Electrocatalytic Reduction of Carbon Dioxide with Mono(bipyridine)carbonylruthenium Complexes in Solution or as Polymeric Thin Films

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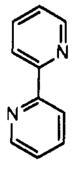
A series of mono(bipyridine)carbonylruthenium(II) complexes, $[Ru(L_1)(CO)_2Cl_2]$, $[Ru(L_1)(CO)_2(CH_3CN)_2][CF_3SO_3]_2$, and $[Ru(L_1)(CO)Cl_3][Me_4N]$ (L_1 = 2,2'-bipyridine), have been found to act as efficient and selective homogeneous electrocatalysts for the reduction of CO_2 into CO in CH_3CN containing 5% water, at a carbon electrode. It has been demonstrated that the electrocatalytic effect is due to the formation of a polymeric film occurring during the electroreduction of the complexes. For $[Ru(L_1)(CO)_2Cl_2]$ and $[Ru(L_1)(CO)_2(CH_3CN)_2][CF_3SO_3]_2$ corresponding films have been identified as the $[\{Ru^0(bpy)(CO)_2\}_n]$ polymer containing Ru^0–Ru^0 bonds. These carbon/$[\{Ru^0(bpy)(CO)_2\}_n]$ modified electrodes appear themselves as efficient molecular cathodes for selective reduction of CO_2 into CO either in CH_3CN + 5% water or in pure aqueous electrolyte. The stability of these modified electrodes can be improved by using a preformed polypyrrolic film functionalized with $[Ru(L_2)(CO)_2Cl_2]$ (L_2 = 4-(2-pyrrol-1-ylethyl)-4'-methyl-2,2'-bipyridine). In this material the formation of Ru^0–Ru^0 bonds occurs in the preformed film during its electroreduction.

Introduction

It has been recently briefly reported that the *trans*-(*Cl*)-$[Ru^{II}(L_1)(CO)_2Cl_2]$ (**C₁**) complex (L_1 = 2,2'-bipyridine) acts as an efficient catalyst in homogeneous solution for the photochemical and electrochemical reduction of carbon dioxide.[2,3] For instance electrochemical reduction of CO_2 at −1.30 V *vs* SCE on a mercury pool catalyzed by $[Ru^{II}(L_1)(CO)_2Cl_2]$ in acetonitrile water (4:1) gave CO as a main product with an 88% current efficiency.[3] However, the identification of the catalytically active species was not investigated. We have previously reported the detailed electrochemical and photochemical behavior of this complex in CH_3CN.[4-6] We have demonstrated that the reduction of $[Ru^{II}(L_1)(CO)_2Cl_2]$ results in the formation of a dark blue strongly adherent electroactive film having the characteristics of a metal–metal bond structure.[4,5] This film has been recently identified as an "open" cluster polymeric $[\{Ru^0(L_1)(CO)_2]$ complex.[7] We report here a detailed investigation concerning the electrocatalytic reduction of CO_2 by this complex, in connection with the role of the $[\{Ru^0(L_1)(CO)_2\}_n]$ film in the electrocatalytic process. The utilization of a preformed polypyrrolic film, containing the $[Ru^{II}(L_2)(CO)_2Cl_2]$ (L_2 = 4-(2-pyrrol-1-ylethyl)-4'-methyl-2,2'-bipyridine) core obtained by electropolymerization of the corresponding monomeric complex with bipyridine ligand having a pyrrole group as substituent, has been also investigated.[8] Moreover, two other mono(bipyridine)carbonylruthenium(II) complexes, $[Ru^{II}(L_1)(CO)_2(CH_3CN)_2]^{2+}$ and $[Ru^{II}(L_1)(CO)Cl_3][Me_4N]$, have been tested as molecular catalysts for the electrochemical reduction of CO_2.



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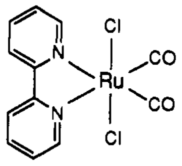

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Experimental Section

Electrochemical Instrumentation and Procedures. Acetonitrile (Rathburn, HPLC grade) was used as received or dried by distillation over P_2O_5. Tetrabutylammonium perchlorate (TBAP) from Fluka was recrystallized from ethyl acetate and dried under vacuum at 80 °C for 3 days. Tetramethylammonium tetrafluoroborate (TMATF) from Fluka was dried under vacuum at 80 °C for 3 days. Water was doubly distilled. Electrochemical experiments were carried out with a Princeton Applied Research Model 273 potentiostat–galvanostat equipped with a Sefram TGM 164 X-Y recorder. Potentials are relative to the Ag/10 mM Ag^+ or saturated calomel (SCE) electrodes in CH_3CN (containing or not containing water) and in water, respectively. Working electrodes for cyclic voltammetry consisted of a vitreous carbon disk (3-mm diameter) polished with 1-μm diamond paste.

All experiments were run under an Ar or CO_2 atmosphere in a conventional three-electrode cell made airtight with vacuum grease (M. Apiezon). The total volume occuped by the gas in the electrolysis cell was 167 mL. Exhaustive electrolyses for the $[\{Ru^0(L_1)(CO)_2\}_n]$ film formation and dissolution were carried out with a 5 cm² platinum cylinder. Anal. Calcd for $[\{Ru^0(L_1)(CO)_2\}_n]$: C, 46.00; H, 2.57; N, 8.94. Found: C, 45.63; H, 2.54; N, 8.71. For electrocatalytic electrolyses a 10 × 10 × 4 mm carbon felt electrode (RVC 2000, 65 mg cm⁻³, from Le Carbon Lorraine) was used. The solution was degased with CO_2 for 20 min with stirring. Films were grown under an argon atmosphere by potentiostating the carbon felt electrode dipped in CH_3CN solution of the appropriate complex (10^{-3} M). The initial solution was removed and the electrode rinsed with a pure CH_3CN solution under argon. This solution was then removed and substituted with a CH_3CN + 0.1 M TBAP solution containing 5% of water or with a H_2O + 0.1 M $LiClO_4$ solution purged

