

been shown to be triclinic (space group  $P1$ ).<sup>18</sup>

The success of the experiments described above for Dy(III) is in large part due to the availability of suitable electronic transitions. The measurement of CPL from the racemic solution requires that both the absorption and emission transitions have large dissymmetry ratios, since, as illustrated in eq 11, the measurement of  $g_{em}^{CP}$  depends on their product. In normal operating conditions, the sensitivity of our experimental apparatus is such that dissymmetry ratios  $>1 \times 10^{-4}$  can be measured easily. In the case of Dy(III), both the absorption and emission transitions used in this work have large dissymmetry ratios (see Table I). This result is consistent with the fact that these intraconfigurational f-f

transitions satisfy magnetic dipole selection rules.<sup>20</sup>

**Acknowledgment** is made to the Monsanto Co. for the award of a postdoctoral research associate (G.L.H.), to the State of Missouri through the Missouri Research Assistant Act, and to the Weldon Spring Fund of the University of Missouri for support of this work.

**Registry No.** Dy(DPA)<sub>3</sub><sup>3+</sup> (isomer I), 113215-76-2; Dy(DPA)<sub>3</sub><sup>3-</sup> (isomer II), 113215-11-5.

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## Photophysical, Photochemical, and Redox Behavior of a Series of Ligand-Bridged (OC)<sub>5</sub>M-L-M'(CO)<sub>5</sub> (M, M' = Cr, Mo, W) Complexes

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Received June 18, 1987

Infrared spectra, electronic absorption data, redox potentials, and photophysical parameters are reported for a series of homonuclear and heteronuclear ligand-bridged (OC)<sub>5</sub>M-L-M'(CO)<sub>5</sub> complexes, where M and M' = Cr, Mo, or W and L = pyrazine (pyz), 4,4'-bipyridine (bpy), *trans*-1,2-bis(4-pyridyl)ethylene (bpe), or 1,2-bis(4-pyridyl)ethane (bpa), and their corresponding mononuclear derivatives. Each complex exhibits low-lying <sup>1</sup>A<sub>1</sub> → <sup>1</sup>E ligand-field (LF) and M → π\*(L) charge-transfer (MLCT) absorptions. The energy position of the MLCT transition is dependent on both the length and conjugation of the binucleating ligand; when L = pyz, bpy, and bpe, the MLCT states are at lowest energy, but when L = bpa, the LF states are lowest lying. Observed electronic absorption and electrochemical data illustrate that the ligand-bridged (OC)<sub>5</sub>W-L-W(CO)<sub>5</sub> complexes vary considerably in the extent of ligand π\*-orbital stabilization upon binucleation, being essentially unperturbed for L = bpa, weakly perturbed for L = bpe and bpy, and strongly perturbed for L = pyz. Calculated conproportionation constants, K<sub>con</sub>, for these binuclear species are 2.5 × 10<sup>4</sup> (L = bpe), 2.9 × 10<sup>8</sup> (L = bpy), and 2.8 × 10<sup>18</sup> (pyz), further illustrating the extent of electronic interaction. Each of the mononuclear and binuclear complexes, where L = bpy, bpe, and pyz, exhibits broad, relatively long-lived (18-770 ns) MLCT emission, centered at 550-720 nm, in deoxygenated solution at 283 K. Obtained photophysical parameters reflect strong electronic effects in the pyz-bridged complex. No emission was observed from the bpa complexes at 283 K, in accordance with the lowest lying LF assignment. On photoexcitation the mononuclear and binuclear complexes both undergo W-N bond cleavage. Effects of varying the ligand and excitation wavelength on the observed photochemical quantum yields are consistent with the model of a reactive <sup>1</sup>A<sub>1</sub> → <sup>1</sup>E LF state lying closely above an unreactive MLCT state.

### Introduction

Since the first report on the now well-known mixed-valence Ru(II)-L-Ru(III) system,<sup>1</sup> there have been extensive studies on the electronic interaction between mononuclear components of ligand-bridged dimer complexes.<sup>2</sup> It has been demonstrated that upon light absorption by one of the chromophores these binuclear systems may undergo intramolecular energy transfer<sup>3,4</sup> or in-

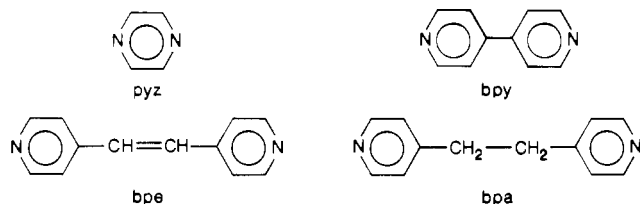
ner-sphere electron transfer<sup>5,6</sup> to the other chromophore. Photochemical reactions have also been documented following these intramolecular energy- and electron-transfer processes.<sup>3,5</sup>

In contrast, there has been relatively little attention paid to photoprocesses of zerovalent organometallic dimer complexes.<sup>7</sup> However, there is ample published spectroscopic and electrochemical evidence illustrating that the binucleating ligand π-system in a ligand-bridged binuclear metal carbonyl compound can be perturbed substantially from that of the corresponding mononuclear complexes.<sup>7,8</sup> Here we describe effects of varying the

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electronic stabilization of the ligand  $\pi^*$  orbitals between the metals for a series of symmetrical ligand-bridged  $(OC)_5W-L-W(CO)_5$  dimer complexes as reflected by their electronic absorption, redox, photophysical, and photochemical properties. The binucleating ligands (L) studied are pyrazine (pyz), 4,4'-bipyridine (bpy),



*trans*-1,2-bis(4-pyridyl)ethylene (bpe), and 1,2-bis(4-pyridyl)ethane (bpa). Also included are the results obtained for a series of heteronuclear  $(OC)_5M(bpy)M'(CO)_5$  ( $M, M' = Cr, Mo, W$ ) complexes.

### Experimental Section

**Materials.** The parent hexacarbonyls ( $M = Cr, Mo, W$ ) were obtained from Strem Chemical Co. and used without further purification. The ligands pyz, bpy, bpe, and bpa were purchased from Aldrich Chemical Co. and recrystallized prior to use. Tetrahydrofuran (THF) used in synthetic procedures was distilled from  $LiAlH_4$  and stored under an argon atmosphere. Solvents used in the spectroscopic experiments were obtained from J. T. Baker Chemical Co. as HPLC or Phorex grade. Methylene chloride used in the electrochemical measurements was of HPLC grade that had been dried over 4-Å molecular sieves and distilled before use. Tetrabutylammonium perchlorate (TBAP) used as supporting electrolyte was rigorously dried (in vacuo at 60 °C for 12 h) prior to use. Nitrogen used for the purging experiments was dried and deoxygenated according to a previously reported method.<sup>9</sup> Other chemicals and solvents used were of the best commercial grade. The complexes were purified by chromatography on 80–200 mesh alumina that had been obtained from Fisher Scientific Co.

