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PHOTOINDUCED INTRAMOLECULAR ENERGY TRANSFER FROM ONE METAL CENTER TO THE OTHER IN A MIXED-METAL RUTHENIUM/RHENIUM COMPLEX

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ABSTRACT

The synthesis and photophysical properties of $[(bpy)_2Ru(Mebpy\text{-}Mebpy)Re(CO)_3py]^{3+}$ are described and compared to similar properties for $[(bpy)_2Ru(Mebpy\text{-}Mebpy)]^{2+}$ and $[(Mebpy\text{-}Mebpy)Re(CO)_3py]^{+}$ (bpy is 2,2'-bipyridine; Mebpy-Mebpy is 1,2-bis(4'-methyl-2,2'-bipyridyl-4-yl)ethane). Excitation of the complexes at 355 nm in methylene chloride at room temperature resulted in emission from each complex. The emission maxima, quantum yields and excited-state lifetimes were as follows: for $[(bpy)_2Ru(Mebpy\text{-}Mebpy)Re(CO)_3py]^{3+}$, λ_{em} = 610 nm, ϕ_r = 0.164, τ_o = 1001 ns; for $[(bpy)_2Ru(Mebpy\text{-}Mebpy)]^{2+}$, λ_{em} = 610 nm, ϕ_r = 0.080, τ_o = 1015 ns; for $[(Mebpy\text{-}Mebpy)Re(CO)_3py]^{+}$, λ_{em} = 552 nm, ϕ_r = 0.179, τ_o = 786 ns. The enhanced radiative quantum yield for the bimetallic complex is attributed to energy transfer from "$(Mebpy\text{-}Mebpy)Re(CO)_3py^{+}$" to "$(bpy)_2Ru(Mebpy\text{-}Mebpy)^{2+}$" which can be accounted for by either a dipole-dipole or electron interchange mechanism. Transient absorption spectra reveal localization of the electron on the "bpy" ligand as an intermediate in each of the complexes upon photoexcitation.

INTRODUCTION

We have reported the synthesis and properties of polynuclear ruthenium(II), rhenium(I) and platinum(II) compounds.[1-9] In a number of cases, the multimetallic complexes retained their luminescence properties, and hence, they maintained their potential for undergoing excited-state

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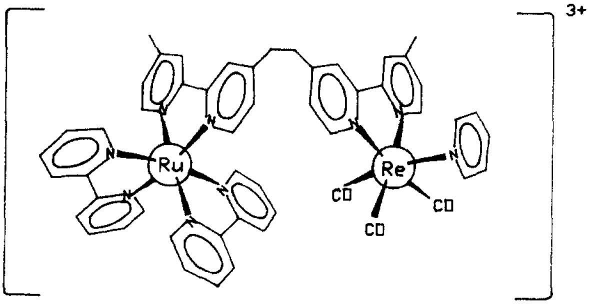
electron transfer reactions. Most recently, we reported that the bimetallic complex illustrated below underwent



luminescence derived from both the rhenium(I) and ruthenium(II) cores. We further reported that the ruthenium(II) based emission was enhanced at the expense of the rhenium(I) based emission and the mechanism responsible for this behavior was postulated to involve energy transfer.[10]

Energy transfer has been reported in other multimetallic systems. Scandola and coworkers[11] found that visible light absorption by the $Ru(bpy)_2^{2+}$ moiety, where bpy is 2,2'-bipyridine, led to phosphorescence from $Cr(CN)_6^{3-}$ in bimetallic $[NC\text{-}Ru(bpy)_2\text{-}NC\text{-}Cr(CN)_5]^{2-}$ and trimetallic $[(CN)_5Cr\text{-}CN\text{-}Ru(bpy)_2\text{-}NC\text{-}Cr(CN)_5]^{4-}$ complexes.[11-12] In an intricate system studied by Meyer and coworkers,[13] light absorption by the $[(bpy)(CO)_3Re(4,4'\text{-}bpy)]^+$ antenna led to luminescence from the $[(4,4'\text{-}bpy)(CO)_3Re((4,4'\text{-}CO_2C_2H_5)_2bpy)]^+$ fragment in $[(bpy)(CO)_3Re(4,4'\text{-}bpy)Re(CO)_3((4,4'\text{-}CO_2C_2H_5)_2bpy)]^{2+}$. Another system closely related to the one reported here was studied by Ryu and Schmehl.[14] Excitation of $[(dmb)_2Ru(b\text{-}b)Ru(dmb)(CN)_2]^{2+}$ at 377 nm, where dmb is 4,4'-dimethyl-2,2'-bipyridine and b-b is 1,4-bis[2-(4'-methyl-bipyridyl-4-yl)ethyl]benzene, resulted in observed emission from both a short-lived component from the $[(dmb)_2Ru(b\text{-}b)]^{2+}$ center and a longer-lived component from the $[(dmb)(CN)_2Ru(b\text{-}b)]$ fragment of the dimer.

In this paper we examine properties of $[(bpy)_2Ru(Mebpy\text{-}Mebpy)Re(CO)_3py]^+$, where Mebpy-Mebpy is 1,2-bis(4'-methyl-2,2'-bipyridyl-4-yl)ethane, in a systematic manner by comparing visible/uv, redox and spectral properties of

$[(bpy)_2Ru(Mebpy\text{-}Mebpy)Re(CO)_3py]^{3+}$ to those of the monometallic precursors, $[(bpy)_2Ru(Mebpy\text{-}Mebpy)]^{2+}$ and $[(Mebpy\text{-}Mebpy)Re(CO)_3py]^+$. In the monometallic complexes, only one Mebpy is coordinated; the other coordination site is unfilled.

EXPERIMENTAL SECTION

Materials

$Re(CO)_5Cl$ was purchased from Pressure Chemical Company; the silver reagents were purchased from Aldrich; HPLC or ACS certified grade solvents were obtained from Fisher Scientific. The reagents were used without further purification. The rhodamine-B was obtained from Wako Pure Chemicals Industry, Ltd. as an ethanolic solution and was diluted using 200 proof ethanol from Midwest Solvent Company of Illinois. Elemental analyses were obtained from Atlantic Microlabs, Norcross, GA.

Preparation of Compounds

$Ru(bpy)_2Cl_2\cdot 2H_2O$ and $Ru(bpy)_3(PF_6)_2$ were available from previous studies. Mebpy-Mebpy and $[(Mebpy\text{-}Mebpy)Ru(bpy)_2]^{2+}$ were prepared following the procedures of Sahai, *et al*.[4] The synthesis of $(Mebpy\text{-}Mebpy)Re(CO)_3Cl$ has been reported elsewhere.[8] All reactions were carried out under a nitrogen atmosphere.