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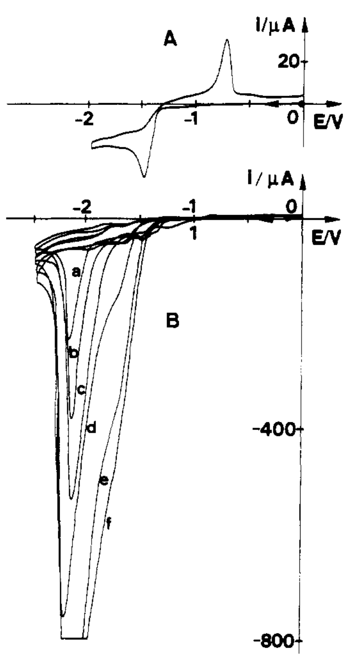


Figure 1. Cyclic voltammograms in CH_3CN solution containing 0.1 M TBAP of $[Ru^{II}(L_1)(CO)_2Cl_2]$ (1 mM) at a vitreous C electrode (0.07 cm^2) at a scan rate of 100 mV s^{-1}: (A) argon-bubbled solution; (B) CO_2-bubbled solution after addition of different percentage of H_2O [(a) 0%, (b) 1%, (c) 2%, (d) 3%, (e) 5%, (f) 10%.]

with CO_2. All experiments were arbitrarely stopped after a determined amount of coulombs (generally 60 C) had been passed. The gas was sampled through a septum. CO was analyzed on a Delsi Model 30 gas chromatograph with a FID detector, with a 120-cm 5-Å molecular sieve column followed by a catalytic oven. Hydrogen was used as a carrier gas. Formate ions were analyzed on a Waters Associates high-pressure chromatograph. A Bio-Rad HPX-87 H cation-exchange resin column was eluated with a 10^{-2} M H_2SO_4 solution. A UV detector set at 224 nm was used. TBAP was removed from the reaction solutions prior to the analyses.

Spectroscopies. Electronic absorption spectra were recorded on a Hewlett-Packard 8452A diode array spectrophotometer equipped with a Compaq 286 computer and a Citizen 120D printer. Spectroelectrochemical measurements on films were made using a conventional sandwich-type cell.[9] The optically transparent electrode (OTE) consisted of doped indium oxide. Infrared spectra were recorded on a Brucker FTIR IFS 25.

Compounds. The preparation and purification of all complexes studied here were previously reported.[4-8]

Results

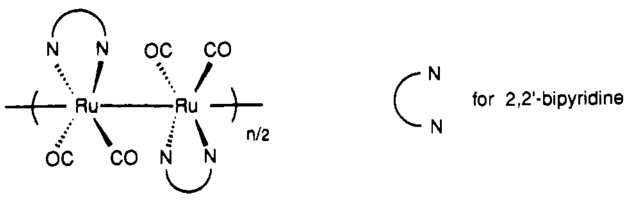
(1) Electrocatalysis with *trans*-(*Cl*)-$[Ru^{II}(L_1)(CO)_2Cl_2]$. In homogeneous solution. Under an argon atmosphere the cyclic voltammogram at a carbon disk electrode of a *trans*-(*Cl*)-$[Ru^{II}(L_1)(CO)_2Cl_2]$ solution (10^{-3} M) in 0.1 M TBAP-CH_3CN exhibits an intense irreversible cathodic peak at −1.48 V which is associated with an anodic peak at −0.74 V on the reverse scan (Figure 1A). The shape of this peak system is typical of an electroprecipitation-redissolution phenomenon and corresponds to the formation and the dissolution of a deep blue film of a polymeric $[\{Ru^0(L_1)(CO)_2\}_n]$ complex on the electrode (see the next paragraph).[4,5,7] When this solution is purged with CO_2, a strong cathodic peak (at −2.18 V), close to that of the direct reduction potential of CO_2 without catalyst, is observed.[3] This shows that *trans*-(*Cl*)-$[Ru^{II}(L_1)(CO)_2Cl_2]$ is a poor catalyst in pure CH_3CN electrolyte. Progressive addition of water to the electrolyte induces a strong increase of the reduction peak while its potential becomes less and less negative until a 10% volume of water (Figure 1B). It should be noted that in the presence of CO_2 the redissolution peak at $E_{pa} = -0.74$ V is partially suppressed. Preparative-scale electrolysis using a carbon felt electrode were performed at −1.55 V in CH_3CN containing various amounts of water (3, 5, 10, 25%) and the *trans*-(*Cl*)-$[Ru^{II}(L_1)(CO)_2Cl_2]$ complex (10^{-3} M). After 60 C was consumed, electrolysis currents were stable and dropped to less than 10% of their initial values. The catalytic current density increases (from 12 to 25 mA) with the percentage of water. Gas-phase and solution analyses show that the main reduction product is CO in all cases, with current efficiencies η as high as 97%. CO is formed according to eq 1.

$$CO_2 + 2H^+ + 2e^- \rightarrow CO + H_2O \qquad (1)$$

Only small amounts of formate were detected. The current efficiency η for formate production lies under 0.5%. These results are in good accordance with literature data except that carbon felt appears to be a more convenient cathodic material than mercury since for CO production our current efficiencies are higher. This could be related to the formation of a polymeric film occurring during the electroreduction of the complex. This polymeric material has been proved to be a very efficient catalyst, and it will be discussed in the next section.

On Polymeric $[\{Ru^0(L_1)(CO)_2\}_n]$ Modified Electrodes. As previously shown[4,5,7] controlled-potential electrolysis at −1.65 V of a solution of *trans*-(*Cl*)-$[Ru^{II}(L_1)(CO)_2Cl_2]$ in 0.1 M CH_3CN resulted in the formation of an strongly adherent electroactive deep blue film on the working electrode (Pt or C). Exhaustive reduction requires the exchange of two electrons per molecule while two Cl^- ions per molecule of complex are released (estimated from the intensity of the well-known quasi-reversible peak system of the Cl^- ions).[11] The reaction is quantitative, and no more complex remains in solution after electrolysis.

We have proposed that this film has a polymeric nature[7] with a basic chemical structure as drawn in **1**. The following mechanism for the film formation can be assumed. The initial step involves a one-electron ligand reduction followed by a fast intramolecular electron transfer associated with a Cl^- loss leading to a Ru^I species (eqs 2 and 3). $[Ru^I(L_1)(CO)_2Cl]$ is probably more easy to reduce than the initial complex and is reduced following a similar pattern to $[Ru^0(L_1)(CO)_2]$ (eqs 4 and 5), the latter being the key species for the polymerization process.



