

Emission and Photochemistry of $M(\text{CO})_4(\text{diimine})$ ($M = \text{Cr}, \text{Mo}, \text{W}$) Complexes in Room-Temperature Solution

David M. Manuta and Alistair J. Lees*

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Electronic absorption, emission, and photochemical data are reported for a series of $M(\text{CO})_4\text{L}$ complexes, where $M = \text{Cr}, \text{Mo}$, or W and $\text{L} = 2,2'$ -bipyridine, 1,10-phenanthroline, or a derivative diimine ligand. Low-energy ligand field (LF) and intense metal-to-ligand charge-transfer (MLCT) transitions are observed in the electronic absorption spectra. The energy positions of the MLCT transitions are extremely sensitive to the nature of ligand substituent and solvent medium. Each complex exhibits dual emission features at 298 K in the 500–850-nm region and two low-lying $M \rightarrow \pi^*(\text{L})$ transitions are implicated in the radiative decay process. Quantum efficiencies for photosubstitution (ϕ) have been determined following excitation into the low-lying excited states. The photoreaction efficiencies depend substantially on the irradiation wavelength; e.g., for $\text{W}(\text{CO})_4(\text{bpy})$ in benzene LF excitation at $\lambda = 395$ nm yields $\phi = 1.2 \times 10^{-2}$, whereas MLCT excitation at $\lambda = 514$ nm yields $\phi = 5.4 \times 10^{-5}$. Photosubstitution data indicate that a LF state is largely responsible for the photochemistry in these $M(\text{CO})_4\text{L}$ complexes. The photoefficiencies following MLCT excitation at 514 nm are only slightly temperature-dependent, indicating that either the MLCT state is intrinsically photoactive or another excited state lies close in energy and contributes to the photochemistry. The suggestion of photoreaction from the low-lying LF triplet state ($^1\text{A} \rightarrow ^3\text{E}$) is discussed. An excited-state scheme relating the photochemical and emission data is presented.

Introduction

There has been a great deal of interest in the photophysical and photochemical processes of transition-metal complexes that exhibit low-lying metal-to-ligand charge-transfer (MLCT) states. Complexes of the general formulas $\text{Ru}(\text{NH}_3)_5\text{L}^{2+}$,¹ $\text{Fe}(\text{CN})_5\text{L}^{3-}$,² $\text{W}(\text{CO})_5\text{L}$,³ and $(\eta^5\text{-C}_5\text{H}_5)\text{M}(\text{CO})_2\text{L}$ ($M = \text{Mn}, \text{Re}$),⁴ where L is CO or a nitrogen, phosphorus, or oxygen donor ligand, have been the subject of extensive investigations. These studies have illustrated that metal complexes which possess a lowest lying MLCT state are relatively unreactive following excitation directly into this state.

A number of metal complexes with low-energy MLCT transitions have been reported to undergo emission at low temperature in a rigid environment, such as a glass or a matrix.^{4–6} In fact, most investigations of the luminescence behavior of transition-metal complexes have been under low-temperature conditions, where nonradiative deactivation processes are effectively reduced.⁷ Consequently, there are relatively few examples of emission from room-temperature solutions of transition-metal complexes. In particular, metal carbonyl complexes were not thought to undergo radiative decay in fluid solution due to their relatively efficient ligand photosubstitution and nonradiative deactivation pathways.

Several $\text{ClRe}(\text{CO})_3\text{L}$ complexes, where L is 2,2'-bipyridine, 1,10-phenanthroline, or a derivative, have been observed to luminesce in room-temperature solution, and the emission has been assigned to originate from a low-energy MLCT state of considerable triplet character.⁸ The emission was noted to be extremely

sensitive to the nature of the environment; these complexes yielded red-orange emission in solution at 298 K and yellow-green emission in glasses at 77 K. Multiple emission characteristics have been reported from the closely related $\text{XRe}(\text{CO})_3\text{L}_2$ complexes, where X is Cl, Br , or I and L is 4,4'-bipyridine, 4-phenylpyridine, or 3-benzoylpyridine.⁹ At 298 K the emission was attributed to a MLCT state, but at 77 K the emitting state was shown to have substantial intraligand ($\pi\text{-}\pi^*$) triplet character.

More recently room-temperature emission has been observed from several group 6 metal carbonyls of the general formulas $\text{M}(\text{CO})_5\text{L}$ and *cis*- $\text{M}(\text{CO})_4\text{L}_2$, where M is Cr, Mo , or W and L is a pyridine or a substituted pyridine.^{3d,10} For each complex the emission was assigned to originate from a low-energy MLCT excited state that overlaps substantially with higher energy ligand field (LF) states. In this respect the $M(\text{CO})_4\text{L}$ complexes, where M is Cr, Mo , or W and L is 2,2'-bipyridine (bpy) or 1,10-phenanthroline (phen), are significant. Their low-lying MLCT states are so well separated from the higher energy LF states that they offer an opportunity to study the photophysical and photochemical properties of the MLCT excited states exclusively. In a previous communication to this journal, these complexes were reported to exhibit unusual dual emission features in solution at 298 K.¹¹ This paper describes the results of our study of the interrelation between photochemistry and emission for a series of $M(\text{CO})_4\text{L}$ complexes under room-temperature conditions, where M is Cr, Mo , or W and L is bpy, phen, or a derivative ligand.

Experimental Section

Materials. The metal hexacarbonyls were obtained from Strem Chemical Co. and used without further purification. The ligands 2,2'-bipyridine (bpy), 4,4'-dimethyl-2,2'-bipyridine (4,4'-Me₂-bpy), 1,10-phenanthroline (phen), 4-methyl-1,10-phenanthroline (4-Me-phen), 5-methyl-1,10-phenanthroline (5-Me-phen), 5-phenyl-1,10-phenanthroline (5-Ph-phen), 5-chloro-1,10-phenanthroline (5-Cl-phen), and 5-nitro-1,10-phenanthroline (5-NO₂-phen) were available at >99% purity (Aldrich or Alfa Chemical Co.) and were used without further purification. Benzene and isooctane were spectroscopic grade (J. T. Baker Chemical Co.); the other solvents used were reagent grade. The solvents used in the emission and photochemical experiments were distilled several times to ensure removal of emitting or quenching impurities. Carbonyl-containing impurities in these solvents were removed according to literature procedures.¹² Nitrogen used for purging was dried and deoxygenated according to a previously described method.¹³ Alumina

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(80–200 mesh) used in the chromatographic purifications was purchased from Fisher Scientific Co.

