Photochemistry of Metal–Metal Bonded Complexes. 5. Cleavage of the M–M Bond in $(OC)_5M–M(CO)_3L$ by Irradiation into a Low-Lying M → L Charge-Transfer Band

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Abstract: The photochemistry and some electronic spectral data are reported for the complexes $Mn_2(CO)_8$(phen) (phen = 1,10-phenanthroline), $Re_2(CO)_8$(phen), and $Re_2(CO)_8$(biquin) (biquin = 2,2′-biquinoline). All three complexes exhibit very intense, solvent sensitive, visible absorption maxima. For example, $Mn_2(CO)_8$(phen) has a maximum at 18.87 kK in acetone which shifts to 16.72 kK in isooctane with a molar absorptivity of about 12 000 l. mol^{-1} cm^{-1}. The lowest energy absorption is associated with a M–M$\sigma_b \rightarrow \pi^*$L transition. Emission from either the pure solid or 77 K EPA solutions of $Re_2(CO)_8$(phen) is found and is associated with radiative decay from the lowest CT state. Consistent with the *depopulation* of a σ_b orbital with respect to the M–M bond we find that the homolytic M–M bond cleavage obtains upon electronic excitation of the complexes in solution at 298 K. The quantum efficiency for disappearance of the M–M bonded species is independent of the excitation wavelength in the range 313 to 633 nm. The quantum yields for disappearance in degassed CH_2Cl_2/CCl_4 (½ by volume) are 0.96 ± 0.10, 0.17 ± 0.02, and 0.02_8 ± 0.004 for $Mn_2(CO)_8$(phen), $Re_2(CO)_8$(phen) and $Re_2(CO)_8$(biquin), respectively. Under these conditions the only metal-containing photoproducts are $M(CO)_5Cl$ and $ClM(CO)_3L$ Flash photolysis of $M_2(CO)_8$(phen) in degassed benzene solution gives $M_2(CO)_{10}$ in good yield.

Mechanistic aspects of the photochemical reactions of dinuclear metal carbonyls containing a metal–metal single bond have been investigated recently.[1-3] In the species investigated thus far the lowest excited states of the M–M bonded species result from one-electron transitions which terminate in an orbital which is σ-antibonding with respect to the M–M bond.[1,4] Consistent with such an excited state, all photoreactions seem to arise from a primary photoprocess involving homolytic cleavage of the M–M bond to generate two ground-state 17-electron metal radicals.[1] Interestingly, it appears that the homolytic cleavage of the M–M bond can occur rather efficiently regardless of whether the orbital origin of the lowest transition is the π-d (essentially nonbonding with respect to the M–M bond) or the orbital which is σ-bonding with respect to the M–M bond. However, one would expect that a $\sigma_b \rightarrow \sigma^*$ transition would result in a greater degree of M–M labilization compared with a π-d $\rightarrow \sigma^*$ transition, and we have observed[1a] some modest decline in the quantum efficiency for homolytic M–M cleavage upon irradiation into the π-d $\rightarrow \sigma^*$ absorption compared with irradiation corresponding to the $\sigma_b \rightarrow \sigma^*$ type excitation.

We have been curious as to whether *population* of the σ^* orbital is *required*. Toward an answer to this question we have sought to investigate a series of complexes where the lowest energy transition does not involve population of the σ^* level. We now report the results of an investigation of $M_2(CO)_8$(phen) (M = Mn, Re) and $Re_2(CO)_8$(biquin) which appear to have lowest energy charge-transfer (CT) electronic transitions which terminate in π^* orbitals of the aromatic ligand. Some qualitative aspects of the photochemistry of such complexes have been reported. For example, irradiation of $Mn_2(CO)_8$(phen) in chlorinated solvents yields[5] $Mn(CO)_5Cl$ and $ClMn(CO)_3$(phen), and irradiation of $(OC)_5MnRe(CO)_3$(phen) in inert media yields[6] $Mn_2(CO)_{10}$ and $Re_2(CO)_6(phen)_2$. These results suggest that photoinduced M–M homolytic cleavage obtains. We now present quantum yield data and electronic absorption and emission spectral studies of the complexes which suggest that the CT state is the photoactive state.

