Inorg. Chem. **1996,** *35,* 6974−6980

Bipyrimidine-Bridged Mixed-Metal Trimetallic Complexes of Ruthenium(II) with Rhodium(III) or Iridium(III), $\{[(bpy)_2Ru(bpm)]_2MCl_2\}^{5+}$

Girlie Naomi A. Nallas, Sumner W. Jones, and Karen J. Brewer*

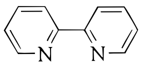
Virginia Polytechnic Institute and State University, Blacksburg, Virginia 24061-0212

Received July 3, 1996[⊗]

Bipyrimidine-bridged trimetallic complexes of the form $\{[(bpy)_2Ru(bpm)]_2MCl_2\}^{5+}$, where M = Rh^{III} or Ir^{III}, bpy = 2,2′-bipyridine, and bpm = 2,2′-bipyrimidine, have been synthesized and characterized. These complexes are of interest in that they couple catalytically active rhodium(III) and iridium(III) metals with light-absorbing ruthenium(II) metals within a polymetallic framework. Their molecular composition is a light absorber−electron collector−light absorber core of a photochemical molecular device (PMD) for photoinitiated electron collection. The variation of the central metal has some profound effects on the observed properties of these complexes. The electrochemical data for the title trimetallics consist of a $Ru^{II/III}$ oxidation and sequential reductions assigned to the bipyrimidine ligands, Ir or Rh metal centers, and bipyridines. In both trimetallic complexes, the first oxidation is Ru based and the bridging ligand reductions occur prior to the central metal reduction. This illustrates that the highest occupied molecular orbital (HOMO) is localized on the ruthenium metal center and the lowest unoccupied molecular orbital resides on the bpm ligand. This bpm-based LUMO in $\{[(bpy)_2Ru(bpm)]_2RhCl_2\}^{5+}$ is in contrast with that observed for the monometallic $[Rh(bpm)_2Cl_2]^+$ where the Rh^{III}/Rh^I reduction occurs prior to the bpm reduction. This orbital inversion is a result of bridge formation upon construction of the trimetallic complex. Both the Ir- and Rh-based trimetallic complexes exhibit a room temperature emission centered at 800 nm with τ = 10 ns. A detailed comparison of the spectroscopic, electrochemical, and spectroelectrochemical properties of these polymetallic complexes is described herein.

Introduction

Investigations leading to the design of photochemically and electrochemically active polypyridyl complexes resulted largely from the fact that $[Ru(bpy)_3]^{2+}$ has a long-lived metal-to-ligand charge transfer (MLCT) excited state and has the ability to undergo facile electron transfer reactions.[1−3] Polymetallic systems incorporating $Ru^{II}(bpy)_2$ fragments have been widely studied.[4−8] To bring together metals into a polymetallic system, a variety of bridging ligands are used.[4−19] Variation of both metal centers and ligands are possible, leading to a tailoring of the spectroscopic and redox properties of these polymetallic systems. It has been proposed that polymetallic systems could be designed to function as photochemical molecular devices.[8e] One of the most commonly utilized bridging ligands in the



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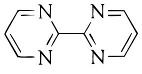

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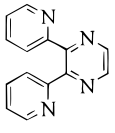

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S0020-1669(96)00792-6 CCC: $12.00

literature is 2,3-bis(2-pyridyl)pyrazine (dpp).[4–6,8–10] This ligand can be used successfully to prepare a wide variety of interesting polymetallic complexes. We have observed that mixed-metal systems constructed with this ligand are not stable in their reduced forms.[4,5f,10] This limits their application as devices for storing reducing equivalents. The dpp ligand binds to each metal through a pyrazine- and pyridine-based nitrogen. These inequivalent nitrogens lead to the presence of a variety of stereoisomers in polymetallic complexes of this ligand.

2,2′-Bipyrimidine (bpm) is able to bridge a variety of metal centers and is expected to electronically couple adjacent metal centers in a polymetallic system.[5c,8b,11–19] This coupling is due to bpm's ability to position two metal centers at a distance of ∼550 pm in a fixed orientation which will allow a direct or indirect $d\pi-d\pi$ interaction.[17b] Monometallic complexes containing bpm as a ligand have been synthesized and characterized by a number of research groups with the objective of utilizing them as precursors for polymetallic synthesis.[6a,14,20,21] $[Ru(bpy)_2(bpm)]^{2+}$ has been made, and its spectroscopic and electrochemical properties have been investigated.[6a,14,21] This monometallic complex exhibits a lowest lying MLCT at 415 nm and an emission centered at 600 nm.[21] Electrochemistry has shown a $Ru^{II/III}$ oxidation at $E = 1.40$ V and a bpm/bpm^- reduction at $E = -1.44$ V vs SSCE in acetonitrile solution.[6a] The metal-based oxidation is ∼300 mV more positive compared with $[Ru(bpy)_3]^{2+}$, reflecting the increased π-accepting ability of the bpm ligand. In symmetric bimetallic systems such as $\{[(bpy)_2Ru]_2(bpm)\}^{4+}$, two closely spaced oxidations are evident, indicative of electronic coupling of the two Ru centers, at $E_{1/2} = 1.60$ and 1.78 V vs SCE.[22] The first bpm localized reduction in $\{[(bpy)_2Ru]_2(bpm)\}^{4+}$ occurs at $E_{1/2} = -1.00$ V vs SCE, positive of $[Ru(bpy)_2(bpm)]^{2+}$ and free bpm ($E_{1/2} = -2.34$ V vs SCE).[22] This positive potential shift of the $bpm^{0/-}$ couple is indicative of the bimetallic formulation of this complex.[22] This is reflected in the red shift of the Ru → bpm CT to 586 nm.[22]

