TABLE IV: Dependence of  ${}^{1}O_{2}$  Phosphorescence Quantum Yields  $Q_{P}(X)$  on Solvent  $X^{a}$ 

solvent X	$Q_{\mathbf{P}}(\mathbf{X})$	
C <sub>6</sub> H <sub>6</sub>	$(4.7 \pm 1.7) \times 10^{-5}$	
CH3CN	$(7.1 \pm 2.8) \times 10^{-5}$	
CHCl <sub>3</sub>	$(3.6 \pm 1.4) \times 10^{-4}$	
CS <sub>2</sub>	$(4.0 \pm 1.8) \times 10^{-2}$	
CCl4	$(9.0 \pm 3.6) \times 10^{-2}$	
Freon 113	$(1.5 \pm 0.6) \times 10^{-1}$	

<sup>a</sup>Standard value  $Q_{\rm P}({\rm B})$  determined by comparison of corrected fluorescence and phosphorescence spectra. The errors in  $Q_{\rm P}({\rm X})$  are mainly determined by the uncertainty of  $Q_{\rm P}({\rm B})$ .<sup>10</sup>

quantum yield  $Q_P$ (Freon 113) = 0.15 ± 0.06 determined in this study agrees excellently with the value  $Q_P$ (Freon 113) = 0.15 ± 0.08 which was obtained from a comparison of the intensities of the spectrally unresolved emissions of TPP and  ${}^{1}O_2$  measured directly with a radiometer.<sup>10</sup> The accordance of both results obtained by completely different techniques confirms impressively the accuracy of the quantum yield data of Table IV.

### Discussion

The quantum yields of  ${}^{1}O_{2}$  formation by the sensitizers DCA, RUB, and TPP have been determined in six different solvents with rather high accuracy. Since  $Q_{\Delta}(X)$  values depend for DCA and RUB distinctly on solvent, probably for both sensitizers S<sub>1</sub>-state and T<sub>1</sub>-state quenching by O<sub>2</sub> produces  ${}^{1}O_{2}$ . In contrast  $Q_{\Delta}(X)$ values for TPP depend only very weakly on solvent nature, indicating that essentially T<sub>1</sub>-state quenching by O<sub>2</sub> leads to the formation of  ${}^{1}O_{2}$  by TPP.

The  ${}^{1}O_{2}$  phosphorescence quantum yield  $Q_{P}(X)$  depends strongly on solvent nature and correlates exactly linear with  $\tau_{\Delta}(X)$ . Consequently the factors controlling  ${}^{1}O_{2}$  deactivation in solution determine also the solvent dependence of phosphorescence quantum yields.

 $^{1}O_{2}$  deactivation by a solvent molecule occurs by a collisional energy-transfer process to a single oscillator of the accepting molecule. Accepting oscillators are terminal atom pairs of the solvent molecule like for example C-H or C-F. During this process electronic energy is converted mainly into vibrational energy. Since the deactivating power of an oscillator increases exponentially with the energy of the largest vibrational quantum, which can be accepted by the oscillator, solvents like CS<sub>2</sub>, CCl<sub>4</sub>, and Freon 113 are distinguished by extremely long lifetimes and consequently by the largest phosphorescence quantum yields.<sup>2</sup> The large <sup>1</sup>O<sub>2</sub> phosphorescence quantum yields found in this study are rather surprising, because from gas-phase absorption experiments it is known that <sup>1</sup>O<sub>2</sub> has an extremely long inherent lifetime of  $\tau_{\rm P} = 3850 \text{ s.}^{23}$  However, already Long and Kearns demonstrated that the oscillator strength of the O<sub>2</sub>( ${}^{3}\Sigma_{\rm g}^{-} \rightarrow {}^{1}\Delta_{\rm g}$ ) transition is by a factor of about 1000 larger in liquid solution than in the diluted gas phase.<sup>3</sup>

They explained the solvent-induced enhancement of the  $O_2({}^{3}\Sigma_{g} \rightarrow {}^{1}\Delta_{g})$  absorption qualitatively by a perturbation of the electronic states of  $O_2$  by the solvent X. In a collisional oxygen-solvent complex exchange mixing of higher excited complex states with the  ${}^{1}({}^{1}\Delta_{g}{}^{1}X_{0})$  complex state should occur, finally introducing intensity from the allowed  ${}^{1}X_{0} \rightarrow {}^{1}X_{1}$  solvent transition into the  $O_2({}^{3}\Sigma_{g}^{-} \rightarrow {}^{1}\Delta_{g})$  transition. Although the solvent oxygen interaction is only of third-order nature its importance was expected to be high, since the  ${}^{3}\Sigma_{g}^{-} \rightarrow {}^{1}\Delta_{g}$  transition is extremely weak compared to allowed solvent transitions.<sup>3</sup> The radiative lifetime of  $\tau_{P} = 5$  s deduced by Long and Kearns from the absorption measurements, however, is still by a factor of 6 larger than our value of  $\tau_{P} = 0.8$  s obtained directly from the phosphorescence measurements.

The solvent independence of the radiative rate constant established by our experiments is properly no unexpected result. Usually radiative lifetimes of excited states in solution depend not or only insignificantly on solvent nature. Even for heavy atom containing solvents like  $C_3F_7I$  no acceleration of the spin-forbidden radiative deactivation of  ${}^{1}O_2$  could be deduced from  $O_2({}^{3}\Sigma_{g} \rightarrow {}^{1}\Delta_{g})$  absorption measurements.<sup>3</sup>

Note Added by Editor. It is recommended that interested readers refer to the Comment on this paper by Ogilby, Peter R. J. Phys. Chem., this issue.

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## Ligand–Ligand Charge-Transfer Excited States of Os(II) Complexes

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This paper examines the photophysics of metal-to-ligand charge-transfer (MLCT) and ligand-to-ligand charge-transfer (LLCT) excited states in a series of  $[(bpy)_2Os^{II}(CO)L]^{2+}$  (Os-L) complexes. For each of the complexes studied, the  $d\pi(Os) \rightarrow \pi^*(bpy)$  absorption band is the lowest energy transition that is apparent. For L = pyridine and benzonitrile, only long-lived, highly luminescent MLCT states are observed. However, when L = an electron-donor aminobenzonitrile (ABN) species (DMABN, TMABN, or CMI; see text), MLCT emission is quenched and in <30 ps LLCT excited states are formed, \* $[(bpy^{-})-(bpy)Os^{II}(CO)ABN^{++}]^{2+}$ . The observed, weighted-average radiationless decays of the LLCT excited states in acetonitrile and dichloromethane follow the sequence Os-DMABN < Os-TMABN < Os-CMI in each solvent, and the calculated energies of the LLCT states for these complexes are in inverse order to the decay rates as expected if an "energy gap law" is followed. Finally, multiexponential relaxations of the LLCT states are pronounced in the nonpolar solvent dichloromethane. The dependence of these relaxations on the concentration of added electrolyte suggests that they may be due to ion-pair structure and dynamics.

## Introduction

During the past 10 years an extensive series of investigations have demonstrated that metal-to-ligand charge-transfer  $(MLCT)^1$ 

<sup>†</sup>University of Florida. <sup>‡</sup>Amoco Research Corporation excited states of d<sup>6</sup> transition metals such as Ru(II), Os(II), and Re(I) are strongly quenched by electron donors and acceptors.<sup>2-8</sup>

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<sup>(1)</sup> Abbreviations: MLCT, metal-to-ligand charge transfer; LLCT, ligand-to-ligand charge transfer; Os-L, [(bpy)<sub>2</sub>Os<sup>II</sup>(CO)L]<sup>2+</sup>; TBAH, tetrabutylammonium hexafluorophosphate; ABN, aminobenzonitrile.

#### SCHEME I



Spectroscopic and kinetic investigations indicate that this quenching is the result of electron transfer between the photoexcited metal complex and an electron donor or acceptor.<sup>2-8</sup> This process is exemplified by the sequence of reactions that follow irradiation of  $Ru(bpy)_3^{2+}$  in the presence of N,N-dimethylaniline (DMA):<sup>9,10</sup>

$$[\operatorname{Ru}^{II}(\operatorname{bpy})_{3}]^{2+} \xrightarrow{h\nu(\operatorname{MLCT})} * [(\operatorname{bpy}^{\bullet-})\operatorname{Ru}^{III}(\operatorname{bpy})_{2}]^{2+}$$
(1)

\*
$$[(bpy^{-})Ru^{II}(bpy)_2]^{2+} + DMA \rightarrow [(bpy^{-})Ru^{II}(bpy)_2]^{+} + DMA^{++} (2)$$

$$[(bpy^{\bullet-})Ru^{II}(bpy)_2]^+ + DMA^{\bullet+} \rightarrow [Ru^{II}(bpy)_3]^{2+} + DMA$$
(3)

Such photodriven electron-transfer reactions have been under intense scrutiny for several reasons. If the ions that are produced in step 2 are prevented from undergoing back-reaction via step 3, the sequence provides a method for storage of the input photon as chemical potential energy.<sup>11-13</sup> On a more fundamental level, these reactions provide a convenient method for studying thermodynamic control of the kinetics of electron-transfer reactions.<sup>2,14-18</sup> Unfortunately, the kinetics of the actual electrontransfer steps 2 and 3 are masked by the kinetics of diffusion of the reactants together.<sup>14-18</sup> Moreover, subtle details regarding the effect of structure on the dynamics of electron transfer are unobtainable. To eliminate these problems, several investigations have recently appeared in which an electron donor or acceptor species is complexed to a d<sup>6</sup> transition-metal complex that contains a redox-active MLCT chromophore.<sup>19-28</sup> Such chromophore-

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quencher complexes afford a unique opportunity to study the effects of structure and reactant energetics on the kinetics of photoinduced electron transfer reactions in systems with known geometry and without the complication of diffusional effects.<sup>19-28</sup>

[(bpy)<sub>2</sub>Os<sup>II</sup>(CO)ABN]<sup>24</sup>

The investigation presented herein focuses upon a series of Os(II) chromophore-quencher complexes having the general structure [(bpy)<sub>2</sub>Os<sup>II</sup>(CO)L]<sup>2+</sup> (Os-L). In this series, each complex contains the  $(bpy)_2Os^{II}(CO)$  - chromophore which possesses a low-lying  $d\pi(Os) \rightarrow \pi^*(bpy)$  MLCT excited state.<sup>29-34</sup> The set of ligands L includes two non-redox-active species (pyridine and benzonitrile, L = N) and three electron-donor aminobenzonitrile species (DMABN, TMABN, and CMI, L = ABN; see Scheme I for structures and abbreviations). These chromophore-quencher systems were chosen for study for the following reasons. (1) The MLCT excited state of the Os-L chromophore is luminescent and is a strong oxidizing agent.<sup>29-34</sup> (2) Synthetic investigations have provided a route into a variety of Os-L complexes where the ligand L is pyridine, nitrile, carboxylate, and hydride.<sup>29,35</sup> Photoexcitation of the Os-ABN chromophorequencher complexes into the MLCT excited state may initiate a sequence of intramolecular electron transfer reactions as summarized in Scheme II.<sup>25,26</sup> This reaction sequence is the innersphere analogue of the diffusion-mediated sequence defined by eq 1-3 above. Importantly, the intramolecular quenching process results in formation of a novel ligand-to-ligand charge-transfer

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excited state (LLCT) which has rarely been observed.<sup>26,36-38</sup>

### **Experimental Section**

Preparations. TMABN. CuCN (12.1 g, 135 mmol), 4bromo-2,6-dimethylaniline (23.1 g, 115 mmol), and 150 mL of pyrrolidone were heated to 135 °C with stirring under N<sub>2</sub> for 4 days. The hot reaction mixture was poured into 600 mL of 50% NH₄OH. After cooling, 500 mL of benzene was added and the mixture was filtered. The benzene layer was separated, washed with three portions of 20% NH4OH and dried over MgSO4. Evaporation of the benzene layer gave 8.9 g of essentially pure 4-amino-2,5-dimethylbenzonitrile, mp 108-110 °C (yield 53%). 4-Amino-2,5-dimethylbenzonitrile (3.0 g, 20.5 mmol) was dissolved with stirring in 13.5 g of 97% formic acid. Then 7.2 mL of 37% formaldehyde was added and the resulting solution was refluxed under  $N_2$  for 10 h. After cooling, the formic acid/formaldehyde solution was evaporated, leaving a brown solid that was recrystallized twice from ethanol. The product was obtained as a white solid, mp 90-90.5 °C (yield 1.95 g, 54%).