Synthesis of $M(\text{CO})_4\text{L}$. The $M(\text{CO})_4\text{L}$ complexes were prepared by irradiation of $M(\text{CO})_6$ in N_2 -purged isooctane containing excess L according to published procedures.¹⁴ Typical yields of 80% were obtained. The $M(\text{CO})_4\text{L}$ complexes were sparingly soluble in isooctane and precipitated during photolysis. Purification was achieved by repeated washings with isooctane to remove reactants, followed by column chromatography on alumina if necessary. Some of the complexes were further purified by recrystallization from benzene/isooctane solution. The product complexes were generally stable in the solid form; storing under nitrogen increases their long-term stabilities. In solution at 298 K the complexes exhibited varying degrees of stability. The $\text{Cr}(\text{CO})_4(5\text{-Ph-phen})$ complex was particularly susceptible to oxidation and underwent some decomposition on exposure to air; in solution it decomposed significantly over a period of a few minutes.

Equipment and Procedures. Infrared spectra were recorded from the complexes as Nujol mulls between NaCl plates on a Perkin-Elmer Model 283B spectrometer. Reported band maxima are considered to be accurate to $\pm 2 \text{ cm}^{-1}$. Electronic absorption spectra were recorded on a Hewlett-Packard Model 8450A spectrophotometer which utilizes a rapid-scanning microprocessor-controlled diode-array detector. Absorption data were obtained from the thermally sensitive solutions within 5 s of complex dissolution. The absorption band maxima are considered accurate to $\pm 2 \text{ nm}$ in the visible region and $\pm 1 \text{ nm}$ in the ultraviolet region.

Emission spectra were recorded on a SLM Instruments Model 8000/8000S spectrometer, which incorporates a photomultiplier-based photon counting detector. The emission data were corrected for variation in detector response as a function of wavelength, and the band maxima in the 500–700-nm region are considered to be accurate to $\pm 8 \text{ nm}$. Maxima in the 700–800-nm region are considered accurate to $\pm 15 \text{ nm}$. Emission quantum yields were determined with the use of a known emitter, $\text{Ru}(\text{bpy})_3^{2+}$,¹⁵ and are considered accurate to $\pm 15\%$. Emission lifetimes were obtained following excitation with a 530-nm (frequency-doubled), 20-ns pulse from a Nd glass laser.¹⁶ Emission decays were recorded at a single wavelength in the 580–600- and 730–750-nm regions with an apparatus comprising a Jarrell-Ash Mark 10 monochromator (with 1-mm slits), an RCA 7265 photomultiplier, and a Tektronix Model 7844 oscilloscope. Corning glass filters placed on the monochromator entrance slit were used to block out the laser light but transmit at wavelengths longer than 580 nm. Plots of $\ln(\text{emission intensity})$ vs. time were linear for each of the complexes, and reported lifetimes are considered accurate to $\pm 10\%$.

Photolyses at 514 nm were performed with a Lexel Corp. Model 95-4 4-W argon ion laser. Typical laser power was in the 50–150-mW range, measured by means of a Lexel Corp. Model 504 power meter. Incident light intensities were further measured by Reineckate actinometry.¹⁷ Irradiation at 395 nm was carried out with an Ealing Corp. 200W mercury-xenon arc lamp, and light intensities were determined by ferrioxalate actinometry.¹⁸ A Baird-Atomic interference filter (10-nm band-pass) was used to isolate the excitation wavelength. In all the photolysis experiments the concentrations of reactants and products were monitored by UV-visible spectroscopy. Photochemical quantum yields (ϕ_{cr}) were obtained by monitoring the disappearance of $M(\text{CO})_4\text{L}$ complex in the 450–550-nm region. These values were corrected for changing degree of light absorption by application of eq 1, where $[M]$ is the

$$d[M]/dt = -\phi_{\text{cr}}I_0(1 - 10^{-D})\epsilon_A l[M]/D \quad (1)$$

concentration of tetracarbonyl complex, I_0 is the incident light intensity, ϵ_A and D are the molar extinction coefficient of the tetracarbonyl complex and the total optical density at the photolysis wavelength, respectively, l is the cell path length, and t is the time of photolysis. Plots of $\ln[(D_t - D_\infty)/(D_0 - D_\infty)]$ vs. $\int_0^t [(1 - 10^{-D})/D] dt$, where D_0 , D_t , and D_∞ are optical densities throughout photolysis at a fixed wavelength, were observed to yield straight lines of slope α . Here $\alpha = -\phi_{\text{cr}}\epsilon_A I_0 l$. Quantum yields were found to be reproducible to $\pm 15\%$.

In the emission and photochemical experiments sample solutions were doubly filtered through 0.22- μm Millipore filters and transferred to a

Table I. Infrared Spectral Data and Assignments for $M(\text{CO})_4\text{L}$ Complexes in the Carbonyl Stretching Region^a

complex	bands, cm^{-1}			
	A_1^a	B_1	A_1^b	B_2
$\text{Cr}(\text{CO})_4(\text{bpy})$	2001	1874	1850 (sh)	1816
$\text{Cr}(\text{CO})_4(4,4'\text{-Me}_2\text{-bpy})$	2002	1879	1875 (sh)	1805
$\text{Cr}(\text{CO})_4(\text{phen})$	1999	1874	1857 (sh)	1824
$\text{Cr}(\text{CO})_4(4\text{-Me-phen})$	2000	1888	1857	1818
$\text{Cr}(\text{CO})_4(5\text{-Me-phen})$	2000	1892	1867	1827
$\text{Cr}(\text{CO})_4(5\text{-Ph-phen})$	2001	1898	1863	1818
$\text{Cr}(\text{CO})_4(5\text{-Cl-phen})$	2000	1897	1869	1821
$\text{Cr}(\text{CO})_4(5\text{-NO}_2\text{-phen})$	2002	1891	1866	1831
$\text{Mo}(\text{CO})_4(\text{bpy})$	2004	1868	1845 (sh)	1818
$\text{Mo}(\text{CO})_4(4,4'\text{-Me}_2\text{-bpy})$	2009	1875	1848 (sh)	1821
$\text{Mo}(\text{CO})_4(\text{phen})$	2004	1887	1866	1837
$\text{Mo}(\text{CO})_4(4\text{-Me-phen})$	2006	1879	1868 (sh)	1839
$\text{Mo}(\text{CO})_4(5\text{-Me-phen})$	2001	1880 (sh)	1863	1822
$\text{Mo}(\text{CO})_4(5\text{-Ph-phen})$	2002	1885	1878 (sh)	1835
$\text{Mo}(\text{CO})_4(5\text{-Cl-phen})$	2005	1880	1863	1824
$\text{Mo}(\text{CO})_4(5\text{-NO}_2\text{-phen})$	2009	1886	1859	1824
$\text{W}(\text{CO})_4(\text{bpy})$	2000	1866	1847 (sh)	1813
$\text{W}(\text{CO})_4(4,4'\text{-Me}_2\text{-bpy})$	2001	1871	1860 (sh)	1800
$\text{W}(\text{CO})_4(\text{phen})$	1996	1863	1852 (sh)	1834
$\text{W}(\text{CO})_4(4\text{-Me-phen})$	2000	1874	1855	1830
$\text{W}(\text{CO})_4(5\text{-Me-phen})$	2000	1888 (sh)	1858	1820
$\text{W}(\text{CO})_4(5\text{-Ph-phen})$	2008	1875	1863 (sh)	1806
$\text{W}(\text{CO})_4(5\text{-Cl-phen})$	2000	1895	1861	1812
$\text{W}(\text{CO})_4(5\text{-NO}_2\text{-phen})$	2001	1896	1851	1829

