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Publication Date	2010-04-21
Publication Information	González-Cardoso, P., Stoica, A.-I., Farràs, P., Pepiol, A., Viñas, C. and Teixidor, F. (2010), Additive Tuning of Redox Potential in Metallacarboranes by Sequential Halogen Substitution. Chem. Eur. J., 16: 6660–6665. doi:10.1002/chem.200902558
Publisher	Wiley
Link to publisher's version	http:/dx.doi.org/10.1002/chem.200902558
Item record	http://hdl.handle.net/10379/5951
DOI	http://dx.doi.org/10.1002/chem.200902558

Additive tuning redox potential in metallacarboranes by sequential halogen substitution

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Abstract: The first artificially made set of electron acceptors derived from a unique platform $Cs[Co(C_2B_9H_{11})_2]^-$ each differing from the predecessor a fix potential is presented. The sequence of electron acceptors is made by substituting one, two or more hydrogen atoms by chlorine atoms, yielding $Cs[Co(C_2B_9H_{11-x}Cl_x)(C_2B_9H_{11-y}Cl_y)]$. The higher the number of chlorine substituents, the more prone the platform is to be reduced. The effect is completely additive so if each substitution implies 0.1 V, ten substitutions imply a reduction of 1 V with regard to the redox potential of the parent.

Keywords: Electron transport chain • metallacarboranes • chlorination • redox tuning • square wave voltammetry

Introduction

Electron transfer (ET) is fundamental in many processes of life, including oxygen binding, photosynthesis and respiration.[1] All organisms obtain energy by transferring electrons from an electron donor to an electron acceptor.[2] Besides, ET attracts considerable attention because of the possible application in energy storage and photovoltaic energy conversion.[3-6]

Maximum efficiency in photosynthesis is obtained when electrons pass from one carrier molecule to another in a downhill direction. Nature has found its way to succeed in this task, but this appears to be hard with man made molecules as incompatibility among the different donors and acceptors may easily occur.[7] By using a unitary platform, this problem could be grossly eliminated facilitating ET. However, an additive stepwise by fixed increments redox potential tuning on a single platform has never been achieved. Typical electrochemical platforms such as ferrocene, C_{60} or perylene diimide have never been proven capable to produce the mentioned stepwise tuning. These first choice platforms have available sites to produce successive substitutions to get a redox potential modulation, but the resulting $E_{1/2}$ is not additive.[8-18]

In this work, we describe the largest set of molecules based on a unique frame that show a stepwise and additive redox potential tuning. This platform is $[Co(C_2B_9H_{11})_2]^-$, $[1]^-$, that has many sites for substitution; besides, the B-Cl bonds are very strong, stronger than the C-Cl sites. This may have been the reason for such uniqueness.
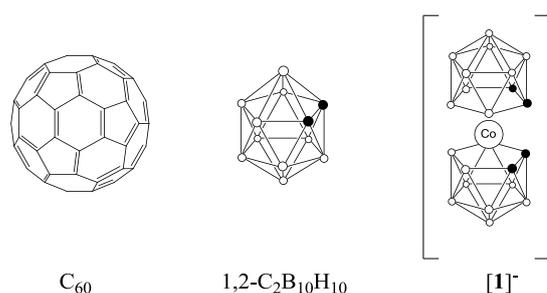

Figure 1. Schematic representation of C_{60}, $1,2-C_2B_{10}H_{10}$ and $Cs[3,3'-Co-(1,2-C_2B_9H_{11})_2]$ molecules.

Boron clusters approximate to deltahedra or to deltahedra with one or more vertices missing. In the early 1970s, it was realized that the geometry of boron clusters is related with the number of electron pairs available for bonding; therefore, redox processes should be able to produce structural change.[19-22]

Although C_{60} and $1,2-$, $1,7-$, and $1,12-C_2B_{10}H_{12}$ *closo*-carboranes, see Figure 1, are all neutral molecules characterized by a closed-cage structure, the first requires much less energy to incorporate $2e^-$ than the carboranes, -0.87 V *vs* -2.5 V, respectively, being both values referred to Saturated Calomel Electrode (SCE).[23,24] The low lying LUMO in C_{60} and the structural rearrangement required upon ET for the carboranes account for this large voltage difference. The low reduction potential of C_{60} has made it very valuable as an electron acceptor in devices,[14-18] and could have been an excellent platform to generate a large sequential set of electron acceptors. However, up to now, this has not been achieved,[25-27] and does not seem to be possible.

