Abstract

Rhenium polypyridyl complexes have long been used as CO$_2$ reduction catalysts both electrochemically and photochemically. The Ruthenium-Rhenium bimetallic complexes [(biq)$_2$Ru($\mu$-dpp)Re(CO)$_3$Cl](PF$_6$)$_2$, [(biq)$_2$Ru($\mu$-dpq)Re(CO)$_3$Cl](PF$_6$)$_2$ and [(biq)$_2$Ru($\mu$-dpb)Re(CO)$_3$Cl](PF$_6$)$_2$ (biq= 2,2'-biquinoline, dpp=2,3-bis(2-pyridyl)pyrazine, dpq= 2,3-bis(2-pyridyl)quinoxaline, dpb = 2,3-bis(2-pyridyl)benzoquinoxaline) were synthesized and studied as potential electrocatalytic and photocatalytic CO$_2$ reduction agents. The catalytic efficiency of the Ru-Re bimetallic complexes is compared to that of each Ru and Re monometallic compound. A total of 9 compounds were investigated.

In cyclic voltammograms of the Re monometallic and Ru-Re bimetallic complexes, current increase was observed under a CO$_2$ atmosphere when compared to measurements conducted under N$_2$. The only CO$_2$ reduction product detected was CO following bulk electrolysis on the complexes using with gas chromatography and $^1$H and $^{13}$C NMR spectroscopy. Photochemically, Re monometallic compounds were shown to reduce CO$_2$ with the assistance of Ru(bpy)$_3^{2+}$ as a photosensitizer. However, Ru-Re bimetallic compounds failed to produce any CO. The possible reasons for the difference in reactivity are discussed.
Dedication

This thesis is dedicated to my family.
Acknowledgement

I would like to thank my advisor Prof. Claudia Turro for her guidance and enthusiasm towards this research. I am especially grateful for Tyler Whittemore for synthesizing all the compounds. I also want to thank Dr. Travis White, Hannah Sayre and Suzanne Witt for teaching me so much and other Turro group members for always being supportive and willing to help.
Vita

June 2014 .......................................................B.S. Chemistry, Beijing University of Chemical Technology

2014 to present ..............................................Graduate Teaching Associate, Department of Chemistry, The Ohio State University

Field of Study

Major Field: Chemistry
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Chapter 1 Introduction

1.1 Background

Carbon dioxide (CO$_2$) is a necessary raw material for most plants and for the industrial preparation of various chemicals. CO$_2$ is produced from combustion and biological processes, including the respiration, fermentation and decomposition of organic materials (Figure 1.1). Under ideal circumstances, the amount of CO$_2$ produced should be balanced with what is consumed to sustain environmental stability.

![Carbon Cycle Diagram](image)

**Figure 1.1 Carbon Cycle**

However, the extensive increase in the emission of CO$_2$ due to human activities in the past few decades has led to excessive CO$_2$ in the atmosphere. Human activities are
changing the natural carbon cycle—both by increasing CO₂ emissions and by inhibiting the ability of natural CO₂ sinks, such as forests and grasslands, to remove CO₂ from the atmosphere. The primary contributor to increased CO₂ emissions is the combustion of fossil fuels, such as coal, natural gas, and oil for industry and transportation.² Global CO₂ emission from the combustion of fossil fuels has dramatically increased since 1900 due to industrialization. Since 1970, CO₂ emission has increased by about 90%, 78% of which is attributed to fossil fuel combustion and other industrial activities (Figure 1.2).³

![Figure 1.2 Global Carbon Emissions from Fossil Fuels 1900-2011](image)

Agriculture, deforestation, desertization, and other uses of land are the second largest contributor to the increased atmospheric CO₂ levels. Excessive CO₂ significantly affects our living environment and the climate of the whole ecosystem. Therefore, it is crucial to limit CO₂ emissions, as well as to convert CO₂ into useful chemicals.³
In addition to global warming, addressing the shortage of fuel and energy sources in the long term is imperative. Therefore, an efficient method for CO$_2$ fixation is highly desirable as a means to not only reduce the amount of CO$_2$ in the atmosphere and alleviate global warming, but also to provide new clean energy sources to solve the energy shortage.$^4$

High CO$_2$ levels have raised a great amount of concern globally. Various governments advocate for the public to reduce their carbon footprint by living a more environmentally conscious lifestyle, as well as to increase their investment in clean energy research. Typically, CO$_2$ conversion may be achieved chemically,$^5$–$^7$ electrocatalytically$^8$–$^{11}$ and photocatalytically.$^{12}$–$^{16}$ However, some large barriers make CO$_2$ capture and conversion difficult. These include the large cost and difficulty for CO$_2$ capture, the large energy demand required for chemical or electrochemical reduction, the selectivity for various CO$_2$ reduction products, and the low yield of certain desirable products.$^1$,$^{17}$ Despite these challenges, researching CO$_2$ capture, conversion and utilization is crucial for society to benefit from this abundant energy source in the future.

CO$_2$ is extremely stable as it is the most oxidized form of carbon. The one-electron reduction of CO$_2$ requires a potential as negative as -1.90V (vs NHE), therefore the direct reduction of CO$_2$ requires significant amount of energy (Equation 1.1). In addition, there is a large kinetic overpotential needed to overcome due to the structural difference between the linear CO$_2$ structure and bent CO$_2^*-\text{structure.}^1^8$

$$\text{CO}_2 + 1\text{e}^- \rightarrow \text{CO}_2^-* \quad -1.90 \text{ V} \quad \text{Equation 1.1}$$
In contrast, proton-assisted multi-electron reduction of CO$_2$ can be performed at more positive potential as shown in equations 1.2 – 1.6 (V vs NHE at 25°C, pH=7 aqueous solution). The various products include formic acid, carbon monoxide (CO), formaldehyde, methanol, methane, and other higher order carbohydrates. Designing catalysts that can facilitate such multi-electron processes is of interest to researchers worldwide. In this regard, transition metal-based catalysts have proven useful due to the availability of multiple oxidation states on both the metal and ligands.

