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Article

# Synthesis and Study of Ru,Rh,Ru Triads: Modulation of Orbital Energies in a Supramolecular Architecture

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Supramolecular trimetallic complexes [{(tpy)RuCl(BL)}$_2$RhCl$_2$]$^{3+}$ where tpy = 2,2′:6′,2″-terpyridine and BL = dpp or bpm {dpp = 2,3-bis(2-pyridyl)pyrazine and bpm = 2,2′-bipyrimidine} have been synthesized and characterized. The mixed-metal complexes couple a reactive rhodium(III) center to two ruthenium(II) light absorbers to form a light absorber–electron collector–light absorber triad. The variation of the bridging (dpp and bpm) and terminal (tpy in lieu of bpy) ligands has some profound effects on the properties of these complexes, and they are remarkably different from the previously reported [{(bpy)$_2$Ru(bpm)}$_2$RhCl$_2$]$^{5+}$ system. The electrochemical data for both title trimetallics consist of overlapping Ru$^{III/II}$ couples for both terminal metals at 1.12 V versus the Ag/AgCl reference electrode. Cathodically an irreversible Rh$^{III/I}$ reduction followed by bridging ligand reductions is seen. This is indicative of highest occupied molecular orbitals (HOMO) localized on the terminal ruthenium metal centers and a lowest unoccupied molecular orbital (LUMO) residing on the rhodium. This rhodium-based LUMO is in contrast to the bpy analogue [{(bpy)$_2$Ru(bpm)}$_2$RhCl$_2$]$^{5+}$, which has a bpm($\pi^*$) localized LUMO. This orbital inversion by terminal ligand variation illustrates the similar energy of these Rh(d$\sigma^*$) and bpm($\pi^*$) orbitals within this structural motif. Both title trimetallics possess broad, low-energy Ru → BL charge transfer absorbances at 540 nm (dpp) and 656 nm (bpm). A comparison of the spectroscopic, electrochemical, and spectroelectrochemical properties of these trimetallic complexes is presented.

## Introduction

Interest in the area of supramolecular chemistry has resulted in the design of many photochemically and electrochemically active ruthenium(II) polypyridyl complexes.[1–17]

Supramolecular complexes have been designed, taking advantage of the long-lived metal-to-ligand charge transfer (MLCT) excited state of the widely studied [Ru(bpy)$_3$]$^{2+}$

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chromophore,[1-3] focused on their use as photochemical molecular devices[4-9] (bpy = 2,2′-bipyridine). Incorporation of ruthenium(II) polypyridyl groups into a supramolecular motif eliminates the need for molecular collision resulting in facile electron or energy transfer. The bridge, which links the metal centers in these supramolecular complexes, is often a multidentate polyazine ligand.[4-17]

Polymetallic complexes incorporating polyazine bridging ligands (BL) have received a great deal of attention.[4-17] The BL serves to bring the metal centers into close proximity and creates a pathway for energy or electron transfer. The commonly used bridging ligand 2,3-bis(2-pyridyl)pyrazine (dpp) binds to two metal centers through a pyridyl and a pyrazine nitrogen, acting as an AB chelate, resulting in a mixture of stereoisomers not typically separated.[4-9,12,14,15] Another BL which performs the same function but has not received as much attention is 2,2′-bipyrimidine (bpm), which binds to two metal centers through two equivalent nitrogens eliminating the stereoisomers associated with the AB chelates.[11,13,16,17]

Within a supramolecular architecture, terminal ligands (TL), typically bpy, are coordinated to the ruthenium light absorbers. Another TL used in supramolecular complexes is 2,2′:6′,2″-terpyridine (tpy). Although $[Ru(tpy)_2]^{2+}$ has a short-lived excited state,[18-20] the tpy ligand brings the advantage of eliminating the Δ and Λ isomeric mixtures associated with the tris-bidentate metal centers giving some stereochemical control in supramolecular complexes. Long-lived excited states are observed for many ruthenium tpy complexes incorporating polyazine bridging ligands.[21-30]
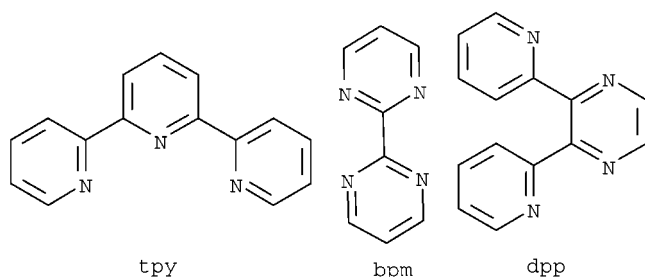
= Ir(III),[31-33] have been studied, and a preliminary report of M = Rh(III) has appeared.[32b] The system with M = Ir and BL = dpb acts as a molecular device for photoinitiated electron collection[31a] and is an electrocatalyst for $CO_2$ reduction.[33] The bpm trimetallic complexes $[\{(bpy)_2Ru-(bpm)\}_2IrCl_2]^{5+}$ and $[\{(bpy)_2Ru(bpm)\}_2RhCl_2]^{5+}$ have Ru-(dπ) based highest occupied molecular orbitals (HOMOs) and bridging ligand, bpm(π*), based lowest unoccupied molecular orbitals (LUMOs).[34]

A number of important studies on the coupling of ruthenium light absorbers to rhodium electron acceptors in supramolecular frameworks have appeared.[32,34-44] Interesting systems with varying bridge length were studied by Indelli, Scandola, Collin, Sauvage, and Sour, $[(tpy)Ru(tpy-(Ph)n-tpy)Rh(tpy)]^{5+}$ (n = 0, 1, or 2).[36] Linked bpy systems of the type $[(Me_2phen)_2Ru^{II}(Mebpy-CH_2CH_2-Mebpy)Rh^{III}(Meb-py)_2]^{5+}$ [36,37] and a dpp bridged system $[(bpy)_2Ru^{II}(dpp)Rh^{III}-(bpy)_2]^{5+}$ [35] have been investigated. Endicott et al. have studied $Ru^{II},Rh^{III}$ cyanide-bridged complexes.[41] Often these systems are reported to undergo intramolecular electron-transfer quenching of the Ru-based MLCT excited state by the rhodium center.

