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Novel homogeneous selective electrocatalysts for CO_2 reduction: an electrochemical and computational study of cyclopentadienyl-phenylendiamino-cobalt complexes

Nicola Melis,[a] Francesca Mocci,[b] Annalisa Vacca [a] and Luca Pilia *[a]

Four cyclopentadienyl-phenylendiamino-cobalt complexes [CoCp(bqdi)] with different substituents (R) at the phenylene moiety (bqdi, **I**; *o*-perfluoro-bqdi, **II**; *p*-NO_2-bqdi, **III**; *p*-COOH-bqdi, **IV**) have been studied with the aim to investigate their capability as catalysts for CO_2 reduction. These compounds were characterized by cyclic voltammetry measurements both under nitrogen and CO_2 atmospheres, showing a increase of the cathodic current ranging from 3.36 (**III**) to 5.59 times (**II**) respect to the measurement under nitrogen. Moreover, by addition of water the current enhancement in the presence of CO_2 arrives till 31.07 times in the case of complex **II**. Interestingly, these complexes present a very good selectivity toward CO_2 reduction respect hydrogen even in the presence of water. Relative turnover frequencies have been also estimated given values ranging from 3.23 (**III**) to 187.21 s^{-1} (**II**) in the presence of water. In addition, these results have been analysed by means of density functional theory (DFT) calculations and Fukui functions analysis. In particular, DFT results clearly show the effects of the different substituents on the electrochemical properties of these compounds. Whereas the Fukui functions analysis indicates that the most favourable positions for electrophilic attack on the reduced complex are the nitrogen and the cobalt atoms.

Introduction

Carbon dioxide (CO_2) is a particularly stable molecule which is the final oxidation state of organic compounds. It is naturally produced by vegetal and animal respiration and mainly, as a consequence of human civilization, by fossil fuels combustion. Despite it is well known to be a green-house gas, it is also one of the most abundant carbon sources and it could be also considered a cheap, fossil-free, building block in the synthesis of organic derivatives and intermediates rather than a waste.[1–3] Indeed, the production of several chemicals from CO_2 can be way cheaper than the current market price.[4] As a matter of fact, the conversion of CO_2 to useful derivatives with a smaller oxidation state necessarily needs energy to be carried out. Among the different approaches for its conversion, electrochemistry represents one of the most promising method because it is a straightforward, clean and very versatile technique.[5–8] Moreover, due to the large amount of studies and technologies on alternative and eco-sustainable manners of energy productions, the use of electricity is becoming more and more sustainable from both economic and environmental point of view. Indeed, the cost of electricity generated from wind and solar photovoltaic has become competitive with fossil fuel based electricity generation technologies.[9] Furthermore, electrochemical reactions (such as H^+, N_2 or CO_2 conversion) can be also used in order to store the excess of electricity produced from sustainable sources in periods of low consumption. However, to achieve these goals, electrocatalysts with high activity and selectivity are absolutely necessary.[10,11]

Unfortunately, CO_2 reduction process does not occur very easily and suffers of high overpotentials because of the CO_2 to $CO_2^{\bullet -}$ reduction step. This reaction has been determined as the first step for CO_2 activation for subsequent reduction reactions and, moreover, it has also been recognized to be the rate determining step for CO_2 reduction. Therefore, CO_2 conversion by electrochemical methods is highly limited by kinetics despite the low and promising equilibrium potential values from a thermodynamic point of view. Additionally, in the right conditions (electrodes, solvent, support electrolyte, *etc*…) some compounds can further react to yield a complex mixture of products that can arise both from different direct reductions of CO_2 and from further electrochemical and chemical reactions of some reduction intermediates (*e.g.* CO, methanol, formaldehyde). The intrinsic difficulties on controlling that number of reaction pathways have to be considered, in addition to other parasite processes such as hydrogen evolution reaction (HER) which is very favourite in aqueous solvents and with the majority of electrodes and conditions. Thus, even the reductive processes that should occur at a

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[a] Dipartimento di Ingegneria Meccanica Chimica e dei Materiali, Università di Cagliari, via Marengo 2, I09123, Cagliari, Italy. E-mail: pilialuc@unica.it
[b] Dipartimento di Scienze Chimiche e Geologiche, Università di Cagliari, S.S. 554 Km 4,500, I09042 Monserrato, Italy.

