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Rhenium Carbonyl Molecular Catalysts for CO₂ Electroreduction. Effects on Catalysis of Bipyridine Substituents Mimicking Anchorage Functions to Modify Electrodes.

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Supporting Information

ABSTRACT: Heterogenization of molecular catalysts on (photo)electrode surfaces is required to design devices performing processes enabling to store renewable energy in chemical bonds. Among the various strategies to immobilize molecular catalysts, direct chemical bonding to conductive surfaces presents some advantages due to the robustness of the linkage. When the catalyst is, as it is often the case, a transition metal complex, the anchoring group has to be connected to the complex through the ligands and an important question is thus raised on the influence of this function on the redox properties and on the catalytic properties of the complex. Herein we analyze the effect of conjugated substituents, structurally closed to anchoring functions previously used to immobilize rhenium carbonyl bipyridyl molecular catalyst for supported CO₂ electroreduction. We show that carboxylic ester groups, mimicking anchoring the catalyst *via* carboxylate binding to the surface, have a drastic effect on the catalytic activity of the complex toward CO₂ electroreduction. The reasons for such an effect are revealed *via* a combined spectro-electrochemical analysis showing that the reducing equivalents are mainly accumulated on the electron withdrawing ester substituents on the bipyridine ligand preventing the formation of the rhenium(0) center and its interaction with CO₂. Alternatively, alkyl-phosphonic ester substituents, not conjugated with the bpy ligand, mimicking anchoring the catalyst *via* phosphonate binding to the surface, allows preserving the catalytic activity of the complex.

Introduction

The electrochemical reduction of CO₂ is a domain of intense activity with the aim to use CO₂ as a source of carbon for fuels or, more broadly, for commodity molecules.¹ Efforts are thus made to develop selective catalysts for CO₂ electroreduction. In that endeavor, molecular catalysts have an advantage compared to “electrocatalysts” due to the fine control of their structure and properties as opposed to elusive active surface states of electrocatalysts.² Molecular catalysts are usually first studied as homogeneous catalysts to evaluate their figure of merits, namely, the faradaic efficiency (*FE*), the maximal turnover frequency (*TOF*^{max}) in given conditions, the limiting turnover number (*TON*^{lim}) and the catalyst standard potential enabling to evaluate the reaction overpotential.³ However, moving forward to applications, it is often better to design systems in which the molecular catalyst is heterogenized on the electrode (or photoelectrode) surface.⁴ Different strategies have been developed to immobilize molecular catalysts including embedment in a 3D polymeric structure deposited on the electrode surface, physical adsorption exploiting π - π and other electrostatic interactions or covalent binding to the electrode surface.^{5,6} Among the variety of molecular linking groups, allowing the catalyst immobilization on the electrode surface or in an electrode material,⁷ aryldiazonium, amine, alkynyl, sulfonyl thiol, phosphonates and carboxylates can be used.⁸ When the catalyst is, as it is often the case, a transition metal complex, one of these immobilizing groups has to be linked to the complex through the ligands and an important question is thus raised on its influence on the redox properties and on the catalytic properties

of the immobilized complex response. Although the role of substituents present on ligands of molecular catalysts has been studied in many cases, mostly to evaluate their implication in modulating the homogeneous catalytic response,^{9,10} the question of the effect of anchoring groups has not been specifically reported.¹¹ Herein we illustrate this issue through the detailed investigation of rhenium tricarbonyl 2,2'-bipyridine (bpy) complexes bearing methyl ester groups directly connected to the bpy ligand in two different positions (5,5' or 4,4') or bearing diethyl phosphonate groups on the bpy 5,5' or 4,4' positions through a methylene alkyl group. Since the first report by Lehn and coworkers,¹² rhenium tricarbonyl bpy complexes are among the most studied molecular catalysts for homogeneous CO₂ electroreduction to CO. The effect of various substituents on the bpy ligand has been reported.^{13,14} However, to the best of our knowledge, among the studied Re complexes, with bpy substituted by alkyl ester groups (*e.g.* [Re(2,2'-bpy-4,4'-(C(O)OR)₂)(CO)₃Cl]) (R = Me or Et),^{15,16} the electrochemical properties in reduction have not been investigated in detail, even if dicarboxy-2,2'-bipyridine derivatives have been used to immobilize Re complexes on surfaces or in organic-inorganic materials.¹⁷ Only few studies, related to the photophysical properties of polypyridyl Re carbonyl complexes, report the redox raw data of [Re(L)(CO)₃Cl] (L = bpy(C(O)OEt)₂).^{16a,18} Conjugated and non-conjugated phosphonated-bpy ligands have also been used to immobilize Re photocatalyst complex, on different substrates such as, mesoporous Cu₂O, TiO₂, ZrO₂ layers, SiO₂, NiO for CO₂ photo(electro)catalytic reactions without detailed study of electrochemical and electrocatalytic properties.¹⁹

Herein, we show that the presence of methyl-ester groups on the

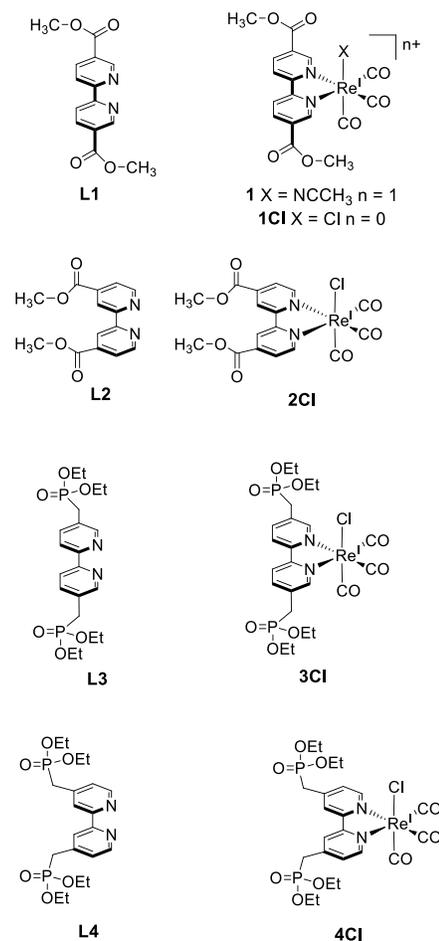
bpy, used as a mimic for covalent attachment of the rhenium complex on a surface or in a material, dramatically change the activity of the complex toward CO_2 electroreduction. A detailed study combining cyclic voltammetry (CV), UV-vis and IR spectroscopies reveals the underlying reasons for such a drastic effect. Then, we show that using another anchoring group (phosphonate) not conjugated with the bpy ligand, modeled here as an alkyl-phosphonic ester group, allows preserving the catalytic activity toward CO_2 reduction in solution.