A trimetallic structural motif would be an interesting framework to exploit the electron acceptor properties of the rhodium metal center. This requires the development of synthetic methods and the ability to modulate orbital energies in a supramolecular architecture. Within this framework the trimetallic complexes $[\{(tpy)RuCl(dpp)\}_2RhCl_2](PF_6)_3$ and $[\{(tpy)RuCl(bpm)\}_2RhCl_2](PF_6)_3$ have been synthesized and characterized by FAB mass spectral analysis, electronic absorption spectroscopy, electrochemistry, and spectroelec-



tpy      bpm      dpp

Trimetallic complexes of the form $[\{(bpy)_2Ru(BL)\}_2-MCl_2]^{5+}$, where BL = dpp, 2,3-bis(2-pyridyl)quinoxaline (dpq), and 2,3-bis(2-pyridyl)benzoquinoxaline (dpb) and M

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trochemistry. These complexes couple two ruthenium light absorbers (LA) to a central electron collecting (EC) rhodium metal center to form a LA−BL−EC−BL−LA assembly. The interesting effects of bridging ligand and terminal ligands on the spectroscopic and electrochemical properties of these complexes is discussed.

## Experimental Section

**Materials.** 2,2′:6′,6″-Terpyridine (tpy) (GFS chemicals), ruthenium(III) chloride hydrate, rhodium trichloride hydrate, and 2,2′-bipyrimidine (bpm) (Alfa), triethylamine (Acros), 2,3-bis(2-pyridyl)-pyrazine (dpp) (Aldrich), (80−200 mesh) adsorption alumina (Fisher), and spectroquality grade acetonitrile and toluene (Burdick and Jackson) were used as received. Tetrabutylammonium hexafluorophosphate $Bu_4NPF_6$ (used as supporting electrolyte for electrochemistry experiments) was prepared by the aqueous metathesis of tetrabutylammonium bromide (Aldrich) with potassium hexafluorophosphate (Aldrich). After several recrystallizations from ethanol the white crystals were dried under vacuum and stored in a vacuum desiccator. Elemental analysis was performed by Galbraith Laboratories, Inc., Knoxville, TN.

**Synthesis.** (tpy)$RuCl_3$,[45] [(tpy)RuCl(dpp)]($PF_6$),[46] [(tpy)RuCl(bpm)]($PF_6$),[47] [{(bpy)$_2$Ru(dpp)}$_2$RhCl$_2$]($PF_6$)$_5$,[32b] and [{(bpy)$_2$Ru(bpm)}$_2$RhCl$_2$]($PF_6$)$_5$[34] were synthesized as described previously.

**[{(tpy)RuCl(dpp)}$_2$RhCl$_2$]($PF_6$)$_3$.** A solution of 0.40 g (0.54 mmol) of [(tpy)RuCl(dpp)]($PF_6$) and 0.080 g (0.36 mmol) of rhodium trichloride hydrate in 2:1 EtOH/$H_2O$ was heated at reflux for 1 h. After being cooled to room temperature, the reaction mixture was added dropwise to an aqueous solution of 100 mL of $H_2O$ and 100 mL of saturated $KPF_6$(aq) solution with stirring. The resulting precipitate was filtered, washed with 30 mL of cold water and 30 mL of cold ethanol followed by 30 mL of ether, and air-dried for 30 min. The product was dissolved in a minimum amount of acetonitrile (ca. 5 mL), flash precipitated in 200 mL of ether, and collected by vacuum filtration to yield a purple powder (0.40 g, 0.22 mmol, 82% yield). Anal. Calcd for [{(tpy)RuCl(dpp)}$_2$RhCl$_2$]($PF_6$)$_3$·8$H_2O$: C, 35.52; H, 2.98; N, 10.00. Found: C, 35.20; H, 2.35; N, 9.93. UV/vis (CH$_3$CN): $\lambda_{max}$ (nm) [$\epsilon \times 10^{-4}$ $M^{-1}$ cm$^{-1}$] = 274 [4.70], 314 [6.48], 360 (sh) [2.72], 460 [1.13], 540 [2.72]. FAB-MS ion (m/z; relative abundance): [{(tpy)RuCl(dpp)}$_2$RhCl$_2$]($PF_6$)$_2$$^+$ (1673, 100); [{(tpy)RuCl(dpp)}$_2$RhCl]($PF_6$)$_2$$^+$ (1636, 10); [{(tpy)RuCl(dpp)}$_2$RhCl$_2$]($PF_6$)$^+$ (1527, 25); [{(tpy)RuCl(dpp)}$_2$RhCl]($PF_6$)$^+$ (1493, 10).

**[{(tpy)RuCl(bpm)}$_2$RhCl$_2$]($PF_6$)$_3$.** A solution of 0.32 g (0.49 mmol) of [(tpy)RuCl(bpm)]($PF_6$) and 0.070 g (0.32 mmol) of rhodium trichloride hydrate in 2:1 EtOH/$H_2O$ was heated at reflux for 2 h. After the reaction mixture was cooled to room temperature, a black residue was removed by filtration. The filtrate was added dropwise to an aqueous solution of 100 mL of $H_2O$ and 100 mL of saturated $KPF_6$(aq) solution with stirring. A brown precipitate formed, which was filtered and washed with 30 mL of cold ethanol followed by 30 mL of ether. The resulting brown product was dissolved in a minimum of acetonitrile (ca. 5 mL), flash precipitated in 200 mL of ether, and collected by vacuum filtration to yield a greenish/brown powder (0.28 g, 0.17 mmol, 72% yield). Anal. Calcd for [{(tpy)RuCl(bpm)}$_2$RhCl$_2$]($PF_6$)$_3$·CH$_3$CN·$H_2O$: C, 33.45; H, 2.28; N, 12.19. Found: C, 33.33; H, 2.40; N, 11.76. UV/vis (CH$_3$-CN): $\lambda_{max}$ (nm) [$\epsilon \times 10^{-4}$ $M^{-1}$ cm$^{-1}$] = 272 [6.21], 312 [5.50], 330 (sh) [3.11], 464 [2.50], 656 [1.00]. FAB-MS ion (m/z; relative abundance): [{(tpy)RuCl(bpm)}$_2$RhCl$_2$]($PF_6$)$_2$$^+$ (1520, 85); [{(tpy)-RuCl(bpm)}$_2$RhCl]($PF_6$)$_2$$^+$ (1485, 15); [{(tpy)RuCl(bpm)}$_2$RhCl$_2$]-($PF_6$)$^+$ (1375, 100); [{(tpy)RuCl(dpp)}$_2$RhCl]($PF_6$)$^+$ (1340, 20).