**Synthesis of  $(OC)_5ML$  Complexes.** The mononuclear  $(OC)_5ML$  ( $M = Cr, Mo, W; L = pyz, bpy, bpe, bpa$ ) compounds were prepared via the  $(OC)_5M(THF)$  complex according to described literature procedures.<sup>8a,10,11</sup> The product complexes are fairly stable as solids but exhibited varying degrees of thermal stability in solution at room temperature, with the chromium complex undergoing the most rapid decomposition.

**Synthesis of  $(OC)_5M-L-M'(CO)_5$  Complexes.** The ligand-bridged dimer compounds ( $M, M' = Cr, Mo, W; L = bpy, bpe, bpa$ ) were prepared by thermally reacting approximately equimolar amounts of  $(OC)_5ML$  with photogenerated  $(OC)_5M'(THF)$  in deoxygenated hexane containing 0.1 M THF according to a previously published method.<sup>7,8d,10</sup> The  $(OC)_5W(py)W(CO)_5$  complex was obtained following direct photolysis of  $W(CO)_6$  (6 mmol) in deoxygenated hexane containing pyz (3 mmol).<sup>7</sup> Elemental analyses (C, H, N) were performed by MICANAL, Inc., and these were satisfactory. Again, the product complexes are moderately stable in the solid form, although their long-term stabilities are enhanced when they are kept in the dark under nitrogen gas at 273 K. The chromium complexes are particularly air-sensitive and were handled accordingly. In solution at room temperature the dimer complexes undergo a very slow thermal reaction, with the exception of  $(OC)_5Cr(bpy)Cr(CO)_5$ , which rapidly decomposed.

**Equipment and Procedures.** Infrared spectra were recorded as Nujol mulls between NaCl plates on a Perkin-Elmer Model 283B spectrometer. Band maxima are considered accurate to  $\pm 2$   $cm^{-1}$ . Electronic absorption spectra were obtained on a Hewlett-Packard 8450A spectrometer, which incorporates a microprocessor-controlled diode-array detector. This en-

abled absorption spectra to be obtained with 5 s of complex dissolution, if necessary. Reported absorption maxima are believed to be accurate to  $\pm 2$  nm.

Emission and excitation spectra were recorded with a SLM Instruments Model 8000/8000S spectrometer, which utilizes a photomultiplier-based photon-counting detector. These spectra were fully corrected for variations in the detector response and excitation lamp intensity as a function of wavelength, and the band maxima are considered accurate to  $\pm 4$  nm. Emission lifetimes were obtained on a PRA System 3000 time-correlated pulsed single-photon-counting apparatus. Samples were excited at 400 nm with light from a PRA Model 510 nitrogen flash lamp that had been transmitted through an Instruments SA Inc. H-10 monochromator. Emission was detected from the sample at 90° by means of a second H-10 monochromator and a thermoelectrically cooled Hamamatsu R955 (red sensitive) photomultiplier tube; the photon counts were stored on a Tracor Northern Model 7200 microprocessor-based multi-channel analyzer. The instrument response function was deconvoluted from the luminescence data to obtain an undisturbed decay that was then fitted by a least-squares method on an IBM PC. Single exponential decays were observed from each sample, and the lifetimes were found to be reproducible to within  $\pm 5$  ns. In the emission and excitation experiments the sample solutions were filtered through a 0.22- $\mu m$  Millipore filter and deoxygenated prior to taking measurements. The solution temperature was controlled to  $\pm 0.1$  K. Emission quantum yields were determined from benzene solutions of the complexes with dilute  $Ru(bpy)_3^{2+}$  in deoxygenated aqueous solution at 283 K as a calibrant ( $\phi_{em} = 0.046$ )<sup>12</sup> and were corrected for differing refractive indices of the solvents by using the equation  $\phi_{em} = \phi_{em}^{obsd}(\eta_s^2/\eta_w^2)$ , where  $\phi_{em}$  and  $\phi_{em}^{obsd}$  are the corrected and experimentally observed quantum yields and  $\eta_s$  and  $\eta_w$  are the refractive indices of benzene and water, respectively.<sup>13</sup> The emission quantum yields are estimated to be accurate to  $\pm 10\%$ .

Photolysis experiments at 458 and 514 nm were performed with a Lexel Corp. Model 95-4 4W argon ion laser with a typical laser power of 40 mW. The photon flux was calculated from the laser power, determined by means of an external Lexel Corp. Model 504 power meter. Irradiations at 405 and 436 nm were carried out with a 200-W medium-pressure Hg lamp with Baird-Atomic and Rolyn Optics Corp. interference filters (10-nm band-pass) to isolate the excitation wavelength. Typical light intensities were  $10^{-9}$ – $10^{-8}$  einstein  $s^{-1}$ , determined by ferrioxalate actinometry.<sup>14</sup> Sample solutions ( $\sim 10^{-4}$  M complex and  $10^{-2}$  M entering ligand in benzene) were filtered through 0.22- $\mu m$  Millipore filters immediately before use and deoxygenated prior to photolysis, and the solution temperature was controlled to  $\pm 0.1$  K. In all photolysis experiments the concentrations of reactants and products were followed by UV-vis spectroscopy. Photochemical quantum yields were corrected for inner-filter effects due to product formation and changing degree of light absorption, when necessary. Measurements were typically made over relatively small (<20%) conversions. Quantum yields were found to be reproducible to  $\pm 10\%$ .

Electrochemical measurements were recorded on a Bio-Analytical Systems Corrosion Model CV-47 voltammograph with a Houston Instruments Model 200 X-Y recorder. Cyclic voltammograms were obtained in deoxygenated dry methylene chloride under a nitrogen atmosphere with a glassy-carbon working electrode, a platinum-wire auxiliary electrode, and a saturated calomel reference electrode (SCE) with 0.1 M tetrabutylammonium perchlorate (TBAP) as supporting electrolyte. The concentration of the metal carbonyl complexes in these measurements was  $\sim 10^{-3}$  M. The scan rate was 80 mV  $s^{-1}$ . The measurements were uncorrected for liquid-junction potentials.

