0 mmol) in hexane to the suspension at 0°C followed by further

reaction at room temperature led to 3,6-I₂-1,2- $C_2B_{10}H_{10}$ in good yield (88 %).



Scheme 1. Synthesis of the periodinated carboranes.

The $^{11}B\{^1H\}$ -NMR shows a pattern 2:2:4:2 from -0.1 to -27.6 ppm, in agreement with a C_{2v} symmetry. The resonance at -27.6 ppm corresponding to B(3,6) does not split in the ^{11}B -NMR spectrum, all others splitting due to B-H coupling. Total boron periodination was achieved reacting 3,6-I₂-1,2- $C_2B_{10}H_{10}$ with triflic acid and ICl to yield 73% of 1,2-H₂-1,2- $C_2B_{10}I_{10}$ (**1**).¹⁵ The $^{11}B\{^1H\}$ -NMR shows a pattern 2:2:4:2 in which no boron resonance splits in ^{11}B -NMR confirming that all boron atoms have one *exocuster* iodine. The structure of **1** (**1** · 1.359DMSO · 0.641acetone) was confirmed by X-ray diffraction analysis.¹⁶ (Figure 1)

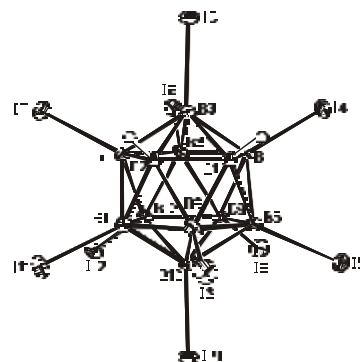
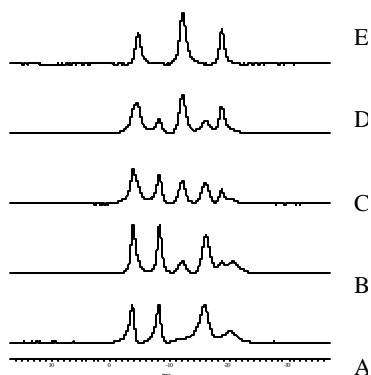


Figure 1. Perspective view of **1** (1,2-H₂-1,2- $C_2B_{10}I_{10}$ · 1.359DMSO · 0.641acetone) with 30% ellipsoids. Solvent molecules and H atoms are omitted for clarity. Selected bond lengths (Å): C(1)-C(2) 1.643(4), B-I 2.122(3) – 2.154(3).

It is of relevance the C-H...O interactions found between the cluster's C-H and the solvating molecules. The 1H -NMR ($CDCl_3$)

C-H resonances of 3,6-I₂-1,2-C₂B₁₀H₁₀ (4.10 ppm), and **1** (7.37 ppm) are most probably consequence of the easiness to produce D-H...A interactions. We related the continuous C-H downfield chemical shift with increasing number of iodine atoms, 1,2-C₂B₁₀H₁₂ (3.55 ppm), 3-I-1,2-C₂B₁₀H₁₁ (3.84 ppm), 3,6-I₂-1,2-C₂B₁₀H₁₀ (4.10 ppm) and **1**, with an increasing acidity. Therefore, would it be possible to remove these C-H protons with relatively weak bases? Would their conjugate acids not be regenerated in water? From a synthetic point of view great benefit is taken from the weak acidity of *o*-carborane, but its conjugate base is so strong that is immediately protonated in protic solvents.⁴ In 1963 Schroeder, and co. reported⁹ the preparation of (HN(C₂H₅)₃)₂(B₁₀Cl₁₀C₂) that was stable in aqueous media. They reacted HN(C₂H₅)₃ and 1,2-H₂-1,2-C₂B₁₀Cl₁₀ in benzene or ethanol. The existence of this salt was later put in doubt by Zakharkin and Ogorodnikova which proved that in aqueous ethanol decachloro-*o*-carborane behaved as a monoprotic acid and not as a diprotic acid. ¹H-NMR of 1,2-H₂-1,2-C₂B₁₀Cl₁₀ was provided indicating that CH's were at 5.89 ppm. Additionally the value of the experimental pK_a was 6.98.¹⁷ According to the ¹H-NMR data, the pK_a of 1,2-H₂-1,2-C₂B₁₀Cl₁₀ should be more positive than this of **1**, and possibly a water stable salt of a carborane derivative could be produced.

Upon dissolution of **1** in CD₃OD and addition of one equivalent of *t*-BuOK, the ¹H-NMR C-H resonance originally present at 7.62 ppm was eliminated. The ¹¹B-NMR also presented an abrupt change now showing three peaks at -7.7, -14.9, -21.1. Further



addition of *t*-BuOK didn't produce any change in the spectrum.