$[(bpy)_2Ru(Mebpy\text{-}Mebpy)Re(CO)_3Cl](PF_6)_2$

Method A: A solution of 0.18 g (0.35 mmol) of $Ru(bpy)_2Cl_2\cdot 2H_2O$ in 50 mL of methanol was brought to reflux and a solution of 0.18 g (0.70 mmol) of $Ag(SO_3CF_3)$ in 20 mL methanol was added. Within 10 min the reaction mixture changed color from purple to deep red. It was allowed to reflux for 16 h before cooling to room temperature and filtering to remove AgCl. The filtrate was added dropwise over a 4 h period to a refluxing solution prepared by dissolving 0.20 g (0.30 mmol) of $(Mebpy\text{-}Mebpy)Re(CO)_3Cl$ in 70 mL of refluxing methanol. The resulting solution was allowed to reflux for ~ 16 h. It was cooled to room temperature and suction filtered through a fine frit to remove solid impurities. The filtrate was evaporated to a small volume

(~ 30 mL) and added to ~ 200 mL of ether. A rust colored precipitate formed which was removed by filtration and dried under vacuum. The yield of crude product was 0.42 g. A two step purification step was followed. First the compound was dissolved in 50 mL of methanol and a saturated NH_4PF_6 solution in methanol was added in excess (~ 5 mL). Addition of this solution to 200 mL of ether resulted in precipitation of a rust-orange powder which was isolated by vacuum filtration. The second purification step involved redissolving this precipitate in a minimum amount of acetonitrile and reprecipitating it by addition to ether. The product was reisolated by vacuum filtration. The yield upon vacuum drying was 0.30 g (75%) of product. Anal. Calcd. for $C_{47}H_{38}ClF_{12}N_8O_3P_2ReRu$: C, 41.03; H, 2.79; N, 8.15. Found: C, 40.87; H, 2.82, N, 8.09.

Method B: In a 100 mL round bottom flask, 0.05 g (0.0467 mmol) of $[(bpy)_2Ru(Mebpy\text{-}Mebpy)](PF_6)_2$ was dissolved in 35 mL of methanol. To this solution, 0.021 g (0.0581 mmol) of $Re(CO)_5Cl$ in 20 mL of methanol was added. The reaction mixture was refluxed for 16 h under a N_2 atmosphere; then methanol was removed with a rotary evaporator. The residue was dissolved in CH_2Cl_2 and reprecipitated by addition to hexane. The precipitate was isolated by vacuum filtration and dried by suction.

$[(bpy)_2Ru(Mebpy\text{-}Mebpy)Re(CO)_3py](PF_6)_3$

A solution of 0.11 g (0.08 mmol) of $[(bpy)_2Ru(Mebpy\text{-}Mebpy)Re(CO)_3Cl](PF_6)_2$ in 20 mL of methanol was warmed to near reflux and 0.03 g (0.12 mmol) of $AgPF_6$ in 50 mL of methanol was added. The resulting suspension was allowed to reflux in the dark for 18 h. It was cooled to room temperature and suction filtered through a fine frit to remove the AgCl precipitate. Then 1 mL of pyridine was added to the filtrate and the resulting solution was refluxed for 24 h. The solution was cooled to room temperature and evaporated to dryness with a rotary evaporator. The residue was dissolved in a small amount of methylene chloride and precipitated by addition to 100 mL of n-hexane. The solid material was collected by vacuum filtration and dried in a vacuum oven.

The yield of fine orange powder was 0.11 g (88%). Anal. Calcd. for $C_{52}H_{43}F_{18}N_9O_3P_3ReRu$: C, 39.33; H, 2.78; N, 8.06. Found: (Method A) C, 39.66; H, 2.82; N, 7.90. (Method B) C, 39.81; H, 2.70; N, 8.03.

[(Mebpy-Mebpy)Re(CO)$_3$py]PF$_6$

A solution of 0.04 g (0.16 mmol) of $AgPF_6$ in 25 mL of acetone was added to a solution containing 0.10 mL of pyridine (1.24 mmol) in 25 mL of acetone. The mixture was stirred at room temperature for 16 h in the dark. Then 0.10 g (0.14 mmol) of (Mebpy-Mebpy)Re(CO)$_3$Cl was added and the solution was allowed to stir at room temperature for 72 h after which 1 mL of pyridine was added. The mixture was warmed to reflux for 48 h. It was cooled to room temperature and suction filtered to remove the AgCl. The yellow filtrate was evaporated to dryness and the residue was dissolved in a minimum amount of methylene chloride. Addition of this solution to 100 mL of n-hexane affords the product as a pale yellow precipitate. It was suction filtered and vacuum dried. The yield was 0.12 g (92%). Anal. Calcd. for $C_{32}H_{27}F_6N_5O_3PRe$: C, 44.65; H, 3.17; N, 8.14. Found: C, 44.41; H, 3.26; N, 8.05.

