# Selective Synthesis and Electrochemical Behavior of *trans*(*Cl*)- and *cis*(*Cl*)-[Ru(bpy)(CO)$_2$Cl$_2$] Complexes (bpy = 2,2′-Bipyridine). Comparative Studies of Their Electrocatalytic Activity toward the Reduction of Carbon Dioxide

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A synthetic procedure for the selective preparation (ca. 75% isolated yield) of *trans*(*Cl*)- and *cis*(*Cl*)-[Ru(bpy)(CO)$_2$Cl$_2$] complexes **1** and **2**, using an oligomeric [Ru(CO)$_2$Cl$_2$]$_n$ precursor, is described. The synthetic methodology also gives access to the *cis*(*CO*)-[Ru(bpy)(CO)$_2$(C(O)OMe)Cl] complex **3**. In contrast to **1**, which gives strongly adherent polymeric [Ru(bpy)(CO)$_2$]$_n$ molecular films, electrochemical reduction of **2** and **3** forms dimers **5** and **6** by a one-electron reduction process accompanied by loss of a chloro ligand. Complexes **2**, **3**, **5**, and **6** function as efficient homogeneous electrocatalysts for the selective reduction of CO$_2$ to CO (95−97% faradaic yield) in aqueous acetonitrile.

## Introduction

In principle, [Ru(L)(CO)$_2$Cl$_2$] complexes (L = bidentate nitrogen ligand) can exist in three stereoisomeric forms,[1,2] although the *trans*(*CO*) isomer is thermodynamically unfavorable.[3] Preparation of these ruthenium carbonyl complexes was earlier accomplished by the so-called “*ruthenium red carbonyl solution*” obtained by reaction of carbon monoxide with RuCl$_3$·3H$_2$O in refluxing ethanol.[4,5] This method has not proven to be reproducible, and recently we have demonstrated that the earlier statment[4] of the existence of a red purple *cis* isomer and a yellow *trans* isomer of [Ru(bpy)(CO)$_2$Cl$_2$] (bpy = 2,2′-bipyridine) was incorrect.[6−8] An alternative synthetic method allowing isolation of the pure *trans*(*Cl*)-[Ru$^{II}$(bpy)(CO)$_2$Cl$_2$] complex has now been developed on the basis of an oligomeric [Ru(CO)$_2$Cl$_2$]$_n$ precursor.[9] The latter arises from reduction of RuCl$_3$·3H$_2$O with HCOOH.[10] We have found that this procedure, after optimization, gives pure *trans*(*Cl*)-[Ru$^{II}$(bpy)(CO)$_2$Cl$_2$] and *cis*(*Cl*)-[Ru$^{II}$(bpy)(CO)$_2$Cl$_2$] isomers **1** and **2** independently and in good yield. A third compound, identified as *cis*(*CO*)-[Ru$^{II}$(bpy)(CO)$_2$(C(O)OMe)Cl] (**3**), is also isolated in pure form but in low yield. During the course of this work, a novel, but nonselective, method for the preparation of these complexes was published using as metal precursor commercially-available [Ru(CO)$_3$Cl$_2$]$_2$. A mixture of *trans* and *cis* isomers was obtained upon reaction of [Ru(CO)$_3$Cl$_2$]$_2$ with 2,2′-bipyridine, and the structure determination of both complexes was established by X-ray crystallography.[11]

We report here the preparation, characterization, and detailed electrochemical behavior of the compounds depicted in Figure 1. In particular, their electrocatalytic activity toward the reduction of carbon dioxide is described. It should be recalled that the *trans*(*Cl*) complex **1** is known to act as an efficient catalyst for the photochemical and electrochemical reduction of carbon dioxide in homogeneous solution.[12−15] For instance, this complex leads to the reduction of CO$_2$ to CO in aqueous CH$_3$CN solution in essentially quantitative yield. We have previously demonstrated that formation of an adherent electroactive polymeric film, formulated as [Ru(bpy)(CO)$_2$]$_n$, on the working electrode is the key step of the electrocatalytic process. This film results from the intermediate formation of a *trans*(*Cl*)-[Ru$^{I}$(bpy)(CO)$_2$Cl]$_2$ dimer **4** and of the corresponding tetrameric species, via an overall two-electron reduction process associated with the loss of the two chloro ligands. On the other hand, we have reported in a preliminary note that reduction of the *cis*(*Cl*) isomer leads only to the formation of a dimer, demonstrating the importance of stereochemistry around the metal center in the electropolymerization mechanism.[16]

## Experimental Section

**Electrochemical Instrumentation and Procedure.** Acetonitrile (Rathburn, HPLC grade) was used as received. DMSO (SDS reagent grade) was distilled from CaH$_2$ under reduced pressure. Tetra-*N*-

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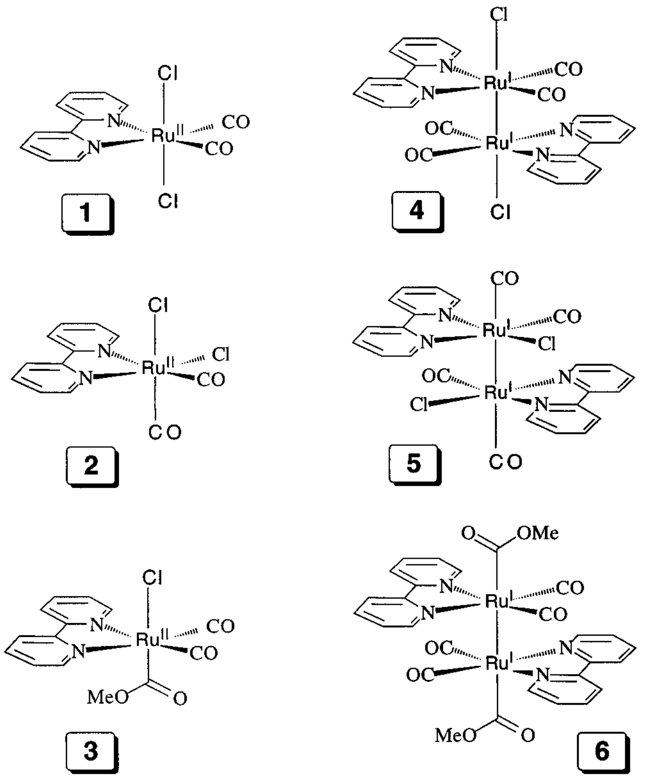


