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Excited-State Properties of (μ-Pyridyl)(μ-hydrido)dirhenium Octacarbonyl and Related Dirhenium Carbonyl Complexes[1]

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A series of dirhenium complexes of the type $Re_2(CO)_7(\mu\text{-}H)(\mu\text{-}py)(L)$, where L = CO or py and py = pyridine or 4-benzoylpyridine, have been synthesized. Excited-state properties of these and related rhenium carbonyl complexes containing pyridine or 4-benzoylpyridine as σ-bound or μ-bridged ligands have been investigated in an effort to design organometallic complexes that possess long-lived excited states generated from the photoexcitation of the M–M σ-bond. Emissive metal-to-ligand charge-transfer states of the type $d_{\pi(M)}\pi^*_L$ or $\sigma_{M\text{-}M}\pi^*_L$ have been observed in complexes containing bridging ligands, and their intermolecular electron-transfer reactions with a variety of neutral or charged donors and acceptors have been studied by emission and transient absorption spectroscopic techniques. Quenching of $[Re_2(CO)_7(\mu\text{-}H)(\mu\text{-}py)(L)]^*$ (py = L = 4-benzoylpyridine) by a series of trialkyl- and triarylphosphines is shown to proceed solely by electron-transfer pathways. We have also studied the electron-transfer reduction of a series of substituted N-methylpyridinium salts by the same excited-state molecule and attempted to correlate the rate of electron transfer with the reduction potential of the quencher.

Introduction

The mechanistic photochemistry of dinuclear metal carbonyl complexes containing an M–M single bond has been extensively investigated in recent years.[2] In the simplest of these complexes, photoexcitation leads to M–M bond homolysis or ligand loss, the former resulting in the generation of transient metal-centered radicals.[3] Such species are known to be reactive as either oxidants or reductants.[4]

The photogenerated transient species has usually been probed by time-resolved absorption spectral measurements,[5] particularly laser flash photolysis experiments.[6] An additional method of probing the photochemistry of organometallic compounds involves study of their emission spectra.[7] Though spin–orbit coupling interactions in transition-metal complexes render the distinction between singlet and triplet states ambiguous, long-lived emissions originating from states predominantly triplet in character have been widely observed. Selected examples typify the nature and diversity of the emissive states as follows. (a) Ligand-field or d–d states: $d_{\sigma(M\text{-}M)}^* \rightarrow {}^3p_{\sigma(M\text{-}M)}$, $Pt_2(pop)_4^{4-}$, $Ir_2(cod)_2(pz)_2$,[8,9] Rh_2-$(tmb)_4^{2+}$, $Pt_2(dppm)_3$;[10,11] $d_{\sigma(M\text{-}M)} \rightarrow {}^3d_{\sigma(M\text{-}M)}^*$, $Pt_2(POP)_4(X)_2^{2-}$;[12]

$^4A_M \rightarrow {}^4T_M$ or ^2E_M, $Cr(bpy)_3^{3+}$.[13] (b) Intraligand states: $\pi_L \rightarrow {}^3\pi_L^*$, $Rh(bpy)_3^{3+}$;[14] $\pi_L/d_{\pi(M)} \rightarrow {}^3\pi_L^*$, $Cu(dmp)(PR_3)^+$.[15] (c) Charge-transfer states: $d_{\pi(M)} \rightarrow {}^3\pi_L^*$, $Ru(bpy)_3^{2+}$;[16] $d_{\sigma(M\text{-}M)} \rightarrow {}^3\pi_L^*$, $Re(CO)_3(phen)(SnPh_3)$.[17]

The emissive properties of the bipyridine complexes of Cr(III), Rh(III), and Ru(II) illustrate how a similar ligand environment can create different emissive states, depending on the nature of the central metal atom and its oxidation state.

Emission from carbonyl complexes has been observed in a series of d⁶ complexes of group VI metals containing pyridine or polypyridyl ligands.[18] Pioneering studies by Gray, Wrighton,[18] and Adamson,[19] as well as more recent work by Lees[20] and Rest[21] have helped to elucidate the photophysical properties and photochemistry in systems of the general type $M(CO)_5L$ and $M(CO)_4L_2$, where M = Cr, Mo, or W and L_2 may be two substituted pyridines or a bidentate nitrogen ligand. Pyridine ligands with electron-withdrawing substituents or polypyridyls lead to low-energy metal-to-ligand charge-transfer (MLCT) absorption bands; quite often, such complexes are also found to luminesce in fluid solution or low-temperature glasses. Photoinduced substitution reactions in these complexes are thought to originate from a higher energy

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ligand-field state that might be thermally equilibrated with the emissive MLCT state in some cases.[19b] Similar results have been obtained[22] in a series of d^6 inorganic complexes of the general formula Ru(NH$_3$)$_5$(py)$^{2+}$.

Other extensively studied d^6 systems include a series of Re(I) complexes of the general formula CpRe(CO)$_2$(L)[23] and XRe-(CO)$_3$L$_2$[24] as well as the corresponding cation, SRe(CO)$_3$L$_2^+$ where X = halide; L may be a substituted pyridine or L$_2$ a bidentate polypyridyl ligand, and S = CH$_3$CN, pyridine, or piperidine.[25] The emissive state has been characterized as an MLCT state, due to the solvatochromic behavior and an observed "rigidochromic shift" (a blue shift in the emission maximum in rigid media).[24a] Low-temperature multiple emission from intraligand (nπ^* or $\pi\pi^*$) and MLCT (dπ^*) emissive states has been observed in certain cases.[24c,d,25a] Recently, a series of *cis*-XRe-(CO)$_4$L (X = Cl, I; L = piperidine, PPh$_3$) complexes have been reported[20f] to exhibit ligand-field emission at room temperature, in fluid solutions. The MLCT emissive state in XRe(CO)$_3$L$_2$ complexes has been shown to be quenched by electron-transfer reagents, both electron donors and acceptors.[24,25] In one such reaction, electron-transfer quenching of the excited state of ClRe(CO)$_3$(4-benzoylpyridine)$_2$ by triethylamine was found to result in catalytic reduction of the 4-benzoylpyridine ligand to α-(4-pyridyl)benzyl alcohol.[25c] An analogous reaction, employing BrRe(CO)$_3$(bpy) and trialkylamines, has been shown to effect the catalytic reduction of CO$_2$.[25d]

Emissive dinuclear organometallic compounds have not been as extensively investigated. Gray and co-workers observed emissive excited states in a series of dirhodium (d^8-d^8) complexes with bridging bis(isocyanide) ligands.[10] These complexes can be formulated in terms of an M–M bond order of zero in the ground state and approximately one in the excited state. Related d^8-d^8 systems, whose emissive behavior has been more extensively investigated in recent years, include Pt$_2$(pop)$_4^{4-}$ and Ir$_2$(cod)$_2$(pz)$_2$ complexes.[8,9] More recently,[11] such emissive behavior has also been observed in a series of d^{10}-d^{10} complexes of the general formula Pt$_2$L$_3$, where L is a bidentate phosphine ligand. The emissive excited state of Pt$_2$(pop)$_4^{4-}$ undergoes atom-transfer reactions with tributyltin hydride[26] or halogen atom donors to generate dinuclear Pt(III)–Pt(III) complexes. One such complex, Pt$_2$(pop)$_4$Br$_2$,[12a] has been cited as the first example of a d^7-d^7 system in which an emissive dinuclear $\sigma\sigma^*$ excited state has been observed in a low-temperature matrix. A d^7-d^7 dirhenium complex, Re$_2$(CO)$_6$(dmpm)$_2$, has been reported[12b] to emit in the solid state, at low temperatures, from a d$_\sigma$d$_\sigma^*$ excited state.

Wrighton investigated a series of dinuclear Re–M compounds that have the general formula Re(CO)$_3$(nn)–ML$_n$ where nn = a bidentate nitrogen ligand and ML$_n$ = Re(CO)$_5$,[27] R$_3$Sn, or R$_3$Ge.[17] These complexes possess low-energy MLCT absorption bands, but in contrast with the mononuclear analogues, photoexcitation is thought to result in the promotion of an electron from the M–M σ bond. The compounds were found to luminesce in fluid solutions from an MLCT emissive state at room temperature, as well as in low-temperature glasses. Photochemical cleavage of the M–M bond was attributed to labilization of the M–M bond resulting from depopulation of the σ orbital in the
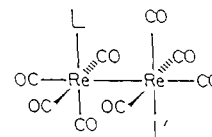
I L = CO, L' = PMe$_3$ (Ia), PPh$_3$ (Ib), CH$_3$CN (Ic), CH$_3$NH$_2$ (Id),

pyridine (Ie), 4-phenylpyridine (If), 4-benzoylpyridine (Ig).

II L = L' = PMe$_3$ (IIa), PPh$_3$ (IIb), CH$_3$CN (IIc), Ph$_2$PCH$_2$PPh$_2$ (IId),

pyridine (IIe), 4-phenylpyridine (IIf), 4-benzoylpyridine (IIg).
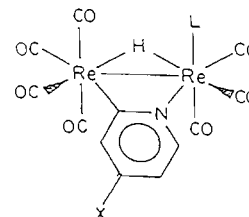
III L = CO, X = H (IIIa) and L = CO, X = Ph-CO- (IIIb).
IV L = py, X = H (IVa), L = 4-bzy, X = Ph-CO- (IVb).

