"Oxidation of *closo*-carboranyldiphosphines by using hydrogen peroxide, sulphur and selenium. Proton mediated Partial Degradation of *closo*-carboranyldiphosphines."

A. Laromaine,[a] I. Rojo,[a] F. Teixidor,[a] R. Kivekääs,[b] R. Sillanpää,[b] C. Viñas[a]*.

[a] *Institut de Ciència de Materials de Barcelona, Campus U.A.B. 08193 Bellaterra, Spain.*

[b] *Department of Chemistry. P.O. Box 55, FIN-00014. University of Helsinki, Finland*

[c] *Department of Chemistry. University of Jyväskylä. FIN-40531, Finland*

RECEIVED DATE (automatically inserted by publisher); clara@icmab.es

Introduction

The *o*-carborane 1,2-$C_2B_{10}H_{12}$ is an icosahedral cluster with the two carbon atoms in adjacent positions. One way to comprehend the orbital set of *o*-carborane is to consider that each participating atom contributes with two **sp** and two $\mathbf{p_t}$ (tangential orbital on cluster carbon) orbitals. This situation is very similar to the atomic orbitals participating in the molecular orbitals of acetylene. In the same way, then, the hydrogen atom connected to the cage carbon (C_c) in *o*-carborane is acidic and may be removed by strong bases. Moreover, the *o*-carborane cluster is electron-withdrawing for the C_c substituents. During our research[1,2,3,4,5] we have observed many structural features, as well as reactivity behaviour, that make the *o*-carboranyl fragment unique in organic chemistry. Bidentate ligands have played an important role in the development of catalytic applications of metal organic complexes since 1959.[6] Our group has reported the synthesis of *closo* diphosphines 1,2-$(PR_2)_2$-1,2-$C_2B_{10}H_{10}$ that incorporate the *closo* 1,2-$C_2B_{10}H_{12}$ cluster,[1e] their partial degradation that produces the anionic diphosphine *nido* [7,8-$(PR_2)_2$-7,8-$C_2B_9H_{10}]^-$ ligands[1e] and the coordinating capability towards metals of both *closo* 1,2-$(PR_2)_2$-1,2-$C_2B_{10}H_{10}$ and *nido* [7,8-$(PR_2)_2$-7,8-$C_2B_9H_{10}]^-$ ligands.[2c,7]

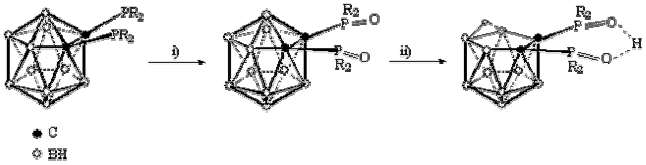
Additionally, diphosphine ligands or their chelating Au(I) complexes are active in several tumoral models in mice.[8] Oxidation and protonation reactions are of particular importance in understanding the anticancer activity of diphosphines.[9]

Despite the well-known affinity of trivalent phosphorous for oxygen and the frustrating destruction of metal catalysts via oxidation of phosphorus-containing ligands, there is a lack of kinetic data and mechanistic studies done on this reaction. In this paper, we report the forced oxidation reaction of *closo* 1,2-$(PR_2)_2$-1,2-$C_2B_{10}H_{10}$ (R= Ph, **1**; ^{i}Pr, **2**) compounds to *closo* 1,2-$(OPR_2)_2$-1,2-$C_2B_{10}H_{10}$ and the partial degradation process of these ligands to the anionic *nido* [7,8-$(OPR_2)_2$-7,8-$C_2B_9H_{10}]^-$ ones. The reactions have been monitoring by ^{31}P-NMR and ^{11}B-NMR spectroscopies. The sequence of the reactions has been proven by the crystal resolution of the *nido* [7,8-$(OP^iPr_2)_2$-7,8-$C_2B_9H_{10}]^-$ ligand as well as this for an intermediate. The phosphine oxide formation rate constant for compound **1** has also been calculated.

Results and discussion

I. Forced oxidation of *closo*-carboranyldiphosphines, 1,2-$(PR_2)_2$-1,2-$C_2B_{10}H_{10}$. Synthesis and characterization of *closo*-1,2-$(OPR_2)_2$-1,2-$C_2B_{10}H_{10}$.

We had observed that, in contrast to other common phosphines, the *closo*-monophosphinocarborane 1-PR_2-2-R'-$C_2B_{10}H_{10}$ (R' = H, Me, Ph; R = Ph, Et, ^{i}Pr) derivatives present a high stability both in solid state and in solution, even under air, in the presence of mild oxidizing agents, alcohols and some acids.[1a] The behaviour of the *closo*-diphosphinocarboranes towards partial degradation,[1e] their high chemical stability both in solution and solid state and the difficulty to coordinate to metal[7g-i] seems to evidence the notable influence of the *closo* cluster on the P atoms. So, *closo*-carboranyldiphosphines have been forced to be oxidized to their corresponding *closo*-carboranyldiphosphine oxides by using hydrogen peroxide in acetone[10] (Scheme 1, i). In the oxidized species, the phosphorus oxidation state has changed from P(III) to P(V).



Scheme 1. Reaction of 1,2-$(PPh_2)_2$-1,2-$C_2B_{10}H_{10}$ with H_2O_2 in acetone. i) Phosphines oxidation. ii) *Closo* cluster partial degradation and zwitterion formation. R= Ph, ^{i}Pr.

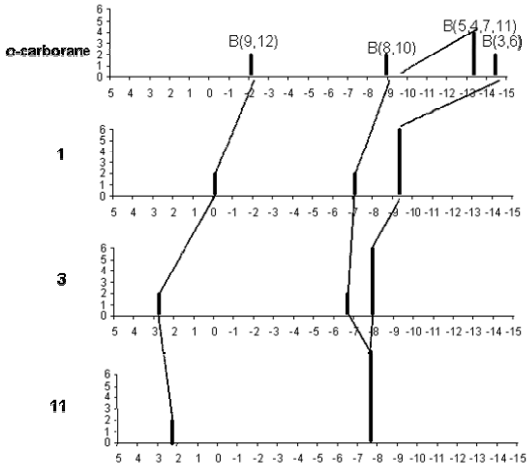


Figure 1. Stick representation of the chemical shifts and relative intensities in the $^{11}B\{^1H\}$-NMR spectra of compounds *closo* 1,2-$C_2B_{10}H_{12}$ (*o*-carborane); *closo* 1,2-$(PPh_2)_2$-1,2-$C_2B_{10}H_{10}$ (**1**) *closo* 1,2-$(OPPh_2)_2$-1,2-$C_2B_{10}H_{10}$ (**3**) and 1,2-$(SPPh_2)_2$-1,2-$C_2B_{10}H_{10}$. (**11**). Lines join equivalent positions in the three compounds.

The *closo* 1,2-$(OPR_2)_2$-1,2-$C_2B_{10}H_{10}$ (R= Ph, **3**; R= ^{i}Pr, **4**) diphosphine dioxide species have been synthesized and characterized by IR, ^{1}H-, ^{13}C-, ^{31}P- and ^{11}B-NMR

spectroscopies. Only one singlet resonance at lower field than the corresponding diphosphine one in the starting (see Table 1) was observed in the ^{31}P-NMR spectra for **3** and **4**.

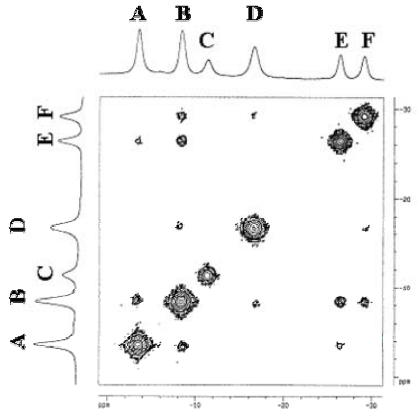


Figure 2. The ^{11}B{^{1}H}-^{11}B{^{1}H} 2D-COSY NMR spectrum of H[**6**]. The resonance marked **A** corresponds to B(9, 11), **B** to B(5, 6), **C** to B(3), **D** to B(2, 4), **E** to B(10), **F** to B(1).

Ligands	^{31}P{^{1}H}-NMR (ppm)
1,2-$(PPh_2)_2$-1,2-$C_2B_{10}H_{10}$	8.22[11]
1,2-$(OPPh_2)_2$-1,2-$C_2B_{10}H_{10}$	23.67
1,2-$(SPPh_2)_2$-1,2-$C_2B_{10}H_{10}$	48.65
1-$SPPh_2$-2-PPh_2-1,2-$C_2B_{10}H_{10}$	49.16 (d, ^{3}J(P,P)=21)/ 12.77 (d, ^{3}J(P,P)=21)
1-$SPPh_2$-2-$OPPh_2$-1,2-$C_2B_{10}H_{10}$	49.96 / 21.65
1-$SePPh_2$-2-PPh_2-1,2-$C_2B_{10}H_{10}$	46.48(dd, ^{3}J(P,P)=27, ^{1}J(P,Se)=807)/ 10.48 (d, ^{3}J(P,P)=27)
1,2-$(P^iPr_2)_2$-1,2-$C_2B_{10}H_{10}$	32.79[1e]
1,2-$(OP^iPr_2)_2$-1,2-$C_2B_{10}H_{10}$	59.08
1-SP^iPr_2-2-P^iPr_2-1,2-$C_2B_{10}H_{10}$	78.0 (d, ^{3}J(P,P)=20)/ 35.55 (d, ^{3}J(P,P)=20)
1-SP^iPr_2-1,2-$C_2B_{10}H_{11}$	77.9
1-SeP^iPr_2-1,2-$C_2B_{10}H_{11}$	83.66
$[NMe_4][7,8\text{-}(PPh_2)_2\text{-}7,8\text{-}C_2B_9H_{10}]$	7.13[1e]
$[NMe_4][7,8\text{-}(OPPh_2)_2\text{-}7,8\text{-}C_2B_9H_{10}]$	29.33
$H[7,8\text{-}(OPPh_2)_2\text{-}7,8\text{-}C_2B_9H_{10}]$	47.09
$H[7,8\text{-}(P^iPr_2)_2\text{-}7,8\text{-}C_2B_9H_{10}]$	31.04
$H[7,8\text{-}(OP^iPr_2)_2\text{-}7,8\text{-}C_2B_9H_{10}]$	77.31

Table 1. ^{31}P{^{1}H}-NMR chemical shifts for the carboranyldiphosphines.

The ν(B-H) in the IR spectrum at 2555 cm^{-1} for **3** and at 2644, 2622, 2596, 2575, 2550 cm^{-1} for **4** are in agreement with a *closo* structure for the cluster fragment. The vibration at 1214 cm^{-1} for **3** and at 1192 cm^{-1} for **4** confirm the presence of P=O group in the molecules. The ^{11}B-NMR spectra for compounds **3** and **4**, with a 2:2:6 pattern in the range +2.8 / –9.1 ppm, fully supports a *closo* structure. Just minor differences with regard to the *closo* 1,2-$(PR_2)_2$-1,2-$C_2B_{10}H_{10}$ precursors (see Figure 1) have been observed in the ^{11}B-NMR spectra of the new diphosphine dioxides 1,2-$(OPR_2)_2$-1,2-$C_2B_{10}H_{10}$. It is worth noticing, though, that the resonance corresponding to the antipodal boron atoms (B9 and B12) in **3** and **4** has been shifted to lower field with regard to the non oxidized starting ones. The ^{1}H-NMR spectrum of **3** shows two different multiplet resonances at 7.52 and 8.03 ppm which indicate two phenyl rings in each –PPh_2 group. The two doublets of doublets in the ^{1}H-NMR spectrum of **4** evidence two non-equivalent methyl groups in each isopropyl unit. The coupling between ^{31}P and ^{13}C nuclei is clearly observed in the ^{13}C{^{1}H}-NMR spectrum of **4**. This shows two different resonances at 17.4 and 18.4 ppm, in agreement with two different methyl groups in each isopropyl unit. The –CH resonance appears as a doublet (^{1}J(P,C)= 61 Hz) at 30.5 ppm and the doublet (^{1}J(P,C)= 19 Hz) at 81.6 ppm corresponds to the carbon cluster atoms (C_c).

II. Partial cluster degradation of the *closo*-carboranyldiphosphine dioxides, 1,2-$(OPR_2)_2$-1,2-$C_2B_{10}H_{10}$. Synthesis and characterization of *nido* [7,8-$(OPR_2)_2$-7,8-$C_2B_9H_{10}$]$^-$ ligands.

Partial degradation of *closo*-diphosphinocarboranes using the well established procedure[12] with alkoxide did not produce the expected new *nido* species, instead it yielded 7,8-dicarba-*nido*-undecaborate(1-) by C_c-P bond cleavage. On the other hand, the reaction carried out in refluxing ethanol in the absence of alkoxide yielded the *closo*-diphosphinocarboranes unaltered, as it was also the case with piperidine-toluene[13] in 1:4 ratio of *closo*-diphosphinocarboranes to piperidine at 20 ºC. Boron removal to yield the *nido* species while preserving the C_c-P bond was successfuly obtained in a 99% yield by reaction of 1,2-$(PR_2)_2$-1,2-$C_2B_{10}H_{10}$ with piperidine in ethanol in a ratio 1:10.[1e]

We later demonstrated that proton can induce partial degradation, thence conversion of the *closo*-C_2B_{10} to the *nido*-$[C_2B_9]^-$ species given the necessary chemical and geometrical arrangements to produce proton chelation.[14] For this purpose, an *o*-carborane adequately C_c-disubstituted with H^+ scavenger elements, such as oxygen was used. The *closo* 1,2-$(OPR_2)_2$-1,2-$C_2B_{10}H_{10}$ species (**3**, **4**) did fulfill these requirements as they are chelating agents and contain oxygen atoms. Hydrogen peroxide which has recently[15] been used to produce *closo*-$[B_{12}(OH)_{12}]^{2-}$ was a suitable oxidizing agent, and a source of H^+. Thus it was expected that upon oxidation of the phosphorus atoms, and the availability of protons, the *closo* cluster would progress to the anionic *nido* cluster [7,8-$(OPR_2)_2$-7,8-$C_2B_9H_{10}]^-$ (R= Ph, [**5**]$^-$, R= ^{i}Pr, [**6**]$^-$) liberating one boron atom and overall producing a neutral species. Indeed this is what happened. The reaction is schematically represented in Scheme 1 ii).

