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Are Halocarboranes Suitable for Substitution Reactions? The Case for 3-I-1,2-*closo*-$C_2B_{10}H_{11}$: Molecular Orbital Calculations, Aryldehalogenation Reactions, ^{11}B NMR Interpretation of *closo*-Carboranes, and Molecular Structures of 1-Ph-3-Br-1,2-*closo*-$C_2B_{10}H_{10}$ and 3-Ph-1,2-*closo*-$C_2B_{10}H_{11}$

Clara Viñas,*,† Gemma Barberà,† Josep M. Oliva,† Francesc Teixidor,† Alan J. Welch,‡ and Georgina M. Rosair‡

Institut de Ciència de Materials de Barcelona (CSIC),Campus U.A.B., E-08193 Bellaterra, Spain, and Department of Chemistry, Heriot-Watt University, Edinburgh EH14 4AS, U.K.

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In this paper, the chemistry of 3-X-1,2-*closo*-$C_2B_{10}H_{11}$ (X = halogen) derivatives is extended. Molecular orbital and ^{11}B and ^{13}C NMR calculations on these species are presented. A qualitative interpretation of the ^{11}B 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*-$C_2B_{10}H_{12}$ (*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*-$C_2B_{10}H_{12}$ is reminiscent of that of R−C≡C−H and arises because of the similar nature of the C atomic orbitals in both *H*C$CB_{10}H_{11}$ and *H*CCR, 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 $AlCl_3$ 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 $AlCl_3$, 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 $AlCl_3$, 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 cocatalyst[10] 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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* Author to whom correspondence should be addressed. Fax: Int. Code +93 5805729. E-mail: clara@icmab.es.

† Institut de Ciència de Materials de Barcelona (CSIC).

‡ Heriot-Watt University.

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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*-$C_2B_{10}H_{11}$,[8] 3-Br-1,2-*closo*-$C_2B_{10}H_{11}$,[11,12] and 3-F-1,2-*closo*-$C_2B_{10}H_{11}$[12] have been synthesized by the alternate strategy of reacting $[C_2B_9H_{11}]^{2-}$ with BX_3 or their adducts. From 3-I-1,2-$C_2B_{10}H_{11}$ may be formed species with B3−C(alkyl) bonds, and 3-R-1,2-*closo*-$C_2B_{10}H_{11}$ (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*-$C_2B_{10}H_{11}$ does exist, the result of the reaction between $[C_2B_9H_{11}]^{2-}$ and $PhBCl_2$.[13]

Density-functional and Hartree−Fock (HF) calculations are also reported on 3-X-1,2-*closo*-$C_2B_{10}H_{11}$ (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*-$C_2B_{10}H_{11}$ 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*-$C_2B_{10}H_{11}$ (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 functional[16] 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 basis set as "Gen". As described in section 4 below, the HF and B3LYP theoretical levels were used with basis sets "Gen" and LANL2DZ[20] (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 ^{11}B NMR chemical shifts in 3-I-1,2-*closo*-$C_2B_{10}H_{11}$. Figure 1 shows the structure of 1,2-*closo*-$C_2B_{10}H_{12}$ with the numbering of the cage atoms.

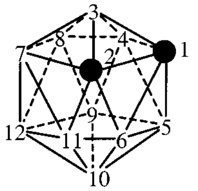

Figure 1. Structure of the 1,2-*closo*-$C_2B_{10}H_{12}$ cluster showing numbering of the cage atoms.

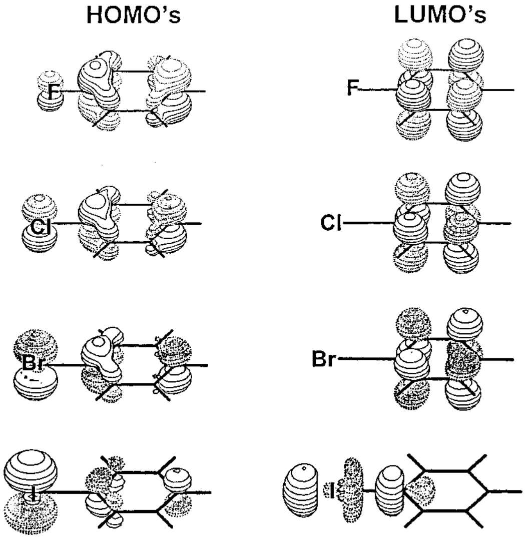

Figure 2. 3D contour plots (±0.075 wave function amplitude units) of HOMO and LUMO orbitals in X−C_6H_5 (X = F, Cl, Br, I) compounds.

