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Photophysical Properties of Re(I) Diimine Complexes: Observation of Room-Temperature Intraligand Phosphorescence

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Abstract: The luminescence behavior of the ligands 4-styryl-4'-methyl-2,2'-bipyridine (mstyb) and 1,4-bis[2-(4'-methyl-2,2'-bipyridyl-4-yl)ethenyl]benzene (dstyb) and the Re(I) complexes $[\text{Re}(\text{CO})_3(\text{CH}_3\text{CN})(\text{mstyb})](\text{PF}_6)$ and $\{[\text{Re}(\text{CO})_3(\text{CH}_3\text{CN})]_2(\text{dstyb})\}(\text{PF}_6)_2$ is discussed. The dstyb ligand exhibits intense fluorescence at room temperature and in frozen (4:1 ethanol-methanol) solutions. The ligand mstyb does not emit at room temperature, but shows both fluorescence and phosphorescence in frozen solutions in the presence of 10% ethyl iodide. The Re(I) complex of mstyb emits from a ${}^3\text{MLCT}$ excited state (558 nm) in room-temperature acetonitrile; however, in frozen solutions structured phosphorescence from an intraligand ${}^3(\pi \rightarrow \pi^*)$ state (595 nm) is observed. The dinuclear Re(I) complex of dstyb exhibits structured intraligand phosphorescence (695 nm) in room-temperature solution and in low-temperature glasses. Gated emission spectra indicate that both intraligand phosphorescence and ${}^3\text{MLCT}$ emission are observed from both complexes immediately following laser excitation at 77 K.

Introduction

Phosphorescence from stilbenes, stilbazoles, and related olefins is observed generally only in the presence of either internal or external heavy atoms in low-temperature glasses.¹⁻⁴ In room-temperature solutions phosphorescence is not observed because trans-cis isomerization and other nonradiative relaxation processes are rapid relative to radiative decay. For styrylpyridines, introduction of a heavy atom into the environment of the olefin can be made by coordination of the pyridine to a transition metal. Studies by Wrighton and co-workers indicate that in *trans*-4-styrylpyridine coordinated to Re(I) in $[(\text{CO})_3\text{XRe}(4\text{-stypy})_2]$ (X

= Br, Cl) efficient trans-cis isomerization in room-temperature solutions is observed upon irradiation.^{5,6} From the cis-trans ratios obtained upon photolysis and spectroscopic data, they concluded that the lowest excited state is an intraligand, ${}^3\text{IL}$, state. They observed no luminescence from the Re complexes at 298 K and did not report spectral data in frozen solutions. Styrylpyridine complexes of Ru, such as $[(\text{bpy})_2\text{Ru}(\text{trans-4-stypy})_2](\text{PF}_6)_2$ are also nonluminescent in solutions.^{7,8} These complexes, however, have ${}^3\text{IL}(\text{trans-4-stypy})$ and $\text{Ru} \rightarrow \text{bpy}$ ${}^3\text{MLCT}$ states that are of comparable energy. Irradiation into the MLCT absorption does not yield trans-cis isomerization, while excitation into the IL absorption results principally in the cis olefin. The results strongly suggest that interconversion between the ${}^3\text{IL}$ and ${}^3\text{MLCT}$ states is slow relative to isomerization and nonradiative relaxation.

(1) Wagner, P. J.; Hammond, G. S. *Adv. Photochem.* **1968**, *5*, 21.
(2) Lewis, F. D. *Adv. Photochem.* **1986**, *13*, 165.
(3) (a) Saltiel, J.; Chang, D. W. L.; Megarity, E. D.; Rousseau, A. D.; Shannon, P. T.; Thomas, B.; Uriarte, A. K. *Pure Appl. Chem.* **1975**, *41*, 559.
(b) Saltiel, J.; Carlton, J. L. In *Rearrangements in Ground and Excited States*; de Mayo, P., Ed.; Academic Press: New York, 1980; Vol. 3, p 25. (c) Saltiel, J.; Khalil, G.-E.; Schanze, K. *Chem. Phys. Lett.* **1980**, *70*, 233.
(4) (a) Lamola, A. A.; Hammond, G. S.; Mallory, F. B. *Photochem. Photobiol.* **1965**, *4*, 259. (b) Ikeyama, T.; Azumi, T. *J. Phys. Chem.* **1985**, *89*, 5332. (c) *Ibid.* **1988**, *92*, 1383.

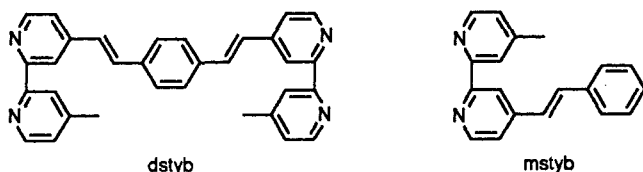
(5) Wrighton, M. S.; Morse, D. L.; Pdungsap, L. *J. Am. Chem. Soc.* **1975**, *97*, 2073.

(6) Geoffroy, G. L.; Wrighton, M. S. *Organometallic Photochemistry*; Academic Press: New York, 1979; pp 188-9.

(7) Zarnegar, P. P.; Whitten, D. G. *J. Am. Chem. Soc.* **1971**, *93*, 3776.

(8) Zarnegar, P. P.; Bock, C. R.; Whitten, D. G. *J. Am. Chem. Soc.* **1973**, *95*, 4367.

Recently Tokumaru's group found that anthrylethylenes have long-lived triplet excited states in room-temperature solutions, and in some cases, one way cis to trans isomerization is observed.^{9,10} However, none of these complexes exhibit room-temperature phosphorescence. We have also observed a relatively long lived triplet $\pi \rightarrow \pi^*$ state in transient absorption spectra of the bipyridine ligand dstyb and in the complexes $[(\text{dmb})_2\text{Ru}(\text{dstyb})](\text{PF}_6)_2$ and $\{[(\text{dmb})_2\text{Ru}]_2\text{dstyb}\}(\text{PF}_6)_4$.¹¹



The photophysics of the three isomers of 3,3',5,5'-tetra-*tert*-butyl-4'-styrylstilbene has recently been reported by Sandros and co-workers.³⁶ The trans, trans isomer exhibits intense, structured fluorescence in room-temperature solutions ($\phi_f = 0.87$), but no phosphorescence is observed. Isomerization is observed from both singlet and triplet states. Dstyb also exhibits strong fluorescence (but no phosphorescence) in room-temperature CH_3CN solutions and both Ru(II) complexes weakly luminesce from metal-to-ligand charge-transfer states (MLCT).