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$$\begin{array}{rcll}
[Ru^{II}(L_1)(CO)_2Cl_2] & \xrightarrow{e^-} & [Ru^{II}(L_1^{\bullet -})(CO)_2Cl_2]^- & (2) \\
[Ru^{II}(L_1^{\bullet -})(CO)_2Cl_2]^- & \longrightarrow & [Ru^{I}(L_1)(CO)_2Cl] + Cl^- & (3) \\
[Ru^{I}(L_1)(CO)_2Cl] & \xrightarrow{e^-} & [Ru^{I}(L_1^{\bullet -})(CO)_2Cl]^- & (4) \\
[Ru^{I}(L_1^{\bullet -})(CO)_2Cl]^- & \longrightarrow & [Ru^{0}(L_1)(CO)_2] + Cl^- & (5) \\
 & & \downarrow & \\
 & & [\{Ru^{0}(L_1)(CO)_2\}_n] &
\end{array}$$

A full characterization of the film is difficult to obtain since it is unstable at potentials higher than −0.60 V, so it cannot be

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handle in air. However, the formulation of structure **1** is strongly supported by the following observations: (1) The great insolubility of films, even in solvents like DMF and DMSO, is in favor of a polymeric structure. (2) Elemental analyses are consistent with the formulation $[\{Ru^0(L_1)(CO)_2\}_n]$ (see Experimental Section). (3) FAB-MS studies (using *m*-nitrobenzyl alcohol (*m*-NBA)/CH_3CN as a matrix) show peaks at m/z values of 1137, 966, and 794 corresponding to the fragments $[Ru_3(L_1)_3(CO)_6(m\text{-NBA})(CH_3CN) + H]$, $[Ru_2(L_1)_3(CO)_5(m\text{-NBA})(CH_3CN) + H]$, and $[Ru_2(L_1)_2(CO)_3(m\text{-NBA})]$, respectively. (4) The absorption of the film electrodeposited on an optically transparent electrode exhibits three intense bands in the visible region (λ_{max} = 475, 600, and 760 nm). The shape of this absorption spectrum strongly suggests the presence of metal–metal bonds in the film as previously demonstrated in the case of the reduction of $[Re^I(bpy)(CO)_3Cl]$, which gave the dimeric $[Re^0(bpy)(CO)_3]_2$ complex.[12–15] (5) The presence of metal–metal bonds (Ru^0–Ru^0) is confirmed by the presence of a band at 170 cm^{-1} in the FT-IR spectrum close to that observed for $Ru_3(CO)_{12}$ for instance. No ν_{Ru-Cl} streching vibration is detected. This film exhibits $\nu_{(CO)}$ at 2017 and 1997 cm^{-1} and the usual bands due to the vibrations of the bipyridine ligand in the 1620–1540-cm^{-1} region. (6) Desorption and dissolution of the film deposited on a platinum cylinder can be accomplished by an exhaustive oxidation at 0 V followed by an other one at 1.1 V after its transfer in pure CH_3CN electrolyte. The involved coulometry corresponds to about two electrons per molecule of the initial complex. Analysis of the resulting colorless solution by means of cyclic voltammetry and spectrophotometry shows that this solution contains the $[Ru^{II}(L_1)(CO)_2(CH_3CN)_2]^{2+}$ complex. A yield >90% was found versus the amount of the starting complex *trans*-(*Cl*)-$[Ru^{II}(L_1)(CO)_2Cl_2]$ used to prepare the $[\{Ru^0(L_1)(CO)_2\}_n]$ films. The cyclic voltammogram of $[Ru^{II}(L_1)(CO)_2\ (CH_3CN)_2]^{2+}$ is described further in the text. This means unambiguously that the basic structure of the starting compound is retained in the polymeric film. In other worlds only simple chemical reactions like dimerization or polymerization (no loss of CO or bpy ligand for instance) occurs during the electroreduction. The two initial Cl^- ligands are replaced by two CH_3CN ligands since the film is dissolved in pure CH_3CN which does not contain any Cl^- anions. Addition of a slight excess of Cl^- as the Et_4N^+ salt to the solution restores the initial complex $[Ru^{II}(L_1)(CO)_2Cl_2]$ with a 90% yield. (7) The *trans*-chloro, *cis*-carbonyl structure of the monomeric $[Ru^{II}(L_1)(CO)_2Cl_2]$ complex favors the structure of the polymer given in **1**. The existence of "open" clusters of the $[\{Ru^0(L_1)(CO)_2\}_n]$ type, based on a geometrical structure of high symmetry, appears not to have been reported previously. It should, however, be noticed that the photochemical preparation[16] and structure determination[17] of an oligomeric form of "Ru(CO)$_4$" have recently been published. (8) $[\{Ru^0(L_1)(CO)_2\}_n]$ films can also be formed from the *trans*-(*Cl*)-$[Ru^{II}(L_1)(CO)_2Cl_2]$ complex by continuously cycling the potential from −0.80 to −2.0 V. The resulting electroactive modified electrode after its transfer to a clean electrolyte exhibits two clear reversible peak systems at $E_{1/2}$ = −0.80 and −1.50 V (Figure 2A) and a third partially reversible peak system at $E_{1/2}$ = −2.25 V under an argon atmosphere. In accordance with the initial cyclic voltammogram of a solution of *trans*-(*Cl*)-$[Ru^{II}(L_1)(CO)_2Cl_2]$ a strong desorption peak is observed at −0.57 V followed by some more or less well-defined irreversible anodic peaks in the anodic area.

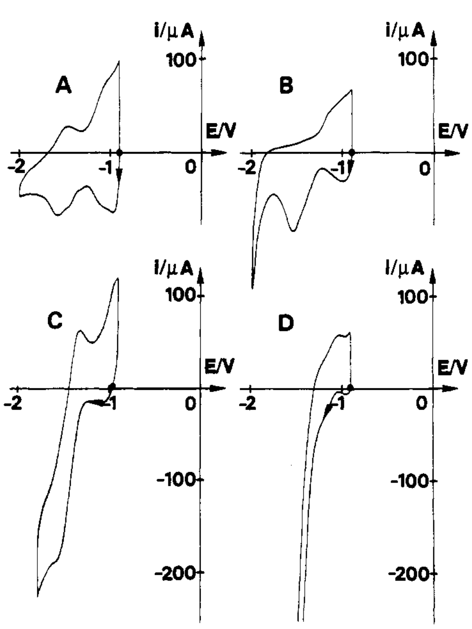

Figure 2. Cyclic voltammograms in CH_3CN solution containing 0.1 M TBAP of C/$[\{Ru^0(L_1)(CO)_2\}_n]$ modified electrode prepared by electrolysis at −1.65 V (charge passed Q = 5 mC) at a scan rate of 100 mV s^{-1}. (A) argon-bubbled solution; (B) after addition of 5% H_2O; (C) CO_2-bubbled solution; (D) after addition of 5% H_2O.

