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Intramolecular Redox Processes Induced in Biquinoline-Centered and Metal to Ligand Charge Transfer Excited States of Ru(II)-(4,4′-bipyridine)-Re(I)- and Ru(II)-(pyrazine)-Re(I)-Containing Dyads

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The photochemical and photophysical properties of the $(CO)_3(biq)Re^I(4,4'\text{-bipy})Ru^{II}(biq)(CO)_2Cl^{2+}$ and $(CO)_3(biq)Re^I(pz)Ru^{II}(biq)(CO)_2Cl^{2+}$ dyads and the monometallic compounds $Re^I(biq)(CO)_3(4,4'\text{-bipy})^+$, $Re^I(biq)(CO)_3(pz)^+$, and $Ru^{II}(biq)(CO)_2Cl_2$ have been investigated. Deaerated solutions of these compounds were irradiated at wavelengths between ∼350 and 532 nm. Intraligand, biq-centered, excited states decay by populating Re(I) to biq charge transfer excited states. In the dyads, the Re(I) to biq charge transfer excited states decay by radiative/radiationless relaxation pathways and by forming reaction intermediates. Oxidants and reductants reacted with these intermediates. The Ru(II) to biq charge transfer excited state, $^3MLCT_{Ru(II)\rightarrow biq}$, could not be observed in a time domain $t \geq 5$ ns, and the transfer of energy from the $^3MLCT_{Re(I)\rightarrow biq}$ to the Ru(II) moiety is an inefficient process.

Introduction

Bichromophoric inorganic molecules, dyads, have been the motive of considerable attention because of the diversity of their thermal and photochemical reactions. Some studies have shown that the dyads may have diverse applications.[1−9] In one of these uses, dyads containing Ru(II) polypyridyl moieties have been anchored to a variety of wide band-gap semiconductors where they work as photosensitizers for light-to-electronic energy conversions.[1−3] Another reason for the interest in these materials is that new synthetic routes could be found in the photochemistry of symmetric Re(I)−Re(I) dyads. Excitation of $(CO)_3(2,2'\text{-bipy})Re^I(\mu\text{-dppene})Re^I(CO)_3(2,2'\text{-bipy})^{2+}$ (μ-dppene = (*E*)-1,2-bis(diphenylphosphino)ethylene) to the Re to 2,2′-bipy MLCT excited state induces stereospecific unsymmetrical substitutions, i.e., to give products $(CO)_3(2,2'\text{-bipy})Re^I(\mu\text{-dppene})Re^I(CO)_2(2,2'\text{-bipy})S^{(2-n)+}$, where S stands for an anionic, S^{n-}, or neutral ligand.[8] The transition metal dyads have also commanded considerable attention because of their intramolecular electron transfer reactions. For example, the Ru(II)−Ru(II) dyads, $[(dpte)_2Ru^{II}(bpe)Ru^{II}Cl(2,2'\text{-bipy})_2]^{3+}$ (bpe = *trans*-1,2-bis(4-pyridyl)ethylene) appear to have a photophysics that includes intramolecular electron transfer processes.[10] While the absorption of light and subsequent processes form the Ru to 2,2′-bipy charge transfer excited state, $^3MLCT_{Ru\rightarrow bipy}$, intramolecular electron transfers give $[(dpte)_2Ru^{III}(bpe)Ru^{II}Cl(2,2'\text{-bipy}^{\bullet-})(2,2'\text{-bipy})]^{3+}$ or a bridge-localized, ππ*, excited state, $[(dpte)_2Ru^{II}(^*bpe)Ru^{II}Cl(bipy)_2]^{3+}$. When the bridge has the appropriate redox potential as in the dyads $[(NH_3)_5Ru^{II}(L)Ru^{II}Cl(2,2'\text{-bipy})_2]^{3+}$, where L = 4,4′-bipy or bpe, the ^3MLCT is rapidly deactivated via an intramolecular electron transfer, i.e., to $[(NH_3)_5Ru^{III}(L^{\bullet-})Ru^{II}Cl(2,2'\text{-bipy})_2]^{3+}$, or via energy transfer, i.e., to give a $\pi(L)-d\pi^*(-Ru^{II}(NH_3)_5)$ excited state. By contrast to the Ru(II)−Ru(II) dyads, a different mechanism appears to operate in Re(I)−Os(II) compounds of the type $(CO)_3(1,10\text{-phen})Re^I(L)Os^{II}(trpy)(2,2'\text{-bipy})^{2+}$ (L = 4,4′-bipy, t-bpe, bpa). It has been proposed that in the latter dyads the $^3MLCT_{Re\rightarrow 2,2'-bipy}$ transfers energy to a $MLCT_{Os\rightarrow L}$ of the Os moiety by a Förster mechanism.[11] The spin−orbit coupling in these dyads must be sufficiently intense and it must lift the main restriction of the mechanism, i.e., that the electronic transition must be an allowed one.[12,13]

The spectral overlap, i.e., between the emission spectrum of the donor and the absorption spectrum of

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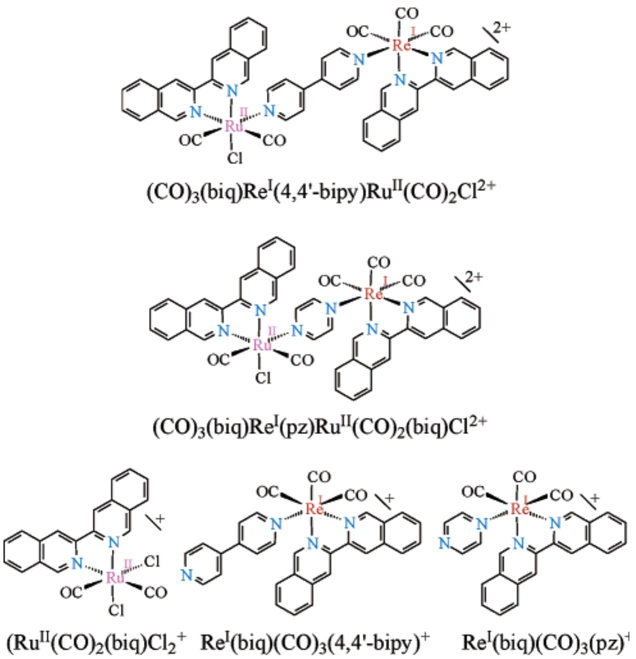
Scheme 1



the acceptor, has been considered insignificant in $(CO)_3$-$(py)Re^I$(Mebpy-Mebpy)$Ru^{II}(2,2'\text{-bipy})_2{}^{3+}$ (Mebpy-Mebpy = 1,2-bis(4′-methyl-2,2′-bipyridyl-4-yl)ethane).[14] On this basis, the "trivial" radiative transfer mechanism has been ruled out. A Förster's dipole−dipole energy transfer mechanism and Dexter's exchange mechanism have been considered possible mechanisms for the deactivation of the Re to 2,2′-bipy MLCT excited state.

The photophysical properties outlined above show that the dyads degrade the electronic excited state energy by a variety of mechanisms. To have a nonemissive acceptor in the dyad, e.g., a Ru(II) moiety, can be a convenient way to probe some of these mechanisms. For example, it may be possible to observe the charge localization in the acceptor and/or the dyad's bridge. Therefore, we have examined the photophysical properties of two dyads containing Re(I) and Ru(II) moieties and related monometallic complexes, Scheme 1.

