A PRELIMINARY STUDY ON ELECTROCATALYTIC REDUCTION OF CO$_2$ USING FAC-Re^I(CO)$_3$(4,4'-DI-METHYL-2,2'-BIPYRIDYL)((E)-2-((3-AMINO-PYRIDIN-4-YLIMINO)-METHYL)-4,6-DI-TERT-BUTYLPHENOL))$^+$ COMPLEX

JUAN CARLOS CANALES[1], ALEXANDER CARREÑO[2,3], DIEGO OYARZÚN[2],*
JUAN MANUEL MANRÍQUEZ[1,3], IVONNE CHÁVEZ[1,3]

[1]Departamento de Quimica Inorganica, Facultad de Quimica, Pontificia Universidad Catolica de Chile,
Avenida Vicuña Mackenna 4860, Macul, Santiago, Chile
[2]Center of Applied Nanosciences (CANS), Universidad Andres Bello, República 275, Santiago, Chile
[3]Núcleo Milenio de Ingeniería Molecular para Catálisis y Biosensores (MECB), ICM, Chile

ABSTRACT

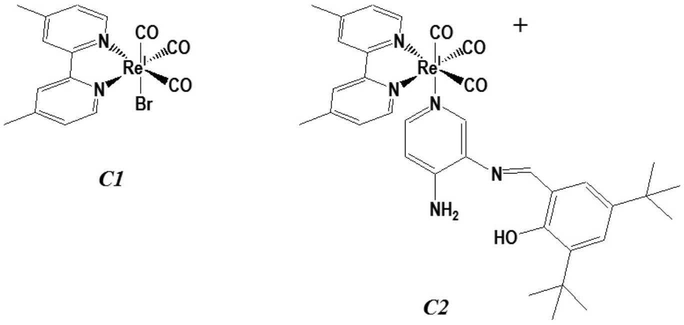
Several research to explore the possible conversion of CO$_2$ using rhenium(I) tricarbonyl complexes have been reported the last years. In the present work, we investigated a potential use of *fac*-Re(CO)3(4,4'-di-methyl-2,2'-bipyridyl)**L**$^+$ complex (**C2**), where **L** is an electron-withdrawing ancillary ligands which present an intramolecular hydrogen bond (IHB), in a preliminary electrocatalytic reduction of CO$_2$. The **C2** complex was synthesized and characterized according to reported methods earlier. The cyclic voltammogram profile for the **C2** complex were studied in dichloromethane under inert atmosphere, and it shows a typical behavior for an electrocatalytic process, the **C2** complex illustrate the electrochemical reaction mechanism corresponds to an electrochemical–chemical–electrochemical pathway (ECE). Also, a Vitreous Carbon plate used as working electrode was employed and modified by cycling the anodic region of **C2** in CH$_2$Cl$_2$ which involve the oxidative redox response for the -NH$_2$ and -OH groups. The voltammogram profile involve shows a polymeric deposit on the plate surface in a CO$_2$ saturated solution (pH=7.0). A strong electrocatalytic discharge of current is obtained with a wave foot of -1.3 V showing that **C2** have the potential to be used in electrocatalyst CO$_2$ reduction.

Keywords: Rhenium tricarbonyl complexes, reduction carbon dioxide, vitreous carbon, electrochemistry.

1. INTRODUCTION

Rhenium (I) tricarbonyl complexes with equatorial heteroaromatic ligands such as bipyridyl or substituted biphosphine (bidentate ligands) have been subject of intense investigations related to their photophysical properties as large Stokes shifts, long luminescence lifetimes and emission in the UV or Visible region upon photoexcitation. [1-6] Indeed, *fac*-Re(CO)$_3$(**X**)**L** (**X**: bidentate ligand and **L**: halogen ligand or others in axial position to the heteroaromatic ring plane named *ancillary* ligand), are the most studied complexes because they allow a systematic modification of their photophysical properties, closely dependent on the ligands nature. [7-9] The effect of the different ancillary ligands have been described for rhenium tricarbonyl complexes.[10-11] Additionally, the general synthetic flexibility and modularity rhenium(I) tricarbonyl syntheses starting from the rhenium-dimmer allowed an easy and systematic preparation for the neutral *fac*-Re(CO)$_3$(X)Br precursors, compared with a traditional synthetic route using reflux under inert atmosphere.[12-13] In this context, we have explored the effect of changing an halogen in the axial position (-Cl or -Br) by **L** as ancillary ligand. **L** is (*E*)-2-((3-amino-pyridin-4-ylimino)-methyl)-4,6-di-*tert*-butylphenol, a kind of Schiff base compounds having an intramolecular hydrogen bond (IHB). In several experiments using **L** on the rhenium(I) core, we concluded that the nature of this ancillary ligand (**L**) is fundamental to emission controlling, electrochemical response and other properties due its electron withdrawing effect.[14-16] On the other hand, the increased stabilization by IHB could be the responsible for the electron withdrawing ability of this **L** ligand. Theoretical evidence, using DFT level of theory that included spin-orbit effect confirm the former effect.[17-20]