**Electronic Spectroscopy.** Electronic absorption spectra were recorded at room temperature using a Hewlett-Packard 8452 diode array spectrophotometer with 2 nm resolution. Samples were run at room temperature in Burdick and Jackson UV-grade acetonitrile in 1 cm quartz cuvettes.

**Electrochemistry.** Cyclic voltammograms were recorded using a one-compartment three-electrode cell, Bioanalytical Systems (BAS), equipped with a platinum wire auxiliary electrode. The working electrode was a 1.9 mm diameter glassy carbon disk from BAS. Potentials were referenced to a Ag/AgCl electrode (0.29 V vs NHE), which was calibrated against the FeCp$_2$/FeCp$_2$$^+$ redox couple (0.67 V vs NHE).[48] The supporting electrolyte was 0.1 M $Bu_4NPF_6$, and the measurements were made in Burdick and Jackson UV-grade acetonitrile, which was dried over 3 Å molecular sieves.

**Spectroelectrochemistry.** Spectroelectrochemical measurements were conducted according to a previously described method using a locally constructed H-cell which uses a quartz cuvette as the working compartment.[49] The working and auxiliary compartments were separated by a fine porous glass frit. The working electrode and auxiliary electrodes were high surface area platinum mesh, and the reference electrode was Ag/AgCl (0.29 V vs NHE). The measurements were made in 0.1 M $Bu_4NPF_6$/acetonitrile solutions that were $2 \times 10^{-5}$ M metal complex. The electrolysis potential was controlled by a BAS 100W electrochemical analyzer.

**FAB Mass Spectrometry.** FAB mass spectral analysis was performed by M-Scan Incorporated, West Chester, PA, on a VG Analytical ZAB 2-SE high-field mass spectrometer using m-nitrobenzyl alcohol as a matrix. The trimetallic gave very nice FAB-MS patterns with sequential loss of each PF$_6$ ion being observed. The fragmentation pattern was consistent with the proposed molecular structure.

## Results and Discussion

**Synthesis.** The supramolecular complexes [{(tpy)RuCl-(dpp)}$_2$RhCl$_2$]($PF_6$)$_3$ and [{(tpy)RuCl(bpm)}$_2$RhCl$_2$]($PF_6$)$_3$ were prepared in good yields under mild conditions using a building-block approach. It is this method that allows for easy variation of structural components within this structural motif. The tpy is first bound to ruthenium followed by BL attachment.[45,46] The trimetallic complexes are assembled by reaction of the [(tpy)RuCl(BL)]($PF_6$), where BL = dpp or bpm, with a slight excess of rhodium(III) trichloride hydrate. The synthesis of [{(tpy)RuCl(bpm)}$_2$RhCl$_2$]($PF_6$)$_3$ by this method is illustrated in Scheme 1. This method of binding the bpm or dpp ligand to the ruthenium metal center first and then binding to the rhodium metal center yields clean reactions with easily purified products. The use of excess rhodium(III) trichloride hydrate ensures that most of the monometallic precursor is reacted. The major product in each case is the desired trimetallic. The excess rhodium(III) trichloride is easily removed by aqueous washings of the precipitated hexafluorophosphate salt of the trimetallic complex.
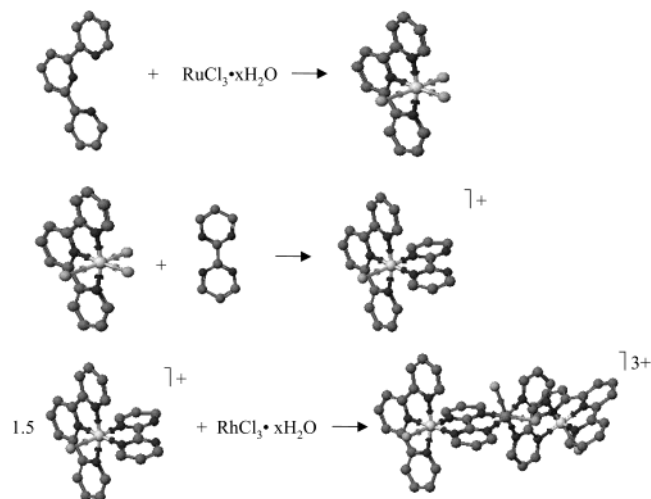
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**Scheme 1.** Building-Block Synthesis of [{(tpy)RuCl(bpm)}₂RhCl₂]³⁺





**Figure 1.** Cyclic voltammograms of the trimetallic complexes [{(tpy)-RuCl(BL)}₂RhCl₂](PF₆)₃ in 0.4 M Bu₄NPF₆ in CH₃CN, where BL = 2,3-bis(2-pyridyl)pyrazine, dpp (A), or 2,2′-bipyrimidine, bpm (B), and tpy = 2,2′:6′,2″-terpyridine. Potentials recorded vs Ag/AgCl reference electrode (0.29 V vs NHE).

The use of dpp as a bridging ligand leads to cis and trans type stereoisomers, around the Ru which are not detectable by cyclic voltammetry or electronic absorption spectroscopy.[46,47] Utilization of the symmetric bridging ligand bpm eliminates the cis/trans type stereoisomers present in the dpp synthons.

These trimetallic complexes were effectively characterized by FAB mass spectral analysis. These supramolecular complexes typically show high mass peaks that are easy to interpret with loss of counterions and intact ligands. Fragmentation patterns for these trimetallics show sequential loss of PF₆⁻ counterions and the chlorides bound to the rhodium center.

**Electrochemistry.** Trimetallic complexes of the form [{(bpy)₂Ru(BL)}₂RhCl₂]⁵⁺ are characterized by reversible ruthenium oxidations, irreversible rhodium reductions, and reversible ligand reductions, with the BLs (dpp or bpm) being reduced prior to the bpy ligands.[32,34] They display a Ru(dπ) HOMO. The LUMO is localized on Rh(dσ*) for dpp and bpm(π*) for the bpm bridged system.

The cyclic voltammogram of [{(tpy)RuCl(dpp)}₂RhCl₂]³⁺ in 0.4 M Bu₄NPF₆/CH₃CN solution is illustrated in Figure 1A and summarized in Table 1.