**Figure 1.** Schematic representations of the *trans*(*Cl*)-[Ru(bpy)(CO)$_2$Cl$_2$] (**1**) and *cis*(*Cl*)-[Ru(bpy)(CO)$_2$Cl$_2$] (**2**) complexes, *cis*(*CO*)-[Ru(bpy)(CO)$_2$(C(O)OCH$_3$)Cl] (**3**) complex, *trans*(*Cl*)-[Ru(bpy)(CO)$_2$Cl]$_2$ (**5**) complex, *trans*(*CO*)-[Ru(bpy)(CO)$_2$Cl]$_2$ (**4**) complex, and *trans*-(C(O)OCH$_3$)-[Ru(bpy)(CO)$_2$(C(O)OCH$_3$)]$_2$ (**6**) complex.

butylammonium perchlorate (TBAP) was purchased from Fluka, recrystallized from ethyl acetate, and 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 quoted relative to the Ag/Ag$^+$ (0.01 M) electrode in CH$_3$CN. Working electrodes for cyclic voltammetry consisted of a platinum or vitreous carbon disc (5 or 3 mm diameter) polished with 2 $\mu$m 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 occupied by the gas in the electrolysis cell was 143 mL. Exhaustive electrolyses for dimer formation were carried out with a 5 cm$^2$ platinum sheet in CH$_3$CN + 0.1 M TBAP. For electrocatalytic electrolyses, a 10 × 10 × 4 mm carbon felt electrode (RVC 2000, 65 mg cm$^{-3}$ (Le Carbon Lorraine)) was used. The solution was purged with CO$_2$ for 20 min with stirring. All experiments were stopped after a predetermined number of coulombs had been passed. The gas was sampled through a septum. CO was analyzed with a Delsi Model 30 gas chromatograph equipped with FID detection, with a 120 cm 5 Å molecular sieve column followed by a catalytic oven. Hydrogen was used as carrier gas. Formate ions were analyzed with a Waters Associates high-pressure chromatograph with detection at 224 nm. A Bio-Rad HPX-87 H cation-exchange resin column was eluted with a 10$^{-2}$ M H$_2$SO$_4$. TBAP was removed from the solutions prior to analysis.

**Synthetic Procedure.** THF was distilled from sodium/benzophenone ketyl under argon while methanol was distilled over MgSO$_4$ under N$_2$. All reactions were performed with oven-dried (140 °C) glassware under an atmosphere of argon. Flash chromatography: Silica gel 60 (Baker: 0.04–0.063 mm). Thin-layer chromatography (TLC): Kieselgel 60 F$_{254}$ glass plates (Merck), visualization being either by a UV lamp, 5% KMnO$_4$ solution in water, iodine vapor, 5% solution of phosphomolybdic acid in ethanol or cerium(IV) sulfate/ammonium molybdate(VI) tetrahydrate/H$_2$SO$_4$ 10% reagent followed by heating to ca. 150 °C on a hot plate.

**Spectroscopies.** Electronic absorption spectra were recorded with Shimadzu UV-260 or Perkin-Elmer Lambda 5 spectrophotometers or with a Hewlett-Packard HP 8452A diode-array spectrometer controlled with a Compaq 286 computer and equipped with a Citizen 120D printer. Spectroelectrochemical measurements were conducted in a drybox (Jaram) under an argon atmosphere. Initial and electrolyzed solutions were transferred to conventional optical cuvettes. The cell was inserted into an optical translator connected to the spectrophotometer via an optical fiber (Photonetics Spectrofip system). The optical fibers pass through the wall of the drybox by means of seals. Infrared spectra were recorded with a Bruker FT-IR IFS 25 spectrometer as KBr pellets or in solution with KBr cells. EPR experiments were made with a Bruker ESP 300E spectrometer. The 200.1 ($^1$H) and 50.3 MHz ($^{13}$C-{$^1$H}) NMR (Bruker SY 200 or AC 200) spectra were recorded at room temperature, unless otherwise specified, using perdeuterated solvents as internal standard: $\delta$ (H) in ppm relative to residual protiated solvent in CD$_3$CN (1.94) and $\delta$ (C) relative to the solvent CD$_3$CN (0.30 and 118.21 ppm). Carbon signals were detected as singlets, and chemical shifts are quoted in ppm on the $\delta$ scale with coupling constants expressed in hertz (Hz).

FAB (positive mode) and DCI (electron capture mode) mass spectra were recorded on a AEI Kratos MS 50 spectrometer fitted with an Ion Tech Ltd gun or on a ZAB-HF-VB-analytical apparatus with *m*-nitrobenzyl alcohol (*m*-NBA) as matrix. Elemental analyses were carried-out by the Service de Microanalyse de l'Université Louis Pasteur de Strasbourg (Strasbourg, France).

Scanning electron microscopy (SEM) analyses were performed with a JEOL JSM 840 microscope. The polymer was sufficiently conducting for the experiment to be performed directly on the polymeric material. Energy dispersion X-ray analysis was performed with an EDXRA-KEVEX Δ.

