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Energy Transfer in Rigid Ru(II)/Os(II) Dinuclear Complexes with Biscyclometalating Bridging Ligands Containing a Variable Number of Phenylene Units

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We have prepared rodlike cyclometalated Ru(II)/Os(II) dinuclear complexes, (ttp)Ru(dpb-(ph)$_n$-dpb)Os(ttp)$^{2+}$, where the biscyclometalating bridging ligands contain dipyridylbenzene fragments, dbp, separated by a variable number, *n*, of phenylene spacers, and the terminal ligand is a terpyridine derivative [dpbH is di-2-pyridyl-1,3-benzene, ttp is 4′-*p*-tolyl-2,2′:6′,2″-terpyridine, and $n = 0-2$]. The rigid bridging ligands keep the metal centers at a distance $r_{MM} = 11$, 15.5, and 20 Å, depending on *n*. Photoinduced energy transfer has been investigated by luminescence spectroscopy in nitrile solvents at room temperature and at 77 K (i.e., in frozen medium). According to a classical description of the process, the energy transfer occurs in a nearly activationless regime, is governed by electronic factors, and can be described in terms of the Dexter-type mechanism. The obtained energy transfer rates roughly span 3 orders of magnitude and indicate (i) that the temperature (i.e., the state of the solvent) has a small influence on the process and (ii) that the interposed phenylene spacers are weak attenuators of intercenter electronic coupling, H [$H = H_0 \exp(-\beta r_{MM})$, with $\beta \sim 0.33$ Å^{-1}].

Introduction

There is currently a great interest in studies of photoinduced electron and energy transfer in supramolecular assemblies.[2] Motivations for this lie in the possibility of mimicking key events triggered by light in natural systems[3] and in the construction of artificial photochemical molecular devices.[4] Among other systems, those including Ru- and Os-based polypyridine chromophores have received a great deal of attention because of their outstanding redox and spectroscopic properties.[5] Important issues in studies concerned with long-range (nm scale) energy or electron transfer[6,7] are related to the geometric and electronic properties of the bridge, BL, in di- and polynuclear complexes. For instance, polymethylene spacers[8] provide a flexible connection between the interacting centers while spacers containing groups like cyanide,[9] ethenyl,[10] ethenylbenzene,[11] ethenylbicyclooctane,[12] ethynylbicyclooctane,[13] ethynyl and ethynylbenzene,[14] polyenes,[15] and polyphenylenes[16] allow a high degree of geometric control of the dinuclear species over an intermetal separation of 10−20 Å or more.[15−17] Concerning the electronic characteristics, the saturated groups[18] of the spacers are responsible for a remarkable

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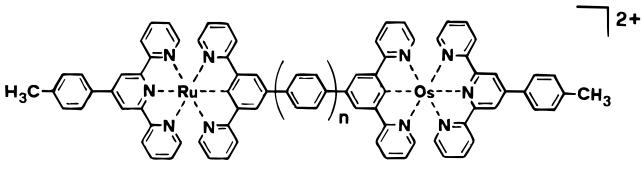
attenuation of the intercenter interaction while bridges containing unsaturated groups like polyene[15] and, possibly, polyphenylene[16] appear to have good conducting properties.

We report here on Ru → Os energy transfer data obtained for a series of Ru(II)/Os(II) dinuclear complexes where the component chromophores are linked by rigid biscyclometalating bridges. These contain tridentate dipyridyl-benzene fragments, dpb, separated by a variable number, *n*, of phenylene units so that the metal-to-metal distances in the (ttp)Ru(dpb-(ph)$_n$-dpb)-Os(ttp)$^{2+}$ species are 11, 15.5, and 20 Å, depending on the number of interposed phenylene groups in the bridging ligand, $n = 0-2$, respectively [dpbH is di-2-pyridyl-1,3-benzene, ttp is 4′-*p*-tolyl-2,2′:6′,2″-terpyridine].[19] With respect to the case of analogous non-cyclometalated species, the σ-donating ability of the C$^-$ sites[20] of the bridge causes a shift of electron density over the metal centers and the terminal ligands. As a consequence, the redox and spectroscopic properties of the component units are subject to relevant changes, and the energetics and excited state dynamics for the energy transfer are also expected to be affected.[21]



(ttp)Ru(dpb-(ph)$_n$-dpb)Os(ttp)$^{2+}$

$n = 0,1,2$

We compare energy transfer results for the investigated cyclometalated complexes with those previously obtained for the analogous series of non-cyclometalated compounds (ttp)-Ru(tpy-(ph)$_n$-tpy)Os(ttp)$^{4+}$, for which we found that energy transfer was very fast, $k \geq 5 \times 10^{10}$ s^{-1} for $n = 0-2$ [tpy is 2,2′:6′,2″-terpyridine].[16,22] In both series the metal-to-metal distances are the same, 11, 15.5, and 20 Å, for $n = 0-2$, respectively. We find that energy transfer is orders of magnitude slower in the cyclometalated series. This outcome is discussed in terms of the role played by energetic and electronic factors.

Experimental Section

Preparation of the Complexes. The bridging ligands were prepared according to a recently published procedure.[24] The synthesis of (ttp)-Ru(dpb-dpb)Os(ttp)(PF$_6$)$_2$ was reported previously.[21] After chromatography and anion exchange, the purity of the highly colored complexes was checked by thin-layer chromatography, UV−visible spectroscopy, high-resolution ^{1}H NMR spectroscopy, and mass spectroscopy.

