Chapter 3. Results and Discussion

Our goal was to develop a device for PEC capable of two electron collection on the central metal and study in detail its redox chemistry. This goal was met by manipulation of the central metal and bridging ligands used within a trimetallic framework. The first generation system for PEC, \([((bpy)_2Ru(dpb))_2IrCl_2](PF_6)_5\), performs two-electron collection when in solution with a sacrificial electron donor, where the electrons are collected on the dpb-Ir\(^{III}\)-dpb portion of the molecule.\(^{54,55}\) Our proposed device uses a central Rh metal center, \([((bpy)_2Ru(dpp))_2RhCl_2](PF_6)_5\). The relative energy level of the Rh d\(\sigma^*\) orbitals is lower than that of Ir. The bridging ligand dpp is a less conjugated system than that of dpb giving a higher \(\pi^*\) energy level. By tuning the bridging ligand and central metal, the orbital energies can be tuned such that electron collection on the central metal is favored in the trimetallic system under investigation, \([((bpy)_2Ru(dpp))_2RhCl_2](PF_6)_5\).

Mixed metal trimetallic systems are commonly studied as a mixture of stereoisomers. The complex under investigation in this thesis, \([((bpy)_2Ru(dpp))_2RhCl_2](PF_6)_5\), is used as a mixture of stereoisomers around the central rhodium metal. The various isomers associated with this complex have not been investigated individually. It should be noted, however, that through our electrochemical studies, we have determined that the two chloride ligands are cis to each other, as illustrated in Scheme 3.1.

The preparation of \([((bpy)_2Ru(dpp))_2RhCl_2](PF_6)_5\) was adapted from the literature.\(^{55}\) (Scheme 3.1) The synthesis of this compound involves coupling the dpp to the Ru first, then coupling to the central Rh. Using this “building block” approach, each bridging ligand and metal center in the complex can be individually modified. In the first step, Ru(bpy)_2Cl_2 was synthesized, with a typical yield of 50%, and purified by washing with diethyl ether and water to remove unreacted starting materials and side products. As the minor impurities that may remain can be removed by purification in subsequent steps,
Scheme 3.1. Synthetic Route to \{[(bpy)_2Ru(dpp)]_2RhCl_2\}(PF_6)_5.

Where bpy (2,2’-bipyridine), dpp (2,3-bis(2-pyridyl)pyrazine), Atom Types: blue = nitrogen, gray = carbon, green = chlorine, white = ruthenium, purple = rhodium.
no further purity tests were performed. In the second step, \([\text{Ru}(bpy)_2(dpp)](\text{PF}_6)_2\) was prepared by reacting \(\text{Ru}(bpy)_2\text{Cl}_2\) with 2 equiv of dpp. \([\text{Ru}(bpy)_2(dpp)](\text{PF}_6)_2\) was purified by column chromatography on alumina. Typical synthetic yield for \([\text{Ru}(bpy)_2(dpp)](\text{PF}_6)_2\) was 43%. In the third step, the target complex \{[(bpy)_2\text{Ru}(dpp)]_2\text{RhCl}_2\}(\text{PF}_6)_5\) was prepared by reacting \(\text{RhCl}_3 \cdot x\text{H}_2\text{O}\) with an excess of \([(bpy)_2\text{Ru}(dpp)](\text{PF}_6)_2\). The crude trimetallic complex was purified by size exclusion chromatography on a Sephadex LH-20 resin, with a 2:1 ethanol/acetonitrile eluent. Separation progress was monitored by UV-vis spectroscopy, combining fractions with superimposable spectra (+/- 5%). The desired fractions were combined and condensed by rotary evaporation. The product was recovered by flash precipitation in diethyl ether. Remaining fractions were combined, evaporated, and rechromatographed to increase product yield. Typical synthetic yield for \{[(bpy)_2\text{Ru}(dpp)]_2\text{RhCl}_2\}(\text{PF}_6)_5\) was 73%. A preliminary report of the electrochemical and spectroscopic characterization of the Ru,Rh mixed-metal trimetallic complex has been reported by the Brewer group.55

The electronic absorption spectrum of \([(bpy)_2\text{Ru}(dpp)](\text{PF}_6)_2\) (Figure 3.1) is dominated by intense intraligand and MLCT transitions. The lowest energy transition at 470 nm (shoulder) is assigned to the \(\text{Ru}(d\pi) \to \text{dpp}(\pi^*)\) charge transfer (MLCT).12 The other band in the visible region, 430 nm, is assigned to the \(\text{Ru}(d\pi) \to \text{bpy}(\pi^*)\) charge transfer (MLCT). In the UV region, absorptions were found at ca. 242, 249, and 294 nm. These bands are attributed to bpy and dpp based \(\pi \to \pi^*\) transitions.13,14 This monometallic complex is the major building block for the trimetallic complex of interest in this investigation, \{[(bpy)_2\text{Ru}(dpp)]_2\text{RhCl}_2\}(\text{PF}_6)_5\). A change in the spectroscopic properties of \([(bpy)_2\text{Ru}(dpp)](\text{PF}_6)_2\) is observed upon incorporation in \{[(bpy)_2\text{Ru}(dpp)]_2\text{RhCl}_2\}(\text{PF}_6)_5\).
The electronic absorption spectrum of \{[(bpy)_2Ru(dpp)]_2RhCl_2\}(PF_6)_5 (Figure 3.2) is also dominated by intense intraligand and MLCT transitions and is virtually superimposable with that of the previously studied complex, \{[(bpy)_2Ru(dpp)]_2IrCl_2\}(PF_6)_5.\textsuperscript{54-56} The lowest energy transition at 512 nm is assigned to the Ru(dπ → dpp(π*) charge transfer (MLCT). The red shift (to lower energy) upon multimetallic formation relative to [Ru(bpy)_2(dpp)]\textsuperscript{2+} is characteristic of a bridging dpp ligand. The other band in the visible region, 410 nm, is assigned to the Ru(dπ → bpy(π*) charge transfer (MLCT). In the UV region, absorptions were found at ca. 240, and 280 nm. These bands are attributed to bpy and dpp based π → π* transitions.\textsuperscript{55}

