SYNTHESIS OF NEW *o*-CARBORANE DERIVATIVES.

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Abstract

B(3)/B(6)-disubstitution of C-unsubstituted *o*-carborane has been achieved by the combination of the boron-degradation and the boron -insertion reactions. Due to the possibility of easy Pd-catalised conversion of B-I to B-C with Grignard reagents, both, simetrical 3,6-R_2-1,2-*closo*-$C_2B_{10}H_{10}$ (R=Me, Biphenyl) and asymmetrical 3-I-6-Me-1,2-*closo*-$C_2B_{10}H_{10}$ have been obtained. Electrophilic halogenation of 3-I-1,2-*closo*-$C_2B_{10}H_{11}$ and 3,6-I_2-1,2-*closo*-$C_2B_{10}H_{10}$ leads nona and deca-B-iodinated carboranes respectively. The degradation process of these highly iodinated compounds has also been studied. Furthermore the electrophilic iodination of 3-Me-1,2-*closo*-$C_2B_{10}H_{11}$ and 3,6-Me_2-1,2-*closo*-$C_2B_{10}H_{10}$ yielded nona and deca B-substituted carboranes respectively.

Keywords

carboranes, iodinated, *nido*

Introduction

Since the utility of carborane units is dependent upon their functionalization,[1] the introduction of functional groups at the boron atoms of the icosaedral carborane cage becomes an important target of synthetic strategies. Whereas the substitution of the carbon hydrogen in the carborane clusters is easy since the C-H vertices may be deprotonated with strong bases, the chemistry of boron-substituted carboranes is less developed than the boron analogues because of the higher difficulty of introducing functional groups at the boron atoms of the carborane cage.

The electrophilic monoiodination at the 9 position[2,3] and the diiodination at the 9 and 12 vertices[2,4] of the *o*-carborane cage by treatment with I_2 in the presence of $AlCl_3$, followed by the reaction with the appropriate Grignard reagents led the obtention of alkyl and aryl substituted carboranes.[4,5] A highly iodinated *o*-carborane, 4,5,7,8,9,10,11,12-octa-B-iodo-1,2-dicarba-*closo*-dodecaborane, was later obtained by reaction with ICl and triflic acid.[6] Not only iodinated carboranes are the derivatives obtained by electrophilic substitution, B-methylated carboranes[7,8] are also part of this group.

Alternatively, another way to B-functionalize the *o*-carborane, concretely at 9 position, is activating a B-I bond by converting a B-carboranyl iodide to the corresponding carboranyl-(phenyl)iodonium salt, which undergoes highly selective nucleophilic substitution at the boron atom under mild conditions.[9]

However, using the proceedings named above, it is possible to derivatize all *o*-carborane cluster positions except the 3 and 6 because the boron atoms adjacent to carbon do not appear to be susceptible to electrophilic substitution. This join to the fact that the selective synthesis of B-substituted derivatives proved to be rather difficult,[10] enhaces the interest in the 3 and 6 carborane substitution. Although studies of a metal-induced selective B(3)/B(6)-disubstitution of *orto*-carborane–1,2-dithiolate has been done,[11] the easily disubstitution of C-unsubstituted 1,2-$C_2B_{10}H_{12}$ needs to resort to the combination of the boron-degradation and the boron -insertion reactions.

Since 1965 when Hawthorne first introduced the boron insertion reaction,[12] several examples of B-substituted carboranes at the 3 vertex have been published.[4,13]

Even a 3,6-disubstituted carborane was obtained by reaction of $[3\text{-Ph-}7,8\text{-}C_2B_9H_{10}]^{2-}$ with BCl_2Ph.[12b] However, this method depends on the availability of dichloroborane derivatives and also on the difficulty to obtain 3,6-disubstituted carboranes with groups that are not retained under degradation basic conditions .

Here we present the synthesis of $3,6\text{-}I_2\text{-}1,2\text{-}C_2B_{10}H_{10}$ which, due to the presence of two iodine atoms at the 3 and 6 positions, have an elevated versatility in order to easily obtain B-derivatives substituted at the less reactive boron atoms in front of an electrophilic attack. The reaction of this species with different Grignard reagents allows the obtention of a new serial of carborane derivatives.

The $3,6\text{-}I_2\text{-}1,2\text{-}closo\text{-}C_2B_{10}H_{10}$ was prepared starting from $3\text{-}I\text{-}1,2\text{-}closo\text{-}C_2B_{10}H_{11}$.[4] Since the deboronation of this monoiodinated compound with KOH/EtOH under reflux conditions and subsequent precipitation with $[HNMe_3]Cl$ led to the formation of $[HNMe_3][3\text{-}I\text{-}7,8\text{-}nido\text{-}C_2B_9H_{11}]$ in good yield,[14] another B-I insertion was possible reacting $[3\text{-}I\text{-}7,8\text{-}C_2B_9H_{10}]^{2-}$ with BI_3 obtaining the $3,6\text{-}I_2\text{-}1,2\text{-}closo\text{-}C_2B_{10}H_{10}$. Due to the possibility of easy Pd-catalised conversion of B-I to B-C with Grignard reagents, both, simetrical $3,6\text{-}R_2\text{-}1,2\text{-}closo\text{-}C_2B_{10}H_{10}$ (R=Me, Biphenyl) and asymmetrical $3\text{-}I\text{-}6\text{-}Me\text{-}1,2\text{-}closo\text{-}C_2B_{10}H_{10}$ have been obtained. Electrophilic halogenation of $3\text{-}I\text{-}1,2\text{-}closo\text{-}C_2B_{10}H_{11}$ and $3,6\text{-}I_2\text{-}1,2\text{-}closo\text{-}C_2B_{10}H_{10}$ led nona[15] and deca-B-iodinated carboranes[16] respectively. The degradation process of these highly iodinated compounds was also studied. Furthermore the electrophilic iodination of $3\text{-}Me\text{-}1,2\text{-}closo\text{-}C_2B_{10}H_{11}$ and $3,6\text{-}Me_2\text{-}1,2\text{-}closo\text{-}C_2B_{10}H_{10}$ yielded nona[15] and deca[17] B-substituted carboranes respectively.

All new carboranes were produced in good yields. Compounds were initially characterised by microanalysis and IR spectroscopy. NMR spectra (^{11}B, ^{13}C, ^{1}H) of the compounds are fully consistent with the proposed formulae.

Results and Discussion

1. Synthetic Studies

I.- Boron iodinated *closo-o-*carborane derivatives:

I.a) New $3,6\text{-}I_2$-*o*-carborane derivative:

That B(3), in $1\text{-}R\text{-}2\text{-}R'\text{-}1,2\text{-}closo\text{-}C_2B_{10}H_{10}$ compounds, is the atom most susceptible to nucleophilic attack was demonstrated long ago by Hawthorne and co-workers.[18] Removal of B(3) leads to the *nido* $[7\text{-}R\text{-}8\text{-}R'\text{-}7,8\text{-}C_2B_9H_{10}]^-$ anion and its rich derivative chemistry. The low electron density at B(3) that facilitates its removal is also what prevents the formation of B3-X bonds by normal electrophilic substitution, a process that readily takes place first at B(9), B(12) followed by B(8) and B(10).[19] Thus there exists the need to have recourse to the insertion of a B-I vertex to obtain iodinated derivatives at the 3 and its equivalent 6 position. Degradation of *o*-carborane and the further insertion of a B-I vertex lead to the monoiodinated 3-I-1,2-*closo*-$C_2B_{10}H_{11}$. Further degradation on it drives to the 3-I-7,8-*nido*-undecaborate(-1) (Sheme a). The bridging hydrogen atom on the open face of 3-I-7,8-*nido*-undecaborate(-1) was removed by basic attack[20] (Scheme b) and the new 3-I-7,8-*nido*-undecaborate(-2) species readily can react with BI_3 to complete a C_2B_{10} *closo* cage in with the icosahedral cage has been reformed with the insertion of a new B-I vertex on afforded the 3,6-diiodo derivative (Scheme b).

I.b) New 3,4,5,7,8,9,10,11,12-nona-B-iodo-1,2-*closo*-$C_2B_{10}H_3$ derivative.

Following a reported procedure on iodination reactions,[6],[21] 3-I-1,2-*closo*-$C_2B_{10}H_{11}$ was mixed with iodine monochloride in the ratio 1:30 in the presence of triflic acid. Following heating at 90ºC for 3 days, and after working up 3,4,5,7,8,9,10,11,12-nona-B-iodo-1,2-dicarba-*closo*-dodecaborane was obtained in a 94% yield. (Scheme c)

I.c) New 3,4,5,6,7,8,9,10,11,12-deca-B-iodo-1,2-*closo*-$C_2B_{10}H_2$ derivative.

Following the same procedure as before, 3,6-I_2-1,2-*closo*-$C_2B_{10}H_{10}$ was mixed with iodine monochloride in the ratio 1:44 in the presence of triflic acid. Following heating at 90ºC for 5 days, and after working up 3,4,5,6,7,8,9,10,11,12-deca-B-iodo-1,2-dicarba-*closo*-dodecaborane was obtained in a 73% yield.

All boron iodinated *o*-carborane derivatives were obtained in a good yield and were initially characterised by microanalysis and IR spectroscopy. NMR spectra (^{11}B, ^{13}C, ^{1}H) and mass spectra of the compounds are fully consistent with the proposed formulae.

II.- Boron alkylated and arylated *closo*-*o*-carborane derivatives:

II.a) Alkyl and Aryl-de-halogenation reactions at B(3) and B(6): In extending the chemistry of 3-R-6-R'-*o*-carborane derivatives, aryl and alkyl-de-halogenation reactions were performed on 3,6-I_2-1,2-*closo*-$C_2B_{10}H_{10}$, using either an alkyl (methyl) or an aryl (biphenyl) substituent.

The reaction consists on the B-C cross coupling reaction on 3,6-I_2-1,2-*closo*-$C_2B_{10}H_{10}$ in the presence of [$PdCl_2(PPh_3)_2$] and CuI using the appropriate aryl or alkyl magnesium bromide reagent as a source of the organic group in THF solution under refluxing conditions (Scheme d). Using a ratio 3,6-I_2-1,2-*closo*-$C_2B_{10}H_{10}$/ Grignard derivative 1:10, new 3,6-R_2-1,2-*closo*-$C_2B_{10}H_{10}$ (R= methyl, biphenyl) species were obtained in a high yield (97, 96%).

Referring to the asymmetric carborane could be obtained following two synthetic procedures. The first one was based on the reaction of the 3,6-I_2-1,2-*closo*-$C_2B_{10}H_{10}$ with the methyl magnesium bromide (1:5). The second one, wich afforded a higher yield, consisted on the combination of a partial degradation of the 3-Me-1,2-*closo*-$C_2B_{10}H_{11}$ and a B-I insertion through the reaction of the [3-Me-7,8-*nido*-$C_2B_9H_{10}$]$^{2-}$ with BI_3.

II.b) New 3,4,5,7,8,9,10,11,12-nona-B-methyl-1,2-*closo*-$C_2B_{10}H_3$ derivative.

Following a reported procedure on methylation reaction,[7,22] 3-I-1,2-$C_2B_{10}H_{11}$ reacted with methyl iodine in the presence of aluminium trichloride. Refluxing the mixture for 2 days, and after working up 3,4,5,7,8,9,10,11,12-nona-B-methyl-1,2-dicarba-*closo*-dodecaborane was obtained in a 98% yield (Scheme e).

II.c) New 9-$I_{0.707}H_{0.293}$-12-$Cl_{0.566}H_{0.434}$-3,4,5,6,7,8,10,11-$(CH_3)_8$-1,2-*closo*-$C_2B_{10}H_2$.

Following the same procedure as before, 3,6-$(CH_3)_2$-1,2-$C_2B_{10}H_{10}$ was mixed with methyl iodide and $AlCl_3$. Refluxing the mixture for 2 days, and after working up a mixture of compounds that was crystallized as 9-$I_{0.707}H_{0.293}$-12-$Cl_{0.566}H_{0.434}$-3,4,5,6,7,8,10,11-$(CH_3)_8$-1,2-*closo*-$C_2B_{10}H_2$ was obtained.