Experimental Section

Flash-Photochemical Procedures. Optical density changes occurring on a time scale longer than 10 ns were investigated with a flash photolysis apparatus, FP, described elsewhere.[15,16] In these experiments, 10 ns (measured at half-width) flashes of 351 nm light were generated with a Lambda Physik SLL-200 excimer laser or 1 ns (measured at half-width) flashes of 355 or 532 nm light were generated with a Continuum Powerlite Nd:YAG laser.[15,16] Flash irradiations at 351 or 355 nm are jointly described by −350 nm in the text. A right angle configuration was used for the excitation and probe beams. Concentrations of the photolytes were adjusted to provide homogeneous concentrations of transient species within the volume of irradiated solution, i.e., optical densities less than or equal to 0.1 at λ_{exc} nm over the cross section of the probe beam. The energy of the laser flash was attenuated to values equal to or less than 20 mJ/pulse by absorbing some of the laser light in solutions of $Ni(ClO_4)_2$ with appropriate optical densities. Time-resolved fluorescence experiments, FF, were carried out with a PTI flash fluorescence instrument. The excitation light was provided by a N_2 laser (λ_{em} = 337 nm, ca. 2 mJ/pulse) or by irradiation at 337 nm of suitable Exciton dyes (λ_{exc} = 350 or 457 nm with a 0.2 ns pulse width and ca. 0.2 mJ/pulse). Solutions for the photochemical and photophysical work were deaerated with streams of ultrahigh-purity N_2 before the irradiations. Relative luminescence quantum yields were determined by following procedures described elsewhere.[17]

Steady State Irradiations. The luminescence of the Re(I) complexes was investigated in an SLM-Aminco-8100 interfaced to a Dell 333P microcomputer.[17] The spectra were corrected for differences in instrumental response and light scattering. Solutions were deaerated with streams of ultrahigh-purity N_2 before and during the irradiations.

Pulse Radiolysis. Pulse radiolysis experiments were carried out with a model TB-8/16-1S electron linear accelerator. The instrument and computerized data collection for time-resolved UV−vis spectroscopy and reaction kinetics have been described elsewhere in the literature.[28−30] Thiocyanate dosimetry was carried out at the beginning of each experimental session. The details of the dosimetry have been reported elsewhere.[18−20] The procedure is based on the concentration of $(SCN)_2{}^{\bullet-}$ radicals generated by the electron pulse in a N_2O-saturated 10^{-2} M SCN^- solution. In the procedure, the calculations were made with $G = 6.13$ and a extinction coefficient, $\epsilon = 7.58 \times 10^3$ M^{-1} cm^{-1} at 472 nm, for the $(SCN)_2{}^{\bullet-}$ radicals.[18−20] In general, the experiments were carried out with doses that in N_2-saturated aqueous solutions resulted in $(2.0 \pm 0.1) \times 10^{-6}$ to $(6 \pm 0.3) \times 10^{-6}$ M concentrations of e^-_{aq}. In these experiments, solutions were deaerated with streams of the O_2-free gas N_2 or N_2O. To irradiate a fresh sample with each pulse, an appropriate flow of the solution through the reaction cell was maintained during the experiment. Radiolyses with ionizing radiation of CH_3OH and CH_3OH/H_2O mixtures have been reported elsewhere in the literature.[21−23] These studies have shown that pulse radiolysis can be used as a convenient source of $e_{sol}{}^-$ and $CH_2OH^\bullet$ radicals.

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(30) The lifetimes of the $^3MLCT_{Re\rightarrow biq}$ excited states in the $(CO)_3(biq)Re^I(4,4'\text{-bipy})Ru^{II}(biq)(CO)_2Cl^{2+}$ and $(CO)_3(biq)Re^I(pz)Ru^{II}(biq)(CO)_2Cl^{2+}$ dyads are marginally smaller, $\tau \approx 50$ ns, than the lifetime of the $Re^I(biq)(CO)_3(4,4'\text{-bipy})^+$ excited state, $\tau \approx 60$ ns. If one ignores a possible increase in the rate of the $^3MLCT_{Re\rightarrow biq}$ excited state radiationless relaxation in the dyads, an upper limit for the combined efficiencies of the formation of the long-lived intermediates and energy transfer to the Ru(II) moiety is $\zeta = 0.15$.

Table 1. Selected Half-Wave Potentials for the Reduction of Re and Ru Compounds and Their Ligands

	$\mathrm{biq}^{0/-1}$	$\mathrm{B}^{0/-1}$	$\mathrm{Re}^{\mathrm{II/I}}$	$\mathrm{Ru}^{\mathrm{III/II}}$
$(\mathrm{CO})_3(\mathrm{biq})\mathrm{Re}^{\mathrm{I}}(4,4'\text{-bipy})\mathrm{Ru}^{\mathrm{II}}(\mathrm{biq})(\mathrm{CO})_2\mathrm{Cl}^{2+}$ [20,21]	−0.65		1.50	1.22
$\mathrm{Re}^{\mathrm{I}}(\mathrm{biq})(\mathrm{CO})_3(4,4'\text{-bipy})^{+}$ [20, 21]	−0.73		1.49[b]	
$\mathrm{Ru}^{\mathrm{II}}(\mathrm{biq})(\mathrm{CO})_2\mathrm{Cl}_2$	−0.94			1.14
$(\mathrm{CO})_3(\mathrm{biq})\mathrm{Re}^{\mathrm{I}}(\mathrm{pz})\mathrm{Ru}^{\mathrm{II}}(\mathrm{biq})\ (\mathrm{CO})_2\mathrm{Cl}^{2+}$	−0.70		1.46	1.18
$\mathrm{Re}^{\mathrm{I}}(\mathrm{biq})(\mathrm{CO})_3(\mathrm{pz})^{+}$ [20,21]	−0.73		1.46	
$2,2'\text{-bipyH}_2{}^{2+}$ [c]	−0.74 [30]			
pz		$-0.25 \leq E° \leq -0.885$[a,e][22]		
$4,4'\text{-bipyH}_2{}^{2+}$ [a,c]		−0.73[22]		

[a] Half-wave potentials relative to the SCE recorded with a scan rate of 2000 or 250 mv/s. The potentials did not change with different scan rates. B = 4,4′-bipy or pz. [b] Peak potentials without counterwave. [c] Diprotonated cation. The reduction of the monoprotonated cation is estimated to be displaced between −0.5 and −1.0 V from the diprotonated cation. [e] Potentials reported in aqueous solutions for various acid concentrations, 0 ≤ pH ≤ 6.8.

Since e_{sol}^- and $\mathrm{CH_2OH}^{\bullet}$ have large reduction potentials, i.e., −2.8 V vs NHE for e^-_{sol} and −0.92 V vs NHE for $\mathrm{CH_2OH}^{\bullet}$, they have been used for the reduction of coordination complexes and for the study of electron transfer reactions. The yield of e_{sol}^- in $\mathrm{CH_3OH}$ ($G \approx 1.1$) is about a third of the G-value in the radiolysis of $\mathrm{H_2O}$ ($G \approx 2.8$).[21] In solutions where e_{sol}^- was scavenged with $\mathrm{N_2O}$,[23] the $\mathrm{CH_2OH}^{\bullet}$ radical appears to be the predominant product (yield > 90%) of the reaction between $\mathrm{CH_3OH}$ and $\mathrm{O}^{\bullet -}$.

Electrochemical Procedures. Electrochemical measurements were carried out with a PAR 173 potentiostat coupled to a PAR 175 universal programmer. Deaerated solutions, 10^{-4} M complex and 10^{-2} M tetraethylammonium perchlorate in a given solvent, were placed in a three-electrode cell with a glassy carbon working electrode, a Pt wire counter electrode, and a saturated calomel reference electrode. Solvents and supporting electrolytes for the electrochemical measurements were dried according to literature procedures.[24–26] The half-wave potentials were calculated according to the relationship $\epsilon_{1/2} = (E_p{}^+ + E_p{}^-)/2$, where $E_p{}^+$ and $E_p{}^-$ are the respective peak potentials of the cathodic and anodic waves. Solutions for the electrochemical work were deaerated with streams of ultra-high-purity $\mathrm{N_2}$.

