

CONCLUSIONS

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1.- S'ha dissenyat un mètode simple i ràpid per a la síntesi amb alt rendiment de borats halogenats de fórmula $[B_6X_6]^{2-}$ (X = Br, I).

2.- S'han sintetitzat i caracteritzat carborans halogenats (iodats i bromats) en la posició 3 del clúster d'*o*-carborà. Per a aquests clústers:

2a.- S'han dut a terme càlculs teòrics dels desplaçaments químics de ^{11}B -RMN que han ajudat a assignar els senyals als diferents àtoms de bor del clúster.

2b.- S'ha estudiat la seva reactivitat davant reactius de Grignard. Això ha permès obtenir derivats alquílics i arílics a la posició 3 del clúster d'*o*-carborà.

2c.- S'ha provat la capacitat d'un dels compostos, el 3-Iodo-1,2-dicarba-*closo*-dodecaborà, de formar una sal de fenil iodoni.

2d.- S'ha estudiat la reactivitat de l'enllaç B-I front a la reacció amb metalls. Metalls com el sodi, el pal·ladi, el coure, el níquel i el magnesi han portat a la reducció de l'enllaç B-I a B-H. A més, l'estudi de la reacció del 3-Iodo-1,2-dicarba-*closo*-dodecaborà amb magnesi ha permès desenvolupar un nou mètode de reducció de l'*o*-carborà.

2e.- S'ha provat la reactivitat del l'enllaç $C_{\text{clúster}}-H$ en el 3-Iodo-1,2-dicarba-*closo*-dodecaborà obtenint la substitució en el carboni.

2f.- Per difracció de raigs X s'ha resolt l'estructura cristal·lina del compost 3-Iodo-1,2-dicarba-*closo*-dodecaborà. En aquesta s'ha evidenciat l'existència d'interaccions intermoleculares.

3.- S'han sintetitzat i caracteritzat *nido*-carborans halogenats en la posició 3 del clúster via degradació parcial dels clústers halogenats *closo*. L'estudi d'aquest procés ha permès determinar, en el cas d'un clúster substituït en B3 i B6, quin dels dos àtoms és l'eliminat.

4.- S'ha sintetitzat i caracteritzat el 3,6-I₂-1,2-dicarba-*closo*-dodecaborà, carborà substituït en les posicions 3 i 6 del clúster d'*o*-carborà. Per a aquest clúster:

4a.- La reacció amb derivats de Grignard ha permès obtenir carborans substituïts en les posicions 3 i 6 amb restes alquilics i arílics.

4b.- El desplaçament químic i en alguns casos l'acidesa dels àtoms d'hidrogen units als àtoms de carboni del clúster depèn del tipus de substituent que es troba en les posicions 3 i 6, essent aquest efecte de tipus additiu.

5.- S'han sintetitzat i caracteritzat derivats de l'*o*-carborà nona i deca-B-substituïts. Aquest últim té substituïts tots els àtoms de bor del clúster:

5a.- S'ha sintetitzat el derivat de l'*o*-carborà iodat en les posicions 3,4,5,7,8,9,10,11 i 12. La síntesi s'ha dut a terme en globalment dues etapes. La primera es basa en la combinació de les reaccions de degradació parcial i inserció que permet obtenir el clúster iodat en posició 3 i la segona en un atac electrofílic amb ICl sobre el clúster monosubstituït que porta a l'obtenció del clúster nonaiodat.

5b.- S'ha sintetitzat el derivat de l'*o*-carborà metilat en les posicions 3,4,5, 7,8,9,10,11 i 12 en dues etapes. La primera es basa en la combinació de les reaccions de degradació parcial i inserció que permet obtenir el clúster metilat en posició 3 i la segona en un atac electrofílic amb MeI sobre el clúster monosubstituït que porta a l'obtenció del clúster nonametilat.

- 5c.- S'ha sintetitzat el derivat de l'*o*-carborà que té les deu posicions de bor 3,4,5,6,7,8,9,10,11 i 12 iodades a partir del clúster d'*o*-carborà mitjançant dues etapes. La primera es basa en la combinació de les reaccions de degradació parcial i inserció que permet obtenir el clúster iodat en posicions 3 i 6 i la segona en un atac electrofílic amb ICl sobre el clúster disubstituint que porta a l'obtenció del clúster per-B-iodat.
- 5d.- Intents de sintetitzar el clúster per-B-metilat, han portat a un carborà octametilat. Aquest fet experimental s'ha atribuït a l'efecte dels grups metils sobre els àtoms de bor del clúster. Aquest efecte ha estat quantificat mitjançant càlculs teòrics. Es pot concloure que a mesura que augmenta el nombre de grups metil en el clúster, augmenta la càrrega total positiva d'aquest i per tant, disminueix la susceptibilitat a l'atac electrofílic.
- 5e.- S'ha estudiat l'acidesa dels àtoms d'hidrogen units als àtoms de carboni del derivat per-B-iodat de l'*o*-carborà front la desprotonació amb diferents bases i la protonació de la seva base conjugada amb diferents àcids.
- 6.- S'han sintetitzat i caracteritzat *nido*-carborans octa i nona-halogenats. L'estudi del procés de degradació parcial ha permès determinar en aquest cas, quin dels dos àtoms de bor B3 o B6 ha estat eliminat.
- 7.- S'ha estudiat l'aplicació de *closo*-carborans halogenats en el camp del radiomarcatge.

ANNEX

ARTICLES PUBLICATS

(Comissió de Doctorat d'Abril del 2002)

Are Halocarboranes Suitable for Substitution Reactions? The Case for 3-I-1,2-*closo*-C₂B₁₀H₁₁: Molecular Orbital Calculations, Aryldehalogenation Reactions, ¹¹B NMR Interpretation of *closo*-Carboranes, and Molecular Structures of 1-Ph-3-Br-1,2-*closo*-C₂B₁₀H₁₀ and 3-Ph-1,2-*closo*-C₂B₁₀H₁₁

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In this paper, the chemistry of 3-X-1,2-*closo*-C₂B₁₀H₁₁ (X = halogen) derivatives is extended. Molecular orbital and ¹¹B and ¹³C NMR calculations on these species are presented. A qualitative interpretation of the ¹¹B NMR spectra of *closo o*-carborane derivatives is also provided. The synthesis of 3-X-1-R-*o*-carborane (X = I, Br and R = Me, Ph) derivatives is reported, and aryldehalogenation at the B3 position is reported for the first time. The molecular and crystal structures of 1-phenyl-3-bromo-1,2-dicarba-*closo*-dodecaborane and 3-phenyl-1,2-dicarba-*closo*-dodecaborane are described.

Introduction

The icosahedral carborane 1,2-*closo*-C₂B₁₀H₁₂ (*o*-carborane) can be viewed as an aromatic moiety,¹ in many respects resembling organic molecules.² For example, the acidity and subsequent reactivity of the C–H group of 1,2-*closo*-C₂B₁₀H₁₂ is reminiscent of that of R–C≡C–H and arises because of the similar nature of the C atomic orbitals in both HCCB₁₀H₁₁ and HCCR, each carbon atom contributing two sp hybrid and two perpendicular p AO's to the molecular orbital set.³

However, the chemistry of boron-substituted carboranes is not as well developed as that of carbon-substituted carboranes because of the difficulty of introducing functional groups at the boron atoms of the carborane cage. In general, boron-halogenated carboranes,⁴ the most accessible boron-substituted derivatives, are of limited value in synthesis due to the low reactivity of the halogen linked to boron, but if this problem could be overcome it would open up many new possibilities in boron cluster chemistry. The strong electron-withdrawing (–I) effect of the cluster on the α substituent at carbon is well established, explaining why it is difficult to add HCl to C-carboranylethene in the presence of AlCl₃ while B-carboranylethylenes readily react under similar conditions.⁵ Thus C-substituted carboranes behave differently from B-substituted

carboranes, and in many aspects the latter better resemble their organic analogues, e.g., 3-amino-*o*-carborane shows reactions typical of aliphatic and aromatic primary amines.⁶ Furthermore, the boron atoms in the cluster are susceptible to electrophilic alkylation in the presence of AlCl₃, under conditions similar to those required for aromatic compounds. The formation of a B–S bond by the action of elemental sulfur on carborane, in the presence of AlCl₃, has also been reported.⁷ These reactions can be better described, however, by the EINS (electrophilic induced nucleophilic substitution) mechanism.

Given that resemblances do exist between B-substituted carboranes and organic analogues, it is difficult to understand why the B-substitution chemistry of carboranes is relatively unexplored. The formation of a B–C bond from B–X through the reaction of iodocarboranes with organomagnesium compounds in the presence of Ni and Pd complexes has been reported.^{8,9} This reaction and a modification introducing CuI as a cocatalyst¹⁰ has become a route to B-substituted *o*-carborane derivatives and has been applied in several systems, mostly on the readily available B9 and/or B12 iodinated species. It could, probably, be extended to the B8 and B10 positions as these

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have also been iodinated. However, the cluster carbon atoms and the boron atoms adjacent to carbon do not appear to be susceptible to electrophilic substitution. Thus compounds 3-I-1,2-*closo*-C₂B₁₀H₁₁,⁸ 3-Br-1,2-*closo*-C₂B₁₀H₁₁,^{11,12} and 3-F-1,2-*closo*-C₂B₁₀H₁₁¹² have been synthesized by the alternate strategy of reacting [C₂B₉H₁₁]²⁻ with BX₃ or their adducts. From 3-I-1,2-C₂B₁₀H₁₁ may be formed species with B3–C(alkyl) bonds, and 3-R-1,2-*closo*-C₂B₁₀H₁₁ (R = ethyl, allyl) have been synthesized.⁸ However, no aryl substitution at B3 has been reported to this time, although 3-Ph-1,2-*closo*-C₂B₁₀H₁₁ does exist, the result of the reaction between [C₂B₉H₁₁]²⁻ and PhBCl₂.¹³

Density-functional and Hartree–Fock (HF) calculations are also reported on 3-X-1,2-*closo*-C₂B₁₀H₁₁ (X = F, Cl, Br, I) and related carboranes. The availability of codes for calculating NMR shielding constants and other magnetic properties from first principles (*ab initio*)^{14,15} allows experimentalists to check, correlate, and compare between experimental and computed NMR shifts, thus assigning NMR signals to the corresponding nuclei. The model calculations assume a single molecule (0 K temperature) in the presence of a constant magnetic field **B**.

In this paper we extend the chemistry of 3-X-1,2-*closo*-C₂B₁₀H₁₁ derivatives. We present molecular orbital calculations (within the framework of density-functional and Hartree–Fock theory) on these species. The synthesis of 1-R-3-X-*o*-carborane derivatives (X = I, Br and R = Me, Ph) is reported, and aryldehalogenation at the B3 position is reported for the first time. The molecular and crystal structures of 1-phenyl-3-bromo-1,2-dicarba-*closo*-dodecaborane and 3-phenyl-1,2-dicarba-*closo*-dodecaborane are described.

Results and Discussion

1. Electronic Structures of 3-X-1,2-*closo*-C₂B₁₀H₁₁ (X = F, Cl, Br, I) and Related Carboranes. A. Theoretical Approach. All calculations in this work were performed with the Gaussian98 suite of programs.¹⁵ The methodology used in the geometry optimizations and NMR calculations is based on density-functional theory (DFT) with Becke's three parameter hybrid functional¹⁶ and the Lee–Yang–Parr correlation functional^{17,18} denoted as B3LYP.¹⁹ The 6-31G* basis set was used for all atoms, except for bromine and iodine, where the 3-21G* and 3-21G** basis sets were used, respectively. These are double- ζ type basis sets with an additional set of polarization functions in all atoms, except hydrogen. We will refer to this

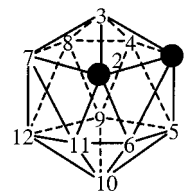


Figure 1. Structure of the 1,2-*closo*-C₂B₁₀H₁₂ cluster showing numbering of the cage atoms.

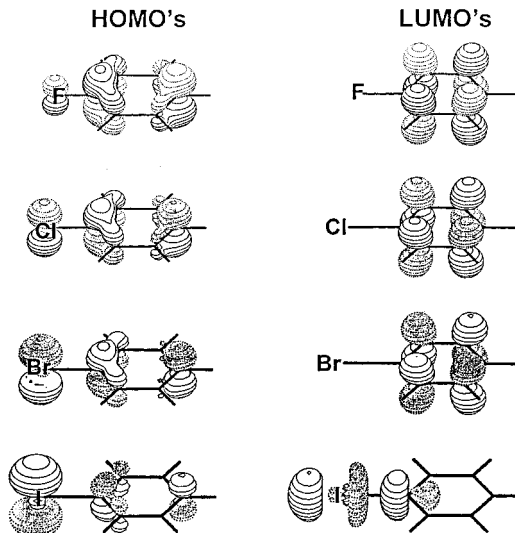


Figure 2. 3D contour plots (± 0.075 wave function amplitude units) of HOMO and LUMO orbitals in X–C₆H₅ (X = F, Cl, Br, I) compounds.

basis set as “Gen”. As described in section 4 below, the HF and B3LYP theoretical levels were used with basis sets “Gen” and LANL2DZ²⁰ (which consists of a Dunning/Huzinaga full double- ζ basis set for H, B, and C atoms, and Los Alamos effective core potential (ECP) plus double- ζ for I) for the calculation of ¹¹B NMR chemical shifts in 3-I-1,2-*closo*-C₂B₁₀H₁₁. Figure 1 shows the structure of 1,2-*closo*-C₂B₁₀H₁₂ with the numbering of the cage atoms.

All optimized molecular geometries are minima in the potential energy hypersurface, that is, all energy second-derivative matrices showed no imaginary frequencies. The NMR spectra calculations were performed on the optimized molecular geometries with gauge-including atomic orbitals (GIAO) and the same level of theory and basis sets noted above.

B. Electronic Structure. In this section the electronic structure of the 3-X-1,2-*closo*-C₂B₁₀H₁₁ carboranes (X = F, Cl, Br, I) is discussed. For comparative purposes on possible chemical reactivity in the former species, and considering the similarity invoked between the carborane cluster and the aromatic ring, discussion of the X–benzene (X = F, Cl, Br, I) molecules is also included.

As shown in Figure 2, the two electrons in the highest-occupied molecular orbital (HOMO) of X-benzene are delocalized around the phenyl ring with wave function amplitudes *decreasing* in the order F > Cl > Br > I. These HOMOs are similar to the 2-fold degenerate (e_{1g}) HOMO in benzene. Notwithstanding this, HOMO p_z wave function amplitudes also appear on the halogen atom in the X-benzene species, *increasing*

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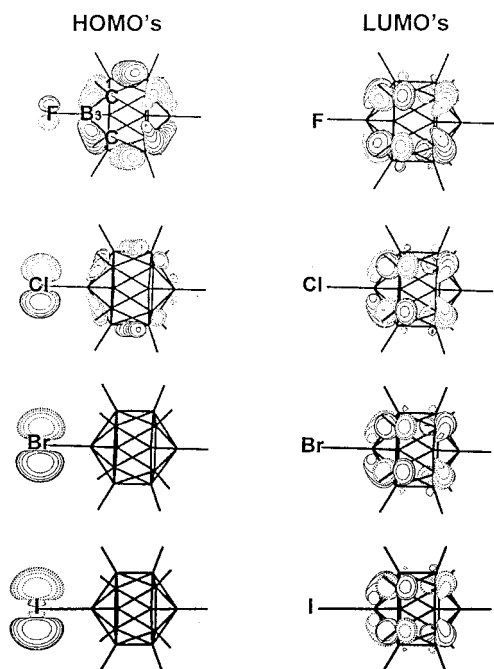


Figure 3. 3D contour plots (± 0.075 wave function amplitude units) of HOMO and LUMO orbitals of 3-X-1,2-closo-C₂B₁₀H₁₁ (X = F, Cl, Br, I) compounds.

in the order $F < Cl < Br < I$. Therefore the lone-pair (or less aromatic) character of the HOMOs in X-benzene is largest for iodobenzene. Turning now to the LUMOs shown in Figure 2, the “hole” amplitudes are also delocalized around the phenyl ring for X = F, Cl, and Br, with very similar amplitudes (all orbitals in Figure 2 and Figure 3 are plotted in a contour of ± 0.075 wave function amplitude units). These LUMOs are also similar to the 2-fold degenerate (e_{2u}) LUMO in benzene. However, when X = I the LUMO is completely different from the above cases, with wave function amplitude along the I–C bond (σ^* symmetry).