According to their reduction potentials, carboranes could not compete with C_{60} as electron acceptors; however, the B-X bond (X = halogen) in boron clusters is much more stable to reduction than

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the C-X bond in sp^2 carbon atoms and this could make it valuable for the sought redox tuning.[28]

As borane clusters are not suited to be redox modulated due to the structural changes caused by addition or removal of electrons, we considered a system that keeps the properties of boron clusters but avoids rearrangement. Thus, attention was set on the less severe electron-counting rules demand of metallacarboranes, and in particular to the well known Co^{III} species Cs[Co(C$_2$B$_9$H$_{11}$)$_2$], Cs[**1**].[29,30] In this work we show how the stepwise dehydrochlorination of [**1**]$^-$ parallels an easier electron reduction in all three redox couples existing in Cs[**1**]. Besides, the ease of electron reduction is additive by a fixed potential amount upon each new dehydrochlorination step.

Results and Discussion

Experimental studies: [Co(C$_2$B$_9$H$_{11}$)$_2$]$^-$ shows three quasi-reversible waves in cyclic voltammetry at +1.67, -1.31 and -2.26 V *vs* Ag/AgCl/KCl$_{sat}$ assigned to Co^{IV}/Co^{III}, Co^{III}/Co^{II} and Co^{II}/Co^I, respectively.[29,31] The negative E$_{1/2}$ peaks indicate that introducing one and two electrons into the Co^{III} system is energy intensive. It was known that the redox potential of the dichlorinated anion [NMe$_4$][Co(C$_2$B$_9$H$_{10}$Cl)$_2$] is -0.99V for the couple Co^{III}/Co^{II},[32] about 0.3 V more positive than for [**1**]$^-$. This corresponded to 0.3V for two steps of dehydrochlorination, and we wanted to learn if it was possible that with a higher number of dehydrochlorination steps, the ease of reduction would increase accordingly. Then, to prove the potential tuning of Cs[**1**], it was necessary to have a wide set of consecutive halogenated derivatives. The only reported synthesis of chlorinated derivatives of Cs[**1**] was based on the reaction of Cl$_2$ with Cs[**1**] that produced mixtures having a number of Cl ranging from 2 to 6.[33] Besides, [HNMe$_3$][Co(C$_2$B$_9$H$_{10}$Cl)$_2$] has been reported to be synthesized pure by reaction of N-chlorosuccinimide with Cs[**1**] in THF.[34] To easily correlate the number of Cl substituents on platform [**1**]$^-$ and the additive potential shift described in this work, we have named the halogenated species as Cs[Cl$_x$-**1**], x stating the number of chlorine atoms on Cs[**1**].

As previously said, only [HNMe$_3$][Cl$_2$-**1**] and Cs[Cl$_6$-**1**] were known before this work, the latter being indeed a mixture of species from Cs[Cl$_2$-**1**] to Cs[Cl$_6$-**1**].[33] This had prevented to accurately calculate the E$_{1/2}$ for Cs[Cl$_6$-**1**] as the cyclic voltammetry (CV) wave was cumbersome (see Fig. 2a). Notwithstanding so, the CV wave corresponding to the Cs[Cl$_2$-**1**] to Cs[Cl$_6$-**1**] mixture was shifted to more positive E$_{1/2}$ values than for Cs[Cl$_2$-**1**]. This, together with the fact that the CV wave corresponding to Cs[Cl$_2$-**1**] was indeed also shifted to more positive values than Cs[**1**], motivated us to find a more efficient chlorination method that eventually would lead to more chlorine enriched mixtures.
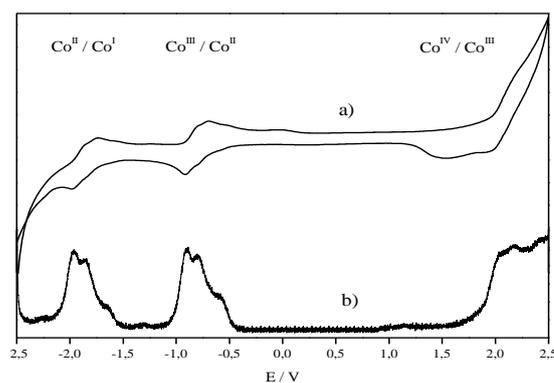

Figure 2. (a) Cyclic voltammogram and (b) Square Wave voltammogram responses recorded at glassy carbon electrode in MeCN of 5·10^{-3}M Cs[Cl$_x$-**1**] (x = 2-6) using [NBu$_4$][PF$_6$] (0.1M) as supporting electrolyte. The electrochemical cell contained Ag/AgCl/KCl$_{sat}$ as the reference electrode and a platinum wire as the auxiliary electrode. Scan rate: a) 0.2 V·s^{-1}, b) 0.025 V·s^{-1}.

