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Aromaticity in boron clusters survives radical structural changes: closo carboranes keep their aromaticity even when deboronated to nido carboranes because they adapt to a different geometry. Combination of lab work and DFT calculations have proven the existence of diatropic currents, hence aromaticity, in these clusters.

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Too Persistent to Give Up: Aromaticity in Boron Clusters Survives Radical Structural Changes

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Abstract

 $o-C_2B_{10}H_{12}$ isometrizes to $m-C_2B_{10}H_{12}$ upon heating at 400 °C. Deboronation in $o-C_2B_{10}H_{12}$ is a relatively easy process, whereas it is more difficult in m-C₂B₁₀H₁₂. These two experimental facts indicate that m- $C_2B_{10}H_{12}$ is thermodynamically more stable than $o-C_2B_{10}H_{12}$. On the other hand, it is widely accepted that closo boranes and carboranes are aromatic compounds. In this work, we relate difficulty in the deboronation of the carboranes with stability and aromaticity. We do this by combining lab work and by means of DFT calculations. Computationally, our results show that the higher thermodynamic stability of m-C₂B₁₀H₁₂ is not related to aromaticity differences but to the location of the C atoms in the carborane structure. It is also demonstrated that the aromaticity observed in *closo* boranes and carboranes is also present in their *nido* counterparts and, consequently, we conclude that aromaticity in boron clusters survives radical structural changes. Further, sandwich metallocenes (e.g. ferrocene) and sandwich metallabis(dicarbollides) (e.g. $[Co(C_2B_9H_{11})_2]$) have traditionally been considered similar. Here it is shown that they are not. Metallabis(dicarbollides) display global aromaticity whereas metallocenes present local aromaticity in the ligands. Remarkable and unique is the double probe given by ¹H- and ¹¹B-NMR tracing the reciprocally antipodal endocyclic open face Hec and B1. These magnetic studies have permitted to correlate both nuclei and relate them to a diatropic current in the plane at the middle of the $nido [C_2B_9H_{12}]^{-}$. This observation is the first and unique data that proves experimentally the existence of diatropic currents, thence aromaticity, in clusters and is comparable to the existence of diatropic currents in planar aromatic compounds. Additionally, heteroboranes with two carbon atoms have been compared to heterocycles with two nitrogen or boron atoms, $C_2B_{10}H_{12}$ carboranes against planar $N_2C_4H_4$ diazines or $[B_2C_4H_4]^{2-1}$ diboratabenzenes, proving the higher persistence of the aromaticity of the tri-dimensional compounds in heteroatom substituted species. This research accounts very well for the "Paradigm for the Electron Requirements of Clusters" in which a *closo*-cluster that is aromatic upon addition of 2e⁻ becomes also an aromatic *nido* species and explains the nice schemes by R.W. Rudolph and R. E. Williams.

Keywords: aromaticity; antiaromaticity; metallabis(dicarbollide); ferrocene; carborane; metallacene.

Introduction

As time goes, metallacarboranes of the type $[M(C_2B_9H_{11})_2]^-$ (M=Co, Fe, Ni), named as metallabis(dicarbollides), have become increasingly important. First signs of application were found in environment in nuclear waste remediation,¹⁻¹⁰ and over the years in advanced materials,¹¹⁻¹³ health,¹⁴ and energy.¹⁵⁻¹⁷ Particularly relevant is their extraordinary stability that features outer sphere electron transfer with the positive consequences this may have in molecular electronics and aspects related to energy. For any application, but very particularly for nuclear waste remediation and electron transfer related aspects, the stability of the molecule is of utmost relevance. Bench chemists have often resorted to the criterion of aromaticity to account for the high stability of certain molecules. An aromatic molecule generally possesses a higher stability and therefore exhibits lower chemical reactivity in comparison to the associated non-aromatic and antiaromatic systems.

It is known that a very large number of transition-metal sandwich or half-sandwich structures are very stable,¹⁸⁻²⁴ and are described as aromatic because as a molecule they keep the ability to undergo aromatic substitution type reactions while maintaining the cyclic conjugated system. Some appealing examples of these aromatic species are ferrocene and dibenzenechromium, that easily undergo electrophilic substitution, but not electrophilic addition. In this sense, for ferrocene, $[Fe(C_5H_5)_2]$, there is scientific consensus on the fact that it is an aromatic molecule, but there is controversy over whether it should be considered global²⁵⁻²⁶ or local²⁷⁻²⁸ aromatic. Be it global or local, what is clear is that the aromaticity of these complexes requires aromaticity of the ligands. This is what happens with $[Cr(\eta^6-C_6H_6)(CO)_3]$ and it is also the case for cyclobutadieneiron tricarbonyl $[Fe(CO)_3(C_4H_4)]$, that displays electrophilic substitution and thus aromaticity as confirmed by the equal four C–C bond lengths and the planarity of the C_4H_4 ring and ¹H NMR spectrum.²⁹ The bonding in this molecule is assumed to involve the triplet state of cyclobutadiene, which is aromatic according to the Baird rule,³⁰ interacting with two singly occupied Fe(0) orbitals.³¹ Remarkably, all these compounds follow the 18 e⁻ rule, that is an additional way to account for stability or lack of reactivity.

All the former complexes had planar conjugated organic ligands, able to perform electrophilic substitution and abiders of the 18 e⁻ rule. At this stage, what is the situation

with $[M(C_2B_9H_{11})_2]^-$ (M = Co, Fe, Ni), that do not contain planar conjugated organic ligands and have been described by computation and for the high stability of $[Co(C_2B_9H_{11})_2]^-$ as aromatic,³² with regard to the aromaticity of their pristine ligands? Metallabis(dicarbollides) $[M(C_2B_9H_{11})_2]^-$ are commonly mononegative (M = Co, Fe, Ni), but dianionic $[Fe(C_2B_9H_{11})_2]^{2-}$ and neutral Ni(C₂B₉H₁₁)₂ are very accessible too. But all of these metallabis(dicarbollides) $[M(C_2B_9H_{11})_2]^{x-}$ (M = Co, Fe, Ni) have an available 18 e⁻ count molecule: $[Fe(C_2B_9H_{11})_2]^{2-}$, $[Co(C_2B_9H_{11})_2]^-$, and $[Ni(C_2B_9H_{11})_2]$.

