Electrocatalytic Reduction of CO$_2$ by Bipyrimidine-Bridged Trimeric Complexes, \{[(bpy)$_2$Ru(bpm)],MCl$_2\}\text{$_5^+$}

Where M=Ir$_{III}$ or Rh$_{III}$

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The electrocatalytic activity of the bipyrimidine-bridged trimetallic complexes of the form, \{[(bpy)$_2$Ru(bpm)],MCl$_2\}\text{$_5^+$}
where bpy = 2,2'-bipyridine, bpm = 2,2'-bipyrimidine and M = Rh$_{III}$ or Ir$_{III}$ in the reduction of carbon dioxide was investigated. The electrochemistry of these complexes differ upon variation of the central metal from iridium to rhodium. In effect, this resulted in a significant shift of the reduction potential for the electrochemical conversion of CO$_2$ into products. Electrocatalytic studies using these bpm systems showed a shift in the CO$_2$ reduction potential from -1.80 V to -1.00 V vs. Ag/AgCl for iridium(III) and rhodium(III) as catalytic centers, respectively. CO and HCOOH were the detectable CO$_2$ reduction products using both trimetallic complexes as electrocatalysts. Details of the catalytic investigations were described herein.

**Key Words**: electrocatalysis, polypyridyl complexes, carbon dioxide conversion, electrochemical reduction, multimetallic catalyst

**INTRODUCTION**

Investigations concerning the development of carbon dioxide (CO$_2$) as a potential alternate carbon source of commercial fuels have increased because of consequential “greenhouse effect” from CO$_2$ accumulation in the atmosphere. Activation of stable CO$_2$ molecule that can lead to a variety of reactions has been achieved via coordination to a transition metal center. This type of interaction was considered a significant step toward an efficient catalytic system for CO$_2$ fixation.

The electrochemical reduction of CO$_2$ produces different products that depend on thermodynamic accessibility from CO$_2$. Examples of these reactions and the corresponding electrode potentials vs NHE are shown below:(Keene 1993)

\[
\begin{align*}
\text{CO}_2 + e^- & \rightarrow \text{CO}_2^- & \text{E} & = -2.10 \text{ V} \\
\text{CO}_{2(g)} + 2\text{H}^+ + 2e^- & \rightarrow \text{HCOOH} & \text{E} & = -0.199 \text{ V} \\
\text{CO}_{2(g)} + 2\text{H}^+ + 2e^- & \rightarrow \text{CO}_{\text{aq}}^- + \text{H}_2\text{O} & \text{E} & = -0.103 \text{ V} \\
\text{CO}_{2(g)} + 6\text{H}^+ + 6e^- & \rightarrow \text{CH}_3\text{OH}[^{\text{aq}}] + \text{H}_2\text{O} & \text{E} & = +0.030 \text{ V} \\
\text{CO}_{2(g)} + 8\text{H}^+ + 8e^- & \rightarrow \text{CH}_4[^{\text{aq}}] + \text{H}_2\text{O} & \text{E} & = +0.169 \text{ V}
\end{align*}
\]

It can be drawn from these data that the reduction of CO$_2$ is favored at lower pH and that the hydrogen evolution, which occurs at E = 0.0 V is more favored than these
Several CO₂-complexes that are based on electron-rich and highly basic transition metal ions, mostly Ir⁵⁺ (Behr et al. 2004), Rh³⁺ (Calabrese et al. 1983; Lundquist et al. 1987; Sakaki et al. 1989; Tsai and Nichols 1992), and Ni²⁺ (Simon-Manso and Kubiak 2005) complexes have been synthesized. Among others, a number of rhodium(I) complexes, particularly phosphine-, carbonyl- and hydride-based rhodium(I) complexes were found to be active toward chemical fixation of CO₂ (Hossain et al. 1981; Lapidus and Savel’ev 1984; Lundquist et al. 1990; Slater and Wagenknecht 1984). These four-coordinate systems can readily bind carbon dioxide to form an isolable CO₂-complex intermediate. This is important in studying the mechanistic pathway for the conversion of carbon dioxide into other molecules. However, though hydrogen carbonate and carbonyl complexes were obtained as fixation products, no further studies were conducted leading to the isolation of reduction products such as free CO₂, CO₂, HCO⁻, etc. Nevertheless, a few rhodium(I) complexes were actually found electrocatalytically active towards CO₂ reduction such as Rh(diphos)Cl where diphos = 1,2-bis(diphenylphosphino)ethane which reduced CO₂ to HCOO⁻ and a small amount of cyanoacetate. (Slater and Wagenknecht 1984)