The fact that the $[\{Ru^0(L_1)(CO)_2\}_n]$ film exhibits reversible electroactivity also argues in favor of a polymeric structure. This electroactivity is probably due to the successive reductions of the bipyridine ligands to the $bpy^{\cdot-}$ ($E_{1/2}$ = −1.50 V) and bpy^{2-} ($E_{1/2}$ = −2.25 V) levels. However, only 8% of the bipyridine sites are electroactive in the polymer (doping level) as evaluated from the ratio of integrated currents for the signals in the film and the total charge involved in the preparation of the film. These modified electrodes are oxidized back at −1.1 V (into the pure $[\{Ru^0(L_1)(CO)_2\}_n]$ state) (undoped level) before their utilization and characterization.

With 5% H_2O added, the cyclic voltammogram of the "blue film" (Fig. 2B) is not basically changed. The redox system at −1.50 V appears less reversible probably as a consequence of the catalytic reduction of water starting from −1.9 V. Figure 2C,D shows the cyclic voltammogram of the film in CH_3CN solution saturated by bubbling CO_2 in the absence and in the presence of 5% water. In accordance with the experiments using *trans*-(*Cl*)-$[Ru^{II}(L_1)(CO)_2Cl_2]$ as a catalyst in solution, the electrocatalytic effect is weak without water. In contrast a strong enhancement of the cathodic current from −1.3 V is observed with 5% water. Repeatedly scanning the potential between −0.9 and −1.8 V shows that this catalytic effect is persistent. No change in the voltammogram is detected after 20 successive cycles. Obviously, cycling at the upper potential (until 0 V) induces the dissolution of the film and the disappearance of the catalytic reduction of CO_2. We have carried out preparative-scale electrolysis using a carbon felt electrode modified with a different amount of $[\{Ru^0(L_1)(CO)_2\}_n]$ in view to confirm its outstanding catalytic activity. Electrolyses were conducted at −1.55 V in CH_3CN + 5% water. Product analysis of the solution shows that in all cases CO is produced with a current yield close to 100%. Table 1 gives the main features of these experiments. As expected, the electrolysis time decreases as the amount of $[\{Ru^0(L_1)(CO)_2\}_n]$ deposited increases. The current drops and reaches a pseudoplateau more or less rapidly depending on the amount $[\{Ru^0(L_1)(CO)_2\}_n]$, indicating probably that some desorption of the film occurs at the beginning of the electrolysis.

Similar experiments have been done in pure aqueous solution (H_2O + 0.1 M $LiClO_4$) showing that films of $[\{Ru^0(L_1)(CO)_2\}_n]$

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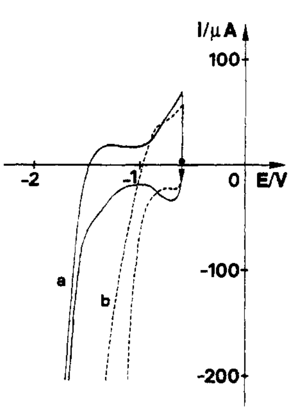


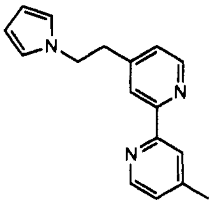
Figure 3. Cyclic voltammograms in H_2O solution containing 0.1 M $LiClO_4$ of C/[$\{Ru^0(L_1)(CO)_2\}_n$] (same conditions as in Figure 2) at a scan rate of 100 mV s^{-1}: (a) argon-bubbled solution; (b) CO_2-bubbled solution.

Table 1. Electrocatalytic Reduction of CO_2 at $E = -1.55$ V on a Carbon Felt [$\{Ru^0(L_1)(CO)_2\}_n$] Modified Electrode in 0.1 M TBAP/CH_3CN Containing 5% H_2O

charge consumed for [$\{Ru^0(L_1)(CO)_2\}_n$] formation (C)	electrolysis time (min)/ coulometry (C)	initial current (mA)	final current (mA)	CO produced (mol × 10^4)	current efficiency η (%)
0.5	96/40	13	6	2.02	97
1	52/60	26	16	3.10	100
1.5	40/60	30	22	3.10	100

are also effective catalysts for CO_2 reduction into CO. Figure 3 displays the cyclic voltammogram under N_2 and CO_2 of the polymer in aqueous medium (all potentials are reported here *vs* SCE). The electroactivity of the film remains quite identical to that observed in CH_3CN, and bubbling of CO_2 strongly increases the cathodic current. Electrolysis at −1.20 V on a carbon felt modified with [$\{Ru^0(L_1)(CO)_2\}_n$] (prepared by using a 1.5-C charge) produced CO with a current efficiency higher than 97% after 60 C has been passed. At this time electrolysis current has dropped to 40% of its initial value while a pseudo plateau was reached.