Os-Pyr. A solution containing 200 mg of [(bpy)<sub>2</sub>Os<sup>II</sup>(CO)-(CF<sub>3</sub>SO<sub>3</sub>)][CF<sub>3</sub>SO<sub>3</sub>]<sup>35</sup> (0.24 mmol) in 10 mL of pyridine was refluxed under Ar for 10 h. After cooling, the solution was concentrated under vacuum and the product was dissolved in 50 mL of  $H_2O$ . Excess aqueous  $NH_4PF_6$  was added to precipitate the complex as the  $PF_6^-$  salt. The resulting solid was collected on a glass frit, washed with excess H<sub>2</sub>O, and dried under vacuum. Purification was effected by column chromatography on neutral alumina eluting with 30% CH<sub>3</sub>CN/CH<sub>2</sub>Cl<sub>2</sub>; yield 50 mg (25%). Spectral Data: <sup>1</sup>H NMR (CD<sub>3</sub>CN) δ 7.36 (d, 1 H, bpy), 7.40 (d, 2 H, Pyr), 7.51 (d, 1 H, Pyr), 7.60 (m, 1 H, bpy), 7.85 (m, 4 H, bpy), 8.14 (m, 3 H, bpy), 8.39 (m, 2 H, bpy), 8.42 (s, 2 H, Pyr), 8.47 (m, 3 H, bpy), 8.65 (d, 1 H, bpy), 9.47 (d, 1 H, bpy); <sup>13</sup>C NMR (75 MHz, CD<sub>3</sub>CN) δ 118.0 (Pyr), 125.8 (Pyr), 126.3 (bpy), 126.5 (bpy), 128.2 (Pyr), 129.0 (bpy), 129.8 (bpy), 129.9 (bpy), 130.5 (bpy), 140.4 (bpy), 140.5 (bpy), 141.0 (bpy), 141.7 (bpy), 142.7 (bpy), 148.7 (bpy), 153.8 (bpy), 154.0 (bpy), 154.0 (bpy), 154.3 (bpy), 155.0 (bpy), 156.5 (bpy), 156.7 (bpy), 159.0 (bpy), 159.3 (bpy).

Anal Calcd for  $OsC_{26}H_{21}N_5OP_2F_{12}$ : C, 34.71; H, 2.35; N, 7.78. Found: C, 34.70; H, 2.35; N, 7.68.

*Os–BN.* The complex was prepared as described for Os–Pyr except that benzonitrile was used in place of pyridine as the reflux solvent; yield 70 mg (32%). Spectral Data: <sup>1</sup>H NMR (CD<sub>3</sub>CN)  $\delta$  7.59 (t, 2 H, bpy), 7.70 (q, 1 H, bpy), 7.78 (m, 5 H, BN), 8.05 (t, 1 H, bpy), 8.11 (t, 1 H, bpy), 8.17 (d, 1 H, bpy), 8.29 (t, 1 H, bpy), 8.37 (t, 1 H, bpy), 8.47 (t, 1 H, bpy), 8.61 (t, 1 H, bpy), 8.81 (d, 1 H, bpy), 8.87 (d, 1 H, bpy), 8.95 (t, 2 H, bpy), 9.65 (d, 1 H, bpy), 9.73 (d, 1 H, bpy); <sup>13</sup>C NMR (75 MHz, CD<sub>3</sub>CN)  $\delta$  110.5 (aromatic), 124.5 (CN), 125.7 (bpy), 125.9 (bpy), 126.4 (bpy), 126.5 (bpy), 129.5 (bpy), 130.19 (aromatic), 130.2 (bpy), 130.6 (bpy), 135.1 (aromatic), 130.6 (bpy), 135.1 (BN), 135.9 (BN), 141.2 (bpy), 141.7 (bpy), 142.2 (bpy), 142.8 (bpy), 149.5 (bpy), 153.3 (bpy), 155.5 (bpy), 176.0 (CO).

Anal Calcd for  $OsC_{28}H_{21}N_5OP_2F_{12}$ : C, 36.41; H, 2.29; N, 7.58. Found: C, 34.84; H, 2.34; N, 7.22.

*Os–DMABN*. A solution containing 200 mg of  $[(bp)_2Os^{II}-(CO)(CF_3SO_3)]$ [CF<sub>3</sub>SO<sub>3</sub>]<sup>35</sup> (0.24 mmol) and 700 mg of DMABN (Aldrich, 4.8 mmol) in DMF was refluxed under Ar for 10 h. Workup and purification of the product was carried out as described for Os–Pyr; yield 50 mg (25%). <sup>1</sup>H NMR (CD<sub>3</sub>CN) δ 3.04 (s, 6 H, NMe<sub>2</sub>), 6.69 (d, 2 H, DMABN), 7.40 (m, 4 H, DMABN, bpy), 7.50 (t, 1 H, bpy), 7.79 (d, 1 H, bpy), 7.84 (t, 1 H, bpy), 7.93 (t, 1 H, bpy), 8.10 (t, 1 H, bpy), 8.18 (t, 1 H, bpy), 8.27 (t, 1 H, bpy), 8.43 (m, 2 H, bpy), 8.50 (d, 1 H, bpy), 8.60 (t, 2 H, bpy), 9.28 (d, 1 H, bpy), 9.41 (d, 1 Hh, bpy); <sup>13</sup>C NMR (75 MHz, CD<sub>3</sub>CN) δ 118.0 (aromatic), 125.8 (Pyr), 126.3

(Pyr), 126.5 (Pyr), 128.2 (bpy), 129.0 (bpy), 129.8 (bpy), 129.9 (bpy), 130.5 (bpy), 140.4 (bpy), 140.5 (bpy), 141.0 (bpy), 141.7 (bpy), 142.7 (bpy), 148.7 (bpy), 153.8 (bpy), 154.0 (bpy), 154.3 (bpy), 155.0 (bpy), 156.5 (bpy), 156.7 (bpy), 159.0 (bpy), 159.3 (bpy).

Anal Calcd for  $OsC_{30}H_{26}N_6OP_2F_{12}$ : C, 37.27; H, 2.71; N, 8.69. Found: C, 36.49; H, 2.76; N, 8.53.

Os-CMI. This complex was prepared as described for Os-DMABN using CMI<sup>39,40</sup> in place of DMABN; yield 60 mg (28%). Spectral Data: <sup>1</sup>H NMR (CD<sub>3</sub>CN)  $\delta$  2.82 (s, 2 H, CH<sub>3</sub>), 2.92 (t, 2 H, CH<sub>2</sub>), 3.54 (t, 2 H, CH<sub>2</sub>), 6.33 (d, 1 H, CMI), 7.09 (s, 1 H, CMI), 7.34 (m, 3 H, CMI, bpy) 7.48 (t, 1 H, bpy), 7.81 (m, 2 H, bpy), 7.93 (t, 1 H, bpy), 8.10 (t, 1 H, bpy), 8.17 (t, 1 H, bpy), 8.27 (t, 1 H, bpy), 8.42 (m, 2 H, bpy), 8.50 (d, 1 H, bpy), 8.57 (t, 2 H, bpy), 9.26 (d, 1 H, bpy), 9.39 (d, 1 H, bpy); <sup>13</sup>C NMR (75 MHz, CD<sub>3</sub>CN)  $\delta$  28.0 (CH<sub>2</sub>), 33.9 (CH<sub>2</sub>), 55.1 (CH<sub>3</sub>), 105.9 (CN), 125.7 (bpy), 125.9 (bpy), 126.4 (bpy), 130.1 (bpy), 130.5 (bpy), 137.3 (aromatic), 140.9 (bpy), 141.4 (bpy), 142.0 (bpy), 142.6 (bpy), 149.4 (bpy), 153.5 (bpy), 155.3 (bpy), 157.3 (bpy).

Anal Calcd for  $OsC_{31}H_{26}N_6OP_2F_{12}$ : C, 38.04; H, 2.68; N, 8.59. Found: C, 37.96; H, 2.72; N, 8.52.

*Os*-*TMABN*. This complex was prepared as described for Os-DMABN using TMABN in place of DMABN; yield 55 mg (25%). Spectral Data: <sup>1</sup>H NMR (300 MHz, CD<sub>3</sub>CN) δ 2.19 (s, 3 H, CH<sub>3</sub>), 2.21 (s, 3 H, CH<sub>3</sub>), 2.80 (s, 6 H, NMe<sub>2</sub>), 7.29 (s, 2 H, TMABN), 7.36 (t, 2 H, bpy), 7.50 (t, 1 H, bpy), 7.77 (d, 1 H, bpy), 7.83 (t, 1 H, bpy), 7.92 (t, 1 H, bpy), 8.11 (t, 1 H, bpy), 8.18 (t, 1 H, bpy), 8.27 (t, 1 H, bpy), 8.43 (m, 2 H, bpy), 8.51 (d, 1 H, bpy), 8.60 (t, 2 H, bpy), 9.27 (d, 1 H, bpy), 9.40 (d, 1 H, bpy); <sup>13</sup>C NMR (75 MHz, CD<sub>3</sub>CN) δ 19.5 (CH<sub>3</sub>), 42.5 (NMe<sub>2</sub>), 125.4 (bpy), 125.6 (bpy), 126.2 (bpy), 129.1 (bpy), 129.8 (bpy), 130.2 (bpy), 135.2 (aromatic), 137.6 (bpy), 140.7 (bpy), 141.3 (bpy), 141.8 (bpy), 142.4 (bpy), 149.2 (bpy), 153.0 (bpy), 155.0 (bpy), 157.1 (bpy).

Anal Calcd for  $OsC_{32}H_{30}N_6OP_2F_{12}$ : C, 38.64; H, 3.04; N, 8.45. Found: C, 38.50; H, 3.02; N, 8.47.

Equipment. Steady-state luminescence spectra were obtained on a Spex Industries F-112A spectrophotometer. Emission spectra were corrected for instrument response using correction factors generated by using a tungsten filament primary standard lamp. Excitation spectra were corrected by using a Rhodamine B/1,2propanediol quantum counter reference. UV-visible spectra were recorded on a Perkin Elmer Model 320 spectrophotometer. NMR spectra were obtained on a Varian VXR-300 instrument.