Rhodium(III), which is another stable oxidation state of rhodium was also studied for catalytic activity. Rhodium(III) complexes of 2,2'-bipyridine were found to have high activity as photocatalysts for the reduction of water to produce hydrogen gas (Kirch et al. 1979). Following this, water soluble derivatives of this group of complexes were used in catalyzing water-gas shift reaction. (Marnot et al. 1981) Furthermore, some rhodium (III) polypyridyl complexes were also found to catalyze the electrochemical reduction of carbon dioxide. (Bolinger et al. 1985; 1988; Rasmussen et al. 1990; Molnar et al. 1994, Nallas and Brewer 1996) Bolinger and co-workers have found that cis-[Rh(bpy)₂X₃]⁺ where bpy = 2,2'-bipyridine and X = Cl⁻ or TFMS (trifluoromethanesulfonate anion) catalyzed the reduction of CO₂ into carbon monoxide and formate ion (80% current efficiency for formate production) in acetonitrile. (Bolinger et al. 1985, 1988) This proton-coupled reaction was augmented by the ability of tetrabutylammonium electrolyte to act as a base under anhydrous conditions. Catalysis was found to occur at E = -1.5V vs SCE, the potential at which the metal complex was reduced by two electrons, [Rh(bpy).]⁺. The polypyridyl ligands which act as electron reservoirs, provided the initial site of reduction.

The complex [Rh(BL)₂Br]⁺ and its iridium analog where BL are the bridging ligands, 2,2'-bipyridine (bpm), 2,3-bis(2-pyridyl)pyrazine (dpb), 2,3-bis(2-pyridyl)quinoxaline (dpq) and 2,3-bis(2-pyridyl)benzoquinoxaline (dpb) were found to catalyze the electrochemical reduction of carbon dioxide to formate in acetonitrile at E = -1.7V vs Ag/AgCl gel reference electrode (Rasmussen et al. 1990). Current efficiency was ca. 40% exclusively for formate production. Variation of the bridging ligands, bpm, dpq, dpb, and dpb, did not significantly affect the catalytic activity of the complex. The utilization of bridging ligands offered the possibility of incorporating other transition metal centers that may have potential application in photoinitiated electron collection and multielectron catalysis. Complexes of the form, [{(bpy)₂Ru(BL)₂}Cl₃]₅⁺ where BL = dpq, dpb, and dpb, and M = Rh(III), Ir(III), Os(III) were synthesized and their photochemical and photophysical properties investigated (Molnar et al. 1994). In addition, the trimetallic complex, [{(bpy)₂Ru(BL)₂}Cl₃]₅⁺ where BL = dpq and dpb were found to catalyze the reduction of carbon dioxide into carbon monoxide with high selectivity and efficiency (Nallas and Brewer 1996).

The trimetallic analog, [{(bpy)₂Ru(bpm)₂}Cl₃]₅⁺ where M = Rh(III) or Ir(III) have been successfully synthesized and characterized in our laboratory (Nallas et al. 1996). The use of bipyrimidine as a bridging ligand eliminated several possible stereoisomers encountered in previously studied rhodium- and iridium-based trimetallic systems using the bridging ligands dpq and dpb. The study presented here involves the investigation of the catalytic activity of these trimetallic complexes in the electrochemical reduction of CO₂. A comparison between rhodium and iridium systems as electrocatalysts is also described.