Electronic Supplementary Information (ESI) available: Synthesis and supplementary fig. S1-S6 and tab. S1-S4. See DOI: 10.1039/x0xx00000x lower potential than HER (*e.g.* methane) are inhibited by kinetic reasons and hydrogen evolution is observed instead. For these reasons, there is an increasing interest in the development of suitable approaches to lower the overpotential of the transformation of interest, force a mechanistic pathway and improve efficiency and selectivity towards a specific product.

As far as the electrochemical methods are concerned, electrocatalysts based on metal complexes have been proved to be a good option in relation to the versatility and tunability of their properties.[12–16] Such molecular species generally possess a good long-term stability and tolerance to experimental conditions and they are amenable of modulation of their catalytic and chemical physical properties. In fact, through variation of the metal centre or a rational ligand design, they can be modified in order to fit to specific purposes such as improve solubility or stability, promote specific inter-molecular interactions or enhance and tune spectroscopic or electrochemical properties. Moreover, they often possess a better selectivity in comparison to solid-phase catalysts and the immobilization of such derivatives on solid supports is gaining increasing importance.[17]

Even though carbon dioxide has been considered to have poor coordinating properties as a ligand due to its general chemical stability,[18] it possesses both electrophilic and nucleophilic characters as proved in many CO_2-metal isolated adducts.[19] Despite the coordination mode involved, it is generally recognized that an interaction between the active form of the complex and CO_2 it is necessary for the reaction to occur. Among the many metal complexes proposed as electrocatalysts for CO_2 reduction, those bearing non-innocent ligands received great attention: in fact, the localized electron density on the ligand portion of the complex in its reduced state allows the ligand to interact with CO_2 via σ and π bonds.[20–23] Moreover, in this context, cobalt as metal centre has gained importance in reductive processes of both hydrogen and carbon dioxide.[24–27]

Therefore, since redox-active ligands and H-bond-active functionalities such as NH seems to exhibit a key role for this purpose, we thought to prepare and test some heteroleptic half sandwich cobalt derivatives with an *o*-phenylendiamino ligand, which is known to be a non-innocent ligand and that can be easily further functionalized.[28] This class of coordination compounds have been previously studied due to their interesting spectroscopic properties and their possible applications in the optoelectronic field. Despite this, these systems received relatively low attention since their first synthesis by Heck in late '60s.[29,30]

In order to rationalize the results and understand the effect of the substituent pattern on the electronic distribution and on the catalytic effect, all the compounds were studied by means of density functional theory (DFT) calculations. Furthermore, the Fukui function analysis was used to verify the region of the reduced catalyst most prone to an electrophilic attack from CO_2.

Results and discussion

We decided to work on a selected group of cyclopentadienyl-phenylendiamino-cobalt complexes [CpCo(bqdi)], whose structures are shown in Chart 1.

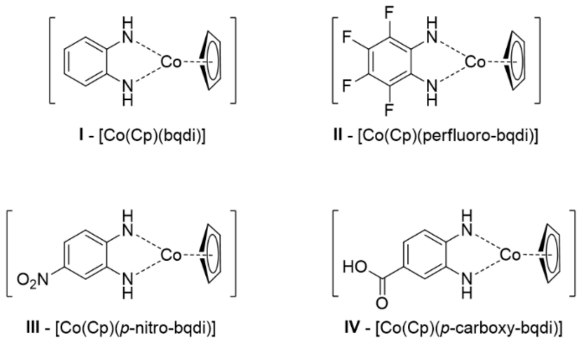


Chart 1 - Chemical structures of complexes **I-IV**.

In particular, we chose the parent compound [CoCp(bqdi)] **I** with a non-susbtituted *o*-phenylendiamine ring and theperfluorinated analogue [CoCp(*o*-perfluoro-bqdi)] **II** in order to evaluate the effect of fluorine in lowering the energy of the molecular orbitals on the catalytic properties. Moreover, the effect of the presence of nitro and carboxy electron withdrawing groups on the catalytic activity, have been studied by preparing the corresponding [CoCp(*p*-NO_2-bqdi)] **III** and [CoCp(*p*-COOH-bqdi)] **IV** complexes.

