Luminescence Properties of Organometallic Complexes

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Contents

I. Introduction

A. Scope of This Review

Most investigations in inorganic photochemistry have been concerned with classical coordination compounds, and these have lead to a good understanding of the

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excited-state processes in these complexes. This field has developed rapidly over the past 30 years, and there already exist a number of review papers that have helped capture the vast expansion of its literature.[1-11]

Although the photoreactivity of metal carbonyls has been studied extensively and has been the subject of several reviews,[1,12-21] the photochemistry of other types of organometallic complexes remains much less understood. Only recently have critical summaries appeared on this topic.[8,22]

This review paper is concerned with the luminescence properties of organometallic complexes and in particular emphasizes how studies of this nature have been used to gain valuable insight on the excited-state processes of these molecules. An indication that this is a rapidly growing area of interest is demonstrated by the frequency of literature citations. There are very few research papers in this area prior to the mid 1970s, and a significant fraction of the early reports on luminescence represent rather isolated examples rather than structured research investigations. It is the primary purpose of this review to link together these reports and thus provide a foundation for future studies in this area. An attempt has been made to be definitive, and the literature has been extensively searched from 1968 to 1986 via both book and online searches of Chemical

Abstracts. Furthermore, this review draws attention to the enormously rich photophysical behavior exhibited by organometallic compounds and describes studies that have characterized various aspects of emission phenomena, including multiple luminescence, electrochemically generated luminescence, low-temperature vibronic coupling, room temperature emission, quenching by energy- or electron-transfer mechanisms, and chemiluminescence. This review is concerned only with transition-metal organometallic complexes and does not include metal cyanides.

B. Types of Excited States in Organometallic Complexes

Organometallic compounds are known to exhibit many of the electronically excited states found in coordination compounds. However, the low-valent metal center and the high degree of covalency associated with the metal–ligand bond in an organometallic complex give rise to some notable differences in the excited-state properties. Like classical coordination compounds, a great deal of photophysical and photochemical behavior can be explained with the use of a localized molecular orbital approach and simple one-electron excitations. A brief summary of the excited states commonly found in organometallic complexes is given below.

1. Ligand Field Excited States

Low-lying ligand field (LF) or metal-centered excited states of organometallic compounds arise from electronic transitions between the metal d orbitals. As carbon-donor ligands are high in the spectrochemical series, the LF transitions of organometallic complexes are normally observed in the ultraviolet and visible regions and are at relatively high energies compared to those of most classical coordination compounds. For example, the lowest energy $t_{2g}^6 e_g^0 \rightarrow t_{2g}^5 e_g^1$ spin-allowed transition ($^1A_{1g} \rightarrow {}^1T_{1g}$) of $Cr(CO)_6$ appears at 317 nm,[23] whereas the lowest energy $t_{2g}^3 e_g^0 \rightarrow t_{2g}^2 e_g^1$ spin-allowed transitions ($^4A_{2g} \rightarrow {}^4T_{2g}$) of Cr(III) complexes are typically in the 450–750-nm region.[24] Furthermore, the high degree of covalency associated with the metal–ligand bond of an organometallic complex means that the metal-centered d $\rightarrow$ d transitions incorporate a fair amount of ligand character. This covalency results in relatively high molar absorptivities, commonly in the 10^3–10^4 M^{-1} cm^{-1} range, for the LF transitions of organometallic species. This contrasts sharply with the molar absorptivities of the d $\rightarrow$ d bands of classical coordination compounds, which are typically in the 10^1–10^2 M^{-1} cm^{-1} range.[24] It is also known that excitation into LF states often brings about efficient ligand dissociation.[18]

2. Metal to Ligand Charge-Transfer Excited States

Metal to ligand charge-transfer (MLCT) states involve electronic transitions from a metal-centered orbital to a ligand-localized orbital. Thus, in a formal sense this excitation results in metal oxidation and ligand reduction. These transitions are commonly observed in organometallic complexes because of the low-valent nature of the metal center and the low-energy position of the acceptor orbitals in many ligands. Depending on the metal center and the coordinating ligands, these transitions may appear in the near-infrared, visible, or ultraviolet regions. Analogous to classical coordination compounds MLCT transitions are typically intense ($\epsilon = 10^4$–10^5 M^{-1} cm^{-1}) and both solvent and substituent dependent.

3. Ligand to Metal Charge-Transfer Excited States

Ligand to metal charge-transfer (LMCT) states involve electronic transitions from a ligand-localized orbital to a metal-centered orbital. As previously noted, carbon donors are high in the spectrochemical series, and this results in large ligand field splitting energies for organometallic systems. Therefore, many complexes exhibit LMCT states that are fairly high in energy. As a consequence, it is generally only the early transition-metal organometallic complexes in high oxidation states that exhibit readily identifiable LMCT excited states.

4. Metal to Solvent Charge-Transfer Excited States

Metal to solvent charge-transfer (MSCT) states originate from electronic transitions from metal-centered orbitals to solvent-localized orbitals. In a formal sense these transitions result in oxidation of the metal and reduction of solvent, and the energy position of these states are dependent on the ease of these processes. Only a few MSCT states have been characterized for organometallic species and these have usually been in halocarbon media.

5. Metal to Metal Charge-Transfer Excited States

Metal to metal charge-transfer (MMCT) states arise from electronic transitions between metal-centered orbitals of two or more metals. The most characterized systems involve metal–metal-bonded binuclear complexes formed by coupling two 17-electron moieties. In these cases the MMCT states are the result of $\sigma_b \rightarrow \sigma^*$ transitions and thus lead to efficient M–M bond breaking. These bands are typically present in the blue or near-ultraviolet regions, and their energies are normally not dependent on solvent. In cluster complexes the metal–metal excited states are more delocalized over the core of metal atoms and are relatively poorly characterized. Furthermore, these states are less consequential with respect to the overall metal–metal bonding.

6. Intraligand Excited States

Intraligand (IL) states derive from electronic transitions between orbitals that are mainly localized on the ligand. Organometallic complexes may exhibit IL transitions that have spectral properties which closely resemble the free ligand states. This is the case where upon coordination there is only a minor perturbation of the ligand orbitals that are involved in the IL transition. When the IL transition arises from a orbital involved in the ligand bonding, however, it is usually of very different character from the free ligand transition.

II. Photoluminescence

A. Metal Carbonyls

Metal carbonyl complexes are recognized as being some of the most light-sensitive inorganic materials, and

TABLE I.[a] **Emission Characteristics of M(CO)$_6^{-b}$**

compound	emission max (width at half-height), 10^{-3} cm^{-1}	ϕ_e ($\pm 20\%$)	τ ($\pm 10\%$), μs
[(n-Bu)$_4$N][Ta(CO)$_6$]	17.20 (3.0)	0.05	23
[Ph$_4$As][Ta(CO)$_6$]	17.36 (2.2)	0.16	63
[(Ph$_3$P)$_3$Au][Ta(CO)$_6$]	17.08 (1.8)	0.25	74
[K(diglyme)$_3$][Nb(CO)$_6$]	17.10 (2.6)		

[a] Reprinted with permission from ref 25. Copyright 1976 American Chemical Society. [b] Recorded from pure powders at 25 K following excitation at 370 nm.