*Electrochemistry.* Cyclic voltammetry was carried out on a Bioanalytical Systems CV-2 voltammograph. Voltammograms were recorded by use of a Linseis Model LY 18100 X-Y recorder. Experiments were carried out in a two-compartment cell in which Pt disk working and Pt wire auxiliary electrodes were separated from the reference electrode (saturated sodium chloride calomel, SSCE) by a medium-porosity glass frit. Tetrabutylammonium hexafluorophosphate (TBAH) (Kodak, recrystallized) at a concentration of 0.1 M was used as supporting electrolyte.

Luminescence Measurements. Solvents used in emission experiments were of Kodak spectroquality. Methylene chloride was further purified to remove acidic impurities by extraction with aqueous base followed by distillation from CaH<sub>2</sub>. For emission scans, sample concentrations were  $\approx 2 \times 10^{-5}$  M, with optical densities at 400 nm  $\approx 0.20$ . For excitation scans, sample concentrations were  $\approx 2 \times 10^{-5}$  M, with optical densities at 400 nm  $\approx 0.20$ . For excitation scans, sample concentrations were  $\approx 2 \times 10^{-6}$  M with maximum optical densities  $\approx 0.20$ . Quantum yield measurements were made relative to an emission actinometer consisting of Zn<sup>II</sup>[5,10,15,20-tetraphenyl-porphyrin] (Zn(TPP)) in air-saturated benzene ( $\Phi_{em} = 0.030$ ).<sup>41</sup> The Os-L samples and the actinometer had matched optical

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densities at the excitation wavelength (400 nm).

Emission decay measurements were carried out with timecorrelated single photon counting<sup>42</sup> on a commercially available system (Photochemical Research Associates, London, Ontario, Canada). The excitation source was an H<sub>2</sub>-filled spark gap (PRA, Model 510B). The instrument response was  $\approx 2.0$  ns fwhm. Excitation light was filtered with a near-UV band-pass filter (Schott, UG-11, maximum transmittance at 350 nm), and emission light was filtered with 70-nm band-pass interference filters. The excitation repitition rate was 30 kHz, and the sampling rate was  $\leq 500$  Hz. For strongly emissive samples 10000 counts were obtained in the maximum channel. Owing to the low fluorescence yields of the "quenched" samples, only 3000–5000 counts were collected in the maximum channel.

Analysis of emission decay data was carried out on an IBM-PC using a deconvolution program from PRA. Fits were judged satisfactory by  $\chi^2 \leq 1.3$  and by random scatter in the residual plots.

Transient Absorption Spectra and Kinetics. The activelypassively mode-locked Nd:YAG laser system was manufactured by Quantel International, Inc. (SN85-350) and employs Kodak 9740 dye in 1,2-dichloroethane solvent. The 1064-nm pulses are approximately 30 ps in duration (fwhm) with the harmonics slightly shorter. The basic experimental arrangement is similar to one described earlier,<sup>43</sup> but some differences do exist and will be described here. A complete schematic of this laser system will be presented in a forthcoming paper.<sup>44</sup>

The laser system's repetition rate is 15 Hz, and its spatially filtered preamplifier output is split into four beams for final amplification. Two are used in this experiment. The excitation pulse at 355 nm is derived from a single-pass 7-mm-diameter final amplifier and SHG and THG crystals. Before entering the sample cell, 1064- and 532-nm wavelengths of light are separated from the 355-nm light with a Pellin-Brocca prism and iris pair. Additionally, a quarter-wave plate is inserted in this beam before the sample cell to eliminate molecular rotational contributions to the transient absorption ( $\Delta A$ ) signal. The probe light is generated with 532-nm pulses by focusing into a 20-cm cell of D<sub>2</sub>O and  $H_2O$  (80:20 by volume). The 532-nm pulse is derived from a double-pass 9-mm-diameter final amplifier and an SHG crystal. A vacuum spatial filter is inserted between this final amplifier and the SHG crystal to produce a spatially pure, well-collimated 1064-nm beam. Another Pellin-Brocca prism and iris pair after this SHG crystal separates 1064-nm light from 532-nm light before the latter is coupled into the water cell. A GPIB controlled translation stage (Anorad-10 System, Anorad Corporation, Hauppauge, NY) with a quartz retroreflector forms an 8-ft-long optical delay line for the 532-nm pulse. It is inserted between the prism and the water cell.

The probe light generated in the water cell is imaged onto an  $800-\mu$ m-diameter aperture in contact with a sandblasted quartz slide. A quartz achromatic depolarizer is placed immediately after this slide to further depolarize the probe light. A beam-splitter cube separates the probe light into sample and reference beams, and each is imaged onto separate monochromators (Model DH10, Instruments SA, Inc., 2 nm/mm dispersion, 1-mm slits) with separate PMTs and detection circuits.

The sample solution is circulated by a variable-speed micropump through a 1 cm path length sample cell followed by a  $10-\mu m$ disk-filter and back into the reservoir flask. This arrangement traps particles in the solution without introducing bubbles into the sample cell. The excitation light is telescoped to yield a collimated 2.8-mm-diameter beam and is directed through the sample cell at a small angle with respect to the 0.8-mm-diameter probe light beam. The angle is such that the probe volume is always completely contained within the excitation volume inside

TABLE I: UV-Visible Absorption of Os-L Complexes and Nitrile Ligands<sup>a</sup>

compound	λ <sub>max</sub> , nm	${}^{\epsilon_{max}}_{mM^{-1}}$ cm <sup>-1</sup>	assignment <sup>b</sup>
Os-Pyr	420	4.5	MLCT
•	299	42	$\pi,\pi^*$ (bpy)
	261	48	$\pi,\pi^*$ (bpy)
Os-BN	398	5.2	MLCT
	298	53	$\pi,\pi^*$ (bpy)
	262	68	$\pi,\pi^*$ (bpy, <b>BN</b> )
Os-DMABN	410 (sh)	4.0	MLCT
	328	39	$\pi,\pi^*$ DMABN
	315	42	$\pi,\pi^*$ (DMABN, bpy)
	255	26	$\pi,\pi^*$ (bpy)
Os-TMABN	410 (sh)	4.0	MLCT
	342	25	$\pi,\pi^*$ (TMABN)
	301	39	$\pi,\pi^*$ (bpy)
	256	48	$\pi,\pi^*$ (TMABN, bpy)
Os-CMI	420 (sh)	4.0	MLCT
	345	48	$\pi,\pi^*$ (CMI)
	315	42	$\pi,\pi^*$ (CMI, bpy)
	255	37	$\pi,\pi^*$ (CMI, bpy)
	245	38	$\pi,\pi^*$ (CMI, bpy)
DMABN	295	30	CT
	220	8.5	$\pi,\pi^*$
TMABN	320	8.0	CT
	235	13	$\pi,\pi^*$
CMI	305	20	СТ
	245 (sh)	6.0	$\pi,\pi^*$
	230	12	$\pi, \pi^*$

<sup>a</sup>CH<sub>3</sub>CN solution. <sup>b</sup>Abbreviations: MLCT,  $d\pi(Os) \rightarrow \pi^*(bpy)$  metal-to-ligand charge transfer; CT, charge transfer.

of the sample cell. The flow rate is adjusted to provide a complete change of sample solution between laser shots. Sample excitation energies are typically less than 2 mJ. In general, the minimum energy that will yield a satisfactory signal-to-noise ratio is used. Importantly, the excellent agreement between transient absorption lifetimes measured on this laser system and emission lifetimes measured under photon-counting conditions provides assurance that the picosecond transient absorption kinetics and spectra result from single-photon excitation of the sample molecules.

Data acquisition follows much the same format as described for the earlier system<sup>43</sup> except that both sample decomposition and fluorescence background corrections are regularly employed. All of the samples in this study emit, some very strongly. In such cases the amount of sample luminescence due to photoexcitation of the sample is measured at each wavelength and used to correct the signal due to probe light transmitted through the photoexcited sample. This is necessary, because this contribution to the signal from sample probe light is absent when "blank" measurements of sample's transmission are made in the absence of excitation light. Fortunately, reproducible fluorescence corrections are usually easy to achieve. In addition, many samples in this study are photoactive. In these cases repeat  $\Delta A$  measurements are made at regular intervals throughout the data acquisition period and used to calculate a geometric progression correction for sample photodecomposition. Use of this correction factor allows later data to be weighted properly with respect to earlier data. Of course, the net sample decomposition must still be kept small (<15%) by switching to fresh solutions as needed.

### Results

UV-Visible Absorption Spectra. Table I lists the absorption bands and corresponding assignments for the Os-L complexes and the free ABN ligands. Figure 1 shows spectra of Os-BN, Os-DMABN, and DMABN for comparison. Each of the metal complexes displays a relatively weak absorption ( $\epsilon \approx 4000 \text{ M}^{-1} \text{ cm}^{-1}$ ) which appears as a shoulder at approximately 400 nm. This low-energy band is assigned to  $d\pi(Os) \rightarrow \pi^*(bpy)$  MLCT and is characteristic of the Os-L chromophore.<sup>29-34</sup> The intense bands in the UV region are assigned to intraligand (IL)  $\pi, \pi^*$  absorptions.

The IL absorptions for the ABN ligands in Os-DMABN, Os-TMABN, and Os-CMI are clearly observable in the spectra

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<sup>(44)</sup> Pourreau, D. B.; Humer, W.; Netzel, T. L. Manuscript in preparation.



Figure 1. UV-visible absorption spectra in CH<sub>3</sub>CN solution: --, Os-BN; -, Os-DMABN; ---, DMABN.

TABLE II	Electrochemical	Potentials <sup>a</sup>
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	CH <sub>3</sub> CN solution		CH₂Cl	2 solution
complex	$\frac{E_{1/2}(L/L^{+})}{L^{+}), V}$	<i>E</i> <sub>1/2</sub> (bpy/ bpy <sup>-</sup> ), V	$\frac{E_{1/2}(L/L)}{L^{+}}, V$	<i>E</i> <sub>1/2</sub> (bpy/ bpy <sup>-</sup> ), V
Os-Pyr		-1.10		
Os-BN		-1.12		-1.06
Os-DMABN	1.18	-1.13	1.34	-1.05
Os-TMABN	1.170	-1.10	1.24 <sup>b</sup>	-1.06
Os-CMI	1.00	-1.12	1.07	-1.08
DMABN	1.16			
TMABN	1.14 <sup>b</sup>			
CMI	0.94			

<sup>a</sup>All potentials relative to SSCE.  ${}^{b}E_{p}$  value for irreversible wave.

of the metal complexes and are slightly red-shifted relative to those of the free ligands. These strong IL absorptions are due to  $\pi,\pi^*$ and intraligand charge transfer excitations; the latter arise from a charge transfer from the alkylamino group to the benzonitrile group.<sup>45-47</sup> Complexation of the nitrile group to the Os(II) center lowers the energy of this charge transfer transition probably by increasing the ability of the aromatic nitrile group to act as an acceptor.

Electrochemistry. Each of the Os complexes was studied by cyclic voltammetry in CH<sub>3</sub>CN and CH<sub>2</sub>Cl<sub>2</sub> solution to measure electrochemical potentials for the various redox processes these complexes undergo. Table II lists relevant potentials for the complexes.