Trimetallic complexes of the type $\{[(bpy)_2Ru(BL)]_2MCl_2\}^{n+}$ incorporating the bridging ligands 2,3-bis(2-pyridyl)pyrazine (dpp), 2,3-bis(2-pyridyl)quinoxaline (dpq), and 2,3-bis(2-pyridyl)benzoquinoxaline) (dpb) and the central metals iridium(III) and osmium(III) have been previously studied in our laboratory.[4a,c,f] The $\{[(bpy)_2Ru(dpb)]_2IrCl_2\}^{5+}$ complex has been shown to function as the first molecular device for photoinitiated electron collection.[4d] These systems exhibit unique photochemical and electrochemical behavior. They undergo a series of reversible redox processes and are stable in a wide variety of oxidation states, making them suitable candidates for multielectron transfer processes.[4] The $\{[(bpy)_2Ru(dpq)]_2IrCl_2\}^{5+}$ and $\{[(bpy)_2Ru(dpb)]_2IrCl_2\}^{5+}$ systems have been utilized as catalysts for the selective and efficient electrochemical reduction of carbon dioxide to carbon monoxide.[4e] A preliminary report of the properties of the Rh^{III}-centered trimetallic complexes $\{[(bpy)_2Ru(BL)]_2RhCl_2\}^{5+}$, where BL = dpp, dpq, and dpb, has appeared.[4c] In this study, the trimetallic complexes of the form, $\{[(bpy)_2Ru(bpm)]_2MCl_2\}^{5+}$ where M = Rh^{III} or Ir^{III}, have been prepared to probe the ability of bipyrimidine to function as a bridging ligand within this mixed-metal framework and to explore how the properties of these complexes will vary as the central metal is changed from Ir^{III} to Rh^{III}.

Experimental Section

Materials. All the reagents used in the syntheses were purchased from Aldrich Chemical Co. unless otherwise indicated. The acetonitrile (Burdick and Jackson) used in the electrochemical experiments was spectroquality and used as received. The supporting electrolyte, Bu_4NPF_6, was prepared from the metathesis of Bu_4NBr and KPF_6, recrystallized two times from hot ethanol, and dried under vacuum. The metals were obtained through the Johnson Matthey precious metal loan program. The bridging ligand, 2,2′-bipyrimidine, was purchased from Lancaster Synthesis and used without further purification. $Ru(bpy)_2Cl_2$[23] and $[Ir(bpm)_2Cl_2](PF_6)$[24] were synthesized according to literature methods.

Syntheses. (a) Bis(2,2′-bipyridine)-2,2′-bipyrimidineruthenium(II) Hexafluorophosphate. The synthesis and purification of $[Ru(bpy)_2(bpm)](PF_6)_2$ was a modification of the method employed by Hunziker and Ludi.[21] A 0.29 g (0.60 mmol) aliquot of $Ru(bpy)_2Cl_2$ and 0.16 g (1.0 mmol) of 2,2′-bipyrimidine were slurried in 12 mL of 2:1 (v/v) ethanol/water solvent mixture. The suspension was stirred and heated at reflux for ∼2 h, and the solution changed color from purple to orange-brown. After being cooled to room temperature, the reaction mixture was added into ∼70 mL of saturated aqueous KPF_6 solution. The dark brown precipitate that formed was removed by vacuum filtration and washed with 10 mL of deionized water. This crude product was purified on adsorption alumina using a 3:2 volume ratio of toluene and acetonitrile as the eluent. The major orange band was collected and the solvent removed by rotary evaporation. The product was dissolved in a minimal amount of acetone, flash precipitated in diethyl ether, and collected by vacuum filtration. Isolation of this purified complex yielded a bright orange powder with a typical yield of 80%.

(b) $\{[(bpy)_2Ru(bpm)]_2RhCl_2\}(PF_6)_5$. This trimetallic complex was prepared by reacting 0.22 g (0.26 mmol) of $[Ru(bpy)_2(bpm)](PF_6)_2$ with 0.027 g (0.13 mmol) of $RhCl_3 \cdot xH_2O$ in 9 mL of 2:1 (v/v) ethanol/water. The mixture was stirred and heated at reflux under nitrogen for 48 h. The reaction solution was then pipetted into ∼50 mL of a saturated solution of KPF_6, where a dark greenish brown precipitate was obtained. This was collected by vacuum filtration and washed with 10 mL of deionized water. Dissolution of the residue in acetone followed by precipitation in diethyl ether and separation by vacuum filtration resulted in the isolation of the crude product (green powder). Purification was achieved by size exclusion chromatography (Sephadex LH-20) using 2:1 (v/v) ethanol/acetonitrile as eluent on a 100 cm column. A large green band eluted first and was collected. The solvent was removed by rotary evaporation. The product was dissolved in a minimal amount of acetone, flash precipitated in diethyl ether, and collected by vacuum filtration. A typical yield for this synthesis is 52%. FAB-MS ion (*m*/*z*; relative abundance): $[\{[(bpy)_2Ru(bpm)]_2RhCl_2\}(PF_6)_5]^+$ (2042; 3), $[\{[(bpy)_2Ru(bpm)]_2RhCl_2\}(PF_6)_4]^+$ (1897; 25), $[\{[(bpy)_2Ru(bpm)]_2RhCl_2\}(PF_6)_3]^+$ (1752; 100), $[\{[(bpy)_2Ru(bpm)]_2RhCl_2\}(PF_6)_2]^+$ (1607; 75), and $[\{[(bpy)_2Ru(bpm)]_2RhCl_2\}(PF_6)]^+$ (1463; 15).