On the other hand, complexes of type neutral *fac*-Re(CO)3(**X**)Cl (with **X**=2,2′-bipyridyl or similar), have demonstrated activity for the selectively reduction of CO$_2$ to CO and the mechanistic pathways have been studied.[21-25] Based on these findings, our group have also been exploring a new kind of rhenium(I) tricarbonyl complexes of type *fac*-Re(CO)3(4,4'-di-methyl-2,2'-bipyridyl)**L**$^+$ (**C2,** See Scheme 1), and its potential properties to the reduction of CO$_2$. The first attempt to the reduction of CO$_2$ mediated by rhenium(I) tricarbonyl complexes using homogenous photocatalysis was reported by Hawecker *et al.* [26] and alter in 1984 they did it by direct electrocatalysis on vitreous carbon electrode to obtain CO with almost 100% of Faradaic efficiency by performing long term experiments.[27-28] More recently, a family of the same kind of complexes using 4,4'-di-substituted-2,2'-bipyridyls with substutuents like -COOH, -CH$_3$, t-Bu, -OMe as equatorial ligands has been prepared and its electrocatalytic properties for the reduction of CO$_2$ evaluated.[29-32] A characteristic voltammetric pattern was observed in acetonitrile for all these compounds that consist on two reduction processes; the first one ranging between -1.34 V to -1.49 V vs SCE (E$_{1/2}$, reversible; 1 electron) and the second one process ranging between -1.70 V to -1.80 V vs SCE (E$_{pc}$, irreversible; 1 electron). The negative trend for the potential values found of both of these reduction peaks match very well with the increasing trend of pKa values on the different ligands used. The best electrocatalytic results is found for the 4,4'-di-tert-Butyl substituted, derivative for the CO$_2$ conversion to CO with Faradaic efficiency close to 100%. [30-32] Motivated by this fact, we initiated studies of chemical design of suitable rhenium (I) tricarbonyl compounds. The main focus of the present manuscript is not the synthesis of **C2** per se, but the study of the **C2** complex regarding its potential properties as electrocatalytic agent for CO$_2$ reduction and compared to previously published experimental observations. This work is just a continuation of previous studies on the use of these kinds of ancillary ligand **L** on the rhenium(I) core employed as biomarker in walled cells. [33-35]



Scheme 1. Chemical structure of neutral *fac*-Re(CO)3(4,4'-di-methyl-2,2'-bipyridyl)**Br** (**C1**) and *fac*-Re(CO)3(4,4'-di-methyl-2,2'-bipyridyl)**L**$^+$ (**C2**) complexes, used in this study.

2. EXPERIMENTAL

All starting materials were purchased from Merck and Aldrich and used without further purification. The **C1** and **C2** complexes employed in this study were synthesized according to report in literature by us. [33-35]

e-mail: jcanales2005@gmail.com

2.1. Electrochemical studies

For the electrochemical experiments, the working solution was prepared with **C2** complex; 9.0 x 10^{-4} mol L^{-1} and 0.1 mol L^{-1} of tetrabutylammonium hexafluorophosphate ($TBAPF_6$) as supporting electrolyte in anhydrous dichloromethane (J.T. Backer, HPLC >99,8%). Prior to each experiment the solution was purged with nitrogen or carbon dioxide (extra pure), and the atmosphere was maintained over the solution during the whole experiment. A vitreous carbon electrode was used as working electrode. Platinum gauze of large geometrical area was employed as counter electrode separated from the cell main compartment by a fine grain sintered glass. An Ag/Ag^+ (KCl sat) was used as reference electrode at room temperature and the potential values finally referred to Saturated Calomel Electrode (SCE). All electrochemical experiments were performed at room temperature on a CHI620 bipotentiostat interfaced to a PC running the CHI 760c software for experimental control and data acquisition. All the experiment were performed in the dark and solutions prepared under inert conditions.

3. RESULTS AND DISCUSSION

The syntheses of neutral fac-[$Re(CO)_3$(4,4'-di-methyl-2,2'-bypiridyl) Br (C1) was prepared by reacting bromotricarbonyl(tetrahydrofuran)rhenium (I) dimer and fac-[$Re(CO)_3$(4,4'-di-methyl-2,2'-bypiridyl)(E-2-((3-amino-pyridin-4-ylimino)-methyl)-4,6-di-tert-butylphenol)](PF6) C2 was carried out by direct reaction of C1 and L in dry THF . For the C2 complex, we observed the stretching azomethine group (–C=N–) of the Schiff base at 1633 cm^{-1} and the presence of carbonyl groups with the characteristic vibrational bands at 2032 and 1923 cm^{-1}, assigned to a facial $Re(CO)_3^+$ arrangement and the signal at 845 cm^{-1} could be assigned to the PF_6^- anion. The purities of their corresponding C1 and C2 complexes were checked by the mentioned techniques (See Section S1 in the S.I.).