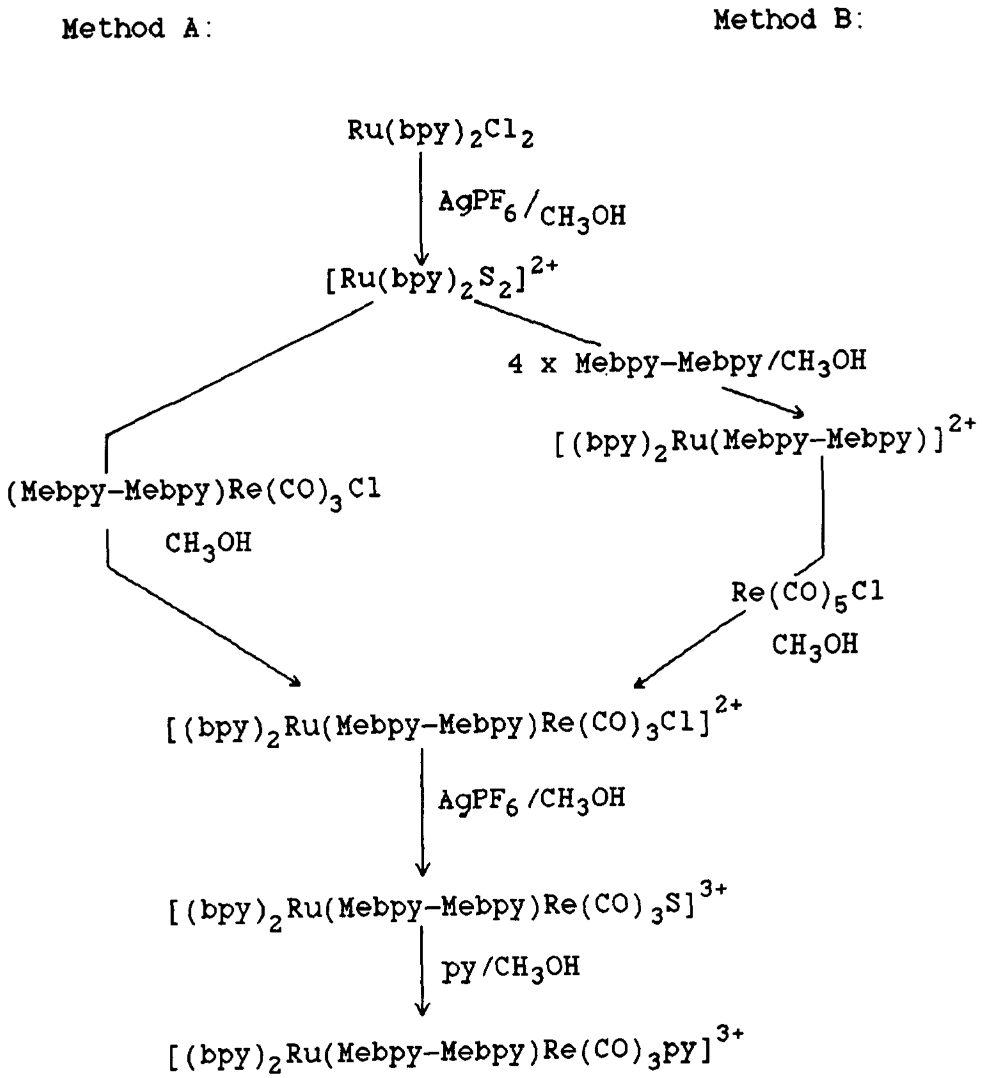
Physical Measurements

Visible-uv spectra were recorded with a Perkin-Elmer Lambda Array 3840 spectrophotometer. Molar absorption coefficients were determined by Beer's law serial dilution methods. Corrected emission spectra, excitation spectra and quantum yields were obtained with a Spex Fluorolog Model 212 system. All samples were adjusted to 0.10 absorbance units at the excitation frequency and then were freeze-pump-thaw degassed. Ru(bpy)$_3^{2+}$, which has a known radiative quantum yield of 0.062 at λ_{ex} = 436 nm in acetonitrile, and rhodamine-B, which has a known radiative quantum yield of 0.69 at λ_{ex} = 355 nm in ethanol, served as standards. Luminescence lifetimes were determined with a PAR LN1000 pulsed N_2 laser, a PAR LN102 Dye laser, a LeCroy 6880A transient digitizer and an IBM PS/2 Model 60 microcomputer. Transient absorption measurements were performed at UNC Chapel Hill using the third harmonic of a Quata Ray DCR-2A Nd:YAG laser as the excitation source. The excitation was at right angles to an Applied Photophysics laser kinetic spectrometer which included a 250 watt pulsed Xe arc probe source, a f/3.4 grading monochrometer and a 5-stage PMT. The output was coupled to the LeCroy 9400 digital oscilloscope interfaced with an IBM PC microcomputer. The laser power was measured before and after each experiment using a Molectron J3-09 power meter coupled to the digital oscilloscope. Electrochemical studies were carried out in acetonitrile with a three electrode system which consisted of a Pt disk working electrode, a Pt wire counter electrode and a saturated sodium chloride calomel standard reference electrode (S.S.C.E.). The solution contained 0.1 M tetrabutylammonium hexafluorophosphate (TBAH) as electrolyte. A PRA 173 potentiostat linked to a PAR 175 programmer was used to obtain cyclic voltammograms which were recorded with a YEW Model 3022 x-y recorder.

RESULTS AND DISCUSSION

Preparation of the Bimetallic Complex

As shown in Scheme 1, the preparation of the final product, the bimetallic pyridinate complex, was effected by the sequential addition of $AgPF_6$ to remove Cl^- from the coordination sphere of $[(bpy)_2Re(Mebpy\text{-}Mebpy)Re(CO)_3Cl]^{2+}$ which was then replaced by pyridine present in solution. The bimetallic chloro complex was the common intermediate formed by two pathways labeled A and B. The two differ in the order of metallation. Method A was originally selected due to the simple preparation and purification of $(Mebpy\text{-}Mebpy)Re(CO)_3Cl$.[11] Reaction of $(Mebpy\text{-}Mebpy)Re(CO)_3Cl$ with $[Ru(bpy)_2S_2]^{2+}$, S = acetone or methanol, affords the mixed-metal $[(bpy)_2Ru(Mebpy\text{-}Mebpy)Re(CO)_3Cl]^{2+}$ cation. The pyridine adduct was then prepared as described above. The emission spectrum of $[(bpy)_2Ru(Mebpy\text{-}Mebpy)Re(CO)_3py]^{3+}$ (λ_{ex} = 355 nm) had a small secondary emission which was initially ascribed to emission from the rhenium component of the molecule. Subsequent experimental work with the monometallic rhenium pyridinate, $[(Mebpy\text{-}Mebpy)Re(CO)_3py]^+$, showed that it was a strong emitter and a small quantity of it, or more likely



Scheme 1. Outline of preparation of the bimetallic complexes by methods A and B.

$\mathrm{[py(CO)_3Re(Mebpy\text{-}Mebpy)Re(CO)_3py]^{2+}}$, could account for this apparent secondary emission.

Method B involved reacting $\mathrm{[(bpy)_2Ru(Mebpy\text{-}Mebpy)]^{2+}}$ with $\mathrm{Re(CO)_5Cl}$ to form $\mathrm{[(bpy)_2Ru(Mebpy\text{-}Mebpy)Re(CO)_3Cl]^{2+}}$ followed by its conversion to $\mathrm{[(bpy)_2Ru(Mebpy\text{-}Mebpy)Re(CO)_3py]^{3+}}$ as described above. The emission spectrum (λ_{ex} = 355 nm) was free of the secondary emission. Method B precluded formation of $\mathrm{[(Mebpy\text{-}Mebpy)Re(CO)_3py]^{+}}$ and $\mathrm{[py(CO)_3Re(Mebpy\text{-}Mebpy)Re(CO)_3py]^{2+}}$ as contaminants but did allow $\mathrm{[(bpy)_2Ru(Mebpy\text{-}Mebpy)Ru(bpy)_2]^{2+}}$ as an impurity. However, there is no real evidence for its presence from elemental analyses or physical property data.