III.- Boron iodinated *nido*-*o*-carborane derivatives:

All these boron substituted carboranes were reacted with KOH/EtOH. While reacting the plain *o*-carborane under these conditions, the low electron density at B(3) facilitates its removal, in the case of 3,6-$(CH_3)_2$-1,2-*closo*-$C_2B_{10}H_{10}$ the presence of methyl groups in B(3)and B(6) prevents its partial degradation. The same happens for the 3,6-$(biph)_2$-1,2-*closo*-$C_2B_{10}H_{10}$. Moreover the 3,4,5,7,8,9,10,11,12-$(CH_3)_9$-1,2-*closo*-$C_2B_{10}H_3$ stays unreactive in front of the typical degradation conditions eventhough the B(6) is bonded to a hydrogen atom. However, the deboronation of the 3,6-diodinated compound with KOH/EtOH under reflux conditions and subsequent precipitation with $[HNMe_3]Cl$ led to the formation of $[HNMe_3][3\text{-}I\text{-}7,8\text{-}\textit{nido}\text{-}C_2B_9H_{11}]$. The reaction of $3,4,5,7,8,9,10,11,12\text{-}I_9\text{-}1,2\text{-}\textit{closo}\text{-}C_2B_{10}H_3$ with KOH/EtOH following a conventional procedure provided, according to MALDI-TOF combined with $^{11}B\{^1H\}$-NMR, gave a mixture of the fully deprotonated $[1,2,3,4,5,6,9,10,11\text{-}I_9\text{-}7,8\text{-}\textit{nido}\text{-}C_2B_9H_2]^{2-}$ and $[1,2,4,5,6,9,10,11\text{-}I_8\text{-}\ \textit{nido}\text{-}7,8\text{-}C_2B_9H_3]^{2-}$ in approximately 50% ratio. The MALDI-TOF analysis of the solid result of precipitating the anions from the solution displayed only two envelops of peaks; one near 1266.8 m/z that matches the simulation for $[1,2,3,4,5,6,9,10,11\text{-}I_9\text{-}7,8\text{-}C_2B_9H_3]^-$ as a result of $[1,2,3,4,5,6,9,10,11\text{-}I_9\text{-}7,8\text{-}C_2B_9H_2]^{2-}$ getting a proton and another near 1140.5 m/z that matches the simulation for $[1,2,4,5,6,9,10,11\text{-}I_8\text{-}7,8\text{-}C_2B_9H_4]^-$ as a result of $[1,2,4,5,6,9,10,11\text{-}I_8\text{-}7,8\text{-}C_2B_9H_3]^{2-}$ getting a proton. The resolution of the crystal structure supported that this can be considered the first dicarbollide stable in a protic solvent like water. On the other hand, during the reaction of the periodinated $3,4,5,6,7,8,9,10,11,12\text{-}I_{10}\text{-}C_2B_{10}H_2$, with KOH/EtOH, since in this case both B(3) and B(6) atoms are bonded to an iodine, the nucleophilic atack takes place in one of these atoms producing only $[1,2,3,4,5,6,9,10,11\text{-}I_9\text{-}\textit{nido}\text{-}7,8\text{-}C_2B_9H_2]^{2-}$. In this case the MALDI-TOF spectrum shows only one envelop of peaks near 1266.8 m/z.

The reaction of the 3-substituted *o*-carboranes $3\text{-}Me\text{-}1,2\text{-}\textit{closo}\text{-}C_2B_{10}H_{11}$ and 3-atracil-$1,2\text{-}\textit{closo}\text{-}C_2B_{10}H_{11}$ with KOH/EtOH led to the obtention of $[3\text{-}Me\text{-}\textit{nido}\text{-}7,8\text{-}C_2B_9H_{11}]^-$ and $[3\text{-antracil-}\textit{nido}\text{-}7,8\text{-}C_2B_9H_{11}]^-$ respectively.

All boron substituted *o*-carborane derivatives were obtained in a good yield and were initially characterised by microanalysis and IR spectroscopy. NMR spectra (^{11}B, ^{13}C, ^{1}H) and MALDI-TOF spectra of the compounds are fully consistent with the proposed formulae

2. Molecular and Crystal Structures of $3,6\text{-}I_2\text{-}1,2\text{-}\textit{closo}\text{-}C_2B_{10}H_{10}$, $3,6\text{-}Me_2\text{-}1,2\text{-}\textit{closo}\text{-}C_2B_{10}H_{10}$, $3\text{-}I\text{-}6\text{-}Me\text{-}1,2\text{-}\textit{closo}\text{-}C_2B_{10}H_{10}$ and $3,4,5,6,7,8,9,10,11,12\text{-}I_{10}\text{-}1,2\text{-}\textit{closo}\text{-}C_2B_{10}H_2\cdot(CH_3)_2COHCH_2COCH_3$.

As an adjunct to our theoretical and synthetic work we have studied the species $3,6\text{-}I_2\text{-}1,2\text{-}\textit{closo}\text{-}C_2B_{10}H_{10}$, $3,6\text{-}Me_2\text{-}1,2\text{-}\textit{closo}\text{-}C_2B_{10}H_{10}$, $3\text{-}I\text{-}6\text{-}Me\text{-}1,2\text{-}\textit{closo}\text{-}C_2B_{10}H_{10}$

and 3,4,5,6,7,8,9,10,11,12-I_{10}-*closo*-1,2-$C_2B_{10}H_2 \cdot (CH_3)_2COHCH_2COCH_3$ by single crystal *X*-ray diffraction.

Molecular structures of 3,6-I_2-1,2-$C_2B_{10}H_{10}$, 3,6-Me_2-1,2-$C_2B_{10}H_{10}$, 3-I-6-Me-1,2-$C_2B_{10}H_{10}$ and 3,4,5,6,7,8,9,10,11,12-I_{10}-1,2-*closo*-$C_2B_{10}H_2 \cdot (CH_3)_2COHCH_2COCH_3$ are presented in Figures 1, 2, 3 and 4, respectively. Selected bond lengths and angles for the compounds are listed in Tables 1, 2, 3 and 4, and crystallographic data are summarized in Table 5.

The structures of 3,6-I_2-*closo*-1,2-$C_2B_{10}H_{10}$, 3,6-Me_2-*closo*-1,2-$C_2B_{10}H_{10}$ and 3-I-6-Me-1,2-closo-$C_2B_{10}H_{10}$ are formed of well-separated molecules without any short contact between them. The molecule of 3,6-I_2-*closo*-1,2-$C_2B_{10}H_{10}$ has approximate C_{2v} symmetry but crystallographic symmetry of the compound is C_1. 3,6-Me_2-*closo*-1,2-$C_2B_{10}H_{10}$ assumes crystallographic two-fold symmetry with the symmetry axis going through the midpoints of the bonds C1-C1^a and B9-B9^a (^{a} refers equivalent position $-x$, y, $-z+3/2$. However, approximate symmetry of the latter molecule is C_{2v}. 3-I-6-Me-1,2-*closo*-$C_2B_{10}H_{10}$ assumes mirror symmetry with the symmetry plane passing through the atoms I3, B3, B6, C6, B8 and B10, and thus the symmetry element is bisecting the C1-C1^b bond (^{b} refers equivalent position $-x$, y, z).

In the structure of 3,4,5,6,7,8,9,10,11,12-I_{10}-1,2-*closo*-$C_2B_{10}H_2 \cdot (CH_3)_2COHCH_2COCH_3$ the carborane cage is connected to the diacetone alcohol with hydrogen bond. The hydrogen bond is formed by the hydrogen atom bonded to the cage carbon C1 and the hydroxyl hydrogen atom O1 of the solvent. Relevant parameters for the hydrogen bond are: C1$\cdot\cdot\cdot$O1 = 3.043(4) Å and C1-H1$\cdot\cdot\cdot$O1 = 158.6°. Moreover, intermolecular hydrogen bond is also formed between O1 and O2 atoms of the solvent molecule.

In these four compounds the $C_{cluster}$-$C_{cluster}$ distances vary in the range 1.613(5) – 1.645(5) Å. These values agree well with the corresponding values observed the 1,2-disubstituted *o*-carborane derivatives.[23] These values are also in line with our earlier tresults for 1,2- dialkylsubstituted *o*-carborane derivatives and longer distances have been found for the derivatives bearing aryl groups, phosphorus or sulfur substituents at the cluster carbons.[24]

3. NMR Spectral Considerations

^{11}B NMR

The sensitivity of the electron distribution in carboranes to the presence of substituents has long been apparent.[25] For *closo* icosahedral carborane derivatives of 1-R-1,2-*closo*-$C_2B_{10}H_{11}$, we showed that the chemical shifts of the cluster boron atoms in the ^{11}B NMR spectra vary with the substituent R.[26] Hermanek and coworkers proposed that the boron atom opposite to the point of attachment of the substituent, the "antipodal atom", increases with the rising electron donation of the substituent.[27]

It was previously demonstrated that the presence of an iodine at the B(3) in *o*-carborane changes considerably the aspect of the ^{11}B NMR spectrum specially the B(3) signal.[13a] The $^{11}B\{^1H\}$ NMR spectrum of 3,6-I_2-1,2-*closo*-$C_2B_{10}H_{10}$ differs from the 3,6-Me_2-1,2-*closo*-$C_2B_{10}H_{10}$. The first present a 2:2:4:2 pattern in the range –0.1/ -27.6 ppm and the second presents the pattern 2:2:6 in the range –2.0/ -11.8 ppm. Neither the resonance at –27.6 ppm for the compound 3,6-I_2-1,2-*closo*-$C_2B_{10}H_{10}$ nor the one at –3.3 ppm for the compound 3,6-Me_2-1,2-*closo*-$C_2B_{10}H_{10}$ split into a doublet in the ^{11}B NMR spectra, indicating that these resonances correspond to the B-I and the B-Me vertexes. If the ^{11}B NMR spectrum of 3,6-I_2-1,2-*closo*-$C_2B_{10}H_{10}$ and 3,6-Me_2-1,2-*closo*-$C_2B_{10}H_{10}$ are compared to that for *o*-carborane, we note that B(3) and B(6) resonances are shifted 13 ppm upfield from *o*-carborane due the dihalosubstitution and 11 ppm downfield due the dialkylsubstitution. Figure 1 shows how the $^{11}B\{^1H\}$ NMR spectra resonances attributable to the different types of boron nuclei in compounds 3,6-I_2-1,2-*closo*-$C_2B_{10}H_{10}$, 3,6-Me_2-1,2-*closo*-$C_2B_{10}H_{10}$ and 1,2-*closo*-$C_2B_{10}H_{12}$ change in chemical shift.

^{1}H-NMR

Not only the substituents affect the ^{11}B NMR spectrum, the ^1H and ^{13}C NMR spectra can be affect by the presence of substituents at B(3) and B(6). Table 6 shows the chemical shifts of 3- substituted and 3,6- disubstituted *o*-carborane derivatives in the ^1H and ^{13}C NMR spectra. If we compare the chemical shift of the $C_{cluster}$-H of the 3-R-1,2-*closo*-$C_2B_{10}H_{11}$ with the chemical shift of the parent 1,2-*closo*-$C_2B_{10}H_{12}$ we observe that the resonance moves down field aproximately 0.28 and 0.18 ppm for R= I and biphenyl respectively and it moves upfield 0.12 ppm for R= Me. The same value and tendency are observed comparing 3,6-R_2-1,2-*closo*-$C_2B_{10}H_{10}$ with 3-R-1,2-*closo*-$C_2B_{10}H_{11}$. In this paper we show how both the ^1H-NMR chemical shift of the cluster $C_{cluster}$-H and the

$^{13}C\{^1H\}$-NMR chemical shift of the carbons of the cluster, depends on the substituent at B(3) and B(6) positions, and that the effect is additive.