Figure 1. Dirhenium carbonyl complexes.

excited state. Electron-transfer quenching and energy-transfer quenching of the emissive excited state were also observed. Emissive behavior and low-temperature photochemistry of similar complexes have been studied by Stufkens et al.[21c]

It would be useful to synthesize dinuclear metal complexes in which it is possible to examine the properties of excited states originating in metal-centered orbitals, particularly the M–M σ bond. Transient metal-centered biradicals[28] and triplet excited states[12] have been generated from M–M-bonded dinuclear complexes, but such species are relatively short-lived. Thus, chemical processes other than recombination or return to the ground state are not easily observed. Introduction of ligand structures that create low-energy MLCT states should lead to more long-lived, emissive excited states from which it should be possible to observe bimolecular processes such as atom transfer or electron transfer. We have investigated a series of dirhenium complexes of the type R$_2$(CO)$_7$(μ-py)(μ-H)L, where L = CO (III) or a pyridine (IV) (Figure 1), to study the effect of incorporating low-energy excited states on the photophysical properties and photostability of dinuclear complexes, as well as on their reactivities in inter- and intramolecular electron-transfer reactions. Our intent in this work has been to create dinuclear complexes that possess long-lived excited states and are stable toward fragmentation to form mononuclear products, by holding the two bonded metal centers together with bridging ligands and by providing accessible charge-transfer excited states.

Experimental Section

General Data. Re$_2$(CO)$_{10}$ was obtained from Pressure Chemical Co. and used without further purification. Pyridines were purchased from Aldrich Chemical Co. and Lancaster Synthesis Co. and used as obtained. Hexane, toluene, and benzene were treated with concentrated H$_2$SO$_4$, washed with water and aqueous bicarbonate, dried over anhydrous MgSO$_4$, and distilled over CaH$_2$. Acetonitrile was stirred over CaH$_2$; both CH$_2$Cl$_2$ and acetonitrile were distilled twice over P$_2$O$_5$. Tetrahydrofuran was distilled over CaH$_2$ and then over LiAlH$_4$. All distillations were carried out under nitrogen, and the distilled solvents were subjected to three freeze–pump–thaw cycles and stored in a nitrogen-atmosphere drybox.

Infrared spectra were obtained on a Beckman IR-4240 spectrophotometer. Electronic spectra were recorded on an IBM-9430 spectrophotometer using 1.0-cm quartz cuvettes. Corrected luminescence spectra were recorded on a Spex Fluo-Log F-212 spectrofluorimeter. Field desorption mass spectra (FDMS) were obtained with ZAB-HF

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Table I. Electronic Absorption Spectral Data for $Re_2(CO)_{10-n}L_n$ ($n = 1, 2$)[a]

compd	ligand	solvent	band A	band B	band C	band D
			$Re_2(CO)_9L$			
I	CO	hexane		309 (16.4)	275 (13.7)	
		CH_2Cl_2		310 (16.4)	275 (13.6)	
		THF[b]		310 (16.5)	273 (14.0)	
Ia	PMe_3	CH_2Cl_2[c]		332 (13.1)	277 (11.9)	
Ib	PPh_3	CH_2Cl_2[c]		320 (18.9)	289 (26.8)	
Ic	CH_3CN	CH_2Cl_2[b]		324 (10.8)	272 (12.7)	
Id	CH_3NH_2	C_6H_{12}[b]	384	335	308	
		THF[b]	380 (2.3)	334 (11.4)	310 (9.7)	
Ie	pyridine	THF[b]		337 (13.6)	312 (10.0)	291 (10.0)
		CH_2Cl_2	352 (3.1)	335 (13.2)	310 (10.2)	290 (10.1)
If	4-phy[d]	CH_2Cl_2	382 (4.2)	338 (12.5)	315 (10.2)	258 (21.1)
Ig	4-bzy[e]	C_6H_{14}	403 (4.0)	337 (11.3)	305 (10.6)	260 (18.2)
		CH_2Cl_2	400 (4.2)	336 (11.3)	306 (10.3)	262 (20.3)
		CH_3CN	393 (3.8)	336 (11.0)	302 (10.1)	259 (19.7)
			$1,2$-eq,eq-$Re_2(CO)_8L_2$			
IIa	PMe_3[c]	CH_2Cl_2		345 (10.7)	301 (8.0)	
IIb	PPh_3[c]	CH_2Cl_2		340 (17.5)	299 (38.9)	
IIc	CH_3CN[b]	CH_2Cl_2	390	344	297	
IId	dppm	CH_2Cl_2		331 (13.8)	289 (8.8)	
IIe	pyridine	CH_2Cl_2	430 (4.9)	355 (13.8)	288 (11.0)	
IIf	4-phy[d]	CH_2Cl_2	435 (6.8)	352 (11.1)	296 (15.4)	264 (34.6)
IIg	4-bzy[e]	CH_2Cl_2	489 (9.9)	353 (14.3)	292 (18.1)	265 (38.8)
		CH_3CN	480 (6)	350 (11)	296 (14)	264 (40)

[a] λ in nm ($\epsilon \times 10^{-3}$ M^{-1} cm^{-1}). [b] Reference 29a. [c] Reference 29 d. [d] 4-Phenylpyridine. [e] 4-Benzoylpyridine.

mass spectrometer in the Mass Spectrometry Laboratory, School of Chemical Sciences, University of Illinois. Elemental analyses were performed by the University of Illinois Microanalytical Laboratory. Cyclic voltammetric studies were performed on a BAS-100 electrochemical analyzer, using a Pt wire as the working electrode, a Pt bead as the counter electrode, and a Ag/AgCl electrode as the reference electrode. All data were obtained by using a 0.002 M solution of the analyte in dry, degassed acetonitrile that was also 0.1 M in tetrabutylammonium tetrafluoroborate (Bu_4NBF_4). Reversible oxidation of ferrocene was reproducibly observed under these conditions to occur at +477 mV.

Synthesis. $Re_2(CO)_8L_2$ (IIa–g), $Re_2(CO)_8(\mu$-py)(μ-H) (IIIa,b), and $Re_2(CO)_7(\mu$-py)(μ-H)(py) (IVa,b) complexes were prepared according to the published procedure.[29a,b] $Re_2(CO)_9L$ (Ia–g) and $Re_2(CO)_7$-(dppm)(4-bzy) (4-bzy = 4-benzoylpyridine) (IIh) complexes were prepared according to the procedure of Koelle.[30] The complexes were purified by column chromatography on a Florisil column using hexane-/CH_2Cl_2 mixtures as eluents and then recrystallized from toluene/hexane mixtures. All compounds were characterized by IR and FD-MS spectroscopy, and satisfactory elemental analyses were also obtained.

Transient Spectroscopy. The laser flash photolysis apparatus and sample preparation methods have been described previously.[31] Solutions were typically 50–100 μM in the complexes in the appropriate solvents. They were prepared and maintained in the dark prior to flash photolysis. All experiments were conducted at ambient temperatures (22 ± 1 °C) unless otherwise stated.

The experimental setup for obtaining emission decay measurements was identical with that used for the transient absorption decay, except that the probe beam was not turned on following the laser pulse. The excitation wavelength remained 337 nm, and the monochromator was set to observe at the emission maximum as determined from luminescence measurements.

Reactions. All reactions were performed under an argon atmosphere, employing inert-atmosphere manipulation techniques and dry solvents that were degassed by three freeze–pump–thaw cycles. Photochemical reactions were performed by irradiation with a General Electric 275-W sunlamp using Pyrex Schlenk vessels. Solutions were maintained at ambient temperature during photolysis by forced-air cooling of the reaction vessels. The course of the reaction was monitored by IR spectroscopy. Products of the reaction were isolated by column chromatography employing Florisil, using dried solvents as eluents, or by preparative TLC with plates (20 × 20 cm, 2.0 mm silica with UV_{254} fluorescent indicator) obtained from Brinkmann instruments. Typical thermolysis

and photolysis procedures are outlined below.

(a) Thermolysis of $Re_2(CO)_9(4$-bzy). A 0.81-g (1.0-mM) sample of the complex was placed in a 50 mL Schlenk flask containing a magnetic stir bar, in a nitrogen-filled drybox, and 30 mL of dry toluene was transferred to the flask. The flask was removed from the drybox and a water-cooled reflux condenser attached under a stream of argon. The flask was then immersed in an oil bath and heated, so as to bring the solution to a steady reflux. Samples were removed from the flask periodically to monitor the extent of reaction by IR spectroscopy. When all of the reactant had been consumed, the solvent was removed under vacuum and the residue subjected to preparative plate chromatography, using 5:1 hexane/dichloromethane as eluent. Each band was extracted into dichloromethane and identified by IR and FDMS techniques. The only organometallic product isolated was $Re_2(CO)_{10}$ (47%).

(b) Photolysis of $Re_2(CO)_8(4$-bzy)$_2$ in the Presence of CCl_4. A 0.96-g (1.0-mmol) sample of the complex was placed in a 50 mL Pyrex Schlenk flask containing a magnetic stir bar, in a nitrogen-filled drybox, and 30 mL of toluene was added to it. Then, 1.0 mL of carbon tetrachloride (10 mmol) was then transferred to the flask by using a syringe, and the flask was removed from the drybox. The solution was irradiated by using a sunlamp, and samples were removed periodically to monitor the course of the reaction by IR spectroscopy. When all of the reactants had been consumed, the solvent was removed under vacuum and the residue was subjected to column chromatography over Florisil, using a 5:1 hexane/dichloromethane mixture as eluent. $ClRe(CO)_4(4$-bzy) was isolated in 78% yield. An unidentified precipitate was also observed at the end of the reaction.

Results and Discussion

Absorption Spectra. A detailed study of mononuclear d^6 complexes containing pyridine ligands has helped to assign the absorption bands in these complexes to the various electronic transitions.[2a] In the dinuclear systems, transitions involving σ_{M-M} or $\sigma_{M-M}*$ orbitals are expected to create additional spectral features. In order to satisfactorily assign these bands, we studied the absorption spectra of a series of dirhenium complexes containing phosphine or nitrogen ligands.