MATERIALS AND METHODS

Materials
All the reagents used in the syntheses were purchased from Aldrich Chemical Co. and used without further purification. The metal salts, RuCl₃·3H₂O, IrCl₃·xH₂O and RhCl₃·xH₂O were purchased from Johnson Matthey or obtained through the precious metal loan program. Bipyrimidine was purchased from Lancaster synthesis. The supporting electrolyte, Bu₄NPF₆, used in all electrochemical experiments was prepared from the metathesis of Bu₄NBr and KPF₆ and recrystallization twice from hot ethanol. This was dried under vacuum and...
kept in a vacuum dessicator prior to use. The acetonitrile used in the electrochemical experiments was Burdick and Jackson spectroquality and obtained from Baxter.

**Synthesis**

The trimetallic complexes, \([\{\text{bpy}\}_2\text{Ir(bpm)}_2\text{RhCl}_3\]^{5+}\) and \([\{\text{bpy}\}_2\text{Ir(bpm)}_2\text{IrCl}_3\]^{5+}\) were synthesized and purified in our laboratory as previously published in the literature (Nallas et al. 1996). The rhodium trimetallic was prepared by the reaction of \([\text{Ru(bpy)}_2\text{Cl}_2]_2\) and \(\text{RhCl}_3\cdot\text{xH}_2\text{O}\), while the iridium trimetallic was synthesized from \([\text{Ir(bpm)}_2\text{Cl}_2]_2\) and \(\text{Ru(bpy)}_2\text{Cl}_2\). Purification was achieved through size exclusion chromatography.

**Electrochemistry**

Cyclic voltammetric measurements were done using a typical three-electrode system, which includes a platinum working electrode, platinum wire auxiliary electrode, and Ag/AgCl (0.29 V vs. NHE) reference electrode. Electrochemical data were obtained using a BioAnalytical Systems 100W electrochemical analyzer interfaced to a computer for data collection. Samples were bubbled with argon prior to analysis, then blanketed the headspace of the solution during the entire experiment. The supporting electrolyte system, 0.1 M \(\text{Bu}_2\text{NPF}_6\) in acetonitrile was used as solvent. This electrolyte solution was dried by passing through a 10-cm alumina column, stored in molecular sieves and filtered through a syringe filter (25 µm) prior to use. The cyclic voltammogram was taken at a sweep rate of 200 mV/sec.

**Electrocatalysis**

To determine the electrocatalytic activity of the trimetallic complexes in \(\text{CO}_2\) reduction, a cyclic voltammogram of the complex under a stream of carbon dioxide was taken and compared with that obtained under an argon atmosphere. The catalyst solution was prepared by dissolving 60-65 mg of the trimetallic complex in 25 mL of electrolyte solution (0.1 M \(\text{Bu}_2\text{NPF}_6\) in acetonitrile) to give a catalyst concentration of ca. 1 mM. Controlled-potential electrolysis experiments were carried out in a gas-tight two-compartment cell. A detailed description of this experimental setup is discussed elsewhere (Nallas and Brewer 1996).

In a typical experiment, 10 mL of the catalyst solution (ca. 1 x \(10^{-5}\) moles) was transferred to the working compartment while the auxiliary compartment contained the solvent electrolyte solution. Prior to electrolysis, both cell compartments were purged with acetonitrile-saturated carbon dioxide for 45 min to ensure saturation. The gas tight working compartment was closed to yield ca. 1 atm \(\text{CO}_2\) headspace with ca. 20 mL volume, while the auxiliary compartment was continuously bubbled with \(\text{CO}_2\) throughout the experiment.

Product analysis was conducted using a gas chromatograph (Gow-Mac Instrument Co. GC Series 580) equipped with a thermal conductivity detector and connected to a Hewlett-Packard 3394A Integrator for data collection and integration. Helium was the carrier gas (25 psi pressure) flowing at 25 mL/min on the Porapak Q column, and at 60 mL/min on the Molecular Sieves 5A column. Both columns were 6 ft. long, o.d. 0.25 in., i.d. 0.210 in, 80/100 mesh and purchased from AllTech. The temperature settings on the chromatograph were: column, 165°C; detector, 180°C; injection port, 150°C. The detector current was set at 150 mA.