**Synthesis of *trans*(*Cl*)-[Ru$^{II}$(bpy)(CO)$_2$Cl$_2$] (1).** To a yellow solution of [Ru(CO)$_2$Cl$_2$]$_n$ (0.741 g, 3.25 mmol, prepared from RuCl$_3$·3H$_2$O and 99% HCOOH[10b]) in methanol (30 mL, adjusted to pH ~7 with triethylamine) at room temperature was added dropwise a solution of 2,2′-bipyridine (0.609 g, 3.90 mmol). After ca. 1 h a copious white-creme precipitate appears. After standing overnight, the precipitate was filtered onto a glass frit and washed twice with cold methanol and finally with diethyl ether. High-vacuum drying afforded the analytically-pure complex **1** ($R_f$ = 0.79 (alumina), 98/2 CH$_2$Cl$_2$/MeOH as eluent) (0.975 g, 78%). $^1$H NMR (CD$_3$CN): $\delta$ = 9.19 (d, 2 H$_{6,6'}$, $^3J_{6-5}$ = 8.1 Hz), 8.47 (d, 2 H$_{3,3'}$, $^3J_{3-4}$ = 8.0 Hz), 8.24 (td, 2 H$_{4,4'}$, $^3J_{4-3}$ = $^3J_{4-5}$ = 8.1 Hz, $^4J_{4-6}$ = 1.5 Hz), 7.76 (td, 2 H$_{5,5'}$, $^3J_{5-6}$ = $^3J_{5-4}$ = 8.1 Hz, $^4J_{4-6}$ = 1.5 Hz). $^{13}$C{$^1$H} (CD$_3$CN): $\delta$ = 197.38 (CO), 155.55 (Cq), 153.84 (CH), 141.38 (CH), 128.73 (CH), 124.98 (CH). FT-IR (cm$^{-1}$ in KBr pellet): 2059 (vs, $\nu_{CO}$), 1999 (vs, $\nu_{CO}$), 1603 (s), 1470, 1443, 1309, 1246, 766, 534. Far FT-IR (cm$^{-1}$ in polyethylene mull): 338 ($\nu_{Ru-Cl}$). FAB$^+$ (*m*/*z* in *m*-NBA): 383.9 [M + H], 355.8 [M + H − CO], 349.0 [M + H − Cl], 327.9 [M + H − 2CO], 321.0 [M + H − Cl − CO], 292.9 [M + H − 2CO − Cl], 257.0 [M − 2CO − 2Cl]. UV–vis [$\lambda_{max}$, nm ($\epsilon$, M$^{-1}$ cm$^{-1}$)]: 352 (1550), 313 (14 100), 300 (11 300), 286 (10 000), 246 (9600). Anal. Calcd (found) for C$_{12}$H$_8$N$_2$O$_2$Cl$_2$Ru ($M_r$ = 384.185): C, 37.51 (37.32); H, 2.10 (2.08); N, 7.29 (7.17).

**Synthesis of *cis*(*Cl*)-[Ru$^{II}$(bpy)(CO)$_2$Cl$_2$] (2).** To a yellow solution of [Ru(CO)$_2$Cl$_2$]$_n$ (2.07 g, 9.08 mmol, prepared from RuCl$_3$·3H$_2$O and a mixture of HCl$_{conc}$/99% HCOOH[9a]) in methanol (ca. 100 mL) was added solid 2,2′-bipyridine (2.04 g, 0.013 mol). After 20 min of stirring at room temperature, a white precipitate appears. This was isolated on a glass fritt, after 3 h of standing. The precipitate was washed twice with cold methanol and diethyl ether (3 × 50 mL). After drying under high-vacuum the analytically-pure complex **2** was obtained ($R_f$ = 0.50 (alumina), 98/2 CH$_2$Cl$_2$/MeOH as eluent) (2.65 g, 76%). $^1$H NMR (CD$_3$CN): $\delta$ = 9.86 (dd, 1 H$_{6 \text{ or } 6'}$, $^3J$ = 5.6 Hz, $^4J$ = 1.3 Hz), 8.92 (dd, 1 H$_{6 \text{ or } 6'}$, $^3J$ = 5.4 Hz, $^4J$ = 1.2 Hz), 8.41 (d, 1 H$_{3 \text{ or } 3'}$, $^3J$ = 8.1 Hz), 8.37 (d, 1H$_{3' \text{ or } 3}$, $^3J$ = 8.2 Hz), 8.19 (td, 1 H$_{4 \text{ or } 4'}$, $^3J$ = 7.7 Hz, $^4J$ = 1.3 Hz), 8.14 (td, 1 H$_{4' \text{ or } 4}$, $^3J$ = 8.1 Hz, $^4J$ = 1.2 Hz), 7.74 (ddd, 1 H$_{5 \text{ or } 5'}$, $^3J$ = 7.6 Hz, $^3J$ = 5.6 Hz, $^4J$ = 1.3 Hz), 7.62 (ddd, 1 H$_{5' \text{ or } 5}$, $^3J$ = 7.7 Hz, $^3J$ = 5.4 Hz, $^4J$ = 1.2 Hz). $^{13}$C{$^1$H} (CD$_3$CN, 125 °C): $\delta$ = 193.04 (CO), 156.51 (Cq), 155.11 (Cq), 153.97, 153.31, 140.89, 140.45, 127.73, 127.29, 124.30. FT-IR (cm$^{-1}$ in KBr pellet): 2051 (vs, $\nu_{CO}$), 1986 (vs, $\nu_{CO}$), 1635 (s), 1599 (m), 1473 (m), 1442 (s), 1056 (s), 770 (s), 584 (m). Far FT-IR (cm$^{-1}$ in polyethylene mull): 319, 297 ($\nu_{Ru-Cl}$). FAB$^+$ (*m*/*z* in *m*-NBA): 385/387 [M + H]$^+$ (expected isotopic profile), 349 [M + H − Cl], 321 [M + H − Cl − CO], 293 [M + H − Cl − 2CO], 258 [M − 2Cl − 2CO]. UV−vis [$\lambda_{max}$, nm ($\epsilon$, $M^{-1}$ $cm^{-1}$)]: 303 (12 200), 293 (10 900), 248 (sh, 11 300), 222 (16 700). Anal. Calcd (found) for $C_{12}H_8N_2O_2Cl_2Ru$ ($M_r$ = 384.185): C, 37.51 (37.39); H, 2.10 (2.03); N, 7.29 (7.15).