We first investigated the electrochemical properties of all the four complexes performing cyclic voltammetry (CV) measurements under nitrogen atmosphere. As can be seen in Figure1a, complex **I** shows a *quasi-reversible* redox couple centred at -1.25 V which is a typical feature of this family of complexes, as previously reported in the literature.[30,31] The fluorinated analogous **II** shows as well the characteristic redox couple, which is consistent with the recently reported study on

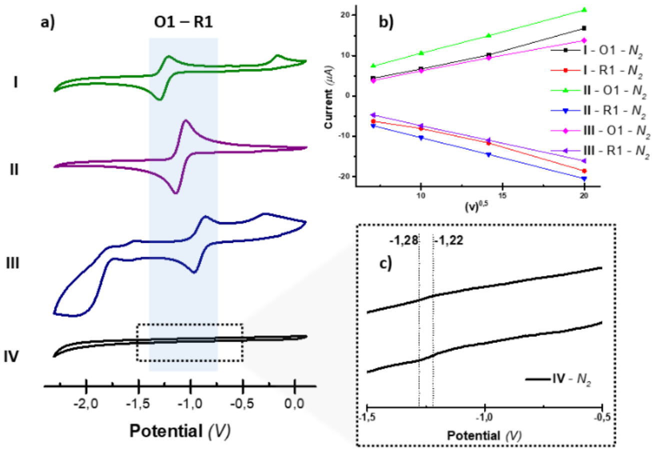


Figure 1 - a) CV measurements of anhydrous complexes **I-IV** under nitrogen atmosphere. b) Correlation of O1 and R1 current with the square root of the scan rate for the complexes **I-III**. c) Magnification of the CV of complex **IV** in the range of -1.5 V and -0.5 V.

this compound.[32] In this case, the redox couple shows a reversible behaviour (I/I=1) and it is shifted to less negative potentials ($E_{1/2}$=-1.10 V) with respect to complex **I** because of the electron-withdrawing effect of the fluorine atoms on the phenyl moiety that make the complex easier to be reduced.

Complex **III** was studied in the same conditions and it showed, similarly to the other two compounds, the characteristic *quasi-reversible* redox couple. The electron-withdrawing effect of the nitro group led to a strong anodic shift of the redox couple ($E_{1/2}$=-0.92 V) with respect to the parent compound. Moreover, being the nitro group electrochemically active, the two additional electrochemical features can be associated to possible reduction processes of this functional group: a *quasi-reversible* peak centred at -1.57 V along with a cathodic wave around -1.90 V are observed. Similar behaviour has been observed by other authors during the reduction of nitrobenzene and nitrophenol in aprotic solvents such as DMF, DMSO and ionic liquids: a first reversible reduction step followed by a chemically irreversible step has been found.[33,34] The current intensities for the redox couple for complexes **I-III** show a linear dependence as a function of the square root of the scan rate (see Figure 1b), indicating a diffusion controlled redox process. Related linear fits and R2 values for these data are reported in S1-S3. Finally, in the case of complex **IV**, the low solubility hampers the CV analyses and neither the magnification of the voltammetry shows appreciable peaks (Figure 1c).

Table 1. Peaks analysis of complexes **I-III** under nitrogen atmosphere.

	O1 (V)	**R1** (V)	**E1/2** (V)	**ΔE** (mV)	Iox/Ired	**n** e^-
I	-1,21	-1,29	-1,25	80,6	0,69	1
II	-1,05	-1,14	-1,10	90.7	1,06	1
III	-0,87	-0,97	-0,92	100.7	0,68	1

Table 1 lists the main electrochemical parameters derived from the analyses of the CVs: as can be seen, the redox potential shift towards less negative potentials starting from complex **I** to **III**. For these complexes the ratio between the cathodic and the anodic current at the related peaks, is almost equal to the unity and the trend of the current at the anodic and cathodic peaks as a function of the square root of the scan rate shows a good linearity indicating reversible redox process involving one electron. Since redox peaks cannot be clearly detected, the analysis of the electrochemical parameters for complex **IV** was not possible.

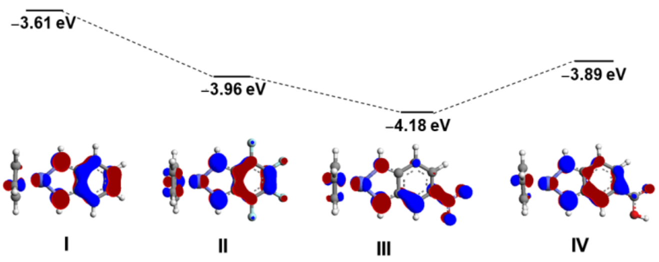


Figure 2 – Single occupied molecular orbitals (SOMOs) of the monoanions of the complexes I-IV with the corresponding energies.

