Intramolecular Energy Transfer Processes in Binuclear Re−Os Complexes

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A series of bimetallic complexes of general formula $[(\text{phen})\text{Re}(\text{CO})_3\text{LOs}(\text{trpy})(\text{bpy})]^{3+}$ (bpy = 2,2′-bipyridine, phen = 1,10-phenanthroline, trpy = 2,2′:6′,2″-terpyridine, and L = 4,4′-bipyridine (4,4′-bpy), *trans*-1,2-bis(4-pyridyl)ethylene (*t*-bpe), or 1,2-bis(4-pyridyl)ethane (bpa)) and the model mononuclear species $[(\text{phen})\text{Re}(\text{CO})_3\text{L}]^+$ and $[\text{Os}(\text{trpy})(\text{bpy})\text{L}]^{2+}$ have been synthesized and their photophysical and photochemical properties studied. In the binuclear species an efficient $\text{Re}^{\text{I}*}-\text{Os}^{\text{II}}$ energy transfer is observed, which is analyzed in terms of Förster theory. In the binuclear $[(\text{phen})\text{Re}(\text{CO})_3(t\text{-bpe})\text{Os}(\text{trpy})(\text{bpy})]^{3+}$ complex, the *trans* to *cis* isomerization of the coordinated *t*-bpe ligand, characteristic of the $[(\text{phen})\text{Re}(\text{CO})_3(t\text{-bpe})]^+$ subunit, is inhibited by competitive intramolecular energy transfer.

Introduction

For the purpose of creating devices in molecular dimensions, highly elaborate supermolecules have been synthesized to combine in a planned way subunits with different functions. Examples can be found in the field of photoinduced charge separation, with supramolecular systems mimicking the primary process in photosynthesis or in light-harvesting systems,[1] with a future application in information storage and signal processing.[2,3]

Complexes consisting of two or more transition-metal complex subunits linked by a bridging ligand have been the subject of several investigations in the research fields of energy and electron transfer. These studies have been reviewed by Balzani and co-workers, with complete literature coverage up to 1996,[4] and in more recent papers focusing on specific classes of compounds.[5−10] Most of the intramolecular energy transfer studies have dealt with binuclear polypyridine complexes of ruthenium, osmium, or rhenium, and with bimetallic complexes containing Re−Ru or Ru−Os metal centers. Studies on binuclear complexes containing polypyridine Re and Os complexes have not been reported in the literature.

We report here the preparation and the photophysical characterization of a series of bimetallic species containing the $(\text{phen})\text{Re}^{\text{I}}(\text{CO})_3$ and $\text{Os}^{\text{II}}(\text{trpy})(\text{bpy})$ units (bpy = 2,2′-bipyridine; phen = 1,10-phenanthroline; trpy = 2,2′:6′,2″-terpyridine) bridged by 4,4′-bipyridine (4,4′-bpy), *trans*-1,2-bis(4-pyridyl)ethylene (*t*-bpe), or 1,2-bis(4-pyridyl)ethane (bpa), and of the model mononuclear constituents $[(\text{phen})\text{Re}^{\text{I}}(\text{CO})_3\text{L}]^+$ and $[\text{Os}^{\text{II}}(\text{trpy})(\text{bpy})\text{L}]^{2+}$ (L = 4,4′-bpy, *t*-bpe, or bpa).

Since the initial work of Wrighton and Morse,[11] considerable attention has been devoted to polypyridyl tricarbonyl complexes of rhenium(I). These complexes have been of value in exploring the fundamental photophysics of metal to ligand charge transfer (MLCT) excited states,[11−14] and in energy and electron transfer studies involving multichromophoric and chromophore−quencher complexes[15−18] Several advantages can be envisioned using *fac*-$[(\text{NN})\text{Re}^{\text{I}}(\text{CO})_3\text{L}]$ complexes (NN = polypyridine ligand; L = ancillary ligand) as chromophoric components in polynuclear species. These lie in the availability of useful synthetic chemistry, which allows substitution reactions to be

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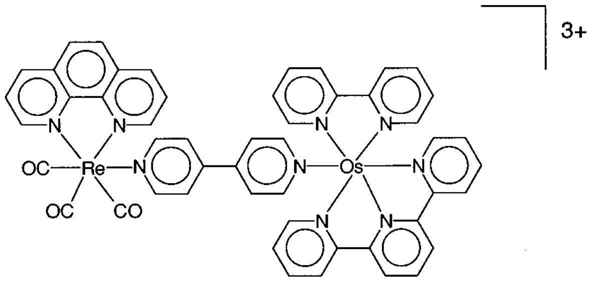

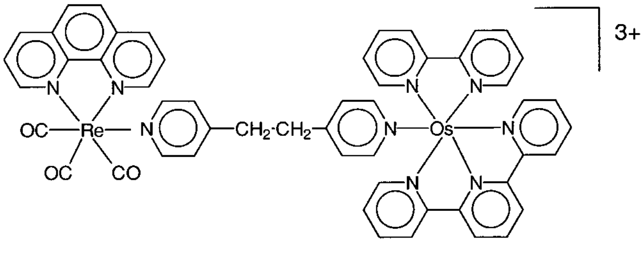

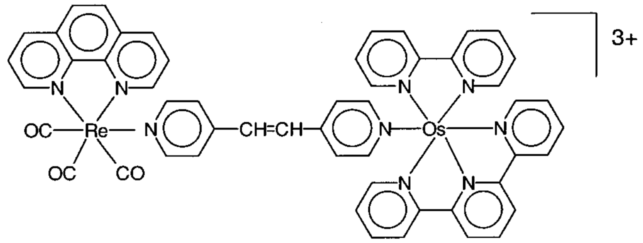

carried out with retention of configuration,[11,12] in the high emission quantum yield, in the oxidizing/reducing ability of the MLCT excited states,[12] and in the presence of intense ν(CO) modes in the infrared region with frequencies responding to changes in the electronic distribution at the Re center.[19,20]

The main goal of this work was the preparation of binuclear Re−Os complexes where electron or energy transfer processes could be observed, exploring the possible role of the bridging ligand in mediating the relevant excited-state intercomponent processes. In addition, this study has led to an interesting observation that photoinduced *trans*−*cis* isomerization of *t*-bpe in the *fac*-$[Re(CO)_3(phen)(t\text{-bpe})]^+$ complex[21] is inhibited in the corresponding Re−Os species due to a competition with Re* → Os intramolecular energy transfer.

Experimental Section

Abbreviations. The following abbreviations are used throughout the text: bpy = 2,2′-bipyridine; phen = 1,10-phenanthroline; trpy = 2,2′:6′,2″-terpyridine; 4,4′-bpy = 4,4′-bipyridine; bpa = 1,2-bis(4-pyridyl)ethane; *t*-bpe = *trans*-1,2-bis(4-pyridyl)ethylene; *c*-bpe = *cis*-1,2-bis(4-pyridyl)ethylene; TFMS = trifluoromethanesulfonic acid; TBAH = tetrabutylammonium hexafluorophosphate.