\[
\begin{align*}
\text{CO}_2 + 2\text{H}^+ + 2\text{e}^- &\rightarrow \text{HCO}_2\text{H} \quad E^\circ = -0.61 \text{ V} \quad \text{Equation 1.2} \\
\text{CO}_2 + 2\text{H}^+ + 2\text{e}^- &\rightarrow \text{CO} + \text{H}_2\text{O} \quad E^\circ = -0.53 \text{ V} \quad \text{Equation 1.3} \\
\text{CO}_2 + 4\text{H}^+ + 4\text{e}^- &\rightarrow \text{HCHO} + \text{H}_2\text{O} \quad E^\circ = -0.48 \text{ V} \quad \text{Equation 1.4} \\
\text{CO}_2 + 6\text{H}^+ + 6\text{e}^- &\rightarrow \text{CH}_3\text{OH} + \text{H}_2\text{O} \quad E^\circ = -0.38 \text{ V} \quad \text{Equation 1.5} \\
\text{CO}_2 + 8\text{H}^+ + 8\text{e}^- &\rightarrow \text{CH}_4 + 2\text{H}_2\text{O} \quad E^\circ = -0.24 \text{ V} \quad \text{Equation 1.6}
\end{align*}
\]

The necessity for CO$_2$-selective reduction must be emphasized since proton reduction occurs at a more positive potential, -0.41V (vs NHE, equation 1.7), than the 2e$^-$ reduction reactions of CO$_2$ (eqs 1.2 and 1.3). Therefore, it is critical for the catalyst to be selective for CO$_2$ reduction rather than proton reduction to limit the competition from competing reactions.

\[
2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2 \quad -0.41 \text{ V} \quad \text{Equation 1.7}
\]
1.2 Catalytic reduction of CO₂

1.2.1 Electrocatalytic reduction of CO₂

Electrocatalytic CO₂ reduction has raised much attention in recent years due to several advantages. First, it is easy to control the potential applied to the electrode. Secondly, it is chemically efficient. The electrolyte can be recycled to minimize chemical waste. Finally, it is possible to industrialize since the electrochemical reactions are compact, modular and feasible for scale-up application. Nevertheless, there are also challenges remaining such as slow kinetics for CO₂ reduction even in the presence of an electrocatalyst and high applied potential, and poor faradaic efficiency due to other undesired reactions on the electrode or in the electrolyte. Current catalytic systems suffer from wide distributions of products and poor stability. The species and yield of various products strongly depend on the catalysts and the potential applied to the electrode. Moreover, the current catalysts usually survive less than 100 h, which is not desirable for future industrial long-term applications. Therefore, it is crucial to design catalysts that can selectively reduce CO₂ to single products over long periods of time at low overpotential.

Among various CO₂ electrocatalysts, transition metal-based catalysts have been extensively researched due to the ability to circumvent the energetically unfavorable CO₂⁻ radical anion and alternatively provide a lower energy pathway for CO₂ reduction through multi-electron processes. There are two prerequisites for a transition metal-based catalyst to work, it should be capable of storing more than a single electron and it should feature at least one open coordination site after reduction to form a CO₂ adduct.
1.2.2 Photocatalytic reduction of CO$_2$

As opposed to electrocatalytic approaches, photocatalytic CO$_2$ reduction utilizes solar energy instead of electricity as a more efficient energy source. In general, a photocatalytic system has three components (Figure 1.2). First, a photosensitizer (PS) absorbs visible light to provide a charge transfer excited state. A desirable PS will absorb at the lower energy region of the visible spectrum (400-700nm) since that is the main component of sunlight on earth. Second, a catalyst to be reduced by the excited state PS by electron transfer and then perform catalysis. Finally, an electron donor (ED) to reduce the oxidized PS to regenerate the PS.

![Figure 1.3 Photocatalytic System](image)

Photocatalytic systems can be classified into three categories: (1). single-component system; (2). two-component system; (3) bimetallic catalysts in which PS and catalyst are connected by bridging ligands.$^{16}$
In single-component systems, the same compound serves as both PS and catalyst. Re(bpy)(CO)$_3$Cl (Figure 1.4) is a well-studied single-component photocatalytic system first introduced by Lehn and coworkers.$^{21}$

![Figure 1.4 Re(bpy)(CO)$_3$Cl](image)

In this system, the complex is first excited to the lowest energy excited state, a triplet metal-to-ligand-charge-transfer state ($^3$MLCT). It is subsequently quenched by the electron donor, triethanolamine (TEOA). The reductive quenching gives one-electron-reduced species, which then followed by the slow loss of Cl$^-$ ligand, it gives rise to a 17-electron species. This complex has an open coordination site for CO$_2$ binding as well as a second electron source for the CO$_2$ bound complexes. Based on these two functions, the reduced complex requires two distinct properties, which are the instability to lose the anionic Cl$^-$ligand for the CO$_2$ adduct to form and the stability to function as the electron donor.$^{16}$ These two opposing requirements are difficult to balance and pose a challenge to the single-component system. Therefore, two-component systems were introduced, in which the PS and catalyst are two separate compounds. The PS can produce stable
reduced catalyst to serve as a second electron donor for the 17-electron species after ligand loss from the catalyst. In both single and two component systems, the electron transfer between the PS and the catalyst may be limited by diffusion. In bimetallic catalyst systems, however, the electrons are transferred via the bridging ligand between a redox PS and catalyst which can provide a faster and more efficient electron transfer pathway.

