Negatively charged Metallacarborane redox couples with both members stable to air.

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ABSTRACT

It was possible to synthesize and isolate redox couples in which both partners are negatively charged. The handy framework is $[3,3'\text{-Co}(1,2\text{-}closo\text{-C}_2\text{B}_9\text{H}_{11})_2]^-$. The $E_{½}$ potential can be tuned by adjusting the nature and number of substituents on B and C. The octaiodinated species $[3,3'\text{-Co}(1,2\text{-}closo\text{-C}_2\text{B}_9\text{H}_7\text{I}_4)_2]^-$ is the most favorable as it is isolatable and stable in air.

KEYWORDS: Metallacarboranes, red-ox tuning, red-ox couple, molecular platform, cobaltabisdicarbollide.

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Introduction

The cobaltabisdicarbollide, [3,3'-Co(1,2-*closo*-$C_2B_9H_{11})_2]^-$, [**1**]$^-$[1], is a remarkable anion: it is chemically and thermally stable in a diverse number of situations;[2] it can be substituted at carbon atoms or at boron atoms,[3] and in the latter ones regioselectively at different sites of each one of the two globes.[4] The central core of this anion, "$Co(C_2B_3)_2$", is very similar to the core of ferrocene, "$Fe(C_5)_2$", thus they bear resemblances in some respects, e.g. the reversible electrochemistry[5] and the high chemical and thermal stability,[6] but are different in others, such an enhanced protection of the Co in [**1**]$^-$ by a canopy of boron hydrogen atoms,[7] and properties derived from the six additional atoms placed in two further planes from the core (B_5 plane and B_1). These vertexes produce a rich variety of substitution sites, and are responsible for additional physicochemical properties. One of the most obvious differences between [**1**]$^-$, and Ferrocene (*Fc*) is the charge of [**1**]$^-$, that makes the latter and its congeners to be some of the few examples of metallocene type complexes with a negative charge. Previous work has shown that [**1**]$^-$ can be modified by halogenations,[8],[9] and it is a unique framework in its ability to produce a stepwise modulation of its redox potential by each new B-X (X = halogen) unit added.[10] We recently demonstrated that sequential substitution of B-H by B-X units produces an average $E_{½}$ shift, near 0.13V, to more positive potential values.[11] This $E_{½}$ cumulative process is very rare[12] and no other redox reversible platform seems to be capable of making it as effectively as [**1**]$^-$. In this work we disclose on i) the $E_{½}$ site dependence of two opposite effect substituents, I- *vs.* Me-, all realized on boron atoms, ii) the power of the $E_{½}$ site dependence shift and iii) the application of these concepts to stabilize the $[Co(C_2B_9H_{11})_2]^{2-}$ framework, [**1**]$^{2-}$, in which the Co is Co^{2+}.

Results and Discussion

Iodine and carbon have similar electronegativities according to the Pauling's scale, X_I= 2.66, X_C= 2.55, X_B= 2.04,[13] thus the polarization of the σ bonds for B-C and B-I shall be similar; further, both have the possibility to donate electron density to the cluster cage: iodine by π-donation and the methyl by hyperconjugation.[14] For both these reasons, we would expect similar effects on $E_{½}$ by B-C and B-I substitution in [**1**]$^-$; however for *Fc*, methyl groups produce an $E_{½}$ shift to more negative potentials,[15] whereas bromo groups, taken as similar to iodo, produce an $E_{½}$ shift towards more positive potentials, all referenced to pristine *Fc*. Therefore, there was the possibility that the opposite trend observed by alkyl or halogen substitution on *Fc* also occurred in [**1**]$^-$, although its redox couple is [**1**]$^{-1/-2}$ in contrast to *Fc* that is *Fc*$^{+/0}$. To provide evidence of this, a set of regioselective derivatives of [**1**]$^-$ were needed. The synthesis of these compounds was now possible due to the great advances in I substitution on the carborane cluster.4 Earlier we and others had demonstrated that starting from monoiodinated metallacarboranes,[4],[16] alkyl derivatives can be produced by a modification of the Kumada reaction. In Scheme 1, the syntheses of [3,3'-Co(9,12-I_2-1,2-*closo*-$C_2B_9H_9$)$_2$]$^-$ (I_4-[**1**]$^-$) and [3,3'-Co(9,12-(Me)$_2$-1,2-*closo*-$C_2B_9H_9$)$_2$]$^-$ ((Me)$_4$-[**1**]$^-$), are shown. Similar protocols have been utilized to produce other I- or Me- polysubstituted [**1**]$^-$ derivatives studied in this work.

Chart 1 indicates the numbering of the [3,3'-Co(1,2-*closo*-$C_2B_9H_{11}$)$_2$]$^-$ platform and its corresponding ligand [7,8-*nido*-$C_2B_9H_{11}$]$^{2-}$. In addition to [**1**]$^-$, two other framework derivatives of the latter have been used, [3,3'-Co(1-Ph-1,2-*closo*-$C_2B_9H_{10}$)$_2$]$^-$, [**2**]$^-$, and [3,3'-Co(1-Me-1,2-*closo*-$C_2B_9H_{10}$)$_2$]$^-$, [**3**]$^-$ (Figure 1). Derivatives of these frames, the site occupation of the substituent, along with their $E_{½}$ values are in Table 1 while Table 2 is dedicated to Me- and I- derivatives of $[\mathbf{1}]^-$. Three fundamental aspects stand out: all Me-derivatives exhibit an $E_{½}$ shift to more negative potential values than the reference value given by $[\mathbf{1}]^-$, whereas the $E_{½}$ for all I- derivatives are shifted to more positive potential values; second, the power of I- in producing a distinct $E_{½}$ shift is far superior to the methyl groups, and third an $E_{½}$ substituent site dependence is clear. Therefore, B–Me or B–I substitution on $[\mathbf{1}]^-$ produce opposite effects on $E_{1/2}$ just as C-Me and C-Br in *Fc*.

The stepwise substitution of B-H by B-Me induces shifts of $E_{½}$ to more negative potential values that are very small, between -10 / -15 mV each, thus one substitution produces -10 mV shift; two substitutions produce -20 mV; four, -40 mV; six, -90 mV; eight, -120 mV. The shift induced by each methyl unit in $[\mathbf{1}]^-$ is about ¼ of the effected on *Fc*. Further, these changes are so small that they cannot be used to define a site effect.

Much more relevant on $E_{½}$ are the stepwise substitutions of B-H by B-I. To interpret the results, it is advisable to formally slice each half of $[\mathbf{1}]^-$ so that four planes are generated. First plane is made of Co; second plane is made of B(4,7,8) and C(1,2); third plane is made of B(5,6,9,11,12); and fourth plane is made by B(10). The site influence on the $Co^{3+/2+}$ couple can be studied by computing the influence of each substituent on each plane on $E_{½}$. The B-I's on B(4,7,8) will tell on the effect of the substituent on the plane C_2B_3 bonded to Co. From Table 2 entry 7, I-B(8) exerts a $\Delta E_{½}$ near +0.30V; the existence of a second I-B in the equivalent position B(8'), I_2-$[\mathbf{1}]^-$ (Table 2 entry 9), induces an average $\Delta E_{½}$ per iodine atom, near +0.24V; the influence of the equivalent B(4) and B(7) sites can be obtained from I_4-$[\mathbf{1}]^-$ in Table 2 entry 12 yielding an average of +0.26V, or from I_2-$[\mathbf{1}]^-$ (Table 2, entry 10) with an average of +0.28V. Thus, it could be assumed that each B-I on the nearest plane to the Co, produces a $\Delta E_{½}$ of +0.27±0.03V. A similar process can be followed for the third plane B_5, the second nearest to Co. In this case, each B-I produces a $\Delta E_{½}$ of 0.15±0.03V.

Finally, a B-I on the fourth plane produces a ΔE½ of +0.14V. Noticeably, these results are related to the B-I vertex distance to the Co metal center. If the rough approximation of the front view of the icosahedron cluster to a hexagon is made, as shown in Figure 2, and the Co is made to occupy one of the vertexes, the distance to the substituted boron in the second plane is ***d***, to the third one is 1.73***d***, and to the fourth one is 2***d***. If ***d*** is taken as 0.27, according to the influence of a B-I in the nearest plane to Co, ***d***/1.73 is 0.16 and ***d***/2 is 0.14 that nicely fits with the ΔE½ values experimentally obtained, 0.27±0.03V, 0.15±0.03V and 0.14V.

The former values validate the additive rule and enlighten the importance of the site where the substitution occurs. These site dependent ΔE½ values indicate that a hypothetical $[\mathbf{1}]^-$ derivative with 6 B-I in the two planes nearest to Co, would induce a global ΔE½ near +1.62V, thus converting $[\mathbf{1}]^-$ with E½= -1.80V into I_6-$[\mathbf{1}]^-$ with E½ near -0.18V. Such a synthesis is still out of the possibility of current state of the art in halogen substitution but a good approach is I_4-$[\mathbf{1}]^-$ (Table 2, entry 12) that with 50% of the B-H replaced in I_8-$[\mathbf{1}]^-$ (Table 2, entry 15) almost reaches the same global ΔE½ as the latter. As a proof of concept, the anion I_6-$[\mathbf{1}]^-$ B(4,4',9,9',12,12') was synthesized and its expected E½ should be near -0.66V. The experimental E½ value is -0.80 V.

Recently, [17] based on seminal works of Pombeiro,[18] Pickett,[19] Lever[20] and Bursten[21] groups, reviewed on the importance of establishing a relationship between the redox potential-structure of complexes that define electrochemical parameters, which are shown for a wide variety of ligands and metal sites. Lever and co-workers reported,[20] an electrochemical parametrization in sandwich complexes of the first row transition metals can be established by assigning electrochemical parameters to the ligands.[22] Due to the sandwich nature of the cobaltabisdicarbollide anions, we adhered recently to Lever's approach[23] to calculate from the experimental $E_{1/2}$ value the E_L contribution of the ligand $[7,8\text{-}C_2B_9H_{11}]^{2-}$ taken for $[3,3'Co\text{-}(1,2\text{-}C_2B_9H_{11})_2]^-$ and two diansa metallacyclophane derivatives, phospha[1]cobaltabisdicarbollidephane and benzene[2]cobaltabisdicarbollidephane. The estimated values were -0.00(0.10), +0.22 and -0.35 V, respectively.[23] The fact that cobaltabisdicarbollide followed Lever's equation derived mostly from metallocenes, indicated that cobaltabisdicarbollide is a metallocene-like molecule that behaves as such.[23] This is why, following the same procedure, E_L contribution of the different methylated and iodinated $[7,8\text{-}C_2B_9H_{11}]^{2-}$ ligand derivatives have been calculated in this work. The E_L ligands' contributions are displayed in Table 2.

The stepwise $\Delta E_{½}$ alteration was correlated with theoretical calculations.[24] Free energy calculations were performed for the three optimized isomers studied (see Figure 3) considering the fifteen Co^{2+} and Co^{3+} complexes **1**-**15**. The calculated stability shows that the c isomer is usually the most stable one (see Table 3), only for the **12** complexes, the simultaneous 4,4',7,7' substitution destabilizes such isomer. The substitution of the hydrogen atoms by Me- groups (entries 1-5 in Table 2) has a small influence in the redox potential due to their low participation in the HOMO orbital (Figure 4).

However, in the case of I_8-[**1**]$^-$ (see **15** in Figure 4) the HOMO energy is considerably stabilized and consequently increases the energy required for the oxidation process (less negative redox potentials). It is worth noting the almost perfect linear correlation between the calculated DFT redox potentials and the calculated HOMO energies for the solvated molecules (Figure 4). Such correction is valuable as the HOMO energies are easily calculated without performing calculations of the vibrations mandatory to estimate thermodynamic magnitudes, such entropy or free energy. As we have been claiming throughout the paper, based on experimental evidence, the computational studies also indicate strong $E_{½}$ dependence on the site of the substituent. As it can be seen in Figure 4 for **15**, the iodine orbital contribution is larger at the 8 and 10 positions (2nd and 4rt planes in Figure 2) than in 9 and 12 (3rd plane). Hence, the existence of substituent in the 2nd and 4th planes should be more efficient in terms of $E_{½}$ tuning than substituent on the 3rd plane. This is in agreement with the values in Table 2 and with Figure 2 for the 2nd and 3rd planes. The mismatch with the 4th plane may have been due to a certain degree of shadowing of the $E_{½}$ tuning at position 10 caused by the substituent on the 3rd level.

It is clear from Table 2 that I_8-[**1**]$^-$ is the [**1**]$^-$ derivative with the highest positive $E_{½}$ value. Further, it undergoes a perfect one-electron reversible redox process. The redox potential of I_8-[**1**]$^-$/I_8-[**1**]$^{2-}$ pair is -0.68 V *vs*. Fc^+/Fc.