As Polypyrrolic Films. We have recently reported that polypyrrolic films containing this kind of complex can be prepared by electropolymerization of the corresponding monomeric molecule *trans-(Cl)*-[$Ru^{II}(L_2)(CO)_2Cl_2$] (C_2), which contains a bipyridine ligands L_2 having one pyrrole as substituent.[8]



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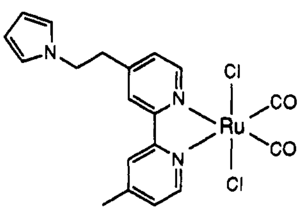


C_2

Electropolymerization was accomplished, for instance, by maintaining the working electrode at 0.95 V dipped in a CH_3CN + 0.1 M TBAP solution of *trans-(Cl)*-[$Ru^{II}(L_2)(CO)_2Cl_2$] (10^{-3} M). Continuous cycling of the poly-[$Ru^{II}(L_1)(CO)_2Cl_2$] modified electrode in the cathodic range (0.9 → −2.0 V) induces the transformation of the film. The former intense cathodic peak ($E_{pc} = -1.68$ V) close to that of the monomer is rapidly replaced by several quasi reversible peak systems at $E_{1/2} = -1.12; -1.51; -1.68$ V (Figure 4A). This is due to the formation of metal–metal bonds in the film *via* a mechanism similar to that proposed for [$\{Ru^0(L_1)(CO)_2\}_n$] formation from *trans-(Cl)*-[$Ru^{II}(L_1)(CO)_2Cl_2$]. However, confinement of the complex in a preformed polypyrrolic film does prevent the obtention of a well-arranged structure such as in **1**. This is in good accordance with spectroelectrochemical experiments conducted on an ITO/poly-[$Ru^{II}(L_2)(CO)_2Cl_2$] electrode.[6] At −1.0 V this film presents an absorption maximum in the red region ($\lambda_{max} = 580$ nm) and at −2.0 V in the blue one ($\lambda_{max} = 680$ nm). These electronic transitions appear at lower wavelenghts than that of the [$\{Ru^0(L_1)(CO)_2\}_n$] polymer indicating a weaker conjugation character of the structure of the film. On the other hand, there is no anodic redissolution peak as observed for the [$\{Ru^0(L_1)(CO)_2\}_n$] polymer since here the polypyrrolic film remains at the electrode surface. However, a weak irreversible peak is detected at −0.90 V corresponding probably to the partial reoxidation of the metal–metal bonds.

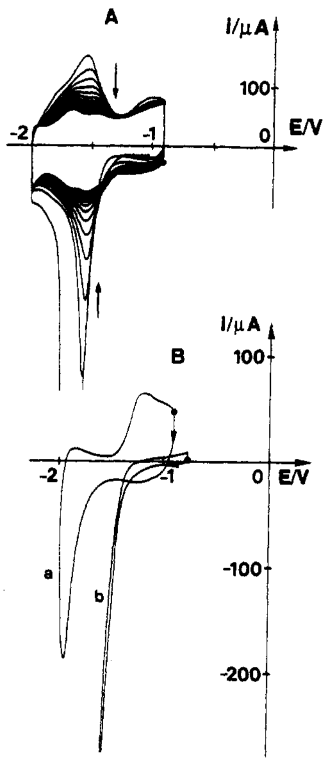


Figure 4. Cyclic voltammograms in CH_3CN solution containing 0.1 M TBAP of C/poly-[$Ru^{II}(L_2)(CO)_2Cl_2$] modified electrode prepared by electrolysis at 0.95 V (charge passed $Q = 1.8$ mC) at a scan rate of 100 mV s^{-1}: (A) evolution of the voltammogram by repeated potential scanning between −0.9 and −2 V; (B) initial voltammograms in CH_3CN after addition of 5% H_2O (a) argon-bubbled solution; (b) CO_2-bubbled solution].

Introduction of water (5% volume) to the CH_3CN solution induces a more marked change in the cathodic electroactivity of the poly-[$Ru^0(L_2)(CO)_2Cl_2$] film than with [$\{Ru^0(L_1)(CO)_2\}_n$] (see above). The redox systems become less reversible (Figure 4B, curve a). When the solution is purged with CO_2, a large catalytic current is observed from −1.50 V (Figure 4B, curve b). Bulk electrolysis carried out with a poly-[$Ru^{II}(L_1)(CO)_2Cl_2$] film either in CH_3CN + 0.1 M TBAP containing 5% water (*E* applied = −1.60 V) or in H_2O + 0.1 M $LiClO_4$ (*E* applied = −1.35 V vs SCE) allows the obtention of CO with a quite high yield (90 and 80% current efficiency, respectively). It is worth noting that the current after 60 C was consumed remains identical to its initial value even in pure aqueous electrolyte. However for the latter case it appears that poly-[$Ru^{II}(L_1)(CO)_2Cl_2$] films reduced previously by two successive scans between −0.9 and −2 V in acetonitrile are more active (when used as an electrocatalyst in H_2O + 0.1 M $LiClO_4$). Complete transformation of those complexes contained in the film into metal–metal-bonded species could account for this observation.

(2) Electrocatalysis with *trans-(CH₃CN)*-[$Ru^{II}(L_1)(CO)_2(CH_3CN)_2$][$CF_3SO_3$]$_2$. In Homogeneous Solution. The cyclic voltammogram of a solution of *trans-(CH₃CN)*-[$Ru^{II}(L_1)$-

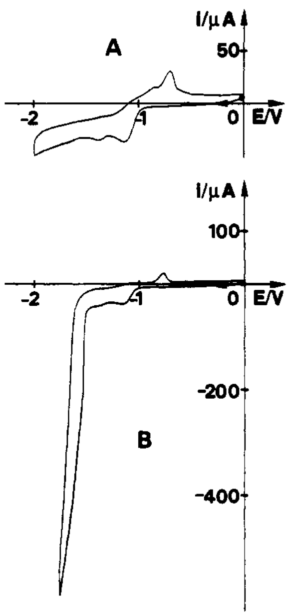


Figure 5. Cyclic voltammograms in CH_3CN solution containing 0.1 M TBAP of *trans-*(*CH_3CN*)-$[Ru^{II}(L_1)(CO)_2(CH_3CN)_2][CF_3SO_3]_2$ (1 mM) at a vitreous C electrode (0.07 cm^2) at a scan rate of 100 mV s^{-1}: (A) argon-bubbled solution; (B) CO_2-bubbled solution after addition of 5% H_2O.