A reversible redox couple at 1.12 V is observed in the positive potential region. This redox couple is attributed to two overlapping Ru$^{II/III}$ oxidations. These LAs are largely electronically uncoupled, allowing them to function independently.[31,34] The Ru$^{II/III}$ couples occur 480 mV less positive in the [{(tpy)RuCl(dpp)}₂RhCl₂]³⁺ systems relative to the bpy systems, resulting from the chloride coordination on the Ru centers in the tpy systems. Reductively an irreversible peak is observed at −0.47 V. This couple results from the overlapping reduction of the Rh(III) to Rh(II) and then to Rh(I). Similar behavior is reported by DeArmond for the [Rh(bpy)₂Cl₂]⁺.[50] Reduction of the Rh(III) to Rh(I) should be followed by conversion of the formally d⁶ pseudooctahedral Rh(III) to a square planar d⁸ Rh(I). This occurs by

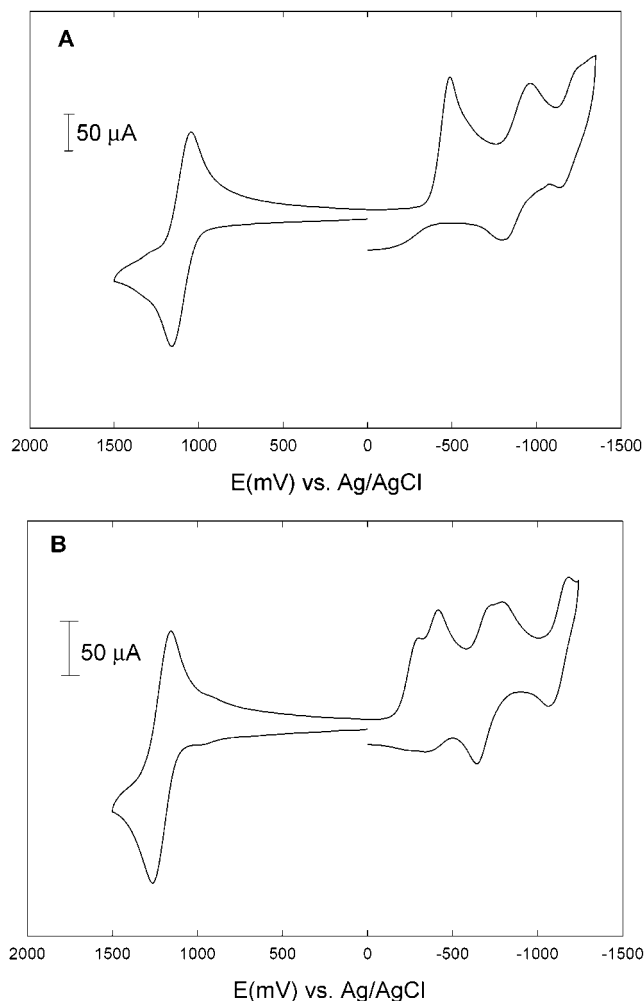(50) (a) Kew, G.; DeArmond, K.; Hanck, K. *J. Phys. Chem.* **1974**, *78*, 727. (b) Kew, G.; Hanck, K.; DeArmond, K. *J. Phys. Chem.* **1975**, *79*, 1828.

chloride loss as evidenced by the presence of free chloride seen in anodic scans that follow cathodic scans through the Rh$^{III/I}$ couple. No evidence of Rh(I) reoxidation is seen in multiple scan experiments. Two quasi-reversible redox couples at −0.87 and −1.20 V are attributed to sequential reduction of the two equivalent dpp bridging ligands, dpp,dpp/dpp,dpp⁻ and dpp,dpp⁻/dpp⁻,dpp⁻, respectively. Further reductive scanning results in a neutral species leading to adsorption of the complex onto the electrode surface. [{(tpy)RuCl(dpp)}₂RhCl₂]³⁺ exhibits a ruthenium(II) based HOMO and a rhodium(III) based LUMO, analogous to [{(bpy)₂Ru(dpp)}₂RhCl₂]⁵⁺. The proposed electrochemical mechanism is shown in Scheme 2. The cyclic voltammogram of [{(tpy)RuCl(bpm)}₂RhCl₂]³⁺ in 0.4 M Bu₄NPF₆/CH₃CN solution is illustrated in Figure 1B and summarized in Table 1. A single reversible oxidation wave is observed at $E_{1/2}$ = 1.21 V and is assigned to the two overlapping Ru$^{II/III}$ redox couples, indicating that the two ruthenium centers are largely electronically uncoupled. Two closely spaced irreversible reductions at −0.26 and −0.38 V in Figure 1B are assigned as sequential one-electron reductions of the rhodium center, Rh$^{III/II}$ and Rh$^{II/I}$. Interestingly, when bpm is used as the BL
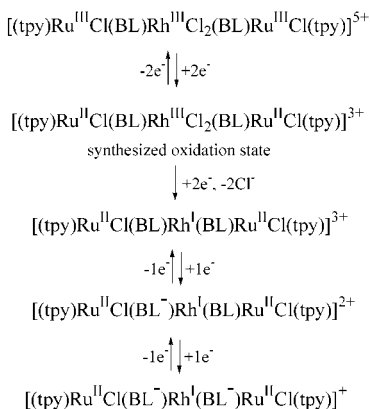
**Table 1.** Electrochemical Properties for a Series of Ru(II) and Ru(II)/Rh(III)/Ru(II) Trimetallic Complexes Where tpy = 2,2′:6′,2″-Terpyridine, dpp = 2,3-Bis(2-pyridyl)pyrazine, and bpm = 2,2′-Bipyrimidine