Conversely, [**1**]$^-$ has a very negative $E_{½}$ value, -1.80 *vs* Fc^+/Fc. The results shown here for I_8-[**1**]$^-$ indicate a strategy to lower, making more positive, the $E_{½}$ value of the platform [**1**]$^-$ to produce the uncommon -1/-2 reversible couples. Moreover, we wanted to learn on the stability of both members of the uncommon redox couple [**1**]$^{-1/-2}$ with a practical $E_{½}$ value. In [**1**]$^-$, the Co is Co^{3+}, and as the dicarbollide is a high field ligand, the 6 electrons d are paired, thus [**1**]$^-$ shall be a diamagnetic species. In [**1**]$^{2-}$, there are 7 electrons d, and a paramagnetic species is expected. For [**1**]$^-$, the independent oxidized and reduced species would be difficult to be observed, indeed the reduced form has never been reported nor isolated, but in I_8-[**1**]$^-$ the chances to observe both redox partners should be much higher. Furthermore, tests on the stability of both forms, oxidized and reduced, in not highly strict anaerobic conditions would be a good indication of possible applications of these complexes. In a typical reaction the $[NMe_4]^+$ salt of I_8-[**1**]$^-$ was dissolved in THF and mixed with freshly prepared $Na[C_{10}H_8]$. Immediately the color of the solution turned from light orange to dark red. Progress of the reaction was followed by NMR analysis directly from the crude and the $^{11}B\{^{1}H\}$-NMR spectrum gave four well defined NMR resonances with intensities 2:6:4:6 in a wide field range (+28 / -95 ppm), clearly suggesting that the generated species was paramagnetic. Following oxidation by air, the sample returned to the original Co^{3+} color and its $^{11}B\{^{1}H\}$-NMR spectrum to the expected range (-2 / -20 ppm). Both $^{11}B\{^{1}H\}$-NMR spectra for I_8-[**1**]$^-$ (in red) and I_8-[**1**]$^{2-}$ (in black) are shown in Figure 5. The $^{11}B\{^{1}H\}$-NMR for I_8-[**1**]$^-$ evidences the diamagnetic nature of the compound. Conversely the ^{11}B-NMR of I_8-[**1**]$^{2-}$ expands significantly evidencing the paramagnetic nature of the reduced form. This is the first reported $^{11}B\{^{1}H\}$-NMR spectrum of one derivative of the cobaltabisdicarbollide platform proving the stability of the reduced species. To detect the presence of Co^{2+}, the EPR spectrum of a 33 mM solution of I_8-[**1**]$^{2-}$ in H_2O was recorded at 130K showing a g= 2,021 (Figure 6). With these results in hand other tests were done to isolate I_8-[**1**]$^{2-}$.

To this objective, the crude of the reaction between I_8-[**1**]$^-$ and $Na[C_{10}H_8]$ was filtered to remove the existing solid whose IR did not display any B-H absorption. The solvent was evaporated and the naphthalene was recovered by low pressure sublimation. The final product was collected as a dark brown solid and the further $^{11}B\{^{1}H\}$-NMR analysis showed that it was not altered during the purification process. Moreover, the stability in both air and inert gas (N_2 and Ar) conditions was also checked. The I_8-[**1**]$^{2-}$ species in solid state was perfectly air-stable for 7 days, while under inert conditions its stability increased to more than 1 month (Figure 7).

The THF solution of the reduced I_8-[**1**]$^{2-}$ species was stable for several hours in air. After one day, some re-oxidation was observed.

Stable paramagnetic compounds derivatives of neutral C_2B_{10} and anionic $[CB_{11}]^-$ clusters have been recently reported[25] but this reduced I$_8$-[**1**]$^{2-}$ species is the first isolated and stable paramagnetic cobaltabisdicarbollide, which is the most commonly used and widely studied metallacarborane.

Conclusions

The wide pattern of possible substitutions in [3,3'-Co(1,2-*closo*- $C_2B_9H_{11})_2]^-$ has facilitated the preparation of a set of regioselective polyiodinated derivatives, which in turn, by a Kumada inspired B-C cross coupling, has led to several regioselective polymethylated derivatives. A singular property of [3,3'-Co(1,2-*closo*-$C_2B_9H_{11})_2]^-$ is that it is redox reversible and permits tailoring the redox potential very accurately. No other platform allows for such an adjustment. Boron dehydromethylation shifts the $E_{½}$ value to more negative potential values, whereas boron dehydroiodination does the opposite effect. The redox potential shift can be large, even larger than 1 V, because of the cumulative individual effects, that are also site dependent. The effect of the B-I unit on the $E_{½}$ value is inversely proportional to the distance. The air exposure of [3,3'-Co(1,2-*closo*-$C_2B_9H_{11})_2]^{2-}$ is totally impractical, however from the $E_{½}$ shift to more positive potentials of the couple [3,3'-Co(8,9,10,12-I$_4$-1,2-*closo*-$C_2B_9H_7)_2]^{-1/-2}$ caused by 8 dehydroiodinations, the $E_{½}$ has shifted from -1.80 to -0.68 V *vs* Fc^+/Fc. This $E_{½}$ shift allows both the oxidized and reduced forms of the couple [3,3'-Co(8,9,10,12-I$_4$-1,2-*closo*-$C_2B_9H_7)_2]^{-1/-2}$ standing in air for several hours and days. These results open an unexplored way to adjust the desired $E_{½}$ value in devices in which $E_{½}$ modification will not imply a sharp molecular modification. In this paper, the redox potential of a series of related complex of Co^{3+} has allowed for the quantification of the ligands electron acceptor/donor properties, which can then be applied as an important characterization parameter.

Experimental section

Instrumentation.

IR spectra (ν, cm^{-1}; ATR or 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) and ^{11}B- and ^{11}B{^{1}H}-NMR (96.29 MHz) spectra were recorded on a Bruker ARX 300 instrument equipped with the appropriate decoupling accessories. All NMR spectra were performed in acetone deuterated solvent at 22ºC. The ^{11}B- and ^{11}B{^{1}H}-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 $SiMe_4$. Chemical shifts are reported in units of parts per million downfield from reference, and all coupling constants in Hz. The mass spectra were recorded in the negative ion mode using a BrukerBiflex 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)].

For voltammetric determinations, an electrochemical system, VoltaLab (Universal Electrochemical Laboratory System) interfaced with a PGZ100 potentiostat (Radiometer Analytical) and controlled by the VoltaMaster 4 software, was used. The electrochemical cell contained glassy carbon electrode as working electrode, a reference Ag/AgCl/KCl$_{sat}$ electrode and platinum wire as auxiliary electrode. The solutions were deaerated with analytical grade nitrogen at the start of each experiment to prevent oxygen interference. All experiments were performed at room temperature. Cyclic voltammogram responses were recorded at glassy carbon electrode in MeCN of $5{\cdot}10^{-3}$M l$_n$-[**1**]$^-$ using [NBu_4][PF_6] (0.1M) as supporting electrolyte. All the potential values were referred to the *Fc*$^+$*/Fc* couple [$E_{1/2}$

(Fc^+/Fc) = 0.64 V *vs*. Standard Hydrogen Electrode (SHE)].

Materials. Unless otherwise noted, all metallacarborane anions prepared are air and moisture stable. All manipulations were carried out under inert atmosphere. 1,2-dimethoxyethane (DME) and THF were distilled from sodium benzophenone prior to use. Reagents were obtained commercially and used as purchased. 1,2-*closo*-$C_2B_{10}H_{12}$ was obtained from Katchem. 1-Me-1,2-*closo*-$C_2B_{10}H_{11}$,[26] 1-Ph-1,2-*closo*-$C_2B_{10}H_{11}$,[27] [9-I-1,2-*closo*-$C_2B_{10}H_{11}$],[28] [9-I-7,8-*nido*-$C_2B_9H_{11}$],[29] [9,11-I_2-7,8-*nido*-$C_2B_9H_{10}$],[30] [5,6-I_2-7,8-*nido*-$C_2B_9H_{10}$]$^-$,[11] [1,5,6,10-I_4-7,8-*nido*-$C_2B_9H_8$]$^-$,[11] [3,3'-Co-(9,12-I_2-1,2-*closo*-$C_2B_9H_9$)$_2$]$^-$,[11] [3,3'-Co-(8,9,10,12-I_4-1,2-*closo*-$C_2B_9H_7$)$_2$]$^-$,[11] [3,3'-Co(8-I-1,2-*closo*-$C_2B_9H_{10}$)(1',2'-*closo*-$C_2B_9H_{11}$)]$^-$,[31] [3,3'-Co(8-I-1,2-*closo*-$C_2B_9H_{10}$)$_2$]$^-$,[11],[31] [3,3'-Co(8-Me-1,2-*closo*-$C_2B_9H_{10}$)(1',2'-*closo*-$C_2B_9H_{11}$)]$^-$,[31] [3,3'-Co-(8-Me-1,2-*closo*-$C_2B_9H_9$)$_2$]$^-$,[31] 3,3'-Co(8,9,10-I_3-1,2-*closo*-$C_2B_9H_8$)$_2$]$^-$,[16] ,3'-Co(8,9,10-Me_3-1,2-*closo*-$C_2B_9H_8$)$_2$]$^-$,[16] were synthesized as reported in the literature. The synthesis of [3,3'-Co-(8-Me-1,2-*closo*-$C_2B_9H_9$)$_2$]$^-$ and [3,3'-Co-(9,12-I_2-1,2-*closo*-$C_2B_9H_9$)$_2$]$^-$ has been also reported by using a different method.[8]

Synthesis of [$HNMe_3$][5-I-7,8-*nido*-$C_2B_9H_{11}$]

To a solution of KOH (418 mg, 7.46 mmol) in degassed EtOH (10 ml), 9-I-1,2-*closo*-$C_2B_{10}H_{11}$ (252 mg, 0.93 mmol) was added. The solution was refluxed for 5 h. After cooling down to room temperature, the solvent was removed under reduced pressure and the solid residue was dissolved in 10 ml of water. The solution was neutralized with HCl 1M. Afterwards, aqueous solution of [$HNMe_3$]Cl was added dropwise until no more precipitate was formed. The white solid was filtered and rinsed with water to give [$HNMe_3$][5-I-7,8-*nido*-$C_2B_9H_{11}$] (250 mg, 83%). Elemental analysis for $C_5H_{21}B_9IN$: calc: C 18.80, H 6.63, N 4.38; found C 18.39, H 6.31, N 4.27. IR (KBr): ν=3020 (s, ν_s(C_c-H), 2947, 2923 (s,

ν_s(C$_{alkyl}$-H), 2531 (s, ν_s(B-H)), 1480 cm^{-1} (s, ν_s(N-CH3)).^{1}H NMR (CDCl$_3$): δ= 3.11 (s, 9H, NH(C*H*$_3$)$_3$), 2.18 (s, 2H, C$_{cluster}$-*H*). ^{1}H{^{11}B} NMR (CD$_3$COCD$_3$): δ=3.11 (s, 9H, NH(C*H*$_3$)$_3$), 2.50-0.5 (s, 8H, B-H), 2.18 (br s, 2H, C$_{cluster}$-*H*), -2.41 ppm (s, 1H, H$_{bridge}$). ^{13}C{^{1}H} NMR (CD$_3$COCD$_3$): δ=46.7 ppm (s, HN(*C*H$_3$)$_3$).^{11}B NMR (CDCl$_3$): δ=-10.7 (d, ^{1}*J*(B,H)=147, 1B, B(9), -11.7 (d, ^{1}*J*(B,H)=149, 1B, B(11), -17.9 (d, ^{1}*J*(B,H)=126, 2B, B(2,4)), -20.6 (d, ^{1}*J*(B,H)=134, 1B, B(6)), -21.8 (d, ^{1}*J*(B,H)=140, 1B, B(3), -24.4 (s, 1B, B(5)), -30.9 (d, ^{1}*J*(B,H)=84, 1B, B(10)), -24.4 (s, 1B, B(5)), -36.1 (d, ^{1}*J*(B,H)=140, 1B, B(1)).MALDI-TOFMS: *m/z*= 261.24 [M, 100%].

Synthesis of [HNMe$_3$][7-Me-5,6-I$_2$-7,8-*nido*-C$_2$B$_9$H$_9$]

The same procedure as for the obtaining of [HNMe$_3$][5-I-7,8-*nido*-C$_2$B$_9$H$_{11}$] was followed. The used reactants quantities were: KOH (102 mg, 1.829 mmol), EtOH (5 ml), 1-Me-9,12-I$_2$-1,2-*closo*-C$_2$B$_{10}$H$_9$ (150 mg, 0.365 mmol). The final white solid [HNMe$_3$][7-Me-5,6-I$_2$-7,8-*nido*-C$_2$B$_9$H$_9$] was obtained with a yield of 87% (151 mg). Elemental analysis for C$_6$H$_{22}$B$_9$I$_2$N: calc: C 15.69, H 4.83, N 3.05; found C 15.83, H 4.57, N 3.13. IR (KBr): ν= 3026 (N-H), 2957 (C$_c$-H), 2925 (C$_{alkyl}$-H), 1480 (N-C), 2541 (B-H).^{1}H NMR (CD$_3$COCD$_3$): δ= 3.47 (s, 12H, N(CH$_3$)$_4$), 1.30 (s, 3H, CH$_3$). ^{1}H{^{11}B} NMR (CD$_3$COCD$_3$): δ= 3.47 (s, 12H, N(CH$_3$)$_4$), 2.40-1.05 (s, B-H), 1.30 (s, 3H, CH$_3$), -1.89 (s, 1H, H$_{bridge}$). ^{13}C{^{1}H} NMR (CDCl$_3$): δ= 55.38 (N(CH$_3$)$_4$), 23.91 (CH$_3$). ^{11}B NMR (CDCl$_3$): δ= -7.6 (d, ^{1}*J*(B,H)= 144, 1B), -8.8 (d, ^{1}*J*(B,H)= 140, 1B), -12.2 (d, ^{1}*J*(B,H)=164, 1B), -16.4 (d, ^{1}*J*(B,H)=171, 1B), -20.2 (d, ^{1}*J*(B,H)=156, 1B), -23.4 (br s, 1B), -24.2 (br s, 1B), -27.3 (d d, ^{1}*J*(B,H)=138, ^{1}*J*(H,H)=34, 1B), -31.8 (d, ^{1}*J*(B,H)=150, 1B).MALDI-TOFMS: *m/z*= 398.60 [M, 100%].