In order to roughly estimate the relative reduction capability of the investigated complexes, the energy of their frontier orbitals, both in the neutral and monoanionic forms, have been calculated by DFT methods (see Figures 2 and S4 and Table S1). As one can see, the trend found is consistent with that of reduction potentials (**I** shows the highest SOMO energy and the most negative R1). Moreover, in the case of complex **IV**, the SOMO energy is just slightly less negative than that of **II**, suggesting a similar reduction potential. In addition, the reduction potential of complex **IV** has been estimated using the empiric relation proposed by D'Andrade *et al.*, which correlates the energy of the frontier orbitals with the experimental redox potential (*vs* $Fc^{0/+}$).[35] In particular, the energy of the calculated lowest unoccupied molecular orbital (LUMO) of the neutral complexes was used to predict the reduction potential (whilst the energy of the highest occupied molecular orbital (HOMO) is related to the oxidation potential) using the following equation (1):

$$\boldsymbol{E_{LUMO}} = (1.4 \pm 0.1) \cdot (q\boldsymbol{V_{CV,red}}) - (4.6 \pm 0.08) \qquad \textbf{(1)}$$

The reduction potentials calculated using this relation correlate well with the experimental data in our conditions, as reported in Figure 3. The linear fit on data of complexes **I-III** (R^2=0.9958) allows to extrapolate the estimated reduction potential of complex **IV**, giving -1.16 V *vs* Pt (reference electrode in our CV measurements). This value, although roughly estimated, is slightly more negative that of complex **II**, in agreement with the findings of DFT calculations reported above.

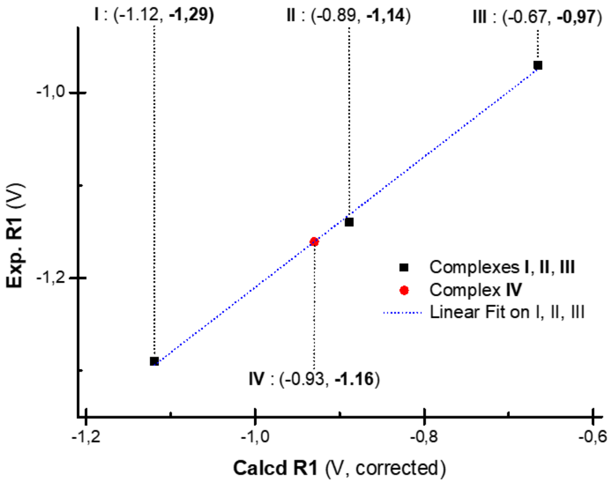


Figure 3 – Correlation between calculated **R1** by using the equation (**3**) and the experimental **R1** of complexes **I**, **II** and **III** (*black data*). Calculated **R1** has been corrected for the used experimental conditions (*vs Pt*). The value for complex **IV** (*red spot*) was calculated by using the equation of the linear fit (*blue line,* see Table S1).

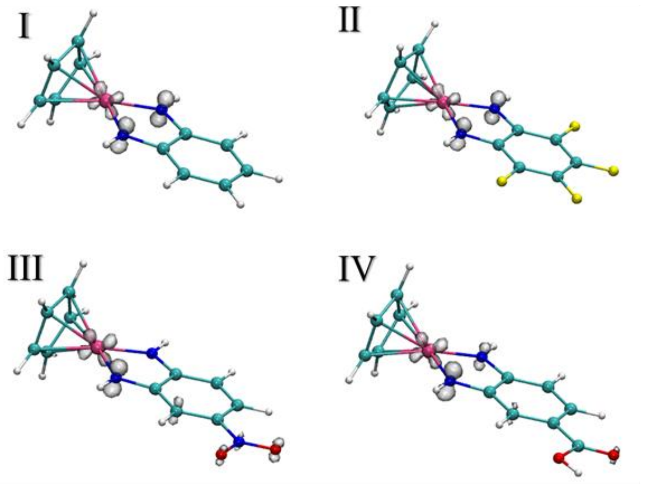


Figure 4 – Representation of the Fukui function *f*- of the monoanions, isodensity level 0.01.