(ttp)Ru(dpb-ph-dpbH)(PF$_6$). This compound was synthesized as described for (ttp)Ru(dpb-dpbH)(PF$_6$)[21] (yield 40%). ^{1}H NMR (400 MHz, CD$_3$CN): δ 8.97 (s, 2H), 8.78 (t, 1H, 0.8 Hz), 8.75 (d, 2H, 4.7 Hz), 8.66 (s, 2H), 8.55 (d, 2H, 8.1 Hz), 8.48 (d, 2H, 1.6 Hz), 8.34 (d, 2H, 8 Hz), 8.11 (m, 6H), 7.99 (d, 2H, 8.3 Hz), 7.92 (t, 2H, 7.8 Hz), 7.68 (m, 4H), 7.55 (d, 2H, 8 Hz), 7.39 (m, 2H), 7.17 (t, 4H, 5.7 Hz), 6.95 (t, 2H, 6.5 Hz), 6.71 (t, 2H, 6.5 Hz), 2.52 (s, 3H). FAB-MS (nitrobenzyl alcohol matrix): $m/z = 961.7$ (C$_{60}$H$_{42}$N$_7$Ru requires 962.1).

(ttp)Ru(dpb-(ph)$_2$-dpbH)(PF$_6$). The same procedure as above was used (yield 53%). ^{1}H NMR (400 MHz, DMSO-d_6): δ 9.44 (s, 2H), 9.02 (d, 2H, 8.1 Hz), 8.87 (t, 1H, 1.4 Hz), 8.83 (s, 2H), 8.78 (d, 2H, 3.8 Hz), 8.57 (d, 2H, 6.4 Hz), 8.52 (d, 2H, 1.6 Hz), 8.35 (d, 2H, 8.2 Hz), 8.26 (m, 4H), 8.03 (m, 8H), 7.98 (td, 2H, 7.0 and 1.1 Hz), 7.84 (td, 2H, 8.1 and 1.4 Hz), 7.73 (m, 2H), 7.56 (d, 2H, 7.9 Hz), 7.44 (m, 2H), 7.21 (t, 2H, 6.5 Hz), 7.14 (t, 2H, 5.9 Hz), 6.80 (t, 2H, 7.1 Hz), 2.5 (s, 3H). FAB-MS (nitrobenzyl alcohol matrix): $m/z = 1038.2$ (C$_{66}$H$_{46}$N$_7$Ru requires 1038.2).

(ttp)Ru(dpb-ph-dpb)Os(ttp)(PF$_6$)$_2$. This compound was synthesized as described for (ttp)Ru(dpb-dpb)Os(ttp)(PF$_6$)$_2$[21] (yield 20%). ^{1}H NMR (200 MHz, CD$_3$CN): δ 9.03 (s, 4H), 8.81 (s, 2H), 8.73 (s, 2H), 8.61 (d, 4H, 8.3 Hz), 8.40 (t, 4H, 7.1 Hz), 8.28 (s, 4H), 8.11 (t, 4H 7.9 Hz), 7.66 (m, 14H), 7.19 (m, 6H), 6.98 (m, 6H), 6.68 (m, 2H), 2.54 (s, 3H), 2.53 (s, 3H). FAB-MS (nitrobenzyl alcohol matrix): $m/z = 1621.2$ (C$_{82}$H$_{58}$N$_{10}$RuOsPF$_6$ requires 1621.3).

(ttp)Ru(dpb-(ph)$_2$-dpb)Os(ttp)(PF$_6$)$_2$. The same procedure as above was used (yield 40%). ^{1}H NMR (200 MHz, CD$_3$CN): δ 9.4 (s, 4H), 9.03 (d, 4H, 5.6 Hz), 8.93 (s, 2H), 8.84 (s, 2H), 8.60 (t, 4H, 8.6 Hz), 8.32 (m, 8H), 8.09 (d, 4H, 8.3 Hz), 7.73 (m, 12H), 7.11 (m, 10H), 6.97 (d, 2H, 5.9 Hz), 6.77 (m, 4H), 2.51 (s, 3H), 2.50 (s, 3H). FAB-MS (nitrobenzyl alcohol matrix): $m/z = 1698.1$ (C$_{88}$H$_{62}$N$_{10}$RuOsPF$_6$ requires 1697.3).

Equipment and Methods. The instruments and procedures used to obtain ^{1}H NMR spectra, mass spectra, and cyclic voltammograms were described previously.[25] Absorption spectra were measured in acetonitrile solution at room temperature with a Perkin-Elmer Lambda 9 spectrophotometer. For the luminescence experiments, butyronitrile solutions of the samples were deaerated via repeated freeze−pump−thaw cycles in 1-cm quartz cuvettes. Luminescence spectra were obtained from solutions whose absorbance values were ≤0.2 at the employed excitation wavelength (514 or 550 nm). At these wavelengths the Ru- and Os-based mononuclear complexes, that we assume to be satisfactory model components of the dinuclear species, absorb light in a (0.6−0.7):1 ratio. Luminescence spectra at room temperature and at 77 K were obtained either with a conventional Spex Fluorolog II

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Table 1. Electrochemical Potentials[a]

	E_{ox}, V		E_{red}, V
	$Os^{3+/2+}$	$Ru^{3+/2+}$	$L^{0/-}$ [c]
(ttp)Ru(dpb)$^{+}$ [b]		+0.485	−1.61
(ttp)Os(dpb)$^{+}$ [b]	+0.335		−1.60
(ttp)Ru(dpb-dpb)Os(ttp)$^{2+}$ [b]	+0.29	+0.51	−1.48
(ttp)Ru(dpb-ph-dpb)Os(ttp)$^{2+}$	+0.33	+0.53	−1.50
(ttp)Ru(dpb-(ph)$_2$-dpb)Os(ttp)$^{2+}$	+0.33	+0.52	−1.50

[a] CH_3CN solutions; *vs* SCE. [b] From ref 21. [c] Irreversible.

spectrofluorimeter equipped with a Hamamatsu R928 phototube or with a near-IR sensitive instrument.