We performed ab initio calculations at the Hartree-Fork 3-21G level on 3-Me-1,2-$C_2B_{10}H_{11}$, 3,6-Me_2-1,2-$C_2B_{10}H_{10}$ and 1,2-$C_2B_{10}H_{12}$ and the calculated Mulliken charges[28] on hydrogen atoms bonded to $C_{cluster}$ gave values of 0.316, 0.327 and 0.334 respectively. These values show an excellent parallel with ^1H-NMR chemical shifts. It seems that the acidity of the C-H in the carborane cluster can be modulated by the nature of the substituent at B(3) and B(6) positions.

As it can be concluded comparing the ^1H chemical shifts of the $C_{cluster}$-H of 1,2-$C_2B_{10}H_{12}$, 3-I-1,2-$C_2B_{10}H_{11}$ and 3,6-I_2-1,2-$C_2B_{10}H_{10}$, the acidity of the hydrogen atom increases with the number of iodines in the molecule. In fact, for the per-B-iodinated *o*-carborane the δC-H ($CDCl_3$) is 7.37 ppm, 3.82 ppm downfield of the the unsubstituted carborane. The acidic character of these $C_{cluster}$-H for the 3,4,5,6,7,8,9,10,11,12-I_{10}-1,2-$C_2B_{10}H_2$ has been proved by the synthesis of the first water stable salt of 1,2-$C_2B_{10}H_{12}$ derivative, $[N(PPh_3)_2]$ $[1,2\text{-}C_2B_{10}I_{10}H]$, obtained through reaction of 1,2-$C_2B_{10}I_{10}H_2$ with different bases. Intents of growing the crystal structure of $N(PPh_3)_2]$ $[1,2\text{-}C_2B_{10}I_{10}H]$ through crystallization in a solution of acetone lead the protonation of the anion and to the obtantion of 3,4,5,6,7,8,9,10,11,12-I_{10}-1,2-*closo*-$C_2B_{10}H_2 \cdot (CH_3)_2COHCH_2COCH_3$.

4. IR Considerations

The BH stretching band of 1,2-dicarba-*closo*-dodecaboranes is a very intense broad band near 2600 cm^{-1}. This broad band is often split into several well-resolved peaks. This splitting can sometimes be used to draw a conclusion about non-equivalent BH bonds, thus treating the IR bands as NMR signals. The stretching and bending CH modes on 1,2-dicarba-*closo*-dodecaboranes are very useful. If the two CH bonds in a 1,2-dicarba-*closo*-dodecaborane derivatives become non-equivalent, two stretching bands, ν(CH), with different frequencies and intensities may be expected in the spectrum. This indicates that these two groups are nonequivalent. In solid state the ν(CH) band are extremely sensitive to the molecular structure as well as to intra- and intermolecular effects. IR spectroscopy can bring information on the ability of carboranes to serve as CH proton donors in hydrogen bonding. Figure 5 shows IR spectra of 1,2-*closo*-$C_2B_{10}H_{12}$ and 1,2-H_2-1,2-*closo*-$C_2B_{10}I_{10}$.

5. Theoretical calculation

Electrophilic iodination of 3,6-I_2-1,2-$C_2B_{10}H_{10}$ yields per-B-iodinated 1,2-$C_2B_{10}I_{10}$, however electrophilic methylation of 3,6-Me_2-1,2-$C_2B_{10}H_{10}$ yielded a mixture of four octa-methylated carboranes (crystallized as 9-$I_{0.707}H_{0.293}$-12-$Cl_{0.566}H_{0.434}$-3,4,5,6,7,8,10,11-$(CH_3)_8$-1,2-*closo*-$C_2B_{10}H_2$) in which the B(9) and B(12) atoms, the most susceptible to electrophilic substitution are not methylated. This supported our first hypothesis that the role of Me groups in boron clusters may not be electron-donating. To aid the synthetic studies, we performed ab initio calculations at the Hartree-Fork 3-21G level[28] on 3-Me-1,2-$C_2B_{10}H_{11}$, 3,6-Me_2-1,2-$C_2B_{10}H_{10}$ and 1,2-$C_2B_{10}H_{12}$. A major difference had appeared; the cluster total charge[29] was increasing parallel to the increasing number of Me groups on boron atoms with each Me group approximately increasing the cluster charge in 0.5 units, as computed from 3-Me-1,2-$C_2B_{10}H_{11}$, or 3,6-Me_2-1,2-$C_2B_{10}H_{10}$. If the original charge on 1,2-$C_2B_{10}H_{12}$ was -0.9, addition of 8 Me groups would alter the cluster's charge to approximately +3.1 (computed HF 3-21G on compound 4,5,7,8,9,10,11,12-Me_8-1,2-*closo*-$C_2B_{10}H_4$ 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 charge and the electrophile, and not the point charges. Hoffmann and Libit pointed out that the substitutent effect of Me groups in $\pi-$electron systems are due not to electron donation by the methyl substituent but to a polarization caused by the $\pi-$system.[30] These conclusions are fully confirmed with the synthesis of 9-X-12-Y-3,4,5,6,7,8,10,11-Me_8-1,2-$C_2B_{10}H_2$ (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-Me_8-1,2-$C_2B_{10}H_2$. If the 9,12 positions are not considered, 9-$I_{0.707}H_{0.293}$-12-$Cl_{0.566}H_{0.434}$-3,4,5,6,7,8,10,11-Me_8-1,2-$C_2B_{10}H_2$ is the complementary compound of 4,5,7,8,9,10,11,12-Me_8-1,2-*closo*-$C_2B_{10}H_4$. Both compounds have methyl substituents at B(4,5,7,8,10,11) vertexes. The compound 4,5,7,8,9,10,11,12-Me_8-1,2-*closo*-$C_2B_{10}H_4$ has Me groups in B(9,12) but not in B(3,6), 9-$I_{0.707}H_{0.293}$-12-$Cl_{0.566}H_{0.434}$-3,4,5,6,7,8,10,11-Me_8-1,2-$C_2B_{10}H_2$ has Me groups in B(3,6) but not in B(9,12). HF/ 3-21G calculations gives a cluster total charge of +3.309

on 9-$I_{0.707}H_{0.293}$-12-$Cl_{0.566}H_{0.434}$-3,4,5,6,7,8,10,11-Me_8-1,2-$C_2B_{10}H_2$ that is very similar to +3.374 obtained with 4,5,7,8,9,10,11,12-Me_8-1,2-*closo*-$C_2B_{10}H_4$. Table 7 shows calculated Mulliken charges by geometry optimizations at the Hartree-Fork 3-21G level on several B-C methylated *o*-carborane derivatives.

Experimental Section

General Pocedures. Elemental analyses were performed using a Carlo Erba EA1108 microanalyser. IR spectra were recorded from KBr pellets on a Shimadzu FTIR-8300 spectrophotometer. ^{1}H and $^{1}H\{^{11}B\}$ NMR (300.13 MHz), $^{13}C\{^{1}H\}$ NMR (75.47 MHz) and ^{11}B NMR (96.29 MHz) spectra were recorded with a Bruker ARX 300 instrument equipped with the appropriate decoupling accessories. Chemical shift values for ^{11}B NMR spectra were referenced to external $BF_3 \leftarrow OEt_2$ and those for ^{1}H, $^{1}H\{^{11}B\}$ and $^{13}C\{^{1}H\}$ NMR spectra were referenced to $SiMe_4$. Chemical shifts are reported in units of parts per million downfield from reference, and all coupling constants in Hz. MS spectra for ionic species were recorded using a Bruker Biflex MALDI-TOF mass spectrometer and using a FIA-ES/MS (Shimadzu AD VP/ API 150) for neutral species.

Unless otherwise noted, all manipulations were carried out under a dinitrogen atmosphere using standard vacuum line techniques. Diethyl ether and THF were distilled from sodium benzophenone prior to use. Hexane was dried over molecular sieves and deoxygenated before use. A 1.6 M solution of *n*-butyllithium in hexanes, iodine monochloride, aluminium trochloride, triflic acid, 4-biphenylmagnesium bromide, methylmagnesium bromide, methyl iodine from Aldrich; and BI_3 from Alfa were used as purchased. 3-I-1,2-*closo*-$C_2B_{10}H_{11}$,[4] 3-antracenyl-1,2-*closo*-$C_2B_{10}H_{11}$,[13a] 3-biphenyl-1,2-*closo*-$C_2B_{10}H_{11}$[13a] and $[HNMe_3][7,8\text{-}C_2B_9H_{11}I]$[14] were synthesized according to the literature.

3,6-diiodo-1,2-dicarba-*closo*-dodecaborane. To a solution of $[HNMe_3][7,8\text{-}C_2B_9H_{11}I]$ (1.3 g, 4 mmol) in anhydrous diethyl ether (20 mL) at 0 ºC, was added dropwise with stirring *n*-butyllithium (5 mL, 8 mmol). Once the addition was completed, the reaction mixture was stirred at room temperature for an additional 2h and then heated to reflux for 4h. After evaporation of the solvent, anhydrous hexane (20 mL) was added to the remaining solid. A solution of BI_3 (2.35 g, 6 mmol) in 20 mL of hexane was then added dropwise with stirring at 0 ºC. Stirring was continued for 5h at room temperature once the addition was completed. The excess boron triiodide was decomposed by carefully addition of 10 mL of water. The organic layer was separated from the mixture and the aqueous layer extracted with hexane (3 x 10 mL). The combined organic phase was dried over $MgSO_4$, and the solvent removed at the water pump. The crude product was recristallized from hexane obtaining 3,6-diiodo-1,2-dicarba-*closo*-dodecaborane. Yield

1.4 g (88 %). Crystals suitable for an X-ray diffraction experiment were grown by slow evaporation of a concentrated hexane solution. Elemental analysis calcd. (%) for: $C_2H_{10}B_{10}I_2$ (396.02): C 6.07, H 2.55; found C 6.52, H 2.47. IR (KBr), ν [cm^{-1}]= 3049, 3038 ($C_{cluster}$ -H), 2598, 2582, 2552 (B-H). ^1H NMR ($CDCl_3$): δ= 4.10 (br s, 2H; $C_{cluster}$-H), 3.50-1.50 (br m, 8H; B-H). $^1H\{^{11}B\}$ NMR: δ= 4.10 (br s, 2H; $C_{cluster}$-H), 3.04 (br s, 2H; B-H), 2.64 (br s, 4H; B-H), 2.54 (br s, 2H; B-H). $^{13}C\{^1H\}$ NMR: δ = 65.0 ($C_{cluster}$). ^{11}B NMR: δ = -0.1 (d, ^1J(B,H)= 153, 2B; (B9, B12), -8.6 (d, ^1J(B,H)= 155, 2B; B8, B10), -9.6 (d, ^1J(B,H)= 111, 4B; B4, B7, B5, B11), -27.6 (s, 2B; B3, B6).

3,6-dibiphenil-1,2-dicarba-*closo*-dodecaborane. To a stirring solution of 3,6-diiodo-1,2-dicarba-*closo*-dodecaborane (396 mg, 1mmol) in THF (10 mL) at 0 ºC, was added, dropwise, a solution of 4- biphenylmagnesium bromide (5 mL, 10 mmol) in the same solvent. After stirring at room temperature for 30 min, [$PdCl_2(PPh_3)_2$] (28 mg, 4% equiv.) and CuI (7.6 mg, 4% equiv.) were added in a single portion, following which the reaction was heated to reflux for 4 days. The solvent was removed, and 20 mL of diethyl ether was added to the residue. The excess of Grignard reagent was destroyed by slow addition of dilute HCl. The organic layer was separated from the mixture, and the aqueous layer was extracted with diethyl ether (3x 10 mL). The combined organic phase was washed with water and dried over $MgSO_4$. The solvent was removed and the residue was extracted with hexane. The final compound was purified by flash silica gel chromatography using dicloromethane: hexane (4:1) as the eluting solvent to give 3,6-dibiphenil-1,2-dicarba-*closo*-dodecaborane. Yield 0.43 g (96 %). Elemental analysis calcd. (%) for $C_{26}H_{28}B_{10}$ (448.62): C 69.6, H 6.29; found C 69.90, H 6.30. IR (KBr), ν [cm^{-1}]= 3076, 3049, 3044 (C_{aryl}-H),($C_{cluster}$-H), 2584, 2547 (B-H). ^1H NMR ($CDCl_3$): δ= 7.73-7.30 (m, 18H; H_{aryl}), 3.92 (br s, 2H; $C_{cluster}$-H), 3.00-1.50 (br m, 8H; B-H). $^1H\{^{11}B\}$ NMR: δ= 7.73-7.30 (m, 18H, H_{aryl}), 3.92 (br s, 2H, $C_{cluster}$-H), 2.62 (br s, B-H), 2.47 (br s, B-H). $^{13}C\{^1H\}$ NMR: δ= 143.4, 142.0, 141.2, 134.3, 130.3, 129.4, 128.4, 127.8 (C_{aryl}), 59.8 (s, $C_{cluster}$). ^{11}B NMR: δ= -2.0 (d, ^1J(B,H)= 150, 2B), -4.7 (s, 2B), -12.6 (d, 6B).