The electrochemical properties of supramolecular complexes like \{[(bpy)_2Ru(dpp)]_2RhCl_2\}(PF_6)_5 can best be understood by considering the electrochemical properties of the building blocks for which it was constructed. A cyclic voltammogram for [Ru(bpy)_2(dpp)](PF_6)_2 is shown in Figure 3.3.\textsuperscript{55} The potentials
measured using our parameters and conditions can be found in Table 3.1.

Figure 3.2. Electronic Absorption Spectrum for \{[(bpy)_2Ru(dpp)]_2RhCl_2\}(PF_6)_5 in Acetonitrile at Room Temperature, where bpy (2,2’-bipyridine), dpp (2,3-bis(2-pyridyl) pyrazine).

![Electronic Absorption Spectrum](image)

<table>
<thead>
<tr>
<th>Wavelength (nm)</th>
<th>ε x 10^4 (M⁻¹ cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>200</td>
<td>0</td>
</tr>
<tr>
<td>300</td>
<td>0.3</td>
</tr>
<tr>
<td>400</td>
<td>0.6</td>
</tr>
<tr>
<td>500</td>
<td>0.9</td>
</tr>
<tr>
<td>600</td>
<td>1.2</td>
</tr>
</tbody>
</table>

Figure 3.3. Cyclic Voltammogram of [Ru(bpy)_2(dpp)](PF_6)_2, where bpy = 2,2’-bipyridine, dpp = 2,3-bis(2-pyridyl)pyrazine. (CH_3CN with 0.1 M Bu_4NPF_6, Ag/AgCl (0.29 V vs. NHE, 0.44 V vs. Cp_2Fe^{0/+1}))

![Cyclic Voltammogram](image)
Table 3.1. Cyclic Voltammetric Data for [(bpy)$_2$Ru(dpp)](PF$_6$)$_2$, where bpy (2,2’-bipyridine), dpp (2,3-bis(2-pyridyl)pyrazine).

<table>
<thead>
<tr>
<th>$E_{1/2}$ (V)</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>+1.41</td>
<td>Ru$^{II/III}$</td>
</tr>
<tr>
<td>-1.02</td>
<td>dpp$^{0/-}$</td>
</tr>
<tr>
<td>-1.45</td>
<td>bpy$^{0/-}$</td>
</tr>
<tr>
<td>-1.63</td>
<td>bpy$^{0/-}$</td>
</tr>
</tbody>
</table>

*In CH$_3$CN with 0.1 M Bu$_4$NPF$_6$, referenced to Ag/AgCl (0.29 V vs. NHE).$^{13,66}$

The electrochemical behavior of this system displays a reversible Ru$^{II/III}$ oxidation, a first reduction as dpp$^{0/-}$, and two subsequent reductions as bpy$^{0/-}$.

The redox properties of the previously studied complex [Rh(dpp)$_2$Cl$_2$]$^{+1}$ are also relevant.$^{24,25}$ In [Rh(dpp)$_2$Cl$_2$]$^{+1}$, the first reduction is an irreversible metal-based reduction at −0.60 V, followed by two subsequent bridging ligand reductions at −1.05 and −1.19 V.$^{24,25}$

A cyclic voltammogram of {(bpy)$_2$Ru(dpp))$_2$RhCl$_2$}(PF$_6$)$_5$ is shown in Figure 3.4 and summarized in Table 3.2. A preliminary report of the electrochemical shows that the first reduction, at −0.35 V, is a Rh$^{III/I}$ irreversible reduction followed by subsequent bridging dpp and bpy reductions.$^{55}$ The two Ru$^{II}$ centers are reversibly oxidized to Ru$^{III}$ at +1.56 V. The oxidation of the two Ru$^{II}$ centers appears to be two overlapping one-electron waves, one for each Ru$^{II}$ oxidation, due to the large Δ$E_p$. This is summarized in the electrochemical mechanism shown below (Scheme 3.2).
Figure 3.4. Cyclic Voltammogram of \([[(\text{bpy})_2\text{Ru(dpp)}]_2\text{RhCl}_2]_5(\text{PF}_6)_5\), where bpy = 2,2’-bipyridine, dpp = 2,3-bis(2-pyridyl) pyrazine. (CH\(_3\)CN with 0.1 M Bu\(_4\)NPF\(_6\), Ag/AgCl (0.29 V vs. NHE, 0.44 V vs. Cp\(_2\)Fe\(^{0+/1}\)))\(^69\)

Table 3.2. Cyclic Voltammetric Data for \([[(\text{bpy})_2\text{Ru(dpp)}]_2\text{RhCl}_2]_5(\text{PF}_6)_5\), where bpy = 2,2’-bipyridine, dpp = 2,3-bis(2-pyridyl) pyrazine.