(c) $\{[(bpy)_2Ru(bpm)]_2IrCl_2\}(PF_6)_5$. A 0.21 g (0.42 mmol) aliquot of $Ru(bpy)_2Cl_2$ was combined with 15 mL of 2:1 (v/v) ethanol/water. The suspension was stirred and heated at reflux under a stream of nitrogen for ∼30 min, after which 0.079 g (0.11 mmol) of $[Ir(bpm)_2Cl_2](PF_6)$ was added and the reaction was heated at reflux for 5 days. A greenish-brown solution was obtained. The reaction mixture was added to saturated aqueous solution of KPF_6 (50 mL) to precipitate the crude product, which was removed by vacuum filtration. Purification of the desired trimetallic complex was achieved by size exclusion chromatography (Sephadex LH-20) using a 2:1 (v/v) ethanol/acetonitrile eluent on a 100 cm column. The first band that eluted was collected, excess solvent was removed by rotary evaporation, and the residue was dissolved in a minimal amount of acetone and flash precipitated in

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diethyl ether. The purified complex was isolated as a dark green solid. A typical yield for this reaction is 60%. FAB-MS ion (*m*/*z*; relative abundance): $[\{[(bpy)_2Ru(bpm)]_2IrCl_2\}(PF_6)_5]^+$ (2131; 3), $[\{[(bpy)_2Ru(bpm)]_2IrCl_2\}(PF_6)_4]^+$ (1986; 29), $[\{[(bpy)_2Ru(bpm)]_2IrCl_2\}(PF_6)_3]^+$ (1841; 10), $[\{[(bpy)_2Ru(bpm)]_2IrCl_2\}(PF_6)_2]^+$ (1697; 95), $[\{[(bpy)_2Ru(bpm)]_2IrCl_2\}(PF_6)]^+$ (1551; 31), and $[\{[(bpy)_2Ru(bpm)]_2IrCl_2\}]^+$ (1406; 26).

Electrochemistry. Cyclic voltammetric measurements were done using a typical three-electrode system which includes a platinum working electrode, platinum wire auxiliary electrode, and a 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 and blanketed during each analysis. Bu_4NPF_6 (0.1 M) in acetonitrile was used as solvent, supporting electrolyte system. The cyclic voltammogram was taken at a sweep rate of 200 mV/s.

Electronic Absorption Spectroscopy. The electronic absorption spectra of the complexes were recorded in acetonitrile at ambient temperature using a HP 8452A diode array spectrophotometer with 2 nm resolution.

Spectroelectrochemistry. Spectroelectrochemical measurements were conducted according to previously described method using a locally constructed H-cell which uses a quartz cuvette as the working compartment.[26,27] The working and auxiliary compartments were separated by a fine porous glass frit. Carbon cloth (GC-12, The Electrosynthesis Co., Inc.) was used as the working electrode, platinum mesh as the auxiliary electrode, and Ag/AgCl as reference electrode (0.29 V vs NHE). All measurements were made on 0.1 M Bu_4NPF_6/acetonitrile solutions that were $\sim 1 \times 10^{-5}$ M metal complex. The electrolyte solution was dried over activated molecular sieves for ~2 h (Fisher), passed through activated alumina (Fisher), and filtered with a 0.25 μm syringe filter (Nalgene PTFE) prior to use. The electrolysis potential was controlled by a BAS100W electrochemical analyzer.

Emission Spectroscopy. The emission spectra were obtained at room temperature on a Photon Technology Inc. (PTI) Alpha-scan spectrofluorometer equipped with a 150 W Xe arc lamp excitation source and a Hamamatsu R666S red-sensitive photomultiplier tube housed in a Products for Research thermoelectrically cooled single photon counting system (0.25 nm resolution). The acetonitrile solution containing the trimetallic complex was deoxygenated by bubbling with high-purity Ar for ~20 min. prior to measurement.

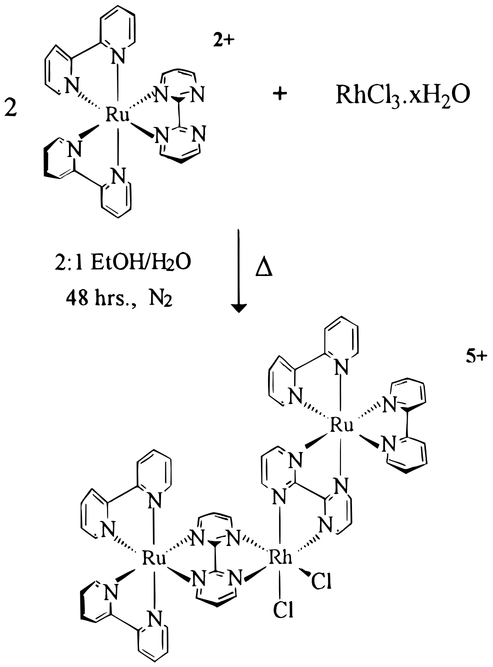
Lifetime Measurements. Emission lifetimes were measured using a PTI PL-2300 nitrogen laser equipped with a PL-201 continuously tunable dye laser (360−900 nm) excitation source. The detector used was a Hamamatsu R928S red-sensitive photomultiplier tube. The signal was recorded on a LeCroy 6880 digitizer (800 ps resolution) and the data transferred to a computer for analysis. Raw data were fit to a single-exponential equation of the form, $Y = A + B(\exp(-X/c))$, where $c = \tau = 1/k$ (in s).

FAB-Mass Spectrometry. FAB mass spectral analysis was conducted on a Fisons VG Quattro triple-stage quadrupole mass spectrophotometer using *m*-nitrobenzyl alcohol as a matrix. These trimetallics gave very nice FAB-MS patterns with sequential loss of each PF_6 ion being observed. Fragmentation patterns were consistent with the proposed molecular structures.

