Additive Tuning of Redox Potential in Metallacarboranes by Sequential Halogen Substitution

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Abstract: The first artificially made set of electron acceptors is presented that are derived from a unique platform Cs-$[3,3'-Co(C_2B_9H_{11})_2]$, for which the redox potential of each differs from its predecessor by a fixed amount. The sequence of electron acceptors is made by substituting one, two, or more hydrogen atoms by chlorine atoms, yielding $Cs[3,3'-Co(C_2B_9H_{11-y}Cl_y)(C_2B_9H_{11-z}Cl_z)]$. The higher the number of chlorine substituents, the more prone the platform is to be reduced. The effect is completely additive, so if a single substitution implies a reduction of 0.1 V of the redox potential of the parent complex, then ten substitutions imply a reduction of 1 V.

Keywords: chlorination · electron transport · metallacarboranes · redox chemistry · 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 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 largely eliminated facilitating ET. However, tuning of a redox potential in an additive and stepwise fashion by fixed increments 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 such 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 tuning of the redox potential. This platform is $[3,3'-Co-(C_2B_9H_{11})_2]^-$ ($\mathbf{1}^-$) and it has many sites for substitution; in addition, the B–Cl bonds are very strong, stronger than the C–Cl sites. This may have been the reason for such uniqueness.

Boron clusters approximate to deltahedra or to deltahedra with one or more vertices missing. In the early 1970s, it was realised that the geometry of boron clusters is related to 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 characterised by a closed-cage structure, the first requires much less energy to incorporate $2e^-$ than the carboranes, -0.87 versus -2.50 V, respectively, being both values referred to saturated calomel electrode (-1.03 and -2.66 V, respectively, referred to the Fc^+/Fc couple; onwards, all the potential values in this paper will be referred to this couple).[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]

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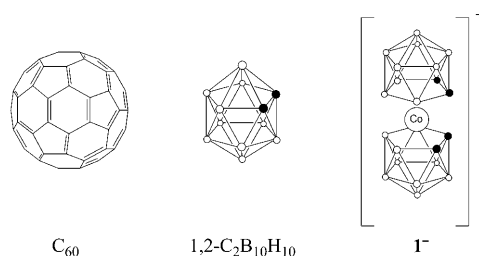
Figure 1. Schematic representation of C_{60}, $1,2\text{-}C_2B_{10}H_{10}$ and $Cs[3,3'\text{-}Co\text{-}(1,2\text{-}C_2B_9H_{11})_2]$ ($Cs[\mathbf{1}]$)molecules.

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 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 known Co^{III} species $Cs[3,3'\text{-}Co(C_2B_9H_{11})_2]$, $Cs[\mathbf{1}]$.[29,30] In this work, we show how the stepwise chlorination of $\mathbf{1}^-$ parallels an easier electron reduction in all three redox couples existing in $Cs[\mathbf{1}]$. Besides, the ease of electron reduction is additive by a fixed amount upon each new chlorination step.

Results and Discussion

Experimental studies: $[3,3'\text{-}Co(C_2B_9H_{11})_2]^-$ shows three quasi-reversible waves in cyclic voltammetry at $+1.47$, -1.51 and -2.46 V versus Fc+/Fc 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 is known that the redox potential of the dichlorinated anion $[NMe_4][3,3'\text{-}Co(C_2B_9H_{10}Cl)_2]$ is -1.19 V for the couple Co^{III}/Co^{II},[32] about 0.3 V more positive than for $\mathbf{1}^-$. This corresponds to 0.3 V for two steps of chlorination, and we wanted to learn if it was possible that with a higher number of chlorination steps whether the ease of reduction would increase accordingly. To prove the potential tuning of $Cs[\mathbf{1}]$, it was necessary to have a wide set of consecutive halogenated derivatives. The only reported synthesis of chlorinated derivatives of $Cs[\mathbf{1}]$ was based on the reaction of Cl_2 with $Cs[\mathbf{1}]$; this reaction produced mixtures of complexes with several Cl atoms ranging from 2 to 6.[33] On the other hand, pure $[HNMe_3][3,3'\text{-}Co(C_2B_9H_{10}Cl)_2]$ has been reported to be syn-

thesised by reaction of *N*-chlorosuccinimide with $Cs[\mathbf{1}]$ in THF.[34] To easily correlate the number of Cl substituents on platform $\mathbf{1}^-$ and the additive potential shift described in this work, we have named the halogenated species $Cs[3,3'\text{-}Co(C_2B_9H_{11-y}Cl_y)(C_2B_9H_{11-z}Cl_z)]$ as $Cs[Cl_x\text{-}\mathbf{1}]$, with x being the total number of chlorine atoms exchanged for hydrogen atoms in $Cs[\mathbf{1}]$.