Turning now to the issue of the aromaticity of a sandwich complex that implies that, in general, its ligands are aromatic, the consequence would be that *nido* $[C_2B_9H_{11}]^{2-}$ is aromatic too. We demonstrated³³ that *closo* boranes $[B_nH_n]^{2-}$ abide to Wade-Mingos's rule³⁴⁻³⁷ and that any of them, with $n \ge 5$, has a polycyclic aromatic hydrocarbon equivalent with an uneven number of π electrons pairs that obeys Hückel's rule.³⁸ Taking this into account, what occurs with the *nido* $[B_nH_n]^{4-}$ series, to which *nido* $[C_2B_9H_{11}]^{2-}$ belongs?³⁹ These have one electron pair more of electrons than *closo* $[B_nH_n]^{2-}$, and therefore if *closo* $[B_nH_n]^{2-}$ are aromatic it is expected that *nido* $[B_nH_n]^{4-}$ should be nonaromatic or antiaromatic if the parallelism between *closo* boranes and flat Hückel's rule abiders holds. This would be the case for typical hydrocarbon aromatic compounds. Is this what is happening with boron clusters? Or, on the contrary, the change in structure from *closo* to *nido* is a strategy at hand by the clusters to skip the aromaticity/antiaromaticity transition upon the addition of two extra electrons to keep the aromaticity? If this was the case their possibilities to maintain a stable structure would be far superior to their organic counterparts.

In this paper, we show the aromatic character of *nido* $[C_2B_9H_{11}]^{2-}$ so that it conforms to the sentence "*the aromaticity of a sandwich complex implies that, in general, its ligands have to be also aromatic*". We will also see that the *nido* $[C_2B_9H_{12}]^-$ precursor of *nido* $[C_2B_9H_{11}]^{2-}$ is aromatic, too, and that the pentagonal ring C_2B_3 in *nido* $[C_2B_9H_{11}]^{2-}$ is not more aromatic than the equivalent C_2B_3 ring in *closo* 1,2-C_2B_{10}H_{12}, despite having a conjugated open face. The C_2B_3 ring is the one that, following the model of metallocenes, is η^5 coordinated to the metal in $[M(C_2B_9H_{11})_2]^-$. Further, we shall see that the aromatic character of a *closo* boron cluster depends on the number of electrons and the confined space⁴⁰⁻⁴¹ available defined by the number of atoms in the cluster. Therefore, we shall see that any of the isomers of *closo* $C_2B_{10}H_{12}$ is aromatic as are *closo* $[B_{12}H_{12}]^2$ -

 and *closo* $[CB_{11}H_{12}]^{-}$. Moreover, we shall also see that the diatropic current in spheres, as can be interpreted the icosahedral boron clusters, is not geometrically restricted as occurs in p_{π} systems and can be present at different parallel planes. In addition, we shall observe that metallabis(dicarbollides) are not a surrogate of the metallocenes, and that their bulky and spherical ligand plays a role to their stability and possibly in their applications, besides the well documented enhanced electrochemical tuning efficiency and photoredox catalysis properties. Finally, we shall also see that boron clusters have access to a morphological detour to skip the aromaticity—antiaromaticity sequence upon the addition of 2e⁻.

Results and Discussion

Deboronation of $closo 1, 7-C_2B_{10}H_{12}, (m-C_2B_{10}H_{12})$

The search for the relationship of aromaticity, stability, and lack of reactivity was triggered as a result of the low throughput of the deboronation of $\frac{closo}{m}$ m-C₂B₁₀H₁₂ to yield <u>*nido*</u> $[7,9-C_2B_9H_{12}]^-$. It is well known the ease to remove the boron atom bound to the two carbon cluster atoms in $\frac{closo}{1,2-C_2B_{10}H_{12}}$ also represented by $o-C_2B_{10}H_{12}$, despite that the electron count of this molecule matches the electron count of $[B_{12}H_{12}]^{2}$, probably one of the most stable aromatic molecules available, following the 4n+2 Wade-Mingos' rule.³⁴⁻³⁷ There are several processes to perform the deboronation successfully.⁴²⁻ ⁵⁰ The most typical one and perhaps the most widely used is the boiling ethanol/KOH procedure. With the aim to produce $[Co(m-C_2B_9H_{11})_2]^{-}$, we investigated the deboronation of closo 1,7-C₂B₁₀H₁₂ (or *m*-C₂B₁₀H₁₂). However, what seemed to be simple became highly difficult as it was reported by Hawthorne et al. because the reaction must be carried out in an autoclave at 150°C for 4 h under autogenous pressure to lead to *nido* [7,9- $C_2B_9H_{12}$]⁻, in our hands with very low yield.⁵¹ Other methods with other reagents have been developed that produce good yields,⁵² however we were interested in the boiling ethanol/KOH procedure, as $m-C_2B_{10}H_{12}$ deboronation can be directly compared with the deboronation of o-C₂B₁₀H₁₂. Why the two, at this stage of the research, apparently aromatic molecules $o-C_2B_{10}H_{12}$ and $m-C_2B_{10}H_{12}$ did behave so different towards the same reagent to yield so similar <u>nido</u> $[7,8-C_2B_9H_{12}]^{-}$ and <u>nido</u> $[7,9-C_2B_9H_{12}]^{-}$ molecules? Would not these be aromatic? Noticeable is that the same reflux temperature used for the *closo* $o-C_2B_{10}H_{12}$ to produce <u>*nido*</u> [7,8-C_2B_9H_{12}]⁻ leaves <u>*closo*</u> m-C_2B_{10}H_{12} unchanged. For the bench chemist this would indicate that *closo* m-C₂B₁₀H₁₂ is more aromatic than *closo* o-