The objective was to see if the CV wave really moved towards more anodic voltages when increasing the chlorination degree of Cs[**1**], and if this tendency was not discontinue. After several unsuccessful trials, we discovered a useful method to increase the chlorination degree of Cs[**1**] by reacting N-chlorosuccinimide with Cs[**1**] in the oven at 200ºC in a vacuum sealed tube (see Supporting Information). By varying the ratio of reagents, a set of series of Cs[Cl$_x$-**1**] (x > 2) was obtained, each series consisting of a limited number of x values in an approximately Gaussian distribution. The Gaussian curve shifted to more enriched chlorinated derivatives of Cs[**1**] when increasing the ratio NCS / Cs[**1**]. The CV of the synthesized mixtures proved our hypothesis that, the higher the degree of chlorination, the more positive the redox potential became. To unambiguously validate the former experiments, it was necessary to find a reliable analytical tool that provided a measure of the components of each mixture. The molecular composition was obtained by MALDI-TOF-MS analysis by comparing the areas under each peak envelop (see Table S1 in Supporting Information) This was possible because the Cs[Cl$_x$-**1**] mixtures are made of chemically and structurally very similar compounds, so their MALDI-TOF-MS represent very well the chemical composition of the studied samples. Each peak in each mixture had the appropriate isotopic composition and was separated from its neighbour either 35 or 36 mass units. The more chlorine enriched derivative produced was the Cs[Cl$_9$-**1**] anion.

Electrochemistry of chlorinated mixtures: The CV of each of these mixtures is very similar to the wave shown in Fig. 2a, but all of them were consistently shifted to anodic potentials as the average x value in the Cs[Cl$_x$-**1**] mixture was increased. Therefore, our hypothesis was qualitatively proven by the CV of the different mixtures, but we had not yet proven the additivity by a fixed amount upon each new dehydrochlorination step on the platform Cs[**1**]. To reach this point, we needed a set of adequate mixtures and an electrochemical method capable of providing E$_{1/2}$ values for each individual species. Thus, we prepared samples A to F (see Table 1) to study their redox potentials. The Square Wave Voltammetry (SWV) was the technique that provided more fine structure in the electrochemical wave to warrant individual E$_{1/2}$ calculations. In Fig. 2b, the SWV for Cs[Cl$_x$-**1**] (x = 2-6) is indicated. When the chemical composition, drawn from MALDI-TOF-MS, and deconvolution into Gaussians of the corresponding SWV were

combined, a set of self-consistent $E_{1/2}$ values for each x value could be obtained, as outlined in Figure 3 for the Co^{III}/Co^{II} redox process. Both MALDI-TOF-MS and SWV are periodic, the first with regard to mass, and the second with regard to potential. Importantly, both also present the same intensity pattern, a property that is related to the quantity of different components in the mixture.

Table 1. Composition of the mixtures of $Cs[Cl_x\text{-}\mathbf{1}]$ used for the calculation of the $E_{1/2}$ values displayed in Figure 4. The composition of each sample has been determined by the analysis of the corresponding MALDI-TOF mass spectrum.

Mixture	$[Cl_2\text{-}\mathbf{1}]^-$	$[Cl_3\text{-}\mathbf{1}]^-$	$[Cl_4\text{-}\mathbf{1}]^-$	$[Cl_5\text{-}\mathbf{1}]^-$	$[Cl_6\text{-}\mathbf{1}]^-$	$[Cl_7\text{-}\mathbf{1}]^-$	$[Cl_8\text{-}\mathbf{1}]^-$	$[Cl_9\text{-}\mathbf{1}]^-$
				%				
A	20.4	62.8	16.8	-	-	-	-	-
B	2.7	49.1	34.1	8.2	5.9	-	-	-
C	-	-	5.2	14.2	16.4	31.1	30.7	2.3
D	-	-	-	-	22.6	42.9	32.4	2.1
E	29.9	25.1	13.7	3.2	11.4	12.9	3.7	-
F	18.4	11.1	15.4	4.7	21.2	23.5	5.8	-