The lowest energy absorption in $Re_2(CO)_{10}$ as well as in $Re_2(CO)_9L$ and $Re_2(CO)_8L_2$, when L is a trialkylphosphine[2a] or an aliphatic nitrogen ligand[29a] (Ia–d and IIa–d, Table I), has been assigned to a $\sigma_{M-M} \rightarrow \sigma_{M-M}*$ transition. This intense absorption shows a systematic red-shift upon increasing ligand substitution [$Re_2(CO)_{10}$ vs I vs II] in all the complexes, and is relatively insensitive to solvent polarity and the electronic requirements of the ligand. On the basis of these observations, absorption band B in the spectra of the corresponding pyridine complexes (Ie–g and IIe–g, Table I) at comparable wavelengths ($\sim$335 nm for I and $\sim$350 nm for II, respectively) can be assigned to a σ_{M-M}

(29) (a) Gard, D. R.; Brown, T. L. *Organometallics* **1982**, *1*, 1143. (b) Nubel, P. O.; Brown, T. L. *Organometallics* **1983**, *2*, 515. (c) Nubel, P. O.; Brown, T. L. *J. Am. Chem. Soc.* **1984**, *106*, 644. (d) Lee, K.-W.; Brown, T. L. *Organometallics* **1985**, *4*, 1030.
(30) Koelle, U. J. *J. Organomet. Chem.* **1978**, *155*, 53.
(31) Herrick, R. S.; Herrinton, T. R.; Walker, H. W.; Brown, T. L. *Organometallics* **1985**, *4*, 42.

Table II. Electronic Absorption Spectral Data for Dirhenium Complexes[a]

no.	compd	band I	band II	band III	band IV
		Re(0) Compounds			
Ie	Re$_2$(CO)$_9$(py)[b]	352 (3.1)	335 (13.2)	310 (10.2)	290 (10.1)
Ig	Re$_2$(CO)$_9$(bzy)	400 (4.2)	336 (10.3)	306 (10.3)	262 (20.2)
IIe	Re$_2$(CO)$_8$(py)$_2$[b]	430 (4.9)	355 (13.8)	288 (11.0)	
IIg	Re$_2$(CO)$_8$(bzy)$_2$	489 (9.9)	353 (14.3)	292 (18.1)	265 (38.8)
IId	Re$_2$(CO)$_8$(dppm)		331 (13.8)	289 (8.8)	
IIh	Re$_2$(CO)$_7$(dppm)(bzy)	499 (4.2)	359 (8.3)	317 (10.7)	262 (19.7)
		Re(I) Compounds			
IIIa	Re$_2$(CO)$_8$(μ-py)(μ-H)[c]		345 (1.1)	291 (10.2)	262 (8.1)
IIIb	Re$_2$(CO)$_8$(μ-bzy)(μ-H)			278 (12.4)	256 (19.3)
IVa	Re$_2$(CO)$_7$(μ-py)(μ-H)(py)			297 (11.3)	264 (13.1)
IVb	Re$_2$(CO)$_7$(μ-bzy)(μ-H)(bzy)			313 (10.1)	254 (25.3)
Va	Re(CO)$_3$(py)$_2$Cl[d]			294 (8)	261 (10)
Vb	Re(CO)$_3$(bzy)$_2$Cl[e]			330 (11.1)	255 (30)

[a] In CH$_2$Cl$_2$ at 22 ± 1 °C; λ in nm ($\epsilon \times 10^{-3}$ M^{-1} cm^{-1}). [b] Reference 29a. [c] Reference 29b. [d] Reference 24a. [e] Reference 24c.

$\rightarrow \sigma_{M-M}*$ transition. Similar results have also been obtained[32] for a series of dirhenium isocyanide complexes of the general formula Re$_2$(CO)$_{10-n}$(CNR)$_n$ ($n = 1, 4$).

In dirhenium phosphine and isocyanide complexes, the d$_{\pi(M)}$ $\rightarrow \sigma_{M-M}*$ transitions as well as the MLCT ($\sigma_{M-M} \rightarrow \pi_L*$) and intraligand transitions are assigned to be at higher energy than the $\sigma \rightarrow \sigma*$ transition.[32,33] Similarly, a common character can be ascribed to the bands listed as band C in Table I. This band may be due to a d$_{\pi(M)} \rightarrow \pi_{CO}*$ transition. Band D is likely to arise from intraligand transitions in the pyridine-substituted complexes. Thus, the ligand effects of pyridine ligand in the electronic spectra of dirhenium complexes are not drastically different from those of phosphine and alkyl isocyanide ligands.

The lowest energy absorption band (band A) in the dinuclear complexes I and II shifts to longer wavelength as the substituent on the pyridine ligand becomes increasingly electron withdrawing. This well-resolved lowest energy absorption in compounds Ie-g and IIe-g (Table I) is broad, low in intensity, and exhibits solvatochromic behavior. It can be assigned, following Stufkens et al.,[21c] to an MLCT absorption corresponding to a d$_{\pi(M)} \rightarrow \pi_L*$ transition. Alternatively, this band could be assigned to a $\sigma_{M-M} \rightarrow \pi_L*$ transition.[27] The data presented here show that the effect of systematic variation in the electronic characteristics of the pyridine ligands upon the absorption spectra of these dinuclear d^7-d^7 complexes parallels that seen in mononuclear d^6 systems.[2a]

The UV-vis absorption spectra of a series of dirhenium complexes containing the 4-benzoylpyridine ligand (Table II) were obtained in order to study the effect of changing the bonding mode and oxidation state on spectral characteristics (Figure 2). Data for the corresponding unsubstituted pyridine complexes are also tabulated to aid the assignment of transitions that terminate in the π_L* level. Of these compounds, Ie,g and IIe,g possess σ-bound pyridines, IIh and IVa,b have a σ-bound pyridine as well as a bridge, consisting of dppm or μ-pyridyl and μ-H ligands, while IIIa,b have bridging pyridine ligands, but lack the σ-bound pyridine, and Va,b are mononuclear Re(I) complexes possessing two σ-bound pyridines.[25a] Analysis of the absorption spectra of these compounds suggests that they fall into two broad categories, those with Re(0) centers and those that have formally Re(I) centers. Members of the former class of compounds (I and II) all show a four-band spectral pattern, the assignment of which has been discussed above.

Compounds III-V all possess formally Re(I) centers, in which the greater nuclear charge should lower the energy of the d orbitals, thus increasing the energies of transitions between the metal-based and ligand-based orbitals, e.g. MLCT transitions; the effect on metal-centered transitions, such as $\sigma \rightarrow \sigma*$, d $\rightarrow$ d or d $\rightarrow \sigma*$, is less easily predicted. X-ray crystallographic data on Re$_2$(CO)$_7$(μ-py)(μ-H)(L), where L = CO or (CH$_3$)$_3$NO,[29b] indicate Re-Re bond distances of 3.20 and 3.23 Å, respectively,
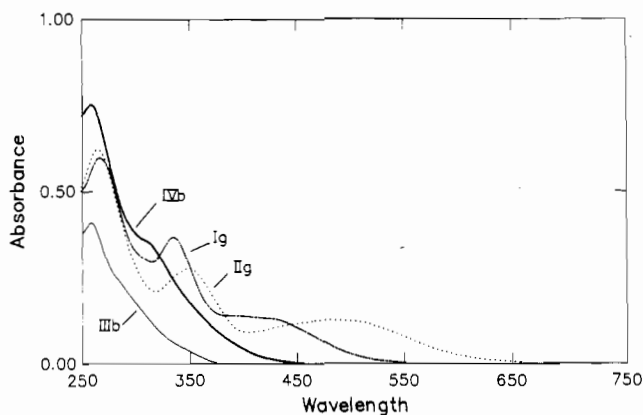

Figure 2. Electronic absorption spectra of dichloromethane solutions of dirhenium 4-benzoylpyridine complexes Ig (- - -) IIg (···) and IIIb (—) at 5 × 10^{-5} M and IVb (—) at 2.5 × 10^{-5} M.

greater than the 3.04 Å observed in Re$_2$(CO)$_{10}$.[34] This observation would suggest that the absorption corresponding to the $\sigma \rightarrow \sigma*$ transition in the bridged species should occur at lower energies than in Re$_2$(CO)$_{10}$, whereas the reverse is observed. However, in a series of isocyanide complexes, substitution of CO by ligands with greater steric requirements does not lead to an increased Re-Re bond length.[32] On the basis of high absorptivity as well as insensitivity to solvent polarity, the lowest energy absorption in IIIb and IVb may be assigned to a $\sigma_{M-M} \rightarrow \sigma_{M-M}*$ transition. In a study of d^8-d^8 systems, Gray et al.[9] have concluded that there is no simple correlation of the $\sigma \rightarrow \sigma*$ absorption energy with the ground-state bond distances and force constants, due to mixing of states. Considerable distortions of an unconstrained Re-Re bond may be expected in compounds III and IV due to the bridging ligands; hence, extension of the results found in compounds I and II to the absorption spectra of these compounds may not be appropriate.

Comparison with the 330-nm band assigned to the d $\rightarrow \pi*$ MLCT absorption in V suggests that the MLCT absorption in IVb would occur at an energy lower than that assigned as the $\sigma \rightarrow \sigma*$ absorption. Though no clear absorption band or shoulder is seen in the spectrum of IVb, the long tail of the lowest energy absorption suggests that a low-intensity MLCT band might be buried under the tail of the more intense absorption assigned to the $\sigma \rightarrow \sigma*$ transition. Indirect evidence for this is found in the excitation spectrum of IVb (vide infra). Attempts to identify the MLCT absorption band by a solvatochromic red shift were unsuccessful; no separate low-energy absorption feature was observed even in nonpolar solvents such as hexane.