 $C_2B_{10}H_{12}$, but we shall see that this is not the case according to the computed aromaticity indicators. The immediate reaction procedure follow up would be to use higher temperature. In this case, however, an important fraction of the *closo meta*-cluster is degraded to boric acid esters, which in turn lead to a low yield of $\frac{nido}{nido}$ [7,9-C₂B₉H₁₂]⁻. Is then <u>*nido*</u> $[7,9-C_2B_9H_{12}]^{-}$ less stable or less aromatic than <u>*nido*</u> $[7,8-C_2B_9H_{12}]^{-}$? Before answering these questions, we decided to optimize the synthetic procedure as the ethanol method would be very practical for the working up. To do it, we searched new parameters to improve the yield of *nido* $[7,9-C_2B_9H_{12}]^-$ and lessen the formation of boric acid and boric acid esters during the process. As we have summarized in the experimental section and after many trials on this partial degradation by altering temperature and/or time of reaction and/or excess of base (Table 3), the yield of the partial degradation reaction was improved notably to 66%. However, it remains poor in comparison to the yield of *nido* $[7,8-C_2B_9H_{12}]^{-}$. This anomalous behavior led us to consider that little was known and much was taken for granted with regard to the stability of the carboranes, their aromaticity, and the stability and aromaticity of their deboronated species. It took us also to revise the old but still actual, magnificent scheme shown by R.W. Rudolph on the relation between *closo*, *nido*, and *arachno* clusters.⁵²⁻⁵⁵ Therefore, we decided to carry on further research with the aim to learn about ligands that now are relevant and for sure will have an important role in the near future.



Figure 1. Closo ortho, meta, and para isomers of $C_2B_{10}H_{12}$, together with $[B_{12}H_{12}]^{2-}$.

Aromaticity of closo-carboranes

The *closo* C₂B₁₀H₁₂ parallels the aromatic *closo* $[B_{12}H_{12}]^{2-.33}$ Both share the same number of valence electrons (50) in the same confined space. *The closo* C₂B₁₀H₁₂ has two heteroatoms that implies three isomers *ortho*, *meta*, and *para* (Figure 1). Further, the difference in electronegativity between the two participating elements in the cluster is $\Delta \chi$ (C,B)=0.51.⁵⁶ Thus, considering the 3D and 2D relationship demonstrated earlier,³³ it Page 7 of 28

was sensible to compare these carborane isomers with planar systems with two heteroatoms, also related to a highly aromatic system, and with a $\Delta \chi$ between the participating atoms as close to $\Delta \chi(C,B)$ as possible. In this regard, C₆H₆ and the three diazines, 1,2-, 1,3-, and 1,4-diazines, commonly known as pyridazine, pyrimidine, and pyrazine, respectively, with $\Delta \chi(N,C)=0.49$,⁵⁷⁻⁵⁸ and 1,2-, 1,3-, and 1,4-diboratabenzenes with $\Delta \chi(C,B)=0.51^{59-61}$ would be the most adequate. It is clear for the bench chemist that both boranes and arenes, as typical aromats, are subject to substitutions restoring the aromaticity, however the diazines are also keen at additions that is contrary to strong aromaticity. In line with this, borate⁶² or diboratabenzenes are subjected to chemical instability, that is also contrary to strong aromaticity. As an example, diazines upon addition they require rearomatization with oxidizing agents, which is not evidence for strong aromaticity, or when treating the 1-phenylboratabenzene anion with excess of acetic acid produces 1,4-pentadiene, cis-1,3-pentadiene, and benzene. Noticeably, everything occurs with the three heterosystems, the *closo* $C_2B_{10}H_{12}$, the diazines, and the diboratabenzenes, for which the difference in electronegativity of the constituents is the same $\Delta \chi(X,Y) \approx 0.50$. All this is supportive of the extraordinary aromaticity of boron clusters, for both homo or heteroboranes, whereas it is not so obvious for arenes.

These experimental evidences based on stability and reactivity are supported by theory. We will restrict our results and discussion section on the most common 12-vertex carboranes, i.e. *closo* $C_2B_{10}H_{12}$ and their *nido* derivatives, with the expectation that the results can be extended to other smaller carborane clusters, and will compare the results with the diazines and diboratabenzenes.

	ortho	meta	para
<i>closo</i> C ₂ B ₁₀ H ₁₂	+19.2	+2.9	0.0
nido [C ₂ B ₉ H ₁₂] ⁻	+16.2	0.0	+26.3
nido [C ₂ B ₉ H ₁₁] ²⁻	+16.6	0.0	+27.5

Table 1. Relative stabilities of closo-C₂B₁₀H₁₂ and their *nido* derivatives (kcal mol⁻¹).

Relative Stability and aromaticity of the dicarboranes. Closo C₂B₁₀H₁₂ is thermally very stable but tend to isomerize to the more stable isomers (Figure 1). Upon heating at 400

°C *o*-C₂B₁₀H₁₂ isomerizes to *m*-C₂B₁₀H₁₂, and near 600°C *m*-C₂B₁₀H₁₂ isomerizes to *p*-C₂B₁₀H₁₂.⁶³

The preparative step from o- to m- is well defined and all o- is converted into m-, and no purification is needed. The step from *m*- to *p*- is far more difficult as a long and troublesome purification process is needed due to the generated mixture of the two isomers. Both *m*- and *p*-isomers are converted into each other, preventing an easy isolation. These experimental conditions indicate that a large difference in thermodynamic stability between the o- and m- is expected, whereas a comparable stability between the m- and p- isomers is likely. Indeed, this is what is computationally found, as shown in Table 1 (first row). Although these relative stabilities are for sure related to the different type of bonds (C–C, B–B, C–B) in the different isomers, they can be more easily explained considering the relative positions of both carbon atoms in the cluster. As $\chi_{\rm C} > \chi_{\rm B}$, C atoms attract higher electron density in its vicinity inducing a repulsive effect with the adjacent C, which is the case of the ortho isomer. Whereas for the *meta* isomer, when one B is inserted in between the two carbon atoms, the repulsive effect is notably diminished in agreement with the Coulomb's inverse-square law. This repulsive effect is even less for the para isomer. These results are easily understood with classical physics, being the *para* isomer the most stable in agreement with the calculations (Table 1), but not so different with regard to the *meta* isomer ($\Delta E = 2.9$ kcal mol⁻¹), a factor to be taken into account for practical applications considering the much higher price of the *p*-isomer.