<table>
<thead>
<tr>
<th>(E_{1/2} ) (V)</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>+1.56</td>
<td>2 Ru(^{II}/III)</td>
</tr>
<tr>
<td>-0.35</td>
<td>Rh(^{III}/I)</td>
</tr>
<tr>
<td>-0.74</td>
<td>dpp, dpp/dpp, dpp(^-)</td>
</tr>
<tr>
<td>-1.01</td>
<td>dpp, dpp/dpp(^-), dpp(^-)</td>
</tr>
</tbody>
</table>

\(^*\)Reference: 55,69
\(^*\)In CH\(_3\)CN with 0.1 M Bu\(_4\)NPF\(_6\), referenced to Ag/AgCl (0.29 V vs. NHE)
Scheme 3.2. Proposed Electrochemical Mechanism for \( \{(bpy)_2Ru(dpp)\}_2RhCl_2\}(PF_6)_5 \), where bpy = 2,2'-bipyridine, dpp = 2,3-bis(2-pyridyl) pyrazine.\(^{55,22}\) (Synthesized Oxidation State Indicated by Bold Lettering)

\[
\begin{align*}
[(bpy)_2Ru^{III}(dpp)Rh^{III}Cl_2(dpp)Ru^{III}(bpy)_2]^{7+} \rightarrow & \quad \text{-1 e-} \uparrow \downarrow \quad \text{+1 e-} \\
[(bpy)_2Ru^{II}(dpp)Rh^{III}Cl_2(dpp)Ru^{III}(bpy)_2]^{6+} \rightarrow & \quad \text{-1 e-} \uparrow \downarrow \quad \text{+1 e-} \\
[(bpy)_2Ru^{II}(dpp)Rh^{II}Cl_2(dpp)Ru^{II}(bpy)_2]^{5+} \rightarrow & \quad \text{-2 e-} \uparrow \downarrow \quad \text{+2 e-} \\
[(bpy)_2Ru(dpp)Rh^{II}Cl_2(dpp)Ru(bpy)_2]^{3+} \rightarrow & \quad \text{-2 Cl} \downarrow \\
[(bpy)_2Ru(dpp)Rh^{II}(dpp)Ru(bpy)_2]^{5+} \rightarrow & \quad \text{-1 e-} \uparrow \downarrow \quad \text{+1 e-} \\
[(bpy)_2Ru(dpp)Rh^{II}(dpp^-)Ru(bpy)_2]^{4+} \rightarrow & \quad \text{-1 e-} \uparrow \downarrow \quad \text{+1 e-} \\
[(bpy)_2Ru(dpp^-)Rh^{II}(dpp^-)Ru(bpy)_2]^{3+} \rightarrow &
\end{align*}
\]

Rh\(^{III}\) species usually undergo a two-electron reduction to Rh\(^{I}\) (d\(^{6}\) to d\(^{8}\)). As previously illustrated, the Rh\(^{III}\) reduction can be due to two closely spaced one-electron waves. The central d\(^{6}\) rhodium in the initial complex, \( \{(bpy)_2Ru(dpp)\}_2RhCl_2\}(PF_6)_5 \), is pseudo-octahedral. Upon conversion to the Rh\(^{I}\) d\(^{8}\) electron configuration, the stable rhodium geometry reverts to square planar, resulting in a chemical step, the loss of two ligands (Figure 3.5\(^{26,55}\)).
A CV-BE-CV (cyclic voltammetry- bulk electrolysis- cyclic voltammetry) experiment was designed to probe the product of the two electron reduction of \([\{(bpy)_2Ru(dpp)\}_2RhCl_2\}(PF_6)_5\) using an H cell (Figure 2.1, pg 22). In this experiment, a series of cyclic voltammograms were performed on the analyte. This is followed by bulk electrolysis of the sample in order to obtain the two-electron reduced species. The progress of the bulk electrolysis is monitored with current vs. time profiles (Appendix I, pg 144) and cyclic voltammetry. Upon completion of the bulk electrolysis (when Rh\text{III/I} is no longer observed, \(i_p^a\) percent remaining = 8.2-18.1\%), the series of CVs is repeated to probe changes in the system.

This experiment was chosen because it allows for a direct comparison of the analyte before and after two-electron reduction without exposure to water or oxygen. In addition, the progress of the bulk electrolysis can be monitored by cyclic voltammetry. We expected that upon Rh reduction, the Rh\text{III/I} couple would not be present in the final cyclic voltammogram due to the irreversible nature of this process. The two Ru\text{II/III} oxidations should remain nearly overlapping, and the dpp, dpp/dpp\(^-\), dpp and dpp, dpp\(^-\)/dpp\(^-\), dpp\(^-\) couples should remain. Finally, the loss of two chloride ligands, resulting was expected.\(^26\) This should lead to the appearance of a 2Cl\(^-/\)Cl\(_2\) irreversible oxidation at +1.01 V.\(^{25}\)
Figure 3.5. A. \{[(bpy)_2Ru(dpp)]_2RhCl_2\}^{+5} and B. Rh^{I} Square Planar
\{[(bpy)_2Ru(dpp)]_2Rh\}^{+5}, where bpy = 2,2'-bipyridine, dpp = 2,3-bis(2-pyridyl)pyrazine.