**Synthesis of *cis*(*CO*)-[$Ru^{II}$(bpy)$(CO)_2$(C(O)OMe)Cl] (3).** This compound was obtained as side product during preparation of complexes **1** and **2**. Complex **3** was isolated by evaporation of the mother liquor (from **1** and **2**) to dryness, followed by chromatography on a column packed with alumina under pressure and eluted with $CH_2Cl_2$ and $CH_2Cl_2$/0.5−1% methanol ($R_f$ = 0.15 (alumina), 98/2 $CH_2Cl_2$/MeOH as eluent), 15−18% respectively from the preparation of complex **1** and **2**. $^1H$ NMR ($CD_3CN$): $\delta = 8.97$ (d, 2 $H_{6,6'}$, $^3J_{6-5} = 5.4$ Hz), 8.41 (d, 2 $H_{3,3'}$, $^3J_{3-4} = 8.1$ Hz), 8.19 (td, 2 $H_{4,4'}$, $^3J_{4-3} = {}^3J_{4-5} = 8.0$ Hz, $^4J_{4-6} = 1.3$ Hz), 7.65 (td, 2 $H_{5,5'}$, $^3J_{5-6} = {}^3J_{5-4} = 5.4$ Hz, $^4J_{5-6} = 1.2$ Hz) 3.31 (s, $3H_{OCH3}$). $^{13}C\{^1H\}$ ($CD_3CN$): $\delta = 198.20$ (*C*(O)$OCH_3$), 193.33 (CO), 155.62 ($C_q$), 153.40 (CH), 140.72 (CH), 127.90 (CH), 124.45 (CH), 51.06 ($OCH_3$). FT-IR ($cm^{-1}$ in KBr pellet): 2053 (vs, $\nu_{CO}$), 1985 (vs, $\nu_{CO}$), 1625 (vs, $\nu_{(CO)OMe}$), 1603 (s), 1499 (s), 1474 (s), 1445 (s),1316 (s), 1066 (s), 780 (s). FT-IR ($cm^{-1}$ in polyethylene mull): 320 ($\nu_{Ru-Cl}$). DCI ($CH_4$): 407 [M − H]. UV−vis [$\lambda_{max}$, nm ($\epsilon$, $M^{-1}$ $cm^{-1}$)]: 312 (15 400), 302 (13 600), 234 (19 800). Anal. Calcd (found) for $C_{14}H_{11}N_2O_4ClRu$ ($M_r$ = 407.777): C, 41.24 (41.09); H, 2.72 (2.62); N, 6.87 (6.73).

**Electrochemical Preparations of [$Ru^I$(bpy)$(CO)_2$Cl]$_2$ Dimer 5 and [$Ru^I$(bpy)$(CO)_2$(C(O)OMe)Cl]$_2$ Dimer 6.** The dimers **5** and **6** were obtained by an exhaustive one-electron reduction at −1.80 and −1.75 V, respectively, of a solution of 10 mM complexes **2** and **3** in $CH_3CN$ + 0.1 M TBAP at a platinum cylinder. After standing for a night in the glovebox, the resulting precipitate was filtered off, washed with few milliliters of $CH_3CN$, and dried under vacuum (respective yields: 90 and 85%).

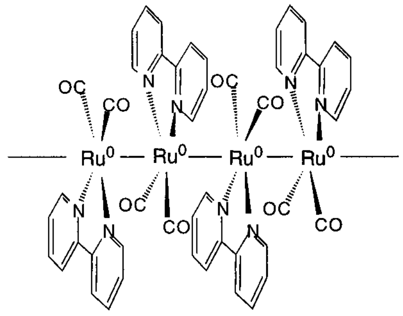
**Characterization of Dimer 5.** $^1H$ NMR (DMSO-$d_6$): $\delta = 8.26$ (d, 4 $H_{6,6'}$, $^3J_{6-5} = 8.2$ Hz), 7.86 (d, 4 $H_{3,3'}$, $^3J_{3-4} = 5.6$ Hz), 7.77 (m, 4 $H_{4,4'}$), 7.12 (m, 4 $H_{5,5'}$). FT-IR ($cm^{-1}$ in KBr pellet): 1987 (vs, $\nu_{CO}$), 1943 (s, $\nu_{CO}$), 1917 (vs, $\nu_{CO}$), 1898 (s, $\nu_{CO}$), 1656 (s). Far FT-IR ($cm^{-1}$ in polyethylene mull): 346 ($\nu_{Ru-Cl}$), 171 ($\nu_{Ru-Ru}$). DCI (electron capture mode): 696 [M − H]. UV−vis ($\lambda_{max}$, nm): 472, 628, 808. Anal. Calcd (found) for $C_{24}H_{16}N_4O_4Cl_2Ru_2$ + $CH_3CN$ ($M_r$ = 697.465 + 41.053): C, 42.29 (42.02); H, 2.59 (2.24); N, 9.48 (9.35).

**Characterization of Dimer 6.** FT-IR ($cm^{-1}$ in KBr pellet): 1995 (vs, $\nu_{CO}$), 1962 (m, $\nu_{CO}$), 1923 (s, $\nu_{CO}$), 1902 (s, $\nu_{CO}$), 1627 (s, $\nu_{C(O)OMe}$), 1600 (m), 1468 (m), 1089 (m), 1047 (s), 1017 (s), 757 (m), 577 (m). UV−vis ($\lambda_{max}$, nm): 474, 626, 786. Anal. Calcd (found) for $C_{28}H_{22}N_4O_8Cl_2Ru_2$ + $CH_3CN$ ($M_r$ = 744.649 + 41.053): C, 45.86 (45.71); H, 3.21 (3.03); N, 8.91 (8.66).

## Results and Discussion

**Synthesis and Characterization.** Ruthenium carbonyl complexes possessing the generic formula [Ru(L)$(CO)_2Cl_2$] (L = bidentate ligand) have been prepared previously in moderate yield from the so-called polymeric "*ruthenium red carbonyl*" solution.[5,9e] An improved and more selective synthesis of both isomers **1** and **2** is described herein and has been acomplished using [$Ru(CO)_2Cl_2$]$_n$ polymer as precursor. Stereoisomers **1** and **2** (Figure 1) could be obtained selectively depending on the conditions used for preparation of the polymer precursor and on the pH of the reaction mixture. When the polymeric [Ru-$(CO)_2Cl_2$]$_n$ precursor was prepared in neat formic acid and with the pH being adjusted to ca. 7 with triethylamine during complexation with 2,2′-bipyridine, the *trans*(*Cl*) stereoisomer **1** was formed preferentially (78%). However, when the [Ru-$(CO)_2Cl_2$]$_n$ precursor was prepared in a mixture of formic and concentrated hydrochloric acids and the solution was kept acidic during complexation with 2,2′-bipyridine, complex **2** was formed in excellent yield (76%). Complex **1** was isolated as a pale yellow solid while **2** was obtained as a white powder. The reason that the *cis*(*Cl*) isomer is prefered under acidic conditions remains obscure but might involve transitory protonation of the bipyridine. A complex, analyzed as *cis*(*CO*)-[Ru(bpy)$(CO)_2$-(C(O)OMe)Cl] (**3**), was formed as a byproduct during preparation of both isomers. This latter complex is presumably formed by methanolic attack on the [Ru(bpy)$(CO)_3$Cl]$^+$ compound formed by reaction of bpy with [$Ru(CO)_3Cl$]$_n^{n+}$ species present in the initial polymer. Formation of complex **3** could be suppressed by using dichloromethane as solvent or enhanced by adding $HCl_{conc}$ (ca. 1%) during preparation.