^a In Nujol mulls at 298 K.

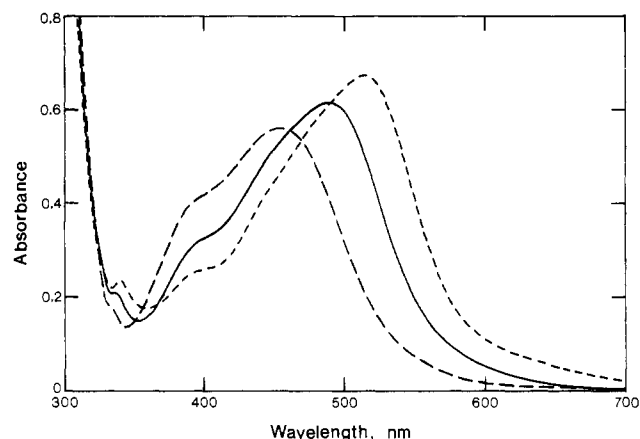


Figure 1. Electronic absorption spectra at 298 K of $\text{W}(\text{CO})_4(\text{phen})$ at equal concentration in dimethylformamide (---), tetrahydrofuran (—), and diethyl ether (-.-).

1-cm quartz glass cell. The solutions were deoxygenated by purging with purified nitrogen for 15 min. The solution temperature was controlled to $\pm 0.2 \text{ K}$ by means of a Brinkmann Instruments K-2/R circulating temperature bath.

Results and Discussion

Infrared Spectra. Infrared absorption spectra have been recorded in the carbonyl stretching region for all of the $M(\text{CO})_4\text{L}$ complexes, and the data are summarized in Table I. The four strong/moderate band maxima are characteristic of a C_{2v} arrangement of the carbonyl ligands at the metal center and are assigned to $2 A_1$, B_1 , and B_2 modes in accordance with previously reported data for closely related $M(\text{CO})_4\text{L}$ and *cis*- $M(\text{CO})_4\text{L}_2$ complexes.^{10b,19}

Electronic Absorption Spectra. Absorption data were recorded from a wide range of $M(\text{CO})_4\text{L}$ complexes, and this has enabled transition assignments to be made. Each complex exhibits an intense absorption band in the visible region that has been assigned to a MLCT transition.²⁰ The MLCT maxima are extremely

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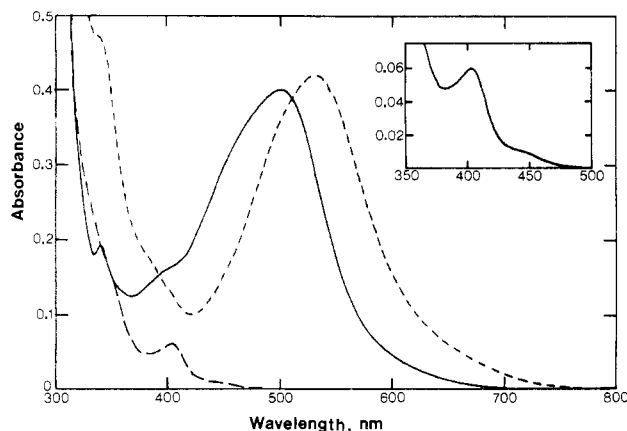


Figure 2. Electronic absorption spectra at 298 K of $W(CO)_4(4\text{-Me-phen})$ (---), $W(CO)_4(5\text{-NO}_2\text{-phen})$ (—), and $W(CO)_4(\text{en})$ (-·-) in benzene at equal concentration. Inset illustrates expanded view of low-lying absorptions of $W(CO)_4(\text{en})$.

Table II. Electronic Absorption Data and Assignments for $M(CO)_4L$ Complexes in Benzene at 298 K

complex	abs max: λ , nm (ϵ , $M^{-1} \text{ cm}^{-1}$)		
	d \rightarrow d	d \rightarrow d	MLCT
$Cr(CO)_4(\text{bpy})$	333 (6650) ^a	398 (sh)	530 (3970)
$Cr(CO)_4(4,4'\text{-Me}_2\text{-bpy})$	335 (8140) ^a	390 (sh)	518 (4230)
$Cr(CO)_4(\text{phen})$	327 (6210) ^a	420 (sh)	519 (5010)
$Cr(CO)_4(4\text{-Me-phen})$	328 (6910) ^a	420 (sh)	512 (5400)
$Cr(CO)_4(5\text{-Me-phen})$	328 (7630) ^a	426 (sh)	518 (5600)
$Cr(CO)_4(5\text{-Ph-phen})^b$	333 (sh) ^a	418 (sh)	524 (5420)
$Cr(CO)_4(5\text{-Cl-phen})$	329 (7390) ^a	420 (sh)	536 (6060)
$Cr(CO)_4(5\text{-NO}_2\text{-phen})$	327 (14 460) ^a	395 (sh)	550 (5400)
$Mo(CO)_4(\text{bpy})$	355 (4890)	390 (sh)	490 (5040)
$Mo(CO)_4(4,4'\text{-Me}_2\text{-bpy})$	355 (5620)	390 (sh)	482 (5410)
$Mo(CO)_4(\text{phen})$	338 (2560)	395 (sh)	490 (6160)
$Mo(CO)_4(4\text{-Me-phen})$	338 (3290)	395 (sh)	482 (7050)
$Mo(CO)_4(5\text{-Me-phen})$	337 (3870)	398 (sh)	490 (7470)
$Mo(CO)_4(5\text{-Ph-phen})$	345 (sh)	395 (sh)	494 (7650)
$Mo(CO)_4(5\text{-Cl-phen})$	345 (3370)	394 (sh)	502 (8070)
$Mo(CO)_4(5\text{-NO}_2\text{-phen})$	340 (8160) ^a	387 (sh)	514 (7700)
$W(CO)_4(\text{bpy})$	364 (5960)	387 (sh)	514 (6480)
$W(CO)_4(4,4'\text{-Me}_2\text{-bpy})$	363 (6310)	395 (sh)	500 (6980)
$W(CO)_4(\text{phen})$	340 (2750)	396 (sh)	510 (7940)
$W(CO)_4(4\text{-Me-phen})$	340 (3550)	391 (sh)	500 (9250)
$W(CO)_4(5\text{-Me-phen})$	346 (3260)	395 (sh)	508 (9900)
$W(CO)_4(5\text{-Ph-phen})$	345 (sh)	393 (sh)	512 (9810)
$W(CO)_4(5\text{-Cl-phen})$	347 (3290)	392 (sh)	520 (10 110)
$W(CO)_4(5\text{-NO}_2\text{-phen})$	341 (8390) ^a	388 (sh)	532 (9670)