The MALDI-TOF-MS in Figure 3 corresponds to a mixture of $Cs[Cl_2\text{-}\mathbf{1}]$, $Cs[Cl_3\text{-}\mathbf{1}]$, $Cs[Cl_4\text{-}\mathbf{1}]$, $Cs[Cl_5\text{-}\mathbf{1}]$ and $Cs[Cl_6\text{-}\mathbf{1}]$, each peak showing the properly isotopic distribution centered at 391.51, 426.53, 461.53, 495.51 and 530.50, respectively. The difference in m/z between these peaks is constant and due to an extra Cl and the loss of a H; the dehydrochlorination step. The SWV plot in Figure 3 deconvolutes into five Gaussians that correspond to the number of chlorinated species in the mixture. The intensities of each Gaussian parallel the intensity of each peak in the MALDI-TOF-MS and they are separated from its neighbours a fixed potential, as happens in the MALDI-TOF-MS where the peaks are separated a fixed m/z. In consequence, mass and potential proceed in a parallel way and one can conclude that the periodic anodic shift in the SWV is also due to the influence of one extra chloride on $Cs[Cl_{x-1}\text{-}\mathbf{1}]$. The periodicity in the $E_{1/2}$ values shown in Figure 3 proves the dehydrochlorination mass and potential additivity described above for the first 6 members of the series. Similar studies have been conducted with directly out of the oven mixtures with higher chlorination patterns or with on purpose made mixtures after combining different synthetic mixtures. The results are displayed in Table 2 together with the whole sequence of $E_{1/2}$ potentials. For each x value, $E_{1/2}$ has been calculated as many times as $Cs[Cl_x\text{-}\mathbf{1}]$ has been found in the different synthetic mixtures; the dispersion of $E_{1/2}(x)$ is very low, proving that the values are self-consistent (see Figure 4). $E_{1/2}$ values for the higher $Cs[Cl_x\text{-}\mathbf{1}]$ members of the series are not given as all mixtures we could prepare contained only traces of such species that prevented an accurate measure of $E_{1/2}$.

Examining the $E_{1/2}$ values, one can see that each Cl addition results in an increase of 0.12 V. Thus, the addition of 8 Cl would imply an increase of 0.96V. For $Cs[Cl_8\text{-}\mathbf{1}]$, an estimated $E_{1/2}$ value near –0.35V = - 1.31 V + 0.96 V would be expected, and the real value is found at -0.36V. The additivity is satisfied very reasonably and also applies to the Co^{II}/Co^{I} couple and most probably to the

Co^{IV}/Co^{III}. Some values are slightly out of the rule, e.g. the $E_{1/2}$ value for $Cs[Cl_9\text{-}\mathbf{1}]$, but this may be due to the always low yield of
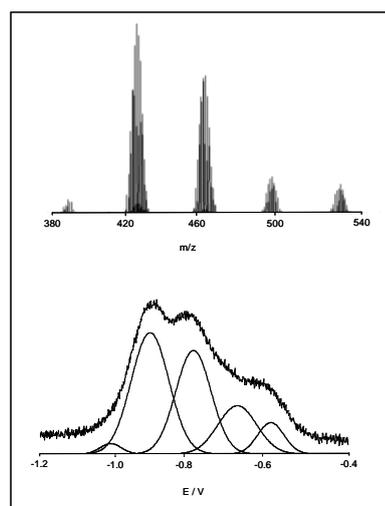

Figure 3. MALDI-TOF mass spectrum of $Cs[Cl_x\text{-}\mathbf{1}]$ with x = 2-6 (up) and deconvolution into Gaussians of its Co^{III}/Co^{II} SWV (down).

this particular anion in any sample produced, more than to a failure of the additivity. In Fig. 2b, the SWV for the Co^{III}/Co^{II} and Co^{II}/Co^{I} look very similar. This has allowed to double check the goodness of fit of the Gaussians deconvolution. Less data has been obtained for the Co^{IV}/Co^{III} couple due to the overall anodic shift upon higher chlorination that has taken the $E_{1/2}$ value for this couple to the anodic edge of the solvent.
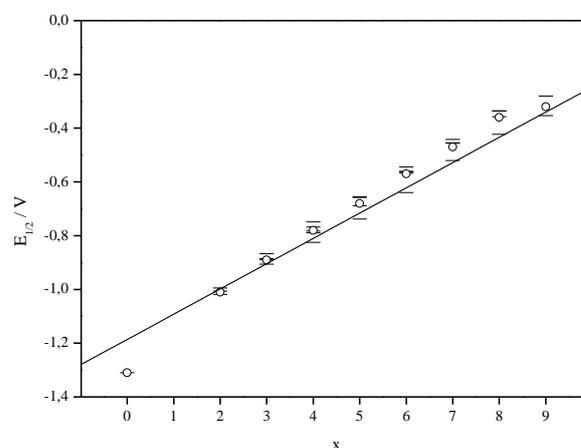

Figure 4. $E_{1/2}$ of all the $Cs[Cl_x\text{-}\mathbf{1}]$ calculated from the deconvolution into Gaussians of the SW voltammograms of the mixtures which contain them. The horizontal lines (—) represent the individual $E_{1/2}$ values whereas the empty circles (○) represent the average $E_{1/2}$ for each number of chlorine atoms.