Results and Discussion

Mimicking carboxy based anchoring group

We study first two novel *fac*-rhenium tricarbonyl dimethoxycarbonyl-2,2'-bipyridine (dmc-bpy) complexes, with dmc at the 5, 5' positions of the 2,2'-bpy (Scheme 1; **1** and **1Cl**). As a preliminary step, we present the redox properties of the free 5,5'-dimethoxycarbonyl-2,2'-bipyridine ligand (**L1**), as its behavior will be useful to rationalize the behavior of the corresponding $[\text{Re}(\text{L1})(\text{CO})_3(\text{CH}_3\text{CN})](\text{PF}_6)$ (**1**) and $[\text{Re}(\text{L1})(\text{CO})_3\text{Cl}]$ (**1Cl**) complexes. Finally, we will extend our result to the Re-carbonyl chloro complexes of the 4,4'-di(methoxycarbonyl)-2,2'-bipyridine ligand (**2** and **L2**; Scheme 1).

Scheme 1.



The synthesis of **L1**, following a two-step preparation starting from 5,5'-dimethyl-2,2'-bipyridine (dmbpy), was already described.²⁰ However, we used slightly different conditions for the two successive steps: (a) oxidation of the two methyl groups of

dmbpy with CrO_3 in orthoperiodic acid to form the 2,2'-bipyridine-5,5'-dicarboxylic acid intermediate (dcbpy)²¹ and, (b) the esterification of the carboxylic acid functions with MeOH in acidic conditions, described for 2,2'-bipyridine-4,4'-dicarboxylic acid, to yield quasi quantitatively the diester based ligand **L1** (see details in the experimental section in the Supporting Information (SI)).²² **L1** redox properties were studied by cyclic voltammetry under Ar in $\text{CH}_3\text{CN} + 0.1 \text{ M NBu}_4\text{PF}_6$ electrolyte. Two reversible one-electron waves are observed in CV on a glassy carbon electrode (GCE) corresponding to the successive formation of the radical anion **L1**^{•-} and the dianion **L1**²⁻ (Figure 1a). The corresponding standard potentials obtained from the midpoint of the anodic and cathodic peak potentials are respectively $E_1^0 = -1.75 \text{ V}$ ($\Delta E_p = 84 \text{ mV}$) and $E_2^0 = -2.06 \text{ V}$ ($\Delta E_p = 70 \text{ mV}$) (unless otherwise stated, all potentials are given vs. Ag^+/Ag). No oxidation of **L1** is observed until 1.50 V (Figure S1).

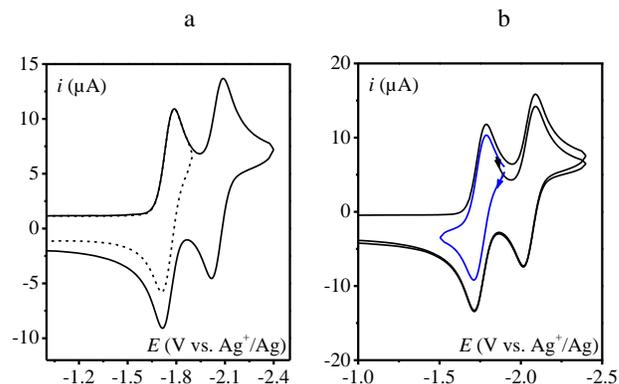


Figure 1. CVs in $\text{CH}_3\text{CN} + 0.1 \text{ M NBu}_4\text{PF}_6$ under Ar at 0.1 V/s on a 3 mm diameter GCE. (a) of **L1** (0.5 mM) (b) of electrogenerated **L1**^{•-} starting at -1.80 V. Initial scanning in the anodic direction (blue) in the cathodic direction, two cycles (black).

Exhaustive electrolysis of a 0.5 mM solution of **L1** was performed by applying a constant potential (-1.80 V) on a vitreous carbon felt until the passage of an equivalent of one mole of electron per mole of **L1** thus leading to the quantitative formation of **L1**^{•-} in solution (stable under Ar). The initially colorless solution of **L1** (Figure 2a, black curve) turns to green upon reduction (Figure 2a, green curve). To monitor absorption changes during the electrogeneration of **L1**^{•-}, UV-visible spectroelectrochemistry (UV-vis SEC) was performed (Figure S2). **L1**^{•-} exhibits several absorption bands (data collected in Table 1). Broad Intra-ligand (IL) absorption bands, centered at 759 nm, are observed in the visible range. In addition, two sharper bands appears at shorter wavelengths ($\lambda_{\text{max}} = 414$ and 446 nm with a shoulder (sh) at 432 nm), they are assigned to the $\pi-\pi^*$ and $\pi^*-\pi^*$ dmc-bpy-localized reduction in bpy species, in accordance with prior assignments.²³ CV performed after exhaustive electrolysis shows that **L1**^{•-} can be reversibly oxidized or reduced (Figure 1b). A second one-electron exhaustive electrolysis was then performed by applying a potential of -2.30 V leading to the dianionic **L1**²⁻ species (Scheme 2). The green solution (**L1**^{•-}) rapidly turns red and is characterized by the electronic absorption spectrum shown in Figure 2a (red curve). **L1**²⁻ exhibits only two intense absorption bands in the visible region at 487 and 520 nm, with a bathochromic shift and higher intensities, compared to those of **L1**^{•-} and shows the disappearance of the broader bands at higher wavelengths (550 -

1000 nm). Such change suggests an electron delocalization onto the dmc moieties of the bpy ligand. This hypothesis is supported by the *ex-situ* IR characterizations of the three species (**L1**, **L1^{•-}** and **L1²⁻**) in electrolytic solution under inert atmosphere (Figure 2b). Each spectrum exhibits one band or two bands (**L1^{•-}**) attributed to $\nu_{C=O}$ of C(O)OMe in dmc-bpy at wavenumbers in agreement with the successive reduction states shown in Scheme 2 (**L1**: 1731, **L1^{•-}**: 1653 and 1572, **L1²⁻**: 1567 cm^{-1}). The di-reduced ligand (**L1²⁻**) is stable under inert atmosphere (at least 30 min). Its exhaustive oxidation at -1.00 V consumes two moles of electron per mole of ligand. The *in-situ* UV-vis SEC experiment shows that this oxidation reaction leads to the quasi-quantitative regeneration of **L1** (Figure S3).