In this paper the photophysical properties of Re(I) complexes of dstyb and 4-methyl-4'-styryl-2,2'-bipyridine (mstyb) are presented. The complex $[(\text{CO})_3(\text{CH}_3\text{CN})\text{Re}(\text{dstyb})\text{Re}(\text{CO})_3(\text{CH}_3\text{CN})](\text{PF}_6)_2$ exhibits weak structured phosphorescence at room temperature from an intraligand excited state, representing the first example of phosphorescence from a stilbene-like chromophore in solution at room temperature.

Experimental Section

Materials. All solvents used for spectrophotometric measurements were spectroquality. Acetonitrile for electrochemical experiments was refluxed and distilled from CaH_2 under N_2 .

$\text{Re}(\text{CO})_5\text{Cl}$ was purchased from Pressure Chemical Co. and used as received. Silver tetrafluoroborate (Aldrich) was stored in the dark in a desiccator.

Reagents for ligand syntheses were used as previously described.¹¹ Benzaldehyde (Aldrich) was vacuum distilled immediately prior to use.

Measurements. UV-vis spectra were recorded on a Hewlett-Packard 8451 single-beam diode array spectrophotometer. Low-temperature (77 K) spectra were obtained in frozen 4:1 ethanol-methanol solutions by using a liquid nitrogen Dewar modified with quartz windows. Infrared spectra were obtained with KBr disks and were recorded on a Mattson Cygnus 100 FTIR. NMR spectra were obtained with an IBM Instruments NR 200 FT-NMR spectrometer; either acetone- d_6 or CDCl_3 was used as solvent and internal reference. Cyclic voltammetric measurements were performed as described previously,¹² using a sodium saturated calomel (SSCE) reference electrode and tetraethylammonium perchlorate (TEAP) electrolyte solutions. Microanalyses were done by Desert Analytics (Tucson, AZ).

Emission spectra were recorded with a SPEX Industries Model 111c photon counting fluorometer equipped with a 450-W Xe arc lamp and a cooled photomultiplier housing. Emission spectra were corrected for PMT (Hammamatsu red-sensitive R928) response. The absorbance of all solutions in emission spectral measurements was <0.2 at the excitation wavelength.

Luminescence lifetime measurements were obtained using apparatus described in other work.^{12,13} Luminescence decays were detected by using a Hammamatsu R928 PMT and a Tektronix 360 AD transient digitizer. All samples were either N_2 bubble degassed or freeze-pump-thaw (FPT) degassed to a final vacuum of $<10^{-5}$ Torr prior to measurement.

Table I. Redox Properties of Re(I) Complexes Obtained by Cyclic Voltammetry at 298 K in CH_3CN ^a

complex	oxidation, $E_{p,a}$	reduction, $E_{p,r}^{\circ}$ (ΔE_p)
$[\text{Re}(\text{dmb})(\text{CO})_3(\text{CH}_3\text{CN})](\text{PF}_6)$	1.79	-1.32 (110)
$[\text{Re}(\text{mstyb})(\text{CO})_3(\text{CH}_3\text{CN})](\text{PF}_6)$	1.9	-1.17 (80)
$\{[\text{Re}(\text{CO})_3(\text{CH}_3\text{CN})]_2(\text{dstyb})\}(\text{PF}_6)_2$	1.84	-1.09 (50)

^a All potentials in volts vs the saturated sodium calomel (SSCE) reference. Peak potential differences, ΔE_p , are in millivolts. Sweep rate for voltammograms is 0.1 V/s. Supporting electrolyte is tetraethylammonium hexafluorophosphate.

Luminescence quantum yields were measured in FPT-degassed CH_3CN solutions relative to $[\text{Ru}(\text{bpy})_3]\text{Cl}_2$ in H_2O ($\phi = 0.042$).³² Integrated intensities were corrected for differences in refractive indices (η) of the solvents by use of the following relationship.³³

$$\phi_f = \phi_f^{\text{obs}}(\eta^2/\eta_{\text{H}_2\text{O}}^2)$$

Gated emission spectra were obtained by using a Princeton Applied Research Model 1455 proximity-focused image-intensified diode array to detect dispersed emission from a Jarrell Ash Monospec 18 spectrograph following pulsed laser excitation. Laser triggering, gating of the image intensifier, and data acquisition from the diode array was controlled by a PAR Model 1461 detector interface equipped with a Model 1462 detector controller, a Model 1303 gate pulse interface, and a Model 1304 pulse amplifier. The PAR 1461 was programmed and controlled by a HP 9826 microcomputer.

Syntheses. *trans*-4-Styryl-4'-methyl-2,2'-bipyridine (mstyb) was prepared by a modification of the method of Juris et al.,¹⁴ using 1 equiv of benzaldehyde instead of 4-(dimethylamino)benzaldehyde. The product was recrystallized from ethanol to yield the styryl derivative. It was shown to be pure by GC-MS and NMR.

1,4-Bis-[2-(4'-methyl-2,2'-bipyridyl-4-yl) ethenyl]benzene (dstyb) was prepared as described elsewhere.¹¹

fac-[Re(CO)₃(dmb)(CH₃CN)](PF₆), prepared by the method of Caspar and Meyer, was available from previous studies.¹⁵

fac-[Re(Re(CO)₃(mstyb)Cl)] was prepared by the procedure of Luong,¹⁶ using mstyb as the chelating ligand. The product was pure by TLC and was used in the subsequent reaction without further purification.

fac-Re(CO)₃(mstyb)(CH₃CN)(PF₆) was prepared by the method of Caspar and Meyer,¹⁵ using AgBF_4 to assist the dehalogenation of $[\text{Re}(\text{CO})_3(\text{mstyb})\text{Cl}]$. The isolated complex was metathesized to the PF_6 salt by using saturated NH_4PF_6 . The product was chromatographed in the dark on neutral alumina (Anspec, activity I) with 2:1 toluene-acetonitrile as eluent. The second nonluminescent band was isolated and precipitated from pentane. IR $\nu(\text{CO}) \text{ cm}^{-1}$: 2033, 2022, 1915. Anal. Calcd for $\text{ReC}_{24}\text{H}_{19}\text{N}_3\text{O}_3\text{PF}_6$: C, 39.56; H, 2.63; N, 5.76. Found: C, 40.31; H, 2.70; N, 5.36.