All of the complexes display an irreversible anodic wave at  $E_{\rm p}$  $\approx 1.75$  V. This wave is assigned to the Os(II)/Os(III) couple by analogy to previously studied Os(II) systems.<sup>29-31</sup> The oxidation potential for the Os(II) site in these complexes occurs at a relatively high potential compared to systems such as Os<sup>II</sup>(bpy)<sub>3</sub><sup>2+</sup> due to the strong  $\pi$ -acceptor ability of the carbonyl ligand. The complexes also exhibit two reversible cathodic waves which occur in the potential region -1.0 to -1.5 V. The first of these two cathodic waves appears between -1.0 and -1.15 V (see Table II); this wave is ascribed to reduction of one of the bipyridine ligands.29-31

The Os-ABN complexes display an additional anodic wave near 1.1 V. This wave was reversible for Os-DMABN and Os-CMI,



Figure 2. Emission spectra of Os-Pyr in CH<sub>3</sub>CN, Os-DMABN in CH<sub>3</sub>CN, and Os-DMABN in CH<sub>2</sub>Cl<sub>2</sub> at 295 K. The spectra reflect relative intensities. Note that the spectra of Os-DMABN are multiplied by a factor of 50 to make them visible on this scale.



Figure 3. Emission spectra of Os-BN and Os-DMABN in MTHF at 77 K.

but not for Os-TMABN.<sup>48</sup> The anodic wave is assigned to oxidation of the ABN ligand, e.g., as written for Os-DMABN:

$$[(bpy)_2Os^{II}(CO)DMABN]^{2+} \rightarrow [(bpy)_2Os^{II}(CO)DMABN^{*+}]^{3+} + e^- (4)$$

Cyclic voltammetry of uncomplexed DMABN, CMI, and TMABN supports this assignment, as each compound exhibits a similar anodic wave at a slightly less positive potential than the respective Os complex (see Table II).

Steady-State Emission and Emission Lifetimes. A. Os-Pyr and Os-BN. Emission spectra, quantum yields, and lifetimes have been obtained for Os-Pyr and Os-BN in several solvents at 295 K and in a 2-methyltetrahydrofuran (MTHF) glass at 77 K. Figures 2 and 3 and Table III contain relevant spectral data. In every solvent examined, Os-Pyr and Os-BN are strongly luminescent; the emission spectra at 295 K are characterized by a broad, featureless band with a maximum between 550 and 600 nm. The emission originates from a  $d\pi(Os) \rightarrow \pi^*(bpy)$  MLCT excited state and is characteristic of Os-bipyridine complexes.<sup>29-34</sup> In a frozen solvent glass, MLCT emission from Os-BN appears in the same spectral region; however, in this environment vibronic bands which are separated by  $\approx 1200$  cm<sup>-1</sup> are resolved. This band structure has been attributed to vibronic bands arising from C-C ring stretching modes associated with the bipyridine ligands.<sup>29,49-51</sup>

Quantum yields were obtained for emission from Os-Pyr and Os-BN in several solvents at 295 K by comparing areas of the

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<sup>(48)</sup> The irreversibility of the oxidative wave for Os-TMABN is attributed to rearrangement of the TMABN-based radical cation. This may occur by a 1,4-shift of a hydrogen atom from the benzylic methyl group to the anilino nitrogen atom. This rearrangement is not possible for DMABN or CMI because these ligands do not have benzylic methyl groups.

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Meyer, T. J.; Woodruff, W. H. J. Am. Chem. Soc. 1984, 106, 3492.
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TABLE III: Emission Spectral Parar	neter
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	295 K			77 K				
complex	solvent	λ <sub>max</sub> , nm	$\Phi_{\rm em}$	$\tau_{\rm em}$ , ns	solvent	$\lambda_{max}$ , nm	$\tau_{\rm em}$ , ns	
Os-BN	PhCN	555	0.25	1500	MTHF	531	5550	
	$CH_2Cl_2$	551						
Os-Pyr	CH <sub>3</sub> CN	595	0.19	1600	MTHF	d	d	
	$CH_2Cl_2$	580						
Os-DMABN	CH <sub>3</sub> CN	а	Ь	с	MTHF	542	5060	
	CH <sub>2</sub> Cl <sub>2</sub>	645	0.0064	с				
	CH <sub>2</sub> Cl <sub>2</sub> /TBAH <sup>e</sup>	645	0.0018	с				
Os-TMABN	CH <sub>3</sub> CN	а	b	с	MTHF	542	5650	
	CH <sub>2</sub> Cl <sub>2</sub>	а	Ь	с				
Os-CMI	CH <sub>3</sub> CN	а	b	С	MTHF	550	4870	
	CH <sub>2</sub> Cl <sub>2</sub>	а	Ь	С				

<sup>a</sup> Emission too weak to assign  $\lambda_{max}$ . <sup>b</sup>  $\Phi_{em} < 5 \times 10^{-4}$ . <sup>c</sup> Multiexponential fits of these emission decays are summarized in Table IV. <sup>d</sup> Insoluble in MTHF. <sup>c</sup> Tetrabutylammonium hexafluorophosphate at 0.1 M.



Figure 4. Time resolved emission decays of Os-DMABN. Lower boxes show the emission decay and the excitation lamp profile along with the computer-calculated fit. Upper boxes show plots of the residuals indicating the quality of the calculated fit. See Table IV for decay parameters. (A)  $CH_3CN$  solution. (B)  $CH_2Cl_2$  solution. (C)  $CH_2Cl_2/0.1$  M TBAH solution.

integrated emission bands with the integrated emission band of Zn(TPP) in benzene. The data compiled in Table III demonstrate that these complexes are relatively efficient emitters having quantum yields  $\geq 0.1$ .

Emission lifetimes were measured for Os–BN and Os–Pyr at 295 and 77 K and are listed in Table III. In both cases the lifetimes are relatively long, consistent with assignment of the emission to a MLCT excited state with a large degree of triplet character.<sup>32</sup>

B. Os-ABN Complexes. Steady-state emission spectra reveal a dramatic difference between the Os-ABN complexes and Os-BN (or Os-Pyr): in fluid solution the Os-ABN complexes display virtually no MLCT emission. Experiments in CH<sub>3</sub>CN show that  $\Phi_{em} < 0.001$  for Os-DMABN, Os-TMABN, and Os-CMI. For each complex in CH<sub>3</sub>CN a weak emission band is apparent which appears in the same spectral region as MLCT emission from Os-BN (see Figure 2). The origin of this emission is uncertain, and it is possible that a small amount of an impurity which contains the unquenched Os-L MLCT state is present in the samples.<sup>52</sup> Evidence supporting this assignment comes from emission lifetime experiments (vide infra) in which a small-amplitude, long-lived decay component is observed. Steady-state emission of the Os-ABN complexes in CH<sub>2</sub>Cl<sub>2</sub> solution also indicates that the MLCT emission is strongly quenched. In CH<sub>2</sub>Cl<sub>2</sub>, Os-TMABN and Os-CMI display little residual emission; however, Os-DMABN exhibits a weak band that is red-shifted relative to the MLCT emission typical of the Os-L chromophore (see Figure 2). A corrected excitation spectrum clearly shows that this emission emanates from Os-DMABN and not from an impurity. While this emission is considerably weaker ( $\Phi_{em} = 0.0064$ ) than the typical MLCT emission, it is stronger than the emission observed for Os-DMABN in CH<sub>3</sub>CN.

Emission decays were monitored by using time-correlated single photon counting.<sup>42</sup> The high sensitivity of this technique allows measurement of decays even for weakly emitting samples. Emission decays for Os-DMABN and Os-TMABN were monitored in CH<sub>3</sub>CN solution at 550 nm. Figure 4A shows the decay observed for Os-DMABN in CH<sub>3</sub>CN solution on a logarithimic scale along with the excitation lamp profile and the computer calculated fit. Table IV contains parameters for multiexponential fits<sup>53</sup> of the emission from Os-DMABN and Os-TMABN in several solvents. Emission decay data for both complexes in CH<sub>3</sub>CN were characterized by the following: (1) one major (>90%) short-lived component ( $\tau_1$  in Table IV) with a lifetime of 610 ps for Os-DMABN and 190 ps for Os-TMABN; (2) one

<sup>(52)</sup> While each of the Os-ABN complexes were highly purified the presence of luminescent impurities could not be alleviated owing to the fact that the complexes undergo slow thermal exchange of the ABN ligand in coordinative solvents. For example, in CH<sub>3</sub>CN solution, this exchange yields  $[(bpy)_2Os^{II}(CO)NCCH_3]^{2+}$ , which has a strongly luminescent MLCT excited state (see ref 29). Experiments demonstrated that only the amplitude of the long-lifetime component was affected by repeated purification—the amplitudes and lifetimes of the short-lived components were not affected.

<sup>(53)</sup> Multiexponential emission decays were fitted by using the following formula:  $I(t) = \sum \alpha_i \exp[-t/\tau_i]$ , where i = 3.

#### TABLE IV: Emission Lifetime Data<sup>a</sup>

complex	solvent	$\tau_1$ , ns ( $\alpha_1$ , %)	$\tau_2$ , ns ( $\alpha_2$ , %)	$\tau_{3}$ , ns ( $\alpha_{3}$ , %)	$\langle \tau \rangle$ , <sup>b</sup> ns
Os-DMABN	CH <sub>3</sub> CN	0.61 (92)	5.6 (6)	280 (2)	0.90
	CH <sub>2</sub> Cl <sub>2</sub>	1.6 (43)	6.8 (19)	36 (38)	16 <sup>d</sup>
	CH <sub>2</sub> Cl <sub>2</sub> /TBAH <sup>c</sup>	0.43 (43)	5.9 (57)	110 (0.3)	3.5
Os-TMABN	CH <sub>3</sub> CN	0.19 (94)	4.6 (5)	270 (1)	0.41
	$CH_2Cl_2$	0.97 (66)	5.0 (33)	95 (1)	2.3
	CH <sub>2</sub> Cl <sub>2</sub> /TBAH <sup>c</sup>	0.85 (96)	5.5 (3)	170 (1)	0.98
Os-CMI	$CH_2Cl_2$	0.62 (83)	6.6 (11)	450 (5)	1.2
	CH <sub>2</sub> Cl <sub>2</sub> /TBAH <sup>c</sup>	0.72 (84)	5.8 (11)	570 (5)	1.2

<sup>a</sup> Lifetimes and relative amplitudes from multiexponential fit (see ref 53). Estimated uncertainty in lifetimes and amplitudes is  $\pm 5\%$ . <sup>b</sup>See ref 54. <sup>c</sup> Tetrabutylammonium hexafluorophosphate, 0.1 M. <sup>d</sup> Mean lifetime calculated using all three lifetime components.

minor ( $\leq 2\%$ ) long-lived component ( $\tau_3$  in Table IV); (3) one intermediate component ( $\tau_2$  in Table IV) with a contribution of approximately 5% and a lifetime of approximately 5 ns. Emission decays of Os-DMABN and Os-TMABN were also measured in CH<sub>3</sub>CN containing 0.1 M TBAH; the decays in this case were identical with those without additional salt.