Results and Discussion

A. Electronic Spectral Studies. In contrast to the colorless $Re_2(CO)_{10}$ and yellow color of $Mn_2(CO)_{10}$, the 1,10-phenanthroline or 2,2′-biquinoline derivatives are highly colored compounds exhibiting a fairly intense, solvent and temperature-sensitive, visible absorption band. The absorption spectra below 30 000 cm^{-1} in EPA at 298 and 77 K are shown in Figures 1, 2, and 3 for $Mn_2(CO)_8$(phen), $Re_2(CO)_8$(phen), and $Re_2(CO)_8$(biquin), respectively. Some absorption spectral data are summarized in Table I in the solvent CH_2Cl_2/CCl_4 (½ by volume), and the solvent dependence of the position of the lowest absorption band is given in Table II. Molar absorptivities are reported for the CH_2Cl_2/CCl_4 solutions since this is the solvent system used for the quantum yield measurements (vide infra).

Aside from the intense visible absorption, each of the complexes exhibits a very intense ($\epsilon > 25\,000$ l. mol^{-1} cm^{-1}) transition in the uv which is very near the position of the absorption found in uncomplexed 1,10-phenanthroline or 2,2′-biquinoline. We therefore ascribe the band found at about 27 000 cm^{-1} in $Re_2(CO)_8$(biquin) as an intraligand 2,2′-biquinoline transition. Likewise, absorption found near 37 000 cm^{-1} in $M_2(CO)_8$(phen) is ascribed to an intraligand 1,10-phenanthroline transition. Intraligand absorptions of this type were also found[7] in $ClRe(CO)_3$(phen) and $ClRe(CO)_3$(biquin).

The $Re_2(CO)_8$(biquin) exhibits a rather prominent absorption shoulder near 23 000 cm^{-1}, and the $M_2(CO)_8$(phen) exhibit shoulders near 24 000-26 000 cm^{-1}. These shoulders are close in position to the *lowest* absorption band in $ClRe(CO)_3$(phen) and $ClRe(CO)_3$(biquin) which was assigned as the Re $\rightarrow \pi^*$L CT absorption. Moreover, the shoulders in the M–M bonded complexes blue-shift upon cooling or upon increasing the polarity or polarizability of the solvent. These effects and the position suggest that the shoulders in the M–M bonded species can be ascribed to the π-dM $\rightarrow \pi^*$ L CT absorption analogous to the lowest energy absorption in $XRe(CO)_3L$.[7] In the present case X = $Re(CO)_5$ rather than Cl.

Obviously though, X = $Re(CO)_5$ has some important consequences which are manifested by the very low-energy visible absorption band. The very substantial change in the position of the lowest energy band in the M–M bonded species compared with $ClRe(CO)_3L$ can be best accommodated by invoking an inherently different spectral assignment. Assignment of the lowest energy transition as a $\sigma_b \rightarrow \sigma^*$ or as a π-d $\rightarrow \sigma^*$

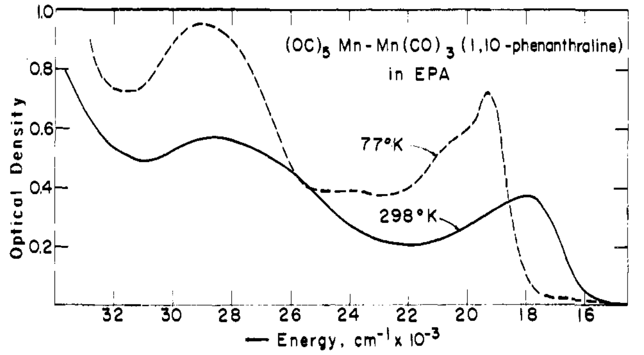

Figure 1. Electronic absorption spectra of $Mn_2(CO)_8(phen)$ in EPA at 298 K (—) and 77 K (- - -). The spectral changes upon cooling have not been corrected for solvent contraction. The spectra are recorded using a 1.0-cm path length cell, and the concentration of the complex is 3.2×10^{-5} M.