{[fac-Re(CO)₃(CH₃CN)]₂(dstyb)}(PF₆)₂ was prepared in two steps. The bischloro complex was prepared by refluxing 2 equiv of $\text{Re}(\text{CO})_5\text{Cl}$ and 1 equiv of the bridging ligand dstyb in 25 mL of CHCl_3 overnight. The solution was cooled to room temperature, evaporated to a small volume, and then added dropwise to pentane. The bright yellow precipitate was collected on a glass frit and dried in a vacuum oven. The bisacetonitrile complex was prepared by the procedure of Caspar and Meyer,¹⁵ using 4 equiv AgBF_4 . After being refluxed for 12 h under N_2 , the reaction was filtered to remove AgCl and metathesized to the PF_6 salt by use of NH_4PF_6 . The complex was chromatographed on Alcoa F-20 alumina, using 1:1 acetonitrile-toluene as eluent. IR $\nu(\text{CO}) \text{ cm}^{-1}$: 2019, 1910, 1885. Anal. Calcd for $\text{Re}_2\text{C}_{42}\text{H}_{33}\text{N}_6\text{O}_6\text{P}_2\text{F}_{12}$: C, 36.58; H, 2.34; N, 6.09. Found: C, 37.20; H, 2.39; N, 5.85.

Results and Discussion

Electrochemistry. Redox data obtained from cyclic voltammograms of $[(\text{mstyb})\text{Re}(\text{CO})_3(\text{CH}_3\text{CN})](\text{PF}_6)$, $\{[\text{Re}(\text{CO})_3(\text{CH}_3\text{CN})]_2(\text{dstyb})\}(\text{PF}_6)_2$, and the parent complex, $[\text{Re}(\text{dmb})(\text{CO})_3(\text{CH}_3\text{CN})](\text{PF}_6)$, are presented in Table I. The metal-centered one-electron oxidation is irreversible in cyclic voltammograms of all the complexes.³⁴ The anodic peak potentials of the mstyb and dstyb complexes are +1.9 and +1.84 V vs SSCE;

(14) Juris, A.; Campagna, S.; Bidd, I.; Lehn, J.-M.; Ziessel, R. *Inorg. Chem.* **1988**, *27*, 4007.

(15) Caspar, J. V.; Meyer, T. J. *J. Phys. Chem.* **1983**, *87*, 952.

(16) Luong, J. C. Ph.D. Dissertation, Massachusetts Institute of Technology, 1981.

(9) Arai, T.; Kuriyama, Y.; Karatsu, T.; Sakuragi, H.; Tokumaru, K.; Oishi, S. *J. Photochem.* **1987**, *36*, 125.

(10) Karatsu, T.; Arai, T.; Sakuragi, H.; Tokumaru, K. *Chem. Phys. Lett.* **1985**, *115*, 9.

(11) Shaw, J. R.; Webb, Ralph T.; Schmehl, Russell H. *J. Am. Chem. Soc.* **1990**, *112*, 1117.

(12) Wacholtz, W. F.; Auerbach, R. A.; Schmehl, R. H. *Inorg. Chem.* **1987**, *26*, 2989.

(13) Wacholtz, W. F.; Auerbach, R. A.; Schmehl, R. H. *Inorg. Chem.* **1986**, *25*, 227.

Table II. Absorption and Luminescence Properties of Ligands and Re(I) Complexes

complex	temp, K	λ_{\max} , nm (log ϵ)	E_{\max}^{em} , cm^{-1}	τ , μs	ϕ_{em}
styp ^a	77		17 200 15 850	<1000	
mstyb	298 77	300 (4.3) 325 340	16 900 ^b 15 500 14 000		
[Re(CO) ₃ (AN)(mstyb)](PF ₆) ^d	298 77	325 (4.25) 325 355	17 920 16 800 15 380 13 900	0.55 3.7 79.4	0.0008
dstyb	298 77	365 (4.65) 355 370 395		<0.01	
{[Re(CO) ₃ (AN)] ₂ (dstyb)}(PF ₆) ₂ ^d	298 77	400 (4.39) 417 443	14 390 12 990 14 390 12 850	4.68 1.5 22.7	<10 ⁻⁴
[Re(CO) ₃ (AN)(dmb)](PF ₆) ^{c,d}	298 77	330	18 790 20 900	0.66 4.28	0.04

^astyp, *trans*-4-styrylpyridine; from ref 23. ^bPhosphorescence maxima. Fluorescence maximum is 23 500 cm^{-1} . ^cFrom Wacholtz, W. F. Ph.D. Dissertation, Tulane University, 1987. ^dAN, acetonitrile.

both are at more positive potentials than the corresponding potential of [Re(dmb)(CO)₃(CH₃CN)](PF₆).

One-electron reduction of Re diimine complexes is localized on the diimine.¹⁷ The first reduction in these complexes can thus be assigned as either dmb, mstyb, or dstyb localized. The mstyb complex first reduction occurs at -1.17 V. The wave is quasi-reversible ($i_{\text{pa}}/i_{\text{pc}} = 0.4$; sweep rate, 0.1 V/s) in cyclic voltammograms when the reductive limit is positive of -1.25 V. Further reduction of Re diimine complexes is complicated by coupled chemical and electrochemical processes. In [(dmb)Re(CO)₃(CH₃CN)](PF₆) one-electron reduction is followed either by a second, irreversible, ligand-localized reduction or loss of CH₃CN and concomitant formation of a dimer, [(dmb)(CO)₃ReRe(CO)₃(dmb)].^{17b,c} The dimer exhibits an irreversible reduction at -1.5 V vs SSCE. Cyclic voltammograms of the mstyb complex are very similar to those of [(dmb)Re(CO)₃(CH₃CN)](PF₆).