The *nido* nature of the cluster was clearly demonstrated in the ^{1}H-NMR by the apical proton resonance at δ –2.05 and –2.56 ppm for compounds H[**5**] and H[**6**] respectively, and by the ^{11}B-NMR, 2:2:1:2:1:1 pattern (low field to high field) observed in the range δ –5.6/-33.9 typical for *nido*-$[C_2B_9]^-$ derivatives.[16] The resonances were separated enough to permit their unambiguous assignment by means of ^{11}B{^{1}H} - ^{11}B{^{1}H} 2D-COSY NMR(see Figure 2). The peak at –29.1 ppm is easily assigned to B(10) since it appears as a doublet of doublets in the ^{11}B-NMR spectrum due to coupling with the H bridge as well as the *exo*-H. The peak at –31.8 ppm, which is at highest field, corresponds to B(1), the antipodal position to the open face. The spectrum also exhibits a singlet at –14.0 ppm that does not show any cross peak and correspond to B(3) which is adjacent to both cluster carbon atoms.[17] With the resonances due to B(1), B(3) and B(10) thus established, analysis of the cross peaks easily allowed the assignment of the 2:2:1:2:1:1 pattern to B(9,11): B(5,6): B(3): B(2,4): B(10): B(1), respectively.

Although the negative charge of the *nido* cluster is maintained in the oxidized species, the phosphorus oxidation state has changed from P(III) to P(V). This is clearly reflected

on the $^{31}P\{^1H\}$-NMR spectra (Table 1) in which the chemical shifts for the oxidized species have shifted to lower field.

The ν(B-H) in the IR spectra at 2605, 2584, 2526 cm^{-1} for H[**5**] and at 2629-2526 cm^{-1} for H[**6**] are in agreement with a *nido* structure of the *o*-carboranyl fragment and the vibration at 1184 and 1081 cm^{-1} respectively confirm the presence of P=O groups.

To ensure that H_2O_2 was the sole agent causing the *closo* to *nido* conversion, an alternative sequential process was developed, which is indicated in Scheme 2. Oxidation of $[NMe_4][7,8\text{-}(PPh_2)_2\text{-}7,8\text{-}C_2B_9H_{10}]$, ($[NMe_4][$**7**$]$),[14] with H_2O_2 was performed in acetone at 0ºC to yield after stirring for 4 h a white solid that corresponds to $[NMe_4][7,8\text{-}(OPPh_2)_2\text{-}7,8\text{-}C_2B_9H_{10}]$, $[NMe_4][$**8**$]$.

III. Identification of the removed boron vertex.

The partial degradation of **1** with hydrogen peroxide in THF and at room temperature for 24 hours was carried out to identify the nature of the removed B^+ containing species. The H[**5**] species was isolated by filtration. The $^{11}B\{^1H\}$ spectrum of the remaining aqueous solution shows a resonance at +19.3 ppm corresponding to a boron atom with no B-H bond. According to the literature, the chemical shift for $B(OH)_3$ appears at +19.3 ppm,[18] confirming that the removed B^+ stays in solution as $B(OH)_3$.

IV. Forced protonation of the *nido*-carboranyldiphosphine dioxides.

As it is well known, phosphines react with perchloric acid in ethanol to give the corresponding phosphonium salts.[19] Acidification of $[NMe_4][$**8**$]$ in CH_2Cl_2 with HCl gas produces a white solid corresponding to $[NMe_4]Cl$. Subsequent evaporation of the CH_2Cl_2 yields a H[**5**].

The ν(O-H) in the IR spectra at 3082 and 3059 cm^{-1} confirmed the formation of the protonated zwitterionic species. This IR data could not be further supported by the observation of a resonance attributed to the chelated proton neither in the ^{1}H-NMR spectra of H[**5**] nor H[**6**]. To get a precise structure determination, crystals were grown from an acetone solution of H[**6**] after slow evaporation.

V. Molecular and crystal structures of two isomers of H[6]

Crystallization of compound H[**6**] from acetone yielded two different needle-shaped crystals, H[**6a**] and H[**6b**], respectively. Compound H[**6a**] crystallizes in the triclinic system while H[**6b**] crystallizes in monoclinic system. Drawings of the molecules are shown in Figures 3a and 3b. For each compound, the X-ray analysis confirmed the expected *nido* structure and similar looking phosphine oxide formation for both phosphorous atoms. Moreover, the analysis confirmed that the proton between the oxygen atoms balances the negative charge of the *nido* carborane cage in each compound.

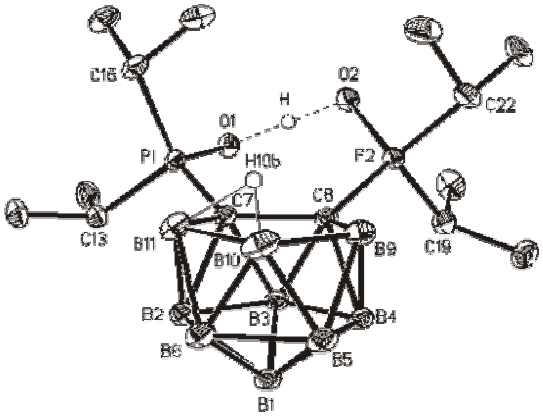


Figure 3a. Drawing of H[**6a**] crystallized from acetone. Thermal displacement ellipsoids are drawn at 30% probability level. Hydrogen atoms, except the chelating hydrogen and H10b, have been omitted.

However there are marked differences between the structural details between H[**6a**] and H[**6b**] like the mutual orientations of the OP^iPr_2 substituents are different in H[**6a**] and H[**6b**], but the most striking difference between the molecules is in the intramolecular O1-H-O2 hydrogen bonds (*cf.* Figures 3a and 3b and Table 3). In H[**6a**] the short O1···O2 distance of 2.3805(15) Å, and the O1-H and O2-H distances of 1.20(3) and 1.19(3) Å together with the O1-H-O2 angle of 173(3)º indicate very strong linear and symmetric hydrogen bond between the oxygen atoms. In H[**6b**] the short O1···O2 distance of 2.4252(16) Å also indicated strong intramolecular hydrogen bond, but the O1-H and O2···H distances of 0.96(3) and 1.47(3) Å, and the O1-H···O2 angle of 171(3)º clearly indicate essentially linear non-symmetric hydrogen bond between the oxygen atoms. This means that in H[**6b**] the positive charge is located at P1, while in H[**6a**] it is on the separate hydrogen atom between the oxygen atoms. These different charge distributions cause the structural differences between H[**6a**] and H[**6b**].

As far as we know, this observation that two different H-bond systems exists in one compound is rare in chemistry. For H[**6a**] there are several comparable zwitterionic compounds like H[**5**][14] and others,[20] where the proton also lies approximately midway between the oxygen atoms and the corresponding hydrogen bond is essentially centrocymmetric and linear. The O1···O2 distance of 2.421(4) Å in H[**5**] is longer than that in H[**6a**] [2.3805(15)] Å, but this is due to the different Lewis acidity of $P(R)_2$ centers.

For H[**6b**] there is no counterpart in the literature, but in $[P(^iPr)_3(OH)]I$[20] there is a similar P center as found in H[**6b**], but in $[P(^iPr)_3(OH)]I$ there is a OH··· I hydrogen bond. The P-O bond length in H[**6b**] is 1.5454(12) Å and in $P(^iPr)_3(OH)]I$ it is 1.573(2) Å. In connection with the different positive charge distribution in H[**6a**] and H[**6b**], clear differences in the P-O and P-C_c distances between the two compounds can be seen. (Table 2). Even the differences are slight, they agree with the general observation that distance of the hydrogen atom from the donor and acceptor atoms affects to the adjacent bonds: the shorter is the O··· H bond the longer is the P=O bond.

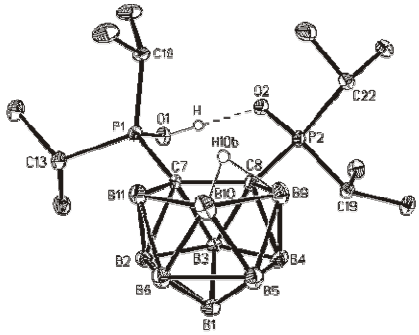


Figure 3b. Drawing of H[6b] crystallized from acetone. Thermal displacement ellipsoids are drawn at 30% probability level. Hydrogen atoms, except the chelating hydrogen and H10b, have been omitted.

The difference of the orientations of P^iPr_2 groups between the H[**6a**] and H[**6b**] is seen in the C8-C7-P1-O1 and C7-C8-P2-O2 torsion angle values that are 23.23(14) and 10.62(14)º for H[**6a**] and 45.64(15) and –3.84(16)º for H[**6b**]. The differences in torsion angles influences on the O···O distances and *vice versa*. So it is difficult to say if the formation of these two crystal modifications is due to packing,

conformational or H-bond interactions. The formation of two crystal forms can also originate from the kinetic reasons.

Additional interesting detail of the structures is the C_c-C_c bond distance. The C7-C8 distances of 1.640(2), 1.624(2) and 1.609(5) Å for H[**6a**], H[**6b**] and H[**5**] are quite close to each other. The positively charged P center in H[**6b**] causes that the C_c-C_c bond distance is in the midway between H[**6a**] and H[**5**].

VI. Mechanistic considerations

The reaction of *closo*-carboranyldiphosphines 1,2-$(PR_2)_2$-1,2-$C_2B_{10}H_{10}$ (R= Ph and ^{i}Pr) with H_2O_2 implies two processes: the partial degradation of the *closo* cluster and the oxidation of the phosphorus atoms. The progress of the reaction has been studied as a function of time to determine which process takes place first. In this sense, the progress of the reaction of both *closo* species **1** and **2** with H_2O_2 was monitored by $^{31}P\{^1H\}$(see Figure 4 for **1** and Figure 5 for **2**) and $^{11}B\{^1H\}$-NMR (see Figure 6 for **1**) spectroscopies. The study provides useful information about the structure of the compounds in solution. The resonance at 8.22 ppm in the $^{31}P\{^1H\}$-NMR spectrum that corresponds to non-altered **1** decreases with time while a new peak at 23.67 ppm increases (See Figure 4). In four hours there is no starting compound left while only the peak at 23.67 ppm is observed. The latter resonance also decreases with time while a new one at 47.09 ppm emerges. This final resonance persists indefinitely. The $^{11}B\{^1H\}$-NMR spectra also shows the process of conversion of the starting *closo* material into a *nido* species (See Figure 6) but is not as informative as the $^{31}P\{^1H\}$-NMR. The peak at 47.09 ppm in the $^{31}P\{^1H\}$-NMR spectrum corresponds to the end species H[7,8-$(OPPh_2)_2$-7,8-$C_2B_9H_{10}$]. Definitive proof of the proton containing P-O-H-O-P moiety has been confirmed by X-ray diffraction.

Scheme 2. Synthesis of H[7,8-$(OPPh_2)_2$-7,8-$C_2B_9H_{10}$] starting from [NMe_4][7,8-$(PPh_2)_2$-7,8-$C_2B_9H_{10}$].

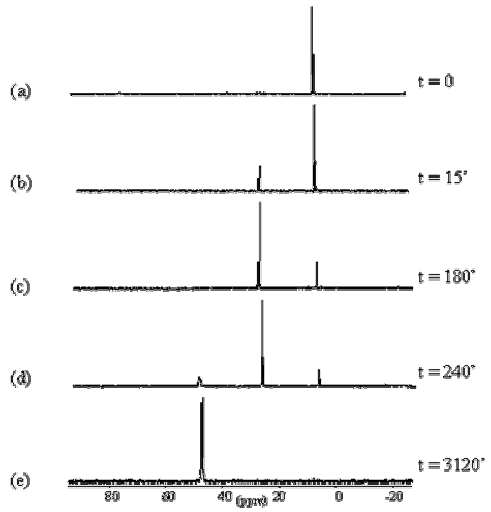


Figure 4. $^{31}P\{^1H\}$ spectra of the *closo* 1,2-$(PPh_2)_2$-1,2-$C_2B_{10}H_{10}$ showing its conversion to *nido* H[7,8-$(OPPh_2)_2$-7,8-$C_2B_9H_{10}$] after *closo* 1,2-$(OPPh_2)_2$-1,2-$C_2B_{10}H_{10}$ formation.

If the reaction is quenched when the peak at 23.67 ppm in the $^{31}P\{^1H\}$-NMR is the dominant one important information about the nature of the intermediate species is obtained. The $^{11}B\{^1H\}$-NMR spectrum indicates that the cluster is *closo*, which is also supported by the lack of hydrogen bridge in the $^{11}H\{^1B\}$-NMR spectrum. The elemental analysis is in agreement with a *closo* species with two P=O units. All these data demonstrate that the first step of the reaction is the phosphorus oxidation with cluster preservation and the second one is cluster decapitation as it is shown in Scheme 1.

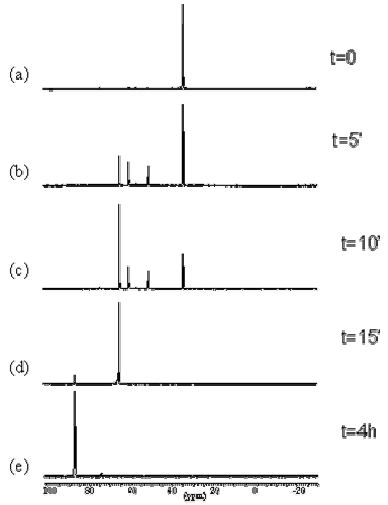


Figure 5. $^{31}P\{^1H\}$ spectra of the *closo* 1,2-$(P^iPr_2)_2$-1,2-$C_2B_{10}H_{10}$ showing its conversion to *nido* H[7,8-$(OP^iPr_2)_2$-7,8-$C_2B_9H_{10}$] after *closo* 1,2-$(OP^iPr_2)_2$-1,2-$C_2B_{10}H_{10}$ formation.

This mechanistic study allows accurate determination of the time to complete the two steps of the reaction: phosphorus oxidation and cluster partial degradation. In the case of 1,2-$(PPh_2)_2$-1,2-$C_2B_{10}H_{10}$ 4 hours are necessary to accomplish the formation of both P=O bonds while the cluster partial degradation of 1,2-$(OPPh_2)_2$-1,2-$C_2B_{10}H_{10}$ into H[7,8-$(OPPh_2)_2$-7,8-$C_2B_9H_{10}$] is essentially done after 52 hours. It is then clear that the slow step of the total process is the cluster partial degradation.

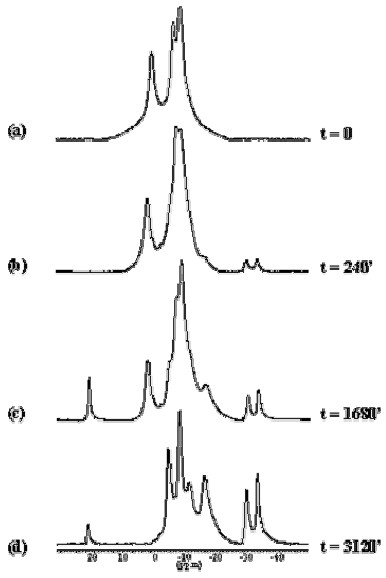


Figure 6. $^{11}B\{^1H\}$ spectra of the *closo* 1,2-$(OPPh_2)_2$-1,2-$C_2B_{10}H_{10}$ showing its partial degradation to *nido* H[7,8-$(OPPh_2)_2$-7,8-$C_2B_9H_{10}$].