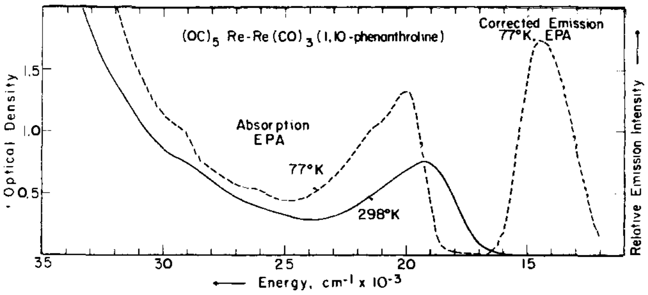

Figure 2. Electronic absorption and emission of $Re_2(CO)_8(phen)$ in EPA at 29S K (—) and K (- - -). Absorption spectral changes upon cooling have not been corrected for solvent contraction. The absorption spectra were recorded using a 1.0-cm path length cell, and the concentration of the complex is 1.1×10^{-4} M. The emission was excited using 514.5-nm light from an argon ion laser.

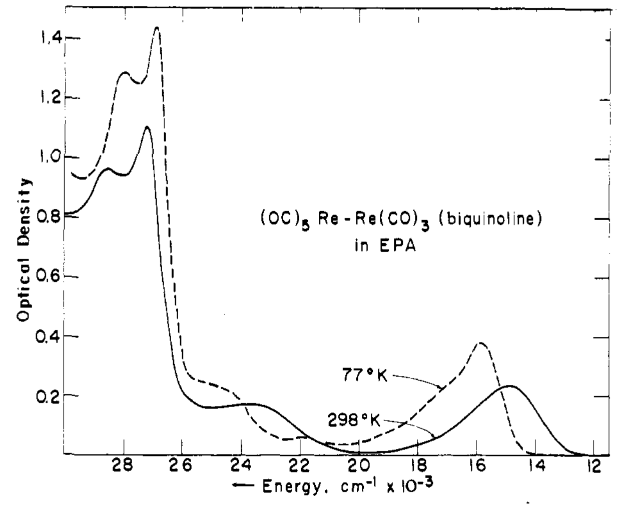

Figure 3. Electronic absorption spectra of $Re_2(CO)_8(biquin)$ in EPA at 298 K (—) and 77 K (- - -). The spectral changes upon cooling have not been corrected for solvent contraction. The spectra are recorded using a 1.0-cm path length cell, and the concentration of the complex is 3.2×10^{-5} M.