The reductive electrochemistry of the dstyb complex is complicated by the observation of several reductive waves in cyclic voltammograms. The first reduction is quasi-reversible ($i_{\text{pa}}/i_{\text{pc}} = 0.2$; sweep rate, 0.1 V/s) and occurs at -1.09 V. It is followed by several poorly resolved irreversible reductions. As is the case for the mstyb complex, the first reduction is ligand localized. The Re-centered reduction in this complex cannot be distinguished since several overlapping reductions occur between -1.25 and -1.5 V.

The first reduction potentials of the Re(I) complexes having mstyb and dstyb are positive relative to the parent complex [(dmb)Re(CO)₃(CH₃CN)](PF₆). There is a +160-mV shift in the potential between the dmb complex and the mstyb complex and a +80-mV shift between the mstyb complex and the dstyb complex. Previous studies of Ru(II), Os(II), and Re(I) diimine complexes have clearly shown that $\Delta E_{1/2}$, the potential difference between the first one-electron reduction and oxidation, is linearly related to the emission energy of the ³MLCT excited states in series of related complexes.^{18,19} The Re(I) complexes discussed here all exhibit irreversible one-electron oxidation by slow-scan (<1 V/s) cyclic voltammetry. However, only a 10-mV difference exists between the reversible one-electron oxidation potentials of the related Ru(II) complexes [(dmb)₃Ru](PF₆)₂, [(dmb)₂Ru]₂(dstyb)(PF₆)₄,¹¹ and [(dmb)₂Ru](dstyb)(PF₆)₂, so it is reasonable

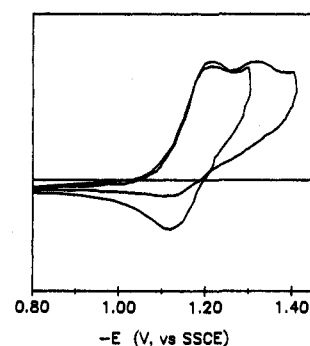


Figure 1. Reductive cyclic voltammograms of [(CO)₃(CH₃CN)Re(mstyb)](PF₆) in CH₃CN. Sweep rate, 0.1 V/s. Supporting electrolyte, tetraethylammonium perchlorate. Reference, SSCE.

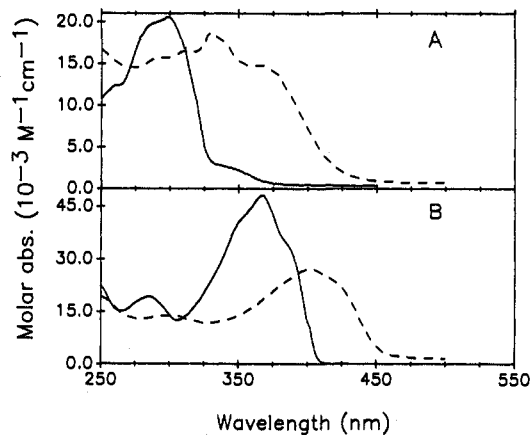


Figure 2. Room-temperature absorption spectra of (A) mstyb (—) and [(CO)₃(CH₃CN)Re(mstyb)](PF₆) (---) and (B) dstyb (—) and [(CO)₃(CH₃CN)Re]₂dstyb(PF₆)₂ (---) in CH₃CN.

to assume that E_{ox}° is nearly the same for the three Re(I) complexes. Given this assumption, differences in the ³MLCT-state energies between the complexes will depend principally on the first reduction potential and both the mstyb and dstyb complexes should luminesce from their ³MLCT states at lower energies than the dmb complex (vide infra).

Absorbance and Luminescence Properties. The absorption and luminescence maxima of the complexes are given in Table II. The primary characteristic of the electronic spectra of the complexes is that they retain the shape of the spectra of the free ligands (Figure 2A,B). In room-temperature acetonitrile solutions the

(17) (a) Sullivan, B. P.; Bolinger, C. M.; Conrad, D.; Vining, W. J.; Meyer, T. J. *J. Chem. Soc., Chem. Commun.* **1985**, 1414. (b) Abruna, H. D.; Breiks, A. I. *J. Electroanal. Chem. Interfacial Electrochem.* **1986**, *201*, 347. (c) O'Toole, T. R.; Sullivan, B. P.; Bruce, M. R.-M.; Margerum, L. D.; Murray, R. W.; Meyer, T. J. *J. Electroanal. Chem. Interfacial Electrochem.* **1989**, *259*, 217.

(18) Juris, A.; Belsler, P.; Barigelletti, F.; von Zelewsky, A.; Balzani, V. *Inorg. Chem.* **1986**, *25*, 256.

(19) Caspar, J. V.; Meyer, T. J. *Inorg. Chem.* **1983**, *22*, 2444.

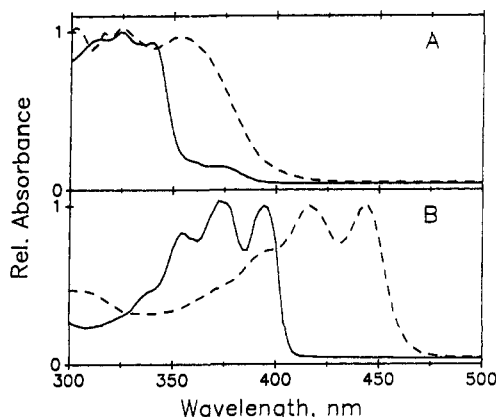


Figure 3. Absorption spectra of (A) mstyb (—) and $[(\text{CO})_3(\text{CH}_3\text{CN})\text{Re}(\text{mstyb})](\text{PF}_6)$ (---) and (B) dstyb (—) and $\{[(\text{CO})_3(\text{CH}_3\text{CN})\text{Re}]_2\text{dstyb}(\text{PF}_6)_2$ (---) in 4:1 ethanol-methanol at 77 K.

absorption maximum of $[\text{Re}(\text{mstyb})(\text{CO})_3(\text{CH}_3\text{CN})](\text{PF}_6)$ is red-shifted 20 nm relative to the free ligand. Wrighton's group found the principal absorption of $[\text{Re}(\text{CO})_3\text{Cl}(\text{trans-4-styrylpyridine})_2]$ and other related styrylpyridine complexes to be ligand localized;^{3,20} however, the lowest energy absorption in diimine complexes such as $[\text{Re}(\text{CO})_3(\text{bpy})\text{Cl}]$ and $[\text{Re}(\text{CO})_3(\text{phen})\text{Cl}]$ ²¹ is metal-to-ligand charge-transfer (MLCT). The shoulder at 360 nm in the absorption spectrum of $[\text{Re}(\text{CO})_3(\text{mstyb})(\text{CH}_3\text{CN})](\text{PF}_6)$ red shifts with increasing solvent polarity, suggesting the transition is $\text{Re}(d\pi) \rightarrow \text{mstyb}(\pi^*)$ MLCT (vide infra). The lowest energy absorption of the dstyb complex is also significantly red-shifted relative to dstyb, as shown in Figure 2B.

