

## **1.3 Volts Inorganic Sequential Redox Chain with an all Anionic Couple 1- /2- in a Single Framework**

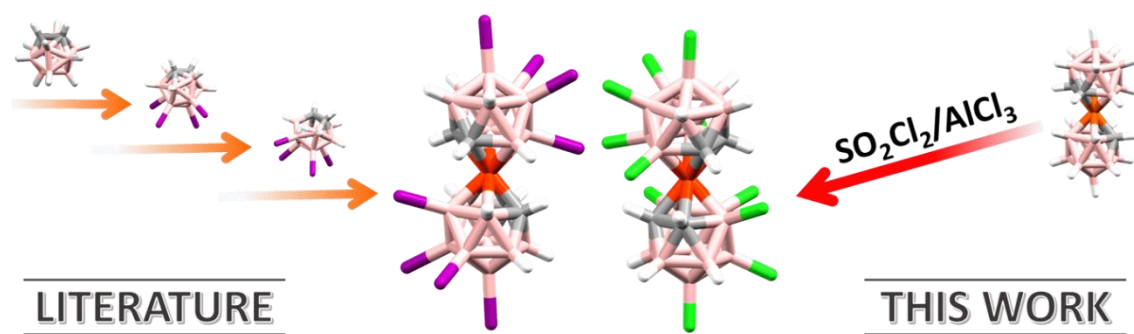
Ana B. Buades,<sup>a</sup> Clara Viñas,<sup>a</sup> Xavier Fontrodona<sup>b</sup> and Francesc Teixidor<sup>a,\*</sup>

<sup>a</sup> Institut de Ciència de Materials de Barcelona (ICMAB-CSIC), Campus UAB, 08193 Bellaterra, Spain.

<sup>b</sup> Dept. de Química and Serveis Tècnics de Recerca, Universitat de Girona, Campus de Montilivi, 17071 Girona, Spain.

Corresponding autor's email: [teixidor@icmab.es](mailto:teixidor@icmab.es)

TOC



## Abstract

The relatively low symmetry of  $[3,3'\text{-Co}(1,2\text{-C}_2\text{B}_9\text{H}_{11})_2]^-$  (**[1]**<sup>-</sup>), along with the high number of available substitution sites, 18 on the boron atoms and 4 on the carbon atoms, allows a fairly regioselective and stepwise chlorination of the platform and therefore a very controlled tuning of the electrochemical potential tuning. This is not so easy to find in other systems, e.g. Ferrocene. In this work, we show how a single platform with B and C in the ligand and only Co can produce a tuning of potentials in a stepwise manner in the 1.3 V range. The platform used is made of two icosahedra sharing one vertex. The  $E_{1/2}$  tuning has been achieved from **[1]**<sup>-</sup> by sequential chlorination which has given potentials whose value increases sequentially and linearly with the number of Chloro groups in the platform. **[Cl<sub>8</sub>-1]**<sup>-</sup>, **[Cl<sub>10</sub>-1]**<sup>-</sup>, and **[Cl<sub>12</sub>-1]**<sup>-</sup>, have been obtained, which are added to the existing **[Cl-1]**<sup>-</sup>, **[Cl<sub>2</sub>-1]**<sup>-</sup>, **[Cl<sub>4</sub>-1]**<sup>-</sup>, **[Cl<sub>6</sub>-1]**<sup>-</sup>, described earlier to give the 1.3 V range. It is envisaged to extend this range also sequentially by changing the metal from Co to Fe. The last successful synthesis of the highest chlorinated derivatives of cobaltabis(dicarbollide) dates back to 1982 and since then no more advances have been done toward more substituted metallacarborane chlorinated compound. The **[Cl<sub>8</sub>-1]**<sup>-</sup>, **[Cl<sub>10</sub>-1]**<sup>-</sup>, and **[Cl<sub>12</sub>-1]**<sup>-</sup> are made with an easy and fast method. The key point of the reaction is the use of the protonated form of  $[\text{Co}(\text{C}_2\text{B}_9\text{H}_{11})_2]^+$ , as a starting material and the use of sulphuryl chloride, a less hazardous and easier to use chlorinating agent. In addition, we present the complete, spectroscopic, crystallographic and electrochemical characterization, together with a study of the influence of the chlorination position in the electrochemical properties.

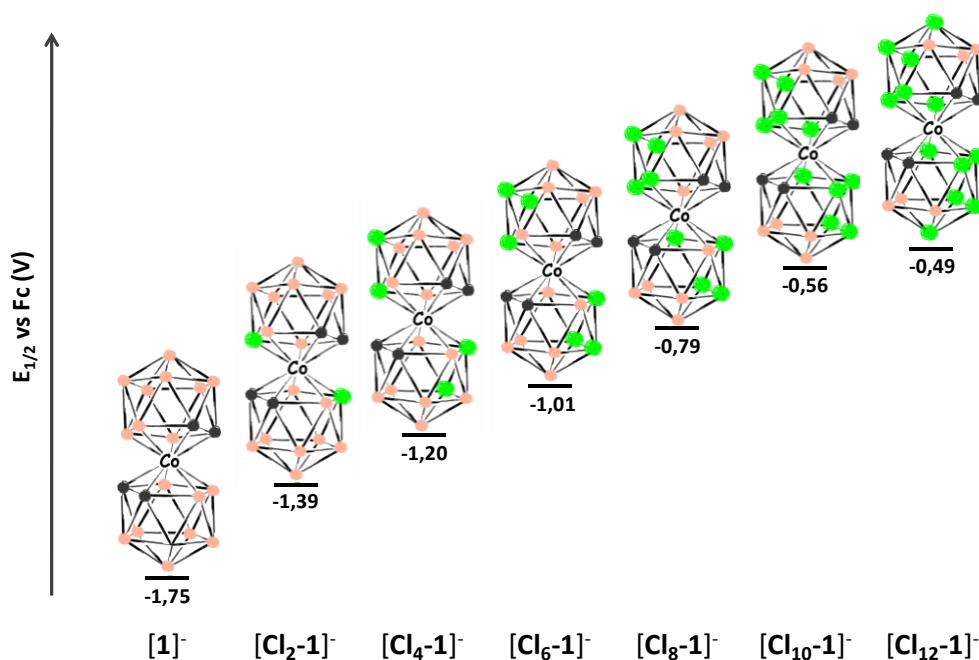
## Keywords

Potential tuning, Sequential potential, Metallacarborane, Cobaltabis(dicarbollide), Electron Transfer.

## Introduction

Redox reactions are key for life both in nature,<sup>1</sup> principally in respiration<sup>2</sup> and photosynthesis,<sup>3</sup> and in any device where electrons are the means to store, release or generate energy.<sup>4-11</sup>

In most of the redox reactions in industry to produce bulk materials or compounds, no fine-tuning of the reduction or oxidation power is sought. But this is not so when it is necessary to ensure the synergy with surrounding materials or compounds that can be affected by an excess of oxidizing or reducing power.  $E^\circ$  tuning of man-made reversible redox systems are largely based first on metals and second in ligands,<sup>18,19</sup> Please notice from this sentence that we emphasize metal based redox reversible systems. We will not deal on non-metal based systems as, for the case of boron clusters, these derived from  $[\text{CB}_{11}\text{H}_{12}]^-$ <sup>20</sup> or  $[\text{B}_{12}\text{H}_{12}]^{2-}$ <sup>21</sup>. It is important to point out that nature succeeds to get a wide range of potential with few metals, few coordinating elements, few ligands for the primary coordination spheres but requires the involvement of one or two extra spheres of influence to modulate  $E^\circ$ .<sup>15</sup> Some robust metal containing scaffolds have been developed on which to tune the redox potential by sequentially adding electron donor or accepting groups or  $\pi$  acceptors. Some of the more studied are due to ferrocene,<sup>22, 23</sup> or metal complexes, most commonly Ru, of polypyridyl ligands, e.g. bipyridine, 2,2'-bipyrimidine, 2,2'-bipyrazine, terpy, phenantroline, and others.<sup>24</sup> These have in common that are usually outer sphere ET octahedral complexes. A quite representative example of the type of  $E^\circ$  tuning in these complexes is given by the ferrocene  $[\text{FeC}_{10}\text{H}_{10-x}\text{Cl}_x]$  chloro derivatives for which brusque, as opposite of stepwise, numbers of chloro units exist, e.g. 10, 5, 2 and 1, which result in brusque  $E_{1/2}$  values, vs  $\text{Fc}^+/\text{Fc}$  of 1.24, 0.77, 0.31 and 0.17 V, respectively. Still, near 1V has been tuned on the same platform.<sup>25, 26</sup> All these complexes are positively charged, e.g.  $[\text{Fe}(\text{C}_5\text{Cl}_5)_2]^+$  or  $[\text{Ru}(\text{bpy})_3]^{2+}$ . Indeed, despite ligands are either negative or neutral, very few chemically stable and robust anionic complexes ready for  $E^\circ$  tuning are available. One could think on the couple  $[\text{Fe}(\text{CN})_6]^{3-/4-}$ , or on the POMs, e.g. keggin  $[\text{XW}_{12}\text{O}_{40}]^{n-}$ ,<sup>27</sup> however, these are difficult to be tuned although efforts are being done for POMs.<sup>28</sup>



**Figure 1.** E<sub>1/2</sub> scheme of the different chloro derivatives of cobaltabis(dicarbollide) in V. (B-H is represented with pink spheres, B-Cl with green and C-H with grey).