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*-$C_2B_{10}H_{11}$ 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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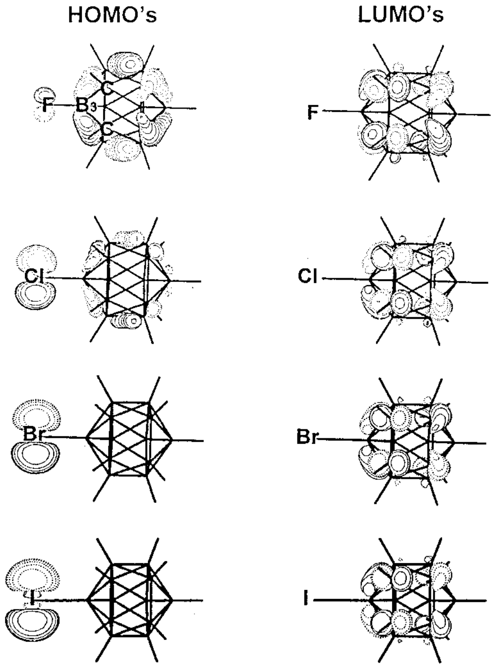


Figure 3. 3D contour plots (±0.075 wave function amplitude units) of HOMO and LUMO orbitals of 3-X-1,2-*closo*-$C_2B_{10}H_{11}$ (X = F, Cl, Br, I) compounds.

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*-$C_2B_{10}H_{11}$ 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*-$C_2B_{10}H_{11}$ 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*-$C_2B_{10}H_{11}$ 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*-$C_2B_{10}H_{11}$ 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*-$C_2B_{10}H_{11}$ 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*-$C_2B_{10}H_{11}$ carboranes have larger HOMO−LUMO gaps, as shown in Figure 4, and therefore they are expected to be less reactive than X-benzene species.

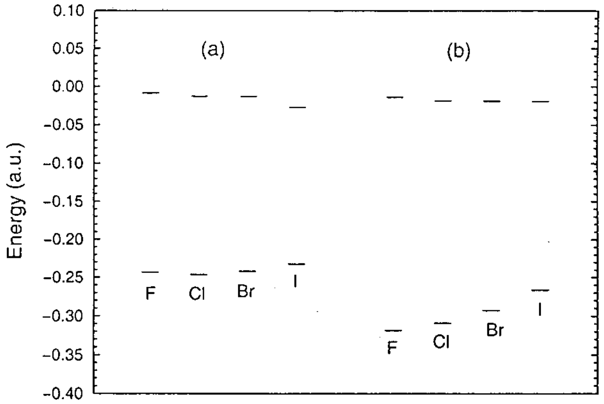
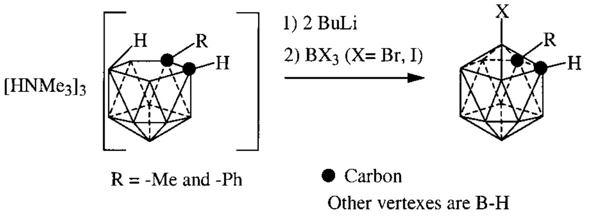


Figure 4. HOMO and LUMO energy levels for (a) X−C_6H_5 and (b) 3-X-1,2-*closo*-$C_2B_{10}H_{11}$ carborane.

Scheme 1



Thus, our calculations suggest that the reactivity of the X-benzene and 3-X-1,2-*closo*-$C_2B_{10}H_{11}$ carboranes should increase in the order F < Cl < Br < I. The 3-I-1,2-*closo*-$C_2B_{10}H_{11}$ 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-R_1-2-R_2-1,2-*closo*-$C_2B_{10}H_{10}$ 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 $[7\text{-}R_1\text{-}8\text{-}R_2\text{-}7,8\text{-}C_2B_9H_{10}]^-$ 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-NH_2-1,2-*closo*-$C_2B_{10}H_{11}$ and 3-CH_2CH-1,2-*closo*-$C_2B_{10}H_{11}$.