^a Overlaps substantially with higher energy $M \rightarrow \pi^*(\text{CO})$ transition.

^b Spectrum of this complex was recorded within 5 s of dissolution.

solvent-sensitive; see Figure 1. In contrast the weaker absorptions in the 330–420-nm region show very little solvent dependence and are attributed to be of ligand field (LF) origin. For each complex the lower and higher energy LF transitions overlap substantially with the intense MLCT and $M \rightarrow \pi^*(\text{CO})$ absorptions, respectively. These two LF absorptions have, in the order of decreasing energy, been assigned to be ${}^1A_1(e^4b_2^2) \rightarrow {}^1A_2(e^3b_2^2a_1)$ and ${}^1A_1(e^4b_2^2) \rightarrow {}^1E(e^3b_2^2b_1)$ transitions.²¹ In accordance with the MLCT assignment, the lowest energy feature exhibits a substantial ligand substituent dependence; see Figure 2. Electronic absorption data for all of the $M(CO)_4(\text{diimine})$ complexes studied are listed in Table II. Similar solvent and ligand substituent effects on the energy of the MLCT transition have been reported for the iso-electronic $Ru(NH_3)_5L^{2+}$, ${}^1Fe(CN)_5L^{3-}$, ${}^3M(CO)_5L$,^{3,10a} and *cis*- $M(CO)_4L_2$ complexes,^{10b} where L is a pyridine or a substituted

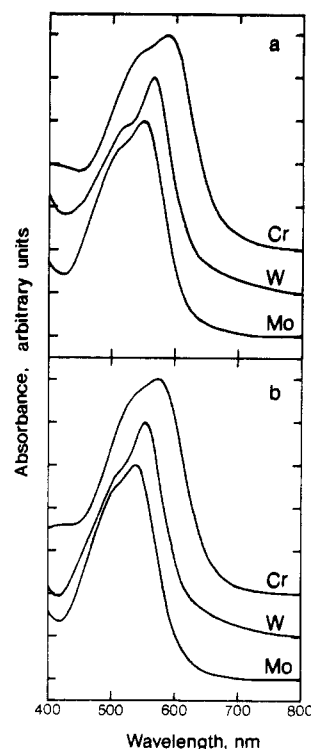


Figure 3. Lowest energy features in the electronic absorption spectra of $M(CO)_4(\text{phen})$ complexes ($M = \text{Cr, Mo, W}$) in (a) isoctane and (b) tetrachloroethylene at 298 K.

pyridine ligand. The MLCT absorption energies for any particular ligand are ordered $Mo > W > Cr$, congruent with other classes of group 6 metal carbonyls.^{10b,22,23} This ordering can be understood by using a relativistic description.²⁴

Further evidence for the LF assignment has been derived from the spectral features of $W(CO)_4(\text{en})$, where en = ethylenediamine (see Figure 2). This complex exhibits a LF state (${}^1A_1 \rightarrow {}^1E$) at approximately the same energy as the $M(CO)_4L$ series but does not possess low-lying MLCT excited states.^{20c} The corresponding weak triplet absorption (${}^1A_1 \rightarrow {}^3E$) at 450 nm can be observed in the absence of an intense MLCT transition. It is noted that there is expected to be substantial spin-orbit coupling in these heavy-metal complexes and that the singlet and triplet designations should be used with caution.

We wish to draw attention to the band structure of the low-lying MLCT absorption. For example, the MLCT absorption of $W(CO)_4(\text{phen})$ in benzene is noticeably asymmetrical (see Figure 1). In isoctane and tetrachloroethylene this absorption red-shifts by $\sim 3000 \text{ cm}^{-1}$ and clearly indicates the presence of two MLCT components (see Figure 3). Similarly resolved spectral features have been observed for the $M(CO)_4L$ series in carbon tetrachloride and triethylamine. Moreover, previously reported electronic absorption spectra of $M(CO)_4L$ complexes ($L = \text{a substituted phen}$) in EPA at 77 K exhibit significant band resolution in the MLCT region.^{20c} Recently, resonance Raman and magnetic circular dichroism measurements have shown that the MLCT band envelope comprises several electronic transitions, of which two have been assigned as y - and z -polarized transitions ($a_1 \rightarrow \pi^*(L)$ and $b_2 \rightarrow \pi^*(L)$, respectively).^{23,25} In conclusion, there is substantial