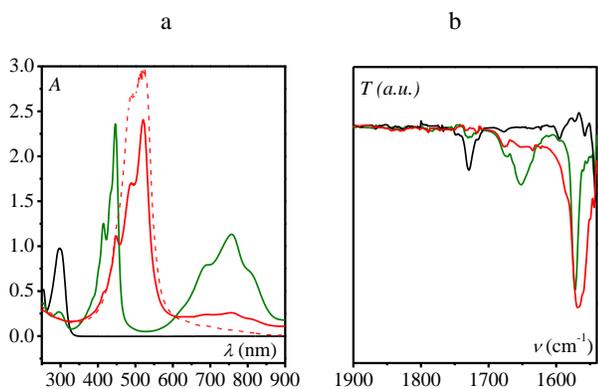
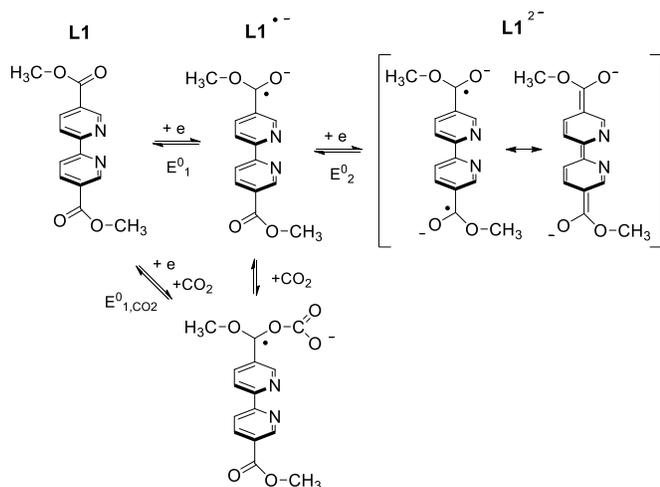


Figure 2. (a) UV-visible absorption spectra of a solution of **L1** (0.5 mM) (black), **L1^{•-}** (green) and **L1²⁻** (red: full line electrolysis not yet completed; dashed line: complete electrolysis but saturation of the absorbance) in $\text{CH}_3\text{CN} + 0.1 \text{ M NBu}_4\text{PF}_6$ ($l = 1 \text{ mm}$). (b) *Ex-situ* IR transmittance spectra of a solution of **L1** (0.5 mM) (black), **L1^{•-}** (green) and **L1²⁻** (red) in $\text{CH}_3\text{CN} + 0.1 \text{ M NBu}_4\text{PF}_6$.

Scheme 2.



The CV of 5,5'-dmc-bpy ligand (**L1**) was further investigated under CO_2 atmosphere. After saturation of an electrolyte **L1** solution with CO_2 the CV is modified (Figure 3a). The first reduction wave shifts to a less negative potential $E_{1,\text{CO}_2}^0 = -1.49 \text{ V}$ and becomes electrochemically slow ($\Delta E_p = 500 \text{ mV}$; Figure 3b). The onset of the reduction of CO_2 being at -2.10 V , the second reduction which might be shifted cathodically is hidden by the large

and intense direct reduction wave of CO_2 , also observed without **L1** (Figure 3a, dotted line). This behavior points out to a stabilization of the mono reduced species **L1^{•-}** radical anion through a Lewis acid/base type interaction with CO_2 . It is in line with previous studies showing that phthalate and benzoate radical anions are able to reduce CO_2 in an innersphere manner involving a nucleophilic addition of the radical anion on CO_2 and forming an oxygen-carbon bonded intermediate (Scheme 2).²⁴ However, in the present case, no catalysis is observed and the behavior is thus reminiscent of CO_2 electrochemical capture by reduced quinones.²⁵ The large separation between the cathodic and anodic peaks on the first chemically reversible wave in the presence of CO_2 (Figure 3b) might be the consequence of the slowness of the electron transfer for the $\{\text{CO}_2\text{-L1}^{0\bullet-}\}$ redox couple revealed by the fast coupled reversible addition of CO_2 .²⁶

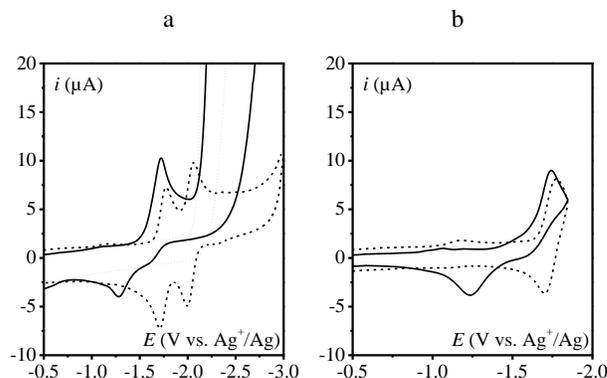


Figure 3. (a) CVs of **L1** (0.5 mM) in $\text{CH}_3\text{CN} + 0.1 \text{ M NBu}_4\text{PF}_6$ under CO_2 (solid line) and under argon (dashed line) at 0.1 V/s on a 3 mm diameter GCE. Dotted line: in the absence of **L1**. (b) Same as (a) but scanning only on the first wave.

We then turned our attention to the novel $[\text{Re}(\text{L1})(\text{CO})_3(\text{CH}_3\text{CN})](\text{PF}_6)$ (**1**) and $[\text{Re}(\text{L1})(\text{CO})_3\text{Cl}]$ (**1Cl**) Re(I)-carbonyl complexes (Scheme 1). **1Cl** was synthesized first, by a reaction between **L1** and pentacarbonylchloro Re(I) following a published procedure described for the preparation of 2,2'-bipyridine-4,4'-bicarboxylic acid Re-carbonyl complex.¹⁵ The substitution of the axial choro ligand in **1Cl**, by an acetonitrile one, was performed by using a previously published synthesis (AgOTf in $\text{CH}_3\text{CN} + \text{NH}_4\text{PF}_6$ metathesis) with slight modifications. **1** was obtained with a 70 % yield (see SI).²⁷

Redox properties of **1** were studied under inert atmosphere in $\text{CH}_3\text{CN} + 0.1 \text{ M NBu}_4\text{PF}_6$ electrolyte. Two reversible one electron reduction waves are observed at respectively $E_3^0 = -1.0 \text{ V}$ ($\Delta E_p = 60 \text{ mV}$) and $E_4^0 = -1.43 \text{ V}$ ($\Delta E_p = 60 \text{ mV}$) (Figure 4a). A reversible one electron oxidation wave is also observed at $E_5^0 = 1.54 \text{ V}$ ($\Delta E_p = 90 \text{ mV}$) characteristic of the oxidation of the rhenium center ($\text{Re}^{\text{II/I}}$) in such complexes.²⁸ Upon scanning toward negative enough potentials, a third reduction wave, irreversible, is observed peaking at -2.49 V . The first two reversible reduction waves are attributed to the reduction of the coordinated ligand **L1** of complex **1**. Comparison with the CV of the free ligand **L1** (Figure 1a) shows that both waves are anodically shifted by $E_3^0 - E_1^0 = 0.75 \text{ V}$ and $E_4^0 - E_2^0 = 0.62 \text{ V}$ respectively. These large shifts agree with the effect of the coordination bonding of dmc-