3.1 Electrochemical behavior

As previously described by Carreño *et al.*[17], under the experimental conditions employed both for **C1** and **C2** complexes in acetonitrile, may undergo two single-electron reduction processes and two single-electron oxidations. The reductions, **C1** and **C2**, behave similarly for both compounds, all reversible and with diffusional control during the first reduction and not diffusional at the second; their electrochemical reaction mechanism corresponds to an electrochemical–electrochemical–chemical pathway (EEC) described elsewhere[36] with slight potential differences between complexes.[37] In both **C1** and **C2** complexes, the electrochemical reaction mechanism for the oxidation corresponds to an electrochemical–chemical–electrochemical pathway (ECE) with three steps: The first electrochemical one-electron oxidation of rhenium center, $Re^I \rightarrow Re^{II}$, followed by an intramolecular Re/ligand redox process ($Re^{II} \rightarrow Re^I$), with ligand substitution by solvent molecule and ends with a second electrochemical one-electron oxidation of rhenium center $Re^I \rightarrow Re^{II}$ (See **Scheme 1** in the S.I.). [38] The difference between **C1** and **C2** complexes is the reversible character and the control mechanism for the reaction rate at the second oxidation process, which is reversible and not-diffusional for **C1**, and irreversible with diffusional control for **C2** due these mechanistic produce broader differences at the oxidation potentials values between complexes.[37] The change when passing from bromide (**C1**), and the **L** ancillary ligand structure (**C2**), is that the first rhenium oxidation shifts towards higher potential values (from 1.46 to 1.88 V vs SCE).[37-41]

On the other hand, in the present study, the electrochemical behavior for the **C2** complex was performed in dichloromethane under inert atmosphere (See **Figure 1**). The cyclic voltammogram exhibit two reduction peaks that were previously described for this kind of compounds; one of them at $E_{1/2}$ = -1.33 V and the other one at c.a. E_{pc} = -1.9 V. The first one is cuasi-reversible (ΔE= 106 mV, 1 electron) is attributed to the bipyridyl ligand by comparing other rhenium(I) tricarbonyl complexes reported.[42-43] The second one (irreversible, 1 electron) is attributed to Re(I)/Re(0) also by comparing with the litarature.[44-45] These potential values match with the usual voltammetric profiles informed for a family of neutral *fac*-$Re(CO)_3$(2,2'-bipyridyl)**Cl** substituted complexes but in acetonitrile (MeCN) [29] and they are negatively shifted regarding the potentials found for the same compound in MeCN ($E_{1/2}$ = -1.25 V and E_{pc} = -1.68 V).[17] An extra reduction process at E_{pc} = -0.90 V (irreversible) is preceding the two described peaks and is the first wave found by scanning on the cathodic direction which is attributed to the reduction of the azomethine group (–CH=N–), the fragment of the Schiff Base on the ancillary ligand (**L**).[46] On the other hand, is very well known that azomethine electroreduction is favored by the presence of H^+. Indeed the group is being affected by multiple intramolecular hydrogen bond (IHB) (See **Scheme S2**; structures #2 and #3 in the S.I.) and additionally dichlorometane have an acidic H^+ so it is the fragment able to be the first easily reduced. The complex concentration used in this study is in the range of 10^{-4} mol L^{-1} so in this work we use a large area Vitreous carbon electrode compared with the literature[29] (28.3 mm^2 instead of 4.7 mm^2) and high scan rate than the commonly used (200 mV/s instead of 100 mV/s) to increase the resolution of the voltammetric profile. Electroanalytic study by cutting potentials it is possible to note that the cuasi-reversible bipyridyl's couple at $E_{1/2}$ = -1.33 V exhibit a composed shape couple which is possible to see in isolated way (See **Figure 2A** and **2B**), like two cuasi-reversible traslaped couples that suggest the presence of a second similar specie in solution. It may come for example by the presence of small amount of *mer*-isomer formed that has been well demonstrated for the conversion of neutral *fac*-$Re(CO)_3$(2,2′-bypiridyl)**Cl** to neutral *mer*- $Re(CO)_3$(2,2′-bipyridyl)**Cl** by hν irradiation, [47] an effect observed even for the simple in solid state in KBr pellets.[48-49] Thus, just a short light exposition during the solution samples preparation for electrochemistry is enough to have a small *mer*-isomer conversion (See **Scheme S3** in the S.I.).