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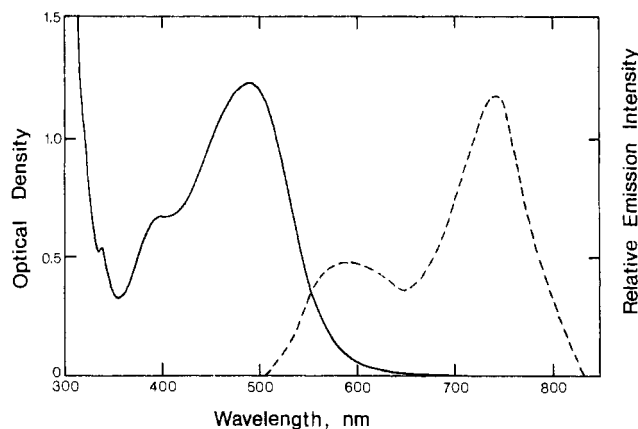
Table III. Emission Maxima for $M(\text{CO})_4\text{L}$ Complexes in Benzene at 298 K^a

complex	emission max, $\text{cm}^{-1} \times 10^3$	
	high energy	low energy
$\text{Cr}(\text{CO})_4(\text{bpy})$	16.00	12.85
$\text{Cr}(\text{CO})_4(4,4'\text{-Me}_2\text{-bpy})$	<i>b</i>	<i>b</i>
$\text{Cr}(\text{CO})_4(\text{phen})$	16.22	12.85
$\text{Cr}(\text{CO})_4(4\text{-Me-phen})$	16.30	12.74
$\text{Cr}(\text{CO})_4(5\text{-Me-phen})$	17.22	12.82
$\text{Cr}(\text{CO})_4(5\text{-Ph-phen})$	<i>c</i>	<i>c</i>
$\text{Cr}(\text{CO})_4(5\text{-Cl-phen})$	16.18	<i>b</i>
$\text{Cr}(\text{CO})_4(5\text{-NO}_2\text{-phen})$	<i>b</i>	<i>b</i>
$\text{Mo}(\text{CO})_4(\text{bpy})$	17.30	12.94
$\text{Mo}(\text{CO})_4(4,4'\text{-Me}_2\text{-bpy})$	17.90	13.19
$\text{Mo}(\text{CO})_4(\text{phen})$	17.33	12.99
$\text{Mo}(\text{CO})_4(4\text{-Me-phen})$	18.42	13.33
$\text{Mo}(\text{CO})_4(5\text{-Me-phen})$	17.85	13.11
$\text{Mo}(\text{CO})_4(5\text{-Ph-phen})$	17.87	12.99
$\text{Mo}(\text{CO})_4(5\text{-Cl-phen})$	17.55	12.99
$\text{Mo}(\text{CO})_4(5\text{-NO}_2\text{-phen})$	<i>b</i>	<i>b</i>
$\text{W}(\text{CO})_4(\text{bpy})$	17.03	12.97
$\text{W}(\text{CO})_4(4,4'\text{-Me}_2\text{-bpy})$	17.15	12.99
$\text{W}(\text{CO})_4(\text{phen})$	17.08	12.97
$\text{W}(\text{CO})_4(4\text{-Me-phen})$	16.73	12.79
$\text{W}(\text{CO})_4(5\text{-Me-phen})$	17.08	12.74
$\text{W}(\text{CO})_4(5\text{-Ph-phen})$	16.83	12.94
$\text{W}(\text{CO})_4(5\text{-Cl-phen})$	16.10	12.74
$\text{W}(\text{CO})_4(5\text{-NO}_2\text{-phen})$	<i>b</i>	<i>b</i>

^aSpectra were corrected for variations in instrumental response as a function of wavelength. The excitation wavelength is 400 nm. ^bEmission not observed. ^cComplex is thermally unstable, and emission data could not be obtained.

evidence that at least two MLCT excited states are present in the broad MLCT band envelope of $M(\text{CO})_4\text{L}$.

Emission Data. Electronic absorption and emission spectra of $\text{Mo}(\text{CO})_4(\text{phen})$ in benzene are illustrated in Figure 4. Emission spectra recorded at 298 K from all of the $M(\text{CO})_4(\text{diimine})$ complexes studied are summarized in Table III. Each of the complexes determined to be emissive at room temperature exhibited two emission features. The dual emission features are assigned to be of MLCT origin and correspond to the symmetry-allowed transitions observed in absorption. The large differences in energy between the two emission maxima suggest that the low-energy MLCT component is considerably more distorted relative to the ground state than the other MLCT state. In several cases the low-energy emission was so far red-shifted that it was only weakly observed as a broad band with a very long tail in the 750–850-nm region. This long-wavelength emission is inferred to be of MLCT character, as it apparently lies much too low in

**Figure 4.** Electronic absorption (—) and emission (---) of 2×10^{-4} M $\text{Mo}(\text{CO})_4(\text{phen})$ in benzene at 298 K. Emission spectrum is corrected for variations in instrumental response as a function of wavelength, and the excitation wavelength is 400 nm.

energy to arise from the ${}^1A_1 \rightarrow {}^1E$ or ${}^1A_1 \rightarrow {}^3E$ (LF) transition (see Figure 4). For any particular ligand the emission energies generally follow the order $\text{Mo} > \text{W} > \text{Cr}$, analogous to that recorded in absorption.

A solvent-dependence study has enabled us to assign the high-energy emission feature. Table IV lists the results obtained for $\text{Mo}(\text{CO})_4(4\text{-Me-phen})$, $\text{Mo}(\text{CO})_4(5\text{-Me-phen})$, and $\text{W}(\text{CO})_4(4\text{-Me-phen})$ at 298 K. The higher energy emission band exhibits solvent shifts parallel to that observed for the MLCT band in absorption, and it is therefore attributed to originate from a MLCT excited state. The variations in half-width data and emission quantum yields are thought to be brought about by overlapping MLCT features; the low-energy MLCT emission overlaps more substantially with the high-energy band in a polar medium. Attempts to record emission data for $M(\text{CO})_4\text{L}$ complexes in extremely nonpolar and nonpolarizable media, such as isooctane, tetrachloroethylene, or carbon tetrachloride, were unsuccessful. This may be attributed either to the sparing solubilities of the $M(\text{CO})_4(\text{diimine})$ complexes in these solvents or, in view of the large solvent dependence in absorption, to the fact that any emission would be so red-shifted (>800 nm) that it would be difficult to detect experimentally. In regard to the latter, low-energy emission was not observed from $\text{Cr}(\text{CO})_4(5\text{-Cl-phen})$.