Apparatus and Procedures. Electrochemical, absorption, emission, and lifetime measurements were carried out as described previously.[21,22] Cyclic voltammetry measurements were performed in acetonitrile (spectroscopic grade) solutions in the presence of 0.1 M TBAH using a glassy carbon or a Pt working electrode, a Pt counter electrode, and an SCE reference electrode.

Transient absorbance difference spectra were measured by using an Applied Photophysics detection system with a J&K System 2000 frequency-doubled ruby laser, delivering 25 ns (half-width) pulses of 347 nm radiation. The maximum absorbance changes observed following the laser pulse were recorded as a function of wavelength at 10 nm intervals between 360 and 860 nm. The transient signals were corrected for variations in the laser pulse intensity by deflecting a small fraction of the laser beam to a photodiode whose output was calibrated against the benzophenone triplet absorption. Corrections of the intensities of these signals were also made for finite laser pulse duration by comparison with a calibration curve of intensity vs lifetime, obtained by quenching of the benzophenone triplet with oxygen in benzene solutions.

Emission spectrum fitting data were obtained following an established protocol.[12,23] Emission quantum yields were measured in deoxygenated acetonitrile solution by integration of the corrected emission spectra relative to that of $[Ru(bpy)_3](PF_6)_2$ ($\phi = 0.062$).[24]

The steady-state photolysis system is described in detail elsewhere.[21] Experiments were performed using an Oriel system with a 200 W Hg(Xe) arc lamp. Monochromatic irradiation was obtained by using Oriel interference filters. The light intensity at each wavelength was determined by tris(oxalate)ferrate(III) actinometry.

Materials. $(NH_4)_2OsCl_4$ was purchased from Johnson Matthey. The polypyridyl ligands were purchased from Aldrich Chemical Co. and used as received. Solvents for the preparations were of reagent grade, and solvents for electrochemistry and photophysical measurements were Aldrich products of spectroscopic or HPLC grade. $[Os(bpy)(Cl)_4]$[25,26] and *fac*-$[Re(phen)(CO)_3Cl]$[12] were prepared according to literature procedures.

Preparations. The mononuclear Re[11,12,29] and Os[25] complexes were prepared by adapting previously published procedures. The reactions were monitored by thin-layer chromatography (TLC) on silica gel or alumina by using a NaCl-saturated methanol solution as eluant.

$[Os(trpy)(bpy)(Cl)]PF_6$. A 0.906 g amount of $[Os(bpy)(Cl)_4]$ (1.86×10^{-3} mol) and 0.495 g of trpy (2.12×10^{-3} mol) were dissolved in 50 mL of ethylene glycol under argon, and the solution was heated to reflux for 1 h. The solution was then cooled to room temperature and was stirred for 5 min after 5 mL of a concentrated aqueous solution of $Na_2S_2O_4$ was added. The complex was precipitated by addition of solid NH_4PF_6, filtered off, and dried under vacuum. The solid was then purified by column chromatography on alumina, using a CH_3CN/toluene (1:1) mixture as eluant. The complex, dissolved in CH_3CN, was loaded onto the alumina column, previously saturated with toluene. The elution, carried out with the solvent mixture, produced a red-brown major band, which was collected and evaporated to dryness. The solid was recrystallized from ethanol/diethyl ether. Anal. Calcd. for $[Os(trpy)(bpy)(Cl)]PF_6$: C, 39.51; N, 9.21; H, 2.52. Found: C, 39.12; N, 9.03; H, 2.54.

$[Os(trpy)(bpy)(4,4'\text{-bpy})](PF_6)_2$. A 0.147 g amount of $[Os(trpy)(bpy)(Cl)]PF_6$ (1.93×10^{-4} mol) was dissolved in 30 mL of acetone, and 0.050 g of AgTFMS (1.9×10^{-4} mol) was added to the solution. The mixture was refluxed for 1 h under argon. The precipitated AgCl was filtered off, and 30 mL of ethylene glycol and 0.74 g of 4,4′-bpy·$2H_2O$ (3.9×10^{-3} mol) were added to the solution. After acetone evaporation, the solution was left refluxing for 6 h. The progress of the reaction was monitored by TLC (R_f of the product 0.09). The reaction mixture was cooled to room temperature, and the product was precipitated by addition of solid NH_4PF_6. The precipitate was dissolved in acetone and chromatographed on silica gel saturated with methanol.

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The elution was performed with methanol to remove the excess of ligand and unreacted [Os(trpy)(bpy)(TFMS)]$^+$, and continued with a NaCl-saturated methanol solution to collect the product. The product fraction was dried, and the solid was dissolved in acetone and precipitated again by adding water and solid NH$_4$PF$_6$. The precipitation was repeated three times to remove chloride ions. The product was finally recrystallized from ethanol/ether. Anal. Calcd. for [Os(trpy)(bpy)(4,4′-bpy)](PF$_6$)$_2$: C, 40.98; N, 9.56; H, 2.65. Found: C, 40.36; N, 9.28; H, 2.71.

[Os(trpy)(bpy)(bpa)](PF$_6$)$_2$. A 0.10 g amount of [Os(trpy)(bpy)(Cl)]PF$_6$ (1.32×10^{-4} mol) was dissolved in 30 mL of acetone, and 0.044 g of AgTFMS was added. The mixture was refluxed for 1 h under argon. The precipitated AgCl was filtered off, and 30 mL of ethylene glycol and 0.48 g of bpa (2.6×10^{-3} mol) were added to the solution. After evaporation of acetone, the reaction mixture was refluxed for 2 h and cooled to room temperature, and the product was precipitated by addition of an aqueous NH$_4$PF$_6$ solution. The solid was redissolved in CH$_3$CN and chromatographed on neutral alumina. The elution was initially performed with toluene and CHCl$_3$ to remove the unreacted bpa ligand, and continued with CH$_3$CN to collect the product. The acetonitrile fraction was dried and the product dissolved in acetone, reprecipitated by slow addition of diethyl ether, and recrystallized from methanol/ether. Anal. Calcd. for [Os(trpy)(bpy)(bpa)](PF$_6$)$_2$: C, 42.17; N, 9.30; H, 2.97. Found: C, 41.80; N, 8.98; H, 2.92.