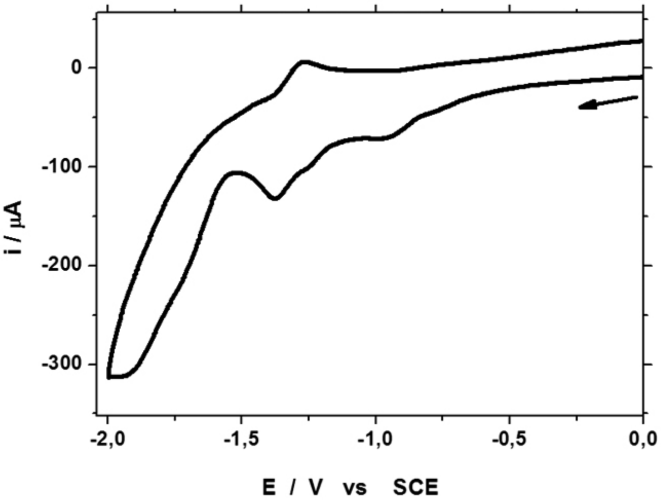


Figure 1. Cyclic voltammogram for the **C2** complex; 9.0 x 10^{-4} mol L^{-1} in CH_2Cl_2 with $TBAPF_6$ 0.1 mol L^{-1} for the cathodic region on vitreous carbon electrode under inert atmosphere. Scan rate 200 mV/s.

Scanning on the anodic direction, a small oxidation process present at E_{pa}= 0.25 V which depends on the presence of the cuasi-reversible couple at $E_{1/2}$ = -1.33 V, could be tentatively attributed to Re(0)/Re(I) and then it could be possible to explain the oxidation process for Re(I)/Re(II) which has been often found at very high positive E values. [50-51] The reduced species formed at E_{pc} = -1.85 V (irreversible) containing Re(0) are being oxidized at E_{pa} = 0.25 for Re(I)/Re(II) and then so far in an extended wave at E_{pa}= 1.05 V in agreement with Re(I)/Re(II).[52] Three oxidation processes appear on anodic region coming from the initial complex in solution; a clear one peak at E_{pa}= 1.45 V and two unsolved peaks at E_{pa}= 1.75 V and E_{pa}= 1.85 V. [5-11]

3.2 CO_2 atmosphere studies

The cyclic voltammogram to the cathodic region exhibit changes for the 2nd and 3th reduction processes (1st one for the azomethine group remains) shifting to a less negative potential values located now at E_{pc} = -1.28 V and E_{pc} = -1.65 V, which is a shift of 110 mV and ~250 mV more favorable than those observed under inert atmosphere (See **Figure 3**), typic behavior waited for an electrocatalytic process. [54-58] However, the current intensity for both peaks doesn't change to much suggesting just an advantage from the thermodynamic point of view but a strong kinetic restriction. When 100 µL of acetic acid (glacial) is added on the same experiment an important change is obtained and the kinetic largely increased by the presence of a Lewis acid in the media giving a current discharge for the electrocatalytic process (See **Figure 4**). The Epc value for the reversible couple that was observed at -1.38 V vs SCE under inert atmosphere is now shifted to -1.30 V vs SCE (80 mV less negative) and the following reduction process is now an intense unsolved current discharge.[59-60]