We did not detect any room-temperature luminescence from $M(\text{CO})_4\text{L}$ complexes, where $M = \text{Cr}, \text{Mo},$ and W and $L = 5\text{-NO}_2\text{-phen}$. Furthermore, low-temperature emission data of these $M(\text{CO})_4\text{L}$ derivatives are notably absent.^{20c} Apparently the presence of a nitro substituent on phen provides an efficient vibrational relaxation route. In this respect the $5\text{-NO}_2\text{-phen}$ ligand

Table IV. Spectral Data of High-Energy Emission Component for $M(\text{CO})_4\text{L}$ Complexes in Various Solvents at 298 K^a

complex	solvent	emission		
		max, $\text{cm}^{-1} \times 10^3$	half-width, $\text{cm}^{-1} \times 10^3$	$10^5 \times$ quantum yield ^c
$\text{Mo}(\text{CO})_4(4\text{-Me-phen})$	dimethyl sulfoxide	19.45	3.30	8.9
	acetone	18.80	3.07	1.4
	ethanol	18.30	3.07	3.2
	benzene	18.10	2.75	1.3
	trichloroethylene	17.45	1.75	0.9
$\text{Mo}(\text{CO})_4(5\text{-Me-phen})$	dimethyl sulfoxide	19.00	2.90	10.7
	acetone	18.85	2.77	1.2
	ethanol	18.35	3.40	4.4
	benzene	17.55	2.05	0.4
	trichloroethylene	17.17	1.88	0.7
$\text{W}(\text{CO})_4(4\text{-Me-phen})$	dimethyl sulfoxide	18.70	2.95	5.5
	acetone	18.10	3.10	2.3
	ethanol	17.95	2.90	3.4
	benzene	17.00	1.80	7.4
	trichloroethylene	16.75	1.95	3.2

^aSpectra were corrected for variations in instrumental response as a function of wavelength. The excitation wavelength is 400 nm. ^bWidth of emission band at half-height. ^cMeasured relative to the emission of $\text{Ru}(\text{bpy})_3^{2+}$; accurate to within 15%.

Table V. Emission Lifetimes for $M(\text{CO})_4\text{L}$ Complexes in Benzene at 293 K^a

complex	emission lifetime, ns	
	high-energy band ^b	low-energy band ^c
$\text{Mo}(\text{CO})_4(4\text{-Me-phen})$	344	357
$\text{Mo}(\text{CO})_4(5\text{-Me-phen})$	362	380
$\text{W}(\text{CO})_4(4\text{-Me-phen})$	348	345

^a Values accurate to within $\pm 10\%$. Excitation wavelength is 530 nm.

^b Emission observed in 730–750-nm region. ^c Emission observed in 580–600-nm region.

has been determined to be the weakest base of the 5-substituted-1,10-phenanthroline series.²⁶ Consequently, the efficient nonradiative deactivation of $M(\text{CO})_4(5\text{-NO}_2\text{-phen})$ may be a result of a M–N cleavage mechanism.

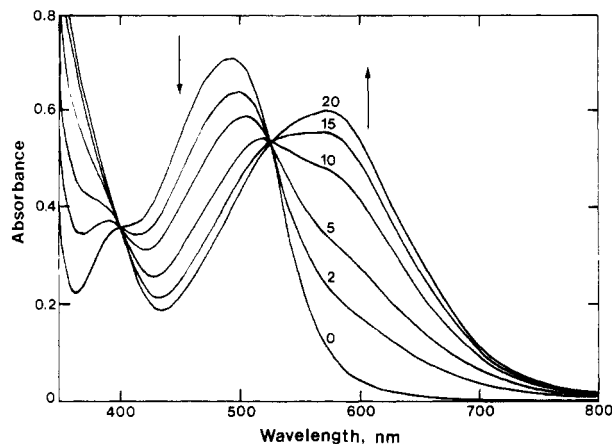
Excitation spectra were recorded from several of the $M(\text{CO})_4(\text{diimine})$ complexes at dilute concentration. An extremely weak and broad excitation band was obtained in the 450–550-nm region for each of the emission maxima. Although these features are consistent with MLCT assignments, the bands were too weak to yield further information.

Further evidence for the MLCT assignment was obtained following a comparison with the spectra of $M(\text{CO})_4(\text{en})$ complexes, where $M = \text{Cr}, \text{Mo},$ or W and $\text{en} = \text{ethylenediamine}$. The $M(\text{CO})_4(\text{en})$ complexes exhibit LF states at approximately the same energy as the other $M(\text{CO})_4(\text{diimine})$ species (see Figure 2) but do not possess low-energy MLCT transitions.^{20c} Importantly, the $M(\text{CO})_4(\text{en})$ complexes were not observed to emit in room-temperature solution following excitation directly into the lowest lying LF state ($^1A \rightarrow ^1E$) at 400 nm.

Emission has previously been observed from $M(\text{CO})_4\text{L}$ complexes in a rigid EPA glass at 77 K, where $M = \text{Mo}$ or W and $L = \text{bpy}, \text{phen},$ or a substituted phen.^{20c} The emission maxima of $M(\text{CO})_4\text{L}$ at low temperature appear in the 14 200–15 500- cm^{-1} range. These maxima are thought to correspond to the low-energy emission bands reported here, as recent observations of emission from other group 6 metal carbonyl complexes in fluid solution have been at longer wavelengths than those determined in a rigid medium.^{3d,10b} This type of energy shift upon changing temperature has also been reported for $\text{ClRe}(\text{CO})_3\text{L}$ complexes, where $L = \text{bpy}, \text{phen},$ or a related derivative ligand.⁸

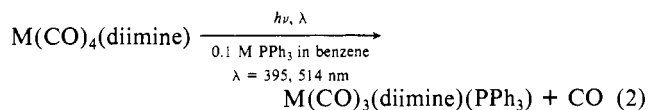
Emission lifetimes have been obtained at 293 K for both the high- and low-energy states of $\text{Mo}(\text{CO})_4(4\text{-Me-phen})$, $\text{Mo}(\text{CO})_4(5\text{-Me-phen})$, and $\text{W}(\text{CO})_4(4\text{-Me-phen})$, following laser excitation at 530 nm with a 20-ns pulse, and the results are shown in Table V. These emission lifetimes are close to those previously obtained for other group 6 metal carbonyl complexes in room-temperature solution and are consistent with emission of MLCT character.^{3d} The relatively long-lived emissions and their energy positions appear to rule out the possibility of a solvent or solvent impurity emission. Moreover, the magnitude of the emission lifetimes suggests that these MLCT states possess considerable triplet character. For each complex, the lifetime values of the emission components are the same within the error limits (see Experimental Section). These results imply that the low-lying MLCT states are in thermal equilibrium. With the facilities of a sensitive subnanosecond-lifetime apparatus and excitation at 358 nm, we have detected at 560 nm a further emission from $\text{Mo}(\text{CO})_4(4\text{-Me-phen})$, with a lifetime of 12.3 (± 0.8) ns. The short-lived emission does not appear to arise from a solvent or reagent impurity; it was observed from the complex in a number of other solvents and was not detected from solutions of the parent hexacarbonyl or free ligand. This emission may originate from a LF state, and it is being further investigated.