Electrochemistry

Redox potentials for the complexes were recorded in acetonitrile and are tabulated in Table 1. The redox potentials for the bimetallic complex were relatively straight forward to assign. Its cyclic voltammogram closely resembled the composite of the ones for the monometallic precursors.

Table 1
Electrochemical Properties of Rhenium(I) and Ruthenium(II) Complexes[a,b]

Complex	Oxidation		Reduction		
	$E_{1/2}(2)$	$E_{1/2}(1)$	$E_{1/2}'(1)$	$E_{1/2}'(2)$	$E_{1/2}'(3)$
(1)		1.19[c]	-1.38[c]	-1.56	-1.93
(2)		1.79[d]	-1.22(70)[e]	-1.56[f]	
(3)	1.78[d]	1.25(60)[e]	-1.36(80)[e,g]	-1.60(100)[e]	-1.81(80)[e]
(4)[h]		1.27	-1.31	-1.50	-1.77

1 = $\mathrm{[(bpy)_2Ru(Mebpy\text{-}Mebpy)]^{2+}}$; 2 = $\mathrm{[(Mebpy\text{-}Mebpy)Re(CO)_3py]^{+}}$; 3 = $\mathrm{[(bpy)_2Ru(Mebpy\text{-}Mebpy)Re(CO)_3py]^{3+}}$; 4 = $\mathrm{[Ru(bpy)_3]^{2+}}$.
a. Potentials are in V vs. SSCE, ± 0.02V, SR = 200 mV/s.
b. Solutions were 0.1 M in TBAH; the solvent was acetonitrile. c. Ref. 4. d. irreversible. e. $\Delta E_p = E_{p,ox} - E_{p,red}$. f. Quasireversible. g. See text about "prewave" located at -1.22 V. h. Ref. 18.

Oxidations of rhenium(I) tricarbonyl and ruthenium(II) monometallic complexes were in accord with other reported systems. The oxidation of $[(\mathrm{Mebpy\text{-}Mebpy})\mathrm{Re(CO)_3py}]^+$ at 1.79 V was irreversible. Previously, in closely related systems, it was assigned to the one electron oxidation of rhenium(I) and is thought to be the case here as well.[15-16] Oxidation of $[(\mathrm{bpy})_2\mathrm{Ru}(\mathrm{Mebpy\text{-}Mebpy})]^{2+}$ occurred with the i_a/i_c ratio near one and ΔE_p($\Delta E_p = E_{p,ox} - E_{p,red}$) on the order of 60 mV indicative of a reversible, one-electron process.[17] It was located at 1.19 V compared to 1.27 V for $[\mathrm{Ru(bpy)_3}]^{2+}$.[18] This shift to more negative potential may be due to the tethered bipyridine unit.

The sequence of oxidations in $[(\mathrm{bpy})_2\mathrm{Ru}(\mathrm{Mebpy\text{-}Mebpy})\mathrm{Re(CO)_3py}]^{3+}$ are assigned in equations 1 and 2. The first electron is removed from the ruthenium center; the

$$[(\mathrm{bpy})_2\mathrm{Ru(II)}(\mathrm{Mebpy\text{-}Mebpy})\mathrm{Re(I)(CO)_3py}]^{3+} \xrightarrow{-e^-} [(\mathrm{bpy})_2\mathrm{Ru(III)}(\mathrm{Mebpy\text{-}Mebpy})\mathrm{Re(I)(CO)_3py}]^{4+} \quad (1)$$

$$[(\mathrm{bpy})_2\mathrm{Ru(III)}(\mathrm{Mebpy\text{-}Mebpy})\mathrm{Re(I)(CO)_3py}]^{4+} \xrightarrow{-e^-} [(\mathrm{bpy})_2\mathrm{Ru(III)}(\mathrm{Mebpy\text{-}Mebpy})\mathrm{Re(II)(CO)_3py}]^{5+} \quad (2)$$

second electron is lost from the rhenium center.

In the past, the first reduction of rhenium(I) and ruthenium(II) heterocycles has been assigned to addition of an electron to the lowest unoccupied molecular orbital localized primarily on the heterocyclic bidentate ligand.[19-20] Reduction of the monometallic rhenium(I) complex followed the process illustrated in equation 3. Equation 4 indicates that the second reduction corresponds to the Re(I/0) couple. The

$$[(\mathrm{Mebpy\text{-}Mebpy})\mathrm{Re(I)(CO)_3py}]^{+} \xrightarrow{+e^-} [(\mathrm{Mebpy\text{-}Mebpy}^-)\mathrm{Re(I)(CO)_3py}] \quad (3)$$

$$[(\mathrm{Mebpy\text{-}Mebpy}^-)\mathrm{Re(I)(CO)_3py}] \xrightarrow{+e^-} [\mathrm{Mebpy\text{-}Mebpy}^-)\mathrm{Re(0)(CO)_3py}]^- \quad (4)$$

first reduction located at -1.22 V is reversible; the second reduction located at -1.56 V is quasireversible.

The initial site of reduction in ruthenium(II) complexes containing various bidentate heterocyclic ligands depends on the ligand with the lowest π^* energy level.[18] The $E_{1/2}$ value for the first reduction in acetonitrile of $[Ru(bpy)_3]^{2+}$ is -1.31 V compared to -1.45 V for $[Ru(dmb)_3]^{2+}$, where dmb is 4,4'-dimethyl-2,2'-bipyridine.[20] Thus, the initial reduction at -1.35 V for $[(bpy)_2Ru(Mebpy\text{-}Mebpy)]^{2+}$ is assigned in equation 5 to one of the bpy ligands.

$$[(bpy)(bpy)Ru(Mebpy\text{-}Mebpy)]^{2+} \xrightarrow{+e^-} [(bpy)(bpy^-)Ru(Mebpy\text{-}Mebpy)]^{+} \qquad (5)$$

In tris chelates such as $[Ru(bpy)_3]^{2+}$, each coordinated ligand is sequencially reduced in 0.2 to 0.3 V intervals, e.g. $E_{1/2}'(1)$, $[Ru(bpy)_3]^{2+/+}$, = -1.31 V; $E_{1/2}'(2)$, $[Ru(bpy)_3]^{+/0}$, = -1.50 V, $E_{1/2}'(3)$, $[Ru(bpy)_3]^{0/-}$, = -1.77 V.[20] A similar series is found for mixed ligand complexes, where each ligand can be placed in the order of its expected reduction based on its $E_{1/2}'(1)$ value in the tris complex plus (absolute value) an additional factor associated with the number of previous reductions. Thus, the second reduction of $[(bpy)_2Ru(Mebpy\text{-}Mebpy)]^{2+}$ located at -1.56 V most likely is associated with addition of an electron to the π^* orbital of the second bpy ligand as illustrated in equation 6.