is unreasonable for two reasons: (1) the position of the lowest energy band is very sensitive to solvent and temperature unlike the bands in $M_2(CO)_n(PPh_3)_{10-n}$ (n = 10, 9, 8);[1,4] and (2) the absolute positions of the lowest absorption in the $M_2(CO)_8L$ complexes reported here is far too removed from the $\sigma_b \rightarrow \sigma^*$ observed in $M_2(CO)_{10}$[1,4] and numerous other derivatives[1,4,8] and other M-M bonded complexes.[9] Additionally, the position of the lowest energy band in $Re_2(CO)_8L$ depends on L, shifting about 5 000 cm^{-1} to the red from 1,10-phenanthroline to 2,2′-biquinoline. We assign the absorption at lowest energy in $M_2(CO)_8L$ as a σ_bM-M → π^*L CT transition; i.e., depopulation of σ_b obtains. A similar sort of transition should occur in the $ClRe(CO)_3L$ complexes, but it likely occurs at fairly high energy. Simple one-electron level diagrams for the complexes might be compared as shown in Scheme I to rationalize our results. The key is that the electrons in the M-M σ bond are among the easiest ionized while those in the Cl-M σ bond are ionized only at higher energy. Photoelectron spectra of $Re_2(CO)_{10}$ and $Mn_2(CO)_{10}$[10] confirm this notion, and photoelectron spectra[10] for $ClRe(CO)_5$ show that the electrons in the Cl-M σ bond are not among the easily ionized electrons and, indeed, are more than 2.0 eV more stable than the easily ionized π-d electrons. Of the three complexes investigated, only $Mn_2(CO)_8(phen)$ exhibits absorption which we can ascribe unequivocally to transitions which involve σ^* population. The rather broad absorption maximizing near 29 000 cm^{-1} likely includes substantial contribution from $\sigma_b \rightarrow \sigma^*$ and π-d $\rightarrow \sigma^*$ transitions. Since the $\sigma_b \rightarrow \sigma^*$ transition of $Mn_2(CO)_{10}$ itself is near 29 000 cm^{-1}, we were certain to purify the complex such that no $Mn_2(CO)_{10}$ was detectable by infrared. Since the d_{z^2} orbitals in $Mn(CO)_5$ species interact to form the σ_b and σ^* levels in $Mn_2(CO)_{10}$, it is likely that axial substituents will have a pronounced effect on the energy of the $\sigma_b \rightarrow \sigma^*$ transition. But in $Mn_2(CO)_8(phen)$ the substitution is equatorial as schemed in I and therefore might be expected to exhibit a $\sigma_b \rightarrow \sigma^*$ transition near that found in $Mn_2(CO)_{10}$. Thus, the 29 000-cm^{-1} band system can be confidently assigned. The important spectral region is seemingly obscured in $Re_2(CO)_8[(biquin)$ by the intraligand absorption. However, in $Re_2(CO)_8(phen)$ a well-defined $\sigma_b \rightarrow \sigma^*$ absorption is not seen. It is possible that the shoulder near 30 000 cm^{-1} is the $\sigma_b \rightarrow \sigma^*$ excitation, but this of course is not certain. Even in some phosphine substituted derivatives of $Re_2(CO)_{10}$, though, we[11]

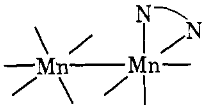

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Table I. Absorption Spectral Data for $M_2(CO)_8L$ Complexes[a]

Complex	Band maxima, kK (ϵ)
$Mn_2(CO)_8(phen)$	17.42 (11 800); 26.31 (12 300) sh; 28.32 (13 500)
$Re_2(CO)_8(phen)$	18.94 (7300); 28.57 (5200) sh
$Re_2(CO)_8(biquin)$	14.53 (7100); 22.94 (5160); 27.17 (35 000)

[a] All data for 298 K solutions in CH_2Cl_2/CCl_4 ½ by volume.

Table II. Solvent Effect on Lowest Energy Absorption Position in $M_2(CO)_8L$ at 298 K

Complex	Solvent	Lowest energy absorption max, kK
$Mn_2(CO)_8(phen)$	Isooctane	16.72
	Benzene	17.78
	CH_2CL_2	18.08
	Acetone	18.87
$Re_2(CO)_8(phen)$	Isooctane	17.48
	Benzene	18.48
	CH_2Cl_2	18.94
	Acetone	19.92
$Re_2(CO)_8(biquin)$	Isooctane	14.08
	Benzene	14.60
	CH_2Cl_2	14.92
	Acetone	15.75

Scheme I

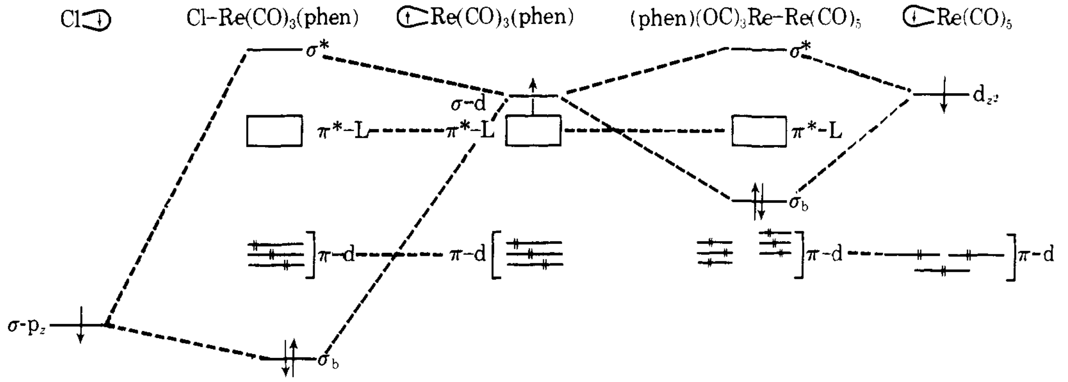

Table III. Quantum Yields for Reaction of $M_2(CO)_8(L)$ Complexes[a]