Figure 2. Additions of *t*-BuOK to 1,2-H₂-C₂B₁₀I₁₀ in DMSO-d₆

The same experiment was run again in DMSO-d₆ with different ratios of **1**:*t*-BuOK; 1:0, 1:0.2, 1:0.4, 1:0.8 and 1:1. The result were different spectra, **A**, **B**, **C**, **D**, **E** in figure 2 which consisted in the cumulative spectra of 1,2-H₂-1,2-C₂B₁₀I₁₀ (**A**) and [1,2-C₂B₁₀I₁₀H]^(E). When H₂O was added to the methanolic or the DMSO solution of [1,2-C₂B₁₀I₁₀H] the spectrum was unaltered and protonation did not occur. Subsequent tests were directly performed in H₂O in which **1** is insoluble, but addition of HNEt₂ (pK_a = 10.9) leads to gradual dissolution. After total dissolution the ¹¹B-NMR spectrum is identical to this obtained after the addition of one equivalent of *t*-BuOK either in DMSO or metanol. Addition of acids with strength higher than 2.9, HCl (pK_a = -7), CCl₃COOH (pK_a = 0.6) and CH₃ClCOOH (pK_a = 2.9) led to insoluble **1**. It is not the case for CH₃COOH (pK_a = 4.7) which is unable to protonate the species existing in **E**. Therefore pK_a of **1** must lie between 2.9 and 4.7, being a stronger acid than 1,2-H₂-1,2-C₂B₁₀Cl₁₀, in agreement with the ¹H-NMR C-H resonance. Can the diprotonated species be generated? Our

experiments say that addition of more than one equivalent of strong base gradually leads to degradation of the cluster. We have tested this with *n*-BuLi in dme and *t*-BuOK in ethanol.

As a last test [N(PPh₃)₂] Cl was added to the aqueous solution of [1,2-C₂B₁₀I₁₀H]^(E) and [N(PPh₃)₂] [1,2-C₂B₁₀I₁₀H] was precipitated. Similarly, [N(PPh₃)₂] Cl in methanol was added to the methanolic solution of [1,2-C₂B₁₀I₁₀H]^(E) to produce same salt. The MALDI-TOF spectrum showed a peak at 1402.4 (m/z = C₂B₁₀I₁₀H^(E)) which demonstrates the anionic character of the cluster.

This work has permitted to isolate for the first time a water stable salt of 1,2-C₂B₁₀H₁₂ derivative, through the synthesis of the boron periodinated *o*-carborane 1,2-H₂-1,2-C₂B₁₀I₁₀ (**1**). This is more acidic than its chlorinated homologous and permits to isolate [N(PPh₃)₂] [1,2-C₂B₁₀I₁₀H]. Our interpretation of Schroeder's salt⁹ is that an adduct C-H...N is generated. It was already treated as an adduct by Zakharkin.¹⁷

Acknowledgements. This work was supported by CICYT (Project MAT01-1575), Generalitat de Catalunya (2001/SGR/00337), and the Academy of Finland (project 41519, RK).

Supporting Information Available: Tables of crystal data for **1** as an X-ray crystallographic file (CIF). This material is available free of charge via Internet at <http://pubs.acs.org>.

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- (15) Synthetic procedure for **1**: To 3,6-I₂-C₂B₁₀H₁₀ (1.00 g, 2.50 mmol) was added under nitrogen flow 10.0 g (66.5 mmol) of triflic acid and 6.0 ml of ICl in this order. The mixture was heated at 90°C for five days. Cold water (10.0 ml) and aqueous NaHSO₃ were added to the cooled mixture. The formed precipitate was filtered and immediately dissolved in 125 ml of hot EtOAc. After evaporation of the solvent the compound was purified by column chromatography using EtOAc as eluent. (Yield 2.55 g, 1.82 mmol, 73%) IR: ν [cm⁻¹] = 3008.2, 2980.3 (C_{cluster}-H). ¹H NMR: CD₃COCD₃, δ = 7.74 (s, 2H, C_{cluster}-H) ¹¹B NMR: δ = -4.3 (s, 2B), -9.2 (s, 2B), -16.9 (s, 4B), -21.4 (s, 2B) ¹³C {¹H} NMR: δ = 63.1 (s, C_{cluster}). Crystals were obtained from DMSO/acetone (1:5) mixture. Crystal data: C_{6,64}H₁₄B₁₀I₁₀O₂S_{1,359} or C₂H₂B₁₀I₁₀; 1.359 DMSO·0.64 Acetone; orthorhombic; *Pbca* (no. 61); colourless; *a* = 17.0878(2) Å; *b* = 19.0063(2) Å; *c* = 19.9227(2) Å; *V* = 6470.41(12) Å³; *Z* = 8; *D_{calc}* = 3.175 g cm⁻³; *m*(Mo K α) = 9.674 mm⁻¹; data collection temperature 173 K; *R*1 = 0.0321; *wR*2 = 0.0566 (*I* > 2 (*I*)); GOF on *F*² = 1.019. Full details are described in the Supporting Information.
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First water-stable dicarbollide.