The 77 K absorption spectra of both of the ligands studied and the corresponding Re complexes exhibit structure as shown in Figure 3. The vibrational spacings in the spectra are between 1400 and 1500 cm^{-1} . Generally, the appearance of vibrational structure coupled with a red shift in the absorption maximum upon cooling is characteristic of intraligand absorption transitions.³ Complexes having lowest energy MLCT transitions usually exhibit a blue shift in the absorption maximum and little or no structure. For instance, the maximum of the MLCT transition of $[\text{Re}(\text{CO})_3\text{Cl}(4\text{-phenylpyridine})_2]$ is at 300 nm both at room temperature and at 77 K, while the intraligand transition red shifts from 265 to 275 nm upon cooling. The ligand mstyb exhibits a bathochromic shift from 295 nm at 298 K to 340 nm at 77 K. In $[\text{Re}(\text{CO})_3(\text{CH}_3\text{CN})(\text{mstyb})](\text{PF}_6)$, the room-temperature maximum at 325 nm becomes structured at 77 K and the shoulder at approximately 355 nm remains broad and does not change upon cooling, suggesting the lowest energy transition is MLCT (Figure 3A, vide infra). By contrast, the dinuclear dstyb complex and the free ligand both exhibit pronounced red shifts and structured absorption upon cooling to 77 K, indicating the lowest energy electronic transition in this complex is ligand localized (Figure 3B).

Luminescence of numerous Re(I)tricarbonyl diimine complexes has been thoroughly studied.^{5,14,15,20-22} Room-temperature emission is usually of ³MLCT origin. The MLCT emission blue shifts upon cooling to 77 K, and as a result, both intraligand and charge-transfer luminescence are observed in frozen solutions of some complexes. The complexes $[\text{Re}(\text{CO})_3\text{Cl}(\text{L})_2]$ (L = 4-phenylpyridine, 3- or 4-benzoylpyridine) all exhibit intraligand phosphorescence at 77 K.²² The 3-benzoylpyridine complex luminesces from both MLCT and ³IL states; the ³IL phosphorescence has a lifetime in excess of 100 ms. The room-temperature and 77 K emission spectra of mstyb, $[\text{Re}(\text{CO})_3(\text{CH}_3\text{CN})(\text{mstyb})](\text{PF}_6)$, and $\{[\text{Re}(\text{CO})_3(\text{CH}_3\text{CN})]_2\text{dstyb}(\text{PF}_6)_2$ in 4:1 ethanol-methanol are shown in Figure 4. Emission maxima,

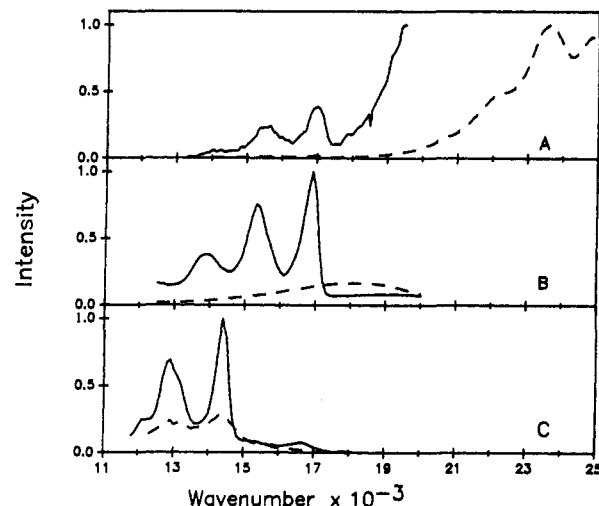


Figure 4. Emission spectra of (A) mstyb, (B) $[(\text{CO})_3(\text{CH}_3\text{CN})\text{Re}(\text{mstyb})](\text{PF}_6)$, and (C) $\{[(\text{CO})_3(\text{CH}_3\text{CN})\text{Re}]_2\text{dstyb}(\text{PF}_6)_2$ at 298 (---) and 77 K (—).

luminescence lifetimes, and radiative quantum yields are given in Table II along with data for other previously reported ligands and complexes.

The ligand mstyb does not luminesce in solution at room temperature. In frozen solutions, strong structured fluorescence is observed, and in solutions with 10% or more ethyl iodide, weak structured phosphorescence also appears as shown in Figure 4A. The phosphorescence maximum is at 16800 cm^{-1} and the vibrational spacing is 1450 cm^{-1} . The Re(I) complex of mstyb has a weak, broad room-temperature luminescence with a maximum at 17900 cm^{-1} . The emission energy is 870 cm^{-1} lower than the ³MLCT luminescence of $[\text{Re}(\text{CO})_3(\text{CH}_3\text{CN})(\text{dmb})](\text{PF}_6)$, consistent with the observed difference in the one-electron reduction potentials of the two complexes (vide supra). The luminescence decay is single exponential with a lifetime of 550 ns. The relatively short lifetime and low-emission quantum yield result in a radiative decay rate constant, k_r , of approximately 1500 s^{-1} (assuming the efficiency for populating the triplet emitting state is unity). The estimated radiative decay rate constant is much smaller than k_r values obtained for other Re(I)(CO)₃ diimine complexes known to luminesce from ³MLCT states at room temperature,¹⁵ but much larger than typical phosphorescence radiative decay rate constants of aromatic hydrocarbons.²³ The implication of the result is that emission arises from a ³MLCT state that is not populated with unit efficiency, although we currently have no evidence for population of any other state (vide infra). The emission of $[\text{Re}(\text{CO})_3(\text{CH}_3\text{CN})(\text{mstyb})](\text{PF}_6)$ also exhibits strong solvent dependence; a red shift of 50 nm is observed between CH_2Cl_2 and DMF. The solvent dependence is characteristic of luminescence from MLCT states. In the complex $[\text{Ru}(\text{dmb})_2(\text{dstyb})](\text{PF}_6)_2$ weak charge-transfer luminescence is observed and the radiative decay rate constant is also very low relative to other Ru(II) diimine complexes.¹¹ However, the Ru(II) complex also has a transient absorption spectrum with a unique absorption feature having a lifetime longer than the luminescence lifetime of the complex, providing direct evidence for population of a triplet intraligand state.