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*-$C_2B_{10}H_{10}$, 3-I-1-Ph-1,2-*closo*-$C_2B_{10}H_{10}$, 3-Br-1-Me-1,2-*closo*-$C_2B_{10}H_{10}$, and 3-I-1-Me-1,2-*closo*-$C_2B_{10}H_{10}$ were produced in good yields. Compounds were initially characterized by microanalysis and

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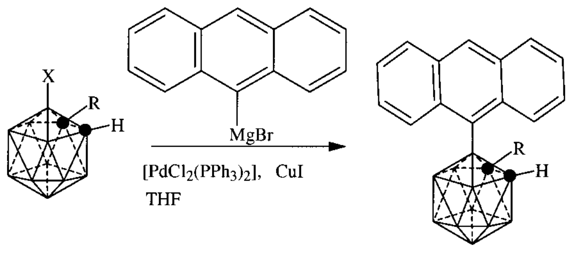
Scheme 2



IR spectroscopy. NMR spectra (^{11}B, ^{13}C, ^{1}H) 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 [7-R-7,8-$C_2B_9H_{10}$]$^{2-}$ 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*-$C_2B_{10}H_{11}$, 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*-$C_2B_{10}H_{11}$ in the presence of [$PdCl_2(PPh_3)_2$] and CuI, in THF solution under refluxing conditions, as denoted in Scheme 2. The compounds 3-R-1,2-*closo*-$C_2B_{10}H_{11}$ (R = aryl) were obtained in good to high yields (≅90%) and were fully characterized by multinuclear NMR data (^{11}B, ^{13}C, ^{1}H).

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*-$C_2B_{10}H_{11}$ in DMF in the presence of Ni[24] or Pd[25] in stoichiometric quantities yielded *o*-carborane.

3. Molecular and Crystal Structures of 1-Ph-3-Br-1,2-*closo*-$C_2B_{10}H_{10}$ and 3-Ph-1,2-*closo*-$C_2B_{10}H_{11}$. As an adjunct to our theoretical and synthetic work we have studied the species 1-Ph-3-Br-1,2-*closo*-$C_2B_{10}H_{10}$ and 3-Ph-1,2-*closo*-$C_2B_{10}H_{11}$ by single-crystal X-ray diffraction.

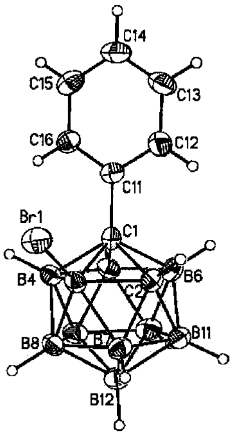


Figure 5. Structure of 1-Ph-3-Br-1,2-*closo*-$C_2B_{10}H_{10}$ showing the atom-labeling scheme.

Table 1. Selected Interatomic Distances (Å) and Interbond and Dihedral Angles (deg) in 1-Ph-3-Br-1,2-*closo*-$C_2B_{10}H_{10}$

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)		

A. 1-Ph-3-Br-1,2-*closo*-$C_2B_{10}H_{10}$. 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*-$C_2B_{10}H_{10}$ and its isomer species 1-Ph-2-Br-1,2-*closo*-$C_2B_{10}H_{10}$.[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*-$C_2B_{10}H_{12}$.[27] In C−Ph 1,2-carboranes we define the orientation of the Ph substituent by the angle θ, the modulus of the average $C_{cage}-C_{cage}-C11-C$ torsion angle.[28] In the present compound θ is 66.8(5)°, 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*-$C_2B_{10}H_{11}$ 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)° and −90.2(5)°, respectively. The B3−Br distance is 1.927(5) Å, in excellent agreement with other such distances in the literature.[30]

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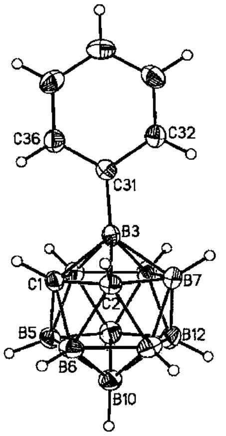

Figure 6. Structure of 3-Ph-1,2-*closo*-$C_2B_{10}H_{11}$ showing the atom-labeling scheme.