When the H_2O_2 reaction study was done on 1,2-$(P^iPr_2)_2$-1,2-$C_2B_{10}H_{10}$, resonances at 33.27, 47.20, 55.08, 59.08, 65.48 and 77.31 ppm were observed in the $^{31}P\{^1H\}$-NMR spectra. There were three additional resonances on top of the awaited ones. The resonance at 33.27 corresponds to the starting *closo* compound **2**, the one at 59.08 corresponds to the *closo*

compound **4** and the one at 77.31 to the *nido* compound H[**6**]. Therefore it seems that the extra resonances at 47.20, 55.08 and 65.48 ppm, might be attributed to other intermediate species. One interpretation is that the two phosphorus atoms are not oxidized at the same time and a *closo* species containing a P(III) atom and P(V) is obtained which would possibly account for the resonances at 55.08 and 47.20 ppm. The additional resonance could correspond to the equivalent phosphorus in the H^+ bonded P-O-H-O-P *closo* species, just the previous step to B^+ removal and zwitterions.

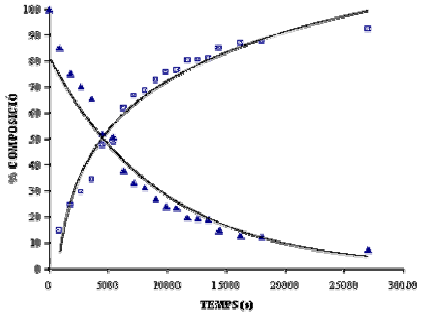


Figure 8. First-order kinetic plot for the reaction between *closo* 1,2-$(PPh_2)_2$-1,2-$C_2B_{10}H_{10}$ and *closo* 1,2-$(OPPh_2)_2$-1,2-$C_2B_{10}H_{10}$.

The mechanistic study shows that **2** is fully oxidized to compound **4** after 15 minutes. So, *closo* 1,2-$(P^iPr_2)_2$-1,2-$C_2B_{10}H_{10}$ is more susceptible to oxidation than *closo* 1,2-$(PPh_2)_2$-1,2-$C_2B_{10}H_{10}$ which is foreseeable considering the greater donating character of the isopropyl group.

VII. Kinetics of formation of 1,2-$(OPPh_2)_2$-1,2-$C_2B_{10}H_{10}$

The P(III) to P(V) oxidation reaction study on both *closo* species **1** and **2** by using H_2O_2 in acetone or tetrahydrofurane at 23°C was monitored by $^{31}P\{^1H\}$ (see Figure 4 for **1** and Figure 5 for **2**) and $^{11}B\{^1H\}$-NMR (see Figure 6 for **1**) spectroscopies. The reaction was found to be first-order rate constant with respect to concentration of 1,2-$(PPh_2)_2$-1,2-$C_2B_{10}H_{10}$. The calculated rate constant is $(1.23 \pm 0.09) \times 10^{-4}$ s^{-1} (Figure 8, 9).

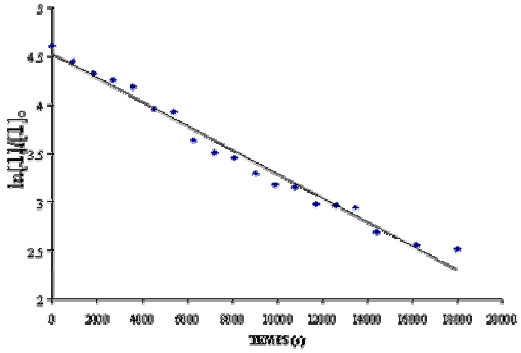
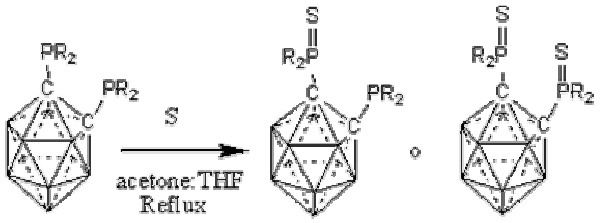


Figure 9. First-order kinetic plot for the reaction between *closo* 1,2-$(PPh_2)_2$-1,2-$C_2B_{10}H_{10}$ and *closo* 1,2-$(OPPh_2)_2$-1,2-$C_2B_{10}H_{10}$.

VIII. Forced oxidation of *closo*-carboranyldiphosphines, 1,2-$(PR_2)_2$-1,2-$C_2B_{10}H_{10}$ with Sulphur. Synthesis and characterization of *closo*-1,2-$(SPR_2)_2$-1,2-$C_2B_{10}H_{10}$.

Closo-carboranyldiphosphines, 1,2-$(PR_2)_2$-1,2-$C_2B_{10}H_{10}$ (R= Ph, ^{i}Pr) have been forced to be oxidized to their corresponding *closo*-carboranyldiphosphinesulphides by using sulphur in acetone:THF (4:1) mixture at reflux (Scheme 3).

a) For R= Ph, the 1-PPh_2-2-$SPPh_2$-1,2-*closo*-$C_2B_{10}H_{10}$, **10** and 1,2-$(SPPh_2)_2$-*closo*-1,2-$C_2B_{10}H_{10}$, **11** species have been synthesized and characterized by IR, ^{1}H-, ^{13}C-, ^{31}P- and ^{11}B-NMR spectroscopies. The ν(B-H) in the IR spectrum at 2574 cm^{-1} for **10** and at 2632, 2603, 2574, 2557 cm^{-1} for **11** are in agreement with a *closo* structure for the cluster fragment. The vibration at 652 cm^{-1} for both species confirms the presence of P=S group in the molecules. The ^{11}B-NMR spectra in the range +2.6 / –9.1 ppm with a 1:1:5:3 and 2:8 pattern for compounds **10** and **11**, respectively, fully support a *closo* structure. Just minor differences have been observed in the ^{11}B-NMR spectra of **11** with regard to **1** and **3** (see Figure 1)**.**



Scheme 3. Reaction of 1,2-$(PR_2)_2$-1,2-$C_2B_{10}H_{10}$ with S in acetone:THF 8:2 at reflux.

The ^{1}H-NMR spectra of **10** and **11** show multiplet resonances in the range 8.41-7.27 ppm which correspond to the phenyl groups. The coupling between ^{31}P and ^{13}C nuclei is clearly observed in the $^{13}C\{^1H\}$-NMR of **10** and **11**.

Purification by preparative thin layer chromatography (silica G, CH_2Cl_2/hexane 8:2) yielded another species 1-$(OPPh_2)$-2-$(SPPh_2)_2$-1,2-*closo*-$C_2B_{10}H_{10}$ **12** that shows two signals in the $^{31}P\{^1H\}$-NMR at 49.96 and 21.65 ppm. The resonance at 21.65 ppm suggests the presence of a phosphorus bonded to an oxygen as in **3** whereas the signal at 49.96 ppm seems to correspond to a phosphorus bonded to a sulphur as in **10**. The ^{11}B-NMR appears in the range 2.98 / -7.52 ppm with a 1:1:8 pattern that fully supports a *closo* structure. The IR exhibits the characteristic ν(B-H) at 2572 cm^{-1} for a *closo* cluster. The vibrations at 652, 690 and 1215 cm^{-1} agree with the presence of both P=S and P=O in **12**.

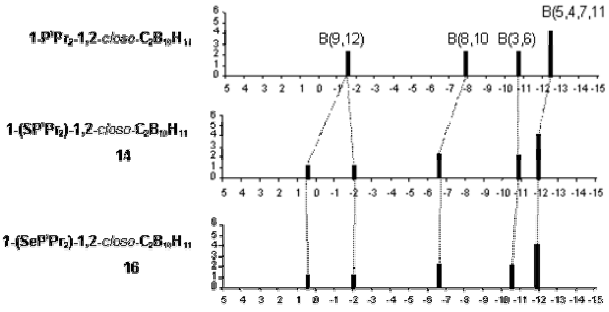


Figure 10 Stick representation of the chemical shifts and relative intensities in the $^{11}B\{^1H\}$-NMR spectra of compounds *closo* 1-P^iPr_2-1,2-$C_2B_{10}H_{11}$, *closo* 1-SP^iPr_2-1,2-$C_2B_{10}H_{11}$ (**14**) *closo* 1-SeP^iPr_2-1,2-$C_2B_{10}H_{11}$ (**16**) Lines join equivalent positions in the three compounds.

b) For R= ^{i}Pr, 1-P^iPr_2-2-SP^iPr_2-1,2-*closo*-$C_2B_{10}H_{10}$, **13** and 1-(SP^iPr_2)-1,2-*closo*-$C_2B_{10}H_{11}$ **14** were obtained after 4 and 48 h. reflux respectively. The $^{11}B\{^1H\}$-NMR of **13** and **14** appear in the range 1.7/-11.98 ppm showing a 1:1:3:5 and 1:1:2:2:4 pattern respectively. Few differences are observed when the $^{11}B\{^1H\}$-NMR spectra of compounds 1-P^iPr_2-1,2-*closo*-$C_2B_{10}H_{11}$ and **14** are compared (see Figure 10). The $^{31}P\{^1H\}$-NMR of **13** displays two resonances at 78.0 and 35.5 ppm whereas only one at 77.96 ppm is observed for **14**. The

IR spectra for **13** and **14** also agree with their *closo* structure and the ν(C-H) at 3029 cm^{-1} for **14** confirms the presence of C_c-H bond.

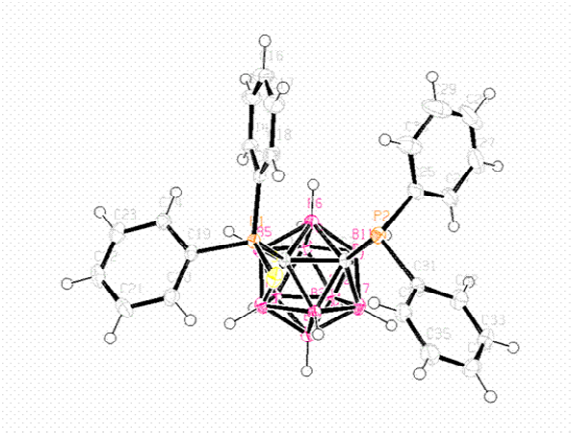


Figure 11. Drawing of 1-PPh_2-2-($SPPh_2$)-1,2-*closo*-$C_2B_{10}H_{10}$, **11.** Thermal displacement ellipsoids are drawn at 30% probability level but minor orientation of the disordered phenyl group have been drawn with open circles and dashed solids. Hydrogen atoms have been omitted.

IX. Molecular and crystal structure of 10 and 11.

Structure analysis of **10** and **11** confirms that compound 1-PPh_2-2-$SPPh_2$-1,2-*closo*-$C_2B_{10}H_{10}$ (Figure 11) and 1,2-($SPPh_2$)$_2$-*closo*-1,2-$C_2B_{10}H_{10}$, (Figure 12) have retained the *closo* architecture during the oxidation with sulphur and only one of the phosphorous atoms has been oxidized in **10** and the two phosphorous atoms has been oxidized in **11**.

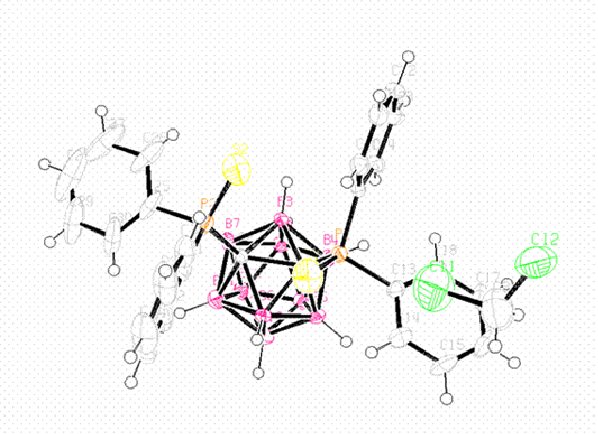


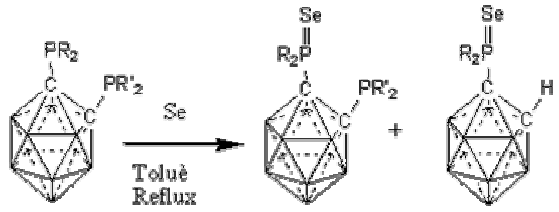
Figure 12. Drawing of 1,2-($SPPh_2$)$_2$-*closo*-1,2-$C_2B_{10}H_{10}$, **12.** Thermal displacement ellipsoids are drawn at 30% probability level but minor orientation of the disordered phenyl group have been drawn with open circles and dashed solids. Hydrogen atoms have been omitted.

X. Forced oxidation of *closo*-carboranyldiphosphines, 1,2-(PR_2)$_2$-1,2-$C_2B_{10}H_{10}$. with Selenium.

Closo-carboranyldiphosphines, 1,2-(PR_2)$_2$-1,2-$C_2B_{10}H_{10}$ (R= Ph, ^{i}Pr) have been forced to be oxidized to their corresponding *closo*-carboranyldiphosphine selenides by using black selenium powder in toluene (Scheme 4) at reflux temperature. Full characterization is at the experimental section. Basically the interpretation is comparable to the earlier discussion described in section VIII for sulphur.

XI. Molecular and crystal structure of 15.

Structure analysis of 15 confirms that compound 1-PPh_2-2-($SePPh_2$)-1,2-*closo*-$C_2B_{10}H_{10}$ has retained the *closo* architecture during selenization reaction and only one of the phosphorous atoms has been oxidized. The P(Se)Ph_2 substituent at C1 is ordered but one of the phenyl groups of the PPh_2 substituent attached to C2 is disordered assuming two orientations (*cf.* Figure 16). As can be seen from Table 4, there are slight differences in the corresponding P-C and P-C_c distances between the phosphorous atoms having different oxidation states. Also P-C_c-C_c angles are different with the P1-C1-C2 being more opened [122.5(4)°] compared with the P2-C2-C1 angle [113.4(4)°] because of more bulky substituent at C1. The C1-C2 distance of 1.732(9) Å equals within experimental errors with the distances of 1.719(3) and 1.722(4) Å in the 1,2-P_2 disubstituted orthocarborane derivatives 1,2-[P(2-^{i}Pr)$_2$]$_2$-1,2-$C_2B_{10}H_{10}$ [1d]and 1,2-[$P(Ph_2)_2$]-1,2-$C_2B_{10}H_{10}$ [21] Likewise, the Se-P1 distance of 2.0982(18) Å is in the range found for comparable Se=P bonds.[22]



Scheme 4. Reaction of 1,2-(PR_2)$_2$-1,2-$C_2B_{10}H_{10}$ with Se in toluene at reflux.