Emission Spectroscopy. The presence of a distinct MLCT absorption in the spectra of pyridine-substituted metal carbonyl

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Table III. Emission Spectral Data for Dirhenium Complexes[a]

compd	solvent	λ_{ab}[b]	λ_{ex}	λ_{em}
Ig	mecyx (77 K)	400	301, 333*, 400, 428	628
IIIb	hexane	278	338	430*, 540
	2-methf (77 K)		294, 335*	430*, 462, 495, 540
	mecyx (77 K)		273, 295, 340*	436*, 468, 505, 550
IVb	hexane	313	291, 341*, 364	563
	toluene	313	292, 340, 365*	570
	CH$_2$Cl$_2$	313	293, 340, 365*	612
	THF	313	293, 345, 365*	617
	9:1 toluene/CH$_3$CN	313	291, 342, 365*	594
	4:1 toluene/CH$_3$CN	312	295, 365*	605
	2:1 toluene/CH$_3$CN	312	298, 365*	616
	1:1 toluene/CH$_3$CN	312	300, 365*	632
	CH$_3$CN	312	303, 365*	645
	polyMMA[c]		300, 355*	540
	2-methf (77 K)		300, 335*, 365	435, 469, 493*
	mecyx (77 K)		300, 340*, 365	543
Vb[d]	benzene	330	330	598
	EPA (77 K)		330	516
4-bzy[e]	CH$_2$Cl$_2$	338	335	415
	mecyx (77 K)		340	420, 451*, 485, 523

[a] At 22 ± 1 °C unless otherwise noted; λ in nm; excitation spectra recorded at λ_{em} = λ of the most intense band (denoted by an asterisk) and vice versa. [b] Lowest energy absorption maximum. [c] IVb dispersed in poly(methyl methacrylate) film at ambient temperature. [d] Reference 24c. [e] 4-Benzoylpyridine.
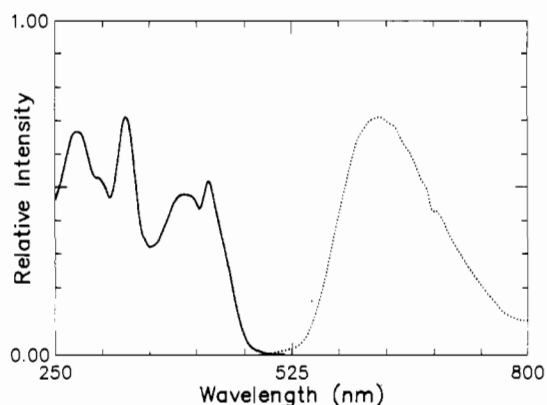

Figure 3. Corrected emission (λ_{ex} = 400 nm) (···) and excitation (λ_{em} = 600 nm) (—) spectra of Ig in methylcyclohexane glass at 77 K.

complexes is often accompanied by a long-lived excited state that decays radiatively.[7b] Compound Ig does not luminesce in hexane solutions at ambient temperatures, and the observed room-temperature emission (λ_{max} = 520 nm) in halocarbon solvents, similar to that of Vb,[24d] is attributed to the presence of emissive ClRe-(CO)$_4$(4-bzy) in solution that is formed by a photochemical atom abstraction reaction. A broad unstructured emission from Ig is observed at 630 nm at 77 K in methylcyclohexane (mecyx) glass (Table III). This emissive state is accessible by excitation into the MLCT band at 400 nm (Figure 3), suggesting that it is a charge-transfer state. The emission from a mononuclear analogue, such as ClRe(CO)$_4$L (L = PPh$_3$[21f] or 4-benzoylpyridine), is blue-shifted as compared to the emission from Ig, suggesting that the emissive state in Ig is $\sigma_{M-M}\pi_L^*$ or $d_M\pi_L^*$. Emission was not observed from compounds IIg and IIh, neither at room temperature nor in low-temperature glasses. It is possible that these complexes emit at wavelengths below 800 nm, the detection limit of the instrument. Compound Vb has been shown to emit both at ambient temperatures in solution as well as in low-temperature glasses.[24d]

Compound IIIb exhibits an intense, short-lived emission at 430 nm in hydrocarbon solvents at ambient temperatures, similar in energy to the fluorescent emission from the free ligand. A weak, unstructured, longer lived emission is also detected at 540 nm. A corresponding emission is not observed from the free ligand in fluid solutions at room-temperature. We assign the weaker 540-nm emission from IIIb to be an MLCT emission, since it is similar in energy to the more intense MLCT emission observed in IVb, to be discussed below. However, since no distinct MLCT
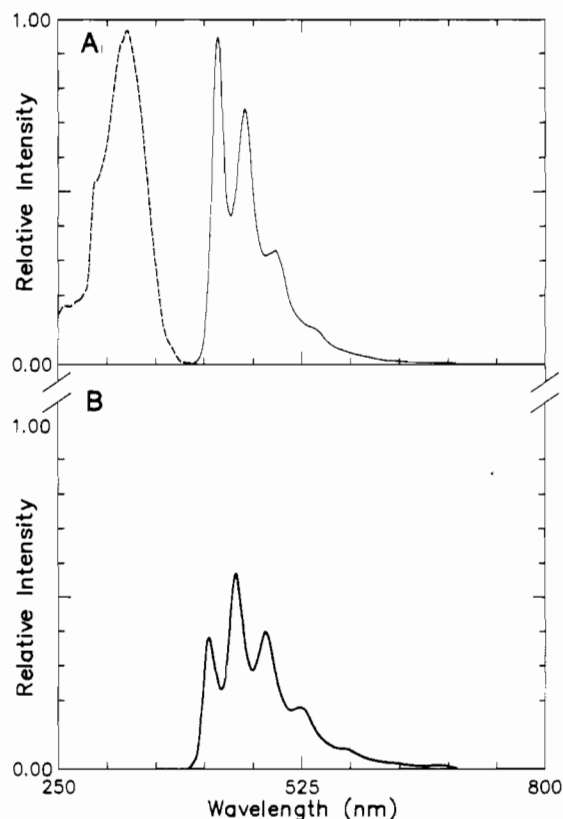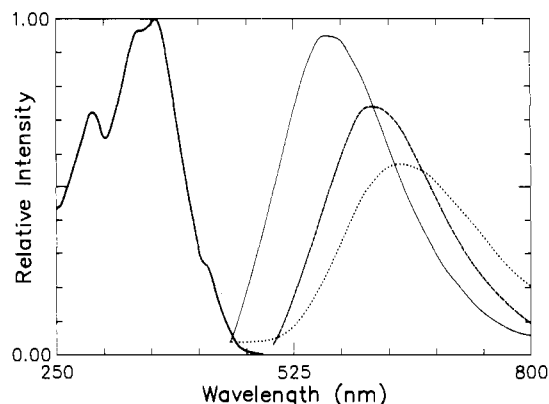

Figure 4. (A) Corrected emission (λ_{ex} = 340 nm) (—) and excitation (λ_{em} = 520 nm) (- - -) spectra of IIIb in 2-methyltetrahydrofuran glass at 77 K. (B) Corrected emission spectrum of 4-benzoylpyridine in 2-methyltetrahydrofuran glass at 77 K.

band is seen in the absorption spectrum of IIIb, it is likely that the observed emission at 540 nm occurs by crossover to the MLCT state from the intraligand excited state.

The emission spectrum of IIIb in 2-methyltetrahydrofuran (2-methf) (Figure 4A) glass at 77 K shows four bands. It closely resembles the emission spectrum of the free ligand at 77 K (Figure 4B), but all the band maxima in the complex are red-shifted relative to that of the free ligand.[23c] The excitation spectrum of IIIb shows an intense band at 338 nm, which also matches with that of the free ligand. Since care was taken to ensure that no free 4-benzoylpyridine was present, these observations suggest that

Figure 5. Corrected emission (λ_{ex} = 370 nm) (---) and excitation (λ_{em} = 600 nm) (—) spectra of IVb in methylene chloride solution in 295 K. Corrected emission spectra in hexane (—) and acetonitrile (···) are also shown.

Table IV. Rate Constants for Transient Absorption Decay of IIIb[a]

solvent	reagent	concn, M	$10^{-6}k_a$, s^{-1}
hexane			30.2 ± 1.1
toluene			28.6 ± 0.9
CH$_3$CN			16.6 ± 0.8
hexane	PMe$_3$	0.001	54.6 ± 2.8
hexane	P^{n}Bu$_3$	0.017	55.3 ± 2.6
hexane	P(O^{i}Pr)$_3$	0.014	41.1 ± 2.1
hexane	BzBr	0.022	30.8 ± 0.9
hexane	Bu$_3$SnH	0.011	31.6 ± 1.2
toluene	MA[b]	0.014	73.8 ± 2.4
CH$_3$CN	4-Bzy$^+$me[c]	0.003	78.9 ± 2.6

[a] At 22 ± 1 °C; monitored at 600 nm. [b] Maleic anhydride. [c] 1-Methyl-4-benzoylpyridinium tetrafluoroborate.