Analysis of gaseous samples was done by withdrawing 0.5 mL sample from the headspace of the catalyst solution in the working compartment using a 0.5 mL pressure-locked syringe (Dynatech Precision Sampling). This 0.5 mL sample was immediately injected into the molecular sieves column. Formate was identified as a reduction product by conversion into methylformate. Ca. 1 mL of the electrolyzed solution was reacted with an excess of the methylating agent, \([\{(\text{CH}_3)_2\text{O}\]}\text{SbCl}_5\) (50-70 mg). A 2.0 µL sample was typically withdrawn (unless otherwise indicated) from the reaction mixture and injected into the Porapak Q column. One (1) mL of each of these standard formate samples was reacted with the methylating agent and the products analyzed by gas chromatography. Formate analysis on this particular experiment resulted to overlapping chromatographic peaks where integration was difficult. For this reason, gas chromatography equipped with mass selective detection (GC-MSD) was used where analyte components were extracted by mass (or molecular weight) identification. The system used was a Hewlett-Packard 5890 Series GC-MSD. Isothermal GC analysis at 30°C was performed. An HP-1, 1% phenylmethyl silicone gum, capillary column (12.5 cm long, 0.22 mm I.D., 0.33 µm film thickness) was used. Duplicate 1.0 µL injection was made for analysis of the methylated electrolyzed catalyst solution.

**RESULTS**

These bipyrimidine-bridged trimetallic complexes have been shown to exhibit unique spectroscopic and electrochemical properties similar to their dpp, dpq, and dpb analogs (Nallas et al. 1996). The electrochemical behavior of iridium trimetallic is different from that of rhodium trimetallic as typically observed in previous...
Preliminary investigations were done to probe the ability of these bipyrimidine based trimetallic complexes to reduce CO$_2$. Cyclic voltammograms under an atmosphere of argon and under CO$_2$ were obtained for both complexes and compared. The cyclic voltammograms are shown in Fig. 1 and Fig. 2. For the trimetallic complex, ([bpy],Ru(bpm)],IrCl]$^{5+}$, current enhancement that starts at ca. -1.70 V vs. Ag/AgCl was observed. In this region, it was also noted that the reversibility of bipyrimidine reductions is lost upon reoxidation that may indicate CO$_2$ reduction.

![Cyclic voltammogram](image)

**Figure 1.** Cyclic voltammogram in 0.1M Bu$_4$NPF$_6$/CH$_3$CN of ([bpy],Ru(bpm)],IrCl]$^{5+}$ where bpy = 2,2'-bipyridine and bpm = 2,2'-bipyrimidine under Ar (——) and under CO$_2$ (---); scan rate at 200 mV/sec

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**Table 1.** Electrochemical data$^a$ in 0.1 M Bu$_4$NPF$_6$/CH$_3$CN for ([bpy],Ru(bpm)],MC]$_2$]$^{5+}$ where M= Rh$^{III}$ or Ir$^{III}$, bpy = 2,2'-bipyridine and bpm = 2,2'-bipyrimidine