bpy ligand to the Re(I) metallic center and indicate a substantial stabilization of the **L1** reduced forms in the corresponding complexes (**1^{•-}** and **1²⁻**). It is well-established that reduction of $[\text{Re}^{\text{I}}(\text{bpy})(\text{CO})_3(\text{CH}_3\text{CN})]^+$ occurs through the bpy ligand and results in the formation of $[(\text{CO})_3(\text{bpy})\text{Re}^0\text{-Re}^0(\text{bpy})(\text{CO})_3]$ dimer.^{29,30} However, due to the electron-withdrawing effect of the dmc moieties, the delocalization of electron onto the rhenium is probably poor in **1^{•-}** as the formation of $[(\text{CO})_3(\text{L1})\text{Re}^0\text{-Re}^0(\text{L1})(\text{CO})_3]$ dimeric species is not observed upon exhaustive one electron reduction of **1** at -1.10 V. Indeed, after such a reduction, the quantitatively obtained product gives a reversible one-electron oxidation wave located at E_3^0 (dashed curve in Figure 4b). A dimer would be oxidized at less negative potential. The one electron reduced species is further reversibly reduced at E_4^0 (Figure 4b). Moreover, this one electron reduced species **1^{•-}** gives well defined intense absorption bands including a broad one at 626 nm (Figure 5a and Table 1) at a lowest wavelength than the characteristic one of Re⁰-Re⁰ bond in dimers such as $[\text{Re}(\text{bpy})(\text{CO})_3]_2$.³¹ These observations point out toward the predominant formation of $[\text{Re}^{\text{I}}(\text{L1}^{\bullet-})(\text{CO})_3(\text{CH}_3\text{CN})]$. Nonetheless, there might be some formation of a mono decarbonylated byproduct, presumably $[\text{Re}^{\text{I}}(\text{L1}^{\bullet-})(\text{CO})_2(\text{CH}_3\text{CN})_2]$, resulting from partial decoordination of CO ligand upon reduction. Based on reported data on the reduction potential of both $[\text{Re}^{\text{I}}(\text{bpy})(\text{CO})_3\text{Cl}]$ and $[\text{Re}^{\text{I}}(\text{bpy})(\text{CO})_2(\text{CH}_3\text{CN})\text{Cl}]$, we anticipate that loss of a carbonyl ligand shifts the reduction potential cathodically.³² Therefore, we attribute the new waves observed in Figure 4b (noted with stars) to the redox system of the bis-carbonyl species, presumably $[\text{Re}^{\text{I}}(\text{L1}^{\bullet-})(\text{CO})_2(\text{CH}_3\text{CN})_2]^{\bullet-}$. We also note that similar waves are observed on the CV of **1** after scanning on the third reduction wave at -2.49 V (stars in Figure 4a). The third reduction of **1** probably further promotes decarbonylation.

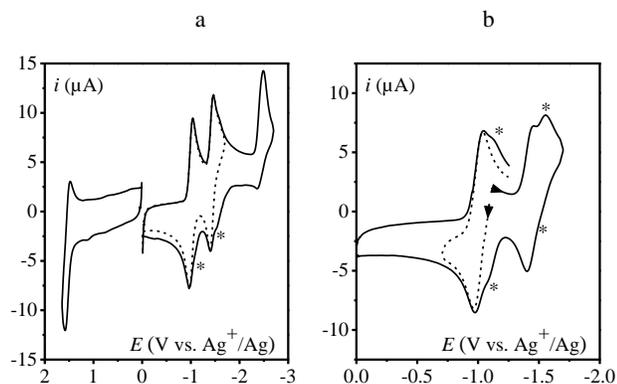


Figure 4. CVs of $[\text{Re}(\text{L})(\text{CO})_3(\text{CH}_3\text{CN})](\text{PF}_6)$ 0.5 mM in CH_3CN + 0.1 M NBu_4PF_6 under argon at 0.1 V/s on a 3 mm diameter GCE. (a) $\text{L} = \text{L1}$ (**1**); (b) $\text{L} = \text{L1}^{\bullet-} (**1^{•-}**).$

The IR spectrum of **1** shows CO bond vibrations with characteristic shape for such metal carbonyl complex (Figure 5b). The presence of two electron-withdrawing groups on 5,5' positions of the 2,2'-bpy induces: (a) a small shift ($\Delta\nu_{\text{C}=\text{O}} \approx 4 \text{ cm}^{-1}$) of the $\text{C}\equiv\text{O}$ stretching to higher energies, compared to the Re-bpy equivalent complex, indicating slightly less effective π -back-bonding to the CO ligands from the Re centre,²⁹ and (b) the presence of a $\nu_{\text{C}=\text{O}}$ stretching band (dmc bpy substituent) at 1738 cm^{-1} (Figure 5b black curve and Table 1).¹⁵ Both reduced species, resulting from the two one-electron successive reductions of **1**

(**1^{•-}** and **1²⁻**) are characterized by *ex-situ* IR in electrolytic solution under inert atmosphere (Figure 5b green and red curves respectively). Based on previous IR report in the literature on Re carbonyl complexes, we expect the two reductions to be occurring on the dmc-bpy ligand. Between 1800 and 2100 cm^{-1} the characteristic $\nu_{\text{C}=\text{O}}$ bands of the three carbonyl ligands are clearly observed with red shifts ($\Delta\nu_{\text{C}=\text{O}} = 19$ and 18 cm^{-1}) indicative without ambiguity of two one-electron reduction on the dmc-bpy ligand³³ as opposed to metal centred in a carbonyl complex. Indeed, when an electron is largely localized on the metallic centre, it has a much larger influence on the vibrational frequencies of the coordinated carbonyl ligands ($\Delta\nu \approx 60 \text{ cm}^{-1}$).³⁴ A focus between 1800 and 1550 cm^{-1} (Figure S4) highlights for both reduced species (**1^{•-}** and **1²⁻**) the existence of electronic density on the $\text{C}(\text{O})\text{OMe}$ function of the **L1** ligand, since substantial shifts of the $\nu_{\text{C}=\text{O}}$ characteristic bands are observed towards lower energy. Finally, additional evidence of a partial decarbonylation of the **1²⁻** complex in solution (*vide supra*), comes from the IR after the second reduction process. A new $\text{C}\equiv\text{O}$ bond vibration (noted with a star in Figure 5b) is observed at lower frequency ($\Delta\nu_{\text{C}=\text{O}} = 16 \text{ cm}^{-1}$) due to the loss of a CO and replacement by CH_3CN which has better σ -donor properties than CO and poor π -accepting properties, increasing the back-donation to the two remaining carbonyl ligands.