3,6-dimethyl-1,2-dicarba-*closo*-dodecaborane. In an analogous manner, 3,6-diiodo-1,2-dicarba-*closo*-dodecaborane (0.50 g, 1.26 mmol) in THF (20 mL) at 0 ºC, was added, dropwise, a solution of methylmagnesium bromide (4.2 mL, 3M, 12.6 mmol).

After stirring at room temperature for 30 minutes [$PdCl_2(PPh_3)_2$] (35.4 mg, 4% equiv.) and CuI (9.6 mg, 4% equiv.) were added in a single portion, following which the reaction was heated to reflux overnight. The solvent was removed and 20 mL of diethylether was added to the residue. The excess of Grignard reagent was destroyed by slow addition of dilute HCl. The organic layer was separated from the mixture, and the aqueous layer was extracted with diethyl ether (3x 10 mL). The combined organic phase was washed with water and dried over $MgSO_4$. The final compound was purified by flash silica gel chromatography using dicloromethane: hexane (3:7) as the eluting solvent to give 3,6-dimethyl-1,2-dicarba-*closo*-dodecaborane. Yield 210 mg (97 %). Crystals suitable for an X-ray diffraction experiment were grown by slow evaporation of a concentrated hexane solution. Elemental analysis calcd. (%) for $C_4H_{16}B_{10}$ (172.28): C 27.89, H 9.36; found C 27.58, H 9.30. IR (KBr), ν [cm^{-1}]= 3057 ($C_{cluster}$-H), 2961, 2918 (C_{alq}-H) 2586, 2571, 2557 (B-H). ^{1}H NMR ($CDCl_3$): δ= 3.31 (br s, 2H; $C_{cluster}$-H), 3.00-1.50 (m, 8H; B-H), 0.65 (s, 6H; CH_3). $^1H\{^{11}B\}$ NMR: δ= 3.31(br s, 2H; $C_{cluster}$-H), 2.26 (br s, 2H; B-H), 2.13 (br s, 4H; B-H), 2.07 (br s, 2H; B-H). $^{13}C\{^1H\}$ NMR: δ= 61.3 (s; $C_{cluster}$), 30.4 (s; CH_3). ^{11}B NMR: δ= -2.0 (d, ^1J(B,H)= 150, 2B; B9, B12), -3.3 (s, 2B; B3, B6), -11.8 (d, ^1J(B,H)= 159, 6B; B4, B5, B7, B8, B10, B11).

3-Iodo-6-methyl-*o*-carborane

a) In an analogous manner, 3,6-diiodo-1,2-dicarba-*closo*-dodecaborane (0.50 g, 1.26 mmol) in THF (20 mL) at 0 ºC, was added, dropwise, a solution of methylmagnesium bromide (2.1 mL, 3M, 6.3 mmol). After stirring at room temperature for 30 minutes [$PdCl_2(PPh_3)_2$] (17.7 mg, 4% equiv.) and CuI (4.8 mg, 4% equiv.) were added in a single portion, following which the reaction was heated at reflux for 5h. The solvent was removed and 20 mL of diethylether was added to the residue. The excess of Grignard reagent was destroyed by slow addition of dilute HCl. The organic layer was separated from the mixture, and the aqueous layer was extracted with diethyl ether (3x 10 mL). The combined organic phase was washed with water and dried over $MgSO_4$. The final compound was purified by flash silica gel chromatography using dicloromethane: hexane (3:5) as the eluting solvent to give 3-yodo-6-methyl-1,2-dicarba-*closo*-dodecaborane. Yield 57.3 mg (16%).

b) To a solution of [$HNMe_3$][3-CH_3-7,8-$C_2B_9H_{11}$] (3.5 g, 16.9 mmol) in anhydrous diethylether (40 mL) at 0 ºC, was added dropwise with stirring butyllithium (21.1 ml, 33.8 mmol). Once the addition was completed the reaction mixture was stirred at room temperature for an additional 2h and then heat to reflux for 4h. After evaporation of the solvent, anhydrous hexane (40 mL) was added to the remaining solid. A solution of BI_3 (9.9 g, 25.35 mmol) in 40 mL of hexane was then added dropwise with stirring at 0 ºC. Stirring was continued for 5h at room temperature once the addition was completed. The excess boron triiodide was decomposed by carefully addition of 10 mL of water. The organic layer was separated from the mixture and the aqueous layer extracted with hexane (3x10mL). The combined organic phase was dried over $MgSO_4$, and the solvent removed at the water pump. The crude product was recristallized in hexane obtaining 3-Iodo-6-methyl-1,2-dicarba-*closo*-dodecaborane. Yield 3.9 g (81 %). Crystals suitable for an X-ray diffraction experiment were grown by slow evaporation of a concentrated dichloromethane solution. Elemental analysis calcd. (%) for $C_3H_{13}B_{10}I$ (284.15): C12.68, H 4.61; found C 12.58, H 4.60. IR (KBr), ν [cm^{-1}]= 3032 ($C_{clúster}$ -H), 2964, 2930 (C_{alkyl}-H), 2594, 2586 (B-H). ^1H NMR ($CDCl_3$): δ= 3.73 (s, 2H; $C_{clúster}$-H), 3.00-1.00 (m, 8H; B-H), 0.70 (s, 3H; CH_3). $^1H\{^{11}B\}$ NMR: δ= 3.73 (s, 2H; $C_{clúster}$-H), 2.70 (s, 1H; B-H), 2.50 (s, 2H; B-H), 2.35 (s, 2H; B-H), 2.24 (s, 2H; B-H), 2.12 (s, 1H; B-H), 0.70 (s, 3H; CH_3). $^{13}C\{^1H\}$ NMR: δ= 62.5 (s, $C_{clúster}$), 33.8 (s, CH_3). ^{11}B NMR: δ= -1.7 (d, $^1J(B,H)$=162, 2B), -3.0 (s, 1B; B6), -11.4 (d, $^1J(B,H)$=155, 6B), -28.8 (s, 1B, B3).

3-methyl-1,2-dicarba-*closo*-dodecaborane. To a stirring solution of 3-iodo-1,2-dicarba-*closo*-dodecaborane (0.5 g, 1.85 mmol) in THF (20 mL) at 0 ºC, was added, dropwise, a solution of methylmagnesium bromide (3.1 mL, 3M, 9.3 mmol). After stirring at room temperature for 30 minutes [$PdCl_2(PPh_3)_2$] (52.0 mg, 4% equiv.) and CuI (14.1 mg, 4% equiv.) were added in a single portion, following which the reaction was heated to reflux overnight. The solvent was removed and 20 mL of diethyl ether was added to the residue. The excess of Grignard reagent was destroyed by slow addition of dilute HCl. The organic layer was separated from the mixture, and the aqueous layer was extracted with diethyl ether (3x 10 mL). The combined organic phase was washed with water and dried over $MgSO_4$. The final compound was recristallized from hexane to give 3-methyl-1,2-dicarba-*closo*-dodecaborane. Yield 285 mg (97 %). Elemental analysis calcd. (%) $C_3B_{10}H_{14}$ (158.25): C 22.77, H 8.92; found C 23.34, H 8.77. IR (KBr), ν [cm^{-1}]= 3063 ($C_{cluster}$-H), 2957, 2924, 2855 (C_{alkyl}-H), 2629, 2598, 2575 (B-H). ^1H NMR ($CDCl_3$): δ= 3.43 (br s, 2H; $C_{cluster}$-H), 3.0-1.0 (br m, 8H;

B-H), 0.65 (s, 3H; CH_3). $^1H\{^{11}B\}$ NMR: δ= 3.43 (br s, 2H; $C_{cluster}$-H), 2.98, 2.46, 2.43, 1.96, 1.84, 1.33 (br s, B-H). $^{13}C\{^1H\}$ NMR: δ= 58.1 (s; $C_{cluster}$), 30.4 (CH_3). ^{11}B NMR: δ= -1.8 (d, ^1J(B,H)= 148, 2B), -4.0 (s, 1B), - 7.8 (d, ^1J(B,H)= 150, 1B), -11.7 (d, ^1J(B,H)= 126, 2B),-12.9 (d, ^1J(B,H)= 150, 4B).

3-methyl-7,8-dicarba-*nido*-undecaborate trimethylamonium salt: To a solution of KOH (0.89 g, 15.79 mmol) in degassed EtOH (50 mL) 3-methyl-1,2-dicarba-*closo*-dodecaborane (500 mg, 3.16 mmol) was added. The solution was refluxed for 3 h. After, it was cooled to room temperature, the solvent was eliminated and the solid residue was dissolved in 20 mL of water. The solution was neutralized with HCl 1M. Afterwards, $[HNMe_3]Cl$ in water was added dropwise to the solution to precipitate the compound. The white solid was rinsed with water and diethyl ether obtaining 3-methyl-7,8-dicarba-*nido*-undecaborate trimethylammonium salt. Yield 550 mg (84 %). Elemental analysis calcd. (%) $C_6H_{24}B_9N$ (207.56): C 34.72, H 11.65, N 6.74; found C 34.69, H 11.56, N 5.62. IR (KBr), ν [cm^{-1}]= 2908, 2856 (C_{alkyl}, H), 2513 (B-H). ^1H NMR (CD_3COCD_3): δ= 3.21 (s, 9H; $[HN(CH_3)_3]$), 2.08 (br s, 2H; $C_{cluster}$-H), 2.09 (s; 3H, CH_3) -2.71 (1H; B-H-B).$^{13}C\{^1H\}$ NMR: δ= 47.5 (m; $C_{cluster}$), 45.1 (s; $[HN(CH_3)_3]$), 25.24 (s; CH_3). ^{11}B NMR: δ= -10.0 (s, 1B), -10.0 (d, ^1J(B,H)=138, 3B), -15.6 (d, ^1J(B,H)=130, 2B), -20.3 (d, ^1J(B,H)=147, 2B), -35.6 (d, ^1J(B,H)=149, 2B).

3-antracenyl-7,8-dicarba-*nido*-undecaborate trimethylamonium salt :To a solution of KOH (150 mg, 2.65 mmol) in degassed EtOH (10 mL) 3-antracenyl-1,2-dicarba-*closo*-dodecaborane (170 mg, 0.53 mmol) was added. The solution was refluxed for 3 h. After, it was cooled to room temperature, the solvent was eliminates and the solid residue was dissolved in 5 mL of water. The solution was neutralized with HCl 1M. Afterwards, $[HNMe_3]Cl$ in water was added dropwise to the solution to precipitate the compound. The white solid was rinsed with water and hexane obtaining 3-antracenyl-7,8-dicarba-*nido*-undecaborate trimethylamonium salt. Yield 165 mg, (84 %).