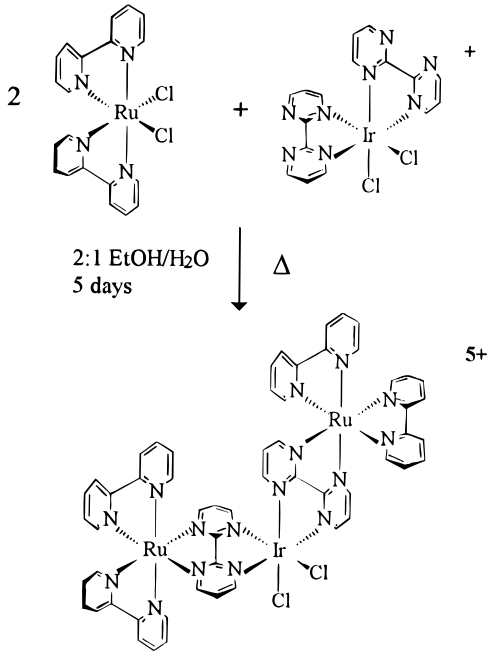
Results and Discussion

Syntheses. These trimetallic complexes can be prepared in reasonable yields with simple synthetic methods. The trimetallic complex $\{[(bpy)_2Ru(bpm)]_2RhCl_2\}^{5+}$ was prepared from the monometallic precursor $[Ru(bpy)_2(bpm)](PF_6)_2$ and $RhCl_3 \cdot xH_2O$ (Scheme 1). This method of bridging the bpm ligand to the ruthenium metal center first and then binding to the Rh metal yields a much cleaner reaction with easily purified products. This reaction produces the trimetallic in good yield, which is lowered to 52% upon size exclusion chromatography to achieve a high-purity product. The corresponding iridium analog was synthesized by reacting the monometallic precursors $Ru(bpy)_2Cl_2$ and $[Ir(bpm)_2Cl_2](PF_6)$ in a 2:1 molar ratio. Due to the high temperature needed for the formation of the iridium−bpm bonds, the reaction proceeds much better if the bpm is first coordinated to Ir and then bound to the Ru center. The reaction produced the trimetallic complex in a 60% yield after purification (Scheme 2).

Scheme 1



Scheme 2



These trimetallics are easily prepared in good yields, but with purification using size exclusion chromatography the yields are reduced to ~50−60%. The utilization of the symmetric bpm bridging ligand has eliminated many stereoisomers possible in the previously studied dpp, dpq, and dpb series. The FAB mass spectral data show that this technique is an effective tool for characterizing these trimetallic complexes. Fragmentation shows the sequential loss of PF_6 counterions while the trimetallic

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Table 1. Electronic Absorption Spectroscopy Data for $\{[(bpy)_2Ru(bpm)]_2MCl_2\}^{5+}$

compound	λ_{max} (nm)	ϵ (M^{-1} cm^{-1})	assignment
$\{[(bpy)_2Ru(bpm)]_2RhCl_2\}^{5+}$	278	9.0×10^4	$n \rightarrow \pi^*, \pi \rightarrow \pi^*$ (bpy)
	412	3.7×10^4	$Ru(d\pi) \rightarrow bpy(\pi^*)$ CT $Ru(d\pi) \rightarrow bpm(\pi^*)$ CT
	594	9.9×10^3	$Ru(d\pi) \rightarrow bpm(\pi^*)$ CT
$\{[(bpy)_2Ru(bpm)]_2IrCl_2\}^{5+}$	280	9.7×10^4	$n \rightarrow \pi^*, \pi \rightarrow \pi^*$ (bpy)
	412	3.0×10^4	$Ru(d\pi) \rightarrow bpy(\pi^*)$ CT $Ru(d\pi) \rightarrow bpm(\pi^*)$ CT
	598	8.3×10^3	$Ru(d\pi) \rightarrow bpm(\pi^*)$ CT

[a] Where M = Rh^{III} or Ir^{III}, bpy = 2,2′-bipyridine, and bpm = 2,2′-bipyrimidine in CH_3CN at room temperature.

framework is kept intact. The molecular composition of these trimetallics, $\{[(bpy)_2Ru(bpm)]_2MCl_2\}^{5+}$, which couples two ruthenium light absorbers to a central Ir or Rh metal, forms the LA−EC−LA core of a molecular device for photoinitiated electron collection (LA = light absorber, EC = electron collector).

Spectroscopy. Table 1 summarizes the electronic absorption spectra of these new trimetallic complexes in acetonitrile at room temperature. The spectroscopies of these two trimetallics, $\{[(bpy)_2Ru(bpm)]_2IrCl_2\}^{5+}$ and $\{[(bpy)_2Ru(bpm)]_2RhCl_2\}^{5+}$, are virtually identical. This verifies the assertion that the two ruthenium centers function as the main chromophores within this trimetallic framework. In the ultraviolet region, intense absorptions due to overlapping bipyridine- and bipyrimidine-based $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions are observed.[1−3,4a,5c,21] $Ru(d\pi) \rightarrow bpy(\pi^*)$ and $Ru(d\pi) \rightarrow bpm(\pi^*)$ charge transfer bands are evident in the visible region of the spectrum. The lowest lying MLCT, the $Ru(d\pi) \rightarrow bpm(\pi^*)$ CT band, for the rhodium complex is at 594 nm, whereas for the iridium complex, this MLCT occurs at 598 nm. For both these trimetallic complexes, the $Ru(d\pi) \rightarrow bpy(\pi^*)$ CT at 412 nm exhibits a distinctly higher extinction coefficient compared to the $Ru(d\pi) \rightarrow bpm(\pi^*)$ CT transition. The previously studied $\{[(bpy)_2Ru(BL)]_2IrCl_2\}^{5+}$ series has been shown to have more intense Ru → BL CT bands (BL = dpp: ϵ_{416} (Ru → bpy CT) = 1.8×10^4 M^{-1} cm^{-1}, ϵ_{522} (Ru → dpp CT) = 2.8×10^4 $M^{-1}cm^{-1}$).[4a] In the previously studied bimetallic complexes bridged by bpm, $\{[(bpy)_2Ru]_2(bpm)\}^{4+}$, the more intense band in the ~420 nm region was attributed to the sum of a second $Ru(d\pi) \rightarrow bpm(\pi^*)$ CT transition and the $Ru(d\pi) \rightarrow bpy(\pi^*)$ CT band.[14] This may be the case for our complexes as well, and spectroelectrochemistry will aid in the verification of this hypothesis.