Synthesis of [HNMe$_3$][7-Ph-5,6-I$_2$-*nido*-7,8-C$_2$B$_9$H$_9$]

The same procedure as for the obtaining of [$HNMe_3$][5-I-7,8-*nido*-$C_2B_9H_{11}$] was followed. The used reactants quantities were: KOH (0.5 g, 1.06 mmol), EtOH (15 ml), 1-Ph-9,12-I_2-1,2-*closo*-$C_2B_{10}H_9$ (500 mg, 1.06 mmol). The final white solid product, [$HNMe_3$][7-Ph-5,6-I_2-7,8-*nido*-$C_2B_9H_9$] was obtained with a yield of 73% (395 mg). Elemental analysis for $C_{11}H_{24}B_9I_2N$: calc: C 25.34, H 4.64, N 2.69; found C 25.23, H 4.81, N 2.42. IR (KBr): ν= 3077 (N-H), 3026 (C_c-H), 2543 (B-H) 1479 (N-C). ^{1}H NMR (CD_3COCD_3): δ= 7.22-7.07 (m, 5H,C_6H_5), δ= 3.46 (s, 12H, $N(CH_3)_4$). ^{1}H{^{11}B} NMR (CD_3COCD_3): δ= 7.22-7.07 (m, 5H,C_6H_5), δ= 3.46 (s, 12H, $N(CH_3)_4$), 2.81-1.24 (s, B-H), -1.58 (s, 1H, H_{bridge}). ^{13}C{^{1}H} NMR ($CDCl_3$): δ= 55.35 ($N(CH_3)_4$), 127.56, 126.65, 125.22 (C_6H_5). ^{11}B NMR ($CDCl_3$): δ= -6.4 (d, ^{1}J(B,H)= 153, 1B), -8.1 (d, ^{1}J(B,H)= 151, 1B), -12.3 (d, ^{1}J(B,H)= 162, 1B), -17.7 (d, ^{1}J(B,H)= 162, 1B), -20.4 (d, ^{1}J(B,H)= 152, 1B), -22.5 (br s, 1B), -23.8 (br s, 1B), -26.4 (d d, ^{1}J(B,H)= 150), -30.9 (d, ^{1}J(B,H)= 147, 1B). MALDI-TOF MS: *m/z*= 462.81 [M, 100%].

Synthesis of [$HNMe_3$][7-Me-1,5,6,10-I_4-7,8-*nido*-$C_2B_9H_7$]

The same procedure as for the obtaining of [$HNMe_3$][5-I-7,8-*nido*-$C_2B_9H_{11}$] was followed. The used reactants quantities were: KOH (0.63 g, 1.13 mmol), EtOH (5 ml), 1-Me-8,9,10,12-I_4-1,2-*closo*-$C_2B_{10}H_7$ (150 mg, 0.226 mmol). The final white solid product, [$HNMe_3$][7-Me-1,5,6,10-I_4-7,8-*nido*-$C_2B_9H_7$], was obtained with a yield of 63% *(*100 mg). Elemental analysis for $C_6H_{20}B_9I_4N$: calc: C 10.13, H 2.83, N 1.97; found C 10.07, H 2.65, N 1.80. IR (KBr):ν= 3115 (s, ν(N-H)), 2923 (w, ν($C_{cluster}$-H st.)), 2865 (w, ν(C_{alkyl}-H st.)), 2555 (s, ν(B-H st.)), 1462 (w, ν(N-C)).^{1}H-NMR: (CD_3COCD_3) δ= 8.51, (t, ^{1}J(N,H) = 111, 1H, $NH(CH_3)_3$), 3.2 (d, ^{3}J(H,H) = 3, 9H, $NH(CH_3)_3$), 2.37 (s, 3H, $CH_{3\ cluster}$).^{1}H{^{11}B} NMR (CD_3COCD_3): δ= 8.51 (t, ^{1}J(N,H) = 111, 1H, $NH(CH_3)_3$), 3.2 (d, ^{3}J(H,H) = 3, 9H,

$NH(CH_3)_3$), 2.60 (m, 4H, B-H), 2.37 (s, 3H, $CH_{3\ \mathrm{cluster}}$), 2.19 (s, 1H, B-H), 0.19 (s, 1H, H_{bridge}).$^{13}C\{^{1}H\}$ NMR (CD_3COCD_3): δ=45.5 (s, $HN(CH_3)_3$), 23.5 (CH_3).^{11}B NMR (CD_3COCD_3): δ= -7.50 (d, ^{1}J (B,H) = 144, 1B), -8.73 (d, ^{1}J (B,H) = 131, 1B), -12.18 (d, ^{1}J (B,H) = 195, 1B), -14.21 (d, ^{1}J (B,H) = 160, 1B), -17.97 (s, 2B, B-I), -17.97 (d, ^{1}J (B,H) = 93, 1B), -35.23 (s, 2B, B-I). MALDI-TOF MS: m/z= 524.98 [M-I, 24%], 651.40 [M, 100%].

Synthesis of [$HNMe_3$][7-Ph-1,5,6,10-I_4-7,8-*nido*-$C_2B_9H_7$]

The same procedure as for the obtaining of [$HNMe_3$][5-I-7,8-*nido*-$C_2B_9H_{11}$] was followed. The used reactants quantities were: KOH (0.77 g, 1.38 mmol), EtOH (5 ml), 1-Ph-8,9,10,12-I_4-1,2-*closo*-$C_2B_{10}H_7$ (200 mg, 0.27 mmol). The final white solid product, [$HNMe_3$][7-Ph-1,5,6,10-I_4-7,8-*nido*-$C_2B_9H_7$], was obtained with a yield of 73% *(*156 mg). Elemental analysis for $C_{11}H_{22}B_9I_4N$: calc: C 17.09, H 2.87, N 1.81; found C 17.20, H 2.97, N 1.74. IR (KBr): ν= 3111 (s, ν(N-H)), 2548 (s, ν(B-H st.)), 1463 (w, ν(N-C)). ^{1}HNMR (CD_3COCD_3): δ= 8.71 (s, ^{1}J(N,H) = 102,1H, $NH(CH_3)_3$), 7.23-7.17 (m, 5H, C_6H_5), 3.19 (d, ^{3}J(H,H) = 6, 9H, $NH(CH_3)_3$). $^{1}H\{^{11}B\}$ NMR (CD_3COCD_3): δ= 8.71 (s, ^{1}J(N,H) = 102,1H, $NH(CH_3)_3$), 7.23-7.17 (m, 5H, C_6H_5), 3.19 (d, ^{3}J(H,H) = 6, 9H, $NH(CH_3)_3$), 2.93-1.2 (m, 5H, B-H), 0.4 (s, 1H, H_{bridge}). $^{13}C\{^{1}H\}$ NMR (CD_3COCD_3): δ= 141.7 (C_{ipso} of C_6H_5), 128.0, 126.6, 126.1 (C_6H_5), 45.5 (s, $HN(CH_3)_3$).^{11}B NMR (CD_3COCD_3): δ= -6.5 (d, ^{1}J (B,H) = 147, 1B), -8.0 (d, ^{1}J (B,H) = 148, 1B), -12.4 (s, 1B, B-I), -15.5 (d, ^{1}J (B,H) = 135, 1B), -17.2 (m, 1B, B-I), -18.2 (m, 2B, B-H), -34.5 (s, 2B, B-I, B(1,10)). MALDI-TOF-MS: m/z= 587 [M-I, 55%], 713 [M, 100%].

Synthesis of [$HNMe_3$][5,6,9-I_3-7,8-*nido*-$C_2B_9H_9$]

In a 100 mL round-bottom flask was placed a magnetic stir bar, [HNMe$_3$][5,6-I$_2$-7,8-*nido*-C$_2$B$_9$H$_{10}$] (508 mg, 1,14 mmol) and 20 mL of MeOH. A solution of I$_2$ (579 mg, 2,28 mmol, 2 eq) in 20 mL of MeOH was added to the reaction flask and the mixture was refluxed overnight. Addition of 10 mL of H$_2$O and subsequent evaporation of the MeOH/H$_2$O solvent resulted in the precipitation of a white solid from the aqueous layer. Recrystallization from boiling H$_2$O gave the desired compound [HNMe$_3$][5,6,9-I$_3$-7,8-*nido*-C$_2$B$_9$H$_9$] (84%, 548 mg). Elemental analysis for C$_5$H$_{19}$B$_9$I$_3$N: calc: C 10.51, H 3.35, N 2.45; found C 10.50, H 3.37, N 2.21. IR (KBr): ν= 3133 (s, ν(N-H)), 2591, 2565, 2539 (s, ν(B-H st.)), 1461 (w, ν(N-C)), 970. ^{1}H NMR (CD$_3$COCD$_3$): δ= 8.51(br t, ^{1}J(N,H)= 4.9, 1H, N-H), 3.23 (s, 9H, NH(C**H**$_3$)$_3$), 2.68 (br s, 1H, C$_c$-H), 2.30 (br s, 1H, C$_c$-H). ^{1}H{^{11}B} NMR (CD$_3$COCD$_3$): δ= 8.51(br t, ^{1}J(N,H)= 4.9, 1H, N-H), 3.23 (s, 9H, NH(C**H**$_3$)$_3$), 2.68 (br s, 1H, C$_c$-H), 2.55 (br s, B-**H**), 2.30 (br s, 1H, C$_c$-H), 1.87 (br s, B-**H**), 1.34 (d, ^{1}J(H,H)= 9, 1H, B(10)-**H**), 1.24 (s, 1H, B(1)-**H)**, -2.25 (t, ^{3}J(H,H)= 9, 1H, BHB). ^{13}C{^{1}H} NMR (CD$_3$COCD$_3$): 51.28-49.61 (br m, C$_c$), 45.51 (s, HN(**C**H$_3$)$_3$), 37,31-35.87 (br m, C$_{cluster}$). ^{11}B NMR (CD$_3$COCD$_3$): -12.6(br s, 2B), -15.7 (d, ^{1}J (B,H) = 167, 2B), -15.7 (s, 1B), -19.1 (d, ^{1}J (B,H) = 162, 1B), -23.2 (d, ^{1}J (B,H) = 136, 1B), -30.3 (s, 1B), 31.7 (d, ^{1}J (B,H) = 146, 1B). MALDI-TOF-MS: m/z= 510.87 [M, 100%].

Synthesis of [NMe$_4$][5,6-Me$_2$-7,8-*nido*-C$_2$B$_9$H$_{10}$]

To a solution of KOH (162 mg, 2.9 mmol) in degassed EtOH (4 mL) 9,12-Me$_2$-1,2-*closo*-C$_2$B$_{10}$H$_{10}$ (100 mg, 0.58 mmol) was added. The solution was refluxed for 20 h. After cooling down to room temperature, the solvent was removed under reduced pressure and the solid residue was dissolved in 5 mL of water. The solution was neutralized with HCl 1M. Afterwards, aqueous solution of [NMe$_4$]Cl was added dropwise until no more precipitate was formed. The white solid was rinsed with water and diethyl ether to give $[NMe_4][5,6\text{-}Me_2\text{-}7,8\text{-}$*nido*$\text{-}C_2B_9H_{10}]$ (77%, 106 mg). IR (KBr): ν= 3048, 3040 (s, $\nu_s(C_c\text{-}H)$), 2925, 2895, 2832 (w, $\nu(C_{alkyl}\text{-}H$ st.)), 2501, 2490 (s, ν(B-H st.)), 1482($\nu_s(N\text{-}CH_3)$), 945 (s, $\nu_{as}(CH_3)$). ${}_1$HNMR (CD_3COCD_3): 3.46 (s, 12H, $N(CH_3)_4$), 1.53 (br s, 2H; $C_{cluster}$-H), -0.04 (s, 6H, CH_3); ${}_1H\{{}_{11}B\}$ NMR (CD_3COCD_3): δ= 3.46 (s, 12H, $N(CH_3)_4$), 1.53 (br s, 2H; $C_{cluster}$-H), 1.96, 1.29, 0.37, 0.19 (br s, B-H), -0.04 (s, 6H, CH_3); -2.47 (d, ${}_1J(H,H)$= 9, 1H, H_{bridge}). ${}_{13}C\{{}_1H\}$ NMR (CD_3COCD_3): 37.62 (qu, ${}_1J(C,B)$= 25, C_c), 55.32 (s, $N(\mathbf{CH_3})_4$), 2.31-0.00 (br m, B-CH_3). ${}_{11}$B NMR (CD_3COCD_3): δ= -6.2 (s, 2B, B-CH_3, B(5,6)), -8.5 (d, ${}_1$J (B,H) = 131, 2B, B(9,11)), -17.2 (d, ${}_1$J (B,H) = 163, 1B, B(3)), -19.7 (d, ${}_1$J (B,H) = 145, 2B, B(2,4)), -27.5(d, ${}_1$J (B,H) = 130, 1B, B(10)), -32.8 (d, ${}_1$J (B,H) = 134, 1B, B(1)). MALDI-TOF-MS: m/z= 161.23 [M, 100%].