Complex	$\Phi_{313\text{ nm}}$[b]	$\Phi_{366\text{ nm}}$	$\Phi_{436\text{ nm}}$	$\Phi_{550\text{ nm}}$	$\Phi_{633\text{ nm}}$
$Mn_2(CO)_8$-(phen)		0.85	1.10	0.93	
$Re_2(CO)_8$-(phen)	0.15	0.22	0.19	0.13	
$Re_2(CO)_8$-(biquin)		0.032	0.02	0.04	0.02

[a] Reactions carried out at 25 °C in CH_2Cl_2/CCl_4 ½ by volume. The photoproducts in every case are stoichiometric yields of $M(CO)_5Cl$ and $ClM(CO)_3L$. [b] All Φ's are ±20%.

have encountered some difficulties in understanding the blue-shift of the $\sigma_b \rightarrow \sigma^*$ transition compared with $Re_2(CO)_{10}$ itself.

The principal result from the electronic absorption spectral studies of the $M_2(CO)_8L$ complexes is that the lowest absorption is a CT transition not involving population of the σ^* orbital. One very important electronic spectral result has yet to be mentioned: the $Re_2(CO)_8$(phen) complex undergoes radiative decay from the lowest excited state. The corrected emission spectrum of $Re_2(CO)_8$(phen) in EPA at 77 K is included in Figure 2. The lifetime is 95×10^{-6} s, and the quantum yield is about 10^{-2} under the same conditions. The emission spectrum and the emission energy at 77 K in EPA are independent of the excitation wavelength. No photochemical reaction of the $Re_2(CO)_8$(phen) complex could be detected at 77 K in EPA. No emission could be detected at room temperature in fluid solutions, but upon 632.8 nm excitation from a He-Ne laser emission is detectable from the pure solid. Detailed studies were not done on the pure solid emission. The lifetime and emission quantum yield at 77 K in EPA reveal a fairly long radiative lifetime, but consistent with other comparisons of first and third row metal carbonyls,[7,12] the $Mn_2(CO)_8$(phen) does not emit under conditions comparable with those for the Re analogue. Thus, the emitting state may not be observable in the absorption spectrum, since the Mn absorption spectrum in the low-energy region is similar to the Re. The long radiative lifetime is still surprising for a Re complex, but is at least explicable by comparison with the Mn analogue. Emission from the $Re_2(CO)_8$(biquin) is expected at an energy below our detection capability. No other M-M bonded carbonyl has been found to luminesce, and we regard the emission from $Re_2(CO)_8$(phen) as very crucial since it convincingly establishes the relaxed excited state as the CT state. We are now in a position to assess the photochemical reactivity of the complexes.

B. Photochemistry of $M_2(CO)_8L$. We have investigated the photochemistry of the $M_2(CO)_8L$ complexes in degassed CH_2Cl/CCl_4 (½ by volume) at 298 K. The chemistry invariably proceeds according to

$$(OC)_5M\text{-}M(CO)_3L \xrightarrow[CH_2Cl_2/CCl_4]{h\nu} Cl\text{-}M(CO)_5 + Cl\text{-}M(CO)_3L \qquad (1)$$