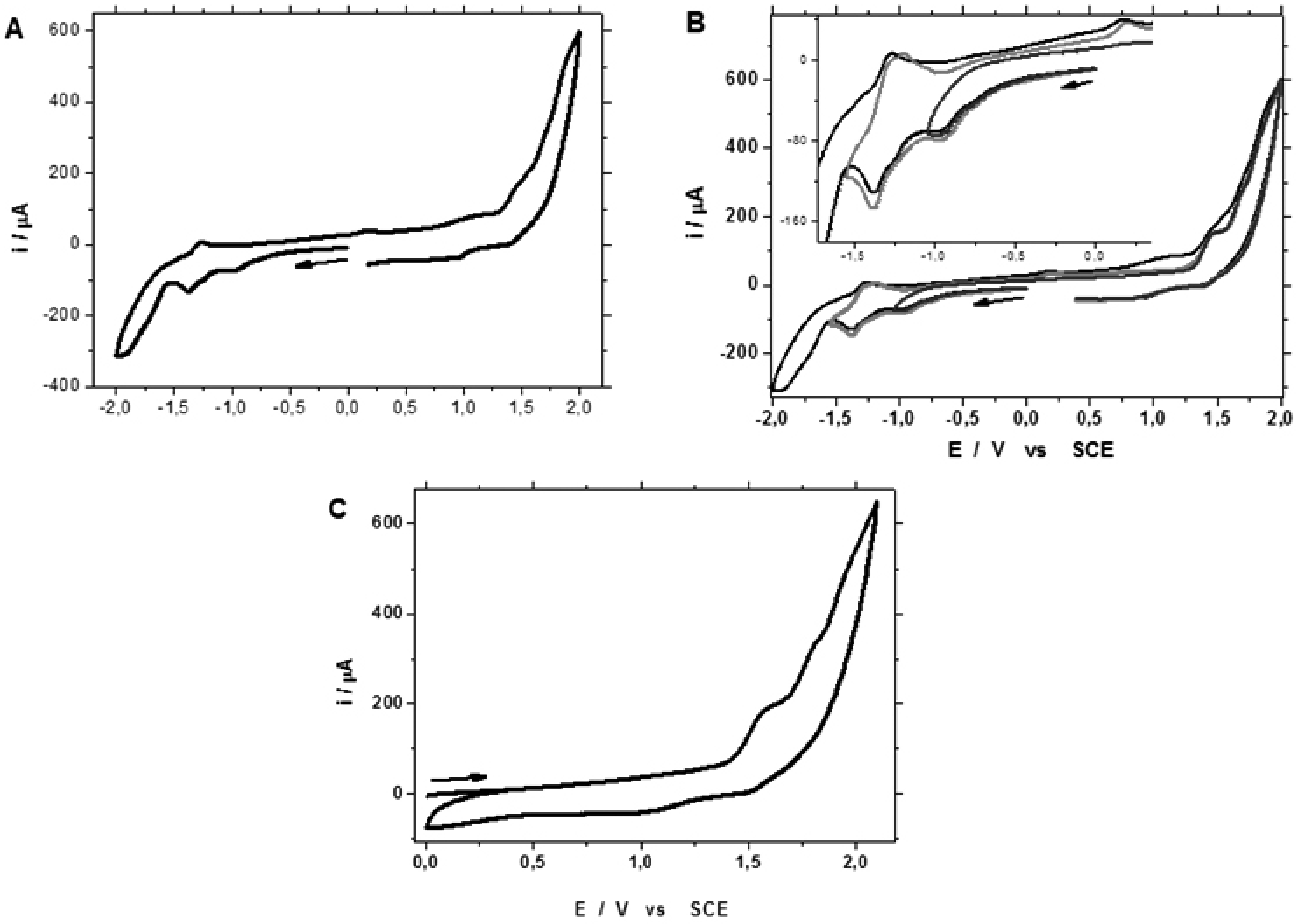


Figure 2. Cyclic voltammogram for **C2** complex; 9.0 x 10^{-4} mol L^{-1} in CH_2Cl_2 with $TBAPF_6$ 0.1 mol L^{-1} on vitreous carbon electrode under inert atmosphere. **A**) and **B**): cathodic scan; **C**): Anodic scan. Scan rate 200 mV/s.

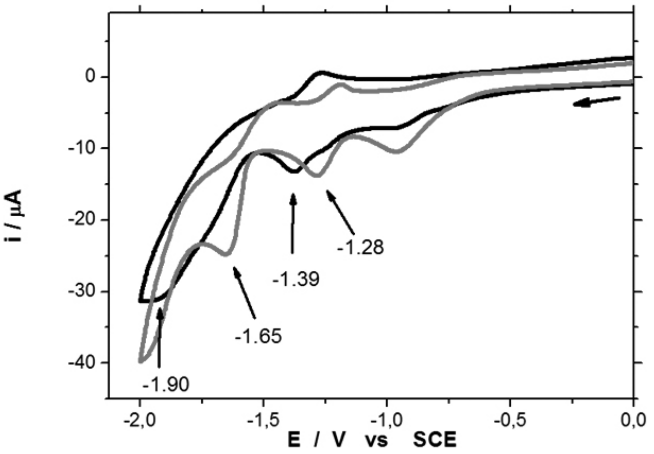


Figure 3. Cyclic voltammogram for the cathodic region of **C2** complex; 9.0 x 10^{-4} mol L^{-1} in CH_2Cl_2 with $TBAPF_6$ 0.1 mol L^{-1} on vitreous carbon electrode. Cathodic region under inert atmosphere (thin line) and under CO_2 atmosphere (bold line). Scan rate 200 mV/s.