$$[(bpy^-)(bpy)Ru(Mebpy\text{-}Mebpy)]^{+} \xrightarrow{+e^-} [(bpy^-)(bpy^-)Ru(Mebpy\text{-}Mebpy)] \qquad (6)$$

The electrochemical reductions of the bimetallic complex follow those of the monometallic precursors. The "$(bpy)_2Ru(Mebpy\text{-}Mebpy)^{2+}$' and "$(Mebpy\text{-}Mebpy)Re(CO)_3{}^+$" fragments behave fairly independently of one another except for small potential shifts. The couple located at $E_{1/2}'(1)$ = -1.22 V in $[(Mebpy\text{-}Mebpy)Re(CO)_3py]^+$ appears as a prewave on the -1.36 V process of the bimetallic complex. This electrochemical process is a two one-electron wave corresponding to equations 3 and 5. The second reduction of the bimetallic complex located at -1.60 V is also a two one-electron process. It corresponds to the electrochemical processes illustrated in equations 4 and 6. The final reduction at -1.81 V has 1/2 the current of the previous one and most likely is associated with addition of an electron to the "Mebpy" ligand in the "$(bpy^-)(bpy^-)Ru(Mebpy-)$" fragment.

Visible/UV Spectra

A summary of the visible/uv properties of the complexes is given in Table 2. The entries are divided into transitions associated with the metal to ligand charge transfer ($d\pi\rightarrow\pi^*$) and intraligand processes ($\pi\rightarrow\pi^*$). These assignments were made on the basis of the well documented optical transitions in $[Ru(bpy)_3]^{2+}$ [21-22] and $[Re(o\text{-}phen)CO_3Cl]$,[23] where o-phen is 1,10-phenanthroline. The $d\pi\rightarrow\pi^*$ transition of the ruthenium complexes occurs near 450 nm whereas the one for the rhenium complexes takes place near 350 nm. Also occurring near 350 nm, is a second $d\pi\rightarrow\pi^*$ transition associated with ruthenium heterocycles of the type reported here.[21-22] The absorption coefficients of the rhenium complexes are typically a factor of three or more less than those of ruthenium analogues, which for the most part can be traced to the number of heterocyclic

Table 2
Visible/UV Properties of Rhenium(I) and Ruthenium(II) Complexes[a]

Complex	$d\pi\rightarrow\pi^*$	$\pi\rightarrow\pi^*$
(1)[b,c]	454(1.7), 430 (1.3) 351(0.71)	289(10.1), 246(4.1)
(2)[d]	354(0.47), 319(1.2)	283(3.4), 250(3.2)
(3)[d]	456(1.4), 435(1.3) 393(0.83), 354(1.2)	319(2.4), 291(9.6) 258(4.4), 247(4.9)

1 = $[(bpy)_2Ru(Mebpy\text{-}Mebpy)]^{2+}$; 2 = $[(Mebpy\text{-}Mebpy)Re(CO)_3py]^+$; 3 = $[(bpy)_2Ru(Mebpy\text{-}Mebpy)Re(CO)_3py]^{3+}$.

a. λ_{max} in nm; ± 1 nm; $\epsilon \times 10^{-4}$ in parenthesis, $M^{-1}cm^{-1}$, ± 1 in last digit, T = 25 ± 2°C. b. CH_3CN. c. Ref 4. d. CH_2Cl_2.

ligands and, hence, is the result of a statistical or probability factor. Previously,[8] we showed that absorption spectra of multimetallic complexes were essentially additive, which appears true for the $d\pi \rightarrow \pi^*$ transitions observed here. For example, the absorption coefficient of the 354 nm band of $[(bpy)_2Ru(Mebpy\text{-}Mebpy)Re(CO)_3py]^{3+}$ is the approximate sum of 0.47×10^4 $cm^{-1}M^{-1}$ for the 354 nm band of $[(Mebpy\text{-}Mebpy)Re(CO)_3py]^+$ and 0.71×10^4 $cm^{-1}M^{-1}$ for the 351 nm band of $[(bpy)_2Ru(Mebpy\text{-}Mebpy)]^{2+}$. However, this statistical treatment breaks down for $\pi \rightarrow \pi^*$ transitions. The absorption coefficient of the 291 nm band of $[(bpy)_2Ru(Mebpy\text{-}Mebpy)Re(CO)_3py]^{3+}$ is less than the sum of its monomeric parts. The transition probability factor of the $\pi \rightarrow \pi^*$ transition here is clearly affected by the presence of more than one metal center. The spectral comparison in Figure 1 illustrate some of these points.

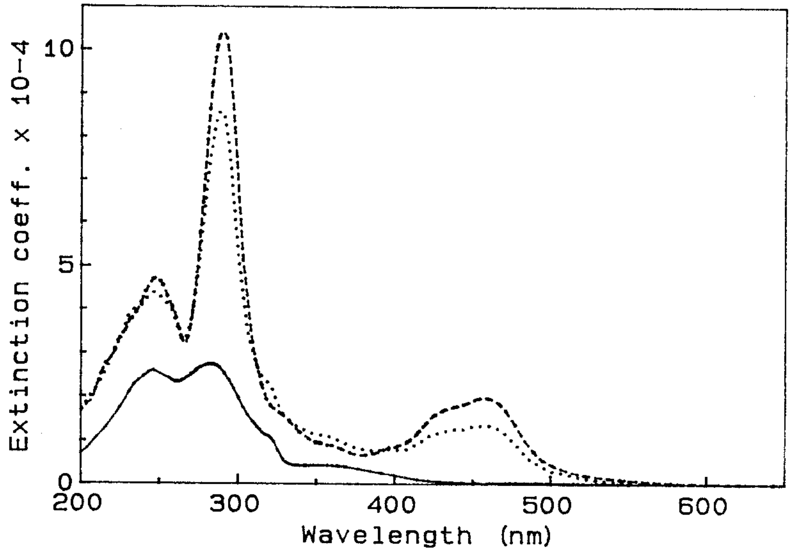


Figure 1. A visible/uv spectral comparison of $[(Mebpy\text{-}Mebpy)Re(CO)_3py]^+$ (——), $[(bpy)_2Ru(Mebpy\text{-}Mebpy)]^{2+}$ (----) and $[(bpy)_2Ru(Mebpy\text{-}Mebpy)Re(CO)_3py]^{3+}$ (····).