As previously said, only $[HNMe_3][Cl_2\text{-}\mathbf{1}]$ and $Cs[Cl_6\text{-}\mathbf{1}]$ were known before this work, the latter being indeed a mixture of species from $Cs[Cl_2\text{-}\mathbf{1}]$ to $Cs[Cl_6\text{-}\mathbf{1}]$.[33] This had prevented an accurate calculation of $E_{1/2}$ for $Cs[Cl_6\text{-}\mathbf{1}]$ as the cyclic voltammetry (CV) wave was very complex (see Figure 2 a). Even so, the CV wave corresponding to the Cs
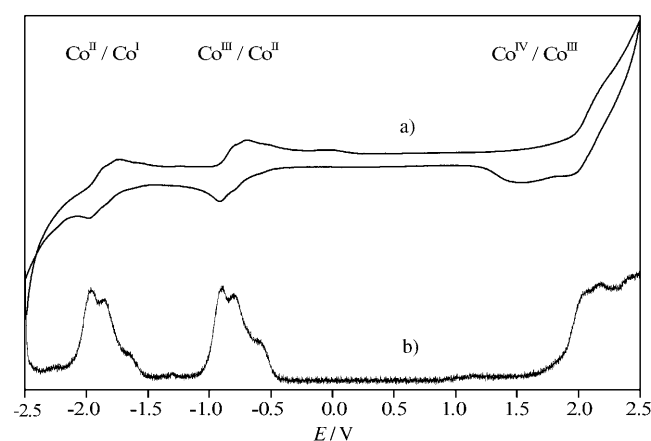

Figure 2. a) Cyclic voltammogram and b) square wave voltammogram responses recorded at a glassy carbon electrode in MeCN of 5×10^{-3} M $Cs\text{-}[Cl_x\text{-}\mathbf{1}]$ ($x = 2$–6) with $[NBu_4][PF_6]$ (0.1 M) as the supporting electrolyte. The electrochemical cell contained $Ag/AgCl/KCl_{sat}$ as the reference electrode and a platinum wire as the auxiliary electrode. The potential values have been referred to Fc+/Fc. Scan rate: a) 0.2 V s^{-1}, b) 0.025 V s^{-1}.

$[Cl_2\text{-}\mathbf{1}]$ to $Cs[Cl_6\text{-}\mathbf{1}]$ mixture was shifted to more positive $E_{1/2}$ values than for $Cs[Cl_2\text{-}\mathbf{1}]$ and, furthermore, the CV wave corresponding to $Cs[Cl_2\text{-}\mathbf{1}]$ was shifted to more positive values than that for $Cs[\mathbf{1}]$. These facts motivated us to find a more efficient chlorination method that eventually would lead to more chlorine-enriched mixtures.

The objective was to see if the CV wave really moved towards more anodic voltages with an increase in the degree of chlorination of $Cs[\mathbf{1}]$. After several unsuccessful trials, we discovered a useful method to increase the chlorination degree of $Cs[\mathbf{1}]$ by reacting *N*-chlorosuccinimide with $Cs[\mathbf{1}]$ in the oven at $200(\pm 6)°$C in a vacuum sealed tube. By varying the ratio of reagents, a set of series of $Cs[Cl_x\text{-}\mathbf{1}]$ ($x > 2$) was obtained, each series consisting of a limited number of x values in an approximately Gaussian distribution (see Supporting Information). The Gaussian curve shifted to more enriched chlorinated derivatives of $Cs[\mathbf{1}]$ by increasing the NCS/$Cs[\mathbf{1}]$ ratio. The CV of the synthesised 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 envelope (see Table S1 in Supporting Information). This was possible because the $Cs[Cl_x-\mathbf{1}]$ mixtures are made of chemically and structurally very similar compounds, so their MALDI-TOF-MS represent the chemical composition of the studied samples extremely well. Each peak in each mixture had the appropriate isotopic composition and was separated from its neighbour either 35 or 36 mass units. The most chlorine-enriched derivative produced was the $Cs[Cl_9-\mathbf{1}]$ salt.