The 77 K luminescence spectrum of $[\text{Re}(\text{CO})_3(\text{CH}_3\text{CN})(\text{mstyb})](\text{PF}_6)$ is shown in Figure 4B. The structured luminescence is nearly identical with the phosphorescence obtained from the noncoordinated ligand in ethyl iodide containing solutions and the luminescence clearly originates from a ³IL state. Further, the very small difference between the phosphorescence spectra of the free ligand and the Re(I) complex indicates that the presence of the Re center does not significantly perturb the emitting triplet state. Recently Görner examined the 77 K luminescence of numerous stilbene derivatives, including *trans*-4-styrylpyridine (4-

(20) Geoffroy, G. L.; Wrighton, M. S. *Organometallic Photochemistry*; Academic Press: New York, 1979; pp 96-101.

(21) Wrighton, M. S.; Morse, D. L. *J. Am. Chem. Soc.* **1974**, *96*, 998.

(22) Giordano, P. J.; Fredricks, S. M.; Wrighton, M. S.; Morse, D. L. *J. Am. Chem. Soc.* **1978**, *100*, 2257.

(23) Görner, H. *J. Phys. Chem.* **1989**, *93*, 1826.

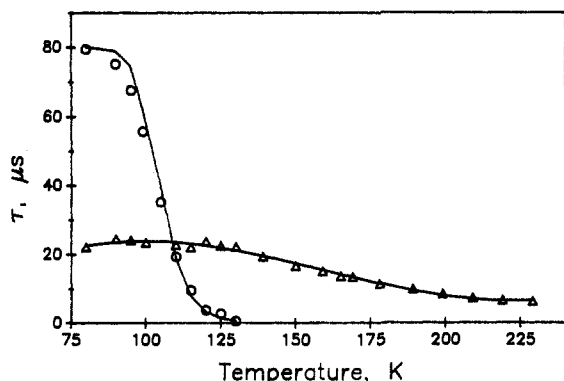


Figure 5. Temperature dependence of the intraligand phosphorescence lifetimes of $[(\text{CO})_3(\text{CH}_3\text{CN})\text{Re}(\text{mstyb})](\text{PF}_6)$ (O) and $[(\text{CO})_3(\text{CH}_3\text{CN})\text{Re}]_2\text{dstyb}(\text{PF}_6)_2$ (Δ) in 4:1 ethanol-methanol.

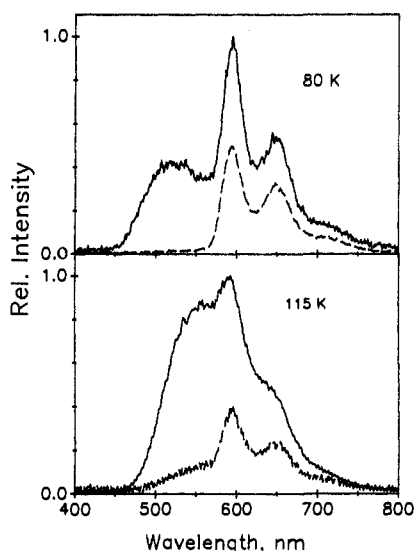


Figure 6. Gated emission spectra of $[(\text{CO})_3(\text{CH}_3\text{CN})\text{Re}(\text{mstyb})](\text{PF}_6)$ in 4:1 ethanol-methanol at 80 K with delays of 100 ns (—) and 10 μs (---) and at 115 K with delays of 100 ns (—) and 1 μs (---). The gate window in each case is 100 ns.

styp).²³ As can be seen from Table II, the luminescence maxima and vibrational spacing of both mstyb and $[\text{Re}(\text{CO})_3(\text{CH}_3\text{CN})(\text{mstyb})](\text{PF}_6)$ strongly resemble those of 4-styp. The luminescence of 4-styp was determined to originate from a $^3(\pi \rightarrow \pi^*)$ state.²³⁻²⁵ In addition, Görner found that quaternization of the pyridine of 3- or 4-styrylpyridine did not change the emission maxima of the $^3(\pi \rightarrow \pi^*)$ luminescence.

Luminescence decays of $[\text{Re}(\text{CO})_3(\text{CH}_3\text{CN})(\text{mstyb})](\text{PF}_6)$ in 4:1 ethanol-methanol at 77 K are double exponential, with short and long components of 3.7 and 79 μs , respectively. As the temperature is raised above the glass transition temperature of the solvent, the lifetime of the long-lived component sharply decreases (Figure 5). Time-resolved spectra of the two emission components at two temperatures are shown in Figure 6. The short-lived emission at 77 K is very similar to that of $[(\text{dmb})\text{Re}(\text{CO})_3(\text{CH}_3\text{CN})](\text{PF}_6)$ and is thus assigned to be of $^3\text{MLCT}$ origin. The longer lived component is the same as the steady-state emission (^3IL origin). Dual emission has been observed at low temperatures for other Re(I) complexes, such as $[\text{Re}(\text{CO})_3\text{Cl}(4\text{-benzoylpyridine})]$,²² having aromatic heterocyclic ligands with low-lying triplet states. Above 250 K, the structured ^3IL emission becomes too weak to be observed and only the $^3\text{MLCT}$ component remains. Disappearance of the ^3IL luminescence above the solvent glass transition temperature may be attributed to trans-cis isomerization, known to be the dominant nonradiative decay path

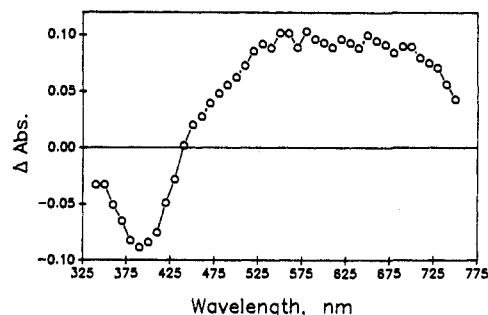


Figure 7. Transient absorption spectrum of $[(\text{CO})_3(\text{CH}_3\text{CN})\text{Re}]_2\text{dstyb}(\text{PF}_6)_2$ in CH_3CN at room temperature 1 μs following excitation at 308 nm.

of stilbene-like chromophores in fluid solutions.

