

Chapter 2. Experimental

Materials.

All chemicals were purchased from Aldrich Chemical Co. and were used as received, unless otherwise noted. Acetonitrile was Burdick and Jackson spectrophotometric grade and was purchased from Baxter. $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ and $\text{RhCl}_3 \cdot x\text{H}_2\text{O}$ were purchased from Johnson Matthey/Alpha Aesar. Tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) used in electrochemical and spectroelectrochemical experiments was prepared by metathesis of tetrabutylammonium bromide and potassium hexafluorophosphate. The Bu_4NPF_6 was recrystallized several times from ethanol, filtered, dried in a vacuum oven for 5-6 hours, and stored in a vacuum desiccator. Adsorption alumina, 80-200 mesh, was purchased from Fisher Scientific Co. Sephadex size-exclusion resin LH-20 was purchased from Sigma.

Electronic Absorption Spectroscopy.

All electronic absorption spectra were recorded at room temperature on a Hewlett Packard 8452A spectrophotometer with a 2 nm resolution and a 190-820 wavelength range. A quartz cell with 1 cm path length was used for measurements. Samples were dissolved in ethanol or acetonitrile.

Extinction coefficients were determined by preparing a sample of analyte in acetonitrile in which the concentration was known. Starting solutions were prepared by dissolving 0.00100 g of analyte in 100 mL of spectral grade acetonitrile. Multiple dilutions (four total) were carried out; each successive dilution contained 10.0 mL of the previous solution, which was diluted to 100.0 mL final volume in a volumetric flask. Electronic absorption spectra measured at each concentration.

Electrochemistry.

Analyses were carried out in UV-grade acetonitrile, unless otherwise noted. Dry acetonitrile was obtained by deoxygenating with Ar then passing the acetonitrile through an activated alumina column in the glovebox. This acetonitrile was stored under inert

atmosphere in a Schlenk vessel, and the appropriate amount transferred by syringe immediately prior to the start of the experiment. Solutions were bubbled with argon for 15 min. prior to each run, and blanketed with argon during. Supporting electrolyte was 0.1 M Bu₄NPF₆.

Cyclic Voltammetry.

Cyclic voltammetry experiments were carried out using a Bioanalytical Systems Inc. 100W system. A standard 3-electrode system was utilized: Ag/AgCl (0.29 V vs. NHE) or Ag/AgNO₃ (0.56 V vs. NHE) reference electrode, a 1.9 mm diameter Pt disk working electrode, and a Pt wire auxiliary electrode.⁶⁹ The reference electrode was checked periodically against a 1.0 mM solution of ferrocene; the FeCp₂⁺/FeCp₂ potential is 0.665 V vs. NHE in 0.1 Bu₄NPF₆ in acetonitrile.⁶⁹ A scan rate of 200 mV/s was used, unless otherwise noted.

Spectroelectrochemistry.

Spectroelectrochemical experiments used a BAS CV-27 potentiostat, an HP 8452A spectrophotometer, a modified spectroelectrochemical cell, an Ag/AgCl reference electrode (0.29 vs. NHE), and platinum cage working and auxiliary electrodes.⁶⁹ Aliquots were taken out of the electrolysis cell, diluted, and electronic absorption spectra obtained from these to monitor the electrolysis. Experiments are all carried out in acetonitrile and 0.1M Bu₄NPF₆, unless otherwise noted. In experiments indicating that dry acetonitrile was used, the acetonitrile was deoxygenated and run down an activated alumina column in the glovebox, and was stored under inert atmosphere. Immediately prior to the start of each experiment, the amount of acetonitrile needed was removed by syringe and filtered, using a 0.25μ syringe filter. Solutions were bubbled with argon for 30 minutes prior to each experiment to reach saturation, and for the duration of the experiment. The solution was electrolyzed until no further significant spectral changes were noted (± 5% at 512 nm).

CV-BE-CV.