TABLE II.[a] **Vibrational Band Maxima in the Emission Spectrum of [Ph$_4$As][Ta(CO)$_6$] at 25 K**

band max, cm^{-1}	$\nu^n - \nu^{n+1}$, cm^{-1}	band max, cm^{-1}	$\nu^n - \nu^{n+1}$, cm^{-1}
19 212		17 848	91
18 788	424	17 363 (max)	485
18 364	424	16 970	393
18 242	122	16 606	364
18 091	151	16 167	439
17 939	152	15 667	500

[a] Reprinted with permission from ref 25. Copyright 1976 American Chemical Society.

the mechanisms of their photoreactions have been investigated in detail for a number of systems. These complexes are now known to exhibit all of the types of excited states discussed in the previous section, and, in fact, the majority of published work on organometallic emission pertains to these important species. These luminescence studies have played an invaluable role in determining the nature of their excited states and their deactivation pathways. The review of the literature on these complexes is divided according to the group of the central metal and presented according to their order from left to right in the periodic table.

1. Vanadium, Niobium, and Tantalum Complexes

Difficulties in preparing V, Nb, and Ta carbonyls have precluded many investigations. Notwithstanding, an extensive study has appeared on the M(CO)$_6^-$ (M = V, Nb, Ta) species, and this is notable as it represents the first report of luminescence from an O$_h$ d^6 low-spin hexacarbonyl complex.[25] It has been shown that the M(CO)$_6^-$ (M = V, Nb, Ta) complexes exhibit low-lying excited states very similar to those of the much studied isoelectronic M(CO)$_6$ (M = Cr, Mo, W) analogues.[23] Consequently, the lowest energy absorptions in the hexacarbonyl anions have been assigned to $^1A_{1g}(t_{2g}^6 e_g^0)$ → $^1T_{1g}(t_{2g}^5 e_g^1)$ and $^1A_{1g}(t_{2g}^6 e_g^0)$ → $^3T_{1g}(t_{2g}^5 e_g^1)$ LF transitions.

The luminescence properties of the M(CO)$_6^-$ species enable considerable insight to be obtained on the character of their excited states. Emission has been determined only from the Nb and Ta salts as powdered samples at low temperature (see Table I) and has been attributed to originate from the lowest energy LF state. It can be seen that although the emission maxima of the Ta salts are relatively unaffected by the nature of the counterion, the emission quantum yield (ϕ_e) and lifetime (τ) show some variation. The absence of emission from the corresponding V compounds is thought to be an indication that spin–orbit coupling is an important factor in bringing about efficient radiative deactivation.
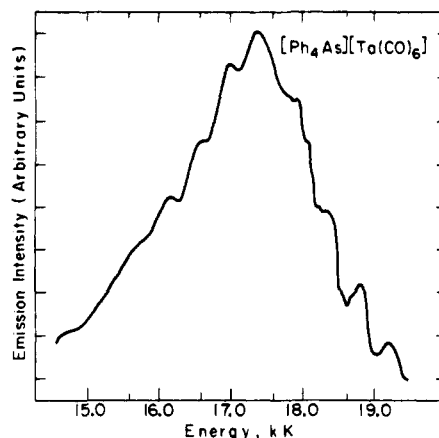

Figure 1. Corrected emission spectrum of [Ph$_4$As][Ta(CO)$_6$] powder at 25 K. Excitation wavelength is 454 nm. Reproduced with permission from ref 25. Copyright 1976 American Chemical Society.
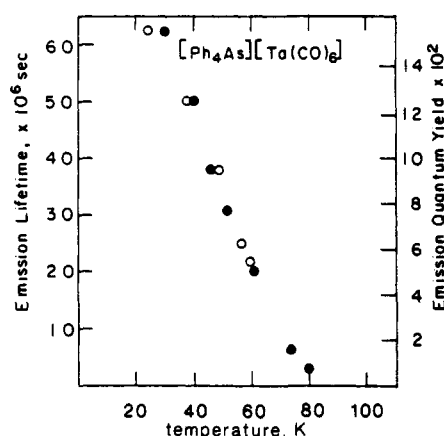

Figure 2. Temperature dependence of emission quantum yields (●) and emission lifetimes (○) for [Ph$_4$As][Ta(CO)$_6$] powder at 25 K. Reproduced with permission from ref 25. Copyright 1976 American Chemical Society.

The emission spectrum of [Ph$_4$As][Ta(CO)$_6$] is particularly informative as it exhibits clear vibrational structure (see Figure 1 and Table II). The highest energy resolved vibrational component is at 19 212 cm^{-1}, and this, together with the lowest energy vibrational component observed in the 25 K absorption spectrum at 19 608 cm^{-1}, provides an accurate bracket of the O–O electronic transition. The vibrational progression on the emission spectrum of this complex (see Table II) is close to the ground-state Ta–C stretching frequency recorded at 410 cm^{-1} by infrared spectroscopy. Furthermore, as this value corresponds with the energy spacing of the vibrational structure in the low-temperature absorption spectrum, it appears that there is rather little distortion of the excited state compared to the ground state in these molecules. Both the small excited-state distortion and the fact that this is the only observation of emission from a powdered sample of a low-spin d^6 octahedral hexacarbonyl can be attributed to additional mixing of M → π^*(CO) CT character in the lowest energy LF state of these complexes.

Temperature studies of the emission lifetime (τ) and emission quantum yield (ϕ_e) have been carried out for the Ta(CO)$_6^-$ system, and the results are displayed in Figure 2.[25,26] The relationship between these emission parameters may be obtained from the definitions of the lifetime and quantum yield with respect to the radiative
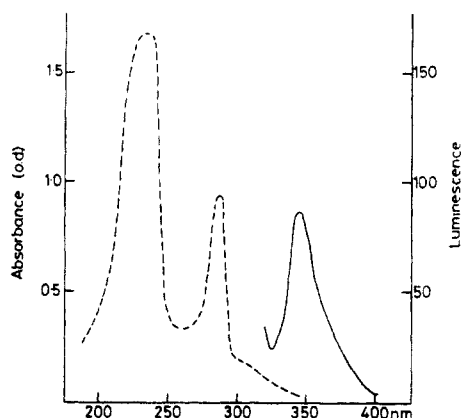
Figure 3. Electronic absorption (- - -) and emission (—) spectra of $Mo(CO)_6$ at dilute concentration in a CH_4 matrix at 12 K. Reproduced with permission from ref 30. Copyright 1979 Royal Society of Chemistry.