Room-temperature luminescence from the dstyb complex, $[(\text{Re}(\text{CO})_3(\text{CH}_3\text{CN}))_2\text{dstyb}(\text{PF}_6)_2]$, sharply contrasts that of all other Re(I) diimine complexes. The very weak, structured luminescence observed from the complex at room temperature is shown in Figure 4C along with the much stronger emission seen at 77 K. The luminescence spectra at the two temperatures have the same maxima and vibrational spacing; the maxima are lower in energy than those observed from mstyb and $[\text{Re}(\text{CO})_3(\text{CH}_3\text{CN})(\text{mstyb})](\text{PF}_6)$. No solvent dependence of the room-temperature luminescence spectrum is observed. The room-temperature excited-state lifetime is 4.7 μs and the luminescence quantum yield is less than 10^{-4} ; if the intersystem-crossing efficiency to populate the $^3(\pi \rightarrow \pi^*)$ state is assumed to be unity,²⁶ the resulting radiative decay rate is less than 20 s^{-1} . This value is much higher than typical radiative decay rate constants of aromatic hydrocarbons in solution (generally $< 0.1 \text{ s}^{-1}$),²³ but much lower than k_r values observed for luminescence from $^3\text{MLCT}$ excited states of Re(I) complexes ($> 10^4 \text{ s}^{-1}$).¹⁵ Since structured luminescence from $^3\text{MLCT}$ states of metal diimine complexes has never been observed at room temperature, the emission is not likely to be of MLCT origin. The similarity of the room-temperature luminescence to the low-temperature intraligand phosphorescence of related ligands, coupled with the lack of a solvent dependence of the emission maxima, strongly suggests that the room-temperature emission is phosphorescence from a $^3(\pi \rightarrow \pi^*)$ state of the ligand. The relatively large value of k_r may result from a small degree of mixing of the $^3\text{MLCT}$ and $^3(\pi \rightarrow \pi^*)$ states.

The transient absorption spectrum of $[(\text{Re}(\text{CO})_3(\text{CH}_3\text{CN}))_2\text{dstyb}(\text{PF}_6)_2]$ in CH_3CN at room temperature is shown in Figure 7. The spectrum consists of ground-state bleaching between 400 and 450 nm and strong absorbance between 500 and 750 nm. The transient absorption decays as a single exponential with a lifetime that matches that of the luminescence. The broad, featureless absorption in the visible ($\lambda_{\text{max}} \approx 625 \text{ nm}$) is not observed in transient spectra of $[(\text{CO})_3(\text{CH}_3\text{CN})\text{Re}(\text{dmb})](\text{PF}_6)$ or $[(\text{CO})_3(\text{CH}_3\text{CN})\text{Re}(\text{mstyb})](\text{PF}_6)$. The transient absorption above 500 nm does, however, resemble that of the triplet state of *trans*-1-alkyl-4-(4-styryl)quinolinium salts previously reported by Görner and co-workers.³⁰ This spectral feature of the excited state further supports assignment as a $^3(\pi \rightarrow \pi^*)$ state.

(26) We have attempted to determine the intersystem-crossing efficiency by using the singlet depletion method to determine the extinction coefficient (ϵ) of the triplet-state absorption across the spectrum.²⁷ By using the ϵ value at a fixed wavelength, the concentration of triplets formed immediately following excitation can be determined and compared with a standard for which η_{isc} is known. With $[\text{Ru}(\text{bpy})_3](\text{PF}_6)_2$ as a standard, $\epsilon_{375} = 29000 \text{ M}^{-1} \text{ cm}^{-1}$,²⁸ the intersystem-crossing efficiency of $[(\text{CO})_3(\text{CH}_3\text{CN})\text{Re}]_2\text{dstyb}(\text{PF}_6)_2$ appears to be nearly unity.

(27) Carmichael, I.; Hug, G. L. *J. Phys. Chem. Ref. Data* **1986**, *15*, 1.

(28) (a) Braterman, P.; Harriman, A.; Heath, G. A.; Yellowlees, L. J. *J. Chem. Soc., Dalton Trans.* **1983**, 1801. (b) Lachish, U.; Infelta, P. P.; Grätzel, M. *Chem. Phys. Lett.* **1979**, *62*, 317.

(29) Sun, Y.-P.; Saltiel, J. J. *J. Phys. Chem.* **1989**, *93*, 8310, and references therein.

(30) Görner, H.; Fojtik, A.; Wroblewski, J.; Currell, L. J. *Z. Naturforsch., A* **1985**, *40*, 525.

(24) Elisei, F.; Mazzucato, U.; Görner, H.; Schulte-Frohlinde, D. *J. Photochem.* **1987**, *37*, 87.

(25) Görner, H.; Schulte-Frohlinde, D. *J. Phys. Chem.* **1985**, *89*, 4105.