A sequence of electrochemical methods was used to probe the product obtained following the reduction of the mixed-metal trimetallic complex, $\{[(bpy)_2Ru(dpp)]_2RhCl_2\}(PF_6)_5$. In this experiment, a series of cyclic voltammograms were performed on a sample of the analyte prior to beginning the bulk electrolysis. The electrolysis was then started at the desired potential. This is a technique that applies a constant potential to the working electrode while monitoring current. Upon completion of the electrolysis, a second series of cyclic voltammograms are completed, utilizing the same parameters as the initial series. Bulk electrolysis was determined to be complete by the disappearance of the $Rh^{III/I}$ wave (i_p^a remaining = 8.2-18.1%). With this technique, the effect of the electrolysis on each electrochemically active portion of the molecule may be studied.

Our experiment required the use of a custom cell to accommodate cyclic voltammetry (CV) and bulk electrolysis (BE) in one compartment (see Figure 2.1). These CV-BE-CV experiments were completed on a Bioanalytical Systems Inc. 100 W potentiostat. A modified H cell was used to perform the CV-BE-CV studies. The working compartment contained all of the electrodes necessary to monitor the progress of the experiment by cyclic voltammetry, and the working and reference electrodes for the bulk electrolysis experiment. These included a Ag/AgCl (0.29 V vs. NHE) or Ag/AgNO₃ (0.59 V vs. NHE) reference electrode (CV and BE), platinum mesh working electrode (BE), a platinum disk or glassy carbon working electrode (CV), and the platinum wire auxiliary electrode (CV).⁶⁹ These electrodes were immersed in a 0.1 M Bu₄NPF₆ in acetonitrile solution, which contained the analyte. The auxiliary compartment was connected to this by fine fritted glass, and contained the carbon cloth auxiliary electrode for the bulk electrolysis. The auxiliary electrode (BE) was immersed in a 0.1 M Bu₄NPF₆ in acetonitrile solution. The same reference electrode was used for both the bulk electrolysis and cyclic voltammetry measurements.

Bulk Electrolysis Studies of $\{[(bpy)_2Ru(dpp)]_2RhCl_2\}(PF_6)_5$.

Initial bulk electrolysis studies making use of a Ag/AgCl reference electrode, untreated acetonitrile, and the experimental design outlined previously gave inconsistent results. These experiments were repeated using varied solvents including dried acetonitrile, 0.01 M H₂O in acetonitrile, and untreated acetonitrile. At this point, it was considered that the water from the aqueous reference electrode may be a factor in the inconsistent results. A Ag/AgNO₃ (non-aqueous) reference electrode was used for the remaining experiments. These include CV-BE-CV experiments in untreated Burdick and Jackson UV-grade (B&J) acetonitrile (0.05% water content), B&J acetonitrile dried over activated alumina, 0.01 M H₂O in acetonitrile, 0.1 M H₂O in acetonitrile, 1.0 M H₂O in acetonitrile, and 3.0 M H₂O in acetonitrile (Table 2.1). New solvent mixtures were prepared immediately before each experiment. The acetonitrile used in the solvent mixtures was taken from a bulk stock of dried acetonitrile that was stored in the glovebox. Acetonitrile was dried by passing it through an activated alumina column in the glovebox.

Figure 2.1. Schematic for the Bulk Electrolysis Modified H Cell.