Table V. Rate Constants for Transient Absorption and Emission Decay of IVb

| solvent/reagent	$10^{-6}k_a$, s^{-1}	$10^{-6}k_e$, s^{-1}
hexane	0.418 ± 0.002	0.391 ± 0.002
toluene	0.428 ± 0.007	0.375 ± 0.004
benzene	0.416 ± 0.006	0.355 ± 0.005
CH$_2$Cl$_2$	2.34 ± 0.04	1.90 ± 0.03
CHCl$_3$	1.77 ± 0.01	1.47 ± 0.01
tetrahydrofuran	1.83 ± 0.09	1.68 ± 0.04
9:1 toluene/CH$_3$CN	1.40 ± 0.02	1.17 ± 0.02
4:1 toluene/CH$_3$CN	2.32 ± 0.03	2.16 ± 0.02
2:1 toluene/CH$_3$CN	3.68 ± 0.04	3.31 ± 0.08
1:1 toluene/CH$_3$CN	5.41 ± 0.09	4.44 ± 0.15
CH$_3$CN	12.1 ± 0.24	9.86 ± 0.16
2-methf (77 K)		
λ = 450 nm		0.0012 ± 0.0001
λ = 550 nm		0.0084 ± 0.0003
mecyx (77 K)		
λ = 550 nm		0.068 ± 0.003
toluene/CCl$_4$ (0.12 M)	0.405 ± 0.003	0.376 ± 0.002
toluene/Bu$_3$SnH (0.05 M)	0.454 ± 0.04	0.402 ± 0.004

[a] At 22 ± 1 °C; monitored at 540 nm (k_a) and 575 nm (k_e) unless otherwise noted.

the low-temperature emission of IIIb occurs from a ligand-based nπ* (IL) state that is only weakly perturbed by ligation to the dirhenium template. The intraligand nature of this emission is also substantiated by the lack of observable emission from compound IIIa under identical conditions.

Replacement of a CO in IIIb by a σ-bound 4-benzoylpyridine ligand to form IVb changes the emissive behavior of the complex. Compound IVb luminesces strongly in fluid solution at ambient temperatures (Figure 5), and the wavelength of the emission maximum shows a solvent dependence, ranging from 563 nm in hexane to 645 nm in acetonitrile (Table III); this red shift in more polar solvents, also observed in other complexes,[24d] suggests that the emission occurs from an MLCT state. Additionally, the rate of emission decay increases (Table V) and the emission intensity
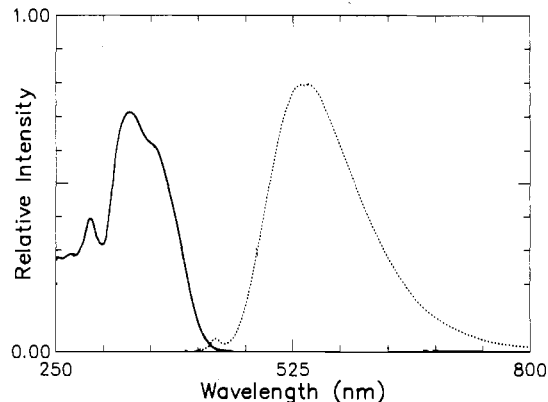
Figure 6. Corrected emission (λ_{ex} = 370 nm) (···) and excitation (λ_{em} = 540 nm) (—) spectra of IVb in methylcyclohexane glass at 77 K.
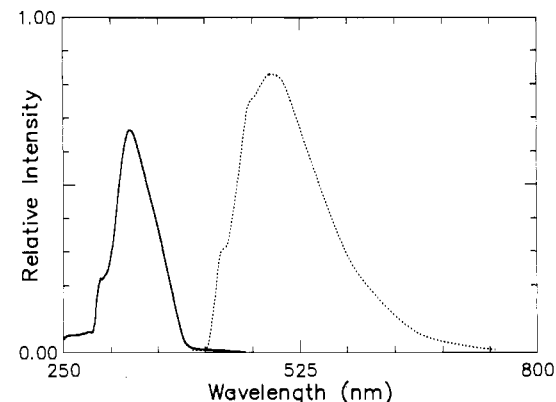
Figure 7. Corrected emission (λ_{ex} = 340 nm) (—) and excitation (λ_{em} = 520 nm) (···) spectra of IVb in 2-methyltetrahydrofuran glass at 77 K.

is diminished in more polar solvents, indicating a faster nonradiative decay in polar media.

Two distinct emissive states may be expected in IVb, due to the presence of both the σ-bound and the μ-bound benzoylpyridine ligands. However, only an unstructured MLCT emission is observed from IVb in fluid solution, in a variety of solvents. The emission spectrum of IVb in mecyx glass at 77 K (Figure 6) or in a poly(methyl methacrylate) film at ambient temperature, also shows a broad, unstructured band, more intense and blue-shifted as compared to the spectrum in fluid solution. The rate of emission decay also decreases by about 5–30-fold; such behavior is typical of an MLCT emission.[6]

The emission from IVb in 2-methf glass at 77 K (Figure 7) is quite different from that in mecyx glass, in that the emission maximum is significantly more blue-shifted and the spectrum shows a good deal of structure; the rate of emission decay appears to be wavelength-dependent as well (Table V). The emission band maxima of IVb match exactly the emission maxima of IIIb. Thus, the structured emission from IVb in 2-methf glass appears to be a composite of the broad, faster MLCT emission and a structured, slower IL emission (similar to that observed from IIIb), suggesting that IVb exhibits multiple emission. The molecular integrity of the compound was confirmed by UV and IR spectroscopy prior to and after acquisition of the emission spectrum, so that the observed multiple emission is unlikely to be due to impurities or decomposition of the compound. DeArmond has attributed[35a] the origin of multiple luminescence to either two spatially isolated multiply emitting systems (as in [Rh(bpy)$_2$(phen)]$^{3+}$)[35b] or two states of distinct orbital origin (as in ClRe(CO)$_3$ (4-phy)$_2$ (4-phy = 4-phenylpyridine)[25a] that do not interconvert with facility. The latter possibility seems to be the more reasonable in the case of IVb. The polarity rather than the rigidity of the glassy medium

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(b) Halper, W.; DeArmond, M. K. *J. Lumin.* **1972**, *5*, 225.

appears to influence the change in emissive behavior of IVb. Multiple emission has usually been observed upon changing the medium from room-temperature fluid solutions to low-temperature glasses; to our knowledge, IVb provides the first instance in which multiple emission can be induced at low temperatures merely by changing the polarity of the glassy medium.

Since the emission maxima of IIIb in 2-methf and mecyx glasses are identical, the polarity of the medium appears not to affect the IL state energy. Thus, the blue shift in the emission maximum of IVb upon going from mecyx (Figure 6) to 2-methf (Figure 7) glass points to a shift in the energy of the MLCT state. In the nonpolar mecyx glass, the MLCT state of IVb is clearly the lowest energy emissive state, because only the MLCT emission is observed. Charge-transfer absorption bands are known to undergo a solvatochromic blue shift in a more polar solvent.[7b] Thus, it is reasonable to assume that the energy gap between the ground and ^{1}MLCT states is raised in a more polar medium, so that it is comparable to the energy gap between the ground and ^{1}IL states; excitation would then lead to the population of both singlet states. Since interconversion between the two states would be slower at 77 K, both the broad MLCT emission and the structured IL emission are observed. In the nonpolar mecyx glass, due to a greater difference in the energy gap between the IL and the MLCT states, the vibronic coupling between the two states is strengthened[7b] and only the lower energy MLCT emission is observed.

Because the emissive states in the two related compounds IIIb (IL) and IVb (MLCT) appeared to be different, the emission excitation spectra of dirhenium 4-benzoylpyridine complexes listed in Table III were obtained to provide information regarding the excitation energy required to populate the emissive state. In most organic and organometallic compounds studied, the positions of the bands in the excitation spectra are found to match those in the absorption spectra. This is also found to be true of Ig in mecyx glass, at 77 K. The excitation spectrum of $Mo(CO)_5$(4-bzy) is reported to differ from its absorption spectrum,[20a] in that a band assigned to a ligand-field transition in the absorption spectrum is absent in the excitation spectrum. Lees suggests that this absorption leads to a dissociative state that results in ligand loss from the complex; hence, the emissive state is not accessible from this state. The excitation spectrum of IIIb in low-temperature glasses shows a maximum at 337 nm, with a shoulder at 295 nm, whereas the lowest energy absorption feature is at 278 nm. Similarly, the excitation spectrum of IVb in fluid solution shows a maximum at λ_{ex} = 365 nm in CH_2Cl_2, with shoulders at 340 and 295 nm, as contrasted with an observed absorption maximum at 313 nm. Thus, the nature of the excited states populated by excitation at 340 and 365 nm cannot be deduced from the absorption spectrum of IVb. It is possible that absorptions at these wavelengths are low in intensity and are buried under the tail of the 313-nm band. If it is assumed that the excitation maximum at 365 nm corresponds to the energy difference between ground and MLCT states, while the lowest energy absorption maximum (at 312 nm) corresponds to the $\sigma \rightarrow \sigma^*$ transition, the discrepancy between the absorption and excitation spectra suggests that the emissive state is only inefficiently accessible from the $\sigma\sigma^*$ state.

Wagner et al. have demonstrated that intramolecular energy transfer, between states where poor orbital overlap is anticipated, is slow enough for fast chemical reactions such as γ-hydrogen abstraction to compete successfully.[36] In the mononuclear Ru(II) systems, energy transfer from an $n\pi^*$ ligand-localized excited state to an MLCT state or an IL state localized on another ligand was estimated to be as slow as 10^8 s^{-1}. In analogous dinuclear complexes such as III or IV, population of the $\sigma\sigma^*$ state by photoexcitation, followed by conversion to the lower energy MLCT state, would constitute an intramolecular electron-transfer reduction of the ligand. Although this process is distinct from the direct population of the MLCT state, it would be practically indistinguishable in most cases. The intramolecular electron-transfer process might, in favorable cases, be seen by transient spectroscopy employing picosecond laser flash photolysis techniques. The excitation spectrum of IVb suggests that irradiation into the $\sigma \rightarrow \sigma^*$ band does lead, albeit with low efficiency, to the formation of the emissive MLCT state. The low efficiency of this process (since the excitation maximum is away from the lowest energy absorption) is indicative of poor overlap between the metal-based ($\sigma\sigma^*$) and MLCT ($\sigma\pi^*$) states, as has been found in other systems.[36b] Since the emission is observed to attain its maximum intensity at the shortest time observable in the experiment, we can estimate the lower limit of the rate constant for the growth of the emissive species (or the intramolecular electron transfer) to be 5×10^7 s^{-1}.