Ishitani and coworkers reported several bimetallic catalysts which have Ru(II) as a photosensitizer unit and Re(I) as a catalyst. The absorption bands of a tris(diimine)ruthenium(II)-type photosensitizers (PSs) are in the visible region with maxima as far to the red as 560 nm, while the fac-Re(NN)(CO)₃Cl-type catalysts absorb in the ultraviolet and visible regions at wavelengths shorter than 450 nm. The difference in absorption between the Ru(II) and Re(I) complexes makes selective excitation of only the PS possible. In their work, the authors proposed three considerations required to design an efficient Ru(II)-Re(I) bimetallic catalyst. First, the electrons captured by the PS should be mostly localized on the bridging ligand rather than the peripheral ligands, since the electrons should be able to transfer efficiently to the catalyst. Second, the electron transfer between the PS and catalyst should not be the rate limiting step compared to other processes, including CO₂ capture by the catalyst, CO₂ reduction on the catalyst, and CO release from the catalyst. And finally, although the conjugation system within the bridging ligand can provide a faster electron transfer, it may also reduce the ability of the Re catalyst to reduce the substrate. It was found that based on these constraints, the photocatalysis by [Ru(4,4’-Me₂bpy)₂(μ-CH₂CH₂)Re(CO)₂{P(p-F-Ph)₃}₂]³⁺ using BIH (1,3-dimethyl-2-phenyl-2,3-dihydro-1H-benzo[d]-imidazole) as the electron donor
(Figure 1.5) performed the best ($\Phi_{\text{CO}} = 0.45$, $\text{TON}_{\text{CO}} = 3029$, and $\text{TOF}_{\text{CO}} = 35.7 \text{min}^{-1}$) among the reported bimetallic catalysts.$^{23}$

Figure 1.5 Bimetallic Catalyst Example and BIH
1.3 New Ru(II)-Re(I) Complexes

The catalysts units used in the present work are Re(dpp)(CO)₃Cl (dpp = 2,3-bis(2-pyridyl)pyrazine), Re(dpq)(CO)₃Cl (dpq = 2,3-bis(2-pyridyl)quinoxaline) and Re(dpb)(CO)₃Cl (dpb = 2,3-bis(2-pyridyl)benzoquinoxaline), with their molecular structure shown in Figure 1.6 These ligand are chosen for three reasons. Firstly, polypyridyl ligands are capable of storing electrons in vacant π* orbitals to make multi-electron CO₂ reduction possible. Secondly, the bidentate ligand has an additional binding site that is able to coordinate a ruthenium complex as a light absorber to generate bimetallic catalysts for photocatalysis. Thirdly, with the extended π systems, these ligands can shift the absorption of the complex to lower energy for improved absorption of sunlight.

![Figure 1.6 Re(NN)(CO)₃Cl (NN = dpp, dpq, and dpb)](image-url)
The ruthenium monometallic compounds [Ru(biq)$_2$(dpp)](PF$_6$)$_2$ (biq= 2,2’- biquinoline), [Ru(biq)$_2$(dpq)](PF$_6$)$_2$ and [Ru(biq)$_2$(dpb)](PF$_6$)$_2$ (Figure 1.7) are control complexes for the Re(I)-Ru(II) dinuclear systems, which served as photosensitizers in the bimetallic structures. They were investigated to determine the influence of the PS component on the catalytic function of the Re catalytic component in the bimetallic systems. The biquinoline ligands were chosen due to their ability to shift the absorption to lower energy for the photocatalytic studies.

![Figure 1.7][1]

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[1]: Figure 1.7 [Ru(biq)$_2$(NN)](PF$_6$)$_2$ (NN =dpp, dpq and dpb)
The bimetallic compounds explored in this work are \([(\text{biq})_2\text{Ru}(\mu\text{-dpp})\text{Re(CO)}_3\text{Cl}(\text{PF}_6)_2, \quad (\text{biq})_2\text{Ru}(\mu\text{-dpq})\text{Re(CO)}_3\text{Cl}(\text{PF}_6)_2\) and \([(\text{biq})_2\text{Ru}(\mu\text{-dpb})\text{Re(CO)}_3\text{Cl}(\text{PF}_6)_2\) (Figure 1.8). As a bimetallic catalyst, Ru acts as the photosensitizer, which is bridged with the Re catalyst via the dpp, dpq and dpb ligands.

![Diagram of bimetallic compounds](image.png)

**Figure 1.8** \([(\text{biq})_2\text{Ru(BL)}\text{Re(CO)}_3\text{Cl}(\text{PF}_6)_2\) (BL = dpp, dpq, and dpb)
Chapter 2 Experimental

2.1 Materials

The chemicals 2,3-bis(2-pyridyl)pyrazine (dpp), ethylenediamine, 2,2'-pyridyl, ruthenium trichloride, rhenium pentacarbonyl chloride, ammonium hexafluorophosphate, silver triflate, and neutral alumina oxide were purchased from Sigma Aldrich used without further purification. Similarly, 2,2'-biquinoline (biq), 2,3-naphthalenediamin and 2,2'-bipyridine were brought from Acro, Spectrum and Alfa Aesar, respectively, and were used as received. Electrochemical grade tetrabutylammonium hexafluorophosphate (TBAPF$_6$) (≥ 99.0%) was purchased from Fluka Analytical, whereas N,N-dimethylformamide (DMF) and acetonitrile (CH$_3$CN) were obtained from Fisher Scientific. DMF was dried with 4 Å molecular sieves prior to use and CH$_3$CN was distilled by refluxing over CaH$_2$ and stored under a N$_2$ atmosphere. Triethanolamine (TEOA) was purchased from Sigma Aldrich and 1-benzyl-1,4-dihydrionicotinamide (BNAH) was obtained from TCI. N$_2$ (99.998%) and CO/He mixture (5:95, v:v) were purchased from Praxair and CO$_2$ (99.998%) from Air Liquide. Water was deionized to 18 MΩ by a Barnstead B-pure cartridge water purification system. The ligand 2,3-bis(2-pyridyl)quinoxaline (dpq) was synthesized according to the method reported by Goodwin and Lions, $^{24}$ and 2,3-bis(2-pyridyl)benzoquinoxaline (dpb) was synthesized based on the procedures reported by Baiano and coworkers.$^{25}$
2.2 Instrumentation
Absorption spectra were measured using a Hewllet-Packard photodiode array spectrometer (HP 8453) in a 1.0 cm path length quartz cuvette. $^1$H NMR spectra were collected utilizing a Bruker 400 MHz NMR spectrometer, and mass spectra were obtained on a Bruker MicrOTOF spectrometer with an electrospray ionization (ESI) ion source.

2.3 Synthesis
Re(dpp)(CO)$_3$Cl was prepared based using the same general method modified from the synthesis of Re(bpy)(CO)$_3$Cl reported by Casper and Meyer.$^{26}$ A mixture of Re(CO)$_5$Cl and a slight excess of polypyridyl ligands was heated in toluene at reflux for 1 h until a precipitate formed. The products were washed three times with octanol and once with diethyl ether, then dried. After separation using a neutral alumina column (3:2 acetone/toluene v: v), the dark brown-orange band of Re(dpp)(CO)$_3$Cl was collected. The product was dried and used without further purification.