### Results and Discussion

**Synthesis and General Properties.** Although this is the first report for several of these metal carbonyl derivatives, the synthetic procedures are not extraordinary and followed earlier methods with only minor modifications (see Experimental Section).<sup>7,8a,8d,11</sup> The compounds are typically stable as solids, though they are somewhat light- and air-sensitive. In room-temperature solution the complexes are moderately stable, with the bpy derivatives exhibiting the greatest thermal decomposition. Both  $(CO)_5Cr(bpy)$  and  $(OC)_5Cr(bpy)Cr(CO)_5$  complexes underwent quite rapid decomposition in room-temperature solution and were not investigated further. The thermal decomposition reaction was, however, generally slow for the other compounds and was only troublesome in polar media. The nature of this thermal process

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**Table I.** Infrared Carbonyl Stretching Frequencies and Assignments for  $(OC)_5ML$  and  $(OC)_5M-L-M'(CO)_5$  Complexes<sup>a</sup>

complex	$\nu_{CO}, \text{cm}^{-1}$			
	$A_1^1$	$B_1$	E	$A_1^2$
$(OC)_5W(py)W(CO)_5$	2075 (m)	1960 (vw)	1946 (s), 1915 (s)	1892 (s)
$(OC)_5W(bpy)W(CO)_5$	2070 (m)	1980 (vw)	1918 (s, br)	1883 (s)
$(OC)_5W(bpe)W(CO)_5$	2069 (m)	1980 (vw)	1920 (s, br)	1882 (s)
$(OC)_5W(bpa)W(CO)_5$	2075 (m)	1990 (vw)	1938 (s, br)	1878 (s)
$(OC)_5W(bpy)Mo(CO)_5$	2072 (m)	1983 (vw)	1930 (s), 1917 (s)	1877 (s)
$(OC)_5W(bpy)Cr(CO)_5$	2073 (m)	1984 (vw)	1929 (s), 1910 (s)	1877 (s)
$(OC)_5Mo(bpy)Mo(CO)_5$	2070 (m)	1985 (vw)	1930 (s, br)	1888 (s)
$(OC)_5Mo(bpy)Cr(CO)_5$	2072 (m)	1993 (vw)	1938 (s), 1918 (s)	1883 (s)
$(OC)_5W(py)z$	2068 (m)	1985 (sh)	1933 (s, br)	1880 (s)
$(OC)_5W(bpy)$	2070 (m)	1988 (vw)	1923 (s, br)	1885 (s)
$(OC)_5W(bpe)$	2070 (m)	1975 (sh)	1925 (s, br)	1880 (s)
$(OC)_5W(bpa)$	2066 (m)	1984 (vw)	1947 (s), 1915 (s)	1870 (s)
$(OC)_5Mo(bpy)$	2077 (m)	1993 (vw)	1939 (s), 1920 (s)	1885 (s)

<sup>a</sup>In Nujol mulls at 298 K; s = strong, m = moderate, vw = very weak, br = broad, sh = shoulder.

**Table II.** Electronic Absorption Spectral Data and Assignments for  $(OC)_5ML$  and  $(OC)_5M-L-M'(CO)_5$  Complexes in Benzene at 298 K<sup>a</sup>

complex	$\lambda_{max}, \text{nm} (10^4\epsilon, \text{M}^{-1}\text{cm}^{-1})$	
	$^1A_1 \rightarrow ^1E$	$M \rightarrow \pi^*(L)$
$(OC)_5W(py)zW(CO)_5$	397 (0.55)	510 (1.20)
$(OC)_5W(bpy)W(CO)_5$	404 (1.18)	438 (1.08)
$(OC)_5W(bpe)W(CO)_5$	404 (1.47)	450 (1.55)
$(OC)_5W(bpa)W(CO)_5$	379 (1.22)	343 (1.29)
$(OC)_5W(bpy)Mo(CO)_5$	402 (1.05)	432 (sh)
$(OC)_5W(bpy)Cr(CO)_5$	402 (0.83)	436 (sh)
$(OC)_5Mo(bpy)Mo(CO)_5$	395 (0.85)	430 (sh)
$(OC)_5Mo(bpy)Cr(CO)_5$	398 (0.45)	432 (sh)
$(OC)_5W(py)z$	398 (0.71)	b
$(OC)_5W(bpy)$	400 (1.03)	b
$(OC)_5W(bpe)$	402 (0.36)	440 (sh)
$(OC)_5W(bpa)$	379 (0.30)	340 (sh)
$(OC)_5Mo(bpy)$	396 (1.00)	428 (sh)

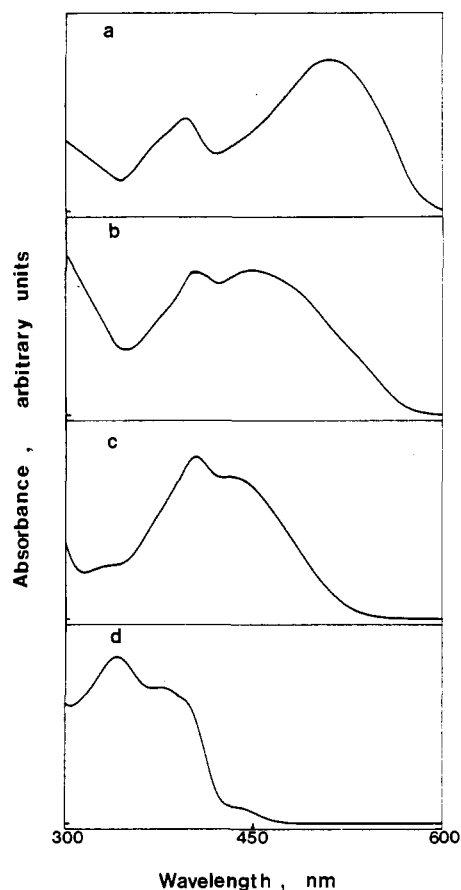
<sup>a</sup>Recorded within 5 s of dissolution to minimize thermal decomposition reaction; sh = shoulder. <sup>b</sup>Overlaps substantially with LF transition.

is thought to involve dissociation of the M-L bond, analogous to the reaction reported previously for  $(OC)_5Mo(py)zMo(CO)_5$ .<sup>15</sup>

**Infrared Spectra.** Infrared carbonyl stretching frequencies obtained from all of the monomer and ligand-bridged dimer complexes studied are shown in Table I. The three moderate/strong band maxima are assigned to  $A_1^1$ , E, and  $A_1^2$  modes and are characteristic of  $C_{4v}$  arrangement of the carbonyl ligands at the metal center.<sup>16</sup> However, there appears to be a slight distortion of the carbonyl ligands'  $C_{4v}$  symmetry in these compounds, as indicated by the weakly infrared-active  $B_1$  mode centered at 1960–1993  $\text{cm}^{-1}$ .

**Electronic Absorption Spectra.** Figure 1 illustrates the electronic absorption spectra of the ligand-bridged  $(OC)_5W-L-W(CO)_5$  (L = pyz, bpy, bpe, bpa) complexes in benzene at room temperature. Spectral data obtained from all of the tungsten mononuclear and binuclear complexes studied and their assignments are summarized in Table II. Each complex exhibits ligand-field (LF)  $^1A_1(e^4b_2^2) \rightarrow ^1E(e^3b_2^2a_1^1)$  and  $M \rightarrow \pi^*(L)$  charge-transfer (MLCT) transitions, as noted previously.<sup>7,8d</sup> Although there is substantial overlap of the  $^1A_1 \rightarrow ^1E$  and  $M \rightarrow \pi^*(L)$  transitions in the spectra of several of these complexes, it may be seen that the  $^1A_1 \rightarrow ^1E$  transitions of the binuclear complexes are relatively unmoved from their corresponding monomer derivatives. This further implies that the approximate  $C_{4v}$  symmetry of the carbonyl ligands in the  $(OC)_5ML$  species is essentially unaltered on forming the ligand-bridged dimers.