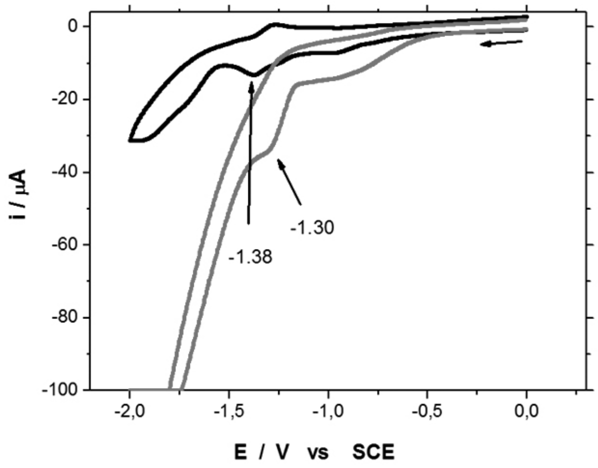
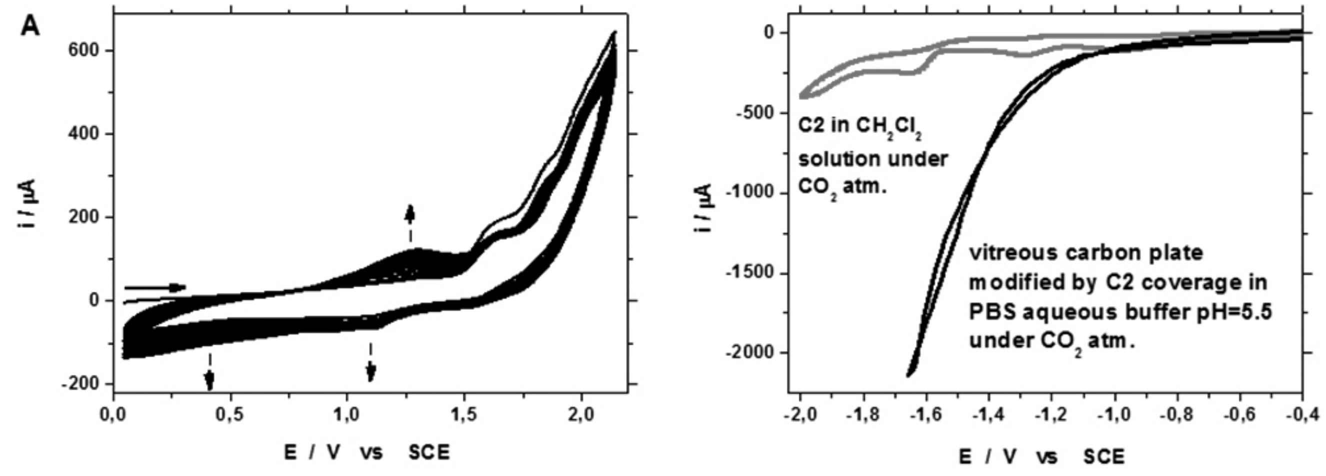


Figure 4. Cyclic voltammogram for the cathodic region of **C2** complex; 9.0 x 10^{-4} mol L^{-1} in CH_2Cl_2 with $TBAPF_6$ 0.1 mol L^{-1} on vitreous carbon electrode. Cathodic region under inert atmosphere (thin line) and under CO_2 atmosphere with 100 µL (1% vol.) of acid acetic added (bold line). Scan rate 200 mV/s.



A B

Figure 5. Cyclic voltammograms for: A) electropolymerization of **C2** complex; 9.0 x 10^{-4} mol L^{-1} in CH_2Cl_2 with $TBAPF_6$ 0.1 mol L^{-1} on large area (~4 cm^2 geom. meas.) vitreous carbon electrode plate, under inert atmosphere. B) Scan rate 200 mV/s. under

3.3 Modified Vitreous Carbon electrode

When a polished Vitreous Carbon plate as working electrode is modified by cycling anodic region of **C2** complex in CH_2Cl_2 which involve the typic oxidative redox profile for amino (-NH_2) and phenolic (-OH) groups presenting in the **L** (cation radical method).[15, 17, 34] The voltammogram profile evolve by growing a polymeric deposit on the plate surface (see **Figure 5, A**). This plate with the immobilized layer of **C2** complex is then transferred to a CO_2 saturated solution buffer, pH=7.0 (allowing it evolve to solution buffer, pH=5.5) and the voltammogram profile registered (see **Figure 5, B).** Under these conditions, a strong electrocatalytic discharge of current is obtained with a wave foot in -1.3 V was observed. [61]

4. CONCLUSIONS

According to the results presented in this study, we conclude that the potential of the *fac*-Re(CO)$_3$(**N,N**)**L**$^+$ complex as electrocatalytic agent depends on the nature of the ancillary ligands. In our case, the use of a Schiff base (*E*)-2-((3-amino-pyridin-4-ylimino)-methyl)-4,6-diterbutylphenol (**L**) on the rhenium(I) core represent an important focus to modulate the mentioned properties in the manuscript. A preliminary study of the electrocatalytic CO_2 reduction mediated by **C2** was electrochemical characterized in dichloromethane. The Epc value for the reversible couple under CO_2 atmosphere was observed at -1.30 V vs SCE (80 mV less negative) and the following reduction process involved an intense unsolved current discharge. Also we observe that when the working electrode is modified by cycling anodic region of **C2** in CH_2Cl_2, a strong electrocatalytic discharge of current is obtained with a wave foot in -1.3 V. Nevertheless, more experimentation is desirable to fully understand this phenomenon. This work is framed in the development of modulating the photophysical properties on the rhenium(I) tricarbonyl core with these kinds of ancillary ligands.[60-61] From the chemical point of view, the modified physicochemical and electrochemical properties modulated the ancillary ligand aimed to obtain catalytic applications of the new rhenium (I) complexes in the CO_2 reduction. [62-63]

Supporting Information: Supplementary data associated with this article can be found, in the online version.