[Os(trpy)(bpy)(*t*-bpe)](PF$_6$)$_2$. A 0.105 g amount of [Os(trpy)(bpy)(Cl)]PF$_6$ (1.38×10^{-4} mol) and 0.035 g of AgTFMS (1.38×10^{-4} mol) were dissolved in 30 mL of acetone. The mixture was refluxed for 1 h under argon. The precipitated AgCl was filtered off, and 30 mL of glycol and 0.504 g of *t*-bpe (2.8×10^{-3} mol) were added to the solution. After evaporation of acetone, the mixture was kept refluxing for 5 h under argon. The complex was purified as described for [Os(trpy)(bpy)(4,4′-bpy)](PF$_6$)$_2$. Anal. Calcd. for [Os(trpy)(bpy)(*t*-bpe)](PF$_6$)$_2$: C, 42.25; N, 9.32; H, 2.78. Found: C, 41.84; N, 9.02; H, 2.74.

***fac*-[Re(phen)(CO)$_3$(4,4′-bpy)]PF$_6$.** A 0.05 g amount of *fac*-[Re(phen)(CO)$_3$(Cl)] (1.03×10^{-4} mol) and 0.026 g of AgTFMS (1.03×10^{-4} mol) were refluxed in 30 mL of CH$_3$OH for 1 h under argon. After AgCl filtration, 0.395 g of 4,4′-bpy•2H$_2$O (2.06×10^{-3} mol) was added and the solution left to reflux for 6 h (product $R_f = 0.45$). The mixture was evaporated to dryness, and the solid was dissolved in acetone and chromatographed on silica gel. The unreacted 4,4′-bpy ligand was eluted with methanol. Elution with NaCl-saturated methanol allowed the product to be collected, which was then methathesized to the PF$_6$ salt as described above for the Os complexes. Anal. Calcd. for *fac*-[Re(phen)(CO)$_3$(4,4′-bpy)]PF$_6$•H$_2$O: C, 39.02; N, 7.28; H, 2.36. Found: C, 38.50; N, 7.03; H, 2.40.

***fac*-[Re(phen)(CO)$_3$(bpa)]PF$_6$.** The complex was prepared as reported for *fac*-[Re(phen)(CO)$_3$(4,4′-bpy)]PF$_6$. Anal. Calcd. for *fac*-[Re(phen)(CO)$_3$(bpa)]PF$_6$•H$_2$O: C, 40.66; N, 7.02; H, 2.78. Found: C, 40.22; N, 6.88; H, 2.80.

***fac*-[Re(CO)$_3$(phen)(*t*-bpe)]PF$_6$.** The complex was prepared with modifications of the literature procedure[16a] by dissolving 0.20 g of *fac*-[(TFMS)Re(CO)$_3$(phen)] (0.35×10^{-3} mol) and 0.46 g of *t*-bpe (2.5×10^{-3} mol) in 45 mL of methanol. The solution was stirred and heated to reflux for 5 h. The reaction was monitored both spectrophotometrically and by TLC.[21]

A yellow solid was obtained by adding a saturated aqueous solution of NH$_4$PF$_6$, which was filtered off and washed with ether. The compound was dissolved in a minimum amount of dimethylformamide, ca. 0.5 mL, purified chromatographically on a silica gel column, and eluted with methanol, at first, to eliminate the excess of the bpe ligand. The pure *fac*-[Re(CO)$_3$(phen)(*t*-bpe)]PF$_6$ was obtained after an NH$_4$PF$_6$-saturated methanol solution was added to the column. The solution was rotatory evaporated to dryness, the solid added in ca. 5 mL of water, and the resulting mixture stirred for 15 min to remove the excess NH$_4$PF$_6$. Filtration followed by additional column chromatography, when necessary, yielded an analytically pure complex. Anal. Calcd. for *fac*-[Re(CO)$_3$(phen)(*t*-bpe)]PF$_6$•H$_2$O: C, 40.72; N, 7.04; H, 2.51. Found: C, 40.61; N, 6.99; H, 2.39.

***fac*-[Re(CO)$_3$(phen)(c-bpe)]PF$_6$.** Attempts to obtain pure *c*-bpe ligand[27,28] did not succeed, and the pure *cis*-1,2-bis(4-pyridyl)ethylene was not isolated. A mixture of *cis*- and *trans*-1,2-bis(4-pyridyl)ethylene (0.48 g, 2.7×10^{-3} mol) was obtained photochemically, irradiating ($\lambda_{irr} = 254$ nm) a methanolic solution of *t*-bpe under N$_2$ atmosphere and controlling the reaction spectrophotometrically. The *fac*-[Re(CO)$_3$(phen)(*c*-bpe)]PF$_6$ complex was prepared by dissolving 0.15 g of *fac*-[(TFMS)Re(CO)$_3$(phen)] (0.24×10^{-3} mol) in a solution of *c*-bpe and heating it to reflux for 2 h. The solid was precipitated by addition of a saturated solution of NH$_4$PF$_6$ and isolated by centrifugation.[21] ^{1}H NMR data indicate a presence of *trans*- and *cis*-complexes. ^{1}H NMR for *fac*-[Re(CO)$_3$(phen)(*c*-bpe)]$^+$ (CD$_3$CN, δ (ppm)): 9.56, dd (2H); 8.83, dd (2H); 8.34, dd (2H); 8.18, s (2H); 8.09, q (2H); 8.06, dd (2H); 6.89, dd (2H); 6.80, d (1H); 6.53 d (1H).

Table 1. Infrared CO Stretching Frequencies (±2 cm^{-1}) for Mononuclear and Binuclear Complexes in KBr

complex	ν(CO), cm^{-1}
[Re(phen)(CO)$_3$(Cl)]	1898, 1932, 2017
fac-[Re(phen)(CO)$_3$(4,4-bpy)]$^+$	1913(sh), 1917, 2033
fac-[Re(phen)(CO)$_3$(bpa)]$^+$	1912(sh), 1919, 2031
fac-[Re(phen)(CO)$_3$(*t*-bpe)]$^+$	1917, 1930(sh), 2032
[Re(phen)(CO)$_3$(4,4-bpy)Os(trpy)(bpy)]$^{3+}$	1917, 1930(sh), 2034
[Re(phen)(CO)$_3$(bpa)Os(trpy)(bpy)]$^{3+}$	1918, 1930(sh), 2033
[Re(phen)(CO)$_3$(*t*-bpe)Os(trpy)(bpy)]$^{3+}$	1918, 1931(sh), 2034

[Re(phen)(CO)$_3$(4,4′-bpy)Os(trpy)(bpy)](PF$_6$)$_3$. A 0.10 g amount of *fac*-[Re(phen)(CO)$_3$(Cl)] (2.06×10^{-4} mol) and 0.053 g of AgTFMS (2.06×10^{-4} mol) were dissolved in 30 mL of CH$_3$OH and refluxed for 1 h under argon. After AgCl filtration, 0.150 g of [Os(trpy)(bpy)(4,4′-bpy)](PF$_6$)$_2$ (1.03×10^{-4} mol) was added and the mixture refluxed for 8 h (R_f(Os monomer) = 0.08; R_f(Re−Os dimer) = 0.04). The reaction mixture was evaporated to dryness and the solid redissolved in acetone and loaded onto the silica gel column. Elution was first performed with CH$_3$OH, to remove unreacted *fac*-[Re(phen)(CO)$_3$(TFMS)]$^+$, and then with a NaCl-saturated methanol solution, to collect the binuclear species. This fraction was dried and the solid methathesized to the PF$_6$ salt as described for the mononuclear Os complexes. Anal. Calcd. for [Re(phen)(CO)$_3$(4,4′-bpy)Os(trpy)(bpy)](PF$_6$)$_3$: C, 37.68; N, 7.99; H, 2.19. Found: C, 37.20; N, 7.94; H, 2.27.