The position of the MLCT absorption band indicates the energies of the ligand  $\pi^*$ -acceptor orbital (see Figure 1 and Table

**Figure 1.** Electronic absorption spectra of  $(OC)_5W-L-W(CO)_5$  complexes (L = pyz (a), bpe (b), bpy (c), bpa (d)) in benzene at 298 K.

II). When L = bpa, the MLCT band lies above the  $^1A_1 \rightarrow ^1E$  LF transition, and the absorption spectra of the bpa mononuclear and ligand-bridged binuclear complexes are very similar. Here, there is apparently no effect on the position of the bpa  $\pi^*$ -acceptor orbital on forming the bridged complex. When L = bpy or bpe, the MLCT state is at slightly lower energy than the  $^1A_1 \rightarrow ^1E$  LF transition for both the mononuclear and binuclear complexes. Moreover, the ligand  $\pi^*$  orbital appears to be only stabilized to a small extent on forming the dimer complexes, as the spectra of the mononuclear (L = bpy, bpe) and corresponding binuclear complexes are fairly similar. In contrast, the energy position of the pyz  $\pi^*$ -acceptor orbital is very substantially lowered as this ligand binucleates to form the bridged complex, as reflected by the relative MLCT energies of the  $(OC)_5W(py)z$  and  $(OC)_5W(py)zW(CO)_5$  species. Overall, the MLCT energies for the ligand-bridged dimers are ordered L = bpa > bpy > bpe > pyz, indicating that the energy of the ligand  $\pi^*$ -acceptor orbital is dependent on both the length and conjugation of the binucleating

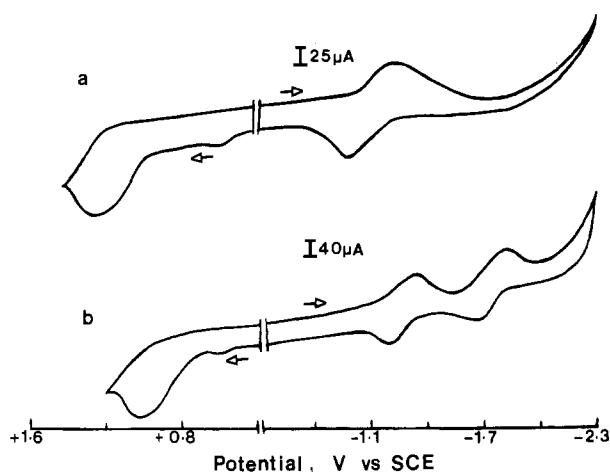
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**Table III.** Redox Potentials and Electronic Absorption Data of Free Ligands (L) and (OC)<sub>5</sub>ML and (OC)<sub>5</sub>M-L-M'(CO)<sub>5</sub> Complexes in Methylene Chloride at 298 K<sup>a</sup>

complex	$E_{ox}$	$E_{red}$ : (0/1-), (1-/2-), (2-/3-)	$\lambda_{max}$ , nm	
			$^1A_1 \rightarrow ^1E$	$M \rightarrow \pi^*(L)$
(OC) <sub>5</sub> W(pyzy)W(CO) <sub>5</sub>	+1.26 (i)	-1.21, >-2.3	395	521
(OC) <sub>5</sub> W(bpy)W(CO) <sub>5</sub>	+1.09 (i)	-1.30, -1.80	402	431
(OC) <sub>5</sub> W(bpe)W(CO) <sub>5</sub>	+1.09 (i)	-1.20, -1.46, -1.80	402	440
(OC) <sub>5</sub> W(bpa)W(CO) <sub>5</sub>	+1.16 (i)	>-2.3	379	335
(OC) <sub>5</sub> W(bpy)Mo(CO) <sub>5</sub>	+1.07 (i)	-1.32, -1.68	397	430 (sh)
(OC) <sub>5</sub> W(bpy)Cr(CO) <sub>5</sub>	+1.06 (i)	-1.37, -1.70	399	432 (sh)
(OC) <sub>5</sub> Mo(bpy)Mo(CO) <sub>5</sub>	+1.16 (i)	-1.38, -1.67	397	426 (sh)
(OC) <sub>5</sub> Mo(bpy)Cr(CO) <sub>5</sub>	+1.06 (i)	-1.43, -1.78	397	428 (sh)
(OC) <sub>5</sub> W(pyzy)	+1.25 (i)	-1.70 (i)	398	b
(OC) <sub>5</sub> W(bpy)	+1.09 (i)	-1.64 (i), -2.04	402	b
(OC) <sub>5</sub> W(bpe)	+1.13 (i)	-1.50 (i), -1.82	400	b
(OC) <sub>5</sub> W(bpa)	c	c	383	b
(OC) <sub>5</sub> Mo(bpy)	+1.16 (i)	-1.40 (i), -1.78	395	b
pyzy		>-2.3		
bpy		-2.10 (i)		
bpe		-1.80 (i), -2.10 (i)		
bpa		>-2.3		

<sup>a</sup> Analyses performed in 10<sup>-3</sup> M deoxygenated solutions containing 0.1 M TBAP. All potentials in volts vs SCE; scan rate 80 mV/s; scan range +1.4 to -2.3 V; i = irreversible process. All reversible potentials were determined to be reproducible to  $\pm 0.01$  V, and the irreversible potentials were reproducible to  $\pm 0.02$  V. <sup>b</sup> Overlaps substantially with LF transition. <sup>c</sup> Value unobtainable due to thermal decomposition of complex.

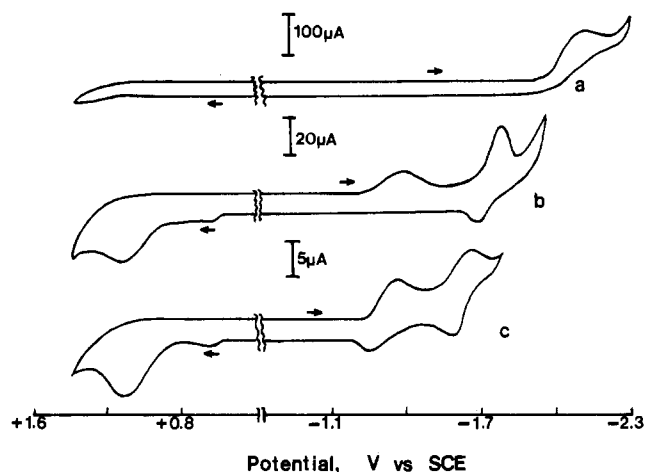


**Figure 2.** Cyclic voltammograms of (a) (OC)<sub>5</sub>W(pyzy)W(CO)<sub>5</sub> and (b) (OC)<sub>5</sub>W(bpy)W(CO)<sub>5</sub> in deoxygenated methylene chloride containing 0.1 M TBAP at 298 K. All potentials are in volts versus SCE; scan rate is 80 mV s<sup>-1</sup>.

ligand. Hence the ligand-bridged dimers studied here represent a range of complexes in which the energies of the ligand  $\pi^*$  orbitals are in effect unperturbed (L = bpa), weakly perturbed (L = bpy, bpe), or strongly perturbed (L = pyzy) on binucleation. Moreover, the absorption spectrum of the heteronuclear (OC)<sub>5</sub>W(bpy)Mo(CO)<sub>5</sub> complex is close to that obtained by adding the spectra of the individual monomer components. In fact, the spectra of all the homonuclear and heteronuclear derivatives bridged via the bpy ligand are similar because the spectra of the (OC)<sub>5</sub>Mo(bpy) and (OC)<sub>5</sub>W(bpy) complexes are so very alike.