Analysis of the Fukui function *f*- of the monoanions, see Figure 4, indicates that the most favourable position for electrophilic attack are the nitrogen and the cobalt atoms. It can be seen that in compound **III**, the highly electronegative nitro group withdraw the electron density from the nitrogen atom in para position with respect to the nitro group, while in compounds **I**, **II** due to the symmetry of the compounds, both the coordinating nitrogen atoms are equally susceptible of electrophilic attack. Compound **IV** is in an intermediate situation with the N atom in para to the carboxylic group being less prone to the electrophilic attack.

To quantify the effect of the substituents attached to the benzene ring on the redox activity, we calculated the Hirschfeld charges in the N-Co-N region of the anions, where, according to the *f*- function, the electrophilic attack should occur, leading to the oxidation of the anion. The charge on the N-Co-N moiety, shown in Figure 5, correlates well with the O1 potential in Table 1.

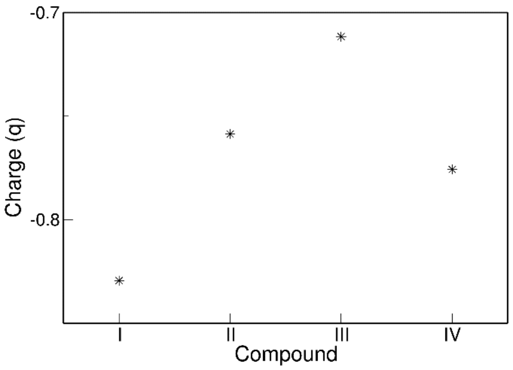


Figure 5 – ADCH partial charge on the N-Co-N portion of the anionic form of the complexes.

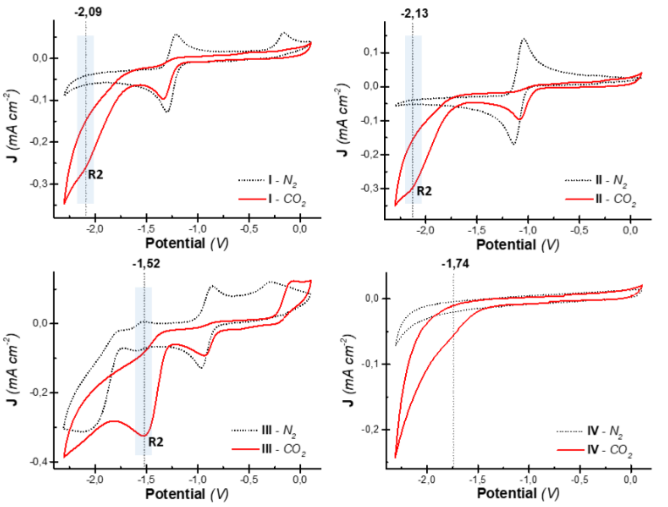


Figure 6 – CVs of anhydrous complexes **I-IV** under nitrogen (*black line*) and carbon dioxide (*red line*) atmosphere.

The results of the cyclic voltammetry analysis of the anhydrous solution of complexes **I-IV** saturated with CO_2 are displayed in Figure 6. As previously reported in several studies,[16] in case of electrocatalysts with a reversible redox couple, the interaction with CO_2 causes the loss of the reversibility and only the reduction process is therefore observed, in accordance with a chemical re-oxidation of the complex by CO_2. Moreover, for all the investigated compounds, an additional cathodic peak, consistent with the CO_2 reduction process, is found at more negative potentials. In the case of complexes **I** and **II** (Figure 6) the above mentioned additional peak starts around -1.6 V, with formation of a shoulder below -2 V. The current enhancements observed upon addition of CO_2, stated as I_{cat}/I_p ratio (I_{cat} = current intensity with CO_2 at a given potential, I_p = current intensity in N_2 atmosphere at the same potential) are 4.12, 5.59 and 4.52 for complex **I**, **II** and **III**, respectively (see Table 2). Complex **IV**, despite its poor electrochemical response, shows a catalytic current in presence of CO_2, with an I_{cat}/I_p of 2.78 in correspondence of a shoulder at -1,74 V.

Since most of the reductive processes of CO_2 involve protons,[5] we decided to investigate the influence of water as

Table 2. Peak analysis of anhydrous complexes **I-IV** under CO_2 and corresponding enhancements.