Atom Types: blue = nitrogen, gray = carbon, green = chlorine, white = ruthenium, purple = rhodium.
Initial bulk electrolysis studies produced confusing results, inconsistent with the anticipated electrochemical behavior for this complex as presented in Scheme 3.2. These studies were repeated and gave the bulk electrolysis result as denoted in Figure 3.6. The cyclic voltammograms shown in Figure 3.6 were taken before and after bulk electrolysis at –1.0 V. This CV shows that the $i_p^c$ for the irreversible Rh$^{III}$ wave at – 0.62 V has been reduced by 91.3%, indicating that reduction from Rh$^{III}$ to Rh$^I$ has taken place. The two overlapping Ru$^{II/III}$ couples originally at +1.26 V now appear as two distinguishable peaks at +1.11 V and +1.25 V. The splitting of the ruthenium oxidations indicates the presence of two types of ruthenium ions. There is only a minor peak at +1.01 V representing free chloride oxidation.

An electronic absorption spectrum for the analyte was obtained before and after the bulk electrolysis experiment (Figure 3.7). The spectrum taken prior to bulk electrolysis is shown as a solid line; the spectrum taken after two-electron reduction of the central rhodium is shown as a dotted line. Upon two-electron reduction, a change in the electronic absorption spectrum of the analyte was seen. The Ru(dπ) → dpp(π*) charge transfer transition at 512 nm blue shifted to 470 nm. The Ru(dπ) → bpy(π*) charge transfer transition at 410 nm which was clear in the initial spectrum was not easily observed in the final spectrum. The MLCT at 470 nm is rather broad, overlapping this region. The UV-region remains essentially unchanged.
Figure 3.6. Cyclic Voltammograms of \{[(bpy)_{2}Ru(dpp)]_{2}RhCl_{2}\}(PF_{6})_{5} Before (A) and After (B) Bulk Electrolysis at –1.0 V, where bpy = 2,2'-bipyridine, dpp 2,3-bis(2-pyridyl)pyrazine. (CH_{3}CN with 0.1 M Bu_{4}NPF_{6}, Ag/AgNO_{3} (0.56 V vs. NHE))
Figure 3.7. Electronic Absorption Spectrum of \([(bpy)_2Ru(dpp)]_2RhCl_2\}(PF_6)_5 in Acetonitrile; Before Bulk Electrolysis at –1.0 V (Solid Line), and After Bulk Electrolysis at –1.0 V (Dotted Line), where bpy = 2,2’-bipyridine, dpp 2,3-bis(2-pyridyl) pyrazine.

A second series of bulk electrolysis experiments yielded instead the originally anticipated electrochemical results. The bulk electrolysis result for this experiment, after two-electron reduction, is shown in Figure 3.8. The same sample of \([(bpy)_2Ru(dpp)]_2RhCl_2\}(PF_6)_5, a Ag/AgCl reference electrode, and a previously opened bottle of acetonitrile were utilized in the experimental procedure. After electrolysis, the \(i_p^c\) for the irreversible RhIII wave was reduced by 73.3%. There was no splitting of the two RuII/III oxidations. A chloride oxidation appeared at +1.01 V. These findings are consistent with the proposed electrochemical scheme (Scheme 3.2, page 31).

Electronic absorption spectroscopy was again used to probe the product of the electrolysis (Figure 3.9). Spectra were obtained before and after the bulk electrolysis experiment. The initial spectrum is shown as a solid line; the spectrum taken after bulk electrolysis is shown as a dotted line. Upon two-electron reduction, a change in the electronic absorption spectrum can be seen. There is a shift in the Ru(d\(\pi\)) \(\rightarrow\) dpp(\(\pi^*\)) charge transfer transition from 512 to 470 nm. The Ru(d\(\pi\)) \(\rightarrow\) bpy(\(\pi^*\)) charge transfer transition is distinct and observable in the final spectrum and has shifted from 410 to 412 nm.
Figure 3.8. Second Series Bulk Electrolysis Result for \{[(bpy)_2Ru(dpp)]_2RhCl_2\}(PF_6)_5. Before (A) and After (B) Bulk Electrolysis at –0.5 V, where bpy = 2,2'-bipyridine, dpp = 2,3-bis(2-pyridyl)pyrazine. (CH_3CN with 0.1 M Bu_4NPF_6, Ag/AgCl (0.29 V vs. NHE, 0.44 V vs. Cp_2Fe^{0.5}))\(^{69}\)
Figure 3.9. Electronic Absorption Spectrum of \(\{(bpy)_2\text{Ru(dpp)}\}_2\text{RhCl}_2\}\{\text{PF}_6\}_5\) in Acetonitrile; Before Bulk Electrolysis at –1.0 V (Dotted Line), and After Bulk Electrolysis at –1.0 V (Solid Line), where bpy = 2,2’-bipyridine, dpp = 2,3-bis(2-pyridyl)pyrazine.