(k_r) and nonradiative (k_{nr}) decay rate constants (see eq 1-3).

$$\tau = 1/(k_r + k_{nr}) \qquad (1)$$

$$\phi_e = k_r/(k_r + k_{nr}) \qquad (2)$$

$$\text{thus} \qquad \phi_e = k_r\tau \qquad (3)$$

The data in Figure 2 illustrate a constancy in the temperature dependencies of τ and ϕ_e over the 20–80 K range. Therefore, it can be deduced for these Ta complexes that k_r does not vary significantly with temperature and that spin–orbit coupling must be so large that a higher energy spin–orbit state cannot be reached by thermal activation in this temperature range. It is notable that these results contrast with those obtained for the isoelectronic d^6 low-spin $Co(CN)_6{}^{3-}$ system in which the emission has been thought to originate from a Boltzmann distribution of A_1, T_1, T_2, and E states derived by spin–orbit perturbation of the $^3T_1$ state.[27,28]

2. Chromium, Molybdenum, and Tungsten Complexes

A featureless luminescence spectrum ($\lambda_{max} = 400$ nm) has been reported from $Cr(CO)_6$ in Ar matrices at 10 K; this emission was only observed following triplet sensitization with toluene, and because of this it has been attributed to $^3T_{1g} \rightarrow {}^1A_{1g}$ LF phosphorescence.[29] More recently emission has been recorded following direct excitation of $M(CO)_6$ (M = Cr, Mo, W) in frozen Ar or CH_4 matrices at 12 K (see Figure 3). The proximity of this emission to the low-lying absorption bands has led to its being assigned as $^1T_{1g} \rightarrow {}^1A_{1g}$ or $^1T_{2g} \rightarrow {}^1A_{1g}$ fluorescence.[30] To date, there are no definitive reports of luminescence from the parent hexacarbonyls at higher temperatures, which is consistent with rapid nonradiative deactivation from these complexes. On the other hand, there are detailed emission data available from a variety of $M(CO)_5L$ (M = Cr, Mo, W) type complexes, and this has greatly enhanced available knowledge of their electronic structures.

Depending on the nature of the coordinated ligand, $M(CO)_5L$ complexes exhibit either LF or d $\rightarrow$ π^*(L) MLCT excited states at lowest energy in the visible and near-ultraviolet regions.[14,18,31–49] The d $\rightarrow$ π^*(CO) charge-transfer transitions are at higher energies in these complexes. The earliest report of emission for any type of metal carbonyl complex concerns a number of $W(CO)_5L$ species either as pure solids or in rigid organic glasses at 77 K, where L is an amine, pyridine, ether, or a ketone ligand.[50] For each case the emission was observed to be centered in the 510–545-nm region and assigned to a $^3E(e^3b_2{}^2a_1) \rightarrow {}^1A_1(e^4b_2{}^2)$ LF transition. Although the emission energies are virtually independent of L, the lifetimes range from 0.6 to 26 μs;[51] these values are fairly typical for spin-forbidden luminescence of heavy transition-metal compounds.[52–55] The variations in emission lifetime have been interpreted in terms of variations in the nonradiative rate constant (k_{nr}) as L is changed.[51] It was also noted that the corresponding chromium and molybdenum complexes were not emissive under identical experimental conditions, and this has been associated with the absence of a $^1A_1 \rightarrow {}^3E$ absorption feature.[50] A number of closely related phosphorous-donor complexes have also been determined to emit in glasses at 77 K.[47] These results closely parallel those of the complexes discussed above with the LF emission maxima independent of phosphorous ligand and occurring at 530 nm. This is rather a peculiar finding as the $^1A_1(e^4b_2{}^2) \rightarrow {}^{1,3}E$-$(e^3b_2{}^2a_1{}^1)$ transitions of the $W(CO)_5$(P-donor) complexes are blue shifted in comparison to the $W(CO)_5$(N-donor) complexes (vide infra).

Interestingly, the emission lifetimes for $W(CO)_5L$ complexes, where L is a series of aliphatic amines, exhibit a dependence on the number of hydrogen atoms attached to the donor nitrogen ligand. Complexes of primary amines yield lifetimes at 77 K of approximately 1 μs, whereas complexes of secondary and tertiary amines lie in the 2.6–5.1- and 6.9–25.5-μs ranges, respectively.[51] This effect is in accordance with the theory of Robinson and Frosch, which states that the high-frequency vibrational modes associated with the geometry changes of a molecule (and its local environment) are the most important with respect to radiationless deactivation.[55] In this particular example the amine N–H stretches may be the key to effective nonradiative decay. Also, in this connection, studies on a series of aliphatic ketones have illustrated that the α-CH stretching modes are a significant factor in the dissipation of energy via radiationless $T_1 \rightsquigarrow S_0$ processes.[56,57]

Further studies of the emission of $W(CO)_5L$ complexes in EPA glasses at 77 K have been carried out for a series of pyridine derivatives.[58,59] Several complexes have been assigned to possess lowest energy LF states, and these exhibit emission maxima in the 18 100–19 700-cm^{-1} region with lifetimes in the 0.82–1.25-μs range. In contrast, when the pyridine ligand contains a highly electron-withdrawing substituent (e.g., 4-cyanopyridine), the d $\rightarrow$ π^*(py) MLCT state is assigned to be at lowest energy and the emission maxima are between 15 200 and 17 000 cm^{-1} with lifetimes ranging from 15.0 to 38.3 μs. Varying degrees of LF and MLCT characters have also been noted for the lowest energy excited states of $W(CO)_5$(cis-diazene) complexes.[60] The emission spectrum reported for $W(CO)_5$(cis-azobenzene) is typical of those attributed to be from a LF state, and this is shown in Figure 4. Emission of MLCT origin has also been observed for a number of these $W(CO)_5$(cis-diazene) compounds but, again, it is at substantially lower energy.[60]
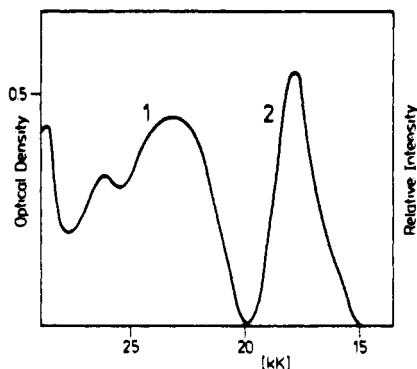
Figure 4. Electronic absorption (curve 1) and uncorrected emission (curve 2) spectra of $W(CO)_5$(cis-azobenzene) in a 2,3-dimethylbutane–n-hexane (8:3 v/v) glass at 77 K. Emission recorded following excitation at 23.2×10^3 cm^{-1}. Reproduced with permission from ref 60. Copyright 1978 American Chemical Society.