Thus, anionic metal containing scaffolds that allow easy tuning with a wide span of voltages are not common. And what could be the advantage of using anionic scaffolds? In our opinion, if the reduced form of the redox couple is negative, it will have an increased tendency to release an electron, and if the oxidized form is negative, it will have less appetite for an electron. And this can be easily spotted with the iodide/triiodide (I<sup>-</sup>/I<sub>3</sub><sup>-</sup>) redox couple in dye-sensitized solar cells in which both the oxidized and reduced partners are negative.<sup>10, 29, 30</sup> Cobalt,<sup>31</sup> Copper-based electrolytes,<sup>32</sup> thiolate/disulphide,<sup>33</sup> ferrocenium/ferrocene (Fc/Fc<sup>+</sup>),<sup>34</sup> hydroquinone/benzoquinone derivatives<sup>35</sup> and the redox couple TEMPO/TEMPO<sup>+</sup><sup>36</sup> all of them either have a partner whose charge is zero, or they have a partner with a + charge, or both partners have a + charge. The success of a DSSC cell relies on the electrons preferring to move through the external circuit to meet the counter electrode, rather than the electrons on the TiO<sub>2</sub> surface to recombine with the dye or the oxidized electrolyte.<sup>37</sup>

We have already indicated that is not simple to have metal-based robust redox couples based on a single scaffold that allow for wide range of potentials. In this work, we show that this is becoming possible with the anionic cobaltabis(dicarbollide) [3,3'-Co(1,2-C<sub>2</sub>B<sub>9</sub>H<sub>11</sub>)<sub>2</sub>]<sup>-</sup> scaffold (abbreviated as [1]<sup>-</sup>). This cluster displays interesting electrochemical and biological properties that have been thoroughly studied.<sup>38-40</sup> Several [1]<sup>-</sup> derivatives have been published with the aim to tailor its properties and find applications in many different fields of science. Some examples are neutron capture therapies,<sup>41, 42</sup> sensors,<sup>43</sup> anticancer therapies,<sup>44-48</sup> electron acceptors,<sup>49</sup> and electroactive electrolyte among others.

The relatively low symmetry of [3,3'-Co(1,2-C<sub>2</sub>B<sub>9</sub>H<sub>11</sub>)<sub>2</sub>]<sup>-</sup> ([1]<sup>-</sup>), along with a high number of available substitution sites allows a fairly regioselective and stepwise chlorination of the platform and therefore a very controlled tuning of the sought property, in this case potential tuning. Such characteristics are not so easy to find in other systems. On the other hand a higher symmetry as in many closo clusters leads more easily to persubstitution but with more difficulty to a step-by-step process.<sup>50</sup>

We present here the three highest chlorinated species of [3,3'-Co(1,2-C<sub>2</sub>B<sub>9</sub>H<sub>11</sub>)<sub>2</sub>]<sup>-</sup> ([1]<sup>-</sup>), that will be named [Cl<sub>8</sub>-1]<sup>-</sup>, [Cl<sub>10</sub>-1]<sup>-</sup>, and [Cl<sub>12</sub>-1]<sup>-</sup>, corresponding to the number of chloro substituents on the scaffold, that span the voltages from -1.75 for [1]<sup>-</sup> to -0.49 for [Cl<sub>12</sub>-1]<sup>-</sup>, vs Fc<sup>+</sup>/Fc in sequential chlorination steps, and very remarkably with very good electrochemical purity and high yield in simple one-pot reactions (see **Figure 1**). This series is the widest range of sequentially tunable potentials on a single metal containing anionic platform available today. And the range of potentials possible can be extended much further by keeping the same platform, changing the metal from cobalt to iron.

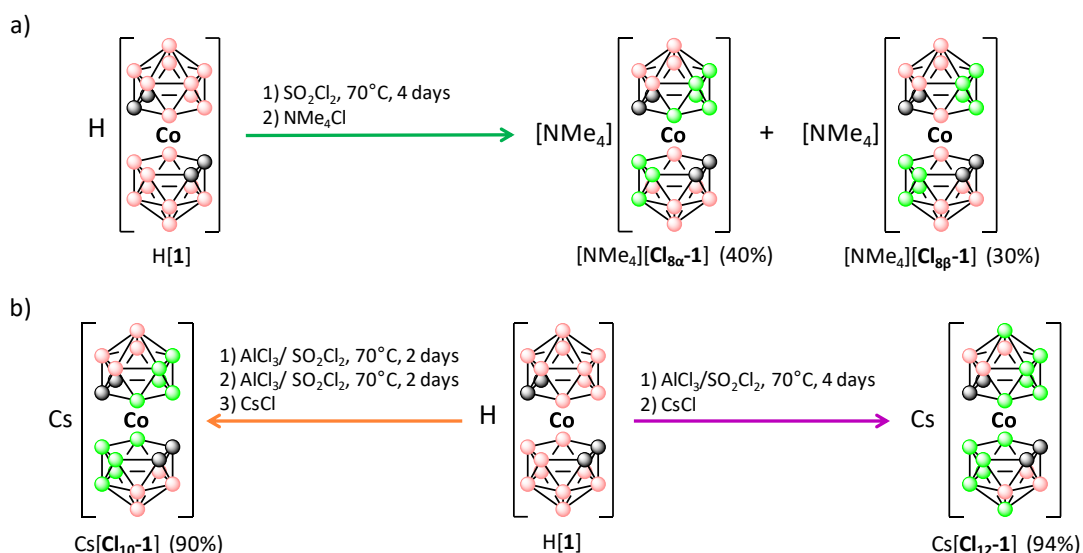
## Results and Discussion

**Synthesis** Since the synthesis of the first halogenated derivative of COSAN, the hexabromocobaltabis(dicarbollide),<sup>51</sup> many strategies have been devised to develop halo derivatives of [1]<sup>-</sup>. The most advanced since the date is the development of iodo derivatives of [1]<sup>-</sup>, whose methodology requires the build-up of the molecule from the components; so the

synthesis of  $[1,5,6,10\text{-I}_4\text{-}7,8\text{-C}_2\text{B}_9\text{H}_{10}]^-$ , followed by their complexation with  $\text{CoCl}_2$  yields  $[3,3'\text{-Co}(8,9,12,10\text{-I}_4\text{-}1,2\text{-C}_2\text{B}_9\text{H}_7)_2]^-$ , that is the halo derivative of cobaltabis(dicarbollide) with the highest number of halo substituents produced until now.<sup>52, 53</sup>

