

Preparation of Thiazine 12.¹⁰ To an ice-cooled solution of 3.28 g (24.7 mmol) of methyl *N*-(thioformyl)glycinate in 50 mL of THF was added 1.38 g (34.5 mmol) of 60% dispersion of NaH. After $\frac{1}{2}$ h, 3.28 g (34.3 mmol) of chloroacetone was added. The reaction was monitored by TLC chromatography (silica gel, 5% of 2-propanol in CH_2Cl_2). After 1 h at 0 °C, THF was evaporated, the residue decomposed by addition of 50 mL of cold 10% aqueous solution of K_2HPO_4 , and the product extracted into ethyl acetate. Evaporation of the solvent gave 5.81 g of a crude product consisting of two isomers of the product and unreacted starting material. Dissolving in 10 mL of diethyl ether and cooling to -15 °C overnight gave 1.167 g (27%) of a crystalline main isomer. The analytical sample was obtained by crystallization from benzene: mp 100–101.5 °C (benzene); $^1\text{H NMR}$ (270 MHz) δ 1.41 (s, 3, CH_3), 2.91 (d, $J = 12.6$ Hz, 1, SCH_2), 3.06 (d, $J = 12.6$ Hz, 1, SCH_2), 3.42 (s, 1, OH), 3.84 (s, 3, CO_2CH_3), 4.20 (s, 1, CHCO_2CH_3), 8.30 (d, $J = 2.2$ Hz, 1, $\text{N}=\text{CHS}$); $^{13}\text{C NMR}$ (67 MHz) δ 26.7, 34.0, 52.3, 62.8, 66.0, 152.9, 171.5; IR (CH_2Cl_2) ν 1730 (s, $\text{C}=\text{O}$), 1604 (s, $\text{C}=\text{N}$) cm^{-1} . Anal. Calcd for $\text{C}_7\text{H}_{11}\text{NO}_3\text{S}$: C, 44.43; H, 5.86; N, 7.40; S, 16.94. Found: C, 44.52; H, 5.75; N, 7.42; S, 16.76.

Preparation of Cepham 13. The procedure for 4b, starting from 1.054 g (3.03 mmol) of the carbene complex and 0.604 g (3.19 mmol) thiazine 12 in 30 mL of ether, gave, after 24-h irradiation, 1.016 g of crude product after the usual isolation. Pure β -lactam 13 (0.893 g, 79%) was obtained after chromatography [Chromatotron, silica gel, *n*-hexane/ether (1:1)] as a yellowish oil. The product was ~1:1 mixture of diastereoisomers (because of the racemic starting thiazine): $^1\text{H NMR}$ (270 MHz) δ 0.88 (m, 6, $\text{CH}(\text{CH}_3)_2$), 1.33 (m, 5, $\text{C}(\text{CH}_3)_2$), 1.59 (s, 1, $\text{C}(\text{CH}_3)_2$), 1.62–1.80 (m, 1, $\text{CH}(\text{CH}_3)_2$), 2.63 (d, $J = 13.8$ Hz, 1, SCH_{2a}), 2.81 (d, $J = 14.4$ Hz, 1, SCH_{2b}), 2.92 (d, $J = 14.8$ Hz, 1, SCH_{2b}), 3.04 (d, $J = 13.8$ Hz, 1, SCH_{2a}), 3.23 (m, 1, NCHCH_2O), 3.36 (br s, 1, OH_a), 3.67 (s, 1, $\text{CHCO}_2\text{CH}_{3b}$), 3.73 (dd, $J = 8.7, 4.3$ Hz, 1, NCHCH_2O), 3.80 (s, 3, OCH_3), 3.82 (dd, $J = 7.8, 10.2$ Hz, 1, NCHCH_2O), 3.88 (s, 3, OCH_3), 4.07 (s, 1, OH_b), 4.22 (d, $J = 1.4$ Hz, 1, COCH_3), 4.27 (d, $J = 1.6$ Hz, 1, COCH_3), 4.47 (s, 1, $\text{CHCO}_2\text{CH}_{3b}$), 4.55 (br s, 1, NCHS_b), 4.78 (d, $J = 1.4$ Hz, 1, NCHS_a); IR (film) ν 1734 (s, $\text{C}=\text{O}$), 1760 (s, $\text{C}=\text{O}$) cm^{-1} . Anal. Calcd for $\text{C}_{17}\text{H}_{28}\text{N}_2\text{O}_5\text{S}$: C, 54.82; H, 7.58; N, 7.52; S, 8.61. Found: C, 54.72; H, 7.46; N, 7.40; S, 8.83.

Synthesis of 14. The reaction of carbene complex 4a (191 mg, 0.500 mmol) and the *N*-benzyl imine of *m*-methoxybenzaldehyde (138 mg, 0.550 mmol) in acetonitrile (22 mL) gave 262 mg of an orange oil after 24 h of irradiation. The product was purified by chromatography [preparative TLC, hexane/EtOAc (1:1)] to yield 21 mg (0.045 mmol, 9%) of a *trans* (14a) isomer and 97 mg (0.21 mmol, 41%) of a 1:1 mixture of two *cis* (14b) isomers. *trans*-14a: $^1\text{H NMR}$ (270 MHz, CDCl_3 , Me_4Si) δ 1.41 (s, 3, CH_3), 1.46 (s, 3, CH_3), 3.38 (dd, $J = 2.3, 8.6$ Hz, 1, $\text{CHCH}=\text{O}$), 3.71 (dd, $J = 4.1, 6.9$ Hz, 1, OCH_2CHN), 3.80 (s, 3, OCH_3), 3.90 (d, $J = 14.9$ Hz, 1, CHPh), 3.99 (d, $J = 2.3$ Hz, 1, $\text{CHC}=\text{O}$), 4.30 (m, 2, OCH_2CHN), 4.45 (d, $J = 14.9$ Hz, 1, CHPh), 5.88 (dd, $J = 8.6, 15.8$ Hz, 1, $\text{CH}=\text{CHPh}$), 6.13 (d, $J = 15.8$ Hz, 1, $\text{CH}=\text{CHPh}$), 6.8 (m, 2, ArH), 7.0 (m, 2, ArH), 7.3 (m, 10, ArH). *cis*-14b: $^1\text{H NMR}$ (270 MHz, CDCl_3 , Me_4Si) δ 1.29 (s, 3, CH_3), 1.39 (s, 3, CH_3), 1.46 (s, 3, CH_3), 1.55 (s, 3, CH_3), 3.64–3.79 (m, 4), 3.80 (s, 3, OCH_3), 3.82 (s, 3, OCH_3), 3.91 (dd, $J = 4.6, 9.2$ Hz, 1, $\text{CHCH}=\text{O}$), 3.97 (d, $J = 4.4$ Hz, 1, $\text{CHC}=\text{O}$), 4.02 (d, $J = 4.6$ Hz, 1, $\text{CHC}=\text{O}$), 4.10 (m, 2), 4.24–4.41 (m, 4), 4.44 (dd, $J = 4.4, 8.3$ Hz, 1, $\text{CHCH}=\text{O}$), 5.48 (dd, $J = 9.2, 15.9$ Hz, 1, $\text{CH}=\text{CHPh}$), 5.95 (dd, $J = 8.3, 16.0$ Hz, 1, $\text{CH}=\text{CHPh}$), 6.15 (d, $J = 16.0$ Hz, 1, $\text{CH}=\text{CHPh}$), 6.25 (d, $J = 15.9$ Hz, 1, $\text{CH}=\text{CHPh}$), 6.61–7.51 (m, 28, ArH). These compounds were not further purified.