The cause for the differing results in the bulk electrolysis experiments was not immediately apparent. One potential uncontrolled variable was water content in the acetonitrile. It is common for acetonitrile to contain water at variable levels. Typically, “dry” acetonitrile has millimolar H_2O content. A potential water effect on the product formed was proposed, as detailed in Scheme 3.3. This was tested in a series of experiments controlling water content.

Scheme 3.3. Proposed Water Modulation of the Reduction Product.

\[
\begin{align*}
\{(bpy)_2\text{Ru(dpp)}\}_{\text{Rh}^{III}}\text{Cl}_2\{(dpp)\text{Ru(bpy)}_2\}\quad & + \quad 2\text{e}^- \\
\{(bpy)_2\text{Ru(dpp)}\}_{\text{Rh}^{I}}\text{Cl}_2\{(dpp)\text{Ru(bpy)}_2\}\quad & + \quad 2\text{Cl}^- \\
\text{Dry CH}_3\text{CN} & \quad \rightarrow & \quad \text{Wet CH}_3\text{CN}
\end{align*}
\]
When \{[(bpy)_2Ru(dpp)]_2RhCl_2\}(PF_6)_5 undergoes two-electron reduction in dry acetonitrile, the product undergoes decomposition to \([(bpy)_2Ru(dpp)]^{+2}\) and \([(bpy)_2Ru(dpp)RhCl_2]^{+1}\) (Scheme 3.4). The initial bulk electrolysis results, although not what was anticipated, support this proposed trimetallic breakdown. This result is attributed to the splitting of the Ru\textsuperscript{II/III} couple and the absence of free chloride. Two Ru\textsuperscript{II/III} waves, at +1.25 V and +1.11 V, were detected in the bulk electrolysis result in dry acetonitrile. The absence of a significant irreversible 2Cl\textsuperscript{-}/Cl\textsubscript{2} anodic peak at +1.01 V was noted. Upon two-electron reduction in the presence of water, loss of two Cl\textsuperscript{-} ligands results. This yields the desired square planar, Rh\textsuperscript{I} trimetallic complex, \{[(bpy)_2Ru(dpp)]_2Rh\}^{+5}.

The basis for the water modulation of product distribution is solubility. Upon two-electron reduction, the d\textsuperscript{6} Rh\textsuperscript{III} converts to a d\textsuperscript{8} Rh\textsuperscript{I}. This looses two ligands to become square planar. This can happen several different ways. Possible ligand loss products may include: \{[(bpy)_2Ru(dpp)]_2Rh\}^{+5}, \([(bpy)_2Ru(dpp)RhCl_2]^{+1}\), or products involving one N-Ru bond breaking. Upon two-electron reduction in the absence of water, the loss of the aromatic, bidentate, N-N ligand in the solvent (acetonitrile) is favored over the loss of Cl\textsuperscript{-}. This leads to the breakdown of the reduced trimetallic into \([(bpy)_2Ru(dpp)]^{+2}\) and \([(bpy)_2Ru(dpp)RhCl_2]^{+1}\). In the presence of water, the loss of Cl\textsuperscript{-} is favored. This leads to the two Cl\textsuperscript{-} ligands being lost, producing a Rh\textsuperscript{I} based trimetallic species.

The steric effects of the trimetallic complex \{[(bpy)_2Ru(dpp)]_2RhCl_2\}(PF_6)_5 also may play a role in product formation upon two-electron reduction. The two-electron reduction of a similar system, \([(bpy)_2RhCl_2]^{+1}\) was previously investigated by DeArmond.\textsuperscript{25} Upon two-electron reduction, a shift in geometry from pseudo-octahedral occurs, resulting in a square planar complex (two ligands must be lost). For \([(bpy)_2Rh\textsuperscript{III}Cl_2]^{+1}\), the chlorides are consistently lost, resulting in \([(bpy)_2Rh\textsuperscript{I}]^{+1}\). We anticipated that \{[(bpy)_2Ru(dpp)]_2RhCl_2\}(PF_6)_5 would exhibit the same behavior upon
two-electron reduction. As \{[(bpy)_2Ru(dpp)]_2RhCl_2\}^{+5} is more sterically hindered around the central rhodium than \[(bpy)_2Rh^{III}Cl_2\]^{+1}, it is very likely that this plays a role in product formation upon two-electron reduction.

Scheme 3.4. Results of Water Modulation of Product Distribution Upon Two-Electron Reduction in Dry Acetonitrile: Breakdown of the \{[(bpy)_2Ru(dpp)]_2RhCl_2\}^{+3} Trimetallic (A) into \{[(bpy)_2Ru(dpp)]RhCl_2\}^{+1} (B) and \[(bpy)_2Ru(dpp)\]^{+2} (C), where bpy (2,2’-bipyridine), dpp (2,3-bis(2-pyridyl)pyrazine).

Atom Types: blue = nitrogen, gray = carbon, green = chlorine, white = ruthenium, purple = rhodium.