Figure 3 depicts HOMOs and LUMOs in the 3-X-1,2-closo-C₂B₁₀H₁₁ carboranes (X = F, Cl, Br, I). It is immediately apparent that the two electrons in the HOMOs are also delocalized, in this case around the carborane cage. As in X-benzene species, the HOMO amplitudes in 3-X-1,2-closo-C₂B₁₀H₁₁ carboranes also decrease in the order $F > Cl > Br > I$. Moreover, no HOMO amplitude whatsoever (at ± 0.075 contour levels) is found in the carborane cage for X = Br, I. Note also that the HOMO p_z amplitude on X also increases in the order $F < Cl < Br < I$.

Turning now to the LUMOs in 3-X-1,2-closo-C₂B₁₀H₁₁ carboranes, Figure 3 shows very similar shapes and amplitudes for all X. Careful inspection of the LUMOs in Figure 3 reveals π^* -type lobes on C1, C2 and on the antipodal atoms B9, B12. LUMO “hole” amplitudes are also found along the B3–B4, B3–B7, B5–B6, and B6–B11 connectivities.

Figure 4 shows the HOMO–LUMO energy levels for (a) X-benzene and (b) 3-X-1,2-closo-C₂B₁₀H₁₁ carborane. As shown in this figure the HOMO–LUMO energy gaps decrease in the order $F > Cl > Br > I$ for a and b. Moreover, the gaps are larger in b than in a.

From the data above and comparing the orbital pictures shown in Figure 2 and Figure 3 we conclude that similar chemical reactivities for both X-benzene and 3-X-1,2-closo-C₂B₁₀H₁₁ carborane species are expected. Electrophiles will thus attack near the HOMO-amplitude region and nucleophiles on the LUMO-amplitude region. Nevertheless, the 3-X-1,2-closo-

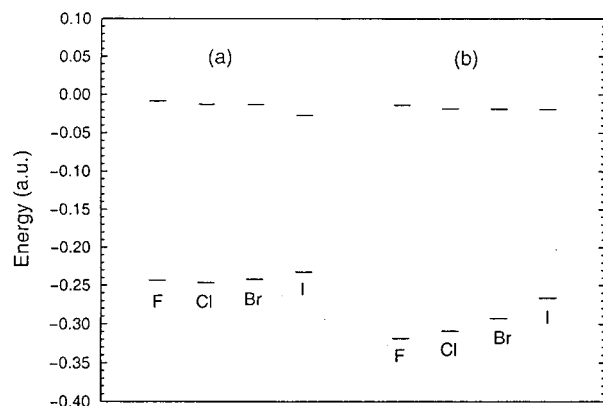
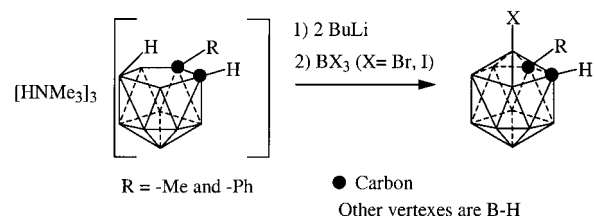


Figure 4. HOMO and LUMO energy levels for (a) X–C₆H₅ and (b) 3-X-1,2-closo-C₂B₁₀H₁₁ carborane.

Scheme 1



C₂B₁₀H₁₁ carboranes have larger HOMO–LUMO gaps, as shown in Figure 4, and therefore they are expected to be less reactive than X-benzene species.

Thus, our calculations suggest that the reactivity of the X-benzene and 3-X-1,2-closo-C₂B₁₀H₁₁ carboranes should increase in the order $F < Cl < Br < I$. The 3-I-1,2-closo-C₂B₁₀H₁₁ compound is predicted to be the best 3-halogenated starting compound for derivative chemistry.

2. Synthetic Studies. A. New 3-X-o-carborane Derivatives.

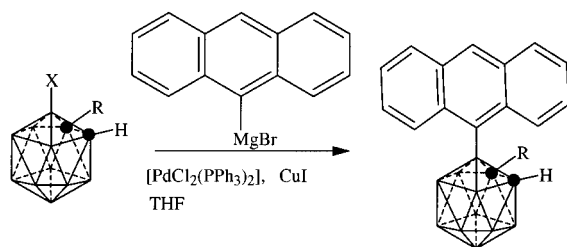
That B3, in 1-R₁-2-R₂-1,2-closo-C₂B₁₀H₁₀ compounds, is the atom most susceptible to nucleophilic attack was demonstrated long ago by Hawthorne and co-workers.²¹ Removal of B3 leads to the nido [7-R₁-8-R₂-7,8-C₂B₉H₁₀][−] anion and its rich derivative chemistry. The low electron density at B3 that facilitates its removal is also what prevents the formation of B3–X bonds by normal electrophilic substitution, a process that readily takes place first at B9, B12 followed by B8 and B10.²² Thus there exists clear evidence that not all the boron atoms in *o*-carborane and its derivatives should be regarded equally. Our calculations suggest that B3–X should have a chemistry comparable to that of C(aryl)–X, an idea supported by the organic-like behavior of 3-NH₂-1,2-closo-C₂B₁₀H₁₁ and 3-CH₂CH-1,2-closo-C₂B₁₀H₁₁.

In extending the chemistry of 3-halogeno *o*-carborane we have first investigated the synthesis of 3-I and 3-Br species which additionally have an electron-donating (–Me) or electron-withdrawing (–Ph) substituent on one of the cage carbon atoms. The reaction is shown in Scheme 1.

All four new carboranes 3-Br-1-Ph-1,2-closo-C₂B₁₀H₁₀, 3-I-1-Ph-1,2-closo-C₂B₁₀H₁₀, 3-Br-1-Me-1,2-closo-C₂B₁₀H₁₀, and 3-I-1-Me-1,2-closo-C₂B₁₀H₁₀ were produced in good yields. Compounds were initially characterized by microanalysis and

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Scheme 2



IR spectroscopy. NMR spectra (^{11}B , ^{13}C , ^1H) of the compounds are fully consistent with the proposed formulas.

Thus it may be concluded that the insertion of a BX^{2+} fragment into the open C_2B_3 face of nido $[\text{7-R-7,8-C}_2\text{B}_9\text{H}_{10}]^{2-}$ derivatives is not much dependent on either the bulkiness of the C-substituent or their electronic properties.

B. Aryldehalogenation Reactions at B(3). Aryldehalogenation reactions were performed on 3-I-1,2-closo- $\text{C}_2\text{B}_{10}\text{H}_{11}$, using three aryl substituents of differing volume: phenyl, biphenyl, and anthracenyl.

The procedure used was a modification of that reported by Hawthorne and Jones for alkyl substitution and consisted of the attack of the appropriate arylmagnesium bromide reagent (prepared from the corresponding aryl bromide) on 3-I-1,2-closo- $\text{C}_2\text{B}_{10}\text{H}_{11}$ in the presence of $[\text{PdCl}_2(\text{PPh}_3)_2]$ and CuI, in THF solution under refluxing conditions, as denoted in Scheme 2. The compounds 3-R-1,2-closo- $\text{C}_2\text{B}_{10}\text{H}_{11}$ (R = aryl) were obtained in good to high yields ($\approx 90\%$) and were fully characterized by multinuclear NMR data (^{11}B , ^{13}C , ^1H).

These reactions thus demonstrate that B–C coupling is a valid route to produce, in addition to B3–C(alkyl) carboranes already described, new B3–C(aryl) derivatives. On the other hand, attempts to produce this B–C coupling but in the reverse way, that is, reaction of a B-carboranylmagnesium reagent with R–X (R = aryl), did not succeed, mainly yielding mostly unreacted reagent. An attempted dehalogen coupling reaction with Cu,²³ intended to lead to B–B formation, was similarly unsuccessful. However, hydrodehalogen reactions of 3-I-1,2-closo- $\text{C}_2\text{B}_{10}\text{H}_{11}$ in DMF in the presence of Ni²⁴ or Pd²⁵ in stoichiometric quantities yielded *o*-carborane.

3. Molecular and Crystal Structures of 1-Ph-3-Br-1,2-closo- $\text{C}_2\text{B}_{10}\text{H}_{10}$ and 3-Ph-1,2-closo- $\text{C}_2\text{B}_{10}\text{H}_{11}$. As an adjunct to our theoretical and synthetic work we have studied the species 1-Ph-3-Br-1,2-closo- $\text{C}_2\text{B}_{10}\text{H}_{10}$ and 3-Ph-1,2-closo- $\text{C}_2\text{B}_{10}\text{H}_{11}$ by single-crystal X-ray diffraction.

A. 1-Ph-3-Br-1,2-closo- $\text{C}_2\text{B}_{10}\text{H}_{10}$. A perspective view of a single molecule is shown in Figure 5, and Table 1 lists key molecular parameters determined. The compound crystallizes as well-separated, individual molecules. There is no relationship between the crystallographic packing in 1-Ph-3-Br-1,2-closo- $\text{C}_2\text{B}_{10}\text{H}_{10}$ and its isomer species 1-Ph-2-Br-1,2-closo- $\text{C}_2\text{B}_{10}\text{H}_{10}$.²⁶ The cage has the expected near-icosahedral geometry with the lengths of the differing types of connectivity increasing in the expected sequence C–C < C–B < B–B, the magnitudes of these connectivities standing in close comparison with those determined for 1,2-closo- $\text{C}_2\text{B}_{10}\text{H}_{12}$.²⁷ In C–Ph 1,2-carboranes

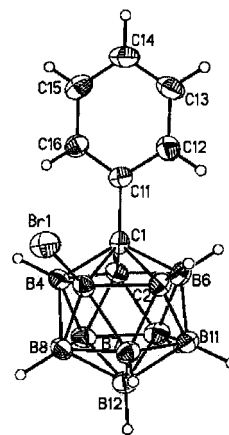


Figure 5. Structure of 1-Ph-3-Br-1,2-closo- $\text{C}_2\text{B}_{10}\text{H}_{10}$ showing the atom-labeling scheme.

Table 1. Selected Interatomic Distances (Å) and Interbond and Dihedral Angles (deg) in 1-Ph-3-Br-1,2-closo- $\text{C}_2\text{B}_{10}\text{H}_{10}$

| | | | |
|-----------------------|----------|-----------------|-----------|
| Br(1)–B(3) | 1.927(5) | B(5)–B(6) | 1.793(7) |
| C(1)–C(11) | 1.521(6) | B(6)–B(10) | 1.770(7) |
| C(1)–C(2) | 1.671(6) | B(6)–B(11) | 1.782(7) |
| C(1)–B(5) | 1.711(6) | B(7)–B(11) | 1.780(7) |
| C(1)–B(4) | 1.712(6) | B(7)–B(12) | 1.782(7) |
| C(1)–B(6) | 1.732(6) | B(7)–B(8) | 1.790(7) |
| C(1)–B(3) | 1.769(6) | B(8)–B(9) | 1.792(7) |
| C(2)–B(7) | 1.696(6) | B(8)–B(12) | 1.796(7) |
| C(2)–B(11) | 1.703(6) | B(9)–B(10) | 1.782(8) |
| C(2)–B(3) | 1.721(7) | B(9)–B(12) | 1.785(7) |
| C(2)–B(6) | 1.730(6) | B(10)–B(12) | 1.779(8) |
| B(3)–B(8) | 1.765(7) | B(10)–B(11) | 1.785(8) |
| B(3)–B(4) | 1.769(7) | B(11)–B(12) | 1.779(7) |
| B(3)–B(7) | 1.780(7) | C(11)–C(16) | 1.382(6) |
| B(4)–B(5) | 1.775(7) | C(11)–C(12) | 1.383(6) |
| B(4)–B(9) | 1.775(7) | C(12)–C(13) | 1.370(7) |
| B(4)–B(8) | 1.779(7) | C(13)–C(14) | 1.392(7) |
| B(5)–B(9) | 1.774(7) | C(14)–C(15) | 1.381(7) |
| B(5)–B(10) | 1.780(7) | C(15)–C(16) | 1.387(6) |
| C(11)–C(1)–C(2) | 118.4(3) | C(2)–B(3)–Br(1) | 119.3(3) |
| C(11)–C(1)–B(5) | 122.3(3) | B(8)–B(3)–Br(1) | 130.0(3) |
| C(11)–C(1)–B(4) | 122.9(4) | C(1)–B(3)–Br(1) | 118.0(3) |
| C(11)–C(1)–B(6) | 116.9(3) | B(4)–B(3)–Br(1) | 123.9(3) |
| C(11)–C(1)–B(3) | 117.6(3) | B(7)–B(3)–Br(1) | 124.5(3) |
| C(2)–C(1)–C(11)–C(16) | | | –159.2(4) |
| B(3)–C(1)–C(11)–C(16) | | | –90.2(5) |
| C(2)–C(1)–C(11)–C(12) | | | 25.6(5) |
| B(3)–C(1)–C(11)–C(12) | | | 94.5(5) |

we define the orientation of the Ph substituent by the angle θ , the modulus of the average $\text{C}_{\text{cage}}-\text{C}_{\text{cage}}-\text{C11}-\text{C}$ torsion angle.²⁸ In the present compound θ is $66.8(5)^\circ$, twisted from its optimum^{29a} value of ca. 25° by the steric requirements of the Br substituent (the potential energy barrier to complete rotation of the Ph substituent in 1-Ph-1,2-closo- $\text{C}_2\text{B}_{10}\text{H}_{11}$ is only 6 kJ mol^{-1} at the DZ//HF/6-31G^* level of theory^{29a}). Thus in the conformation adopted the torsion angles B3–C1–C11–C12 and B3–C1–C11–C16 are nearly equal and opposite, $94.5(5)^\circ$ and $-90.2(5)^\circ$, respectively. The B3–Br distance is $1.927(5) \text{ \AA}$, in excellent agreement with other such distances in the literature.³⁰

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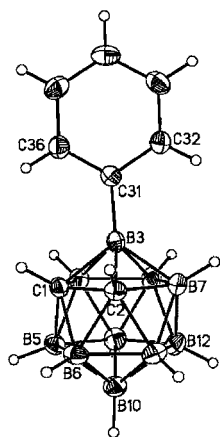


Figure 6. Structure of 3-Ph-1,2-*closo*-C₂B₁₀H₁₁ showing the atom-labeling scheme.

Table 2. Selected Interatomic Distances (Å) and Interbond and Dihedral Angles (deg) in 3-Ph-1,2-*closo*-C₂B₁₀H₁₁

| | | | |
|---------------|------------|---------------|------------|
| C1—C2 | 1.626(3) | B5—B6 | 1.782(3) |
| C1—B4 | 1.692(3) | B5—B10 | 1.787(3) |
| C1—B5 | 1.699(3) | B6—B10 | 1.766(3) |
| C1—B6 | 1.725(3) | B6—B11 | 1.779(3) |
| C1—B3 | 1.734(3) | B7—B12 | 1.774(3) |
| C2—B7 | 1.695(3) | B7—B11 | 1.780(3) |
| C2—B11 | 1.700(3) | B7—B8 | 1.786(3) |
| C2—B6 | 1.724(3) | B8—B9 | 1.789(3) |
| C2—B3 | 1.740(3) | B8—B12 | 1.791(3) |
| B3—C31 | 1.566(3) | B9—B12 | 1.786(3) |
| B3—B8 | 1.774(3) | B9—B10 | 1.786(3) |
| B3—B4 | 1.791(3) | B10—B11 | 1.783(3) |
| B3—B7 | 1.793(3) | B10—B12 | 1.790(3) |
| B4—B8 | 1.774(3) | B11—B12 | 1.778(3) |
| B4—B9 | 1.780(3) | C31—C32 | 1.396(2) |
| B4—B5 | 1.781(3) | C31—C36 | 1.400(3) |
| B5—B9 | 1.779(3) | | |
| C31—B3—C1 | 121.44(14) | C31—B3—B7 | 125.27(15) |
| C31—B3—C2 | 122.33(15) | B3—C31—C32 | 120.04(16) |
| C31—B3—B8 | 128.74(15) | B3—C31—C36 | 122.64(16) |
| C31—B3—B4 | 123.50(16) | C32—C31—C36 | 117.12(17) |
| C1—B3—C31—C32 | 155.93(16) | C1—B3—C31—C36 | -29.3(3) |
| C2—B3—C31—C32 | 89.0(2) | C2—B3—C31—C36 | -96.2(2) |

B. 3-Ph-1,2-*closo*-C₂B₁₀H₁₁. Figure 6 shows a perspective view of a single molecule of 3-Ph-1,2-*closo*-C₂B₁₀H₁₁, and Table 2 lists key interatomic distances, interbond angles, and torsion angles determined.