The title trimetallics are weakly emissive at room temperature in acetonitrile solution compared with their ruthenium monometallic precursor.[21] Emission maxima for both the rhodium- and iridium-based systems occurred at a relatively low energy (800 nm) typical for these types of polymetallic complexes. These complexes emit at a region where the photomultiplier tube (PMT) response is weak, making it difficult to accurately determine the emission maxima. Emission lifetimes are ~10 ns for both the rhodium- and iridium-based trimetallics. This similarity in the photophysical properties of these Ir- and Rh-based trimetallics results from the similar Ru → bpm CT nature of their lowest lying excited state.

Electrochemistry. Cyclic voltammograms were taken in 0.1 M Bu_4NPF_6 in CH_3CN under argon and are illustrated in Figure 1. The cyclic voltammogram for the bpm-bridged iridium trimetallic is quite similar to the dpp, dpq, and dpb complexes, $\{[(bpy)_2Ru(BL)]_2IrCl_2\}^{5+}$,[4a] with the bpm complex giving distinctly sharper waves. This may be the result of the other BL complexes having the ability to exist as a mixture of stereoisomers that vary in the coordination mode of the unsymmetric BL to the central Ir core.[4a] In the reductive scan of $\{[(bpy)_2Ru(bpm)]_2IrCl_2\}^{5+}$, two pairs of closely spaced reversible reductions were evident. These reductions are assigned as sequential bpm-based reductions, bpm,bpm/bpm$^-$,bpm and bpm$^-$,bpm/bpm$^-$,bpm$^-$ (−0.08 and −0.21 V) followed by bpm$^-$,bpm$^-$/bpm^{2-},bpm$^-$ and bpm^{2-},bpm$^-$/bpm^{2-},bpm^{2-} (−0.90 and −1.07 V). These equivalent bpm ligands reduce at different potentials due to a small degree of electronic coupling through the Ir center. The presence of bpm$^-$/bpm^{2-} waves prior to bpy/bpy$^-$ reductions is indicative of the trimetallic formulation of these complexes.[4a] The reversible reduction at −1.60 V is tentatively assigned as a bpy$^{0/-}$ reductive couple, and the Ir^{III}/Ir^{I} and the other bpy reductions appear to occur at −1.70 and −1.75 V although

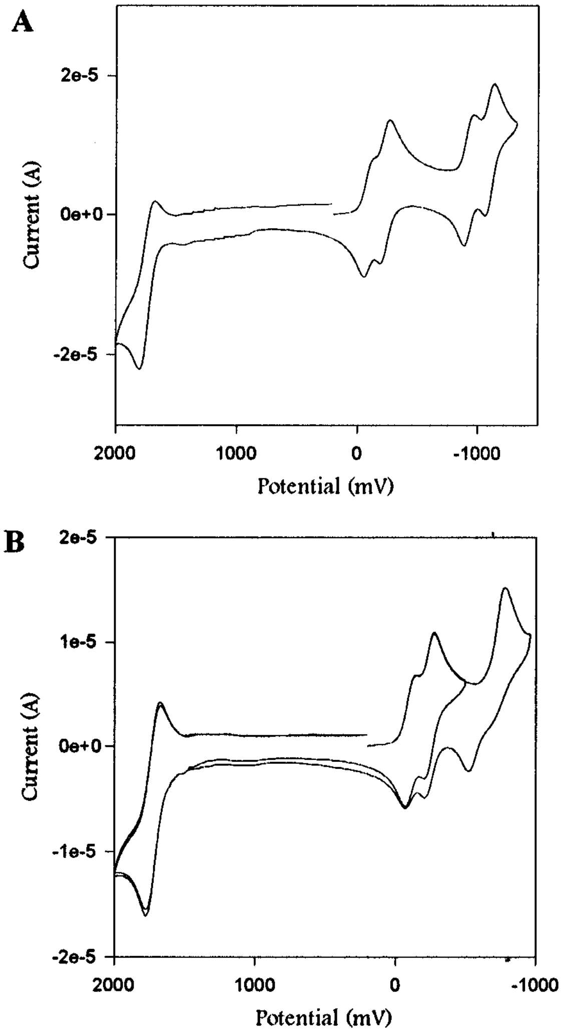


Figure 1. Cyclic voltammograms of the trimetallic complexes $\{[(bpy)_2Ru(bpm)]_2MCl_2\}^{5+}$ in 0.1 M Bu_4NPF_6 in CH_3CN, where M = Ir^{III} (A) or Rh^{III} (B), bpy = 2,2′-bipyridine, and bpm = 2,2′-bipyrimidine, Potentials recorded vs Ag/AgCl reference electrode (0.29 V vs NHE).