[Re(phen)(CO)$_3$(bpa)Os(trpy)(bpy)](PF$_6$)$_3$. An 0.11 g amount of [Re(phen)(CO)$_3$(Cl)] (2.28×10^{-4} mol) and 0.058 g of AgTFMS (2.25×10^{-4} mol) were refluxed in 20 mL of methanol for 1 h under argon. The precipitated AgCl was filtered off, and 0.080 g of [Os(trpy)(bpy)(bpa)](PF$_6$)$_2$ (7.6×10^{-5} mol) in 30 mL of ethylene glycol was added. After evaporation of methanol, the mixture was refluxed for an additional 20 h under argon (R_f(Os monomer) = 0.11, R_f(Re−Os dimer) = 0.05). The crude product was precipitated by addition of an NH$_4$PF$_6$ aqueous solution. The solid was purified on an alumina column. Elution was first performed with 1:2 acetonitrile/toluene to remove the unreacted Re complex followed by 1:1 acetonitrile/methanol to collect the Re−Os dimer. This fraction was evaporated and the solid dried under vacuum. Anal. Calcd. for [Re(phen)(CO)$_3$(bpa)Os(trpy)(bpy)](PF$_6$)$_3$: C, 38.40; N, 7.70; H, 2.40. Found: C, 38.20; N, 7.60; H, 2.50.

[Re(phen)(CO)$_3$(*t*-bpe)Os(trpy)(bpy)](PF$_6$)$_3$. The complex was prepared as reported for [Re(phen)(CO)$_3$(4,4′-bpy)Os(trpy)(bpy)](PF$_6$)$_3$. Anal. Calcd. for [Re(phen)(CO)$_3$(*t*-bpe)Os(trpy)(bpy)](PF$_6$)$_3$: C, 37.9; N, 7.60; H, 2.30. Found: C, 37.70; N, 7.50; H, 2.40.

Results

Infrared Spectra. The infrared spectra of *fac*-[Re(phen)(CO)$_3$(L)]$^+$ complexes (L = Cl$^-$, bpa, 4,4′-bpy, or *t*-bpe) are characterized by intense carbonyl stretching vibrations, ν(CO), which are consistent with C_s symmetry. Three intense ν(CO) modes (2A′ + A″) are in general observed between 1900 and 2050 cm^{-1}, the frequencies of which are reported in Table 1. These values show clearly that the $d_{\pi-\pi^*}$(CO) back-bonding interaction is generally high. In fact the ν(CO) mode energies

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Table 2. Electrochemical Properties of Mononuclear and Binuclear Complexes in Acetonitrile Solution

complex	half-wave potentials ($E^{1/2}$) (V vs SCE) Re^{II}/Re^{I}	Os^{III}/Os^{II}	L/L$^-$
fac-$[\mathrm{Re(bpy)(CO)_3(4\text{-}Etpy)}]^+$ [c]	1.75[a,c]		−1.18[b,c]
fac-$[\mathrm{Re(phen)(CO)_3(4,4'\text{-}bpy)}]^+$	1.84[a]		−1.18[b]
fac-$[\mathrm{Re(phen)(CO)_3(bpa)}]^+$	1.78[a]		−1.18[b]
fac-$[\mathrm{Re(phen)(CO)_3}(t\text{-}\mathrm{bpe})]^+$	1.80[a]		−1.14[b]
$[\mathrm{Os(bpy)_3}]^{2+}$ [d]		0.81[d]	−1.21[d]
$[\mathrm{Os(trpy)_3}]^{2+}$ [c]		0.97[c]	−1.25[e]
$[\mathrm{Os(bpy)(trpy)(4,4'\text{-}bpy)}]^{2+}$		0.84	−1.19
$[\mathrm{Os(bpy)(trpy)(bpa)}]^{2+}$		0.80	−1.21
$[\mathrm{Os(bpy)(trpy)}(t\text{-}\mathrm{bpe})]^{2+}$		0.81	−1.21
$[\mathrm{Re(phen)(CO)_3(4,4'\text{-}bpy)Os(trpy)(bpy)}]^{3+}$	1.84	0.84	−1.25[b]
$[\mathrm{Re(phen)(CO)_3(bpa)Os(trpy)(bpy)}]^{3+}$	1.80	0.80	−1.20
$[\mathrm{Re(phen)(CO)_3}(t\text{-}\mathrm{bpe})\mathrm{Os(trpy)(bpy)}]^{3+}$	1.78	0.82	−1.12

[a] Anodic peak potential. [b] Cathodic peak potential. [c] Values taken from ref 28. [d] Values taken from ref 29. [e] Values taken from ref 30.

are appreciably lower than those observed for other carbonyl complexes of transition metals and increase as the π acceptor ability of the ligand L increases. The comparable ν(CO) frequencies of mononuclear Re complexes and corresponding binuclear Re−Os species (Table 1) are indicative of a low electronic coupling between the Re^{I} and Os^{II} metal centers.

