



# Photoinduced intramolecular electron transfer in bimetallic donor–acceptor assemblies

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## Abstract

A series of bimetallic complexes containing an ( $\alpha$ -diimine)(CO)<sub>3</sub>Re<sup>I</sup> chromophore and a covalently attached ruthenium pentaammine moiety has been prepared and characterized. Ground state properties, including absorption spectra and redox potentials, are consistent with very weak metal–metal interaction in these systems. However, picosecond luminescence decay profiles indicate that emission from the Re  $\rightarrow$   $\alpha$ -diimine <sup>3</sup>MLCT excited state is strongly quenched by attachment of the Ru center for complexes in both Re<sup>I</sup>/Ru<sup>II</sup> and Re<sup>I</sup>/Ru<sup>III</sup> oxidation states. Such behaviour is consistent with extremely rapid photoinduced intramolecular electron transfer processes, and the data are interpreted in light of the ‘superexchange’ mechanism. No short-lived transients are observed for the Re<sup>I</sup>/Ru<sup>III</sup> bimetallic complexes, suggesting that electron transfer may occur from the <sup>1</sup>MLCT state in these systems.

**Keywords:** Photoinduced intramolecular electron transfer; Rhenium complexes; Ruthenium complexes; Carbonyl complexes; Diimine complexes; Bimetallic complexes

## 1. Introduction

Over the last 30 years, a considerable amount of effort has been devoted to probing the mechanisms of long range electron transfer (ET), and a detailed theoretical treatment has gradually emerged [1–3]. However, experimental studies have been hampered by the inherent difficulty of designing (and building) systems in which each variable can be controlled independently. As a result, many interesting theoretical predictions remain virtually untested. For example, while numerous studies have focused on the distance dependence of ET rates [4–10], little quantitative information regarding the modulation of this distance dependence by reaction driving force is available. Further, there are few reported studies of intramolecular photoinduced electron transfer between two transition metal centers [11,12].

In order to gain a better understanding of ET fundamentals in such systems, we have designed and synthesized a series of molecules containing both an inorganic chromophore and an inorganic electron transfer quenching agent, separated by a suitable bridging ligand.

Transition metal complexes based on the parent species [(LL)(CO)<sub>3</sub>Re(BL)]<sup>+</sup> (where LL represents 2,2′-bipyridine or a related  $\alpha$ -diimine ligand and BL represents a pyridine-based bridging ligand) have been used as the chromophores in this study. Rhenium complexes of this type possess a highly emissive Re  $\rightarrow$  bpy MLCT excited state, and their attractive photophysical properties have been previously exploited to probe intramolecular long range energy transfer and electron transfer processes [13–18]. The <sup>3</sup>MLCT excited state of [(bpy)(CO)<sub>3</sub>ReCl] has been shown to undergo both oxidative and reductive quenching [19–21], and the excited state redox potentials can be ‘tuned’ by making appropriate substitutions on the bpy ligand without causing any gross change in the nature of the excited state or in the magnitude of electronic coupling with a covalently attached quencher [13,22]. In the current work, the [–Ru(NH<sub>3</sub>)<sub>5</sub>]<sup>n+</sup> ( $n = 2, 3$ ) moiety is employed as the quenching functionality.

The bimetallic systems described herein possess several features relevant to the study of intramolecular photoinduced electron transfer. First, the direction of electron transfer can be controlled simply by changing the oxidation state of the quencher portion of the molecule. Assuming a through-bond pathway, observation of a rapid rate for the oxidative quenching

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direction (Re chromophore as  $e^-$  donor) would suggest that the unoccupied orbitals of the bridging ligand serve to mediate the ET process [23–27]. Conversely, rapid reductive quenching (Re chromophore as  $e^-$  acceptor) would imply metal–metal coupling through the occupied orbitals of the bridging ligand ('hole' transfer) [23–27]. Second, as noted above, the reaction energetics are well-defined and easily altered via simple ligand substitution. This not only allows for the study of electron transfer versus hole transfer mechanisms in finer detail, but also offers the opportunity to more fully explore the interplay between reaction driving force, distance and rate without the heroic synthetic efforts typically required for model systems employing covalently attached organic donors and/or acceptors.

In this report, we describe the synthesis of several heterobimetallic  $\text{Re}^I/\text{Ru}^{II/III}$  complexes, along with their electrochemical and spectroscopic characterization. Preliminary investigations of photoinduced electron transfer in these systems have focused on the measurement of ET rates by monitoring luminescence decay profiles. The kinetic results are interpreted in terms of quantum mechanical ET theory.

## 2. Experimental

### 2.1. Materials

$\text{Re}(\text{CO})_5\text{Cl}$  (Pressure Chemical Co.), 2,2'-bipyridine (bpy, GFS Chemicals) and 1,2-bis(4-pyridyl)ethane (bpa, Aldrich) were used as received. 4,4'-Dimethyl-2,2'-bipyridine ( $\text{Me}_2\text{bpy}$ ) and 4,4',5,5'-tetramethyl-2,2'-bipyridine ( $\text{Me}_4\text{bpy}$ ) were generous gifts from Professor C.M. Elliott. 4,4'-Di(isopropylcarboxylate)-2,2'-bipyridine (DCObpy) was prepared from  $\text{Me}_2\text{bpy}$  by the method of Delaive et al. [28]. The 1,3-bis(4-pyridyl)propane (bpp) used in this study was obtained from Reilly Tar and Chemical and was recrystallized twice from methanol and diethyl ether.  $^1\text{H}$  NMR spectroscopy was utilized to confirm the purity of all ligands. Tetraalkylammonium salts (electrometric grade, Southwestern Analytical) were dried overnight in a vacuum oven (60 °C) before being employed in the electrochemical measurements. All solvents were HPLC or spectral grade and were purified and dried by distillation using established procedures. Elemental analyses were performed by Atlantic Microlab, Inc., Norcross, GA.

### 2.2. *Fac*-(LL)(CO)<sub>3</sub>ReCl (LL = py, $\text{Me}_4\text{bpy}$ )

These compounds were prepared by refluxing a stoichiometric mixture of  $\text{Re}(\text{CO})_5\text{Cl}$  and the desired ligand in isooctane for several hours under a nitrogen blanket. The solution was then cooled, filtered, and washed liberally with isooctane to remove any unreacted

$\text{Re}(\text{CO})_5\text{Cl}$ . Typical yields of isolated product were 90–95%.

### 2.3. *Fac*-(DCObpy)(CO)<sub>3</sub>ReCl

900 mg of  $\text{Re}(\text{CO})_5\text{Cl}$  (2.49 mmol) and 817 mg of DCObpy (2.49 mmol) were dissolved together in 100 ml of isopropanol and heated to 60 °C for 3 h. The crude product, a bright red solid, was isolated by filtration and washed several times with copious amounts of isooctane. Final purification was achieved by the slow addition of anhydrous diethyl ether to a concentrated solution of the complex in  $\text{CH}_2\text{Cl}_2$ , followed by filtration and washing with ether to give a pure red solid. Yield 1.44 g, 91%.

### 2.4. *Fac*-[(LL)(CO)<sub>3</sub>Re(CH<sub>3</sub>CN)](PF<sub>6</sub>) (LL = bpy, $\text{Me}_4\text{bpy}$ , DCObpy)

These complexes were prepared by refluxing the corresponding *fac*-(LL)(CO)<sub>3</sub>ReCl compound in  $\text{CH}_3\text{CN}$  containing excess  $\text{AgCF}_3\text{SO}_3$  for 12 h under nitrogen. AgCl was removed by filtration and the solvent was evaporated in vacuo, after which the residue was dissolved in a minimum of  $\text{CH}_2\text{Cl}_2$  and added dropwise to stirred anhydrous diethyl ether to precipitate the *fac*-[(LL)(CO)<sub>3</sub>Re(CH<sub>3</sub>CN)](CF<sub>3</sub>SO<sub>3</sub>) salt. These were converted to the desired PF<sub>6</sub><sup>-</sup> salts by dissolving in  $\text{CH}_3\text{CN}$  and adding solid  $\text{NH}_4\text{PF}_6$ . The mixture was then reduced to one-third of its original volume by rotary evaporation, and the resulting precipitate was collected and washed with water and ether. Finally, the product was redissolved in  $\text{CH}_3\text{CN}$  and diethyl ether was slowly added to yield the product in crystalline form. Typical yields were 90%.