<table>
<thead>
<tr>
<th>Complex</th>
<th>$E_{1/2}$ (V)</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>([bpy],Ru(bpm)],MCl]$_2$]$^{5+}$</td>
<td>+1.70</td>
<td>Ru$^{III}$/Ru$^{IV}$</td>
</tr>
<tr>
<td></td>
<td>-0.13</td>
<td>bpm,bpm/bpm,bpm</td>
</tr>
<tr>
<td></td>
<td>-0.26</td>
<td>bpm',bpm/bpm,bpm'</td>
</tr>
<tr>
<td></td>
<td>-0.78 (E$_a$)</td>
<td>Rh$^{III}$/Rh$^{I}$</td>
</tr>
<tr>
<td></td>
<td>-1.19</td>
<td>2Ru(bpy)$'/2Ru(bpy)'(bpy)$$_2$</td>
</tr>
<tr>
<td></td>
<td>-1.45</td>
<td>Ru(bpy)$'/2Ru(bpy)'(bpy)$$_2$</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>([bpy],Ru(bpm)],IrCl]$^{5+}$</th>
<th>+1.70</th>
<th>Ru$^{III}$/Ru$^{IV}$</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>-0.08</td>
<td>bpm,bpm/bpm,bpm</td>
</tr>
<tr>
<td></td>
<td>-0.21</td>
<td>bpm',bpm/bpm,bpm'</td>
</tr>
<tr>
<td></td>
<td>-0.90</td>
<td>bpm',bpm/bpm,bpm'</td>
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<tr>
<td></td>
<td>-1.07</td>
<td>bpm',bpm/bpm,bpm'</td>
</tr>
<tr>
<td></td>
<td>-1.60</td>
<td>2Ru(bpy)$'/2Ru(bpy)'(bpy)$$_2$</td>
</tr>
<tr>
<td></td>
<td>-1.70</td>
<td>Ir$^{III}$/Ir$^{IV}$</td>
</tr>
<tr>
<td></td>
<td>-1.75</td>
<td>2Ru(bpy)$'/2Ru(bpy)'(bpy)$$_2$</td>
</tr>
</tbody>
</table>

$^a$Potentials reported vs. Ag/AgCl (0.29 V vs. NHE) at a scan rate of 200 mV/s

$^b$Resolution of these waves was difficult
Different electrochemical behavior was observed with the rhodium-based complex, \([\{(bpy)_2Ru(bpm)\}_2RhCl_2]^{5+}\). The cyclic voltammogram taken under an atmosphere of CO\(_2\) exhibited a drastic increase in cathodic current starting at ca. -0.80 V vs. Ag/AgCl. The apparent disappearance of the Rh\(^{III}/Rh^{II}\) reductive couple may indicate a cathodic shift which, in effect, gets embedded in the CO\(_2\) reduction current. Bipyrimidine reductions lost reversibility upon passing an atmosphere of CO\(_2\) in the system. This may indicate CO\(_2\) reduction leading to a reoxidation of bpm ligands. The current enhancement in the cyclic voltammetric data of this rhodium-based system which occurs at a much more positive potential compared to the iridium analog illustrates a very significant effect of the central metal variation in the catalytic activity of these trimetallic complexes. CO\(_2\) reduction can therefore be conducted at a minimum potential of -0.80 V for \([\{(bpy)_2Ru(bpm)\}_2RhCl_2]^{5+}\) compared to a more negative value of -1.80 V for \([\{(bpy)_2Ru(bpm)\}_2IrCl_2]^{5+}\). These electrochemical potentials correspond to the central metal, M\(^{III}/M^{IV}\) reductive couple (Nallas et al. 1996). This observation further verifies earlier assertion that the trimetallic has singly reduced bridging ligands and a twice-reduced central metal, Rh\(^{II}\)(bpm\(^\cdot\))\(_2\).

Controlled potential electrolysis experiments were performed to verify the formation of CO\(_2\) reduction products using the bipyrimidine bridged trimetallic complexes as electrocatalysts. A summary of these results is tabulated in Table 2. Ca. 1 mM solution of the complex \([\{(bpy)_2Ru(bpm)\}_2IrCl_2]^{5+}\) was electrolyzed at -1.80 V vs. Ag/AgCl. From the cyclic voltammogram under an atmosphere of CO\(_2\), these potential values correspond to the onset of current enhancement. At the beginning of the electrolysis, the catalyst solution was observed to gradually change color from dark green to deep brown. Deposition of dark brown precipitate in the working compartment of the bulk electrolysis cell was also observed at prolonged electrolysis. At -1.80 V, a steady increase in the charging current was observed during the electrolysis. After 10-15 min. of electrolysis, the current dropped exponentially, and then remained fairly constant (±5%) until the experiment was halted at desired total charge passed. Electrolyzing this iridium trimetallic in sufficiently dried solvent electrolyte solution to reach a total charge of 67 C resulted in the formation of CO and formate as reduction products. In this electrocatalysis experiment, CO was produced with a current efficiency of 23%. Analysis of the electrolyzed solution for formate gave a 16% current efficiency for formate production. At a longer electrolysis time where a total charge of 127 C was passed, a decrease in current efficiency for CO production with a corresponding increase in current efficiency for formate production was observed. This observation is