**Electrochemistry.** Redox potential values obtained from cyclic voltammetry data of the free ligands and their mononuclear and binuclear complexes in deoxygenated methylene chloride solution are listed in Table III. Also included are relevant absorption data. Cyclic voltammograms of (OC)<sub>5</sub>W(pyzy)W(CO)<sub>5</sub> and (OC)<sub>5</sub>W(bpy)W(CO)<sub>5</sub> are typical of these complexes and are illustrated in Figure 2. These recorded reduction potentials represent ligand-centered one-electron processes for the LUMO levels of the complexes. The first reduction potentials of the ligand-bridged (OC)<sub>5</sub>W-L-W(CO)<sub>5</sub> complexes follow the order L = bpa > bpy > bpe ~ pyzy, reflecting the energy position of the ligand  $\pi^*$ -acceptor orbital, and are in agreement with that noted from absorption data (vide supra).

Representative cyclic voltammograms of the bpy ligand and the (OC)<sub>5</sub>Mo(bpy) and (OC)<sub>5</sub>Mo(bpy)Mo(CO)<sub>5</sub> complexes are depicted in Figure 3. These results (and data listed in Table III)



**Figure 3.** Cyclic voltammograms of (a) bpy ligand, (b) (OC)<sub>5</sub>Mo(bpy), and (c) (OC)<sub>5</sub>Mo(bpy)Mo(CO)<sub>5</sub> in deoxygenated methylene chloride containing 0.1 M TBAP at 298 K. All potentials are in volts versus SCE; scan rate is 80 mV s<sup>-1</sup>.

illustrate that the first reduction potentials (0/1-) follow the order bpy > (OC)<sub>5</sub>M(bpy) > (OC)<sub>5</sub>M(bpy)M'(CO)<sub>5</sub>. The first reduction potentials of all compounds studied indicate that the binuclear complexes (where L = bpy, bpe, and pyzy) are more easily reduced compared to the corresponding mononuclear complexes. These values again reflect the stabilization of the ligand  $\pi^*$  orbitals in the bridged compounds, and this is most pronounced for the pyzy species in accordance with the above rationale.<sup>17</sup> In all cases the first reduction potentials were observed to be quasi-reversible for one-electron processes of the ligand-bridged dimer complexes ( $E_{pc} - E_{pa} \approx 0.058/n$  V;  $E_{pc}$  = cathodic peak potential,  $E_{pa}$  = anodic peak potential,  $n$  = number of electrons transferred per molecule) but were found to be irreversible ( $E_{pc} - E_{pa} \gg 0.058$  V) for the mononuclear complexes and the free ligands (see Table III).<sup>8k,18</sup> This further illustrates the lowering in energy of the ligand  $\pi^*$ -acceptor orbitals in the binuclear complexes. All the oxidation processes were observed to be irreversible, and the oxidation potentials indicate that the HOMO levels of the mononuclear species are not appreciably affected on forming the ligand-bridged compounds.

Cyclic voltammograms of the ligand-bridged complexes exhibit either two or three reduction potentials. For molecules with two

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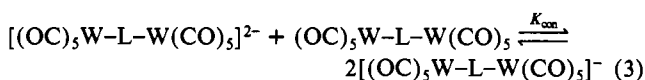
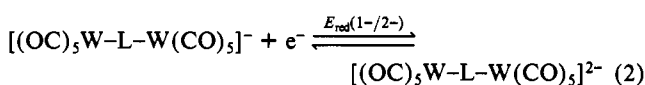
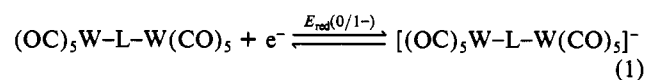
(18) Mabbott, G. A. *J. Chem. Educ.* **1983**, *60*, 697.

**Table IV.** Emission Data and Derived Radiative Rate Constants ( $k_r$ ) for (OC)<sub>5</sub>ML and (OC)<sub>5</sub>M-L-M'(CO)<sub>5</sub> Complexes in Benzene at 283 K<sup>a,b</sup>

complex	$\lambda_{\max}$ , nm	half-width, <sup>c</sup> cm <sup>-1</sup> × 10 <sup>3</sup>	10 <sup>4</sup> $\phi_{em}$ <sup>d</sup>	$\tau$ , <sup>e</sup> ns	$k_r$ , s <sup>-1</sup> × 10 <sup>2</sup>
(OC) <sub>5</sub> W(py <sub>2</sub> )W(CO) <sub>5</sub>	721	3.80	4.40	186	23.7
(OC) <sub>5</sub> W(bpy)W(CO) <sub>5</sub>	654	3.90	1.59	394	4.0
(OC) <sub>5</sub> W(bpe)W(CO) <sub>5</sub>	560	4.00	0.13	123	1.0
(OC) <sub>5</sub> W(bpa)W(CO) <sub>5</sub>	<sup>f</sup>				
(OC) <sub>5</sub> W(bpy)Mo(CO) <sub>5</sub>	651	3.50	1.23	428	2.9
(OC) <sub>5</sub> W(bpy)Cr(CO) <sub>5</sub>	642	2.85	0.62	368	1.7
(OC) <sub>5</sub> Mo(bpy)Mo(CO) <sub>5</sub>	606	2.50	0.99	547	1.8
(OC) <sub>5</sub> Mo(bpy)Cr(CO) <sub>5</sub>	602	2.65	0.40	767	0.5
(OC) <sub>5</sub> W(py <sub>2</sub> )	645	3.40	0.20	18 <sup>g</sup>	11.1
(OC) <sub>5</sub> W(bpy)	643	3.15	0.72	415	1.7
(OC) <sub>5</sub> W(bpe)	549	3.60	0.10	120	0.8
(OC) <sub>5</sub> W(bpa)	<sup>f</sup>				
(OC) <sub>5</sub> Mo(bpy)	595	2.46	0.56	699	0.8