### 2.5. *Fac*-[(LL)(CO)<sub>3</sub>Re(BL)](PF<sub>6</sub>) (LL = bpy, $\text{Me}_4\text{bpy}$ , DCObpy; BL = bpa, bpp, 4-ethylpyridine)

This series of complexes was prepared by the method of Luong [29], which involves the direct reaction of an approximately tenfold excess of the appropriate ligand with *fac*-[(LL)(CO)<sub>3</sub>Re(CH<sub>3</sub>CN)](PF<sub>6</sub>) in THF solution at reflux under a nitrogen atmosphere for 2 h. After cooling, anhydrous diethyl ether was added dropwise to give crystalline product. Typical yields were 80–85%.

### 2.6. [Ru(NH<sub>3</sub>)<sub>5</sub>(BL)](PF<sub>6</sub>)<sub>2</sub> (BL = bpa, bpp)

These compounds were prepared by the method of Ford [30], using  $[\text{Ru}(\text{NH}_3)_5(\text{H}_2\text{O})](\text{PF}_6)_2 \cdot \text{H}_2\text{O}$  generated essentially as described by Harrison et al. [31]. Yields 80–85%.

2.7. *Fac*-[(LL)(CO)<sub>3</sub>Re(BL)Ru(NH<sub>3</sub>)<sub>5</sub>](PF<sub>6</sub>)<sub>3</sub>  
(LL = bpy, Me<sub>4</sub>bpy, DCObpy; BL = bpa, bpp)

The syntheses of these systems were carried out by a procedure which is described in detail below for the case LL = bpy and BL = bpp. In a typical experiment, [(bpy)(CO)<sub>3</sub>Re(CH<sub>3</sub>CN)](PF<sub>6</sub>) (0.24 g, 0.38 mmol) and [Ru(NH<sub>3</sub>)<sub>5</sub>(bpp)](PF<sub>6</sub>)<sub>2</sub> (0.24 g, 0.35 mmol) were placed in a 100 ml Schlenk flask which was wrapped with aluminum foil to afford protection from light, and the flask was deoxygenated on a vacuum line. Deoxygenated acetone (30 ml) was added via syringe to the flask, and the reaction mixture was stirred for 4 h at room temperature. No significant color change was observed during this period. The solution was filtered into a 150 ml Schlenk flask and 100 ml of deoxygenated CH<sub>2</sub>Cl<sub>2</sub> was slowly added to yield a yellow precipitate, which was subsequently dissolved in 10 ml of deoxygenated acetone and reprecipitated by the addition of CH<sub>2</sub>Cl<sub>2</sub>. The resulting yellow solid was collected and dried in vacuo, then redissolved in 10 ml of acetone and reprecipitated by the addition of deoxygenated water (100 ml). The bright yellow salt was dissolved in 20 ml of acetone, filtered to remove insoluble impurities, and precipitated as the trichloride salt by the addition of a saturated solution of tetra(n-butyl)ammonium chloride in acetone (5 ml). The dark orange material was collected by filtration and dried by washing with several 10 ml portions of anhydrous diethyl ether. The trichloride salt was then immediately dissolved in 15 ml of water and filtered. A saturated aqueous solution of NH<sub>4</sub>PF<sub>6</sub> was then slowly added, and the solution was cooled to 4 °C. The yellow solid was collected, washed with cold water, ethanol and ether. The [(bpy)(CO)<sub>3</sub>Re(bpp)-Ru(NH<sub>3</sub>)<sub>5</sub>](PF<sub>6</sub>)<sub>3</sub> was dried in vacuo and stored under argon at 4 °C (protected from light). Yield 390 mg, 90% based on Ru.

*Note:* the [(DCObpy)(CO)<sub>3</sub>Re(BL)Ru(NH<sub>3</sub>)<sub>5</sub>](PF<sub>6</sub>)<sub>3</sub> compounds are somewhat soluble in CH<sub>2</sub>Cl<sub>2</sub>, so diethyl ether rather than CH<sub>2</sub>Cl<sub>2</sub> was used to precipitate all DCObpy complexes.

2.8. *Fac*-[(LL)(CO)<sub>3</sub>Re(BL)Ru(NH<sub>3</sub>)<sub>5</sub>](PF<sub>6</sub>)<sub>4</sub>  
(LL = bpy, Me<sub>4</sub>bpy, DCObpy; BL = bpa, bpp)

The syntheses of these systems were carried out by a procedure which is described in detail below for the case LL = bpy and BL = bpa. The entire preparation was carried out in the absence of light. [(bpy)(CO)<sub>3</sub>Re(bpp)Ru(NH<sub>3</sub>)<sub>5</sub>](PF<sub>6</sub>)<sub>3</sub> (110 mg, 0.084 mmol) was dissolved in deoxygenated CH<sub>3</sub>CN (5 ml). A solution of Br<sub>2</sub> in CH<sub>3</sub>CN (16.5 ml, 2.8 × 10<sup>-3</sup> M, 0.045 mmol) was slowly added to the stirred solution. After 15 min, the resulting solution was added dropwise to stirred anhydrous diethyl ether (100 ml), giving a yellow precipitate. The crude product was collected on

a frit, washed with several portions of CH<sub>2</sub>Cl<sub>2</sub> and redissolved in acetone (5 ml). A saturated aqueous solution of NH<sub>4</sub>PF<sub>6</sub> (5 ml) was added and the mixture was cooled to 4 °C. The resulting yellow solid was collected, washed with cold water and ether. The product was placed in a glass vial under argon, protected from light, and stored at 4 °C. Yield 738 mg, 60%.

## 2.9. Methods

<sup>1</sup>H NMR spectra were acquired either in d<sub>6</sub>-acetone or d<sub>6</sub>-dimethyl sulfoxide (Cambridge Isotopes) using a Varian Gemini 200 MHz NMR spectrometer. All chemical shifts are reported versus TMS as an internal standard.

Electronic absorption spectra were recorded on an Aviv model 14DS spectrophotometer equipped for computerized data acquisition. Excitation and emission spectra were obtained using a Perkin-Elmer LS50 luminescence spectrometer.

Electrochemical measurements were performed using an EG&G PAR model 273 potentiostat/galvanostat and a Houston Instrument model 200 XY recorder. Cyclic voltammetry was conducted with a freshly polished glassy carbon working electrode, a Pt wire auxiliary electrode, and a saturated sodium calomel (SSCE) reference electrode. The working electrode was cleaned by polishing with 0.05 μm alumina (Buehler), followed by ultrasonication (10 min) and rinsing with water and acetone. Samples were dissolved in spectral grade acetonitrile or dimethyl sulfoxide (to ~10<sup>-3</sup> M) with 0.1 M tetrabutylammonium hexafluorophosphate (TBAH) as supporting electrolyte. All solutions were deoxygenated by bubbling with argon for at least 5 min prior to scanning. All potentials are reported versus SSCE and are uncorrected for junction potentials.

Spectrophotometric titrations were performed in the absence of light using deoxygenated solvents. Titration was carried out by adding aliquots of a standardized Br<sub>2</sub> solution to a solution of the complex and monitoring the change in the absorbance spectrum. A solution of Br<sub>2</sub> in CH<sub>3</sub>CN (0.1 N) was prepared for this purpose by adding 0.68 ml of bromine to 250 ml of deoxygenated CH<sub>3</sub>CN. This stock solution was then standardized by titration using thiosulfate as a primary standard and diluted as necessary.

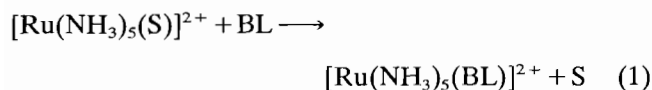
Samples were deoxygenated for at least four freeze-pump-thaw cycles and then sealed with a high vacuum Teflon stopcock prior to emission measurements. Luminescence lifetimes greater than 50 ns were obtained by monitoring the emission decay subsequent to 355 nm pulse excitation (~7 ns fwhm) from a Lumonics HY750 Nd:YAG pulsed laser system. The signal from the Hamamatsu R955 PMT was collected by a LeCroy model 3500SA transient digitizer and lifetimes were determined by a least-squares fitting

procedure. Plots of  $\ln(I_{em})$  versus time were linear for at least four half-lives. Lifetime measurements on shorter-lived species were performed at the NSF Center for Photoinduced Charge Transfer at the University of Rochester. Those data were collected with a single photon counting system incorporating a Quantronix 116 Mode-Locked Nd:YAG laser and capable of  $\sim 2$  ps resolution. A more complete description of this instrument is available elsewhere [32].