There are in the structure of **15** four Se···H(Ph) contacts shorter than 3.0 Å, all of those to the three ordered phenyl groups. Three of the contacts are intramolecular (2.76-2.87 Å) and one intermolecular (2.96 Å). Thus we may assume that disordering of one of the phenyl groups may partly arise from the lack of Se···H(Ph) interaction.

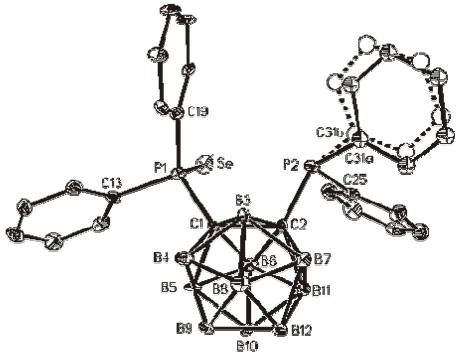


Figure 15. Thermal displacement ellipsoids are drawn at 30% probability level but minor orientation of the disordered phenyl group have been drawn with open circles and dashed solids. Hydrogen atoms have been omitted.

Conclusions

The carborane influence into the directly connected phosphorus atom is not only perceived in the chemical shift but also in the chemical properties. The electron-acceptor character of the cluster induces a lower charge density in the phosphorus atom which causes the P resonance to be shifted at lower field in the ^{31}P-NMR spectra. In addition, it makes the ligand to have a lower coordinating capacity towards transition metals and a higher stability in solid state and in solution, even under air. An influence of the R group in *closo* 1,2-(PR_2)$_2$-1,2-$C_2B_{10}H_{10}$ compounds agent has also been recognized. In this sense, an electron donating group (^{i}Pr) facilitates the oxidation reaction more than an electron withdrawing group (Ph).

When H_2O_2 is used on 1,2-(PR_2)$_2$-*closo*-1,2-$C_2B_{10}H_{10}$ (R= Ph, ^{i}Pr), these first suffer oxidation to 1,2-(OPR_2)$_2$-*closo*-1,2-$C_2B_{10}H_{10}$ (R= Ph, ^{i}Pr) and later the cluster suffers partial degradation to [7,8-(PR_2)$_2$-*nido*-7,8-$C_2B_9H_{10}$]$^-$ (R= Ph, ^{i}Pr).

When S is used on 1,2-(PPh_2)$_2$-*closo*-1,2-$C_2B_{10}H_{10}$, mono- and dioxidation takes place and both compounds can be

isolated. When S is used on 1,2-(P^iPr_2)$_2$-*closo*-1,2-$C_2B_{10}H_{10}$, only mono-oxidation takes place and if the reaction is continued, the second C_c-P^iPr_2 breaks to yield 1-SP^iPr_2-*closo*-1,2-$C_2B_{10}H_{11}$.

When Se is used on 1,2-(PR_2)$_2$-*closo*-1,2-$C_2B_{10}H_{10}$ (R= Ph, ^{i}Pr), only mono-oxidation takes place and, if the reaction is continued, the second C_c-PR_2 breaks to yield 1-SePR_2-*closo*-1,2-$C_2B_{10}H_{11}$.

Acknowlegment

We thank ENRESA and Carburos Metál.licos for the partial support of this research and MCyT (MAT01-1575), and Generalitat de Catalunya 2001/SGR/00337.

Experimental Section

Instrumentation.

Elemental analyses were performed in our laboratory using a Carlo Erba EA1108 microanalyzer. IR spectra (ν, cm^{-1}; KBr pellets) were obtained on a Shimadzu FTIR-8300 spectrophotometer. The ^{1}H- and ^{1}H{^{11}B}-NMR (300.13 MHz), ^{13}C{^{1}H}-NMR (75.47 MHz), ^{11}B-NMR (96.29 MHz) and ^{31}P{^{1}H}-NMR (121.48 MHz) spectra were recorded on a Bruker ARX 300 instrument equipped with the appropriate decoupling accessories. All NMR spectra were performed in deuterated solvents at 22 ºC. The ^{11}B-NMR shifts were referenced to external $BF_3{\cdot}OEt_2$, while the ^{1}H, ^{1}H{^{11}B}, and ^{13}C{^{1}H}-NMR shifts were referenced to $SiMe_4$ and the ^{31}P{^{1}H}-NMR to external 85% H_3PO_4. Chemical shifts are reported in units of parts per million downfield from reference, and all coupling constants in Hz.

Materials.

All manipulations were carried out under atmosphere. THF was distilled from sodium benzophenone prior to use. EtOH was dried over molecular sieves and deoxygenated prior to use. Reagents were obtained commercially and used as purchased. 1,2-Bis(diphenylphosphino)-1,2-dicarba-*closo*-dodecaborane[23] and 1,2-bis(diisopropylphosphino)-1,2-dicarba-*closo*-dodecaborane[1e] were prepared from *o*-carborane according to the literature.

Synthesis of 1,2-($OPPh_2$)$_2$-1,2-$C_2B_{10}H_{10}$ (3). To a round bottom flask (25 mL) containing 1,2-bis(difenylfosfino)-1,2-dicarba-*closo*-dodecaborane (50 mg, 0.10 mmol) was added tetrahydrofuran (5 mL). The mixture was cooled (ice-water) during the dropwise addition of a 0.2 M solution of H_2O_2 (1.5 mL, 0.40 mmol). After stirring for 3 h and 25 min at room temperature the solvent was removed. The evaporation of the solvent yield a white solid. Yield: 48 mg (98 %). Anal. Calcd for $C_{26}H_{30}B_{10}O_2P_2$: C: 57.34, H: 5.55 %. Found: C: 57.12, H: 5.80 %. FTIR: 3048, 2962 (C_{aryl}-H), 2555 (B-H), 1214, 1191 (P=O). ^{1}H NMR ($CDCl_3$) δ: 8.03 (m, 10H, Ph), 7.52 (m, 10H, Ph), 2.68-2.09 (br m, 10H, B-H). ^{1}H{^{11}B} NMR ($CDCl_3$): 8.03 (m, 10H, Ph), 7.52 (m, 10H, Ph), 2.68 (br s, 2H, B-H), 2.49 (br s, 1H, B-H), 2.35 (br s, 2H, B-H), 2.30 (br s, 3H, B-H), 2.09 (br s, 2H, B-H). ^{13}C{^{1}H} NMR ($CDCl_3$) δ: 132.58 (d, ^{2}J(C,P)= 8, Ph), 132.27, 130.80, 129.33 (s, Ph), 128.25 (d, ^{2}J(C,P)= 14, Ph). ^{11}B-NMR ($CDCl_3$) δ: 2.8 (d, ^{1}J(B,H)= 88, 2B), -6.7 (4B), -7.9 (4B). ^{31}P{^{1}H}-NMR ($CDCl_3$) δ: 23.67 (s, $OPPh_2$).

Synthesis of 1,2-(OP^iPr_2)$_2$-1,2-$C_2B_{10}H_{10}$ (4). To a round bottom flask (25 mL) containing 1,2-bis(diisopropilfosfino)-1,2-dicarba-*closo*-dodecaborà (50 mg, 0.13 mmol) was added tetrahydrofuran (5 mL). The mixture was cooled (ice-water) during the dropwise addition of a 0.2 M solution of H_2O_2 (2.0 mL, 0.40 mmol). After stirring for 40 min at room temperature the solvent was removed. The evaporation of the solvent yield a white solid. Yield: 54 mg (99 %). Anal. Calcd for $C_{14}H_{38}B_{10}O_2P_2$= C: 41.16, H: 9.38 %. Found: C: 41.04, H: 9.25 %. FTIR: 2996, 2970, 2933, 2878 (C-H_{alkyl}), 2644, 2622, 2596, 2575, 2550 (B-H), 1192 (P=O). ^{1}H NMR ($CDCl_3$) δ: 3.10 (br s), 2.02 (m, 4H, CH), 1.41 (dd, ^{3}J(P,H)= 11, ^{3}J(H,H)= 7, 12H, Me), 1.35 (dd, ^{3}J(P,H)= 13, ^{3}J(H,H)= 7, 12H, Me). ^{13}C{^{1}H} NMR ($CDCl_3$) δ: 81.61 (d, ^{1}J(C,P)= 19, C_c), 30.53 (d, ^{1}J(C,P)= 61, CH), 17.4 (s, Me), 18.4 (s, Me). ^{11}B NMR ($CDCl_3$) δ: 2.8 (d, ^{1}J(B,H)= 140, 2B, B(9,12)), -6.5 (d, ^{1}J(B,H)= 211, 2B, B(8,10)), -9.1 (d, ^{1}J(B,H)= 138, 6B, B(3,4,5,6,7,11)). ^{31}P NMR ($CDCl_3$) δ: 59.08 (d, ^{3}J(P,H)= 16, OP^iPr_2).

Synthesis of H[7,8-($OPPh_2$)$_2$-7,8-$C_2B_9H_{10}$] (H[5]). Procedure a: A solution of [NMe_4][7,8-($OPPh_2$)$_2$-7,8-$C_2B_9H_{10}$] (1.0 g, 1.64 mmol) in CH_2Cl_2 (50 mL) was bubbled with a HCl stream for 15 min. A precipitate of [NMe_4]Cl was separated, and the solution was evaporated in vacuo. A white solid was obtained. Yield: 0.86 g (98 %).

Procedure b: To a solution of [1,2-(PPh_2)$_2$-1,2-$C_2B_{10}H_{10}$] (0.1 g, 0.20 mmol) in THF at 0ºC was added 5.56 mL (0.56 mmol) of a solution of 0.1 M H_2O_2. The mixture was stirred for 24 hours, and a precipitate was formed. The solid was filtered off, washed with water, and dried in vacuo. Yield: 0.10 g (94 %). Anal. Calcd for $C_{26}H_{31}B_9O_2P_2$: C: 58.40, H: 5.84 %. Found: C: 58.22, H: 5.78 %. FTIR: 3082, 3059 (O-H), 3016, 2961, 2918 (C-H_{aryl}), 2605, 2584, 2526 (B-H), 1184 (P=O). ^{1}H NMR ($CDCl_3$): 7.91 (m, 5H, Ph), 7.51 (m, 5H, Ph), 7.38 (m, 5H, Ph), 7.20 (m, 5H, Ph), 3.10-0.74 (br s, 9H, B-H), -2.05 (br s, 1H, BHB). ^{1}H{^{11}B} NMR ($CDCl_3$) δ: 7.91 (m, 5H, Ph), 7.51 (m, 5H, Ph), 7.38 (m, 5H, Ph), 7.20 (m, 5H, Ph), 3.10 (br s, 1H, B-H), 2.65 (br s, 1H, B-H), 1.84 (br s, 3H, B-H), 1.07 (br s, 3H, B-H), 0.74 (br s, 1H, B-H), -2.10 (br s, 1H, BHB). ^{13}C{^{1}H} NMR ($CDCl_3$) δ: 133.95, 133.82 (s, Ph), 133.05 (d, ^{1}J(P,C)= 21, Ph), 129.18 (d, ^{2}J(P,C)= 41, Ph). ^{11}B NMR ($CDCl_3$) δ: -5.6 (d, ^{1}J(B,H)= 128, 2B), -8.9 (d, ^{1}J(B,H)= 133, 2B), -12.1 (1B), -17.0 (2B), -30.4 (d, ^{1}J(B,H)= 123, 1B), -33.9 (d, ^{1}J(B,H)= 147, 1B). ^{31}P{^{1}H} NMR ($CDCl_3$) δ: 47.09 (s, $OPPh_2$).

Synthesis of H[7,8-(OP^iPr_2)$_2$-7,8-$C_2B_9H_{10}$] (H[6]). To a solution of 1,2-bis(diisopropylfosfino)-1,2-dicarba-*closo*-dodecaborane (50 mg, 0.13 mmol) in THF at 0ºC was added 2.0 mL (0.40 mmol) of a solution of 0.2 M H_2O_2. The mixture was stirred during a weekend. Acetone (8 mL) was added to the white solid and 2.4 mL (0.96 mmol) of a solution of 0.4 M H_2O_2 were added at room temperature. The solution was stirred for another weekend. Then this was concentrated until a white solid precipitated. The solid was filtered off and dried in vacuo. Yield: 38 mg (71 %). Anal. Calcd for $C_{14}H_{39}B_9O_2P_2$: C: 42.17, H: 9.86 %. Found: C: 41.82, H: 10.04 %. FTIR: 2995, 2973, 2936, 2877 (O-H, C-H_{alkyl}), 2629, 2596, 2587, 2581, 2543, 2552, 2536, 2526, 2608 (B-H), 1081 (P=O). ^{1}H NMR (CD_3COCD_3) δ: 2.82 (m, 2H, CH), 2.59 (m, 2H, CH), 1.47 (dd, ^{3}J(P,H)= 11, ^{3}J(H,H)= 7, 6H, Me), 1.42 (dd, ^{3}J(P,H)= 11, ^{3}J(H,H)= 7, 6H, Me), 1.37 (dd, ^{3}J(P,H)= 17, ^{3}J(H,H)= 7, 6H, Me), 1.31 (dd, ^{3}J(P,H)= 15, ^{3}J(H,H)= 7, 6H, Me), 2.49-0.68 (br s, 9H, B-H), -2.56 (br s, 1H, BHB). ^{1}H{^{11}B} NMR (CD_3COCD_3) δ: 2.82 (m, 2H, CH), 2.59 (m, 2H, CH), 2.49 (br s, 1H, B-H), 2.42 (br s, 1H, B-H), 1.77 (br s, 2H, B-H), 1.61 (br s, 3H, B-H), 1.47 (dd, ^{3}J(P,H)= 11, ^{3}J(H,H)= 7, 6H, Me), 1.42 (dd, ^{3}J(P,H)= 11, ^{3}J(H,H)= 7, 6H, Me), 1.37 (dd, ^{3}J(P,H)= 17, ^{3}J(H,H)= 7, 6H, Me), 1.31 (dd, ^{3}J(P,H)= 15, ^{3}J(H,H)= 7, 6H, Me), 0.68 (br s, 2H, B-H), -2.56 (br s, 1H, BHB). ^{13}C{^{1}H} NMR (CD_3COCD_3) δ: 16.78, 16.71, 16.67, 16.31, 16.21 (s, CH, Me). ^{11}B NMR (CD_3COCD_3): -6.2 (d, ^{1}J(B,H)= 138, 2B, B(9,11)), -11.1 (d, ^{1}J(B,H)= 142, 2B, B(5,6)), -14.0 (d, ^{1}J(B,H)= 169, 1B, B(3)), -19.4 (d, ^{1}J(B,H)= 155, 2B, B(2,4)), -29.1 (dd, ^{1}J(B,H)= 138, ^{1}J(B,H)= 30, 1B, B(10)), -31.8 (d, ^{1}J(B,H)= 143, 1B, B(1)). ^{31}P{^{1}H} NMR (CD_3COCD_3) δ: 77.31 (s, OP^iPr_2).