Materials. The complexes $[(\mathrm{CO})_3(\mathrm{biq})\mathrm{Re}^{\mathrm{I}}(4,4'\text{-bipy})\mathrm{Ru}^{\mathrm{II}}(\mathrm{biq})(\mathrm{CO})_2\mathrm{Cl}](\mathrm{OTF})_2$,[27] $[\mathrm{Re}^{\mathrm{I}}(\mathrm{biq})(\mathrm{CO})_3(4,4'\text{-bipy})]\mathrm{OTF}$,[27] $\mathrm{Ru}^{\mathrm{II}}(\mathrm{biq})(\mathrm{CO})_2\mathrm{Cl}_2$,[27] $[\mathrm{Re}^{\mathrm{I}}(\mathrm{biq})(\mathrm{CO})_3(\mathrm{pz})]\mathrm{OTF}$,[28] and $[\mathrm{Co}^{\mathrm{III}}(\mathrm{Me}_6\text{-}[14]\mathrm{dieneN}_4)\mathrm{Cl}_2]\mathrm{ClO}_4$ shown in Scheme 1 were available from a previous work and used without further purification.

$[(\mathrm{CO})_3(\mathrm{biq})\mathrm{Re}^{\mathrm{I}}(\mathrm{pz})\mathrm{Ru}^{\mathrm{II}}(\mathrm{biq})(\mathrm{CO})_2\mathrm{Cl}](\mathrm{OTF})_2$ was obtained by a modification of procedures communicated elsewhere for the preparation of the 4,4′-bipy-containing species. In these procedures the amount of 4,4′-bipy and $[\mathrm{Re}^{\mathrm{I}}(\mathrm{biq})(\mathrm{CO})_3(4,4'\text{-bipy})]\mathrm{OTF}$ were respectively substituted by the equivalent amounts of pz and $[\mathrm{Re}^{\mathrm{I}}(\mathrm{biq})(\mathrm{CO})_3(\mathrm{pz})]\mathrm{OTF}$. The preparation and purification of the compounds were conducted otherwise as previously described. Tables 1 and 2 in the Supporting Information list the frequencies from the IR and NMR spectra of the complexes with 4,4′-bipy or pz ligands. Elemental analysis of $[(\mathrm{CO})_3(\mathrm{biq})\mathrm{Re}^{\mathrm{I}}(\mathrm{pz})\mathrm{Ru}^{\mathrm{II}}(\mathrm{biq})(\mathrm{CO})_2\mathrm{Cl}](\mathrm{OTF})_2$ yield: Anal. Calcd for $\mathrm{ReC_{18}H_{11}N_4O_5}$: H, 2.10; C, 40.00; N, 6.20. Found: H, 2.14; C, 40.12; N, 6.00.

Solvents, $\mathrm{CH_3CN}$, $\mathrm{CH_2Cl_2}$, or MeOH, were spectroquality grade and used without further purification.

Results

The compound $[(\mathrm{CO})_3(\mathrm{biq})\mathrm{Re}^{\mathrm{I}}(\mathrm{pz})\mathrm{Ru}^{\mathrm{II}}(\mathrm{biq})(\mathrm{CO})_2\mathrm{Cl}](\mathrm{OTF})_2$ used for our photochemical and electrochemical experiments was characterized by comparing its spectroscopic properties with those of closely related compounds. The IR and NMR spectra of $[\mathrm{Re}^{\mathrm{I}}(\mathrm{biq})(\mathrm{CO})_3(\mathrm{pz})]\mathrm{OTF}$ and $[(\mathrm{CO})_3(\mathrm{biq})\mathrm{Re}^{\mathrm{I}}(\mathrm{pz})\mathrm{Ru}^{\mathrm{II}}(\mathrm{biq})(\mathrm{CO})_2\mathrm{Cl}](\mathrm{OTF})_2$ in Tables 1 and 2 in the Supporting Information showed that they are structurally related to previously prepared Re(I) compounds containing 4,4′-bipy instead of pz.[27, 28]

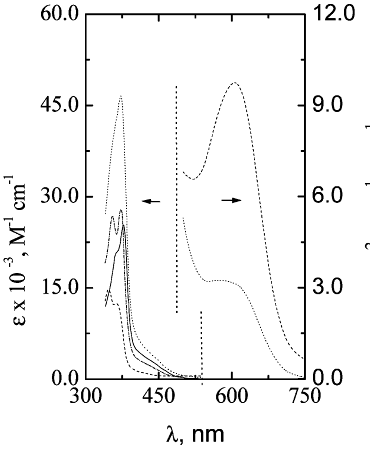

Figure 1. Absorption spectra of $\mathrm{Re}^{\mathrm{I}}(\mathrm{biq})(\mathrm{CO})_3(4,4'\text{-bipy})^+$ (—), $\mathrm{Ru}^{\mathrm{II}}(\mathrm{biq})(\mathrm{CO})_2\mathrm{Cl}_2$ (- - -), and $(\mathrm{CO})_3(\mathrm{biq})\mathrm{Re}^{\mathrm{I}}\mathrm{L}\mathrm{Ru}^{\mathrm{II}}(\mathrm{biq})(\mathrm{CO})_2\mathrm{Cl}^{2+}$, L = 4,4′-bipy (···), pz (·-·), in $(\mathrm{CH_3})_2\mathrm{CO}$.

Electrochemical Properties. The cyclic voltammograms of the complexes were recorded in $\mathrm{N_2}$-deaerated $\mathrm{CH_3CN}$ by procedures communicated in literature reports.[28] Results of the electrochemical experiments are presented in Table 1 together with those of the monometallic complexes and ligands. Since the $\epsilon_{1/2}$ for the metal-centered couples in the dyads were close to those calculated from the cyclic voltammograms of the monometallic moieties, it was possible to make reliable assignments of the electrochemical processes, Table 1. Ligand-centered processes in the dyads were also in accordance with values reported for the same ligands in monometallic Re(I) complexes.

UV−Vis Absorption Spectroscopy. Some spectral features in the spectra of the $\mathrm{Re}^{\mathrm{I}}(\mathrm{biq})(\mathrm{CO})_3(4,4'\text{-bipy})^+$ and $\mathrm{Ru}^{\mathrm{II}}(\mathrm{biq})(\mathrm{CO})_2\mathrm{Cl}_2$ monometallic complexes were also found in the spectrum of the binuclear species, Figure 1. A comparison of the position of the absorption bands in the spectra of the dyads and monometallic complexes aided in the assignment of the optical transitions, Table 3, Supporting Information. Absorption bands centered at $\lambda_{\max} \approx 570 \pm 30$ nm in the spectra of the mono- and bimetallic $\mathrm{Ru}^{\mathrm{II}}$ complexes were associated with the Ru(II) to biq charge transfer transitions. A shoulder, $\lambda_{\mathrm{sh}} \approx 400$ nm, in the spectrum of the Re(I)-biq complexes has been previously assigned to a Re(I) to 2,2′-biq charge transfer transition. It is also a feature in the spectrum of the dyads. The 2,2′-biq ligand-centered electronic transitions give rise to absorption bands with $\lambda_{\max} < 400$ nm in the spectrum of the free ligand. Therefore, two maxima near 370 nm in the spectra of $\mathrm{Re}^{\mathrm{I}}(\mathrm{biq})(\mathrm{CO})_3(4,4'\text{-bipy})^+$ and $(\mathrm{CO})_3(\mathrm{biq})\mathrm{Re}^{\mathrm{I}}(4,4'\text{-bipy})\mathrm{Ru}^{\mathrm{II}}(\mathrm{biq})(\mathrm{CO})_2$-

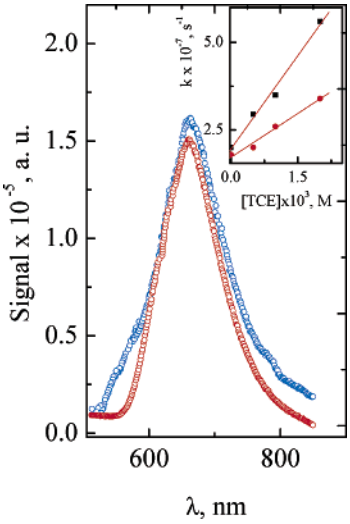

Figure 2. Emission spectra of 1.3×10^{-5} M $Re^{I}(biq)(CO)_3(4,4'\text{-}bipy)^{+}$ (○) and 8.0×10^{-6} M $(CO)_3(biq)Re^{I}(4,4'\text{-}bipy)Ru^{II}(biq)(CO)_2Cl^{2+}$ (△) in deaerated CH_3CN. Both solutions were irradiated at ~350 nm. The dependence on TCE concentration of the rate constant for the decay of the $(CO)_3(biq)Re^{I}LRu^{II}(biq)(CO)_2Cl^{2+}$ (■) and $Re^{I}(biq)(CO)_3(4,4'\text{-}bipy)^{+}$ (●) luminescence is shown in the inset. Solutions of the compounds in CH_3CN were irradiated at 450 nm.