Table 2. Selected Interatomic Distances (Å) and Interbond and Dihedral Angles (deg) in 3-Ph-1,2-*closo*-$C_2B_{10}H_{11}$

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*-$C_2B_{10}H_{11}$. Figure 6 shows a perspective view of a single molecule of 3-Ph-1,2-*closo*-$C_2B_{10}H_{11}$, 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*-$C_2B_{10}H_{11}$ bears no relationship to those of two crystalline modifications of 1-Ph-1,2-*closo*-$C_2B_{10}H_{11}$ 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*-$C_2B_{10}H_{11}$, ^{11}B NMR studies have shown that 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]

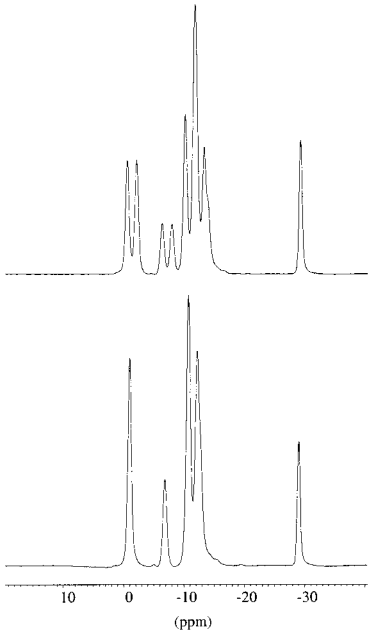

Figure 7. ^{11}B and $^{11}B\{^1H\}$ spectra of 3-I-1,2-*closo*-$C_2B_{10}H_{11}$.

The ^{11}B NMR spectrum of 3-I-1,2-*closo*-$C_2B_{10}H_{11}$ presents a 2:1:3:3:1 pattern in the range −1.04 to −29.02 ppm. Figure 7 shows the ^{11}B and $^{11}B\{^1H\}$ NMR spectra of 3-I-1,2-*closo*-$C_2B_{10}H_{11}$. The resonance at −29.02 ppm does not split into a doublet in the ^{11}B NMR spectrum, indicating that this resonance corresponds to the B−I vertex. Once the B3 resonance is known, the two-dimensional 2D-COSY NMR spectrum[33] is helpful for the assignment of the remaining peaks. Figure 8 shows a typical spectrum, that of 3-I-1,2-*closo*-$C_2B_{10}H_{11}$, with the assignments deduced from the off-diagonal resonances.

A. Qualitative Description of the ^{11}B NMR Spectra. The ^{11}B 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*-$C_2B_{10}H_{12}$ 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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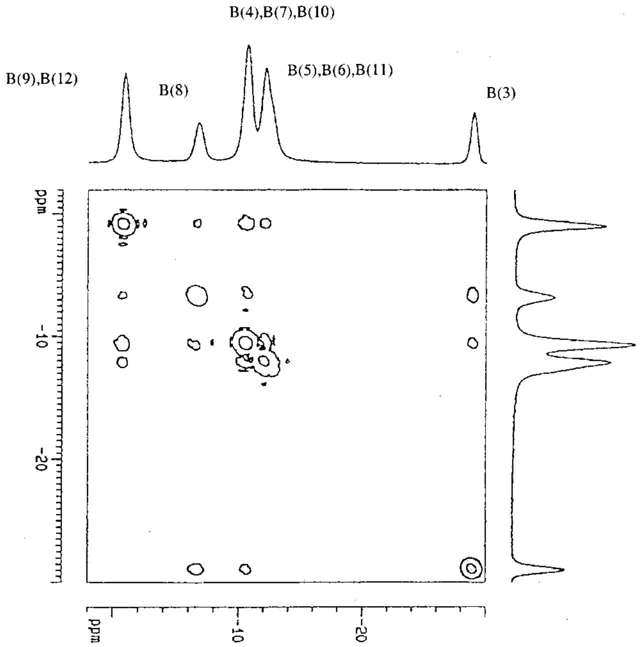

Figure 8. $^{11}B\{^1H\}-^{11}B\{^1H\}$ 2D-COSY NMR spectrum of 3-I-1,2-*closo*-$C_2B_{10}H_{11}$.