Emission-Excitation Properties

Emission energy maxima, quantum yields and lifetimes are summarized in Table 3. Data were acquired at two excitation frequencies, 355 and 436 nm. At 436 nm excitation, only the "$(bpy)_2Ru(Mebpy-Mebpy)^{2+}$" moiety absorbs light and emits; "$(Mebpy-Mebpy)Re(CO)_3py^+$" is inactive. Comparison of the data (λ_{ex} = 436 nm) for $[(bpy)_2Ru(Mebpy-Mebpy)]^{2+}$ and $[(bpy)_2Ru(Mebpy-Mebpy)Re(CO)_3py]^{3+}$ indicates that the emission maxima remain near 610 nm. However, in contrast to the normal decrease in emission lifetime and quantum yield of multimetallic complexes coupled by conducting bridging ligands[24] or the similarity of values for multimetallic complexes coupled by saturated or nonconducting bridging ligands,[4,25] the excited-state lifetime and radiative quantum yield actually increase by about 10%.

Table 3

Luminescence Properties of Rhenium(I) and Ruthenium(II) Complexes in Dichloromethane at Room Temperature[a]

Complex	λ_{ex}, nm[b]	λ_{em}, nm[b]	τ_o,[c]ns	ϕ_r
(1)	436	609	1048	0.097[d]
	355	609	1015	0.080[d]
(2)	436	---	----	-----
	355	552	786	0.179[e]
(3)	436	610	1191	0.119[f]
	355	610	1001	0.164[g]

1 = $[(bpy)_2Ru(Mebpy-Mebpy)]^{2+}$; 2 = $[(Mebpy-Mebpy)Re(CO)_3py]^+$; 3 = $[(bpy)_2Ru(Mebpy-Mebpy)Re(CO)_3py]^{3+}$.

a. T = 25 ± 2°C. b. ± 2 nm. c. ± 10%. d. ± 0.001. e. ± 0.004. f. ± 0.002. g. ± 0.003, corrected for the 62%/38% Ru/Re absorbance at 355 nm.

At 355 nm excitation, both $[(bpy)_2Ru(Mebpy-Mebpy)]^{2+}$ and $[(bpy)_2Ru(Mebpy-Mebpy)Re(CO)_3py]^{3+}$ emit, each with its own characteristic features. In comparison to 436 nm excitation, the luminescence maximum of $[(bpy)_2Ru(Mebpy-Mebpy)]^{2+}$ remains near 610 nm, the emission lifetime remains just over 1000 ns, and the emission quantum yield is 0.080. These data are in accord with the reported intersystem crossing quantum efficiency near one from higher energy ^{1}MLCT states to emitting states in the $[Ru(bpy)_3]^{2+}$ model compound.[26] $[(Mebpy\text{-}Mebpy)Re(CO)_3py]^{3+}$, on the other hand, emits near 552 nm, has an emission lifetime of 786 ns, somewhat less than 1015 ns for $[(bpy)_2Ru(Mebpy\text{-}Mebpy)]^{2+}$, and has an emission quantum yield of 0.179, approximately two times larger than 0.080 found for $[(bpy)_2Ru(Mebpy\text{-}Mebpy)]^{2+}$. The positions and intensities of the emission bands for $[(bpy)_2Ru(Mebpy\text{-}Mebpy)]$ and $[(Mebpy\text{-}Mebpy)Re(CO)_3py]^+$ are illustrated in Figure 2.

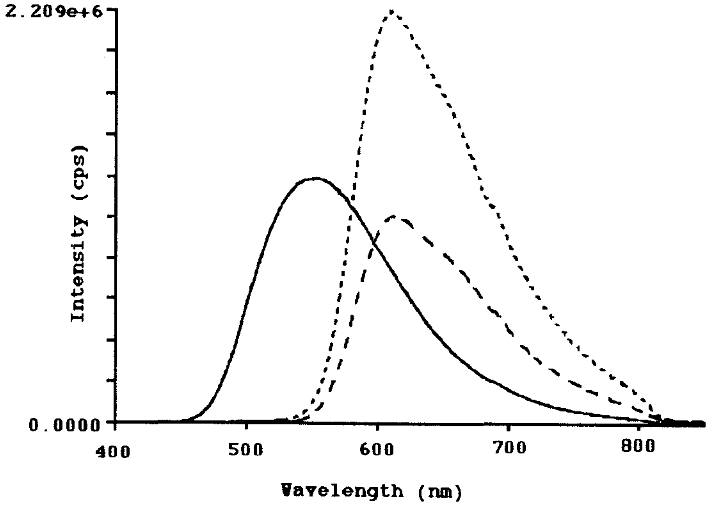


Figure 2. An emission spectral comparison of $[(Mebpy\text{-}Mebpy)Re(CO)_3py]^+$ (——), $[(bpy)_2Ru(Mebpy\text{-}Mebpy)]^{2+}$ (----), and $[(bpy)_2Ru(Mebpy\text{-}Mebpy)Re(CO)_3py]^{3+}$ (····) in CH_2Cl_2 (λ_{ex} = 355 nm).

The luminescence behavior of the heterobimetallic complex is also illustrated in Figure 2. Excitation at 436 nm in CH_2Cl_2 results in an increased emission intensity at 610 nm compared to $[(bpy)_2Ru(Mebpy\text{-}Mebpy)]^{2+}$. The radiative quantum yields are 0.119 compared to 0.080, respectively. Excitation of the heterobimetallic complex at 355 nm results in a decrease in excited-state lifetime from 1191 ns to 1001 ns but an increase in radiative quantum yield from 0.119 to 0.164 compared to excitation at 436 nm. This observation is significant because normally within a series of similar compounds, as the excited-state lifetime increases, the radiative quantum yield also increases.[27] The increase in radiative quantum yield can only be explained by energy (or electron) transfer from the "(Mebpy-Mebpy)Re$(CO)_3py^+$" fragment to the "$(bpy)_2$Ru(Mebpy-Mebpy)$^{2+}$" fragment in the bimetallic complex. A crude calculation based on 62% absorbance by the "$(bpy)_2$Ru(Mebpy-Mebpy)$^{2+}$" fragment and 38% absorbance by "(Mebpy-Mebpy)Re$(CO)_3py^+$" fragment and the radiative quantum yields of 0.119 for $[(bpy)_2Ru(Mebpy\text{-}Mebpy)Re(CO)_3py]^{3+}$ at 436 nm excitation and 0.179 for $[(Mebpy\text{-}Mebpy)Re(CO)_3py]^+$ at 355 nm excitation, 0.62(0.119) + 0.38(0.179), results in $\phi_r \approx$ 0.14. The actual radiative quantum yield is 0.16. Clearly, the energy transfer process is efficient.