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The reaction of 3,4,5,7,8,9,10,11,12-*I*₉-C₂B₁₀H₃ with KOH/EtOH gave a mixture of the boron periodinated *nido* [1,2,3,4,5,6,9,10,11-*I*₉-7,8-C₂B₉H₂]²⁻ and [1,2,4,5,6,9,10,11-*I*₉-7,8-C₂B₉H₃]²⁻ in approximately 50% ratio. Moreover, 3,4,5,6,7,8,9,10,11,12-*I*₁₀-C₂B₁₀H₂ was mixed with KOH/EtOH to purely produce [1,2,3,4,5,6,9,10,11-*I*₉-7,8-C₂B₉H₂]²⁻.

It has been reported that 1,2-dicarbocloso-dodecaborane is readily partially degraded, one boron atom removal, by bases under controlled conditions to [7,8-C₂B₉H₁₂]⁻.¹ The deprotonation of these monoanions generates alkali metal salts of the carborane dianions [7,8-C₂B₉H₁₁]²⁻ which are easily protonated by moisture.² Boron removal from the cluster takes place via nucleophilic attack to one of the two most positive boron atoms, B(3) or B(6), which are adjacent to both cluster carbon atoms. A nucleophilic shielding process is operative on B(3) or B(6) when a bond B-R exists. This shielding prevents removal of this particular boron atom; instead the boron occupying the second reactive position is removed if it is a BH. Exceptions to this behaviour are limited to R=NH₂,³ OH,³ CH₂(CH₂)₂OH.⁴

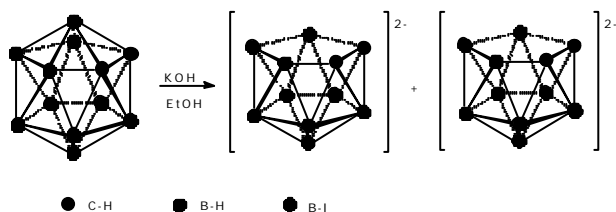
In this regard partial degradation of 3-OH-1,2-C₂B₁₀H₁₁ and 3-CH₂(CH₂)₂OH-1,2-C₂B₁₀H₁₁ yields [7,8-C₂B₉H₁₂]⁻, and partial degradation of 3-NH₂-1,2-C₂B₁₀H₁₁ yields a mixture of [7,8-C₂B₉H₁₂]⁻ and [3-NH₂-7,8-C₂B₉H₁₁]⁻. As a further example of the applicability of the nucleophilic shielding we recently reported the partial degradation of 3-*I*-1-*R*-1,2-C₂B₁₀H₁₀ (R = H, -CH₃, -C₆H₅). Again two positions were ready to the nucleophilic attack, the B(3)-*I* and the B(6)-H, however only the B(6)-H was attacked and [3-*I*-7-*R*-7,8-C₂B₉H₁₀]⁻ was generated.⁵ We will be back to this later. We decided to study what would happen if both B(3) and B(6) positions hold B-*I* *exo* bonds. The large size of *I* could facilitate that for the first time a 3,6-disubstituted species could be partially degraded. First studies were, however, directed to study the partial degradation of the recently described 3,4,5,7,8,9,10,11,12-*I*₉-C₂B₁₀H₃, *closo-1*.⁶ This has all boron positions with B-*I* bonds except B(6) where a B(6)-H exists. The large size of *I* could facilitate B-*I* removal instead of B-H removal to release steric energy. The reaction of *closo-1* with KOH/EtOH following a conventional procedure provided,⁷ according to MALDI-TOF and ¹¹B{¹H}-NMR, gave a

mixture of the boron periodinated *nido-1a* [1,2,3,4,5,6,9,10,11-*I*₉-7,8-C₂B₉H₂]²⁻ and *nido-1b* [1,2,4,5,6,9,10,11-*I*₈-7,8-C₂B₉H₃]²⁻ in approximately 50% ratio. (Scheme 1)

The MALDI-TOF analysis of the solid result of precipitating the anions from the solution with [HNMe₃]Cl displayed only two envelopes of peaks; one near 1266.8 m/z matching the simulation for [*nido-1a*+1H⁺] and a second near 1140.7 m/z that matches the simulation for [*nido-1b*+1H⁺].⁸ The solution ¹¹B-NMR spectrum of the mixture reminds very much ¹¹B-NMR spectrum of the dicarbollide [7,8-C₂B₉H₁₂]²⁻ anion.⁹ This fact along with the absence of resonances upfield, near -2/-3 ppm of the ¹H-NMR spectrum led us to hypothesize that dianions were obtained as a result of partial degradation of *closo-1*. The resolution of the crystal structure of *nido-1b* corroborated our hypothesis.¹⁰ (Figure 1) Although dianionic dicarbollides are readily generated, their synthesis requires either an aprotic solvent or a quick stabilization through metal complexation. The precipitation of this dianion represents, to the best of our knowledge, the first dicarbollide stable in a protic solvent like water.