Chlorine gas was the most popular chlorinating agent for  $[\mathbf{1}]^-$ <sup>54-56</sup> being  $[3,3'\text{-Co}(8,9,12\text{-Cl}_3\text{-}1,2\text{-C}_2\text{B}_9\text{H}_8)_2]$ ,<sup>53</sup> the highest chlorinated  $[\mathbf{1}]^-$  obtained as a pure compound since 1982. In 1980 sulfuryl chloride was used as a source of chlorine and solvent in the synthesis of  $[\text{B}_9\text{Cl}_9]^{2-}$ .<sup>57</sup> Sulfuryl chloride is less hazardous, cheaper and easier to handle than chlorine gas and has been successfully applied as a chlorinating agent in organic chemistry.<sup>58, 59</sup> To achieve chlorination in boron clusters it was needed to solubilize the cesium and tetramethylammonium (the most common) salts of the different boron clusters but these are not fully soluble in sulfuryl chloride. In 2010 a step forward was achieved by mixing acetonitrile to the sulfuryl chloride to increase the solubility. This new method permitted the synthesis of  $[\text{B}_{12}\text{Cl}_{12}]^{2-}$  pure<sup>60</sup> and afterwards, the same methodology was used to obtain the hexachloroferrabisdicarbollide,<sup>61</sup> tetrachloro<sup>62</sup> and hexachlorocobaltabis(dicarbollide).<sup>63</sup> However we did not succeed to go beyond with this mixture, even after several days of refluxing and reposition of acetonitrile and sulfuryl chloride. Therefore, the combination of sulfuryl chloride with acetonitrile was not considered the best option. Instead, we have gone for  $\text{H}[\mathbf{1}]$  that is more soluble in neat sulfuryl chloride.<sup>64</sup> As sulfuryl chloride has a relatively low boiling point, 69°C, we aimed at increasing the reaction pressure to lower reaction times and increase the reaction temperature. Stainless steel autoclaves, even lined with Teflon, were proven not to be suitable as extensive damage was caused by the generated  $\text{Cl}_2$  at the autogenous pressure induced by external heating at 120°C. We then moved to thick-walled glass pressure tubes with Ace-Thred PTFE bushing and FETFE® O-ring. The O-rings were replaced every 4 experiments. These proved to be adequate for our purposes.

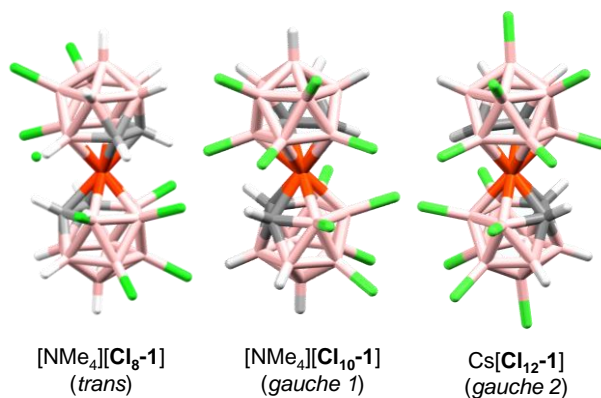
The reaction of  $\text{H}[3,3'\text{-Co}(1,2\text{-C}_2\text{B}_9\text{H}_{11})_2]$  with an excess of  $\text{SO}_2\text{Cl}_2$  (650 equiv.) in an ace pressure tube at 70°C for 4 days is a convenient route to synthesize the octachloro derivative presented as an isomeric mixture of  $[3,3'\text{-Co}(4,7,8,9,12\text{-Cl}_5\text{-}1,2\text{-C}_2\text{B}_9\text{H}_6)(8',9',12'\text{-Cl}_3\text{-}1',2'\text{-C}_2\text{B}_9\text{H}_8)]^-$  ( $[\text{Cl}_{8\alpha}\text{-}\mathbf{1}]^-$ ), and  $[3,3'\text{-Co}(4,8,9,12\text{-Cl}_4\text{-}1,2\text{-C}_2\text{B}_9\text{H}_7)_2]^-$  ( $[\text{Cl}_{8\beta}\text{-}\mathbf{1}]^-$ ) (**Figure 2a**). This turned out to be the maximum chlorination degree achievable by this method. Attempts to increase the chlorination degree by increasing the reaction time to a few weeks or use of higher temperatures did not lead to notable amounts of  $[\text{Cl}_9\text{-}\mathbf{1}]^-$  or  $[\text{Cl}_{10}\text{-}\mathbf{1}]^-$  derivatives. It was then proven that a convenient and easy method leading to constitutionally although not isomerically pure  $[\text{Cl}_8\text{-}\mathbf{1}]^-$  was available. To increase the number of chloro groups in the molecule, a Lewis acid such as  $\text{AlCl}_3$  (1 equiv.) was added to the reaction mixture and this turned to be determinant to get a higher chlorination degree leading to produce  $[3,3'\text{-Co}(4,7,8,9,10,12\text{-Cl}_6\text{-}1,2\text{-C}_2\text{B}_9\text{H}_5)_2]^-$  ( $[\text{Cl}_{12}\text{-}\mathbf{1}]^-$ ), the highest imaginable chlorinated redox reversible couple (**Figure 2b**). In addition, the amount of  $\text{SO}_2\text{Cl}_2$  was optimized to control the chlorination degree leading  $[3,3'\text{-Co}(4,7,8,9,12\text{-Cl}_5\text{-}1,2\text{-C}_2\text{B}_9\text{H}_6)_2]^-$  ( $[\text{Cl}_{10}\text{-}\mathbf{1}]^-$ ). Thus, while the synthesis of  $[\text{Cl}_{12}\text{-}\mathbf{1}]^-$  requires a huge excess of  $\text{SO}_2\text{Cl}_2$  (650 equiv.), the synthesis of  $[\text{Cl}_{10}\text{-}\mathbf{1}]^-$  demand less chlorinating agent (65 equiv.). The methodology consists on a mixture of 0.1 and 65 equivalents of  $\text{AlCl}_3$  and  $\text{SO}_2\text{Cl}_2$  with 1 equivalent of  $\text{H}[\mathbf{1}]$  in an ace pressure tube at 70°C for 2 days. Then the tube is open and the solvent is removed under reduced pressure. Then, 0.1 and 65 equivalents more of  $\text{AlCl}_3$  and  $\text{SO}_2\text{Cl}_2$  are added to the solid reaction mixture, the tube is closed again and is lead at 70°C for 2 more days. (see **Figure 2b**).



**Figure 2.** Reaction conditions for the synthesis of compounds a)  $[\text{Cl}_{8\alpha-1}]^-$ ,  $[\text{Cl}_{8\beta-1}]^-$  and b)  $[\text{Cl}_{10-1}]^-$ ,  $[\text{Cl}_{12-1}]^-$  (B-H is represented with pink spheres, B-Cl with green and C-H with grey).

**Characterization** All new compounds were characterized by  $^1\text{H}$ -,  $^1\text{H}\{^{11}\text{B}\}$ -,  $^{13}\text{C}\{^1\text{H}\}$ -,  $^{11}\text{B}$ -,  $^{11}\text{B}\{^1\text{H}\}$ -NMR, MALDI-TOF-MS at the negative mode, EA, IR and X-ray diffraction. The complete spectral information and the crystallographic data can be found in the S.I.. The IR spectra give us a qualitative analysis of the reaction through the monitoring of the B-H band around  $2600\text{ cm}^{-1}$ . In addition, the comparison of the FT-IR spectrum of the  $\text{Na}[1]$  with the spectra of  $[\text{NMe}_4][\text{Cl}_8-1]$ ,  $[\text{NMe}_4][\text{Cl}_{10-1}]$  and  $\text{Cs}[\text{Cl}_{12-1}]$  unveil a band at  $992\text{ cm}^{-1}$  corresponding to the B-Cl bond, this band appears in other boron clusters in the literature such as  $[\text{B}_{12}\text{Cl}_{12}]^{2-}$  demonstrating the hypothesis.<sup>65</sup> On the other hand, the MALDI-TOF-MS at the negative mode provides faster and reliable information about the exact number of chloro substituents in the  $[1]^-$  skeleton. MALDI-TOF-MS of the 8, 10 and 12 chlorinated derivatives of  $[1]^-$  show a main peak at 598.7, 666.8 and 734.8 m/z that corresponds to  $[\text{Cl}_8-1]^-$  in  $[\text{NMe}_4][\text{Cl}_8-1]$ ,  $[\text{Cl}_{10-1}]^-$  in  $[\text{NMe}_4][\text{Cl}_{10-1}]$  and  $[\text{Cl}_{12-1}]^-$  in  $\text{Cs}[\text{Cl}_{12-1}]$  and represent the 82, 90 and 97 % of the sample, respectively. However, the MALDI-TOF-MS unveils a percentage less than 10 % of side products corresponding to compounds with one chloro plus or less (see S.I.).<sup>56</sup>

The study of NMR spectra together with x-ray diffraction led us to unveil the exact position of the chloro substituents. Suitable single crystals of  $[\text{NMe}_4][\text{Cl}_8-1]$  and  $[\text{NMe}_4][\text{Cl}_{10-1}]$  were obtained by slow evaporation in acetone; for  $\text{Cs}[\text{Cl}_{12-1}]$ , crystals were obtained in  $\text{CH}_2\text{Cl}_2$  and as far as we are concerned, they are the highest halogenated derivatives of metallacarborane ever crystallized (Figure 3).