To test if \[(bpy)_2Ru(dpp)\]^{+2} was being produced upon two-electron reduction in dry acetonitrile, a cyclic voltammogram of \[(bpy)_2Ru(dpp)\]^{+2} was run using a Ag/AgNO_3
reference electrode. This was compared to cyclic voltammograms of
\( \{(bpy)_2Ru(dpp)\}_2Rh^{III}Cl_2\}^{+5} \) taken after bulk electrolysis which result in the trimetallic
breakdown into \( \{(bpy)_2Ru(dpp)\}^{+2} \) and \( \{(bpy)_2Ru(dpp)RhCl_2\}^{+1} \) (Figure 3.10).

When cyclic voltammograms of \( \{(bpy)_2Ru(dpp)\}^{+2} \) and the dry bulk electrolysis
product are compared, the following points are noted. The Ru\(^{II/III}\) oxidation for
\( \{(bpy)_2Ru(dpp)\}^{+2} \) occurs at +1.11 V, as does the first Ru\(^{II/III}\) oxidation for the bulk
electrolysis product. The dpp\(^0/-\) reduction also occurs at the same potential in both cyclic
voltammograms, at -1.29 V. When the cyclic voltammograms are overlaid, each
\( \{(bpy)_2Ru(dpp)\}^{+2} \) oxidation or reduction overlaps with the corresponding wave in the
bulk electrolysis result. The dry bulk electrolysis product contains \( \{(bpy)_2Ru(dpp)\}^{+2} \).
The remaining Ru\(^{II/III}\) oxidation for the bulk electrolysis product occurs at +1.25 V. This
is consistent with the oxidation potential for the multimetallic system, supporting the
other proposed product, \( \{(bpy)_2Ru(dpp)RhCl_2\}^{+1} \). This experiment supports the proposal
that upon two-electron reduction in the absence of water the trimetallic complex
\( \{(bpy)_2Ru(dpp)\}_2Rh^{I}Cl_2\}^{+3} \) breaks down into \( \{(bpy)_2Ru(dpp)\}^{+2} \) and
\( \{(bpy)_2Ru(dpp)RhCl_2\}^{+1} \).

An electronic absorption spectroscopy subtraction study was also completed
(Figure 3.11). An electronic absorption spectrum of \( \{(bpy)_2Ru(dpp)\}_2Rh^{III}Cl_2\}^{+5} \) was
taken after bulk electrolysis at -1.0 V in the absence of water. It was clear that this
subtraction contained peaks consistent with the presence of \( \{(bpy)_2Ru(dpp)\}^{+2} \). To
attempt to observe the spectrum of the other product, the electronic absorption spectrum
of \( \{(bpy)_2Ru(dpp)\}^{+2} \) was subtracted from the spectrum of the reaction product. To
achieve this, the spectrum of \( \{(bpy)_2Ru(dpp)\}^{+2} \) is multiplied by 2 so that the maximum
absorbance would match that of the trimetallic product. When the subtraction is
performed, the resulting spectrum has the lowest energy transition at 508 nm, consistent
with a Ru(d\(\pi\)) \( \rightarrow \) dpp(\(\pi^*\)) charge transfer (MLCT) for a bridging dpp ligand. This
further supports the breakdown of the trimetallic upon two-electron reduction in the
Figure 3.10. Cyclic Voltammogram of $\{[(\text{bpy})_2\text{Ru(dpp)}]_2\text{Rh}^{\text{III}}\text{Cl}_2\}^{+5}$ After Bulk Electrolysis at −1.0 V (A), Cyclic Voltammogram of $\{[(\text{bpy})_2\text{Ru(dpp)}]\}^{+2}$ (B), and A and B overlaid (C), where bpy = 2,2'-bipyridine, dpp = 2,3-bis(2-pyridyl)pyrazine. (CH$_3$CN with 0.1 M Bu$_4$NPF$_6$, Ag/AgNO$_3$ (0.56 V vs. NHE))\textsuperscript{69}
Figure 3.11. (A) Electronic Absorption Spectrum of: \([\text{[(bpy)}_2\text{Ru(dpp)}]_2\text{RhCl}_2\text{]}\text{(PF}_6\text{)}_5\) in Acetonitrile, After Bulk Electrolysis at –1.0 V (Light Line); \([\text{[(bpy)}_2\text{Ru(dpp)}]\text{(PF}_6\text{)}_2\) (Heavy Line), (B) Result of Subtraction of Spectrum of \([\text{[(bpy)}_2\text{Ru(dpp)}]\text{(PF}_6\text{)}_2\) (Heavy Line) from Spectrum of \([\text{[(bpy)}_2\text{Ru(dpp)}]_2\text{RhCl}_2\text{]}\text{(PF}_6\text{)}_5\) After Bulk Electrolysis at –1.0 V (Light Line), where bpy = 2,2’-bipyridine, dpp = 2,3-bis(2-pyridyl)pyrazine.
absence of water to $[(\text{bpy})_2 \text{Ru(dpp)}]^{2+}$ and $[(\text{bpy})_2 \text{Ru(dpp)RhCl}_2]^{+1}$.