Electrochemistry of chlorinated mixtures: The CV of each of these mixtures is very similar to the wave shown in Figure 2a, but all of them were consistently shifted to anodic potentials as the average x value in the $Cs[Cl_x-\mathbf{1}]$ 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 chlorination step on the platform $Cs[\mathbf{1}]$. 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–F (see Table 1) to study their redox potentials. The square wave voltammetry (SWV) was the technique that provided more fine structure
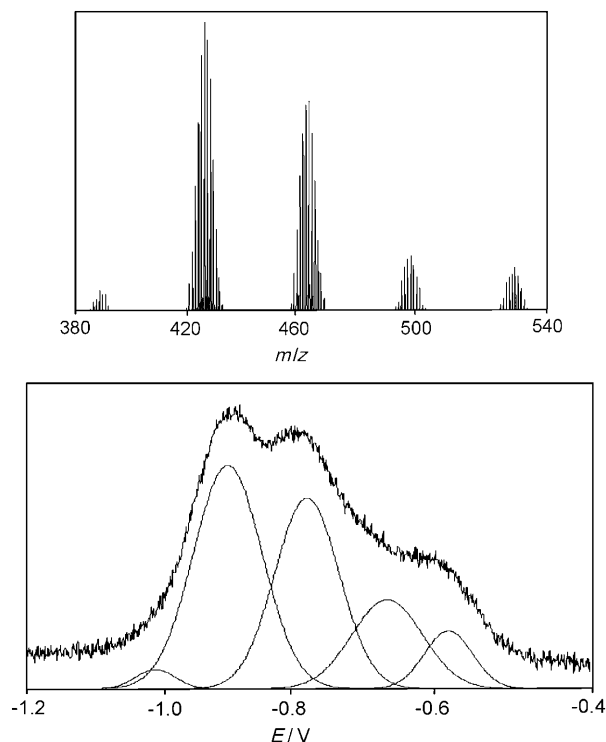

Figure 3. MALDI-TOF mass spectrum of $Cs[Cl_x-\mathbf{1}]$ with $x=2$–6 (top) and deconvolution into Gaussians of its Co^{III}/Co^{II} SWV (bottom) from sample B.

Table 1. Percentage composition of the mixtures of $Cs[Cl_x-\mathbf{1}]$ 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.

	$[Cl_2-\mathbf{1}]^-$	$[Cl_3-\mathbf{1}]^-$	$[Cl_4-\mathbf{1}]^-$	$[Cl_5-\mathbf{1}]^-$	$[Cl_6-\mathbf{1}]^-$	$[Cl_7-\mathbf{1}]^-$	$[Cl_8-\mathbf{1}]^-$	$[Cl_9-\mathbf{1}]^-$
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	–

in the electrochemical wave to warrant individual $E_{1/2}$ calculations. In Figure 2b, the SWV for $Cs[Cl_x-\mathbf{1}]$ ($x=2$–6) is indicated. When the chemical composition, drawn from MALDI-TOF MS, and deconvolution into Gaussian curves of the corresponding SWV were combined, a set of self-consistent $E_{1/2}$ values for each x value could be obtained for the Co^{III}/Co^{II} redox process, as outlined in Figure 3. The MALDI-TOF MS and SWV data 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.

The MALDI-TOF MS in Figure 3 (top) corresponds to sample B, made up of $Cs[Cl_2-\mathbf{1}]$, $Cs[Cl_3-\mathbf{1}]$, $Cs[Cl_4-\mathbf{1}]$, $Cs[Cl_5-\mathbf{1}]$ and $Cs[Cl_6-\mathbf{1}]$; each peak shows the proper isotopic distribution centred 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 the addition of an extra chlorine atom

and the loss of hydrogen; that is, the chlorination step. The SWV plot in Figure 3 deconvolutes into five Gaussian curves 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 by a fixed potential, as also happens in the MALDI-TOF MS in which the peaks are separated a fixed m/z. In consequence, the change in mass and potential proceeds in a parallel fashion and one can conclude that the periodic anodic shift in the SWV is also due to the influence of one extra chloride on $Cs[Cl_{x-1}-\mathbf{1}]$. The periodicity in the $E_{1/2}$ values shown in Figure 3 (bottom) proves the chlorination mass and potential additivity described above for the first six members of the series. Similar studies have been conducted with directly out of the oven mixtures with higher chlorination patterns or with purposely prepared mixtures after combining different synthetic procedures. 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 $Cs[Cl_x-\mathbf{1}]$ 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). The $E_{1/2}$ values for the higher $Cs[Cl_x-\mathbf{1}]$ members of the series are not given, only

Table 2. Calculated energy values of the HOMO and LUMO of $Cs[Cl_x\text{-}1]$ compared with the $E_{1/2}$ value for their corresponding Co^{III}/Co^{II} process (versus Fc^+/Fc).