**Figure 3.** Crystal structures of  $[\text{NMe}_4][\text{Cl}_8\text{-1}]$ ,  $[\text{NMe}_4][\text{Cl}_{10}\text{-1}]$  and  $\text{Cs}[\text{Cl}_{12}\text{-1}]$  (from left to right).

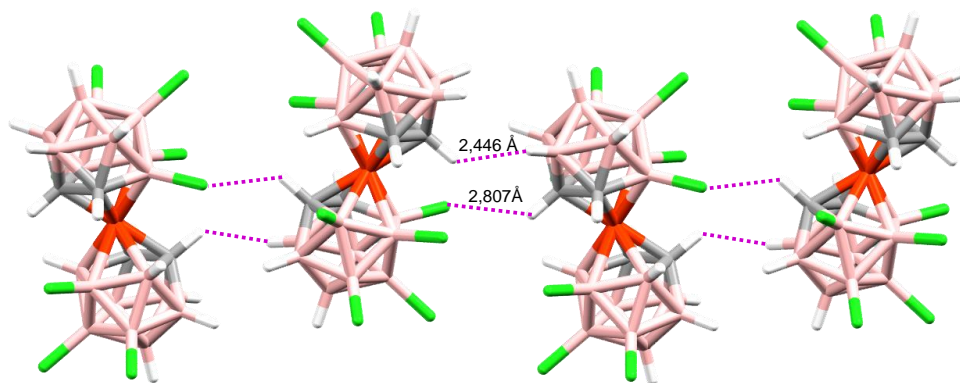
**Structures and intermolecular non-bonding interactions.** The representation of a chloro and a hydrogen atom in B(4,4') positions of  $[\text{NMe}_4][\text{Cl}_8\text{-1}]$  indicates the isomers present in the crystal (B in pink, C in grey, H in white, Cl in green and  $\text{Co}^{3+}$  in orange). The X-ray analysis of  $[\text{NMe}_4][\text{Cl}_8\text{-1}]$  revealed the solid solution nature of the crystal due to the existence of two isomers in the same monocystal. Specifically, the crystal demonstrated the existence of  $[\text{NMe}_4][\text{Cl}_{8\alpha}\text{-1}]$  isomer in 80% and the  $[\text{NMe}_4][\text{Cl}_{8\beta}\text{-1}]$  in 20% (Figure 3).

Structures  $[\text{NMe}_4][\text{Cl}_8\text{-1}]$  and  $[\text{NMe}_4][\text{Cl}_{10}\text{-1}]$  show different types of intermolecular interactions due to its cation (see S.I.). The dihydrogen bond  $\text{C}_{\text{Me}}\text{-H}\cdots\text{H-B}$  that is the most abundant interaction in tetramethylammonium metallocarboranes<sup>66</sup> becomes less abundant in these derivatives due to the high chlorination degree of the molecules. Instead, the moderated hydrogen bonds  $\text{C}_{\text{Me}}\text{-H}\cdots\text{Cl-B}$  with distances from 2.745 to 2.911 Å dominate the intermolecular interaction for  $[\text{NMe}_4][\text{Cl}_{10}\text{-1}]$  with seven hydrogen bonds for each  $[\text{NMe}_4]^+$ . In contrast, the  $\text{C}_{\text{Me}}\text{-H}\cdots\text{H-B}$  interaction is more abundant than the  $\text{C}_{\text{Me}}\text{-H}\cdots\text{Cl-B}$  in the  $[\text{NMe}_4][\text{Cl}_8\text{-1}]$  structure because the chlorination degree is less. To end the most important interaction in the crystal structure of  $[\text{NMe}_4][\text{Cl}_{10}\text{-1}]$  is the double contact between Cl-B<sub>B</sub>(4) of the metallocarborane (B) and the C<sub>C</sub>-H of the near metallocarborane (A). Specifically the  $\text{C}_{\text{CA}}(1)\text{-H}\cdots\text{Cl-B}_A(4)$  and  $\text{B}_{\text{CB}}(4)\text{-Cl}\cdots\text{H-C}_{\text{CA}}(1')$  with distances of 2.877 and 2.657 Å respectively, with an angle of 51.4°.<sup>67</sup> The study of the structure  $\text{Cs}[\text{Cl}_{12}\text{-1}]$  reveals other types of interactions. The double contact  $\text{B}_A(9')\text{-Cl}\cdots\text{Cs}\cdots\text{Cl-B}_B(9)$  with distances of 3.597 and 3.671 Å and the interaction of  $\text{B}_A(7)\text{-Cl}\cdots\text{H-B}_B(11)$  and  $\text{B}_A(8')\text{-Cl}\cdots\text{H-B}_C(5)$  between three nearby metallocarboranes with distances of 3.118 and 2.999 Å respectively are the most significant. In addition, the structure shows interactions between two metallocarboranes and the  $\text{CH}_2\text{Cl}_2$  solvent. Specifically, the solvent molecule interacts with the B(5)-H and B(9)-Cl positions of two metallocarboranes with distances of 2.251 and 2.902 Å. Finally, the H-C<sub>C</sub> position of  $\text{Cs}[\text{Cl}_{12}\text{-1}]$  surprisingly, do not show any intermolecular interaction in the structure.

As a result of all these contacts, the three structures revealed the less common conformations in cobaltabis(dicarbollide) derivatives.<sup>66</sup> The crystal structure of  $[\text{NMe}_4][\text{Cl}_8\text{-1}]$  show a *transoid* rotamer in solid-state, even though this conformation should be the least energetic, the intermolecular interactions and the crystal packaging used to be the key factors (Figure 4). However, in this structure we have a solid solution hence the packaging should permit the



exchange of Cl by H and vice-versa in the B(4) and B(4') positions and the conformation more advantageous to get it is the *trans*.

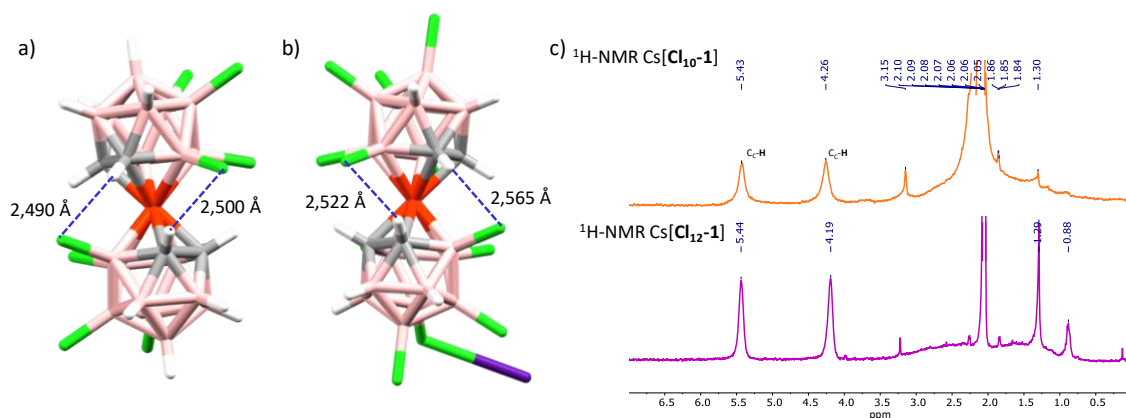


**Figure 4.** Interactions  $C_A(2)H \cdots Cl-B_B(4')$  and  $B_A(6)-H \cdots H-C_B(1)$  between near  $[Cl_8-1]^-$  molecules forming a chain in the crystal packing (B in pink, C in grey, H in white, Cl in green and  $Co^{3+}$  in orange).