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Intersystem Crossing to both Ligand-Localized and Charge-Transfer Excited States in Mononuclear and Dinuclear Ruthenium(II) Diimine Complexes

John R. Shaw, Ralph T. Webb, and Russell H. Schmehl*

Contribution from the Department of Chemistry, Tulane University, New Orleans, Louisiana 70118. Received September 6, 1988

Abstract: The unsaturated bridging ligand 1,4-bis[2-(4'-methyl-2,2'-bipyrid-4-yl)ethenyl]benzene (dstyb) was prepared in a simple two-step sequence. The ruthenium complexes $[(\text{dmb})_2\text{Ru}]_n(\text{dstyb})^{2+}$ ($n = 1, 2$; $\text{dmb} = 4,4$ -dimethyl-2,2'-bipyridine) were prepared, and their redox and photophysical properties were examined. Both complexes have a single oxidation in cyclic voltammetry at 1.10 V vs SSCE, and for the dinuclear complex $n = 2$. The first one-electron reductions are localized on the dstyb ligand and occur at -1.32 and -1.26 V for the mononuclear and dinuclear complexes, respectively. The emission maximum in room-temperature CH_3CN is 680 nm for $[(\text{dmb})_2\text{Ru}(\text{dstyb})]^{2+}$ and 720 nm for $[(\text{dmb})_2\text{Ru}]_2(\text{dstyb})^{4+}$. For both complexes emission quantum yields are <0.005 , and luminescence lifetimes are 622 ns for the monomer and 2.02 μs for the dimer at room temperature. The very low radiative decay rates (ϕ_{em}/τ) observed result from low intersystem crossing efficiencies for population of the emitting $^3\text{MLCT}$ state. Transient absorption spectra of the two complexes provide evidence for the presence of a $^3(\pi \rightarrow \pi^*)$ state. In the mononuclear complex the lifetime of the $T_1 \rightarrow T_2$ absorbance of the $^3(\pi \rightarrow \pi^*)$ state is 1.6 μs , much longer than the emission lifetime. The $^3\text{MLCT}$ emission and the $^3(\pi \rightarrow \pi^*)$ absorption lifetimes of the dinuclear complex are within experimental error, indicating the states are equilibrated. Quenching of the transient absorbance with a series of triplet quenchers provides a measure of the triplet energy of the $^3(\pi \rightarrow \pi^*)$ state of the complexes.

There has been considerable recent interest in the photochemical and photophysical properties of binuclear and multinuclear transition-metal complexes having bridging ligands that allow varying degrees of electronic interaction between the coupled metal centers.¹⁻¹¹ Complexes of this type are of interest as potential

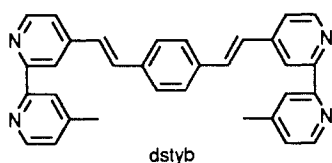
chromophores for multielectron photoredox processes. Studies of coupled ruthenium(II) diimine complexes have shown that the

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redox and luminescence properties of symmetrically bridged dimers differ appreciably from those of the corresponding mononuclear complexes when electronic communication between the metal centers is strong.^{2b,6a} In a thorough survey of pyrazine, quinoxaline, and bipyrimidine complexes of the type $[(bpy)_2Ru]_n(BL)$ ($n = 1, 2$), Gafney and co-workers showed that the dinuclear complexes ($n = 2$) luminesce at much lower energies than the mononuclear complexes ($n = 1$).^{2b} Further, the emission yields of the dinuclear complexes are lower than those of the corresponding mononuclear complexes, and luminescence lifetimes are generally much shorter. The luminescence was thus assigned as originating from a metal-to-ligand charge-transfer (MLCT) state, similar to the case for mononuclear complexes. The lowering of the emission energies of the dinuclear complexes was attributed to a large decrease in the energy of the lowest π^* orbitals of the bridging ligand upon coordination of the second metal center to the bridging ligand.

A possible consequence of the large stabilization of ligand π^* orbitals is the appearance of ligand-localized excited states (IL) at energies comparable to the MLCT states. Examples exist of ³IL phosphorescence from mononuclear Re(I) complexes having ligands known to possess relatively low energy $^3(\pi \rightarrow \pi^*)$ excited states.¹²⁻¹⁴ Also, cis-trans isomerization of styrylpyridine coordinated to Ru(II) has been shown to result from intraligand excited states.¹⁵ In binuclear complexes, the excited-state manifold is sufficiently complex that observation of intraligand excited states could be obscured by relaxation of charge-transfer states. This paper describes the preparation and photophysical investigation of the bidentate bridging ligand 1,4-bis[2-(4'-methyl-2,2'-bipyrid-4-yl)ethenyl]benzene (dstyb) and the corresponding complexes $\{[(dmb)_2Ru]_n(dstyb)\}^{2+}$ ($n = 1, 2$). Both the mononuclear



and dinuclear complexes have transient spectra with absorption in the red/near-infrared. For the mononuclear complex the lifetime of the transient absorption is longer than the ³MLCT emission. The long-lived state is populated via direct intersystem crossing from the ¹MLCT state formed upon visible light exci-

tation. This behavior is unique for complexes having emissive ³MLCT states. Direct sensitization of ³IL states by excitation into ¹MLCT states can result in a decrease in the efficiency of excited-state electron-transfer reactions of the ³MLCT state if the two states are not in equilibrium.

Experimental Section

Materials. Lithium diisopropylamide was prepared in situ from equimolar amounts of butyllithium (Aldrich, 2.5 mol) and diisopropylamine (Aldrich) freshly distilled from KOH. Terephthalaldehyde (Aldrich) and phosphoryl chloride (Aldrich) were used as received. Pyridine was distilled from KOH under an N₂ blanket and stored over molecular sieves (5 Å). Preparations for the ligand 1,4-bis[2-(4'-methyl-2,2'-bipyrid-4-yl)ethenyl]benzene (b-b) and the complex $[(dmb)_2Ru(b-b)](PF_6)_2$ have been published previously.^{4b} 4,4'-Dimethyl-2,2'-bipyridine (dmb) was purchased from Reilly Tar and Chemical and was purified by recrystallization from ethanol before use. $[Ru(dmb)_2Cl_2]$ was prepared according to the method of Sprintschnik et al.¹⁶ Acetonitrile used in electrochemical experiments (Burdick and Jackson) was refluxed over CaH₂ under N₂ and distilled immediately prior to use. Microanalyses were performed by Desert Analytics (Tucson, AZ). The triplet quenchers used were all obtained from Aldrich and used without further purification.