The clear difference in stability between the *o*- and *m*-isomers ($\Delta E = 16.3$ kcal mol⁻¹), does it result in loss of aromaticity between one isomer and the other? The answer is no, if we attend to the magnetically-based nucleus independent chemical shift (NICS) values given in Table 2. If we look at Scheme 1, there are two layers enlightened, the C₂B₃/CB₄/B₅ and the CB₄/B₅. This sketch is valid for *closo* [B₁₂H₁₂]²⁻ and for *closo o*-, *m*-, and *p*-C₂B₁₀H₁₂. In *closo* [B₁₂H₁₂]²⁻ each B₅ ring displays a NICS of -34.6 ppm, that indicates high aromaticity, and this value is just a little bit lower for C₂B₃ in *closo o*-C₂B₁₀H₁₂ (-33.7 ppm) and -32.7 ppm for B₅ (Table 2). Interestingly, it again increases for *closo m*-C₂B₁₀H₁₂ with -34.2 ppm for C₂B₃ and -33.1 ppm for B₅ and matches the B₅ values found for *closo* [B₁₂H₁₂]²⁻ and that of CB₄ for *closo p*-C₂B₁₀H₁₂ (-34.6 ppm). For a bench chemist it is clear that *closo* [B₁₂H₁₂]²⁻ is by all means more stable or, in other words, less reactive than *closo o*-C₂B₁₀H₁₂, as it is also demonstrated in the following two equations:

$[B_{12}H_{12}]^{2-} \rightarrow [B_{11}H_{11}]^{2-} + BH \text{ compared to } o-C_2B_{10}H_{12} \rightarrow C_2B_9H_{11} + BH,$ (1)
in which all components share the same number of electrons. At the B3LYP/6-
311++G(d,p) level of theory, removal of a BH from closo [B ₁₂ H ₁₂] ²⁻ requires 29 kcal
mol ⁻¹ more than from <i>closo</i> o-C ₂ B ₁₀ H ₁₂ following this scheme. The isoelectronic and
isostructural <i>closo</i> $[B_{12}H_{12}]^{2-}$ and <i>closo o</i> -, <i>m</i> -, and <i>p</i> -C ₂ B ₁₀ H ₁₂ are a clear example that
<i>molecules having similar aromaticity may have very much distinct reactivity</i> . ^{57, 64-66} This
was demonstrated in the deboronation of $\frac{closo}{closo}$ o- and $\frac{closo}{closo}$ m-C ₂ B ₁₀ H ₁₂ discussed in the
previous section, and agrees well with the results of diazines and diboratabenzenes that
can be compared with the aromaticity of C_6H_6 (NICS(0)= -8.05 ppm) and the three
diazines, 1,2-diazine (NICS(0)= -5.35), 1,3-diazine (NICS(0)= -5.53) and 1,4-diazine
(NICS(0)= -5.36), ⁶⁷ and 1,2-diboratabenzene (NICS(0)= -1.92), 1,3-diboratabenzene
(NICS(0)= -2.18), and 1,4-diboratabenzene (NICS(0)= -1.46). It is informative the
percentage discrepancy between the NICS(0) values of the diazine isomer and the
benzene reference that are 33.5% for closo o-, 31.3% for closo m-, and 33.4% for closo
<i>p</i> -, much larger than for the carboranes with respect to $\frac{closo}{[B_{12}H_{12}]^2}$, being 2.6% for
<i>closo o-</i> , 1.2% for <i>closo m-</i> , and 0% for <i>closo p-</i> , but smaller than between the NICS(0)
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Scheme 1. Two five-membered rings in 12-vertex carboranes and [B₁₂H₁₂]²⁻.

	- rin	ng
<mark>carborane</mark>	C2B3/CB4	CB4/B5
0-C2B10H12	<mark>-33.7</mark>	<mark>-32.7</mark>
<mark>o-[C2B9H12]⁻</mark>	<mark>-23.4</mark>	<mark>-35.4</mark>
<mark>0-[C2B9H11]²⁻</mark>	<mark>-19.5</mark>	<mark>-37.0</mark>
<mark>m-C2B10H12</mark>	<mark>-34.2</mark>	<mark>-33.1</mark>
<mark>m-[C₂B₉H₁₂]⁻</mark>	<mark>-21.3</mark>	<mark>-33.9</mark>
m-[C2B9H11] ²⁻	<mark>-18.7</mark>	<mark>-36.7</mark>
<mark>p-C₂B₁₀H₁₂</mark>	<mark>-34.6</mark>	<mark>-34.6</mark>
p-[C2B9H12] ⁻	<mark>-23.2</mark>	<mark>-36.2</mark>
<mark>p-[C₂B₉H₁₁]²⁻</mark>	<mark>-19.6</mark>	<mark>-37.9</mark>

Table 2. NICS (in ppm) of the C_2B_3 , CB_4 , and B_5 rings (measured at the centre) of *closo* carboranes under analysis.^a

^a NICS for B_5 ring in <u>closo</u> $[B_{12}H_{12}]^{2-}$ is -34.6 ppm.

Aromaticity of the closo dicarboranes with regard to deboronation. It is known experimentally that *closo* dicarboranes can lead to deboronation; more easily if the two carbon atoms are adjacent, *ortho*, than if they are separated by a boron atom, *meta*, as described in the above "Deboronation of m-C₂B₁₀H₁₂" section and in the Experimental Section, and even more easily than when they are separated by two carbon atoms, *para*, an unpractical process. *nido* species with the formula, *nido* [C₂B₉H₁₂]⁻ are produced from *closo o*- and *m*-C₂B₁₀H₁₂ but with different positions of the two carbon atoms. The deboronation easiness of the *closo* dicarboranes shall be related to the relative stability and/or reactivity of the *closo o*-, *m*-, and *p*-C₂B₁₀H₁₂, and the kinetics of the involved reaction. Interestingly, it correlates very well with the percentage discrepancy between the NICS(0) value of the *closo* carborane isomer and the *closo* [B₁₂H₁₂]²⁻ reference, although their aromatic character are very similar, as we have demonstrated earlier. The degree of deboronation difficulty of the *closo* carborane can also be interpreted with classical physics on the grounds of the deboronated compound, *nido* [C₂B₉H₁₂]⁻. Simply one has to consider the relative stabilities of the *nido* [C₂B₉H₁₂]⁻ isomer clusters by which