The molecule crystallizes with no imposed symmetry. The plane of the Ph substituent is more or less symmetrically disposed with respect to C2 but lies in no special orientation with respect to C1 (and C1 and C2 are unambiguously located). There are no significant intermolecular contacts, and the crystal structure of 3-Ph-1,2-*closo*-C₂B₁₀H₁₁ bears no relationship to those of two crystalline modifications of 1-Ph-1,2-*closo*-C₂B₁₀H₁₁ recently reported.²⁹

C1—C2 is 1.626(3) Å, C(cage)—B distances lie in the range 1.69–1.74 Å, and B—B lies in the range 1.76–1.80 Å. The phenyl ring is attached to B3 at B3—C31 1.566(3) Å.

4. NMR Spectral Considerations. The sensitivity of the electron distribution in carboranes to the presence of substituents has long been apparent.² For icosahedral carborane derivatives of 1-R-1,2-*closo*-C₂B₁₀H₁₁, ¹¹B NMR studies have shown that

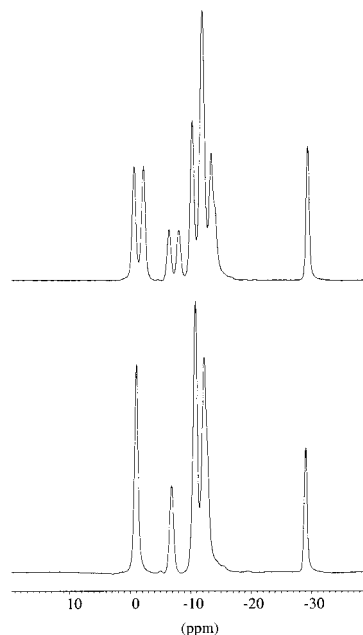


Figure 7. ¹¹B and ¹¹B{¹H} spectra of 3-I-1,2-*closo*-C₂B₁₀H₁₁.

the chemical shifts of the cage boron atoms vary with the substituent R,³¹ particularly the boron atom opposite to the point of attachment of the substituent, the “antipodal atom”.³²

The ¹¹B NMR spectrum of 3-I-1,2-*closo*-C₂B₁₀H₁₁ presents a 2:1:3:3:1 pattern in the range -1.04 to -29.02 ppm. Figure 7 shows the ¹¹B and ¹¹B{¹H} NMR spectra of 3-I-1,2-*closo*-C₂B₁₀H₁₁. The resonance at -29.02 ppm does not split into a doublet in the ¹¹B NMR spectrum, indicating that this resonance corresponds to the B—I vertex. Once the B3 resonance is known, the two-dimensional 2D-COSY NMR spectrum³³ is helpful for the assignment of the remaining peaks. Figure 8 shows a typical spectrum, that of 3-I-1,2-*closo*-C₂B₁₀H₁₁, with the assignments deduced from the off-diagonal resonances.

A. Qualitative Description of the ¹¹B NMR Spectra. The ¹¹B NMR spectra of icosahedral *closo*-carboranes could be easily understood if dominated by the diamagnetic shielding term σ^d : the further a boron atom was from the more electronegative carbon atoms, the more shielded it would be and the more negative its chemical shift. Thus, 1,2-*closo*-C₂B₁₀H₁₂ would display a 2:4:2:2 pattern from high to low frequency due to B(3,6), B(4,5,7,11), B(8,10), and B(9,12), respectively. However, this is not the case as the experimental spectrum has resonances at -2.1: -8.9: -13.4: -14.5 (2:2:4:2) ppm arising from atoms B(9,12), B(8,10), B(4,5,7,11), and B(3,6), respectively; thus the real spectrum is the reverse of that predicted on the basis of σ^d .³⁴ This certainly implies that a paramagnetic deshielding term σ^p is very relevant as has been stated earlier,^{35,36} the magnitude of this term decreasing as B(9,12) > B(8,10) > B(4,5,7,11) > B(3,6). The strong σ^p term is a

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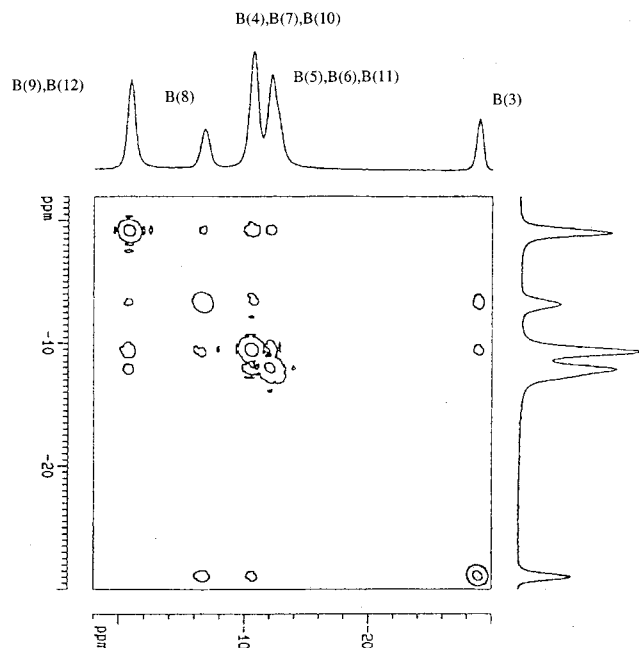


Figure 8. $^{11}\text{B}\{^1\text{H}\}\text{-}^{11}\text{B}\{^1\text{H}\}$ 2D-COSY NMR spectrum of 3-I-1,2-*closo*- $\text{C}_2\text{B}_{10}\text{H}_{11}$.

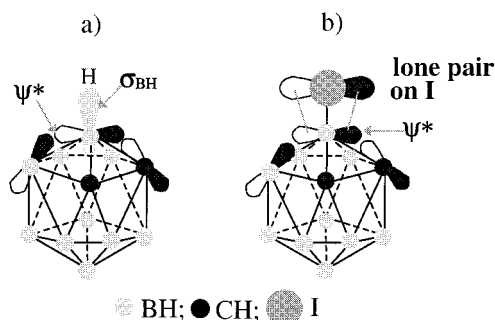


Figure 9. ^{11}B NMR in closo carboranes. (a) In 1,2- $\text{C}_2\text{B}_{10}\text{H}_{12}$, perpendicular disposition of the occupied σ_{BH} and the atomic p_\perp orbitals. The last one participates in the low-lying ψ^* unoccupied orbital. Only some atomic orbitals are represented. (b) In 3-I-1,2- $\text{C}_2\text{B}_{10}\text{H}_{11}$, lone-pair electron back-donation from the I atom to the ψ^* , largely spread on the cluster.

consequence of low-lying unoccupied p_\perp orbitals allowed efficient combination with appropriate energy-rich occupied orbitals. Figure 9a depicts the $\sigma_{\text{BH}}/\text{p}_\perp$ combination, possibly responsible for the strong ^{11}B NMR dependency of the σ^{p} term. According to selection rules the combination of an occupied and an unoccupied orbital is magnetically active only when the corresponding (hypothetical) electron transfer comprises an angular momentum.³⁷ Thus, perpendicularly placed σ/p_\perp combinations are active in NMR, yielding deshielding contributions perpendicular to the σ/p_\perp plane of charge circulation. It is also reasonable to assume that the magnitude of the individual σ^{p} contributions will depend on the electron density in the particular B–H bond. The last follows the pattern $\text{B-H}(9,12) > \text{B-H}(8,10) > \text{B-H}(4,5,7,11) > \text{B-H}(3,6)$; thus the largest individual σ^{p} contribution would be for B–H(9,12), the smallest for B–H(3,6), corresponding very well with the observed pattern indicated above.

The ^{11}B NMR spectrum of *o*-carborane was rationalized in 1986 following a set of empirical rules incorporating antipodal, rhomboidal, butterfly, and neighbor effects.³⁸ The description

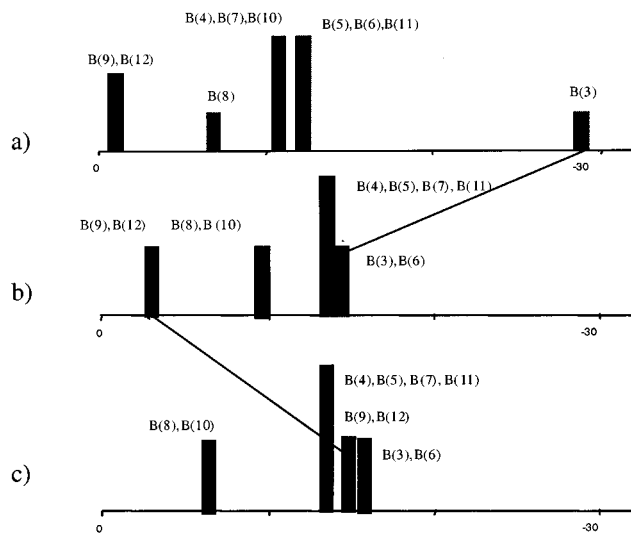


Figure 10. Raw ^{11}B NMR spectra with the peak assignments for the compounds: (a) 3-I-1,2-*closo*- $\text{C}_2\text{B}_{10}\text{H}_{11}$, (b) 1,2-*closo*- $\text{C}_2\text{B}_{10}\text{H}_{12}$, and (c) 9,12- I_2 -1,2-*closo*- $\text{C}_2\text{B}_{10}\text{H}_{10}$.

above provides a rationale for these effects. Now, if the ^{11}B NMR spectrum of 3-I-1,2-*closo*- $\text{C}_2\text{B}_{10}\text{H}_{11}$, with resonances at -1.04 (B9,B12), -6.82 (B8), -10.73 (B4,B7,B10), -12.18 (B5,B11,B6), and -29.02 (B3) ppm, is compared to that for *o*-carborane, we note that all resonances are shifted about 3 ppm to lower field, except that due to B3, considerably shifted to higher field, by about 14 ppm. Figure 10 shows how the resonances attributable to the different types of boron nuclei in compounds 1,2-*closo*- $\text{C}_2\text{B}_{10}\text{H}_{12}$, 3-I-1,2-*closo*- $\text{C}_2\text{B}_{10}\text{H}_{11}$, and 9,12- I_2 -1,2-*closo*- $\text{C}_2\text{B}_{10}\text{H}_{10}$ change in chemical shift. All the resonances show some changes, but the largest upfield shift, over 14 ppm, is always due to the B–I resonances.

We will not discuss the smaller shifts, a general phenomenon when a heteroatom participating with more electrons than BH is incorporated into the cluster, this already anticipating that B3 is electron rich compared to BH's in the molecule.

Let us focus on the B3 shift. It is known that the σ/p_\perp combination is more efficient the closer in energy are the participating orbitals. Considering that lone pairs of non-electronegative elements like iodine are reasonably basic in terms of Lewis acid/base theory, they should interact efficiently with the p_\perp orbitals on B3. See Figure 9b. This will enrich considerably the electron density at B3 enhancing its shielding σ^{d} term, and consequently shifting the B3 resonance to high field. This back-donation to B3 will diminish in the sequence $\text{I} > \text{Br} > \text{Cl} > \text{F}$, thus shifting the B3 resonance to lower field upon substitution of one halogen by another. The increasing electronegativity in the former sequence will, moreover, cause B3 to become even more deshielded, explaining its considerable downfield shift. This qualitative explanation suffices to explain the ^{11}B NMR pattern of these icosahedral closo species. Their main novelty is the inclusion of a local σ^{p} contribution, thus avoiding the concept of tangential p_x and p_y , “ π ” orbitals which are NMR active, and radial p_z orbitals which are chemically active.^{35,39} The π back-donation power (the mesomeric (+M) effect) had been invoked earlier to explain an increase in the electron density at the antipodal position.³¹

B. Quantitative Description of the ^{11}B and ^{13}C NMR Spectra. To our knowledge no comprehensive literature exists

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Table 3. Experimental $^{11}\text{B}\{^1\text{H}\}$ and $^{13}\text{C}\{^1\text{H}\}$ Chemical Shifts (ppm) in Carboranes 3-X-1,2- $\text{C}_2\text{B}_{10}\text{H}_{11}$ (X = F, Cl, Br, I, Ph) and 3-X-1-R-1,2- $\text{C}_2\text{B}_{10}\text{H}_{10}$ (X = Br, I and R = Me, Ph)^a

| nuclei | F ^b | Cl ^c | Br | I | Ph | (Br, Me) | (Br, Ph) | (I, Me) | (I, Ph) |
|-------------------------|----------------|-----------------|------------|------------|------------|------------|------------|------------|------------|
| ^{11}B | 0.0 (1) | 6.02 | -1.42 (2) | -1.04 (2) | -2.06 (2) | -2.32 (1) | -3.26 (2) | -1.24 (1) | -1.98 (1) |
| ^{11}B | -5.4 (2) | -3.1 | -7.56 (1) | -6.82 (1) | -4.71 (1) | -5.60 (1) | -7.80 (1) | -5.06 (1) | -3.00 (1) |
| ^{11}B | -12.1 (1) | -10.10 | -11.27 (3) | -10.73 (3) | -8.16 (1) | -7.74 (1) | -8.61 (1) | -6.41 (1) | -6.49 (1) |
| ^{11}B | -14.0 (1) | -15.02 | -12.5 (4) | -12.18 (3) | -12.62 (3) | -9.10 (1) | -9.59 (1) | -8.17 (1) | -9.43 (5) |
| ^{11}B | -14.4 (2) | -16.55 | | -29.02 (1) | -13.29 (3) | -9.97 (4) | -10.53 (3) | -10.05 (4) | -12.75 (1) |
| ^{11}B | -15.5 (2) | -17.7 | | | | -12.31 (1) | -11.38 (1) | -12.09 (1) | -23.19 (1) |
| ^{11}B | -19.2 (1) | | | | | -13.14 (1) | -13.88 (1) | -24.32 (1) | |
| ^{13}C cluster | | | 59.17 | 60.30 | 56.69 | 72.04 | 78.23 | 71.47 | 78.15 |
| ^{13}C cluster | | | 59.17 | 60.30 | 56.69 | 66.24 | 62.32 | 66.84 | 62.59 |
| ^{13}C | | | | | 133.06 | 25.73 | 132.70 | 28.35 | 134.24 |
| ^{13}C | | | | | 132.03 | | 130.77 | | 130.78 |
| ^{13}C | | | | | 129.77 | | 129.53 | | 129.53 |
| ^{13}C | | | | | 128.30 | | 127.79 | | 127.67 |

^a The numbers within parentheses correspond to the equivalent boron atoms. ^b Reference 46. ^c Reference 47.

on GIAO/IGLO calculations of ^{11}B NMR spectra in B(3)-substituted *o*-carboranes.⁴⁰ We should emphasize here the IGLO calculations of Brain et al.²⁹ on the C-substituted 1-Ph-1,2-*closo*- $\text{C}_2\text{B}_{10}\text{H}_{11}$. Their computed ^{11}B NMR chemical shift results agree well with experiment up to a difference of ca. 4 ppm (B(8,10)) for the minimum energy conformer ($\Pi''/\text{HF}/6\text{-}31\text{G}^*$ calculations). Similar results are found in a recent work Oliva et al.³⁶ where ^{11}B and ^{13}C NMR experimental and computed chemical shifts for dodecaborane, *o*-carborane, and 1,2-(SH)₂-*o*-carborane are reported. Also, Diaz et al.⁴¹ report experimental/calculational correlations of ^{13}C NMR signals in a series of carboranes and derivatives, including *o*-carborane.