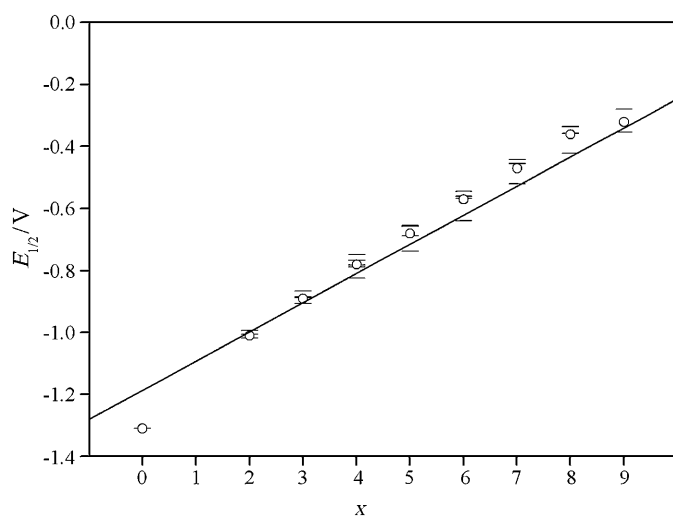|	$E_{1/2}$ [V]	$-E_{HOMO}$ [eV]	$-E_{LUMO}$ [eV]	CTC
Cs[1]	−1.51	3.963	−0.546	−3.48
Cs[Cl$_1$-1]	–	4.060	−0.379	−3.25
Cs[Cl$_2$-1]	−1.21	4.163	−0.153	−3.10
Cs[Cl$_3$-1]	−1.09	4.261	0.019	−2.94
Cs[Cl$_4$-1]	−0.98	4.409	0.195	−2.79
Cs[Cl$_5$-1]	−0.88	4.492	0.344	−2.65
Cs[Cl$_6$-1]	−0.77	4.609	0.496	−2.51
Cs[Cl$_7$-1]	−0.67	4.698	0.596	−2.37
Cs[Cl$_8$-1]	−0.56	4.784	0.698	−2.24
Cs[Cl$_9$-1]	−0.52	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

Figure 4. $E_{1/2}$ of all the $Cs[Cl_x\text{-}1]$ 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 $E_{1/2}$ versus Fc^+/Fc for each number of chlorine atoms.

traces of such species were found in all the mixtures prepared, preventing 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 eight chloride ions would imply an increase of 0.96 V. For $Cs[Cl_8\text{-}1]$, an estimated $E_{1/2}$ value near $-0.55\,V = -1.51 + 0.96\,V$ would be expected, and the real value is found at $-0.56\,V$. 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} couple. Some values are slightly out of the rule, for example, the $E_{1/2}$ value for $Cs[Cl_9\text{-}1]$, but this may be due to the always low yield of this particular anion in any sample produced, more than to a failure of the additivity. In Figure 2b, the SWV for the Co^{III}/Co^{II} and Co^{II}/Co^{I} look very similar. This has allowed us to double check the goodness of fit of the Gaussian deconvolution. Less data has been ob-

tained 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.

Preliminary results show that the $E_{1/2}$ additivity modulation also occurs with Br and I derivatives of Cs.[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.

DFT calculations: To find a theoretical basis on the redox tunability of $Cs[Cl_x\text{-}1]$ 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 natural population analysis (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 $Cs[Cl_x\text{-}1]$ compound to be oxidised is that with $x = 0$, which is the one with the more positive HOMO energy, in agreement with the Koopman's theorem. Conversely, the easiest $Cs[Cl_x\text{-}1]$ to be reduced is that with $x = 12$, as it has the more stable LUMO. There is also noticeable correlation between $E_{1/2}$ and the CTC: the species with a more negative CTC charge are more difficult to reduce; see, for example, Cs[1], which has the highest negative CTC. In contrast, the compounds that are reduced most easily are those with the more positive CTC charge.

Conclusion

These redox values are very comparable to the first two reduction waves of C_{60} at -0.64 V for $[C_{60}]^{0/-I}$ and -1.03 V for $[C_{60}]^{-I/-II}$ versus Fc^+/Fc, which is remarkable considering that C_{60} is a neutral molecule, whereas $[3,3'-Co(C_2B_9H_{11})_2]^-$ 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 us to synthesise specific species up to the $Cs[Cl_{12}\text{-}1]$.

Experimental Section

Materials and instrumentation: All metallacarborane anions prepared were air and moisture stable. *N*-Chlorosuccinimide (NCS) was purchased from Aldrich and used as received. $Cs[3,3'-Co(C_2B_9H_{11})_2]$ was supplied by Katchem. The mass spectra were recorded in the negative ion mode

by using Bruker Biflex MALDI-TOF MS [N$_2$ laser; λ_{exc} 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 a 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. All the potential values were referred to the Fc$^+$/Fc couple [$E_{1/2}$ (Fc$^+$/Fc) = 0.20 V versus Ag/AgCl/KCl$_{sat}$].

General synthetic procedure for the preparation of chlorinated derivatives of [3,3′-Co(1,2-C$_2$B$_9$H$_{11}$)$_2$]$^-$: Cs[**1**] ($\approx$0.1 mmol), and the corresponding molar quantity of N-chlorosuccinimide (NCS), for the main target anion expected in the resulting mixture, were crushed together in a glove box until a homogeneous powder was obtained. As an example, if [Cl$_6$-**1**]$^-$ was the desired dominant anion in the mixture, a 1:6 ratio of Cs[**1**] and NCS was to 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 h at 194 ± 6 °C. 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 characterisation 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 optimised 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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