Structures  $[NMe_4][Cl_{10-1}]$  and  $Cs[Cl_{12-1}]$  surprisingly, present *gauche 1* and *gauche 2* rotamers with centroid distances between  $\eta^5-C_2B_3$  and  $Co^{III}$  of 1.514 and 1.539 Å respectively, typical distances of this conformation (see **Figure 3**).<sup>66</sup> These conformations are not the most common or the least energetic neither. However, while the structure of  $[Cl_8-1]^-$  presents the distances around 2.75 Å between atoms of two cluster cages of the same molecule; both crystal structures  $[NMe_4][Cl_{10-1}]$  and  $Cs[Cl_{12-1}]$  present shorter intramolecular interactions that force the *gauche* conformation of the molecules. Namely, the interactions  $B(7)-Cl \cdots H-C(1')$  and  $C(2)-H \cdots Cl-B(4')$  with distances of 2.490 and 2.500 Å respectively, for the crystal of  $[NMe_4][Cl_{10-1}]$  and 2.522 and 2.565 Å, respectively for the crystal structure of  $Cs[Cl_{12-1}]$  (**Figure 5a** and **b**). In addition, these intermolecular interactions are so strong that persist in solution explaining the extra peaks that appear in the  $^{11}B\{^1H\}$ -NMR spectra of both compounds (See S.I.). The *gauche* conformation in the crystal structures of  $[NMe_4][Cl_{10-1}]$  and  $Cs[Cl_{12-1}]$  breaks all the symmetry of the molecule and consequently, the  $^1H$ -NMR spectrum shows two  $C_C-H$  resonances with 2:2 intensities because the two  $C_C-H$  are spectroscopically different (**Figure 5c**). Moreover, the signal at downfield supports that the intramolecular  $B-Cl \cdots H-C_c$  interactions are kept in solution.

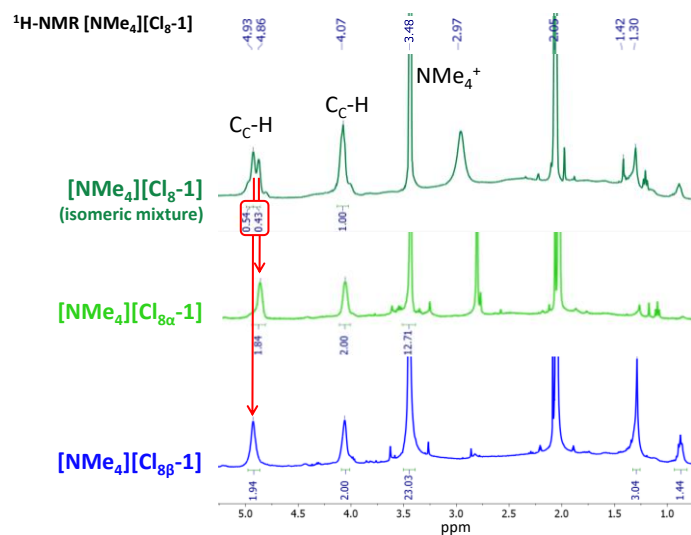
The  $^{11}B$ -NMR spectrum of  $Cs[Cl_{10-1}]$  displays three singlets at 12.4, 6.4 and 1.6 ppm with intensities 2:6:2 corresponding to ten B-Cl units at B(8,8'), B(4,4', 9,9',12,12') and B(7,7'). In addition, the four doublets that appear in the  $^{11}B$ -NMR spectrum at 0.2, -14.3, -17.1 and -27.7 ppm with intensities 2:2:2:2, correspond to the B-H units of the boron atoms B(10,10'), B(5,5',11,11') and B(6,6') respectively. In contrast, the  $^{11}B$ -NMR spectrum of the  $Cs[Cl_{12-1}]$  presents three singlets at 11.5, 5.6 and 0.7 ppm with intensities 2:8:2, corresponding to B(8,8'), B(4,4',9,9',10,10',12,12') and B(10,10') respectively, that confirms the twelve boron cluster vertices substitution. Two further doublets with intensities 4:2 corresponding to B(5,5',11,11') and B(6,6') B-H vertices are also observed respectively (see S.I.).

Moreover, the  $^{11}B$ -NMR spectra for  $Cs[Cl_{10-1}]$  and  $Cs[Cl_{12-1}]$  unveil a B(4)-Cl signal very different from its supposed equivalent B(7)-Cl ( $\Delta ppm=4.81$ ) demonstrating again that the compounds retain the intramolecular  $B-Cl \cdots H-C_c$  interactions in solution as it was shown above by  $^1H$ -NMR.



**Figure 5.** B(7)-Cl $\cdots$ H-C(1') and C(2)-H $\cdots$ Cl-B(4') intramolecular interactions of the structures a) [Cl<sub>10</sub>-1]<sup>-</sup> and b) [Cl<sub>12</sub>-1]<sup>-</sup>, responsible to their *gauche* conformation; c) <sup>1</sup>H-NMR spectra in (CD<sub>3</sub>)<sub>2</sub>CO of Cs[Cl<sub>10</sub>-1] (in orange) and Cs[Cl<sub>12</sub>-1] (in purple).

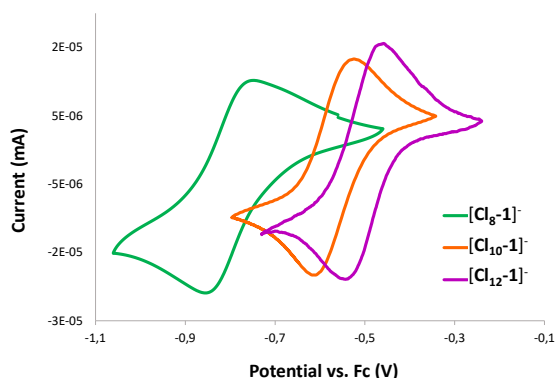
Concerning the NMR characterization of [NMe<sub>4</sub>][Cl<sub>8</sub>-1], the situation is very different (**Figure 6**). Even though the EA and MALDI-TOF-MS at the negative mode confirm the purity of the product, the <sup>11</sup>B-NMR spectrum shows many signals difficult to characterize due to the presence of the different structural isomers [Cl<sub>8 $\alpha$ ]-1]<sup>-</sup> and [Cl<sub>8 $\beta$ ]-1]<sup>-</sup>. The <sup>1</sup>H-NMR show two signals at 4.92 and 4.87 ppm and one broad signal at 4.07 ppm indicating the existence of isomeric mixture but, the integration of the proton peaks corresponding to the C<sub>c</sub>-H signals of the <sup>1</sup>H-NMR spectrum provides a rough ratio  $\alpha$ : $\beta$  isomers of 55:45 (Figure 6). Fortunately, the separation of the mixture was possible thanks to the different polarity of isomers. Particularly, the isomer [Cl<sub>8 $\beta$ ]-1]<sup>-</sup> was very insoluble in chloroform, leading to an isomeric pure product that could be analyzed by <sup>1</sup>H-<sup>11</sup>B- and <sup>13</sup>C{<sup>1</sup>H}-NMR (see S.I.).</sub></sub></sub>



**Figure 6.** <sup>1</sup>H-NMR in (CD<sub>3</sub>)<sub>2</sub>CO, of the mixture [NMe<sub>4</sub>][Cl<sub>8</sub>-1] (dark green), isolated [NMe<sub>4</sub>][Cl<sub>8 $\alpha$ ]-1] (light green) and isolated [NMe<sub>4</sub>][Cl<sub>8 $\beta$ ]-1] (blue).</sub></sub>

**Electrochemical redox couples** The  $E_{1/2}(\text{Co}^{\text{III}}/\text{Co}^{\text{II}})$  values for [Cl<sub>8</sub>-1]<sup>-</sup>, [Cl<sub>10</sub>-1]<sup>-</sup> and [Cl<sub>12</sub>-1]<sup>-</sup> were experimentally obtained by cyclic voltammetry and compared with the other chlorinated derivatives available in the literature, see **Figure 7**, **Figure 8** and **Table 1**. These results indicated not only the redox potential of Co(III)/Co(II) but also the reversibility of the system. For [NMe<sub>4</sub>][Cl<sub>10</sub>-1] and [NMe<sub>4</sub>][Cl<sub>12</sub>-1] their  $\Delta mV$  values are less than 100mV, 99.8 and 62 mV

respectively. On the other hand,  $[\text{NMe}_4][\text{Cl}_8\text{-1}]^-$  shows a broader signal, with a  $\Delta\text{mV}$  of 183, see **Figure 7** and **Table 1**, most probably due to the mixture of isomers that causes slightly different potentials, and due to the overlap of the two traces it is found a thicker signal.