Table 3 shows ^{11}B and ^{13}C NMR experimental chemical shifts for the carboranes 3-X-1,2-*closo*- $\text{C}_2\text{B}_{10}\text{H}_{11}$ (X = F, Cl, Br, I, Ph) and 3-X-1-R-1,2-*closo*- $\text{C}_2\text{B}_{10}\text{H}_{10}$ (X = Br, I; R = Me, Ph). Attempts to reproduce these ^{11}B and ^{13}C NMR chemical shifts using rigorous calculational methods⁴² have been used. All of them broadly reproduce trends for most cage atoms except B3. Possible solvent molecule–molecule interactions of the iodocarboranes when measuring the ^{11}B NMR signals, and/or intermolecular hydrogen bonding noted in the crystal structure of 3-I-1,2-*closo*- $\text{C}_2\text{B}_{10}\text{H}_{11}$,⁴³ should not be disregarded to explain the degree of inaccuracy found. However, it is necessary to consider that small differences (up to 2 ppm) are experimentally observed when recording ^{11}B NMR spectra of *o*-carborane derivatives in different solvents.

Experimental Section

General Considerations. Elemental analyses were performed using a Carlo Erba EA1108 microanalyzer. IR spectra were recorded from KBr pellets on a Shimadzu FTIR-8300 spectrophotometer. ^1H and $^1\text{H}\{^{11}\text{B}\}$ NMR (300.13 MHz), $^{13}\text{C}\{^1\text{H}\}$ 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. All NMR spectra were recorded from CDCl_3 solutions at 25 °C. Chemical shift values for ^{11}B NMR spectra were referenced to external $\text{BF}_3 \cdot \text{OEt}_2$, and those for ^1H , $^1\text{H}\{^{11}\text{B}\}$, and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra were referenced to SiMe_4 . Chemical shifts are reported in units of parts per million downfield from reference, and all coupling constants are reported in hertz.

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 prior to use. A 1.6 M solution of *n*-butyllithium in hexanes from Lancaster was used as purchased. BI_3 and BBr_3 were used as purchased from Alfa. 3-I-1,2-*closo*- $\text{C}_2\text{B}_{10}\text{H}_{11}$ ⁸ and 3-Br-1,2-*closo*- $\text{C}_2\text{B}_{10}\text{H}_{11}$ ¹¹ were synthesized according to the literature.

3-Bromo-1-methyl-1,2-dicarba-*closo*-dodecaborane. To a solution of $[\text{HNMe}_3][7\text{-Me-}7,8\text{-C}_2\text{B}_9\text{H}_{11}]$ (5.0 g, 24 mmol) in anhydrous diethyl ether (50 mL) at 0 °C was added dropwise with stirring butyllithium (30 mL, 48 mmol). Once the addition was completed, the reaction mixture was stirred at room temperature for an additional 2 h and then heated to reflux for 4 h. After evaporation of the solvent, anhydrous hexane (100 mL) was added to the remaining solid. BBr_3 (9.0 g, 36 mmol) was then added dropwise with stirring at 0 °C. Stirring was continued for 5 h at room temperature once the addition was completed. The excess boron tribromide was decomposed by careful addition of 20 mL of water. The organic layer was separated from the mixture and the aqueous layer extracted with hexane (3 × 15 mL). The combined organic phase was dried over MgSO_4 and the solvent removed at the water pump. The crude product was purified by flash silica gel chromatography using dichloromethane/hexane (2:1) as the eluting solvent to give 3-bromo-1-methyl-1,2-dicarba-*closo*-dodecaborane. Yield: 3.5 g (62%). Anal. Calcd for $\text{C}_3\text{H}_{13}\text{B}_{10}\text{Br}$: C, 15.19; H, 5.53. Found: C, 15.50; H, 5.64. IR: ν [cm^{-1}] = 3057 ($\text{C}_{\text{cluster}}\text{-H}$), 2960–2854 ($\text{C}_{\text{Me}}\text{-H}$), 2590 (B–H). ^1H NMR: δ = 3.56 (br s, 1H, $\text{C}_{\text{cluster}}\text{-H}$), 2.17 (s, 3H, CH_3), 3.50–1.50 (br m, 9H, B–H). $^{13}\text{C}\{^1\text{H}\}$ NMR: δ = 72.04, 66.24 (s, $\text{C}_{\text{cluster}}$), 25.73 (s, CH_3). ^{11}B NMR: δ = -2.32 (d, $^1J(\text{B,H})$ = 151, 1B), -5.60 (d, $^1J(\text{B,H})$ = 151, 1B), -7.74 (d, $^1J(\text{B,H})$ = 110, 1B), -9.10 (s, 1B, B(3)), -9.97 (d, 4B), -12.31 (d, 1B), -13.14 (d, $^1J(\text{B,H})$ = 96, 1B).

3-Bromo-1-phenyl-1,2-dicarba-*closo*-dodecaborane. Similarly were reacted $[\text{HNMe}_3][7\text{-Ph-}7,8\text{-C}_2\text{B}_9\text{H}_{11}]$ (5.0 g, 19 mmol) and butyllithium (24 mL, 38 mmol) in anhydrous diethyl ether (50 mL) at 0 °C, followed by addition of anhydrous hexane (100 mL) and BBr_3 (7.1 g, 28.5 mmol). Workup and purification as previously gave 3-bromo-1-phenyl-1,2-dicarba-*closo*-dodecaborane. Yield: 3.1 g (55%). Anal. Calcd for $\text{C}_8\text{H}_{15}\text{B}_{10}\text{Br}$: C, 32.11; H, 5.05. Found: C, 32.42; H 5.07. IR: ν [cm^{-1}] = 3068 ($\text{C}_{\text{cluster}}\text{-H}$), 3056, 3040 ($\text{C}_{\text{aryl}}\text{-H}$), 2642, 2609, 2599, 2589, 2577, 2558 (B–H). ^1H NMR: δ = 7.47–7.27 (m, 5H, H_{aryl}), 4.23 (br s, 1H, $\text{C}_{\text{cluster}}\text{-H}$), 3.90–2.10 (br m, 9H, B–H). $^{13}\text{C}\{^1\text{H}\}$ NMR: δ = 132.70, 130.77, 129.53, 127.79 (C_{aryl}), 78.23, 62.32 (s, $\text{C}_{\text{cluster}}$). ^{11}B NMR: δ = -3.26 (d, $^1J(\text{B,H})$ = 143, 2B), -7.80 (d, 1B), -8.61 (s,

(40) Non-boron-substituted *nido*-undecaborates and icosahedral *closo* *o*-carboranes have respectively chemical shift windows ca. (0:–40 ppm) and (0:–15 ppm). More extensive literature is found for the GIAO-MP2/GIAO/IGLO computations of ^{11}B NMR spectra in the *nido* and related carboranes; see, e.g.: (a) Schleyer, P. v. R.; Gauss, J.; Buehl, M.; Greatrex, R.; Fox, M. A. *J. Chem. Soc., Chem. Commun.* **1993**, 23, 1766. (b) Onak, T.; Tran, D.; Tseng, J.; Diaz, M.; Arias, J.; Herrera, S. *J. Am. Chem. Soc.* **1993**, *115*, 9210. (c) Jaballas, J.; Onak, T. *J. Organomet. Chem.* **1998**, *550*, 101. (d) Hosmane, N. S.; Maguire, J. A. In *Organometallic and Organometalloidal Compounds: Borane, Carbocation Continuum*; Casanova, J. Ed.; Wiley: New York, 1998; p 397.

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1B, B(3)), -9.59 (d, 1B), -10.53 (d, 3B), -11.38 (d, 1B), -13.88 (d, $^1J(\text{B,H}) = 164, 1\text{B})$.

3-Iodo-1-methyl-1,2-dicarba-closo-dodecaborane. In an analogous manner were reacted $[\text{HNMe}_3][7\text{-Me-7,8-C}_2\text{B}_9\text{H}_{11}]$ (5.0 g, 24 mmol) and butyllithium (30 mL, 48 mmol) in anhydrous diethyl ether (50 mL) at 0 °C, followed by addition of anhydrous hexane (100 mL) and BI_3 (14.1 g, 36 mmol). Workup as previously and purification by flash silica gel chromatography using dichloromethane/hexane (4:1) as the eluting solvent gave 3-iodo-1-methyl-1,2-dicarba-closo-dodecaborane. Yield: 4.8 g (71%). Anal. Calcd for $\text{C}_3\text{H}_{13}\text{B}_{10}\text{I}$: C, 12.68; H, 4.61. Found: C, 13.04; H 4.56. IR: ν [cm^{-1}] = 3058 ($\text{C}_{\text{cluster}}\text{-H}$), 2956–2857 ($\text{C}_{\text{Me}}\text{-H}$), 2594 (B–H). $^1\text{H NMR}$: $\delta = 3.60$ (br s, 1H, $\text{C}_{\text{cluster}}\text{-H}$), 2.24 (s, 3H, CH_3), 3.50–1.10 (br m, 9H, B–H). $^{13}\text{C}\{^1\text{H}\}$ NMR: $\delta = 71.47, 66.84$ (s, $\text{C}_{\text{cluster}}$), 28.35 (s, CH_3). $^{11}\text{B NMR}$: $\delta = -1.24$ (d, $^1J(\text{B,H}) = 151, 1\text{B}$), -5.06 (d, $^1J(\text{B,H}) = 156, 1\text{B}$), -6.41 (d, $^1J(\text{B,H}) = 122, 1\text{B}$), -8.17 (d, $^1J(\text{B,H}) = 176, 1\text{B}$), -10.05 (d, $^1J(\text{B,H}) = 180, 4\text{B}$), -12.09 (d, $^1J(\text{B,H}) = 161, 1\text{B}$), -24.32 (s, 1B, B(3)).

3-Iodo-1-phenyl-1,2-dicarba-closo-dodecaborane. Similarly, $[\text{HNMe}_3][7\text{-Ph-7,8-C}_2\text{B}_9\text{H}_{11}]$ (5.0 g, 19 mmol) was deprotonated with butyllithium (24 mL, 38 mmol) in anhydrous diethyl ether (50 mL), followed by evaporation of the solvent and addition of anhydrous hexane (100 mL) and BI_3 (11.1 g, 28.5 mmol) in hexane (50 mL). After reaction and workup as previously, chromatography using dichloromethane/hexane (1:1) as eluting solvent gave 3-iodo-1-phenyl-1,2-dicarba-closo-dodecaborane. Yield: 3.42 g (52%). Anal. Calcd for $\text{C}_8\text{H}_{15}\text{B}_{10}\text{I}$: C, 27.75; H, 4.37. Found: C, 27.64; H, 4.34. IR: ν [cm^{-1}] = 3059 ($\text{C}_{\text{cluster}}\text{-H}$), 2544 (B–H). $^1\text{H NMR}$: $\delta = 7.50\text{--}7.00$ (m, 5H, H_{aryl}), 4.22 (br s, 1H, $\text{C}_{\text{cluster}}\text{-H}$), 3.10–1.50 (br m, 9H, B–H). $^{13}\text{C}\{^1\text{H}\}$ NMR: $\delta = 134.24, 130.78, 129.53, 127.67$ (C_{aryl}), 78.15, 62.59 (s, $\text{C}_{\text{cluster}}$). $^{11}\text{B NMR}$: $\delta = -1.98$ (d, $^1J(\text{B,H}) = 140, 1\text{B}$), -3.00 (d, $^1J(\text{B,H}) = 114, 1\text{B}$), -6.49 (d, $^1J(\text{B,H}) = 164, 1\text{B}$), -9.43 (d, $^1J(\text{B,H}) = 158, 5\text{B}$), -12.75 (d, $^1J(\text{B,H}) = 169, 1\text{B}$), -23.19 (s, 1B, B(3)).

3-Phenyl-1,2-dicarba-closo-dodecaborane. To a stirring solution of 3-iodo-1,2-dicarba-closo-dodecaborane (1.35 g, 5 mmol), in THF (50 mL) at 0 °C, was added, dropwise, a solution of phenylmagnesium bromide (20 mmol) in the same solvent. After stirring at room temperature for 30 min, $[\text{PdCl}_2(\text{PPh}_3)_2]$ (140 mg, 4% equiv) and CuI (38 mg, 4% equiv) were added in a single portion, following which the reaction mixture was heated to reflux for 3 days. The solvent was removed, and 100 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 (3 \times 10 mL). The combined organic phase was washed with water and dried over MgSO_4 . The solvent was removed and the residue purified by flash silica gel chromatography using dichloromethane/hexane (1:4) as the eluting solvent to give 3-phenyl-1,2-dicarba-closo-dodecaborane. Yield: 0.95 g (86%). Anal. Calcd for $\text{C}_8\text{H}_{16}\text{B}_{10}$: C, 43.61; H, 7.32. Found: C, 43.75; H, 7.34. IR: ν [cm^{-1}] = 3064 ($\text{C}_{\text{cluster}}\text{-H}$), 3010 ($\text{C}_{\text{aryl}}\text{-H}$), 2646, 2635, 2619, 2608, 2602, 2596, 2556 (B–H). $^1\text{H NMR}$: $\delta = 8.00\text{--}7.30$ (m, 5H, H_{aryl}), 3.71 (br s, 2H, $\text{C}_{\text{cluster}}\text{-H}$), 3.50–0.50 (br m, 9H, B–H). $^{13}\text{C}\{^1\text{H}\}$ NMR: $\delta = 133.06, 132.03, 129.77, 128.30$ (C_{aryl}), 56.69 (s, $\text{C}_{\text{cluster}}$). $^{11}\text{B NMR}$: $\delta = -2.06$ (d, $^1J(\text{B,H}) = 149, 2\text{B}$), -4.71 (s, 1B, B(3)), -8.16 (d, $^1J(\text{B,H}) = 147, 1\text{B}$), -12.62 (d, 3B), -13.29 (d, $^1J(\text{B,H}) = 169, 3\text{B}$).

3-Biphenyl-1,2-dicarba-closo-dodecaborane. An entirely analogous reaction, but using 4-biphenylmagnesium bromide (20 mmol) and chromatography using dichloromethane/hexane (4:1) as eluting solvent, gave 3-biphenyl-1,2-dicarba-closo-dodecaborane. Yield: 1.4 g (94%). Anal. Calcd for $\text{C}_{14}\text{H}_{20}\text{B}_{10}$: C, 56.73; H, 6.80. Found: C, 56.64; H, 6.78. IR: ν [cm^{-1}] = 3060 ($\text{C}_{\text{cluster}}\text{-H}$), 3028 ($\text{C}_{\text{aryl}}\text{-H}$), 2623, 2601, 2567 (B–H), 1479 (γ (C-C_{aryl})). $^1\text{H NMR}$: $\delta = 7.70\text{--}7.20$ (m, 9H, H_{aryl}), 3.73 (br s, 2H, $\text{C}_{\text{cluster}}\text{-H}$), 2.50–1.10 (br m, 9H, B–H). $^{13}\text{C}\{^1\text{H}\}$ NMR: $\delta = 142.66, 141.24, 140.43, 134.28, 129.44, 128.43, 127.86, 127.68$ (C_{aryl}), 57.35 (s, $\text{C}_{\text{cluster}}$). $^{11}\text{B NMR}$: $\delta = -2.01$ (d, $^1J(\text{B,H}) = 150, 2\text{B}$), -4.75 (s, 1B, B(3)), -8.14 (d, $^1J(\text{B,H}) = 150, 1\text{B}$), -12.63 (d, 6B).