Synthesis of [NMe_4][7,8-($OPPh_2$)$_2$-7,8-$C_2B_9H_{10}$] ([NMe_4][8]). To a solution of [NMe_4][7,8-(PPh_2)$_2$-7,8-$C_2B_9H_{10}$] (0.5 g, 0.87 mmol) in acetone (15 mL) at 0ºC was

added dropwise 17.4 mL (1.74 mmol) of a solution of 0.1 M in H_2O_2. The mixture was stirred for 4 hours at room temperature and then an aqueous solution with an excess of $[NMe_4]Cl$ was added to precipitate the white product. This was filtered off, washed with water (3x10 mL) and dried in vacuo. Yield: 0.39 g (74 %). Anal. Calcd for $C_{30}H_{42}B_9NO_2P_2$: C: 59.27, H: 6.96, N: 2.30 %. Found: C: 58.95, H: 7.00, N: 2.45 %. FTIR: 3019 ($C\text{-}H_{aryl}$), 2959 ($C\text{-}H_{alkyl}$), 2535 (B-H), 1183 (P=O). ^1H NMR (CD_3COCD_3) δ: 7.91-7.23 (m, 20H, Ph), 3.43 (s, 12H, NMe_4), 2.84-0.42 (br m, 9H, B-H), -1.95 (br s, 1H, BHB). $^1H\{^{11}B\}$-NMR (CD_3COCD_3) δ: 7.91-7.23 (m, 20H, Ph), 3.43 (s, 12H, NMe_4), 2.84 (br s, 2H, B-H), 2.33 (br s, 1H, B-H), 1.59 (br s, 2H, B-H), 1.20 (br s, 2H, B-H), 0.88 (br s, 1H, B-H), 0.42 (br s, 1H, B-H), -1.95 (br s, 1H, BHB). $^{13}C\{^1H\}$ NMR (CD_3COCD_3) δ: 137.72 (d, $^1J(C,P)$= 87, Ph), 136.34 (d, $^1J(C,P)$= 88, Ph), 132.53 (s, *p*-Ph), 132.01 (s, *p*-Ph), 129.63 (d, $^2J(C,P)$= 25, *o*-Ph), 126.82 (s, *m*-Ph), 126.21 (s, *m*-Ph), 54.89 (s, NMe_4). ^{11}B NMR (CD_3COCD_3) δ: -5.6 (d, $^1J(B,H)$= 119, 2B), -11.1 (d, $^1J(B,H)$= 133, 3B), -19.0 (d, $^1J(B,H)$= 111, 2B), -32.2 (d, $^1J(B,H)$= 142, 1B), -34.0 (d, $^1J(B,H)$= 150, 1B). $^{31}P\{^1H\}$ NMR (CD_3COCD_3): 29.33 (s, $OPPh_2$).

Oxidation of 1,2-$(PPh_2)_2$-1,2-$C_2B_{10}H_{10}$ with S. To a round bottom flask (25 mL) containing 1,2-bis(difenilfosfino)-1,2-dicarba-*closo*-dodecaborane (100 mg, 0.20 mmol) was added acetone (4 mL) and THF (1ml). Then, S powder (13 mg, 0.40 mmol) was added to the solution and the mixture was refluxed for two days. After evaporation of the solvent a white solid appeared which was extracted with diethyl ether (10mL). From the suspension solid **10** was filtered (Yield: 33 mg, 31%). Purification by preparative thin layer chromatography (silica G, CH_2Cl_2/Hexane 8:2) yielded two compounds **11** (R_f: 0.56, 22 mg, 20%) and **12** (R_f 0.3125, 23mg, 20 %).

1-$(SPPh_2)$-2-(PPh_2)-1,2-$C_2B_{10}H_{10}$ (10). Anal. Calcd for $C_{26}H_{30}B_{10}SP_2.0.3\ CH_2Cl_2$: C, 55.20; H, 5.39; S, 5.60 %. Found: C, 55.24; H, 5.66; S, 5.94 %. FTIR: 3053(C_{aryl}-H), 652 (P=S). ^1H NMR ($CDCl_3$) δ: 8.43 (d, $^2J(H,H)$= 7, 2H, Ph), 8.39 (d, $^2J(H,H)$= 7, 2H, Ph), 7.63-7.27 (m, 16H, Ph), 3.1-2.00 (br m, B-H). $^1H\{^{11}B\}$ NMR ($CDCl_3$): 8.43 (d, $^2J(H,H)$= 7, 2H, Ph), 8.39 (d, $^2J(H,H)$= 7, 2H, Ph), 7.63-7.27 (m, 16H, Ph), 3.06 (br s, 1H, B-H), 2.32 (br s, 4H, B-H), 2.23 (s, 4H, B-H), 1.63 (br s, 1H, B-H). $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ: 135.8 (d, J(C,P)= 10, Ph), 135.1 (d, J(C,P)= 23, Ph), 134.6 (d, J(C,P)= 10, Ph), 133.9 (d, J(C,P)= 18, Ph), 132.5 (s, *p*-Ph), 130.2 (s, *p*-Ph), 128.2 (d, J(C,P)= 8, Ph), 127.8 (d, J(C,P)= 12, Ph), 85.5 (d, $^1J(C,P)$= 87, C_c), 82.5 (q, $^3J(C,P)$= 15, $^1J(C,P)$= 32, C_c). ^{11}B-NMR ($CDCl_3$) δ: 2.15 (d, $^1J(B,H)$= 151, 1B), 1.05 (d, $^1J(B,H)$= 140, 1B), -6.83 (d, $^1J(B,H)$= 135, 5B), -9.11 (d, $^1J(B,H)$= 153, 3B). $^{31}P\{^1H\}$-NMR ($CDCl_3$) δ: 49.16 (d, $^3J(P,P)$= 21, $SPPh_2$), 12.77 (d, $^3J(P,P)$= 21, PPh_2).

1,2-$(SPPh_2)_2$-1,2-$C_2B_{10}H_{10}$ (11)

Anal. Calcd for $C_{26}H_{30}B_{10}S_2P_2.2CH_2Cl_2$: C, 45.05, H, 4.59, S, 8.59 %. Found: C, 44.56, H, 4.85, S, 8.98 %. FTIR: 3058 (C_{aryl}-H), 2632, 2603, 2574, 2557 (B-H), 1434, 1089, 652 (P=S), 688, 507 (PPh_2).^1H NMR (CD_3COCD_3) δ: 8.26 (m, 8H, Ph), 7.60 (m, 12H, Ph), 3.7-0.80 (br m, B-H). $^1H\{^{11}B\}$ NMR (CD_3COCD_3): 8.26 (m, 8H, Ph), 7.60 (m, 12H, Ph), 3.61, 2.34, 2.20, 1.28, 0.86 (br s, B-H). $^{13}C\{^1H\}$ NMR (CD_3COCD_3) δ: 133.7 (d, J(C,P)= 10, Ph), 132,3 (s, Ph), 130.5 (s, Ph),127.9 (d, J(C,P)= 14, Ph), 87.7 (d, $^1J(C,P)$= 21, C_c). ^{11}B-NMR (CD_3COCD_3) δ: 2.59 (d, $^1J(B,H)$= 140, 2B), -7.70 (d, $^1J(B,H)$= 134, 8B). $^{31}P\{^1H\}$-NMR (CD_3COCD_3) δ: 48.65 (s, $SPPh_2$).

1-$(SPPh_2)$-2-$(OPPh_2)$-1,2-$C_2B_{10}H_{10}$, (12)

Anal. Calcd for $C_{26}H_{30}B_{10}SP_2O.CHCl_3$: C, 47.69, H,4.59, S 4.72%. Found: C, 47.78, H,5.04, S 4.98%. FTIR: 3060 (C_{aryl}-H), 2572, 2621(B-H), 1215 (P=O), 652, 690 (P=S). ^1H NMR (CD_3COCD_3) δ: 8.37. (q, $^2J(H,H)$= 7, 5H, Ph), 7.96 (q, $^2J(H,H)$= 8, 5H, Ph), 7.63-7.54 (m, 10H, Ph), 3.1-2.00 (br m, B-H). $^1H\{^{11}B\}$ NMR (CD_3COCD_3): 8.37. (q, $^2J(H,H)$= 7, 5H, Ph), 7.96 (q, $^2J(H,H)$= 8, 5H, Ph), 7.63-7.54 (m, 10H), 3.33 (br s, 1H, B-H), 2.36 (br s, 1H, B-H), 2.25 (br s, 4H, B-H), 2.04 (br s, 4H, B-H). $^{13}C\{^1H\}$ NMR (CD_3COCD_3) δ: 134.16 (d, J(C,P)= 11, Ph), 132.62 (d, J(C,P)= 3, Ph), 132.29-132.18, 131.37 (s, Ph), 130.91 (s, Ph), 128.31 (d, J(C,P)= 12, Ph), 121.55 (d, J(C,P)= 12, Ph), 86.47 (d, $^1J(C,P)$= 19, C_c), 82.26 (d, $^1J(C,P)$= 28, C_c). ^{11}B-NMR (CD_3COCD_3) δ: 2.98 (d, $^1J(B,H)$= 146, 1B), 1.40 (d, $^1J(B,H)$= 138, 1B), -7.52 (8B). $^{31}P\{^1H\}$-NMR (CD_3COCD_3) δ: 49.96 (s, $SPPh_2$), 21.65 (s, $OPPh_2$).

Synthesis of 1-SP^iPr_2-2-P^iPr_2-1,2-*closo*-$C_2B_{10}H_{10}$ (13)

To a round bottom flask (25 mL) containing 1,2-bis(diisopropilfosfino)-1,2-dicarba-*closo*-dodecaborane (102 mg, 0.27 mmol) was added acetone (4 mL), THF (1ml) and S powder (17 mg, 0.54 mmol). The mixture was refluxed four hours and then cooled to room temperature. Evaporation of the solvent yielded a yellow oil. Then, diethyl ether (10mL) and water (10 mL) were added in this order. The mixture was thoroughly shaken and the two layers separated. The organic layer was dried with $MgSO_4$, filtered, and evaporated. Compound **13** was isolated. FTIR: 3058 (C_{aryl}-H), 2633, 2629, 2570(B-H), 655 (P=S). ^{11}B-NMR ($CDCl_3$) δ: 1.7 (d, $^1J(B,H)$= 132, 1B), 0.8 (d, $^1J(B,H)$= 153, 1B), -6.2 (d, $^1J(B,H)$= 151, 3B), -9.2 (d, $^1J(B,H)$= 145, 5B). $^{31}P\{^1H\}$-NMR ($CDCl_3$) δ: 78.0 (d, $^3J(P,P)$= 20, SP^iPr_2), 35.5 (d, $^3J(P,P)$= 20, P^iPr_2).

Synthesis of 1-SP^iPr_2-1,2-*closo*-$C_2B_{10}H_{11}$ (14)

To a round bottom flask (25 mL) containing 1,2-bis(diisopropilfosfino)-1,2-dicarba-*closo*-dodecaborane (102 mg, 0.27 mmol) was added acetone (4 mL), THF (1ml) and S powder (17 mg, 0.54 mmol). The mixture was refluxed two days and then cooled to room temperature. Evaporation of the solvent yielded a yellow oil. Then, diethyl ether (10mL) and water (10 mL) were added in this order. The mixture was thoroughly shaken and the two layers separated. The organic layer was dried with $MgSO_4$, filtered, and evaporated. The oily residue was purified by preparative thin layer chromatography using CH_2Cl_2: Hexane ((8:2). Compound **14** (R_f: 0.71, 55 mg, 22%) was isolated. Anal. Calcd for $C_8H_{24}B_{10}SP.0.4CH_3COCH_3$: C, 35.12, H, 8.46, S, 10.19 %. Found: C: 34.96, H 9.04, S, 11.03 %. FTIR: 2999, 2972, 2875 (C_{alkyl}-H), 2570 (B-H), 655 (P=S). ^1H NMR ($CDCl_3$) δ: 2.63 (h, $^3J(H,H)$= 7, 2H, ^iPr), 1.42 (t, $^3J(H,H)$= 7, 6H, ^iPr), 1.33 (t, $^3J(H,H)$= 7, 6H, ^iPr), 2.5-2.00 (br m, B-H). $^1H\{^{11}B\}$ NMR ($CDCl_3$): 2.63 (h, $^3J(H,H)$= 7, 2H, ^iPr), 1.42 (t, $^3J(H,H)$= 7, 6H, ^iPr), 1.33 (t, $^3J(H,H)$= 7, 6H, ^iPr), 2.42 (br s, B-H), 2.27 (br s, B-H), 2.12 (br s, B-H). $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ: 71 (s, C_c), 31.16 (d, $^1J(C,P)$= 47, CH), 18.73 (d, $^2J(C,P)$= 28, CH_3).^{11}B-NMR ($CDCl_3$) δ: 0.77 (d, $^1J(B,H)$= 152, 1B), -1.97 (d, $^1J(B,H)$= 152, 1B), -6.42 (d, $^1J(B,H)$= 151, 2B), -10.84 (d, $^1J(B,H)$= 160, 2B), -11.98 (d, $^1J(B,H)$= 160, 4B). $^{31}P\{^1H\}$-NMR ($CDCl_3$) δ: 77.96 (s, SP^iPr_2).