M = Mn, L = 1,10-phenanthroline
Re, L = 1,10-phenanthroline or 2,2′-biquinoline

The quantitative formation (within 10%) of the $ClM(CO)_5$ and $ClM(CO)_3L$ was determined by quantitative infrared spectroscopic determinations by comparison with authentic samples. The quantum yields for the disappearance of the $M_2(CO)_8L$ complexes are given in Table III for several irradiating wavelengths. We have only been able to obtain accurate quantum yields for rigorously degassed solutions. Solutions irradiated in air often gave quantum yields in excess of 1.0, and instead of obtaining $ClM(CO)_5$ a substantial fraction of $[M(CO)_4Cl]_2$ was obtained. These observations have not been followed up in detail but can be accommodated by reactions with O_2 and/or N_2 which result in new metal carbonyl radicals which can react with ground-state $M_2(CO)_8L$ to propagate radical chain decompositions. Substitution lability of metal radicals of this sort has already been reported.[1a,3]

Table IV. Photoinduced Cross-Coupling Reactions of $M_2(CO)_8$(phen)[a]

Starting complex (moles)	Photolysis[b] conditions	Moles reacted	Moles M_2-$(CO)_{10}$ formed
$Mn_2(CO)_8$(phen) (8.37×10^{-6})	Six flashes at 400 J	7.66×10^{-6}	1.50×10^{-6}
$Re_2(CO)_8$(phen) (1.17×10^{-5})	Five flashes at 250 J	7.21×10^{-6}	0.52×10^{-6}
$Re_2(CO)_8$(phen) (1.11×10^{-5})	Seven flashes[c] at 300 J	1.11×10^{-5}	0.68×10^{-6}

[a] 3.0-ml degassed benzene solutions of $M_2(CO)_8$(phen) in Pyrex ampules. [b] Flash photolyzed using the full output of the emission from a Xenon Corp. flash photolysis apparatus except where noted. [c] The flash was filtered to pass only visible light (wavelength longer than 420 nm).

Photolyses of $M_2(CO)_8$(phen) (M = Mn, Re) have also been carried out in degassed benzene solutions. We have measured the yield of the expected $M_2(CO)_{10}$ photoproducts and find the yields to be respectable, but not quantitative (Table IV). The $M_2(CO)_6L_2$ complexes are also formed, but were not determined quantitatively. The metal radicals likely generated by a flash photolysis competitively react with impurities or undergo unimolecular decomposition. Some attempts were made to induce the cross-coupling of metal radicals by flash photolyzing the $Re_2(CO)_8$(biquin), but we could detect no

$Re_2(CO)_{10}$. We ascribe this difficulty to the low quantum efficiency for Re–Re cleavage in $Re_2(CO)_8$(biquin) prohibiting the generation of a sufficiently high concentration of $Re(CO)_5$ radicals to couple at a rate comparable with the other reaction pathways.

The photochemistry obtained here parallels the more qualitative studies[5,6] reported earlier. Importantly, the photochemistry occurs with good quantum efficiency at the lowest excitation energies. The variations in quantum efficiency for the various wavelengths are rather small and are not highly reproducible. However, the data allow us to firmly conclude that the lowest excited state is reactive and leads to homolytic M–M bond cleavage. Assignment of the lowest transition as σ_bM–M $\rightarrow$ π^*L CT is, then, quite compatible with all results. We conclude that the *depopulation* of the σ_b orbital is sufficient to labilize the M–M bond. Within our simple electronic formulations the σ_bM–M $\rightarrow$ π^*L and the π-d $\rightarrow$ σ^* transitions should labilize the M–M bond to about the same extent, as each reduces the M–M bond order by one-half. The essential wavelength independence of the quantum yields is consistent with all photochemistry originating from the lowest excited state.

Our results and conclusions raise at least one interesting question: is the $M(CO)_3L$ photofragment formed in an electronic excited state? The answer depends on whether the 17-electron $M(CO)_3L$ is a metal-centered radical or is a d^6 complex with L coordinated as a radical anion. We are currently investigating this question and the reactivity of other M–M bonded complexes containing a low-energy CT absorption.