3-Anthracenyl-1,2-dicarba-closo-dodecaborane. An entirely analogous reaction, but using 9-anthracylmagnesium bromide (25 mmol) and chromatography using dichloromethane/hexane (1:4) as eluting solvent, gave 3-anthracenyl-1,2-dicarba-closo-dodecaborane. Yield: 1.50 g (94%). Anal. Calcd for $\text{C}_{16}\text{H}_{20}\text{B}_{10}$: C, 59.97; H, 6.29. Found: C, 58.41; H, 6.11. IR: ν [cm^{-1}] = 3089 ($\text{C}_{\text{cluster}}\text{-H}$), 3010 ($\text{C}_{\text{aryl}}\text{-H}$), 2603–2550 (B–H), 1436 (γ (C-C_{aryl})). $^1\text{H NMR}$: $\delta = 8.80$ (d, $^2J(\text{H,H}) = 8.80, 2\text{H}, \text{H}_{\text{aryl}}$), 8.47 (s, 1H, H_{aryl}), 8.01 (d, $^2J(\text{H,H}) = 7.5, 2\text{H}, \text{H}_{\text{aryl}}$), 7.54–7.46 (m, 4H, H_{aryl}), 3.86 (s, 2H, $\text{C}_{\text{cluster}}\text{-H}$), 3.50–1.50 (br m, 9H, B–H). $^{13}\text{C}\{^1\text{H}\}$ NMR: $\delta = 137.41, 132.22, 131.91, 130.15, 127.92, 126.95, 125.62$ (C_{aryl}), 59.0 (s, $\text{C}_{\text{cluster}}$). $^{11}\text{B NMR}$: $\delta = -2.15$ (d, $^1J(\text{B,H}) = 147, 2\text{B}$), -3.89 (s, 1B, B(3)), -7.83 (d, $^1J(\text{B,H}) = 150, 1\text{B}$), -11.02 (d, $^1J(\text{B,H}) = 134, 1\text{B}$), -11.81 (d, $^1J(\text{B,H}) = 132, 2\text{B}$), -13.34 (d, $^1J(\text{B,H}) = 159, 3\text{B}$).

Crystallographic Studies. Intensity data collected on a Bruker P4 diffractometer, with $\text{Mo K}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) to $2\theta_{\text{max}} = 50^\circ$, ω scans, corrections for absorption (φ scans), Lorentz and polarization effects,⁴⁴ and structures were solved by direct methods and refined (against F^2) by full-matrix least-squares refinement.⁴⁵ Cage C atoms were unambiguously identified by inspection of U values following isotropic refinement of all cage vertexes as boron, and confirmed by C–C distances. H atoms were treated as riding model.

For 1-Ph-3-Br-1,2-closo- $\text{C}_2\text{B}_{10}\text{H}_{10}$, $\text{C}_8\text{H}_{15}\text{B}_{10}\text{Br}$, 160(2) K, $M_r = 299.21$: crystal size $0.25 \times 0.38 \times 0.30$ mm, monoclinic, $P2_1/n$, $a = 7.0131(6) \text{ \AA}$, $b = 20.213(3) \text{ \AA}$, $c = 10.5327(14) \text{ \AA}$, $\beta = 107.005(9)^\circ$, $V = 1427.8(3) \text{ \AA}^3$, $Z = 4$, $\rho_{\text{calcd}} = 1.392 \text{ g cm}^{-3}$, $F(000) = 592$, $\mu = 2.848 \text{ mm}^{-1}$, of 3332 unique reflections 2500 were observed [$F_o > 2\sigma(F_o)$], 173 parameters, $R1 = 0.0455$, $wR2 = 0.1176$ (for observed data), $S = 1.080$; maximum and minimum residual electron density, 0.601 and $-1.404 \text{ e \AA}^{-3}$ (near Br3).

For 3-Ph-1,2-closo- $\text{C}_2\text{B}_{10}\text{H}_{11}$, $\text{C}_8\text{H}_{16}\text{B}_{10}$, 293(2) K, $M_r = 220.31$: crystal size $0.10 \times 0.68 \times 0.24$ mm, monoclinic, $P2_1/c$, $a = 10.405(2) \text{ \AA}$, $b = 9.779(2) \text{ \AA}$, $c = 12.746(2) \text{ \AA}$, $\beta = 99.26(2)^\circ$, $V = 1280.0(4) \text{ \AA}^3$, $Z = 4$, $\rho_{\text{calcd}} = 1.143 \text{ cm}^{-3}$, $F(000) = 356$, $\mu = 0.053 \text{ mm}^{-1}$, of 2246 unique reflections 1724 were observed [$F_o > 4\sigma(F_o)$], 197 parameters, $R1 = 0.0708$, $wR2 = 0.1399$ (for observed data), $S = 1.042$; maximum and minimum residual electron density, 0.237 and $-0.202 \text{ e \AA}^{-3}$.

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Supporting Information Available: Crystallographic data for 1-Ph-3-Br-1,2- $\text{C}_2\text{B}_{10}\text{H}_{10}$ and 3-Ph-1,2- $\text{C}_2\text{B}_{10}\text{H}_{11}$ in CIF format. GIAO calculated ^{11}B and ^{13}C NMR chemical shifts in carboranes 3-X-1,2-closo- $\text{C}_2\text{B}_{10}\text{H}_{11}$ (X = F, Cl, Br, I, Ph) and 3-X-1-R-1,2-closo- $\text{C}_2\text{B}_{10}\text{H}_{10}$ (X = Br, I and R = Me, Ph). Experimental and GIAO computed ^{11}B NMR chemical shifts in 3-I-1,2-closo- $\text{C}_2\text{B}_{10}\text{H}_{11}$ using the Hartree–Fock and B3LYP approaches with the “Gen” and LANL2DZ basis sets. This material is available free of charge via the Internet at <http://pubs.acs.org>. Crystallographic data (excluding structure factors) for the structures reported in this paper also have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications no. CCDC-162671 and CCDC-154906 for 1-Ph-3-Br-1,2- $\text{C}_2\text{B}_{10}\text{H}_{10}$ and 3-Ph- $\text{C}_2\text{B}_{10}\text{H}_{11}$, respectively. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. (fax, (+44) 1223-336-033; E-mail, deposit@ccdc.cam.ac.uk).

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The B–I activation in *o*-carborane clusters: their fate towards B–H. Easy synthesis of $[7,10\text{-C}_2\text{B}_{10}\text{H}_{13}]^-$

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Abstract

The reaction of 3-*I-o*-carborane with Cu, Cu/PPh₃, [Ni(PPh₃)₃], or [Pd(PPh₃)₄] has been studied to find the suitability of B–iodine substituted carboranes as sources of new boron-derivatives. In all these reactions a hydrodehalogenation reaction to yield *o*-carborane has been produced, indicating that B–I activation takes place. It may be considered that B–I adds oxidatively to M, but alternative explanations can be given. Reaction of 3-*I-o*-carborane with Na/naphthalene also produced *o*-carborane showing that albeit an oxidative addition is impossible for sodium the same hydrodehalogenation had taken place. The same result was also formed with Mg. Addition of 1,2-dibromoethane to the Mg/*o*-carborane reaction yielded $[7,10\text{-C}_2\text{B}_{10}\text{H}_{13}]^-$. Then, the sequence 3-*I-o*-carborane → *o*-carborane → $[7,10\text{-C}_2\text{B}_{10}\text{H}_{13}]^-$ can be generated with only reducing agents. The synthetic procedure for $[7,10\text{-C}_2\text{B}_{10}\text{H}_{13}]^-$ is very simple and produces a 97% yield of [NMe₄][7,10- $\text{C}_2\text{B}_{10}\text{H}_{13}$]. Basically, 1,2- $\text{C}_2\text{B}_{10}\text{H}_{12}$ and Mg in excess are refluxed in THF in the presence of I₂ and 1,2-dibromoethane. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Carboranes; Cluster; Iodine; *Nido*; Magnesium; Oxidative addition

1. Introduction

It is well known that the chemistry of boron-substituted carboranes is not as developed as that of the carbon analogues due to the difficulty of introducing functional groups at the boron atom of the carborane cage. B-halogenated carboranes would be an excellent source of new B-derivatives if they were not so inert to substitution reactions [1]. Notwithstanding so, these can be adequate starting materials through reaction of a iodocarborane with organomagnesium compounds in the presence of Ni and Pd complexes [2], or if the B–I bond is activated to the corresponding carboranyl(phenyl)iodonium salt [3,4]. None of these methods provide, however, a nucleophilic boron atom. Considering the similarities between aryl and carboranyl fragments [5] one would expect the ready formation of B-carboranyl Grignard reagents. In this case a formally negative B-carboranyl fragment could be produced. Another way of activating the B–I bond would be via the oxidative addition to metal ions in low oxidation states, as is the case in cross-coupling reac-

tions [6]. Neither in one case nor in the other, we were able to obtain the desired final products. The recent paper by Grushin and coworkers [4] on the activation of B–I by Pd(0) motivated us to present our results which are in agreement and complement the observations indicated there.

2. Results and discussion

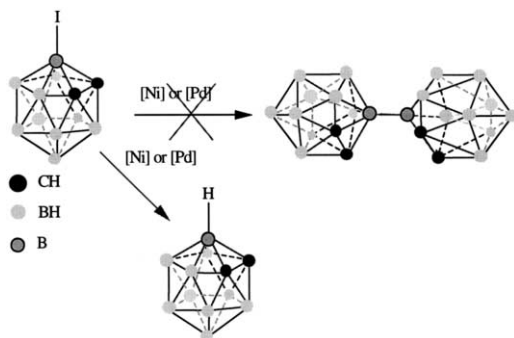
Grushing et al. utilized 9-*I-m*-carborane while we did utilize 3-*I-o*-carborane [7]. They reasoned to use the *m*-carborane to avoid the nucleophilic induced partial degradation of the *closo*-carborane framework. They used [Pd(PPh₃)₄], and precursors of [Pd(PPh₃)_{*n*}] (*n* = 1 or 2), while we did use Cu, Cu/PPh₃, [Ni(PPh₃)₃], and [Pd(PPh₃)₄]. The reagents are comparable and, as expected, the conclusions were, too. Our interest in these reactions was motivated to generate 3-(3'-*o*-carboranyl)-*o*-carborane as shown in Scheme 1.

Contrary to Grushing et al., who had used the metal complexes in catalytic amounts, in our case the metal complex was used in stoichiometric amounts. The reaction of 3-*I-o*-carborane with Cu, Cu/PPh₃, [Ni(PPh₃)₃],

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or $[\text{Pd}(\text{PPh}_3)_4]$ has been studied. The reaction conditions are the ones used to generate coupling of organic iodides [8]. The result in all cases was a hydrodehalogenation to produce *o*-carborane. This hydrodehalogenation reaction, however, does not take place when 9-*I*-*m*-carborane is reacted with $[\text{Pd}(\text{PPh}_3)_4]$ [4,9]. For this to occur, it is required to use $[\text{Pd}(\text{PPh}_3)_n]$ ($n = 1$ or 2) that provides more accessibility to the metal ion. Although this proves that some differences exist between 3-*I*-*o*-carborane and 9-*I*-*m*-carborane, which are the result of the different electronic surroundings, it seems clear that B–I activation takes place by M(0) transition metal complexes. This is, however, not synthetically satisfactory as it reverts to *o*-carborane. It may happen, as it has been indicated, that B–I adds oxidatively to M. In fact there is data that seems to support it [4], although from our point of view the source of H is controversial. Due to the special characteristics of the cluster an interaction such as the one shown in Fig. 1 could not be excluded.

To discern on the fate of the Pd complex, the reaction between 3-*I*-*o*-carborane and $\text{Pd}[(\text{PPh}_3)_4]$ in DMF at reflux for 24 h, was carried out. The reaction was monitored by boron and phosphorous NMR spectra. The $^{11}\text{B}\{^1\text{H}\}$ -NMR spectrum of the initial reaction mixture displayed a spectrum with pattern 2:1:3:3:1 in the range -1.0 to -29.0 ppm characteristic of 3-*I*-*o*-carborane while both the $^{31}\text{P}\{^1\text{H}\}$ and ^{31}P spectra showed a singlet at 15.66 ppm characteristic of $[\text{Pd}(\text{PPh}_3)_4]$ complex [10]. After completion of the reaction, the $^{11}\text{B}\{^1\text{H}\}$ -NMR spectrum of the reaction crude



Scheme 1. Hydrodehalogenation of 3-*I*-*o*-carborane to produce *o*-carborane. On top, the sought 3-(3-*o*-carboranyl)-*o*-carborane dicluster.

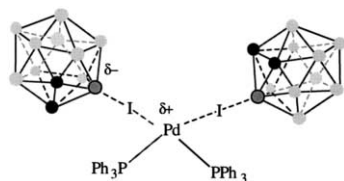
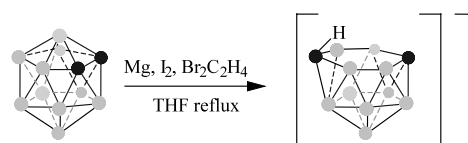


Fig. 1. Possible explanation for B–I activation and formation of $[\text{PdI}_2(\text{PPh}_3)_2]$.

showed an independent broad resonance at -5 ppm corresponding to the removed boron vertex and a pattern spectrum 2:2:1:2:1:1 in the range -10.6 to -37.6 ppm characteristic of *nido*- $[7,8\text{-C}_2\text{B}_9\text{H}_{12}]^-$ species and the $^{31}\text{P}\{^1\text{H}\}$ and ^{31}P spectra showed two singlets at -5.35 and 25.9 ppm in a ratio 1:1. The resonance at -5.35 ppm could be attributed to triphenylphosphine [11] and the second one most probably to *cis*- $[\text{PdI}_2(\text{PPh}_3)_2]$ [12].

Electron density from the electron-rich metal would be transferred to the easily polarizable iodine, ultimately forming an electron-rich boron, which could be subjected to an electrophilic attack by a proton. An alternative pathway would be a homolytic cleavage of the B–I bond, but there seems to be evidence that it does not take place with $[\text{Pd}(\text{PPh}_3)_4]$ [4]. To see if an electron transfer, basically a reduction, could also explain the formation of the *o*-carborane, a reducing agent that cannot undergo additive oxidation was chosen. Although the coupling of two aryl halides with sodium is impractical [13], the fate of 3-*I*-*o*-carborane with this metal was tested. Reaction of 3-*I*-*o*-carborane with Na/naphthalene produced after working up the *o*-carborane. Thus, the hydrodehalogenation has again taken place, albeit an oxidative addition is impossible in this case. We pursued this issue further by performing the reaction with Mg. It is well known that aryl iodides react directly with magnesium to give Grignard reagents, and the similarity of 3-*I*-*o*-carborane with iodophenyl should have produced, a priori, the Grignard derivatives of 3-*o*-carborane. Furthermore it is generally accepted that the mechanism of this reaction involves free radicals [13]. The reaction was done in THF, adding a few crystals of I_2 as a catalyst. Under these conditions the reaction proceeded very slowly. After 10 days at reflux, and following the sequential addition of minor amounts of I_2 , the reaction was considered terminated. The ^{11}B -NMR of the mother liquor, done in a concentric tube, proved that *o*-carborane had been produced. The reaction was considerably accelerated when 1,2-dibromoethane, that produces ethene, was added as a catalyst. Within 12 h at room temperature, the total conversion of 3-*I*-*o*-carborane to *o*-carborane had taken place. Another observation was that upon reaction of 3-*I*-*o*-carborane with Mg for 12 h, in THF, at reflux and with 1,2-dibromoethane, an anionic species was generated. This could be isolated as the $[\text{NMe}_4]^+$ salt. The ^{11}B -NMR displayed a 2:1:1:2:2:2 pattern, with resonances at 16.4, 12.1, $+0.8$, -7.9 , -15.8 , -22.2 ppm that could be assigned to $[7,10\text{-C}_2\text{B}_{10}\text{H}_{13}]^-$ according to published data [14]. To ascertain if 3-*I*-*o*-carborane was necessary to produce this reaction, *o*-carborane was treated under the same conditions, to say in THF, at reflux, with Mg and 1,2-dibromoethane, for 9 h. The result was identical. This

Scheme 2. Synthesis of $[7,10\text{-C}_2\text{B}_{10}\text{H}_{13}]^-$.

indicates that the sequence 3-*I-o*-carborane \rightarrow *o*-carborane $\rightarrow [7,10\text{-C}_2\text{B}_{10}\text{H}_{13}]^-$ is the one that takes place.