<table>
<thead>
<tr>
<th>Complex</th>
<th>(E_{\text{red, CO}_2}) (V)</th>
<th>Coulombs passed (C)(^a)</th>
<th>Current efficiency(^c)</th>
<th>Turnover(^d)</th>
</tr>
</thead>
<tbody>
<tr>
<td>([{(bpy)_2Ru(bpm)}_2MCl_2]^{5+})</td>
<td>-1.80</td>
<td>63</td>
<td>23% (CO)</td>
<td>7</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>16% (HCOOH)</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>127</td>
<td>12% (CO)</td>
<td>8</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>48% (HCOOH)</td>
<td>34</td>
</tr>
<tr>
<td>([{(bpy)_2Ru(bpm)}_2IrCl_2]^{5+})</td>
<td>-1.00</td>
<td>67</td>
<td>40% (CO)</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td></td>
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<td>31% (HCOOH)</td>
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<tr>
<td></td>
<td></td>
<td>90</td>
<td>12% (CO)</td>
<td>4</td>
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<td></td>
<td></td>
<td></td>
<td>44% (HCOOH)</td>
<td>15</td>
</tr>
<tr>
<td></td>
<td>-1.40</td>
<td>44</td>
<td>70% (CO)</td>
<td>16</td>
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<td></td>
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<td>6% (HCOOH)</td>
<td>2</td>
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<tr>
<td></td>
<td></td>
<td>56</td>
<td>76% (CO)</td>
<td>26</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>22% (HCOOH)</td>
<td>8</td>
</tr>
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</table>

\(^a\)Experiments were conducted in CO\(_2\)-saturated CH\(_3\)CN containing 0.1 M Bu\(_4\)NPF\(_6\)/CH\(_3\)CN and ca. 10 mmoles of added catalysts.

\(^b\)Total charge passed by the electrode.

\(^c\)Percent current attributed to production of CO, or HCOOH; current efficiency = \(\frac{Q_{\text{red, CO}_2} \times 100\%}{Q_{\text{theor}}}\) where \(Q_{\text{theor}}\) = \(\frac{nFE}{n}\) and \(n\) is the no. of moles of product.

\(^d\)Turnover = no. of moles product \(\div\) no. of moles catalyst.
similar to that observed for the dpq and dpb bridged systems studied in our laboratory, \{[(bpy)₂Ru(dpq)]IrCl₃\}^{5+} and \{[(bpy)₂Ru(dpq)]IrCl₃\}^{5+}, where the increasing amount of water in the system shifts the reduction of CO₂, from CO formation to formate formation. This trimetallic complex, \{[(bpy)₂Ru(bpm)]IrCl₃\}^{5+}, remained catalytically active at the end of electrolysis. Electrolysis at a more positive potential (-1.60 V) was also done, but did not result in any significant current passage across the system, and no detectable amount of CO or formate as reduction products were observed.