Luminescence data have also been obtained from $W(CO)_5L$ (L = Cl$^-$, Br$^-$, I$^-$, NCO$^-$, N$_3^-$) complexes in 77 K glasses.[48] Again, the emission of each complex has been assigned to occur from a LF excited state. In general, these complexes are less photoactive and exhibit longer lifetimes than the aforementioned neutral nitrogen- or phosphorus-donor species, and this indicates that the nonradiative deactivation routes are more favorable for the complexes which undergo efficient ligand photosubstitution.[48,58,59] It has been hypothesized that the nonradiative decay pathway in these species may involve rearrangement of the excited state from a square pyramidal to a trigonal bipyramidal geometry.[48,61]

An extensive study of the electronic, vibrational, luminescence, and magnetic circular dichroism spectra of $W(CO)_5(N_3)^-$ has led to a proposed description of the lowest energy excited-state potential surface for this molecule.[49] This model incorporates a high degree of configuration interaction between low-lying ligand field (LF) and azide to metal charge-transfer (LMCT) excited states. Experimentally determined photoreactivity routes may be rationalized on this model; azide photodecomposition and CO photosubstitution are thought to arise from LMCT and LF reaction channels on the excited-state potential surface. The lowest point on the potential surface may represent the LF potential well because the luminescence of $W(CO)_5(N_3)^-$ is similar to that of other types of $W(CO)_5L$ complexes which exhibit LF emission.[47,48,59]

Matrix isolation studies of $M(CO)_5L$ complexes, where M = Mo or W and L = pyridine, 3-bromopyridine, pyridazine, piperidine, trimethylphosphine, or trichlorophosphine, are significant as they have provided the first reports of fluorescence from substituted metal carbonyls.[30,62,63] The absorption and emission spectra of matrix-isolated $W(CO)_5$(pip) (pip = piperidine) are illustrated in Figure 5. It is notable that two emission bands were recorded from a number of the $W(CO)_5L$ complexes in either Ar or CH$_4$ matrices at 12 K.[63] The long-wavelength feature (λ_{max} = 520 nm) has been assigned to a $^3E_a \rightarrow ^1A_1$ LF phosphorescence; this energy position and its lifetime (e.g., 3.4 ± 0.2 μs for $W(CO)_5$(pyridine) in a 12 K Ar matrix) are in good agreement with the earlier studies in glasses at 77 K.[51,58,59] The higher energy emission feature (λ_{max} = 420 nm) has been attributed to $^1E_a \rightarrow ^1A_1$ fluorescence as
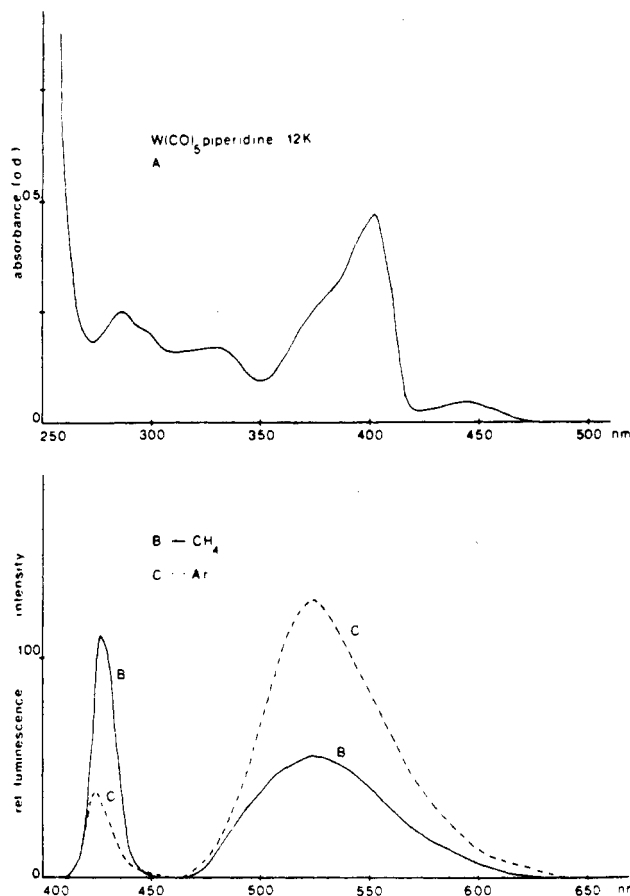

Figure 5. Electronic absorption and emission spectra of $W(CO)_5$(pip) isolated in CH$_4$ (—) and Ar (- - -) matrices at 12 K. Reproduced with permission from ref 63. Copyright 1981 American Chemical Society.

it has only a small Stokes shift of approximately 1300 cm^{-1} from the corresponding spin-allowed absorption band (see Figure 5). Excitation spectra obtained on this system have provided further evidence for the fluorescence and phosphorescence assignments.[63]

Although the fluorescence lifetime has not been obtained experimentally, it may be estimated with the application of eq 4.[63,64] In eq 4 values of $\phi_f \sim 10^{-2}$ and

$$\tau_f = \phi_f \tau_{rad} = \phi_f (10^{-4}/\epsilon_{max}) \qquad (4)$$

$\epsilon_{max} \sim 5000$ may be used to yield $\tau_f \sim 200$ ps at 12 K. Additionally, as fluorescence has not been observed in room temperature fluid conditions an upper limit of ϕ_f = 10^{-4} may be entered into eq 4, which yields an upper estimate of the fluorescence lifetime to be 2 ps. Although this procedure for estimating excited-state lifetimes involves several approximations, it has been demonstrated to be accurate to ±10% for a number of aromatic molecules.[65]

Changing the matrix material has been shown to affect the fluorescence and phosphorescence intensities of $W(CO)_5L$ in an inverse relationship. When CH$_4$ is replaced by Ar, the fluorescence is decreased, whereas the phosphorescence increases in intensity (see Figure 5). In a Kr matrix any fluorescence is completely undetectable, whereas the phosphorescence is further enhanced. This trend is thought to indicate an enhancement of intersystem crossing rates because of an external heavy-atom effect of the matrix material. Similar observations have previously been made for benzene and perdeuteriobenzene phosphorescence in
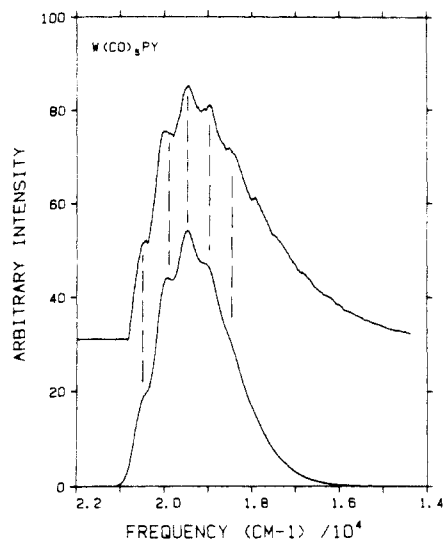
Figure 6. Top: Experimental emission spectrum of $W(CO)_5(py)$ at 10 K. Bottom: Calculated emission spectrum. Reproduced with permission from ref 69. Copyright 1982 American Chemical Society.