The bridging ligand 1,4-bis[2-(4'-methyl-2,2'-bipyrid-4-yl)ethenyl]benzene (dstyb) was prepared in two steps. To a solution of dmb (1 equiv), dissolved in a minimum of THF in a three-necked round-bottomed flask equipped with a pressure-equalizing dropping funnel and cooled to 0 °C, a THF solution of LDA (1 equiv) was added dropwise. The deep purple solution was allowed to equilibrate for 1 h after which terephthalaldehyde (0.5 equiv) dissolved in THF was added dropwise. The reaction mixture was allowed to warm to room temperature and was stirred until the deep purple color of the dmb anion disappeared (12 h). The mixture was quenched with water and evaporated to dryness. The crude product was recrystallized from ethanol to yield the dialcohol (mp 185–190 °C). The dialcohol (1 equiv), dissolved in freshly distilled pyridine, was mixed with a pyridine solution of phosphoryl chloride (2.5 equiv) in an Erlenmeyer flask. The solution was stirred for 1 h and evaporated to dryness. The crude dehydration product was recrystallized from hot toluene to yield pure dstyb: mp 240–242 °C; ¹H NMR (CDCl₃) δ 8.60 (m), 8.27 (s), 7.59 (s), 7.51 (s), 7.40 (m), 7.17 (m), 2.44 (s). Anal. Calcd for C₃₂H₂₆N₄·1.5H₂O: C, 77.87; H, 5.72; N, 11.34. Found: C, 77.79; H, 5.45; N, 10.78.

$[(dmb)_2Ru(dstyb)](PF_6)_2$ was prepared by refluxing $[(dmb)_2RuCl_2]$ (1 equiv) with dstyb (5 equiv) in ethanol for 5 h under an Ar blanket. After cooling, the solution was evaporated to dryness. The orange solid was taken up in water, filtered to remove excess ligand, and precipitated with aqueous NH₄PF₆. The precipitate was collected by vacuum filtration and dried in a vacuum oven. The crude product was purified by chromatography on neutral alumina (Anspec, activity I) using toluene/acetonitrile mixtures as eluent. With 2:1 toluene/acetonitrile the unreacted ligand not removed by filtration eluted. Increasing the CH₃CN to 50% resulted in elution of the monomeric complex as an orange band. A second orange band followed the monomer. Anal. Calcd for RuC₃₆H₅₀N₈P₂F₁₂: C, 54.86; H, 4.11; N, 9.13. Found: C, 54.30; H, 4.01; N, 9.10.

The dinuclear complex $\{[(dmb)_2Ru]_2(dstyb)\}^{4+}$ was prepared in a manner similar to that used to prepare the monomer except that a threefold excess of $[(dmb)_2RuCl_2]$ over dstyb was used. Purification of the dinuclear complex was achieved by using acidic alumina (1 in. × 6 in., Anspec, activity I) and 1:1 toluene/acetonitrile as eluent. Any mononuclear complex adsorbed to the acidic column irreversibly. Anal. Calcd for Ru₂C₈₀H₇₄N₁₂P₄F₂₄·H₂O: C, 47.96; H, 3.82; N, 8.39. Found: C, 47.95; H, 3.83; N, 8.49.

Apparatus. All UV-vis absorption spectra were recorded on a Hewlett-Packard 8451 single-beam diode-array spectrophotometer. IR spectra were obtained as KBr disks or mulls on NaCl plates and recorded on a Mattson Cygnus 100 FTIR. Emission spectra were recorded with a Spex Industries Model 111C photon-counting fluorometer equipped with a 450-W Xe arc lamp (Osram) and a cooled photomultiplier tube (PMT) housing (Hamamatsu R928, select red sensitive). All emission spectra were corrected for PMT response. The absorbance of all solutions used in emission spectral measurements was <0.2 at the excitation wavelength. NMR spectra were obtained by using an IBM Instruments NR/200 FT NMR spectrometer with CDCl₃ as both solvent and internal reference. Differential pulse polarograms (DPP) were recorded on a Sargent-Welch Model 4001 polarograph. Cyclic voltammograms were

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Table I. Redox Properties of Monomeric and Dimeric Complexes in CH₃CN^a

complex	oxidation $E_1^\circ(\text{Ox}),$ V ($\Delta E_p, \text{mV}$)	reduction $E_1^\circ(\text{Red}),$ V ($\Delta E_p, \text{mV}$)	$\Delta E_{1/2}, \text{V}$
$[(\text{dmb})_2\text{Ru}(\text{b-b})]^{2+}$	1.11 (60)	-1.44 (60)	2.55
$[(\text{dmb})_2\text{Ru}(\text{dstyb})]^{2+}$	1.10 (60)	-1.32 (60)	2.42
$\{[(\text{dmb})_2\text{Ru}]_2(\text{dstyb})\}^{4+}$	1.10 (60)	-1.26 (60)	2.36
$[(\text{styb})_3\text{Ru}]^{2+}$	1.14 (—)		

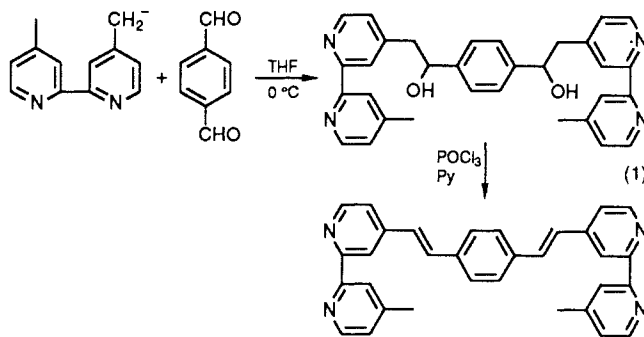
^a Potentials determined by cyclic voltammetry (0.2 V/s) referenced to SSCE in 0.1 M tetraethylammonium perchlorate. All potentials ± 0.005 V. ^b styb = 4,4'-distyryl-2,2'-bipyridine; b-b = 1,4-bis[2-(4'-methyl-2,2'-bipyrid-4-yl)ethyl]benzene.

obtained as described previously.¹⁷ In all electrochemical measurements the sodium saturated calomel electrode (SSCE) served as reference with tetraethylammonium perchlorate (TEAP) as the supporting electrolyte. Luminescence lifetime measurements were obtained by using an apparatus described elsewhere.¹⁷ All samples for emission lifetime and transient absorption measurements were freeze-pump-thaw degassed to a final pressure $< 5 \times 10^{-5}$ Torr.

Transient absorption spectra were obtained by using excitation from the total emission of a coumarin-460 dye cell pumped by a Lambda Physik EMG-52 XeCl₂ excimer laser. Excitation was perpendicular to the spectrophotometric optical path. Absorption measurements were made by focusing the output of an Ealing Instruments 250-W mercury-xenon lamp through a 1-mm hole in a home-built 1-cm² cell holder and imaging the transmitted light into a CGA-McPherson Model 270 monochromator. Transient absorption spectral changes were detected by monitoring the output of a Hammamatsu R-928 PMT housed in a home-built base, using a Tektronix 390 AD transient digitizer optically triggered by laser pulses. Shutters were used to minimize exposure of samples to the analyzing light source. Control of shutter movement, monochromator scanning, laser triggering, and storage of transient signals was achieved by using a Hewlett-Packard 9826 microcomputer. Each transient represents the average of 5–10 laser pulses; spectra were typically acquired with 10-nm wavelength intervals.