Re(dpq)(CO)$_3$Cl was synthesized using the same procedure as Re(dpp)(CO)$_3$Cl except that the dark red-orange band of Re(dpq)(CO)$_3$Cl was collected.

Re(dpb)(CO)$_3$Cl was synthesized using the same procedure as Re(dpp)(CO)$_3$Cl except that the dark orange band of Re(dpb)(CO)$_3$Cl was collected.

[Ru(biq)$_2$(dpb)][PF$_6$]$_2$ was prepared based on the method reported by Albani and Turro.$^{27}$ ESI MS m/z = 474, corresponding to [Ru(biq)$_2$(dpb)]$^{2+}$. 
[Ru(biq)₂(dpp)][PF₆]₂ was prepared using modified procedure according to Albani and Turro,²⁷ where dpp ligand was used instead of dpb ligand. A dark pink mixture was collected after heating, refluxing and stirring for 72 h. After the addition of a saturated aqueous solution of NH₄PF₆ to the filtrate, a dark pink precipitate was formed and collected. After a neutral alumina column (acetone/toluene, 3:2 v:v) the dark pink band was than collected. A dark pink solid was collected after drying. ESI MS m/z = 424, corresponding to [Ru(biq)₂(dpp)]²⁺.

[Ru(biq)₂(dpq)][PF₆]₂: was prepared using modified procedure reported by Albani and Turro,²⁷ where dpq ligand was used instead of dpb ligand. A deep red mixture was collected after heating, refluxing and stirring for 72 h. After the addition of a saturated aqueous solution of NH₄PF₆ to the filtrate, a deep red precipitate was formed and collected. After a neutral alumina column (acetone/toluene, 3:2 v:v) the deep red band was than collected. A deep red solid was collected after drying. ESI MS m/z = 449, corresponding to [Ru(biq)₂(dpq)]²⁺.

[(biq)₂Ru(µ-dpb)Re(CO)₃Cl][PF₆]₂ was prepared based on the method reported by Albani and Turro.²⁷ ESI MS m/z = 1399, corresponding to [(biq)₂Ru(dpb)Re(CO)₃Cl][PF₆]⁺, IR carbonyl stretches (cm⁻¹): 2025, 1937(sh), and 1915.

[(biq)₂Ru(µ-dpp)Re(CO)₃Cl][PF₆]₂ was prepared using modified procedure according to Albani and Turro,²⁷ where [Ru(biq)₂(dpp)][PF₆]₂ was used instead of [Ru(biq)₂(dpb)][PF₆]₂. The reaction was cooled and dried by Rotovap to yield a dark purple crude product which was further washed with octanol/ether. The dark purple solid
was collected. ESI MS m/z = 577, corresponding to \((\text{biq})_2\text{Ru(dpp)Re(CO)}_3\text{Cl}]^{2+}\), IR carbonyl stretches (cm\(^{-1}\)): 2020 and 1893.

\[\text{[(biq)}_2\text{Ru(µ-dpq)Re(CO)}_3\text{Cl]}\text{[PF}_6\text{]}_2\]: was prepared using modified procedure according to Albani and Turro,\(^{27}\) where [Ru(biq)]_2(dpq)][PF_6]_2 was used instead of [Ru(biq)(dpb)]PF_6_2. The reaction was cooled and dried by Rotovap to yield a dark purple crude product which was further washed with octanol/ether. The dark purple solid was collected. ESI MS m/z = 602, corresponding to \((\text{biq})_2\text{Ru(dpq)Re(CO)}_3\text{Cl}]^{2+}\). m/z = 1349, corresponding to \((\text{biq})_2\text{Ru(dpq)Re(CO)}_3\text{Cl]}\text{[PF}_6\text{]}^+\), IR carbonyl stretches (cm\(^{-1}\)): 2023 and 1898.

2.4 Electrochemistry

2.4.1 Cyclic Voltammetry

Electrochemical measurements were performed by using a BASi model CV-50W voltammetric analyzer (Bioanalytical Systems). Cyclic voltammograms (CV) were obtained using a standard three-electrode configuration with a Ag/AgCl (3 M NaCl (aq)) reference electrode in a glass tube capped with a Vycor tip, glassy carbon (3 mm diameter) working electrode, and a Pt wire auxiliary electrode (Figure 2.1). The glassy carbon working electrode were polished with alumina powder before each scan. The cell was deoxygenated with N_2 or CO_2 prior to use. Typical CVs were obtained using the following conditions: 0.5 mM Re, Ru monometallic complexes or Ru-Re bimetallic complexes in MeCN or DMF, 0.1 M TBAPF_6 supporting electrolyte, 100 mV/s scan rate, and under a N_2 or CO_2 atmosphere at 298 K.
2.4.2 Bulk Electrolysis

Bulk electrolysis (BE) experiments were carried out in a custom-built, airtight two-compartment cell separated by a glass frit as shown in Figure 2.2. A Pt wire electrode was placed in the right auxiliary compartment which was filled with electrolyte solution without any catalysts. The left side represents the working compartment with a Ag/AgCl (3 M NaCl (aq)) reference electrode and a high density extruded graphite rod (Graphtek LLC) working electrode. A magnetic stir bar was placed in the bottom of the cell and the solution level in the auxiliary and working compartment were kept at the same height.
The cell was deoxygenated with N\textsubscript{2} or bubbled with CO\textsubscript{2} for 20 min prior to the experiment and setting of the cell at -1.5 V (vs NHE).