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Supporting Information

A PRELIMINARY STUDY ON ELECTROCATALYTIC REDUCTION OF CO_2 USING *FAC*-$Re^I(CO)_3$(4,4'-DI-METHYL-2,2'-BIPYRIDYL)((*E*)-2-((3-AMINO-PYRIDIN-4-YLIMINO)-METHYL)-4,6-DI-*TERT*-BUTYLPHENOL))$^+$ COMPLEX

JUAN CARLOS CANALES[1], ALEXANDER CARREÑO[2,3], DIEGO OYARZÚN[2], JUAN MANUEL MANRÍQUEZ[1,3], IVONNE CHÁVEZ[1,3]*

[1]Departamento de Quimica Inorganica, Facultad de Quimica, Pontificia Universidad Catolica de Chile,
Avenida Vicuña Mackenna 4860, Macul, Santiago, Chile
[2]Center of Applied Nanosciences (CANS), Universidad Andres Bello, República 275, Santiago, Chile
[3]Núcleo Milenio de Ingeniería Molecular para Catálisis y Biosensores (MECB), ICM, Chile

Section S1 of the supporting information.

***-Synthesis of (E)*-2-((3-amino-pyridin-4-ylimino)-methyl)-4,6-di-tert-butylphenol), (L).** This ligand was synthesized according to literature procedure. Yield 78 %. (See reference 1 and 2)

***-Synthesis of fac*-[Re(CO)$_3$(4,4'-di-methyl-2,2'-bipyridyl)Br], (C1) complex.** This complex was synthesized by direct reaction with bromotricarbonyl(tetrahydrofuran)rhenium(I) dimmer and 4,4'-di-methyl-2,2'-bipyridyl (1:2) in toluene at room temperature. (See reference 3, 4 and 5) Yield 89 %. ^{1}H NMR (400 MHz, CD_3CN): δ= 2.41 [s, 3H, ($-CH_3$)], 7.36 [d, J=5.7 Hz; 1H; H2], 8.20 [s, 1H; H3], 8.76 [d, J=5.7 Hz; 1H;H1]. FTIR (cm^{-1}) 2027; 1929; 1907 (νCO); 1590 (νCC).

***-Synthesis of fac*-[Re(CO)$_3$(4,4'-di-methyl-2,2'-bipyridyl)((*E*)-2-((3-amino-pyridin-4-ylimino)-methyl)-4,6-di-*tert*-butylphenol)](PF$_6$), (C2).** This complex was synthesized according to literature. (See reference 5 and 6) Yield 88%. ^{1}H NMR (400 MHz, CD_3CN): δ=1.36 [s, 9H; $-C(CH_3)_3$], 1.40 [s, 9H; $-C(CH_3)_3$], 1.43 [s,6H, ($-CH_3$)], 5.59 [s, 2H, $-NH_2$],6.44 [d, J=6.4 Hz; 1H; H2´], 7.26 [s; 2H; H5´ and H6´], 7.44 [s, 1H; H3´], 7.55 [s, 1H; H1´], 7.58 [d; J=5.5 Hz; 1H; H2], 8.08 [s, 1H; H4´], 8.24[s; 1H; H3], 9.03 [d; J=5.5 Hz; 1H; H1], 12.55 [s; 1H; -OH]. FTIR (cm^{-1}): 3407 (νOH); 2871 (νNH_2); 2027 and 1929 (νCO), 1623 (νCN); 847 (νPF_6^-).