Synthesis of 1-$SePPh_2$-2-PPh_2-1,2-$C_2B_{10}H_{10}$ (15)

To a round bottom flask (25 mL) containing 1,2-bis(difenilfosfino)-1,2-dicarba-*closo*-dodecaborane (35 mg, 0.068 mmol) was added toluene (8 mL) and Se powder (11 mg, 0.14 mmol). The mixture was refluxed overnight and cooled to room temperature. The Selenium in excess was filtered. Evaporation of the solvent yielded a yellow solid. Yield: 24 mg, (0.041 mmol, 61 %). Anal. Calcd for $C_{26}H_{30}B_{10}SeP_2$: C, 52.79, H, 5.11 %. Found: C: 52.59, H 4.98 %. FTIR: 3049, 2927(C_{aryl}-H), 2532 (B-H), 692 (P=Se). ^1H NMR ($CDCl_3$) δ: 7.61 (m, 10H, Ph), 7.38 (m, 10H, Ph), 3.1-2.00 (br m, B-H). $^1H\{^{11}B\}$ NMR ($CDCl_3$): 7.61 (m, 10H, Ph), 7.38 (m, 10H, Ph), 3.09 (br s, 1H, B-H), 2.27- 2.01 (br s, 9H, B-H). $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ: 135.79 (d, J(C,P)= 10, Ph),

135.11 (d, J(C,P)= 23, Ph), 134.58 (d, J(C,P)= 10, Ph), 133.95 (d, J(C,P)= 18, Ph), 132.49 (s, *p*-Ph), 130.17 (s, *p*-Ph), 128.19 (d, J(C,P)= 8, Ph), 127.83 (d, J(C,P)= 12, Ph), 86.21 (s, C_c), 79.81 (s, C_c). ^{11}B-NMR ($CDCl_3$) δ: 1.26 (d, ^{1}J(B,H)= 149, 1B), -0.34 (d, ^{1}J(B,H)= 134, 1B), -7.89 (d, ^{1}J(B,H)= 140, 8B). ^{31}P{^{1}H}-NMR ($CDCl_3$) δ: 46.48 (d, ^{3}J(P,P)= 27, ^{1}J(P,Se)= 807, $SePPh_2$), 10.48 (d, ^{3}J(P,P)= 27, PPh_2).

Synthesis of 1-SeP^{i}Pr$_2$-1,2-C$_2$B$_{10}$H$_{11}$ (16)

To a round bottom flask (25 mL) containing 1,2-bis(diisopropilfosfino)-1,2-dicarba-*closo*-dodecaborane (82 mg, 0.22 mmol) was added 5 mL toluene and Se powder (35 mg, 0.44 mmol). The mixture was refluxed five days and cooled to room temperature. Evaporation of the solvent yielded a yellow oil. Purification by preparative thin layer chromatography (Hexane) gave compound **16** (R_f: 0.79, 25mg, 11%). ^{1}H NMR ($CDCl_3$) δ: 2.69 (m, 2H, C**H**$(CH_3)_2$), 1.37 (d, ^{3}J(H,H)=2, 3H, CH_3), 1.35 (d, ^{3}J(H,H)=2, 3H, CH_3), 2.7-1.5 (br m, B-H). ^{1}H{^{11}B} NMR ($CDCl_3$): 2.69 (m, 2H, C**H**$(CH_3)_2$), 1.37 (d, ^{3}J(H,H)=2, 3H, CH_3), 1.35 (d, ^{3}J(H,H)=2, 3H, CH_3), 2.48, 2.29, 2.20 (br s, B-H). ^{31}P{^{1}H}-NMR ($CDCl_3$) δ: 83.67(s, SeP^{i}Pr$_2$). ^{13}C{^{1}H} NMR ($CDCl_3$) δ: 66.29 (s, C_c), 21.18 (s, CH), 20.19 (s, CH_3), 18.92 (s, CH_3). ^{11}B-NMR ($CDCl_3$) δ: 0.5 (d, ^{1}J(B,H)= 147, 1B), -2.1 (d, ^{1}J(B,H)= 151, 1B), -6.8 (d, ^{1}J(B,H)= 150, 2B), -10.6 (d, ^{1}J(B,H)= 166, 2B), -11.8 (d, ^{1}J(B,H)= 175, 4B).

X-ray Structure Determinations. Single-crystal data collections for H[**6a**], H[**6b**], **10**, **11** and **15** were performed at –100º with an Enraf Nonius KappaCCD diffractometer using graphite monochromatized Mo Kα radiation. A totals of 7073, 7738 and 22651 reflections were collected for H[**6a],** H[**6b] 10**, **11** and **15** giving 4035, 4359 and 4785 unique reflections (R_{int} = 0.0180, 0.0251 and 0.1392).

The structures of H[**6a**] and H[**6b**] were solved by direct methods and refined on F^2 by the SHELXL97 program[24] , and all non-hydrogen atoms were refined with anisotropic displacement parameters for both compounds. Positional parameters of the hydrogen atoms connected to the boron atoms were refined with fixed isotropic displacement parameters. For both compounds, the chelating hydrogen atom was picked from difference Fourier map, and both coordinates and isotropic thermal displacement parameters of the atom were refined. Rest of the hydrogen atoms were treated as riding atoms using the SHELX97 default parameters.

The structure of **15** was solved by direct methods and refined on F^2 by the SHELXL97 program.[24] One of the phenyl groups is disordered assuming two orientations. The disordered group was refined isotropically as rigid group but rest of the non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were treated as riding atoms using the SHELX97 default parameters. Crystallographic parameters for H[**6a**], H[**6b**] and **15** are gathered in Table 2.

Supporting material available: Tables listing detailed crystallographic data, atomic positional and thermal displacement parameters, and bond lengths and angles for H[**6a**], H[**6b**] and **10**, **11** and **15**. This material is available free of charge via the Internet at http://pubs.acs.org.

(1) (a) Núñez, R.; Viñas, C.; Teixidor, F.; Sillanpää, R.; Kivekäs, R. J. Organomet. Chem. 1999, 592, 22. (b) McWhannell, M. A.; Rosair, G. M.; Welch, A. J.; Teixidor, F.; Viñas, C. Acta Cryst. C52 1996, 3135. (c) Kivekäs, R.; Teixidor, F.; Viñas, C.; Núñez, R. Acta Cryst. C51 1995, 1868. (d) Kivekäs, R.; Sillanpää, R.; Teixidor, F.; Viñas, C.; Núñez, R.; Abad, M. Acta Cryst. C51 1995, 1864. (e) Teixidor, F.; Viñas, C.; Abad, M. M.; Núñez, R.; Kivekäs, R.; Sillanpää, R. J. Organomet. Chem. 1995, 503, 193. (f) Kivekäs, R.; Sillanpää, R.; Teixidor, F.; Viñas, C.; Núñez, R. Acta Cryst. C50 1994, 2027. (g) Sillanpää, R.; Kivekäs, R.; Teixidor, F.; Viñas, C.; Núñez, R. Acta Cryst. C52 1996, 2223.

(2) (a) Viñas, C.; Abad, M. M.; Teixidor, F.; Sillanpää, R.; Kivekäs, R. J. Organomet. Chem. 1998, 555, 17. (b) Teixidor, F.; Viñas, C.; Abad, M. M.; Kivekäs, R.; Sillanpää, R. J. Organomet. Chem. 1996, 509, 139. (c) Kivekäs, R.; Sillanpää, R.; Teixidor, F.; Viñas, C.; Abad, M. M. Acta Chem. Scand. 1996, 50, 499.

(3) (a) Teixidor, F.; Viñas, C.; Benakki, R.; Kivekäs, R.; Sillanpää, R. Inorg. Chem. 1997, 36, 1719. (b) Viñas, C.; Cirera, M. R.; Teixidor, F.; Kivekäs, R.; Sillanpää, R.; Llibre, J. Inorg. Chem. 1998, 37, 6746. (c) Teixidor, F.; Rius, J.; Romerosa, A. M.; Miravitlles, C.; Escriche, L.; Sánchez, E.; Viñas, C.; Casabó, J. Inorg. Chim. Acta 1990, 176, 287. (d) Teixidor, F.; Viñas, C.; Casabó, J.; Romerosa, A. M.; Rius, J.; Miravitlles, C. Organometallics 1994, 139,14.

(4) (a) Teixidor, F.; Romerosa, A. M.; Rius, J.; Miravitlles, C.; Casabó, J.; Viñas, C.; Sánchez, E. J. Chem. Soc., Dalton Trans. 1990, 525. (b) Teixidor, F.; Viñas, C.; Sillanpää, R.; Kivekäs, R.; Casabó, J. Inorg. Chem. 1994, 33, 2645. (c) Viñas, C.; Cirera, M. R.; Teixidor, F.; Sillanpää, R.; Kivekäs, R. J. Organomet. Chem. 1997, 530, 89.

(5) Teixidor, F.; Núñez, R.; Viñas, C.; Sillanpää, R.; Kivekäs, R. Angew. Chem. Int. Ed. 2000, 39, 4290.

(6) (a) Van Leeuwen, P. W. N. M; Kamer, P. C. J.; Reek, J. N. H.; Dierkes, P. Chem. Rev. 2000, 100, 2741. (b) Ittel, S. D.; Johnson, L. K.; Brookhart, M. Chem. Rev. 2000, 100 1169. (c) Issleib, K.; Müller, D. Chem. Ber. 1959, 92, 3175.

(7) (a) Teixidor, F.; Viñas, C.; Abad, M. M.; López, M.; Casabó, J. Organometallics 1993, 12, 3766. (b) Teixidor, F.; Viñas, C.; Abad, M. M.; Kivekäs, R.; Sillanpää, R. J. Organomet. Chem. 1996, 509, 139. (d) Teixidor, F.; Viñas, C.; Abad, M. M.; Whitaker, C.; Rius, J. Organometallics 1996, 15/14, 3154. (e) Viñas, C.; Abad, M. M.; Teixidor, F.; Sillanpää, R.; Kivekas, R. J. Organomet. Chem. 1998, 555, 17. (f) Núñez, R.; Viñas, C.; Teixidor, F.; Abad M. M. Appl. Organomet. Chem. 2003, 17, 509. (g) Paavola, S.; Kivekäs, R.; Teixidor, F.; Viñas, C. J. Organomet. Chem. 2000, 606, 183. (h) Paavola, S.; Teixidor, F.; Viñas, C.; Kivekäs, R. J. Organomet. Chem. 2002, 645, 39. (i) Paavola, S.; Teixidor, F.; Viñas, C.; Kivekäs. R. J. Organomet. Chem. 2002, 657, 187.

(8) (a) Berners-Price, S. J.; Mirabelli, C. K.; Johnson, R. K.; Mattern, M. R.; McCabe, F. L.; Faucette, L. F.; Sung, C.-M-; Mong, S.-M.; Sadler, P. J.; Crooke, S. T. Cancer Research 1986, 46, 5486. (b) Johnson, R. K.; Mirabelli, C. K.; Faucette, L. F.; McCabe, F. L.; Sutton, B. M.; Bryan, D. L.; Girad, G. R.; Hill, D. T. Proc. Amer. Assoc, Cancer Res. 1985, 26, 254.

(9) (a) Buckler, S. A. J. Am. Chem. Soc. 1962, 84, 3093. (b) Floyd, M. B.; Boozer, C. E. J. Am. Chem. Soc. 1963, 85, 984. (c) Ogata, Y.; Yamashita, M. J. Chem. Soc., Perkin Trans II 1972, 730.

(10) Malone, J. F.; Marrs, D. J.; Mckervey, M. A.; O'Hagan, P.; Thompson, N.; Walker, A.; Arnaud-Neu, F.; Mauprivez, O.; Schwing-Weill, M. J.; Dozol, J. F.; Rouquette, H.; Simon, N. J. Chem. Soc., Chem. Commun. 1995, 2151.

(12) (a) Wiesboeck, R. A.; Hawthorne, M. F. J. Am. Chem. Soc. 1964, 86, 1642. (b) Garret, P. M.; Tebbe, F. N.; Hawthorne, M. F. J. Am. Chem. Soc. 1964, 86, 5016. (c) Hawthorne, M. F.; Young, D. C.; Garret, P. M.; Owen, D. A.; Schwerin, S. G.; Tebbe, F. N.; Wegner, P. M. *J. Am. Chem Soc.* **1968**, *90*, 862.

(13) Zakharkin, L. I.; Kalinin, V. N. Tetrahedron Letters 1965, 407.

(14) Viñas, C.; Núñez, R.; Rojo, I.; Teixidor, F.; Kivekäs, R.; Sillanpää, R. Inorg. Chem. 2001, 14, 3259.

(15) Peymann, T.; Herzog, A.; Knobler, C. B.; Hawthorne, M. F. Angew. Chem. Int. Ed. Engl. 1999, 38, 1062.

(16) Buchanan, J.; Hamilton, E. J. M.; Reed, D.; Welch, A. J. J. Chem. Soc., Dalton Trans. 1990, 677.

(17) (a) M. Bown, J. Plesek, K. Base, B. Stibr Mag. Reson, Chem. 1989, 27, 947. (b) X. L. R. Fontaine, N. N. Greenwood, J. D. Kennedy, K. Nestor, M. Thornton-Pett J. Chem. Soc., Dalton Trans. 1990, 681. (c) G. G. Hlatlky, R. R. Eckman, H. W. Turner Organometallics 1992, 11, 1413. (d) R. Uhrhammer, Y. S. Su, D. C. Swenson, R. F. Jordan Inorg. Chem., 1994, 33, 43978.

(18) (a) Dewar, M.J.S.; Jones, R., J. Amer. Chem. Soc. 1967, 89, 4251. (b) H. Nöth, B. Wrackmeyer, Magnetic Nuclear Resonance Spectroscopy of Boron Compounds. Ed. P. Diehl, E. Fluck, R. Kosfeld. Spring-Verlag, Berlin heildelberg 1978.

(19) Wanda, M.; Higashizaki, S.; Tsuboi, A. J. Chem. Research 1985, 38.

(20) (a) Ruthe, F.; Jones, P. G.; du Mont, W. -W.; Deplano P.; Mercuri, M. L. Z. Anorg. Allg. Chem. 2000, 626, 1105. (b)Godfrey, S. M.; Ho, N.; McAuliffe, C. A.; Pritchard, R. G. Angew. Chem., Int. Ed. Engl. 1996, 35, 2344. (c)Carmalt,C. J.; Norman, N. C.; Farrugia, L. J. Polyhedron 1993, 12, 2081. (d) Boraei, A. A.; du Mont, W. W.; Ruthe, F.; Jones, P. G. Acta Crystallog., Sect. C: Cryst. Struct. Commun. 2002, C58, o318.(e) Halvorson, K. E.; Willett, R. D.; Massabni, A. C.. J. Chem. Soc, Chem. Commun. 1990, 246. (f) Lane, H. P.; Godfrey, S. M.; McAuliffe, C. A.; Pritchard, R. G. J. Chem. Soc., Dalton Trans. 1994 3249-56.

(21) Paavola, S. PhD thesis (URL: http://ethesis.Helsinki.fi/julkaisut/mat/kemia/vk/paavola University of Helsinki, Finland, 2002.