Emission decays for Os-DMABN, Os-TMABN, and Os-CMI were also obtained in CH<sub>2</sub>Cl<sub>2</sub> solution both with and without added TBAH. Table IV contains the parameters for multiexponential fits of the emission data and parts B and C of Figure 4 show the emission decays of Os-DMABN in CH<sub>2</sub>Cl<sub>2</sub> and CH<sub>2</sub>Cl<sub>2</sub> with 0.1 M TBAH, respectively. The decay of Os-DMABN in CH<sub>2</sub>Cl<sub>2</sub> was characterized by three lifetime components each having significant amplitudes, 1.6, 6.8, and 36 ns. Interestingly, the decay kinetics of Os-DMABN were quite different when salt was added to the CH<sub>2</sub>Cl<sub>2</sub>. With 0.1 M TBAH the emission decay was characterized by two main components with lifetimes of 430 (43%) and 5.9 ns (57%). Although the emission decays are multiexponential in both the presence and absence of added salt, it is clear that the weighted-average lifetime of the emission decay decreases substantially upon addition of salt to the  $CH_2Cl_2$ . This effect can be visualized by comparing Figure 4B and Figure 4C. The emission decay of Os-TMABN in CH2Cl2 was also biexponential and was characterized by two lifetime components having lifetimes of 970 (66%) and 5.0 ns (33%). Addition of 0.1 M TBAH to a CH<sub>2</sub>Cl<sub>2</sub> solution of Os-TMABN also had a marked effect on the emission decay kinetics. In this case the decay was characterized mainly (96%) by a lifetime of 850 ps. With Os-TMABN it is again clear that addition of salt to  $CH_2Cl_2$  leads to a decrease in the weighted-average emission decay lifetime (Table IV). The emission decay of Os-CMI in CH<sub>2</sub>Cl<sub>2</sub> was dominated (83%) by a lifetime of 620 ps. In addition, two other low-amplitude components were resolved with lifetimes of 6.6 (11%) and 450 ns (5%). The emission decay of Os-CMI in CH<sub>2</sub>Cl<sub>2</sub> was unaffected by the addition of 0.1 M TBAH.

To compare the emission kinetics of the three Os-ABN complexes, a weighted-average (mean) decay lifetime  $(\langle \tau \rangle)$  was calculated<sup>54</sup> and is listed in the last column of Table IV. This value allows us to note the following general trends. First, for both CH<sub>3</sub>CN and CH<sub>2</sub>Cl<sub>2</sub> the mean lifetimes of the complexes decrease along the series: Os-DMABN > Os-TMABN > Os-CMI. Second, for Os-DMABN and Os-TMABN, the mean lifetime is longer in CH<sub>2</sub>Cl<sub>2</sub> than in CH<sub>3</sub>CN.

C. Os-ABN Complexes at 77 K. Steady-state emission spectra were obtained for Os-DMABN, Os-TMABN, and Os-CMI in MTHF at 77 K. Each complex emits strongly with band shapes and intensities similar to those of Os-BN under the same conditions. Figure 3 shows the normalized emission spectra of Os-DMABN and Os-BN in MTHF at 77 K for comparison. The similarity of these emission spectra suggests that in all cases the  $d\pi(Os) \rightarrow \pi^*(bpy)$  MLCT excited state is responsible for the observed emission. This assignment is also supported by emission lifetime data at 77 K in MTHF (see Table III). Importantly, the emission lifetimes are similar and virtually identical with the



## Wavelength, nm

Figure 5. Picosecond absorption-difference spectra after excitation with a 30-ps pulse of 355-nm light. (A) Os-BN in benzonitrile,  $c = 1.2 \times 10^{-4}$  M, 100-ps delay time. (B) Os-DMABN in CH<sub>2</sub>Cl<sub>2</sub>,  $c = 4.8 \times 10^{-5}$  M, 100-ps delay time. (C) Os-TMABN in CH<sub>2</sub>Cl<sub>2</sub>,  $c = 3.3 \times 10^{-5}$  M, 15-ps delay time. (D) Os-CMI in CH<sub>2</sub>Cl<sub>2</sub>,  $c = 1.3 \times 10^{-5}$  M, 15-ps delay time.

lifetime of Os-BN under these conditions.

Picosecond Absorption-Difference Spectra. Absorption-difference ( $\Delta A$ ) experiments were carried out on several of the Os complexes using the third harmonic of a mode-locked Nd:YAG laser for excitation (355 nm, 30 ps fwhm). Time-resolved difference spectra of the intermediates produced by photoexcitation were measured in the 30-ps-16-ns time range over the spectral region from 370 to 730 nm. Lifetimes of the transients were determined by monitoring the relaxation of the absorbance differences at several wavelengths.

A. Os-BN and Os-Pyr. Figure 5A shows the difference spectrum produced 100 ps after photoexcitation of Os-BN in benzonitrile. The spectrum is characterized by a strong absorption that increases steadily at wavelengths less than 390 nm. Spectral data could not be acquired at wavelengths less than 370 nm due to scattered laser excitation light and lack of monitor light. As a result, the peak of this absorption band is unresolved. In addition to the strong absorption feature in the near-UV, the complex displays weak absorption throughough the visible region with weak maxima at approximately 450 and 510 nm. Time-resolved experiments indicate that these transient absorbances do not decay at delay times up to 15 ns, demonstrating that this photoproduct is relatively long-lived.

The difference spectrum of Os-Pyr in  $CH_3CN$  was obtained at 100 ps after photoexcitation and is very similar to that described above for Os-BN. Like Os-BN, Os-Pyr displays a strong absorption that increases steadily at wavelengths less than 390 nm; the band maximum for this near-UV absorption is also unresolved. Finally, Os-Pyr displays only very weak absorption in the spectral region ranging from 390 to 730 nm, and the spectrum does not decay for delay times up to 15 ns.

B. Os-DMABN. The absorption-difference spectrum produced by picosecond photoexcitation of Os-DMABN was measured in CH<sub>3</sub>CN and CH<sub>2</sub>Cl<sub>2</sub> solution. The  $\Delta A$  spectrum of the complex in CH<sub>2</sub>Cl<sub>2</sub> at a delay time of 100 ps is shown in Figure 5B; the spectrum observed in CH<sub>3</sub>CN is virtually identical and therefore is not shown. Comparison of parts A and B of Figure 5 shows that the  $\Delta A$  spectrum of Os-DMABN differs from the spectrum

<sup>(54)</sup> The mean decay lifetime,  $\langle \tau \rangle$ , was calculated using the multiexponential decay data in Table IV with the formula  $\langle \tau \rangle = \alpha_1 \tau_1 + \alpha_2 \tau_2$ . The  $\tau_3$  component was neglected in the calculation because this component is ascribed to impurity emission.



# Time, ps

**Figure 6.** Absorption-difference decay kinetics for Os-DMABN monitored at 450 nm after excitation with a 30-ps pulse of 355-nm light. The circles represent the experimental data points, and the lines represent the calculated fits. (A) CH<sub>3</sub>CN solution  $c = 7.3 \times 10^{-4}$  M, fit using a single-exponential decay with  $\tau = 640$  ps. (B) CH<sub>2</sub>Cl<sub>2</sub> solution  $c = 3.8 \times 10^{-5}$  M, fit using a double-exponential decay with  $\tau_1 = 3.3$  ns (15%),  $\tau_2 = 27$  ns (85%). (C) CH<sub>2</sub>Cl<sub>2</sub>/0.1 M TBAH solution  $c = 4.5 \times 10^{-5}$  M, fit using a triple-exponential decay with  $\tau_1 = 0.15$  ns (11%),  $\tau_2 = 5.1$  ns (78%),  $\tau_3 > 50$  ns (11%).

of Os-BN in several key features. The Os-DMABN spectrum shows a strong absorbance with a *resolved* maximum at 375 nm. In addition, moderately strong absorption is noted in the 390-460-nm wavelength region, with shoulders appearing at 410 and 440 nm. At wavelengths greater than 460 nm only weak, nearly unstructured absorption is noted. Spectra taken at later delay times in both solvents show that all of the spectral features decrease uniformly in time, indicating that only one kind of transient species is present on the time scale of the experiment (30-15000 ps).

Decay kinetics of absorbance differences for Os-DMABN were monitored at several wavelengths in CH<sub>3</sub>CN, CH<sub>2</sub>Cl<sub>2</sub>, and  $CH_2Cl_2/0.1$  M TBAH. In each solvent the temporal behavior of the signal was found to be the same at the different wavelengths studied. Figures 6A–C shows the  $\Delta A$  kinetics monitored at 450 nm in the above three solvent systems. The circles represent the experimental data, and the solid lines are computer-calculated fits of the data. Comparison of these figures demonstrates that the transient decays much more rapidly in CH<sub>3</sub>CN than in CH<sub>2</sub>Cl<sub>2</sub> solution. The decay in CH<sub>3</sub>CN was fitted by using a single-exponential function with a lifetime of 640 ps. The transient absorption decay in  $CH_2Cl_2$  was fitted by using either of two types of functions. The first type used lifetimes of 8.9 (60%) and >50 ns (40%). However, the data were equally well described by a second type of biexponential function with lifetimes of 3.3 (15%)and 27 ns (85%) as shown by the solid line in Figure 6B. Clearly, the limited time scale of this experiment cannot distinguish between these two fits. However, if emission data (vide infra) is used to determine the longest decay lifetime, one can use this  $\Delta A$ data to determine the shorter lifetime. This was done in the case of the second fit. Therefore the 3.3-ns component can be independently compared to the short components of the corresponding emission experiment (vide infra). The absorption difference at 450 nm in CH<sub>2</sub>Cl<sub>2</sub>/0.1 M TBAH decays considerably more rapidly than in neat CH<sub>2</sub>Cl<sub>2</sub> (compare Figure 6B,C). In the presence of added salt, the decay is multiexponential and required three lifetimes for adequate simulation. The computer-generated best fit line shown in Figure 6C used the following parameters:

0.15 (11%), 5.1 (78%), and >50 ns (11%).

C. Os-TMABN and Os-CMI. The  $\Delta A$  spectra taken 15 ps after 355-nm excitation of the complexes in CH<sub>2</sub>Cl<sub>2</sub> solution are shown in Figure 5C,D. The spectra of these complexes again differ significantly from the transient absorption spectra of Os-BN and Os-Pyr. The  $\Delta A$  spectrum of Os-CMI is virtually identical with that of Os-DMABN, showing a resolved band at 370 nm and shoulders at 390 and 430 nm. Os-TMABN shows not only the strong  $\Delta A$  increase at 370 nm but in addition a broad, moderately strong absorption ranging from 380 to 520 nm. It is now apparent that the absorption-difference spectra of the Os-L complexes fall into two general categories: (1) Os-Pyr and Os-BN have unresolved near-UV absorptions and almost no 400-450-nm absorption. (2) Os-DMABN, Os-TMABN, and Os-CMI, in contrast, have resolved 370-nm peaks with moderate, structured absorptions in the 400-450-nm region.

### Discussion

MLCT Quenching and Production of the LLCT Excited State. Scheme II presents an energy level diagram that suggests the relative ordering of excited states for the Os-L complexes. In addition, decay rate constants (k) for the various states are labeled.

UV-visible absorption spectra show that all of the complexes possess a low-energy  $d\pi(Os) \rightarrow \pi^*(bpy)$  MLCT absorption band. Excitation into this absorption band  $(+h\nu_1)$  results in population of the MLCT excited state.<sup>29-34</sup> In Os-Pyr and Os-BN, production of the MLCT state is signaled by the appearance of a strong, long-lived MLCT emission  $(-h\nu_1;$  see Figure 2 and Table III). In these complexes, the MLCT state decays via "normal" radiative and nonradiative  $(k_d^{MLCT})$  paths (see Scheme II).<sup>29-34</sup> A good approximation for the electronic structure of the MLCT state is \*[(bpy\*-)(bpy)Os<sup>III</sup>(CO)L]<sup>2+</sup>; this electronic distribution indicates that optical excitation promotes an electron from a metal-based  $d\pi$  orbital into a bipyridine  $\pi^*$  orbital.<sup>29-34</sup> An important consequence of this electronic distribution is that a strongly oxidizing Os(III) center exists in the MLCT excited state.