Further proof of the energy transfer phenomenon in the bimetallic complex is rationalized on the basis of the excitation spectra which are compared in Figure 3. The excitation envelope of $[(bpy)_2Ru(Mebpy\text{-}Mebpy)]^{2+}$ covers the range from about 250 to 500 nm and consists of several peaks above 400 nm. The excitation spectrum of $[(Mebpy\text{-}Mebpy)Re(CO)_3py]^+$ consists of two broad peaks in the 250-400 nm region, but only tailing is observed in the wavelength region above 400 nm. The excitation spectrum of the "$(bpy)_2$Ru(Mebpy-Mebpy)$^{2+}$" end of the bimetallic complex is a composite of the excitation spectra for the monomeric components. The peaks related to the excitation spectrum of the "(Mebpy-Mebpy)Re$(CO)_3py^+$" fragment are present in the emission at 610 nm from the "$(bpy)_2$Ru(Mebpy-Mebpy)$^{2+}$" fragment. This phenomenon is indicative of energy transfer from one chromaphoric site to another.[14]

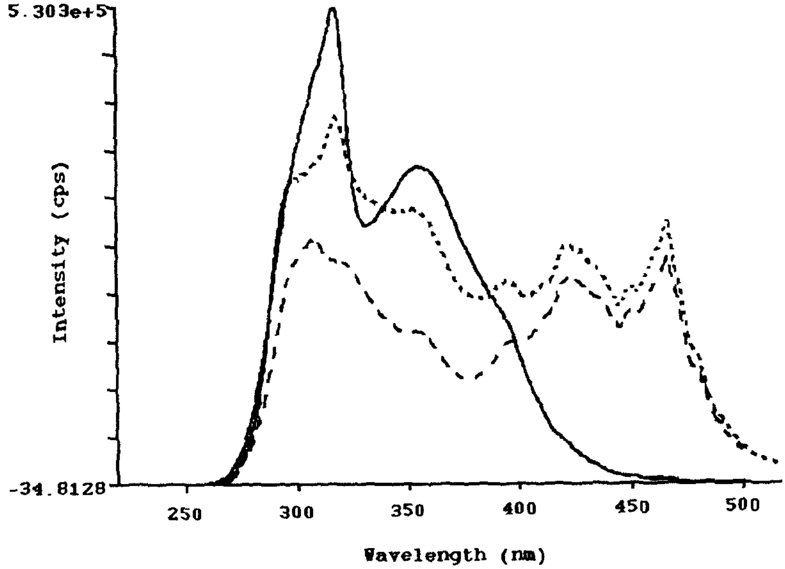


Figure 3. A comparison of the excitation spectra of $[(bpy)_2Ru(Mebpy\text{-}Mebpy)]^{2+}$ (——), $[(Mebpy\text{-}Mebpy)Re(CO)_3py]^+$ (----), and $[(bpy)_2Ru(Mebpy\text{-}Mebpy)Re(CO)_3py]^{3+}$ (••••). The $[(bpy)_2Ru(Mebpy\text{-}Mebpy)Re(CO)_3py]^{3+}$ emission was monitored at 610 nm; the $[(bpy)_2Ru(Mebpy\text{-}Mebpy)]^{2+}$ emission was monitored at 610 nm (its excitation spectrum was multiplied by 0.62); the $[(Mebpy\text{-}Mebpy)Re(CO)_3py]^+$ emission was monitored at 550 nm (its excitation spectrum was multiplied by 0.38).

Transient Absorption Spectra

Transient absorbance measurements for $[(bpy)_2Ru(Mebpy\text{-}Mebpy)]^{2+}$, $[(Mebpy\text{-}Mebpy)Re(CO)_3py]^+$ and $[(bpy)_2Ru(Mebpy\text{-}Mebpy)Re(CO)_3py]^{3+}$ were obtained in CH_2Cl_2 using the third harmonic of the Nd:YAG laser as the excitation source. The spectra shown in Figure 4 were obtained 30 ns after excitation. Within experimental error, transient absorptions decayed at the same rate as luminescence.

As shown in Figure 4, a large positive peak at ~ 370 nm is obtained in all three complexes and a negative peak related to bleaching of the MLCT absorption band of "$(bpy)_2Ru(Mebpy-Mebpy)^{2+}$" occurs when it is present. The bleach is less in the bimetallic complex than the monometallic species indicating that the "$(Mebpy-Mebpy)Re(CO)_3py^+$" fragment also absorbs excitation energy. The transient absorption spectrum for $[(bpy)_2Ru(Mebpy-Mebpy)]^{2+}$ is similar to the one obtained for $[Ru(bpy)_3]^{2+}$ under similar experimental conditions. The $[Ru(bpy)_3]^{2+*}$ transient absorption spectrum has been assigned to formation of the $Ru(III)(bpy^-)$ fragment.[28] It follows, that in the case of $[(Mebpy-Mebpy)Re(I)(CO)_3py]^+$, the transient responsible for its absorption spectrum in Figure 4 is formation of $[(Mebpy-Mebpy^-)Re(II)(CO)_3py]^{+*}$. Here the radical anion "bpy^-" dominates the absorption at ~ 370 nm and bleaching is not observed in the 450 nm region in accord with

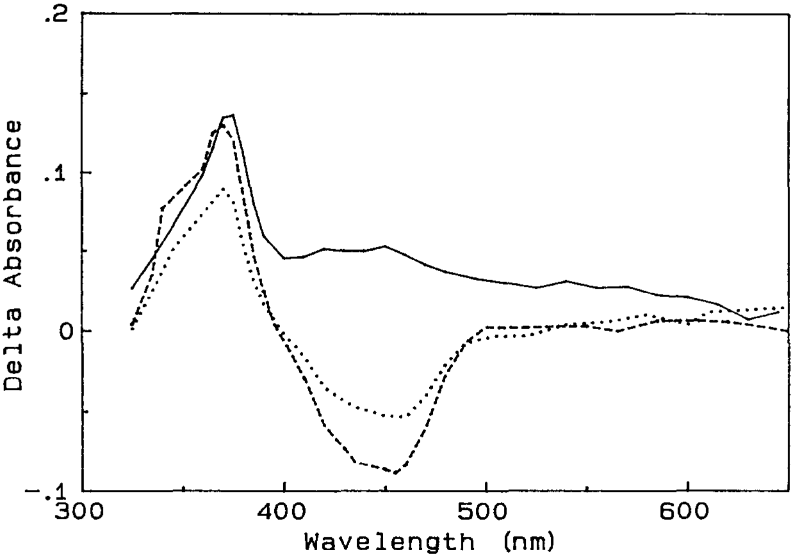
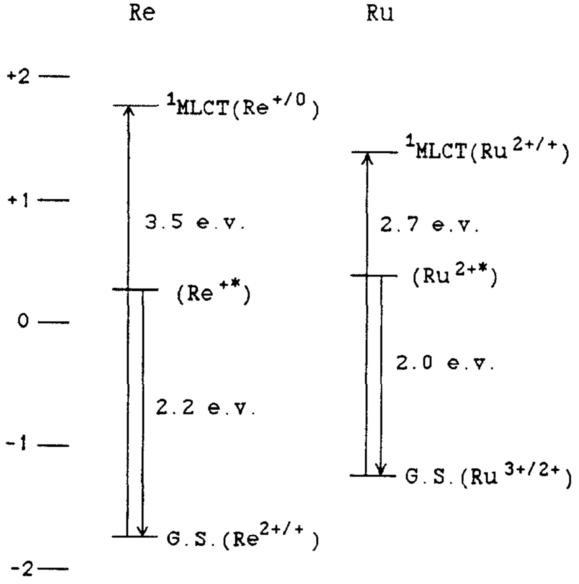