Electrochemical Properties. The electrochemical behavior of the mononuclear and binuclear complexes was studied in Ar-saturated acetonitrile solution, and the relevant redox potentials are listed in Table 2. For the mononuclear Re complexes, no corresponding oxidation/reduction peaks were observed at scan rates in the range 50−500 mV/s, indicating coupled chemical reactions; anodic and cathodic peak potentials at a scan rate of 100 mV/s are reported. The Os^{II} complexes presented a couple of peaks characteristic of reversible processes, with separation between the anodic and cathodic peak potentials in the range of 60−65 mV. No appreciable difference was observed between the reduction potentials of Re and Os metal centers in the mononuclear and binuclear metal complexes. In the cathodic region (0 to −2 V vs SCE) several reduction processes involving electron transfer to π^* orbitals of the aromatic ligands were observed for the Os^{II} and Re^{I}−Os^{II} binuclear species. The half-wave potentials of the first one-electron reduction process are reported in Table 2. All assignments are based on comparisons with analogous polypyridine complexes of Re[29] and Os.[30,31]

UV−Vis Spectra. The electronic absorption spectra of the binuclear Re−Os complexes are shown in Figure 1 and compared with the absorption spectra of the mononuclear *fac*-$[\mathrm{(phen)Re^{I}(CO)_3(L)}]^+$ and $[\mathrm{Os^{II}(trpy)(bpy)(L)}]^{2+}$ (L = 4,4′-bpy, bpa, or *t*-bpe) species. Usually the lowest energy absorption band (in the range 350−450 nm) for the Re complexes is assigned to MLCT transitions involving d$_\pi$Re^{I} orbitals and π^* orbitals of the phen ligand,[11,12] although some complexes such as *fac*-$[\mathrm{(phen)Re^{I}(CO)_3}(t\text{-}\mathrm{bpe})]^+$ also present contributions of intraligand (IL) $\pi-\pi^*_{t\text{-bpe}}$ and MLCT $d_\pi\mathrm{Re}-\pi^*_{t\text{-bpe}}$ transitions in this region.[21] These bands are not resolved and appear as shoulders of the more intense ligand-based $\pi-\pi^*$ transitions that dominate the UV region. The Os complexes show intense ^{1}MLCT transitions in the 380−600 nm region and intraligand $\pi-\pi^*$ transitions in the UV region. Owing to the high spin−orbit coupling constant of Os,[23b,32] intense (ϵ = 1600−1800 M^{-1} cm^{-1}) spin-forbidden transitions to the ^{3}MLCT states are observed between 700 and 800 nm. The absorption spectra of the binuclear species are consistent with the superimposition of bands characteristic of the $[\mathrm{(phen)Re^{I}(CO)_3(L)}]^+$ and $[\mathrm{Os^{II}(trpy)(bpy)(L)}]^{2+}$ (L = 4,4′-bpy, *t*-bpe, or bpa) complexes.

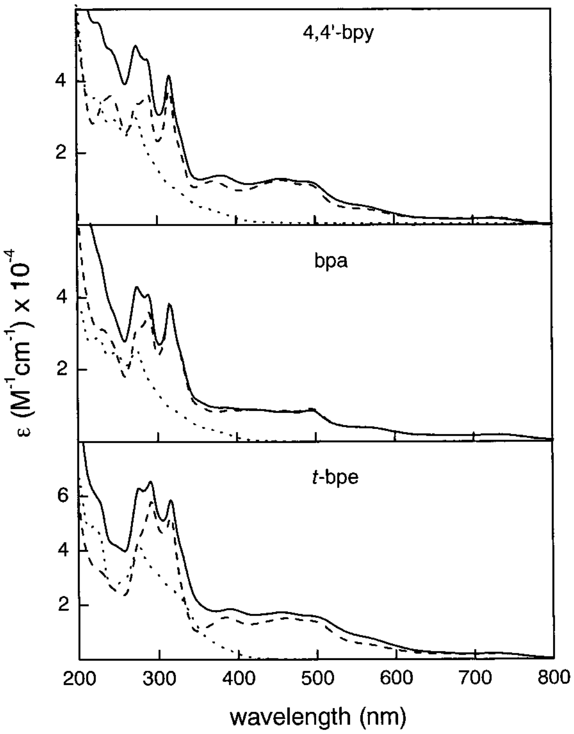

Figure 1. UV−vis absorption spectra of *fac*-$[\mathrm{Re(phen)(CO)_3(L)}]^+$ (dotted lines), $[\mathrm{Os(trpy)(bpy)(L)}]^{2+}$ (dashed lines), and $[\mathrm{Re(phen)(CO)_3(L)Os(trpy)(bpy)}]^{3+}$ (continuous lines) complexes (L = 4,4′-bpy, bpa, or *t*-bpe) in acetonitrile solution.

Photophysical and Photochemical Properties of Mononuclear Complexes. Most of the investigated mononuclear complexes were found to emit in fluid solution at room temperature. The emission maxima, lifetimes, and relative emission quantum yields in acetonitrile solution are reported in Table 3. Excited-state redox potentials are also reported in Table 3. These values were calculated from standard equations $E(\mathrm{S^+/S^*}) = E(\mathrm{S^+/S}) - E^{0-0}$ and $E(\mathrm{{}^*S/S^-}) = E(\mathrm{S/S^-}) + E^{0-0}$, where $E(\mathrm{S^+/S})$ and $E(\mathrm{S/S^-})$ are the redox potentials corresponding to the oxidation of the metal center and first ligand reduction and E^{0-0} represents the zero−zero spectroscopic energy of the excited state. E^{0-0} was estimated from the spectral fitting of the room-temperature emission spectrum of the excited complexes. The fitting procedure, based on a single-mode Franck−Condon analysis of the emission spectra, has been previously described.[23] Given the approximations involved in these calculations, the reported excited-state potentials are meaningful only as comparisons in the series of complexes.

With the exception of *fac*-$[\mathrm{(phen)Re^{I}(CO)_3}(t\text{-}\mathrm{bpe})]^+$, intense emissions and no appreciable photoreaction were observed for solutions of Re complexes in acetonitrile or methanol. As described below, intraligand and/or MLCT excitation of *fac*-$[\mathrm{(phen)Re^{I}(CO)_3}(t\text{-}\mathrm{bpe})]^+$ was observed to give spectral changes consistent with *trans* to *cis* isomerization of the coordinated *t*-bpe ligand.[21]

Steady-state photolysis of *fac*-$[\mathrm{(phen)Re^{I}(CO)_3}(t\text{-}\mathrm{bpe})]^+$ in methanol was performed by excitation at 313, 334, or 365 nm.

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Table 3. Photophysical Properties of Mononuclear and Binuclear Complexes in Acetonitrile Solution at Room Temperature

complex	$\lambda_{\text{max em}}$ (nm)	Φ_{em}	τ_{em} (ns)	E^{0-0} (V)^{a}	$E(S^+/S^*)$ (V)	$E(S^*/S^-)$ (V)
fac-[Re(phen)(CO)$_3$(4,4-bpy)]$^+$	560	0.16	1607	2.69	−0.82	1.51
fac-[Re(phen)(CO)$_3$(bpa)]$^+$	565	0.14	1437	2.67	−0.86	1.49
[Os(bpy)(trpy)(4,4-bpy)]$^{2+}$	793	0.017	52	1.72	−0.88	0.53
[Os(bpy)(trpy)(bpa)]$^{2+}$	803	0.014	47	1.71	−0.87	0.50
[Os(bpy)(trpy)(*t*-bpe)]$^{2+}$	790	0.017	54	1.72	−0.91	0.51
[Re(phen)(CO)$_3$(4,4-bpy)Os(trpy)(bpy]$^{3+}$	792	0.020	58	1.72	−0.88	0.47
[Re(phen)(CO)$_3$(bpa)Os(trpy)(bpy]$^{3+}$	802	0.015	51	1.70	−0.90	0.50
[Re(phen)(CO)$_3$(*t*-bpe)Os(trpy)(bpy]$^{3+}$	800	0.021	51	1.71	−0.89	0.59

[a] Estimated from the spectral fitting of the room-temperature emission spectra,[23] by using one vibrational acceptor mode with a quantum spacing of 1450 cm^{-1}.