(22) (a)Stampfl, T.; Gutmann, R.; Czermak, G.; Langes, C.; Dumfort, A.; Kopacka, H.; Ongania, K.-H.; Brüggeller, P. Dalton Trans., 2003, 3425. (b) Stampfl, T.; Czermak, G.; Gutmann, R.; Langes, C.; Kopacka, H.; Ongania, K.-H.; Brüggeller, P. Inorg. Chem. Commun. 2002, 5, 490. (c) Hitchcock, P. B.; Nixon, J. F.; Sakaray, N. Chem. Commun. 2000, 1745.

(23) Alexander R.P., Schroeder H. A.: Inorg. Chem. 1963, 2, 1107.

(24) Sheldrick, G. M. SHELX97. University of Göttingen, Germany, 1997

"Total Chemical Reduction of 1,2-*closo*-$C_2B_{10}H_{12}$ cluster in Carbon Substituted Derivatives to *nido* $[C_2B_{10}H_{13}]^-$".

Clara Viñas,[a] Gemma Barberà,[a] Anna Laromaine,[a] Francesc Teixidor,[a] Reijo Sillanpää,[c] Raikko Kivekas[b a a]
Institut de Ciència de Materials de Barcelona, C.S.I.C., Campus U.A.B., 08193 Bellaterra, Spain
[b] *Department of Chemistry, POBox 55, FIN-00014 University of Helsinki, Finland*
[c] *Department of Chemistry, University of Jyväskylä, FIN-40351 Jyväskylä, Finland*

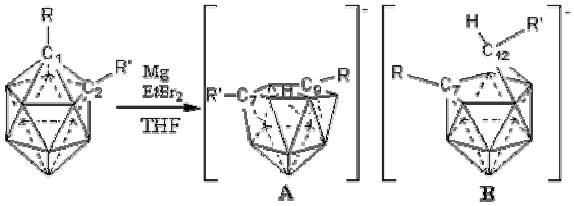
Introduction

It is well known that similar to its *meta* and *para* isomers, 1,2-*closo*-$C_2B_{10}H_{12}$, undergoes a two-electron reduction reaction by alkaline metals[1-3] to form a *nido* $[C_2B_{10}H_{12}]^{2-}$ carborane dianion. Protonation of this dianion leads to the formation of two monoanions $[C_2B_{10}H_{13}]^-$.[4, 5] One of them is the kinetic or "reactive" compound, [7-R-9-R'-7,9-*nido*-$C_2B_{10}H_{13}]^-$, and the other is the thermodynamic or "non-reactive" compound, [7-R-μ-(9,10-HR'C)-7-*nido*-$CB_{10}H_{11}]^-$. Recent studies verified the denomination as a kinetic and thermodynamic by theoretical calculations. It was found that at the MP2/6-31G* /3-21G+ZPE level, the thermodynamic isomer is 6.7 Kcal/mol more stable than the reactive one.[6] The crystal structures of both, kinetic and thermodynamic compounds were reported. X-ray structures related to the thermodynamic compound, [7-Me-μ-(9,10-HMeC)-7-*nido*-$CB_{10}H_{11}]^-$ were reported by Churchill and DeBoer[7] in 1973 and [7-Ph-μ-(9,10-HPhC)-7-*nido*-$CB_{10}H_{11}]^-$ by Tolpin and Lipscomb.[8] These structures were defined by an open five membered CB_4 face and a bridging methylene group. The molecular structure of kinetic compound wasn't solved until 1990.[9] It has an open six-membered face with the "extra" hydrogen symmetrically bridging two boron atoms in the C_2B_4 open face.

The kinetic isomer undergoes typical reactions with transition metals to form organometallic complexes.[10,11, 12] For the kinetic isomer are known many 13 vertex metalloboranes complexes such as Rh,[13] Co,[7, 14] Ti,[15] Pd,[11] Ir,[11] Fe,[14] Ni,[14] Mo,[14] W,[14] Ti,[14, 16] V,[16] Zr,[16] Cr, Mn and Hf. More recently metallacarboranes complexes of lanthanides Sm,[17-20] Nd,[19, 20] Eu,[21, 22,] Er,[23] Y,[22] and U[24] have been synthesized. All these complexes are incorporating the $[^6$-$C_2B_{10}H_{12}]^{2-}$ ligand which is a powerful reducing agent. Concretely [7-R-9-R'-7,9-*nido*-$C_2B_{10}H_{12}]^{2-}$ (R= H, Me) has been known to reduce M(IV) to M(III) (M=Ti, Zr, Hf)[15] and Eu(III) to Eu(II).[21, 22] This fact was confirmed by the reaction of $TiCl_4$ with $Na_2[C_2B_{10}H_{12}]$ in THF yielding a diamagnetic derivatives of Ti(II). The recovery of the *closo*-1,2-$C_2B_{10}H_{12}$ from the reaction mixture without exposure to air, identified the 12 vertex carborane dianion, [7-R-9-R'-7,9-*nido*-$C_2B_{10}H_{12}]^{2-}$, as the reducing agent for the formal Ti(II) compound. Recent improvements carried out by our group demonstrated that the thermodynamic isomer known as "inert" one is reactive as well.[25, 26]

Studies related to the polyhedral expansion of 1,2-*closo*-$C_2B_{10}H_{12}$ yielding to "supercarboranes" have been recently highlighted by Welch and Xie and coworkers as an emerging field getting through the icosahedral barrier.[27-29]

Due to the renewest interest of 12 vertices *nido* $[C_2B_{10}H_{12}]^{2-}$ anions not only for the possibility of expanding the cluster and for its capacity to produce complexes in a [6] fashion but also in a [7] fashion,[30, 31] we have re-investigated the two-electron reduction of 1,2-*closo*-$C_2B_{10}H_{12}$ with magnesium in this paper.[32]



Scheme 1.- Reduction process of 1,2-R_2-1,2-*closo*-$C_2B_{10}H_{10}$ clusters to [7-R-9-R-7,9-*nido*-$C_2B_{10}H_{11}]^-$ and [7-R-μ-(9,10-HR'C)-7-*nido*-$CB_{10}H_{11}]^-$.

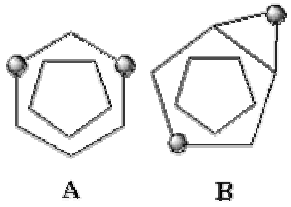


Figure 1.- Schematic view of the positional [7-R-9-R'-7,9-*nido*-$C_2B_{10}H_{11}]^-$ and [7-R-μ-(9,10-HR'C)-7-*nido*-$CB_{10}H_{11}]^-$ isomers from the top of the open face.

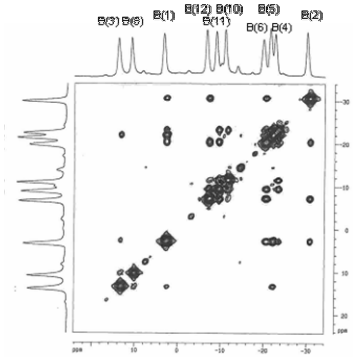


Figure 2.- $^{11}B\{^1H\}$-$^{11}B\{^1H\}$ COSY 2D NMR spectrum of $[NMe_4][7\text{-Me-9-Me-7,9-}nido\text{-}C_2B_{10}H_{11}]$.

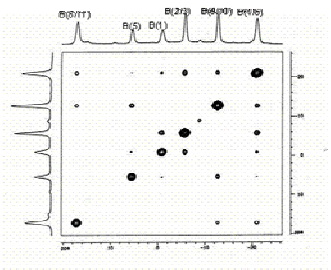


Figure 3.- $^{11}B\{^1H\}$-$^{11}B\{^1H\}$ COSY 2D NMR spectrum of $[NMe_4][$ [7-Me-μ-(9,10-HMeC)-7-*nido*-$CB_{10}H_{11}$].

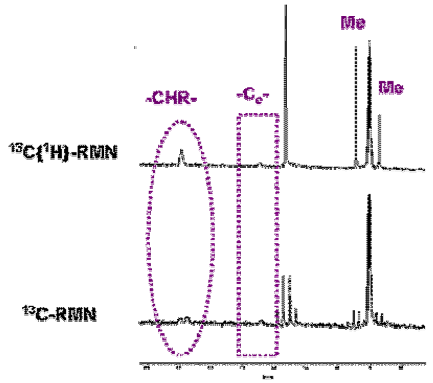


Figure 3. ^{13}C and $^{13}C\{^1H\}$-NMR spectra of $[NMe_4][7$-Me-μ-(9,10-HMeC)-7-*nido*-$CB_{10}H_{11}$].

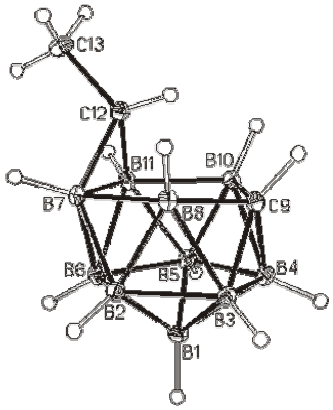
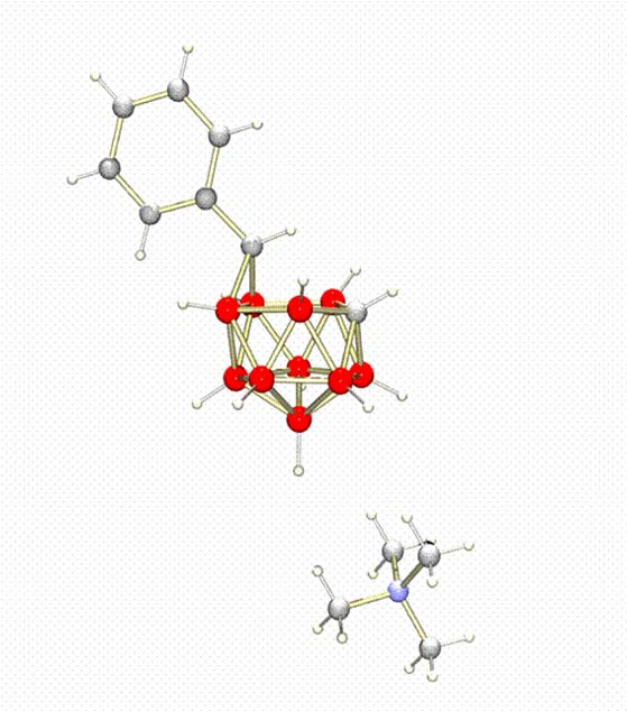


Figure 4.- Perspective view of the anion in $[N(CH_3)_4][$μ-(9,10-CHMe)-7-$CB_{10}H_{11}$] **4** with the cation omitted to aid clarity and 40% thermal ellipsoids. Selected distances (Å): C7-B8 1.640(3), C7-B11 1.620(3), B8-B9 1.857(3), B9-C12 1.641(3), B9-B10 1.849(3), B10-C12 1.651(3), B10-B11 1.862(3), C12-C13 1.529(3), and angles (º): B9-C12-B10 68.35(11), C13-C12-B9 113.11(15), C13-C12-B10 114.85(15).

Acknowledgements. This project was supported by CICYT (Project MAT98-0921), Generalitat de Catalunya (**SGR2000/00108**) and the Academy of Finland (project 41519, RK).

Figure 6.- Perspective view of the anion in $[NMe_4][$μ-(9,10-CHPh)-7-$CB_{10}H_{11}$] **8 .**



Experimental

General Considerations. Elemental analyses were performed using a Carlo Erba EA1108 microanalyzer. IR spectra were recorded using KBr pellets on a Shimadzu FTIR-8300 spectrophotometer. The mass spectra were recorded in the negative ion mode using a Bruker Biflex MALDI-TOF-MS [N_2 laser; λ_{exc} 337 nm (0.5 ns pulses); voltage ion source 20.00 kV (Uis1) and 17.50 kV (Uis2)]. The ^1H, $^1H\{^{11}B\}$ NMR (300.13 MHz), ^{11}B NMR (96.29 MHz) and $^{13}C\{^1H\}$ NMR (75.47 MHz) spectra were recorded on a Bruker ARX 300 spectrometer. All NMR spectra were recorded from acetone-d_6 solutions at 25ºC. 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 $Si(CH_3)_4$. Chemical shifts are reported in units of parts per million downfield from reference, and all coupling constants are reported in Hertz.

All reactions were performed under an atmosphere of dinitrogen employing standard Schlenk techniques. THF was distilled from sodium benzophenone prior to use. Compounds 1,2-*closo*-$C_2B_{10}H_{10}$, 1-Me-1,2-*closo*-$C_2B_{10}H_{11}$ and 1-Ph-1,2-*closo*-$C_2B_{10}H_{11}$ were supplied by Katchem Ltd. (Prague) and used as received. 1,2-$(Me)_2$-1,2-*closo*-$C_2B_{10}H_{10}$,[33] 1,2-$(Ph)_2$-1,2-*closo*-$C_2B_{10}H_{10}$ was synthesized according to the procedures described in the literature.

Synthesis of $[N(Me)_4][7,9\text{-}C_2B_{10}H_{13}]$ (1)

To a 100 ml schlenk flask were added Mg metal (5.0 g, 0.2 mol), 2ml of THF and a crystal of I_2. Then, a solution of 1,2-*closo*-$C_2B_{10}H_{12}$ (1.0 g, 6.9 mmol) in THF (20ml) and dibromoethane (5 ml, 12.21 mmol) were added drop wise, at the same time, to the Mg suspension. Once the addition was completed the reaction mixture was left at room temperature and then refluxing 12h. After that the mixture was evaporated to dryness in vacuo and water (100 ml) was added to the residue in a little portions, filtered and the anion was precipitated from the aqueous solution with an excess of $[N(CH_3)_4]Cl$. The white solid was washed with water and diethylether. The compound was obtained in 90% yield (1.55 g, 6.3 mmol).Anal. Calcd. for $C_6H_{25}B_{10}N$: N, 6.38, C, 32.85; H, 11.49. IR: ν[cm^{-1}] =. 2530 (B-H), $^1H\{^{11}B\}$-NMR: δ= 4.4 (s, C-H, 2H), 3.42 (s, $[N(Me)_4]$, 12H), 4.03, 3.08, 2.3, 1.50, 1.21, 0.71 (s, B-H), -4.56 (s, B-H-B). ^{11}B-NMR: δ= +12.0 (d, ^1J(B, H)= 129, 1B), +2.5 (d, ^1J(B, H)= 136,2B), -5.0 (d, ^1J(B, H)= 145,1B), -8.1 (d, ^1J(B, H)= 138, 2B), -17.8 (d, ^1J(B, H)= 145, 1B), -20.3 (d, ^1J(B, H)= 189, 1B), -21.6 (d, ^1J(B, H)= 146, 2B).