In order to test the hypothesis that water concentration modulated the product distribution, adventitious sources of water were identified. The aqueous Ag/AgCl reference electrode, the acetonitrile, and the electrolyte (Bu$_4$NPF$_6$) could all introduce water into the system. A typical CV-BE-CV experiment can take as long as five hours. Sufficient leakage of water from the reference electrode could occur. To limit extraneous sources of water, all subsequent experiments were carried out using a non-aqueous, acetonitrile-based Ag/AgNO$_3$ reference electrode. Acetonitrile is hygroscopic. To limit the water content, acetonitrile was deoxygenated and passed through activated alumina in the glovebox. The acetonitrile was stored in the glovebox until it was used and transferred by syringe as needed. Bulk electrolysis experiments were performed in solutions of varying, but quantitatively measured water concentration, from no added water to 3.0 M H$_2$O in CH$_3$CN.

The first CV-BE-CV experiment was completed in dry acetonitrile with no added water. This was done to confirm the result obtained under these initial conditions. The cyclic voltammogram for the product, shown in Figure 3.12, matches the result obtained in initial bulk electrolysis experiments (see Figure 3.7). The cyclic voltammogram shows the splitting of the Ru$^{II/III}$ oxidations and shows little indication of free chloride. This is consistent with the proposed dry mechanism of the breakdown of the reduced Rh$^{I}$ trimetallic species $\{(\text{bpy})_2 \text{Ru(dpp)}\}_2 \text{RhCl}_3$ into $[(\text{bpy})_2 \text{Ru(dpp)}]^{2+}$ and $[(\text{bpy})_2 \text{Ru(dpp)RhCl}_2]^{+1}$.

Next, bulk electrolyses were run with increasing amounts of added water. At concentrations 0.01 M and 0.1 M water in acetonitrile, the bulk electrolysis result matched the dry result, as shown above. When the water concentration was increased to 1.0 M, a mixed bulk electrolysis product resulted (Figure 3.13).
Figure 3.12. Bulk Electrolysis Result for \{[(bpy)\textsubscript{2}Ru(dpp)]\textsubscript{2}RhCl\textsubscript{2}\}(PF\textsubscript{6})\textsubscript{5} – Dry. Before (A) and After (B) Bulk Electrolysis at –1.0 V, where bpy = 2,2’-bipyridine, dpp = 2,3-bis(2-pyridyl)pyrazine. (CH\textsubscript{3}CN with 0.1 M Bu\textsubscript{4}NPF\textsubscript{6}, Ag/AgNO\textsubscript{3} (0.56 V vs. NHE))\textsuperscript{69}
Figure 3.13. 1.0 M H₂O in Acetonitrile Bulk Electrolysis Result for \{[(bpy)₂Ru(dpp)]₂RhCl₂\}(PF₆)₅. Before (A) and After (B) Bulk Electrolysis at -1.0 V, where bpy = 2,2'-bipyridine, dpp = 2,3-bis(2-pyridyl)pyrazine. (CH₃CN with 0.1 M Bu₄NPF₆, Ag/AgNO₃ (0.56 V vs. NHE))\(^{69}\)
At 0.1 M water in acetonitrile, both a significant splitting of the Ru\textsuperscript{II/III} oxidation and a significant Cl\textsuperscript{−} wave were observed. This indicates that both the products which result in the presence of water, \{[(bpy)\textsubscript{2}Ru(dpp)]\textsubscript{2}Rh\textsuperscript{1+}Cl\textsuperscript{−}\}\textsuperscript{5+}, and 2 Cl\textsuperscript{−}, and the products which result in the absence of water, [(bpy)\textsubscript{2}Ru(dpp)]\textsuperscript{+2} and [(bpy)\textsubscript{2}Ru(dpp)RhCl\textsubscript{2}]\textsuperscript{+1} are present. Both however, are present in smaller quantities than in bulk electrolysis experiments, producing only wet or dry results. This mixed result with both the wet and dry products was also seen in previous bulk electrolysis studies.