	R1 (V)	**Ep/2** (V)	**R2** (V)	**Ep/2** (V)	E (V)	I_{cat}/I_p
I	-1.32	-1.26	-2.06	-1.80	-2,09	4,12
II	-1.08	-1.01	-2.11	-1.97	-2,13	5,59
III	-0.93	-0.86	-1.50	-1.39	-1,52	4.52
IV	-	-	-	-	-1.74	2.78

proton source with progressive additions of 200 μL in a range of 0-9%$_{v/v}$ H_2O/DMSO. Moreover, in order to spotlight any hydrogen evolution current and therefore, investigate the selectivity of these complexes towards the CO_2 reduction in aqueous media, we explored the effect of water under saturation conditions of both N_2 and CO_2 (see Figure 7 and Table 3 and S3). We were glad to notice in all the cases we studied, an increased reductive current due to the effect of water. In particular, complexes **I** and **II** show considerable current enhancements (I_{cat}/I_p) at 9.09%$_{v/v}$ in the amount of 24.4- and 31.1–folds, respectively. Pleasingly, very poor residual currents were observed when, after the addition of water, the system has been saturated with nitrogen again (1.08 and 1.04 times for **I** and **II**, respectively). These findings rule out any relevant contribution of hydrogen evolution and therefore, show a high selectivity of these complexes toward the catalytic reduction of CO_2 in the presence of water, which is of paramount importance from an application point of view.

Complex **III** behaved differently; in fact, with only CO_2 under anhydrous condition we observed a significant enhancement at -1.52: at this potential the addition of water led to a small decreasing of current density (from 3.98 to 3.24 I_{cat}/I_p). Moreover, the residual current with water and under nitrogen saturated atmosphere is 1.9 folds more intense compared to that observed in anhydrous condition. Interestingly, in the presence of water complex **III** exhibits a more noticeable enhancement at a lower potential (-2.13 V) similar to that observed for the other complexes. Despite these consideration, as reported in Table 3, the best results are related to the peak at -1.52 V even if the calculated TOF is low and the complex seems to be more effective under anhydrous conditions.

Complex **IV** showed three possible potential values depending on the amount of water. At -1.74 V, a maximum enhancement of 7.85 times with 7.4%$_{v/v}$ amount of water and 1.78 times of residual current with 9.1% of water under nitrogen atmosphere. With the addition of water, a new shoulder at -1.91 V can be observed: in this case a maximum enhancement of 9.5 times with 5-7% of water and a higher residual current (2.5 times). Moreover, with the increase of the water content, a third shoulder at -2.13 can be observed and at this potential value a catalytic current 9.1 times higher than the anhydrous complex under nitrogen is recorded. Nevertheless, in this condition the residual current is 5 times more intense, suggesting hydrogen evolution process.

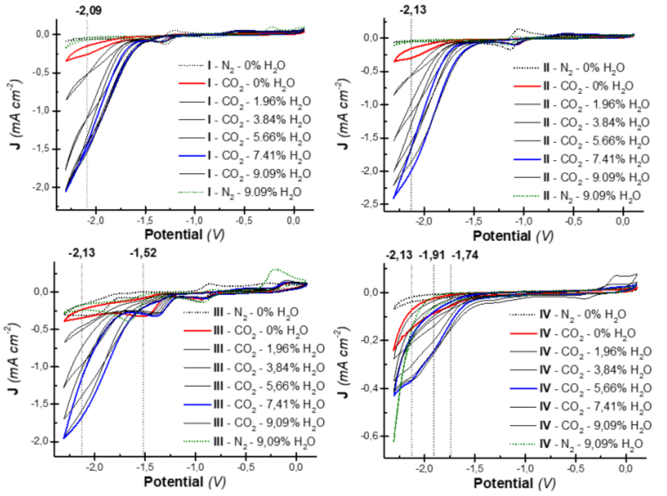


Figure 7 - Effect of water on the CVs of complexes **I-IV**. Black dotted line is referred to anhydrous complexes under N_2, the red line to anhydrous complex under CO_2, blue line to the maximum enhancement under CO_2 due to water and the green dotted line to the maximum amount of water under N_2.

Moreover, we also calculated the turnover frequency (TOF) value using the following equation (2) with the aim of an easy comparison between the catalysts we tested.