The former apparatus is suited for monitoring the Ru-based portion of the luminescence spectra for the investigated cyclometalated complexes ($\lambda_{em} < 800$ nm; vide infra). With this instrument, corrected luminescence profiles could be obtained by using a correction curve provided by the firm or by employing a calibrated 45-W quartz−halogen tungsten filament lamp by Optronic Laboratories as a standard for correction of the phototube response. The correction procedure provided band maxima and relative luminescence intensities which were affected by large uncertainties, 5−20 nm and ~25%, respectively. From the area of the corrected luminescence spectra on an energy scale, we obtained luminescence quantum yields for samples (s) with reference to a standard (r) according to eq 1, where *A* stands for absorbance, *n*

$$\frac{\Phi_s}{\Phi_r} = \frac{A_r {n_s}^2 a_s}{A_s {n_r}^2 a_r} \tag{1}$$

is the refraction index of the solvent, and *a* is the spectral area. As a reference, we chose $Os(bpy)_3^{2+}$ in deaerated CH_3CN at room temperature ($\Phi_r = 0.005$,[26] corrected $\lambda_{em}^{max} = 742$ nm). For the sake of comparison with previously reported data, we use uncorrected band maxima throughout the text.

For the observation of the Os-based portion of the steady state luminescence spectra of the investigated cyclometalated complexes ($\lambda_{em} > 820$ nm), the 514-nm line of a Spectra-Physics 265 Ar^+ laser was used for excitation in a modified Edinburgh Instruments FS900 spectrofluorimeter. Detection was accomplished using a cooled (77 K) North Coast EO-817L Ge detector in combination with a Stanford Research SR lock-in amplifier. With this near-IR equipment, only relative intensities were measured from samples exhibiting identical absorbances at the selected excitation wavelengths. The uncertainty in band maxima and luminescence intensities is estimated lower than with the conventional spectrofluorimeter.

In order to obtain lifetimes for the decay of the Ru-based luminescence, we used $\lambda_{exc} = 337$ nm from an IBH single-photon counter or 532 nm from a picosecond fluorescence spectrometer using a Continuum PY62-10 Nd:YAG laser and a Hamamatsu C1587 streak camera. Both apparatuses have been described previously.[21] Concerning the Os-based luminescence, lifetimes at 77 K were obtained by using the single-photon counting equipment, while at room temperature ($\lambda_{em} > 900$ nm for the investigated cyclometalated complexes; vide infra), it was not possible to perform time-resolved measurements with the available equipment. The uncertainty in the lifetime values is 10%.

Results

Electrochemistry. Electrochemical potentials for the dinuclear species and for the reference mononuclear complexes, (ttp)Ru(dpb)$^+$ and (ttp)Os(dpb)$^+$, are collected in Table 1. Oxidations are metal centered and reductions are ligand centered processes, respectively. Table 1 shows potentials consistent with previous assignments.[21] From the reported values, one concludes that (i) oxidation of an osmium center is easier than that involving a ruthenium center and (ii) reduction is irreversible and occurs practically at the same potential in the three dinuclear species, *ca.* −1.5 V. The ligand localization of the added electron (i.e., whether on the terminal ttp or on the bridging ligands) will be discussed later.

Absorption Spectra. Table 2 reports absorption maxima and intensities. The absorption features in the UV region ($\epsilon \sim 10^4$−10^5 M^{-1} cm^{-1}) are ascribed to ligand-centered (^{1}LC) transitions, and those occurring in the visible region (500−550 nm, $\epsilon \sim 10^4$ M^{-1} cm^{-1}) correspond to metal-to-ligand charge-transfer (^{1}MLCT) transitions.[21] Comparison with data for the mononuclear complexes shows that in the dinuclear species the ^{1}MLCT bands consist of overlapping bands of Ru → L (ttp or BL) and Os → L (ttp or BL) origin. Weak absorptions at ca. 770 nm ($\epsilon \sim 10^3$ M^{-1} cm^{-1}) correspond to direct population of Os → L CT triplet excited states. As previously noted for the heterometallic (ttp)Ru(dpb-dpb)Os(ttp)$^{2+}$ complex and the homometallic (ttp)Ru(dpb-dpb)Ru(ttp)$^{2+}$ and (ttp)Os(dpb-dpb)Os(ttp)$^{2+}$ complexes,[21] the absorption spectra exhibited by the dinuclear species in the visible region do not overlap with the sum of those of the component moieties, (ttp)Ru(dpb)$^+$ and (ttp)Os(dpb)$^+$.

Luminescence Properties. Table 3 lists luminescence band maxima and lifetimes obtained in dilute (~10^{-5} M) butyronitrile solutions of the three cyclometalated dinuclear complexes. For comparison purposes, in the table are also reported results for the mononuclear complexes. From the luminescence maxima at 77 K, one sees that the Ru → Os energy transfer step is energetically allowed by *ca.* 0.18 eV. In principle, in order to

Table 2. Ground State Absorption Maxima[a]

(ttp)Ru(dpb)$^{+}$ [b]	286 (43 000)	504 (10 800)	550 (8250)	
(ttp)Os(dpb)$^{+}$ [b]	288 (48 000)	503 (13 650)	537 (13 000)	765 (2000)
(ttp)Ru(dpb-dpb)Os(ttp)$^{2+}$ [b]	288 (119 000)	511 (35 450)	542 (35 700)	770 (2700)
(ttp)Ru(dpb-ph-dpb)Os(ttp)$^{2+}$	288 (135 000)	511 (39 100)	534 (40 100)	770 (2900)
(ttp)Ru(dpb-(ph)$_2$-dpb)Os(ttp)$^{2+}$	289 (136 000)	511 (37 530)	532 (37 000)	770 (3000)

[a] CH_3CN solutions; room temperature. [b] From ref 21.