Dual emission bands involving MLCT and intraligand (IL) states have been previously observed by Wrighton et al. for *fac*- $\text{XRe}(\text{CO})_3\text{L}$ and *fac*- $\text{XRe}(\text{CO})_3\text{L}_2$ complexes at low tempera-

**Figure 5.** Electronic absorption spectral changes accompanying the 514-nm photolysis (time intervals in minutes) at 298 K of $\text{Mo}(\text{CO})_4(5\text{-Ph-phen})$ in benzene containing 0.1 M PPh_3 .

ture.^{8,9} Double emission features have also been reported by Sexton, Ford, and Magde for a series of haloamminerhodium(III) complexes at room temperature and attributed to fluorescence and phosphorescence from a lowest lying LF state.²⁷ Patterson et al. have detected two emissions from the *cis* and *trans* isomers of $\text{PtCl}_2(\text{py})_2$ in an ethanol glass at 78 K.²⁸ Furthermore, two emitting MLCT states have been reported from a $\text{Cu}(\text{dmp})_2^+$ complex at room temperature, where $\text{dmp} = 2,9\text{-dimethyl-1,10-phenanthroline}$.²⁹ Therefore, only a few inorganic systems are known to exhibit dual luminescence properties and the results reported here are the first of their kind for metal carbonyl complexes in fluid solution.

Photochemistry. The photosubstitution reactivities of a number of $M(\text{CO})_4(\text{diimine})$ complexes have been previously described.^{20c,23} We have studied the relationship of the photochemistry of these complexes to their absorption and emission properties via excitations directly into the low-energy LF and MLCT states. The photosubstitution reaction shown in eq 2 was



monitored for each of the $M(\text{CO})_4\text{L}$ complexes. Figure 5 illustrates a typical spectral sequence observed following the 514-nm photolysis at 298 K of $\text{Mo}(\text{CO})_4(5\text{-Ph-phen})$ in benzene. The spectra show a clean progression to the spectral features of $\text{Mo}(\text{CO})_3(5\text{-Ph-phen})(\text{PPh}_3)$. Isosbestic points at 400 and 525 nm were retained throughout $>75\%$ conversions, indicating that over this period the reaction is uncomplicated by side or subsequent reactions. This was the only reaction we observed at each of the irradiation wavelengths, and no evidence was found for photosubstitution of diimine.

Quantum yields (ϕ) for reaction 2 have been determined for each of the complexes, and the results are listed in Table VI. These photoreactivity values are low and typical of those observed from compounds that possess a lowest lying MLCT state, which is virtually unreactive. For complexes where L is a highly electron-withdrawing ligand (e.g., 5- $\text{NO}_2\text{-phen}$) the photosubstitution reaction proceeds with an extremely low quantum efficiency. It is concluded from the wavelength and ligand substituent dependence of ϕ that a LF excited state is largely responsible for the photochemistry of the $M(\text{CO})_4\text{L}$ complexes. As noted previously, the MLCT transition overlaps substantially with the $^1A \rightarrow ^1E$ LF absorption and therefore 395-nm excitation should not be regarded

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Table VI. Photosubstitution Quantum Yields (ϕ) for $M(\text{CO})_4\text{L}$ Complexes at 298 K following 395- and 514-nm Excitations^a

complex	quantum yields	
	$10^2\phi_{395\text{nm}}$	$10^4\phi_{514\text{nm}}$
$\text{Cr}(\text{CO})_4(\text{bpy})$	37	170
$\text{Cr}(\text{CO})_4(4,4'\text{-Me}_2\text{-bpy})$	15	290
$\text{Cr}(\text{CO})_4(\text{phen})$	50	220
$\text{Cr}(\text{CO})_4(4\text{-Me-phen})$	41	160
$\text{Cr}(\text{CO})_4(5\text{-Me-phen})$	24	220
$\text{Cr}(\text{CO})_4(5\text{-Ph-phen})$	<i>b</i>	<i>b</i>
$\text{Cr}(\text{CO})_4(5\text{-Cl-phen})$	25	190
$\text{Cr}(\text{CO})_4(5\text{-NO}_2\text{-phen})$	1.5	4.1
$\text{Mo}(\text{CO})_4(\text{bpy})$	2.7	3.9
$\text{Mo}(\text{CO})_4(4,4'\text{-Me}_2\text{-bpy})$	0.58	2.9
$\text{Mo}(\text{CO})_4(\text{phen})$	1.3	0.34
$\text{Mo}(\text{CO})_4(4\text{-Me-phen})$	1.8	8.3
$\text{Mo}(\text{CO})_4(5\text{-Me-phen})$	1.1	6.1
$\text{Mo}(\text{CO})_4(5\text{-Ph-phen})$	0.78	3.3
$\text{Mo}(\text{CO})_4(5\text{-Cl-phen})$	1.1	0.16
$\text{Mo}(\text{CO})_4(5\text{-NO}_2\text{-phen})$	0.75	0.025
$\text{W}(\text{CO})_4(\text{bpy})$	1.2	0.54
$\text{W}(\text{CO})_4(4,4'\text{-Me}_2\text{-bpy})$	0.18	0.072
$\text{W}(\text{CO})_4(\text{phen})$	0.19	0.10
$\text{W}(\text{CO})_4(4\text{-Me-phen})$	0.76	2.0
$\text{W}(\text{CO})_4(5\text{-Me-phen})$	0.65	0.49
$\text{W}(\text{CO})_4(5\text{-Ph-phen})$	0.52	0.83
$\text{W}(\text{CO})_4(5\text{-Cl-phen})$	0.35	0.28
$\text{W}(\text{CO})_4(5\text{-NO}_2\text{-phen})$	0.21	0.081

^a Photolysis carried out in $\sim 10^{-4}$ M solutions of $M(\text{CO})_4\text{L}$ in benzene containing 0.1 M PPh_3 . ^b Complex is thermally unstable, and photosubstitution data could not be obtained.

as populating the LF state exclusively.