### 3. Results

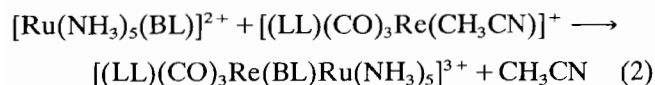
#### 3.1. Synthesis

The majority of the preparations described in Section 2 utilize  $[\text{Ru}(\text{NH}_3)_5(\text{H}_2\text{O})](\text{PF}_6)_2$  dissolved in acetone as a synthetic intermediate. The reactions (Eq. (1)) in acetone are rapid, apparently quantitative, and particularly useful for cases where the entering ligand is insoluble in water.

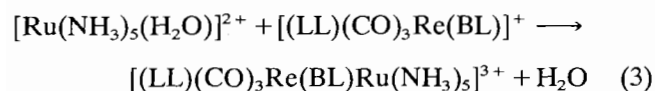


(S=acetone or water; BL=bpa or bpp)

In the preparation of the ligand-bridged heterobinuclear complexes, the reactivity of  $[(\text{LL})(\text{CO})_3\text{Re}(\text{CH}_3\text{CN})]^+$  was exploited (Eq. (2)).



The reaction can be also carried out by the addition of the ruthenium pentaammine moiety to the rhenium complex (Eq. (3)).



However, this latter route is noticeably slower, more prone to undesirable side reactions and less synthetically useful than reaction (2).

$[(\text{LL})(\text{CO})_3\text{Re}(\text{BL})\text{Ru}(\text{NH}_3)_5]^{3+}$  can be oxidized by bromine in acetonitrile to obtain  $[(\text{LL})(\text{CO})_3\text{Re}(\text{BL})\text{Ru}(\text{NH}_3)_5]^{4+}$ . Careful control of reactant stoichiometry is required, since excess bromine produces side products which complicate the kinetic analysis.  $^1\text{H}$  NMR spectra suggest that excess  $\text{Br}_2$  results in substitution on the  $\alpha$ -diimine ligand rings.

The stoichiometry of  $[(\text{LL})(\text{CO})_3\text{Re}(\text{BL})\text{Ru}(\text{NH}_3)_5]^{3+}$  oxidation by bromine in acetonitrile was determined by spectrophotometric titration, and typical data are shown in Fig. 1 (for  $[(\text{bpy})(\text{CO})_3\text{Re}(\text{bpp})\text{Ru}(\text{NH}_3)_5](\text{PF}_6)_3$ ). The ratio of moles of bromine consumed per mole of binuclear complex was determined to be

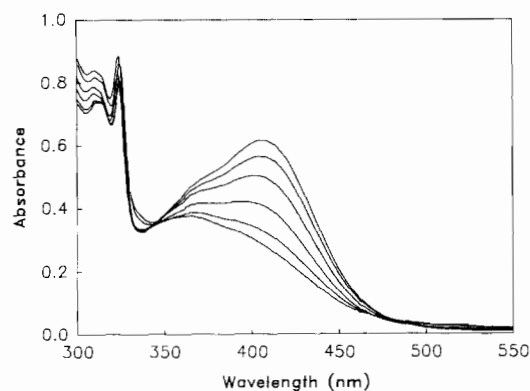
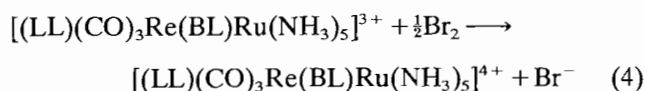


Fig. 1. Electronic absorption spectra recorded during the titration of  $[(\text{bpy})(\text{CO})_3\text{Re}(\text{bpp})\text{Ru}(\text{NH}_3)_5](\text{PF}_6)_3$  by  $\text{Br}_2$  in  $\text{CH}_3\text{CN}$  (see text).

$0.5 \pm 0.01$  for each of the six complexes, thus confirming the expected stoichiometry



The product obtained by bromine oxidation could be readily converted back to the reduced starting material via reaction with  $\text{Zn}(\text{Hg})$ , as confirmed by  $^1\text{H}$  NMR spectroscopy.

Elemental analysis data for all compounds are shown in Table 1.

#### 3.2. NMR spectroscopy

Several representative  $^1\text{H}$  NMR spectra are shown in Fig. 2. For each of the 3+ binuclear complexes, peak assignments are easily determined by comparison with the spectra of the corresponding mononuclear complexes. Indeed, the chemical shifts of the protons on the chelating  $\alpha$ -diimine ligands and  $\text{NH}_3$  groups are virtually unaffected by formation of the bimetallic species. The ring protons of the bridging ligands (bpa, bpp) show two doublet-doublet (AA'BB') splitting patterns due to the attachment of different metal centers. The peak assignments for bridging ligands in the binuclear complexes can be readily made by comparisons to the spectra of  $[\text{Ru}(\text{NH}_3)_5(\text{BL})]^{2+}$  and  $[(\text{LL})(\text{CO})_3\text{Re}(\text{Etpy})]^+$  (Etpy is 4-ethylpyridine).

Upon oxidation of  $[(\text{LL})(\text{CO})_3\text{Re}(\text{BL})\text{Ru}(\text{NH}_3)_5]^{3+}$  to  $[(\text{LL})(\text{CO})_3\text{Re}(\text{BL})\text{Ru}(\text{NH}_3)_5]^{4+}$ , all proton signals shift upfield except the *ortho*-proton resonances on the bridging ligand ring attached to the ruthenium center. The latter peaks are shifted downfield and show significant peak broadening. Meanwhile, the signals from both *cis*- and *trans*- $\text{NH}_3$  groups (at 2.21 and 2.76 ppm, respectively, in the  $\text{Ru}^{\text{II}}$  complexes) completely disappear. These observations are attributed to the effect of the paramagnetic  $\text{Ru}^{\text{III}}$  center [33].

Table 1

Elemental analysis data for  $[(LL)(CO)_3Re(BL)]^+$  and  $[(LL)(CO)_3Re(BL)Ru(NH_3)_5]^{3+/4+}$  complexes

Complex	Calc. (Found)		
	C	H	N
$[(DCObpy)(CO)_3Re(bpa)]PF_6 \cdot 2H_2O$	40.36 (40.37)	3.82 (3.32)	5.70 (5.70)
$[(DCObpy)(CO)_3Re(bpp)]PF_6 \cdot H_2O$	42.54 (42.35)	3.78 (3.54)	5.83 (5.86)
$[(Me_4bpy)(CO)_3Re(bpa)]PF_6 \cdot 2H_2O$	40.23 (40.13)	3.96 (3.38)	6.47 (6.31)
$[(Me_4bpy)(CO)_3Re(bpp)]PF_6 \cdot H_2O$	42.70 (42.41)	3.82 (3.69)	6.64 (6.38)
$[(bpy)(CO)_3Re(bpa)Ru(NH_3)_5](PF_6)_3$	24.38 (24.43)	2.86 (2.83)	10.23 (10.09)
$[(bpy)(CO)_3Re(bpp)Ru(NH_3)_5](PF_6)_3$	25.07 (25.22)	2.99 (3.04)	10.12 (10.04)
$[(DCObpy)(CO)_3Re(bpa)Ru(NH_3)_5](PF_6)_3$	28.23 (28.19)	3.38 (3.34)	8.90 (8.98)
$[(DCObpy)(CO)_3Re(bpp)Ru(NH_3)_5](PF_6)_3$	28.76 (28.80)	3.48 (3.45)	8.89 (8.81)
$[(Me_4bpy)(CO)_3Re(bpa)Ru(NH_3)_5](PF_6)_3$	27.05 (27.07)	3.37 (3.33)	9.79 (9.73)
$[(Me_4bpy)(CO)_3Re(bpp)Ru(NH_3)_5](PF_6)_3$	27.68 (27.58)	3.48 (3.46)	9.68 (9.60)
$[(bpy)(CO)_3Re(bpa)Ru(NH_3)_5](PF_6)_4$	21.81 (22.57)	2.56 (2.69)	9.16 (9.42)
$[(bpy)(CO)_3Re(bpp)Ru(NH_3)_5](PF_6)_4$	22.45 (22.27)	2.68 (2.88)	9.06 (9.33)
$[(DCObpy)(CO)_3Re(bpa)Ru(NH_3)_5](PF_6)_4$	25.59 (25.71)	3.09 (3.07)	8.14 (8.13)
$[(Me_4bpy)(CO)_3Re(bpa)Ru(NH_3)_5](PF_6)_4$	25.31 (25.09)	3.02 (3.22)	8.80 (8.90)