Table 3. Luminescence Data[a]

	298 K				77 K			
	Ru		Os		Ru		Os	
	λ_{max},[b] nm	τ, ns	λ_{max},[c] nm	τ, ns	λ_{max},[b] nm	τ, ns	λ_{max},[c] nm	τ, ns
(ttp)Ru(dpb)$^+$	784[d]	4.5[d]			752	496[e]		
(ttp)Os(dpb)$^+$			920	*f*			844[g]	400
(ttp)Ru(dpb-dpb)Os(ttp)$^{2+}$	~816	0.35	940	*f*	~750	0.720	837	400
(ttp)Ru(dpb-ph-dpb)Os(ttp)$^{2+}$	800	3.5	920	*f*	750	42	837	370
(ttp)Ru(dpb-(ph)$_2$-dpb)Os(ttp)$^{2+}$	792	4.9	916	*f*	750	178	840	*h*

[a] In butyronitrile. Luminescence spectra were obtained with $\lambda_{exc} = 514$ or 550 nm and luminescence lifetimes were obtained with $\lambda_{exc} = 337$ or 532 nm; see text. [b] From the conventional spectrofluorimeter. [c] From the IR-sensitive equipment. [d] $\Phi = 4.5 \times 10^{-5}$, ref 21. [e] $\Phi = 7.2 \times 10^{-4}$. [f] Not detectable. [g] A different value (832 nm) was reported in ref 21. [h] Hidden by the tail of the Ru-based emission.

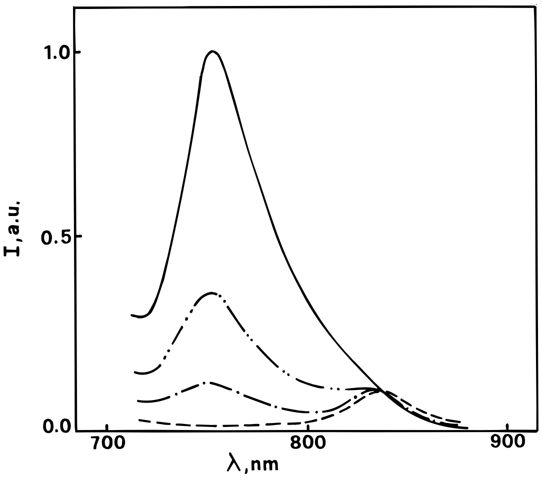

Figure 1. Relative luminescence spectra at 77 K: (ttp)Ru(dpb)$^+$ (—); (ttp)Ru(dpb-(ph)$_2$-dpb)Os(ttp)$^{2+}$ (−••−); (ttp)Ru(dpb-ph-dpb)Os(ttp)$^{2+}$ (−•−); (ttp)Ru(dpb-dpb)Os(ttp)$^{2+}$ and (ttp)Os(dpb)$^+$ (— — —).

monitor this step through luminescence spectroscopy, one should selectively excite the Ru-based chromophore and monitor the Ru- and Os-based luminescence properties. We could not follow this approach because the absorption spectra of the mononuclear (ttp)Ru(dpb)$^+$ and (ttp)Os(dpb)$^+$ complexes, which we take as model compounds, overlap extensively (Table 2). Excitation was therefore performed into the MLCT absorption band system of the dinuclear complexes at 550 and 514 nm. At these wavelengths the ratio of the extinction coefficients for the (ttp)Ru(dpb)$^+$ and (ttp)Os(dpb)$^+$ mononuclear species varies between 0.6 and 0.7 (Table 2). By assuming that the Ru- and Os-based chromophores in the dinuclear species maintain the same ratio of absorption intensities, one obtains *ca.* 40% and 60% excitation of the Ru- and Os-based component chromophores, respectively, at the employed excitation wavelengths.

From the results of Table 3, one concludes that each of the dinuclear complexes exhibits a dual luminescence, both at room temperature and at 77 K. Comparison with data for the mononuclear complexes allows identification of the emission bands as Ru-based and Os-based, according to the assignments reported in the table. In particular, the band maximum of the Ru-based luminescence occurs in the 792−816 nm interval at room temperature and at 750 nm in frozen solvent. The band maximum of the Os-based luminescence is in the 916−940 nm interval at room temperature and in the 837−840 nm interval at 77 K.

For the dinuclear species, we observed quenching of the luminescence of the donor moiety and sensitization of the luminescence of the acceptor moiety, as illustrated below from data obtained at (a) 77 K and (b) room temperature.

(a) Figure 1 shows the luminescence spectra obtained at 77 K with the conventional fluorimeter (see Experimental Section). The intensity of the band centered at 750 nm (Ru-based luminescence) is maximized when the bridging ligand contains two phenylene units and gradually decreases for $n = 1$ and 0. In Figure 1, the portion of the luminescence spectra falling at $\lambda > 800$ nm corresponds to the Os-centered luminescence and apparently peaks at *ca.* 830 nm.[21] Given the dramatic drop of the phototube response for $\lambda > 800$ nm, a reliable assessment on quantitative grounds of the sensitization of the Os-based luminescence was not possible.