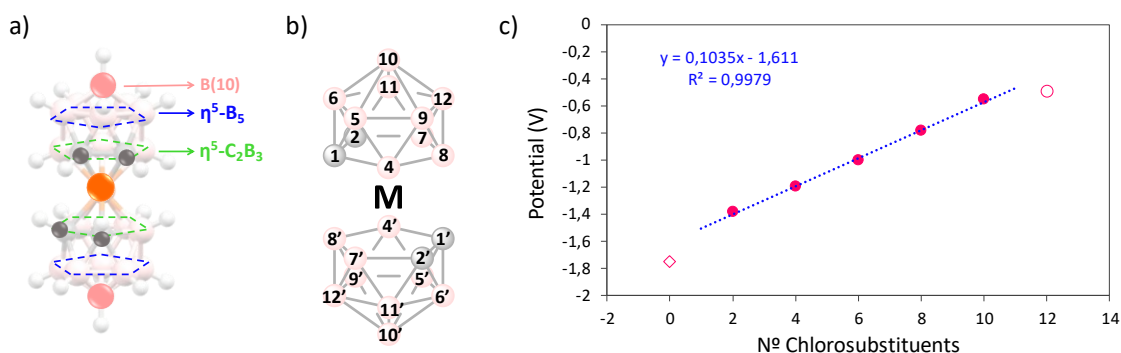
**Figure 7.** Cyclic voltammetry of  $[\text{Cl}_8\text{-1}]^-$  (in green),  $[\text{Cl}_{10}\text{-1}]^-$  (in orange) and  $[\text{Cl}_{12}\text{-1}]^-$  (in purple) carried out in dry acetonitrile as solvent and  $[\text{NBu}_4][\text{PF}_6]$  (0.1M) as supporting electrolyte. For the electrodes, Glassy carbon as working electrode, Ag as pseudoreference electrode and Pt wire as the counter electrode. Measurements were referenced to internal  $\text{Fc}^+/\text{Fc}$  couple.

As a rule of thumb, it was considered that each new chloro added to the structure contributes +0.12V to the  $E_{1/2}(\text{Co}^{\text{III}}/\text{Co}^{\text{II}})$ .<sup>56</sup> **Figure 8** shows that indeed the increment of  $E_{1/2}(\text{Co}^{\text{III}}/\text{Co}^{\text{II}})$  ( $\Delta E_{1/2}$ ) is quasilinear, except for the first  $[\text{Cl}_2\text{-1}]^-$  and last points ( $[\text{Cl}_{12}\text{-1}]^-$ ) showing a considerable deviation from the expected values. This accounts for the importance of the chlorinated position, a phenomenon previously observed in the iodinated derivatives.<sup>68</sup> It has been demonstrated that the anionic  $[\mathbf{1}]^-$  cluster is a global 3D aromatic system<sup>69</sup> with a negative charge delocalized all over the system.<sup>70</sup> Considering that chloro substituent is an electron-withdrawing group, each additional chloride makes the redox site more positive, and consequently the redox potential of the couple  $\text{Co}^{\text{III}}/\text{Co}^{\text{II}}$  becomes more positive, then easier to be reduced. In addition, the impact of this effect depends on the distance of the chlorinated position to the Co atom. The substituents that are in the plane nearest to Co ( $\eta^5\text{-C}_2\text{B}_3$ ) affect more the redox potential of the  $\text{Co}^{\text{III}}/\text{Co}^{\text{II}}$  couple than those on a more distant plane ( $\text{B}_5$ ) or in the B(10) position (Figure 8a). Theoretical studies<sup>71</sup> and the crystal structures of  $[\text{NMe}_4][\text{Cl}_8\text{-1}]^-$ ,  $[\text{NMe}_4][\text{Cl}_{10}\text{-1}]^-$  and  $\text{Cs}[\text{Cl}_{12}\text{-1}]^-$  suggest that the chlorination order for  $[\mathbf{1}]^-$  is first B(8) followed by B(9,12) (equivalent positions), B(4,7), B(8) B(5,11) and finally B(6), the last three are very difficult to chlorinate. Therefore, the largest potential gaps are found for  $[\text{Cl}_2\text{-1}]^-$ , and  $[\text{Cl}_{12}\text{-1}]^-$ , that correspond to the chlorination of B(8) and B(10), respectively. To demonstrate our hypothesis, we synthesized  $[\text{NMe}_4][3,3'\text{-Co}(4,7\text{-Cl}_2\text{-1},2\text{-C}_2\text{B}_9\text{H}_9)_2]$  and studied its electrochemistry. The synthesis was done following the methodology already described with some minor modifications, (see S.I. for the synthesis and characterization of  $[\text{NMe}_4][3,3'\text{-Co}(4,7\text{-Cl}_2\text{-1},2\text{-C}_2\text{B}_9\text{H}_9)_2]$ )<sup>53</sup>; to notice are the distinct positions of chlorination of  $[\text{NMe}_4][3,3'\text{-Co}(4,7\text{-Cl}_2\text{-1},2\text{-C}_2\text{B}_9\text{H}_9)_2]$  with regard to what we name  $[\text{Cl}_4\text{-1}]^-$ ,  $[\text{NMe}_4][3,3'\text{-Co}(8,9\text{-Cl}_2\text{-1},2\text{-C}_2\text{B}_9\text{H}_9)_2]$ . In  $[\text{Cl}_4\text{-1}]^-$ , one B-Cl is in the plane  $\eta^5\text{-C}_2\text{B}_3$  next to Co and the second B-Cl is in the more distant plane  $\text{B}_5$ . In  $[\text{NMe}_4][3,3'\text{-Co}(4,7\text{-Cl}_2\text{-1},2\text{-C}_2\text{B}_9\text{H}_9)_2]$  both B-Cl are in the plane next to Co. Thus the  $E_{1/2}(\text{Co}^{\text{III}}/\text{Co}^{\text{II}})$  should be more positive in  $[\text{NMe}_4][3,3'\text{-Co}(4,7\text{-Cl}_2\text{-1},2\text{-C}_2\text{B}_9\text{H}_9)_2]$ . The cyclic voltammetry experiment present a redox potential of -1.13 V vs.  $\text{Fc}^+/\text{Fc}$ , a value of  $E_{1/2}(\text{Co}^{\text{III}}/\text{Co}^{\text{II}})$  0.07 V more

positive than the -1.20 V for  $[\text{NMe}_4][3,3'\text{-Co}(8,9\text{-Cl}_2\text{-}1,2\text{-C}_2\text{B}_9\text{H}_9)_2]$ ,  $[\text{Cl}_4\text{-}1]^-$  (**Table 1**). In addition, this experiment demonstrate the hypothesis of a broad  $\Delta mV$  value for  $[\text{Cl}_8\text{-}1]^-$  due to the overlap of the two redox curves for the two isomers  $[\text{Cl}_{8\alpha}\text{-}1]^-$  and  $[\text{Cl}_{8\beta}\text{-}1]^-$ , proving that both are reversible systems.

**Table 1.**  $E_{1/2}$  of  $(\text{Co}^{\text{III}}/\text{Co}^{\text{II}})$  data for  $[\text{Cl}_n\text{-}1]^-$ , ( $n= 0, 1, 2, 4, 6, 8, 10$  and  $12$ ). The superindex indicate the reference. Besides,  $\Delta mV$  data indicate the potential difference between the reduction and oxidation peaks. Finally,  $\Delta E_{1/2}$  is the redox potential difference between compounds  $[\text{Cl}_n\text{-}1]^-$  and  $[\text{Cl}_{(n-2)}\text{-}1]^-$ .