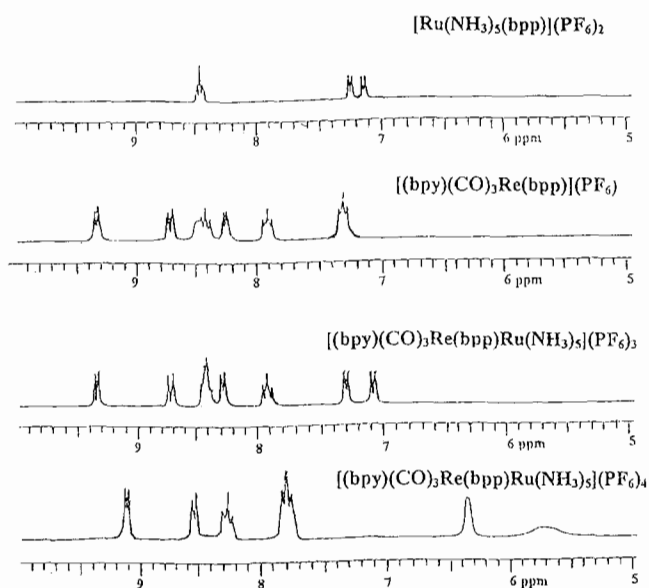


Fig. 2.  $^1H$  NMR spectra of  $[Ru(NH_3)_5(bpp)](PF_6)_2$ ,  $[(bpy)(CO)_3Re(bpp)](PF_6)$ ,  $[(bpy)(CO)_3Re(bpp)Ru(NH_3)_5](PF_6)_3$  and  $[(bpy)(CO)_3Re(bpp)Ru(NH_3)_5](PF_6)_4$  in  $d_6$ -DMSO.

### 3.3. Electronic absorption spectra

Electronic absorption data for  $[(LL)(CO)_3Re(BL)Ru(NH_3)_5]^{3+}$ ,  $[(LL)(CO)_3Re(BL)Ru(NH_3)_5]^{4+}$  and the related monomeric complexes,  $[Ru(NH_3)_5(BL)]^{2+}$  and  $[(LL)(CO)_3Re(BL)]^+$  (BL = bpa, bpp), are summarized in Table 2.

The electronic spectra of  $[Ru(NH_3)_5(BL)]^{2+}$  complexes are dominated by intense ( $\epsilon > 10^4 M^{-1} cm^{-1}$ ) visible bands at 410 nm which have been assigned as  $Ru \rightarrow BL$  transitions [30]. Bands in the UV region for such complexes have been assigned to ligand-localized  $\pi \rightarrow \pi^*$  (LL) transitions involving the aromatic N-het-

Table 2

Electronic absorption data for  $[(LL)(CO)_3Re(BL)]^+$  and  $[(LL)(CO)_3Re(BL)Ru(NH_3)_5]^{3+}$  complexes in  $CH_3CN$  at room temperature

LL	BL	$\lambda_{max}$ ( $10^{-3} \epsilon_{max}$ ( $M^{-1} cm^{-1}$ ))			
$[(LL)(CO)_3Re(BL)]^+$					
DCObpy	bpa	390 (3.72)	325 (9.69)	297 (12.4)	
DCObpy	bpp	390 (3.64)	325 (8.98)	297 (11.9)	
bpy	bpa	350 (3.89)	321 (9.70)	303 (12.5)	
bpy	bpp	350 (3.58)	321 (9.23)	303 (12.0)	
Me <sub>4</sub> bpy	bpa	343 (5.67)	318 (10.9)	310 (16.9)	
Me <sub>4</sub> bpy	bpp	343 (5.57)	318 (9.80)	310 (15.9)	
$[(LL)(CO)_3Re(BL)Ru(NH_3)_5]^{3+}$					
DCObpy	bpa	410 (4.50)	390 (3.72)	325 (9.69)	297 (12.4)
DCObpy	bpp	410 (4.62)	390 (3.64)	325 (8.98)	297 (11.9)
bpy	bpa	410 (4.83)	350 (3.89)	321 (9.70)	303 (12.5)
bpy	bpp	410 (4.90)	350 (3.58)	321 (9.23)	303 (12.0)
Me <sub>4</sub> bpy	bpa	410 (5.20)	343 (5.67)	318 (10.9)	310 (16.9)
Me <sub>4</sub> bpy	bpp	410 (5.20)	343 (5.57)	318 (9.80)	310 (15.9)

erocyclic ligand. Ligand field absorption bands have not been observed for  $[Ru(NH_3)_5(BL)]^{2+}$ , presumably because such bands are masked by the more intense MLCT absorptions [30].

For complexes of the type  $[(LL)(CO)_3Re(BL)]^+$ , the very intense bands occurring below 320 nm have been assigned to  $\pi \rightarrow \pi^*$  (LL) transitions. The somewhat weaker bands which occur at 345–390 nm have been assigned as  $Re \rightarrow LL$  MLCT transitions [17–19]. As expected, the energies of the MLCT absorption bands of  $[(LL)(CO)_3Re(BL)]^+$  in  $CH_3CN$  are very sensitive to the nature of the substituents. For example, the absorption spectrum of  $[(DCObpy)(CO)_3Re(BL)]^+$  displays an MLCT band at about 390 nm while the MLCT band of  $[(Me_4bpy)(CO)_3Re(BL)]^+$  is shifted to  $\sim 340$

nm. These differences are visually obvious; while  $[(\text{Me}_4\text{bpy})(\text{CO})_3\text{Re}(\text{LL})](\text{PF}_6)$  is a yellow solid,  $[(\text{DCObpy})(\text{CO})_3\text{Re}(\text{BL})](\text{PF}_6)$  is a red solid.

The spectrophotometric data also show that the  $[(\text{LL})(\text{CO})_3\text{Re}(\text{BL})\text{Ru}(\text{NH}_3)_5]^{3+}$  spectra are essentially the sum of the spectra of  $[\text{Ru}(\text{NH}_3)_5(\text{BL})]^{2+}$  ( $\lambda_{\text{max}} = 410$  nm) and  $[(\text{LL})(\text{CO})_3\text{Re}(\text{BL})]^+$ , suggesting that interaction between the metal centers is weak. Upon oxidation of  $[(\text{LL})(\text{CO})_3\text{Re}(\text{BL})\text{Ru}(\text{NH}_3)_5]^{3+}$ , the only change in the spectrum is the disappearance of the 410 nm Ru  $\rightarrow$  BL MLCT band (see Fig. 1). As a result, the spectra of  $[(\text{LL})(\text{CO})_3\text{Re}(\text{BL})\text{Ru}(\text{NH}_3)_5]^{4+}$  are almost identical with those of  $[(\text{LL})(\text{CO})_3\text{Re}(\text{BL})]^+$ .