Table 1. Characteristic UV-visible and IR selected data

Compound	λ_{max} (nm)	ν (cm^{-1})
L1	299	1731
L1 ^{•-}	299, 414, 432 (sh), 446, 687, 759, 810, 909	1653, 1572
L1 ²⁻	292, 431 (sh), 489, 522	1567
$[\text{Re}^{\text{I}}(\text{L1})(\text{CO})_3(\text{CH}_3\text{CN})]^+$	370	2044, 1942 ^a , 1738
$[\text{Re}^{\text{I}}(\text{L1}^{\bullet-})(\text{CO})_3(\text{CH}_3\text{CN})]$	386, 438, 626	2025, 1918 ^a , 1692, 1586
$[\text{Re}^{\text{I}}(\text{L1}^{2-})(\text{CO})_3(\text{CH}_3\text{CN})]^-$	439, 470, 533, 590, 641	2007, 1894 ^a , 1631, 1589
$[\text{Re}^{\text{I}}(\text{L1})(\text{CO})_3\text{Cl}]$	416	2025, 1921, 1906, 1737
$[\text{Re}^{\text{I}}(\text{L1}^{\bullet-})(\text{CO})_3\text{Cl}]^-$	404, 639	2009, 1896, 1880, 1686, 1585

^a large

a

b

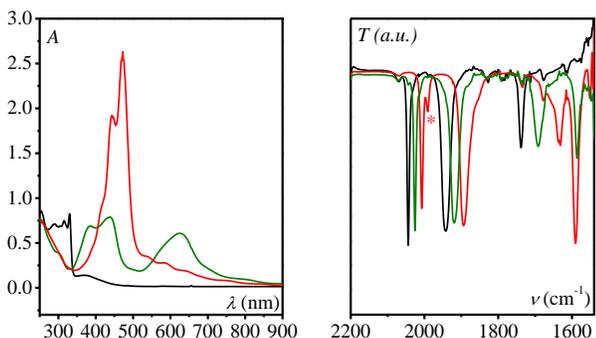
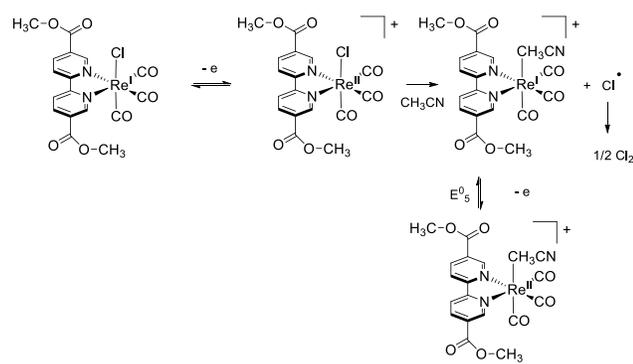


Figure 5. (a) UV-vis absorption spectra of a 0.5 mM solution of $[\text{Re}^{\text{I}}(\text{L1})(\text{CO})_3(\text{CH}_3\text{CN})](\text{PF}_6)$ (black), after one-electron reduction (green), after two-electron reduction (red) ($l = 1$ mm). (b) Ex-situ IR transmittance spectra of a solution of $[\text{Re}^{\text{I}}(\text{L1})(\text{CO})_3(\text{CH}_3\text{CN})](\text{PF}_6)$ (black), after one-electron reduction (green), after two-electron reduction (red). Both in $\text{CH}_3\text{CN} + 0.1$ M NBu_4PF_6 .

The behavior of $[\text{Re}(\text{L1})(\text{CO})_3\text{Cl}]$ (**1Cl**) complex in reduction is different from the $[\text{Re}(\text{bpy})(\text{CO})_3\text{Cl}]$ complex,¹² as it gives two reversible waves (Figure 6a) quite similar to the $[\text{Re}(\text{L1})(\text{CO})_3(\text{CH}_3\text{CN})](\text{PF}_6)$ (**1**) complex (Figure 4a), with a shift of standard potentials of each wave towards more negative values ($E_6^0 = -1.10$ V ($\Delta E = 110$ mV), $E_7^0 = -1.47$ V ($\Delta E_p = 70$ mV)) and a third irreversible wave observed at -2.44 V. This shift of potentials is characteristic of a Cl/ CH_3CN substitution, in agreement with the poorer electron donating ability of CH_3CN compared to chloro ligand. This was already reported for several metal-carbonyl bipyridyl complexes and also for $[\text{Re}(\text{bpy})(\text{CO})_3\text{X}]$.³⁵ On the oxidation side, there is an irreversible wave at 1.14 V which was not observed with complex **1** (Figure 4a). It is attributed to the oxidation of the complex leading to the cleavage of the Re-Cl bond and to the formation of the Re(I) oxidized solvated complex (**1**) and free Cl^\bullet , which immediately chemically evolves towards Cl_2 . It is then followed by the reversible oxidation of the Re center of **1** at E_5^0 (Figure 6a; Scheme 3).

35

Scheme 3.



a

b

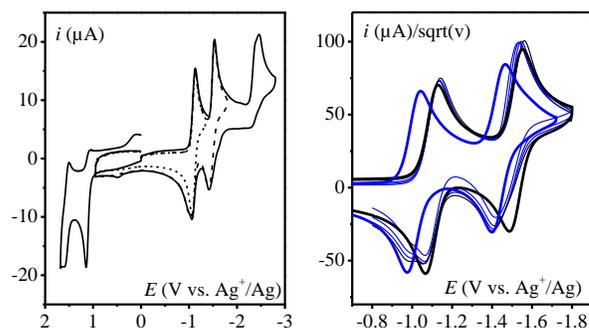
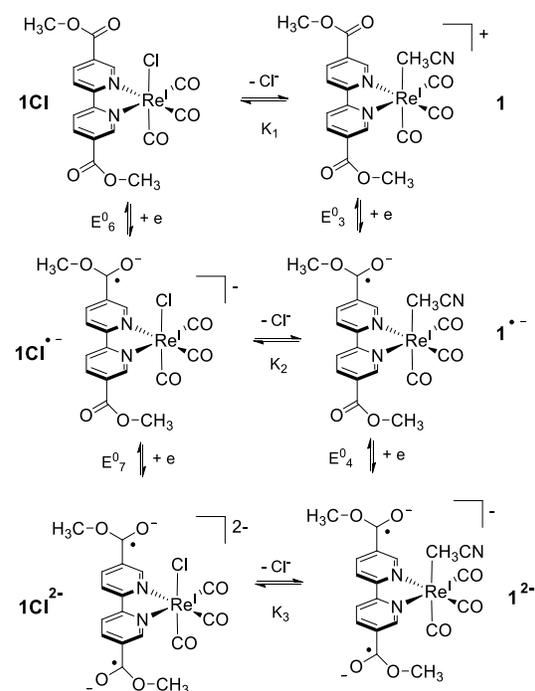


Figure 6. (a) CVs of $[\text{Re}(\text{L1})(\text{CO})_3\text{Cl}]$ (**1Cl**) 0.5 mM in $\text{CH}_3\text{CN} + 0.1$ M NBu_4PF_6 under argon at 0.1 V/s in a 3 mm diameter GCE. All scans start at 0 V (b) Thin lines: Normalized CVs of $[\text{Re}(\text{L1})(\text{CO})_3\text{Cl}]$ at various scan rates ($v = 50, 100, 200, 500$ mV/s) under argon. Thick black line: normalized CV of **1Cl** at 0.1 V/s with 40 mM NET_4Cl . Thick blue line: normalized CV of **1** at 0.1 V/s.