Cl^{2+} were assigned to an intraligand transition, IL, in the biq ligand. A shoulder, $\lambda_{sh} \approx 358$ nm, in the spectrum of pz-containing complexes is absent in the spectrum of complexes free of this ligand. It was assigned to a pz-centered optical transition.

Luminescence of the Mono- and Bimetallic Complexes. Deaerated 8.0×10^{-6} or 4.0×10^{-6} M solutions of $(CO)_3(biq)Re^{I}(pz)Ru^{II}(biq)(CO)_2Cl^{2+}$ or $(CO)_3(biq)Re^{I}(4,4'\text{-}bipy)Ru^{II}(biq)(CO)_2Cl^{2+}$ in CH_3CN were steady state irradiated at ~350 nm, i.e., within the absorption band of the biq-centered π to π^{*} electronic transition. The solutions luminesced with $\lambda_{max} = 660$ nm, Figure 2. A similar luminescence spectrum, Figure 2, was recorded when deaerated 1.1×10^{-5} M $Re^{I}(biq)(CO)_3(4,4'\text{-}bipy)^{+}$ in CH_3CN was irradiated at ~350 nm, i.e., within the biq-centered optical transition of the monometallic Re(I) complex. A comparison of the luminescence spectrum of $(CO)_3(biq)Re^{I}(4,4'\text{-}bipy)Ru^{II}(biq)(CO)_2Cl^{2+}$ and $Re^{I}(biq)(CO)_3(4,4'\text{-}bipy)^{+}$ in Figure 2 shows that they exhibit similar features. However, the luminescence of $(CO)_3(biq)Re^{I}(4,4'\text{-}bipy)Ru^{II}(biq)(CO)_2Cl^{2+}$ was characterized by a slightly smaller emission quantum yield than the monometallic Re(I) complex, i.e., $\phi_{ems}((CO)_3(biq)Re^{I}(4,4'\text{-}bipy)Ru^{II}(biq)(CO)_2Cl^{2+}) \approx 0.87\phi_{ems}(Re^{I}(biq)(CO)_3(4,4'\text{-}bipy)^{+}) \approx 2 \times 10^{-2}$.

In flash fluorescence experiments, solutions containing 7.3×10^{-5} M $(CO)_3(biq)Re^{I}(4,4'\text{-}bipy)Ru^{II}(biq)(CO)_2Cl^{2+}$ or $(CO)_3(biq)Re^{I}(pz)Ru^{II}(biq)(CO)_2Cl^{2+}$ in CH_3CN were irradiated at wavelengths of the biq-centered transition, $\lambda_{exc} \approx 350$ nm, and within the absorption band of the Re(I) to 2,2′-biq charge transfer transition, $\lambda_{exc} = 457$ nm. In either of the excitation wavelengths, the luminescence of the dyads was monitored at 640 nm. The luminescence was fitted to a single-exponential, $\exp(-t/\tau)$, with lifetimes $\tau = 50 \pm 6$ ns for $(CO)_3(biq)Re^{I}(4,4'\text{-}bipy)Ru^{II}(biq)(CO)_2Cl^{2+}$ and $\tau = 46 \pm 5$ ns for $(CO)_3(biq)Re^{I}(pz)Ru^{II}(biq)(CO)_2Cl^{2+}$. On the basis of these experimental observations, it is possible to assign the luminescence of the dyads to the radiative decay of the $^{3}MLCT_{Re(I)\rightarrow biq}$ when these compounds are irradiated at wavelengths of the IL or MLCT absorption bands.[17,28]

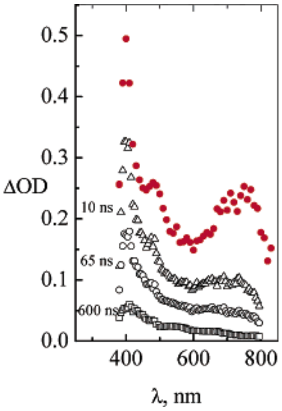

Figure 3. Transient spectra generated when 1.0×10^{-5} M $(CO)_3(biq)Re^{I}(4,4'\text{-}bipy)Ru^{II}(biq)(CO)_2Cl^{2+}$ solution in deaerated CH_3CN was irradiated at ~350 nm (black symbols). The delays, starting from the top spectrum, are 10, 65, and 600 ns after the flash. The spectrum of the $^{3}MLCT_{Re\rightarrow biq}$ (○) generated when 1.0×10^{-5} M $Re^{I}(biq)(CO)_3(4,4'\text{-}bipy)^{+}$ in deaerated CH_3CN was irradiated at ~350 nm (this work and ref 21) was added for comparison purposes.

Steady state irradiations of 4.0×10^{-4} M $(CO)_3(biq)Re^{I}(4,4'\text{-}bipy)Ru^{II}(biq)(CO)_2Cl^{2+}$ or 2.0×10^{-4} M $Ru^{II}(biq)(CO)_2Cl_2$ in CH_3CN at the longer wavelengths of the electronic Ru to biq charge transfer transition, i.e., $\lambda_{exc} \geq 550$ nm, led to no detectable luminescence.

Quenching of the Luminescence. The decay of the luminescence induced with 457 nm flash irradiations of $(CO)_3(biq)Re^{I}(4,4'\text{-}bipy)Ru^{II}(biq)(CO)_2Cl^{2+}$ in CH_3CN solutions containing also tetracyanoethylene, TCE, was fitted to a single exponential. The lifetimes of the luminescence decreased with the concentrations of TCE, 1×10^{-5} M $\leq$ [TCE] $\leq 2.0 \times 10^{-3}$ M. A straight line was fitted to a plot of the rate constant vs the TCE concentration, k_{obs} vs [TCE], and the rate constants, $k_0 = 2\ 10^{7}$ s^{-1}, for the decay of the excited state in the absence of quencher and $k_q = 7.5\ 10^{9}$ M^{-1} s^{-1}, for the reaction between quencher and excited state, were respectively derived from the intercept and the slope of the line, Figure 2. In similar experiments with $Re^{I}(biq)(CO)_3(4,4'\text{-}bipy)^{+}$, the calculated rate constants were $k_0 = 1.8 \times 10^{7}$ s^{-1} from the intercept and $k_q = 6.0 \times 10^{9}$ M^{-1} s^{-1} from the slope of the plot of k_{obs} vs [TCE], Figure 2.