IR: ν [cm^{-1}]= 3070 (C_{aryl}-H), 2527 (B-H). ^1H NMR: CD_3COCD_3**,** δ= 8.5-7.0 (m, 9H, H_{aryl}), 3.07 (s; $[HN(CH_3)_3]$), -2.75 (1H; B-H-B). $^{13}C\{^1H\}$ NMR: δ= 134.3, 133.5, 128.7, 128.1, 126.8, 126.3, 126.0, 125.4.^{11}B NMR: δ= -8.83 (s, 1B; B3), -10.8 (d, ^1J(B,H)= 142, 2B), -16.2 (d, ^1J(B,H)= 135, 2B), -21.1 (d, ^1J(B,H)= 150, 2B), -35.4 (d, ^1J(B,H)= 161, 1B), -36.9 (d, ^1J(B,H)= 144, 1B). MALDI-TOF: *m/z* = 309.8 (M).

3,4,5,7,8,9,10,11,12-nona-B-iodo-1,2-dicarba-*closo*-dodecaborane: 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 90ºC during three days and after that was allowed to cool to room temperature. Cold water (10 mL) and then an aqueous $NaHSO_3$ 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. Yield 4.45g (94%). Elemental analysis calcd. (%) for $C_2B_{10}I_9H_3$ (1277.30): C 1.89, H 0.24; found C 1.97, H 0.20. IR (KBr), ν [cm^{-1}]= 3013, 2981 ($C_{cluster}$-H), 2650 (B-H). ^1H NMR (CD_3COCD_3): δ= 6.98 (br s; $C_{cluster}$-H, B-H). $^{13}C\{^1H\}$ NMR: δ= 72.5 (s; $C_{cluster}$). ^{11}B NMR: δ= -4.2 (s, 2B), -9.7 (s, 1B), -11.1 (1B, B6), -12.6 (s, 1B), -17.2 (s, 2B), -20.3 (s, 2B), -22.1 (s, 1B). MS: 1277.0. The $^1H\{^{11}B\}$ NMR spectrum of the crystals *closo*-**1**. $CH_3COOCH_2CH_3$ was run in CD_3COCD_3, 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; CH_2), 3.54 (s, 3H; CH_3), 1.2 (t, ^2J(H, H)= 7.1 Hz, 3H; CH_3). MS-EI: *m/z* = 1277.0 (M), 1152.0 (M-I).

3,4,5,7,8,9,10,11,12-nona-B-methyl-1,2-dicarba-*closo*-dodecaborane:
To a mixture of 3-methyl-1,2-dicarba-*closo*-dodecaborane (700 mg, 4.4 mmol) and $AlCl_3$ (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 hydrolized and extracted with pentane. The combined organic phases were treated with $Na_2S_2O_3$ and dried over $MgSO_4$. 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 (98 %). Elemental analysis calcd. (%) for $C_{11}B_{10}H_{30}$ (270.47): C 48.85, H 11.18; found C 48.98, H 11.25. IR (KBr), ν [cm^{-1}]= 3056 ($C_{cluster}$-H), 2945, 2904, 2833 (C_{alkyl}-H), 2590 (B-H). $^1H\{^{11}B\}$ NMR ($CDCl_3$): δ= 0.32 (br s, 3H; CH_3), 0.13 (br s, 6H; CH_3), 0.05 (br s, 6H; CH_3), 0.01 (br s, 3H; CH_3), -0.12 (br s, 3H; CH_3), -0.23 (br s, 6H; CH_3), 2.89 (d, ^3J(H, H)= 43 Hz, 2H; $C_{clúster}$-H), 1.86 (br s, 1H; B-H). $^{13}C\{^1H\}$ NMR: δ= 54.2 (s, $C_{cluster}$), -3.0 (br, CH_3). ^{11}B NMR: δ= 5.4 (s, 2B), -2.1 (s, 1B), -4.2 (s, 1B), -8.8 (s, 5B), -17.2 (d, ^1J(B, H)= 161 Hz, 1B). MS-EI: *m/z* = 270.05 (M), 255.05 (M- CH_3).

9-$I_{0.707}H_{0.293}$-12-$Cl_{0.566}H_{0.434}$-3,4,5,6,7,8,10,11-$(CH_3)_8$-1,2-*closo*-$C_2B_{10}H_2$. A mixture of 3,6-$(CH_3)_2$-1,2-$C_2B_{10}H_{10}$ (0.50 g, 2.9 mmol), MeI (4.2 ml) and $AlCl_3$ (0.78g, 5.8 mmol) was refluxed for 2 days. The excess of MeI was removed and water was added to the residue. The aqueous layer was extracted with pentane and $Na_2S_2O_3$ was added to the organic phase to remove I_2. The product was purified by flash silica gel chromatography using pentane as the eluting solvent obtaining 0.75 g of product. ^1H NMR ($CDCl_3$): δ= 4.47 (br s; C-$H_{clúster\ (H,H)}$), 3.16 (d, ^3J(H, H)= 4.1; C-$H_{clúster\ (H,Cl)}$), 2.99 (d, ^3J(H, H)= 4.1; C-$H_{clúster\ (H,Cl)}$), 3.04 (d, ^3J(H, H)= 3.8; C-$H_{clúster\ (I,Cl)}$); 2.94 (d, ^3J(H, H)= 3.8; C-$H_{clúster\ (I,Cl)}$), 2.77 (d, ^3J(H, H)= 3.8; C-$H_{(I,H)}$), 2.74 (d, ^3J(H, H)=3.8; C-$H_{(I,H)}$) (2H; C-H_{total}), 0.58, 0.38, 0.36, 0.31, 0.24, 0.18, 0.12, 0.11, 0.09, 0.05, -0.01, -0.08, -0.12, -0.14, -0.20 (s, 24H; CH_3). ^{13}C NMR: δ= 81.7, 81.3, 80.9, 58.6, 56.4, 54.8 (br s; C_c-H), -2.9 (m, B-CH_3). ^{11}B RMN: δ= 7.2, 5.6 (br s, 2B), -4.0, -5.0, -8.2 (br s, 8B).

3,4,5,6,7,8,9,10,11,12-deca-B-iodo-1,2-dicarba-*closo*-dodecaborane

To 3,6-diiodo-1,2-dicarba-*closo*-dodecaborane (1.0g , 2.5 mmol) were added under nitrogen flow first 10g (66.5 mmol) of triflic acid and then 6 mL of ICl. The mixture was let at 90ºC during five days and after that was allowed to cool to room temperature. Cold water (10 mL) and then an aqueous $NaHSO_3$ were added to the mixture The precipitate was filtered and was immediately dissolved in 125 mL of hot EtOAc and a chromatography column was done using EtAc as eluent (2.55, 73%). Elemental analysis calcd. (%) for $C_2B_{10}I_{10}H_2$ (1403.19): C 1.71, H 0.14; found C1.69, H 0.12. IR (KBr), ν [cm^{-1}]= 3008, 2980 ($C_{cluster}$-H). ^1H NMR (CD_3COCD_3): δ= 7.74 (s, 2H; $C_{cluster}$-H). $^{13}C\{^1H\}$ NMR: δ= 63.1 (s, $C_{cluster}$). Crystals suitable for an X-ray diffraction experiment were grown by slow evaporation of a concentrated acetone solution.

1,2,4,5,6,9,10,11-octa-B-iodo-7,8-dicarba-*nido*-undecaborate trimethylamonium salt. To a solution of KOH (110 mg, 1.95 mmol) in degassed EtOH (50 mL), 3,4,5, 7,8,9,10,11,12-nona-B-iodo-1,2-dicarba-*closo*-dodecaborane (500 mg, 0.39 mmol) was added. The solution was refluxed for 3 h. After, it was cooled to room temperature, the solvent was eliminates and the solid residue was dissolved in 20 mL of water. The solution was neutralized with HCl 1M. Afterwards, $[HNMe_3]Cl$ in water was added dropwise to the solution to precipitate the compound. The white solid was rinsed with water and diethyl ether obtaining a mixture of 1,2,4,5,6,9,10,11-octa-B-iodo-7,8-dicarba-*nido*-undecaborate trimethylammonium salt and 1,2,3,4,5,6,9,10,11-nona-B-iodo-7,8-dicarba-*nido*-undecaborate trimethylammonium salt (1:1). After recristallization we could obtain 1,2,4,5,6,9,10,11-octa-B-iodo-7,8-dicarba-*nido*-undecaborate trimethylammonium salt. ^{1}H NMR: CD_3COCD_3**,** δ= 3.18 (s, 9H; $[HN(CH_3)_3]$). $^{13}C\{^{1}H\}$ NMR: δ= 45.4 (s; $[HN(CH_3)_3]$), 41.3 (m; $C_{cluster}$). ^{11}B NMR: δ= -16.1 (s, 2B), -19.1 (s, 4B; B3), -27.0 (s, 2B), -41.0 (s, 1B). MALDI-TOF: *m/z* =1140.5 (M), 1013.7 (M-I).

1,2,3,4,5,6,9,10,11–nona-B-iodo-7,8-dicarba-*nido*-undecaborate trimethylamonium salt. To a solution of KOH (100mg, 1.78 mmol) in degassed EtOH (50 mL) 3,4,5,6,7,8,9,10,11,12-decaiodo -1,2-dicarba-*closo*-dodecaborane (500 mg, 0.35 mmol) was added. The solution was refluxed for 3 h. After, it was cooled to room temperature, the solvent was eliminates and the solid residue was dissolved in 20 mL of water. The solution was neutralized with HCl 1M. Afterwards, $[HNMe_3]Cl$ in water was added dropwise to the solution to precipitate the compound. The white solid was rinsed with water and diethyl ether obtaining 1,2,3,4,5,6,9,10,11-nona-B-iodo-7,8-dicarba-*nido*-undecaborate trimethylammonium salt. (415 mg, Rendiment: 86 %). Elemental analysis calcd. (%) for $C_8B_9I_9H_{22}N_2$ (1385.72): C 6.93, H 1.60; found C 6.89, H 1.65. ^{1}H NMR (CD_3COCD_3): δ= 3.18 (s, 9H; $[HN(CH_3)_3]$). $^{13}C\{^{1}H\}$ NMR: δ= 45.4 (s; $[HN(CH_3)_3]$), 40.4 (m; $C_{cluster}$). ^{11}B NMR: δ= -15.9 (s, 2B), -19.3 (s, 3B), -24.9 (s, 2B), -26.7 (s, 1B; B3), -38.9 (s, 1B). MALDI-TOF: *m/z* =1266.8 (M), 1139.9 (M-I), 1013.9(M-2I).

$[N(CH_3)_4][1\text{-}BH_3\text{-}1,2\text{-}C_2B_{10}H_{10}I]$

To 3-I-1,2-$C_2B_{10}H_{11}$ (40 mg, 0.15 mmol) in 2mL of dry THF at 0ºC, BuLi (0.1 mL, 0.16 mmol) was added dropwise. The solution was cooled to –70ºC and BH3 (0.3 mL, 0..3 mmol) was added. The solution was let stir at room temperature for 6 h and when the solvent was evaporated, water was added. The aqueous part was precipitated with tetramethylammonium chloride. Elemental analysis calcd. (%) for $C_6B_{11}H_{25}IN$ (282.95): C 8.49, H 4.63; found C 8.40, H 4.59. IR (KBr), ν [cm^{-1}]= 2958 ($C_{cluster}$-H), 2522 (B-H). ^{1}H NMR (CD_3COCD_3): δ= 3.45 (s, 12; $[N(CH_3)_4]$), 2.80 (s,1H; $C_{cluster}$-H), 3.00-1.50 (br m, 9H; B-H), 1.35 (s, 3H; BH_3). $^{1}H\{^{11}B\}$ NMR (CD_3COCD_3): δ= 3.45 (s, 12; $[N(CH_3)_4]$), 2.80 (s,1H; $C_{cluster}$-H), 2.48 (br s, 4H; B-H), 2.31 (br s, 2H; B-H), 2.05 (br s, 2H; B-H), 1.8 (br s, 1H; B-H), 1.35 (1:1:1:1, $^1J(B,H)= 90$, 3H; BH_3). $^{13}C\{^1H\}$ NMR: $\delta=$ 55.1 (s; $[N(CH_3)_4]$), 61.3, 70.4 (s; $C_{cluster}$). ^{11}B NMR: $\delta= -2.1$ (d, $^1J(B,H)= 142$, 1B), -6.3 (d, $^1J(B,H)=150$, 3B), -7.6 (d, $^1J(B,H)=150$, 1B), -8.9 (d, $^1J(B,H)=167$, 3B), -11.8 (d, $^1J(B,H)= 157$, 1B), -18.6 (q, $^1J(B,H)=90$, 1B), -22.9 (s, 1B). MALDI-TOF: m/z= 284.2 (M), 270.4 (M-BH_3).