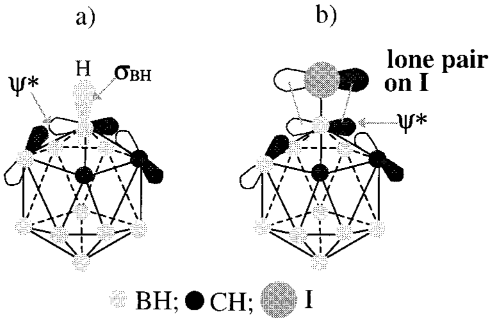

Figure 9. ^{11}B NMR in closo carboranes. (a) In 1,2-$C_2B_{10}H_{12}$, perpendicular disposition of the occupied $\boldsymbol{\sigma}_{\mathbf{BH}}$ and the atomic $\mathbf{p}_\perp$ orbitals. The last one participates in the low-lying ψ^* unoccupied orbital. Only some atomic orbitals are represented. (b) In 3-I-1,2-$C_2B_{10}H_{11}$, lone-pair electron back-donation from the I atom to the ψ^*, largely spread on the cluster.

consequence of low-lying unoccupied $\mathbf{p}_\perp$ orbitals allowed efficient combination with appropriate energy-rich occupied orbitals. Figure 9a depicts the $\boldsymbol{\sigma}_{\mathbf{BH}}/\mathbf{p}_\perp$ combination, possibly responsible for the strong ^{11}B NMR dependency of the $\boldsymbol{\sigma}^{\mathbf{p}}$ 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 $\boldsymbol{\sigma}/\mathbf{p}_\perp$ combinations are active in NMR, yielding deshielding contributions perpendicular to the $\boldsymbol{\sigma}/\mathbf{p}_\perp$ plane of charge circulation. It is also reasonable to assume that the magnitude of the individual $\boldsymbol{\sigma}^{\mathbf{p}}$ contributions will depend on the electron density in the particular B−H bond. The last follows the pattern B−H(9,12) > B−H(8,10) > B−H(4,5,7,11) > B−H(3,6); thus the largest individual $\boldsymbol{\sigma}^{\mathbf{p}}$ contribution would be for B−H(9,12), the smallest for B−H(3,6), corresponding very well with the observed pattern indicated above.

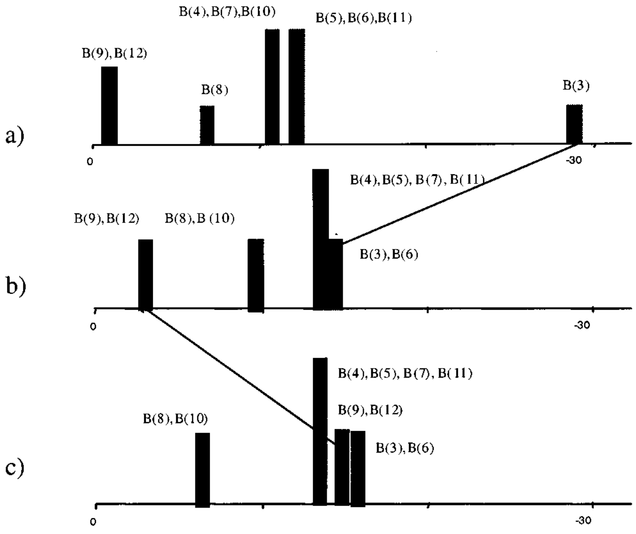

Figure 10. Raw ^{11}B NMR spectra with the peak assignments for the compounds: (a) 3-I-1,2-*closo*-$C_2B_{10}H_{11}$, (b) 1,2-*closo*-$C_2B_{10}H_{12}$, and (c) 9,12-I_2-1,2-*closo*-$C_2B_{10}H_{10}$.