Scheme 4.



Taking a closer look at the first two reversible waves, we note that both oxidations waves are actually composed of an overlap of two waves which contributions are scan rate dependent (Figure 6b). This behavior is attributed to a partial dechlorination of the di-reduced complex thus leading to a mixture of 1Cl^{2-} and 1^{2-} . Consequently, on the reoxidation scan, the waves are split in two. The contribution at the more positive potential for each oxidation wave is attributed to the oxidation of the dechlorinated species as it matches the oxidation peak potentials obtained with compound **1** (thick blue CV in Figure 6b). Importantly, the relative intensity of both contribution is a function not only of the thermodynamics of the various equilibrium (constants K_1 to K_3 defined in Scheme 4) but also on their kinetics as well as the diffusion toward the bulk solution of the released chloride. These kinetics effects are illustrated by the scan rate dependence of oxidation peaks splitting. In the presence of an excess of free chloride in solution (40 mM NET_4Cl), only two simple reversible waves are

obtained (thick black CV in Figure 6b) leading to the corresponding standard potentials $E_6^0 = -1.10$ V and $E_7^0 = -1.53$ V. In such conditions, it thus appears that neither $\mathbf{1Cl}^{\bullet-}$ nor $\mathbf{1Cl}^{2-}$ lose a chloride on the time scale of the CV. Then, the ratio of the chloride association constants (K_1 to K_3) are obtained from the following thermodynamical relationships:

$$E_3^0 - E_6^0 = \frac{RT}{F} \ln \frac{K_1}{K_2} \quad \text{and} \quad E_4^0 - E_7^0 = \frac{RT}{F} \ln \frac{K_2}{K_3},$$

leading to: $\frac{K_1}{K_2} = 72.8$ and $\frac{K_2}{K_3} = 72.4$. As expected, the release of chloride is more and more favorable as the complex is reduced.

After exhaustive electrolysis at -1.20 V corresponding to the transfer of one electron, only one species is formed with no release of chloride as attested by CV (Figure S5). This indicates that $K_2 \gg 1$. This is further confirmed by the fact that the UV-vis spectrum of the formed species is identical whether the electrolysis is performed with or without excess of free chloride in solution (Figure S6a). The absence of chloride release also indicates that the formed species is not a $\text{Re}^0\text{-Re}^0$ dimer but simply $[\text{Re}^{\text{I}}(\text{L}^{\bullet-})(\text{CO})_3\text{Cl}]^-$. It is clearly at variance with the classical $[\text{Re}(\text{bpy})(\text{CO})_3\text{Cl}]$ complex which leads to a dimer upon reductive electrolysis. Moreover, if a dimer is formed upon one electron reduction of $\mathbf{1}$ and $\mathbf{1Cl}$, the same species would be observed which is not the case based on the UV-vis spectra (Figure 5a, Figure S6a and Table 1). Note that complexation of $\text{L}1$ by Re induces a characteristic shift of the charge transfer band for both $\mathbf{1}^{\bullet-}$ and $\mathbf{1Cl}^{\bullet-}$ compared to $\text{L}1^{\bullet-}$ ($\Delta\lambda_{\text{max}} = 132$ and 118 nm respectively), in line with electronic effect induced by coordination reaction, CH_3CN and chloro ligands. The evolution of the IR spectrum upon reduction of $\mathbf{1Cl}$ to $\mathbf{1Cl}^{\bullet-}$ is also consistent with a simple reduction with a shift of the vibration bands of the C=O of the order of 20 cm^{-1} and 50 cm^{-1} for C=O (Figure S6b) similar to what is observed for $\mathbf{1}^{0/\bullet-}$ (Figure 5b). Finally, a further one electron reduction of $\mathbf{1Cl}^{\bullet-}$ via application of a constant potential at -1.60 V leads to a mixture of products corresponding to the loss of chloride in agreement with CV (Figure 6 and Figure S7b) and $K_3 < K_2$ and also concomitantly partial loss of one carbonyl (IR, Figure S7b). ~~The mono-decarbonylation is completed if the reduction is continued for one more one electron reducing process, at a more negative potential beyond the 3rd reduction (-2.70 V) which corresponds to the reduction of the metal center ($\text{Re}^{0\text{I}}$) in mono-decarbonylated $\mathbf{1}^{2-}$ species ($\Delta\nu_{\text{C=O}} = -34\text{ cm}^{-1}$ (1860 cm^{-1}) and $\Delta\lambda_{\text{max}} = -15\text{ nm}$ (487 nm)).~~

The complexes $[\text{Re}(\text{L}1)(\text{CO})_3(\text{CH}_3\text{CN})](\text{PF}_6)$ ($\mathbf{1}$) and $[\text{Re}(\text{L}1)(\text{CO})_3\text{Cl}]$ ($\mathbf{1Cl}$) were then put in electrolyte solution under CO_2 atmosphere. In both cases, no significant effect is observed on the first and second reduction waves (Figure 7). This indicates that reduced forms of $\mathbf{1}$ and $\mathbf{1Cl}$ are not catalysts for the electrochemical reduction of CO_2 (at least on the timescale of the CV). This is actually in line with the fact that the added electrons are mostly delocalized and stabilized on the $\text{L}1$ ligand. There is not reduction of the Re(I) center that would allow its interaction and binding to CO_2 , a necessary condition to trigger catalysis. On the other hand, it appears that, as opposed to what has been mentioned above, with the free ligand $\text{L}1$, the charge density is not concentrated enough on the $\text{L}1$ ligand in the complex to react with CO_2 . Note also that, in the case of $\mathbf{1Cl}$, formation of $\mathbf{1Cl}^{2-}$

leads to loss of the chloride ligand. Hence another condition for CO_2 binding, *i.e.* existence of an open position on the metal, is not a sufficient condition. ~~QWe also note that our results do not exclude that $\mathbf{1Cl}$ could act as a catalyst at more negative potential (third wave); however, as shown in figure 7a, this would overlay with the direct reduction of CO_2 on GCE.~~