X-ray structure determinations of 3,6-I_2-*closo*-1,2-$C_2B_{10}H_{10}$, 3,6-Me_2-*closo*-1,2-$C_2B_{10}H_{10}$, 3-I-6-Me-1,2-*closo*-$C_2B_{10}H_{10}$ and 3,4,5,6,7,8,9,10,11,12-I10-1,2-*closo*-$C_2B_{10}H_2$.

Single-crystal data collection for 3,6-I_2-*closo*-1,2-$C_2B_{10}H_{10}$ was performed at ambient temperature on a Rigaku AFC5S diffractometer, and data collections for 3,6-Me_2-*closo*-1,2-$C_2B_{10}H_{10}$, 3-I-6-Me-*closo*-1,2-$C_2B_{10}H_{10}$ and 3,4,5,6,7,8,9,10,11,12-I_{10}-1,2-*closo*-$C_2B_{10}H_2\cdot (CH_3)_2COHCH_2COCH_3$ were performed with Enraf Nonius FR590 diffractometer at -100ºC using monochromatized Mo Kα radiation.

The structures were solved by direct methods and refined on F^2 by the SHELXL97 program.[31]

For 3,6-I_2-1,2-$C_2B_{10}H_{10}$ and 3,6-Me_2-1,2-$C_2B_{10}H_{10}$, non-hydrogen atoms were refined with anisotropic displacement parameters, and hydrogen atoms were treated as riding atoms using the SHELX97 default parameters. 3,6-I_2-1,2-$C_2B_{10}H_{10}$ crystallizes in non-centrosymmetric space group and absolute configuration of the compound was determined by refinement of Flack *x* parameter.

For 3-I-6-Me-1,2-$C_2B_{10}H_{10}$, non-hydrogen atoms were refined with anisotropic displacement parameters, and hydrogen atoms were treated as riding atoms using the SHELX97 default parameters. The methyl group is disordered showing rotational disorder with each hydrogen atom occupying two positions. 3-I-6-Me-1,2-$C_2B_{10}H_{10}$ crystallizes in non-centrosymmetric space group and absolute configuration of the compound was determined by refinement of Flack *x* parameter.

For 3,4,5,6,7,8,9,10,11,12-I_{10}-1,2-*closo*-$C_2B_{10}H_2\cdot (CH_3)_2COHCH_2COCH_3$, non-hydrogen atoms were refined with anisotropic displacement parameters, and hydrogen atoms, except the hydroxyl hydrogen atom H1a of the solvent molecule, were treated as riding atoms using the SHELX97 default parameters. H1a was refined isotropically with fixed thermal displacement parameter.

Supporting information available:

Tables of crystal, structure solution and refinement, atomic coordinates, bond lengths and angles, and anisotropic thermal parameters for *closo* 3,6-I_2-1,2-$C_2B_{10}H_{10}$ (**1**), *closo* 3,6-Me_2-1,2-$C_2B_{10}H_{10}$ (**2**), *closo* 3-I-6-Me-1,2-C2B10H10 (**3**) and *closo* 3,4,5,6,7,8,9,10,11,12-I_{10}-1,2-*closo*-$C_2B_{10}H_2$· $(CH_3)_2COHCH_2COCH_3$ (**4**).

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC- and CCDC- . Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44)1223 336-033; e-mail: deposit@ccdc.cam.ac.uk.

Figure Captions

Figure 1.- Molecular structure of 3,6-I_2-*closo*-1,2-$C_2B_{10}H_{10}$.

Figure 2.- Molecular structure of 3,6-Me_2-1,2-*closo*-$C_2B_{10}H_{10}$.

Figure 3.- Molecular structure of 3-I-6-Me-1,2-*closo*-$C_2B_{10}H_{10}$.

Figure 4.- Molecular structure of 3,4,5,6,7,8,9,10,11,12-I_{10}-1,2-*closo*-$C_2B_{10}H_2 \cdot (CH_3)_2COHCH_2COCH_3$.

Figure 5.- Raw ^{11}B NMR spectra with the pick assignments for the compounds 3,6-I_2-*closo*-1,2-$C_2B_{10}H_{10}$, 1,2-*closo*-$C_2B_{10}H_{12}$ and 3,6-Me_2-1,2-*closo*-$C_2B_{10}H_{10}$.

Figure 6.- IR spectra for compounds 1,2-*closo*-$C_2B_{10}H_{12}$ (a) and 3,4,5,6,7,8,9,10,11,12-I_{10}-1,2-*closo*-$C_2B_{10}H_2$ (b).

Figure 1.- Molecular structure of 3,6-I_2-1,2-*closo*-$C_2B_{10}H_{10}$. Hydrogen atoms are omitted.

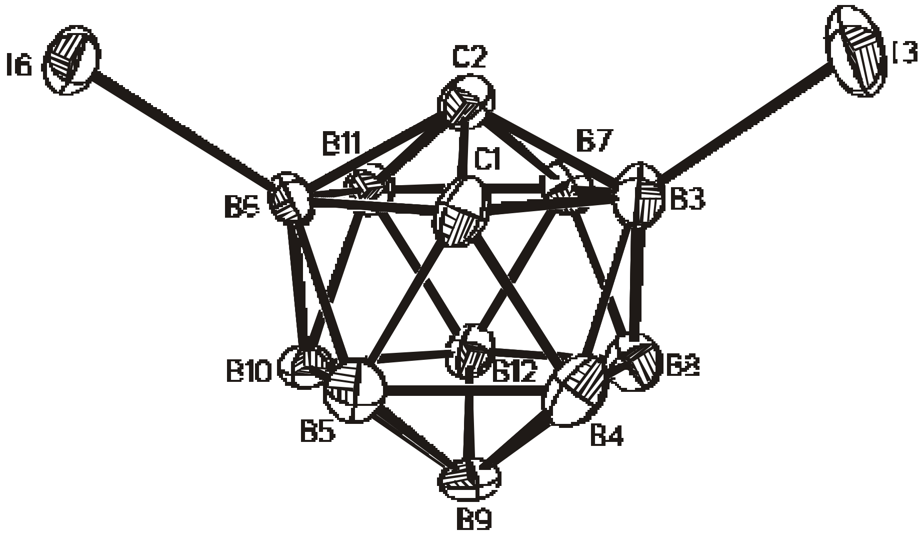


Figure 2.- Molecular structure of 3,6-Me_2-1,2-*closo*-$C_2B_{10}H_{10}$. Hydrogen atoms are omitted. Small letter "a" refers equivalent position –*x*, *y*, -*z*+3/2.

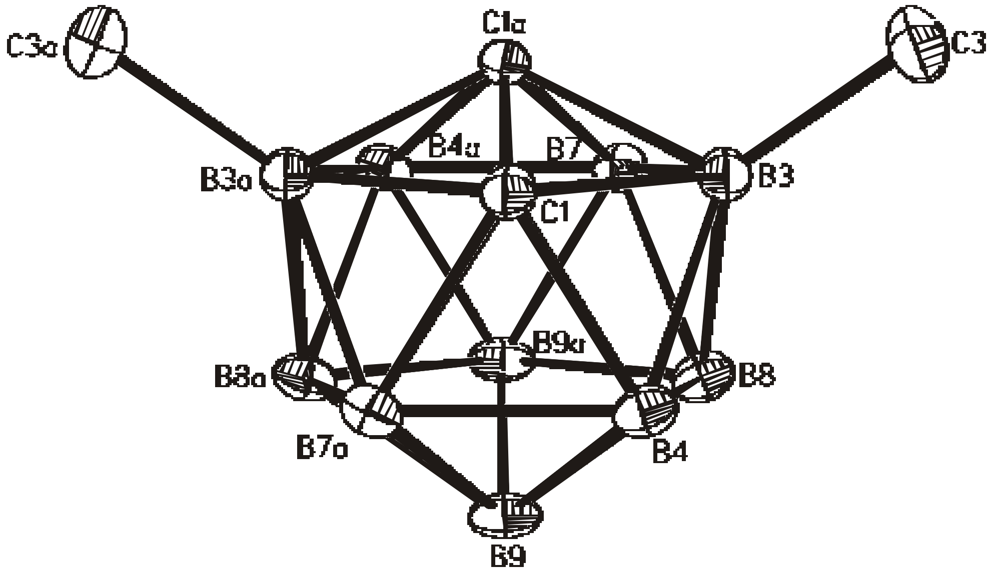


Figure 3.- Molecular structure of 3-I-6-Me-1,2-*closo*-$C_2B_{10}H_{10}$. Hydrogen atoms are omitted. Small letter "b" refers equivalent position $-x$, y, z.

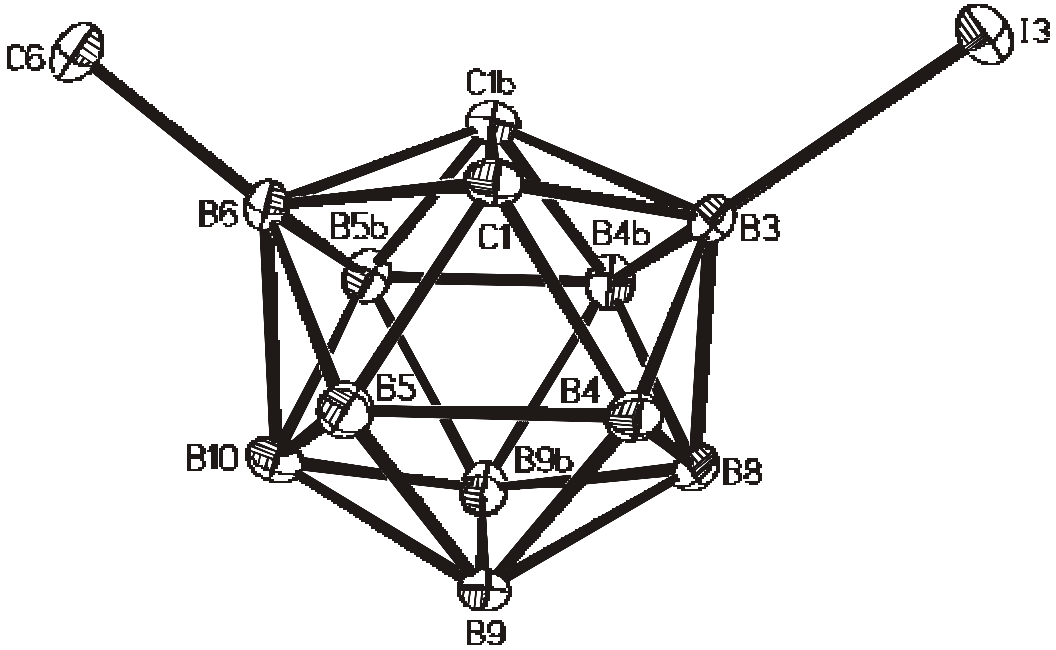


Figure 4.- Molecular structure of 3,4,5,6,7,8,9,10,11,12-I_{10}-1,2-*closo*-$C_2B_{10}H_2 \cdot (CH_3)_2COHCH_2COCH_3$. Hydrogen atoms bonded to cage carbons and the hydroxyl hydrogen have been drawn, others are omitted. Hydrogen bonds have been drawn with dashes.