Each of the Os-ABN complexes displays the MLCT absorption feature; however, they differ from Os-Pyr and Os-BN in that their MLCT emission is strongly quenched in fluid solution. A reasonable mechanism for this MLCT emission quenching is ultrafast production of a ligand-to-ligand charge-transfer excited state (LLCT) via a thermally activated, intramolecular electron transfer reaction:

\*[(bpy<sup>•-</sup>)(bpy)Os<sup>III</sup>(CO)ABN]<sup>2+</sup> 
$$\xrightarrow{k_l^{ILCI}}$$
  
\*[(bpy<sup>•-</sup>)(bpy)Os<sup>II</sup>(CO)ABN<sup>•+</sup>]<sup>2+</sup> (5)

In the Os-ABN complexes, population of the LLCT state from the MLCT state is thermodynamically favorable because the Os(III) center in the MLCT state is a strong enough oxidant to remove an electron from the ABN ligand (vide infra). That the LLCT state is formed in a thermally activated step from the MLCT state and not directly from the ground state by light absorption is indicated by two lines of evidence. First, the visible absorption spectra of the Os-ABN complexes are nearly identical with the spectrum of Os-BN: no bands, therefore, can be assigned to LLCT absorption. Since no apparent LLCT absorptions are present, direct photoexcitation of the LLCT state is a very low probability event. Second, the Os-ABN complexes in a glass at 77 K display a strong, long-lived MLCT emission, indicating that under these conditions the LLCT state is not formed. Apparently, thermal energy is necessary to effect the intramolecular and solvent reorganizations that accompany the MLCT to LLCT transition.<sup>22b</sup>

The energy of the LLCT excited state ( $E_{LLCT}$ ) can be estimated for the Os-ABN complexes by the following equation:<sup>15,55-58</sup>

$$E_{\text{LLCT}} = E_{1/2}(L/L^{\bullet+}) - E_{1/2}(bpy/bpy^{\bullet-}) - 14.45/\epsilon R_{\text{DA}}$$
(6)

In (6),  $E_{1/2}(L/L^{*+})$  is the oxidation potential of the ABN ligand and  $E_{1/2}(bpy/bpy^{*-})$  is the reduction potential of the bpy ligand. The last term represents the Coulombic stabilization energy of the LLCT excited state that results from interaction of the electron

### LLCT Excited States of Os(II) Complexes

and hole at separation distance  $R_{DA}$  (in angstrom units) in a solvent of dielectric constant  $\epsilon^{55-58}$  The first two terms in (6) are available from electrochemical measurements in CH<sub>2</sub>Cl<sub>2</sub> and CH<sub>3</sub>CN solution (Table II). The last term is estimated by using the respective dielectric constants and taking  $R_{DA} = 5.0$  Å. Table V lists calculated values of  $E_{LLCT}$  for the Os-ABN complexes in CH<sub>3</sub>CN and CH<sub>2</sub>Cl<sub>2</sub> solutions.

The energy of the MLCT excited state  $(E_{MLCT})$  for the Os-ABN complexes is unavailable owing to the fact that MLCT emission is not observed. However, an estimate of a lower limit for  $E_{MLCT}$  is obtained from the emission maximum of Os-BN  $(E_{MLCT} \ge 2.30 \text{ eV})$ . Comparison of this value with the  $E_{LLCT}$ values listed in Table V indicates that this state lies lower in energy than the MLCT state in the Os-ABN complexes.

Photophysics of Os-DMABN. A. Picosecond Transient Absorption Studies. The transient absorption spectrum of Os-BN provides information concerning the absorption features characteristic of the Os-L MLCT state. The prominent feature in the spectrum of Os-BN (Figure 5A) is a strong, unresolved band in the near-UV region. This band is observed in the MLCT excited-state spectra of many metal-bipyridine complexes, and it is assigned to a  $\pi,\pi^*$  absorption of the bipyridine anion radical.<sup>7,22b,25,26,30</sup>

Comparison of Figure 5A and Figure 5B indicates that the spectrum of photoexcited Os-DMABN is different from the corresponding Os-BN spectrum. The features that are unique to Os-DMABN are the resolved peak at 370 nm and the shoulders at 410 and 440 nm. Interestingly, the DMABN radical cation (DMABN<sup>++</sup>) has absorption features that correspond with the bands in the spectrum of photoexcited Os-DMABN (DMABN<sup>++</sup>: peak at 368 nm, shoulder at 393 nm, shoulder at 432 nm).<sup>59</sup> This correspondence strongly suggests that the DMABN ligand is formally oxidized in the photoexcited metal complex. While further information cannot be deduced from the transient absorption spectrum, it is compelling to assign the transient species observed following flash excitation of Os-DMABN to the LLCT excited state.

The transient absorption kinetics are now interpreted based on the assumption that the absorbing transient species is the LLCT state. The temporal behavior of the LLCT state in CH<sub>3</sub>CN is given by the kinetic profile in Figure 6A. The data clearly indicates that the LLCT state is produced promptly (during the laser excitation pulse, fwhm = 30 ps) and that it decays with a lifetime of 640 ps. These observations imply the following rate constants for the complex in CH<sub>3</sub>CN:  $k_f^{LLCT} \ge 10^{11} \text{ s}^{-1}$  and  $k_d^{LLCT} = 1.6 \times 10^9 \text{ s}^{-1}$ . The temporal behavior of the LLCT state in CH<sub>2</sub>Cl<sub>2</sub> is described by the kinetic profile in Figure 6B. In CH<sub>2</sub>Cl<sub>2</sub>, formation of this state also occurs during the laser pulse, but the decay is significantly slower than in CH<sub>3</sub>CN. The decay can not be fit to a single-exponential function (vide supra); however, a good double-exponential fit is given by lifetimes of 3.3 (15%) and 27 ns (85%). The transient absorption kinetics for Os-DMABN in CH<sub>2</sub>Cl<sub>2</sub> suggest the following weight-averaged rate constants:  $k_f^{LLCT} \ge 10^{11} \text{ s}^{-1}$  and  $k_d^{LLCT} \approx 4.3 \times 10^7 \text{ s}^{-1}$ .

B. Emission Studies of Os-DMABN. This complex luminesces only weakly in CH<sub>3</sub>CN solution; the emission is characterized by a band which is in the spectral region typical for MLCT emission (Figure 2). Due to the weakness of the emission, it is difficult to rule out the possibility that the band is due to a minor impurity that contains the unquenched Os-L MLCT state.<sup>52</sup> The emission decay of the complex in CH<sub>3</sub>CN (Figure 4A, Table IV) is dominated by a short-lived component with a lifetime of 610 ps (93%). In addition, two other low-amplitude components are resolved with lifetimes of 6 and 280 ns. The long-lived, low-amplitude component (280 ns) is attributed to a minor impurity.<sup>52</sup> The shortand intermediate-lived components are apparently due to emission from Os-DMABN. It is important to note the close correspondence between the lifetime of the dominant, short-lived emission lifetime component and the lifetime obtained for the LLCT state from transient absorption kinetics (610 and 640 ps, respectively). This close agreement strongly suggests that *the LLCT state is weakly emissive* and that its decay kinetics are given by the emission lifetime experiments.

In CH<sub>2</sub>Cl<sub>2</sub> solution, Os-DMABN exhibits a weak, broad emission with a maximum at 645 nm. This band is considerably weaker and is red-shifted compared to typical MLCT emission from the Os-L chromphore (see Figure 2 and Table III). A corrected excitation spectrum reveals that this emission is due to Os-DMABN and not an impurity. The emission decay of the complex in CH<sub>2</sub>Cl<sub>2</sub> is clearly multiexponential and is characterized by three lifetime components having lifetimes of 1.6 (43%), 6.8(19%), and 36 ns (38%). The weighted-average of the first two emission lifetimes is 3.2 ns. An important fact is that this emission decay is similar to the decay of the LLCT state determined by transient absorption kinetics: the transient absorption assigned to the LLCT state is well simulated by a two component decay function with lifetimes of 3.3 and 27 ns (see Figure 6B).<sup>60</sup> The origin of the multiexponential decay kinetics will be discussed below; however, this correspondence in emission and transient absorption lifetimes indicates that the red-shifted band observed for Os-DMABN in CH<sub>2</sub>Cl<sub>2</sub> can be assigned to emission from the LLCT state.

A lower limit for the 0–0 energy of the LLCT state can be approximated from the maximum of this emission band; the value thus approximated is 1.95 eV. As described previously, the energy of the LLCT state for Os-DMABN in  $CH_2Cl_2$  was estimated to be 2.09 eV by (6). As expected, these values are in reasonable agreement.

C. Model for Photophysics of Os-DMABN. On the basis of the transient absorption and emission data, a kinetic model is defined for the excited-state processes that occur following excitation of Os-DMABN. Photolysis of the complex into the lowest absorption band produces primarily the MLCT state. This state then rapidly relaxes to the LLCT state with  $k_f^{LLCT} \ge 10^{11} \text{ s}^{-1}$ . The rapid rate for this transition is not surprising considering the fact that this process is an exothermic electron transfer between a donor and an acceptor that are in close proximity and interact strongly.<sup>61</sup> Since  $k_f^{LLCT} \gg k_d^{MLCT}$ , formation of the LLCT state from the MLCT state occurs with near unit quantum efficiency.

The LLCT state has a lifetime that is sufficiently long to allow its observation by picosecond transient absorption and to allow radiative decay to compete with radiationless decay processes. Inefficient radiative decay of the LLCT state accounts for the observation of weak emission from the complex by time-resolved photon counting in CH<sub>3</sub>CN and by both time-resolved and steady-state photon counting in CH<sub>2</sub>Cl<sub>2</sub> solution. Although LLCT emission has not been reported for other d<sup>6</sup> transition-metal complexes, such emission has been reported from a series of Zn(II) and Cd(II) complexes.<sup>36–38</sup> Consideration of the electronic structure of the LLCT state suggests a similarity between this state and organic intramolecular<sup>62–65</sup> and intermolecular<sup>66</sup> charge

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<sup>(58)</sup> Oevering, H.; Paddon-Row, M. N.; Heppener, M.; Oliver, A. M.; Cotsaris, E.; Verhoeven, J. W.; Hush, N. S. J. Am. Chem. Soc. 1987, 109, 3258.

<sup>(59)</sup> Forster, M.; Hester, R. E. J. Chem. Soc., Faraday Trans. 2 1981, 77, 1521.

<sup>(60)</sup> The signal to noise of the  $\Delta A$  data in Figure 6B is not good enough to determine two lifetimes that differ by a factor of 4. Rather, only their average would be fit.

<sup>(61)</sup> Evidence for a strong interaction between the ABN ligands and the metal complex is given by the shifts in the ABN ligand based  $\pi,\pi^*$  absorption bands (Table I) and electrochemical potentials (Table II) for the Os complexes compared to the free ligands.

<sup>(62)</sup> Pasman, P.; Mes, G. F.; Koper, N. W.; Verhoeven, J. W. J. Am. Chem. Soc. 1985, 107, 5839.

<sup>(63)</sup> Mes, G. F.; van Ramesdonk, H. J.; Verhoeven, J. W. Recl. Trav. Chim. Pays-Bas 1983, 102, 55.

<sup>(64)</sup> Mes, G. F.; van Ramesdonk, H. J.; Verhoeven, J. W. J. Am. Chem. Soc. 1984, 106, 1335.