Results and Discussion

Synthesis. The ligand dstyb was prepared by an approach analogous to that used in the preparation of 4-methyl-4'-vinyl-2,2'-bipyridine.^{18,19} Reaction of the monoanion of 4,4'-dimethyl-2,2'-bipyridine with terephthalaldehyde in THF (eq 1) resulted in formation of the dialcohol. Dehydration of the dialcohol was accomplished with POCl₃ in anhydrous pyridine. The complexes $[(\text{dmb})_2\text{Ru}(\text{dstyb})]^{2+}$ and $\{[(\text{dmb})_2\text{Ru}]_2(\text{dstyb})\}^{4+}$ were prepared by standard methods,^{4a} using $[(\text{dmb})_2\text{RuCl}_2]$ as the metalating agent. Repeated chromatography of the PF₆⁻ salts on either neutral or acidic alumina was required to remove unreacted dstyb.



Electrochemistry. One measure of the degree of electronic interaction between coupled ruthenium centers in symmetrically bridged dimers, $[(L)_n\text{Ru}(\text{bridge})\text{Ru}(L)_n]$, is the relative Ru(3⁺/2⁺) potentials of each metal. Cyclic voltammograms and differential pulse polarograms of weakly interacting complexes have a single

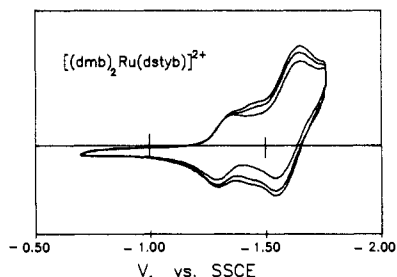
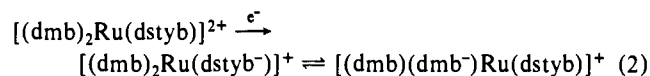


Figure 1. Reductive cyclic voltammogram of $[(\text{dmb})_2\text{Ru}(\text{dstyb})]^{2+}$ in CH₃CN at room temperature. Current increases with cycling result from deposition of complex on the electrode. Sweep rate: 100 mV/s. Supporting electrolyte: tetraethylammonium perchlorate.

Ru(3⁺/2⁺) wave at a potential nearly equal to that of the mononuclear complex. As the degree of interaction increases, the two Ru(3⁺/2⁺) waves split into two distinct waves reflecting partial delocalization of metal d* electrons between the two centers.^{2,3,6,20} Table I summarizes redox data obtained for $[(\text{dmb})_2\text{Ru}(\text{dstyb})]^{2+}$ and $\{[(\text{dmb})_2\text{Ru}]_2(\text{dstyb})\}^{4+}$ from cyclic voltammograms in acetonitrile solution. Both complexes exhibit a single oxidative wave in cyclic voltammograms. The Ru(3⁺/2⁺) potential of both complexes is very close to that of $[(\text{dmb})_2\text{Ru}(\text{b-b})]^{2+}$, in which the ethenyl groups of the bridge between the bipyridines of dstyb are saturated. Only a single anodic wave is observed for $\{[(\text{dmb})_2\text{Ru}]_2(\text{dstyb})\}^{4+}$, indicating a small degree of electronic interaction between the linked metal centers. Coulometric analysis of the anodic wave of the dimer yields $n = 2$, demonstrating that both the complex 6⁺/5⁺ and 5⁺/4⁺ waves occur at the same potential. This behavior sharply contrasts with that of the bridged dimer $\{[(\text{bpy})_2\text{Ru}]_2(\text{dpp})\}^{4+}$, where the 6⁺/5⁺ and 5⁺/4⁺ potentials are separated by 190 mV (dpp = 2,3-bis(2-pyridyl)pyrazine).^{2a}

Cyclic voltammograms for the mononuclear and dinuclear complexes indicate the relative effect of coordination of the Ru(II) centers on the π^* level of the bridging ligand since reduction of tris(diimine) Ru(II) complexes is known to be ligand localized.²¹ A reductive cyclic voltammogram of $[(\text{dmb})_2\text{Ru}(\text{dstyb})]^{2+}$ is shown in Figure 1. Two reductive waves are observed at potentials positive of -1.8 V vs SSCE. The first reduction occurs at -1.32 V, 120 mV positive of the first reduction of $[(\text{dmb})_2\text{Ru}(\text{b-b})]^{2+}$. Results of EPR²² and spectroelectrochemical²³ studies of reduced mixed-ligand Ru(II) diimine complexes show that the reducing electron resides principally on the more easily reduced ligand (eq 2). An interesting feature of reduction of this complex is that



repeated reductive cycling results in a steady increase in peak currents and accumulation of the complex on the electrode. The electrodeposition is probably the result of reductive electropolymerization, a process that has been thoroughly studied for Ru(II) diimine complexes having olefinic moieties.²⁴ We are currently further characterizing adsorbed films formed upon reduction of $[(\text{dmb})_2\text{Ru}(\text{dstyb})]^{2+}$.

The first reduction of $\{[(\text{dmb})_2\text{Ru}]_2(\text{dstyb})\}^{4+}$ occurs at -1.26 V, only 60 mV positive relative to corresponding reduction of the mononuclear complex. Related complexes having completely conjugated bridging ligands typically exhibit 300–400-mV shifts in the first bridging-ligand reduction. The small positive shift in the first reduction of $\{[(\text{dmb})_2\text{Ru}]_2(\text{dstyb})\}^{4+}$ may simply result from the increased positive charge of the complex, although no difference is observed in the first one-electron reductions of

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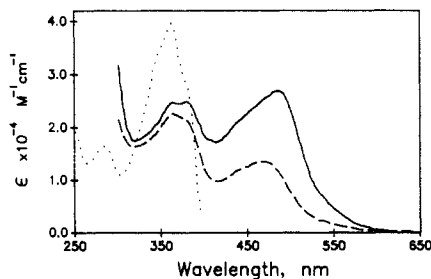
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Table II. Absorption and Luminescence Properties of Ru(II) Complexes in CH₃CN at 25 °C

complex ^a	λ_{\max} , nm (log ϵ)	E_{em} , ^b cm ⁻¹	τ_{em} , ^b ns	ϕ_{em} ^b	$10^4 k'_r$, ^c s ⁻¹	η_{isc}
{[(dmb) ₂ Ru] ₂ (b-b)} ⁴⁺	460 (4.15)	16 200	820	0.066	8.0	1.0
{[(dmb) ₂ Ru(dstyb)] ²⁺	468 (4.21)	14 700	622	0.006	0.91	0.30
{[(dmb) ₂ Ru] ₂ (dstyb)} ⁴⁺	484 (4.57)	13 900	2020	0.001 ₅	0.075	
{styb) ₃ Ru] ²⁺	487 (4.52)	14 700	720	0.03	4.2	

^aLigand descriptions are the same as those of Table I. ^b $E_{\text{em}} \pm 50$ cm⁻¹; $\tau_{\text{em}} \pm 10$ ns; $\phi_{\text{em}} \pm 0.0005$. ^c $k'_r = \phi_{\text{em}}/\tau_{\text{em}}$.