As in the mstyb complex, time resolution of the luminescence of $\{[\text{Re}(\text{CO})_3(\text{CH}_3\text{CN})_2\text{dstyb}](\text{PF}_6)_2$ at 77 K reveals that two components are observed. The short-lived emission component has spectral characteristics indicative of luminescence from a $^3\text{MLCT}$ state and the longer component (Table II) arises from intraligand phosphorescence. Figure 5 shows the temperature dependence of the lifetime of the long-lived emission between 77 and 220 K. The relatively small change in the lifetime between 100 and 130 K, the glass transition region of 4:1 ethanol-methanol, is expected if trans-cis isomerization is a minor nonradiative relaxation path. Activation parameters were obtained from temperature-dependent excited-state decay rate constants for the two complexes by assuming a single thermally activated decay component with a base line representing the intrinsic decay. For the long-lived emission component of $[(\text{CO})_3(\text{CH}_3\text{CN})\text{Re}(\text{mstyb})](\text{PF}_6)_2$, the preexponential factor, activation energy, and baseline term are $1.1 \times 10^{14} \text{ s}^{-1}$, 1800 cm^{-1} , and $12\,500 \text{ s}^{-1}$, respectively. For $\{[(\text{CO})_3(\text{CH}_3\text{CN})\text{Re}]_2\text{dstyb}(\text{PF}_6)_2$ the corresponding values are $3.8 \times 10^6 \text{ s}^{-1}$, 540 cm^{-1} , and $39\,000 \text{ s}^{-1}$. The intrinsic decay rate for excited-state decay in the absence of rotation, $k_r + k_{nr}$, will depend on the rate constant for intersystem crossing from the $^3(\pi \rightarrow \pi^*)$ state back to the ground state. The observed rate constant for the dstyb complex is faster than that of the mstyb complex, reflecting the presence of multiple heavy atoms and/or the smaller energy gap. Also, as noted above, the dstyb complex excited-state decay has a weak temperature dependence, characteristic of aromatic hydrocarbons exhibiting decay unimolecularly from $^3(\pi \rightarrow \pi^*)$ states.³¹ The much larger temperature dependence of the mstyb complex may reflect either (a) thermally activated internal conversion to populate the $^3\text{MLCT}$ state (the emitting state at room temperature) or (b) nonradiative relaxation via twisting of the olefin. Since we currently have no evidence indicating that photoinduced isomerization of the mstyb complex occurs, population of the $^3\text{MLCT}$ state is the more likely explanation.

The isomerization rate constant for *trans*-stilbene in hydrocarbon solvents is approximately 10^{10} s^{-1} .²⁹ Since no room-temperature isomerization is observed for $\{[\text{Re}(\text{CO})_3(\text{CH}_3\text{CN})_2\text{dstyb}](\text{PF}_6)_2$, the isomerization rate must be considerably slower than the room-temperature excited-state decay rate of $2.5 \times 10^5 \text{ s}^{-1}$. Recently trans-cis isomerization rate constants for the singlet excited state of *trans*-stilbene in different environments have been analyzed by using modified versions of Kramer's model for diffusive barrier crossing.²⁹ The model describes Brownian motion of a particle over a barrier of height E_0 , which exists in a potential energy curve that is piecewise parabolic. When applied to olefin twisting processes, expressions such as eq 1 are used where ω and ω' are the frequency of the initial

$$k_{\text{obs}} = (\omega/2\pi)(\beta/2\omega')[[1 + (2\omega'/\beta)^2]^{1/2} - 1] \exp(-E_0/rt) \quad (1)$$

well and the curvature at the top of the barrier, respectively, and β is the reduced friction coefficient. The reduced friction coefficient can be expressed in terms of the ratio of the friction coefficient for the twisting portion of the molecule to the moment of inertia (eq 2) where r and m are the radius and mass of the

$$\beta = \alpha\pi\eta_s r^2/m \quad (2)$$

twisting part of the molecule, η_s is shear viscosity of the solvent, and α is a constant defined by the boundary conditions used. Both the radius and mass of the twisting part of $\{[\text{Re}(\text{CO})_3(\text{CH}_3\text{CN})_2\text{dstyb}](\text{PF}_6)_2$ are larger than the same values of stilbene (the radius is approximately twice that of stilbene and the mass is approximately 5.5 times larger), but the difference in the friction coefficient alone cannot account for the obviously very slow twisting rate ($k_{\text{obs}} \ll 10^5 \text{ s}^{-1}$) relative to *trans*-stilbene. The implication is that, given Kramer's model, either the frequency of the initial well is much lower than that of stilbene or the activation barrier for the twisting process is significantly higher than the 14 kJ/mol barrier of stilbene. Recently Ramamurthy and co-workers have shown that *trans*-stilbene trapped in zeolites having heavy atom dopants is phosphorescent at room temperature.^{35,36} The zeolite serves to concentrate stilbene in the environment of the heavy atom dopant and inhibit rotation of the excited triplet. The Re(I) centers of the dstyb complex serve a similar function; clearly formation of the $^3(\pi \rightarrow \pi^*)$ state is enhanced by the heavy atom.

Summary

The photophysical properties of the two Re(I) complexes having stilbene-like chromophoric components reflect the varying degree of π conjugation in the ligands. The mstyb complex, $[(\text{CO})_3(\text{CH}_3\text{CN})\text{Re}(\text{mstyb})](\text{PF}_6)_2$, has close-lying $^3\text{MLCT}$ and $^3(\pi \rightarrow \pi^*)$ excited states. The relative energy of the states depends on the temperature of the medium. The $^3\text{MLCT}$ state is lower at room temperature but moves to higher energy upon cooling to 77 K, whereupon the intraligand $^3(\pi \rightarrow \pi^*)$ phosphorescence predominates. The intraligand excited state of $\{[(\text{CO})_3(\text{CH}_3\text{CN})\text{Re}]_2\text{dstyb}(\text{PF}_6)_2$ is the lowest energy state at all temperatures between 77 K and room temperature. In room-temperature CH_3CN solutions, unique structured phosphorescence is observed for this complex. The observation of phosphorescence results from both a decreased rate of excited-state isomerization and an increased rate of radiative decay relative to stilbene.

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(31) Turro, N. J. *Modern Molecular Photochemistry*; Benjamin/Cummings: Reading, PA, 1978; pp 190-2.

(32) Van Houten, J.; Watts, R. J. *J. Am. Chem. Soc.* **1976**, *98*, 4853.

(33) Demas, J. N.; Crosby, G. A. *J. Phys. Chem.* **1971**, *75*, 991.

(34) Luong, J. C.; Nadjo, L.; Wrighton, M. S. *J. Am. Chem. Soc.* **1978**, *100*, 5790.

(35) Ramamurthy, V.; Caspar, J. V.; Corbin, D. R. *Tetrahedron Lett.* **1990**, *31*, 1097. (b) Ramamurthy, V.; Caspar, J. V.; Corbin, D. R.; Schlyer, B. D.; Maki, A. H. *J. Phys. Chem.* **1990**, *94*, 3391.

(36) Sandros, K.; Sundahl, M.; Wennerstrom, O.; Norinder, U. *J. Am. Chem. Soc.* **1990**, *112*, 3082.