TABLE V: Estimated Energies for the LLCT State in Os-ABN Complexes<sup>a</sup>

complex	E <sub>LLCT</sub> , CH <sub>3</sub> CN	$E_{\text{LLCT}}, \\ \text{CH}_2\text{Cl}_2$	
Os-DMABN	2.23	2.09	
Os-TMABN	2.19	2.00	
Os-CM1	2.04	1.85	

<sup>a</sup>Energies in eV calculated by using eq 6; see text.

transfer excited states. Here the organic donor and acceptor subunits of the LLCT excited state are held in proximity by a central metal ion.

Photophysics of Os-TMABN and Os-CM1. A. Os-TMABN. The transient absorption spectrum of photoexcited Os-TMABN in CH<sub>2</sub>Cl<sub>2</sub> (Figure 5C), like that of Os-DMABN, is quite different from the spectrum of the Os-L MLCT excited state typified by Os-BN. This difference is explained by assigning the absorption observed in the Os-TMABN spectrum to the LLCT excited state. In Os-TMABN the MLCT excited state is not observed and is therefore thought to rapidly ( $k > 10^{11} \text{ s}^{-1}$ ) convert to the LLCT state following photoexcitation. If this is correct, any emission observed from this complex must come from the LLCT state.

The steady-state emission of Os-TMABN in CH<sub>3</sub>CN is exceedingly weak. A band is observed in the spectral region typical for MLCT emission; however, owing to the low intensity of the emission it is difficult to eliminate the possibility that the band may be due to an impurity.<sup>52</sup> The emission decay of the complex in CH<sub>3</sub>CN is characterized predominantly by a short-lived component (190 ps, 94%) and by two low-amplitude components (4.6 and 270 ns). The long-lived component (270 ns, 1%) is assigned to an impurity, and the short-lived components are assigned to emission intrinsic to Os-TMABN. Neglecting for now the 4.6-ns component (5%), we conclude that the predominant, short-lived decay component is due to the LLCT state and therefore that its lifetime is 190 ps in CH<sub>3</sub>CN.

The steady-state emission of Os-TMABN in CH<sub>2</sub>Cl<sub>2</sub> is also exceedingly weak; however, the band shape is different that the band shape of the weak emission observed in CH<sub>3</sub>CN. While there is weak intensity in the region typical for MLCT emission, there is a distinct tail on the low-energy side of the emission band. It is difficult to determine the maximum of the low-energy emission, as the band is not clearly resolved; however, it is reasonable to assign this low-energy emission to the LLCT excited state. The total emission decay of this complex in CH<sub>2</sub>Cl<sub>2</sub>, like that of Os-DMABN, is multiexponential, and is qualitatively described by two main components having lifetimes of 970 (66%) and 5.0 ns (33%). Assuming that this emission comes from the LLCT excited state, we conclude that this state decays significantly more slowly in  $CH_2Cl_2$  solution than in  $CH_3CN$ . This behavior is also paralleled by the LLCT excited-state decay of Os-DMABN in the same two solvents.

B. Os-CMI. The transient-difference spectrum of this complex in  $CH_2Cl_2$  (Figure 5D) is remarkably similar to the transientdifference spectrum of Os-DMABN, suggesting again that the excited state responsible for the transient absorption is the LLCT state. Therefore, in the following analysis it is assumed that the emission observed for this complex also emanates from the LLCT state.

Emission measurements in CH<sub>3</sub>CN were not possible due to the instability of the complex in this solvent. A slow increase in emission intensity over time was observed, indicating that the complex undergoes a reaction to produce a strongly emissive species. This behavior is clearly due to slow replacement of the CMI ligand by solvent.<sup>52</sup> On the other hand, Os-CMI is very stable in the noncoordinating solvent CH<sub>2</sub>Cl<sub>2</sub>. Steady-state emission of Os-CMI in CH<sub>2</sub>Cl<sub>2</sub> reveals only a weak emission band which is centered in the region typical for MLCT emission. An excitation spectrum indicates that the emission is due to an impurity. For this complex, LLCT emission is obscured by the impurity emission in the steady-state spectrum. The emission decay of Os-CMI in CH<sub>2</sub>Cl<sub>2</sub> is dominated by a short-lived component having a lifetime of 620 ps (83%). In addition, smallamplitude components were resolved having lifetimes of 6.6 (11%) and 450 ns (5%). Again the long-lived emission component (450 ns) is attributed to an impurity. This was confirmed through experiments in which the emission of Os-CMI was monitored after repeated purification. Purification resulted only in a decrease in the amplitude of the long-lived component; the lifetimes of the short-lived components were unaffected. Therefore, the short-lived decay components are assigned to emission from the LLCT state, indicating that in Os-CMI this state has a lifetime of approximately 620 ps.

General Considerations. A. Spectroscopic and Kinetic Model Used To Explain Photophysics of Os-ABN Complexes. Discussion of the specific photophysical processes of the Os-ABN complexes is based on a model that assumes the following sequence: (1) Photoexcitation produces primarily the MLCT excited state. (2) The MLCT state rapidly undergoes conversion to the LLCT state. (3) The LLCT state decays on a time scale of 0.2-30 ns depending upon the nature of the Os-L complex and on the solvent. This sequence follows naturally from assignment of the transient that is observed following picosecond flash excitation to the LLCT excited state. This assignment is based on two observations: first, the transient spectra of the Os-ABN complexes are quite different in band shape compared to those of Os-BN and Os-Pyr, which typify the absorption of the MLCT excited state, and second, the bands in the transient absorption spectra of Os-DMABN correspond to those expected for the bpy<sup>•-</sup> and DMABN\*\* radicals. Assignment of the transient absorption to the LLCT excited state leads to the conclusion that the weak, short-lived emission that is observed from each of the Os-ABN complexes also comes from this state. This conclusion is substantiated by the similarity of the decay kinetics for transient absorption and luminescence from Os-DMABN in CH<sub>3</sub>CN,  $CH_2Cl_2$ , and  $CH_2Cl_2/TBAH$ .

B. Origin of the Multiexponential Decay Kinetics. Salt Effects. As pointed out several times in the preceding sections, multiexponential decay kinetics were observed in both transient absorption and emission experiments; the complexity of the decay kinetics was most pronounced in  $CH_2Cl_2$  solution. An important question that must be examined here concerns the origin of these multiexponential decays. The first factor that must be considered is whether or not the samples contain impurities. Examination of the emission decay data for Os-DMABN and Os-TMABN in  $CH_3CN$  and Os-CMI in  $CH_2Cl_2$  (Figure 4A and Table IV) shows that long-lived luminescent impurities are present. Each complex displays a long-lived component with a relatively low amplitude ( $\tau_3$ ); this component is associated with contamination of the samples with a small amount of an Os-L complex lacking an amino group.<sup>52</sup>

In addition to this long-lived emission component, the complexes display at least two other decay components. Importantly, this multiexponential decay behavior is considerably more pronounced in CH<sub>2</sub>Cl<sub>2</sub> than in CH<sub>3</sub>CN, suggesting that the effect may in some way be associated with solvent polarity. In order to probe the origin of the complicated kinetics in CH<sub>2</sub>Cl<sub>2</sub> solution, experiments were conducted in the presence of varied concentrations of added salt (TBAH). These experiments provide revealing data: for example, addition of TBAH to CH2Cl2 solutions of Os-DMABN has a dramatic effect on the decay kinetics observed in both transient absorption and emission experiments. While the decay kinetics remain complex, the mean lifetime decreases significantly on addition of TBAH (compare Figure 4B with 4C and Figure 6B with 6C). This decrease in lifetime is paralleled by a decrease in the emission quantum yield (see Table III). Addition of TBAH to CH<sub>2</sub>Cl<sub>2</sub> solutions of Os-TMABN has a similar effect on the emission decay kinetics. On the other hand, addition of TBAH to CH<sub>3</sub>CN solutions of Os-DMABN or Os-TMABN has ab-

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TABLE VI: Estimated Decay Rates for LLCT Excited State<sup>a</sup>

complex	k <sub>d</sub> <sup>llCT</sup> , CH₃CN	$k_{d}^{LLCT}$ , CH <sub>2</sub> Cl <sub>2</sub>	
Os-DMABN	$1.1 \times 10^{9}$	$6.3 \times 10^{7}$	
Os-TMABN	$2.4 \times 10^{9}$	$4.3 \times 10^{8}$	
Os-CMI		$8.1 \times 10^{8}$	

<sup>a</sup> First-order rate constants in units of s<sup>-1</sup>. Calculated from weighted mean lifetime of principal emission decay components ( $\langle \tau \rangle$ , Table IV).

### solutely no effect on the emission decay kinetics.

These experiments strongly suggest that ion pairing plays an important role in determining the decay lifetime of the luminescent excited state in nonpolar solvents. In  $CH_2Cl_2$ , a relatively nonpolar solvent, the metal complexes exist as ion pairs with their counterions.<sup>67</sup> On the other hand, in a polar solvent such as  $CH_3CN$  the metal complexes exist as free ions. Apparently there is a strong relationship between the structural organization of the metal complex and its counterions and the decay kinetics of the LLCT excited state. The multiexponential decay kinetics might result from the existence of a distribution of ion-pair types.

A recent report examined salt effects on the lifetime of MLCT excited states of several Os(II)-bipyridine and Os(II)phenanthroline complexes in  $CH_2Cl_2$  solution.<sup>67</sup> These experiments demonstrated that there is a small effect of counterion on the lifetime of the MLCT state, but no evidence for multiexponential decay kinetics was reported. However, multiexponential excited-state decay kinetics have been reported for many systems in which chromophores are in environments that are inhomogenous on a microscopic scale.<sup>68-71</sup> Especially noteworthy in this regard is the recent report of multiexponential decay kinetics for a series of Ru(II)-bipyridine and Ru(II)-phenanthroline MLCT excited states in polyelectrolyte solutions.<sup>71</sup>

The salt effect on the lifetime of the LLCT state in the Os-ABN complexes might have its origin in one of several possible mechanisms. First, a trivial mechanism is the increase in bulk dielectric constant that accompanies addition of electrolyte to the solvent. A change in solvent dielectric is expected to affect the energy of the dipolar LLCT state, and this would be reflected by a change in its decay rate. However, a change in solvent dielectric constant through addition of electrolyte is a nonspecific effect and cannot explain the multiexponential decay kinetics. For this reason, another mechanism must be considered. Given the relatively low symmetry of the Os-L complexes, the distribution of the two PF<sub>6</sub><sup>-</sup> anions around the ground-state metal complex in CH<sub>2</sub>Cl<sub>2</sub> solution is expected to be random. On the other hand, the extended dipole in the LLCT excited state, [(bpy<sup>•-</sup>)(bpy)-Os<sup>II</sup>(CO)ABN<sup>•+</sup>]<sup>2+</sup>, provides a basis for an electrostatic preference for certain anion orientations. However, since formation of the LLCT state occurs extremely rapidly ( $k \ge 10^{11} \text{ s}^{-1}$ ), the orientation of the anions in the initially formed state will remain random, as they were in the ground state.<sup>72-74</sup> Indeed, rearrangement of the anions around the LLCT state's dipole must occur during the lifetime of the LLCT state. Both the existence of a distribution of ion-pair types and the change from ground-state distributions of these pair geometries can give rise to multiexponential decay kinetics for this "extended dipole" excited state.