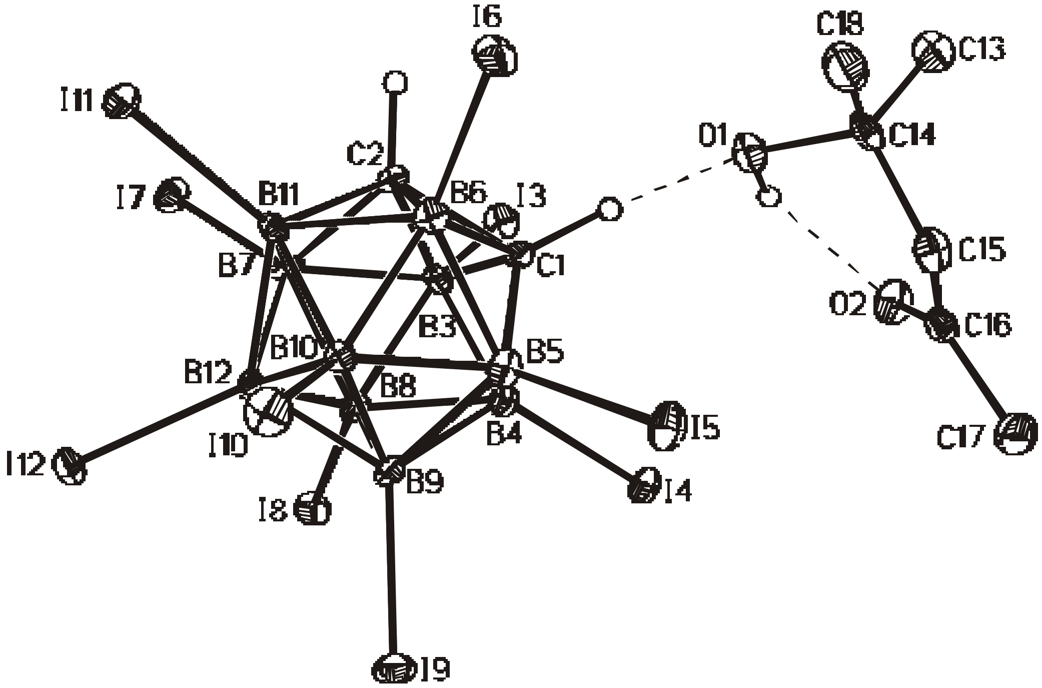


Figure 5.- Raw ^{11}B NMR spectra with the pick assignments for the compounds: a) 3,6-I_2-1,2-*closo*-$C_2B_{10}H_{10}$, b) 1,2-*closo*-$C_2B_{10}H_{12}$ and c) 3,6-Me_2-1,2-*closo*-$C_2B_{10}H_{10}$.

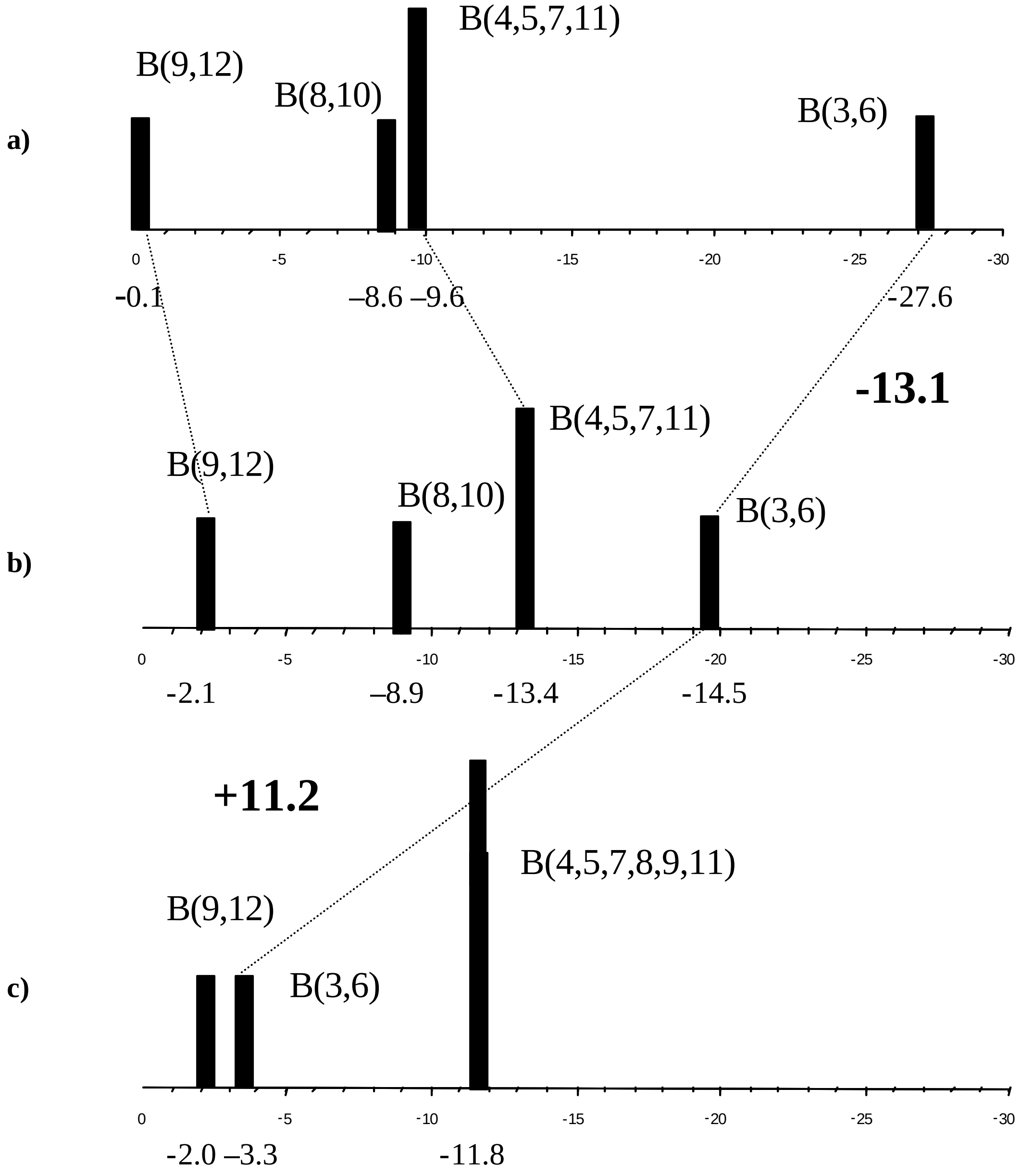
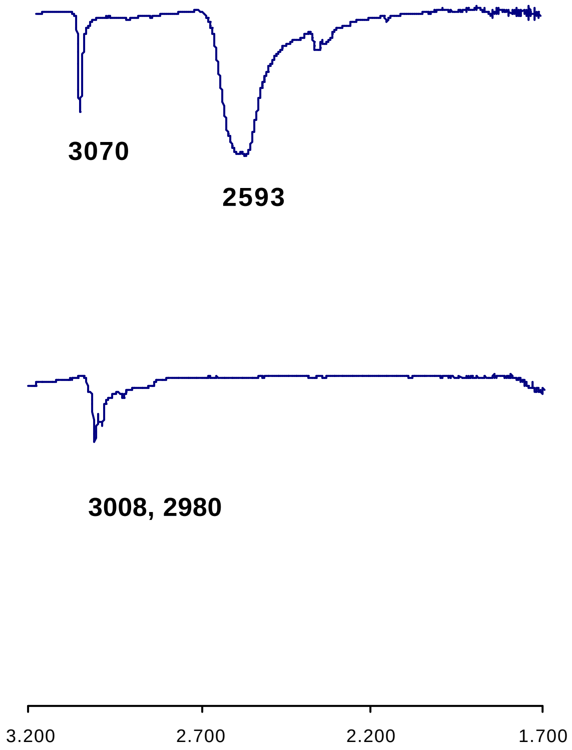


Figure 6.- IR spectra for compounds 1,2-*closo*-$C_2B_{10}H_{12}$ (a) and 3,4,5,6,7,8,9,10,11,12-I_{10}-1,2-*closo*-$C_2B_{10}H_2$ (b).



Scheme Captions

Scheme a: Partial degradation process on 3-I-1,2-*closo*-$C_2B_{10}H_{11}$.

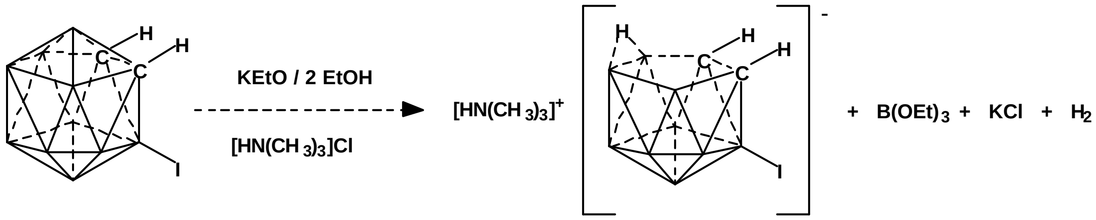
Scheme b: Deprotonation process on the [3-I-7,8-*nido*-$C_2B_9H_{11}$]$^-$ species and new boron insertion reaction.

Scheme c: Iodination reaction.

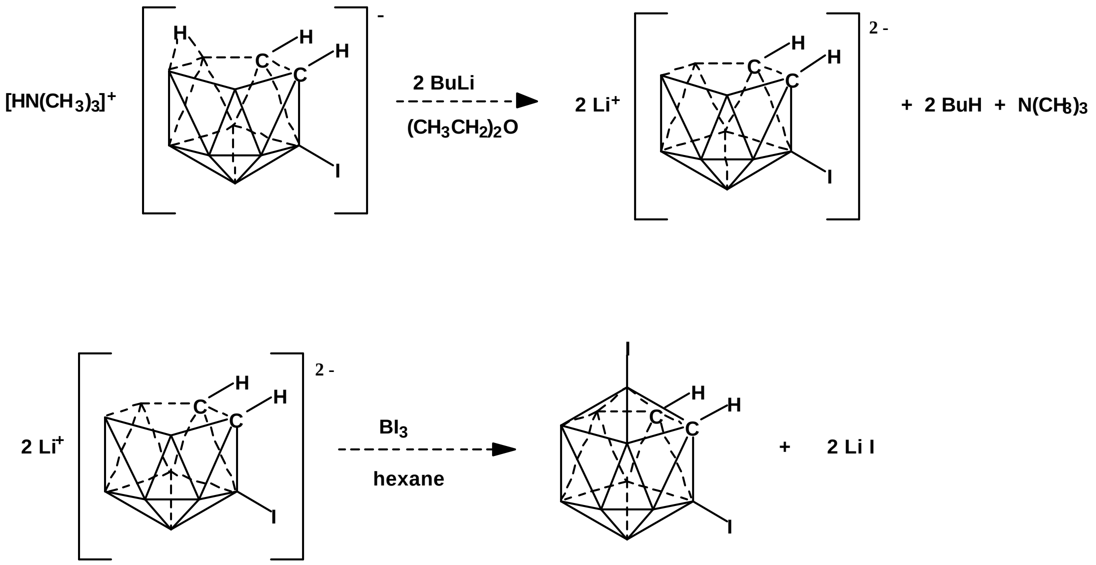
Scheme d: B-C bond formation via a cross coupling reaction.

Scheme e: Electrophilic methylation reaction.

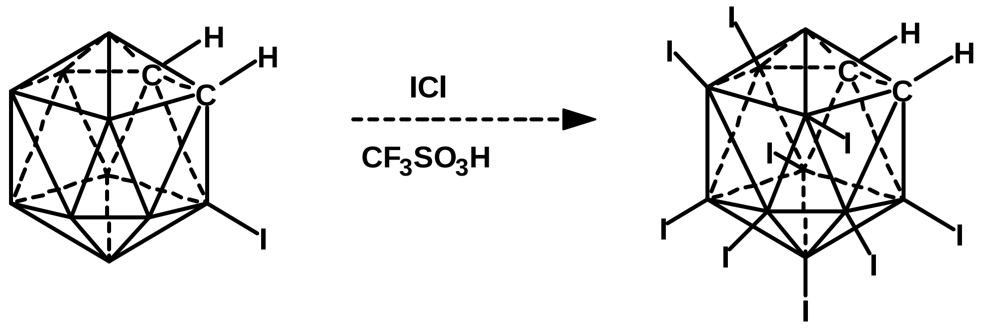
Scheme a: Partial degradation process on 3-I-1,2-*closo*-$C_2B_{10}H_{11}$.