Compound	$E_{1/2}$ vs. $F_c^+/F_c$ (V) [ $\Delta mV$ ]	$\Delta E_{1/2}$ (V)
$[1]^-$	-1.75 [56] <sup>72</sup>	
$[\text{Cl}_2\text{-}1]^-$	-1.39 <sup>73</sup>	0.36
$[\text{Cl}_4\text{-}1]^-$	-1.20 <sup>62</sup>	0.19
$[\text{Cl}_6\text{-}1]^-$	-1.01 <sup>63</sup>	0.19
$[\text{Cl}_8\text{-}1]^-$	-0.79 [183]	0.22
$[\text{Cl}_{10}\text{-}1]^-$	-0.56 [100]	0.23
$[\text{Cl}_{12}\text{-}1]^-$	-0.49 [63]	0.07



**Figure 8.** a) Representation of the different planes of  $[1]^-$ ; b) scheme of  $[1]^-$  representing the vertex numbering; c) Graphical representation of  $E_{1/2}$  ( $\text{Co}^{\text{III}}/\text{Co}^{\text{II}}$ ) (V) varying with the number of chloro substituents in the  $[1]^-$  structure.

## Conclusions.

In this paper we have demonstrated that with a single platform,  $[3,3'\text{-Co}(1,2\text{-C}_2\text{B}_9\text{H}_{11})_2]$ ,  $[1]^-$ , with a restricted number of equivalent sites, it has been possible by sequential halogenations to chlorinate up to 12 positions out of 18 possible. Earlier work indicated that each chloro substitution results in a potential modulation in the range 0.1-0.13 V. But as is demonstrated here it depends on the distance of the substitution site to the metal center. As a rule of thumb, the number of chloro substituents  $\times 0.1$  is a quite predictive equation for the voltage modulation. We mentioned earlier that our system was quite simple. To do this we synthesize the molecule with the desired potential in a single reaction in a single flask, and this was achieved. In this way we have made the derivatives with 8, 10 and 12 chloro,  $[\text{Cl}_8\text{-}1]^-$ ,  $[\text{Cl}_{10}\text{-}1]^-$ , and  $[\text{Cl}_{12}\text{-}1]^-$ , where  $[1]^-$

is  $[\text{Co}(\text{C}_2\text{B}_9\text{H}_{11})_2]^-$ . They add to the  $[\text{Cl-1}]^-$ ,  $[\text{Cl}_2-1]^-$ ,  $[\text{Cl}_4-1]^-$ ,  $[\text{Cl}_6-1]^-$ , described earlier. A total of 1.3V that are modulated stepwise with the particularity that each molecule occupies the same or very similar volume so that solid solutions have crystallographically been encountered. This is a major breakthrough, but we cannot go further with  $[\text{1}]^-$  because substitutions with more than 12 chloro substituents are very difficult, at least with the current procedure. Does this mean that we cannot go beyond these potential values with metallacarboranes? The answer is yes, it is possible, and this is what we are working on now. If instead of using only Co, we use the much more abundant Fe, i.e. we move from  $[\text{Co}(\text{C}_2\text{B}_9\text{H}_{11})_2]^-$  to  $[\text{Fe}(\text{C}_2\text{B}_9\text{H}_{11})_2]^-$ , we shift at once 1 V to more positive values. It is only to be expected that the tuning achieved by halogenation is comparable to  $[\text{1}]^-$  and the first results support this. The  $[\text{Fe}(\text{C}_2\text{B}_9\text{H}_{11})_2]^-$  in terms of potential is equivalent to  $[\text{Cl}_8-1]^-$ . We hope that with only two metals and the same platform, a potential range equivalent to 2V can be achieved.

Up to now,  $[\text{Cl}_6-1]^-$  was the highest chloro derivative of COSAN synthetically quasi pure. Now, after 39 years since the first synthesis of  $[\text{Cl}_6-1]^-$ , three new high chlorinated derivatives of  $[\text{1}]^-$  are introduced in good yields into the group of chloro derivatives of  $[\text{1}]^-$ :  $[\text{Cl}_8-1]^-$ ,  $[\text{Cl}_{10}-1]^-$  and  $[\text{Cl}_{12}-1]^-$ .

## Experimental

### Materials

$\text{SO}_2\text{Cl}_2$ ,  $\text{AlCl}_3$  were purchased from Sigma-Aldrich.  $\text{H}[\text{COSAN}]$  was synthesized from  $\text{Cs}[\text{COSAN}]$  as previously described.

### Synthesis

#### Synthesis of $[\text{NMe}_4][\text{Cl}_8-1]$ (isomeric mixture)

50 mg (0.15 mmol) of  $\text{H}[3,3'\text{-Co-(1,2-C}_2\text{B}_9\text{H}_{11})_2]$  in 8 mL of  $\text{SO}_2\text{Cl}_2$  (49.5 mmol) was heated in an ace pressure tube at  $70^\circ\text{C}$  for 4 days. When the reaction has finished, the closed tube was left cool at room temperature. The tube was opened and the solvent was removed under reduced pressure. The solid was extracted with diethyl ether and  $\text{HCl}$  0.1M three times and the organic layer was cleaned with water once more. The solvent of the organic layer was removed under reduced pressure, the solid was dissolved in 5 ml of  $\text{H}_2\text{O}$  and a saturated solution of  $\text{NMe}_4\text{-HCl}$  was added appearing a red solid precipitate identified as isomeric mixture  $\text{NMe}_4[\text{Cl}_{8\alpha}-1]$  and  $\text{NMe}_4[\text{Cl}_{8\beta}-1]$ . The solid was filtered and dried obtaining 64.5 mg of orange solid (yield: 70%). The  $\text{NMe}_4[\text{Cl}_{8\beta}-1]$  isomer was isolated using chloroform as a cleaning solvent (the  $\beta$  isomer is completely insoluble in Chloroform). FTIR ( $\nu$  in  $\text{cm}^{-1}$ ): 3046.01 and 2923.56 (C-H), 2593.79 (B-H), 2360.44 and 2339.23 (B-Cl). MALDI-TOF: Teor. 598.96m/z. Found 598.72m/z. Elemental analysis: Found: C, 6.51; H, 1.97. Calc. for  $\text{CsCl}_8\text{CoC}_4\text{B}_{18}\text{H}_{14}$ : C, 6.56; H, 1.91%. **NMR characterization of  $[\text{NMe}_4][3,3'\text{-Co-(4,7,8,9,12-Cl}_5\text{-1,2-C}_2\text{B}_9\text{H}_6)$  ( $8',9',12'\text{-Cl}_3\text{-1',2'-C}_2\text{B}_9\text{H}_8$ ) ( $[\text{NMe}_4][\text{Cl}_{8\alpha}-1]$ ).**  $^1\text{H}$   $\{^{11}\text{B}\}$  NMR (400MHz,  $\text{CD}_3\text{COCD}_3$ )  $\delta$ : 4.93 (2H, s, C-H), 4.06 (2H, s, C-H), 3.45 (12H, s,  $\text{N}(\text{CH}_3)_4$ ).  $^{11}\text{B}$  NMR (128MHz,  $\text{CD}_3\text{COCD}_3$ )  $\delta$ : 12.8 (2B, s, B(8,8')-Cl), 5.4(-3.01)(8B, B(4,7,8,8',9,9',12,12')-Cl and B(4',7')-H), -2.3 (1B, d,  $^1\text{J}_{\text{B-H}}$  125, B10-H), -3.2(1B, d,  $^1\text{J}_{\text{B-H}}$  122.9, B10'-H), -17.5 (2B, d,  $^1\text{J}_{\text{B-H}}$  166.4 B(5,11)-H), -19.7 (2B, d,  $^1\text{J}_{\text{B-H}}$  174.1, B(5',11')-H), -24.4 (1B, d,  $^1\text{J}_{\text{B-H}}$  151.0, B6-H), -27.2 (1B, d,  $^1\text{J}_{\text{B-H}}$  193.3, B6'-H).  $^{13}\text{C}$   $\{^1\text{H}\}$  NMR (100MHz,  $\text{CD}_3\text{COCD}_3$ )  $\delta$ : 55.25. **NMR characterization of**