| $E_{1/2}$ in V$^a$ ($\Delta E_p$ in mV) | assignment |
|---|---|
| [{(tpy)RuCl(dpp)}$_2$RhCl$_2$](PF$_6$)$_3$ | |
| 1.12 (85) | 2Ru$^{III/II}$ |
| $E_p^c = -0.47$ | Rh$^{III/I}$ |
| −0.87 (140) | dpp,dpp/dpp,dpp$^-$ |
| −1.20 (95) | dpp,dpp$^-$/dpp$^-$,dpp$^-$ |
| [{(tpy)RuCl(bpm)}$_2$RhCl$_2$](PF$_6$)$_3$ | |
| 1.12 (100) | 2Ru$^{III/II}$ |
| $E_p^c = -0.26$ | Rh$^{III/II}$ |
| $E_p^c = -0.38$ | Rh$^{II/I}$ |
| −0.70 (100) | bpm,bpm/bpm,bpm$^-$ |
| −1.12 (115) | bpm,bpm$^-$/bpm$^-$,bpm$^-$ |
| [{(bpy)$_2$Ru(dpp)}$_2$RhCl$_2$](PF$_6$)$_5$$^{32b}$ | |
| 1.60 | 2Ru$^{III/II}$ |
| $E_p^c = -0.39$ | Rh$^{III/I}$ |
| −0.79 | dpp,dpp/dpp,dpp$^-$ |
| −1.02 | dpp,dpp$^-$/dpp$^-$dpp$^-$ |
| [{(bpy)$_2$Ru(bpm)}$_2$RhCl$_2$](PF$_6$)$_5$$^{34}$ | |
| 1.70 | 2Ru$^{III/II}$ |
| −0.13 | bpm,bpm/bpm,bpm$^-$ |
| −0.26 | bpm,bpm$^-$/bpm$^-$,bpm$^-$ |
| −0.78 | Rh$^{III/I}$ |
| [(tpy)RuCl(dpp)](PF$_6$)$^{47}$ | |
| 1.00 | Ru$^{III/II}$ |
| −1.21 | dpp$^{0/-}$ |
| −1.54 | tpy$^{0/-}$ |
| [(tpy)RuCl(bpm)](PF$_6$)$^{47}$ | |
| 1.01 | Ru$^{III/II}$ |
| −1.15 | bpm$^{0/-}$ |
| −1.56 | tpy$^{0/-}$ |

$^a$ Potentials reported versus the Ag/AgCl (0.29 V vs NHE) reference electrode in 0.1 M Bu$_4$NPF$_6$ CH$_3$CN.

**Scheme 2.** Electrochemical Mechanism for the Ru,Rh,Ru Triads

[(tpy)Ru$^{III}$Cl(BL)Rh$^{III}$Cl$_2$(BL)Ru$^{III}$Cl(tpy)]$^{5+}$

-2e$^-$ ↑↓ +2e$^-$

[(tpy)Ru$^{II}$Cl(BL)Rh$^{III}$Cl$_2$(BL)Ru$^{II}$Cl(tpy)]$^{3+}$

synthesized oxidation state

↓ +2e$^-$, -2Cl$^-$

[(tpy)Ru$^{II}$Cl(BL)Rh$^I$(BL)Ru$^{II}$Cl(tpy)]$^{3+}$

-1e$^-$ ↑↓ +1e$^-$

[(tpy)Ru$^{II}$Cl(BL$^-$)Rh$^I$(BL)Ru$^{II}$Cl(tpy)]$^{2+}$

-1e$^-$ ↑↓ +1e$^-$

[(tpy)Ru$^{II}$Cl(BL$^-$)Rh$^I$(BL$^-$)Ru$^{II}$Cl(tpy)]$^+$

these two couples shift apart relative to the dpp analogue, indicating some stability of the Rh(II) oxidation state. This is an unusual property for a [Rh(NN)$_2$Cl$_2$]$^+$ system. Reversing the scan after the Rh$^{III/II}$ couple but prior to the Rh$^{II/I}$ couple does lead to the observation of a small return wave corresponding to Rh(II) reoxidation, but this couple remains largely irreversible. Further cathodic scanning past the Rh$^{II/I}$ couple reveals the sequential one-electron reduction of the bpm bridging ligands, bpm,bpm/bpm,bpm$^-$ and bpm,bpm$^-$/bpm$^-$,bpm$^-$. Further reduction leads to adsorption.

The new bpm-based trimetallic complex [{(tpy)RuCl-(bpm)}$_2$RhCl$_2$]$^{3+}$ displays a Rh(d$\sigma$*) LUMO in marked

**Scheme 3.** Orbital Energy Diagram for [{(tpy)RuCl(bpm)}$_2$RhCl$_2$]$^{3+}$ and [{(bpy)$_2$Ru(bpm)}$_2$RhCl$_2$]$^{5+}$
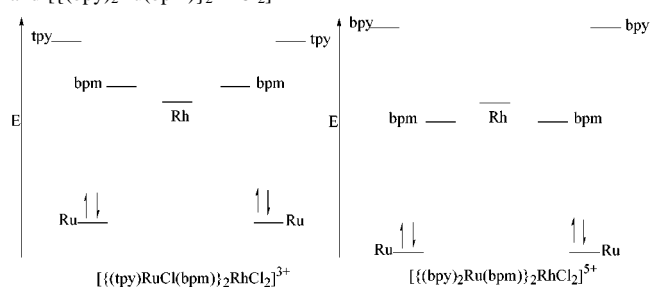


**Scheme 4.** Orbital Energy Diagram for [{(tpy)RuCl(dpp)}$_2$RhCl$_2$]$^{3+}$ and [{(bpy)$_2$Ru(dpp)}$_2$RhCl$_2$]$^{5+}$
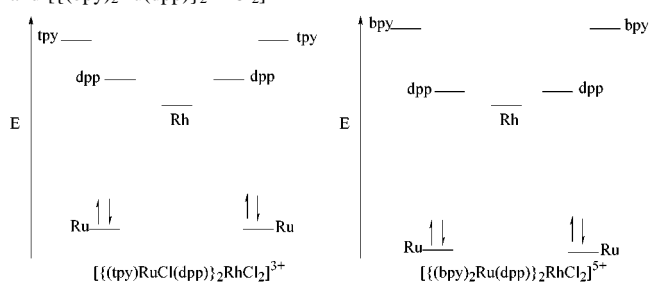


contrast to the bpm($\pi$*) LUMO in [{(bpy)$_2$Ru(bpm)}$_2$RhCl$_2$]$^{5+}$. The redox chemistry of [{(bpy)$_2$Ru(bpm)}$_2$RhCl$_2$]$^{5+}$ is characterized by two reversible one-electron bpm-based reductions at −0.13 and −0.26 V followed by the irreversible reduction of the rhodium center, Rh$^{III/I}$, at −0.78 V.$^{34}$ Variation of the terminal ligands on the Ru metals indirectly modulates the energy of the bpm ligand orbitals. Coordination of the Cl$^-$ ligand to ruthenium in [{(tpy)RuCl-(bpm)}$_2$RhCl$_2$]$^{3+}$ results in a more electron rich Ru center. This leads to less stabilization of the bpm($\pi$*) orbitals relative to the bis-bpy analogue. As the bpm($\pi$*) and Rh(d$\sigma$*) orbitals are very close in energy, this modulation of the bpm($\pi$*) orbital energies by terminal ligand variation leads to orbital inversion, Schemes 3 and 4.