The values of k_q/k_0, 3.8×10^{2} and 3.3×10^{2} s^{-1}, obtained respectively from the flash fluorescence experiments with $(CO)_3(biq)Re^{I}(4,4'\text{-}bipy)Ru^{II}(biq)(CO)_2Cl^{2+}$ and $Re^{I}(biq)(CO)_3(4,4'\text{-}bipy)^{+}$ were in good agreement with the Stern−Volmer constants derived from the quenching of the luminescence with TCE in steady state irradiations. When the irradiation of the complexes, 4.0×10^{-4} M $(CO)_3(biq)Re^{I}(4,4'\text{-}bipy)Ru^{II}(biq)Cl^{2+}$ and the monometallic $Re^{I}(biq)(CO)_3(4,4'\text{-}bipy)^{+}$ in CH_3CN, was performed at ~350 nm, TCE quenched their luminescence and the corresponding Stern−Volmer plots, i.e., $I_{em}{}^{0}/I_{em}$ vs TCE concentration, were linear. The constants $K_{SV} = (3.6 \pm 0.4) \times 10^{2}$ M^{-1} and $K_{SV} = (3.0 \pm 0.1) \times 10^{2}$ M^{-1} were calculated from the Stern−Volmer plots respectively obtained from the quenching of the

Table 2. Lifetimes of the Luminescence and Quenching of the Luminescence by TCE

	λ_{exc},[a] nm	λ_{ob},[a] nm	τ_{em}, ns	$k_q \times 10^{-9}$,[b] $M^{-1}\ s^{-1}$	$K_{SV} \times 10^{-2}$,[c] M^{-1}
$Re^I(biq)(CO)_3(4,4'\text{-}bipy)^+$	~350	630	58 ± 3[d]	6	3.0 ± 0.1
$Re^I(biq)(CO)_3(pz)^+$	~350	610	11 ± 4[d]		
$(CO)_3(biq)Re^I(4,4'\text{-}bipy)Ru^{II}$	457	630	55 ± 5	7.5	3.6 ± 0.4
$(biq)(CO)_2Cl^{2+}$	~350	630	52 ± 5		
$(CO)_3(biq)Re^I(4,4'\text{-}bipy)Ru^{II}$	~350	650	46 ± 5	7.2	3.3 ± 0.6
$(biq)(CO)_2Cl^{2+}$					

[a] The luminescence was followed at λ_{ob} when solutions of the complexes in deaerated CH_3CN were irradiated at λ_{ob}. [b] Rate constant for the quenching of the luminescence by TCE. [c] Stern–Volmer constant for the quenching of the luminescence by TCE. [d] This work and ref 21.

$(CO)_3(biq)Re^I(4,4'\text{-}bipy)Ru^{II}(biq)(CO)_2Cl^{2+}$ and $Re^I(biq)(CO)_3(4,4'\text{-}bipy)^+$ luminescence.

Time-Resolved Absorption Spectroscopy. Flash irradiation, $\lambda_{exc} \approx 350$ nm, of 1.0×10^{-5} M $(CO)_3(biq)Re^I(4,4'\text{-}bipy)Ru^{II}(biq)(CO)_2Cl^{2+}$ in CH_3CN produced a transient spectra between 400 and 600 nm, Figure 3. Spectra recorded with 10 or 20 ns delay after the laser irradiation were different from those of spectra recorded with 10^2 ns or longer delays. The spectral changes were in accordance with the presence of two different transients, and the decay of the optical density between 380 and 800 nm could not be fitted to a single exponential. Oscillographic traces were fitted with acceptable deviations to a double exponential, $\Delta OD(\lambda_{ob}) = \Delta OD(\lambda_{ob})_0' e^{-t/\tau'} + \Delta OD(\lambda_{ob})_0'' e^{-t/\tau''}$. The lifetimes $\tau' = 46 \pm 3$ ns and $\tau'' = 1.25 \pm 0.06\ \mu s$ were independent of λ_{ob}, and τ' approached the lifetime of the luminescence, Table 2. The shortest-lived transient spectrum can be associated with the spectrum of the $^3MLCT_{Re(I)\rightarrow biq}$ excited state, and the long-lived transient will be identified by I hereafter, eqs 1 and 2.

$$(CO)_3(biq)Re^I(4,4'\text{-}bipy)Ru^{II}(biq)(CO)_2Cl^{2+} \underset{-h\nu'}{\overset{h\nu}{\rightleftharpoons}} {}^3MLCT \quad \tau' = 46 \text{ ns} \quad (1)$$

$$\underset{\tau'' = 1.25\ \mu s}{^3MLCT \quad \rightarrow I \rightarrow ...} \quad (2)$$

The assignment is in agreement with a previous literature report where the flash irradiation of $Re^I(biq)(CO)_3(4,4'\text{-}bipy)^+$ in CH_3CN produced the spectrum of the $^3MLCT_{Re(I)\rightarrow biq}$ excited state, which closely resembles those of the short-lived transient in Figure 3.[28]

The ~350 nm flash irradiation of 8.0×10^{-6} M $(CO)_3(biq)Re^I(pz)Ru^{II}(biq)(CO)_2Cl^{2+}$ in CH_3CN produced transient spectra that disappeared by a complex process, Figure 4. The disappearance of the spectra proceeded through three steps that were followed in very different time scales, inset to Figure 4. These processes are kinetically of first-order. Each of them was fitted to a single exponential with lifetimes $\tau_1 = 46 \pm 3$ ns, $\tau_2 = 50 \pm 4\ \mu s$, and $\tau_3 = 1.2 \pm 0.1$ ms that was independent of the flash-generated concentrations. A comparison with the spectrum of the $^3MLCT_{Re(I)\rightarrow biq}$ excited state in related Re(I) complexes[28] indicated that the transient with a lifetime $\tau_1 = 46 \pm 3$ ns, identical to the luminescence lifetime, is the $^3MLCT_{Re(I)\rightarrow biq}$ excited state in the dyad.

No transient spectra with a lifetime $\tau > 10$ ns were detected when $Ru^{II}(biq)(CO)_2Cl_2$ was irradiatied at $\lambda_{exc} = 532$ nm, i.e., a wavelength corresponding to the Ru(II) to biq charge transfer transition. In contrast, the irradiation at $\lambda_{exc} \approx 350$ nm, a wavelength corresponding to a biq intraligand transition, produced transient spectral changes, Figure 5. Oscillographic traces recorded between 400 and 650 nm were fitted to a double exponential, $\Delta OD(t) = A_1 e^{-t/\tau'} + A_2 e^{-t/\tau''}$, with lifetimes $\tau' = 51 \pm 1$ ns and $\tau'' = 4.92 \pm 0.07\ \mu s$. The ratio of the

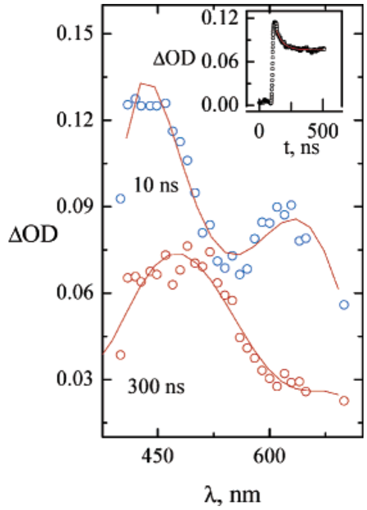

Figure 4. Spectral changes observed when a solution 8.0×10^{-6} M $(CO)_3(biq)Re^I(pz)Ru^{II}(biq)(CO)_2Cl^{2+}$ in deaerated CH_3CN was flash irradiated at ~350 nm. The delays, starting from the top spectrum, are 10, 100, and 525 ns after the laser irradiation. The trace in the inset shows the multiple steps in the decay of the 400 nm optical density.