### 3.4. Electrochemistry

Cyclic voltammetric data for these complexes are collected in Table 3, and a representative voltammogram is depicted in Fig. 3. The redox properties of the mixed-metal complexes can be readily understood by comparison to their monometallic precursors. The initial oxidation of the heterobinuclear 3+ complexes appears to be largely localized on the ruthenium center and is observed in all cases at  $E_{1/2} = +0.30$  V versus SSCE [30]. This ruthenium-based oxidation is electrochemically reversible, with differences between anodic and cathodic peak potentials of 60–65 mV (at  $10 \text{ mV s}^{-1}$ ) and ratios of anodic to cathodic peak currents near unity. Such behaviour suggests that the binuclear com-

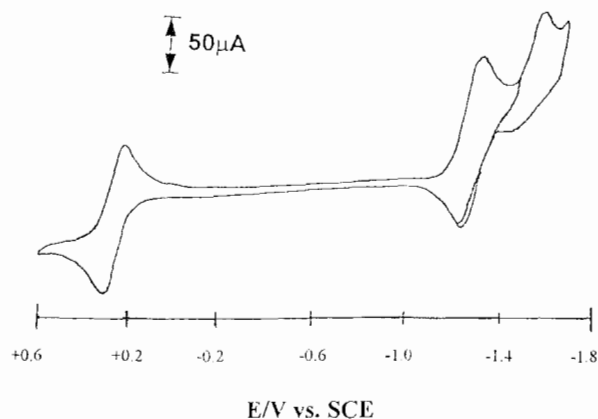


Fig. 3. Cyclic voltammogram of  $[(\text{bpy})(\text{CO})_3\text{Re}(\text{bpp})\text{Ru}(\text{NH}_3)_5](\text{PF}_6)_3$  in 0.1 M TBAH/ $\text{CH}_3\text{CN}$ , recorded at a glassy carbon disk. Scan rate =  $25 \text{ mV s}^{-1}$ .

plexes are stable in both Ru<sup>II</sup> and Ru<sup>III</sup> oxidation states, at least on the voltammetric timescale.

The rhenium center undergoes a one-electron chemically irreversible oxidation at more positive potentials [19–21], and the electrochemical data show the presence of small substituent effects. The  $E_{\text{ox}}[\text{Re}^{\text{II}}/\text{Re}^{\text{I}}]$  values for  $[(\text{LL})(\text{CO})_3\text{Re}(\text{BL})\text{Ru}(\text{NH}_3)_5]^{3+}$  complexes decrease with increasing electron donation by the substituents:  $\text{DCObpy} > \text{bpy} > \text{Me}_4\text{bpy}$ . However, a comparison of the oxidation potentials of the binuclear and mononuclear complexes shows that there is no discernible effect of secondary metal attachment, again suggestive of very weak metal–metal interaction [11,12].

The electrochemical data also illustrate the effect of substituents on the reduction potentials of the chelating ligands. The  $E_{\text{red}}(0/-)$  values of the chelating ligands in both the  $[(\text{LL})(\text{CO})_3\text{Re}(\text{BL})]^+$  and  $[(\text{LL})(\text{CO})_3\text{Re}(\text{BL})\text{Ru}(\text{NH}_3)_5]^{3+}$  series are identical and shift to more negative potentials with increasing electron donation by the substituents, reflecting the substituent effect on the  $\pi^*$  energy level of the chelating ligand. In the case of  $\text{Me}_4\text{bpy}$  complexes, assignment of the first reduction is somewhat ambiguous, since the observed redox potential is very close to the value one would predict for reduction of either the electron-rich  $\text{Me}_4\text{bpy}$  ligand or the rhenium center itself [13,19–21,34].

### 3.5. Emission properties

Each of the mononuclear complexes exhibits a broad emission band in room temperature acetonitrile solution. Peak maxima and bandshapes are independent of excitation wavelength over the region 300–400 nm, consistent with the Re  $\rightarrow$  LL <sup>3</sup>MLCT origin. The emission band maxima also depend on the nature of the substituent; the band shifts to higher energy with increasing electron donation from the substituents (see Table 4).

The single-photon counting data for each of the mononuclear model complexes  $[(\text{LL})(\text{CO})_3\text{Re}(\text{BL})]^+$

Table 3  
Electrochemical data for  $[(\text{LL})(\text{CO})_3\text{Re}(\text{BL})]^+$  and  $[(\text{LL})(\text{CO})_3\text{Re}(\text{BL})\text{Ru}(\text{NH}_3)_5]^{3+}$  complexes<sup>a</sup>

LL	BL	$E_{1/2}$ (V)	$E_p^b$ (V)			
			LL <sup>0/-</sup>	Re <sup>+0</sup>	Ru <sup>3+/2+</sup>	Re <sup>2+/+</sup>
$[(\text{LL})(\text{CO})_3\text{Re}(\text{BL})]^+$						
DCObpy	bpp	-0.83	-1.24		+1.88	
DCObpy	bpa	-0.83	-1.24		+1.88	
bpy	bpp	-1.09	-1.30		+1.75	
bpy	bpa		-1.30		+1.76	
Me <sub>4</sub> bpy	bpp		-1.40 <sup>c</sup>		+1.67	
Me <sub>4</sub> bpy	bpa		-1.40 <sup>c</sup>		+1.66	
$[(\text{LL})(\text{CO})_3\text{Re}(\text{BL})\text{Ru}(\text{NH}_3)_5]^{3+}$						
DCObpy	bpp	-0.83	-1.24	+0.30	+1.88	
DCObpy	bpa	-0.83	-1.24	+0.30	+1.88	
bpy	bpp	-1.09	-1.30	+0.30	+1.75	
bpy	bpa	-1.09	-1.30	+0.30	+1.76	
Me <sub>4</sub> bpy	bpp		-1.40 <sup>c</sup>	+0.30	+1.67	
Me <sub>4</sub> bpy	bpa		-1.40 <sup>c</sup>	+0.30	+1.66	

<sup>a</sup>Potential measurements are referred to the saturated sodium calomel electrode in 0.1 M TBAH/ $\text{CH}_3\text{CN}$  at room temperature; scan rate =  $25 \text{ mV s}^{-1}$ .

<sup>b</sup>The  $\text{Re}^{2+/+}$  couple is chemically irreversible;  $E_p$  values represent anodic peak potentials.

<sup>c</sup>Assignment of this reduction is somewhat ambiguous.

Table 4

Photophysical data for  $[(LL)(CO)_3Re(BL)]^+$  and  $[(LL)(CO)_3Re(BL)Ru(NH_3)_5]^{3+/4+}$  complexes in deoxygenated  $CH_3CN$  at room temperature<sup>a</sup>

Complex	$\lambda_{max}$ (nm)	$\tau$ (ns)	$\ln k_{et}$
$[(bpy)(CO)_3Re(bpa)]PF_6$	564	210	
$[(bpy)(CO)_3Re(bpp)]PF_6$	567	170	
$[(DCObpy)(CO)_3Re(bpa)]PF_6$	629	65	
$[(DCObpy)(CO)_3Re(bpp)]PF_6$	629	60	
$[(Me_4bpy)(CO)_3Re(bpa)]PF_6$	521	1110	
$[(Me_4bpy)(CO)_3Re(bpp)]PF_6$	523	1070	
$[(bpy)(CO)_3Re(bpa)Ru(NH_3)_5](PF_6)_3$	564	0.23	22.2
$[(bpy)(CO)_3Re(bpp)Ru(NH_3)_5](PF_6)_3$	567	0.20	22.3
$[(DCObpy)(CO)_3Re(bpa)Ru(NH_3)_5](PF_6)_3$	629	0.15	22.6
$[(DCObpy)(CO)_3Re(bpp)Ru(NH_3)_5](PF_6)_3$	629	0.14	22.7
$[(Me_4bpy)(CO)_3Re(bpa)Ru(NH_3)_5](PF_6)_3$	521	0.28	22.0
$[(Me_4bpy)(CO)_3Re(bpp)Ru(NH_3)_5](PF_6)_3$	523	0.25	22.1
$[(bpy)(CO)_3Re(bpa)Ru(NH_3)_5](PF_6)_4$	564	<sup>b</sup>	<sup>b</sup>
$[(bpy)(CO)_3Re(bpp)Ru(NH_3)_5](PF_6)_4$	567	<sup>b</sup>	<sup>b</sup>
$[(DCObpy)(CO)_3Re(bpa)Ru(NH_3)_5](PF_6)_4$	629	<sup>b</sup>	<sup>b</sup>
$[(DCObpy)(CO)_3Re(bpp)Ru(NH_3)_5](PF_6)_4$	629	<sup>b</sup>	<sup>b</sup>
$[(Me_4bpy)(CO)_3Re(bpa)Ru(NH_3)_5](PF_6)_4$	521	<sup>b</sup>	<sup>b</sup>
$[(Me_4bpy)(CO)_3Re(bpp)Ru(NH_3)_5](PF_6)_4$	521	<sup>b</sup>	<sup>b</sup>

<sup>a</sup>Excitation wavelength = 335 nm.<sup>b</sup>No short-lived component observed (see text).