This electrochemical data indicates that, in the trimetallic complexes [{(tpy)RuCl(BL)}$_2$RhCl$_2$]$^{3+}$ and [{(bpy)$_2$Ru(BL)}$_2$RhCl$_2$]$^{5+}$, the BL($\pi$*) and Rh(d$\sigma$*) orbitals are close in energy. In all cases the HOMO is localized on the Ru(d$\pi$) orbitals. The localization of the LUMO can be modulated, being Rh(d$\sigma$*) in nature for [{(tpy)RuCl(BL)}$_2$RhCl$_2$]$^{3+}$ (BL = dpp or bpm) and [{(bpy)$_2$Ru(dpp)}$_2$RhCl$_2$]$^{5+}$ and bpm($\pi$*) in nature for [{(bpy)$_2$Ru(bpm)}$_2$RhCl$_2$]$^{5+}$.

**Electronic Absorption Spectroscopy.** The electronic absorption spectral data in acetonitrile of the new trimetallic complexes, [{(tpy)RuCl(dpp)}$_2$RhCl$_2$]$^{3+}$ and [{(tpy)RuCl-(bpm)}$_2$RhCl$_2$]$^{3+}$, as well as their monometallic precursors and trimetallic bpy analogues are assembled in Table 2. The UV regions of the spectra for all of these complexes show BL (dpp or bpm) and terminal ligand (tpy or bpy) $\pi \rightarrow \pi$* transitions with the BLs expected to show the lowest lying $\pi \rightarrow \pi$* bands.$^{1,4-9,34,47,51}$ The visible regions of the spectra are dominated by overlapping Ru(d$\pi$) $\rightarrow$ BL($\pi$*) and Ru(d$\pi$) $\rightarrow$ bpy or tpy($\pi$*) charge transfer (CT) transitions with BL based bands occurring at lower energy.

(51) Krause, E.; Ferguson, J. *Prog. Inorg. Chem.* **1989**, *37*, 293.

**Table 2.** Electronic Absorption Spectroscopy for a Series of Ru(II) and Ru(II)/Rh(III)/Ru(II) Trimetallic Complexes Where tpy = 2,2′:6′,2″-Terpyridine, dpp = 2,3-Bis(2-pyridyl)pyrazine, and bpm = 2,2′-Bipyrimidine[a]

| $\lambda_{max}$ (nm) | $\epsilon \times 10^{-4}$ (M$^{-1}$ cm$^{-1}$) | assignments |
|---|---|---|
| [{(tpy)RuCl(dpp)}$_2$RhCl$_2$](PF$_6$)$_3$ |
| 274 | 4.70 | tpy ($\pi \rightarrow \pi^*$) |
| 314 | 6.48 | tpy ($\pi \rightarrow \pi^*$) |
| 330(sh) | 5.41 | Ru(d$\pi$) $\rightarrow$ tpy($\pi^*$) CT |
| 360(sh) | 2.72 | dpp ($\pi \rightarrow \pi^*$) |
| 460 | 1.13 | Ru(d$\pi$) $\rightarrow$ tpy($\pi^*$) CT |
| 540 | 2.72 | Ru(d$\pi$) $\rightarrow$ dpp($\pi^*$) CT |
| [{(tpy)RuCl(bpm)}$_2$RhCl$_2$](PF$_6$)$_3$ |
| 272 | 6.21 | tpy ($\pi \rightarrow \pi^*$) |
| 312 | 5.50 | tpy ($\pi \rightarrow \pi^*$) |
| 330(sh) | 3.11 | Ru(d$\pi$) $\rightarrow$ tpy($\pi^*$) CT |
|  |  | bpm ($\pi \rightarrow \pi^*$) |
| 464 | 2.50 | Ru(d$\pi$) $\rightarrow$ tpy($\pi^*$) CT |
|  |  | Ru(d$\pi$) $\rightarrow$ bpm($\pi^*$) CT |
| 656 | 1.00 | Ru(d$\pi$) $\rightarrow$ bpm($\pi^*$) CT |
| [{(bpy)$_2$Ru(dpp)}$_2$RhCl$_2$](PF$_6$)$_5$b |
| 242 | 6.53 | bpy ($\pi \rightarrow \pi^*$) |
| 284 | 9.64 | bpy ($\pi \rightarrow \pi^*$) |
| 344(sh) | 2.87 | dpp ($\pi \rightarrow \pi^*$) |
| 414 | 1.74 | Ru(d$\pi$) $\rightarrow$ bpy ($\pi^*$) CT |
| 514 | 2.01 | Ru(d$\pi$) $\rightarrow$ dpp ($\pi^*$) CT |
| [{(bpy)$_2$Ru(bpm)}$_2$RhCl$_2$](PF$_6$)$_5$34 |
| 278 | 9.00 | bpy ($\pi \rightarrow \pi^*$) |
| 412 | 3.70 | Ru(d$\pi$) $\rightarrow$ bpy ($\pi^*$) CT |
|  |  | Ru(d$\pi$) $\rightarrow$ bpm($\pi^*$) CT |
| 594 | 0.99 | Ru(d$\pi$) $\rightarrow$ bpm($\pi^*$) CT |
| [(tpy)RuCl(dpp)](PF$_6$)47 |
| 238 | 2.32 | dpp ($\pi \rightarrow \pi^*$) |
| 276 | 2.00 | tpy ($\pi \rightarrow \pi^*$) |
| 314 | 2.91 | tpy ($\pi \rightarrow \pi^*$) |
| 370 | 0.44 | Ru(d$\pi$) $\rightarrow$ tpy($\pi^*$) CT |
| 514 | 0.89 | Ru(d$\pi$) $\rightarrow$ tpy($\pi^*$) CT |
|  |  | Ru(d$\pi$) $\rightarrow$ dpp($\pi^*$) CT |
| [(tpy)RuCl(bpm)](PF$_6$)47 |
| 240 | 3.94 | bpm ($\pi \rightarrow \pi^*$) |
| 266 | 2.92 | tpy ($\pi \rightarrow \pi^*$) |
| 316 | 3.31 | tpy ($\pi \rightarrow \pi^*$) |
| 370 | 0.96 | Ru(d$\pi$) $\rightarrow$ tpy($\pi^*$) CT |
| 516 | 0.99 | Ru(d$\pi$) $\rightarrow$ tpy($\pi^*$) CT |
|  |  | Ru(d$\pi$) $\rightarrow$ bpm($\pi^*$) CT |

[a] Absorption spectra taken in acetonitrile at room temperature. [b] Lowest energy CT transitions taken from ref 32b; other assignments and extinction coefficients result from this work.