**Chart 1**



As might be expected, the two isomers exhibit disparate spectroscopic behavior. The infrared spectrum of both complexes shows two $\nu_{CO}$ stretching frequencies (ca. 2060−1980 $cm^{-1}$), indicative of *cis* terminal carbonyl groups. The presence of a single $\nu_{Ru-Cl}$ stretching vibration at 338 $cm^{-1}$ in **1**, compared to the presence of two $\nu_{Ru-Cl}$ stretches at 319 and 297 $cm^{-1}$ in **2**, is consistent with a *trans*(*Cl*) stereochemical assignment for complex **1** but a *cis*(*Cl*) arrangement in complex **2**. Lowering of the Ru−Cl stretching vibration in the *cis*(*Cl*) complex relative to the *trans*(*Cl*) complex has been observed previously for somewhat related complexes.[17] A significant hypsochromic effect in the absorption spectrum recorded for complex **2** (see Experimental Section) strongly supports a *cis* stereochemical arrangement of the Cl groups, on the basis of reported values.[17]

Finally, the $^1H$ and $^{13}C$ NMR spectra (see Experimental Section) are markedly different for these two isomeric complexes and this difference permits their unique assignment. The *trans*(*Cl*) complex **1** exhibits a symmetrical pattern for the bipyridine chelator (four sets of aromatic protons being observed) while the *cis*(*Cl*) complex **2** shows a nonsymmetrical pattern for the bpy ligand (eight sets of aromatic protons are observed). It is noteworthy that no thermal or photochemical isomerization of these complexes in solution could be observed by NMR spectroscopy.

For complex **3**, the presence of two $\nu_{Ru-CO}$ and one $\nu_{Ru-Cl}$ vibrational modes, taken together with a symmetrical environment about the bipyridine ligand (four sets of aromatic protons) is strong support for a *cis* stereochemical arrangement of the carbonyl ligands located in the 2,2′-bipyridine plane. As expected, the presence of an ester ligand in complex **3**, compared to a chloro ligand in complex **1**, induces shielding of the aromatic protons by ca. 0.2 ppm. The X-ray structure of this complex, as prepared by refluxing [$Ru(CO)_3Cl$]$_2$ with excess 2,2′-bipyridine in methanol, recently appeared in the literature.[11]

**Electrochemical Behavior.** We have previously demonstrated that electrochemical reduction of the *trans*(*Cl*) isomer **1** leads to deposition on the working electrode of an electroactive polymeric film having the generic chemical structure [$Ru^0$(bpy)-$(CO)_2$]$_n$ and containing metal−metal bonds (Chart 1).[15]

Polymerization results from the overall addition of two electrons per mole of *trans*(*Cl*)-[$Ru^{II}$(bpy)$(CO)_2Cl_2$] and is

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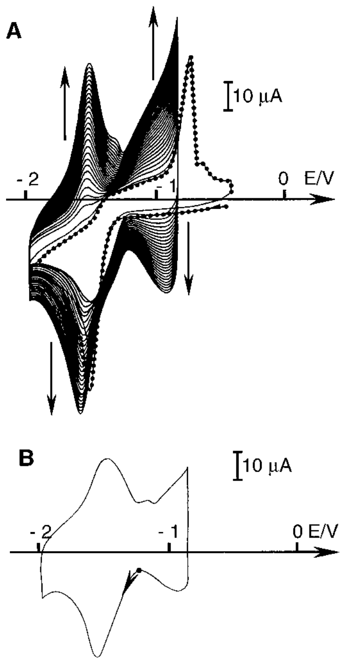

**Figure 2.** (A) Cyclic voltammograms recorded for **1** (0.99 mM) in CH$_3$CN containing 0.1 M TBAP and at a carbon electrode (7.1 mm$^2$): (···) First scan between −0.45 and −2.00 V; (—) 2nd to 28th successive scans between −0.85 and −2.00 V ($v$ = 100 mV s$^{-1}$). (B) Cyclic voltammogram of the resulting modified electrode transfered to fresh CH$_3$CN containing 0.1 M TBAP, at $v$ = 100 mV s$^{-1}$.

associated with the loss of both coordinated chloride ligands (eq 1). Electropolymerization proceeds via transient formation of dimeric and tetrameric complexes.[16]

$$n\ trans(Cl)\text{-}[\mathrm{Ru^{II}(bpy)(CO)_2Cl_2}] + 2ne^- \rightarrow [\mathrm{Ru^0(bpy)(CO)_2}]_n + 2n\mathrm{Cl}^- \quad (1)$$

Film formation at a Pt or C electrode can be followed by continuously cycling the potential for a solution of **1** ($10^{-3}$ M) in CH$_3$CN or DMSO TBAP (0.1 M). Figure 2A shows the growth of the electroactive film on a carbon electrode as the potential is repeatedly scanned between −0.85 and −2.00 V. Two peak systems become evident ($E_{\rm pc}$ = −0.92 V and $E_{1/2}$ = −1.51 V) and progressively increase in size. The resultant modified electrode, after its transfer to fresh electrolyte solution (CH$_3$CN + 0.1 M TBAP), retains two quasi-reversible systems (Figure 2B). The more cathodic peak corresponds to the reduction of the bpy ligand to the bpy$^{\bullet-}$ level in the film while the less cathodic peak, which is associated with an intense desorption peak (not shown here), is attributed to the partial oxidation of the polymer. This oxidation step induces breakage of the Ru−Ru bonds and causes desorption of the film. Further oxidation leads to formation of the soluble complex [Ru(bpy)(CO)$_2$S$_2$]$^{2+}$ (S = solvent).