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 above provides a rationale for these effects. Now, if the ^{11}B NMR spectrum of 3-I-1,2-*closo*-$C_2B_{10}H_{11}$, 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*-$C_2B_{10}H_{12}$, 3-I-1,2-*closo*-$C_2B_{10}H_{11}$, and 9,12-I_2-1,2-*closo*-$C_2B_{10}H_{10}$ 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 $\boldsymbol{\sigma}/\mathbf{p}_\perp$ 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 $\mathbf{p}_\perp$ orbitals on B3. See Figure 9b. This will enrich considerably the electron density at B3 enhancing its shielding $\boldsymbol{\sigma}^{\mathbf{d}}$ term, and consequently shifting the B3 resonance to high field. This back-donation to B3 will diminish in the sequence I > Br > Cl > 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 $\boldsymbol{\sigma}^{\mathbf{p}}$ 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 $^{11}B\{^1H\}$ and $^{13}C\{^1H\}$ Chemical Shifts (ppm) in Carboranes 3-X-1,2-$C_2B_{10}H_{11}$ (X = F, Cl, Br, I, Ph) and 3-X-1-R-1,2-$C_2B_{10}H_{10}$ (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*-$C_2B_{10}H_{11}$. 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 (II″//HF/6-31G* 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*-$C_2B_{10}H_{11}$ (X = F, Cl, Br, I, Ph) and 3-X-1-R-1,2-*closo*-$C_2B_{10}H_{10}$ (X = Br, I; R = Me, Ph). Attempts to reproduce these ^{11}B and ^{13}C NMR chemical shifts using rigorous calculational methods[42] 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*-$C_2B_{10}H_{11}$,[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 $^1H\{^{11}B\}$ NMR (300.13 MHz), $^{13}C\{^1H\}$ 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 $BF_3 \cdot OEt_2$, and those for ^1H, $^1H\{^{11}B\}$, and $^{13}C\{^1H\}$ 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*-$C_2B_{10}H_{11}$[8] and 3-Br-1,2-*closo*-$C_2B_{10}H_{11}$[11] were synthesized according to the literature.

3-Bromo-1-methyl-1,2-dicarba-*closo*-dodecaborane. To a solution of $[HNMe_3][7\text{-}Me\text{-}7,8\text{-}C_2B_9H_{11}]$ (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 $C_3H_{13}B_{10}Br$: C, 15.19; H, 5.53. Found: C, 15.50; H, 5.64. IR: ν [cm^{-1}] = 3057 ($C_{cluster}$−H), 2960−2854 (C_{Me}−H), 2590 (B−H). ^1H NMR: δ = 3.56 (br s, 1H, $C_{cluster}$−H), 2.17 (s, 3H, CH_3), 3.50−1.50 (br m, 9H, B−H). $^{13}C\{^1H\}$ NMR: δ = 72.04, 66.24 (s, $C_{cluster}$), 25.73 (s, CH_3). ^{11}B NMR: δ = − 2.32 (d, ^1J(B,H) = 151, 1B), −5.60 (d, ^1J(B,H) = 151, 1B), −7.74 (d, ^1J(B,H) = 110, 1B), −9.10 (s, 1B, B(3)), −9.97 (d, 4B), −12.31 (d, 1B), −13.14 (d, ^1J(B,H) = 96, 1B).

3-Bromo-1-phenyl-1,2-dicarba-*closo*-dodecaborane. Similarly were reacted $[HNMe_3][7\text{-}Ph\text{-}7,8\text{-}C_2B_9H_{11}]$ (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 $C_8H_{15}B_{10}Br$: C, 32.11; H, 5.05. Found: C, 32.42; H 5.07. IR: ν [cm^{-1}] = 3068 ($C_{cluster}$−H), 3056, 3040 (C_{aryl}−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, $C_{cluster}$−H), 3.90−2.10 (br m, 9H, B−H). $^{13}C\{^1H\}$ NMR: δ = 132.70, 130.77, 129.53, 127.79 (C_{aryl}), 78.23, 62.32 (s, $C_{cluster}$). ^{11}B NMR: δ = −3.26 (d, ^1J(B,H) = 143, 2B), −7.80 (d, 1B), −8.61 (s,

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[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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[42] We have used the following GIAO methods: HF/LANL2DZ, HF/Gen, B3LYP/LANL2DZ, and B3LYP/Gen.

[43] Viñas, C.; Barberà, G.; Teixidor, F.; Welch, A. J., Rosair, G. M. To be published.