<sup>a</sup>  $4 \times 10^{-5}$ – $2 \times 10^{-4}$  M deoxygenated solutions. <sup>b</sup> Spectra corrected for variation in instrumental response as a function of wavelength; the excitation wavelength is 400 nm. <sup>c</sup> Width of emission band measured at half-height. <sup>d</sup> Absolute quantum yields measured relative to the emission of Ru(bpy)<sub>3</sub><sup>2+</sup>; accurate to within  $\pm 10\%$ . <sup>e</sup> Lifetimes accurate to within  $\pm 5$  ns, unless otherwise stated. <sup>f</sup> No emission observed. <sup>g</sup> Lifetime accurate to within  $\pm 2$  ns.

chemically equivalent and reversible redox sites the differences ( $\Delta$ ) between these reduction potentials may be related to the comproportionation (or anion-radical stability) constant  $K_{con}$  (see eq 1–4).<sup>81,19</sup> A large difference between the first and second



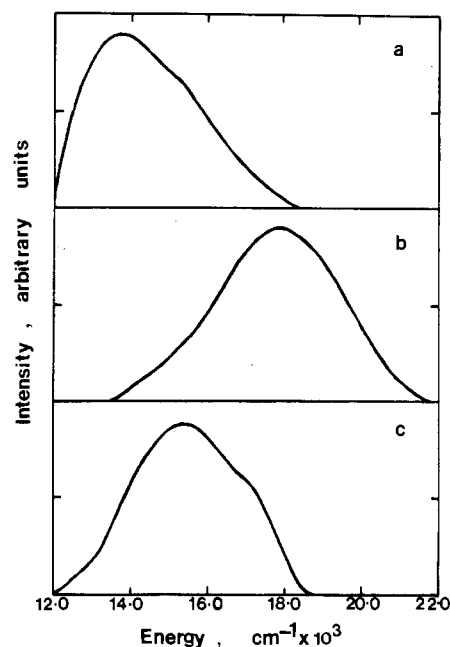
$$\Delta = E_{red(0/1-)} - E_{red(1-/2-)} = 0.0591 \log K_{con} \quad (\text{at } 25^\circ \text{C}) \quad (4)$$

reduction potentials indicates a strong energy stabilization of the ligand  $\pi^*$ -acceptor orbital. For the (OC)<sub>5</sub>W-L-W(CO)<sub>5</sub> complexes the calculated values of  $K_{con}$  are  $2.5 \times 10^4$  (L = bpe),  $2.9 \times 10^8$  (L = bpy), and  $2.8 \times 10^{18}$  (L = pyz), providing further evidence for the varying degrees of ligand  $\pi^*$ -orbital stabilization in this system. Previously obtained values for other ligand-bridged group 6 metal carbonyl systems are  $K_{con} \sim 10^{11}$  for 2,2'-bipyrimidine<sup>81</sup> and  $K_{con} > 10^{20}$  for 1,2,4,5-tetrazine complexes.<sup>20</sup> In addition,  $K_{con}$  values between  $5$  and  $5 \times 10^8$  have been reported for a number of binuclear molybdenum tetracarbonyl complexes bridged through various types of  $\alpha, \alpha'$ -diimine ligands.<sup>81</sup> The reduction potential differences ( $\Delta$ ) for these binuclear complexes can be rationalized in terms of energy repulsion between the two electrons in the highest occupied antibonding orbital of [(OC)<sub>5</sub>W-L-W(CO)<sub>5</sub>]<sup>2-</sup>, as previously noted for related ligand-bridged metal carbonyl complexes<sup>81</sup> and other organic systems.<sup>21</sup> The repulsion energy follows the order pyz > bpy > bpe and may relate to the distance between the W(CO)<sub>5</sub> fragments in the dimeric species.

The data of Table III also indicate a relationship between the redox potential difference,  $E_p$  (see eq 5), and the MLCT transition

$$E_p = E_{ox} - E_{red(0/1-)} \quad (5)$$

energy for the (OC)<sub>5</sub>W-L-W(CO)<sub>5</sub> complexes. When L = pyz, the determined  $E_p$  value of 2.47 eV (for a one-electron process) approximates the MLCT transition energy of 2.38 eV. In contrast,



**Figure 4.** Corrected emission spectra of (OC)<sub>5</sub>W-L-W(CO)<sub>5</sub> complexes (L = pyz (a), bpe (b), bpy (c)) in deoxygenated benzene at 283 K. Excitation wavelength is 400 nm.

the  $E_p$  values for (OC)<sub>5</sub>W-L-W(CO)<sub>5</sub> (where L = bpy, bpe, and bpa) illustrate that an additional energy term ( $\chi$ ) must be included to justify the MLCT transition energies. This energy term may be a result of resonance and exchange energies or a Franck-Condon perturbation effect (see eq 6).<sup>22</sup> In eq 6  $E_{od}$  is the optical

$$E_{od} = E_p + \chi \quad (6)$$

absorption energy and  $\chi$  comprises contribution to the Franck-Condon energy from intramolecular and intermolecular vibrations. For the ligand-bridged complexes, where L = bpy, bpe, and bpa, the energy term  $\chi$  may consist of Franck-Condon contributions resulting from twisting between the pyridyl rings. This has previously been suggested for biphenyl-like molecules.<sup>23</sup>

**Photophysical Properties.** Emission spectra recorded from deoxygenated benzene solutions of the (OC)<sub>5</sub>W-L-W(CO)<sub>5</sub> complexes (L = pyz, bpe, bpy) are shown in Figure 4. Spectral data, emission quantum yields, and lifetime values obtained from

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 (20) (a) Troll, T. *Electrochim. Acta* **1982**, *27*, 1311. (b) Kaim, W. *J. Chem. Soc., Perkin Trans. 2* **1985**, 1633.  
 (21) Saji, T.; Aoyagi, S. *J. Electroanal. Chem. Interfacial Electrochem.* **1983**, *144*, 143.

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 (23) (a) Suzuki, H. *Electronic Absorption Spectra and Geometry of Organic Molecules*; Academic: New York, 1967. (b) Sullivan, B. D.; Fong, J. Y. *Chem. Phys. Lett.* **1976**, *38*, 555.

all of the complexes in deoxygenated benzene at 283 K are listed in Table IV.