Transient Spectroscopy. Flash photolysis techniques may be employed to obtain the rate of decay of absorption due to a photogenerated transient species and also to obtain the rate of decay of emissive transients. In previous studies of excited-state spectra of emissive inorganic compounds, the rate of decay of the absorption transient was found to match the rate of emissive decay.[7a] Thus, it is possible to probe the excited state reactivity of such complexes by transient absorption as well as emission spectroscopy. The absorption spectrum of Ig, IIg, and IIh in the visible region interferes in each case with acquisition of the transient absorption spectra. No absorption transients were detected from compounds IIIa or IVa. Upon excitation at 337 nm with a pulsed N_2 laser, compound IIIb exhibits a broad transient absorption with a maximum at ~630 nm, which decays in hexane and acetonitrile solutions at ambient temperature with first-order rate constants of 3.7×10^7 s^{-1} and 1.66×10^7 s^{-1}, respectively. Neither 4-benzoylpyridine nor 1-methyl-4-benzoylpyridinium tetrafluoroborate shows a transient absorption at 630 nm under the same conditions, suggesting that the transient absorption of IIIb corresponds to an MLCT state. The rate constant for transient absorption decay is comparable to the rate constant for the decay of the emission (~1×10^7 s^{-1}) of IIIb at λ_{em} = 540 nm, suggesting that the observed absorption transient corresponds to this MLCT emissive state.

The rate of transient absorption decay of IIIb is not enhanced by the addition of atom-transfer reagents such as benzyl bromide or tributyltin hydride. Addition of phosphines increases the rate of decay; maleic anhydride and 1-methyl-4-benzoylpyridinium tetrafluoroborate also effect a similar rate enhancement, suggesting that electron-transfer quenching of the transient may be implicated. The first-order rate constants of the decay of transient absorption of IIIb by selected reactants are listed in Table IV. In addition to the intense transient absorption, a longer-lived absorption, much lower in intensity, is also observed in hexane solutions. This residual absorption is not observed in a coordinating solvent such as acetonitrile; it is likely to be due to an intermediate resulting from photochemical CO loss.

Compound IVb also shows an intense transient absorption in hexane solution, with λ_{max} at ~580 nm. The growth of the absorption is complete within the shortest time scales examined, suggesting that the lower limit on the rate of formation of this state is 5×10^7 s^{-1}. This broad absorption appears to be solvent-dependent; the absorption maximum shifts to shorter wavelengths (~540 nm) in a more polar solvent such as acetonitrile. The rate of transient absorption decay is 30-fold faster in acetonitrile as compared with hexane (Table V). The enhancement in the rate of decay parallels the increased dielectric constant of the medium. As seen in other complexes that possess MLCT emissive states,[7b] the solvent dependence of the rate of transient absorption or emission decay is likely to be due to an enhancement in the rates of nonradiative decay in more polar solvents. The rate of transient absorption decay matches the rate of emissive decay in a number of solvents and in the presence of a variety of reagents, suggesting that the emissive state is the one giving rise to the transient absorption.

Transient absorption is quenched by reagents such as trialkylphosphines, triphenylamine, maleic anhydride, quinones, anthracene, *trans*-stilbene, and a series of substituted *N*-

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methylpyridinium salts. The kinetics of the transient absorption decay as well as emission decay of IVb in the presence of energy- and electron-transfer reagents are discussed in a separate section.

Chemistry of the Dirhenium Complexes. To better understand the chemistry of the bridged pyridyl compounds III and IV, the reactivities of dirhenium complexes containing both the 4-benzoylpyridine ligand and a "free" Re–Re bond, i.e. compounds Ig and IIg, as well as IIh with a bridging ligand, need to be examined. As noted earlier, the intense absorptions of these complexes in the visible region interfere with the study of their reaction kinetics by transient absorption spectral measurements. Thermolysis or photolysis of Ig in hydrocarbon solvents leads to the formation of Re$_2$(CO)$_{10}$. We observe that both Ig and IIg are thermally and photochemically reactive toward atom-transfer reagents such as CCl$_4$ and tributyltin hydride. Thermal and photochemical substitution reactions of Ig and IIg, by phosphines or pyridine, are also observed.

In analogy to the reactivity of the corresponding pyridine complex IIe, refluxing IIg in toluene results in the formation of IVb, traces of IIIb, and Re$_2$(CO)$_{10}$. A similar reaction obtains under photolysis, but decomposition, with the formation of Re$_2$(CO)$_{10}$, predominates. The photochemical atom-transfer reaction of IIh with CCl$_4$ is much less efficient than that of Ig or IIg. Our results are similar to those obtained in other dirhenium complexes,[21c,27] suggesting that the presence of a low-energy MLCT absorption in Ig and IIg is not sufficient to prevent homolysis of the "free" dirhenium compounds. On the other hand, the dppm-bridged compound IIh shows a greater stability under thermal and photochemical reaction conditions.

As in the case of the corresponding pyridine compounds IIIa and IVa,[29a] both IIIb and IVb are quite robust thermally and photochemically, presumably due to the presence of the bridging ligands. Prolonged reflux or photolysis in toluene leads to decomposition in both cases; mononuclear rhenium complexes and Re$_2$(CO)$_{10}$ have been identified in the resulting solution by IR spectroscopy. Both IIIb and IVb are less reactive than Ig or IIg to thermal or photochemical ligand substitution, but the σ-bound 4-benzoylpyridine in IVb can be replaced by CO to form IIIb, with prolonged heating under CO pressure. However, a similar thermal reaction with PMe$_3$ leads to a slow formation of CO-substituted product rather than replacement of 4-benzoylpyridine; photoreaction also yields similar results. That the σ-bound pyridine is not substituted under photolysis is not surprising, since the binding of benzoylpyridine to Re in the charge-separated MLCT state should be stronger than that in the ground state.[2a]

The photoreactivity of IIIb and IVb might be expected to result from the generation of an orbital vacancy at the dinuclear metal center in the MLCT excited state. However, no photochemically induced atom-transfer reactions are observed. Photolysis of IIIb and IVb in neat CCl$_4$ or in the presence of a 100-fold excess of Bu$_3$SnH did not lead to any new products, based upon monitoring the reaction products by IR spectroscopy; additionally, the first-order rate constant for the decay of the transient absorption and emission were found to be no faster in the presence of these reagents (Table VI). The observed lack of reactivity is thought to be the result of steric crowding around the dirhenium center by the ligands, preventing the approach of atom-transfer reagents. Thus, compounds III and IV appear to be significantly less reactive, both thermally and photochemically, than the corresponding unbridged compounds. However, reactivity toward electron-transfer donors confirms the presence of a metal-centered SOMO in the excited state.

Electron-Transfer Reactivity of IVb. (a) Reactivity toward Electron Donors. If photoexcitation of IVb leads to the creation of a SOMO in the Re–Re σ bonding orbital, it is reasonable to expect that the resulting excited state should behave as a better electron acceptor than the ground state. We observe that N,N-dimethyl-p-toluidine quenches both the excited state emission and transient absorption of IVb, at concentrations low enough to suggest diffusion-controlled rates of quenching (Table VI). Triphenylamine also quenches the excited state; the resulting long-lived cationic species, NPh$_3^+$, can be observed by its transient

Table VI. Rate Constants for Reactions of IVb with Neutral Electron Donors[a]

donor	concn, M	$10^{-6}k_a$, s^{-1}	$10^{-6}k_e$, s^{-1}	$10^{-8}k_q$, M^{-1} s^{-1} (r)[b]
none		0.428 ± 0.007	0.375 ± 0.004	
N,N-dmp[c]	0.0005	>40	>40	d
Ph$_3$N	0.0041		7.96 ± 0.18	19.4 (1.00)
pyridine	0.12	0.720 ± 0.003	0.623 ± 0.005	
4-bzy	0.011	0.577 ± 0.05	0.610 ± 0.03	
PMe$_3$	0.053	23.6 ± 0.7	20.5 ± 0.6	3.64 (0.98)
P(^{n}Bu)$_3$	0.051	18.7 ± 0.1	16.5 ± 0.3	2.15 (0.99)
P(^{i}Pr)$_3$	0.036	7.36 ± 0.08	6.7 ± 0.07	1.02 (1.00)
P(OEt)$_3$	0.058	0.448 ± 0.009	0.427 ± 0.010	0.046 (0.99)
P(O^{i}Pr)$_3$	0.202	0.582 ± 0.003	0.566 ± 0.002	0.011 (0.99)
P(OPh)$_3$	0.0060	5.03 ± 0.05	4.92 ± 0.47	6.27 (1.00)
P(C$_6$H$_5$)$_3$	0.010	1.71 ± 0.49	1.60 ± 0.27	1.13 (1.00)
P(p-tolyl)$_3$	0.010	3.05 ± 0.66	2.84 ± 0.10	3.71 (1.00)
P(p-anisyl)$_3$	0.011	14.6 ± 0.4	12.7 ± 0.6	13.2 (0.99)
P(p-ClPh)$_3$	0.010	0.737 ± 0.016	0.677 ± 0.025	0.57 (0.98)
dppb	0.010	4.21 ± 0.26	3.75 ± 0.20	2.12 (1.00)

[a] At 22 ± 1 °C in toluene; monitored at 540 nm (k_a) and 575 nm (k_e) unless otherwise noted. [b] From a Stern–Volmer plot using first-order emission rate constants obtained at five different concentrations; r = correlation coefficient. [c] N,N-Dimethyl-p-toluidine. [d] Diffusion limited.

absorption at 650 nm,[37] consistent with an electron-transfer mechanism for the quenching reaction. A Stern–Volmer plot yields a quenching rate constant of 1.9 × 10^9 M^{-1} s^{-1}.