**Figure 2.** Absorption spectra of dstyb (···), [(dmb)₂Ru(dstyb)]²⁺ (---), and {[(dmb)₂Ru]₂(dstyb)}⁴⁺ (—) in CH₃CN at room temperature.

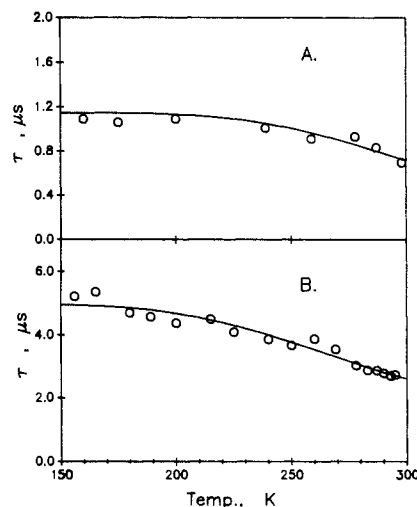
{[(dmb)₂Ru(b-b)]²⁺ and {[(dmb)₂Ru]₂(b-b)}⁴⁺.^{4b}

Spectral Properties and Luminescence Decays. Absorption and emission spectral data for the complexes in CH₃CN at room temperature are summarized in Table II. The absorption spectra of dstyb and of the mononuclear and dinuclear complexes of dstyb are shown in Figure 2. The ligand has an absorption maximum at 360 nm and also exhibits strong fluorescence at room temperature with a maximum at 420 nm. Irradiation of CH₃CN solutions of the ligand on the red edge of the absorption (380 nm) results in a shift of the absorption maximum to 340 nm. The spectrophotometric change is reversible upon photolysis at 300 nm. Spectral changes of this type are analogous to those observed upon trans-cis isomerization of styrylpyridines.^{25,26}

The spectra of [(dmb)₂Ru(dstyb)]²⁺ and {[(dmb)₂Ru]₂(dstyb)}⁴⁺ have both intraligand (IL) and lower energy metal-to-ligand charge-transfer (MLCT) transitions (Figure 2). A single broad MLCT absorption is observed for the complexes; the independent Ru(dπ) → dmb(π*) and Ru(dπ) → dstyb(π*) transitions are not resolved as in other mixed-ligand diimine complexes.^{2,3,4,17} A 16-nm (800 cm⁻¹) difference in the lowest energy MLCT absorption maxima is observed between the mononuclear and dinuclear complexes bridged by dstyb.

It has been shown that for complexes having MLCT absorption and emission, linear correlations exist between absorption or emission energies and $\Delta E_{1/2}$, the difference between the potentials for metal-centered oxidation and the first coordinated ligand reduction (Table I).^{2b,27-32} Comparison of data from Tables I and II indicates that red shifts in the absorption and emission (800 cm⁻¹) energies of the dimer relative to the monomer are comparable to the observed difference in $\Delta E_{1/2}$ of 500 cm⁻¹. The correlation of electrochemical and spectroscopic properties is consistent with both the lowest energy absorption and emission of both complexes being MLCT transitions.

More careful spectroscopic examination reveals idiosyncracies of the complexes. The observed radiative decay rates, k'_r (Table

**Figure 3.** Luminescence lifetimes in 4:1 ethanol/methanol as a function of temperature for [(dmb)₂Ru(dstyb)]²⁺ (A) and {[(dmb)₂Ru]₂(dstyb)}⁴⁺ (B). The solid lines represent the best fit of the data to eq 4; fitting parameters are given in Table III.

II), of both [(dmb)₂Ru(dstyb)]²⁺ and {[(dmb)₂Ru]₂(dstyb)}⁴⁺ are much lower than those of most Ru(II) diimine complexes (10⁴–10⁵ s⁻¹).^{21,33} Since emission in Ru(II) polypyridine complexes is generally from triplet MLCT states, k'_r is actually the product of the intersystem crossing efficiency, η_{isc} , and the radiative decay rate of the emitting excited state (eq 3). Thus one explanation

$$k'_r = \phi_{\text{em}}/\tau_{\text{em}} = \eta_{\text{isc}}k_r \quad (3)$$

of the low radiative decay rates observed is that η_{isc} is lower than that of other Ru(II) diimine complexes. Although η_{isc} has been determined for only a few complexes of this type, values are typically close to unity.^{34,35}

A second explanation for the low radiative decay rates is that emission occurs from an intraligand, ³($\pi \rightarrow \pi^*$) state rather than a ³MLCT state. The observation of phosphorescence from coordinated ligands is not unique.^{12-14,36,37} Giordano and Wrighton have reported efficient intraligand (IL) phosphorescence from [ReX(CO)₃(4-phenylpyridine)₂] at 77 K (X = Cl, Br, I) and *fac*-[ReX(CO)₃(3-benzoylpyridine)₂].¹² Further, Juris and co-workers have recently reported IL phosphorescence from 4,4'-bis[2-(*p*-(diethylamino)styryl)]-2,2'-bipyridine (DEAS-bpy) in the complex [ReCl(CO)₃(DEAS-bpy)] at room temperature in DMF solution.¹⁴ However, room-temperature phosphorescence from styrylpyridines and 1,2-bis(pyridyl)ethylenes, either free or as coordinated ligands, has not been observed, and trans-cis isomerization is the principal reaction mode of the triplet excited state ($\phi_{\text{isc}} = 0.3$).^{25,26} Trans-cis isomerization of coordinated styrylpyridine in [(bpy)₂Ru(4-styrylpyridine)₂]²⁺ has been observed only upon direct irradiation into the styrylpyridine $\pi \rightarrow \pi^*$ absorption, suggesting weak coupling of the ³($\pi \rightarrow \pi^*$) and the lower energy ³MLCT states of the complex.¹⁵ Irradiation of

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Table III. Activation Parameters Obtained from Temperature Dependent Luminescence Decays^a

complex	$\tau_{em}(77\text{ K}),^b$ μs	k_0, s^{-1}	k_0', s^{-1}	$E_a,$ cm^{-1}
$[(\text{dmb})_2\text{Ru}(\text{dstyb})]^{2+}$	2.87	8.7×10^5	9.0×10^8	1550
$\{[(\text{dmb})_2\text{Ru}]_2(\text{dstyb})\}^{4+}$	5.3	2.0×10^5	3.9×10^7	1115
$[(\text{dmb})_3\text{Ru}]^{2+c}$	4.0	5.2×10^5	3.0×10^{11}	2740

^aMargins of error: $k_0 \pm 5\%$, $k_0' \pm 80\%$, $E_a \pm 20\%$. ^bIn 4:1 ethanol/methanol glass. ^cReference 17.