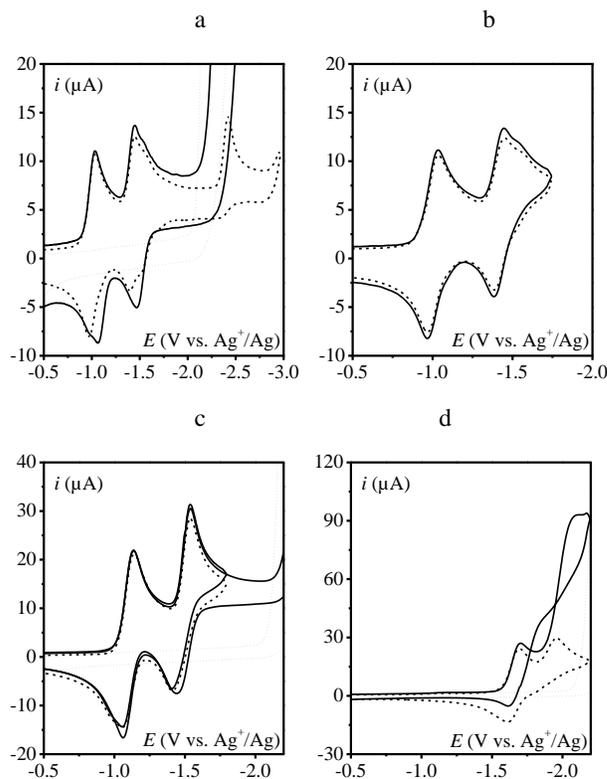


Figure 7. CVs in $\text{CH}_3\text{CN} + 0.1\text{ M NBu}_4\text{PF}_6$ at 0.1 V/s on a 3 mm diameter GCE. (a) $[\text{Re}(\text{L}1)(\text{CO})_3(\text{CH}_3\text{CN})](\text{PF}_6)$ ($\mathbf{1}$) under CO_2 (solid line) and under argon (dashed line). Dotted line: direct reduction of CO_2 in the absence of $\mathbf{1}$. (b) Same as (a) but scanning only on the first two waves. (c) $[\text{Re}(\text{L}1)(\text{CO})_3\text{Cl}]$ ($\mathbf{1Cl}$) under CO_2 (solid line) and under argon (dashed line). Dotted line: direct reduction of CO_2 in the absence of $\mathbf{1Cl}$. (d) CV of $[\text{Re}(\text{bpy})(\text{CO})_3\text{Cl}]$ under CO_2 (solid line) and under argon (dashed line). Dotted line: direct reduction of CO_2 in the absence of $[\text{Re}(\text{bpy})(\text{CO})_3\text{Cl}]$.

For the sake of comparison, CVs have been recorded under similar conditions with $[\text{Re}(\text{bpy})(\text{CO})_3\text{Cl}]$ as catalyst (Figure 7d).¹² It is clearly seen that in the absence of ester substituents, the two-electron reduced rhenium complex catalyzes the reduction of CO_2 in CH_3CN electrolyte, whereas this catalysis is inexistent (on the timescale of the CV) when the ester substituents are present on the bpy ligand.

One may then wonder if the position of the carboxylate anchoring groups with respect to the nitrogen of the bpy may modify the above observation that the injected electrons are mainly localized on the methoxycarbonyl groups and then prevent catalysis of CO_2 reduction. To that end, we have also investigated $[\text{Re}(\text{L}2)(\text{CO})_3\text{Cl}]$ ($\mathbf{2Cl}$) with $\text{L}2 = 4,4'$ -di(methoxycarbonyl)-2,2'-bipyridine ligand (Scheme 1). $\text{L}2$ and $\mathbf{2Cl}$ were synthesized as already described^{21,22} with slight modification (see SI). The CV behavior of $\mathbf{2Cl}$ under argon (Figure 8a) is very similar to the behavior of $\mathbf{1Cl}$ (Figure 6a). Two reversible waves are observed upon reduction until -2V. Scanning at more negative potential

leads to a third reversible wave located at *ca.* -2.50 V. The first two waves are not purely single electron transfer waves due to partial loss of chloride at the level of the second reduction wave *via* a reaction scheme akin to Scheme 4. On the oxidation waves, the behavior is similar to **1Cl** and corresponds to an oxidative dechlorination of the complex as described in Scheme 3 for **1Cl**. Based on the similar behavior of **2Cl** and **1Cl**, it is not surprising that no catalysis is observed on one of the two first reduction waves upon running CV of **2Cl** under CO₂ atmosphere (Figure 8b). As a consequence, whether at position 5,5' or 4,4' on the bpy ligand, the electron withdrawing effect of ester carboxylic groups, mimicking anchoring groups, is so strong that, in the case of rhenium carbonyl complexes, it prevents any catalytic activity toward CO₂ reduction. We note that such an effect is likely dependent on the nature of the metal as electronic distribution between the ligand and the metal is a subtle interplay between the orbitals of both. Indeed, for example, in the case Ru-carbonyl-bipyridyl complexes, the addition of an alkyl ester function on the bpy ligand has a positive influence on the catalytic activity and selectivity towards the electroreduction of CO₂ and does not prevent the formation of the active species, as we have seen above for the Re.^{36,37} Note also that previous studies with rhenium tris-carbonyl chloride complex with 2,2'-bipyridine-4,4'-dicarboxylic acid ligand reported that this complex had no activity toward CO₂ reduction, in line with our findings.¹³

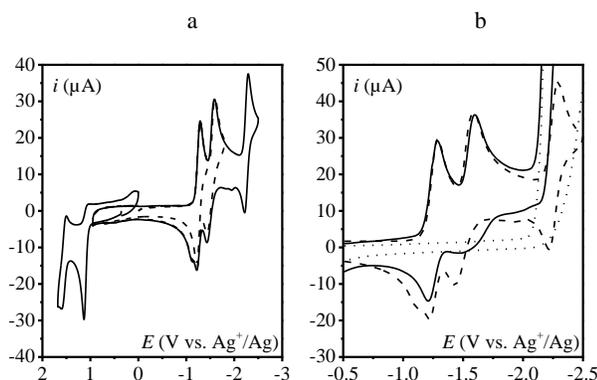


Figure 8. CVs in CH₃CN + 0.1 M NBu₄PF₆ at 0.1 V/s on a 3 mm diameter GCE (a) [Re(L2)(CO)₃Cl] (**2Cl**) under argon. (b) **2Cl** under CO₂ (solid line) and under argon (dashed line). Dotted line: direct reduction of CO₂ in the absence of **2Cl**.

Mimicking phosphonic anchoring group

Phosphonate groups are alternative to carboxylate groups to anchor complexes onto surfaces or materials. They have been used in particular to functionalize metallic oxide electrodes.³⁸ Taking lessons from the above study showing that electron withdrawing anchoring groups conjugated with the bpy ligand can have deleterious effect on catalysis, we have studied [Re(L3)(CO)₃Cl] (**3Cl**) and [Re(L4)(CO)₃Cl] (**4Cl**) complexes, with **L3** = 5,5'-diethylmethylphosphonate-2,2'-bipyridine ligand and **L4** = 4,4'-diethylmethylphosphonate-2,2'-bipyridine ligand (Scheme 1), containing phosphonic ester groups with non-conjugated linker with bpy, as mimicking phosphonate anchoring groups.