$(CO)_2(CH_3CN)_2][CF_3SO_3]_2$ (10^{-3} M) under an argon atmosphere in CH_3CN + 0.1 M TBAP shows an irreversible process similar to that of *trans-*(*Cl*)-$[Ru^{II}(L_1)(CO)_2Cl_2]$ (Figure 5A). However, this reduction occurs at a less negative potential ($E_{pc} = -1.20$ V). This reduction corresponds to the formation of a similar polymeric film (vide supra). As for *trans-*(*Cl*)-$[Ru^{II}(L_1)(CO)_2Cl_2]$, the electrocatalytic reduction of CO_2 is efficient only in the presence of water. Curve B of Figure 5 shows the cyclic voltammogram in CH_3CN + 0.1 M TBAP + 5% water purged with CO_2. It should be noted that the continuous cycling of the electrode between -0.9 and -2.0 V induces an increase of the catalytic effect with a continuous positive shift of the cathodic current as a consequence of the growth of a polymeric film on the electrode surface. Preparative-scale electrolysis at -1.55 V using a carbon felt electrode and a *trans-*(*CH_3CN*)-$[Ru^{II}(L_1)(CO)_2(CH_3CN)_2][CF_3SO_3]_2$ solution (10^{-3} M) gives only CO with a 100 % electrical yield after 60 C. At this stage of electrolysis the current was stable and dropped to less than 10% of its initial value.

On a Polymeric Modified Electrode. Formation of a polymeric film with electrochemical and spectroscopic characteristics identical to those resulting from the electroreduction of *trans-*(*Cl*)-$[Ru^{II}(L_1)(CO)_2Cl_2]$ is obtained by cycling the potential between -0.85 and -1.60 V (Figure 6A) or by potentiostating the electrode at -1.30 V. Figure 6B shows the cyclic voltammogramm of the resulting film under an argon atmosphere. The film formation process probably involves the electrogeneration of the $[Ru^{I}(L_1)(CO)_2(CH_3CN)_2]^+$ species (eqs 6 and 7) followed by a second one-electron transfer leading to $[Ru^0(bpy)(CO)_2]$ (eq 8 and 9) which polymerizes.

$$[\mathrm{Ru^{II}(L_1)(CO)_2(CH_3CN)_2}]^{2+} \xrightarrow{e^-} [\mathrm{Ru^{II}(L_1^{\bullet -})(CO)_2(CH_3CN)_2}]^{+} \tag{6}$$

$$[\mathrm{Ru^{II}(L_1^{\bullet -})(CO)_2(CH_3CN)_2}]^{+} \longrightarrow [\mathrm{Ru^{I}(L_1)(CO)_2(CH_3CN)}]^{+} + \mathrm{CH_3CN} \tag{7}$$

$$[\mathrm{Ru^{I}(L_1)(CO)_2(CH_3CN)}]^{+} \xrightarrow{e^-} [\mathrm{Ru^{I}(L_1^{\bullet -})(CO)_2(CH_3CN)}] \tag{8}$$

$$[\mathrm{Ru^{I}(L_1^{\bullet -})(CO)_2(CH_3CN)}] \longrightarrow \underset{\displaystyle [\{\mathrm{Ru^0(L_1)(CO)_2}\}_n]}{\underset{\displaystyle\downarrow}{[\mathrm{Ru^0(L_1)(CO)_2}\}}} + \mathrm{CH_3CN} \tag{9}$$

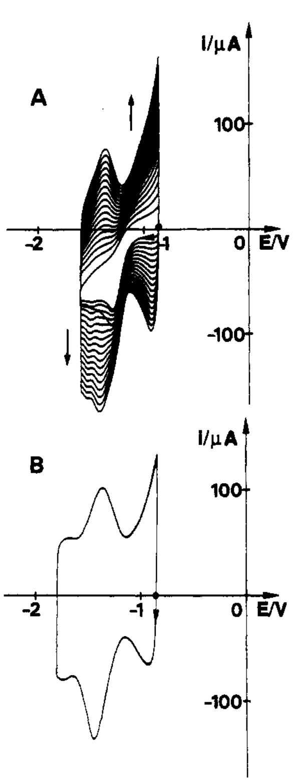


Figure 6. (A) Cyclic voltammograms in CH_3CN solution containing 0.1 M TBAP of *trans-*(*CH_3CN*)-$[Ru^{II}(L_1)(CO)_2(CH_3CN)_2][CF_3SO_3]_2$ (2.1 mM) at a Pt electrode (0.2 cm^2) at a scan rate of 100 mV s^{-1} (scans 1–18). (B) Cyclic voltammograms in CH_3CN solution containing 0.1 M TBAP of the resulting $[\{Ru^0(L_1)(CO)_2\}_n]$ modified electrode.

The release of one CH_3CN ligand does not require as much energy as the release of one Cl^- ligand in accordance with the less cathodic potential of *trans-*(*CH_3CN*)-$[Ru^{II}(L_1)(CO)_2(CH_3CN)_2]$-$[CF_3SO_3]_2$ compared to *trans-*(*Cl*)-$[Ru^{II}(L_1)(CO)_2Cl_2]$.

Desorption and dissolution of the "blue film", obtained after an exhaustive reduction on a platinum cylinder (2 electrons per molecule are involved in that process), can be achieved by two successive oxidations at 0 and 1.1 V in pure CH_3CN + 0.1 M TBAP. Two electrons per molecule of the initial complex are needed. The resulting solution exhibits the same cyclic voltammogram and absorption spectrum as those of the starting solution of the *trans-*(*CH_3CN*)-$[Ru^{II}(L_1)(CO)_2(CH_3CN)_2]^{2+}$ complex. This experiment reinforces our assumption about the proposed structure of the polymeric film. Obviously, exhaustive electrolyses relative to the CO_2 reduction can be conducted with these films. They give results identical to those carried out with $[\{Ru^0(L_1)(CO)_2\}_n]$ films prepared from *trans-*(*Cl*)-$[Ru^{II}(L_1)(CO)_2Cl_2]$ with a quantitative formation of CO.