It has been well documented that alkali metals can reduce the neutral carborane $\text{C}_2\text{B}_{10}\text{H}_{10}\text{R}_2$ to the carborane dianion $[\text{nido-C}_2\text{B}_{10}\text{H}_{10}\text{R}_2]^{2-}$, which is able to form the 13-vertex *closo*-metallacarboranes with the metal ions in a η^6 fashion [15]. The $[\text{C}_2\text{B}_{10}\text{H}_{12}]^{2-}$ anions have recently experienced a renewed interest [16], mainly in its capacity to produce U, Dy, Y, Er and Sm complexes. The monoanion $[7,10\text{-C}_2\text{B}_{10}\text{H}_{13}]^-$ can be produced by reduction of any of the $\text{C}_2\text{B}_{10}\text{H}_{12}$ isomers [17] although the more convenient is 1,2- $\text{C}_2\text{B}_{10}\text{H}_{12}$. Upon its reduction with sodium metal, in THF at room temperature for 15 h, the dianion $[\text{C}_2\text{B}_{10}\text{H}_{12}]^{2-}$ is obtained. Treatment of the $\text{Na}_2\text{C}_2\text{B}_{10}\text{H}_{12}$ solution in THF with aqueous 0.1 N NaOH yielded after considerable working up $[\text{NMe}_4][7,10\text{-C}_2\text{B}_{10}\text{H}_{13}]$, in overall 20% yield. The procedure reported here is considerably more simple and produces a 97% yield of $[\text{NMe}_4][7,10\text{-C}_2\text{B}_{10}\text{H}_{13}]$. It uses Mg instead of Na, which already represents an advantage for the easiness of use, and requires an easy working up. Basically, 1,2- $\text{C}_2\text{B}_{10}\text{H}_{12}$ and Mg in excess are refluxed in THF for 9 h in the presence of I_2 and 1,2-dibromoethane. After working up and treatment of the water solution with $[\text{NMe}_4]\text{Cl}$ the species $[\text{NMe}_4][7,10\text{-C}_2\text{B}_{10}\text{H}_{13}]$ is obtained.

In conclusion, in this report we have intended to produce new information concerning the reactivity of B–I in *o*-carborane. Our results are in agreement with those reported by Grushing et al., however, it is not so clear whether the mechanism goes through an oxidative addition. While the end product is the same, the *o*-carborane, we have shown that Na, which cannot undergo oxidative addition leads to the same product. Also, the statement that the reaction does not take place via a radical mechanism is not supported by the fact that the *o*-carborane is also produced by a Grignard reaction which is accepted to take place via this mechanism. Most possibly, different mechanisms take place. What seems to be clear is that the *o*-carborane formation is a favored process, probably due to kinetic considerations, which compete favorably with other desired products. More efforts are needed to activate the B–I bond, avoiding the competition of hydrogen, either radical or a proton that prevents their use as a convenient starting material.

Finally we have proven that $[7,10\text{-C}_2\text{B}_{10}\text{H}_{13}]^-$ an anion that surprisingly has not received much attention, can be synthesized in high yield by reduction with Mg with the concurrence of 1,2-dibromoethane (Scheme 2).

3. Experimental

3.1. General

^1H -NMR (300.13 MHz), ^{11}B -NMR, $^{11}\text{B}\{^1\text{H}\}$ -NMR (96.29 MHz) and ^{31}P -, $^{31}\text{P}\{^1\text{H}\}$ -NMR (121.5 MHz) spectra were recorded in a Bruker ARX 300 instrument equipped with the appropriate decoupling accessories. Most of the NMR spectra were recorded from acetone- d_6 concentric tubes at 25 °C. The acetone- d_6 was in the inner tube. The outer tube contained the sample in a non-deuterated dry solvent. Chemical shift values for ^{11}B -NMR spectra were referenced to external $\text{BF}_3\cdot\text{OEt}_2$ and those for ^1H -, $^1\text{H}\{^{11}\text{B}\}$ -NMR spectra were referenced to Me_4Si . ^{31}P - and $^{31}\text{P}\{^1\text{H}\}$ -NMR spectra were referenced to an external 85% H_3PO_4 . Chemical shifts are reported in units of parts per million downfield from Me_4Si , and all coupling constants are reported in Hz.

Unless otherwise noted, all manipulations were carried out under N_2 atmosphere using standard vacuum line techniques. Toluene and THF were distilled from sodium benzophenone prior to use. DMF was distilled from CaO and Py from CaH. $[\text{Ni}(\text{PPh}_3)_3]$ [18] and $[\text{Pd}(\text{PPh}_3)_4]$ [19] were synthesized by published methods.

3.2. Reaction of 3-*I-o*-carborane with Cu

3.2.1. In the presence of PPh_3

3-*I-o*-Carborane (100 mg, 0.37 mmol), triphenylphosphine (97 mg, 0.37 mmol) and activated Cu metal (235 mg, 3.7 mmol) were placed in a capillary. After sealing, it was heated in the oven at 300 °C for 24 h. After it was cooled down, the residue was extracted with acetone and evaporated to dryness to get *o*-carborane (53 mg) in 100% yield.

3.2.2. In the absence of PPh_3

As above with 3-*I-o*-carborane (100 mg, 0.37 mmol) and activated Cu metal (235 mg, 3.7 mmol) to get 25 mg of *o*-carborane in 48% yield.

3.3. Reaction of 3-*I-o*-carborane with $[\text{Ni}(\text{PPh}_3)_3]$

3.3.1. In toluene, THF or pyridine

To a 25 ml Schlenk flask were added $[\text{NiCl}_2(\text{PPh}_3)_2]$ (653 mg, 1 mmol), PPh_3 (524 mg, 2 mmol), Zn (66 mg, 1 mmol) and 5 ml of the dry solvent. The mixture was heated at 50 °C in an oil bath for 1 h. A solution of 3-*I-o*-carborane (270 mg, 1 mmol) in dry solvent was added to the mixture. Stirring was continued under N_2

at 50 °C for 24 h. The solution contained only *o*-carborane.

3.3.2. In DMF

The same as above was done but in DMF, obtaining a mixture of *o*-carborane (95%) and *nido-o*-carborane (5%).

3.4. Reaction of 3-*I-o*-carborane with [Pd(PPh₃)₄]

To a 25 ml Schlenk flask were added [Pd(PPh₃)₄] (577 mg, 0.5 mmol), K₂CO₃ (691 mg, 5 mmol) and 5 ml of dry DMF. The mixture was heated at 50 °C in an oil bath for 1 h. A solution of 3-*I-o*-carborane (135 mg, 0.5 mmol) in dry DMF was added to the mixture and was continued stirring under N₂ at 50 °C during 24 h. The solution contained *nido-o*-carborane in 100% yield as the only final product.

3.5. Synthesis of [N(CH₃)₄][7,10-C₂B₁₀H₁₃]

To a 100 ml Schlenk flask were added Mg metal (1.0 g, 41 mmol), 2 ml of THF and a crystal of I₂. Then, dibromoethane (0.5 ml, 6.0 mmol) and a solution of *o*-carborane (1.0 g, 7.0 mmol) in THF (40 ml) were added dropwise, at the same time, to the Mg suspension at 0 °C. Once the addition was completed the reaction mixture was left at room temperature for 30 min. After 9 h at reflux the mixture was evaporated to dryness in vacuo and water (60 ml) was added to the residue, filtered and the anion was precipitated from the aqueous solution with an excess of [NMe₄]Cl. The white solid was washed with water and Et₂O. The compound [NMe₄][7,10-C₂B₁₀H₁₃] was obtained in 97% yield (1.5 g, 6.8 mmol). ¹H-NMR (CD₃COCD₃, 25 °C): δ 3.40 (s, N(CH₃)₄, 12H), 3.21 (d, C–H, 1H, *J*(H,H) = 7.4 Hz), 2.81 (d, C–H, 1H, *J*(H,H) = 7.4 Hz), 2.54 (s, C–H, 1H). ¹¹B-NMR (CD₃COCD₃, 25 °C): δ +16.4 (d, 2B, *J*(B–H) = 151 Hz), +12.1 (d, 1B, *J*(B–H) = 135 Hz), +0.8 (d, 1B, *J*(B–H) = 135 Hz), –7.9 (d, 2B, *J*(B–H) = 148 Hz), –15.8 (d, 2B, *J*(B–H) = 135 Hz), –22.2 (d, 2B, *J*(B–H) = 139 Hz).

Acknowledgements

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Retention of the B(3)–X (X = Br, I) bond in *closo-o*-carborane derivatives after nucleophilic attack. The first synthesis of [3-X-7-R-7,8-*nido*-C₂B₉H₁₀][−] (X = Br, I). Crystal structure of [HNMe₃][3-I-7,8-*nido*-C₂B₉H₁₁]

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Abstract

The synthesis of new 3-halogeno *nido* derivatives of *o*-carborane, [3-X-7-R-7,8-*nido*-C₂B₉H₁₀][−] (X = Br, I; R = H, CH₃, C₆H₅) is described, through deboronation of the compounds 3-X-1-R-1,2-*closo*-C₂B₁₀H₁₀, previously synthesised in our laboratory. These *nido* products have been fully characterised using ¹H-, ¹¹B- and ¹³C-NMR spectroscopies, MALDI-TOF and, for [3-I-7,8-*nido*-C₂B₉H₁₁][−] by an X-ray crystallographic study. The influences of the halogen moiety on both the B(3) resonance and that of the bridge proton are discussed. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: *nido* Carborane derivatives; Deboronation; Iodinated ligands

1. Introduction

Recently, the chemistry of boron-halogenated carboranes has received considerable attention, as evidenced by many relevant publications [1]. Previously, we have reported the synthesis of a series of 3-iodo and 3-bromo *closo-o*-carboranes and demonstrated that they could be excellent starting compounds for the preparation of new carborane-derivatives following substitution reactions [2]. More recently, the reactivity of 3-I-*o*-carborane towards Mg, Cu, Cu in the presence of PPh₃, [Ni(PPh₃)₃], or [Pd(PPh₃)₄] has also been studied in our group to establish the suitability of B-iodine substituted carboranes as sources of new derivatives [3]. In spite of the fact that halogenated *nido* carboranes have potential relevance to important topics such as radioiodine carry and as boron neutron capture therapy (BNCT) reagents [4]; relatively few iodinated and brominated *nido* carboranes are known. The iodination of [7,8-*nido*-C₂B₉H₁₂][−] was first reported by

Hawthorne et al. in 1965, [5] an electrophilic substitution at the 9-position of the open face of the *nido* precursor. The synthesis of 9,11 disubstituted [7,8-*nido*-C₂B₉H₁₂][−] was later described either by electrophilic halogenation with iodine [6,7] and bromine [7] or through the reaction of the anion with *N*-halosuccinimide (iodo and bromo) [8]. The synthesis of the 5-iodo-derivative, has also been described, [9,7] and, recently, some *nido* carborane species have been radioiodinated for labelling studies [10].

In this work, we describe the synthesis of new 3-halogeno *nido* derivatives of *o*-carborane, [3-X-7-R-7,8-*nido*-C₂B₉H₁₀][−] (X = Br, I; R = H, CH₃, C₆H₅), through the deboronation of the appropriate 3-X-1-R-1,2-*closo*-C₂B₁₀H₁₀, compounds previously synthesised in our laboratory [2].

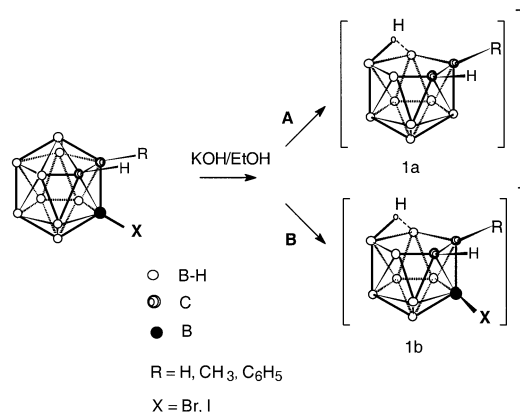
2. Results and discussion

Since the best method of obtaining halocarboranes is by electrophilic halogenation with iodine or bromine of the boron atom vertices, the most common halogenated

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nido carboranes are those substituted at the 9 and 11 positions, the sites of highest electron density as a result of their position in the open pentagonal face of the *nido* cluster [5]. Consequently, producing iodo and bromo derivatives substituted in other positions of the *nido* cluster is relatively difficult, due to the unsusceptibility of these sites to electrophilic attack. As far as we are aware, bromination of a *nido* carborane is only known at the 9 and 11 positions. For iodocarboranes the *nido* anion enantiomers 5-*I-nido*-7,8-dicarbaundecaborate and 6-*I-nido*-7,8-dicarbaundecaborate have been additionally obtained, through the deboronation of 9-*I-o*-carborane with KOH [7] or tetrabutylammonium fluoride hydrate, TBAFH [9]. In this paper we describe the deboronation with EtO^- in EtOH of a series of *closo* derivatives of *o*-carborane 3-*X-1-R-closo-1,2-C₂B₁₀H₁₀* (X = Br, I; R = H, CH₃, C₆H₅) iodinated or brominated at the 3-position, i.e. that connected both cluster carbon atoms. As it is well established, the deboronation of an icosahedral *closo-o*-carborane cluster always takes place at the 3 or 6 positions, equivalent in the case of non-B-substitution. However, the equivalence is removed in our case, because B(3) is halogenated. Therefore, one of the aims of this work was to establish which deboronation path, either the elimination of the B(3)–X vertex (X = I, Br) or the removal of the B(6)–H vertex (Scheme 1), would be followed.

Hawthorne et al. established that the partial degradation of 3-*R-closo*-compounds (R = Et, Ph) [11] by nucleophilic attack with ethanolic hydroxide ion at reflux temperature took place at the non-substituted boron atom, due to the steric demand of the R group, thus affording partially degraded products in which the organic substituent remains attached to boron(3). Hawthorne later reported [12] that B–OR carborane derivatives can also undergo degradation under basic conditions with retention of the substituent, but that, for substituted carboranes such as 3-(CH₂(CH₂)₂OH)-1,2-*closo-C₂B₁₀H₁₁*, the B(3) vertex was removed. In general it has been shown that the deboronation of 3-substituted



Scheme 1. Possible paths of the degradation process in B-derivatives.

ortho-carboranes, 3-*R-1,2-closo-C₂B₁₀H₁₁* in alcoholic KOH solution gives either [3-*R-7,8-nido-C₂B₉H₁₁*][−] (R = Ph, Et, NC, NHR) or [7,8-*closo-C₂B₉H₁₂*][−] (R = OH) or both possible *nido* anions when R = NH₂ [13]. Therefore, it is apparent that the outcome of nucleophilic attack is not just affected by steric considerations, and that electronic effects should also be taken into account. Fox et al. [9] calculated the Mulliken charges for some halogenated *closo* carboranes and demonstrated that the boron atom removed remains the one bearing the highest positive charge, thus the preferred site for nucleophilic attack.

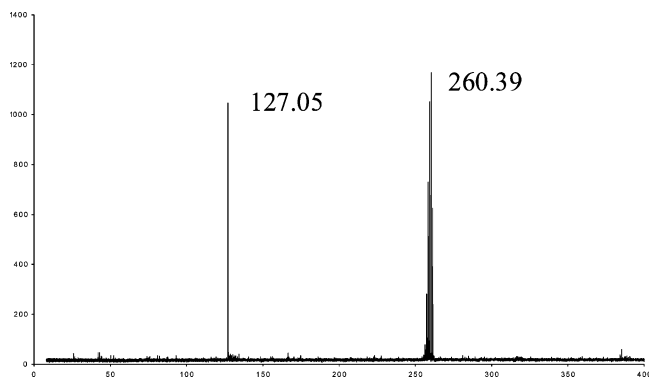
In our case, B(3) is either substituted with iodine or bromine. Both are electron-withdrawing atoms that can deplete electron density on B(3) making this atom more susceptible to nucleophilic attack; in contrast, they are also bulky atoms, which could prevent B(3) removal by steric effects, forcing attack at B(6) instead.