In an effort to further elucidate the nature of the photochemically active state (or states), we have measured the temperature dependence of ϕ following MLCT excitation at 514 nm. For $\text{Mo}(\text{CO})_4(5\text{-Me-phen})$ the quantum yields at 283, 293, 303, and 313 K are 4.0×10^{-4} , 4.4×10^{-4} , 5.3×10^{-4} , and 6.2×10^{-4} , respectively. These data were plotted on an Arrhenius type plot ($\ln \phi$ vs. $1/T$), and the least-squares line yielded an apparent activation energy of $11.5 (\pm 4.2)$ kJ mol⁻¹. In the corresponding experiment with $\text{Cr}(\text{CO})_4(5\text{-NO}_2\text{-phen})$ (the most red-shifted of the complexes), the quantum yields at the above temperatures are 3.5×10^{-4} , 4.1×10^{-4} , 6.3×10^{-4} , and 7.9×10^{-4} , respectively, yielding an apparent energy of $21.2 (\pm 4.2)$ kJ mol⁻¹. These activation energies appear to be too small to be attributed to thermal back-population of the lowest energy LF singlet state ($^1A_1 \rightarrow ^1E$). If thermal back-population of a higher energy LF state does indeed lead to photoreaction, it would seem more feasible to implicate the corresponding LF triplet ($^1A_1 \rightarrow ^3E$) state at 450 nm (see Figure 2). As noted earlier, the MLCT absorption band envelope comprises several electronic transitions, and a broad MLCT component centered in the 470–490-nm region^{23,25} may thermally back-populate this ^3LF state. Therefore, the estimated energy differences between the ^3LF and higher energy MLCT states range from 11 to 22 kJ mol⁻¹ and are within the experimental errors of our activation values. In summary, the results indicate that either the MLCT state is very weakly photoactive or another state, possibly the low-lying LF triplet, is close in energy to a MLCT component and is responsible for the long-wavelength photochemistry.

Summary

An excited-state scheme summarizing the experimental observations is shown in Figure 6. The relative positions of the ^1LF and MLCT states identified in the absorption spectra are depicted in the diagram. The $^1A_1 \rightarrow ^3E$ state observed in the absorption spectrum of $\text{W}(\text{CO})_4(\text{en})$ is included in this scheme, although this

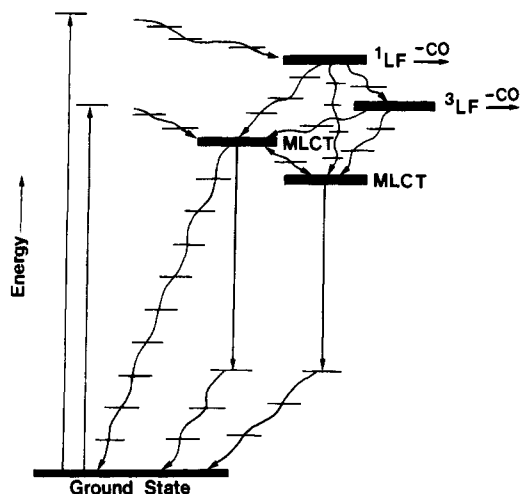


Figure 6. Excited-state scheme for $M(\text{CO})_4\text{L}$. Heavy horizontal lines represent thermally equilibrated excited states. Light horizontal lines denote successive complex-solvent cage energies as vibrationally excited states relax (only a few of these lines are shown). Vertically and wavy lines depict radiative and nonradiative processes, respectively.

transition is very weak ($\epsilon = 400 \text{ M}^{-1} \text{ cm}^{-1}$)²¹ and for the other $M(\text{CO})_4(\text{diimine})$ complexes is hidden by the intense $M \rightarrow \pi^*$ (diimine) transitions. It should also be noted that the positions of the MLCT states will be dependent on the nature of solvent medium and ligand substituent.

Dual emissions were observed from the $M(\text{CO})_4\text{L}$ complexes following ^1LF excitation. From the energy positions, solvent sensitivity characteristics, and emission lifetimes, these features were assigned to originate from two low-energy MLCT states; the vertical lines from these states denote those processes. The low-lying ^1LF state thus populates the emitting MLCT states; the wavy line between these states denotes this process. The MLCT states are close in energy and in thermal equilibrium.

The photoreactivity results are expressed in the excited-state scheme (Figure 6). Excitation at 395 nm results in appreciable population of the ^1LF state and relatively efficient photosubstitution. This LF state is thus assigned as a reactive excited state, and this is illustrated by the loss of a CO ligand. However, intersystem crossing from the ^1LF state to the ^3LF state (at ~ 450 nm) may be efficient and may contribute to the photoreactivity. The results indicate that the low-energy MLCT excited states are not very (if at all) reactive with respect to ligand loss.

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Registry No. $\text{Cr}(\text{CO})_4(\text{bpy})$, 15668-63-0; $\text{Cr}(\text{CO})_4(4,4'\text{-Me}_2\text{-bpy})$, 15740-68-8; $\text{Cr}(\text{CO})_4(\text{phen})$, 14168-63-9; $\text{Cr}(\text{CO})_4(4\text{-Me-phen})$, 101056-23-9; $\text{Cr}(\text{CO})_4(5\text{-Me-phen})$, 59136-57-1; $\text{Cr}(\text{CO})_4(5\text{-Ph-phen})$, 101056-24-0; $\text{Cr}(\text{CO})_4(5\text{-Cl-phen})$, 59136-56-0; $\text{Cr}(\text{CO})_4(5\text{-NO}_2\text{-phen})$, 16632-86-3; $\text{Mo}(\text{CO})_4(\text{bpy})$, 15668-64-1; $\text{Mo}(\text{CO})_4(4,4'\text{-Me}_2\text{-bpy})$, 15740-82-6; $\text{Mo}(\text{CO})_4(\text{phen})$, 15740-78-0; $\text{Mo}(\text{CO})_4(4\text{-Me-phen})$, 101056-25-1; $\text{Mo}(\text{CO})_4(5\text{-Me-phen})$, 35270-49-6; $\text{Mo}(\text{CO})_4(5\text{-Ph-phen})$, 101056-26-2; $\text{Mo}(\text{CO})_4(5\text{-Cl-phen})$, 35270-50-9; $\text{Mo}(\text{CO})_4(5\text{-NO}_2\text{-phen})$, 16632-98-7; $\text{W}(\text{CO})_4(\text{bpy})$, 15668-66-3; $\text{W}(\text{CO})_4(4,4'\text{-Me}_2\text{-bpy})$, 26546-43-0; $\text{W}(\text{CO})_4(\text{phen})$, 14729-20-5; $\text{W}(\text{CO})_4(4\text{-Me-phen})$, 87655-71-8; $\text{W}(\text{CO})_4(5\text{-Me-phen})$, 59136-52-6; $\text{W}(\text{CO})_4(5\text{-Ph-phen})$, 87655-72-9; $\text{W}(\text{CO})_4(5\text{-Cl-phen})$, 59136-53-7; $\text{W}(\text{CO})_4(5\text{-NO}_2\text{-phen})$, 16785-76-5; dimethyl sulfoxide, 67-68-5; acetone, 67-64-1; ethanol, 64-17-5; benzene, 71-43-2; trichloroethylene, 79-01-6.