1B, B(3)), −9.59 (d, 1B), −10.53 (d, 3B), −11.38 (d, 1B), −13.88 (d, ^1J(B,H) = 164, 1B).

3-Iodo-1-methyl-1,2-dicarba-*closo*-dodecaborane. In an analogous manner were reacted [$HNMe_3$][7-Me-7,8-$C_2B_9H_{11}$] (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 $C_3H_{13}B_{10}I$: C, 12.68; H, 4.61. Found: C, 13.04; H 4.56. IR: ν [cm^{-1}] = 3058 ($C_{cluster}$−H), 2956−2857 (C_{Me}−H), 2594 (B−H). ^{1}H NMR: δ = 3.60 (br s, 1H, $C_{cluster}$−H), 2.24 (s, 3H, CH_3), 3.50−1.10 (br m, 9H, B−H). ^{13}C{^{1}H} NMR: δ = 71.47, 66.84 (s, $C_{cluster}$), 28.35 (s, CH_3). ^{11}B NMR: δ = −1.24 (d, ^1J(B,H) = 151, 1B), −5.06 (d, ^1J(B,H) = 156, 1B), −6.41 (d, ^1J(B,H) = 122, 1B), −8.17 (d, ^1J(B,H) = 176, 1B), −10.05 (d, ^1J(B,H) = 180, 4B), −12.09 (d, ^1J(B,H) = 161, 1B), −24.32 (s, 1B, B(3)).

3-Iodo-1-phenyl-1,2-dicarba-*closo*-dodecaborane. Similarly, [$HNMe_3$][7-Ph-7,8-$C_2B_9H_{11}$] (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 $C_8H_{15}B_{10}I$: C, 27.75; H, 4.37. Found: C, 27.64; H, 4.34. IR: ν [cm^{-1}] = 3059 ($C_{cluster}$−H), 2544 (B−H). ^{1}H NMR: δ = 7.50−7.00 (m, 5H, H_{aryl}), 4.22 (br s, 1H, $C_{cluster}$−H), 3.10−1.50 (br m, 9H, B−H). ^{13}C{^{1}H} NMR: δ = 134.24, 130.78, 129.53, 127.67 (C_{aryl}), 78.15, 62.59 (s, $C_{cluster}$). ^{11}B NMR: δ = −1.98 (d, ^1J(B,H) = 140, 1B), −3.00 (d, ^1J(B,H) = 114, 1B), −6.49 (d, ^1J(B,H) = 164, 1B), −9.43 (d, ^1J(B,H) = 158, 5B), −12.75 (d, ^1J(B,H) = 169, 1B), −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, [$PdCl_2(PPh_3)_2$] (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 × 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 dicloromethane/hexane (1:4) as the eluting solvent to give 3-phenyl-1,2-dicarba-*closo*-dodecaborane. Yield: 0.95 g (86%). Anal. Calcd for $C_8H_{16}B_{10}$: C, 43.61; H, 7.32. Found: C, 43.75; H, 7.34. IR: ν [cm^{-1}] = 3064 ($C_{cluster}$−H), 3010 (C_{aryl}−H), 2646, 2635, 2619, 2608, 2602, 2596, 2556 (B−H). ^{1}H NMR: δ = 8.00−7.30 (m, 5H, H_{aryl}), 3.71 (br s, 2H, $C_{cluster}$−H), 3.50−0.50 (br m, 9H, B−H). ^{13}C{^{1}H} NMR: δ = 133.06, 132.03, 129.77, 128.30 (C_{aryl}), 56,69 (s, $C_{cluster}$). ^{11}B NMR: δ = −2.06 (d, ^1J(B,H) = 149, 2B), −4.71 (s, 1B, B(3)), −8.16 (d, ^1J(B,H) = 147, 1B), −12.62 (d, 3B), −13.29 (d, ^1J(B,H) = 169, 3B).