Synthesis of $[NBu_4][1,5,6,10\text{-}Me_4\text{-}7,8\text{-}$*nido*$\text{-}C_2B_9H_8]$

A stirred mixture of $8,9,10,12\text{-}Me_4\text{-}1,2\text{-}$*closo*$\text{-}C_2B_{10}H_8$ (150 mg, 0.74 mmol) and Bu_4NF hydrate (978 mg, 3.74 mmol) in THF (10 mL) was heated under reflux for 4 hours. After cooling, the solvent was removed. The solid was dissolved in dichloromethane, washed with water (100 mL), dried over $MgSO_4$ and the solvent vaccum removed. The resulting oil was washed with hexane to give $[NBu_4][1,5,6,10\text{-}Me_4\text{-}7,8\text{-}$*nido*$\text{-}C_2B_9H_8]$ as a white solid (298 mg, 92%). IR (KBr): ν= 2964, 2933, 2895, 2877, 2831 (s, $\nu(C_{alkyl}\text{-}H)$), 2527, 2496 (s, ν(B-H st.)), 1471, 974 (w, ν(N-C)). ${}_1$H NMR (CD_3COCD_3): δ= 3.45 (t, ${}_3J(H,H)$ =9, 8H, $(CH_3CH_2CH_2C\mathbf{H}_2)_4N$), 1.83 (m, ${}_3J(H,H)$= 9, 8H, $(CH_3CH_2C\mathbf{H}_2CH_2)_4N$), 1.46 (m, ${}_3J(H,H)$=6, 8H, $(CH_3C\mathbf{H}_2CH_2CH_2)_4N$), 0.99 (t, ${}_3J(H,H)$ =6, 12H, $(C\mathbf{H}_3CH_2CH_2CH_2)_4N$), 0.05 (br s, 3H, $C\mathbf{H}_3$), -0.29 (br s, 9H, $C\mathbf{H}_3$). ${}_1H\{{}_{11}B\}$ NMR (CD_3COCD_3): δ= 3.45 (t, ${}_3J(H,H)$ =9, 8H, $(CH_3CH_2CH_2C\mathbf{H}_2)_4N$), 1.84 (m, ${}_3J(H,H)$= 9, ${}_3J(H,H)$=6, 8H,

$(CH_3CH_2C\mathbf{H}_2CH_2)_4N$), 1.73 (br s, 2H, B-H), 1.46 (m, ^3J(H,H)= 9, ^3J(H,H)=6, 8H, $(CH_3C\mathbf{H}_2CH_2CH_2)_4N$),1.13 (br s, 3H, B-H), 0.99 (t, ^3J(H,H) =6, 12H, $(C\mathbf{H}_3CH_2CH_2CH_2)_4N$), 0.05 (s, 3H, $C\mathbf{H}_3$), -0.28 (s, 6H, $C\mathbf{H}_3$), -0.31 (s, 3H, $C\mathbf{H}_3$), -1.87 (s, 1H, H_{bridge}). $^{13}C\{^1H\}$ NMR (CD_3COCD_3): 58.5 (s, $CH_3CH_2CH_2\mathbf{C}H_2)_4N^+$), 37.81 (m, $\mathbf{C}_cH$), 23.5 (s, $CH_3CH_2\mathbf{C}H_2CH_2)_4N^+$), 19.4 (s, $CH_3\mathbf{C}H_2CH_2CH_2)_4N^+$), 12.9 (s, $\mathbf{C}H_3\mathbf{C}H_2CH_2CH_2)_4N^+$), -0.6/-1.9 (br s, $B\mathbf{C}H_3$). ^{11}B NMR (CD_3COCD_3): δ= -6.6 (s, 2B, B-CH_3), -8.7 (d, ^1J (B,H) = 132, 2B), -18.0 (d, ^1J (B,H) = 173, 1B), -19.9 (d, ^1J (B,H) = 155, 2B), -22.6 (s, 1B, B-CH_3), -27.0 (s, 1B, B-CH_3). MALDI-TOF-MS: m/z= 190,29 [M, 100%].

Synthesis of [NHMe$_3$][3,3'-Co-(9-I-1,2-*closo*-C$_2$B$_9$H$_{10}$)$_2$]

The same procedure as for the obtaining of compound [NMe$_4$][3,3'-Co-(1-Me-9,12-I$_2$-1,2-*closo*-C$_2$B$_9$H$_8$)$_2$] was followed. The used reactants quantities were: [HNMe$_3$][5-I-7,8-*nido*-C$_2$B$_9$H$_{11}$] (8.2 mg, 0.45 mmol), THF (10mL), solution of butyllithium in hexanes (0.98 mL, 1.4M, 1.37 mmol), CoCl$_2$ (356.8 mg, 2.74 mmol), 10mL of diethyl ether, 10mL of HCl (37%, 0.25M) aqueous solution. The final orange solid [NHMe$_3$][3,3'-Co-(9-I-1,2-*closo*-C$_2$B$_9$H$_{10}$)$_2$] was obtained with a yield of 74% (130 mg). Elemental analysis for $C_7H_{30}B_{18}CoI_2N$: calc: C 13.23, H 4.76, N 2.20; found C 13.18, H 4.97, N 2.31. IR (ATR): ν= 3022 (s, $\nu_s(C_{cluster}$-H)), 2955, 2924, 2855 (s, $\nu_s(C_{alkyl}$-H), 2545 (vs, ν_s(B-H)), 1473 (ν_s(**N-C**H3)). ^1H NMR (CD_3COCD_3): δ= 4.26 (br s, 2H, $C_{cluster}$-*H*), 4.16 (br s, 2H, $C_{cluster}$-*H*), 3.09 (s, 9H, NH(C*H*$_3$)$_3$). $^1H\{^{11}B\}$ NMR (CD_3COCD_3): δ= 4.26 (br s, 2H, $C_{cluster}$-*H*), 4.16 (br s, 2H, $C_{cluster}$-*H*), 3.09 (s, 9H, NH(C*H*$_3$)$_3$), 3.95-1.62 (s, 16H, B-*H*). $^{13}C\{^1H\}$ NMR (CD_3COCD_3): δ= 67.15 (*C*$_{cluster}$), 44.8 (s, HN(CH_3)$_3$)). ^{11}B NMR (CD_3COCD_3): δ= 7.3 (d,

^{1}J(B,H)=147, 2B), 4.0 (d, ^{1}J(B,H)=143, 2B), -4.4 (d, 8B, ^{1}J(B,H)=105), -16.9 (s, 4B), -21.9 (d, 2B, ^{1}J(B,H)=166). MALDI-TOF MS: *m/z*= 575.8 [M, 100%].

Synthesis of [NMe$_4$][3,3’-Co-(4-I-1,2-*closo*-C$_2$B$_9$H$_{10}$)$_2$]

The same procedure as for the obtaining of compound [NMe$_4$][3,3’-Co-(1-Me-9,12-I$_2$-1,2-*closo*-C$_2$B$_9$H$_8$)$_2$] was followed. The crude of reaction was refluxed for 36 hours. The used reactants quantities were: [HNMe$_3$][9-I-7,8-*nido*-C$_2$B$_9$H$_{11}$] (400 mg, 1.26 mmol), THF (20 ml), solution of K*t*BuO in THF (7.6 ml, 1M, 7.6mmol), CoCl$_2$ (1313mg, 10.11mmol), 10ml of THF, 10ml of HCl (37%, 0.25M) aqueous solution. The final orange solid compound, [NMe$_4$][3,3’-Co-(4-I-1,2-*closo*-C$_2$B$_9$H$_{10}$)$_2$] was obtained with a yield of 62% (260 mg), after purification on silica gel column chromatography, using CH$_2$Cl$_2$ for elution. Elemental analysis for C$_8$H$_{32}$B$_{18}$CoI$_2$N: calc: C 14.79, H 4.96, N 2.16; found C 14.54, H 4.97, N 2.31. IR (ATR): ν= 3029 (s, ν_s(C$_{cluster}$-H)), 2959, 2929 (s, ν_s(C$_{alkyl}$-H), 2537 (vs, ν_s(B-H)), 1473 (ν_s(**N-C**H3)). ^{1}H NMR (CD$_3$COCD$_3$): δ= 4.69 (s, 2H, C$_{cluster}$*H*), 4.50 (br s, 4H, C$_{cluster}$*H*), 4.04 (s, 2H, C$_{cluster}$*H*), 3.47 (s, 12H, N(C*H*$_3$)$_4$). ^{1}H{^{11}B} NMR (CD$_3$COCD$_3$): δ= 4.69 (s, 2H, C$_{cluster}$*H*), 4.50 (br s, 4H, C$_{cluster}$*H*), 4.04 (s, 2H, C$_{cluster}$*H*), 3.70 (s, 1H, B-H) 3.47 (s, 12H, N(C*H*$_3$)$_4$), 3.05-1.89 (s, 15H, B-*H*). ^{13}C{^{1}H} NMR (CD$_3$COCD$_3$): δ= 59.33 (*C*$_{cluster}$), 55.68 (s, N(CH$_3$)$_4$)). ^{11}B NMR (CD$_3$COCD$_3$): δ= 11.2 (d, ^{1}J(B,H)=139), 7.8 (d, ^{1}J(B,H)=141), 4.1 (d, ^{1}J(B,H)=144), -0.6 (d, ^{1}J(B,H)=113), -1.8 (d, ^{1}J(B,H)=110), -2.7 (d, ^{1}J(B,H)=95), -3.9 (d, ^{1}J(B,H)=135), -11.1 (d, ^{1}J(B,H)=191), -13.2 (d, ^{1}J(B,H)=86), -13.8 (s, 2B, B-I), -15.1 (br s), -16.2 (d, ^{1}J(B,H)=110), -21.1 (d, ^{1}J(B,H)=75). MALDI-TOF MS: *m/z*= 574.8 [M, 100%].

Synthesis of [NMe$_4$][3,3’-Co-(1-Me-9,12-I$_2$-1,2-*closo*-C$_2$B$_9$H$_8$)$_2$] To a stirring solution of [HNMe$_3$][7-Me-5,6-I$_2$-7,8-*nido*-C$_2$B$_9$H$_9$] (120 mg, 0.25 mmol) in THF (10 ml) cooled to 0 ºC in an ice-water bath was added, dropwise, a solution of K*t*BuO in THF (1.3ml, 1M, 1.26mmol). In parallel a $CoCl_2$ (165mg, 01.26mmol) solution in THF (5ml) was prepared. The solution was then transferred via a syringe over the initial reaction mixture, previously cooled to 0 ºC. The resulted mixture was heated to reflux for 6 hours. The solvent was then removed under reduced pressure. 10ml of diethyl ether and 10ml of HCl (37%, 1M) aqueous solution were then added to the residue. The mixture was hardly shaken and the two layers were separated. The organic layer was separated from the mixture and the aqueous layer was extracted with diethyl ether (3 x 10ml). The combined organic phase was dried over $MgSO_4$, filtered and the solvent removed under reduce pressure. Afterwards, an aqueous solution of $[NMe_4]Cl$ was added dropwise until no more precipitate was formed. The orange solid was filtered and rinsed with water to give $[NMe_4]$[3,3'-Co-(1-Me-9,12-I_2-1,2-*closo*-$C_2B_9H_8)_2$] (165 mg, 70%). Elemental analysis for $C_{10}H_{34}B_{18}CoI_4N$: calc: C 12.92, H 3.69, N 1.51; found C 12.52, H 3.59, N 1.20. IR (KBr): ν= 3020 (C_c-H), 2922, 2853 (C_{alkyl}-H), 2577 (B-H), 1479 (N-CH_3). $^1H(CD_3COCD_3)$: δ= 3.45 (N(C*H*$_3)_4$), 2.42 (s, 3H, $C_{cluster}$-CH_3), 2.29 (s, 3H, $C_{cluster}$-CH_3)). $^1H\{^{11}B\}$ NMR (CD_3COCD_3): δ= 3.76-1.71 (m, B-*H*), 3.48 (s, 12H, N(C*H*$_3)_4$), 2.42 (s, 3H, $C_{cluster}$-CH_3), 2.29 (s, 3H, $C_{cluster}$-CH_3)). $^{13}C\{^1H\}$ NMR (CD_3COCD_3): δ= 65.47 (*C*$_{cluster}$-CH_3), 55.52 (N(*C*H$_3)_4$), 54.13 (*C*$_{cluster}$-H), 22.45 (CH_3). ^{11}B NMR (CD_3COCD_3): δ= 8.9, 5.0, -2.7, -4.2 (m, B-H), -8.8, -12.9, -14.9 (m, B-I). MALDI-TOF MS: *m/z*= 1117.6 [M+2I, 47%], 990.1 [M+I, 100%], 862.6 [M, 88%].