An additional but partially reversible peak ($E_{1/2}$ = −2.02 V) can be observed. It corresponds to the second reduction of the bpy ligand in the polymeric material. Identical films can be deposited by potentiostating the electrode at −1.60 V after a few millicoulombs have been passed in the solution.

The [Ru(bpy)(CO)$_2$]$_n$ polymer (Chart 1) has been characterized by several chemical and physical techniques.[14] Morphology of the film has been examined by scanning electron microscopy (SEM). The surface of the film exhibits a quasi-homogeneous distribution of the polymeric nuclei (~3000−6000 Å). Some excrescences are clearly visible and are attributed to partial growth of the polymer as "cotton flower" on the nuclei. The presence of ruthenium atoms is confirmed by a strong signal observed at 2.5 keV during EDXRA experiments.

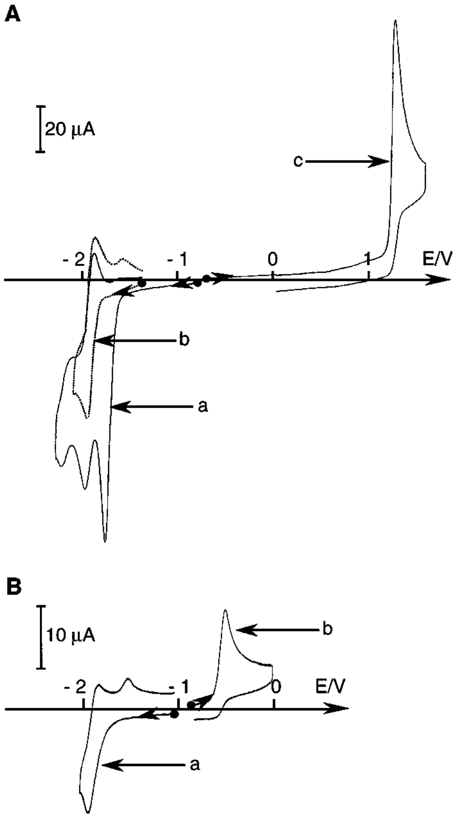

**Figure 3.** (A) Cyclic voltammograms recorded for **2** (1.3 mM) in CH$_3$CN containing 0.1 M TBAP and at a Pt electrode (19.6 mm$^2$): (a) initial solution between 0 and −2.40 V; (b) solution after exhaustive electrolysis at $E_{\rm app}$ = −1.80 V; (c) initial solution between 0 and 1.60 V at $v$ = 100 mV s$^{-1}$. (B) Cyclic voltammograms in DMSO containing 0.1 M TBAP of **5** (0.3 mM) at a Pt electrode (19.6 mm$^2$): (a) between −1.00 and −2.10 V; (b) between −0.90 and 0 V at $v$ = 100 mV s$^{-1}$.

**Electrochemical Behavior of 2.** Complex **2** exhibits redox behavior markedly different from that of **1**, because of the change in stereochemistry. Thus, **2** is irreversibly reduced at a more negative potential ($E_{\rm pc}$ = −1.79 V compared to −1.52 V for **1**) and this process is followed by a fairly reversible system ($E_{1/2}$ = −1.96 V) (Figure 3A, curve a). Continuous cycling of the potential between −0.65 and −2.20 V does not induce film deposition on the electrode surface. Exhaustive electrolysis at −1.80 V consumes only one electron per mole of complex and leads to development of a greenish solution from which a dark blue precipitate appears after standing for a few hours. Chemical and spectroscopic analysis of this precipitate shows it to be the corresponding dimer **5** (Figure 1; see Experimental Section for electrochemical preparation of **5**). Elemental analysis and mass spectroscopy (DCI, electron capture mode, [M − 2H] at 696) strongly support this formulation. The following mechanism is suggested for dimer formation: (i) the initial step involves a one-electron reduction of ligand associated with the ejection of a Cl$^-$, generating a Ru$^{\rm I}$ center (eq 2); (ii) two such Ru$^{\rm I}$ entities dimerize to form complex **5** by way of metal-metal bond formation (eq 3).

$$cis(Cl)\text{-}[\mathrm{Ru^{II}(bpy)(CO)_2Cl_2}] + e^- \rightarrow [\mathrm{Ru^I(bpy)(CO)_2Cl}] + \mathrm{Cl}^- \quad (2)$$

$$2[\mathrm{Ru^I(bpy)(CO)_2Cl}] \rightarrow [\mathrm{Cl(CO)_2(bpy)Ru^I{-}Ru^I(bpy)(CO)_2Cl}] \quad (3)$$

Cyclic voltammogram recorded for the reduced solution obtained after removal of the precipitate shows, in the positive region, the typical quasi-reversible peak system at 0.66 V due to oxidation of the released $Cl^-$ anion.[18]

The complexity of the IR spectrum (4 $\nu_{CO}$ bands) indicates the coexistence of rotamers, as was recently observed for the chemically prepared dimer **4**, in which the two Cl ligands occupy axial positions.[11] The presence of a metal−metal bond ($Ru^I-Ru^I$) is confirmed by the profile of the absorption spectrum recorded for a solution of **5** in $CH_3CN$, which shows intense bands at 472, 628, and 808 nm and which is comparable to that recorded for $[Ru(bpy)(CO)_2]_n$ films.[15] Far-IR spectral analysis reveals the presence of the Ru−Ru bond at 171 $cm^{-1}$ and of one Ru−Cl stretching vibration at 346 $cm^{-1}$. Another striking feature of dimer **5** is the absence of any EPR signal, either in solid or fluid phases, indicating strong electronic coupling between the two paramagnetic Ru(I) metal centers. Cyclic voltammograms recorded after exhaustive reduction of **2** (Figure 3A, curve b) or after isolation and redissolution of **5** in DMSO (Figure 3B) are basically identical. A poorly reversible monoelectronic system ($E_{1/2} = -1.96$ V) corresponding to the monoreduced form of **5** (eq 4) is seen in the negative

$$[Cl(CO)_2(bpy)Ru^I-Ru^I(bpy)(CO)_2Cl] + e^- \rightarrow [Cl(CO)_2(bpy^{\bullet -})Ru^I-Ru^I(bpy)(CO)_2Cl]^- \quad (4)$$

area and agrees with that found upon reduction of **2** following its irreversible reduction (Figure 3A, curve a). On the reverse scan a new anodic peak appears at a less negative potential ($E_{pa} = -1.58$ V) resulting from the evolution of the one electron reduced form of **5** (see above).