(where BL = bpa, bpp or Etpy) could be readily fit using simple first-order decay kinetics (see Fig. 4). In particular, no short-lived transients were ever observed prior to attachment of the ruthenium center. Such results provide an important demonstration of the absence of emissive impurities in these samples.

By contrast, the emission decay curves for all  $[(LL)(CO)_3Re(BL)Ru^{II}(NH_3)_5]^{3+}$  complexes show strong deviations from first-order kinetics (see Fig. 5), and cannot be adequately fit by a single exponential

(two adjustable parameters). Rather, such decay profiles require the use of 4–6 parameters to achieve satisfactory fits. In each case, however, the longest-lived component could be fit using a lifetime equal to that of the corresponding  $[(LL)(CO)_3Re(BL)]^+$  mononuclear complex. In view of the relatively small amplitude of this component, these results suggest the presence of small amounts of mononuclear impurities. Rough calculations illustrate that, because of the large difference in lifetime between mononuclear and binuclear complexes (vide

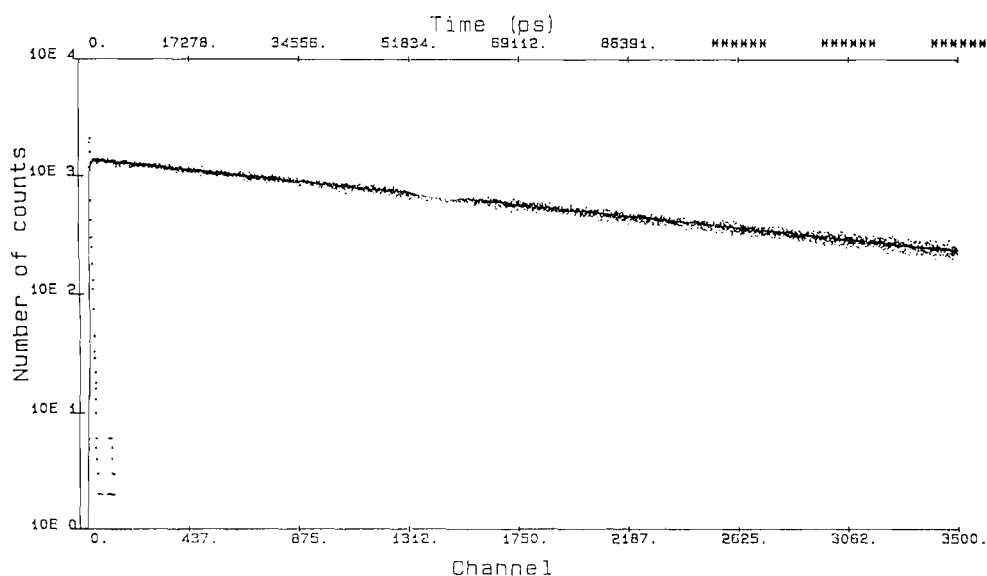


Fig. 4. Emission decay profile (log plot) for  $[(DCObpy)(CO)_3Re(bpp)](PF_6)_3$  in deoxygenated  $CH_3CN$  at room temperature. Solid line represents the best fit to a single exponential. Excitation wavelength = 300 nm.

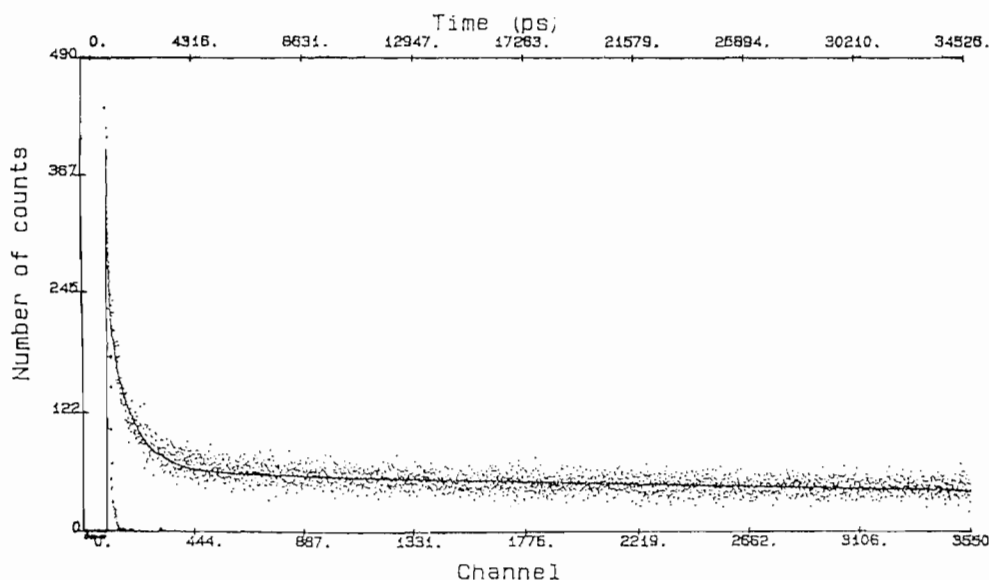


Fig. 5. Emission decay profile (linear plot) for  $[(bpy)(CO)_3Re(bpp)Ru(NH_3)_5](PF_6)_3$  in deoxygenated  $CH_3CN$  at room temperature. Solid line represents the best fit to a biexponential. Excitation wavelength = 300 nm.

infra), impurity levels <0.3% can account for the observed behaviour. It should be noted that it was not possible to detect such impurities by steady-state luminescence methods since the emission maximum is insensitive to the introduction of the ruthenium center.

For all Re/Ru<sup>II</sup> binuclear complexes, the largest amplitude component is a very short-lived (~250 ps) transient. In several cases, the amplitude of this feature is nearly 20 times that of the slower component. Thus, it seems reasonable to assign the fastest component to  $[(LL)(CO)_3Re(BL)Ru^{II}(NH_3)_5]^{3+}$ . A few of the samples show a third component of intermediate lifetime (a few ns). However, the amplitude of this middle component is generally very small (<5% of the short-lived transient) and will be ignored in the subsequent analysis.

The emission decay profiles for all Re/Ru<sup>III</sup> complexes also exhibit biexponential behavior, requiring four adjustable parameters to obtain satisfactory fits. Again, the lifetime of the longer-lived component is identical to that of the corresponding  $[(LL)(CO)_3Re(BL)]^+$  mononuclear complex, but the total emission amplitude represents only ~5% of the signal expected for a pure sample of the monometallic species (see Fig. 6). Therefore, we assign the longer-lived component to a small amount of  $[(LL)(CO)_3Re(BL)]^+$  impurity. Surprisingly, however, such impurities are responsible for most of the total emission amplitude from the Re/Ru<sup>III</sup> samples. A second, minor component yields a lifetime of 2–6 ns, but its amplitude is typically only 10% of the slower (impurity) signal. Thus, it seems unreasonable to assign either component to  $[(LL)(CO)_3Re(BL)Ru(NH_3)_5]^{4+}$ , yet the total emission intensity drops by factor of 20 upon binucleation. No shorter-lived transients were ever

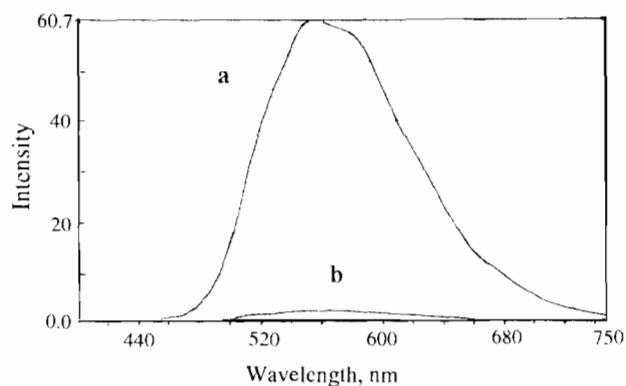


Fig. 6. Emission spectra of  $[(bpy)(CO)_3Re(bpa)](PF_6)$  (a) and  $[(bpy)(CO)_3Re(bpa)Ru(NH_3)_5](PF_6)_4$  (b) in deoxygenated  $CH_3CN$  at room temperature, recorded under identical conditions on the same intensity scale. Excitation wavelength = 355 nm. The absorbance at this wavelength is 0.5 for each of the samples.