(3) Electrocatalysis with $[Ru(L_1)(CO)Cl_3][Me_4N]$. In Homogeneous Solution. At negative potential the cyclic voltammogram of this complex 6.5×10^{-4} M in CH_3CN, H_2O (5%) + 0.1 M TBAP shows an irreversible peak at $E_{pc} = -1.90$ V on a carbon electrode (Figure 7A); no return peak is detected on the reverse scan. We have previously reported that controlled-potential reduction at -2.0 V does not produce films on the working electrode[4], however thin films can be made by maintaining the electrode at a less cathodic potential (see further on in the text). Under a CO_2 atmosphere in CH_3CN + 5% of water no clear catalytic enhancement of the current is observed on the first cathodic scan. Continuous cyclic over the range -0.9 to -2.0 V induces cycle by cycle an anodic shift of the wave and a large increase of the current. After 5 successive cycles the catalytic effect starts from -1.40 V as a consequence of an electroactive film formation (Figure 7B). Quantitative production of CO (η

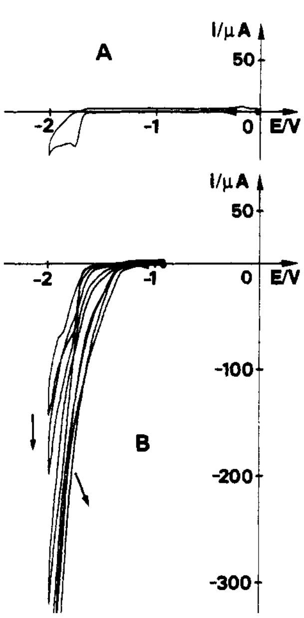
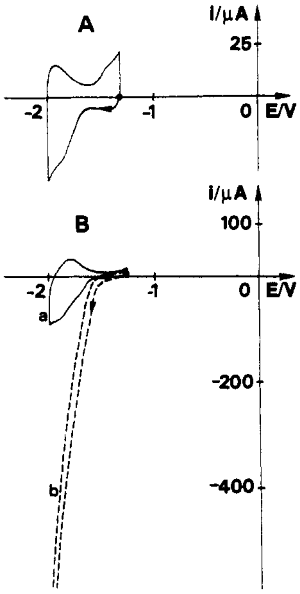


Figure 7. Cyclic voltammograms in CH_3CN solution containing 0.1 M TBAP and 5% H_2O of $[Ru^{II}(L_1)(CO)Cl_3][Me_4N]$ (0.65 mM) at a C electrode (0.07 cm^2) at a scan rate of 100 mV s^{-1}: (A) argon-bubbled solution; (B) CO_2-bubbled solution, with five successive scan between -0.9 and -2 V.

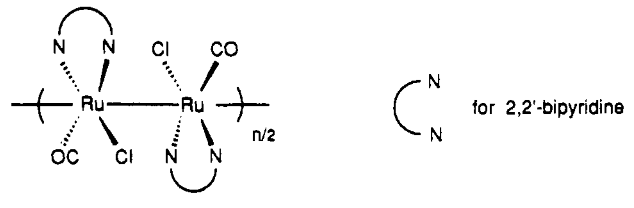


0q; y = 222q

Figure 8. (A) Cyclic voltammograms in CH_3CN solution containing 0.1 M TBAP of a Pt/$[\{Ru^0(L_1)(CO)Cl\}_n]$ modified electrode prepared by electrolysis at -1.9 V (charge passed Q = 20 mC) at a scan rate of 100 mV s^{-1}. (B) Cyclic voltammograms in CH_3CN solution containing 0.1 M TBAP and 5% of H_2O of a C/$[\{Ru^0(L_1)(CO)Cl\}_n]$ modified electrode at a scan rate of 100 mV s^{-1} [(a) argon-bubbled solution; (b) CO_2-bubbled solution].

= 100%) is obtained after an exhaustive electrolysis was made (60 C has been passed). The initial applied potential was -1.80 V and next was decreased reduced gradually to -1.70 V, the current was remarkably stable at that stage.

As Polymeric Films. Thin electroactive films can be obtained by potentiostating the electrode at -1.90 V. Figure 8, curve a, shows the cyclic voltammogram of the resulting film (20 mC has been passed for its preparation) after its transfer into a clean electrolyte. Two quasi-reversible stable systems located at -1.35 and -1.90 V are displayed. Although we did not yet try to fully characterize this material we suggest by analogy with $[\{Ru^0(L_1)(CO)_2\}_n]$ a similar polymeric structure $[\{Ru^0(L_1)(CO)Cl\}_n]$, polymer **2**. The FT-IR spectrum of this polymer shows ν_{CO} at 1998 cm^{-1}, a ν_{Ru-Cl} stretching vibration at 330 cm^{-1}, and strong bands at 231 and 173 cm^{-1}.



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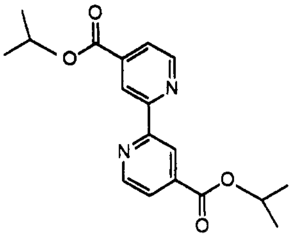
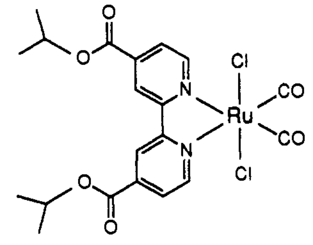
This is in accordance with the fact that exhaustive reduction of the initial solution of $[Ru^{II}(bpy)(CO)Cl_3][Me_4N]$ required two electrons per complex while two Cl^- ions per molecule are released. Moreover the redox couples of these films lie at a more cathodic potential than those of $[\{Ru^0(L_1)(CO)_2\}_n]$ as a consequence of the substitution of one Cl^- ligand by one CO. In CH_3CN, H_2O (5%) + 0.1 M TBAP electrolyte saturated with CO_2, this film also exhibits a large catalytic peak starting from -1.5 V. Exhaustive electrolysis conducted at -1.75 V on a carbon felt modified electrode yields CO with a 60% faradic yield, after 32 C has been passed. This lower faradic yield might be due to some unstability of the film owing to the presence of Ru–Cl bonds.

(4) Electrocatalysis with Complexes Having 4,4'-Bis(isopropoxycarbonyl)-2,2'-bipyridine (L_3) as a Ligand. The electrochemical behavior of *trans*-(*Cl*)-$[Ru^{II}(L_3)(CO)_2Cl_2]$ (C_3), and



L_3



C_3

trans-(*CH_3CN*)-$[Ru^{II}(L_3)(CO)_2(CH_3CN)_2][CF_3SO_3]_2$ in CH_3CN + 0.1 M TBAP is basically the same as that of *trans*-(*Cl*)-$[Ru^{II}(L_1)(CO)_2Cl_2]$ and *trans*-(*CH_3CN*)-$[Ru^{II}(L_1)(CO)_2(CH_3CN)_2][CF_3SO_3]_2$. Their reductions are irreversible despite the electron-withdrawing properties of the ester substituents. The potentials of the cathodic peaks are positively shifted (~200 mV) against peaks of complexes containing the unsubstituted bipyridine ligand. In the cyclic voltammogram of *trans*-(*Cl*)-$[Ru^{II}(L_3)(CO)_2Cl_2]$ in CH_3CN and in CH_3CN + 5% water, the presence of CO_2 does not induces a strong increase of the cathodic current. Only a weak enhancement and anodic shift of the initial peak located at -1.90 V is observed. A controlled electrolysis at -1.70 V does not produce a significant quantity of CO (η = 0.5%) although a quite high catalytic steady-state current (~10 mA) is obtained. Only a rather small amount of formate is detected (η = 10%) while H_2 appears as the main product of reduction.