the electron enriched atoms prefer the edge sites, thus the positions on the pentagonal open face are preferred to the lateral sites (Figure 2). In this regard, the *nido ortho* and *nido meta* isomers should be more stable than the *nido para*, and between *nido ortho* and *nido meta*, the *nido meta* is preferred over *nido ortho* because of the Coulomb's law. This is what is shown in Table 1 for *nido* isomers *o*- ($\Delta E = 16.6$ kcal mol⁻¹), *m*- ($\Delta E = 0.0$ kcal mol⁻¹), and *p*-[C₂B₉H₁₁]²⁻ ($\Delta E = 27.5$ kcal mol⁻¹). The same argumentation is valid for the protonated species *nido* isomers *o*-, *m*-, and *p*-[C₂B₉H₁₂]⁻. The higher stability of the *nido m*- *vs* the *nido o*-[C₂B₉H₁₂]⁻ indicates that the difficulty in its formation originates in the much less reactivity of the corresponding *closo* species, as evidenced experimentally.



Figure 2. Nido ortho-, meta-, and para- isomers of [C₂B₉H₁₂]⁻.



Scheme 2. Deboronation process of *closo* o-C₂B₁₀H₁₂, incorrectly showing a circle meaning aromaticity.

 Aromaticity of the nido dicarborane species [7,8-C₂B₉H₁₂]. Scheme 2 shows the deboronation process leading, in this case, to <u>*nido*</u> $[7,8-C_2B_9H_{12}]^{-}$. The C₂B₃ open face reminds closely the cyclopentadiene, precursor of $[C_5H_5]^-$. We found that the on top of the face proton (endocyclic, ec)⁶⁹ in $[7,8-C_2B_9H_{12}]^-$ resonates near -2.5 ppm in the ¹H-NMR spectrum. As this endocyclic hydrogen can be removed by a strong base it is certainly acidic, and the question that arises is how could a proton resonate at such high field? The customary answer is simple; the point is whether it was correct or not. The endocyclic proton (Hec) does resonate at high magnetic field because there is an induced ring current in the delocalized π system of the aromatic C₂B₃ ring. Because of this interpretation, it was not uncommon to draw the ring shown in the C₂B₃ face of the *nido* $[C_2B_9H_{12}]$ ⁻ representing aromaticity (see Scheme 3a). However, if we think in terms of Hückel aromaticity, there is a major incongruence with this as, to have the conjugation, no p_{π} open face orbital should be part of a covalent bond, as is the B-H_{ec}. Therefore, and contrarily to what has been assumed, the p_{π} ring in the open face cannot be responsible for the upfield chemical shift of the endocyclic proton. Further, besides the anomalous chemical shift in the ¹H-NMR of the endocyclic proton, there is also another anomalous chemical shift due to B_1 at -37.2 ppm. This is at the highest magnetic field of the spectrum. Again, it can be interpreted to be originated in an induced ring current, but this cannot be due to the supposed delocalized system of π -electrons at the C₂B₃ open face as it would be too far. Moreover, the anomalous chemical shifts due to the endocyclic proton and the B_1 seem to be related. This indicates that their origin would be the same, supporting the proposition that is not due to the C_2B_3 open face ring current, but to one diatropic current in an intermediate plane equidistant to both nuclei, H and B₁. The ¹H-NMR of the upfield endocyclic proton and the upfield ¹¹B-NMR of the B₁ resonances prove the existence of diatropic currents and therefore prove the aromaticity of the *nido* dicarborane.



Scheme 3. Possible location of the ring currents in *nido* $[C_2B_9H_{12}]^-$ and *nido* $[C_2B_9H_{11}]^{2-}$.

 This relationship between the chemical shift of the endocyclic proton and B_1 can be visualized with Scheme 3b, which explains why H_{ec} and B_1 are related considering that one is measured with ¹H-NMR and the second by ¹¹B-NMR. The same Scheme 3b also shows a red circle suggesting a ring current placed in the centre of the pentagonal antiprism in which the centre of the icosahedron lies. This would explain the anomalous chemical shifts of the endocyclic proton and the apical B_1 , and their common origin (*vide infra*).

Is this view supported by the NICS of nido $[C_2B_9H_{12}]^2$ Largely yes. Remarkably, the C₂B₃ layer, although being definitely aromatic according to the NICS value of -27.4 ppm, loses aromaticity with regard to the same layer in *closo* 1,2-C₂B₁₀H₁₂ (-33.7 ppm). Conversely, the B₅ layer increases aromaticity (NICS = -35.4 ppm) with regard to B₅ in *closo* 1,2-C₂B₁₀H₁₂ (-32.7 ppm). Thus, it is clear that the diatropic loop has descended from the open C₂B₃ face to the B₅ layer as it was inferred from the H_{ec} and B₁ anomalous chemical shifts (Scheme 3c).

Aromaticity of the nido $[C_2B_9H_{11}]^{2-}$ coordinating ligand. We have seen that the diatropic ring current in *nido* $[C_2B_9H_{12}]^-$ has descended from the coordinating face. Does it find its continuation in <u>*nido*</u> $[C_2B_9H_{11}]^{2-}$ that is the real, in terms of metal sandwich formation, analogue of $[C_5H_5]$? The answer seems to follow the same trend (Table 2). The tendency is the same as it appears that the B₅ ring is the most aromatic one. We should say unexpectedly because it is contrary to what would be common reasoning for a π arene system to coordinate to metal by haptic covalent bonds. The "coordinating face" $C_2B_3/CB_4/B_5$ follows the tendency to lose aromaticity manifested in the order *closo* $[B_{12}H_{12}]^{2} > \frac{closo}{C_2B_{10}H_{12}} > \frac{nido}{C_2B_9H_{12}} > \frac{nido}{C_2B_9H_{11}} [C_2B_9H_{11}]^{2}$, with NICS values for the ortho isomer of -34.6, -33.7, -23.4, and -19.5 ppm, respectively. On the contrary, for the B₅/C₄B non-coordinating ring the tendency is reversed, $\frac{closo}{C_2B_{10}H_{12}} < \frac{nido}{C_2B_{10}H_{12}}$ $[C_2B_9H_{12}]^- < nido [C_2B_9H_{11}]^2$, with NICS values of -32.7, -35.4, and -37.0 ppm, respectively. To account for this situation, a similar scheme as this for $\frac{nido}{[C_2B_9H_{12}]^{-1}}$ is suggested for <u>*nido*</u> $[C_2B_9H_{11}]^{2-}$ but with the aromatic ring somehow closer to B₁ (Scheme 3c). And how this should be manifested? If the density of magnetic field lines is higher on B₁ in *nido* $[C_2B_9H_{11}]^{2}$ than in *nido* $[C_2B_9H_{12}]^{-}$ due to a higher aromaticity of the B₅ ring, then the chemical shift of B₁ in *nido* $[C_2B_9H_{11}]^{2-}$ shall be more negative than in *nido* $[C_2B_9H_{12}]^{-}$, as it is the case (δ -46.1 vs -37.2 ppm, respectively).⁷⁰