Figure 7. Corrected emission spectra at 298 K of (a) $W(CO)_5$-(4-AC-py), (b) $W(CO)_5$(4-BN-py), (c) $W(CO)_5$(4-CN-py), and (d) $W(CO)_5$(4-FM-py); (—) solid, (- - -) (6–8) × 10^{-5} M $W(CO)_5L$ in methylcyclohexane and (—·—) (4–6) × 10^{-5} M $W(CO)_5L$ in benzene. Intensities are scaled to make maxima equal. Excitation wavelength is 400 nm. Reproduced with permission from ref 80. Copyright 1982 American Chemical Society.

CH_4, Ar, and Kr matrices.[66-68]

Fluorescence has also been determined from W-$(CO)_5(PMe_3)$ and $W(CO)_5(PCl_3)$ in Ar and CH_4 matrices at 12 K. These emission spectra are blue shifted 4000–5000 cm^{-1}, in accordance with their absorption spectra and the increased π-backbonding character of phosphorus-donor ligands compared to that of nitrogen-donor ligands. Phosphorescence of these molecules, however, is conspicuously absent, and this has been explained in terms of ineffective internal heavy-atom-induced spin–orbit coupling in the phosphorus-donor complexes. These results also suggest that the earlier observations of emission at 530 nm (which is at the same energy position as several of the nitrogen-donor analogues) from $W(CO)_5$(P-donor) complexes in glasses at 77 K[47] may have arisen from photolysis decomposition products.[63]

Vibrational structure in the luminescence spectrum of $W(CO)_5(py)$ (py = pyridine) shown in Figure 6 has been studied in detail.[69,70] Although the vibronic spectral features of $W(CO)_5(py)$ are regularly spaced at 550 cm^{-1}, there is no ground-state normal mode that corresponds to this frequency.[69,71,72] This effect has been referred to as the "missing mode effect" or MIME, as the normal mode that appears to be present in the emission spectrum does not actually exist. The MIME effect has been interpreted in terms of a time-dependent picture of electronic transitions by employing a Franck–Condon analysis;[73-76] with this analysis and an estimate of the excited-state displacement (from experimentally determined preresonance Raman intensities), a calculated spectrum can be derived that is in good agreement with the experimental data (see Figure 6).[69,70] The normal modes that give rise to the 550-cm^{-1} MIME frequency for $W(CO)_5(py)$ are predominantly the W–C stretch in the 400–500-nm region, the W–N stretch at 195 cm^{-1}, and the WCO bend at 636 cm^{-1}. Additionally, it has been shown that the MIME effect can occur under a variety of conditions and that it may, in fact, not be uncommon.[77]

High-resolution polarized luminescence spectra have been obtained from a series of $W(CO)_5L$ single crystals in the 1.9–80 K temperature range.[78] When L = pyr-
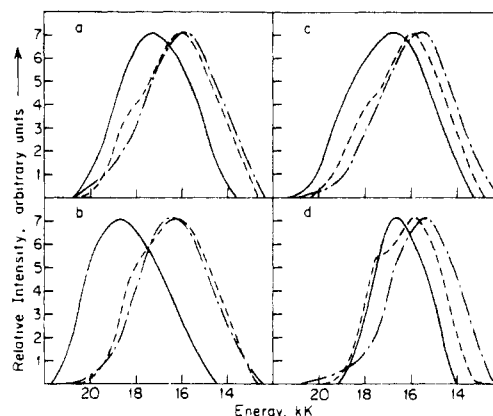
idine, 4-methylpyridine, 4-tert-butylpyridine, 3,4-dimethylpyridine, and 4-aminopyridine, the emission spectra are observed to be extremely temperature dependent and exhibit distinct sharp-lined fine structure at low temperature. These spectra have been attributed to LF luminescence from A_2', $2A_1'$, and E' levels that are derived from spin-orbit coupling of a ^3E state. In addition, these LF emissions are sensitive to the application of a homogeneous magnetic field and these magnetic field effects have been explained in terms of a reduction of molecular symmetry from C_{4v} to C_4. When L = 3-acetylpyridine, 3,5-dibromopyridine, 3-benzoylpyridine, and 4-formylpyridine, the observed luminescence spectra are structureless and not temperature dependent and have been assigned to arise from lowest-lying MLCT states.

In the above studies luminescence has been detected from $M(CO)_5L$ (M = Mo, W) complexes at low temperature either as pure solids, in frozen glasses, or in a matrix environment. Metal carbonyl complexes were not thought to emit in room temperature solution because of rapid ligand dissociation and efficient nonradiative relaxation to the ground state.[14,18] Recently, however, several reports concerning room temperature luminescence of $M(CO)_5L$ (M = Mo, W) complexes have appeared.[79-82] These studies have illustrated that complexes which possess a MLCT state as the lowest energy excited state undergo relatively slow radiative deactivation and that this can be readily detected under fluid conditions. Hence, only the $M(CO)_5L$ complexes, where M = Mo or W and L is a pyridine derivative with an electron-withdrawing substituent, exhibit luminescence at room temperature; reported lifetimes and emission quantum yields of the W complexes in methylcyclohexane at 298 K range from 0.25 to 0.46 μs and 2.2 × 10^{-4} to 7.7 × 10^{-4}, respectively.[79-82] Importantly, the complexes that emit in room temperature solution undergo ligand photosubstitution with a much reduced photoreactivity efficiency.[59,80,82] Emission under fluid conditions has not been observed from the $M(CO)_5L$ complexes in which the LF excited state has been established as lowest lying, and these latter complexes undergo ligand photosubstitution with much greater photoreactivity efficiency values.
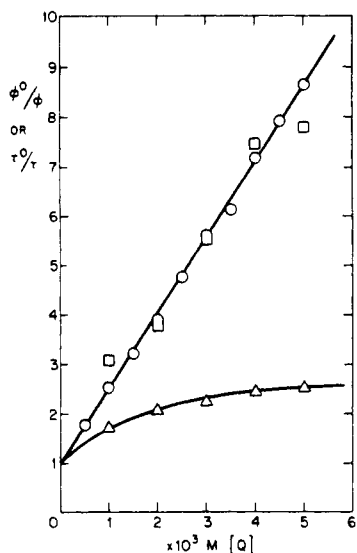
Figure 8. Quenching of $W(CO)_5$(4-CN-py) photosubstitution quantum yields (ϕ) and emission lifetimes (τ) at 298 K by anthracene in methylcyclohexane containing 0.05 M ethanol (O τ^0/τ; □ ϕ^0/ϕ; △ ϕ^0/ϕ). Excitation wavelengths are (O) 530, (□) 520, and (△) 430 nm. The 530-nm wavelength corresponds to MLCT excitation; the 430-nm wavelength corresponds to excitation into overlapping LF and MLCT states. Reproduced with permission from ref 80. Copyright 1982 American Chemical Society.