Synthesis of $[NMe_4]$[3,3'-Co-(1-Ph-9,12-I_2-1,2-*closo*-$C_2B_9H_8)_2$]

The same procedure as for the obtaining of compound $[NMe_4]$[3,3'-Co-(1-Me-9,12-I_2-1,2-*closo*-$C_2B_9H_8)_2$] was followed. The used reactants quantities were: $[HNMe_3]$[7-Ph-5,6-I_2-

7,8-*nido*-$C_2B_9H_9$] (200 mg, 0.39 mmol), THF (10 ml), solution of K*t*BuO in THF (1.95 ml, 0.195 mmol), $CoCl_2$ (254 mg, 1.95 mmol), 5ml of THF, 10ml of HCl (37%, 0.25M) aqueous solution. The final orange solid compound, [NMe_4][3,3'-Co-(1-Ph-9,12-I_2-1,2-*closo*-$C_2B_9H_8$)$_2$] was obtained with a yield of 71% (295 mg). Elemental analysis for $C_{20}H_{38}B_{18}CoI_4N$: calc: C 22.80, H 3.64, N 1.33; found C 22.58, H 3.84, N 1.32. IR (KBr): ν= 3027 (C_c-H), 2951, 2923, 2854 (C_{alkyl}-H), 2558 (B-H), 1479 (**N-C**H_3). $_1$H NMR (CD_3COCD_3): δ= 7.66-7.14 (m, 10H, C_6H_5), 4.63 (s, 2H, $C_{cluster}$-H), 3.47 (N(C*H*$_3$)$_4$). $_1$H{$_{11}$B} NMR (CD_3COCD_3): δ= 7.66-7.14 (m, 10H, C_6H_5), 4.80-1.53 (m, B-H), 4.63 (s, 2H, $C_{cluster}$-H), 3.47 (N(C*H*$_3$)$_4$). $_{13}$C{$_1$H} NMR (CD_3COCD_3): δ= 141.45, 140.70 (C_{ipso} of C_6H_5), 129.15, 128.45, 127.97, 127.29, 125.59, 122.88 (C_6H_5), 71.29 (*C*$_{cluster}$-C_6H_5), 55.46 (N(*C*H_3)$_4$), 53.94, 50.59 (*C*$_{cluster}$-H). $_{11}$B NMR (CD_3COCD_3): δ= 9.4, 5.6, -3.7, -9.4 (m, B-H), -14.6 (s, B-I). MALDI-TOF MS: *m/z*= 1115.8 [M+I, 17%], 988.2 [M, 100%], 860.8 [M-I, 17%].

Synthesis of [NMe_4][3,3'-Co-(4,7-I_2-1,2-*closo*-$C_2B_9H_9$)$_2$]

The same procedure as for the obtaining of compound [NMe_4][3,3'-Co-(1-Me-9,12-I_2-1,2-*closo*-$C_2B_9H_8$)$_2$] was followed. The used reactants quantities were: [$HNMe_3$][9,11-I_2-7,8-*nido*-$C_2B_9H_{10}$] (200 mg, 0.63 mmol), THF (20 ml), solution of K*t*BuO in THF (3.8ml, 1M, 3.8mmol), $CoCl_2$ (656mg, 5.05mmol), 10ml of THF, 10ml of HCl (37%, 0.25M) aqueous solution. The final orange solid compound, [NMe_4][3,3'-Co-(4,7-I_2-1,2-*closo*-$C_2B_9H_9$)$_2$] was obtained with a yield of 57% (350 mg), after purification on silica gel column chromatography, using CH_2Cl_2 for elution. Elemental analysis for $C_8H_{30}B_{18}CoI_4N$: calc: C 10.66, H 3.35, N 1.55; found C 10.76, H 3.21, N 1.43. IR (ATR): ν= 3018 (s, $ν_s$($C_{cluster}$-H)), 2955, 2922, 2858 (s, $ν_s$(C_{alkyl}-H), 2564 (vs, $ν_s$(B-H)), 1478 ($ν_s$(**N-C**H3)). $_1$H NMR

(CD_3COCD_3): δ= 4.83 (s, 2H, $C_{cluster}$*H*), 4.73 (s, 2H, $C_{cluster}$*H*), 3.47 (s, 12H, N(C*H*$_3$)$_4$). $^{1}H\{^{11}B\}$ NMR (CD_3COCD_3): δ= 4.83 (s, 2H, $C_{cluster}$*H*), 4.73 (s, 2H, $C_{cluster}$*H*), 3.47 (s, 12H, N(C*H*$_3$)$_4$), 3.06-2.30 (s, 14H, B-*H*). $^{13}C\{^{1}H\}$ NMR (CD_3COCD_3): δ= 63.17 (*C*$_{cluster}$), 55.25 (s, $N(CH_3)_4$)). ^{11}B NMR (CD_3COCD_3): δ= 14.9 (d, ^{1}J(B,H)=145), 4.7 (d, ^{1}J(B,H)=137), 3.4 (d, ^{1}J(B,H)=138), -0.8 (d, ^{1}J(B,H)=147), -9.1 (d, B-H + 2B-I), -11.4 (d, B-H), -12.9 (s, 2B-I), -20.6 (d, ^{1}J(B,H)=162). MALDI-TOF MS: *m/z*= 827.9 [M, 100%], 702 [M-1, 39%], 576 [M-2I, 27%].

Synthesis of $[NMe_4][3,3'\text{-}Co\text{-}(1\text{-}Me\text{-}8,9,10,12\text{-}I_4\text{-}1,2\text{-}\mathit{closo}\text{-}C_2B_9H_6)_2]$

The same procedure as for the obtaining of compound $[NMe_4][3,3'$-Co-(1-Me-9,12-I_2-1,2-*closo*-$C_2B_9H_8)_2]$ was followed. The used reactants quantities were: $[HNMe_3][7$-Me-1,5,6,10-I_4-7,8-*nido*-$C_2B_9H_7]$ (60 mg, 0.08 mmol), THF (5 ml), solution of butyllithium in hexane (0.105ml, 1.6M, 0.168mmol), $CoCl_2$ (32.8g, 0.253mmol), 10ml of diethyl ether, 10ml of HCl (37%, 0.25M) aqueous solution. The final orange solid compound, $[NMe_4][3,3'$-Co(1-Me-8,9,10,12-I_4-1,2-*closo*-$C_2B_9H_6)_2]$, was obtained with a yield of 65% *(64 mg).* Elemental analysis for $C_{10}H_{30}B_{18}CoI_8N$: calc: C 8.38, H 2.11, N 0.98; found C 8.21, H 2.36, N 1.04. IR (KBr): ν= 3022 (w, ν($C_{cluster}$-H)), 2952, 2924, 2853 (s, ν($C_{cluster}$-CH_3), ($N(CH_3)_4$)), 2590 (s, ν(B-H)). ^{1}H NMR (CD_3COCD_3): δ= 5.18 (s, 2H, $C_{cluster}$-H), 3.45 (s, 12H, $N(CH_3)_4$), 2.55 (s, 3H, $C_{cluster}$-CH_3). $^{1}H\{^{11}B\}$ NMR (CD_3COCD_3): δ= 5.18 (s, 2H, $C_{cluster}$-H), 4.25 (s, B-H), 3.45 (s, 12H, $N(CH_3)_4$), 2,93 (s, B-H), 2.84 (s, 3H, $C_{cluster}$-CH_3), 2.55 (s, 3H, $C_{cluster}$-CH_3). $^{13}C\{^{1}H\}$ NMR (CD_3COCD_3): δ= 69.77 ($C_{cluster}$-CH_3), 60.66 ($C_{cluster}$-H), 55.36 ($N(CH_3)_4$), 22.42 (CH_3). ^{11}B NMR (CD_3COCD_3): δ= -0.5, -1.3, -3.2, -4.9 (m, B-H), -7.4, -9.4 (m, 4B, B-I), -11.7, -13.2 (m, B-H). MALDI-TOF-MS: m/z= 1363 [M, 27%], 1237 [M-I, 10%], 837 [M-4I, 100%].

Synthesis of [NMe_4][3,3'-Co-(1-Ph-8,9,10,12-I_4-1,2-*closo*-$C_2B_9H_6$)$_2$]

The same procedure as for the obtaining of compound [NMe_4][3,3'-Co-(1-Me-9,12-I_2-1,2-*closo*-$C_2B_9H_8$)$_2$] was followed. The used reactants quantities were: [$HNMe_3$][7-Ph-1,5,6,10-I_4-7,8-*nido*-$C_2B_9H_7$] (100 mg, 0.12 mmol), THF (5 ml), solution of butyllithium in hexane (0.16ml, 1.6M, 0.258mmol), $CoCl_2$ (50.2g, 0.387mmol), 10ml of diethyl ether, 10ml of HCl (37%, 0.25M) aqueous solution. The final orange solid compound, [NMe_4][3,3'-Co(1-Ph-8,9,10,12-I_4-1,2-*closo*-$C_2B_9H_6$)$_2$], was obtained with a yield of 69% *(42 mg).* Elemental analysis for $C_{20}H_{34}B_{18}CoI_8N$: calc: C 15.43, H 2.20, N 0.90; found C 15.27, H 2.17, N 0.87. IR (KBr): ν= 3030 (w, ν($C_{cluster}$-H)), 2952, 2923, 2853 (s, ν(N(CH_3)$_4$), 2606 (s, ν(B-H). ^1H NMR (CD_3COCD_3): δ= 7.26-6.98 (m, 10H, C_6H_5), 5.71 (s, 2H, $C_{cluster}$-H), 3.45 (s, 12H, N(CH_3)$_4$). $^1H\{^{11}B\}$ NMR (CD_3COCD_3): δ= 7.26-6.98 (m, 10H, C_6H_5), 5.71 (s, 2H, $C_{cluster}$-H), 4.50 (s, B-H), 2.63 (s, B-H), 2.41 (s, B-H), 3.45 (s, 12H, N(CH_3)$_4$). $^{13}C\{^1H\}$ NMR (CD_3COCD_3): δ= 137.40 (C_{ipso} of C_6H_5), 129.93, 128.73, 128.12, 127.03, 126.63 (C_6H_5) 64.01 ($C_{cluster}$-H), 55.29 (N(CH_3)$_4$). ^{11}B NMR (CD_3COCD_3): δ= -1.89, -6.70, -11.30, -14.02 (m, 18B, B-H + B-I). MALDI-TOF-MS: m/z= 1486 [M, 17%], 1359 [M-I, 33%], 1232 [M-2I, 20%], 1104 [M-3I, 12%], 978 [M-4I, 16%], 840 [M-5I, 32%], 713 [M-6I, 100%].

Synthesis of [NMe_4][3,3'-Co-(4,9,12-I_3-1,2-*closo*-$C_2B_9H_8$)$_2$]

To a stirring solution of [$HNMe_3$][5,6,9-I_3-7,8-*nido*-$C_2B_9H_9$] (90mg, 0.15mmol) in THF (3 mL) was added, dropwise, a solution of potassium K*t*BuO in THF (0.94 mL, 1M, 0.94mmol). After 50 minute, the resulting solution was then transferred via a syringe onto a $CoCl_2$ anhydrous solution (122mg, 0.94 mmol) in THF (5mL), following which the reaction was heated to reflux overnight. After removal of the solvent, 10 mL of diethyl ether was added. This solution was extracted three times with 10 mL of diluted HCl (37%, 0.25M). The organic layer was separated and dried over anhydrous MgSO4. The solvent was removed, the product was redissolved in the minimum volume of water and an aqueous solution containing an excess of $[NMe_4]Cl$ was added to precipitate the product. The precipitate was collected by filtration and dried in vacuum. The final orange solid $[NMe_4][3,3'$-Co-$(4,9,12$-I_3-1,2-*closo*-$C_2B_9H_8)_2]$, was obtained with a yield of 83% (76 mg). Elemental analysis for $C_8H_{28}B_{18}CoI_6N$: calc: C 8.33, H 2.45, N 1.21; found C 8.41, H 2.26, N 1.23. IR (KBr): ν= 3019 (s, ν($C_{cluster}$-H)), 2947, 2918, 2855 (C_{alkyl}-H), 2589 (s, νs(B-H)), 1477 (νs(N-CH_3)), 941 (s, νas(CH_3)). ^{1}HNMR (CD_3COCD_3): δ= 5.8 (br s, $C_{cluster}$-H), 5.2 (s, $C_{cluster}$-H), 5.0(s, $C_{cluster}$-H), 4.5(s, $C_{cluster}$-H) 3.46 (s, 12H, $N(CH_3)_4$), $^1H\{^{11}B\}$ NMR (CD_3COCD_3): δ= 5.8 (br s, $C_{cluster}$-H), 5.2 (s, $C_{cluster}$-H), 5.0(s, $C_{cluster}$-H), 4.5 (s, $C_{cluster}$-H), 4.4, 3.9, 3.8, 2.6, 2.5, 2.0 (br s, B-H), 3.46 (s, 12H, $N(CH_3)_4$). $^{13}C\{^1H\}$ NMR (CD_3COCD_3): 59.0, 56.9 (s, $C_{cluster}$-H), 55.3(s, $(CH_3)_4$) ^{11}B NMR (CD_3COCD_3): δ= 12.0, 7.5 and -1.1(br s, 6B, B-H + B-I), -10.0,-10.7, -13.4, -14.1, -19.2 (br s, 12B, B-H + B-I). MALDI-TOF-MS: m/z= 695.7[M-3I, 46%], 953.8[M-I, 15%] 1079.8 [M, 100%], 1205.7[M+I, 15%].