Synthesis of $[N(Me)_4][\mu\text{-}(9,10\text{-}CH_2)\text{-}7\text{-}nido\text{-}CB_{10}H_{11}]$ (2)

We use the product **1**, 250 mg, 1.14 mmol $[N(Me)_4][7,9\text{-}C_2B_{10}H_{13}]$ and isomerized at 90ºC during 1h in solid state and we obtained the 94% of the thermodynamic isomer. Yield. 235mg, 1.07 mmol, 94%. The characterization is the same we find in the literature.[34] IR: ν[cm^{-1}] = 2531 (B-H). $^1H\{^{11}B\}$-NMR: δ= 3.93 (s, 1B, B-H), 3.71(s, 1B, B-H), 3.40 (s, $[N(Me)_4]$, 12H), 3.21 (d, C-H, ^1J(H, H)=7.4, 1H), 2.81 (d, C-H, ^1J(H, H)=7.4, 1H), 2.54 (s, C-H, 1H), 1.68 (s, 2B, B-H), 1.46 (s, 2B, B-H), 0.95 (s, 2B, B-H), -4.41 (s, 1H, B-H-B).^{11}B-NMR: δ= 16.4 (d, ^1J(B, H)=151, 2B, B(8/11)), 12.1 (d, ^1J(B, H)= 135, 1B, B(5)), 0.8 (d, ^1J(B, H)= 135, 1B, B(1)), -7.9 (d, ^1J(B, H)= 148, 2B, B(2/3)), -15.8 (d, ^1J(B, H)= 135, 2B, B(9/10)), -22.2 (d, ^1J(B, H)= 139, 2B, B(4/6)). ^{13}C-NMR: +77.2 (d, ^1J(C, H) = 156, CH_2), 55.11 (s, $[N(Me)_4]$), 45.0 (d, ^1J(C, H) = 144, CH).

Synthesis of $[N(Me)_4][7\text{-}Me\text{-}7,9\text{-}C_2B_{10}H_{12}]$ (3)

The same procedure described for **1** were added Mg metal (5.0 g, 0.2 mol), 2ml of THF a crystal of I_2, a solution of 1-Me-1,2-*closo*-$C_2B_{10}H_{11}$ (1.0 g, 6.3 mmol) in THF (20ml) and dibromoethane (5 ml, 12.21 mmol) were added drop wise. After 12h refluxing and the work up we obtained the product in 88% yield (1.30 g, 5.6 mmol).Anal. Calcd. for $C_7H_{27}B_{10}N$: N, 6.0; C,36.02; H,11.66. Found: N, 5.98; C, 35.95, H, 5.77 %.IR: ν[cm^{-1}] = 2531 (B-H). $^1H\{^{11}B\}$-NMR: δ= 3.40 (s, $[N(Me)_4]$, 12H), 2.24 (s, Me, 3H), 4.05 (s, 1H, C-H), 2.35, 1.02, 1.21, 1.59, 1.30, -1.03, -4.41 (B-H).^{11}B-NMR: δ= 15.6 (d, ^1J(B, H)=135, 1B, B(3)), 12.8 (d, ^1J(B, H)= 129, 1B, B(8)), 5.0 (d, ^1J(B, H)= 136, 1B, B(1)), -4.8 (d, ^1J(B, H)= 150, 1B, B(12)), -7.1 (d, ^1J(B, H)= 177, 1B, B(11)), -9.1 (d, ^1J(B, H)= 137, 1B, B(10)), -18.1 (d, ^1J(B, H)= 146, 1B, B(6)), -19.7 (d, ^1J(B, H)= 154, 1B, B(5)), -20.6 (d, ^1J(B, H)= 142, 1B, B(4)), -28.2 (d, ^1J(B, H)= 143, 1B, B(2)). $^{13}C\{^1H\}$-NMR: δ= 32.28 (Me), 49.28 ($C_{cluster}$), 55.11 ($[N(Me)_4]$.

Synthesis of $[N(Me)_4][\mu\text{-}(9,10\text{-}CHMe)\text{-}7\text{-}nido\text{-}CB_{10}H_{12}]$ (4)

Similarly that for the compound **2**, 250 mgr, 1.07 mmol $[N(Me)_4][7\text{-}Me\text{-}7,9\text{-}C_2B_{10}H_{12}]$, 90C, 1h. Yield, 93%, 232mg, 0.98 mmol. Anal. Calcd. for $C_7H_{27}B_{10}N$: N,6.00; C,36.02; H,11.66. Found: N,5.70; C,34.80; H,11.71%. IR : ν (cm^{-1}) 2960 - 2852 (C-H_{alkyl}), 2513 (B-H). $^1H\{^{11}B\}$-NMR : δ 3.59 (s, ^3J(H, H)= 1.5, Me -C**H**, 1H), 3.45 (s, $[N(Me)_4]$, 12H), 2.54 (s, Me -$C_{cluster}$, 3H), 1.30 (d, ^3J(H, H)= 1.5, Me -CH, 3H). ^{11}B-NMR : δ +15.1 (d, ^1J(B, H)= 148, 2B), +9.3 (d, ^1J(B, H)= 132, 1B), -1.2 (d, ^1J(B, H)= 133, 1B), -8.8 (d, ^1J(B, H)= 146, 2B), -12.7 (d, ^1J(B, H)= 132, 2B), -20.0 (d, ^1J(B, H)= 135, 2B). $^{13}C\{^1H\}$-NMR : δ 92.5 (**C**$_{bridge}$, ^1J(C, H)= 156), 55.2 ($[N(Me)_4]$), 53.3 (**C**$_{cluster}$), 33.2 (Me). MALDI-TOF (m/z): 158.3 (M; 100%).

Synthesis of $[N(Me)_4][7,9\text{-}(Me)_2\text{-}C_2B_{10}H_{11}]$ (5)

The same procedure described for **1** were added Mg metal (5.0 g, 0.2 mol), 2ml of THF a crystal of I_2, a solution of 1,2-$(Me)_2$-1,2-*closo*-$C_2B_{10}H_{10}$ (1.0 g, 5.8 mmol) in THF (20ml) and dibromoethane (5 ml, 12.21 mmol) were added drop wise. After 12h refluxing and the work up we obtained the product in 91% yield (1.31 g, 5.3 mmol). IR: ν[cm^{-1}] = 2538 (B-H). $^1H\{^{11}B\}$-NMR: δ= 3.44 (s, $[N(Me)_4]$, 12H), 1.67 (Me, s, 3H), 0.92 (Me, s, 3H), 3.76, 3.74, 2.79, 2.39, 1.41, 1.39, 0.68, 1.1, -4. 28 (s, B-H) ^{11}B-NMR: δ= +14.1 (d, ^1J(B, H)= 128, 1B), +4.4 (d, ^1J(B, H)= 146, 2B), -0.9 (d, ^1J(B, H)= 148, 1B), -8.9 (d, ^1J(B, H)= 137, 2B), -15.5 (d, ^1J(B, H)= 147, 2B), -18.7 (d, ^1J(B, H)= 138, 1B), -20.1 (d, ^1J(B, H)= 157, 1B).

Synthesis of $[N(Me)_4][7\text{-}Me\text{-}\mu\text{-}(9,10\text{-}CHMe)\text{-}nido\text{-}CB_{10}H_{11}]$ (6)

Similarly that for the compound **2**, 250 mg, 1.01 mmol $[N(Me)_4][7,9\text{-}(Me)_2\text{-}C_2B_{10}H_{10}]$, 90ºC, 1h. Yield, 94%, 234mg, 0.94 mmol. Anal. Calcd. for $C_8H_{29}B_{10}N$: N,5.66; C,38.83; H,11.81. Found: N,6.37; C,38.85; H,12.15%. IR : ν (cm^{-1}) 2978-2866 (C-H_{alkyl}), 2527 (B-H). $^1H\{^{11}B\}$-NMR: δ 3.55 (q, ^3J(H, H)= 6.2, Me-C**H**, 1H), 3.40 (s, $[N(Me)_4]$, 12H), 1.69 (s, Me-$C_{cluster}$, 3H), 1.34 (d, ^3J(H, H)= 6.2, Me-CH, 3H). ^{11}B-NMR: δ +17.2 (d, ^1J(B, H) 148, 2B), +5.5 (d, ^1J(B, H) 137, 1B), -0.9 (d, ^1J(B, H) 135, 1B), -5.7 (d, ^1J(B, H) 146, 2B), -12.7 (d, ^1J(B, H) 133, 2B), -21.0 (d, ^1J(B, H) 135, 2B). ^{13}C-NMR: δ 88.5 (d, **C**$_{bridge}$, ^1J(C, H)=154), 64.2 (**C**$_{cluster}$), 56.2 ($[N(Me)_4$), 34.2 (Me), 26.9 (Me). MALDI-TOF (m/z): 173.3 (M; 100%), 160.3 (M- Me, 1%).

Synthesis of $[N(Me)_4][7\text{-}Ph\text{-}7,9\text{-}C_2B_{10}H_{12}]$ (7)

The same procedure described for **1** were added Mg metal (5.0 g, 205 mmol), 2ml of THF a crystal of I_2, a solution of 1-Ph-1,2-*closo*-$C_2B_{10}H_{11}$ (0.8 g, 3.6 mmol) in THF (20ml) and dibromoethane (5 ml, 12.21 mmol) were added drop wise. After 12h refluxing and the work up we obtained the product in 65 % yield (kinetic isomer), 33% of thermodynamic isomer. IR: ν[cm^{-1}] = 3023(C-H_{aryl}), 2534 (B-H). $^1H\{^{11}B\}$-NMR: δ= 7.1 (m, Ph, 12H), 4.37 (br s, CH, 2H), 3.98 (s, BH), 3.92 (s, BH), 3.78 (s, BH), 3.72 (s, BH), 3.44 (s, $[N(Me)_4]$, 12H), 2.8, 2.4, 2.2, 1.7, 1.53, 1.39, 1.23, 0.99, 0.68 (s, BH), -4. 22 (s, B-H-B, 1H). ^{11}B-NMR: δ= +17.8(d, ^1J(B, H)= 135, 1B), +12.7 (d, ^1J(B, H)= 129, 1B), +7.0 (d, ^1J(B, H)= 138, 1B), -4.7 (d, ^1J(B, H)= 150, 2B), -9.9 (d, ^1J(B, H)= 182, 1B), -15.9 (d, ^1J(B, H)= 130, 1B), -18.6 (d, ^1J(B, H)= 130, 1B), -21.7 (d, ^1J(B, H)= 139, 1B), -30.6 (d, ^1J(B, H)= 144, 1B).

Synthesis of $[N(Me)_4][\mu\text{-}(9,10\text{-}CHPh)\text{-}nido\text{-}CB_{10}H_{11}]$ (8)

Similarly that for the compound **2**, 250 mg, 0.88 mmol $[N(Me)_4][7\text{-}Ph\text{-}7,9\text{-}C_2B_{10}H_{12}]$ 90ºC, 1h. Yield, 86%, 215 mg, 0.75mmol. Anal. Calcd. for $C_{12}H_{29}B_{10}N$: N,4.74; C,48.78; H,9.89. Found: N,4.66; C,48.52, H,9.64%. IR: ν (cm^{-1})= 3012-2920 (C- H_{aryl}), 2518 (B-H). $^1H\{^{11}B\}$-NMR : δ 7.1-7.0 (m, Ph-$C_{cluster}$, 5H), 4.38 (s, C-**H**, 1H), 3.40 (s, $[N(Me)_4]$, 12H). ^{11}B-NMR : δ +17.4 (d, ^1J(B, H)= 144, 2B), +9.4 (d, ^1J(B, H)= 134, 1B), +0.0 (d, ^1J(B, H)= 127, 1B), -8.8 (d, ^1J(B, H)= 146, 2B), -12.3 (d, ^1J(B, H)= 132, 2B), -17.9 (d, ^1J(B, H)= 135, 2B). ^{13}C-NMR : δ 128.2, 126.9, 124.7 (**Ph**), 92.9 (**C**$_{bridge}$, ^1J(C, H) 213), 74.5 (**C**$_{cluster}$), 55.16 ($[N(Me)_4]$). MALDI-TOF (m/z): 220.3 (M; 100%)

Synthesis of $[N(CH_3)_4][\ ][\mu\text{-}(9,10\text{-}CHPh)\text{-}7\text{-}Ph\text{-}nido\text{-}CB_{10}H_{11}]$ (10)

Anal. Calcd. for $C_{18}H_{34}B_{10}N$: N,3.77; C,58.18; H,8.95. Found: N,3.64; C,57.98, H,8.72%. IR: ν (cm^{-1})= 3022-2918 (C-H_{aryl}), 2525 (B-H),. ^1H NMR : δ 7.60-6.90 (m, C_6**H**$_5$-$C_{cluster}$, 10H), 4.79 (s, C-**H**, 1H), 3.42 (s, $[N(Me)_4]$, 12H).^{11}B-NMR : δ +19.3 (d, ^1J(B, H)= 141, 2B), +8.8 (d, ^1J(B, H)= 136, 1B), +0.9 (d, ^1J(B, H)= 136, 1B), -6.0 (d, ^1J(B, H)= 148, 2B), -11.7 (d, ^1J(B, H)= 134, 2B), -18.3 (d, ^1J(B, H)= 137, 2B). ^{13}C-NMR : δ 152.3, 149.5, 128.1, 127.8, 127.2, 127.1, 124.9, 124.5 (s, Ph), 92.1 (d, **C**$_{bridge}$, ^1J(C, H)= 198), 76.1 (**C**$_{cluster}$), 56.7 ($[N(Me)_4]$). MALDI-TOF (m/z): 296.4 (M; 100%).

Reaction with $3,6\text{-}(Me)_2\text{-}1,2\text{-}closo\text{-}C_2B_{10}H_{10}$

We use the same procedure described for **1** adding Mg metal (1.25 g, 51.4 mmol), 2ml of THF a crystal of I_2, a solution of 3,6-$(Me)_2$-1,2-*closo*-$C_2B_{10}H_{10}$ (0.20 g, 1.13 mmol) in THF (5ml) and dibromoethane (1.25 ml,3 mmol) were added drop wise. We monitored the reaction and after 12h refluxing no reaction was observed we left the reaction 5 h more refluxing and no reaction was observed. We recovered all the starting material in 97% yield (0.19 g, 1.12 mmol).

Reaction with $1,7\text{-}closo\text{-}C_2B_{10}H_{12}$

We use the same procedure described for **1** adding Mg metal (1.25 g, 51.4 mmol), 2ml of THF a crystal of I_2, a solution of 1,7-*closo*-$C_2B_{10}H_{12}$ (0.20 g, 1.4 mmol) in THF

(5ml) and dibromoethane (1.25 ml, 3 mmol) were added drop wise. We monitored the reaction and after 15h refluxing no reaction was observed we left the reaction 48h more refluxing and no reaction was observed. We recovered all the starting material in 95% yield (0.19 g, 1.32 mmol).