![Bulk Electrolysis Cell](image)

**Figure 2.2 Bulk Electrolysis Cell**

The reaction solution contained 0.5 mM of each Re and Ru monometallic complex or 0.5 mM Ru-Re bimetallic complex in 3 mL mixture of DMF/H\textsubscript{2}O (10% H\textsubscript{2}O) or acetonitrile with 0.1 M TBAPF\textsubscript{6} supporting electrolyte. Aliquots (200 μL) of the 37 mL headspace were removed using a Hamilton gastight syringe and injected into a Shimadzu GC-2014 gas chromatograph (He carrier gas) with a ShinCarbon column (2 m long × 1/8 in. OD × 2.0 mm ID) and a Shimadzu TCD-2014 thermal conductivity detector. The GC conditions were as follows: injector temperature, 62.0 °C; column temperature, 60 °C; detector temperature, 200 °C; and gas flow, 20 mL/min. The liquid products were
analyzed by performing $^1$HNMR with a Bruker DPX 400 MHz spectrometer and $^{13}$CNMR with a Bruker AVIII 600 MHz NMR spectrometer.

2.5 Photochemistry

A solution (4 mL, N, N–dimethylformamide and triethanolamine mixture (DMF-TEOA, 5:1 v/v) containing the catalyst (0.25 mM) was placed into a vial (volume brim, 23.5 mL) with septum bonded cap purchased from Thermo Scientific. The solution was saturated with CO$_2$ and then irradiated. A 150 W Xe lamp with 385 nm longpass filter was used to irradiate the single-component system for Re monometallic compounds. Self-assembled neutral white 4100 K LEDs were used to irradiate two-component system and bimetallic catalyst system. The relative spectral power distribution of the white LED is shown in Figure 2.3.

![Figure 2.3 Relative Spectral Power Distribution of Neutral White 4100 K LED](image-url)
After irradiation, aliquots (200 μL) of the 19.5 mL headspace from the vial were removed using a Hamilton gastight syringe and injected into a Shimadzu GC-2014 gas chromatograph (He carrier gas) to identify and quantify the amount of gaseous products.

2.6 CO calibration

The amount of CO in the headspace was determined by external calibration of the gas chromatography. In order to build a calibration curve, 10 μL, 20 μL, 30 μL, 40 μL and 50 μL of the standard ultra-high purity CO/He mixture (5:95) was injected into GC under the conditions mentioned in 2.4.2 three times. The average CO peak area was plotted versus the corresponding amount of CO (Figure 2.4).

![CO Calibration Curve](image)

**Figure 2.4 CO Calibration Curve**

\[ y = 9.2240 \times 10^{-6}x \]

\[ R^2 = 9.9161 \times 10^{-1} \]
Chapter 3 Results and Discussion

3.1 Electrochemistry

3.1.1 Re monometallic compounds

1. Cyclic Voltammetry

The mononuclear Re(NN)(CO)\textsubscript{3}Cl (NN = dpp, dpq, and dpb) compounds were investigated first to help understand the function and efficiency of the catalytic unit of the bimetallic compounds. Cyclic voltammetry was performed for all three compounds under saturated N\textsubscript{2} (the black curve) and CO\textsubscript{2} (the colored curve) atmosphere (Figure 3.1).
Figure 3.1 Cyclic voltammograms of Re(NN)(CO)₃Cl (NN = dpp, dpq, and dpb) under N₂ and CO₂. Potentials were determined in DMF with 0.50 mM catalyst and 0.1 M TBAPF₆ as the supporting electrolyte.
The three mononuclear Re complexes display two reductions in the potential region from 0 to \(-1.80\) V. The first reduction in each of the three compounds is assigned to reversible ligand localized event, \(L^{0/-}\), which appears at \(-0.85\) V, \(-0.58\) V and \(-0.46\) V for dpp, dpq and dpb under \(N_2\), respectively. The half-wave potential (\(E_{1/2}\)) is calculated from the average of the peak cathodic potential (\(E_{pc}\)) and peak anionic potential (\(E_{pa}\), Equation 3.1).

\[
E_{1/2} = \frac{E_{pc} + E_{pa}}{2}
\]

Equation 3.1

The second, irreversible reduction is assigned to be metal centered \(Re^{I0}\), which appear at \(-1.40\) V, \(-1.28\) V and \(-1.10\) V for the dpp, dpq and dpb in the monometallic Re compounds under \(N_2\), respectively. The CV correspond to that of the well-studied Re(bpy)(CO)\(_3\)Cl compound with both reductions shifting to more negative potential. The \(E_{1/2}\) and \(E_{pc}\) values for all four compounds are summarized in Table 3.1.\(^{25}\)

<table>
<thead>
<tr>
<th>Compound</th>
<th>(E_{1/2}) (V)</th>
<th>(E_{pc}) (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Re(bpy)(CO)(_3)Cl</td>
<td>-1.18</td>
<td>-1.66</td>
</tr>
<tr>
<td>Re(dpp)(CO)(_3)Cl</td>
<td>-0.85</td>
<td>-1.40</td>
</tr>
<tr>
<td>Re(dpq)(CO)(_3)Cl</td>
<td>-0.58</td>
<td>-1.28</td>
</tr>
<tr>
<td>Re(dpb)(CO)(_3)Cl</td>
<td>-0.46</td>
<td>-1.10</td>
</tr>
</tbody>
</table>

\(^{a}\) Potentials (V vs 3 M NaCl Ag/AgCl Reference Electrode) were determined in DMF with 0.50mM catalyst and 0.1 M TBAPF\(_6\) as the supporting electrolyte.
It is evident from the data in Table 3.1 that both the ligand-centered and metal-centered reduction potentials shift to more positive values as the π-system on the ligand is extended. An extended π-system makes the addition of electrons more favorable, thus the ligand within each compound is reduced at more positive potentials as the π-system is increased. In addition, in the reduction of the larger ligands, the electron is placed in an orbital further from the metal, such that in those systems the reduction of the metal is more facile, resulting in a positive shift to the metal-centered couple as a function of the size of the ligand π-system.

In solutions saturated with CO₂ (0.28 M), the ligand-centered reduction waves remain unchanged, but current enhancement is observed in the presence of CO₂ at an E_{pc} of approximately –1.4 V for the dpp compound and –1.5 V for the dpq and dpb compounds vs Ag/AgCl. This observation indicates that the compounds may interact with CO₂ and undergo electrochemical catalytic reaction with each complex at the respective potential.