(b) At room temperature, both Ru- and Os-based luminescence maxima shift toward longer wavelengths than at 77 K; see Table 3. In this case it was possible to monitor the Os-based luminescence by employing the near-IR spectrofluorimeter, which reliably covers the wavelength interval from 820 to 1200 nm. Figure 2 shows luminescence spectra obtained from isoabsorptive solutions at $\lambda_{exc} = 514$ nm. At this wavelength one excites 40% and 60% of the Ru- and Os-based chromophores, respectively. Relevant results are as follows. (i) For (ttp)Ru(dpb-dpb)Os(ttp)$^{2+}$, the Os-based luminescence is as intense as that of the (ttp)Os(dpb)$^+$ complex, consistent with nearly complete Ru → Os energy transfer.[21] (ii) For (ttp)Ru(dpb-(ph)$_2$-dpb)Os(ttp)$^{2+}$, the Os-based luminescence intensity is about six-tenths that of (ttp)Os(dpb)$^+$, indicating that no or very little sensitization takes place. The Ru-based relative luminescence intensities in the series (ttp)Ru(dpb-(ph)$_n$-dpb)Os(ttp)$^{2+}$, as monitored with the conventional spectrofluorimeter in the 790−820 nm interval, are *ca.* 1, 0.8, and 0.1 for $n = 2$, 1, and 0, respectively. These results show a satisfactory agreement with the observations of points i and ii above.

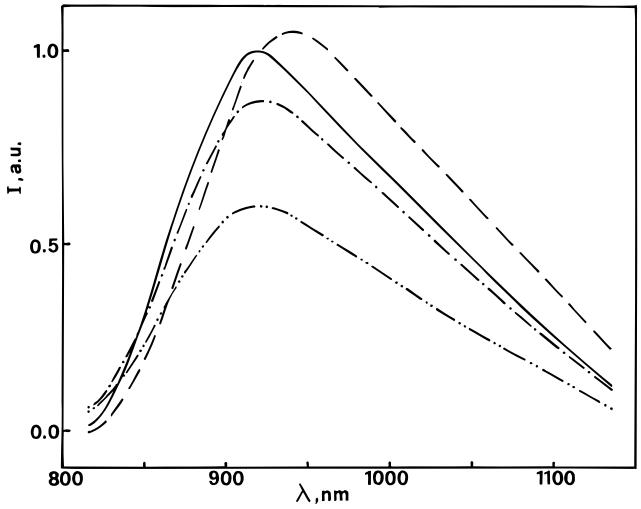

Figure 2. Relative luminescence spectra at room temperature: (ttp)Os(dpb)$^+$ (—); (ttp)Ru(dpb-(ph)$_2$-dpb)Os(ttp)$^{2+}$ (−••−); (ttp)Ru(dpb-ph-dpb)Os(ttp)$^{2+}$ (−•−); (ttp)Ru(dpb-dpb)Os(ttp)$^{2+}$ (— —).

The obtained results indicate that quenching of the Ru-based luminescence and parallel sensitization of the Os-based luminescence *via* intramolecular photoinduced energy transfer are related to the length of the bridging ligand, i.e. to the number of interposed phenylene units. In principle, the energy transfer rate constant, k, can be obtained from eq 2, where τ and I are

$$k = \frac{1}{\tau} - \frac{1}{\tau_0} \qquad (2a)$$

$$k = \frac{1}{\tau_0}\left(\frac{I_0}{I} - 1\right) \qquad (2b)$$

the luminescence lifetime and intensity of the Ru-based luminescence of the dinuclear complexes and τ_0 and I_0 are the lifetime and intensity of the (ttp)Ru(dpb)$^+$ species, taken as a reference model for the energy donor moiety in the dinuclear species. As noticed above, the luminescence intensity measurements are affected by large uncertainties and only provide a qualitative assessment of the energy transfer step. Thus, we have obtained the energy transfer rates at room temperature and 77 K in accord with eq 2a. The evaluated rates are collected in Table 4.

Discussion

Electronic Consequences of Cyclometalation. Cyclometalated complexes exhibit remarkably different properties with

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(26) Kober, E. M.; Caspar, J. V.; Lumpkin, R. S.; Meyer, T. J. *J. Phys. Chem.* **1986**, *90*, 3722.

Table 4. Energy Transfer Rates[a]

	k, s^{-1}	
	298 K	77 K
$(ttp)Ru(dpb\text{-}dpb)Os(ttp)^{2+}$	2.6×10^9	1.4×10^9
$(ttp)Ru(dpb\text{-}ph\text{-}dpb)Os(ttp)^{2+}$	6.3×10^7	2.2×10^7
$(ttp)Ru(dpb\text{-}(ph)_2\text{-}dpb)Os(ttp)^{2+}$	$<2.2 \times 10^7$ [b]	3.6×10^6

[a] From eq 2a of text. [b] Estimated on the basis of the fact that there is no quenching of the Ru-based luminescence, so that, within a 10% uncertainty, $k < 0.1/\tau_0$, where τ_0 is taken to be the lifetime of the $(ttp)Ru(dpb)^+$ complex; see text.

respect to those of their non-cyclometalated counterparts.[20] For instance, the Os- and Ru-centered oxidation processes occur at +0.34 and +0.90 V in $(ttp)Os(dpb)^+$ and $Os(ttp)_2{}^{2+}$, respectively, and at +0.49 and +1.30 V in $(ttp)Ru(dpb)^+$ and $Ru(ttp)_2{}^{2+}$, respectively, showing that cyclometalation causes a remarkable increase of electron density in the metal centers. The electrochemical and spectroscopic properties of the homometallic Ru and Os dinuclear species containing the (dpb-(ph)$_n$-dpb) bridges are consistent with a high degree of covalency for the various metal−ligand interactions.[27,28] Because of this effect, one expects that the two metal centers interact strongly. For instance, for the species $(ttp)Ru(dpb\text{-}dpb)Ru(ttp)^{3+}$, intervalence studies[27] revealed a very strong metal−metal interaction ($\epsilon = 27\,000$ M^{-1} cm^{-1} at 1820 nm, to be compared with $\epsilon = 1618$ M^{-1} cm^{-1} at 1580 nm for the related non-cyclometalated complex $(ttp)Ru(tpy\text{-}tpy)Ru(ttp)^{5+}$ [23]).