Trialkyl- and triarylphosphines are also found to quench the excited state emission of IVb efficiently. A slow photochemical CO substitution reaction by phosphines is observed upon continuous photolysis, but the rates are not nearly rapid enough to suggest that substitution is the cause for quenching of the excited state. Additionally, a solution of IVb and a 100-fold excess of trimethylphosphine shows identical infrared spectra prior to and after laser flash photolysis, suggesting that extensive substitution has not occurred. The quenching of the emission by phosphines obeys Stern–Volmer kinetics (Table VI). The relative insensitivity of the quenching rate constant (k_q) to the changes in steric requirements of the donor [PMe$_3$ vs P(^{i}Pr)$_3$ or PPh$_3$], as contrasted with a very strong dependence on the electron donor ability [P(^{i}Pr)$_3$ vs P(O^{i}Pr)$_3$], also points to an electron-transfer mechanism. Electronic effects are manifested in the relative reactivities of a series of para-substituted triphenylphosphines (Table VI); p-methyl (k_q = 3.71 × 10^8 s^{-1}) and p-methoxy (13.2 × 10^8 s^{-1}) substituents enhance the rate as compared to PPh$_3$ (1.13 × 10^8 s^{-1}), while a p-chloro (0.57 × 10^8 s^{-1}) substituent retards the rate of quenching. A bidentate phosphine such as bis(diphenylphosphino)butane (dppb), which can stabilize its substitution product by chelation, also leads to no net substitution after flash photolysis. The quenching rate constant of dppb (2.12 × 10^8 s^{-1}) is almost twice that of triphenylphosphine, probably because two donor sites are available per molecule. All these observations suggest that the phosphines react solely as electron-transfer reagents in these reactions. No net reaction is observed as a result of flash photolysis, presumably because a back-electron-transfer reaction occurs upon diffusive recombination of the charged products. Energy-transfer quenching processes by trialkylphosphines can be ruled out, since no low-lying acceptor levels are present in these compounds.

Another evidence for an electron-transfer quenching mechanism is the observation of a new absorption transient at 420 nm in the reactions of IVb with triarylphosphines and triphenyl phosphite as donors. This transient absorption, which grows in at a rate comparable to the rate of emission decay of IVb*, is not observed during laser flash photolysis of the phosphines or IVb separately. The transient triphenylphosphine cation, PPh$_3^+$, is known to absorb at 400–425 and 520–600 nm,[38] suggesting that the transient absorption at 420 nm in the flash photolysis of IVb in the presence of PPh$_3$ is due to this species. A similar reactivity of phosphines

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Table VII. Rate Constants for Reactions of IVb with Cationic Quenchers[a]

reagent	E_T, kcal mol^{-1} ($E_{1/2}$, V)[b]	concn, M	$10^{-6}k_a$, s^{-1}	$10^{-6}k_e$, s^{-1}	$10^{-8}k_q$, M^{-1} s^{-1} (r)[c]
none			0.428 ± 0.007	0.375 ± 0.004	
naphthalene	60 (−2.25)	0.020	0.441 ± 0.010	0.393 ± 0.012	
fluorene	68 (−2.27)	0.010	0.484 ± 0.011	0.456 ± 0.010	
trans-stilbene	49 (−2.22)	0.0030	3.15 ± 0.17	2.83 ± 0.03	2.31 (0.99)
anthracene	42 (−1.41)	0.0005	>40	>40	g
MA[d]	(−0.84)	0.010	1.38 ± 0.07	1.20 ± 0.12	0.68 (0.99)
2,3-Me$_2$MA		0.020	3.02 ± 0.05	2.84 ± 0.04	0.54 (0.98)
2,3-Cl$_2$MA		0.0080	2.59 ± 0.06	2.35 ± 0.04	1.34 (0.99)
PA[e]	(−1.31)	0.014	1.46 ± 0.03	1.19 ± 0.03	0.58 (0.99)
p-quinone	50 (−0.48)	0.0050	2.84 ± 0.05	2.89 ± 0.07	1.87 (0.97)
2,6-dmq[f]	(−0.67)	0.010	1.78 ± 0.04	1.64 ± 0.04	0.98 (0.98)
duroquinone	52 (−0.84)	0.014	2.98 ± 0.04	2.84 ± 0.03	0.74 (0.98)

[a] At 22 ± 0.2 °C in toluene; monitored at 540 nm (k_a) and 575 nm (k_e). [b] E_T = triplet energy of the acceptor from ref 40b,c. $E_{1/2}$ = polarographic half-wave potential for the A/A$^-$ couple, vs SSCE, in CH$_3$CN, μ = 0.1 M (Et$_4$NClO$_4$), from ref 40a. [c] From a Stern–Volmer plot using first-order emission rate constants obtained at five different concentrations; r = correlation coefficient. [d] Maleic anhydride. [e] Phthalic anhydride. [f] 2,6-Dimethyl-*p*-quinone. [g] Diffusion limited.

Table VIII. Rate Constants for Reactions of IVb with Cationic Electron Acceptors[a]

reagent	concn, M	$E_{p,c}$,[b] V	$10^{-6}k_a$, s^{-1}	$10^{-6}k_e$, s^{-1}	$10^{-8}k_q$, M^{-1} s^{-1} (r)[c]
none			5.41 ± 0.07	4.44 ± 0.15	
^{n}Bu$_4$NBF$_4$	0.020		5.64 ± 0.08	4.84 ± 0.04	
MV(BF$_4$)$_2$[d]	0.0005	−0.44		11.2 ± 0.1	e
Acceptor = [X$_n$C$_5$H$_{5-n}$NCH$_3$]$^+$BF$_4^-$					
X = 4-COPh	0.0050	−0.62	19.2 ± 0.2	18.5 ± 0.3	24.3 (1.00)
X = 3-COPh	0.010	−0.81	5.64 ± 0.09	5.25 ± 0.08	0.90 (0.98)
X = 2-COPh	0.010	−0.68	16.7 ± 0.2	15.2 ± 0.1	6.42 (1.00)
X = 4-CN	0.0030	−0.60	17.5 ± 0.7	17.4 ± 0.2	26.4 (1.00)
X = 3-CN	0.0060	−0.76	6.31 ± 0.14	5.92 ± 0.11	2.66 (0.98)
X = 2-CN	0.010	−0.57	14.2 ± 0.2	14.0 ± 0.2	8.82 (0.99)
X = 4-COOMe	0.0060	−0.72	6.68 ± 0.06	6.42 ± 0.07	3.63 (0.98)
X = 4-CONH$_2$	0.012	−0.88	8.51 ± 0.19	7.93 ± 0.12	0.77 (0.99)
X = 2-Cl	0.010	−1.01	5.36 ± 0.07	4.95 ± 0.10	
X = 4-NMe$_2$	0.022	>−1.7	5.32 ± 0.19	4.86 ± 0.18	
X = 2-OMe	0.018	−1.36	6.25 ± 0.12	6.45 ± 0.12	
X$_2$ = 3,5-Me$_2$	0.017	−1.32	5.59 ± 0.32	5.37 ± 0.09	

[a] At 22 ± 0.2 °C in 1:1 (v/v) toluene/CH$_3$CN; monitored at 540 nm (k_a) and 600 nm (k_e). [b] $E_{p,c}$ peak potential vs Ag/AgCl, from the cathodic cycle of a cyclic voltammogram, μ = 0.1 M (^{n}Bu$_4$NBF$_4$) in CH$_3$CN (+477 mV for the F$_p$/F$_p$$^+$ couple): Burke, M.; Brown, T. L. Manuscript in preparation. [c] From a Stern-Volmer plot using first-order emission rate constants obtained at five different concentrations; r = correlation coefficient. [d] Methyl viologen. [e] Diffusion limited.

has been suggested in the electron-transfer catalysis of the photochemical substitution of [Re(CO)$_3$(phen)(CH$_3$CN)]$^+$ by PPh$_3$[25a] and of (CO)$_5$Re–Re(CO)$_3$(dab).[22c]

Triphenyl phosphite is found to behave differently from the other phosphites studied, in that its rate of quenching of the emission or transient absorption of IVb appears to be faster than those for all the phosphines studied. Such a fast rate of quenching is not explained by the stereoelectronic characteristics of this quencher. The mechanism of quenching is likely to be a combination of electron- and energy-transfer processes.

(b) Reactivity toward Electron Acceptors. The emission and transient absorption of the charge-separated MLCT excited state of IVb is found to be quenched by both neutral (Table VII) and charged (Table VIII) electron acceptors. Stern–Volmer plots obtained by using substituted maleic anhydrides as acceptors in toluene yield quenching rate constants in the range (0.54–1.34) × 10^8 M^{-1} s^{-1}. Electronic effects are manifested in the relative rates of quenching: 2,3-dichloromaleic anhydride is found to be a better quencher than the unsubstituted anhydride or 2,3-dimethylmaleic anhydride. It can be inferred that energy transfer is not the dominant quenching pathway, because maleic anhydride is found to be a better quencher than phthalic anhydride; the latter compound would be expected to possess low-lying acceptor levels that could facilitate energy transfer. Similar reactivity is also observed with the series of methyl-substituted *p*-quinones, whose quenching rate constants range from 0.91 × 10^8 M^{-1} s^{-1} for duroquinone to 1.87 × 10^8 M^{-1} s^{-1} for benzoquinone.