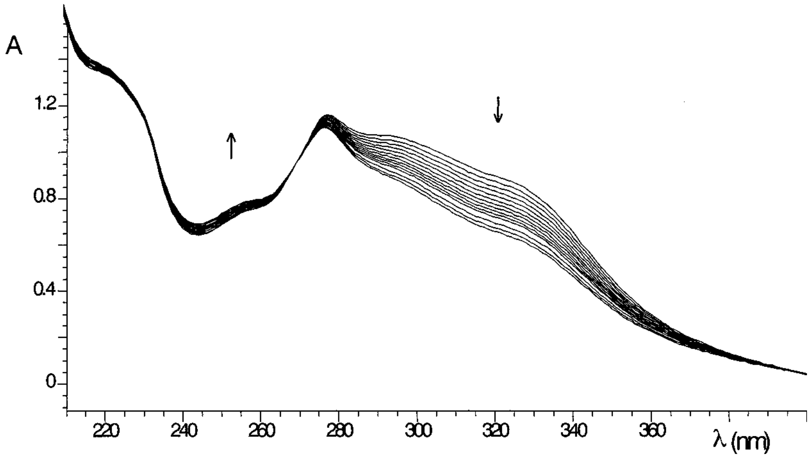

Figure 2. Spectral variations observed following irradiation at 365 nm of *fac*-[Re(phen)(CO)$_3$(*t*-bpe)]$^+$ in methanol solution.

Table 4. Quantum Yields for Isomerization of *t*-bpe by Direct Photolyses at 313,^{a} 334,^{b} or 365^{c} nm

compound	quantum yield	% photolysis^{d}
t-bpe[1]	0.17 ± 0.03^{a}	(5.05, 10.80)^{e}
protonated *t*-bpe[1]	0.19 ± 0.02^{a}	(5.61, 10.89)^{f}
	0.15 ± 0.01^{b}	(3.49, 5.04, 6.89, 8.514)^{g}
fac-[Re(CO)$_3$(phen)(*t*-bpe)]$^+$	0.32 ± 0.02^{a}	(3.41, 6.92, 10.30)^{h}
		(3.61, 7.35, 10.59)^{i}
	0.35 ± 0.03^{b}	(2.63, 5.59, 8.26, 10.76)^{j}
		(2.07, 4.13, 6.11, 8.08)^{k}
	0.25 ± 0.02^{c}	(2.96, 6.25, 9.38)^{l}
		(3.72, 7.12, 9.03)^{m}

[a] Interference filter (313 nm). [b] Interference filter (334 nm). [c] Interference filter (365 nm). [d] All the numbers in the columm "% photolysis" represent individual photolysis experiments using distinct conditions—different photolysis times and concentrations of the complex at each wavelength. [d–l] Concentration of the compounds 0.16, 0.12, 0.26, 0.17, 0.16, 0.19,0.26, 0.35, and 0.33 mmol·L^{-1}, respectively.

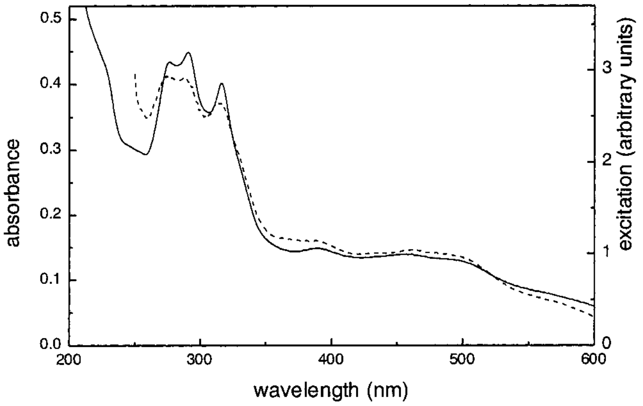

Figure 3. Absorption (continuous line) and excitation (dotted line) spectra of [Re(phen)(CO)$_3$(*t*-bpe)Os(trpy)(bpy)]$^{3+}$ in acetonitrile solution.

The spectral changes observed at the three irradiation wavelengths were similar (Figure 2), with observation of isosbestic points at 200, 270, and 384 nm. Quantum yields for the isomerization of the coordinated ligand at the 313, 334, and 365 excitation wavelengths were determined at different photolysis percentages, and their values are listed in Table 4 for both the free *t*-bpe and the coordinated one. These values are much higher than those obtained for the *trans* to *cis* isomerization in methanol of the uncoordinated *t*-bpe, 0.17 ± 0.03, and of its protonated form, 0.19 ± 0.02, for 313 nm irradiation.[21] The photoproduced *fac*-[(phen)Re^{I}(CO)$_3$(*c*-bpe)]$^+$ showed an intense emission at room temperature in acetonitrile solution.

Photophysical Properties of Binuclear Species. The binuclear [Re(phen)(CO)$_3$(L)Os(trpy)(bpy)](PF$_6$)$_3$ complexes (L = 4,4′-bpy, bpa, or *t*-bpe) were found to be emissive in fluid solution, with emission spectra and emission quantum yields similar to those observed for the model [Os^{II}(trpy)(bpy)(L)]$^{2+}$ complexes (Table 3). Emission decays were observed to be exponential with lifetimes comparable to those of the Os species. As shown in Figure 3 for the binuclear [Re(phen)(CO)$_3$(*t*-bpe)Os(trpy)(bpy)]$^{3+}$ complex, taken as an example, corrected excitation spectra in the 300–600 nm range were found to match closely the corresponding absorption spectra. No photochemical reaction was observed following irradiation of these species in the UV–vis region, which presented no spectral changes under irradiation for hours.