resolution is difficult.[4a,c,e] Reduction in this potential region leads to adsorption of the trimetallic onto the electrode surface. In the positive potential region, only one reversible oxidative process is observed, which is attributed to two overlapping Ru^{II}/Ru^{III} oxidations.[4a] The presence of these nearly overlapping waves for these two equivalent ruthenium centers indicates that they are largely electronically uncoupled within this framework. This indicates that they can function independently as separate light absorbers.

$$[(bpy)_2Ru^{III}(bpm)Ir^{III}Cl_2(bpm)Ru^{III}(bpy)_2]^{7+}$$

$$+2e^- \downarrow\uparrow -2e^-$$

$$[(bpy)_2Ru^{II}(bpm)Ir^{III}Cl_2(bpm)Ru^{II}(bpy)_2]^{5+}$$

synthesized oxidation state

$$-1e^- \uparrow\downarrow +1e^-$$

$$[(bpy)_2Ru^{II}(bpm^-)Ir^{III}Cl_2(bpm)Ru^{II}(bpy)_2]^{4+}$$

$$-1e^- \uparrow\downarrow +1e^-$$

$$[(bpy)_2Ru^{II}(bpm^-)Ir^{III}Cl_2(bpm^-)Ru^{II}(bpy)_2]^{3+}$$

$$-1e^- \uparrow\downarrow +1e^-$$

$$[(bpy)_2Ru^{II}(bpm^{2-})Ir^{III}Cl_2(bpm^-)Ru^{II}(bpy)_2]^{2+}$$

$$-1e^- \uparrow\downarrow +1e^-$$

$$[(bpy)_2Ru^{II}(bpm^{2-})Ir^{III}Cl_2(bpm^{2-})Ru^{II}(bpy)_2]^{1+}$$

The electrochemistry indicates that this $\{[(bpy)_2Ru(bpm)]_2IrCl_2\}^{5+}$ system has a ruthenium ($d\pi$)-based highest occupied molecular orbital (HOMO) and a bpm-based lowest unoccupied molecular orbital (LUMO). This would predict the observed lowest lying $Ru(d\pi) \rightarrow bpm(\pi^*)$ CT transition in the electronic spectroscopy of this system.[28]

For the rhodium trimetallic complex, $\{[(bpy)_2Ru(bpm)]_2RhCl_2\}^{5+}$, different electrochemical behavior is observed (Figure 2). There are two closely spaced, reversible bridging ligand reductions at −0.13 and −0.26 V, and they occur prior to the Rh^{III}/Rh^{I} reduction. The presence of bpm/bpm^- couples prior to the Rh^{III}/Rh^{I} couple is in contrast to the $[Rh(bpm)_2Cl_2]^+$ monometallic, which exhibits a Rh^{III}/Rh^{I} couple at −0.62 V followed by two bpm/bpm^- couples at −1.34 and −1.70 V.[24] This trimetallic complex, $\{[(bpy)_2Ru(bpm)]_2RhCl_2\}^{5+}$, has stabilized bpm π^* orbitals relative to $[Rh(bpm)_2Cl_2]^+$ due to the coordination of the Ru^{II} metal centers to the remote nitrogens on the bpm ligand. This stabilization of the bpm π^* orbitals shifts them below the Rh $d\sigma^*$ orbitals, giving rise to the observed electrochemical behavior. This orbital inversion results from the fact that these bpm π^* orbitals and Rh $d\sigma^*$ orbitals, are close in energy, and slight modifications in the bpm π^* orbital energy, can lead to this inversion of the LUMO in this trimetallic framework. Our preliminary report of $\{[(bpy)_2Ru(dpp)]_2RhCl_2\}^{5+}$ indicates that the rhodium reductive couple is observed prior to the bridging ligand reductions in this system.[4c] The irreversible reduction for $\{[(bpy)_2Ru(bpm)]_2RhCl_2\}^{5+}$ observed at −0.78 V accounts for the two-electron reduction of Rh^{III} to Rh^{I} followed by the rapid loss of the two chlorides.[4c,25] The bipyridine reductions appear to follow at −1.19 and −1.45 V, but resolution of these waves is difficult and reduction in this potential region leads to adsorption onto the electrode surface. One oxidative wave is observed in the positive potential region for $\{[(bpy)_2Ru(bpm)]_2RhCl_2\}^{5+}$ and is assigned to a Ru^{II}/Ru^{III} oxidation for both metal centers indicating that these two ruthenium centers are largely electronically uncoupled. This ruthenium oxidation occurs at the same potential as that observed for the iridium-based system.

$$[(bpy)_2Ru^{III}(bpm)Rh^{III}Cl_2(bpm)Ru^{III}(bpy)_2]^{7+}$$

$$+2e^- \downarrow\uparrow -2e^-$$

$$[(bpy)_2Ru^{II}(bpm)Rh^{III}Cl_2(bpm)Ru^{II}(bpy)_2]^{5+}$$

synthesized oxidation state

$$-1e^- \uparrow\downarrow +1e^-$$

$$[(bpy)_2Ru^{II}(bpm^-)Rh^{III}Cl_2(bpm)Ru^{II}(bpy)_2]^{4+}$$

$$-1e^- \uparrow\downarrow +1e^-$$

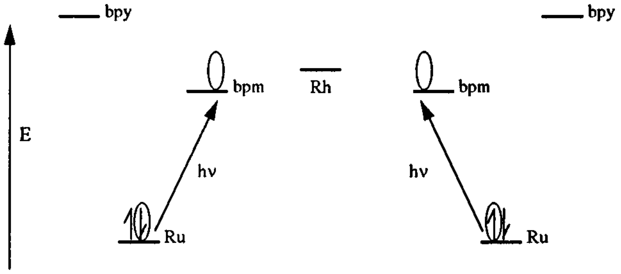
$$[(bpy)_2Ru^{II}(bpm^-)Rh^{III}Cl_2(bpm^-)Ru^{II}(bpy)_2]^{3+}$$