Ring currents of closo $[B_{12}H_{12}]^2$, closo $C_2B_{10}H_{12}$, nido $[C_2B_9H_{12}]^2$ and nido $[C_2B_9H_1]^2$. The magnetic induced current densities of $\frac{closo}{closo}$ $[B_{12}H_{12}]^{2-}$, $\frac{closo}{closo}$ o-C₂B₁₀H₁₂, $\frac{nido}{closo}$ o- $[C_2B_9H_{12}]^{-}$, and <u>*nido*</u> o- $[C_2B_9H_{11}]^{2-}$ were computationally obtained by applying an external magnetic field B₀ as shown in Figure 3. The currents for the *meta*- and *para*isomers are similar to those obtained for the ortho-species (see Supporting Information). As a reference, the Supporting Information contains the magnetic induced current densities of benzene. By convention, it is considered that the direction of the diatropic ring currents indicating aromaticity is clockwise. The magnetic induced current densities of <u>closo</u> $[B_{12}H_{12}]^{2}$ reaches a maximum in the center of the icosahedron (see Figure 4). Interestingly, the most inner ring current in the center is paratropic. Antiaromatic molecules have paratropic inner and outer ring currents, whereas aromatic molecules present paratropic inner and diatropic outer ring currents.⁷¹ Ring currents perpendicular to the external magnetic field at the center of $[B_{12}H_{12}]^{2-}$ are typical of an aromatic compound. Other planes perpendicular to the external magnetic field located at 1, 2, or 3 bohr above or below the central plane show also the same picture, although the intensity of the ring currents is somewhat reduced.



Figure 3. Representation of (a) the integration plane for the calculation of the currentdensity and the magnetic field vector (B₀) for the <u>closo</u> $[B_{12}H_{12}]^{2-}$ system. (b) Representation of the different system orientations with respect to the magnetic field vector B₀ (blue arrow) for the <u>closo</u> o-C₂B₁₀H₁₂, <u>closo</u> m-C₂B₁₀H₁₂, <u>closo</u> p-C₂B₁₀H₁₂, <u>nido</u> o-[C₂B₉H₁₂]⁻, <u>nido</u> o-[C₂B₉H₁₁]²⁻, <u>nido</u> m-[C₂B₉H₁₂]⁻, <u>nido</u> m-[C₂B₉H₁₁]²⁻, <u>nido</u> m-[C₂



Figure 4. Representation of the current-density vector field for the <u>closo</u> $[B_{12}H_{12}]^{2-}$ system. Top view of the currents in the perpendicular plane with respect to the magnetic field vector B_0 located at 0, 1, 2, and 3 bohrs (from left to right, respectively) above the central plane. Units are nA T⁻¹. See Supporting Information for pictures with larger resolution.



Figure 5. Representation of the current-density vector field for the *closo* o-[C₂B₁₀H₁₂] system in orientation **III** (Figure 3). See Supporting Information for the rest of orientations of the external magnetic field. Top view of the currents in the σ_{xy} plane located at -2, 0, and 2 bohrs (from left to right, respectively) above the plane located in the middle of the two 5-membered rings (parallel to the 5-membered ring planes). Color scale given in Figure 4. Units are nA T⁻¹. See Supporting Information for pictures with larger resolution.

Figure 5 depicts the magnetic induced current densities of *closo* o-C₂B₁₀H₁₂. Change of BH⁻ by CH does not produce a notable change of the observed ring currents. One can conclude that the aromaticity of the system is affected only slightly by moving from *closo* $[B_{12}H_{12}]^{2-}$ to *closo* o-C₂B₁₀H₁₂. This is not unexpected as we keep the *closo* aromatic structure of the borohydride. On the other hand, when we move from *closo* o-C₂B₁₀H₁₂ carborane to *nido* o-[C₂B₉H₁₂]⁻, there is a clear decrease of the diatropic intensity in the central part of the polyhedron (the central plane is considered the plane in the middle of the two pentagonal rings), indicating a reduction of the aromatic character of this species (see Figure 6). Still, the picture of the ring currents indicates that we are dealing with an aromatic compound, despite it is less aromatic than the *closo* $[B_{12}H_{12}]^{2-}$ or *closo* o-C₂B₁₀H₁₂. As we move from the central plane, the currents tend to be more disorganized.

Finally, for species *nido* o-[C₂B₉H₁₁]²⁻, the ring currents are similar to those obtained for *nido* o-[C₂B₉H₁₂]⁻ (see Figure 7).



Figure 6. Representation of the current-density vector field for the *nido* o-[C₂B₉H₁₂]⁻ system. Top view of the currents in the perpendicular plane with respect to the magnetic field vector B₀ located at -2, -1, 0, 1, and 2 bohr (from left to right, respectively) above the plane located in the middle of the two 5-membered rings (parallel to the 5-membered ring planes). Color scale given in Figure 4. Units are nA T⁻¹. See Supporting Information for pictures with larger resolution.



Figure 7. Representation of the current-density vector field for the *nido* o-[C₂B₉H₁₁]²system. Top view of the currents in the perpendicular plane with respect to the magnetic field vector B₀ located at -2, -1, 0, 1, and 2 bohr (from left to right, respectively) above the plane located in the middle of the two 5-membered rings (parallel to the 5-membered ring planes). Color scale given in Figure 4. Units are nA T⁻¹. See Supporting Information for pictures with larger resolution.