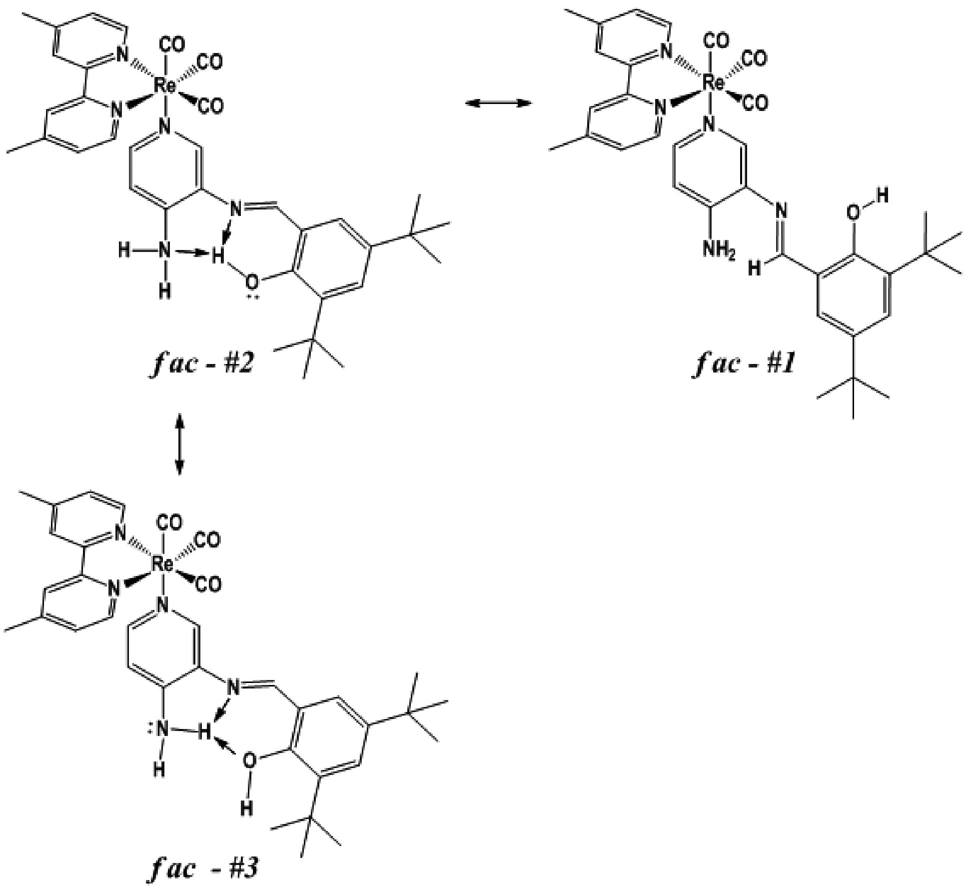
Section S2 of the supporting information.: Schemes

-Scheme S1. Electrochemical–electrochemical–chemical reaction mechanism (EEC). (See reference 7-10)

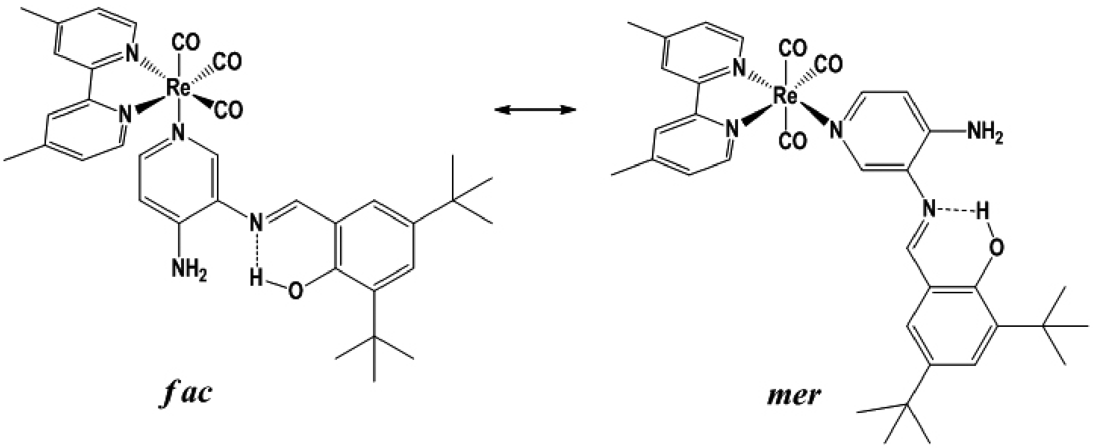
$[Re(dmb)(CO)_3Br] + e \rightarrow [Re(dmb)(CO)_3Br]^-$ $E_{1/2}$: -0.94 V (i)
$[Re(dmb)(CO)_3Br]^- \rightarrow [Re(dmb)(CO)_3] + Br^-$, slow (ii)
$[Re(dmb)(CO)_3Br]^- + e \rightarrow [Re(dmb)(CO)_3Br]^{2-}$ $E_{1/2: -1.25}$ V (iii)
$[Re(dmb)(CO)_3Br]^{2-} \rightarrow [Re(dmb)(CO)_3]^- + Br-$, fast (iv)

4,4'-di-methyl-2,2'-bipyridyl = dmb

-Scheme S2: Intramolecular H-bridge species involved to the ((*E*)-2-((3-amino-pyridin-4-ylimino)-methyl)-4,6-di-*tert*-butylphenol) (**L**) ancillary ligand. (See reference 2, 4 and 5)



-Scheme S3. Equilibrium *facial-meridional* structures proposed in this study. (See reference 11)



Section S3 of the supporting information: References

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