To better understand the electrocatalytic ability of these compounds, Re(dpp)(CO)₃Cl is chosen as an example to compare with the well-studied Re(bpy)(CO)₃Cl catalyst under the same electrochemical conditions. The cyclic voltammograms under saturated CO₂ atmosphere for the dpp and bpy compounds are shown in Figure 3.2.
Figure 3.2 Cyclic voltammograms of Re(bpy)(CO)$_3$Cl (yellow) and Re(dpp)(CO)$_3$Cl (blue) under CO$_2$. Potentials were determined in DMF with 0.50 mM catalyst and 0.1 M TBAPF$_6$ as the supporting electrolyte.

The first ligand-centered reduction bpy$^{0/-}$ for Re(bpy)(CO)$_3$Cl is observed at $-1.18$ V vs Ag/AgCl, a potential that is the more negative than the dpp, dpq and dpb reductions (Table 3.1). By coordinating to the least electron-rich bidentate ligand, bpy, Re(bpy)(CO)$_3$Cl has the most electron positive Re center for CO$_2$ reduction. Re(bpy)(CO)$_3$Cl also shows the largest current at $-1.80$ V vs Ag/AgCl among all four compounds, suggesting that more electrons are being transferred to and utilized in the reaction of the Re(bpy)(CO)$_3$Cl with the substrate, CO$_2$. Therefore, the comparison of the current enhancement under the same electrochemical conditions can be used as a predictor of the catalytic ability of the compounds, among which Re(bpy)(CO)$_3$Cl is the
most efficient CO$_2$ reducing agent, followed by Re(dpb)(CO)$_3$Cl, Re(dpp)(CO)$_3$Cl and Re(dpq)(CO)$_3$Cl. This prediction was confirmed by bulk electrolysis.

2. Bulk Electrolysis

In bulk electrolysis (BE), a graphite rod working electrode is used to provide a larger surface area compared to a glassy carbon disc electrode used in cyclic voltammetry. Therefore, BE can be used to impart a larger electrochemical change on a system. During a BE experiment, the working electrode is held at a constant potential (Volts) and current (Amps) is monitored over time (seconds). The analyte is quantitatively reduced or oxidized from its original oxidation state to a new oxidation state. After the electrochemical reaction is performed on the working electrode, the products can be characterized and quantified.

The gas phase products of electrocatalytic CO$_2$ reduction by Re(NN)(CO)$_3$Cl (NN = bpy, dpp, dpq, and dpb) were investigated by injection of headspace samples from the airtight bulk electrolysis cell into a gas chromatogram (GC). In CO$_2$ saturated solutions of each complex (0.50 mM, 0.1 M TBAPF$_6$ DMF/10%H$_2$O), the potential was held at $-1.50$ V vs Ag/AgCl for 2 h. For all four Re(I) complexes, carbon monoxide (CO) was determined as the only gaseous product, and the amount of CO generated was calculated from the calibration curve described in the Experimental Section. CO production is important as it can serve as a feedstock chemical for the synthesis of alkanes through the Fischer-Tropsch reaction. The absence of liquid products was confirmed by $^1$H and $^{13}$C NMR.
Figure 3.3 CO production during bulk electrolysis by Re(NN)(CO)$_3$Cl (NN= dpp, dpq, and dpb) complexes.

The efficiency of the catalyst is determined by the turnover number (TON), which is given by the total moles of all products divided by the moles of catalyst (Equation 3.2). The larger the TON the greater the catalytic efficiency. The TONs for the four compounds are listed in Table 3.2.

\[
TON = \frac{\text{Total moles product}}{\text{Moles catalyst}}
\]

Equation 3.2
Table 3.2 CO Production (µmol) and TON for Re(NN)(CO)₃Cl(NN = bpy, dpp, dpq, and dpb) from Bulk Electrolysis in 2 h.

<table>
<thead>
<tr>
<th>Compound</th>
<th>CO (µmol)</th>
<th>TON</th>
</tr>
</thead>
<tbody>
<tr>
<td>Re(dpp)(CO)₃Cl</td>
<td>0.4</td>
<td>0.2</td>
</tr>
<tr>
<td>Re(dpq)(CO)₃Cl</td>
<td>0.4</td>
<td>0.2</td>
</tr>
<tr>
<td>Re(dpb)(CO)₃Cl</td>
<td>1.5</td>
<td>0.6</td>
</tr>
<tr>
<td>Re(bpy)(CO)₃Cl</td>
<td>29.5</td>
<td>19.7</td>
</tr>
</tbody>
</table>

To be an efficient CO₂ reduction catalyst, Re tricarbonyl polypyridyl compounds, Re(NN)(CO)₃X (X = halide), should yield a TON of at least 3 because the compound itself contains three carbonyl ligands, so one may argue that if TON < 3 is achieved, then the CO production may originate from ligand dissociation and not from substrate reduction. However, the dpp, dpq and dpb Re monometallic compounds only produce TONs of 0.2, 0.2 and 0.69, respectively, all of which are smaller than 3, such that they are not efficient CO₂ reduction electrocatalysts, especially compared to the model complex Re(bpy)CO₃Cl with TON ~ 20 in 2 h. The relative activity toward CO production for the four compounds also agrees with the cyclic voltammetry observations, in which the bpy compound shows the greatest current enhancement.

The mechanistic studies of electrocatalytic CO₂ reduction of Re(NN)(CO)₃X complexes show that two electrons are added to the complex to provide the electrocatalytically active species [Re(NN)(CO)₃]⁻.²⁹,³⁰ This species has a singlet ground state and processes the formal charge distribution Re₀(NN)⁻ with one electron on the π* orbital of the polypyridyl ligand and the other on the dz² orbital of Re.³¹
can selectively interact with CO$_2$ rather than H$^+$ to reduce CO$_2$ first with a small activation barrier, thus making Re(NN)(CO)$_3$X complexes efficient CO$_2$ reducing agents$^{32}$. The dissociation of the halide ligand X during this process provides an open coordination site for a CO$_2$ adduct to form, followed by a two-electron reduction. The halide ligand dissociation is slow and is considered the rate-limiting step of the catalytic cycle. Therefore, the ease of chloride dissociation affects the catalytic ability of the compounds.

Since bpy is the most electron donating ligand in the series, Re(bpy)(CO)$_3$Cl has a more nucleophilic metal center to weaken the Re-Cl bond. As a result, the bpy compound is the most efficient electrocatalytic CO$_2$ reducing agent.