As previously demonstrated, formation of polymeric films with electrochemical and spectroscopic characteristics similar to those resulting from the electroreduction of *trans*-(*Cl*)-$[Ru^{II}(L_1)(CO)_2Cl_2]$ or *trans*-(*CH_3CN*)-$[Ru^{II}(L_1)(CO)_2(CH_3CN)_2][CF_3SO_3]_2$ is achieved[4] by cycling the potential between -0.60 and -1.65 V or by potentiostating the electrode at -1.38 V for instance. The cyclic voltammogram of a film prepared at -1.38 V exhibits two characteristic reversible systems at -1.13 and -1.60 V. The system at the more negative potential is much more intense than the other; an enhancement of the second cathodic peak under CO_2

atmosphere is obtained although the system remains largely reversible. Continuous cycling of the potential between −0.8 and −1.75 V induces the rapid decrease of the electrochemical signal as a consequence of the poor stability of this film under these conditions. An exhaustive electrolysis experiment carried out at −1.7 V with this modified electrode confirms these observations since after 30 C has been passed the current is lower than 20% of its initial value. Analyses of the solution and the atmosphere show that the electrochemical reduction with the film gives a result quite similar to that obtained with *trans-(Cl)*-$[Ru^{II}(L_3)(CO)_2Cl_2]$ in solution. The amounts of formate and CO produced are higher but the electrochemical efficiency remains low (η_{CO} = 8%, $\eta_{formate}$ = 15%), H_2 remaining the major product of reduction.

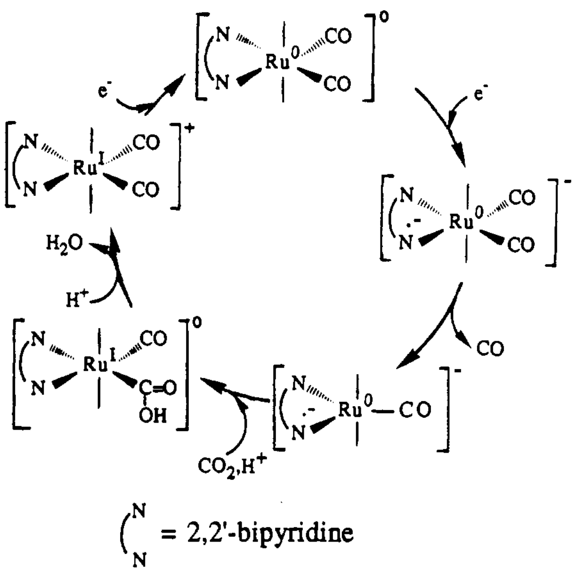
Discussion

The preceding experiments reveal that the polymeric film $[\{Ru^0(L_1)(CO)_2\}_n]$ is the active catalyst in the electrochemical CO_2 reduction by *trans-(Cl)*-$[Ru^{II}(L_1)(CO)_2Cl_2]$ or *trans-(CH$_3$CN)*-$[Ru^{II}(L_1)(CO)_2(CH_3CN)_2]^{2+}$ complexes in solution. This film is formed as the electrocatalytic process takes place. Taking into account the proposed structure of the polymer, we suggest the following mechanism for the electrocatalytic cycle (Scheme 1).

The initial step involves the one-electron reduction of the electroactive $[Ru(bpy)(CO)_2]$ subunit in the polymer to give $[Ru(bpy^{\cdot-})(CO)_2]^-$. This species is not fully stable and may liberate CO, generating a pentacoordinated species $[Ru(bpy^{\cdot-})(CO)]^-$. In the presence of CO_2, the latter coordinates this species to produce $[Ru(bpy)(CO)_2]^+$, *via* $[Ru(bpy)(CO)(COOH)]$ in the presence of water acting as a proton source. At that potential $[Ru(bpy)(CO)_2]^+$ is reduced back to $[Ru(bpy)(CO)_2]$. The electrogenerated pentacoordinated metallic carbonyl complexes like $[Ru^0(bpy)_2CO]$ and $[Re^I(bpy)(CO)_2Cl]^-$ have been previously proposed as key species in some homogeneous electrocatalytic reduction of CO_2 processes.[2,3,19]

The substitution of the bpy ligand by the strong electron-withdrawing ester groups stabilizes the one-electron reduced form of the complex. This markedly prevents the formation of the pentacoordinated species making the corresponding film a poor electrocatalyst.

Scheme 1



Conclusion

This study demonstrates that the reductive formation of an electroactive polymeric film is the key step in the electrocatalytic reduction of CO_2 with mono(bipyridine)carbonylruthenium complexes in solution. Carbon electrodes modified by these films exhibit an outstanding catalytic activity either in aqueous–CH_3CN solution or in pure aqueous electrolyte. These materials provide the first examples of extended inorganic polymers which acts as efficient molecular cathodes for the electrocatalytic reduction of CO_2 especially in pure aqueous electrolyte. They display a high selectivity for the process (only CO is formed with an quantitative faradic yield) and a good accessibility of the applied potential. At least the stability of these cathodes based on polymeric metallic catalytic entities can be markedly improved by using a preformed polypyrrolic film.

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(18) The reversible system located at $E_{1/2}$ = −0.80 V associated with the intense desorption peak at −0.57 V could be attributed to the partial oxidation of the polymer into $[\{Ru^I(L_1)(CO)_2\}_n]^{n+}$. Then some break of the Ru–Ru bonds can occur leading to the desorption of the film.

(19) Haweker, J.; Lehn, J.-M.; Ziessel, R. *Helv. Chim. Acta* **1986**, *69*, 1990.