Preliminary results show that the $E_{1/2}$ additivity modulation also occurs with Br and I derivatives of $Cs[\mathbf{1}]$. For the same number of halogen substituents, the anodic shift follows the next order: $E_{1/2}(Cl) < E_{1/2}(Br) < E_{1/2}(I)$. Each redox potential is shifted near 0.10 V for Co^{III}/Co^{II} and 0.07 V for Co^{II}/Co^{I} when moving from Cl to Br and 0.10 V for both redox processes when moving from Br to I.

Table 2. Calculated energy values of the HOMO and the LUMO of Cs[Cl$_x$-**1**] compared with the E$_{1/2}$ value for their corresponding Co^{III}/Co^{II} process (*vs* Ag/AgCl/KCl$_{sat}$).

Compound	E$_{1/2}$ / [V]	-E$_{HOMO}$ / [eV]	-E$_{LUMO}$ / [eV]	CTC
Cs[**1**]	-1.31	3.963	-0.546	-3.48
Cs[Cl$_1$-**1**]	-	4.060	-0.379	-3.25
Cs[Cl$_2$-**1**]	-1.01	4.163	-0.153	-3.10
Cs[Cl$_3$-**1**]	-0.89	4.261	0.019	-2.94
Cs[Cl$_4$-**1**]	-0.78	4.409	0.195	-2.79
Cs[Cl$_5$-**1**]	-0.68	4.492	0.344	-2.65
Cs[Cl$_6$-**1**]	-0.57	4.609	0.496	-2.51
Cs[Cl$_7$-**1**]	-0.47	4.698	0.596	-2.37
Cs[Cl$_8$-**1**]	-0.36	4.784	0.698	-2.24
Cs[Cl$_9$-**1**]	-0.32	4.838	0.819	-2.13
Cs[Cl$_{10}$-**1**]	-	4.984	0.925	-2.01
Cs[Cl$_{11}$-**1**]	-	5.017	1.026	-1.90
Cs[Cl$_{12}$-**1**]	-	5.149	1.130	-1.78

DFT calculations: To find a theoretical basis on the redox tunability of Cs[Cl$_x$-**1**] species, the E$_{1/2}$ values for the redox couple Co^{III}/Co^{II} have been correlated with their HOMO and LUMO energies. Table 2 displays the HOMO and the LUMO energies along with the E$_{1/2}$ for the couple Co^{III}/Co^{II}. The Cluster Total Charge (CTC) is also shown.[35] CTC is a useful property to interpret the behaviour of boron clusters since it computes all charges on the cluster atoms, not only these in the periphery. In this case, CTC has been computed with the NPA method.[36]

There is a good parallel between the plots of E$_{1/2}$ and -E$_{LUMO}$, as well as between E$_{1/2}$ and -E$_{HOMO}$. Although the E$_{1/2}$ correlation with both E$_{LUMO}$ and E$_{HOMO}$ may seem contradictory, it is not if the first relates to the reduction of Co^{III} to Co^{II} and the second relates to the oxidation of Co^{III} to Co^{IV}. The easiest Cs[Cl$_x$-**1**] to be oxidized is the one with x = 0, which is the one with the more positive HOMO energy, in agreement with the Koopman's theorem. Conversely, the easiest Cs[Cl$_x$-**1**] to be reduced is the one with x = 12, as it has the more stable LUMO. It is also noticeable the correlation between E$_{1/2}$ and the CTC: the species with a more negative CTC charge are the ones that are more difficult to reduce, see Cs[**1**] that has the highest negative CTC. On the contrary, the easiest to be reduced are the ones with the more positive CTC charge.