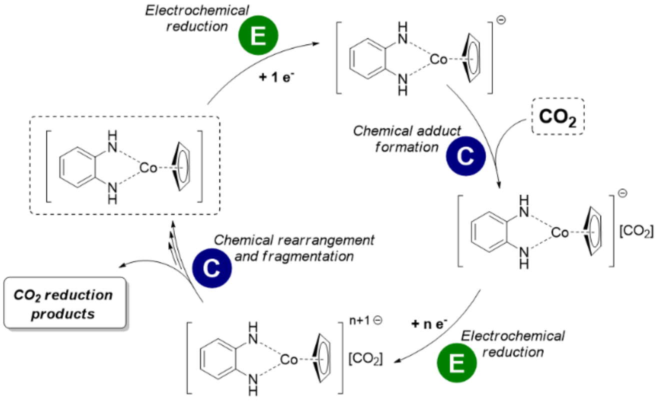
$$TOF = 0.1992\left(\frac{F\nu}{RT}\right)\left(\frac{n_p^3}{n_{cat}^2}\right)\left(\frac{i_{cat}}{i_p}\right)^2$$

(2)

In this approach, already exploited by McKinnon *et al.* very recently,[36] we considered the first reduction step of CO_2 to CO and we therefore assume n_{cat} to be 2, while n_p=1 as calculated for the first reduction wave. Table 3 and S4 summarize the TOF calculated at the values of potential and water amount corresponding to those at which we observed the best results. As expected, the highest TOF is found for complex **II** (187.21 s^{-1}) followed by **I** (115.46 s^{-1}) whereas compound **III** presents the smallest values (3.24 s^{-1}).

Looking closer to the results, it seems that the presence of electron-withdrawing groups capable of mesomeric effect (-NO_2 and -COOH), allows the catalytic CO_2 reduction at potentials lower than those observed in the case of **I** and **II**. However, in the presence of water, it seems that these groups reduce both catalytic efficiency and selectivity. The reason of this different behavior may be related to existence on -NO_2 and -COOH groups of the electron density highlighted by the Fukui function analysis (see above).

The reported results can be used to postulate a possible catalytic cycle for the CO_2 reduction in anhydrous conditions. This class of complexes presents a typical one-electron reversible redox process which can be observed under nitrogen and carbon dioxide atmosphere as well. Since all the



Scheme 1 – Hypothesis of the ECEC catalytic cycle involved.

Table 3. Summary table for complexes I-IV of I_{cat}/I_p and TOF values under anhydrous conditions and in presence of water calculated at the corresponding potential.

	I		**II**		**III**		**IV**	
$\mathbf{E}_{cat}$ (V)	-2.09		-2.13		-1.52		-1.91	
$\mathbf{H_2O}$ (%v/v)	0	9.09	0	9.09	0	7.41	0	9.09
$\mathbf{I}_{cat}$ / $\mathbf{I}_p$	4.12	24.40	5.59	31.07	4.53	3.49	3.36	9.97
TOF (s-1)	3.29	115.46	6.06	187.21	3.98	3.24	2.19	19.27
Residual $\mathbf{I}_{cat}$ / $\mathbf{I}_p$[a]	1.09		1.04		1.89		2.49	

[a] Calculated at 9.09 $\%_{v/v}$ of water under nitrogen atmosphere.

differences in the electrochemical behaviour in presence of CO_2 are observed at lower potentials with respect to this first reduction, the active form of the catalyst is likely to be the reduced specie $[CoCp(bqdi)]^-$, with which CO_2 should interact to form an adduct susceptible of further reduction. The formation of such adducts should allow the reduction process to occur at higher (less negative) potential than molecular CO_2 due to the presence of the complex; indeed, no CO_2 reduction is observed if the CV measurements are performed in the same condition of those reported in Figure 6 but without catalyst. The absence of any kind of re-oxidation peak in the cyclic voltammetry suggests a chemical oxidation of the complex in order to ensure a closed catalytic cycle, which is hypothesised to happen intramolecularly with a chemical rearrangement of the reduced CO_2-complex adduct and a subsequent rearrangement/fragmentation to yield reduced CO_2 product(s) and the pre-active form of the catalysts. A hypothesis of this kind is compatible with an ECEC mechanism,[37] as reported in scheme 1. Deeper experimental and theoretical studies are necessary to further support the proposed cycle and to elucidate the important role played by water in the mixed solvent reactions (Figure 7).