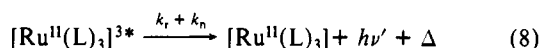
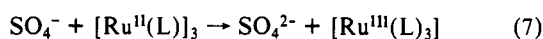
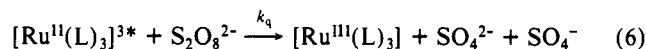
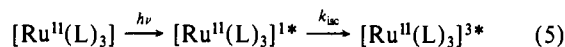
$[(\text{dmb})_2\text{Ru}(\text{dstyb})]^{2+}$ in CH_3CN solutions at $\lambda > 450\text{ nm}$ results in a blue shift in the IL ($\pi \rightarrow \pi^*$) absorption of the complex, similar to spectral changes observed upon photolysis of free dstyb. The reactivity of the $^3(\pi \rightarrow \pi^*)$ state observed following MLCT excitation suggests that the emitting state could be $^3(\pi \rightarrow \pi^*)$.

Since phosphorescence of $^3(\pi \rightarrow \pi^*)$ states is generally medium and temperature dependent, the temperature dependence of the luminescence decay of both complexes was examined (Figure 3). Data obtained at temperatures above the glass transition temperature of the solvent can be fit by assuming a single thermally activated nonradiative decay path exists for the emitting excited state (eq 4),^{21,33} where k_0 is the sum of the intrinsic radiative and

$$k_{obs} = k_0 + k_0' \exp[-E_a/RT] \quad (4)$$

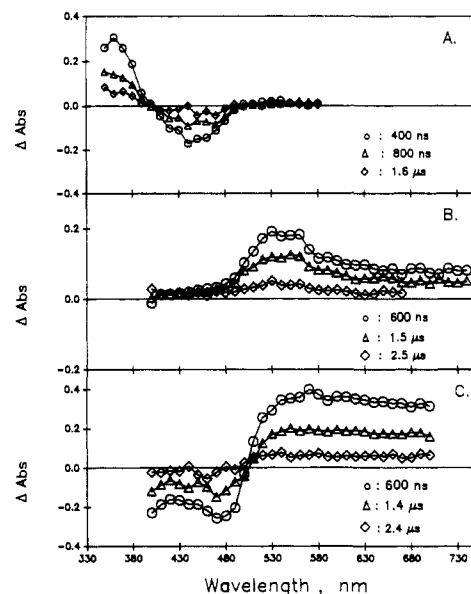
nonradiative decay rate constants of the emitting state. If the state populated in the surface crossing is *not* in equilibrium with the emitting state, then k_0' and E_a represent the prefactor and activation barrier for the process. If the two states are in equilibrium, then k_0' is a function of the prefactors for both forward and back internal conversion between the equilibrated states and the decay rate of the nonemitting state and E_a equals the energy difference between the two states. In Ru(II) diimine complexes, both types of thermally activated surface crossings have been observed.³³ When the prefactor k_0' is near the vibrational limit (10^{13} s^{-1}), the surface crossing results in population of a metal-centered (^3MC) state. Lower values of k_0' (10^6 – 10^8 s^{-1}) are observed in mixed-ligand complexes having one low-lying $^3\text{MLCT}$ state. In these complexes ^3MC photochemistry is not observed, and the thermally activated process is ascribed to population of a higher lying MLCT state possessing significant singlet character.^{33,40} Parameters obtained from fits of the temperature-dependent lifetimes of $[(\text{dmb})_2\text{Ru}(\text{dstyb})]^{2+}$ and $\{[(\text{dmb})_2\text{Ru}]_2(\text{dstyb})\}^{4+}$ are given in Table III. Both complexes have small prefactors and low activation barriers. The data can be explained either as resulting from back intersystem crossing to the $^1\text{MLCT}$ state or as an equilibrium process (vide infra). The lifetimes obtained in frozen solutions (77 K) are typical of $^3\text{MLCT}$ emission²¹ and are much shorter than lifetimes observed for phosphorescence from coordinated ligands such as DEAS-bpy.¹⁴ The frozen-solution behavior, combined with the correlation of redox and emission properties, strongly suggests the emission of both complexes is of MLCT origin. In order to account for the observed radiative decay rates, η_{isc} must be less than unity for both complexes.

A photochemical approach to approximating η_{isc} in ruthenium polypyridyl complexes was devised by Bolletta and involves the irreversible photooxidation of the Ru(II) center by peroxydisulfate (eq 5–8).³⁸



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**Figure 4.** Transient absorption spectra obtained following flash excitation at 460 nm of $[(\text{dmb})_3\text{Ru}]^{2+}$ (A), $[(\text{dmb})_2\text{Ru}(\text{dstyb})]^{2+}$ (B), and $\{[(\text{dmb})_2\text{Ru}]_2(\text{dstyb})\}^{4+}$ (C) in CH_3CN at room temperature.**Table IV.** Lifetimes of Transients Observed in Flash Photolysis of Complexes in CH_3CN at 298 K^a

complex	$\tau(525\text{ nm}), \text{ns}$	τ_{em}, ns
$[(\text{dmb})_2\text{Ru}(\text{dstyb})]^{2+}$	1660 ± 20	660 ± 10
$\{[(\text{dmb})_2\text{Ru}]_2(\text{dstyb})\}^{4+}$	2500 ± 50	2000 ± 100

^aDye laser excitation at 460 nm. Lifetime obtained as average of 10 decays.

The limiting quantum yield for the process is twice the intersystem crossing efficiency, provided $\text{S}_2\text{O}_8^{2-}$ does not react with the excited singlet MLCT state. For $[\text{Ru}(\text{bpy})_3]^{2+}$ the limiting quantum yield is 2.0.^{33–35,38} The value of η_{isc} obtained by this approach for the mononuclear complex of dstyb is given in Table II. A reliable estimate of η_{isc} for $\{[(\text{dmb})_2\text{Ru}]_2(\text{dstyb})\}^{4+}$ could not be obtained because precipitation of the $\text{S}_2\text{O}_8^{2-}$ salt of the complex occurs at concentrations of $\text{S}_2\text{O}_8^{2-}$ above $5 \times 10^{-4}\text{ M}$. The radiative decay rate, k_r , calculated for $[(\text{dmb})_2\text{Ru}(\text{dstyb})]^{2+}$ is $3.2 \times 10^4\text{ s}^{-1}$ when the intersystem crossing efficiency is included. This value is typical of radiative decay rates for $^3\text{MLCT}$ state emission.^{41,42} The low intersystem crossing efficiency may result from either rapid nonradiative relaxation from the $^1\text{MLCT}$ state or competitive population of another state.