Synthesis of $[NMe_4][3,3'$-Co-$(9,12$-Me_2-1,2-*closo*-$C_2B_9H_9)_2]$

A solution of $[NMe_4][3,3$-Co$(9,12$-I_2-1,2-*closo*-$C_2B_9H_9)_2]^-$ (300 mg, 0.33mmol) in THF (40 mL) was treated with methylmagnesium bromide (1.1 mL, 3.0 M in diethyl ether; 3.32 mmol) at -84^{o}C, forming a brown precipitate. The mixture was allowed to warm to room temperature and then $[PdCl_2(PPh_3)_2]$ (28.5 mg, 0.04 mmol) and CuI (9.57mg, 0.05 mmol) were added. The mixture was refluxed 15h. Twenty drops of water were then added to quench the excess Grignard reagent, and the solvent was removed in vacuum. The residue was extracted with diethyl ether, leaving some dark material, which was discarded and the combined organic layers were dried over anhydrous magnesium sulfate. The solvent was removed, the product was redissolved in the minimum volume of ethanol and an aqueous solution containing an excess of $[NMe_4]Cl$ was added to precipitate the product. The precipitate was collected by filtration and dried in vacuum. The solid was subjected to flash silica gel chromatography using the next solvent mixture methylene chloride:acetonitrile 7:4. The final orange solid compound, $[NMe_4][3,3\text{-}Co(9,12\text{-}Me_2\text{-}1,2\text{-}\textit{closo}\text{-}C_2B_9H_9)_2]$, was obtained with a yield of 77% *(*120 mg*)*. Elemental analysis for $C_{12}H_{42}B_{18}CoN$: calc: C 31.75, H 9.32, N 3.09; found C 32.66, H 8.63, N 3.23. IR (KBr): ν= 3040, 3029 (s, ν($C_{cluster}$-H)), 2933, 2897, 2830 (C_{alkyl}-H), 2541, 2516 (s, ν_s(B-H)), 1481 (ν_s(N-CH_3)), 945 (s, ν_{as}(CH_3)). $_1$HNMR (CD_3COCD_3): δ= 3.75 (s, 4H, $C_{cluster}$-H), 3.47 (s, 12H, $N(CH_3)_4$), 0.08 (s, 12H, BCH_3); $_1$H{$_{11}$B} NMR (CD_3COCD_3): δ= 3.75 (s, 4H, $C_{cluster}$-H), 3.47 (s, 12H, $N(CH_3)_4$), 3.17 (br s, 2H, B-*H*), 2.77 (br s, 2H, B-*H*), 2.66 (br s, 2H, B-H), 2.64 (br s, 2H, B-H), 1.53 (br s, 6H, B-H), 0.08 (s, 12H, BCH_3); $_{13}$C{$_1$H} NMR (CD_3COCD_3): δ= 55.7 (s, $(CH_3)_4$) 45.9 (s, $C_{cluster}$-H), 5.07-2.57 (br m, B-CH_3). $_{11}$B NMR (CD_3COCD_3): δ= 10.9 (d, $_1$J(B,H) = 137, 2B, B(8,8’)), 4.1 ((4BC+2BH) , B(9,9’,10,10’,12,12’), -3.7 (d, $_1$J (B,H) = 146, 4B, B(4,4’,7,7’)), -16.9 (d, $_1$J (B,H) = 148, 4B, B(5,5’,11,11’)), -22.1 (d, $_1$J (B,H) =164, 2B, B(6,6’)). MALDI-TOF-MS: m/z= 379.6 [M, 100%].

Synthesis of $[NMe_4][3,3'\text{-}Co\text{-}(8,9,10,12\text{-}Me_4\text{-}1,2\text{-}\textit{closo}\text{-}C_2B_9H_7)_2]$

To a stirring solution of $[NBu_4][1,5,6,10\text{-}Me_4\text{-}7,8\text{-}\textit{nido}\text{-}C_2B_9H_8]$ (100mg, 0.23mmol) in THF (6 mL) was added, dropwise, a solution of potassium K*t*BuO in THF (1.38 mL, 1M, 1.38mmol). After 20 minute, the resulting solution was then transferred via a syringe onto a $CoCl_2$ anhydrous solution (180mg, 1.38 mmol) in THF (5mL), following which the reaction was heated to reflux for 7h. After removal of the solvent, 10 mL of diethyl ether was added. This solution was extracted three times with 10 mL of diluted HCl (37%, 0.25M). The organic layer was separated and dried over anhydrous $MgSO_4$. The solvent was removed and the orange solid was flash-chromatographed over silica gel using ethyl acetate as eluent. The final orange solid compound, $[NBu_4][3,3\text{-}Co(8,9,10,12\text{-}Me_4\text{-}1,2\text{-}$*closo*-$C_2B_9H_7)_2]$, was obtained with a yield of 60% (47 mg). IR (KBr): ν= 2955, 2925, 2855 (C_{alkyl}-H), 2598, 2557, 2531 (s, ν_s(B-H)). ^{1}HNMR (CD_3Cl): δ= 4.00 (s, 4H, $C_{cluster}$-H), 3.16 (t, ^{3}J(H,H) = 6, 8H, $(CH_3CH_2CH_2CH_2)_4N$), 1.63 (m, ^{3}J(H,H) = 9, 8H, $(CH_3CH_2CH_2CH_2)_4N$), 1.48 (m, ^{3}J(H,H) = 6, 8H, $(CH_3CH_2CH_2CH_2)_4N$), 1.07 (t, ^{3}J(H,H) = 6, 12H, $(CH_3CH_2CH_2CH_2)_4N$), 0.09 (s, 6H, CH_3), 0.05 (s, 6H, CH_3), -0.19 (s, 12H, CH_3). ^{1}H{^{11}B} NMR (CD_3Cl): δ= 4.00 (s, 4H, $C_{cluster}$-H), 3.16 (t, ^{3}J(H,H) = 6, 8H, $(CH_3CH_2CH_2CH_2)_4N$), 2.27 (br s, B-H), 1.63 (m, ^{3}J(H,H) = 9, 8H, $(CH_3CH_2CH_2CH_2)_4N$), 1.48 (m, ^{3}J(H,H) = 6, 8H, $(CH_3CH_2CH_2CH_2)_4N$), 1.07 (t, ^{3}J(H,H) = 6, 12H, $(CH_3CH_2CH_2CH_2)_4N$), 0.09 (s, 6H, CH_3), 0.05 (s, 6H, CH_3), -0.19 (s, 12H, CH_3). ^{11}B NMR (CD_3Cl): δ= 12.8 (s, 2B, B-CH_3), 9.9 (s, 2B, B-CH_3), 1.9 (s, 4B, B-CH_3), -5.0 (d, ^{1}*J*(B,H) = 138), -17.2 (d, ^{1}*J*(B,H) = 135), -24.0 (d, ^{1}*J*(B,H) = 137). MALDI-TOF-MS: m/z= 422.4 [M-1Me, 43.7%], 436.4 [M, 100%], 450.4 [M+1Me, 51.5%].

Synthesis of Na $[NMe_4][3,3'\text{-}Co\text{-}(8,9,10,12\text{-}I_4\text{-}1,2\text{-}$*closo*-$C_2B_9H_7)_2]\cdot 2.5H_2O$

A freshly prepared solution of $Na[C_{10}H_8]$ (35 mg, 1.52 mmol) in THF (10 ml) was added over the $[NMe_4]^+$ salt of $[3,3'\text{-}Co\text{-}(8,9,10,12\text{-}I_4\text{-}1,2\text{-}$*closo*-$C_2B_9H_7)_2]^-$ (200 mg, 0.14 mmol) dissolved in THF (10 ml). The mixture was stirred at room temperature for 30 min. Next, the formed grey suspension was removed by filtration. After stripping off the solvent from the filtrate under reduced pressure, a brown solid powder was obtained. Naphthalene was removed by vacuum sublimation to give $[3,3'\text{-}Co\text{-}(8,9,10,12\text{-}I_4\text{-}1,2\text{-}$*closo*-$C_2B_9H_7)_2]^{2-}$ (180 mg). Elemental analysis for $C_8H_{26}B_{18}CoI_8NNa\cdot 2.5H_2O$: calc: C 6.51, H 2.10, N 0.96; found

C 6.42, H 2.14, N 0.94. ^{11}B NMR (CD_3COCD_3): δ= 28.4 (s, 2B), 20.7 (s, 6B), -55.1 (s, 4B), -95.7 (s, 6B). ^{1}H{^{11}B} NMR (CD_3COCD_3): δ= +45.98 (br s, $C_{cluster}$-*H*), 3.45 (s, $N(CH_3)_4$), -15.85 (s, B-*H*). IR (KBr): ν= 3396 (O-H), 3025 (C_c-H), 2923, 2853 (C_{alkyl}-H), 2587, 2535 (B-H), 1660, 1596 (H-O-H), 1475, 944 (**N-C**).

Electron paramagnetic resonance spectra (EPR) of I_8-[1]$_2$-in H_2O at 130 K (33 mM).

EPR spectra were obtained in an X-Band Bruker ELEXYS E500 spectrometer equipped with a TE102 microwave cavity, a Bruker variable temperature unit and a field frequency lock system Bruker ER 033 M. The signal to noise ratio of spectra was increased by accumulation of scans using the F/F lock accessory to guarantee large field reproducibility. Line positions were determined with an NMR Gaussmeter Bruker ER 035 M. The modulation amplitude was kept well below the line width, and the microwave power was well below saturation.

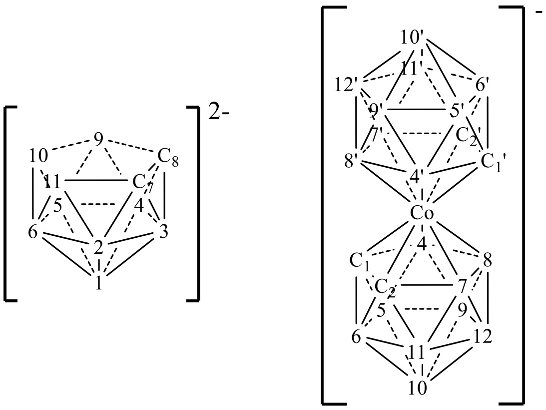
Computational Details

Calculations were performed using the Gaussian09 (revisión D01)[32] with the hybrid B3LYP functional[33] together with LANL2DZ basis set (Hay-Wadt effective core potentials for the iodine and cobalt atoms[34]). In order to improve the convergence of the Co^{2+} systems, the option of switching quadratic convergence algorithm and direct inversion in the iterative subspace (DIIS) method was employed. In the calculation of the redox potentials, in order to circumvent the problems to perform the calculation of the thermodynamic magnitudes (free energy) including solvent effects (polarizable conductor calculation model) a thermodynamic cycle was employed.[35] Thus, the free energy to calculate the redox potentials was estimated using the gas phase free energy difference between the oxidized and reduced species, while the solvation energies were calculated as the energy difference between the solvated and non-solvated molecules.

Acknowledgments

The authors are grateful to the following organizations for financial support: the Ministerio de Ciencia e Innovación (MICINN, project numbers CTQ2011-23862-C02-01 and CTQ2013-44670-R), the Generalitat de Catalunya (projects number 2014SGR149). M. Lupu thanks MICINN for FPU grant. M. Lupu and A. Zaulet are enrolled in the UAB PhD program.

Chart 1.- Icosahedral dianionic [7,8-*nido*-$C_2B_9H_{11}$]$^{2-}$ ligand and pristine monoanionic cobaltabisdicarbollide [3,3’-Co(1,2-*closo*-$C_2B_9H_{11}$)$_2$]$^{-}$ with their vertex numbering.