Cyclic voltammetric measurements of selected dirhenium complexes were performed in acetonitrile under the following conditions: μ = 0.1 M (^{n}Bu$_4$NBF$_4$), reference electrode = Ag/AgCl, counter electrode = Pt wire, sweep rate = 500 mV s^{-1}. Reversible oxidation of ferrocene was observed under these conditions to occur at $E_{1/2}$ = 0.477 V, with a peak separation (ΔE) of 69 mV. Re$_2$(CO)$_{10}$ shows an irreversible oxidation wave with $E_{p,a}$ = +1.55 V and irreversible reduction with $E_{p,c}$ = −2.13 V under these conditions. A cyclic voltammogram of IVb indicates that it is oxidized at $E_{p,a}$ = +1.73 V (irreversible), while one-electron-reduction waves are observed at $E_{1/2}$ = −1.02 V (reversible, ΔE = 72 mV) and at $E_{p,c}$ = −1.38 V (quasi-reversible, ΔE = 93 mV). The cyclic voltammogram of IIIb shows an irreversible oxidation wave at $E_{p,a}$ = +1.66 V, while IIIa shows a reversible oxidation wave at $E_{1/2}$ = +1.48 V (ΔE = 66 mV). The reduction waves of 1-methyl-4-benzoylpyridinium tetrafluoroborate are seen at $E_{1/2}$ = −0.64 V (reversible) and $E_{p,c}$ = −1.20 V (irreversible), suggesting that the reduction of IVb is ligand-localized. A reversible oxidation at about +1.6 V, observed in all three dirhenium compounds, suggests that the site of oxidation is the dinuclear metal center. Assuming an excited state energy of +2.48 eV (500 nm) for the emissive IVb* and the oxidation potential of IVb/IVb$^+$ to be +1.65 V ($E_{p,a}$ − ΔE_{fp}), the approximate excited state potential for the IVb*/IVb$^+$ couple can be estimated to be −0.83 V.

A series of substituted *N*-methylpyridinium tetrafluoroborate salts were employed as electron acceptors in 1:1 acetonitrile/toluene (v/v) solutions, to study the electron-transfer reactivity of IVb toward ionic acceptors. One of the difficulties in employing a mixed-solvent system is that the microenvironment around the reactant molecules may be thought to be different than in the bulk
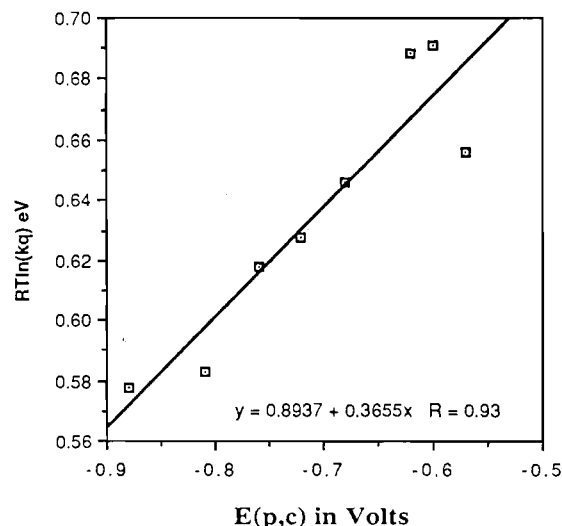
Figure 8. Plot of $RT \ln k_q$ (eV) for the emission quenching of IVb* by a series of substituted N-methylpyridinium tetrafluoroborate salts vs $E_{p,c}$ (V), the cathodic peak potential of the irreversible reduction wave vs Ag/AgCl electrode (μ = 0.1 M (Bu$_4$NBF$_4$), in acetonitrile) determined by cyclic voltammetry.

solvent. The increase in the rates of emission and transient absorption decay correlate well with increasing polarity of the solvent mixture (Table V), suggesting that the solvent composition at a molecular level closely parallels the bulk composition. Also, the rates of emission decay, with or without added Bu$_4$NBF$_4$ (0.02 M), were the same within error limits, indicating that the presence of an ionic species by itself does not affect the rates of emission or transient absorption decay of IVb. We believe that the observed decrease in the lifetime of the transient species caused by the pyridinium salts is indeed due to electron-transfer quenching.

Quenching rate constants, obtained from Stern–Volmer plots of the first-order rate constants for the quenching of emission from IVb as a function of free ion concentration,[4b] are found to be near the diffusion-controlled limit when an electron-withdrawing substituent is present on the pyridinium salt, as in the cases of X = –CN, –COPh, or –COOMe. The rates are slower for 4-CONH$_2$ and 2-Cl. For a series of similarly substituted quenchers (–CN or –COPh), the quenching rates follow the order of increasing ease of reduction of the acceptor, or less negative $E_{p,c}$ (X = 4- = 2- > 3-). The quenching rate constants for the 2-COPh- and 2-CN-substituted pyridinium salts are lower than would be anticipated from their reduction potentials, suggesting that the proximity of polar, electron-withdrawing substituents adjacent to the nitrogen on the ring plays a significant role in determining the rate of electron transfer to these acceptors. When the substituent has little electron-withdrawing ability, the pyridinium salts were found not to quench the excited state of IVb. Thus, N-methylpyridinium salts with 2-methoxy, 4-(dimethylamino) and 3,5-dimethyl substituents were observed not to quench the emission at concentrations as high as 0.02 M, close to the saturation solubility of these acceptors in the solvent mixture. The results suggest that the MLCT emissive state is easily oxidized by good oxidants, a reactivity that is also seen in a number of mononuclear d^6 complexes.[18]

The reactivity of IVb toward the 1-methyl-4-benzoylpyridinium BF$_4$ salt is particularly interesting, since the ligand-based SOMO of IVb* (MLCT) might be expected to be very similar to the acceptor orbital. Thus, a reaction resembling a self-exchange (the back-reaction would then appear to be a disproportionation reaction), A*$^-$ + A$^+$ $\rightleftharpoons$ A$^\bullet$ + A$^\bullet$, might be envisaged between the two reactants. The rate constant for this electron-transfer reaction is 2.4 × 10^9 M^{-1} s^{-1}.

The Stern–Volmer quenching rate constants are found to decrease with increasing cathodic peak potential ($E_{p,c}$) of the acceptor; a plot of $RT \ln k_q$ vs $E_{p,c}$ for a series of quenchers yields a poor linear fit (Figure 8). The slope of the plot (0.37) is less than the theoretical limit of 0.50 for an outer-sphere electron-transfer process.[9] This, however, is to be expected, given that the quenching rates are within an order of magnitude of the diffusion limit.

Reactions of IVb with Triplet Quenchers. As with other excited-state triplet species,[39] IVb is reactive toward energy-transfer quenchers (Table VII). The excited-state energy can be bracketed by employing quenchers of known triplet energies. Anthracene, a typical triplet quencher (E_T = 42 kcal mol^{-1}), totally quenches the emission from IVb* at concentrations as low as 5 × 10^{-4} M, suggesting that energy transfer takes place at a diffusion-limited rate. An acceptor with higher $\pi\pi^*$ energy such as *trans*-stilbene (E_T = 49 kcal mol^{-1}) quenches the emission of IVb*, but at higher concentrations (k_q = 2.31 × 10^8 M^{-1} s^{-1}). Naphthalene (E_T = 60 kcal mol^{-1}) and fluorene (E_T = 67 kcal mol^{-1}) do not quench the emission from IVb*. From these observations, the triplet-state energy of IVb* can be estimated to be about 54 kcal mol^{-1}, in good agreement with the emission spectral data.

In many instances it is not clear whether quenching occurs via electron transfer or energy transfer. For instance, the rate constants for emission quenching of IVb* by substituted p-benzoquinones are found to be relatively insensitive to the change in $E_{p,c}$ of the quenchers; a large difference in $E_{p,c}$ in going from duroquinone (–0.84 V vs SSCE) to 1,4-benzoquinone (–0.48 V vs SSCE) results in only a modest increase in k_q from 0.91 × 10^8 to 1.87 × 10^8 M^{-1} s^{-1}. Such an increase in quenching rate constants is more compatible with the relative triplet energies of these two quenchers, 52 and 50 kcal mol^{-1}, respectively. The triplet energies of both acceptors are 2–4 kcal mol^{-1} below the estimated triplet energy of IVb*, so that they can act as emission quenchers by an energy-transfer mechanism. It is difficult to choose electron transfer or energy transfer as the likely reaction pathway in the absence of detectable products of the quenching reaction.

Conclusions

The dirhenium complexes IIIb and IVb provide the first examples of dinuclear carbonyl complexes with long-lived intraligand or charge-transfer excited states that are relatively inert to thermal and photochemical degradation. A long-lived charge-transfer excited state of IVb has been characterized by its emissive behavior at ambient temperature as well as low temperature. Transient absorption spectroscopy has been employed to study its electron-transfer reactivity. The MLCT state of IVb has been shown to be quenched by trialkyl- and triarylphosphines and trialkyl and triaryl phosphites, solely through electron-transfer oxidation, at close to diffusion-limited rates, while electron-transfer reduction of a variety of acceptors such as anhydrides, quinones, and N-methylpyridinium salts also occur with facility. The electron-transfer reactivity of IIIb and IVb in the photoexcited state, combined with their greater stability toward thermal and photochemical degradation, makes them attractive as neutral, lipophilic organometallic sensitizers or as photocatalysts for solar energy conversion. In addition, the solvatochromism of IIIb and IVb in emission, a 30-fold enhancement in the rate of nonradiative decay of the emissive state in a polar as contrasted with a nonpolar solvent, and their low symmetry suggest that it might be possible to observe nonlinear optical behavior in these complexes.

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