Transient Absorption Spectra and Triplet Quenching. Transient absorption spectra of $[(\text{dmb})_3\text{Ru}]^{2+}$, $[(\text{dmb})_2\text{Ru}(\text{dstyb})]^{2+}$, and $\{[(\text{dmb})_2\text{Ru}]_2(\text{dstyb})\}^{4+}$ following pulsed dye laser excitation at 460 nm are shown in Figure 4. Both complexes containing dstyb have a strong absorption feature in the red ($>550\text{ nm}$) that differs from tris(diimine) complexes such as $[(\text{dmb})_3\text{Ru}]^{2+}$. The lifetimes of the red absorption feature and the luminescence, obtained with the same dye laser excitation, are given in Table IV. In $[(\text{dmb})_2\text{Ru}(\text{dstyb})]^{2+}$ the red absorption feature has a significantly longer lifetime than the luminescence decay. Excimer laser flash excitation (308 nm) of free dstyb in CH_3CN produces a transient with absorption maxima at 445 ± 10 and $500 \pm 10\text{ nm}$ and a lifetime of $5.9\text{ }\mu\text{s}$ at room temperature. Recent work by Tokumaru and co-workers has shown that a series of anthryl ethylenes have low triplet energies ($<15000\text{ cm}^{-1}$) and long triplet lifetimes for the trans isomers.³⁹ For example, 2-styrylanthracene has a triplet energy of 14300 cm^{-1} ($\tau = 190\text{ }\mu\text{s}$), and the $T_1 \rightarrow T_n$ absorption

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Table V. Rate Constants for Quenching of Transient Absorbance and Luminescence of Complexes^a

quencher	[[dmb] ₂ Ru(dstyb)] ²⁺			{[(dmb) ₂ Ru] ₂ (dstyb)} ⁴⁺	
	<i>E</i> _T , cm ⁻¹	<i>k</i> _q ^{abs} × 10 ⁻⁸	<i>k</i> _q ^{em} × 10 ⁻⁸	<i>k</i> _q ^{abs} × 10 ⁻⁸	<i>k</i> _q ^{em} × 10 ⁻⁸
acridine (Acr)	15 900	0.23	20.1		
phenazine (Phen)	15 400	0.97	28.0	0.05	
anthracene (Anth)	15 000	8.9	30.5	1.3	1.2
1-chloroanthracene (1-ClA)	14 750	14.0	59.1	3.3	2.7
9,10-diphenyl- anthracene (DPA)	14 500	16.0	20.1	14.7	13.0
9,10-dichloro- anthracene (DCA)	14 150	77.0	159.0	57.4	57.3
perylene (PER)	12 300	73.5	110.0	62.8	85.6
methylviologen		0.54	3.8	0.73	0.77

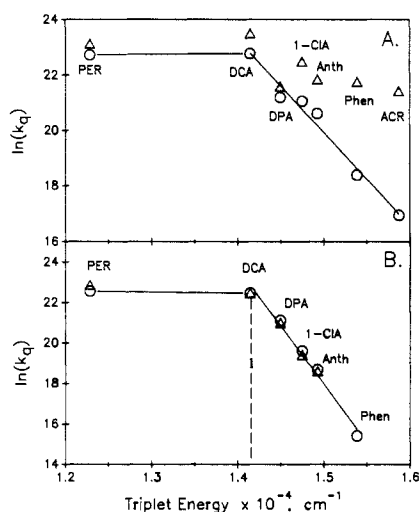
^a All rate constants are second order (M⁻¹ s⁻¹).

Figure 5. Rates for triplet quenching of transient absorbance (O) and luminescence (Δ) of [(dmb)₂Ru(dstyb)]²⁺ (A) and {[(dmb)₂Ru]₂(dstyb)}⁴⁺ (B) as a function of quencher triplet-state energy in CH₃CN at room temperature. The solid line in the regions of decreasing ln(*k*_q) vs *E*_T represents the best-fit straight line through the points.

spectrum has maxima at 450 and 620 nm in benzene at room temperature. Given the literature precedent and these observations, the long-lived transients observed for dstyb, [(dmb)₂Ru(dstyb)]²⁺, and {[(dmb)₂Ru]₂(dstyb)}⁴⁺ may all be assigned as T₁ → T_n absorption of a ³(π → π*) IL state. The fact that the luminescence and T₁ → T_n absorption lifetimes differ by a factor of nearly 3 for the mononuclear complex indicates that the ³MLCT and ³(π → π*) states are not in equilibrium. This is consistent with the results of Whitten et al. for styrylpyridine isomerization in [(bpy)₂Ru(4-styrylpyridine)]²⁺.¹⁵

To further examine the relative energies of the ³MLCT and ³(π → π*) states, quenching of both the T₁ → T_n absorption and ³MLCT emission was examined, using a series of aromatic hydrocarbons of known triplet energy (*E*_T) as quenchers. Table V lists quenching rate constants obtained assuming Stern–Volmer kinetics, and Figure 5 shows ln(*k*_q) as a function of the triplet energy for each complex; both plots have a slope close to 1/*RT*, where *k*_q decreases with increasing *E*_T. Results for quenching of both transient absorbance and luminescence of {[(dmb)₂Ru]₂(dstyb)}⁴⁺ are nearly identical. Although the data are relatively limited, the ³(π → π*) energy is close to that of 9,10-dichloroanthracene (14 150 cm⁻¹), which is only slightly higher than the ³MLCT emission maximum (13 900 cm⁻¹). Quenching of {[(dmb)₂Ru]₂(dstyb)}⁴⁺ with methylviologen, which can only react with the ³MLCT state via electron transfer,⁴⁴ results in quenching of both ³MLCT emission and intraligand transient

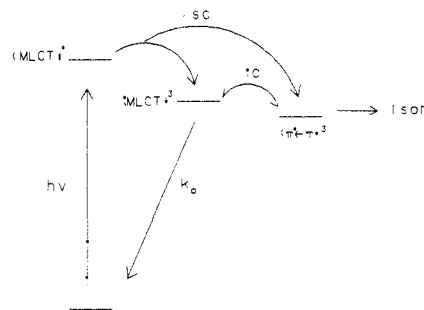


Figure 6. General state diagram for dstyb complexes.

absorbance at comparable rates (Table V). This observation suggests the two states are in equilibrium. The small prefactor and low activation barrier obtained from temperature-dependent luminescence decays of {[(dmb)₂Ru]₂(dstyb)}⁴⁺ (vide supra) may result from equilibrium internal conversion between the emitting ³MLCT state and the ³(π → π*) state.

Triplet quenching of [(dmb)₂Ru(dstyb)]²⁺ by the series of quenchers is shown in Figure 5A. The data for quenching of T₁ → T_n absorption indicates the ³(π → π*) state is nearly the same energy as the same state of the dinuclear complex. However, greater quenching of the ³MLCT emission is observed for all of the quenchers. This is consistent with the higher (>550 cm⁻¹) energy of the ³MLCT state of the complex. Oxidative electron-transfer quenching of the ³MLCT emission with methylviologen is 7 times faster than quenching of the ³IL absorption; this is consistent with slow back internal conversion from the ³(π → π*) state to the ³MLCT state. Given the different lifetimes and quenching rates of the ³(π → π*) and ³MLCT states and the measured intersystem crossing efficiency to the ³MLCT state of 0.3, it is reasonable to conclude that the ¹MLCT state populates both of the observed triplet states directly. The ³(π → π*) state can also be populated by internal conversion from the ³MLCT state. If it is assumed that the activation parameters of Table III correspond to internal conversion from the ³MLCT state to the lower energy ³(π → π*) state of [(dmb)₂Ru(dstyb)]²⁺, then the room-temperature internal conversion efficiency is approximately 0.35. Internal conversion from the ³MLCT state into the ³MC state is not likely to be an important decay path for the dstyb complex since the ligand field of [(dmb)₂Ru(dstyb)]²⁺ is nearly the same as that of [(dmb)₃Ru]²⁺ but the ³MLCT state is lower in energy; this has been demonstrated for other mixed-ligand complexes.^{17,21}

Figure 6 shows a general state diagram for [(dmb)₂Ru(dstyb)]²⁺ and {[(dmb)₂Ru]₂(dstyb)}⁴⁺. Excitation into the MLCT absorption is followed by intersystem crossing into both ³MLCT and ³(π → π*) manifolds. Relaxation of the ³MLCT state occurs by either radiative or nonradiative paths and the ³(π → π*) is nonemissive. Internal conversion between the two states differs for the two complexes. In [(dmb)₂Ru(dstyb)]²⁺, back internal conversion from the ³IL state is slower than nonradiative relaxation and the two states are not in equilibrium. In the dimer, emission lifetime and electron-transfer quenching results suggest that equilibration of the states is rapid relative to relaxation processes. Absorption spectral changes observed upon photolysis of the free ligand and the mononuclear complex suggest that relaxation of the ³(π → π*) state is accompanied by some degree of isomerization.