Electrochemical and spectroscopic properties can be employed to discuss the localization of the MLCT excited states involved in energy transfer. For instance, for the non-cyclometalated $(ttp)Ru(tpy\text{-}(ph)_n\text{-}tpy)Os(ttp)^{4+}$ series, first reduction occurred at −1.01, −1.20, and −1.22 V for $n = 0-2$, respectively, while it occurred at −1.29 and −1.25 V in $Ru(ttp)_2{}^{2+}$ and $Os(ttp)_2{}^{2+}$, respectively.[16] These data indicate that reduction is centered on the bridging ligand (BL) in the dinuclear species. EHMO calculations provide support for this interpretation because the LUMO levels of tpy-tpy and ttp are calculated at −9.62 and −9.88 eV, respectively, but the LUMO of the bridge is expected to be further stabilized by the presence of the second metal center.[29] Similarly, we found a correlation between the reduction potentials seen above and the energy levels corresponding to the lowest wavelength MLCT bands of the absorption spectra and to the luminescence spectra.[16] Thus, for the series $(ttp)Ru(tpy\text{-}(ph)_n\text{-}tpy)Os(ttp)^{4+}$, we concluded that the MLCT excited states involved in the Ru → Os energy transfer step are *localized on BL*, as in eq 3, where the ligand localization of the promoted electron is indicated as $L^{\bullet-}$.

$$*[(ttp)Ru^{3+}(tpy^{\bullet-}\text{-}(ph)_n\text{-}tpy)Os^{2+}(ttp)]^{4+} \rightarrow *[(ttp)Ru^{2+}(tpy\text{-}(ph)_n\text{-}tpy^{\bullet-})Os^{3+}(ttp)]^{4+} \quad (3)$$

According to the above equation, the energy transfer step involves the movement of (i) a positive charge over a distance *equal to* and (ii) a negative charge over a distance *lower than* the metal-to-metal separation. It is worth noticing that, for all of the $(ttp)Ru(tpy\text{-}(ph)_n\text{-}tpy)Os(ttp)^{4+}$ complexes, the Ru-based luminescence was completely quenched and it was demonstrated that sensitization of the Os-based luminescence took place at a rate larger than 5×10^{10} s^{-1}, *both at room temperature and at 77 K*.[16] These results indicated that the phenylene groups apparently behave like good conductors toward energy transfer and that the process is not inhibited in rigid solvent, at odds with electron transfer processes if the driving force is ≤0.6 eV.[30]

For the series of investigated cyclometalated complexes, the shift of electron density caused by the dianionic bridges toward both the metal centers and the terminal ligands results in first reduction at ∼−1.5 V and metal-centered oxidations at +0.29 to +0.33 V and +0.51 to +0.53 V for the Os- and Ru-centered processes, respectively (Table 1). Comparison of the redox and absorption properties for the dinuclear and mononuclear species, Tables 1 and 2, does not allow us to draw a clear-cut conclusion about which type of ligand, i.e. whether ttp or BL, is involved in the lowest lying MLCT excited states. From the luminescence band maxima at room temperature, Table 3, one sees that the Ru- and Os-based luminescent levels become higher and higher in energy for $n = 0$, 1, and 2, respectively. This behavior parallels that exhibited by the non-cyclometalated series,[16] which apparently suggests the involvement of BL. However, when the dinuclear species contain a dianionic BL, it seems reasonable that first reduction and the lowest-lying MLCT states are *centered on the terminal ttp ligands*. In this case, the energy transfer step would be described by eq 4, implying the

$$*[(ttp^{\bullet-})Ru^{3+}({}^{-}dpb\text{-}(ph)_n\text{-}dpb^{-})Os^{2+}(ttp)]^{2+} \rightarrow *[(ttp)Ru^{2+}({}^{-}dpb\text{-}(ph)_n\text{-}dpb^{-})Os^{3+}(ttp^{\bullet-})]^{2+} \quad (4)$$

movement of (i) a positive charge over a distance *equal to* and (ii) a negative charge over a distance *greater than* the metal-to-metal separation.

According to eqs 3 and 4, one sees that the effective site-to-site distance covered in the energy transfer step should be larger for the cyclometalated series than for the non-cyclometalated series.

Mechanism of Intramolecular Energy Transfer. Energy transfer may be described in terms of exchange (Dexter)[31] and Coulombic (Förster)[32] mechanisms. The former case may be visualized in a simple way as a simultaneous double electron exchange between the donor and the acceptor. The Förster mechanism takes into account the interaction between the transition dipoles[33] for deactivation of the excited state of the donor and excitation of the acceptor.