The electronic absorption spectra for [{(tpy)RuCl(dpp)}$_2$-RhCl$_2$]$^{3+}$ and [{(tpy)RuCl(bpm)}$_2$RhCl$_2$]$^{3+}$ in acetonitrile are characterized by high-energy tpy and BL ($\pi \rightarrow \pi^*$) transitions, with tpy bands at 274 nm and 314 nm. A shoulder observed at ca. 340 or 360 nm is attributed to the BL($\pi \rightarrow \pi^*$) transition for dpp and bpm, respectively.[31b] Significant spectral differences between these two trimetallics becomes apparent when the visible regions of the spectra are compared. The lowest energy transition at 540 nm for [{(tpy)RuCl(dpp)}$_2$RhCl$_2$]$^{3+}$, which contains the Ru(d$\pi$) $\rightarrow$ dpp($\pi^*$) CT transition, is 116 nm higher in energy than the corresponding transition for the bpm analogue. This suggests that the impact of the rhodium coordination on the BL $\pi^*$ orbitals is more dramatic for bpm than dpp, consistent with the electrochemical behavior.[47]

A comparison of the electronic absorption spectra of the trimetallic, [{(tpy)RuCl(dpp)}$_2$RhCl$_2$]$^{3+}$, and its monometallic precursor, [(tpy)RuCl(dpp)]$^+$, reveals some interesting fea-

tures. The UV regions of the spectra are virtually identical, consisting of dpp and tpy based $\pi \rightarrow \pi^*$ transitions. As expected, these transitions are more intense for the trimetallic complex, in keeping with its molecular structure. Coordination of two monometallic precursors, [(tpy)RuCl(dpp)]$^+$, to the rhodium metal center red shifts the Ru(d$\pi$) $\rightarrow$ dpp($\pi^*$) CT transition from 516 nm for the monometallic to 540 nm. This results from rhodium coordination stabilizing the dpp-($\pi^*$) orbitals of the trimetallic, consistent with the electrochemical behavior of the title trimetallic. The Ru(d$\pi$) $\rightarrow$ dpp($\pi^*$) CT band at 540 nm in [{(tpy)RuCl(dpp)}$_2$RhCl$_2$]$^{3+}$ is red shifted relative to 514 nm in [{(bpy)$_2$Ru(dpp)}$_2$RhCl$_2$]$^{5+}$. This shift is due to higher energy Ru(d$\pi$) orbitals in [{(tpy)RuCl(dpp)}$_2$RhCl$_2$]$^{3+}$ due to the coordinated chloride, also consistent with the electrochemical data.

The UV regions of the spectra for the bpm monometallic, [(tpy)RuCl(bpm)]$^+$, and the trimetallic, [{(tpy)RuCl(bpm)}$_2$-RhCl$_2$]$^{3+}$, complexes are very similar, with intense intraligand $\pi \rightarrow \pi^*$ transitions from bpm and tpy. Upon coordination of the monometallic to the rhodium metal center, the Ru(d$\pi$) $\rightarrow$ bpm($\pi^*$) CT transition at 516 nm red shifts to 656 nm. This is the result of stabilization of the bpm($\pi^*$) orbitals from coordination of the electron-withdrawing rhodium center. This 656 nm Ru(d$\pi$) $\rightarrow$ bpm($\pi^*$) CT transition of the title trimetallic is red shifted relative to the 594 nm peak in the bpy analogue [{(bpy)$_2$Ru(bpm)}$_2$RhCl$_2$]$^{5+}$, consistent with the electrochemical data.

Both title trimetallics [{(tpy)RuCl(BL)}$_2$RhCl$_2$]$^{3+}$ possess Ru(d$\pi$) based HOMOs and Rh(d$\sigma^*$) LUMOs. Spectroscopically, no optical transition is seen representing this metal-to-metal charge transfer (MMCT) excitation. This likely results from the high extinction coefficient for the lowest energy Ru(d$\pi$) $\rightarrow$ BL($\pi^*$) CT transition and the low overlap of the Ru(d$\pi$) and Rh(d$\sigma^*$) orbitals leading to low intensity of the MMCT transition. Energetically, this MMCT state lies lower in energy than the optically populated MLCT state. This should lead to the intramolecular electron transfer to the Rh center in these complexes leading to quenching of the MLCT emission, discussed below.

**Spectroelectrochemistry.** Spectroelectrochemistry was used to study the electronic absorption spectroscopy and cyclic voltammetry of the title trimetallics. The spectroelectrochemistry of [{(tpy)RuCl(dpp)}$_2$RhCl$_2$]$^{3+}$ and [{(tpy)RuCl(bpm)}$_2$RhCl$_2$]$^{3+}$ is shown in Figures 2 and 3.