Relation to Other Complexes. The observation of both ³MLCT emission and T₁ → T_n absorption of the ³(π → π*) state in these complexes is unusual. There are numerous reports of multiple-state emission from transition-metal complexes,^{12–14,36,37} particularly at low temperatures; however, direct observation of both emitting and nonluminescent states of the same spin multiplicity is rare. Studies of photoanation of Ru(II) diimine complexes provide evidence for thermal equilibration of ³MLCT and ³MC states;^{21,33,43} in these complexes available evidence indicates that population of the ³MLCT state precedes internal conversion to the ³MC state. For the mononuclear complex reported here intersystem crossing occurs from the ¹MLCT to both ³MLCT and ³(π → π*) states. The related complex [(bpy)₂Ru(4-styryl-

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pyridine)₂]²⁺ exhibits very different behavior.¹⁵ Results from ligand isomerization studies suggest that intraligand states, ³IL, are formed only upon photolysis directly into the ligand ³($\pi \rightarrow \pi^*$) absorption. Photolysis into the lower energy MLCT absorption results in a cis:trans ratio reasonably close to the thermodynamic ratio, implying the ¹MLCT manifold does not sensitize the ³IL state, which yields nearly equal amounts of cis and trans isomers. In [(dmb)₂Ru(dstyb)]²⁺, MLCT irradiation results in an intersystem crossing efficiency into the ³IL state of 0.7. The difference in behavior between styrylpyridine and dstyb complexes may simply reflect the fact that the ³IL state of dstyb (14 150 cm⁻¹) is lower than that of styrylpyridine (17 500 cm⁻¹). Another difference between the styrylpyridine complex and the dstyb complexes is that the lowest MLCT absorption in [(bpy)₂Ru(4-styrylpyridine)]²⁺ is Ru(d π) \rightarrow bpy(π^*) whereas for both dstyb

complexes the transition is Ru(d π) \rightarrow dstyb(π^*). We are currently examining other complexes that will address this question more directly.

Many of the complexes prepared as potential sensitizers for multielectron redox reactions employ bridging ligands having extended conjugation similar to that of dstyb. The presence of low-energy, nonluminescent ³IL states, as in complexes of dstyb, coupled with low yields for population of ³MLCT states, can serve to decrease the efficiency of reactions of this type.

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Reactions of Triplet Carbonyl Compounds and Nitro Derivatives with Silanes

Angelo Alberti,[†] Sergio Dellonte,[‡] Carmen Paradisi,[§] Sergio Roffia,[§] and Gian Franco Pedulli^{*,\u00b1}

Contribution from the I.Co.C.E.A.—C.N.R., Via della Chimica 8, I-40064 Ozzano Emilia, Italy, F.R.A.E.—C.N.R., Via dei Castagnoli 1, I-40126 Bologna, Italy, Dipartimento di Chimica G. Ciamician, Universit\u00e0 di Bologna, Via Selmi 2, I-40126 Bologna, Italy, and Dipartimento di Chimica Organica, Universit\u00e0 di Bologna, Via S. Donato 15, I-40127 Bologna, Italy.
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Abstract: The photoinduced reactions of aromatic and aliphatic carbonyl compounds and nitro derivatives with tetramethylsilane, hexamethyldisilane, and tetrakis(trimethylsilyl)silane were investigated by EPR spectroscopy. The photoreaction of benzophenone with the three silanes was also studied by time-resolved optical techniques. Triplet ketones and quinones reacted with Me₃SiSiMe₃ and with (Me₃Si)₄Si by a radical-like displacement mechanism. Homolytic substitution was also observed by reacting photoexcited nitro compounds with the same silanes. The nature of the radical adducts being formed suggests that this reaction is likely to proceed, at least for some of the investigated compounds, via a partial or complete electron transfer (ET). Corroborating evidence for the latter process was sought in polarographic, cyclic voltammetric, and controlled-potential coulometric experiments.

Group IVB organometallic compounds can undergo homolytic substitution reactions, S_H2, at the metal atom. These processes take place more readily when the heavier elements of the group, such as tin and lead, are involved;¹⁻³ examples have also been reported of homolytic displacement at silicon and germanium brought about by halogen atoms.² Generally, metal-to-metal bonds are more easily cleaved via an S_H2 mechanism than metal-to-carbon bonds,² this being in agreement with the different bond strengths involved, i.e., 80.5 (Me₃Si-SiMe₃), 89.4 (Me₃Si-Me),⁴ 73 (Ge-Ge), 76 (Ge-Me), 56 (Sn-Sn), and 65 kcal/mol (Sn-Me).⁵

The capability of bringing about homolytic displacement reactions is not a peculiarity of free radicals and is also exhibited by other species containing unpaired electrons such as triplet-state molecules. Indeed, we have shown in previous papers that the reaction of triplet diphenylcarbene with sulfides, disulfides, diselenides,⁶ some trivalent phosphorus compounds,⁷ and group IVB organometallic derivatives containing metal-metal bonds⁸ is analogous to the familiar homolytic substitution process, S_H2. Also triplet carbonyl compounds have been shown to give homolytic displacements, in particular at phosphorus⁷ and boron⁹ derivatives.

We report here the results of an investigation on the photochemical reactions between a number of carbonyl and nitro de-

rivatives with some silanes. This study has been carried out by using electron paramagnetic resonance spectroscopy (EPR) to identify the radicals formed, electrochemical techniques to determine redox potentials, and time-resolved optical techniques to measure the rate of quenching of a representative triplet ketone, i.e., benzophenone, by several silanes.

Results and Discussion

The silicon-containing compounds that have been used are tetramethylsilane and two derivatives containing the silicon-silicon bond, i.e., hexamethyldisilane and tetrakis(trimethylsilyl)silane.

Carbonyl Compounds. EPR Measurements. The reactions of triplet ketones with group IVB metal hydrides have been exten-

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[†] I.Co.C.E.A.—C.N.R.

[‡] F.R.A.E.—C.N.R.

[§] Dipartimento di Chimica G. Ciamician, Universit\u00e0 di Bologna.

^{\u00b1} Dipartimento di Chimica Organica, Universit\u00e0 di Bologna.