Scheme 1.- Syntheses of [3,3'-Co(9,12-I$_2$-1,2-*closo*-C$_2$B$_9$H$_9$)$_2$]$^-$ (I$_4$-[**1**]$^-$) and [3,3'-Co(9,12-(Me)$_2$-1,2-*closo*-C$_2$B$_9$H$_9$)$_2$]$^-$ (Me$_4$-[**1**]$^-$).

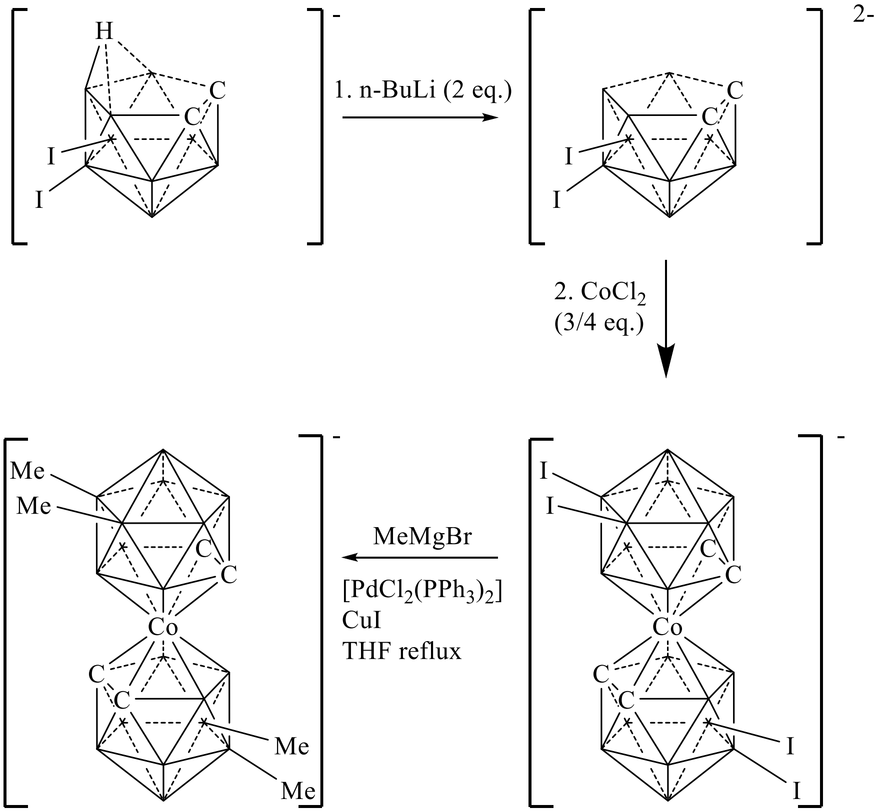


Table 1. $E_{1/2}(Co^{3+/2+})$ dependence upon the number and position of iodine substituent in platforms [**1**]$^-$, [**2**]$^-$ and [**3**]$^-$. $E_{1/2}$ as well as E_L(L) are given in Volts.

Compound	Substituents Position	$E_{1/2}$ *vs.* Fc^+/Fc	$\Delta E_{1/2}$ with respect to **[1]**$^-$	***E**L***(**L**)
[**1**]$^-$	-	-1,80	-	0.00
[**2**]$^-$	C_c-Me	-1,72	+ 0.08	+0.07
[**3**]$^-$	C_c-Ph	-1,66	+ 0.14	+0.12
I_4-[**1**]$^-$	B(9,9',12,12')	-1,15	+ 0.65	+0.56
I_4-[**2**]$^-$	B(9,9',12,12');C(1,1')	-1,03	+ 0.77	+0.66
I_4-[**3**]$^-$	B(9,9',12,12');C(1,1')	-1,00	+ 0.80	+0.69
I_8-[**1**]$^-$	B(8,8',9,9',10,10',12,12')	-0,68	+ 1.12	+0.96
I_8-[**2**]$^-$	B(8,8',9,9',10,10',12,12');C(1,1')	-0,61	+ 1.19	+1.02
I_8-[**3**]$^-$	B(8,8',9,9',10,10',12,12');C(1,1')	-0,54	+ 1.26	+1.09

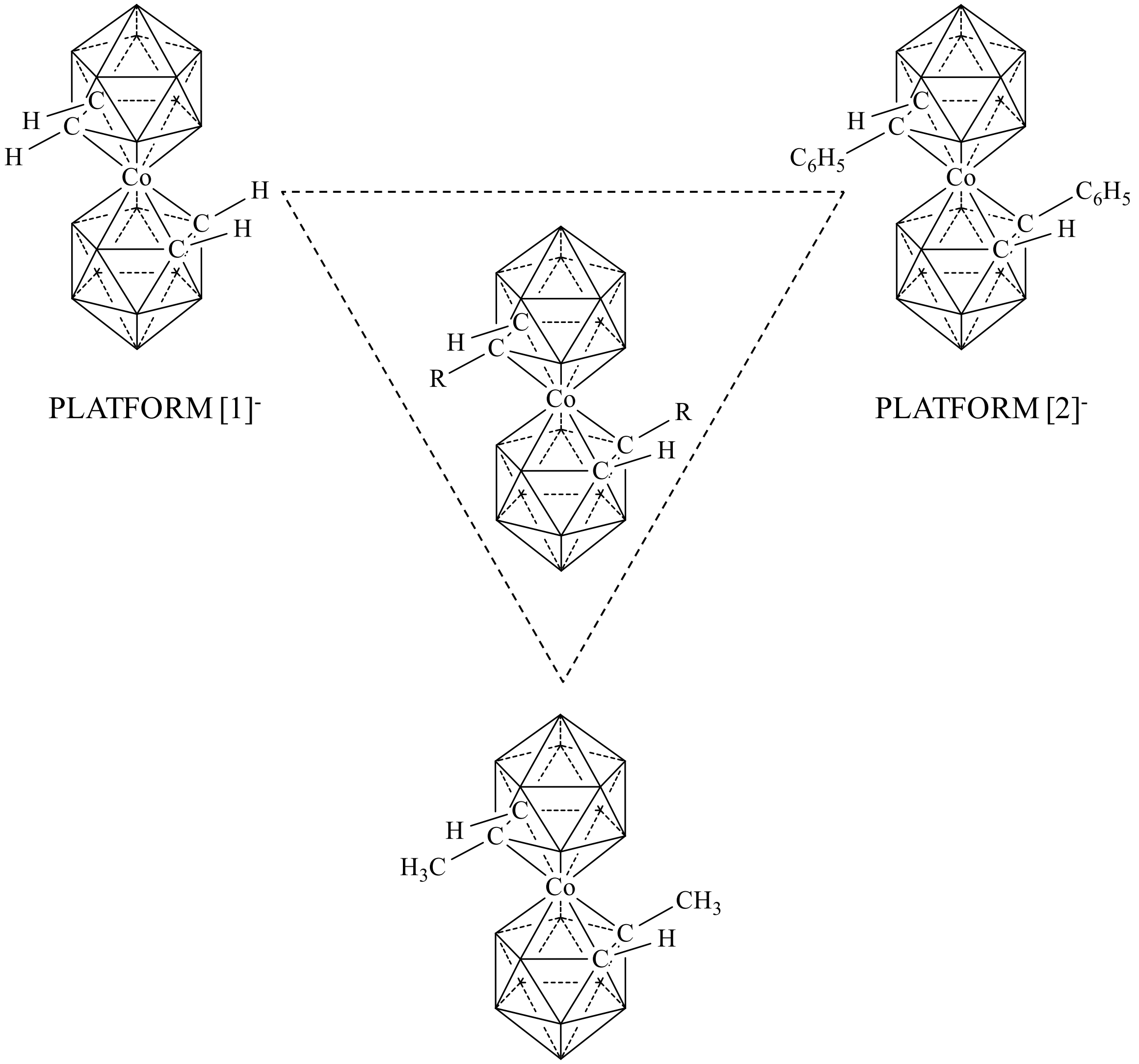
Table 2. $E_{1/2}(Co^{3+/2+})$ dependence upon the number and position of iodine substituents in platform [**1**]$^-$. $E_{1/2}$ are given in Volts.

Entry	**Compound**	**Substituent' Position**	**$E_{1/2}$ *vs.* *Fc*$^+$/*Fc***	**$\Delta E_{1/2}$ with respect to [1]$^-$**	***E_L*(L)**
1	Me_8-[**1**]$^-$	B(8,8',9,9',10,10',12,12')	-1,92	**- 0,12**	**-0.07**
2	Me_6-[**1**]$^-$	B(8,8',9,9',12,12')	-1,89	**- 0,09**	**-0.05**
3	Me_4-[**1**]$^-$	B(9,9',12,12')	-1,84	**- 0,04**	**-0.02**
4	Me_2-[**1**]$^-$	B(8,8')	-1,82	**- 0,02**	**-0.01**
5	Me-[**1**]$^-$	B(8)	-1,81	**- 0,01**	**0.00**
6	[**1**]$^-$	-	-1,80	**-**	**0.00**
7	I-[**1**]$^-$	B(8)	-1,50	**+ 0,30**	**+0.18**
8	I_2-[**1**]$^-$	B(9,9')	-1,46	**+ 0,34**	**+0.29**
9	I_2-[**1**]$^-$	B(8,8')	-1,32	**+ 0,48**	**+0.41**
10	I_2-[**1**]$^-$	B(4,4')	-1,24	**+ 0,56**	**+0.48**
11	I_4-[**1**]$^-$	B(9,9',12,12')	-1,15	**+ 0,65**	**+0.56**
12	I_4-[**1**]$^-$	B(4,4',7,7')	-0,77	**+ 1,03**	**+0.89**
13	I_6-[**1**]$^-$	B(8,8',9,9',12,12')	-0,82	**+ 0,98**	**+0.84**
14	I_6-[**1**]$^-$	B(4,4',9,9',12,12')	-0,80	**+ 1,00**	**+0.86**
15	I_8-[**1**]$^-$	B(8,8',9,9',10,10',12,12')	-0,68	**+ 1,12**	**+0.97**

Table 3. B3LYP calculated free energies (in a.u.) for the three optimized isomers (a, b and c in Figure 3) for the fifteen Co^{2+} and Co^{3+} compounds **1-15**. The values in parenthesis correspond to the free energy difference between the isomers (in kcal/mol) taking as reference the usually most stable c isomer. Only for the compound **12**, the c isomer is significantly less stable than the other two isomers due to the simultaneous 4,4',7,7' substitution on each C_2B_3 face.

	Co^{2+} a		**Co^{2+} b**		**Co^{2+} c**	**Co^{3+} a**		**Co^{3+} b**		**Co^{3+} c**
1	-1072.2653	(4.3)	-1072.2708	(0.8)	-1072.2721	-1072.2897	(4.7)	-1072.2976	(-0.3)	-1072.2972
2	-993.6799	(5.0)	-993.6867	(0.8)	-993.6879	-993.7010	(6.3)	-993.7093	(1.1)	-993.7111
3	-915.1049	(2.6)	-915.1065	(1.6)	-915.1091	-915.1257	(2.7)	-915.1301	(0.0)	-915.1300
4	-836.5090	(5.0)	-836.5137	(2.0)	-836.5169	-836.5270	(5.6)	-836.5349	(0.7)	-836.5360
5	-797.2175	(5.4)	-797.2238	(1.5)	-797.2261	-797.2398	(3.6)	-797.2435	(1.3)	-797.2455
6	-757.9246	(6.9)	-757.9327	(1.7)	-757.9355	-757.9485	(3.7)	-757.9523	(1.3)	-757.9544
7	-768.7472	(20.8)	-768.7798	(0.3)	-768.7803	-768.7722	(8.6)	-768.7808	(3.3)	-768.7860
8	-779.6126	(5.6)	-779.6174	(2.6)	-779.6216	-779.6103	(4.5)	-779.6151	(1.5)	-779.6174
9	-779.5996	(14.8)	-779.6112	(7.5)	-779.6232	-779.5915	(15.1)	-779.6082	(4.6)	-779.6155
10	-779.5908	(5.9)	-779.5938	(4.0)	-779.6001	-779.5855	(4.9)	-779.5846	(5.4)	-779.5932
11	-801.2783	(10.6)	-801.2912	(2.5)	-801.2952	-801.2649	(5.2)	-801.2709	(1.4)	-801.2731
12	-801.2415	(-6.5)	-801.2575	16.5)	-801.2311	-801.2161	(-5.3)	-801.2296	(-13.7)	-801.2076
13	-822.9299	(17.0)	-822.9443	(8.0)	-822.9570	-822.8902	(17.9)	-822.9101	(5.4)	-822.9187
14	-822.9267	(8.8)	-822.9332	(4.7)	-822.9406	-822.8903	(5.5)	-822.8909	(5.1)	-822.8991
15	-844.5851	(16.5)	-844.5996	(7.4)	-844.6113	-844.5352	(18.4)	-844.5552	(5.9)	-844.5646

Figure 1. Cobaltabisdicarbollide-based electroactive frameworks.



PLATFORM [1]$^-$

PLATFORM [2]$^-$

PLATFORM [3]$^-$

Figure 2. Rough approximation of the front view of the icosahedron cluster in a hexagonal representation.