In the weak-interaction limit, the exchange mechanism can be described in terms of thermodynamic quantities by using eqs 5−7,[34,35] according to a classical approach which parallels

$$k = \nu \exp(-\Delta G^{\ddagger}/RT) \quad (5)$$

$$\nu = \frac{2H^2}{h}\left(\frac{\pi^3}{\lambda RT}\right)^{1/2} \quad (6)$$

$$\Delta G^{\ddagger} = \frac{\lambda}{4}\left(1 + \frac{\Delta G^{\circ}}{\lambda}\right)^2 \quad (7)$$

that for nonadiabatic electron transfer.[36]

In these equations ν is a frequency factor, λ is the reorganization energy, H is the intercomponent electronic interaction

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(32) (a) Förster, Th. *Discuss. Faraday Soc.* **1959**, *27*, 7. (b) Förster, Th. In *Modern Quantum Chemistry*; Sinanoglu, O., Ed.; Academic Press: New York, 1965; Part III.

Table 5. Calculated Parameters for Energy Transfer

		298 K			77 K		
	r_{MM}	H,[a] cm^{-1}	k_D,[b] s^{-1}	k_F,[c] s^{-1}	H,[a] cm^{-1}	k_D,[b] s^{-1}	k_F,[c] s^{-1}
(ttp)Ru(dpb-dpb)Os(ttp)$^{2+}$	11	2.05	1.7×10^9	5.6×10^7	1.2	8.9×10^8	6.7×10^6
(ttp)Ru(dpb-ph-dpb)Os(ttp)$^{2+}$	15.5	0.32	4.2×10^7	7.2×10^6	0.15	1.4×10^7	8.5×10^5
(ttp)Ru(dpb-(ph)$_2$-dpb)Os(ttp)$^{2+}$	20	<0.19	$<1.5 \times 10^7$	1.6×10^6	0.06	2.2×10^6	2.1×10^5

[a] Interaction term; see eqs 5−7 of text. [b] Calculated according to eqs 8 and 10 of text. [c] Calculated according to eqs 9 and 11 of text.

energy, and $\Delta G^{\ddagger}$ and ΔG° are the activation energy and the free energy change, respectively, for the process.

Within usual assumptions, the free energy change ΔG° is −0.18 eV, corresponding to the energy gap between the 77 K band maxima for (ttp)Ru(dpb)$^{+}$ and (ttp)Os(dpb)$^{+}$, Table 3, taken as donor and acceptor component models, respectively. By contrast with the case of electron transfer,[36] contributions to the reorganization energy for energy transfer only come from intramolecular processes taking place in the donor and acceptor components.[34,35] For (ttp)Os(dpb)$^{+}$, the reorganization energy can be evaluated from the spectroscopic Stokes shift,[37] obtained from the absorption and luminescence data reported in Tables 2 and 3. By assuming that the structurally similar (ttp)Ru(dpb)$^{+}$ and (ttp)Os(dpb)$^{+}$ complexes exhibit the same value for the reorganization energy, one obtains $\lambda \sim 0.15$ eV. Thus the Ru → Os energy transfer for the investigated dinuclear complexes occurs in a nearly activationless regime, $-\Delta G^{\circ} \sim \lambda$. According to eqs 5−7, using the experimentally determined rate constants, one obtains the electronic interaction term, H. Calculated values for H are collected in Table 5.

It is possible to estimate the energy transfer rate constants according to both Dexter (D) and Förster (F) mechanisms by calculating the pertinent overlap integrals, J_D[31] and J_F,[32] between the luminescence spectrum of the donor, $F(\bar{\nu})$, and the absorption spectrum of the acceptor, $\epsilon(\bar{\nu})$, as taken on an energy scale (cm^{-1}), eqs 8 and 9.

$$J_D = \frac{\int F(\bar{\nu})\, \epsilon(\bar{\nu})\, d\bar{\nu}}{\int F(\bar{\nu})\, d\bar{\nu} \int \epsilon(\bar{\nu})\, d\nu} \tag{8}$$

$$J_F = \frac{\int F(\bar{\nu})\, \epsilon(\bar{\nu})/\bar{\nu}^4\, d\bar{\nu}}{\int F(\bar{\nu})\, d\bar{\nu}} \tag{9}$$

Thus, from the luminescence spectrum of (ttp)Ru(dpb)$^{+}$ as a donor model and the absorption spectrum of (ttp)Os(dpb)$^{+}$ as an acceptor model, one obtains $J_D = 3.5 \times 10^{-4}$ cm and $J_F = 5.5 \times 10^{-12}$ cm^3 M^{-1} at room temperature and $J_D = 5.5 \times 10^{-4}$ cm and $J_F = 6.1 \times 10^{-12}$ cm^3 M^{-1} at 77 K. The energy transfer rate constants according to Dexter and Förster treatments are then evaluated according to eqs 10[38] and 11, respectively.

$$k_D = \frac{4\pi^2 H^2}{h} J_D \tag{10}$$

$$k_F = \frac{8.8 \times 10^{-25} K^2 \Phi}{n^4 \tau r^6} J_F \tag{11}$$

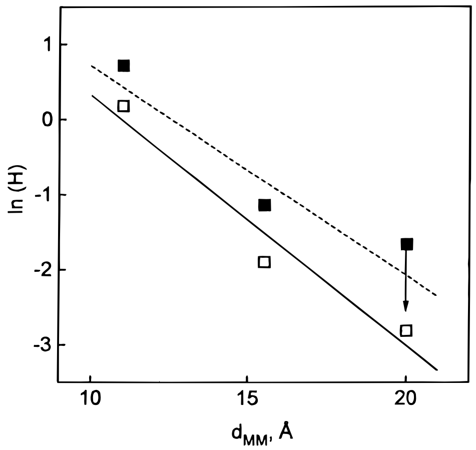

Figure 3. Distance dependence of the interaction term H at room temperature (■) and 77 K (□); see text.