$$\downarrow +2e^-, -2Cl^-$$

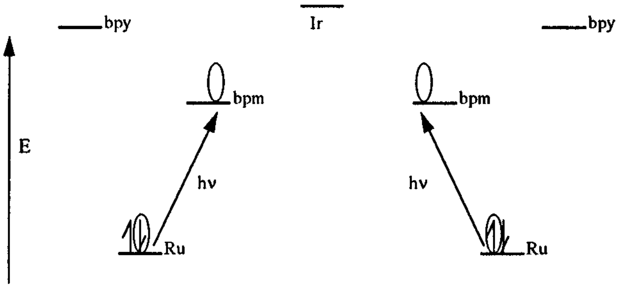
$$[(bpy)_2Ru^{II}(bpm^-)Rh^{I}(bpm^-)Ru^{II}(bpy)_2]^{3+}$$

These electrochemical data indicate that this $\{[(bpy)_2Ru(bpm)]_2RhCl_2\}^{5+}$ trimetallic possesses a Ru ($d\pi$)-based HOMO and a bpm-based LUMO with the Rh $d\sigma^*$ orbitals lying very close in energy. This would imply a lowest lying $Ru(d\pi) \rightarrow bpm(\pi^*)$ CT excited state, consistent with the observed spectroscopy.

Comparison of the electrochemistry of these trimetallic complexes, $\{[(bpy)_2Ru(bpm)]_2MCl_2\}^{5+}$ (M = Rh^{III} or Ir^{III}) gives us the following orbital pictures.



Orbital Energy Diagram for $\{[(bpy)_2Ru(bpm)]_2RhCl_2\}^{5+}$



Orbital Energy Diagram for $\{[(bpy)_2Ru(bpm)]_2IrCl_2\}^{5+}$

Both systems have the appropriate orbital energies to function as the central LA−EC−LA core of a molecular device for photoinitiated electron collection.[4c,d,8e]

Spectroelectrochemistry. Spectroelectrochemistry can aid in the verification of the spectroscopic and electrochemical

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(28) A discussion of the correlation of $\Delta E_{1/2}$ and E_{op} can be found in: Dodsworth, E. S.; Lever, A. B. P. *Chem. Phys. Lett.* **1986**, *124*, 152.

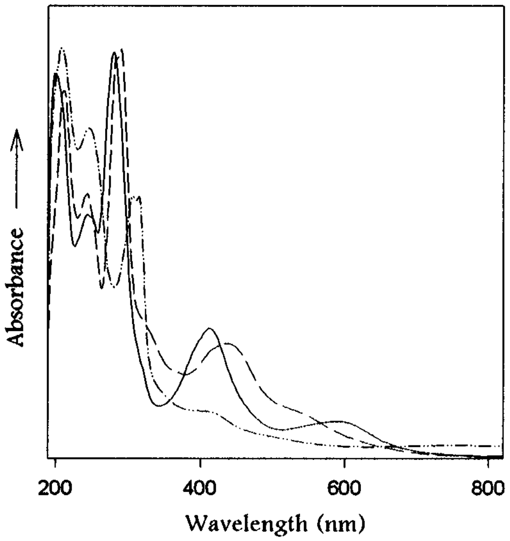

Figure 2. Spectroelectrochemical results for $\{[(bpy)_2Ru(bpm)]_2IrCl_2\}^{5+}$, where bpy = 2,2′-bipyridine and bpm = 2,2′-bipyrimidine in 0.1 M Bu_4NPF_6 in CH_3CN at room temperature: (—) $\{[(bpy)_2Ru(bpm)]_2IrCl_2\}^{5+}$, (– –) $\{[(bpy)_2Ru(bpm)]_2IrCl_2\}^{3+}$, (– ·· –) $\{[(bpy)_2Ru(bpm)]_2IrCl_2\}^{7+}$.

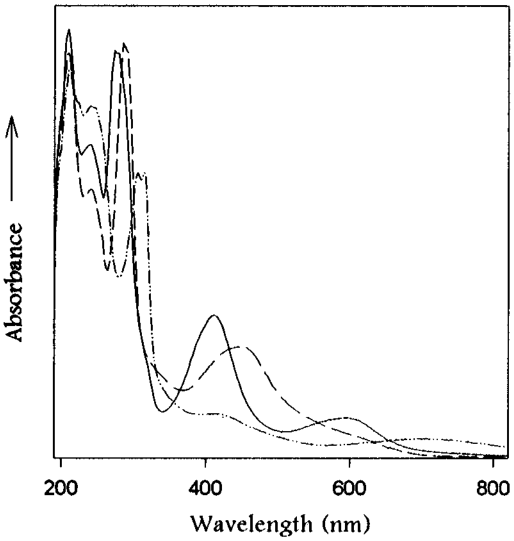

Figure 3. Spectroelectrochemical results for $\{[(bpy)_2Ru(bpm)]_2RhCl_2\}^{5+}$, where bpy = 2,2′-bipyridine and bpm = 2,2′-bipyrimidine in 0.1 M Bu_4NPF_6 in CH_3CN at room temperature: (—)$\{[(bpy)_2Ru(bpm)]_2RhCl_2\}^{5+}$, (– –) $\{[(bpy)_2Ru(bpm)]_2RhCl_2\}^{3+}$, (– ·· –) $\{[(bpy)_2Ru(bpm)]_2RhCl_2\}^{7+}$.

properties of these new trimetallics as well as provide the spectroscopic features of the reduced and oxidized forms of these complexes. The spectroelectrochemistry of $\{[(bpy)_2Ru(bpm)]_2RhCl_2\}^{5+}$ and $\{[(bpy)_2Ru(bpm)]_2IrCl_2\}^{5+}$ are shown in Figures 2 and 3. The electronic absorption spectra reported were acquired from a single solution at room temperature. Relative absorption intensities for the transitions are shown.