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 $C_{14}H_{20}B_{10}$: C, 56.73; H, 6.80. Found: C, 56.64; H, 6.78. IR: ν [cm^{-1}] = 3060 ($C_{cluster}$−H), 3028 (C_{aryl}−H), 2623, 2601, 2567 (B−H), 1479 (γ (C−C)$_{aryl}$). ^{1}H NMR: δ = 7.70−7.20 (m, 9H, H_{aryl}), 3.73 (br s, 2H, $C_{cluster}$−H), 2.50−1.10 (br m, 9H, B−H). ^{13}C{^{1}H} NMR: δ = 142.66, 141.24, 140.43, 134.28, 129.44, 128.43, 127.86, 127.68 (C_{aryl}), 57.35 (s, $C_{cluster}$). ^{11}B NMR: δ = −2.01 (d, ^1J(B,H) = 150, 2B), −4.75 (s, 1B, B(3)), −8.14 (d, ^1J(B,H) = 150, 1B), −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-anthracyl-1,2-dicarba-*closo*-dodecaborane. Yield: 1.50 g (94%). Anal. Calcd for C_{16} H_{20} B_{10}: C, 59.97; H, 6.29. Found: C, 58.41; H, 6.11. IR: ν [cm^{-1}] = 3089 ($C_{cluster}$−H), 3010 (C_{aryl}−H), 2603−2550 (B−H), 1436 (γ (C−C)$_{aryl}$). ^{1}H NMR: δ = 8.80 (d, ^2J(H,H) = 8.80, 2H, H_{aryl}), 8.47 (s, 1H, H_{aryl}), 8.01 (d, ^2J(H,H) = 7.5, 2H, H_{aryl}), 7.54−7.46 (m, 4H, H_{aryl}), 3.86 (s, 2H, $C_{cluster}$−H), 3.50−1.50 (br m, 9H, B−H). ^{13}C{^{1}H} NMR: δ = 137.41, 132.22, 131.91, 130.15, 127.92, 126.95, 125.62 (C_{aryl}), 59.0 (s, $C_{cluster}$). ^{11}B NMR: δ = −2.15 (d, ^1J(B,H) = 147, 2B), −3.89 (s, 1B, B(3)), −7.83 (d, ^1J(B,H) = 150, 1B), −11.02 (d, ^1J(B,H) = 134, 1B), −11.81 (d, ^1J(B,H) = 132, 2B), −13.34 (d, ^1J(B,H) = 159, 3B).

Crystallographic Studies. Intensity data collected on a Bruker P4 diffractometer, with Mo Kα radiation (λ = 0.71073 Å) to $2\theta_{max}$ = 50°, 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*-$C_2B_{10}H_{10}$, $C_8H_{15}B_{10}Br$, 160(2) K, M_r = 299.21: crystal size 0.25 × 0.38 × 0.30 mm, monoclinic, $P2_1/n$, a = 7.0131(6) Å, b = 20.213(3) Å, c = 10.5327(14) Å, β = 107.005(9)°, V = 1427.8(3) Å^3, Z = 4, ρ_{calcd} = 1.392 g cm^{-3}, F(000) = 592, μ = 2.848 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 eÅ^{-3} (near Br3).

For 3-Ph-1,2-*closo*-$C_2B_{10}H_{11}$, $C_8H_{16}B_{10}$, 293(2) K, M_r = 220.31: crystal size 0.10 × 0.68 × 0.24 mm, monoclinic, $P2_1/c$, a = 10.405(2) Å, b = 9.779(2) Å, c = 12.746(2) Å, β = 99.26(2) °, V = 1280.0 (4) Å^3, Z = 4, ρ_{calcd} = 1.143 cm^{-3}, F(000) = 356, μ = 0.053 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 e Å^{-3}.

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Supporting Information Available: Crystallographic data for 1-Ph-3-Br-1,2-$C_2B_{10}H_{10}$ and 3-Ph-1,2-$C_2B_{10}H_{11}$ in CIF format. GIAO calculated ^{11}B and ^{13}C NMR chemical shifts in carboranes 3-X-1,2-*closo*-$C_2B_{10}H_{11}$ (X = F, Cl, Br, I, Ph) and 3-X-1-R-1,2-*closo*-$C_2B_{10}H_{10}$ (X = Br, I and R = Me, Ph). Experimental and GIAO computed ^{11}B NMR chemical shifts in 3-I-1,2-*closo*-$C_2B_{10}H_{11}$ 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-$C_2B_{10}H_{10}$ and 3-Ph-$C_2B_{10}H_{11}$, 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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