Figure 4. Transient absorption spectra of $[(Mebpy-Mebpy)Re(CO)_3py]^+$ (——), $[(bpy)_2Ru(Mebpy-Mebpy)]^{2+}$ (----) and$[(bpy)_2Ru(Mebpy-Mebpy)Re(CO)_3py]^{3+}$ (····). See text for details.

the fact that the rhenium complex does not absorb in this region of the spectrum.

Proposed Energy Transfer Mechanism

Based on absorption energy maxima, emission energy maxima, and electrochemical potentials, an absolute energy comparison of "$(bpy)_2Ru(Mebpy\text{-}Mebpy)^{2+}$" to "$(Mebpy\text{-}Mebpy)Re(CO)_3py^{+}$" is given in Scheme 2. According to this scheme, the ground state energies differ by ~ 0.5 eV, with the



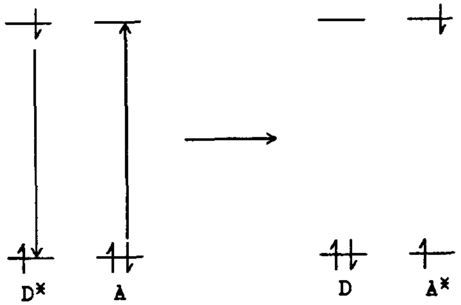
Scheme 2. An absolute energy comparison of the Re(I) and Ru(II) components in $[(bpy)_2Ru(Mebpy\text{-}Mebpy)Re(CO)_3py]^{3+}$.

Re(I) component having the lowest energy ground state. The Re(I) component also has the highest energy ^{1}MLCT state. The ^{3}MLCT states of the Re(I) and Ru(II) fragments are approximately located at the same energy, although the Re(I) unit is approximately 0.1 eV lower.

Several mechanisms can be postulated to account of energy transfer from "$(Mebpy\text{-}Mebpy)Re(CO)_3py^{+*}$" to "$(bpy)_2Ru(Mebpy\text{-}$

Mebpy)$^{2+}$". The first of these, radiative energy transfer, can be discounted. The mechanism involves excitation of the acceptor by the emission of the donor. This requires overlap of the emission spectrum of the donor with the absorption spectrum of the acceptor.[29] This does not appear to be the case in $[(bpy)_2Ru(Mebpy\text{-}Mebpy)Re(CO)_3py]^{3+}$. The "(Mebpy-Mebpy)$Re(CO)_3py]^{+}$" emission is centered at 552 nm, the "$(bpy)_2Ru(Mebpy\text{-}Mebpy)^{2+}$" absorption is located at 456 nm.

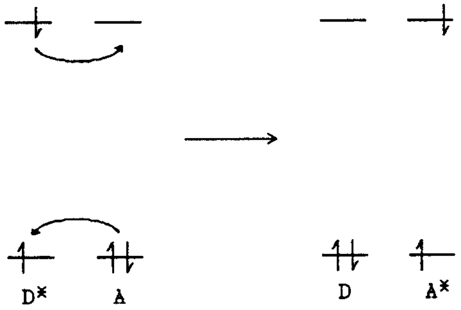
The second mechanism considered is the one postulated by Förster.[30] This mechanism requires through space coulombic interaction. According to this mechanism, the dipole of the excited-state donor interacts with the dipole of the acceptor, thereby simultaneously exciting the acceptor and relaxing the donor. This mechanism is illustrated in Scheme 3. The



Scheme 3. The dipole-dipole interchange mechanism.

Förster mechanism does not require molecular contact (collision) in order to occur and can take place with up to 100 Å separation between donor and acceptor.

The third mechanism as described by Dexter[31] entails actual electron exchange from one molecular center to the other. This is illustrated in Scheme 4. The electron exchange mechanism is exponentially dependent upon distance between the donor and acceptor and becomes negligible at distances greater than 10 Å.



Scheme 4. Energy transfer by electron exchange.

Energy transfer in $[(bpy)_2Ru(Mebpy\text{-}Mebpy)Re(CO)_3py]^{3+}$ can be explained by either the Dexter of Förster mechanism. The Förster mechanism depends upon oscillator strength and preliminary evidence[32] suggests a direct correlation exists between the radiative quantum yield and the oscillator strength of the bimetallic complex. Energy transfer by the Dexter mechanism is also possible. The edge to edge distance of the Mebpy-Mebpy pyridine rings is 3.4 Å and the maximum distance between the nitrogen atoms of Mebpy-Mebpy is 10.5 Å. Clearly the extension of $d\pi \rightarrow \pi^*$ orbitals on "$(bpy)_2Ru(Mebpy\text{-}Mebpy)^{2+}$" and "$(Mebpy\text{-}Mebpy)Re(CO)_3py^+$" fall within the 10 Å range. According to Scheme III, there is sufficient thermodynamic driving force to allow the Dexter mechanism to occur. Upon photoexcitation of the "$(Mebpy\text{-}Mebpy)Re(CO)_3py^+$" fragment, a hole is generated in the ground state which can readily be filled by one of the electrons in the ground state of "$(bpy)_2Ru(Mebpy\text{-}Mebpy)^{2+}$. Simultaneously the electron in the ^{3}MLCT state on "$(Mebpy\text{-}Mebpy)Re(CO)_3py^+$" can transfer to the ^{3}MLCT state of "$(bpy)_2Ru(Mebpy\text{-}Mebpy)^{2+}$" with a net release of energy.

Additional work is underway to seek answers to whether both mechanisms occur, or one is dominant over the other.

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