The observation of room temperature luminescence has made possible studies of quenching, temperature, and solvent dependency. Figure 7 depicts the luminescence of $W(CO)_5L$ complexes, where L = acetyl-pyridine (4-AC-py), 4-benzoylpyridine (4-BN-py), 4-cyanopyridine (4-CN-py), and 4-formylpyridine (4-FM-py), as solids or in solution at room temperature. On the basis of energy position and ligand dependence the luminescence features have been assigned to the MLCT excited states in these complexes. In nonpolar solvents the emission lifetimes and efficiencies were noted to be considerably greater than in the more polar solvents. This phenomenon has been attributed to an increased rate of nonradiative decay from the MLCT excited state; this may be due to collisional deactivation of the emitting state or, because the energy gap between the LF and MLCT states is reduced, an increased population of the photochemically active LF excited state in the polar solvents.

An extensive series of quenching experiments have been undertaken to bracket the energies of the MLCT states of $W(CO)_5L$. For example, the luminescence of $W(CO)_5$(4-AC-py) is quenched by 1,2-benzanthracene ($E_T = 16\,500$ cm^{-1})[83] and acenaphthaquinone ($E_T = 17\,900$ cm^{-1}),[84] but not by 1,2:5,6-dibenzanthracene ($E_T = 18\,300$ cm^{-1})[83] and fluoranthene ($E_T = 18\,500$ cm^{-1}).[83] Thus, it can be concluded that the lowest lying MLCT transition of $W(CO)_5L$ lies between 17 900 and 18 300 cm^{-1}. This quenching process is thought to be energy transfer as the $W(CO)_5L$ complexes also act as quenchers at diffusion-controlled rates for benzo-phenone and biacetyl phosphorescence. The luminescence of $W(CO)_5L$ is also quenched by dissolved oxygen. Therefore, both the luminescence and energy-transfer properties of these complexes indicate that they behave much like organic triplet donors and acceptors, even though the heavy metal center precludes a "pure" triplet description. In metal carbonyls, however, the MLCT excited state will have substantial ligand character, and
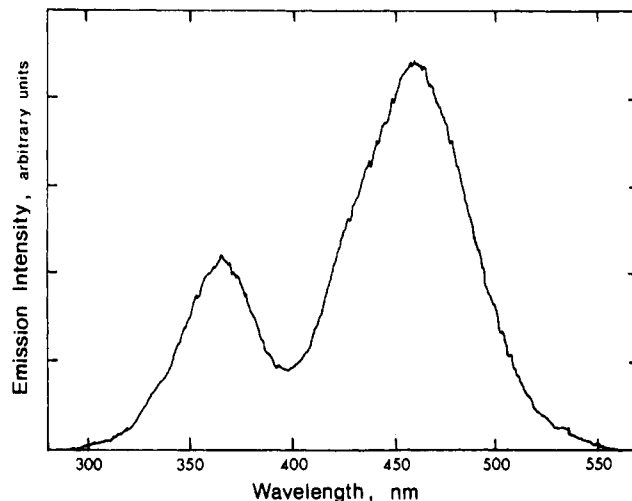

Figure 9. Emission excitation spectrum of 10^{-4} M $Mo(CO)_5$(4-BN-py) in benzene at 298 K. The excitation spectrum was recorded with emission monitored at 640 nm. Reproduced with permission from ref 82. Copyright 1986 American Chemical Society.

this will tend to lower the effects of spin–orbit coupling.

The emission lifetime (τ) of $W(CO)_5$(4-CN-py) has been shown to be quenched by anthracene according to Stern–Volmer kinetics with a bimolecular quenching rate constant (k_q) approaching that of the diffusion limit. This slope is in agreement with that for the photosubstitution reaction quenching following MLCT excitation (see Stern–Volmer plot of Figure 8). The common slope indicates that the emitting state of this complex is implicated in the photochemical pathway; that is, chemical reaction occurs from or via this excited state. Photosubstitution quantum yield data indicate that a higher lying $^1A_1(e^4b_2{}^2) \rightarrow {}^1E(e^3b_2{}^2a_1{}^1)$ LF state is responsible for the photochemistry in these molecules. Furthermore, quantum efficiency data obtained following 430-nm excitation do not obey Stern–Volmer kinetics (see Figure 8). This behavior can be explained in terms of direct population of this LF excited state which can chemically react at a rate competitive with internal conversion to the lower lying MLCT states.[80]

Temperature-dependence studies of the luminescence intensity of $W(CO)_5L$ complexes have indicated behavior that is not characteristic of a single emitting state. These results have been interpreted in terms of two MLCT excited states in which the higher state is thermally populated by the lower energy state.[80]

Several $Mo(CO)_5L$ complexes, where L = a substituted pyridine ligand, are also known to luminesce under fluid conditions.[81,82] The emission of the complexes are broad and unstructured and exhibit maxima in the 630–668-nm region. From the relative position of the bands in the absorption and emission spectra, the emission has been assigned to a low-lying MLCT excited state that is estimated to lie at 19 200 ± 500 cm^{-1} for each complex. Excitation spectra of these complexes have revealed a wavelength dependence for ϕ_e and indicate the energy deactivation pathway; an excitation spectrum of $Mo(CO)_5$(4-BN-py) in benzene at 298 K is shown in Figure 9. The most intense feature in the excitation spectrum at 455 nm has been attributed to the low-lying MLCT excited state. The excitation band at 366 nm suggests the presence of a higher lying excited state that effectively populates the emitting state. The
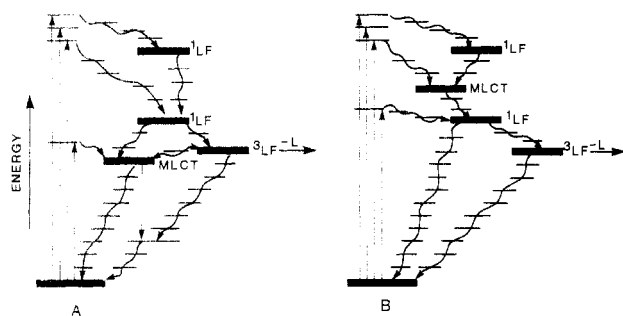
Figure 10. Excited-state schemes for $Mo(CO)_5L$ complexes. Vertical and wavy lines depict radiative and nonradiative processes, respectively. Heavy horizontal lines denote successive complex–solvent cage energies as vibrationally excited states relax (only a few of these lines are shown). Scheme A illustrates energy degradation processes in complexes where the MLCT state is at lowest energy (e.g., L = 4-CN-py). Scheme B depicts energy degradation processes in complexes where the LF state is lowest lying (e.g., L = 3-CN-py). Reproduced with permission from ref 82. Copyright 1986 American Chemical Society.

minimum in the excitation spectrum at 398 nm corresponds to the energy of the $^1A_1(e^4b_2{}^2) \rightarrow {}^1E(e^3b_2{}^2a_1{}^1)$ LF absorption, implying that this state does not efficiently populate the emitting MLCT state and that its energy degradation is by an alternative nonradiative route, possibly by ligand dissociation.[81] Further studies on the wavelength dependence of photosubstitution quantum yields have illustrated that these complexes do indeed undergo efficient LF photochemistry. It has also been suggested that a triplet LF state which lies very close in energy to the MLCT state may be reactive.[82] Reactive LF excited states have been determined for the isoelectronic $Ru(NH_3)_5L^{2+}$[9,85–91] and $Fe(CN)_5L^{3-}$[92] complexes.