When the water concentration was increased to 3.0 M water in acetonitrile and the bulk electrolysis experiment was repeated, the desired electrolysis product was not clearly produced (Figure 3.14). The cyclic voltammograms taken both before and after two-electron reduction show that the analyte concentration is low, as the waves are consistently very small as compared to the background. For each of the bulk electrolysis experiments, the amount of \{[(bpy)\textsubscript{2}Ru(dpp)]\textsubscript{2}RhCl\textsubscript{2}\}(PF\textsubscript{6})\textsubscript{5} to be used was weighed out, and was approx. 0.047 g. For this experiment, 0.046 g of \{[(bpy)\textsubscript{2}Ru(dpp)]\textsubscript{2}RhCl\textsubscript{2}\}(PF\textsubscript{6})\textsubscript{5} was used. When the initial cyclic voltammograms were run, the waves were very small, indicating low concentration. The solution was remade, doubling the analyte concentration. The low concentration seen in the cyclic voltammogram indicates that there is presumably excess salt (KPF\textsubscript{6}) present in the sample. This was not detected prior to running the bulk electrolysis experiments, as purity of \{[(bpy)\textsubscript{2}Ru(dpp)]\textsubscript{2}RhCl\textsubscript{2}\}(PF\textsubscript{6})\textsubscript{5} was established by cyclic voltammetry and this does not detect electroinactive impurities. The solvent being used is 3.0 M water in acetonitrile. At this concentration, the electrolysis of the water in the solvent may begin to be a factor. These factors lower the signal/noise in Figure 3.14. To try to further elucidate the results of the bulk electrolysis at 3.0 M water in acetonitrile, a background subtraction was performed, the results of which are shown in Figure 3.15. This background subtraction has made the oxidative and reductive waves more visible. The chloride peak is clear, and the Ru\textsuperscript{II/III} oxidation as well as the ligand reductions are more prominent than in the previous figure.
Figure 3.14. 3.0 M H2O in Acetonitrile Bulk Electrolysis Result for \{[(bpy)_2Ru(dpp)]_2RhCl_2\}(PF_6)_5. Before (A) and After (B) Bulk Electrolysis at –1.0 V, where bpy = 2,2’-bipyridine, dpp = 2,3-bis(2-pyridyl) pyrazine. (CH3CN with 0.1 M Bu4NPF6, Ag/AgNO3 (0.56 V vs. NHE))
Osteryoung square wave voltammograms (OSWV) were also completed on the sample after bulk electrolysis in 3.0 M water (Figure 3.16). This square wave electrochemical technique is more sensitive than cyclic voltammetry, and can be used to detect species in lower concentration due to the higher signal-to-noise. The oxidative OSWV results (A) indicate the presence of free chloride. There is a small amount of splitting of the two Ru$^{II/III}$ oxidations. The predominant Ru oxidation at +1.25 V is the $\{[(bpy)_2Ru(dpp)]_2Rh^1\}^{+5}$ oxidation. A small amount of $[(bpy)_2Ru(dpp)]^{+2}$ is also present in the solution, as indicated by the Ru oxidation at +1.11 V. The reductive OSWV results (B) indicate that the Rh$^{III/I}$ reduction has taken place. A moderate amount of Rh$^{III}$ does remain, however, as indicated by the peaks at –0.9 to –1.0 V (percent rhodium remaining, $i_p$ remaining = 39.8%). These findings are consistent with the proposed electrochemical
scheme (see Scheme 3.2, pg 32). The results indicate that although a small amount of 
\[ [(\text{bpy})_2\text{Ru(dpp)}]^+ \] has been produced, this is the “mixed” result portion, the primary 
result is the desired square planar, Rh\(^I\) trimetallic: 
\[ \{[(\text{bpy})_2\text{Ru(dpp)}]_2\text{Rh}\}^{+5} \], as shown in 
Figure 3.5. This will be addressed further in the Future Work section.

Figure 3.16. Osteryoung Square Wave Voltammograms for the 3.0 M H\(_2\)O in Acetonitrile 
Bulk Electrolysis Result for 
\[\{[(\text{bpy})_2\text{Ru(dpp)}]_2\text{RhCl}_2\}(\text{PF}_6)_5\], Oxidative (A), Reductive 
(B). After Bulk Electrolysis at –1.0 V, where bpy = 2,2’-bipyridine, 
dpp = 2,3-bis(2-pyridyl) pyrazine. (CH\(_3\)CN with 0.1 M Bu\(_4\)NPF\(_6\), Ag/AgNO\(_3\) (0.56 V vs.
NHE)).
The bulk electrolysis experiment at 3.0 M in water used a platinum disk-working electrode. This working electrode had been sufficient at all other water concentrations. However, at 3.0 M in water significant background current resulted, as platinum lowers the overpotential for water reduction. Making use of a glassy carbon-working electrode should help to control the water redox problems. Preliminary studies were completed using wet acetonitrile and both platinum and glassy carbon working electrodes. Cyclic voltammograms of \[((bpy)_2Ru(dpp))^{+2} \] used 3.0 M water in acetonitrile as the solvent, Ag/AgNO₃ reference electrode, with both a glassy carbon and platinum disk working electrode (Figure 3.17). These results showed first that larger amounts of analyte need to be added to the solution to get a reasonable signal. Secondly, in comparing Figure 3.17 (A) and (B), it is clear that at this water concentration (3.0 M) the glassy carbon working electrode improves the signal in the resulting cyclic voltammogram. This point is addressed in further detail in the future work section.

I conclude that upon two-electron reduction in the absence of water, the \{[(bpy)_2Ru(dpp)]_2Rh^ICl_2\}^{+3} trimetallic complex breaks down into \[((bpy)_2Ru(dpp))^{+2} \] and \[((bpy)_2Ru(dpp)RhCl_2)^{+1} \] (see Scheme 3.4). This breakdown is attributed to the instability of the d⁶ Rh^I intermediate in an octahedral configuration, resulting in decomposition to square planar will occur. The \[((bpy)_2Ru(dpp))(PF₆)_2 \] is more readily solubilized than the chloride in dry acetonitrile. Therefore, I propose that in dry acetonitrile the loss of the \[((bpy)_2Ru(dpp))^{+2} \] portion of the molecule will result, which leaves the square planar bimetallic, \[((bpy)_2Ru(dpp)RhCl_2)^{+1} \].
Figure 3.17. Cyclic Voltammogram of [(bpy)$_2$Ru(dpp)](PF$_6$)$_2$ in 3.0 M H$_2$O in Acetonitrile using a Platinum Disk (A) and Glassy Carbon (B) Working Electrode, where bpy = 2,2'-bipyridine, dpp = 2,3-bis(2-pyridyl) pyrazine. (CH$_3$CN with 0.1 M Bu$_4$NPF$_6$, Ag/AgNO$_3$ (0.56 V vs. NHE))$^{69}$