Continuation of the cathodic scan to −2.70 V in $CH_3CN$ indicates that some further reduction occurs. There is a weak but reversible signal at $E_{1/2} = -2.09$ V, probably corresponding to the doubly-reduced form of **5**, followed by a large irreversible peak at $E_{pc} = -2.52$ V (not shown on Figure 3). Exhaustive electrolysis at −2.00 V confirms the instability of the $[Cl(CO)_2(bpy^{\bullet -})Ru-Ru(bpy)(CO)_2Cl]^-$ species since a volumous black precipitate is then obtained. We have not yet tried to fully identify this new compound. As shown in Figure 3B curve b, the dimer **5** is easily, but irreversibly, oxidized at a peak potential ($E_{pa} = -0.50$ V) close to that of the polymer oxidation. However, dimerization is a chemically reversible process. As a matter of fact, the in situ exhaustive oxidation of a freshly prepared solution of dimer **5** in $CH_3CN$ ($E_{app} = 0.4$ V) consumed two electrons and afforded in turn monomer **2** in 90% yield. Traces of *trans*(*Cl*) complex **1** are also obtained (10% yield) showing that some rearrangement of the coordination sphere around the ruthenium center occurs during the Ru−Ru bond-breaking process.

It should also be noted that oxidation of monomer **2** is fully irreversible, unlike **1**. The peak potential is less anodic ($E_{pa} = 1.37$ V; Figure 3A, curve c) because of the different stereochemistry. We have not investigated further this electrochemical process.

**Electrochemical Behavior of 3.** Electrochemical behavior of this complex is similar to that described for **2**, with formation of the corresponding dimer **6** (Figure 1). Cyclic voltammograms recorded for **3** in $CH_3CN$ show the same pattern as found for **2** with an irreversible reduction peak ($E_{pc} = -1.66$ V) followed by a reversible one at $E_{1/2} = -1.97$ V. After exhaustive electrolysis at −1.80 V, which consumes one electron per mole of complex, the initial irreversible cathodic peak is suppressed while the partially reversible one remains. The dimeric structure of **6** has been confirmed by elemental analysis (see Experimental Section) while IR and visible spectra remain comparable to those of dimer **5** (see Experimental Section for electrochemical preparation of **6**). Four $\nu_{CO}$ bands are also observed while the ester stretching vibration at 1627 $cm^{-1}$ remains, thus confirming that the "$C(O)OCH_3$" group is a poor axial leaving group. On the other hand, three bands are present in the electronic absorption spectrum ($\lambda_{max} = 474$, 626, and 786 nm). As for **2**, this dimer gives no EPR signal because of strong electronic coupling between the two $Ru^I$ centers.

Compound **6** is fairly soluble in DMSO. Unfortunately, rapid decomposition occurs in this solvent and it has not been possible to undertake accurate NMR measurements. When a fresh electrochemically prepared solution of **6** in $CH_3CN$ is oxidized at 0.40 V, the initial monomer **3** is recovered in 80% yield while traces of the *trans*(*Cl*) complex **1** is also formed. The latter species is detected by its characteristic irreversible reduction peak centered at −1.52 V.

**Electroreduction of $CO_2$.** The mono(bipyridine) complex *trans*(*Cl*)-$[Ru^{II}(bpy)(CO)_2Cl_2]$ (**1**) is known to act as an efficient homogeneous catalyst for the electrochemical reduction of $CO_2$.[15] In aqueous $CH_3CN$ solution (10/90), CO is produced in essentially quantitative yield (97% current efficiency) while only traces of formate are found (0.5%). In addition, we have recently demonstrated that formation of an electroactive $[Ru(bpy)(CO)_2]_n$ polymeric film, which occurs during reduction of complex **1**, is the key step for electrocatalytic behavior. It is interesting, therefore, to measure the capability of monomers **2** and **3** and dimers **5** and **6** to act as homogeneous electrocatalysts since these systems are unable to enter into heterogeneous catalytical processes.

**Electrocatalysis with 2 *and* 5.** When a solution of **2** in $CH_3CN$ containing TBAP (0.1 M) is saturated with $CO_2$, a strong catalytic current appears around −1.50 V (Figure 4A, curve b). Addition of water (10%) to the electrolyte induces a shift of the electrocatalytic peak to less negative potential (Figure 4A, curve c). Preparative-scale electrolyses using a carbon felt electrode were performed at −1.55 V in the presence of 10% of water and complex **2** (0.9 mM). Gas phase and solution analyses showed the main reaction product to be CO (95%, turnover number 11 after consumption of 60 C), accompanied by a small amount of formate (5%). The absence of film formation on the working electrode during the electrocatalytic process was verified by a similar experiment but using a platinum disc electrode. However, under these latter conditions some black precipitate is formed as a consequence of the dimer formation.

Dimer **5**, as prepared by reduction of **2**, also appears to be an efficient homogeneous electrocatalyst. Figure 4B shows cyclic voltammograms of a solution of **5** electrochemically prepared in $CH_3CN$ containing TBAP (0.1 M) under $CO_2$ in the absence and presence of 10% water. A catalytic current is observed in both cases, with the peak potential being markedly less negative in the presence of water. Exhaustive electrolysis at −1.55 V affords CO and $HCOO^-$ in yields (95 and 5%, respectively) similar to those obtained using monomeric complex **2** as electrocatalyst. The current is relatively stable, only a 20% loss of the current being observed after passage of 75 C (turnover number 28).