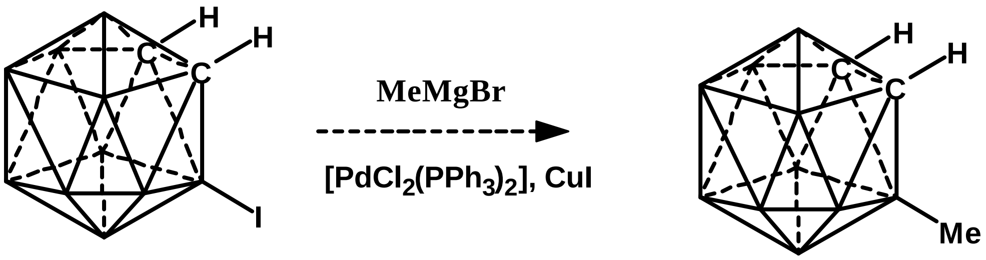
Scheme b: Deprotonation process on the [3-I-7,8-*nido*-$C_2B_9H_{11}$]$^-$ species and new boron insertion reaction.



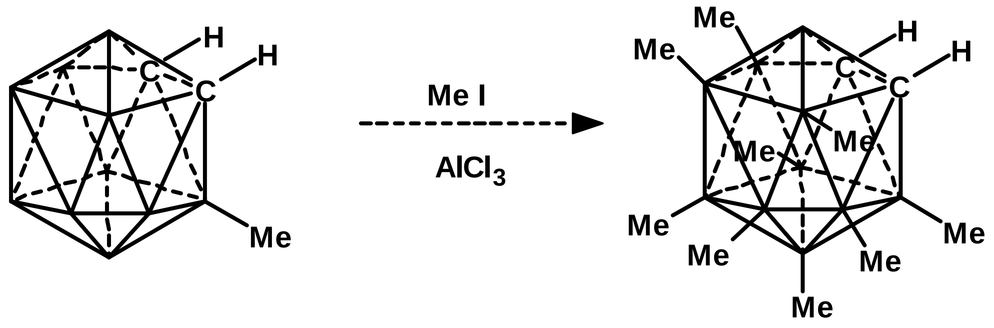
Scheme c: Iodination reaction.



Scheme d: B-C bond formation via a cross coupling reaction.



Scheme e: Electrophilic methylation reaction.



Tables caption.

Table 1.- Selected Bond Lengths (Å) and Angles (deg) for 3,6-I_2-1,2-*closo*-$C_2B_{10}H_{10}$.

Table 2.- Selected Bond Lengths (Å) and Angles (deg) for 3,6-Me_2-1,2-*closo*-$C_2B_{10}H_{10}$.

Table 3.- Selected Bond Lengths (Å) and Angles (deg) for 3-I-6-Me-1,2-*closo*-$C_2B_{10}H_{10}$.

Table 4.- Selected Bond Lengths (Å) and Angles (deg) for 3,4,5,6,7,8,9,10,11,12-I_{10}-1,2-*closo*-$C_2B_{10}H_2$· $(CH_3)_2COHCH_2COCH_3$.

Table 5.- Crystallographic Data and Structural Refinement Details for Compounds 3,6-I_2-1,2-$C_2B_{10}H_{10}$ (**1**), 3,6-Me_2-1,2-$C_2B_{10}H_{10}$ (**2**), 3-I-6-Me-1,2-$C_2B_{10}H_{10}$ (**3**) and 3,4,5,6,7,8,9,10,11,12-I_{10}-1,2-*closo*-$C_2B_{10}H_2$· $(CH_3)_2COHCH_2COCH_3$ (**4**).

Table 6. δ ^{1}H NMR and δ $^{13}C\{^1H\}$ NMR ($C_{cluster}$-H) of substituted carboranes.

Table 7.- Calculated Mulliken charges by geometry optimizations at the Hartree-Fork 3-21G level on several B-C methylated *o*-carborane derivatives .

Table 1.- Selected Bond Lengths (Å) and Angles (deg) for 3,6-I_2-1,2-*closo*-$C_2B_{10}H_{10}$.

I3-B3	2.156(11)
I6-B6	2.146(9)
C1-C2	1.623(13)
C1-B3	1.723(14)
C1-B6	1.711(12)
C2-B3	1.700(14)
C2-B6	1.727(13)
C1-B3-I3	120.1(7)
C2-B3-I3	119.4(7)
I3-B3-B8	128.8(7)
C1-B6-I6	119.8(6)
C2-B6-I6	119.9(6)
I6-B6-B10	129.5(6)

Table 2.- Selected Bond Lengths Distances (Å) and Angles (deg) for 3,6-Me_2-1,2-$C_2B_{10}H_{10}$.

C1-C1[a]	1.613(5)
C1-B3	1.738(4)
C1-B3[a]	1.742(4)
C3-B3	1.572(4)
C3-B3-C1	119.4(2)
C3-B3-C1[a]	119.8(2)
C3-B3-B8	132.1(2)

[a] Equivalent position –*x*, *y*, -*z*+3/2.

Table 3.- Selected Bond Lengths (Å) and Angles (deg) for 3-I-6-Me-1,2-$C_2B_{10}H_{10}$.

I3-B3	2.132(3)
C1-C1[b]	1.625(4)
C1-B3	1.718(4)
C1-B6	1.736(4)
C6-B6	1.571(5)
C1-B3-I3	121.5(2)
C1[b]-B3-I3	121.5(2)
I3-B3-B8	127.7(3)
C1-B6-C6	120.8(2)
C1[b]-B6-C6	120.8(2)
C6-B6-B10	130.9(3)

[b] Equivalent position –*x*, *y*, *z*.

Table 4.- Selected Bond Lengths (Å) and Angles (deg) for 3,4,5,6,7,8,9,10,11,12-I_{10}-1,2-*closo*-$C_2B_{10}H_2\cdot (CH_3)_2COHCH_2COCH_3$.

I3-B3	2.127(4)
I6-B6	2.142(4)
C1-C2	1.645(5)
C1-B3	1.747(5)
C1-B6	1.737(5)
C2-B3	1.724(5)
C2-B6	1.758(5)
I9-B9	2.132(4)
I10-B10	2.142(4)
O1-C14	1.445(4)
O2-C16	1.197(5)
C1-B3-I3	119.5(2)
C2-B3-I3	120.5(3)
I3-B3-B8	129.6(2)
C1-B6-I6	119.5(2)
C2-B6-I6	117.7(3)
I6-B6-B10	130.4(3)

Table 5.- Crystallographic Data and Structural Refinement Details for Compounds 3,6-I_2-1,2-$C_2B_{10}H_{10}$ (**1**), 3,6-Me_2-1,2-$C_2B_{10}H_{10}$ (**2**), 3-I-6-Me-1,2-$C_2B_{10}H_{10}$ (**3**) and 3,4,5,6,7,8,9,10,11,12-I_{10}-1,2-*closo*-$C_2B_{10}H_2$· $(CH_3)_2COHCH_2COCH_3$ (**4**).

compound	(**1**)	(**2**)	(**3**)	(**4**)
empirical formula	$C_2H_{10}B_{10}I_2$	$C_2H_{16}B_{10}$	$C_3H_{13}B_{10}I$	$C_8H_{14}B_{10}I_{10}O_2$
formula weight	396.00	172.27	284.13	1519.29
crystal system	orthorhombic	monoclinic	orthorhombic	monoclinic
space group	*P*212121	*C*2/*c*	*Pmn*21	*P*21/*c*
a (Å)	9.0602(4)	14.8528(7)	7.2615(2)	9.8179(2)
b (Å)	17.4247(17)	6.8281(3)	9.6534(3)	14.6436(3)
c (Å)	7.7457(16)	11.5332(6)	8.0861(2)	22.1195(5)
b (deg)	90	114.220(5)	90	97.3310(7)
V ($Å^3$)	1222.8(3)	1066.70(9)	566.82(3)	3154.11(12)
Z	4	4	2	4
T (°C)	21	-100	-100	-100
λ (Å)	0.71069	0.71073	0.71073	0.71073
r (g cm-3)	2.151	1.073	1.665	3.199
m(cm-1)	50.88	0.46	27.66	98.32
goodness-of-fit	1.071	1.044	1.076	1.012
R^a [$I>2\sigma(I)$]	0.0332	0.0965	0.0278	0.0333
Rw^b [I>2σ(I)]	0.0847	0.2576	0.0560	0.0607

$^aR = \Sigma||F_o|-|Fc||/\Sigma|Fo|$

$^bRw = \{\Sigma[w(Fo^2-Fc^2)^2]/\Sigma[\ w(Fo^2)^2\ ]\}^{1/2}$

Table 6. δ ^{1}H NMR and δ ^{13}C {^{1}H} NMR ($C_{cluster}$-H) of substituted carboranes.

Compound	δ ^{1}H NMR of $C_{cluster}$- H(ppm)	Difference	δ ^{13}C NMR of $C_{cluster}$- H(ppm)	Diference
1,2-*closo*-$C_2B_{10}H_{12}$	3.55		55.1	
3-Me-1,2-*closo*-$C_2B_{10}H_{11}$	3.43		58.1	
		upfield 0.12		downfield 3.0
3,6-Me_2-1,2-*closo*-$C_2B_{10}H_{10}$	3.31		61.3	
		upfield 0.12		downfield 3.2
3-I-1,2-*closo*-$C_2B_{10}H_{11}$	3.84		60.3	
		downfield 0.29		downfield 5.2
3,6-I_2-1,2-*closo*-$C_2B_{10}H_{10}$	4.10		65.0	
		downfield 0.26		downfield 4.7
3-I-6-Me-1,2-*closo*-$C_2B_{10}H_{10}$	3.73	downfield 0.18 0.28 - 0.12= 0.16	62.5	downfield 7.4 3.0+4.7= 7.7
3-biPh-1,2-*closo*-$C_2B_{10}H_{11}$	3.73		57.4	
		downfield 0.18		downfield 2.3
3,6-$(biPh)_2$-1,2-*closo*-$C_2B_{10}H_{10}$	3.92		59.8	
		downfield 0.19		downfield 2.4

Table 7.- Calculated Mulliken charges by geometry optimizations at the Hartree-Fork 3-21G level on several B-C methylated *o*-carborane derivatives .

HF/3-21G	*o*-carborane	1,2-$(CH_3)_2$-*o*-carborane	3-CH_3-*o*-carborane	3,6-$(CH_3)_2$-*o*-carborane	3,6,8,10-$(CH_3)_4$-*o*-carborane	3,4,5,6,7,8,10,11-$(CH_3)_8$-*o*-carborane	4,5,7,8,9,10,11,12-$(CH_3)_8$-*o*-carborane
C1	-0,919	-0,809	-0,942	-1,005	-0,980	-1,060	-1,005
C2	-0,919	-0,804	-0,942	-1,005	-0,980	-1,063	-1,000
B3	0,266	0,294	**0,834**	**0,775**	**0,861**	**0,865**	0,242
B4	0,096	0,110	0,088	0,113	0,079	**0,675**	**0,652**
B5	0,096	0,112	0,095	0,113	0,082	**0,657**	**0,679**
B6	0,266	0,296	0,263	**0,775**	**0,861**	**0,858**	0,234
B7	0,096	0,110	0,088	0,113	0,082	**0,632**	**0,653**
B8	-0,008	-0,016	-0,007	0,018	**0,517**	**0,536**	**0,511**
B9	0,013	0,014	0,009	0,011	0,012	0,005	**0,621**
B10	-0,008	-0,021	-0,009	0,018	**0,517**	**0,540**	**0,509**
B11	0,096	0,102	0,095	0,113	0,079	**0,655**	**0,646**
B12	0,013	0,010	0,009	0,011	0,012	0,009	**0,632**
Cluster total charge	**-0,912**	**-0,602**	**-0,419**	**0,050**	**1,142**	**3,309**	**3,374**

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