In eq 10, H is the interaction energy evaluated above. In eq 11, K^2 is a geometric factor which can assume values in the range 0−4, depending on the relative orientation of the interacting dipoles.[32] We tentatively assume a statistical orientation of the dipoles, and $K^2 = 2/3$. Φ and τ are the luminescence quantum yield and lifetime of the donor component, (ttp)Ru(dpb)$^{+}$, n is the refraction index of the solvent, and r is taken as the metal-to-metal separation. Results of calculations for k_F and k_D are collected in Table 5. As one can see, the values obtained for k_F are orders of magnitude lower than the experimentally obtained rate constants, Table 4, and the Förster mechanism cannot play any role in the present cases.

Effect of Distance. For the series of investigated dinuclear species, the intramolecular energy transfer process, which is mediated by phenylene units, takes place according to a Dexter (double electron exhange) mechanism. The transfer step occurs under nearly activationless conditions, $\Delta G^{\circ} \sim -0.18$ and $\lambda \sim 0.15$ eV, eq 7, and is governed by electronic factors. These can be described by the intercomponent interaction energy, H, whose distance dependence is expected to follow eq 12[36] where β can be seen as an attenuation factor.

$$H = H_0 \exp(-\beta r_{MM}) \tag{12}$$

Actually, by plotting ln(H) *vs* r_{MM}, one sees that the experimental points lie on a straight line, and from the slope one obtains $\beta \sim 0.33$ Å^{-1} at both 77 K and room temperature, Figure 3. It is interesting to notice that McLendon *et al.* found $\beta_{ET} = 0.4$ Å^{-1} for photoinduced electron transfer (ET) through phenylene spacers[39,40] to be compared with $\beta \sim 1$ Å^{-1} found for saturated groups.[18] Because of the relation between electron and energy (double electron exchange) transfer it has been proposed that $\beta = \beta_{HT} + \beta_{ET}$, where HT stands for hole

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(33) Higher order interactions are usually disregarded. For examples of more complete treatments, see: (a) Scholes, G. D.; Ghiggino, K. P. *J. Photochem. Photobiol. A: Chem.* **1994**, *80*, 355. (b) Scholes, G. D.; Ghiggino, K. P.; Oliver, A. M.; Paddon-Row, M. N. *J. Phys. Chem.* **1993**, *97*, 11871.

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transfer.[41] In the light of our and McLendon's results on the role of polyphenylene bridges, this simplified description seems not to hold unless one assumes that $\beta_{HT} \sim 0$. In simple terms this would mean that the metal-to-metal hole transfer, presumably occurring through a superexchange mechanism involving the HOMO level of the bridge,[4,42] takes place very easily. At the moment, we have no evidence supporting this view, even if one might notice that, for the homometallic species (ttp)Ru(dpb-(ph)$_n$-dpb)Ru(ttp)$^{2+}$ and (ttp)Os(dpb-(ph)$_n$-dpb)Os(ttp)$^{2+}$, the σ-donation of the cyclometalated sites was reported to cause a high inter-metal coupling[27,28,43] resulting, for the Ru-containing series, in $\beta \sim 0.12$ Å^{-1}.

Concerning the high-energy transfer rate constants ($k_{en} > 5 \times 10^{10}$ s^{-1}) previously obtained for the series (ttp)Ru(tpy-(ph)$_n$-tpy)Os(ttp)$^{4+}$, a possible explanation may be based on the fact that the MLCT excited states involved in the Ru → Os energy transfer step are partly delocalized over BL (see eq 3); as discussed above, this is equivalent to saying that the *effective* intercenter distance is significantly shorter than the metal-to-metal separation. A report by Lehn, Harrimann, and colleagues dealing with binuclear complexes containing Ru(bpy)$_3^{2+}$ units linked by polyene chains of variable length illustrates a similar case for which the bridge effectively delocalizes the MLCT states.[15] In that case, the attenuation factor for the intermetal electronic coupling was found very low, $\beta \sim 0.06$ Å^{-1}.

Conclusion

Stepwise complexation of ruthenium(II) and osmium(II) to symmetrical biscyclometalating bridging ligands allowed preparation of rigid, rodlike asymmetrical compounds containing two different complex subunits. By introducing phenylene spacers in the bridges, one could modulate the Ru−Os distance between 11 and 20 Å. Photoinduced Ru → Os energy transfer was studied by luminescence spectroscopy, and the energy transfer rate constants were found to vary substantially with the Ru−Os distance ($k_{en} = 2.6 \times 10^9$ and $< 2.2 \times 10^7$ s^{-1} for $r_{MM} = 11$ and 20 Å, respectively, at room temperature) being little affected by temperature. Energy transfer was found to take place according to a Dexter mechanism. Comparison with analogous complexes containing non-cyclometalating bridging ligands, where the MLCT excited states involved in the energy transfer step are localized in the bridge and very fast energy transfer takes place ($k > 5 \times 10^{10}$ s^{-1}),[16] suggests that the energy transfer step in the cyclometalated complexes is slower because the involved MLCT excited states are directed toward the terminal ligands. This apparently results in a longer transfer pathway. The present results in combination with those obtained for analogous non-cyclometalated species indicate that it should be possible to control energy transfer directionality and rate in multicomponent transition-metal-based systems by combining various types of cyclometalating and/or non-cyclometalating bridges and terminal ligands.

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(43) Similar results were obtained with Phbpy tridentate environments: Constable, E. C.; Cargill Thompsom, A. M. W.; Greulich, S. *J. Chem. Soc., Chem. Commun.* **1993**, 1444.