Conclusion

These redox values are very comparable to the first two reduction waves of C$_{60}$ at -0.48 V for [C$_{60}$]$^{0/-I}$ and -0.87 V for [C$_{60}$]$^{-I/-II}$ *vs* SCE, which is remarkable considering that C$_{60}$ is a neutral molecule whereas [Co(C$_2$B$_9$H$_{11}$)$_2$]$^-$ is an anionic species. These results show that, with a higher degree of chlorination, it should be possible to attain even positive values of E$_{1/2}$. We are currently developing a new method of synthesis that should allow to synthesize species expectedly up to the Cs[Cl$_{12}$-**1**].

Experimental Section

Materials and instrumentation: All metallacarborane anions prepared are air and moisture stable. N-Chlorosuccinimide (NCS) was purchased from Aldrich and used as received. Cs[Co(C$_2$B$_9$H$_{11}$)$_2$] was supplied by Katchem. The mass spectra were recorded in the negative ion mode using Bruker Biflex MALDI-TOF-MS [N$_2$ laser; λexc 337 nm (0.5 ns pulses); voltage ion source 20.00 kV. 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.

General synthetic procedure for the preparation of [3,3'-Co(1,2-C$_2$B$_9$H$_{11}$)$_2$]$^-$ chlorinated derivatives: Cs[3,3'-Co(1,2-C$_2$B$_9$H$_{11}$)$_2$], Cs[**1**], near 0.1 mmol, and the corresponding molar quantity of N-chlorosuccinimide, NCS, for the main target anion in the expected resulting mixture, were crushed together in a glove box until a homogeneous powder was obtained. As an example, if [Cl$_6$-**1**]$^-$ was aimed as one of the dominant anions in the mixture, a 1:6 ratio of Cs[3,3'-Co(1,2-C$_2$B$_9$H$_{11}$)$_2$] and NCS would be mixed. A thick-walled Pyrex tube (20 cm long, 5 mm id and 8 mm od) was charged with the powder. The lower part of the tube was then cooled with liquid N$_2$, evacuated and sealed under vacuum with an energetic flame. Afterwards, the tube was placed inside a protective iron cylinder and put inside a preheated tubular furnace. The temperature of the furnace was maintained for 2 hours at 194±6ºC. The protective cylinder containing the tube was then carefully removed and the whole cooled down to room temperature. The tube was then opened and THF was added in order to perform the characterization by negative MALDI-TOF-MS and get the CV and SWV for the mixture of anions.

Computational methods: Calculations were performed with the Gaussian 03 suite of programs.[37] Geometries of [3,3'-Co(1,2-C$_2$B$_9$H$_{11}$)$_2$]$^-$ and its chlorinated derivatives were fully optimized and HOMO-LUMO energies and NPA (natural population analysis) charges calculated at the B3LYP/3-21G* and B3LYP/6-31+G(d,p) level of theory, respectively.[36] All stationary points were found to be true minima (number of imaginary frequencies, N$_{imag}$=0).

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Tuning Redox Potentials ─────

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Additive tuning redox potential in metallacarboranes by sequential halogen substitution

- 1.31 V

- 0.89 V

- 0.57 V

- 0.32 V

- 0.11 V

- 1 H⁻
+ 1 Cl⁻
+ 0.1 V

$E_{1/2}$ vs. Ag/AgCl/KCl$_{sat}$
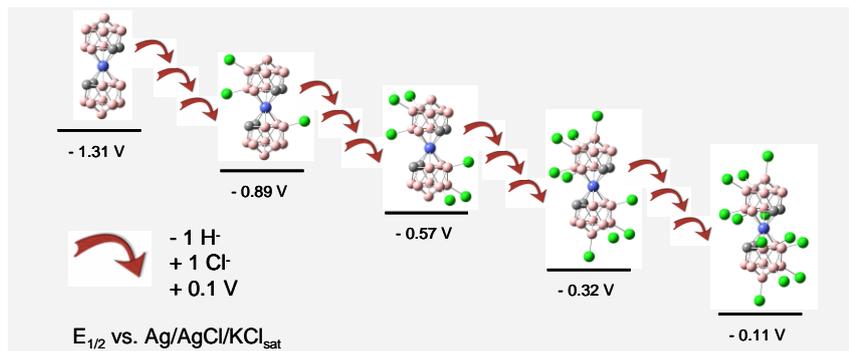
The first artificially made set of electron acceptors derived from a unique platform $Cs[Co(C_2B_9H_{11})_2]^-$ each differing from the predecessor a fix potential is presented. The sequence of electron acceptors is made by substituting one, two or more hydrogen atoms by chlorine atoms.

The higher the number of chlorine substituents, the more prone the platform is to be reduced. The effect is completely additive so that each substitution implies a 0.1 V anodic shift.