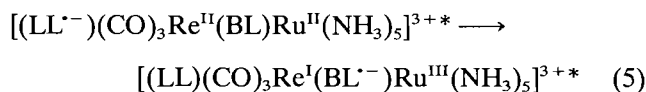
observed for the Re/Ru<sup>III</sup> bimetallic complexes (2 ps resolution).

#### 4. Discussion

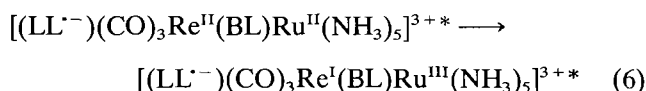
Based on the lifetime data and emission intensities of the Re/Ru<sup>II</sup> binuclear complexes, it is clear that the  $\alpha$ -diimine ligand-based MLCT states are efficiently quenched by the attached  $-Ru(NH_3)_5^{2+}$  moiety. Several possible quenching mechanisms must be considered. First, these binuclear complexes might undergo *intermolecular* electron transfer, but this possibility is unlikely since the experiments are done at very low concentration (about  $10^{-5}$  M) and the observed quenching rate is too rapid to ascribe the process to a binuclear reaction.



A second possible quenching mode of the LL-based MLCT state may involve energy transfer to the Ru → BL MLCT state:



However, this pathway is also considered unlikely because the spectral overlap between the rhenium-based <sup>3</sup>MLCT emission and the Ru<sup>II</sup> → LL MLCT absorption is so small that energy transfer via the Coulombic mechanism can be effectively ruled out [35]. Further evidence against an energy transfer mechanism in this system is provided by the insensitivity of the quenching rate to Re → LL MLCT energy. Meanwhile, energy transfer via the exchange mechanism [36] is expected to be more strongly dependent on distance than is electron transfer and hence less important in systems with large separation distances. Closs et al. [37] have quantitatively investigated the dependence of electron and energy transfer rates on distance, and their results show that  $k_{en} \propto \exp(-2\alpha R)$  ( $k_{en}$  is the rate constant for energy transfer) while  $k_{et} \propto \exp(-\alpha R)$ . For these reasons, we believe that quenching occurs by intramolecular electron transfer:



In this process, the MLCT excited state of the rhenium chromophore undergoes reductive quenching by  $-Ru(NH_3)_5^{2+}$ , i.e., electron transfer from the ruthenium center to the rhenium center.

Energy transfer in the  $[(LL)(CO)_3Re(BL)Ru(NH_3)_5]^{4+}$  systems is even less likely than in the Re/Ru<sup>II</sup> complexes because of the lack of a low-lying Ru → LL MLCT state. In addition, the ligand-field excited states lie at higher energy for Ru<sup>III</sup> than for Ru<sup>II</sup>.

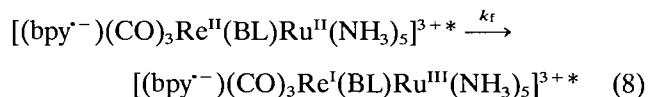
If the rate constants for the photophysical processes by which the excited state decays remain constant between the D–A system and a similarly structured reference molecule that does not undergo photoinduced electron transfer, the forward electron transfer rate constant may be determined from the relation

$$k_f = 1/\tau_1 - 1/\tau_2 \quad (7)$$

where  $\tau_1$  is the fluorescence lifetime of D\* in D–A and  $\tau_2$  is the corresponding lifetime of the reference molecule [38]. Rate constants for photoinduced ET in each of the bimetallic complexes are given in Table 4. The  $k_{et}$  values ( $2\text{--}9 \times 10^9 \text{ s}^{-1}$ ) are consistent with a highly exergonic electron transfer process, and our data suggest that electronic interaction between centers is sufficiently large to support rapid intramolecular ET.

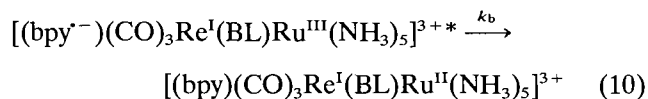
The free energy change for photoinduced electron transfer processes can be calculated with data obtained

by cyclic voltammetry and emission spectroscopy. For example, the calculation of driving force ( $= -\Delta G$ ) for ‘forward’ ET (quenching) in a prototypical heterobinuclear complex is shown below.



$$\Delta G_1 = -E_{1/2}^{\circ}(bpy^{0/-}) + E_{1/2}^{\circ}(Ru^{3+/2+}) - E_{em}^* \quad (9)$$

Meanwhile, the free energy change for ‘back’ ET is readily obtained from ground state reduction potentials alone:



$$\Delta G_2 = E_{1/2}^{\circ}(bpy^{0/-}) - E_{1/2}^{\circ}(Ru^{3+/2+}) \quad (11)$$

Calculated values of  $-\Delta G$  for forward and back ET reactions of all complexes are collected in Table 5. These numbers indicate that the MLCT excited states of  $(LL)(CO)_3Re(BL)^+$  complexes should readily undergo both reductive quenching by an attached  $-Ru(NH_3)_5^{2+}$  group and oxidative quenching by  $-Ru(NH_3)_5^{3+}$ .

Rate constants for ET quenching of the bpy, DCObpy and Me<sub>4</sub>bpy binuclear complexes by the pendant  $-Ru(NH_3)_5^{2+}$  moiety are very similar. This is not surprising since the expected free energy changes for the three binuclear complexes ( $-\Delta G = 0.93 \pm 0.05 \text{ eV}$ ) do not vary appreciably. Further, the reaction driving force is nearly equal to the reorganization energy (1.1 eV, vide infra), and the sensitivity of  $k_{et}$  to driving force is small when  $-\Delta G/\lambda \approx 1$ . (Here we assume that  $\lambda$  is constant for bpy, DCObpy and Me<sub>4</sub>bpy complexes containing the same bridging ligand.)

Calculation of the reorganization energy ( $\lambda$ ) is more difficult than calculation of  $-\Delta G$  owing to a lack of available parameters, but it is still possible to estimate  $\lambda$  using published data. The inner-sphere reorganization energy associated with the Ru center,  $\lambda_{Ru}$ , has been estimated to be about 0.17 eV ( $4.0 \text{ kcal mol}^{-1}$ ) for the  $Ru(NH_3)_5(L)^{3+/2+}$  couple (L = pyridine) [39–41]. Unfortunately, a reliable value for  $\lambda_{Re}$  has not been well established to date. However, both experimental and theoretical evidence suggest that  $\lambda_{Re}$  is small, since analogous rhenium(I) complexes undergo photoinduced electron transfer reactions at the diffusion-controlled limit [13,19–21]. Thus, the reorganization energy associated with the Re center,  $\lambda_{Re}$  is estimated to be 0.1 eV. Using these values for  $\lambda_{Ru}$  and  $\lambda_{Re}$  gives  $\lambda_{in} = (\lambda_{Ru} + \lambda_{Re})/2 = 0.14 \text{ eV}$ .

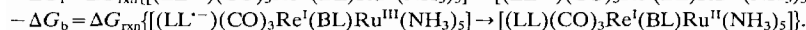
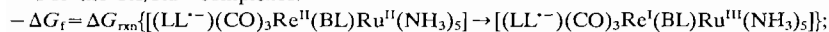
A theoretical value for the outer-sphere reorganization energy,  $\lambda_{out}$ , can be calculated from Eq. (12).

$$\lambda_{out} = e^2(1/2r_D + 1/2r_A - 1/r_{DA})(1/n^2 - 1/D) \quad (12)$$

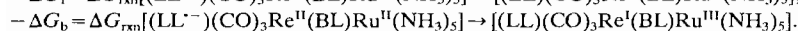
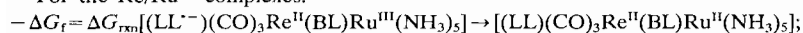
Table 5  
Thermodynamic data for photoinduced intramolecular electron transfer in [(LL)(CO)<sub>3</sub>Re(BL)Ru(NH<sub>3</sub>)<sub>5</sub>]<sup>3+/4+</sup> complexes