The photophysical and photochemical properties of these $Mo(CO)_5L$ complexes are greatly dependent on the nature of the ligand substituent.[82] For example, when L = 4-cyanopyridine (4-CN-py), the MLCT excited state is at lowest energy and luminescence is observed under room temperature solution conditions. In contrast, when L = 3-cyanopyridine (3-CN-py), the LF states are lowest lying and no room temperature emission has been determined. Furthermore, when the LF states are lowest lying, the quantum yields depict fairly efficient photoreaction; this may be rationalized on the basis of the above $e^4b_2{}^2 \rightarrow e^3b_2{}^2a_1{}^1$ LF assignment, where the weak field (pyridine) ligand is labilized following population of the metal $d_z{}^2$ orbital.[82] When the MLCT states are lowest lying, the quantum yields indicate substantially reduced photochemistry. Excited-state schemes summarizing the ordering of the energy levels and the photophysical and photochemical properties of these $Mo(CO)_5L$ complexes are shown in Figure 10. Schemes A and B of Figure 10 depict energy degradation processes in complexes where the MLCT and LF states are at lowest energy, respectively. Thus, the 4-CN-py complex is representative of $Mo(CO)_5L$ complexes that exhibit room temperature luminescence (scheme A), and the 3-CN-py complex represents those which have efficient photoreactivity pathways (scheme B).

A few reports have dealt with the luminescence characteristics of cis-$M(CO)_4L_2$ complexes, where M = Cr, Mo, or W and L = pyridine or a substituted pyridine. The cis-$W(CO)_4L_2$ complexes have been reported to luminesce in EPA or 1:1 toluene/methylcyclohexane

TABLE III.[a] **Emission Spectral Data for cis-$M(CO)_4L_2$ (M = Mo, W) Complexes in Benzene at 298 K**[b,c]

complex	emission[d]		
	max, nm	half-width,[e] 10^{-3} cm^{-1}	$10^4\phi_e{}^f$
cis-$Mo(CO)_4(py)_2$	610	2.8	0.1
cis-$Mo(CO)_4(4$-Ph-py$)_2$	636	3.2	3.0
cis-$Mo(CO)_4(3,5$-Cl$_2$-py$)_2$	645	3.1	0.2
cis-$Mo(CO)_4(4$-BN-py$)_2$	665	4.1	0.4
cis-$Mo(CO)_4(4$-CN-py$)_2$	650	3.4	1.4
cis-$W(CO)_4(4$-Et-py$)_2$	565	5.7	0.5
cis-$W(CO)_4(4$-Me-py$)_2$	575	6.0	0.3
cis-$W(CO)_4(py)_2$	629	5.1	1.4
cis-$W(CO)_4(4$-Ph-py$)_2$	641	6.5	56.4
cis-$W(CO)_4(3,5$-Cl$_2$-py$)_2$	678	3.5	0.9
cis-$W(CO)_4(4$-BN-py$)_2$	>700		
cis-$W(CO)_4(4$-CN-py$)_2$	>700		

[a] Reprinted with permission from ref 97. Copyright 1984 American Chemical Society. [b] Recorded at 283 K for molybdenum complexes. [c] 8×10^{-5}–4×10^{-4} M deaerated solutions. [d] Spectra were corrected for variation in instrumental response as a function of wavelength. The excitation wavelength is 400 nm. [e] Width of emission band at half-height. [f] Measured relative to the emission of $Ru(bpy)_3{}^{2+}$. Accurate to within ±15%.

glasses at 77 K.[93] For complexes where L = pyridine, 3,4-dimethylpyridine, or 4-ethylpyridine, the emission maxima are approximately at 560 nm and the emission has been attributed to originate from a LF excited state; these emission energies are close to the 545-nm emission of cis-$W(CO)_4(pip)_2$ (pip = piperidine), which clearly exhibits low-lying LF transitions.[94] For complexes where L = 3-benzoylpyridine, 4-phenylpyridine, 3,5-dichloropyridine, 3,5-dibromopyridine, 4-benzoylpyridine, and 4-cyanopyridine, the emission maxima are at lower energies (600–735-nm region), and in each case they are assigned to a MLCT excited state. In either type of emission the lifetimes are fairly long (6.2–28.5 μs) and the emitting states can be inferred to have considerable triplet character.[93] In this connection, no emission has been detected from the closely related cis-$W(CO)_4(trans$-4-styrylpyridine) complex either as a pure solid or in solution at 77 or 298 K despite the MLCT assignment for its lowest energy band.[95]

Room temperature luminescence spectra have been obtained from a number of cis-$Mo(CO)_4L_2$ and cis-$W(CO)_4L_2$ complexes (see Table III).[96,97] For each complex the emission has been assigned to be from a single M → π^*(L) MLCT excited state. The emission maxima shift to lower energies as the L becomes more electron withdrawing; this energy shift is parallel to that observed in absorption. It is also noted that for any given ligand the emission energies are ordered Mo > W, corresponding to the position of the MLCT transition seen in the absorption spectra. In accordance with the MLCT assignment the emission energies are solvent dependent; for example, cis-$W(CO)_4(4$-Ph-py$)_2$ (4-Ph-py = 4-phenylpyridine) yields emission maxima at 641 nm in benzene and at 671 nm in tetrachloroethylene. Analogous to the $W(CO)_5L$ type complexes emission was not observed from the cis-$W(CO)_4L_2$ complexes in more polar solvents. Emission quantum yields for cis-$W(CO)_4L_2$ complexes also show considerable variation with ligand changes. Accompanying these increases in emission quantum efficiencies are reductions in the photosubstitution reactivities of these molecules (see Table III); this is particularly striking in the case of the Mo and W complexes where L = 4-Ph-py. A higher

TABLE IV.[a] Emission Data for M(CO)₄L Complexes in EPA Solution at 77 K[b]

M	L	band maxima (±50), cm⁻¹	half-width (±50), cm⁻¹	τ (±10%), μs	ϕ_e[c] (±20%)
Mo	bpy	15 250	3440		
	phen	15 660	3150	11.6	0.09
	5-CH₃-phen	15 550	3260	13.2	0.08
	5-Cl-phen	14 400	2940	13.3	0.04
	5-Br-phen	14 900	3325	9.5	
W	bpy	15 100	3500		
	phen	15 300	3210	11.6	0.05
	5-CH₃-phen	14 900	3200	12.5	0.04
	5-Cl-phen	14 400	2950	7.9	0.02
	5-Br-phen	14 400	3340	7.9	
	en	18 320		23.5	