It is then proven that the B-*I* vertex in a sterically crowded species can be removed in the same way as a B-H can be removed in a non-crowded species. The expected higher positive charge on boron in B-*I* than in B-H, and the expected higher release of steric energy in the crowded *closo-1* has not facilitated a larger removal of B-*I* than B-H, as approximately a 50% of *nido-1a* and *nido-1b* have been obtained, but it may be a necessary condition when competing B-*I* and B-H groups are present. According to the former data it could be anticipated that partial degradation of the periodinated 3,4,5,6,7,8,9,10,11,12-*I*₁₀-C₂B₁₀H₂, *closo-2*,¹¹ by B-*I* removal could take place. In a similar reaction to *closo-1*, *closo-2* was mixed with KOH/EtOH to purely produce *nido-1a*. As expected the MALDI-TOF spectrum matches the envelope near 1266.8 m/z observed for [*nido-1a*+1H⁺] from *closo-1*.

At this stage it was clear that B-*I* was susceptible to be removed in partial degradation reactions, however both *closo-1* and *closo-2* are very constrained and B-*I* removal could be the result of such crowdedness. To prove that crowdedness is not necessary to remove a B-*I* vertex, partial degradation of a non-crowded species, 3,6-*I*₂-1,2-C₂B₁₀H₁₀ (*closo-3*) with KOH/EtOH was done producing [3-*I*-7,8-C₂B₉H₁₁]⁻.

Scheme 1 Partial degradation of *closo-1*.

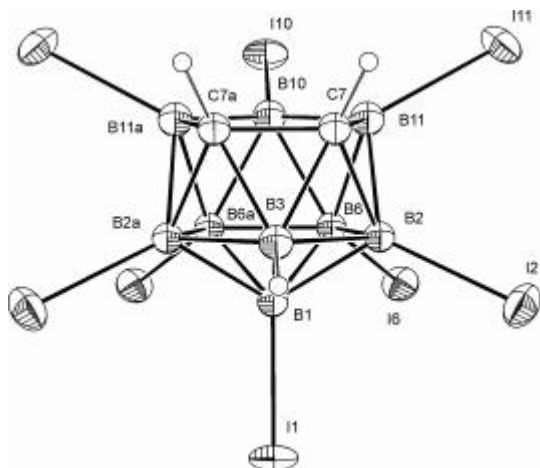


Figure 1. Perspective view of $[\text{HNMe}_3]_2[\text{nido-1b}]$ with 30% ellipsoids. (Trimethylammonium groups are omitted for clarity.) $[\text{nido-1b}]^{2-}$ anion has a mirror going through atoms I1, B1, B3, H3, B10 and I10. Selected bond lengths (\AA): C7-C7a 1.593(11) ($a = -x - \frac{1}{2}y, z$), B1-I1 2.171(11), B2-I2 2.157(8), B6-I6 2.182(7), B10-I10 2.220(13), B11-I11 2.211(9).

Therefore we have demonstrated that in addition to B-H, B-I as a vertex can also be removed from the cluster to produce an open face C_2B_3 . Results seem to confirm that chances to remove one or the other in crowded species are very comparable. However given the option to remove a B-I or B-H vertex in a non-crowded species, the vertex attacked by the nucleophile is the B-H as proven in the partial degradation of 3-I-1-R-1,2- $\text{C}_2\text{B}_{10}\text{H}_{11}$ described earlier, in which there is retention of the B-I in the resulting *nido* cluster. Furthermore we have proven the stability of the *nido-1a* $[\text{1,2,3,4,5,6,9,10,11-I}_9\text{-7,8-C}_2\text{B}_9\text{H}_2]^{2-}$ and *nido-1b* $[\text{1,2,4,5,6,9,10,11-I}_8\text{-7,8-C}_2\text{B}_9\text{H}_3]^{2-}$ species in aqueous solution that may represent the first examples of stable dicarbollide anions in water. This stability is dependent on the number of iodine groups in the molecule. In this way the $[\text{3-I-7,8-C}_2\text{B}_9\text{H}_{10}]^{2-}$ can not be isolated.

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