3.1.2 Ru Monometallic Compounds

Ru acts as a photosensitizer (PS) when bound to Re monometallic compounds through the dpp, dpb, and dpq bridging ligands, making bimetallic catalysts. [Ru(biq)$_2$(NN)](PF$_6$)$_2$ (NN = dpp, dpq and dpb) monometallic compounds were investigated to understand their role in Ru-Re catalysts. According to the structural information, Ru monometallic compounds do not possess an open coordination site upon reduction, thus no CO$_2$ adduct can be formed for catalysis to occur. Bulk electrolysis supports this conclusion, as neither gaseous nor liquid products were detected after 2 hours with these Ru(II) complexes. It may therefore be concluded that the [Ru(biq)$_2$(NN)](PF$_6$)$_2$ (NN = dpp, dpq and dpb) complexes alone do not function as CO$_2$ reduction electrocatalysts.
3.1.3 Ru-Re Bimetallic Compounds

In the bimetallic complexes \([((bi)q)_2Ru(BL)Re(CO)_3Cl](PF_6)_2\), \(BL = \text{dpp, dpq, and dpb}\), the Ru photosensitizer component is bound to the Re catalyst component with dpp, dpq or dpb bridging ligands. The electrocatalytic properties of these complexes are discussed in section 3.1 and the photocatalytic properties will be introduced in section 3.2.

1. Cyclic Voltammetry

Similar to the corresponding Re monometallic compounds, the bimetallic compounds show current increase under \(\text{CO}_2\) when compared to scans under \(\text{N}_2\) (Figure 3.4), which indicates that the bimetallic compounds can electrochemically and catalytically reduce \(\text{CO}_2\).

![Cyclic voltammograms of \([((bi)q)_2Ru(BL)Re(CO)_3Cl](PF_6)_2\) under \(\text{N}_2\) (black lines) and \(\text{CO}_2\) (colored lines)](image)

Figure 3.4 Cyclic voltammograms of \([((bi)q)_2Ru(BL)Re(CO)_3Cl](PF_6)_2\) (BL=dpp, dpq, and dpb) under \(\text{N}_2\) (black lines) and \(\text{CO}_2\) (colored lines)
2. Bulk Electrolysis

In CO\textsubscript{2} saturated solutions of the compounds (0.50 mM, 0.1 M TBAPF\textsubscript{6} DMF/10% H\textsubscript{2}O), the potential was held at –1.50 V for 2 h and CO was determined as the only product. In these experiments, [(biq)\textsubscript{2}Ru(\mu-dpp)Re(CO)\textsubscript{3}Cl]\textsuperscript{2+}, [(biq)\textsubscript{2}Ru(\mu-dpq)Re(CO)\textsubscript{3}Cl]\textsuperscript{2+}, and [(biq)\textsubscript{2}Ru(\mu-dpb)Re(CO)\textsubscript{3}Cl]\textsuperscript{2+} produced 0.76 µmol (TON = 0.51), 0.72 µmol (TON = 0.48), and 0.30 µmol CO (TON = 0.20), respectively (Table 3.3). Table 3.3 also compares the CO production and TONs for each bimetallic complex and the corresponding mononuclear compound.

Table 3.3 CO Production (µmol) and TONs for Re( NN)(CO)\textsubscript{3}Cl ( NN = dpp, dpq, and dpb) and [(biq)\textsubscript{2}Ru(BL)Re(CO)\textsubscript{3}Cl](PF\textsubscript{6})\textsubscript{2} (BL = dpp, dpq, and dpb) Following 2 h of Bulk Electrolysis.

<table>
<thead>
<tr>
<th>Compound</th>
<th>CO (µmol)</th>
<th>TON</th>
</tr>
</thead>
<tbody>
<tr>
<td>[(biq)\textsubscript{2}Ru(\mu-dpp)Re(CO)\textsubscript{3}Cl]\textsuperscript{2+}</td>
<td>0.8</td>
<td>0.5</td>
</tr>
<tr>
<td>Re(dpp)(CO)\textsubscript{3}Cl</td>
<td>0.4</td>
<td>0.2</td>
</tr>
<tr>
<td>[(biq)\textsubscript{2}Ru(\mu-dpq)Re(CO)\textsubscript{3}Cl]\textsuperscript{2+}</td>
<td>0.8</td>
<td>0.5</td>
</tr>
<tr>
<td>Re(dpq)(CO)\textsubscript{3}Cl</td>
<td>0.5</td>
<td>0.2</td>
</tr>
<tr>
<td>[(biq)\textsubscript{2}Ru(\mu-dpb)Re(CO)\textsubscript{3}Cl]\textsuperscript{2+}</td>
<td>0.3</td>
<td>0.2</td>
</tr>
<tr>
<td>Re(dpb)(CO)\textsubscript{3}Cl</td>
<td>1.5</td>
<td>0.6</td>
</tr>
</tbody>
</table>

When compared to the corresponding Re monometallic compounds, the CO production is similar in the bimetallic complexes since the Ru photosensitizer does not enhance
catalysis. As a result, the catalytic ability of the Ru-Re bimetallic compounds is primarily dependent on the Re portion. Due to the low catalytic efficiency of the Re monometallic compounds, it may also be concluded that the bimetallic compounds are not efficient electrocatalytic reducing agents, as is the case in the corresponding mononuclear Re(I) complexes.

3.2 Photochemistry

In electrocatalysis the electrons for CO$_2$ reduction are provided by the working electrode, which ultimately requires electricity. In contrast, in photocatalysis, the energy is provided by photons. If photocatalytic CO$_2$ reduction can be achieved, this would be a more energy-efficient way for CO$_2$ fixation, as solar energy is an abundant and renewable resource.

3.2.1 Single-component system

In single-component system, a complex functions both as a photosensitizer and a catalyst. The well-studied Re tricarbonyl polypyridyl catalyst, Re(bpy)(CO)$_3$Cl, is such an example. The Re monometallic compounds used in the present work were tested for photocatalytic activity. A solution (4 ml DMF-TEOA, 5:1 v/v) containing the catalyst (0.05 mM) was placed into a sealed vial. The solution was saturated with CO$_2$ and then irradiated by a 150W Xe lamp with 385nm long-pass filter for 3 h. No reaction products were detected in either the gaseous or liquid phases.