Using the trimetallic complex, \{[(bpy)₂Ru(bpm)]IrCl₃\}^{5+}, a different type of electrocatalytic activity was observed. Bulk electrolysis experiments performed on the system used similar conditions as described earlier. Different electrolysis potentials were used based on cyclic voltammetric results under CO₂ atmosphere. A gradual change in color from dark green to deep brown solution was also observed in the first 5-10 min of electrolysis. Formation of dark brown precipitate was observed at the end of the electrolysis. The amount of charge passed steadily increased throughout the experiment illustrating the relatively unaltered catalytic activity of this trimetallic complex. Electrolyses of ca. 1 mM solution of \{[(bpy)₂Ru(bpm)]IrCl₃\}^{5+} in 0.1M Bu₄NPF₆/CH₃CN at -1.40 V vs. Ag/AgCl readily formed CO as reduction product. After a total charge of ca. 44 C was passed, 70% current efficiency for CO production was obtained. This was accompanied by formate production with 6% current efficiency. Increasing the total charge passed to 56 C performed in a similar experiment resulted in a similar efficiency for the production of CO and formate (76% and 22%, respectively). At an electrolysis potential of -1.00 V, this rhodium based trimetallic complex remains catalytically active. Ca. 1.5 mM concentration of the catalyst was used and electrolyzed for a total of 67 C charge passed. This experiment resulted in the production of CO and formate with 40% and 31% current efficiencies, respectively. No other reduction products were observed. Similar to the iridium based system, at prolonged electrolysis where a total charge of 90 C was passed across the catalyst solution, a decrease in CO production and enhanced efficiency for formate production was observed. From the above results, it is noted that at -1.0 V, formate production was favored over CO production, whereas at a more negative electrolysis potential (-1.40 V), CO was the predominant reduction product. Electrolysis at a more positive potential of -0.80 V did not result to a significant passage of current across the catalyst solution. No detectable amounts of reduction products were obtained from gas chromatographic analysis. This illustrates that the minimum catalytic potential using \{[(bpy)₂Ru(bpm)]IrCl₃\}^{5+} is at -1.00 V vs. Ag/AgCl.

**DISCUSSION**

The aforementioned results from controlled potential electrolysis experiments using \{[(bpy)₂Ru(bpm)]IrCl₃\}^{5+} and \{[(bpy)₂Ru(bpm)]IrCl₃\}^{5+} as catalysts demonstrate the effect of central metal variation on the electrocatalytic activity of these polynuclear trimetallic complexes. It is evident that when rhodium is substituted for iridium as the central metal, a significant shift in the electrocatalytic potential for CO₂ reduction is obtained. The 800 mV drop in the potential needed for efficient catalysis when the rhodium based trimetallic is used instead of the iridium based trimetallics, illustrates the ability of central metal variation to tune the electrocatalytic properties of these systems. This large variation may be attributed to the differences in orbital energy levels of the central metals, Ir III or Rh III. The catalytically active species for the Rh based trimetallic is of the form Rh⁺(bpm)₃, which is quite similar to the previously studied mononuclear systems, [Rh(bpy)X₂]⁺ (Bolinger et al. 1985) and [Rh(BL)Br₂]⁺ (Rasmussen et al. 1990) where X = Cl⁻ or CF₃SO₃⁻ and BL = bpm, dpq, and dpb where the active form of the catalysts are [Rh⁺(bpy)³]⁺ and [Rh⁺(BL)³]⁺, respectively. One advantage of this trimetallic complex over the mononuclear complexes is that the electrocatalytic potential is shifted to a more positive value. This is attributed to the anodic shift in reduction potential of the bipyridine ligand brought about by coordination to two electropositive ruthenium centers. This shift is so large that it effectively occurs prior to metal reduction with activation. Both CO and formate are observed as reduction products wherein CO becomes more favored at more negative electrolysis potentials. For the iridium based system, the catalytically active species is of the form Ir⁺(bpm)³, similar to the trimetallic systems, \{[(bpy)₂Ru(dpq)]IrCl₃\}^{5+} and \{[(bpy)₂Ru(dpq)]IrCl₃\}^{5+}. However, CO₂ reduction using this complex resulted in a different product distribution that involves CO and HCOOH formation. Further investigations leading to a more detailed elucidation of the electrocatalytic activity of these trimetallic complexes toward the reduction of CO₂ are currently underway.

**ACKNOWLEDGMENT**

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