These experimental results seem to indicate that dimer formation is probably the first step in the overall electrocatalyzed reduction of $CO_2$ by **2**, with the reduced form of the dimer being the active catalytic species. We tried to confirm this hypothesis

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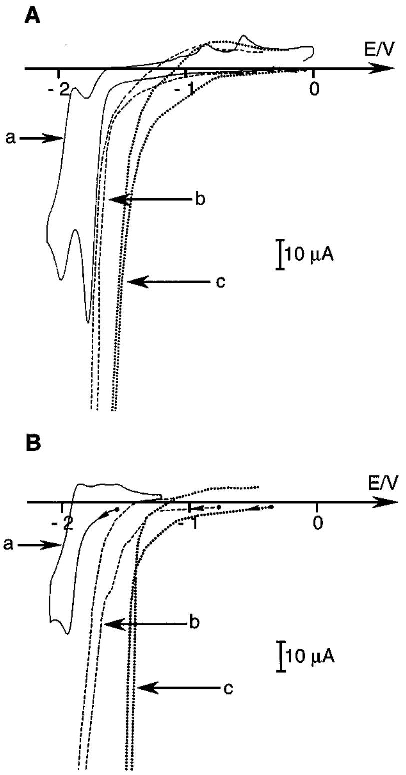

**Figure 4.** Cyclic voltammograms recorded at a Pt electrode (19.6 mm$^2$) in CH$_3$CN containing 0.1 M TBAP. (A) Voltammograms of **2** (0.9 mM): (a) on Ar; (b) on CO$_2$; (c) on CO$_2$ in the presence of 10% of water. (B) Voltammograms of **5** (0.5 mM): (a) on Ar; (b) on CO$_2$; (c) on CO$_2$ in the presence of 10% of water at $v = 100$ mV s$^{-1}$.

by measuring the dependance of the catalytic current as a function of concentration of monomer **2**. No linear dependence or square dependence are observed, reflecting that several catalytical processes are involved. Taking into account the low yield of HCOO$^-$, we suggest that the major pathway for CO$_2$ reduction involves interaction of the reduced form of **5** with CO$_2$ to form a metallocarboxylate intermediate. In turn, this species can lose CO and undergo further reduction in competition to metal hydride formation. This mechanism is in agreement with that proposed for the electrocatalytic reduction of CO$_2$ using [Ru(bpy)(CO)$_2$]$_n$ polymeric films.[14]

**Electrocatalysis with 3 *and* 6.** Similar catalytic effects are found for **3** in CO$_2$-saturated CH$_3$CN containing water (2%). Exhaustive electrolysis at −1.55 V affords CO with a 95% faradaic yield, after 80 C had been consumed (turnover number 14). However, it should be noted that some formation of the [Ru(bpy)(CO)$_2$]$_n$ polymeric film occurs during catalysis. Here the electrochemical formation of [Ru(bpy)(CO)$_2$]$_n$ arises by way of substitution of the methoxycarbonyl ligand (C(O)OCH$_3$) by a solvent molecule. Hydrolysis of the activated "Ru$^{II}$−C(O)-OCH$_3$" ester by water results in formation of a metallocarboxylate "Ru$^{II}$−C(O)O$^-$" which rapidly decomposes to form [Ru(bpy)(CO)$_2$(CH$_3$CN)Cl]$^+$. This latter intermediate possesses two axial leaving groups, a situation known to be extremely favorable for formation of the [Ru(bpy)(CO)$_2$]$_n$ polymer during reduction.

Finally, dimer **6** presents a strong catalytic ability toward CO$_2$ reduction. Electrocatalysis conducted at −1.45 V with a solution of electrochemically prepared **6** gives results identical to those carried out with monomer **3** and giving almost quantitative formation of CO (97% electrical yield after 70 C, turnover number 26).

**Performances of the Catalysts.** The results obtained for complexes **2**, **3**, **5**, and **6** regarding the electrocatalytic reduction of carbon dioxide differ markedly from previously reported homogeneous systems based on monometallic Co, Ni, Rh, and various polypyridyl-type transition metal complexes.[19] In many of these examples the chemical nature of the active is ill-defined and, in particular, it is unclear if the catalyst is monomeric, polymeric or chemically adsorbed onto the working electrode. In the specific case of [Re(bpy)(CO)$_3$Cl] an electrogenerated dimer has been isolated, but detailed studies have revealed that this species is inactive toward the reduction of carbon dioxide.[20] The results obtained in the present work with respect to selectivity and efficiency compare well with all previous systems. However, this is the first time where the electrogenerated dimeric species, formed from the monomeric complex during catalysis, are found to be the active catalysts for reduction of carbon dioxide. Polymetallic transition metal complexes have also recently been used to selectively electroreduce carbon dioxide at low overpotential.[21]

## Conclusion

The essential feature of this work concerns the selective synthesis of the *trans*(*Cl*)-[Ru(bpy)(CO)$_2$Cl$_2$] and *cis*(*Cl*)-[Ru(bpy)(CO)$_2$Cl$_2$] complexes and the comparison of their electrochemical behavior and catalytic activity versus CO$_2$ reduction. For the *cis*(*Cl*) isomer, electrochemical reduction leads to a dimer, while the *trans*(*Cl*) isomer conducts to the formation of a polymeric film of [Ru(bpy)(CO)$_2$]$_n$. A similar dimer is also formed when a single chloride ligand is present in a mixed *trans*-(chloro/ester) complex. The ester ligand is a relatively poor leaving group in the reduced form of the complex. This strategy provides a valuable synthetic route for the clean generation of Ru(I) dimers, under ambient conditions, in moderate to excellent yield especially for the *cis* isomer.

These dimers exhibit strong electrocatalytic activity toward CO$_2$ reduction. As such, the present system permits close comparison of homogeneous (monomers and dimers) and heterogeneous (polymer) electrocatalysts under very similar experimental conditions. An unusual aspect of this work is that a choice can be made between homogeneous and heterogeneous systems using the same experimental setup by simply changing the stereochemistry of the precursor. An advantage of the homogeneous system is that the active species could be studied, and it is significant to note that identical product distributions and efficiencies are obtained for the two systems. Furthermore the intense coloration and characteristic spectroscopic properties shown by these dimers should enable detailed mechanistic studies to be undertaken that might identify the exact manner in which the two-electron reduction of CO$_2$ is facilitated. Such mechanistic investigations are currently underway.

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