Experimental

Synthesis

All the reagents and solvents were purchased from Aldrich and used with no further purification. Synthesis of derivatives I and III has been performed as previously described by Heck,[29] while the fluorinated analogue II was prepared adapting the same procedure as reported very recently by Pilia and co-workers.[32] Synthesis of the carboxyl-substituted derivative IV, which has not been synthesized before at the best of our knowledge, was also carried out adjusting the general Heck's procedure for this class of compounds. The cyclopentadienyl-cobalt intermediate complex $CpCoI_2CO$ was prepared as reported by King.[38]

Electrochemical methods

The electrochemical behaviour of complexes **I-IV** have been evaluated by means of voltammetric techniques under nitrogen and carbon dioxide atmosphere. If not otherwise specified, all the measurements have been carried out at 100 mV s^{-1} with a three-electrode cell using a glassy carbon electrode as working electrode, a platinated titanium net as counter electrode and a platinum wire as *pseudo*-reference electrode. All the solutions were prepared in anhydrous degassed dimethylsufoxide (DMSO) solution with 0.1 M $[nBu_4N][PF_6]$ as supporting electrolyte. DMSO was chosen as a model solvent mainly for its typical high boiling point which should reasonably avoid any changes in concentration by evaporation of solvent during nitrogen and CO_2 insufflation processes. In these conditions the redox couple $Fc^{0/+}$ is centred at +0.45 V.

The number of electrons involved in the reversible redox processes were calculated by using the following equation (3):

$$\left|E_p - E_{\frac{p}{2}}\right| = \frac{59\,mV}{n}$$

(3)

Computational methods

The structure of all of the studied compounds both in the neutral and anionic form were optimized by means of DFT calculations. In details, geometry optimization was performed employing the B3LYP functional as implemented in the commercially available suite of programs Gaussian 16[39] using the 6-311++G(d,p) basis set for all atoms. The same level of theory was used to perform the vibrational analysis on all of the optimized structures in order to verify the character of the stationary points (no imaginary frequencies were found) and to compute the thermodynamic parameters at 298.15 K.

The solvent effect on the geometry and on the electronic properties was estimated by further optimizing the *in vacuo* global minimum of each species using a polarizable continuum model (PCM) and the current implementation in Gaussian 16, performing a reaction field calculation using the integral equation formalism IEF-PCM.[40] All PCM calculations were carried out at 298.15 K, and the molecular cavity was constructed using the default procedure in which the radii of the spheres placed around each atom are derived from the UFF force field and scaled by a factor of 1.1. Graphics of molecular models were generated using VMD[41] or ArgusLab 4.0.[42]

Electron attachment enthalpies were calculated as the enthalpy difference at 298.15 K and 1 atm, between the anionic and neutral forms of each compound, considering the minimum energy geometry of each species.

The Fukui function is extensively used to predict reactive sites, and its calculation with the DFT approach was originally defined by Parr and Yang.[43] We used the program Multiwfn[44] to calculate the Fukui function f^{-} in order to predict the regions for the electrophilic attack. This function (4) is defined as:

$$f^{-}(\vec{r}) = \rho_N(\vec{r}) - \rho_{N-1}(\vec{r})$$

(4)

with $\rho_N(\vec{r})$ being in our case the electronic density between of the 6-311++g(d,p) optimized anion and $\rho_{N-1}(\vec{r})$ that of the corresponding neutral form with the same geometry. Multiwfn was also used to calculate the ADCH (atomic dipole moment corrected Hirshfeld population) charge.[45]

Conclusions

In summary, the electrochemical behaviour of a selection of neutral half-sandwich cobalt complexes with cyclopentadienyl and phenylendiamine ligands have been explored in combination with DFT calculations. They revealed to be an efficient class of catalysts for the reduction of CO_2 via electrochemical methods in presence of water as a proton donor, showing up to 31-fold catalytic current in the case of complex **II**, which is based on fluorinated phenylendiamine ligand. Moreover, in the presence of water, complexes **I** and **II** show a very good selectivity toward CO_2 reduction respect to hydrogen. Fukui functions have been employed as a useful tool for the prediction of the chemical reactivity of the catalytic specie and for a preliminary study of the mechanism. In this regard, experimental and computational data suggest an ECEC mechanism. Our laboratories are currently involved in deeper studies for the determination of the intermediates and the reduction products of the reaction in order to better rationalize the mechanism behind the process and the role of the proton donor.

Conflicts of interest

There are no conflicts to declare.

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