The *closo* halogenated compounds 3-*X-1-R-1,2-closo-C₂B₁₀H₁₀* (X = Br, I; R = H, Me, Ph) have been used as starting materials. The deboronation of these compounds with KOH–EtOH under reflux conditions for 3 h and subsequent precipitation with [HNMe₃]Cl led to the formation of [HNMe₃][3-*X-1-R-7,8-nido-C₂B₉H₁₀*] (X = Br, I; R = H, Me, Ph; compounds I–VI) in good to high yield (Scheme 1b). Therefore, it is clear that nucleophilic attack takes place at the non-substituted atom B(6) leaving B(3)–X intact. This can be interpreted either in terms of the bulkiness of the substituent or the π back-donation power (the mesomeric (+M) effect) of the halogen atoms. Given that the lone pairs of weakly electronegative elements like iodine are reasonably basic in terms of Lewis acid–base theory, they could interact fairly efficiently with the tangential p-orbitals on B(3) transferring electron density to this atom, [2] thus causing B(6) to become the atom most susceptible to nucleophilic attack.

Compounds I–VI represent the first examples of 3-halogeno *nido* derivatives of *o*-carborane, and they can be used as precursors to synthesise carborane-containing macromolecules. I–VI have been fully characterised using ¹H-, ¹¹B-, ¹³C-NMR spectroscopy, and, in the case of [3-*I-7,8-nido-C₂B₉H₁₁*][−], MALDI-TOF and X-ray diffraction. The MALDI-TOF spectrum (Fig. 1) shows a peak with isotopic distribution at $m/z = 260.39$ corresponding to [IC₂B₉H₁₁][−]. A peak at 127.05 corresponding to lost iodine is also observed.

2.1. The B(3)–X influence on the bridging proton

The bridging proton in [7,8-*nido-C₂B₉H₁₂*][−] derivatives is relatively acidic and can be removed by the addition of strong base. Comparing the chemical shift of this bridging proton in unsubstituted [7,8-*nido-C₂B₉H₁₂*][−], −2.90 ppm, with that in [3-*X-7,8-nido-C₂B₉H₁₁*][−] (X = I, $\delta = -2.67$ ppm; X = Br, $\delta = -2.68$

Fig. 1. MALDI-TOF of $[\text{HNMe}_3][3\text{-I-}7,8\text{-C}_2\text{B}_9\text{H}_{11}]$ (I).

ppm) we observe that, although the variation is small, the presence of an halogen group on B(3) moves δ to lower field. The effect is similar for both iodine and bromine. The same phenomenon is apparent for $[3\text{-X-}7\text{-Me-}7,8\text{-nido-C}_2\text{B}_9\text{H}_{10}]^-$ (X = I, Br) in which the BHB resonance is found at the same position in both species, in both cases at lower field than in $[7\text{-Me-}7,8\text{-nido-C}_2\text{B}_9\text{H}_{11}]^-$. Moreover, this pattern also extends to the $\text{C}_{\text{cluster}}\text{-Ph}$ derivatives (see Table 1). It is also noteworthy that, when a halogen group is substituted on B(3), in most cases the bridge proton appears in the $^1\text{H}\{^{11}\text{B}\}$ -NMR spectrum as a multiplet instead of the broad singlet usually observed in *nido* carboranes.

2.2. The B(3)-X substitution influence on the ^{11}B -NMR spectrum

The presence of an iodine substituent on B(3) in $[3\text{-I-}7,8\text{-nido-C}_2\text{B}_9\text{H}_{11}]^-$ ($\delta_{\text{B}(3)} = -28.8$), causes the resonance to appear at higher field in comparison to the unsubstituted anion $[7,8\text{-nido-C}_2\text{B}_9\text{H}_{12}]^-$ ($\delta_{\text{B}(3)} = -17.4$). In contrast, a bromine substituted on B(3) shifts the resonance to lower field; $[3\text{-Br-}7,8\text{-nido-C}_2\text{B}_9\text{H}_{11}]^-$ ($\delta_{\text{B}(3)} = -14.2$). The same effect was earlier observed in the case of halogeno *closo*-carborane derivatives [2]. We also note that the influence of a carbon substituent, either methyl or phenyl, on the chemical shift of B(3) in 3-I or 3-Br-*nido*-carborane is comparable in both cases, causing a shift to low field of ca. 5 ppm in the iodo case and ca. 3 ppm in the bromo case ($\delta_{\text{B3-I,C-Me}} = -23.1$, $\delta_{\text{B3-I,C-Ph}} = -23.6$; $\delta_{\text{B3-Br,C-Me}} = -11.1$, $\delta_{\text{B3-Br,C-Ph}} = -10.9$) (see Table 2).

Table 1
Chemical shifts of bridge BHB protons in halogenated *nido*-carboranes

| | $\text{C}_{\text{cluster}}\text{-H}$ (ppm) | $\text{C}_{\text{cluster}}\text{-Me}$ (ppm) | $\text{C}_{\text{cluster}}\text{-Ph}$ (ppm) |
|---------|--|---|---|
| B(3)-H | -2.90 | -2.71 | -2.46 |
| B(3)-I | -2.67 | -2.54 | -2.31 |
| B(3)-Br | -2.68 | -2.54 | -2.31 |

Table 2

^{11}B -NMR data of B(3) in $[3\text{-X-}7\text{-R-}7,8\text{-nido-C}_2\text{B}_9\text{H}_{10}]^-$ (X = Br, I; R = H, CH_3 , C_6H_5) compounds (I–VI)

| Compound | $[3\text{-X-R-}7,8\text{-nido-C}_2\text{B}_9\text{H}_{10}]^-$ | | |
|---|---|-------------------------|----------------|
| | X, R | δ (B(3)-X) (ppm) | Δ (ppm) |
| $[\text{C}_2\text{B}_9\text{H}_{12}]^-$ | -, H | -17.4 | 0 |
| (I) | I, H | -28.8 | -11.4 |
| (II) | Br, H | -14.2 | +3.2 |
| (III) | I, Me | -23.1 | -5.7 |
| (IV) | I, Ph | -23.6 | -6.2 |
| (V) | Br, Me | -11.1 | +6.3 |
| (VI) | Br, Ph | -10.9 | +6.5 |

The $^{11}\text{B}\{^1\text{H}\}$ -NMR spectrum of $[3\text{-I-}7,8\text{-nido-C}_2\text{B}_9\text{H}_{11}]^-$ displays a 2:2:2:1:1 pattern (low field to high field) in the range -9.3 to -35.8 ppm characteristic of $[7,8\text{-nido-C}_2\text{B}_9\text{H}_{12}]^-$ species, [15] with the resonances sufficiently separated enough to permit their unambiguous assignment by means of $^{11}\text{B}\{^1\text{H}\}\text{-}^{11}\text{B}\{^1\text{H}\}$ COSY. The peak at -34.1 ppm is easily assigned to B(10) since it appears as a doublet of doublets in the ^{11}B -NMR spectrum due to coupling with the H bridge as well as the *exo*-H. The peak at -35.8 ppm, at highest field, corresponds to B(1), the position antipodal to the open face (Fig. 2). The spectrum also exhibits a singlet at -28.8 ppm corresponding to B(3). With the resonances due to B(1), B(3) and B(10) thus established, analysis of the cross peak easily allowed the assignment of the 2:2:2:1:1 pattern to B(9,11): B(5,6): B(2,4): B(3): B(10): B(1), respectively (see Fig. 3).

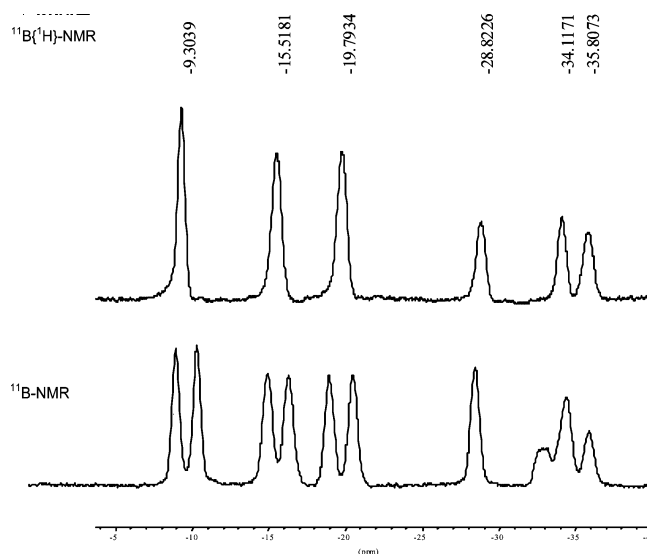
Fig. 2. Comparison of ^{11}B - and $^{11}\text{B}\{^1\text{H}\}$ -NMR spectra of $[\text{HNMe}_3][3\text{-I-}7,8\text{-nido-C}_2\text{B}_9\text{H}_{11}]$ (I).

Table 3
Selected interatomic distances (Å) and angles (°) for [HNMe₃][3-I-7,8-*nido*-C₂B₉H₁₁] (I)

| Interatomic distances | | Interatomic angles | |
|-----------------------|-----------|--------------------|----------|
| I(1)–B(3) | 2.163(10) | B(4)–B(1)–B(3) | 61.4(6) |
| B(1)–B(4) | 1.744(13) | B(3)–B(1)–B(2) | 59.9(6) |
| B(1)–B(3) | 1.755(14) | B(2)–B(1)–B(6) | 57.8(6) |
| B(1)–B(2) | 1.772(14) | B(4)–B(1)–B(5) | 58.7(5) |
| B(1)–B(6) | 1.808(14) | B(6)–B(1)–B(5) | 60.4(6) |
| B(1)–B(5) | 1.817(14) | C(7)–B(2)–B(3) | 58.5(5) |
| B(2)–C(7) | 1.729(13) | B(6)–B(2)–B(1) | 62.1(6) |
| B(2)–B(6) | 1.730(14) | B(3)–B(2)–B(1) | 59.6(6) |
| B(2)–B(3) | 1.762(15) | C(7)–B(2)–B(11) | 54.8(5) |
| B(2)–B(11) | 1.776(14) | B(6)–B(2)–B(11) | 59.7(6) |
| B(3)–C(8) | 1.700(12) | C(8)–B(3)–C(7) | 54.3(5) |
| B(3)–C(7) | 1.707(13) | C(7)–B(3)–B(2) | 59.8(6) |
| B(3)–B(4) | 1.787(13) | B(1)–B(3)–B(2) | 60.5(6) |
| B(4)–C(8) | 1.721(11) | C(8)–B(3)–B(4) | 59.1(5) |
| B(4)–B(5) | 1.747(14) | B(1)–B(3)–B(4) | 59.0(5) |
| B(4)–B(9) | 1.792(13) | C(8)–B(3)–I(1) | 123.1(6) |
| B(5)–B(10) | 1.773(14) | C(7)–B(3)–I(1) | 125.6(6) |
| B(5)–B(9) | 1.782(14) | B(1)–B(3)–I(1) | 124.9(6) |
| B(5)–B(6) | 1.823(14) | B(2)–B(3)–I(1) | 123.2(6) |
| B(6)–B(11) | 1.744(13) | B(4)–B(3)–I(1) | 122.1(6) |
| B(6)–B(10) | 1.795(14) | B(1)–B(4)–B(5) | 62.7(6) |
| C(7)–C(8) | 1.555(13) | C(8)–B(4)–B(3) | 57.9(5) |
| C(7)–B(11) | 1.613(14) | B(1)–B(4)–B(3) | 59.6(5) |
| C(8)–B(9) | 1.636(14) | C(8)–B(4)–B(9) | 55.5(5) |
| B(9)–B(10) | 1.857(16) | B(5)–B(4)–B(9) | 60.5(6) |
| B(9)–H(10A) | 1.37(10) | B(4)–B(5)–B(9) | 61.0(6) |
| B(10)–B(11) | 1.845(15) | B(10)–B(5)–B(9) | 63.0(6) |
| B(10)–H(10A) | 1.17(10) | B(4)–B(5)–B(1) | 58.5(5) |
| C(21)–N(1) | 1.514(12) | B(10)–B(5)–B(6) | 59.9(6) |
| C(22)–N(1) | 1.481(12) | B(1)–B(5)–B(6) | 59.5(6) |
| C(23)–N(1) | 1.495(12) | B(2)–B(6)–B(11) | 61.5(6) |
| N(1)–H(1N) | 0.88(9) | B(11)–B(6)–B(10) | 62.8(6) |
| | | B(2)–B(6)–B(1) | 60.1(6) |
| | | B(10)–B(6)–B(5) | 58.7(6) |
| | | B(1)–B(6)–B(5) | 60.1(5) |
| | | C(8)–C(7)–B(11) | 116.0(8) |
| | | C(8)–C(7)–B(3) | 62.6(6) |
| | | B(11)–C(7)–B(2) | 64.1(6) |
| | | B(3)–C(7)–B(2) | 61.7(6) |
| | | C(7)–C(8)–B(9) | 111.3(8) |
| | | C(7)–C(8)–B(3) | 63.1(6) |
| | | B(9)–C(8)–B(4) | 64.5(6) |
| | | B(3)–C(8)–B(4) | 63.0(5) |
| | | C(8)–B(9)–B(4) | 60.1(5) |
| | | B(5)–B(9)–B(4) | 58.5(5) |
| | | C(8)–B(9)–B(10) | 106.3(8) |
| | | B(5)–B(9)–B(10) | 58.3(6) |
| | | B(5)–B(10)–B(6) | 61.4(6) |
| | | B(6)–B(10)–B(11) | 57.2(6) |
| | | B(5)–B(10)–B(9) | 58.7(6) |
| | | B(11)–B(10)–B(9) | 101.1(7) |
| | | C(7)–B(11)–B(2) | 61.1(6) |
| | | B(6)–B(11)–B(2) | 58.9(5) |
| | | C(7)–B(11)–B(10) | 105.0(7) |
| | | B(6)–B(11)–B(10) | 59.9(6) |
| | | C(22)–N(1)–C(23) | 112.1(8) |
| | | C(22)–N(1)–C(21) | 111.5(8) |
| | | C(23)–N(1)–C(21) | 111.1(7) |
| | | C(22)–N(1)–H(1N) | 108(6) |
| | | C(23)–N(1)–H(1N) | 108(6) |
| | | C(21)–N(1)–H(1N) | 106(6) |

2.3. Description of the structure of [HNMe₃][3-I-7,8-*nido*-C₂B₉H₁₁] (I)

Only three crystal structures of iodinated *nido* compounds, [HNMe₃][9,11-I₂-7,8-*nido*-C₂B₉H₁₀] [6], [HNMe₃][9-I-7,8-*nido*-C₂B₉H₁₁] [6] and Cs[7-(*p*-C₆H₄NCS)-9-I-7,8-*nido*-C₂B₉H₁₁] [4] have been reported. That of [HNMe₃][3-I-7,8-*nido*-C₂B₉H₁₁] (I), reported here, is the first in which the iodine is not attached to one of the symmetry equivalent positions 9 or 11.

The salt I crystallise as ion pairs (Fig. 4) with no close inter-ion contacts. The anion has the anticipated *nido* icosahedral geometry with the iodine substituent at position 3. Table 3 lists selected interatomic distances and angles. B(3)–I is 2.163(10) Å, wholly typical of similar distances in the literature [14]. Molecular parameters within the *nido* cage are consistent with those in the parent compound [7,8-*nido*-C₂B₉H₁₂][–] [15], with C(7)–C(8) 1.555(13) Å. The atom H(10A) appears to be intermediate between *endo* on B10 and bridging between B(10) and B(9), B(9)–H(10A) 1.37(10) Å, B(10)–H(10A) 1.17(10) Å. All other distances and angles, and those in the cation, are quite normal.

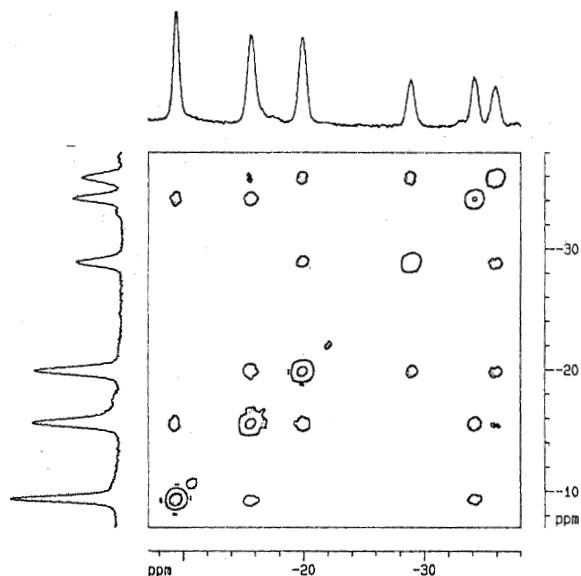


Fig. 3. $^{11}\text{B}\{^1\text{H}\}-^{11}\text{B}\{^1\text{H}\}$ COSY spectrum of $[\text{HNMe}_3][3\text{-I-7,8-nido-C}_2\text{B}_9\text{H}_{11}]$ (**I**).