Each of the complexes gives rise to a single broad emission band in the 500–750-nm region; the emission is assigned to the lowest energy  $M \rightarrow \pi^*(L)$  MLCT excited state, as previously noted for  $(OC)_5W(py)W(CO)_5$ <sup>7</sup> and several mononuclear group pentacarbonyl derivatives.<sup>10,24</sup> When  $L = bpy$  and  $bpe$ , the emission maxima of the ligand-bridged dimer complexes are only slightly red-shifted from the emission maxima of the corresponding mononuclear species. In contrast, when  $L = pyz$ , the emission maximum for the binuclear complex is considerably more red-shifted than that for the  $(OC)_5W(py)W(CO)_5$  complex (see Table IV); this further reflects the effects of strong ligand  $\pi^*$ -orbital perturbation in the  $pyz$ -bridged binuclear complexes. Recorded emission maxima of these complexes illustrate that the MLCT energies follow the order  $L = bpa > bpe > bpy > pyz$ ; this is generally in agreement with the absorption and redox potential data. However, we note that the energy positions of the emission maxima from the  $bpy$  and  $bpe$  dimer complexes have been reversed from the previous trend. It is not clear what is the exact reason for this change in the order of MLCT energies, but it may be a result of varying degrees of excited-state distortion about the pyridyl rings in these molecules. Importantly, when  $L = bpa$ , no emission was observed from either the mononuclear or the binuclear complexes, implying that the MLCT state is raised so high in energy that it lies above the  $^1A_1 \rightarrow ^1E$  LF state and that this energy level ordering provides an efficient nonradiative deactivation pathway. Hence, photophysically the  $(OC)_5W(bpa)W(CO)_5$  complex behaves like its respective mononuclear complex, and again we conclude that the ligand  $\pi^*$  orbital of this binuclear complex is essentially unperturbed.

For the ligand-bridged complexes where  $L = pyz$  and  $bpy$  the recorded spectra do exhibit some band structure (see Figure 4), suggesting the presence of two emitting levels. However, these states would appear to be thermally equilibrated as single exponential decays with constant lifetimes that were observed at any wavelength under the broad emission band. Moreover, the spectral distribution of the emission from each complex was observed to be independent of excitation wavelengths greater than 300 nm, consistent with emission from a single state or from two states in thermal equilibrium. In this connection, previously reported electronic absorption and resonance Raman measurements have indicated that there are several MLCT transitions that comprise the low-energy absorption band of  $(OC)_5W(py)W(CO)_5$  of which two have been assigned as symmetry-allowed  $y$ - and  $z$ -polarized transitions.<sup>7b,8c</sup> A detailed investigation of the emission behavior of these complexes at low temperature is presently being carried out and will be fully reported in a later paper.

Radiative rate constants ( $k_r$ ) have been derived from the emission quantum yield ( $\phi_{em}$ ) and lifetime ( $\tau$ ) data, according to eq 7, and the values are included in Table IV. These exper-

$$k_r = \phi_{em} / \tau \quad (7)$$

imentally observed emission quantum yields and lifetimes and the derived radiative rate constants provide further evidence for the effects of ligand  $\pi^*$ -orbital stabilization in these ligand-bridged metal complexes. As noted above, the photophysical behavior can be interpreted in terms of an unreactive emitting MLCT state that lies below a reactive LF ( $^1A_1 \rightarrow ^1E$ ) state. When the MLCT state lies close in energy to the LF state, the photochemical pathway is efficient (vide infra) and the complexes are only weakly emissive. When the MLCT state lies far below the LF state, the radiative route is enhanced. Alternatively, the emission data can

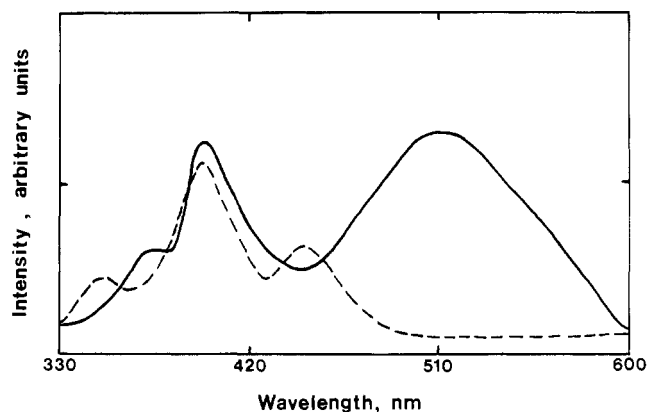


Figure 5. Corrected excitation spectra of (—)  $(OC)_5W(py)W(CO)_5$  and (---)  $(OC)_5W(bpy)W(CO)_5$  in deoxygenated benzene at 283 K. Emission was monitored at the emission maximum of each complex.

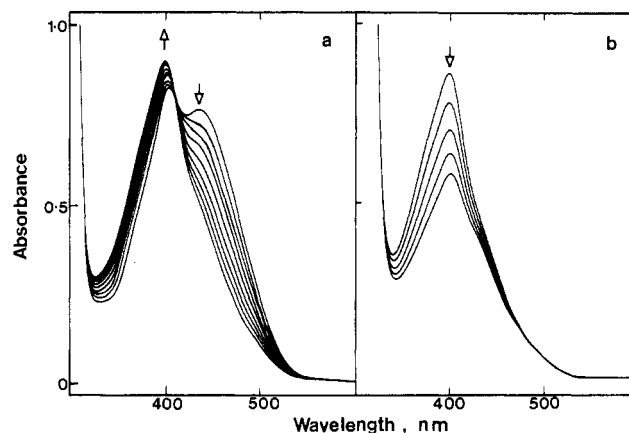


Figure 6. Electronic absorption spectral changes accompanying the 430-nm photolysis (equal time intervals) of (a)  $(OC)_5W(bpy)W(CO)_5$  and (b)  $(OC)_5W(bpy)$  in deoxygenated benzene at 283 K. Solutions contain (a) 0.01 M  $bpy$  and (b) 0.01 M  $PPH_3$  as entering ligand, respectively.

Table V. Excitation Spectral Data for  $(OC)_5ML$  and  $(OC)_5M-L-M'(CO)_5$  Complexes in Benzene at 283 K<sup>a,b</sup>

complex	$\lambda_{max}$ , nm
$(OC)_5W(py)W(CO)_5$	370, 395, 510
$(OC)_5W(bpy)W(CO)_5$	364, 400, 432
$(OC)_5W(bpe)W(CO)_5$	354, 400, 448
$(OC)_5W(bpy)Mo(CO)_5$	358, 398, 421 (sh)
$(OC)_5W(bpy)Cr(CO)_5$	361, 399, 424 (sh)
$(OC)_5Mo(bpy)Mo(CO)_5$	359, 400, 423 (sh)
$(OC)_5Mo(bpy)Cr(CO)_5$	360, 404, 421 (sh)
$(OC)_5W(py)$	364, 396, 434 (sh)
$(OC)_5W(bpy)$	366, 398, 429
$(OC)_5W(bpe)$	354, 398, 430 (sh)
$(OC)_5Mo(bpy)$	358, 402, 422 (sh)

<sup>a</sup>  $4 \times 10^{-5}$ – $2 \times 10^{-4}$  deoxygenated solutions. <sup>b</sup> Corrected excitation spectra with emission monitored at the emission maxima; sh = shoulder.