Experimental Section

Materials. Synthesis of $Mn_2(CO)_8$(phen) was by photolysis of a mixture of Mn_2CO_{10} and 1,10-phenanthroline. The resulting mixture of $Mn_2(CO)_{10}$, $Mn_2(CO)_6(\text{phen})_2$, and $Mn_2(CO)_8$(phen) was separated by chromatography on alumina. The $Mn_2(CO)_8$(phen) was purified by recrystallization from CH_2Cl_2 by addition of *n*-pentane. The purple solid was identified by comparison of the ir spectrum with the reported spectrum.[5]

Synthesis of $Re_2(CO)_8L$ was by airless addition (in the dark) of a tetrahydrofuran solution of $NaRe(CO)_5$[13] to a deoxygenated $ClRe(CO)_3L$ solution. The displacement[13] of Cl^- by $Re(CO)_5^-$ occurs rapidly at 298 K to yield a highly colored solution containing the desired complex and NaCl precipitate. The colored solution was decanted and reduced in volume by rotary evaporation. The $Re_2(CO)_8$(phen) was purified by column chromatography on alumina, recrystallization from CH_2Cl_2 by addition of *n*-pentane, and sublimation. $Re_2(CO)_8$(phen) is a red-purple solid which gives a satisfactory elementary analysis. Anal. Calcd: C, 30.9; H, 1.03; N, 3.60. Found. C, 30.70; H, 1.03; N, 3.74. The mp is 252–254 °C (cor), and the complex has ir bands in the CO stretching region at 2073 (m), 2012 (s), 1992 (m), 1959 (m), 1915 (m), and 1889 (m) cm^{-1} in CH_2Cl_2 in good agreement with the reported values for $Mn_2(CO)_8$(phen).[5] $Re_2(CO)_8$(biquin) is a blue-green solid with ir bands in the CO stretching region at 2076 (m), 2020 (s), 1986 (m), 1958 (m), 1915 (m), 1889 (m).

Spectra. All uv-visible-near-ir spectra were obtained using a Cary 17 uv-visible-near-ir spectrophotometer. Ir spectra were recorded using a Perkin-Elmer 521 or 237 grating infrared spectrometer. Low-temperature uv-visible-near-ir spectra were obtained using a quartz liquid nitrogen dewar with optical quality quartz flats as windows. Emission measurements were made using the Cary 17 by placing the sample where the lamp is usually positioned and exciting with a Spectra-Physics argon ion laser or by using an Aminco-Bowman spectrofluorometer utilizing a dry-ice cooled RCA 7102 photomultiplier tube. The emission spectrum was corrected using the equipment and procedure reported previously.[14]

Lifetime Measurement. Emission lifetimes were measured using a TRW Model 75A decay time fluorometer equipped with a Xenon Corp. Model 437 nanopulser exciting source. The photomultiplier was a Hamamatsu 446 UR at 750 V powered by a Kepco Model ABC high-voltage power supply. Output of the PMT was monitored with a Tektronix oscilloscope and recorded with a Polaroid camera. Plots of log (luminescence intensity) against time were linear over at least 3 lifetimes.

Photolysis Procedures. Solutions of the complex in CH_2Cl_2/CCl_4 ($\frac{1}{2}$ v/v) in 3-ml aliquots were placed in 13 × 100 mm Pyrex test tubes with constrictions. Samples were degassed in a least three freeze-pump-thaw cycles and were then hermetically sealed. Photolyses was performed with the use of merry-go-round[15] apparatus equipped with 450- or 550-W Hanovia medium-pressure Hg source, filtered with Corning glass filters and filter solutions to isolate the 313-, 366-, 436-, and 550-nm Hg emissions. A Spectra-Physics Model He-Ne laser equipped with a 6X beam expander was used in 632.8-nm irradiations. Ferrioxalate[16] or Reinecke's salt[17] actinometry was used to measure light intensity. Analysis for $M_2(CO)_8L$ disappearance was by uv-visible-near-ir spectral measurements.

Flash Photolysis Procedure. Flash photolysis of weighed samples of complex in degassed ampules in benzene solution was accomplished using a Xenon Corp. Model F-710 flash photolysis apparatus. Analysis was by column chromatographic separation of products on alumina, followed by electronic spectrophotometric determinations.

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