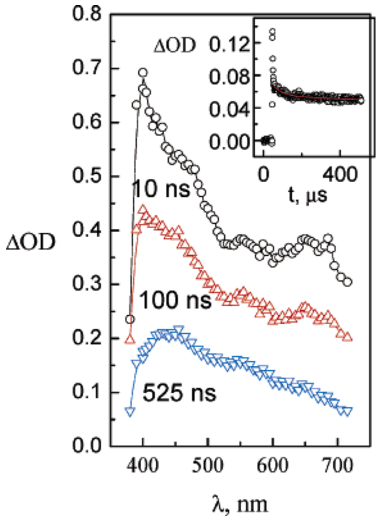

Figure 5. Transient spectra recorded when 3.0×10^{-5} M $Ru^{II}(biq)(CO)_2Cl_2$ in deaerated CH_3CN was flash irradiated at ~350 nm. The trace in the inset shows multiple steps in the decay of the 490 nm optical density.

preexponential factors, A_1/A_2, obeys the relationship $A_1/A_2 = (\Delta OD_0 - \Delta OD_e)/\Delta OD_e$, where ΔOD_0 is the prompt OD change and $\Delta OD_e \approx \Delta OD_0/2.71$. These are the functional conditions expected for two sequential reactions that are kinetically of first-order. The photoinduced spectral change at $\lambda_{ob} < 410$ nm was a prompt bleach of an absorption band of the biq ligand. A large fraction of the bleached OD, ~98%, was recovered by a first-order process with a lifetime $\tau = 4.9 \pm 0.3$ μs. The final 2% recovery of the OD occurs on a much longer time scale, i.e., $t \geq 50$ ms.

The experimental observations strongly suggested that the photochemical transformations of the dyads and $Ru^{II}(biq)(CO)_2Cl_2$ were almost photoreversible. Indeed, only an insignificant discoloration of the complexes' solutions was noted after they were irradiated at $\lambda_{exc} \approx 350$ nm with 100 laser flashes.

Redox Reactions of Photogenerated Products. It was observed that the long-lived intermediates generated in the flash photochemical experiments with the bimetallic complexes participate in redox reactions. Electron transfer reactions of the long-lived intermediates with oxidants, i.e., TCE and $Co(Me_6\text{-}[14]dieneN_4)Cl_2^+$, gave products with spectra where the prominent absorptions of the $biq^{\bullet-}$ chromophore were absent. In addition, reactions of the long-lived intermediates with reductants, i.e., 2,2′,2″-nitrilotriethane, TEA, and 2,2′,2″-nitrilotriethanol, TEOA, gave products with spectra where the contributions of the Re(II) and Ru(III) chromophores were missing. For example, the reactions of the intermediate generated in the photolysis of $(CO)_3(biq)Re^I(4,4'\text{-bipy})Ru^{II}(biq)(CO)_2Cl^{2+}$ are shown in eqs 3 and 4.

$$I \xrightarrow[-\text{oxidant}^{\bullet-}]{+\text{oxidant}} (CO)_3(biq)Re^I(4,4'\text{-bipy})Ru^{III}(CO)_2(biq)Cl^{3+} \quad (3)$$

$$\text{oxidant} = \text{TCN}, Co(Me_6\text{-}[14]dieneN_4)Cl_2^+$$

$$\text{oxidant}^{\bullet-} = \text{TCN}^{\bullet-}, Co(Me_6\text{-}[14]dieneN_4)Cl_2$$

$$I \xrightarrow[-\text{TEA}^{\bullet+}\text{ or TEOA}^{\bullet+}]{+\text{TEA or TEOA}} \begin{cases} (CO)_3(biq^{\bullet-})Re^I(4,4'\text{-bipy})Ru^{II}(CO)_2Cl^+ \\ \text{and/or} \\ (CO)_3(biq)Re^I(4,4'\text{-bipy})Ru^{II}(CO)_2(biq^{\bullet-})Cl^+ \end{cases} \quad (4)$$

Indeed, the prompt spectrum recorded when solutions containing 1.4×10^{-4} M $(CO)_3(biq)Re^I(4,4'\text{-bipy})Ru^{II}(biq)(CO)_2Cl^{2+}$ and 1.0×10^{-3} M $Co^{III}(Me_6\text{-}[14]dieneN_4)Cl_2^+$ were flash irradiated at ~350 nm was that of the $^3MLCT_{Re(I)\rightarrow biq}$ excited state, Figure 6. The lifetime of the $^3MLCT_{Re(I)\rightarrow biq}$ excited state was the same in the presence and absence of the Co(III) complex, denoting the absence of a reaction between them. There was however a reaction between I and the Co(III) complex. The spectrum of the reaction product was recorded with delays ensuring a complete decay of the $^3MLCT_{Re(I)\rightarrow biq}$ excited state. A maximum at 450 nm in the spectrum of the reaction product was the same observed in the absorption spectrum of the oxidized complex, $(CO)_3(biq)Re^I(4,4'\text{-bipy})Ru^{III}(biq)(CO)_2Cl^{3+}$. A back electron transfer reaction between this Ru(III) species and the reduced scavenger was followed by means of the decay of the transient spectrum at wavelengths between 400 and 690 nm. Linear plots of the reciprocal of the change in optical density, $\Delta OD(\lambda_{ob})^{-1}$, vs time confirmed that the back electron transfer reaction was kinetically of second-order. The value $2kC_0 = (5.8 \pm 0.6) \times 10^6$ s^{-1} was calculated from traces collected between $\lambda_{ob} = 410$ and $\lambda_{ob} = 670$ nm, and the ratio of the rate constant to the extinction coefficient, $k/\epsilon = (5.0 \pm 0.3) \times 10^7$ cm s^{-1}, was calculated from traces recorded at $\lambda_{ob} = 420$ nm. The experimental observations made when the dyad was irradiated at 532 nm were similar to those made when the irradiation was at ~350 nm.

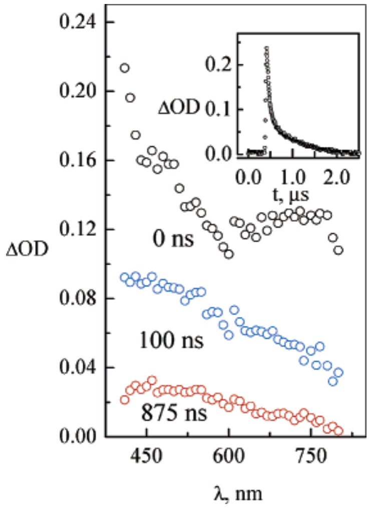

Figure 6. Transient spectra recorded when a solution containing 1.4×10^{-4} M $(CO)_3(biq)Re^I(4,4'\text{-bipy})Ru^{II}(biq)(CO)_2Cl^{2+}$ and 1.0×10^{-3} M $Co(Me_614]dieneN_4)Cl_2^+$ in deaerated CH_3CN was laser flash irradiated at ~350 nm. The trace in the inset shows the back electron transfer reaction between the reduced Co complex and oxidized dyad.

No reaction between $Co(Me_6\text{-}[14]dieneN_4)Cl_2^+$ and the $^3MLCT_{Re\rightarrow biq}$ excited state of the $Re^I(biq)(CO)_3(4,4'\text{-bipy})^+$ complex was observed when the concentration of Co(III) scavenger was equal to or less than 3×10^{-3} M. The absence of a reaction between the Co(III) complex and the respective $^3MLCT_{Re\rightarrow biq}$ excited states of $(CO)_3(biq)Re^I(4,4'\text{-bipy})Ru^{II}(biq)(CO)_2Cl^{2+}$ and $Re^I(biq)(CO)_3(4,4'\text{-bipy})^+$ suggests that the reaction is slow by comparison with the lifetime of the excited state.