The two-electron oxidation of [{(tpy)RuCl(dpp)}$_2$RhCl$_2$]$^{3+}$ is greater than 95% reversible. Electrolysis at 1.35 V, past the Ru$^{III/II}$ redox couple, shows a loss of the absorption band at 540 nm. This is consistent with its assignment as a Ru(d$\pi$) $\rightarrow$ dpp($\pi^*$) CT transition. The absorption band at 314 nm and its lowest energy shoulder at 360 nm broaden and shift to lower energy upon oxidation of the ruthenium metal centers, consistent with a ligand-based ($\pi \rightarrow \pi^*$) transition.[31] A component (at ca. 330 nm) is lost upon oxidation of the ruthenium centers, consistent with a higher energy Ru(d$\pi$) $\rightarrow$ tpy($\pi^*$) CT transition occurring in this region. Similar behavior has been reported for the oxidation
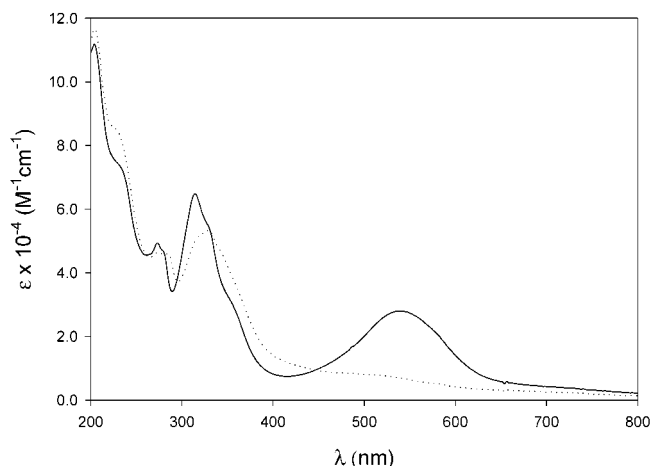
**Figure 2.** Spectroelectrochemistry for [{(tpy)RuCl(dpp)}$_2$RhCl$_2$](PF$_6$)$_3$ where tpy = 2,2':6',2''-terpyridine and dpp = 2,3-bis(2-pyridyl)pyrazine in 0.1 M Bu$_4$NPF$_6$ in CH$_3$CN at room temperature: (—) [{(tpy)RuCl(dpp)}$_2$RhCl$_2$]$^{3+}$, (···) [{(tpy)RuCl(dpp)}$_2$RhCl$_2$]$^{5+}$.
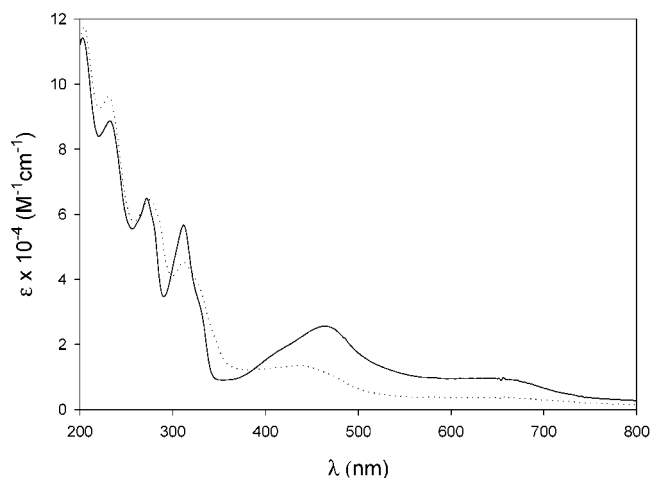


**Figure 3.** Spectroelectrochemistry for [{(tpy)RuCl(bpm)}$_2$RhCl$_2$](PF$_6$)$_3$ where tpy = 2,2':6',2''-terpyridine and bpm = 2,2'-bipyrimidine in 0.1 M Bu$_4$NPF$_6$ in CH$_3$CN at room temperature: (—) [{(tpy)RuCl(bpm)}$_2$RhCl$_2$]$^{3+}$, (···) [{(tpy)RuCl(bpm)}$_2$RhCl$_2$]$^{5+}$.

of an array of Ru(tpy) moieties.[52,53] Reduction of the trimetallic complex was irreversible due to reaction of the reduced rhodium center, consistent with the Rh(d$\sigma$*) nature of the LUMO.

Very similar spectroelectrochemistry is observed for the bpm-bridged trimetallic, [{(tpy)RuCl(bpm)}$_2$RhCl$_2$]$^{3+}$, Figure 3. Oxidation of the ruthenium centers at 1.45 V is greater than 95% reversible. This electrolysis leads to the loss of the absorption bands at ca. 330, 464, and 656 nm, consistent with their assignment as higher energy Ru(d$\pi$) → tpy($\pi$*), Ru(d$\pi$) → tpy($\pi$*), and Ru(d$\pi$) → bpm($\pi$*) CT transitions, respectively. A broadening and red shift of the absorption

band at 312 nm and shoulder at ca. 340 nm is consistent with overlapping intraligand $\pi \rightarrow \pi$* transitions. Reduction was irreversible, consistent with a Rh(d$\sigma$*) LUMO.

We were unable to detect any emission from the title trimetallics at room temperature or 77 K in acetonitrile solutions. This may result from the weak response of the photomultiplier tube in the region in which these complexes are expected to emit, a low quantum yield for emission, or a quenching of the MLCT excited state by the expected intramolecular electron transfer to the rhodium metal center. The [{(bpy)$_2$Ru(bpm)}$_2$RhCl$_2$]$^{5+}$ system displays an emission at 800 nm,[34] supporting the role of intramolecular electron-transfer quenching of the MLCT excited state in the title trimetallics in quenching their MLCT emission.

## Conclusions

The trimetallic complexes [{(tpy)RuCl(dpp)}$_2$RhCl$_2$]$^{3+}$ and [{(tpy)RuCl(bpm)}$_2$RhCl$_2$]$^{3+}$ were synthesized in good yield using a building-block approach. These systems assemble two ruthenium light absorbers to a central rhodium electron collector in the form LA−BL−EC−BL−LA. Use of excess rhodium leads to the trimetallic products, which are easily purified by aqueous washing followed by flash precipitation. The complexes displayed FAB mass spectra consistent with their formulation. The use of a tridentate capping ligand (tpy) with the sixth coordination site of the ruthenium centers occupied by a monodentate chloride ligand results in interesting spectroscopic and electrochemical behavior.

Both trimetallic complexes [{(tpy)RuCl(dpp)}$_2$RhCl$_2$]$^{3+}$ and [{(tpy)RuCl(bpm)}$_2$RhCl$_2$]$^{3+}$ contain ruthenium-based HOMOs and rhodium-based LUMOs. Coordination of the weak field Cl$^-$ ligand to the ruthenium centers of the trimetallic complex results in higher energy bpm($\pi$*) orbitals relative to the bpy system localizing the LUMO on the Rh(d$\sigma$*) orbital. This orbital inversion by remote ligand variation is quite unique. Interestingly, this [{(tpy)RuCl(bpm)}$_2$RhCl$_2$]$^{3+}$ system shows separate Rh$^{III/II}$ and Rh$^{II/I}$ couples indicating a somewhat stable Rh$^{II}$ state. The ruthenium orbitals of the title trimetallics are higher in energy relative to the bpy analogues. This new [{(tpy)RuCl(BL)}$_2$RhCl$_2$]$^{3+}$ structural motif has resulted in systems that display interesting properties. Studies are underway probing the photochemistry of these systems.[54] Interestingly, the properties of these complexes could be further tuned by substitution of the chloride which occupies the sixth coordination site of the ruthenium centers.

(52) Vrana, L. M.; Brewer, K. J. *J. Photochem. Photobiol., A* **1997**, *109*, 2013.
(53) *J. Organomet. Chem.* **1998**, *554*, 29.

(54) Swavey, S.; Brewer, K. J. Work in progress.