As discussed in the introduction, in order to work as a single-component system, once the complex is reduced by one electron, the balance of two distinct properties must be
considered. These are the exchange of an anionic halide ligand for CO$_2$ and the stability of the reduced complex during the time required for the electron donor to provide a second electron. In contrast to Re(bpy)(CO)$_3$Cl, it is apparent from the present work that the corresponding Re(NN)(CO)$_3$Cl (NN = dpp, dpq and dpb) complexes are not be able to balance both properties to photocatalytically reduce CO$_2$.

3.2.2 Two-component system

In order to reconcile the opposing requirements for the one electron reduced complex in the single-component system, a second compound was introduced. [Ru(bpy)$_3$]$^{2+}$ serves as a redox photosensitizer to initiate photochemical electron transfer. The ground state [Ru(bpy)$_3$]$^{2+}$ is excited to its metal to ligand charge transfer (MLCT) state [Ru(bpy)$_3$]$^{2+*}$ upon absorption of a photon in the visible region, which can be accomplished through irradiation with a white LED. The excited state [Ru(bpy)$_3$]$^{2+*}$ transfer electron to Re monometallic compound catalyst. The oxidized Ru(III) is then reduced by an electron donor, triethanolamine (TEOA), to regenerate the ground state Ru(II) photosensitizer. PS to catalyst ratio was 2:1. CO was detected as the only product of this two-component system after 2 h of irradiation, however, the calculated TONs remain small (Table 3.4).
In electrochemistry, the reaction is more controllable since the applied potential can be readily manipulated. In contrast, photochemical systems are more difficult to control. For example, if the excited state PS relax back to ground state before it transfers electron to the catalyst, the catalyst would not be reduced to perform CO₂ reduction. As a result, if electrochemically the catalysts are not efficient, photochemically, they would be expected to be inefficient as well. Based on the experimental results, Re monometallic compounds are not efficient electrocatalytic or photocatalytic CO₂ reducing agents.

3.2.3 Ru-Re Bimetallic catalysts

In two-component systems, the electron transfer requires collision between the one electron reduced complex of the PS and the catalyst which maybe the rate-limiting step of the photocatalytic reaction. Excess PS relative to the catalyst is usually added to the system to avoid this problem. Therefore, systems where the PS is covalently bound to the catalyst are designed to overcome these problems. In this work, a Ru PS unit is bound to
Re monometallic catalyst through a bridging ligands, BL, to form the bimetallic catalysts 
[(biq)₂Ru(BL)Re(CO)₃Cl](PF₆)₂ (BL = dpp, dpq, and dpb). The sacrificial electron donor 
1-benzyl-1,4-dihydronicotinamide (BNAH) was used in the present work, since the 
³MLCT excited state of the bimetallic compounds is not oxidizing enough to remove an 
electron from the typical electron donor TEOA. However, TEOA is still required in the 
system to prevent the back-electron transfer from the OERS to oxidized BNAH.³³ A 
solution of 0.05 mM catalyst and 0.1M BNAH was prepared in 4 mL DMF/TEOA (5:1, 
v:v) and saturated with CO₂ before excited with white LED for 3 h. No CO was detected 
from this system.

There are a few possible reasons why the bimetallic catalysts cannot photocatalytically 
reduce CO₂. First, the electrocatalytic and photocatalytic studies of the Re monometallic 
compounds, Re(NN)(CO)₃Cl (NN = dpp, dpq, and dpb) were shown to be inefficient 
catalysts, such that the bimetallic complexes containing these catalysts are also expected 
to perform poorly. Second, the electron transfer from PS to catalyst is hindered by the 
bridging ligands because the conjugated bridging ligands dpp, dpq, and dpb are stable 
upon reduction thus acting as electron sinks. Third, the excited state lifetime of the Ru-Re 
bimetallic complex is too short to transfer electrons to the catalyst unit before it relaxes 
back to ground state. The excited state ³MLCT lifetime of [(biq)₂Ru(µ-
dpb)Re(CO)₃Cl](PF₆)₂ was determined τ = 2-20 ns by Albani and Turro²⁷ which is 
relatively short as a photosensitizer. Finally, after the first electron transfer from Ru to Re, 
back electron transfer maybe faster than the regeneration of Ru(II) from Ru(III) by 
BNAH.
Chapter 4 Conclusion

The Ruthenium-Rhenium bimetallic complexes \((\text{biq})_2\text{Ru}(\mu\text{-dpp})\text{Re(CO)}_3\text{Cl}[\text{PF}_6]_2\), \((\text{biq})_2\text{Ru}(\mu\text{-dpq})\text{Re(CO)}_3\text{Cl}[\text{PF}_6]_2\) and \((\text{biq})_2\text{Ru}(\mu\text{-dpb})\text{Re(CO)}_3\text{Cl}[\text{PF}_6]_2\) were synthesized and investigated as potential electrocatalytic and photocatalytic \(\text{CO}_2\) reduction agents. The catalytic efficiency of the Ru-Re bimetallic complexes were compared with the corresponding Ru(II) and Re(I) monometallic compounds.

Electrochemically, both the Re monometallic complexes and Ru-Re bimetallic compounds showed current increase under a \(\text{CO}_2\) atmosphere when compared to measurements conducted under \(\text{N}_2\). The only \(\text{CO}_2\) reduction product detected was \(\text{CO}\) following bulk electrolysis. However, neither series of compounds produced significant TON values, which indicates they are not efficient electrocatalytic \(\text{CO}_2\) reduction agent.

Photochemically, Re monometallic compounds were shown to reduce \(\text{CO}_2\) to \(\text{CO}\) with the assistance of \([\text{Ru(bpy)}_3]^{2+}\) as a photosensitizer. However, the Ru-Re bimetallic compounds failed to produce any \(\text{CO}\) upon irradiation with visible light. The inability of these systems to reduce \(\text{CO}_2\) may be due to the inefficient catalytic unit, electron transfer barrier, short excited state lifetime and back-electron transfer.
Reference


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