Considerations on the aromaticity of $[Co(C_2B_9H_{11})_2]^{-}$ as an example of *metallabis(dicarbollides)* and their singularity versus the metallocenes. Since their discovery, metallabis(dicarbollides) $[M(C_2B_9H_{11})_2]^{-}$ (M=TM) (Figure 8) have been considered the equivalent in boron clusters to the metallocenes, but they are not as we shall demonstrate here. They share the property of having one solid structure difficult to be reorganized, thus allowing outer electron transfer that is commonly fast. Both undergo typical aromatic substitution reactions. And both show continuous electron delocalization, at least in part of the molecule. However, inspection of both molecular structures shows a remarkable difference. The word sandwich, which is applied to both molecules, is adequate for the metallocenes because in their case two parallel planar ligands, to follow the aromatic typical concept, have a metal filling in between. However,

the generated pentagonal pyramid does not fit in the classical concept of aromaticity as in fact, what is happening is that coordination to metal by the cyclopentadienyl ligand does not prevent that they exhibit aromatic properties, although the aromaticity of the ligands can be somewhat reduced as it was demonstrated for the benzene ring of $[Cr(n^6 C_{6}H_{6}$ (CO)₃.⁷² Thus, it would seem adequate to say that ferrocene exhibits aromatic properties rather than refer to it as an aromatic compound. This conclusion is reinforced by the work of Fowler et al. showing that the two cyclopentadienyl anions support individual diatropic ring currents.²⁸ Conversely, the metallabis(dicarbollides) are made of two icosahedra in which the metal occupies one vertex. If we take into account the definition of aromaticity of Chen and Schleyer as "a manifestation of electron delocalization in closed circuits, either in two or three dimensions",⁶⁸ the $[M(C_2B_9H_{11})_2]$ conforms to a structure, the icosahedron, that is compatible with aromaticity because it can generate a closed circuit. Therefore, metallabis(dicarbollides) are aromatic compounds, whereas metallocenes display aromatic behavior. In other words, metallabis(dicarbollides) display global aromaticity whereas metallocenes present local aromaticity in the ligands.

This can be well observed by the ring currents depicted in Figure 9 with the direction of the magnetic field shown in Figure 8. For $[Co(C_2B_9H_{11})]^+$, there is a clear external diatropic ring current from 1 to 5 bohrs with a maximum located at around the center. The intensity of the current density seems to indicate a slightly loss of aromaticity when moving from *nido o*- $[C_2B_9H_{11}]^2$ to *closo* $[Co(C_2B_9H_{11})]^+$, although care has to be taken when using the ring currents and the NICS as indicators of aromaticity when metal atoms do participate, as paratropic currents are produced in this situation that perturb the diatropic current leading to misunderstandings.⁷³ A similar situation is found for *closo* $[Co(C_2B_9H_{11})_2]^-$ (Figure 10), but now the intensity of the current density seems to be as large as that of *nido o*- $[C_2B_9H_{11}]^2$. Interestingly, the highest intensity of current density is found inside the icosahedron of the cobaltabis(dicarbollides, not far from the Co atom, whereas in ferrocene the highest intensity of current density is found outside the pentagonal pyramid and far from Fe.²⁸ We think that this result is a clear indication that we have global aromaticity in metallabis(dicarbollides) and local in ferrocenes.



Figure 8. Representation of the orientation of the magnetic field vector, magnetic field vector B_0 (blue arrow) for the *closo* $[Co(C_2B_9H_{11})]^+$ and *closo* $[Co(C_2B_9H_{11})_2]^-$ systems.



Figure 9. Representation of the current-density vector field using the LIC method for the *closo* $[Co(C_2B_9H_{11})]^+$ system. Top view of the currents in the planes parallel to the 5membered rings located 0, 1, 2, and 3 bohr (on top, and from left to right, respectively); and 4, 5, 6, and 7 bohr (on bottom, and from left to right, respectively). Being the plane at 0 bohr the one containing the Co atom, and the plane at 4 bohr the one in the middle of the two 5-membered rings Color scale given in Figure 4. Units are nA T⁻¹. See Supporting Information for pictures with larger resolution.



Figure 10. Representation of the current-density vector field using the LIC method for the *closo* $[Co(C_2B_9H_{11})_2]^-$ system. Top view of the currents in the planes parallel to the 5-membered rings located 0, 1, 2, and 3 bohr (on top, and from left to right, respectively); and 4, 5, 6, and 7 bohr (on bottom, and from left to right, respectively). Being the plane at 0 bohr the one containing the Co atom, and the plane at 4 bohr the one in the middle of the two 5-membered rings. Color scale given in Figure 4. Units are nA T⁻¹. See Supporting Information for pictures with larger resolution.

Conclusions

There are several conclusions that can be drawn from this research; these refer to aromaticity of *closo* carboranes, aromaticity of *nido* carboranes, aromaticity of sandwich metallabis(dicarbollides), aromaticity and antiaromaticity, aromaticity and reactivity, and planar and spherical aromaticity.

The resistance of the *closo* m-C₂B₁₀H₁₂ deboronation as compared to the easiness to deboronate the *closo* o-C₂B₁₀H₁₂, together with the isomerization of *closo* o-C₂B₁₀H₁₂ to *closo* m-C₂B₁₀H₁₂ upon heating agrees with the B3LYP/6-311++G(d,p) results indicating that the isomer *meta* is 16.3 kcal mol⁻¹ more stable than the *ortho*. However, this difference is not related to aromaticity but to the location of the C atoms in the carborane structure.