The two-electron oxidation of the Ir trimetallic is achieved with 70% reversibility. Electrolysis past the Ru^{II}/Ru^{III} oxidation at 1.90 V shows a shift and splitting of the absorption at 280 nm to 308 and 318 nm. This has been observed in the past for trimetallic complexes with remote $Ru^{II}(bpy)_2$ moieties.[4a] This is indicative of overlapping bpy-based n → π^* and $\pi \rightarrow \pi^*$ bands at 280 nm. The MLCT absorptions at 412 and 598 nm are lost upon ruthenium oxidation, consistent with their Ru → ligand CT assignments.[4a,5f,10]

Electrogeneration of the two-electron-reduced iridium trimetallic was achieved with ~80% regeneration of the original oxidation state. This state generated at −0.50 V has two singly reduced bpm ligands. The two-electron-reduced species showed a loss of the lowest energy MLCT at 598 nm consistent with its assignment to a Ru → bpm CT transition. A decrease in intensity and shift to lower energy of the transition at 412 nm is seen upon reduction of both bpm ligands. This can be attributed to overlapping Ru → bpy and Ru → bpm CT transitions. The Ru → bpm CT component should be lost when the bpm is reduced while the Ru → bpy CT component would shift to lower energy.[4a,5f,10] The loss in intensity is not consistent with only a Ru → bpy CT band in this 412 nm region and provides further evidence of an underlying Ru → bpm CT band. The two-electron reduction has little effect on the absorbance at 280 nm, consistent with a bpm-based reduction and a primarily bpy-based absorbance.[4a,5f,10]

The rhodium trimetallic exhibits oxidative and reductive spectroelectrochemistry very similar to that observed for the iridium-based complex. The two-electron oxidation of the Rh trimetallic at 1.90 V to produce two Ru^{III} centers results in the loss of absorption at 412 and 594 nm, consistent with their Ru → ligand CT assignment. There is a more evident, broad and weak absorption centered at ~700 nm that appears upon Ru oxidation. This observation is also seen in the dpp analog and may represent a bpm → Ru^{III} LMCT.[4a] A shift and splitting of the absorption at 280 nm to 308 and 318 nm is also observed as a result of oxidative electrolysis. This illustrates the presence of overlapping bpy-based n → π^* and $\pi \rightarrow \pi^*$ transitions in this region of the spectrum of the Rh-based trimetallic.[4a] The similarity of results in oxidative spectroelectrochemistry gives further evidence for the dominance of the two ruthenium chromophores on the observed spectroscopy of these systems. Reduction of this oxidized species is achieved with 70% efficiency. The absorption spectrum of the $2e^-$-reduced species generated at −0.45 V to give a species with two reduced bpm ligands shows a loss of the lowest energy transition at 594 nm consistent with its assignment as a Ru → bpm CT transition. The higher energy transition at 412 nm exhibited a decrease in intensity and shift to lower energy. These observations are consistent with the assignment of overlapping Ru → bpy and Ru → bpm CT transitions.[4a,5f,10] Reoxidation of this reduced complex can be accomplished with 80% efficiency.

Conclusions

The trimetallic complexes $\{[(bpy)_2Ru(bpm)]_2MCl_2\}^{5+}$, where M = Rh^{III} or Ir^{III}, were prepared under relatively mild conditions with reasonable yields. Size exclusion chromatography to obtain a highly purified complex decreases the purified yield to ~50–60%. The bpm ligand functions well as a bridging ligand within this framework. FAB mass spectral analysis proved very useful in identifying these complexes. The use of this symmetric bpm bridging ligand instead of the previously studied dpp-type ligands has eliminated the stereoisomers on the central $M^{III}(BL)_2Cl_2$ moiety associated with the arrangement of the pyrazine and pyridine rings of the dpp ligand. This leads to sharper waves in the cyclic voltammograms of these complexes. These bpm-based systems exhibit unique spectroscopic and electrochemical properties with the $Rh^{III}(bpm)_2Cl_2$ moiety undergoing orbital inversion upon bridge formation to prepare $\{[(bpy)_2Ru(bpm)]_2RhCl_2\}^{5+}$. These Rh- and Ir-based trimetallic systems exhibit spectroscopic properties that are dominated by the two ruthenium chromophores and do not change significantly as the central metal is varied from Rh^{III} to Ir^{III}. This is true in both the synthesized oxidation state and the electrogenerated $\{[(bpy)_2Ru(bpm)]_2MCl_2\}^{7+}$ and $\{[(bpy)_2Ru(bpm)]_2MCl_2\}^{3+}$ states. Both trimetallics are emissive at room temperature, displaying an emission that is centered at 800 nm with $\tau = 10$ ns. Both the Ir- and Rh-based trimetallic systems have appropriate orbital energies to function as the central LA−EC−LA core for a molecular device for photoinitiated electron collection.[29]

Acknowledgment. The authors thank the National Science Foundation (Grant CHE-9313642) and the Department of Science and Technology (Philippines) for financial support of this project and Johnson Matthey, an Alfa Aesar Company, for the loan of the metals used in this study. Special gratitude to Ms. Cindy Kaminer for her assistance in the synthetic work.

Supporting Information Available: A table of the electrochemical data and a figure of the electronic absorption spectroscopy (2 pages). Ordering information is given on any current masthead.

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(29) Jones, S. W., Nallas, G. N., Brewer, K. J., work in progress, 1996.