Quenching reactions were also used for the investigation of the short, $\tau' = 51$ ns, and long-lived, $\tau'' = 4.9$ μs, transients generated in the ~350 nm photolysis of $Ru^{II}(biq)(CO)_2Cl_2$. When a solution of 2.0×10^{-4} M $Ru^{II}(biq)(CO)_2Cl_2$ in CH_3CN containing 1.5×10^{-3} M $Co(Me_6\text{-}[14]dieneN_4)Cl_2^+$ was flash irradiated at ~350 nm, a transient difference spectrum assigned to the oxidized complex, $Ru^{III}(biq)(CO)_2Cl_2^+$, was recorded after the reaction of the Co(III) complex with the long-lived transient. The formation of $Ru^{III}(biq)(CO)_2Cl_2^+$ is indicative of an electron transfer reaction with the Co(III) complex. As expected for a back electron transfer reaction between the Ru(III) and Co(II) products, the linear dependence of ΔOD^{-1} on time showed that the process is kinetically of second-order with $2kC_0 = (1.2 \pm 0.4) \times 10^6$ s^{-1} and $k/\epsilon = (2.4 \pm 0.3) \times 10^7$ cm s^{-1} at $\lambda_{ob} = 420$ nm. The short-lived transient, $\tau' = 51$ ns, that was also generated in these irradiations did not react with the limited range of Co(III) concentrations used in the experiments, i.e., $\leq 3 \times 10^{-3}$ M.

By contrast to Co(Me$_6$-[14]dieneN$_4$)Cl$_2$$^+$, TCE proved to be an electron acceptor that did not discriminate between the ^{3}MLCT$_{\mathrm{Re(I)}\rightarrow\mathrm{biq}}$ excited state and long-lived intermediates. It oxidized the ^{3}MLCT$_{\mathrm{Re}\rightarrow\mathrm{biq}}$ of dyads and Re$^{\mathrm{I}}$(biq)(CO)$_3$(4,4′-bipy)$^+$, and it also reacted with the short- and long-lived transients photogenerated with the dyad and the Ru$^{\mathrm{II}}$(biq)(CO)$_2$Cl$_2$.

TEA or TEOA were respectively used as reductants of the transients photogenerated in the ~350 nm flash photolysis of Re$^{\mathrm{I}}$(biq)(CO)$_3$(4,4′-bipy)$^+$ or (CO)$_3$(biq)Re$^{\mathrm{I}}$-(4,4′-bipy)Ru$^{\mathrm{II}}$(biq)(CO)$_2$Cl^{2+}. Reaction of these intermediates with the electron donors produced long-lived products, i.e., with lifetimes $\tau \gg 20$ μs. The spectra of the products comapared very well with the spectra products obtained by the reduction of the complexes with pulse radiolytically generated e$^-_{\mathrm{solv}}$ and CH$_2$OH$^\bullet$ radicals. The spectra were assigned to species with metal-coordinated biq$^{\bullet-}$ radicals.[28]

Radiolytically Generated Reduced Moieties. Either in the ^{3}MLCT$_{\mathrm{Re}\rightarrow\mathrm{biq}}$ excited state or in the quenching reaction, eq 2, charge is transferred and/or localized in the biq ligand. In terms of their characterization, it was useful to compare the UV–vis spectra of these products with those generated when the dyads and monometallic complexes of Re(I) and Ru(II) reacted with pulse radiolytically generated e$_{\mathrm{solv}}$$^-$ and CH$_2$OH$^\bullet$ radicals. The reduction of N$_2$-deaerated 10^{-3} M biq in MeOH with e$^-_{\mathrm{solv}}$ produces a transient spectrum with spectral features attributable to the biq$^{\bullet-}$ radical anion. Since negligible spectral changes where observed when the biq solution was saturated with N$_2$O, it must be concluded that the reaction of CH$_2$OH$^\bullet$ radicals with biq is too slow by comparison with the fast radical disproportionation. Spectral features related to those in the spectrum of the biq$^{\bullet-}$ radical anion were found in the spectra produced when e$^-_{\mathrm{solv}}$ reacted with the biq complexes in the scheme. In these pulse radiolysis experiments, the N$_2$-deaerated solutions were 10^{-3} M in a given complex and the products were formed on a time scale $t < 1$ μs. Although CH$_2$OH$^\bullet$ radicals were unable to reduce the biq ligand, they reacted with the pz ligand of the dyads and monomeric complexes. These reactions occurred on a longer time scale than the e$^-_{\mathrm{solv}}$ reactions and caused new growths of the optical density between 500 and 700 nm. These spectral changes were also observed when the solutions of the complexes were staurated with N$_2$O, i.e., when only CH$_2$OH$^\bullet$ radicals reacted with the complexes. As an example of these processes, the reactions of e$_{\mathrm{solv}}$$^-$ and CH$_2$OH$^\bullet$ radicals with (CO)$_3$(biq)Re$^{\mathrm{I}}$(4,4′-bipy)Ru$^{\mathrm{II}}$(biq)(CO)$_2$Cl^{2+} are shown in eqs 5 and 6.

$$(\mathrm{CO})_3(\mathrm{biq})\mathrm{Re}^{\mathrm{I}}(\mathrm{pz})\mathrm{Ru}^{\mathrm{II}}(\mathrm{biq})(\mathrm{CO})_2\mathrm{Cl}^{2+} + \mathrm{e_{solv}}^- \rightarrow \begin{cases} (\mathrm{CO})_3(\mathrm{biq}^{\bullet-})\mathrm{Re}^{\mathrm{I}}(\mathrm{pz})\mathrm{Ru}^{\mathrm{II}}(\mathrm{biq})(\mathrm{CO})_2\mathrm{Cl}^+ \\ \text{and/or} \\ (\mathrm{CO})_3(\mathrm{biq})\mathrm{Re}^{\mathrm{I}}(\mathrm{pz})\mathrm{Ru}^{\mathrm{II}}(\mathrm{biq}^{\bullet-})(\mathrm{CO})_2\mathrm{Cl}^+ \end{cases} \quad (5)$$

$$(\mathrm{CO})_3(\mathrm{biq})\mathrm{Re}^{\mathrm{I}}(\mathrm{pz})\mathrm{Ru}^{\mathrm{II}}(\mathrm{biq})(\mathrm{CO})_2\mathrm{Cl}^{2+} + \mathrm{CH_2OH}^\bullet \rightarrow (\mathrm{CO})_3(\mathrm{biq})\mathrm{Re}^{\mathrm{I}}(\mathrm{pz}^{\bullet-})\mathrm{Ru}^{\mathrm{II}}(\mathrm{biq})(\mathrm{CO})_2\mathrm{Cl}^+ \quad (6)$$

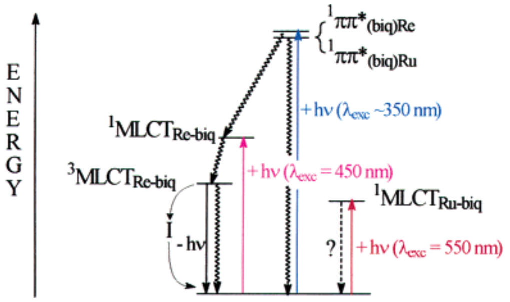

Figure 7. Jablonski diagram showing the excited states populated in the irradiation of the dyads at three different wavelengths. Intraligand biq excited states of the biq respectively coordinated to Re(I) or Ru(II) have been identified as $\pi\pi^*_{\mathrm{(biq)Re}}$ and $\pi\pi^*_{\mathrm{(biq)Ru}}$ in the curly bracket. Long-lived reaction intermediates, I, produced when the ^{1}MLCT$_{\mathrm{Re-biq}}$ is populated are summarily indicated in the diagram.

Discussion

The results show that irradiations within the bands of the dyads' biq-centered electronic transitions induce luminescence from the Re(I) to biq charge transfer excited states and the formation reaction intermediates. These processes are individually discussed in the following paragraphs on the basis of the scheme in Figure 7.

(a) ^{3}MLCT$_{\mathrm{Ru}\rightarrow\mathrm{biq}}$ Excited States. The redox potentials in Table 1 suggest that the lowest energy absorption band in complexes containing the –Ru$^{\mathrm{II}}$(biq) moiety, Figure 1 and Table 3 (Supporting Information), must be assigned to a Ru(II) to biq charge transfer transition. Irradiation of Ru$^{\mathrm{II}}$(biq)(CO)$_2$Cl$_2$ or the Ru(II)-containing dyads at 532 nm is within this band. The absence of luminescence and/or long-lived transients shows that, in fluid solution at room temperature, radiationless processes rapidly relax the ^{3}MLCT$_{\mathrm{Ru}\rightarrow\mathrm{biq}}$ excited state, i.e., with a lifetime $\tau \leq 5$ ns, Figure 7. The participation of LF excited states of Ru(II) in the radiationless processes cannot be ruled out.