Transient absorbance (TA) difference spectra of the binuclear complex species are shown in Figure 4b. These spectra are analogous to those obtained for the mononuclear Os complexes and present a pronounced bleaching in the 400–700 nm MLCT region. These spectra markedly differ from those obtained for *fac*-[(phen)Re^{I}(CO)$_3$(bpa)]$^+$ and *fac*-[(phen)Re^{I}(CO)$_3$(4,4′-bpy)]$^+$ (Figure 4a) that present a broad absorption in the 400–800 nm region with a maximum at 450 nm. Both transient absorbance

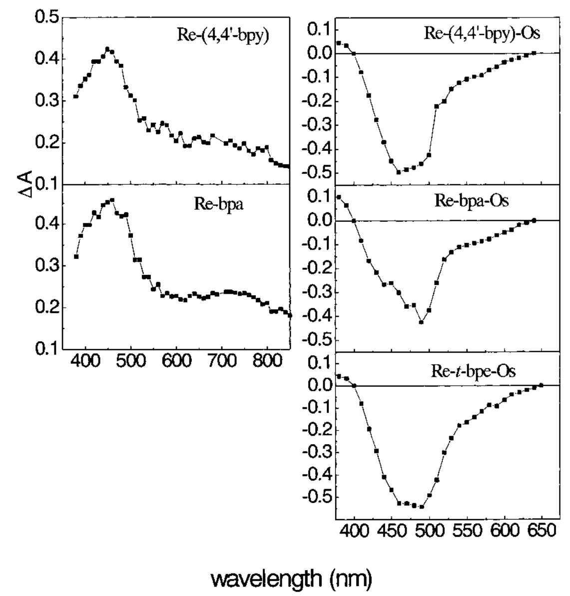

Figure 4. Transient absorbance difference spectra of mononuclear *fac*-$[Re(phen)(CO)_3(L)]^+$ (L = 4,4′-bpy or bpa) and binuclear $[Re(phen)(CO)_3(L)Os(trpy)(bpy)]^{3+}$ (L = 4,4′-bpy, bpa, or *t*-bpe) complexes in acetonitrile solution.

and emission intensity decays were similar within an experimental error of ±5%. For *fac*-$[(phen)Re^I(CO)_3(t\text{-bpe})]^+$ a short-lived transient giving a broad positive absorption in the visible was observed. The transient spectrum was not well resolved due to the lifetime of the transient comparable to the laser pulse width (25 ns).

Oxidative Experiments. One-electron-oxidized forms of the binuclear complexes were observed to decompose in acetonitrile solution. Addition of stoichiometric amounts of $(NH_4)_2Ce(NO_3)_6$ or Br_2 to acetonitrile solutions of the binuclear Re^I-Os^{II} complexes was accompanied by an intensity decrease of the typical Os^{II} MLCT bands and by the appearance of an emission with a maximum and lifetime similar to those exhibited by *fac*-$[(phen)Re^I(CO)_3(bpa)]^+$ or *fac*-$[(phen)Re^I(CO)_3(4,4'bpy)]^+$.

Discussion

The general synthetic methods for generating the mononuclear Re^I and Os^{II} complexes were mainly based on previous studies.[11,12,25,29] The binuclear compounds $[Re(phen)(CO)_3(L)Os(trpy)(bpy)]^{3+}$ (L = bpa, 4,4′-bpy, or *t*-bpe) were prepared by reacting $[Os(trpy)(bpy)(L)]^{2+}$ species with an excess of *fac*-$[(phen)Re^I(CO)_3(TFMS)]^+$ to simplify the product purification from unreacted starting materials. Elemental analyses of the complexes were satisfactory.

The absorption spectra of the binuclear species were consistent with the presence of additive contributions of bands arising from electronic transitions localized on the Re^I and Os^{II} centers, and indicative of a weak coupling character of the bridging ligands.[33] Consistently, ν(CO) bands of *fac*-$[Re(phen)(CO)_3(L)]^+$ were unaffected by coordination of L to the Os^{II} moieties, and oxidative $Re^{I/II}$ and $Os^{II/III}$ waves were observed at potentials comparable to those of the model mononuclear compounds.

The lack of the reductive peak in cyclic voltammograms observed for the Re^I complexes is most probably due to a release of strong ligand field ligands in the nascent Re^{II} species. The mechanisms of these processes were not investigated in detail, as was done for the analogous *fac*-$[Re(CO)_3(bpy)(X)]$ (X = CN^- or Cl^-) species,[34] and will be addressed in a future work. Oxidation of the Os moieties in the binuclear complexes was observed to be reversible on the time scale of cyclic voltammetry (50−500 mV/s), although affected by chemical steps that follow the electron transfer on the time scale of bulk electrolysis or chemical oxidation. The $Os^{III}-L$ bond breaking in $[Re^I(phen)(CO)_3(L)Os^{III}(trpy)(bpy)]^{4+}$ is in accord with the change of the emission spectra that show an increase of the typical $[Re(phen)(CO)_3(L)]^+$ (L = 4,4′-bpy or bpa) emission as a function of time.

Photophysical and Photochemical Properties. The main aim of this work was the investigation of the excited-state behavior of the new binuclear Re−Os complexes, and the study of the mechanism of the excited-state relaxation processes involving upper lying electronic states localized on the Re moieties. The lack of isomerization in the Re−*t*-bpe−Os complex, as well as in similar Re−*t*-bpe−Ru and Ru−*t*-bpe−Os complexes, can be ascribed to the presence of the low-lying MLCT states, which quench the chemical reaction. For the same reason, the analogous mononuclear Ru−bpe complex does not promote the ligand isomerization, showing that the Re compounds are the most appropriate ones to sensitize the ligand isomerization due to the adequate energy of their MLCT states.

The photophysical properties of the model *fac*-$[Re(phen)(CO)_3(L)]^+$ and $[Os(trpy)(bpy)(L)]^{2+}$ (L = bpa, 4,4′-bpy, and *t*-bpe) complexes have also been studied and are listed in Table 3. As for the analogous phen- and bpy-containing rhenium(I) tricarbonyl chloro complexes,[11,12] the *fac*-$[Re(phen)(CO)_3(L)]^+$ species (L = 4,4′-bpy or bpa) presented no photochemical reaction and exhibited long emission lifetimes and high emission quantum yields, consistent with an emitting ^{3}MLCT state. On the contrary, no emission was observed for *fac*-$[Re(phen)(CO)_3(t\text{-bpe})]^+$ in fluid solution. It also presented a fascinating photochemistry, similar to that observed by Wrighton,[35] and recently by Yam,[36] for *trans*-styrylpyridine complexes of the type $[(X)Re(CO)_3(L)_2]$ (X = Cl^- or Br^-; L = *trans*-3-styrylpyridine or *trans*-4-styrylpyridine) and other rhenium complexes with stilbene-like ligands.[17,18] The photoproduct was characterized by ^{1}H NMR as the *cis*-isomer *fac*-$[Re(phen)(CO)_3(c\text{-bpe})]^+$,[21] and its highly emitting property after isomerization also showed a possibility of the use of the photoisomerizable properties of pyridyl−ethenyl-type ligands in the design and development of photochemical molecular devices.