System	$E_{1/2}^{\text{Ru}}$	$E_{1/2}^{\text{Re}}$	$E_{1/2}^{\text{LL}}$	$E^*$ (eV)	$-\Delta G_f^{a,b}$ (eV)	$-\Delta G_b^{a,b}$ (eV)
[Ru(NH <sub>3</sub> ) <sub>5</sub> (BL)] <sup>2+</sup>	0.29					
[(DCObpy)(CO) <sub>3</sub> Re(BL)Ru(NH <sub>3</sub> ) <sub>5</sub> ] <sup>3+</sup>	0.30	1.88	-0.83	2.10	0.97	1.13
[(bpy)(CO) <sub>3</sub> Re(BL)Ru(NH <sub>3</sub> ) <sub>5</sub> ] <sup>3+</sup>	0.30	1.73	-1.16	2.39	0.93	1.46
[(Me <sub>4</sub> bpy)(CO) <sub>3</sub> Re(BL)Ru(NH <sub>3</sub> ) <sub>5</sub> ] <sup>3+</sup>	0.30	1.67	-1.40	2.58	0.88	1.70
[(DCO)bpy(CO) <sub>3</sub> Re(BL)Ru(NH <sub>3</sub> ) <sub>5</sub> ] <sup>4+</sup>	0.30	1.88	-0.83	2.10	0.52	1.58
[(bpy)(CO) <sub>3</sub> Re(BL)Ru(NH <sub>3</sub> ) <sub>5</sub> ] <sup>4+</sup>	0.30	1.73	-1.16	2.39	0.96	1.43
[(Me <sub>4</sub> bpy)(CO) <sub>3</sub> Re(BL)Ru(NH <sub>3</sub> ) <sub>5</sub> ] <sup>4+</sup>	0.30	1.67	-1.40	2.58	1.21	1.37

<sup>a</sup>For the Re/Ru<sup>II</sup> complexes:



For the Re/Ru<sup>III</sup> complexes:



<sup>b</sup>All values are calculated assuming the electron transfer process occurs from the Re → LL <sup>3</sup>MLCT state.

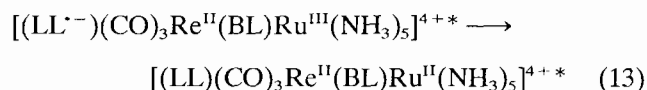
For CH<sub>3</sub>CN at 20 °C,  $n^2 = 1.80$  and  $D = 37.5$ , and using  $4.0 \times 10^{-10}$  m for  $r(\text{Ru}(\text{NH}_3)_5(\text{bpa})^{2+})$ ,  $6.5 \times 10^{-10}$  m for  $r(\text{bpy})(\text{CO})_3\text{Re}^+$  and  $r(\text{Re}-\text{Ru}) = 13.5 \times 10^{-10}$  m gives  $\lambda_{\text{out}} = 0.97$  eV. The estimates of molecular radii used in the calculation above have been obtained from crystallographic data or from appropriate models. These values of  $\lambda_{\text{in}}$  and  $\lambda_{\text{out}}$  yield an estimate for  $\lambda$  of  $1.1 \pm 0.1$  eV.

$k_{\text{et}}$  values for the Re/Ru<sup>II</sup> bimetallic complexes containing bridging ligands (bpa, bpp) are only slightly different, with  $k_{\text{et}}$  values for the bpp-bridged binuclear complexes being generally larger than those of the corresponding bpa-bridged derivatives. This trend is the opposite of what one would expect if the bridging ligands are considered to be in the fully extended conformation and conformationally rigid. However, because the differences in both bridge length and  $k_{\text{et}}$  are small, no definite conclusions can be reached.

Two other points regarding the distance dependence of  $k_{\text{et}}$  should also be considered. First, both bpa and bpp are quite flexible, and a variety of conformers, each possessing a distinct D–A separation distance, can be envisioned. While electrostatic effects will tend to favor the more fully extended conformation [6], it is conceivable that electron transfer may occur only upon close approach of the two metal centers. On the other hand, the fact that emission decay in such systems is dominated by a single very fast component argues against contributions to the observed ET rate from multiple conformations. Second, the effect of the relative spatial orientation of D and A may also be important. A theoretical treatment of the effect of mutual donor–acceptor orientation on ET rates has been presented by Cave et al. [42]. The results of this analysis indicate that ET rates should be a very sensitive function of both the orientation and the nature of the orbitals involved. Therefore, the small change in  $k_{\text{et}}$  between

the bpa- and bpp-containing binuclear complexes may reflect subtle orientation effects.

A striking observation in the current study is the apparent complete lack of emission from the Re/Ru<sup>III</sup> bimetallic species. One possible explanation is that very fast electron transfer occurs from the *singlet* MLCT excited state of the rhenium chromophore to the ruthenium center:



In this mechanistic model, the emission is quenched by virtue of the fact that the emissive state is never produced.

Intramolecular quenching from excited singlet states by electron transfer is very common in organic systems. For example, in a covalently linked porphyrin–amide–quinone system, the singlet excited state of the porphyrin chromophore is quenched by the quinone moiety via intramolecular electron transfer with a rate  $\sim 10^9$  s<sup>-1</sup> [43]. Such phenomena are also occasionally observed in metal complexes. In cobalt(III)–copper(I) binuclear complexes containing aminoalkene and alkenylpyridine bridging ligands, the Cu<sup>I</sup> → olefin <sup>1</sup>MLCT state is quenched by Co<sup>III</sup> via intramolecular electron transfer with a rate constant of 10<sup>8</sup> s<sup>-1</sup> [44]. A recent report by Lucia et al. [45] suggests that Re–C bond homolysis may occur from an *unrelaxed* MLCT state upon photolysis of Re<sup>I</sup> alkyl complexes.

In two particularly relevant studies, the effect of a covalently attached d<sup>5</sup> metal center in the MLCT luminescence of a d<sup>6</sup> complex was monitored [11,12]. Curtis et al. report that neither the excited state lifetime nor the emission quantum yield of [(bpy)<sub>2</sub>RuCl(bpa)]<sup>+</sup> is strongly perturbed by the attachment of a pendant –Ru(NH<sub>3</sub>)<sub>5</sub><sup>3+</sup> group [11]. On the other hand, Schanze

et al. find that  $[(\text{bpy})_2(\text{CO})\text{Os}^{\text{II}}(\text{bpa})\text{Os}^{\text{III}}(\text{phen})(\text{dppe})\text{-Cl}]^{4+}$  (phen = 1,10-phenanthroline; dppe = diphenylphosphinoethane) displays emission properties which closely parallel our observations on these Re<sup>I</sup>/Ru<sup>III</sup> systems [12]. That is, while the lifetime of the bimetallic species is not unusually short, the emission quantum yield is approximately five times less than that of  $[(\text{bpy})_2(\text{CO})\text{Os}(\text{bpa})]^{2+}$ . These authors suggest (as we have) that rapid quenching of a short-lived upper state (possibly <sup>1</sup>MLCT in character) in competition with its decay to the luminescent <sup>3</sup>MLCT level may be responsible for the suppressed emission [12].

For such an explanation to be viable, electron transfer which occurs from the <sup>1</sup>MLCT state must compete effectively with intersystem crossing to the <sup>3</sup>MLCT state. Since intersystem crossing rate constants for similar systems have been established to be  $\geq 10^9 \text{ s}^{-1}$  [45,46], an electron transfer rate constant of  $\sim 10^{10} \text{ s}^{-1}$  or more is required. This value does not appear totally unreasonable, despite the 13.5 Å separation distance, since the driving force is about 0.2–0.3 eV higher than the values calculated above (see also Table 5) due to the energetic separation between the <sup>1</sup>MLCT and <sup>3</sup>MLCT states. The Re/Ru<sup>II</sup> complexes described herein also undergo rapid electron transfer ( $k_{\text{et}} = 2\text{--}5 \times 10^9 \text{ s}^{-1}$ ), but such processes are apparently unable to compete with intersystem crossing in those systems. Both picosecond transient absorption and low temperature time-resolved emission studies are being undertaken to test the model presented above.

However, because of the inherent flexibility of the bridging ligands employed in this study, conformations representing a range of separation distances in solution are possible, and interpretation of the ET rate data becomes difficult. For this reason, studies of rigidly linked molecules in which the donor and acceptor are held at known orientations and spacing are critically important for a quantitative understanding of the influence of bridge length on photoinduced intramolecular electron transfer.

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