It is to be noticed that the closed or partially closed structure of boranes permits to draw conclusions on aromaticity that otherwise would be difficult to observe in other morphologies. Experimentally, it is found that the endocyclic and acid proton on top of a pentagonal C_2B_3 face resonates near -2.5 ppm in the ¹H-NMR and its antipodal boron resonates at -37.2 ppm at the ¹¹B-NMR. Both are at the highest upfield parts of their respective spectra that prove the existence of diatropic currents in the plane at the middle of the cluster. Upon removal of the endocyclic proton, the C_2B_3 generated plane is not the most aromatic of the possible cluster pentagonal planes according to NICS values. This situation contrasts with ferrocene in which the highest aromaticity is in the Cp⁻ planes. Calculations at the B3LYP/6-311++G(d,p) level of theory also prove that the C₂B₃ ring in *nido* carborane is not more aromatic than that in *closo*, despite the former represents a conjugated open face, which coordinates with the metal in metallabis(dicarbollides). More importantly, and at difference to p_{π} systems, the strongest diatropic ring currents are not found at *ca*. 1 Å from the ring plane, but to different parallel planes between the two main five-membered rings of the cluster. This latter is responsible of the anomalous chemical shift in the ¹H-NMR of the endocyclic proton, as well as that of B_1 .

For completeness, comparison to metallocenes allows to conclude that whereas metallabis(dicarbollides) are clearly aromatic, as mentioned above, metallocenes display aromatic character; alternatively, metallabis(dicarbollides) display global aromaticity whereas metallocenes present local aromaticity in the ligands. *closo* boranes, e.g. $[B_{12}H_{12}]^{2-}$ and *closo* carboranes, e.g. *o-*, *m-*, *p-*C₂B₁₀H₁₂ display very similar aromaticity properties, with very large NICS negative values, about -33 ppm, despite the existence of

 heteroatoms with $\Delta \chi(C,B)=0.51$. This contrasts markedly with the planar diazines and diboratabenzenes also having *o*-, *m*-, *p*-N₂C₄H₄ and *o*-, *m*-, *p*-[C₄B₂H₆]²⁻ isomers, which can be referenced to C₆H₆. These have similar $\Delta \chi(N,C)=0.49$ and precise $\Delta \chi(C,B)$ but the discrepancies with the NICS values between C₆H₆ and the diazines surpass 30%, and between C₆H₆ and the diboratabenzenes surpass 75%, whereas between *closo* [B₁₂H₁₂]²⁻ and *closo* carboranes is near 1%. The *nido* carboranes present an aromatic character very similar to that of *closo*-carboranes, despite *nido* carboranes have lost the spherical shape of the *closo*-carboranes or boranes. Both NICS magnetic aromaticity criteria, as well as their diatropic ring currents, support the aromatic character of *nido* carboranes.

Thus, it is proven the initial hypothesis that if metallabis(dicarbollides) are aromatic, their ligands must be also aromatic. Unlike aromatic hydrocarbons that become antiaromatic when two electrons are either added or removed, carboranes keep their aromaticity even when deboronated because they adapt to a different geometry. Therefore, aromaticity in boron clusters survives radical structural changes. When two electrons are added to a *closo* with n vertexes it becomes a *nido* with n-1 vertexes to preserve the initial aromaticity. This possibility is not feasible to planar conjugated organic molecules with $4n+2\pi$ electron counting, and highlights the uniqueness of boron clusters with regard to the aromaticity. Further it accounts very well for the "Paradigm for the Electron Requirements of Clusters" by R.W. Rudolph in which a *closo* cluster that is aromatic upon addition of 2e- becomes a *nido* species (actually also aromatic according to this work), and explains the nice schemes by R.W. Rudolph and R. E. Williams.

Experimental Section

Bench work: Partial degradation or deboronation of *closo* $1,2-C_2B_{10}H_{12}$ and *closo* $1,7-C_2B_{10}H_{12}$ has been done in a comparative way to show the differences of the apparently similar but in reality very different isomers. Despite there are alternative methods of partial degradation of *closo* $1,7-C_2B_{10}H_{12}$ indicated in the text, the reported autoclave method⁵¹ with KOH in ethanol can be convenient for the simplicity in the working up procedure. All details of the partial degradation procedures done and the NMR characterization are extensively indicated in the S.I.

The reported general procedure is: 200 mg (1.38 mmols) of *closo* $1,7-C_2B_{10}H_{12}$ and 388 mg (6.94 mmols) of KOH were mixed with 5 mL of ethanol in an autoclave to preserve the solvent at 130°C for 4h. The resulting white precipitate was filtered off and the solvent

evaporated in vacuum to give *nido* $[7,9-(C_2B_9H_{11})]^{2-}$. Water (15-20 mL) were added followed by drops of a diluted HCl solution until having a pH equal to 3. The precipitation by adding 132 mg (1.38 mmols) of [HNMe₃]Cl gave 176 mg of [HNMe₃][7,9-*nido*-(C₂B₉H₁₂)] (66%).

Table 3: Summary of the different parameters used for the partial degradation of the *closo* $m-C_2B_{10}H_{12}$ cluster

Working conditions				
T(°C)	Time (hours)	n _{eq} of KOH	Presence of the starting closo m-C ₂ B ₁₀ H ₁₂ cluster	nido meta [HNMe3][m-C2B9H12] Yield (%)
110 115 120 130	4 1 2 3	<mark>5</mark>	<mark>√</mark>	38.2 40.8 45.3
150	4	3 5	√	47.2
<mark>160</mark>	<mark>4</mark>			

Computational work: All calculations were performed with the Gaussian 09 package⁷⁴ by means of the B3LYP⁷⁵⁻⁷⁷ hybrid density functional and the 6-311++G(d,p) basis set.⁷⁸ The geometry optimizations were carried out without symmetry constraints, and analytical Hessians were computed to characterize the optimized structures as minima (zero imaginary frequencies). Aromaticity was evaluated by means of the nucleus-independent chemical shift (NICS),^{33, 40-41, 68} proposed by Schleyer and co-workers as a magnetic descriptor of aromaticity. NICS is defined as the negative value of the absolute shielding computed at a ring center or at some other point of the system. Rings with large negative NICS values are considered aromatic. NICS values were computed using the gaugeincluding atomic orbital method (GIAO).⁷⁹ The magnetic shielding tensor was calculated for ghost atoms located at the center of the rings (or polyhedra) determined by the nonweighted mean of the heavy atoms coordinates. These values are denoted as NICS(0).⁸⁰ Reported ring currents were computed using the GIMIC program⁸¹⁻⁸³ using the gaugeincluding atomic orbitals (GIAO) procedure with the B3LYP/6-311++G(d,p) method.⁸⁴ A more detailed explanation of the GIMIC calculations is provided in the Supporting Information.

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Graphic for the TOC