Known **4Cl** complex was prepared as previously described with slight modifications and the new **3Cl** Re tris carbonyl chloride complex with the substitution at the 5- and 5'-bpy positions, was synthesized by adapting published procedure (see SI).²⁷ CV of **3Cl** and **4Cl** under argon (Figure 9a and 9c respectively) are very similar to the CV of the classical [Re(bpy)(CO)₃Cl] complex

(Figure 7b dashed line). A first reversible one electron wave is observed corresponding to reduction on the ligand. It is followed by an irreversible wave corresponding to reduction of the metal coupled with decoordination of the chloride. This wave is slightly smaller than a one electron wave because this process is in competition with a spontaneous decoordination of the chloride on [Re^I(L⁺)(CO)₃Cl]⁻ (L = **L3** or **L4**) and formation of the corresponding [Re⁰(L)(CO)₃]₂ dimer. Oxidation of this dimer is observed on the reverse scan at *ca.* -0.4 V. Formation of a dimer upon one-electron reduction is confirmed by UV-vis after an exhaustive electrolysis conducted at -1.70 V (Figure S8). We can thus conclude that, as opposed to the methyl-ester groups directly conjugated to the bpy, the ethyl-phosphonic ester groups not conjugated to the bpy do not substantially modify the electronic distribution between the ligand and the metal upon reduction. The activity as a catalyst toward CO₂ electroreduction is indeed preserved as attested by CV. Under CO₂ atmosphere, a catalytic wave is observed at *ca.* -2.00 V (Figure 9b, thin solid line) as in the case of [Re(bpy)(CO)₃Cl] complex (Figure 7d). Addition of water leads to an increase of the catalytic current (Figure 9b and 9d, thick solid line). The addition of a weak Brønsted acid, including water, is known to boost catalysis, presumably *via* a stabilization of the rhenium-CO₂ intermediate through protonation and then it facilitates the cleavage of a C-O bond leading to the formation of CO as a product.³⁹

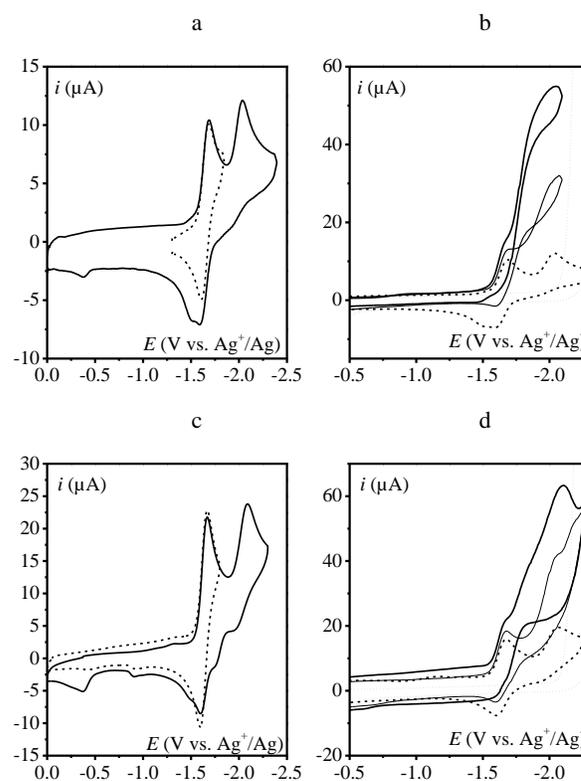


Figure 9. CVs in CH₃CN + 0.1 M NBu₄PF₆ at 0.1 V/s on a 3 mm diameter GCE. (a) [Re(L3)(CO)₃Cl] (**3Cl**) 0.5 mM under argon. (b) [Re(L3)(CO)₃Cl] (**3Cl**) 0.5 mM under CO₂ (thin solid line), under CO₂ + 15% H₂O. (c) [Re(L4)(CO)₃Cl] (**4Cl**) 1 mM under argon. (d) [Re(L4)(CO)₃Cl] (**4Cl**) 1 mM under CO₂ (thin solid line), under CO₂ + 5% H₂O (solid line) and under argon (dashed line). Dotted lines: direct reduction of CO₂ in the absence of catalyst.

The selective formation of CO as a product of the electroreduc-

tion of CO₂ with [Re(L3)(CO)₃Cl] (**3CI**) as catalyst was confirmed by a controlled potential electrolysis at -1.70 V of a solution containing the complex at a concentration of 1 mM in CH₃CN/H₂O (90/10) under CO₂ (see SI for details). After 2.5 h and the passage of 60 C (average current 6.5 mA, Figure S9), the analysis of the gas in the headspace by gas chromatography indicates that CO is the major product formed with a faradaic yield of 83% (Figure S10), the only other product detected was H₂ at a concentration corresponding to a 10% FY.

Conclusion

We have investigated rhenium tricarbonyl bipyridine complexes bearing substituents mimicking anchoring functionalities toward their catalytic properties for CO₂ electroreduction in solution. We have shown that substituent groups conjugated with the bpy ligand have a dramatic deleterious effect on the catalytic activity. This effect can be rationalized via the analysis of both the free ligand and the complexes which shows that upon reduction the added electrons mostly localize on the ester groups thus preventing the reduction of the metal to become nucleophilic enough to bind CO₂, a required step to initiate and activate CO₂ reduction. The behavior is the same whether ester groups are at the 5, 5' or 4, 4' positions on the bpy. A side consequence of the electron withdrawing effect of the ester groups, leading to small unpaired spin density in the d_{z²} orbital of the Re center, is that it prevents the formation of a Re⁰-Re⁰ dimer. It is also in line with the observation that there is no dechlorination of the reduced [Re^I(L1^{•-})(CO)₃Cl]⁻. Alternatively, we have shown that alkylphosphonic ester groups not conjugated with the bpy do not alter the catalytic activity of the corresponding rhenium tricarbonyl bipyridine complex which efficiently catalyze the electroreduction of CO₂ to CO.

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This study shows that the necessary heterogenization of Re based molecular catalysts on (photo)electrode surfaces, directly or through an extra host material, to design devices enabling to store renewable energy in chemical bonds, has to be done wisely to preserve the catalytic activity.

ASSOCIATED CONTENT

Supporting Information

Experimental details. Additional data.

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Notes

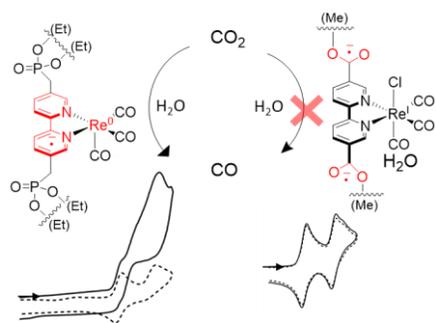
The author declares no competing financial interest.

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TOC



Synopsis: Heterogenization of molecular catalysts on (photo)electrode surfaces, to design devices enabling to store renewable energy in chemical bonds, has to be done wisely to preserve the catalytic activity. Indeed, substituent groups mimicking anchorage functions and conjugated with the bpy ligand have a dramatic deleterious effect on the catalytic activity of Rhenium triscarbonyl bipyridine complexes. Alternatively, anchorage functions not conjugated with the bipyridine (e.g. alkyl-phosphonic ester) do not alter the catalytic activity of the corresponding.