**[NMe<sub>4</sub>][3,3'-Co-(4,8,9, 12-Cl<sub>4</sub>-1,2-C<sub>2</sub>B<sub>9</sub>H<sub>7</sub>)<sub>2</sub>] ([NMe<sub>4</sub>][Cl<sub>8</sub>-1]).** <sup>1</sup>H {<sup>11</sup>B} NMR (400MHz, CD<sub>3</sub>COCD<sub>3</sub>) δ: 4.88 (2H, s, C-H), 4.08 (2H, s, C-H), 3.45 (12H, s, N(CH<sub>3</sub>)<sub>4</sub>). <sup>11</sup>B NMR (128MHz, CD<sub>3</sub>COCD<sub>3</sub>) δ: 9.1 (2B, s, B8-Cl), 4.4 (2B, s, B7-Cl), 3.0 (4B, s, B(9,12)-Cl) -0.2 (2B, d, <sup>1</sup>J<sub>B-H</sub> 153.6, B4-H), -4.0 (2B, d, <sup>1</sup>J<sub>B-H</sub> 169.0, B10-H), -17.5 (2B, d, <sup>1</sup>J<sub>B-H</sub> 163.6, B11-H), -21.9 (2B, d, <sup>1</sup>J<sub>B-H</sub> 165.2, B5-H), -25.8 (2B, d, <sup>1</sup>J<sub>B-H</sub> 169.0, B6-H). <sup>13</sup>C {<sup>1</sup>H} NMR (100MHz, CD<sub>3</sub>COCD<sub>3</sub>) δ: 55.21

### **Synthesis of [NMe<sub>4</sub>][3,3'-Co-(4,7,8,9,12-Cl<sub>5</sub>-1,2-C<sub>2</sub>B<sub>9</sub>H<sub>6</sub>)<sub>2</sub>]**

The mixture of 500 mg (1.54 mmol) of H[3,3'-Co-(1,2-closo-C<sub>2</sub>B<sub>9</sub>H<sub>11</sub>)<sub>2</sub>], 20.5 mg of AlCl<sub>3</sub> (0.15 mmol) and 8 mL of SO<sub>2</sub>Cl<sub>2</sub> (99 mmol) was heated in an ace pressure tube at 70°C for 2 days. When the reaction has finished, the closed tube was left cool at room temperature. The tube was opened and the solvent was removed under reduced pressure. 20.5 mg (0.15 mmol) of AlCl<sub>3</sub> was added again and the mixture was dissolved in 8 mL of SO<sub>2</sub>Cl<sub>2</sub> in the same ace pressure tube. The reaction was heated at 70°C for other 2 days. When the reaction has finished, the closed tube was left cool at room temperature. The product was purified following the same treatments used with the compound [NMe<sub>4</sub>][Cl<sub>8</sub>-1]. The solid was filtered, dried and 924 mg of a red solid corresponding to product NMe<sub>4</sub>[Cl<sub>10</sub>-1] was obtained (yield: 90%). <sup>1</sup>H{<sup>11</sup>B} NMR (300MHz, CD<sub>3</sub>COCD<sub>3</sub>) δ: 5.43 (2H, s, C<sub>Cluster</sub>-H), 4.26 (2H, s, C<sub>Cluster</sub>-H), 11B NMR (96.3MHz, CD<sub>3</sub>COCD<sub>3</sub>) δ: 12.4 (2B, s, B8-Cl), 6.4 (6B, s, B4-Cl, B9-Cl or B12-Cl), 1.6 (2B, s, B7-Cl), 0.2 (2B, d, <sup>1</sup>J<sub>B-H</sub> 142.1, B10-H), -14.3 (2B, d, <sup>1</sup>J<sub>B-H</sub> 173.3, B-H), -17.1 (2B, d, <sup>1</sup>J<sub>B-H</sub> 183.0, B-H), 27.7 (2B, d, <sup>1</sup>J<sub>B-H</sub> 182.0, B6-H). <sup>13</sup>C{H} NMR (75.5MHz, CD<sub>3</sub>COCD<sub>3</sub>) δ: 50.12(C<sub>Cluster</sub>-H), 48.12 (C<sub>Cluster</sub>-H). FTIR (ν in cm<sup>-1</sup>): 3059.51 and 3.037.34 (C-H), 2601.5 (B-H), 2360.4 and 2339.23 (B-Cl). MALDI-TOF: Teor. 666.88 m/z. Found 666.75m/z. Elemental analysis: Found: C, 5.92; H, 1.56. Calc. for CsCl<sub>10</sub>CoC<sub>4</sub>B<sub>18</sub>H<sub>12</sub>: C, 5.99; H, 1.49%.

### **Synthesis of [NMe<sub>4</sub>][3,3'-Co-(4,7,8,9,10,12-Cl<sub>6</sub>-1,2-C<sub>2</sub>B<sub>9</sub>H<sub>5</sub>)<sub>2</sub>]**

The mixture of 50 mg (0.15 mmol) of H[3,3'-Co-(1,2-C<sub>2</sub>B<sub>9</sub>H<sub>11</sub>)<sub>2</sub>], 20.5 mg of AlCl<sub>3</sub> (0.15mmol) and 8 mL of SO<sub>2</sub>Cl<sub>2</sub> (99 mmol) was heated in an ace pressure tube at 70°C for 4 days. When the reaction has finished, the closed tube was left cool at room temperature. The product was purified following the same treatments used with the compound [NMe<sub>4</sub>][Cl<sub>8</sub>-1]. The solid was filtered, dried and 106 mg of a red solid corresponding to the product was obtained (yield: 94%). <sup>1</sup>H{<sup>11</sup>B} NMR (300MHz, CD<sub>3</sub>COCD<sub>3</sub>) δ: 5.44 (2H, s, C<sub>Cluster</sub>-H), 4.19 (2H, s, C<sub>Cluster</sub>-H), 2.34 (4H, s, B5-H or B11-H). <sup>11</sup>B NMR (96.3MHz, CD<sub>3</sub>COCD<sub>3</sub>) δ: 11.5 (2B, s, B8-Cl), 5.5 (8B, s, B4-Cl, B7-Cl, B9-Cl, B12-Cl), 0.8 (2B, s, B10-Cl), 14.2 (2B, d, <sup>1</sup>J<sub>B-H</sub> 173.3, B5-H), 17.05 (2B, d, <sup>1</sup>J<sub>B-H</sub> 183.0, B11-H), 27.93 (2B, d, <sup>1</sup>J<sub>B-H</sub> 173.3, B6-H). <sup>13</sup>C{<sup>1</sup>H} NMR (75.5MHz, CD<sub>3</sub>COCD<sub>3</sub>) δ: 48.18 (C<sub>Cluster</sub>-H), 46.28 (C<sub>Cluster</sub>-H). FTIR (ν in cm<sup>-1</sup>): 3060.48 and 2866.67 (C-H), 2591.86 (B-H), 2360.44 and 2339.23 (B-Cl). MALDI-TOF: Teor. 734.81 m/z. Found 735.71 m/z. Elemental analysis: Found C, 8.9; H, 1.94. Calc. for NaCl<sub>12</sub>CoC<sub>4</sub>B<sub>18</sub>H<sub>10</sub> · CH<sub>3</sub>COOH: C, 8.77; H, 1.70%.

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**“ASSOCIATED CONTENT”: Supporting Information Available:**

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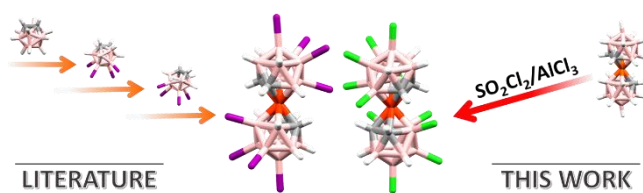
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### For Table of Contents Only



By sequential halogenations of  $[\text{Co}(\text{C}_2\text{B}_9\text{H}_{11})_2]^-$ ,  $[\mathbf{1}]^-$  with Cl, the  $[\mathbf{Cl}_8\text{-}\mathbf{1}]^-$ ,  $[\mathbf{Cl}_{10}\text{-}\mathbf{1}]^-$ , and  $[\mathbf{Cl}_{12}\text{-}\mathbf{1}]^-$  derivatives of  $[\mathbf{1}]^-$  have been prepared and isolated. The  $E_{1/2}$  potentials increase sequentially and linearly with the number of Chloro groups in the platform. If these potentials are added to the existing  $E_{1/2}$  due to  $[\mathbf{Cl}\text{-}\mathbf{1}]^-$ ,  $[\mathbf{Cl}_2\text{-}\mathbf{1}]^-$ ,  $[\mathbf{Cl}_4\text{-}\mathbf{1}]^-$ ,  $[\mathbf{Cl}_6\text{-}\mathbf{1}]^-$ , described earlier a 1.3 V range is obtained. This permits to tune the wanted potentials to the purpose as done by nature.