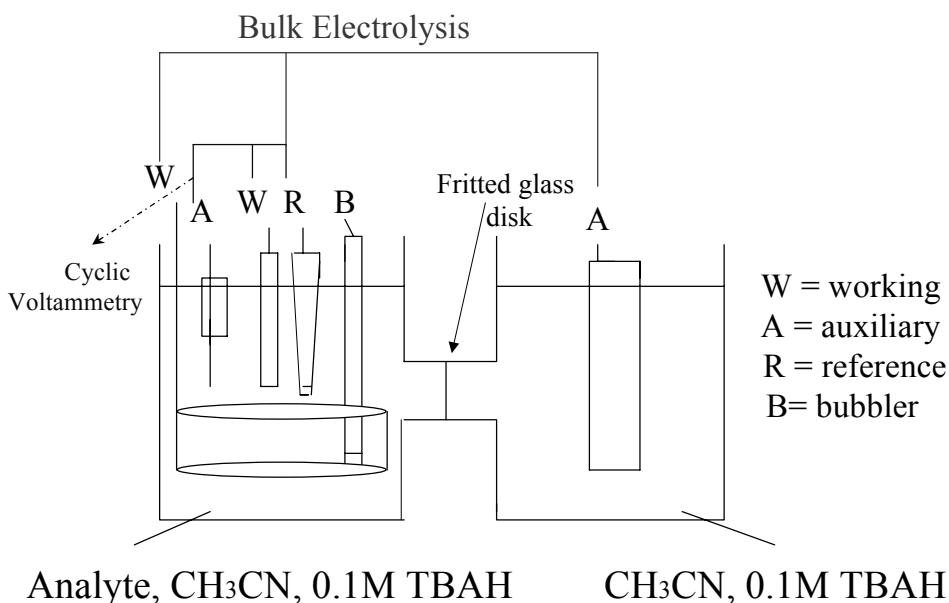


Table 2.1. Water Concentrations in Acetonitrile Used in Bulk Electrolysis Studies.

<u>Sample in CH₃CN</u>	<u>Vol. H₂O (mL)</u>	<u>Vol. Total (mL)</u>
dry	0	200
0.01 M H ₂ O	0.036	200
0.1 M H ₂ O	0.372	200
1.0 M H ₂ O	3.6	200
3.0 M H ₂ O	10.8	200

Synthesis.

Ru(bpy)₂Cl₂:

The synthesis of Ru(bpy)₂Cl₂ is a modification of a literature preparation.⁷⁰ LiCl (8.427 g, 0.1986 mol), 2,2'-bipyridine (9.362 g, 0.06000 mol), RuCl₃·3H₂O (7.799 g, 0.03760 mol) were combined in 50 mL dimethylformamide in a 250 mL round bottom flask. The mixture was heated at reflux with stirring for eight hours. The solution changed in color from red-brown to dark purple. The mixture was removed from heat and cooled overnight. The solution was then added to 250 mL of acetone in a large beaker, covered, and placed in a freezer overnight to induce precipitation. The black product was then collected by vacuum filtration, rinsed three times with 25 mL of water, and rinsed three times with 25 mL of diethyl ether. The product was then dried and stored in a vacuum desiccator. Yield: 50%, 8.24 g, 0.017 mol.

[(bpy)₂Ru(dpp)](PF₆)₂:

The synthesis of this compound is a modification of the literature preparation.¹² 2,3-bis(2-pyridyl)pyrazine (1.463 g, 0.006240 mol), Ru(bpy)₂Cl₂ (2.072 g, 0.004280 mol), and 90 mL 2:1 ethanol/water were combined in a 250 mL round-bottom flask. The mixture was heated at reflux with for 3 h. The product was flash precipitated by the addition of the reaction mixture to saturated aqueous KPF₆ (approximately 400 mL). The crude product was isolated by vacuum filtration and dried in a vacuum desiccator. The

crude product was purified by column chromatography on alumina, with a 3:2 toluene/acetonitrile eluent. The desired product is an orange band, which elutes first, followed by a purple byproduct band. Chromatography was repeated twice to insure purity. Yield: 43%, 1.724 g, 1.84×10^{-3} mol.

{{(bpy)₂Ru(dpp)}₂RhCl₂}(PF₆)₅:

The synthesis of this compound is a modification of one developed in our laboratory.⁵⁵ [(bpy)₂Ru(dpp)](PF₆)₂ (0.3155g, 0.3367 mmol), RhCl₃·xH₂O (0.0450 g, 0.215 mmol) were combined with 15 mL 2:1 ethanol/water in a one-neck 100 mL round-bottom flask. The mixture was heated at reflux with stirring for 1 h. The product was then flash precipitated by the addition of the reaction mixture to saturated aqueous KPF₆ (approximately 100 mL). The crude product was isolated using vacuum filtration, and dried in a vacuum desiccator. The crude product was purified by size exclusion chromatography using a Sephadex LH-20 resin, with a 2:1 ethanol/acetonitrile eluent. The column was approximately 106.7 cm in length and 2.5 cm in diameter. A berry-colored band eluted first, followed very closely by an orange band. Fractions were collected and checked by electronic absorption spectroscopy. The berry-colored fractions were combined after comparing their UV-visible spectra to give the desired trimetallic product. Solvent was removed from these samples by rotary evaporation. The product was dissolved in acetonitrile and precipitated in diethyl ether. Purified product was isolated using vacuum filtration. “Impure” fractions were rechromatographed to increase yield. Yield: 73%, 0.271 g, 1.23×10^{-4} mol.