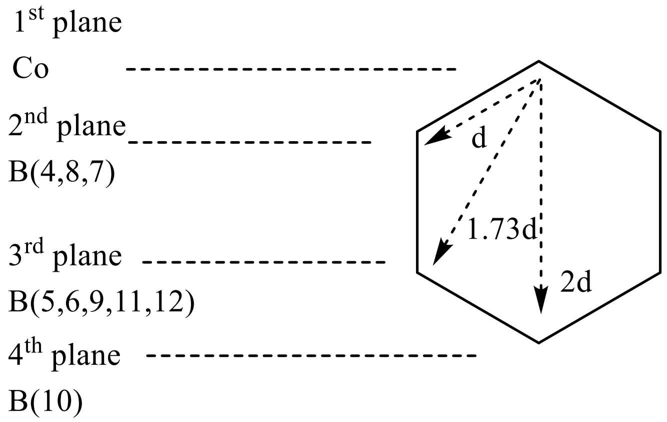
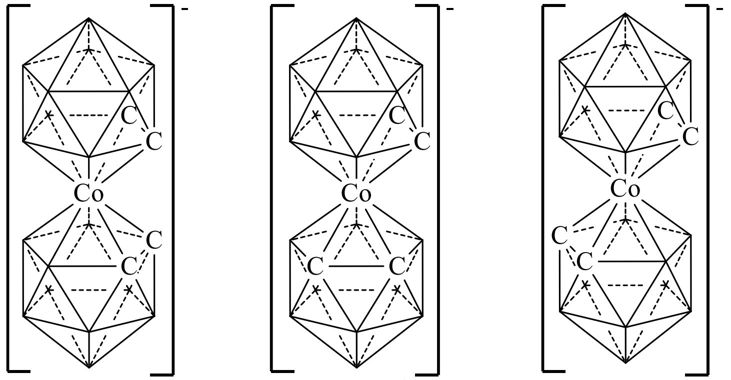


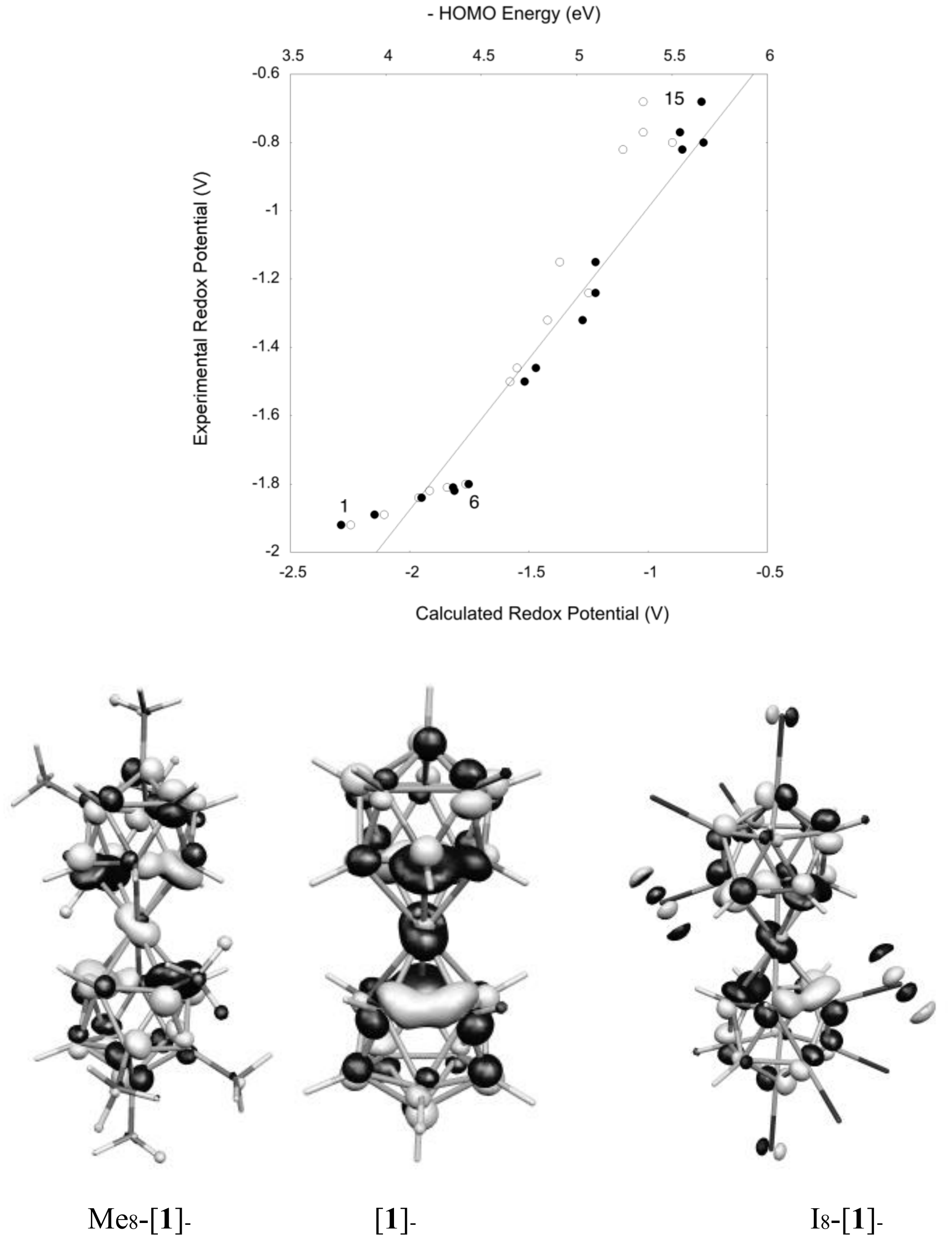
Figure 3.- Model structures of the three isomers studied for the fifteen complexes **1-15**.



Isomer a Isomer b Isomer c

Figure 4. (a) Dependence of the experimental redox potential for cobaltabisdicarbollide derivatives (1-15 entries in Table 2) with the DFT calculated values (black circles) and the -HOMO energies corresponding to the solvated molecule (white circles). (b) Representation of the HOMO orbitals corresponding to Me$_8$-[**1**]$^-$, [**1**]$^-$ and I$_8$-[**1**]$^-$ (entries 1, 6 and 15, respectively, in Table 2).

(a)



(b) Me$_8$-[**1**]$^-$ [**1**]$^-$ I$_8$-[**1**]$^-$

Figure 5. $^{11}B\{^{1}H\}$-NMR of the reduced form [3,3'-Co(8,9,10,12-I_4-1,2-*closo*-$C_2B_9H_7$)$_2$]$^{2-}$ (I_8-[**1**]$^{2-}$) in black *vs* the oxidized one [3,3'-Co(8,9,10,12-I_4-1,2-*closo*-$C_2B_9H_7$)$_2$]$^{-}$ (I_8-[**1**]$^{-}$) in red.

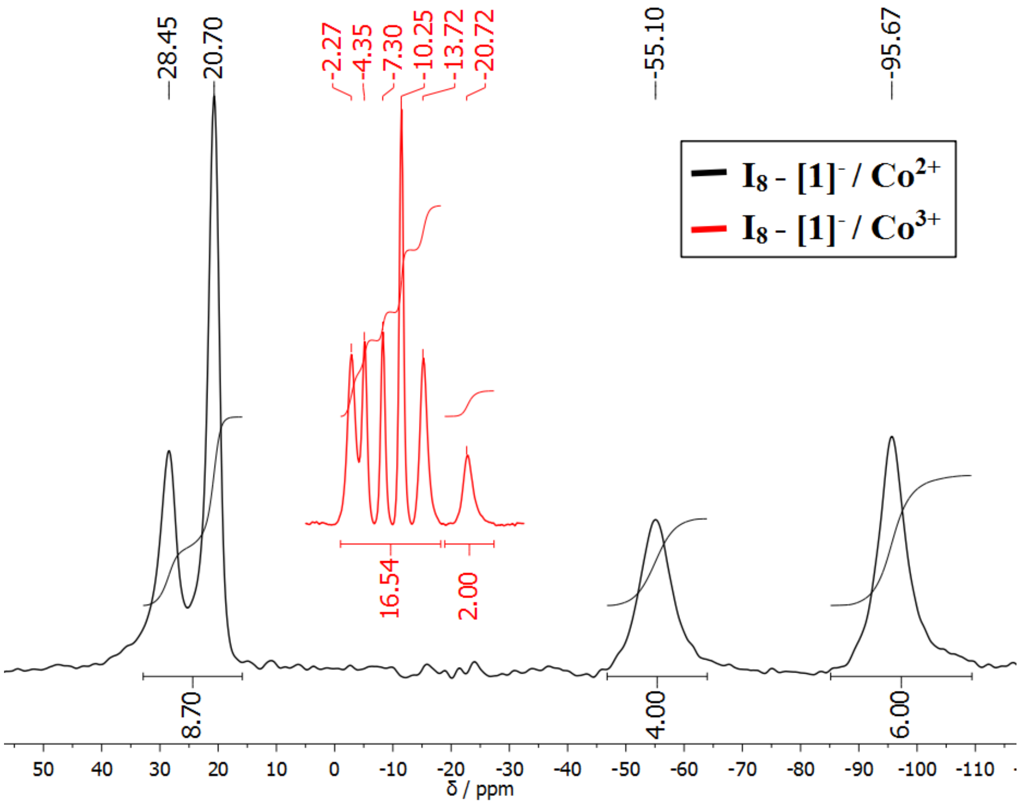


Figure 6.- Electron paramagnetic resonance spectra (EPR) of I_8-[**1**]$_2$-.

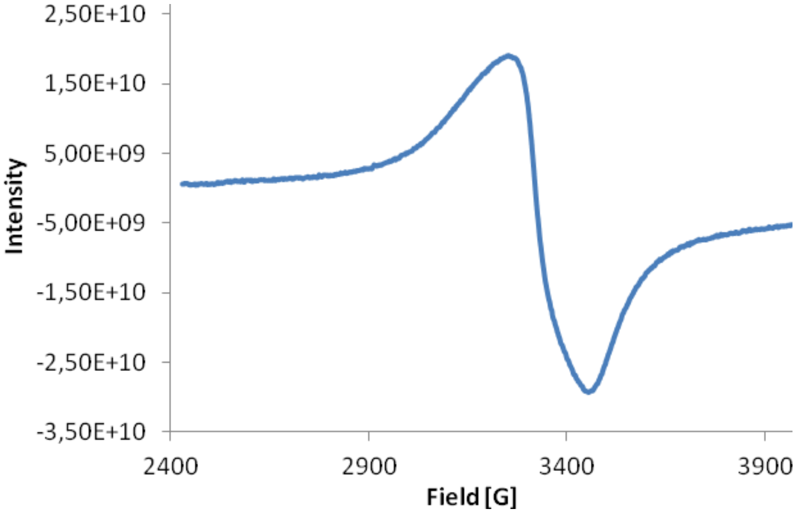
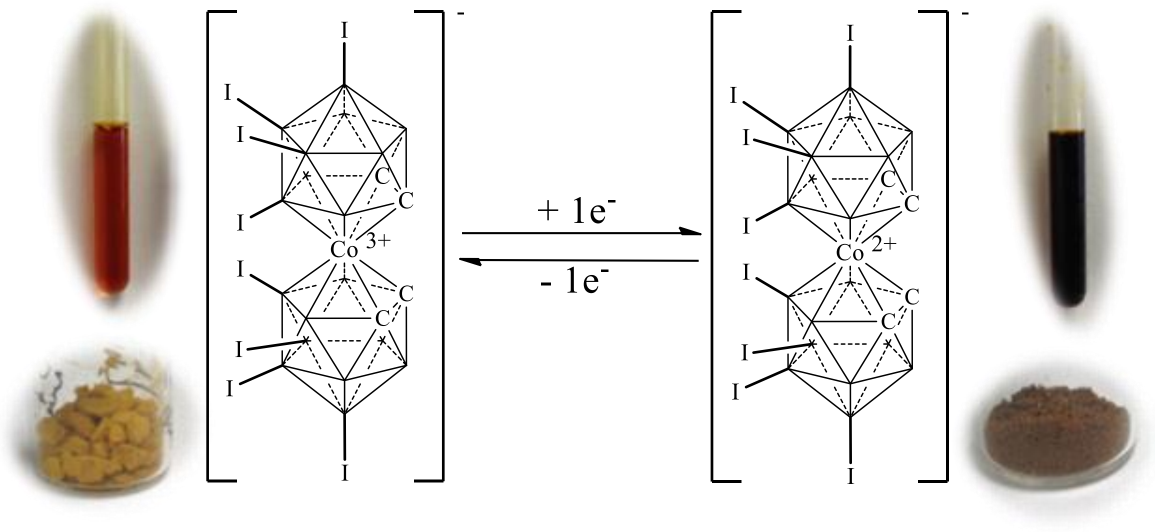


Figure 7. Air stability of both compounds in the couple [3,3’-Co(8,9,10,12-I_4-1,2-*closo*-$C_2B_9H_7$)$_2$]$_{-1}$/$_{-2}$.



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