The data reported here show higher quantum yields for the ligand isomerization when *t*-bpe is coordinated to the rhenium complex. Moreover, the coordination allows irradiation at lower energy, such as at 365 nm, where the free ligand has no absorption. The photosensitization results in an efficient *trans* to *cis* isomerization process with a quantum yield as high as 0.25 even for 365 nm excitation. This shows clearly that the metal complex serves as a chromophore and sensitizes the ligand-localized $^3\pi\pi^*$ state responsible for the photoisomerization process[37] and that the optical energy is dissipated into chemical paths by a *trans* → *cis* isomerization.

Recently, the *trans* to *cis* isomerization of bpe in *fac*-$[Re(phen)(CO)_3(c\text{-bpe})]^+$ was investigated by time-resolved absorption and TRIR measurements[37] at room temperature,

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showing that the lowest lying excited state is a bpe-based $^3\pi-\pi_1^*$ for the *trans*-isomer ligand. This state is short-lived due to a rapid crossing to a bpe excited state, which decays to *fac*-$[Re(phen)(CO)_3(c\text{-bpe})]^+$.[37]

Considering the good reducing ability and very high oxidizing power of the electronically excited $[Re(phen)(CO)_3(L)]^+$complexes (Table 3), both oxidative (eq 1) and reductive (eq 3) intramolecular electron transfer can be envisioned as feasible processes leading to the relaxation of the excited $Re^{I*}-Os^{III}$ and $Re^{I*}-Os^{II}$ species:

$$[Re^{II}(phen^{\bullet -})(CO)_3(L)Os^{III}(trpy)(bpy)]^{4+} \rightarrow [Re^{II}(phen)(CO)_3(L)Os^{II}(trpy)(bpy)]^{4+} \quad (1)$$

$$[Re^{II}(phen)(CO)_3(L)Os^{II}(trpy)(bpy)]^{4+} \rightarrow [Re^{I}(phen)(CO)_3(L)Os^{III}(trpy)(bpy)]^{4+} \quad (2)$$

$$[Re^{II}(phen^{\bullet -})(CO)_3(L)Os^{II}(trpy)(bpy)]^{3+} \rightarrow [Re^{I}(phen^{\bullet -})(CO)_3(L)Os^{III}(trpy)(bpy)]^{3+} \quad (3)$$

$$[Re^{I}(phen^{\bullet -})(CO)_3(L)Os^{III}(trpy)(bpy)]^{3+} \rightarrow [Re^{I}(phen)(CO)_3(L)Os^{II}(trpy)(bpy)]^{3+} \quad (4)$$

While dissociation of $[Re^{II}(phen^{\bullet -})(CO)_3(L)Os^{III}(trpy)(bpy)]^{4+}$ prevented verification of the occurrence of process 1, deactivation of $[Re^{II}(phen^{\bullet -})(CO)_3(L)Os^{II}(trpy)(bpy)]^{3+}$ via reductive electron transfer (eq 3) could be ruled out on the basis of the observation of the typical Os* emissions, with excitation spectra matching the absorption spectra of the corresponding binuclear species. This observation points to the occurrence of an efficient intramolecular $Re^{I*} \rightarrow Os^{II}$ energy transfer in the binuclear $[Re^{I}(phen)(CO)_3(L)Os^{II}(trpy)(bpy)]^{3+}$ complexes, independent of the type of bridging ligand. The fact that these bridging ligands may support fast and efficient energy and electron transfer processes in binuclear metal complexes has been previously established.[38−40] In particular, in the binuclear complex $[Ru(bpy)_2(H_2O)(4,4'\text{-bpy})Os(trpy)(bpy)]^{4+}$,[39] MLCT excitation is followed by rapid ($k_{en} > 10^{10}$) and efficient energy transfer to low-lying MLCT states localized on the Os moiety.

The lack of residual Re* emission in laser flash photolysis experiments allows a limit to be placed for the energy transfer rate constant, $k_{en} > 4 \times 10^7\ s^{-1}$. The actual rates, however, are believed to be much higher for the reasons discussed below.

Exchange energy transfer[41,42] from the lowest spin-forbidden excited state is expected to be almost a rule for metal complexes;[43,44] on the other hand, the *Coulombic* or Förster mechanism[45] can be very important in heavy metal systems, where spin−orbit coupling gives some dipole-allowed character to the electronic transitions in the donor. The relationship between the rate constant for Coulombic energy transfer and the spectroscopic and photophysical properties of the two molecular components is given by the classical Förster formula (eq 5).

$$k_{en}^{Coul} = (1.25 \times 10^{17}) \frac{\phi_A}{n^4 \tau_A r_{AB}^{6}} \int_0^\infty F_A(\bar{\nu}) \epsilon_B \frac{d\bar{\nu}}{\bar{\nu}^4} \quad (5)$$

ϕ_A is the quantum yield of donor emission, n is the solvent refractive index, τ_A is the lifetime of the donor emission, r_{AB} is the distance (nm) between the donor and acceptor, F_A is the emission spectrum of the donor (wavenumbers, normalized to unity), and ϵ_B is the decadic molar extinction coefficient of the acceptor.[42] Calculations according to eq 5, by using estimated metal to metal distances of 10.6, 13.4, and 13.45 Å for the 4,4′-bpy, bpa, and *t*-bpe dimers, respectively,[46] give k_{en} values of $1.5 \times 10^9\ s^{-1}$ for the 4,4′-bpy dimer and $4 \times 10^8\ s^{-1}$ for the bpa- and *t*-bpe-containing species. Considering that the calculated k_{en} for the bpe dimer is 1 order of magnitude higher than the crossing rate to a bpe excited state in *fac*-$[Re^{I}(phen)(CO)_3(t\text{-bpe})]^+$,[37] the lack of observation of *trans*−*cis* photochemistry in $[Re^{I}(phen)(CO)_3(t\text{-bpe})Os^{II}(trpy)(bpy)]^{3+}$ can be rationalized in terms of a favorable competition of Förster energy transfer over nonradiative crossing to a twisted intraligand state. Although these arguments are speculative in the absence of an experimental evaluation of k_{en}, it can be noted that the occurrence of a Coloumbic energy transfer in these species is further supported by the calculated values of the critical separation distance, R_0,[45,47] which represents the donor−acceptor separation for which k_{en} and the deactivation rate of the donor are equal. For the 4,4′-bpy and bpa dimers, the R_0 values are higher than the metal−metal distances (R_0 = 27 and 38 Å, respectively), indicating that $Re^{I*} \rightarrow Os^{II}$ Förster energy transfer dominates Re^{I*} deactivation processes.

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$$R_0^{6} = \frac{9000(\ln 10)\phi_A}{128\pi^6\eta^4 N} \int_0^\infty F_A(\bar{\nu})\epsilon_B \frac{d\bar{\nu}}{\bar{\nu}^4}$$

where N is the Avogadro number, η is the refractive index of the solvent, and the other parameters are defined in eq 5 (see the Discussion).