(b) ^{3}MLCT$_{\mathrm{Re}\rightarrow\mathrm{biq}}$ Excited States. Absorption bands related to the Re(I) to biq charge transfer transitions are observed as shoulders in the spectrum of the dyads and Re$^{\mathrm{I}}$(biq)(CO)$_3$(4,4′-bipy)$^+$ at $\lambda > 420$ nm, Figure 1. Irradiation of the dyads within the Re(I) to biq charge transfer band, i.e., at 450 nm, or within the band of a biq-centered IL transition, i.e., at ~350 nm, induced luminescence that is independent of the excitation wavelength, Figure 7. Indeed, the same emission spectrum and the same kinetics of the luminescence resulted when the irradiation was performed at wavelengths of the IL and Re to biq charge transfer transitions. An efficient conversion of the biq-centered IL excited states to the luminescent ^{3}MLCT$_{\mathrm{Re}\rightarrow\mathrm{biq}}$ excited states accounts for these observations. Moreover, internal conversions of ^{3}MLCT$_{\mathrm{Re}\rightarrow\mathrm{biq}}$ excited states to the nonluminescent and short-lived ^{3}MLCT$_{\mathrm{Ru}\rightarrow\mathrm{biq}}$ must be inefficient processes.[23] If internal conversions of the ^{3}MLCT$_{\mathrm{Re}\rightarrow\mathrm{biq}}$ excited states to the nonluminescent and short-lived ^{3}MLCT$_{\mathrm{Ru}\rightarrow\mathrm{biq}}$ were efficient processes, the charge transfer luminescence of the Re(I) chromophores would have been quenched.

(c) Biquinoline-Centered Excited States, IL($\pi\pi^*$). Intense bands with maxima at 373 nm in the absorption spectrum of $(CO)_3(biq)Re^I(pz)Ru^{II}(biq)(CO)_2Cl^{2+}$ and a maximum at 375 nm in the spectrum of $(CO)_3(biq)Re^I$-(4,4′-bipy)$Ru^{II}(biq)(CO)_2Cl^{2+}$ can be assigned to a biq-centered, π to π^*, electronic transition by comparison with the spectra of related Re(I) complexes and the free biq ligand, Figure 1 and Table 3 (Supporting Information).[17,28] In accordance with the assignment, similar features can be found in the spectra of $Re^I(biq)(CO)_3$-(4,4′-bipy)$^+$ and $Ru^{II}(biq)(CO)_2Cl_2$. The positions of these bands in the spectra of the dyads imply that there is a small difference, $-140\ cm^{-1}$, between the energies of the biq-centered, IL($\pi\pi^*$), excited states of the Re(I) and Ru(II) moieties. Because of the small gap between these excited states in relation to the excitation energy, $28.5 \times 10^3\ cm^{-1}$ when $\lambda_{exc} \approx 350$ nm, it is possible to populate either or both IL($\pi\pi^*$) excited states of the Re(biq) and Ru(biq) moieties with $\lambda_{exc} \approx 350$ nm, Figure 7.

The envelope of the short-lived transient spectrum observed when the dyads are flash irradiated at ~350 nm, Figures 3 and 4, appears to be shaped mostly by the spectrum of the $^3MLCT_{Re\rightarrow biq}$ excited state. Indeed, the spectra exhibited most of the features and have the lifetimes previously ascribed to $^3MLCT_{Re\rightarrow biq}$ excited states of complexes containing $Re^I(biq)(CO)_3$ chromophores, e.g., $Re^I(biq)(CO)_3$(4,4′-bipy)$^+$.[17,28] Also the luminescence spectra of the dyads can be assigned to the radiative decay of the $^3MLCT_{Re\rightarrow biq}$ because they closely resemble the charge transfer emission spectrum of $Re^I(biq)(CO)_3$(4,4′-bipy)$^+$, Figure 3. It must be concluded, therefore, that in the dyads and $Re^I(biq)(CO)_3$-(4,4′-bipy)$^+$ internal conversions of the IL($\pi\pi^*$) excited states populate luminescent $^3MLCT_{Re\rightarrow biq}$ excited states, Figure 7.

Since irradiation within the intraligand π to π^* transition results in emission from the $^3MLCT_{Re\rightarrow biq}$ excited state, internal conversion between these manifolds must be rapid, i.e., $k > 109\ s^{-1}$. Fast conversions of the IL($\pi\pi^*$) excited states to the luminescent $^3MLCT_{Re\rightarrow biq}$ have been previously communicated for the monometallic complexes $Re^I(biq)(CO)_3Cl$ and Re^I (biq)-$(CO)_3(pz)^+$,[16,21] as well as in other related Re(I) complexes. Similar conversions of the IL($\pi\pi^*$) excited states to the $^3MLCT_{Re\rightarrow biq}$ excited states in the $(CO)_3(biq)Re^I$-(4,4′-bipy)$Ru^{II}(biq)(CO)_2Cl^{2+}$ and $(CO)_3(biq)Re^I(pz)Ru^{II}$-$(biq)(CO)_2Cl^{2+}$ dyads are expected to be equally fast processes, a proposition supported by the time-resolved absorption and emission spectroscopies.

(d) Reaction Intermediates. Marked differences were observed between the spectrum of the $^3MLCT_{Re\rightarrow biq}$ excited state of Re^I $(biq)(CO)_3$(4,4′-bipy)$^+$ and the transient spectra generated in the ~350 nm flash irradiations of the dyads, Figures 3−5. The transient spectra recorded with delays shorter than 10^2 ns have larger optical densities at $\lambda_{ob} < 450$ nm than those expected for the spectrum of the $^3MLCT_{Re\rightarrow biq}$ excited state alone. The spectral differences were ascribed to the presence of the long-lived reaction intermediates, I, together with the$^3MLCT_{Re\rightarrow biq}$ excited state. In the flash irradiation of the dyads the spectra of these transients are more clearly seen when they are recorded with delays $t > 10^2$ ns after the flash. Because the lifetime of the lowest lying $^3MLCT_{Ru\rightarrow biq}$ of the Ru(II) moieties is too short, $\tau < 5$ ns, it cannot be related to any of these transients. Although the long-lived transients could be generated in photoinduced ligand substitution reactions,[31] photoreactions that substitute CO by other ligands would have led to an irreversible change of the dyads' spectra. Contrary to this expectation, the photoinduced spectral changes vanished on a long time scale. In addition, the observed redox reactions of the long-lived intermediates are uncharacteristic of the products of a ligand substitution. The electron transfer reactions of the intermediates with oxidants, i.e., TCE and Co(Me_6-[14]dieneN_4)Cl_2^+, or reductants, i.e., TEA and TEOA, respectively leave absorption features of the Re(II), Ru(III), or $biq^{\bullet-}$ chromophores in the spectra of the reaction products. Species that may account for this chemical behavior are unstable ortho-metalated or charge-separated complexes. Ortho-metalated complexes of d^6 second- and third-row transition metal ions have been isolated and the biq ligand in the dyads has an adequate geometry for this type of coordination.[32,33] Also charge-separated species have been observed in the photochemistry of Re and other metal complexes.[34−37] In the case of the dyads investigated here, the long lifetime of the charge-separated intermediates must be interpreted in terms of some structural anomaly. It is possible that a stabilization of the charge separation can be achieved by some intrinsic distortion of the flexible biq ligand or $biq^{\bullet-}$ ligand-radical.

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Supporting Information Available: Tables 1, 2, and 3. This material is available free of charge via the Internet at http://pubs.acs.org.

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