also be interpreted with considerations of the energy gap law;<sup>25</sup> this aspect is presently being further investigated for these compounds in rigid media at low temperatures. Thus, the lifetimes and quantum yield data of Table IV indicate that it is only the mononuclear  $pyz$  complex that is substantially affected as the ligand binucleates to form the bridged complex. By comparison, the emission parameters of the  $bpy$  and  $bpe$  complexes are rela-

(24) (a) Lees, A. *J. Chem. Rev.* **1987**, *87*, 711. (b) Wrighton, M.; Hammond, G. S.; Gray, H. B. *Mol. Photochem.* **1973**, *5*, 179. (c) Wrighton, M. S.; Abrahamson, H. B.; Morse, D. L. *J. Am. Chem. Soc.* **1976**, *98*, 4105. (d) Dahlgren, R. M.; Zink, J. I. *Inorg. Chem.* **1977**, *16*, 3154. (e) Boxhoorn, G.; Stufkens, D. J.; Van de Coolwijk, P. J. F. M.; Hezemans, A. M. F. *Inorg. Chem.* **1981**, *20*, 2778. (f) Lees, A. J.; Adamson, A. W. *J. Am. Chem. Soc.* **1980**, *102*, 6874. (g) Lees, A. J.; Adamson, A. W. *J. Am. Chem. Soc.* **1982**, *104*, 3804. (h) Lees, A. J. *J. Am. Chem. Soc.* **1982**, *104*, 2038.

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**Table VI.** Wavelength Dependence of Photodissociation Quantum Yields ( $\phi_{cr}$ ) for  $(OC)_5WL$  and  $(OC)_5W-L-W(CO)_5$  Complexes in Benzene at 283 K<sup>a</sup>

complex	entering ligand	$10^2\phi_{cr}$ ( $\lambda_{ex} = 405$ nm)	$10^2\phi_{cr}$ ( $\lambda_{ex} = 436$ nm)	$10^5\phi_{cr}$ ( $\lambda_{ex} = 458$ nm)	$10^5\phi_{cr}$ ( $\lambda_{ex} = 514$ nm)
$(OC)_5W(pyzo)W(CO)_5$	pyz	3.9	2.8	7.0	1.0
$(OC)_5W(bpy)W(CO)_5$	bpy	3.5	1.8	4.4	b
$(OC)_5W(bpe)W(CO)_5$	bpe	3.6	1.7	4.4	b
$(OC)_5W(bpa)W(CO)_5$	bpa	11.0	8.6	b	b
$(OC)_5W(pyzo)$	$PPh_3$	47.8	40.0	b	b
$(OC)_5W(bpy)$	$PPh_3$	26.8	10.0	b	b
$(OC)_5W(bpe)$	$PPh_3$	9.9	9.1	b	b
$(OC)_5W(bpa)$	$PPh_3$	c	c	c	c

<sup>a</sup> Photolysis performed in deoxygenated solutions of  $\sim 10^{-4}$  M complex in benzene containing 0.01 M entering ligand; quantum yields accurate to  $\pm 10\%$ . <sup>b</sup> These complexes absorb insufficiently at these wavelengths to obtain accurate quantum yields. <sup>c</sup> Value unobtainable due to thermal decomposition of complex.

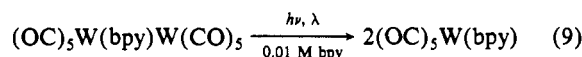
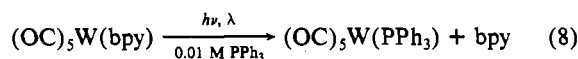
tively unchanged on moving from the mononuclear to the binuclear species.

The calculated  $k_r$  values of the homonuclear and heteronuclear  $(OC)_5M(bpy)M'(CO)_5$  series reveal a general dependence on the metal, following the order  $Cr < Mo < W$ . This is analogous to internal heavy-atom effects that are well recognized for spin-forbidden processes of numerous organic systems.<sup>26</sup> This observation, and the fact that these are relatively long emission lifetimes for organometallic complexes in fluid solution, lead us to conclude that the emitting MLCT excited states of these molecules are triplet centered. We also note that  $k_r$  increases on going from the mononuclear to the binuclear tungsten complexes, in accordance with the additional heavy-atom effect on coordination of the second  $W(CO)_5$  moiety; this effect is significant for  $L = pyzo$  and  $bpy$ , but not for  $L = bpe$ .

Excitation spectra recorded from  $(OC)_5W(pyzo)W(CO)_5$  and  $(OC)_5W(bpy)W(CO)_5$  in deoxygenated benzene at 283 K are shown in Figure 5. Excitation maxima observed from all of the emissive mononuclear and ligand-bridged binuclear complexes are listed in Table V. Three features are observed in all of the excitation spectra. The lowest energy bands in the 420–510-nm region are associated with the MLCT emitting state(s) and their energies follow the order  $bpy > bpe > pyzo$ , in agreement with the above discussion. The band maxima at 395–405 nm are attributed to the LF ( $^1A_1 \rightarrow ^1E$ ) states that effectively populate the emitting states. The band maxima in the 350–370-nm region indicate the participation of a higher lying excited state in the radiative deactivation process; this state can be observed as a weak feature in the absorption spectra (see Figure 1) and is thought to be another LF state.

**Photochemical Behavior.** Figure 6 illustrates spectral sequences that have been observed on photolysis of  $(OC)_5W(bpy)$  and

$(OC)_5W(bpy)W(CO)_5$  in deoxygenated benzene solution containing an excess amount of entering ligand. The following reactions occur on photoexcitation:



$$\lambda = 405, 436, 458, 514 \text{ nm}$$

These reactions proceed to products without interference from secondary processes, as evidenced by the clear spectral progressions with retention of isosbestic points. Photochemical quantum yields determined from all of the complexes studied are shown in Table VI. The photoreactivities of these complexes are concordant with those observed from other types of mononuclear group 6 pentacarbonyl complexes<sup>24</sup> and those previously reported for  $(OC)_5W(pyzo)W(CO)_5$ ,<sup>7b</sup> and they are indicative of labilization of the weak-field N-donor ligand following  $^1A_1(e^4b_2^2) \rightarrow ^1E(e^3b_2^2a_1^1)$  excitation. The observed effects of ligand and excitation wavelength are consistent with the proposed photophysical model of a reactive LF state lying closely above an unreactive MLCT state. Thus, the  $bpa$ -bridged complex undergoes efficient photochemistry following excitation at either 405 nm or 436 nm whereas the quantum efficiencies determined from the other dimers are excitation wavelength dependent. Moreover, the mononuclear complexes ( $L = bpy, bpe, pyzo$ ), which have MLCT states lying close in energy to the reactive LF states, undergo photodissociation more efficiently than their corresponding binuclear species.

**Acknowledgment.** We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research. M.M.Z. gratefully acknowledges receipt of a South African CSIR/Mintek Fellowship. We also thank Prof. B. McDuffie for several helpful discussions and access to the electrochemical equipment.

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