3. Experimental

3.1. Instrumentation

Elemental analyses were performed using a Carlo Erba EA1108 microanalyser. IR spectra were recorded from KBr pellets on a Shimadzu FTIR-8300 spectrophotometer. ^1H - and $^1\text{H}\{^{11}\text{B}\}$ -NMR (300.13 MHz), $^{13}\text{C}\{^1\text{H}\}$ -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. All NMR spectra were recorded from CD_3COCD_3 solutions at 25 °C. Chemical shift values for ^{11}B -NMR spectra were referenced to external $\text{BF}_3\cdot\text{OEt}_2$ and those for ^1H -, $^1\text{H}\{^{11}\text{B}\}$ - and $^{13}\text{C}\{^1\text{H}\}$ -NMR spectra were referenced to SiMe_4 . Chemical shifts are reported in units of parts per million downfield from reference, and all coupling constants are in Hz. MS

spectra were recorded using a Bruker Biflex MALDI-TOF mass spectrometer.

3.2. Materials

Unless otherwise noted, all manipulations were carried out under a dinitrogen atmosphere using standard vacuum line techniques. 3-I-*o*-carborane, [16] 3-I-1-Me-*o*-carborane, [2] 3-I-1-Ph-*o*-carborane, [2] 3-Br-*o*-carborane, [17] 3-Br-1-Me-*o*-carborane, [2] 3-Br-1-Ph-*o*-carborane, [2] were synthesised according to the bibliography. Ethanol, KOH and $[\text{HNMe}_3]\text{Cl}$ were purchased from commercial sources and used as received.

3.3. Trimethylammonium 3-iodo-7,8-dicarba-nido-undecaborate (**I**)

A solution of 1.95 g (7.2 mmol) of 3-iodo-1,2-dicarba-*closo*-dodecaborane and 2.0 g (36 mmol) of KOH in 60 ml of ethanol was heated under reflux for 3 h. The alcohol was then distilled off and the residue was dissolved in water (50 ml), neutralised and precipitated with aqueous $[\text{HNMe}_3]\text{Cl}$. After filtration, the solid was washed with cold water (2×15 ml) and hexane (2×15 ml) yielding compound **I** as a white powder. Yield 2.0 g (87%). Anal. Calc. for $\text{C}_5\text{H}_{21}\text{B}_9\text{NI}$: C, 18.81; H, 6.62; N, 4.38. Found: C, 19.53; H, 6.76; N, 4.21%. IR: ν [cm^{-1}] = 3163 (N–H), 2518 (B–H). $^1\text{H}\{^{11}\text{B}\}$ -NMR: δ = 3.22 (s, 9H, $\text{HN}(\text{CH}_3)_3$), 3.00–0.00 (br m, 8H, B– $\text{H}_{\text{terminal}}$), 1.95 (br s, 2H, $\text{C}_{\text{cluster}}\text{-H}$), –2.67 (br m, 1H, B– H_{bridge}). $^{13}\text{C}\{^1\text{H}\}$ -NMR: δ = 48.0 ($\text{C}_{\text{cluster}}$), 45.2 (s, $\text{HN}(\text{CH}_3)_3$). ^{11}B -NMR: δ = –9.3 (d, $^1J(\text{B,H}) = 139$, 2B, B(9,11)), –15.5 (d, $^1J(\text{B,H}) = 136$, 2B, B(5,6)), –19.8 (d, $^1J(\text{B,H}) = 153$, 2B, B(2,4)), –28.8 (s, 1B, B(3)), –34.1 (dd, $^1J(\text{B,H}_{\text{terminal}}) = 138$, $^1J(\text{B,H}_{\text{bridge}}) = 55$, 1B, B(10)), –35.8 (d, $^1J(\text{B,H}) = 154$, 1B, B(1)).

3.4. Trimethylammonium 3-bromo-7,8-dicarba-nido-undecaborate (**II**)

Similarly were reacted 1.60 g (7.2 mmol) of 3-bromo-1,2-dicarba-*closo*-dodecaborane and 2.0 g (36 mmol) of KOH in 60 ml of ethanol. Work-up gave compound **II**. Yield 1.62 g (83%). Anal. Calc. for $\text{C}_5\text{H}_{21}\text{B}_9\text{NB}$: C, 58.57; H, 4.13; N, 2.73. Found: C, 59.20; H, 4.12; N, 2.70%. IR: ν [cm^{-1}] = 3167 (N–H), 2514 (B–H). $^1\text{H}\{^{11}\text{B}\}$ -NMR: δ = 3.21 (s, 9H, $\text{HN}(\text{CH}_3)_3$), 3.0–0.00 (br m, 8H, B– $\text{H}_{\text{terminal}}$), 1.95 (br s, 2H, $\text{C}_{\text{cluster}}\text{-H}$), –2.68 (br m, 1H, B– H_{bridge}). $^{13}\text{C}\{^1\text{H}\}$ -NMR: δ = 47.0 ($\text{C}_{\text{cluster}}$), 45.2 (s, $\text{HN}(\text{CH}_3)_3$). ^{11}B -NMR: δ = –10.0 (d, $^1J(\text{B,H}) = 137.6$, 2B), –14.2 (s, 1B), –16.1 (d, $^1J(\text{B,H}) = 137.6$, 2B), –20.7 (s, $^1J(\text{B,H}) = 152.1$, 2B), –36.6 (d, $^1J(\text{B,H}) = 137.2$, 2B).

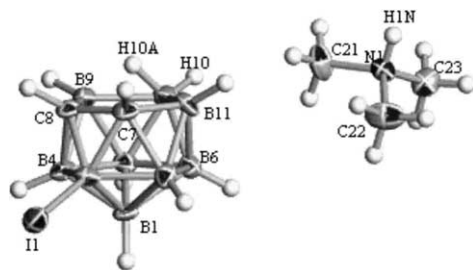


Fig. 4. Perspective view of the ion pair $[\text{HNMe}_3][3\text{-I-7,8-nido-C}_2\text{B}_9\text{H}_{11}]$ (**I**).

Table 4
Details of structural study of [HNMe₃][3-I-7,8-*nido*-C₂B₉H₁₁] (**I**)

| | |
|---|---|
| Empirical formula | C ₅ H ₂₁ B ₉ IN |
| Formula weight | 319.42 |
| Temperature (K) | 160(2) |
| Wavelength (Å) | 0.71073 |
| Crystal system | Monoclinic |
| Space group | <i>P</i> 2 ₁ / <i>c</i> |
| Unit cell dimensions | |
| <i>a</i> (Å) | 11.9951(16) |
| <i>b</i> (Å) | 12.640(3) |
| <i>c</i> (Å) | 9.6449(17) |
| β (°) | 94.070(13) |
| Volume (Å ³) | 1458.6(4) |
| <i>Z</i> | 4 |
| <i>D</i> _{calc} (Mg m ⁻³) | 1.455 |
| Absorption coefficient (mm ⁻¹) | 2.161 |
| <i>F</i> (000) | 624 |
| Crystal size (mm ³) | 0.06 × 0.32 × 0.28 |
| θ range for data collection (°) | 2.34–25.00 |
| Index ranges | –14 ≤ <i>h</i> ≤ 14, –1 ≤ <i>k</i> ≤ 15, –1 ≤ <i>l</i> ≤ 11 |
| Reflections collected | 3306 |
| Independent reflections | 2545 [<i>R</i> _{int} = 0.0709] |
| Completeness to θ = 25.00° | 99.2% |
| Absorption correction | Empirical |
| Max/min transmission | 1.00, 0.7195 |
| Refinement method | Full-matrix least-squares on <i>F</i> ² |
| Data/restraints/parameters | 2545/10/182 |
| Goodness-of-fit on <i>F</i> ² | 1.116 |
| Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)] | <i>R</i> ₁ = 0.0544, <i>wR</i> ₂ = 0.1324 |
| <i>R</i> indices (all data) | <i>R</i> ₁ = 0.0853, <i>wR</i> ₂ = 0.1536 |
| Largest difference peak, hole (e Å ⁻³) | 1.630, –1.688 |

3.5. Trimethylammonium 3-iodo-7-methyl-7,8-dicarbanido-undecaborate (**III**)

In the same manner were reacted 2.05 g (7.2 mmol) of 3-iodo-1-methyl-1,2-dicarba-*closo*-dodecaborane and 2.0 g (36 mmol) of KOH in 60 ml of ethanol. Work-up gave compound **III**. Yield 1.90 g (79%). Anal. Calc. for C₆H₂₃B₉NI: C, 21.61; H, 6.95; N, 4.20. Found: C, 21.71; H, 6.95; N, 4.19%. IR: ν [cm⁻¹] = 3155 (N–H), 2962–2860 (C_{alk}–H), 2523 (B–H). ¹H{¹¹B}-NMR: δ = 3.21 (s, 9H, HN(CH₃)₃), 3.0–0.0 (br m, 8H, B–H_{terminal}), 1.61 (br s, 2H, C_{cluster}–H), 1.50 (s, 3H, CH₃), –2.54 (br m, 1H, B–H_{bridge}). ¹³C{¹H}-NMR: δ = 52.1 (C_{cluster}), 45.2 (s, HN(CH₃)₃), 25.1 (s, CH₃). ¹¹B-NMR: δ = –8.5 (d, ¹*J*(B,H) = 153, 1B), –10.3 (d, ¹*J*(B,H) = 153, 1B), –16.2 (d, ¹*J*(B,H) = 173, 2B), –18.4 (d, ¹*J*(B,H) = 115, 1B), –19.1 (d, ¹*J*(B,H) = 115, 1B), –23.1 (s, 1B), –34.1 (d, ¹*J*(B,H) = 115, 2B).

3.6. Trimethylammonium 3-iodo-7-phenyl-7,8-dicarbanido-undecaborate (**IV**)

Similarly were reacted 2.5 g (7.2 mmol) of 3-iodo-1-phenyl-1,2-dicarba-*closo*-dodecaborane and 2.0 g (36 mmol) of KOH in 60 ml of ethanol. After working-up

compound **IV** was obtained. Yield 2.0 g (70%). Anal. Calc. for C₁₁H₂₅B₉NI: C, 33.40; H, 6.37; N, 3.54. Found: C, 33.84; H, 6.38; N, 3.55%. IR: ν [cm⁻¹] = 3100 (N–H), 2524 (B–H). ¹H{¹¹B}-NMR: δ = 7.20–6.90 (br m, 5H, C–H_{aryl}), 3.21 (s, 9H, HN(CH₃)₃), 3.0–0.0 (br m, 8H, B–H_{terminal}), 2.40 (br s, 2H, C_{cluster}–H), –2.31 (br s, 1H, B–H_{bridge}). ¹³C{¹H}-NMR: δ = 144.1, 127.5, 126.6, 124.9 (C_{aryl}), 47.1 (C_{cluster}), 45.5 (s, HN(CH₃)₃). ¹¹B-NMR: δ = –6.2 (d, ¹*J*(B,H) = 138, 1B), –9.9 (d, ¹*J*(B,H) = 138, 1B), –15.8 (d, ¹*J*(B,H) = 167, 1B), –17.05 (d, ¹*J*(B,H) = 146, 1B), –19.1 (d, ¹*J*(B,H) = 145, 2 B), –23.6 (s, 1B), –33.3 (d, ¹*J*(B,H) = 143, 2B).

3.7. Trimethylammonium 3-bromo-7-methyl-7,8-dicarbanido-undecaborate (**V**)

In the same manner were reacted 1.71 g (7.2 mmol) of 3-bromo-1-methyl-1,2-dicarba-*closo*-dodecaborane and 2.0 g (36 mmol) of KOH in 60 ml of ethanol. Work-up gave compound **V**. Yield 1.55 g (75%). Anal. Calc. for C₆H₂₃B₉NBr: C, 25.16; H, 8.09; N, 4.89. Found: C, 25.26; H, 8.06; N, 4.80%. IR: ν [cm⁻¹] = 3165 (N–H), 2900–2749 (C_{alk}–H), 2524 (B–H). ¹H{¹¹B}-NMR: δ = 3.18 (s, 9H, HN(CH₃)₃), 3.0–0.0 (br m, 8H, B–H_{terminal}), 1.97 (br s, 2H, C_{cluster}–H), 1.43 (s, 3H, CH₃), –2.54 (br m, 1H, B–H_{bridge}). ¹³C{¹H}-NMR: δ = 52.1 (C_{cluster}), 45.2 (s, HN(CH₃)₃), 25.4 (s, CH₃). ¹¹B-NMR: δ = –8.6 (d, ¹*J*(B,H) = 135, 1B), –11.1 (d, ¹*J*(B,H) = 146, 1B), –11.1 (s, 1B), –17.3 (d, ¹*J*(B,H) = 145, 2B), –18.6 (d, ¹*J*(B,H) = 151, 1B), –20.2 (d, ¹*J*(B,H) = 158, 1B), –35.85 (d, ¹*J*(B,H) = 131, 2B).

3.8. Trimethylammonium 3-bromo-7-phenyl-7,8-dicarbanido-undecaborate (**VI**)

Similarly were reacted 2.15 g (7.2 mmol) of 3-bromo-1-phenyl-1,2-dicarba-*closo*-dodecaborane and 2.0 g (36 mmol) of KOH in 60 ml of ethanol. After working-up compound **VI** was obtained. Yield 1.50 g (69%). Anal. Calc. for C₁₁H₂₅B₉NBr: C, 37.9; H, 7.2; N, 4.01. Found: C, 38.0; H, 7.3; N, 4.09%. IR: ν [cm⁻¹] = 3165 (N–H), 2527 (B–H). ¹H{¹¹B}-NMR: δ = 7.20–6.90 (br m, 5H, C–H_{aryl}), 3.20 (s, 9H, HN(CH₃)₃), 3.0–0.0 (br m, 8H, B–H_{terminal}), 2.37 (br s, 2H, C_{cluster}–H), –2.31 (br s, 1H, B–H_{bridge}). ¹³C{¹H}-NMR: δ = 143.4, 127.2, 126.8, 124.5 (C_{aryl}), 47.2 (C_{cluster}), 45.3 (s, HN(CH₃)₃). ¹¹B-NMR: δ = –6.6 (d, ¹*J*(B,H) = 140, 1B), –10.9 (d, 1B), –10.9 (s, 1B), –17.1 (d, ¹*J*(B,H) = 139, 2B), –19.7 (d, ¹*J*(B,H) = 183, 1B), –19.9 (d, ¹*J*(B,H) = 180, 1 B), –35.1 (d, ¹*J*(B,H) = 135, 2B).

3.9. X-ray crystallographic study of **I**

A single crystal was mounted on a glass fibre and studied using a Bruker P4 diffractometer [18] operating

with graphite-monochromated Mo–K α radiation ($\lambda = 0.71069 \text{ \AA}$) with cooling via an Oxford Cryostreams device. Intensity data were collected using ω scans. No significant deviation of the intensities of standard reflections periodically remeasured was detected. Data were corrected for absorption effects by psi scans. The structure was solved by direct methods and difference Fourier methods and refined [19] by full-matrix least-squares. Cage H atoms and the ammonium H atom were located from a difference Fourier map. *Exo*-H atoms on the cage were restrained to 1.10(2) Å from boron or 1.15(2) Å from carbon, but the atoms H(10A) and H(1N) were allowed free refinement. Methyl H atoms were set in idealised positions. All H atom displacement parameters were treated as riding on their respective bound atom, with U_{H} set at $1.2 \times U_{\text{B}}$, $1.2 \times U_{\text{C}_{\text{cage}}}$ or $1.5 \times U_{\text{C}_{\text{methyl}}}$. Table 4 lists relevant data.

4. Supporting information available

Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications CCDC no. 169772. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>).

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