C. Comparison of Kinetic Results for the Os-ABN Complexes. While the photophysical properties of the Os-ABN complexes are similar, some differences exist in their excited-state dynamics. In order to simplify comparison of the kinetic data for the various complexes, decay rates for the LLCT state have been approximated from mean lifetime data (Table IV) according to the relation,  $k_{\rm d}^{\rm LLCT} = 1/\langle \tau \rangle$ . Decay rate constants calculated by using this expression are collected in Table VI. The rates span the range from  $2.4 \times 10^9$  s<sup>-1</sup> for Os-TMABN in CH<sub>3</sub>CN to  $6.3 \times 10^7$  s<sup>-1</sup> for Os-DMABN in CH<sub>2</sub>Cl<sub>2</sub>. The fact that each of these complexes are weak emitters indicates that  $k_d^{LLCT}$  gives directly the nonradiative decay rate of the LLCT state.<sup>67</sup> The decay rates observed for the LLCT states in the Os-ABN complexes compare well with kinetic data from the only other system which has been studied to date that has a similar LLCT excited state. In this system, which contains a Re(I)-bipyridine center covalently bonded to an electron-donating phenothiazine moiety, a LLCT excited state was clearly identified by transient absorption spectroscopy and observed to decay with a rate constant of  $4 \times 10^7$ s<sup>-1</sup> in CH<sub>3</sub>CN solution.<sup>26</sup>

One clear trend that emerges from inspection of the kinetic data for the three Os-ABN complexes is that  $k_d^{LLCT}$  follows the sequence Os-DMABN < Os-TMABN < Os-CMI in each solvent examined.<sup>75</sup> A possible explanation for this trend is suggested from work on nonradiative decay rates for MLCT states of Ru(II) and Os(II) polypyridyl complexes.<sup>29,76</sup> This work demonstrates that the energy gap law is followed for a series of structurally related complexes: a correlation is observed in which the nonradiative decay rate increases as the excited-state energy decreases. Interestingly, for the Os-ABN complexes the correlation that is expected from the energy gap law is found between  $k_d^{LLCT}$  and  $E_{LLCT}$ . The data in Table V indicate that the ordering of  $E_{LLCT}$ in both CH<sub>3</sub>CN and CH<sub>2</sub>Cl<sub>2</sub> is Os-DMABN > Os-TMABN > Os-CMI, which is inverse to the ordering of  $k_d^{LLCT}$ .

It is interesting to note that the decay rates of the LLCT states for the Os-ABN complexes are 100–1000 times greater than the decay rates of the MLCT states for Os-N chromophores. An explanation for this may be that there is a difference in the spin character of these two excited states. Studies of the electronic structure of Ru(II) and Os(II) MLCT states demonstrate that the emitting levels have a significant degree of triplet spin character.<sup>32,77</sup> Because of this there is an unfavorable spin factor that accounts for the relatively slow decay of MLCT states. The enhanced decay rate of the LLCT state may be a consequence of greater singlet spin character in this state compared to the MLCT state in the Os-ABN chromophores.

#### Conclusion

This study has focused on a unique series of Os-L complexes that each have a common chromophore based on an Os  $\rightarrow$  bipyridine MLCT transition. In Os-N complexes the MLCT excited state is long-lived and strongly luminescent, as typified by the photophysics of Os-BN and Os-Pyr. Studies on the Os-ABN complexes establish that when an electron-donating ABN ligand is added to the coordination environment, the MLCT excited state is strongly quenched. Quenching of the MLCT excited state is clearly associated with the intervention of a new low-lying LLCT excited state, \*[(bpy<sup>-</sup>)(bpy)Os<sup>II</sup>(CO)ABN<sup>++</sup>]<sup>2+</sup>.

Although the qualitative aspects of the photophysical events that occur for the Os-ABN complexes are clear, details concerning the kinetics for decay of the LLCT state are complicated by the observation of multiexponential relaxations. The detailed origin of these complicated kinetics has not been made clear; however, experiments with varied concentrations of electrolyte suggest that they may be due to ion-pair structure and dynamics especially in nonpolar solvents. Experiments are in progress to examine further solvent and salt effects on LLCT excited-state relaxations in these and related chromophore-quencher systems.

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Registry No. BN, 100-47-0; Pyr, 110-86-1; DMABN, 1197-19-9; TMABN, 60082-00-0; CMI, 57413-40-8; Os-BN, 119999-01-8; Os-Pyr, 89689-79-2; Os-DMABN, 119999-02-9; Os-TMABN, 119999-03-0; Os-CMI, 119999-04-1; [(bpy)<sub>2</sub>Os<sup>II</sup>(CO)(CF<sub>3</sub>SO<sub>3</sub>)][CF<sub>3</sub>SO<sub>3</sub>], 89689-72-5; pyrrolidone, 616-45-5; 4-bromo-2,6-dimethylaniline, 24596-19-8; 4-amino-2,5-dimethylbenzonitrile, 72917-37-4.

# ESR and Optical Evidence on Formation of the Cl<sup>-</sup>···CCl<sub>3</sub><sup>+</sup> Ion Pair in 3-Methylpentane Matrices $\gamma$ -Irradiated at 77 K

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The well-known absorption band at 470 nm in CCl<sub>4</sub>-alkane systems is investigated. The results obtained are as follows: (1) The absorption band due to the radical cation of 5-methyldecane (5MD<sup>+</sup>) in 5MD-CCl<sub>4</sub>-3MP systems converts into the 470-nm band. (2) In the conversion, the positive charge of the 5MD<sup>+</sup> reacts with the unpaired electron of the CCl<sub>3</sub>. radical. (3) CBrCl<sub>3</sub> and CCl<sub>3</sub>F in 3MP glasses produce the absorption bands at 480 and 438 nm, respectively, and the nature of these bands is the same with that of the 470-nm band in the all points examined. Results 1 and 2 lead to the formation of CCl<sub>3</sub><sup>+</sup> cations. We also obtain evidence on the formation of CCl<sub>3</sub><sup>+</sup> cations from CBrCl<sub>3</sub> and CCl<sub>2</sub>F<sup>+</sup> cations from CCl<sub>3</sub>F. It is evident that the band shift observed in the case of CBrCl<sub>3</sub> is not attributable to the free ions CCl<sub>3</sub><sup>+</sup> nor to the solvent-separated ion pairs Br-solvent|CCl<sub>3</sub><sup>+</sup> but to the formation of charge-transfer contact ion pairs Br-wCl<sub>3</sub><sup>+</sup>. Therefore, it is concluded that CCl<sub>4</sub> and CCl<sub>3</sub>F in 3MP produce Cl<sup>-</sup>...CCl<sub>3</sub><sup>+</sup> and Cl<sup>-</sup>...CCl<sub>2</sub>F<sup>+</sup>, respectively. We also obtain the results that CBrF<sub>3</sub>,  $CClF_3$ , and  $CCl_2F_2$  in 3MP glasses yield the corresponding radical anions with absorption bands at 314, 300, and 314 nm, respectively, and that these radical anions are neutralized with the migrating positive charges of the 5MD<sup>+</sup> formed.

### Introduction

It is well-known from the work of Hamill and co-workers<sup>1</sup> that the 77 K radiolysis of 3-methylpentane (3MP) glasses containing small amounts of CCl<sub>4</sub> produces a prominent absorption band in the visible region ( $\lambda_{max} = 470 \text{ nm}$ ). The band is readily bleached by light and suppressed by olefins and proton acceptors.<sup>1a,b</sup> They found that a 370-nm band produced in 3-methylheptane glasses decays at 77 K to form the 470-nm band and attributed the 370-nm band to CCl<sub>4</sub><sup>+</sup> radical cations.<sup>ic</sup> Thus, the 470-nm band was assumed to be a charge-transfer complex Cl-CCl<sub>4</sub>, resulting from charge recombination of Cl- with CCl4+. Willard and coworkers found that the 370-nm band is mainly produced in the 20 K radiolysis of CCl<sub>4</sub>-3MP glasses and that the band in the 3MP glasses decays very rapidly at 77 K.<sup>2a</sup> They also found that the 20 K radiolysis of polycrystalline methylcyclohexane (MCH) containing CCl<sub>4</sub> produces an intense 425-nm absorption band and attributed the band to a charge-transfer complex between a CCl<sub>4</sub> molecule and a MCH<sup>+</sup> radical cation.<sup>2b</sup>

After these pioneer works, the radiolysis of CCl<sub>4</sub>-alkane systems has been extensively studied. The models proposed for the 470-nm species are the following: solvent-separated ion pairs between Clanions and CCl<sub>4</sub><sup>+</sup> radical cations, Cl<sup>-</sup>|solvent|CCl<sub>4</sub><sup>+</sup>;<sup>3</sup> solventseparated ion pairs between Cl<sup>-</sup> anions and CCl<sub>3</sub><sup>+</sup> cations, Cl<sup>-</sup>|solvent [CCl<sub>3</sub><sup>+;4</sup> and contact ion pairs between Cl<sup>-</sup> anions and CCl<sub>3</sub> cations, Cl<sup>-</sup>...CCl<sub>3</sub><sup>+,5</sup> Suwalski and Kroh<sup>6</sup> proposed a Cl...CCl<sub>4</sub> complex for the 470-nm species observed in CCl<sub>4</sub>-MCH systems. Recently, Klassen and Ross<sup>7</sup> attributed the 370-nm species observed in the pulse radiolysis of  $CCl_4$ -3MP glasses to  $CCl_4^-$  radical anions and the observed 470-nm species to CCl<sub>3</sub><sup>+</sup> cations. Thus, the postulated models for the 470-nm band are classified as paramagnetic or nonparamagnetic species. These works, however, were based on studies performed by use of an optical spectrometer. Optical studies alone sometimes lead to erroneous conclusion.

In the present work, CCl<sub>4</sub>-3MP glasses containing a small amount of 5-methyldecane (5MD) are mainly investigated at 77 K by combined optical method with ESR method. Glasses of 3MP containing other halocarbon electron scavengers (CCl<sub>3</sub>Br, CCl<sub>3</sub>F,  $CCl_2F_2$ , and  $CClF_3$ ) are also studied for comparison. It has been found by ESR and optical experiments that  $77 \text{ K} \gamma$ -radiolysis of 5MD-3MP glasses with electron scavengers produces 5MD radical cations (5MD<sup>+</sup>).<sup>8a</sup> Louwrier and Hamill have extensively studied the nature of alkane radical cations formed in  $\gamma$ -irradiated 3MP glasses.<sup>8b</sup> The mechanism forming 5MD<sup>+</sup> may be explained in terms of positive charge transfer from the radical cations of matrix molecules, i.e.,  $3MP^{+}$ . The ionization potential (IP) of 5MD is lower than that of 3MP, and the reaction  $3MP^+ + 5MD \rightarrow 3MP$ + 5MD<sup>+</sup> is expected to be exothermic.<sup>9</sup> The reason 5MD is added to CCl<sub>4</sub>-3MP glasses comes from our recent ESR observations<sup>10</sup> that 77 K radiolysis of n-hexane matrices with 1-chloropentane (electron scavenger) and *n*-octane (positive-charge scavenger) produces pentyl radicals (RCH<sub>2</sub><sup>•</sup>) and *n*-octane radical cations  $(nC_8^+)$ , respectively, and that photobleaching of  $nC_8^+$  by IR light  $(\lambda \ge 1200 \text{ nm})$  induces a decrease in RCH<sub>2</sub>. For the photo-

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