[a] Reprinted with permission from ref 94. Copyright Elsevier Sequoia S.A. [b] From corrected emission spectra; emission half-width is the width of the emission band at half-height; excitation from an argon ion laser at 351.1 and 363.4 nm. [c] Measured relative to rhodamine B.

lying LF state has been shown to be responsible for the photochemistry in this system. Apparently the non-radiative processes that intercommunicate the LF and MLCT excited states depend on the coordinated ligand and become much more competitive for the cis-M-(CO)₄(4-Ph-py)₂ complexes.[97]

Several studies have characterized LF and MLCT excited states in the low-energy absorption system of M(CO)₄(α-diimine) complexes.[94,98-106] Luminescence data have been reported for M(CO)₄L, where M = Cr, Mo or W and L = 2,2′-bipyridine (bpy), 1,10-phenanthroline (phen), or a derivative of these ligands, in EPA glasses at 77 K.[94,107] Early reports of emission spectra of M(CO)₄(bpy) (M = Cr, Mo, W) noted that

M(CO)₄(bpy)
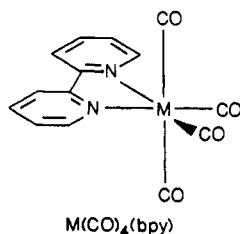
these molecules underwent rapid relaxation to their lowest M → π*(bpy) excited triplet states. These complexes are thus able to undergo emission without substantial CO dissociation because the photoactive d → d excited states are higher in energy than the lowest MLCT state.[107,108] Emission data obtained from several Mo(CO)₄L and W(CO)₄L complexes are shown in Table IV.[94] The luminescence of W(CO)₄(en) (en = ethylenediamine) has been assigned to originate from a LF excited state, analogous to a number of the previously discussed cis-W(CO)₄L₂ complexes. Emission spectra from the other M(CO)₄(α-diimine) complexes are at significantly longer wavelength and have consequently been assigned to arise from MLCT excited states. These latter compounds are also emissive as solids at room temperature with maxima determined in the 14 230–15 450-cm⁻¹ region.

The photophysical properties of M(CO)₄(α-diimine) complexes are especially interesting as they are known to exhibit dual luminescence features in room temperature solution.[109-111] Although multiple-state emission has now been established for a number of classical
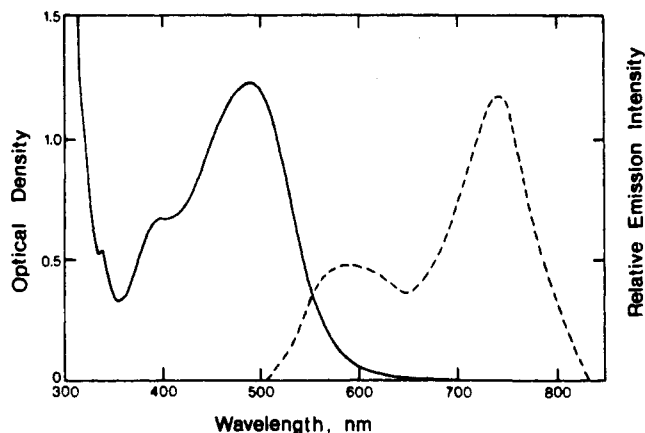

Figure 11. Electronic absorption (—) and emission (---) of 2 × 10⁻⁴ M Mo(CO)₄(phen) in benzene at 298 K. Emission spectrum is corrected for variations in instrumental response as a function of wavelength, and the excitation wavelength is 400 nm. Reproduced with permission from ref 110. Copyright 1986 American Chemical Society.

TABLE V.[a] Emission Maxima for M(CO)₄L Complexes in Benzene at 298 K[b]

complex	emission max, 10⁻³ cm⁻¹ high energy	emission max, 10⁻³ cm⁻¹ low energy
Cr(CO)₄(bpy)	16.00	12.85
Cr(CO)₄(4,4′-Me₂-bpy)	c	c
Cr(CO)₄(phen)	16.22	12.85
Cr(CO)₄(4-Me-phen)	16.30	12.74
Cr(CO)₄(5-Me-phen)	17.22	12.82
Cr(CO)₄(5-Ph-phen)	d	d
Cr(CO)₄(5-Cl-phen)	16.18	c
Cr(CO)₄(5-NO₂-phen)	c	c
Mo(CO)₄(bpy)	17.30	12.94
Mo(CO)₄(4,4′-Me₂-bpy)	17.90	13.19
Mo(CO)₄(phen)	17.33	12.99
Mo(CO)₄(4-Me-phen)	18.42	13.33
Mo(CO)₄(5-Me-phen)	17.85	13.11
Mo(CO)₄(5-Ph-phen)	17.87	12.99
Mo(CO)₄(5-Cl-phen)	17.55	12.99
Mo(CO)₄(5-NO₂-phen)	c	c
W(CO)₄(bpy)	17.03	12.97
W(CO)₄(4,4′-Me₂-bpy)	17.15	12.99
W(CO)₄(phen)	17.08	12.97
W(CO)₄(4-Me-phen)	16.73	12.79
W(CO)₄(5-Me-phen)	17.08	12.74
W(CO)₄(5-Ph-phen)	16.83	12.94
W(CO)₄(5-Cl-phen)	16.10	12.74
W(CO)₄(5-NO₂-phen)	c	c

[a] Reprinted with permission from ref 110. Copyright 1986 American Chemical Society. [b] Spectra were corrected for variations in instrumental response as a function of wavelength. The excitation wavelength is 400 nm. [c] Emission not observed. [d] Complex is thermally unstable, and emission data could not be obtained.

coordination compounds,[112-125] this phenomenon has been largely unrecognized for organometallic systems, particularly under fluid solution conditions. Figure 11 depicts the absorption and emission spectra recorded from Mo(CO₄(phen) in benzene at 298 K.[109] Similar dual luminescence features have been reported from a series of M(CO)₄(diimine) complexes, and these are summarized in Table V.[110] The dual emission bands may be associated with the a₁ → π*(L) and b₂ → π*(L) y- and z-polarized MLCT absorptions;[100-104,106] the higher energy transition shows a solvent sensitivity comparable to that observed in absorption,[126,127] and the lower energy transition appears too red shifted to be

TABLE VI.[a] Spectral Data of High-Energy Emission Component for Mo(CO)$_4$(4-Me-phen) in Various Solvents at 298 K[b]

	emission		
solvent	max, 10^{-3} cm^{-1}	half-width,[c] 10^{-3} cm^{-1}	$10^5 \phi_e$[d]
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

[a] Reprinted with permission from ref 110. Copyright 1986 American Chemical Society. [b] Spectra were corrected for variations in instrumental response as a function of wavelength. The excitation wavelength is 400 nm. [c] Width of emission band at half-height. [d] Measured relative to the emission of Ru(bpy)$_3{}^{2+}$; accurate to within 15%.

a LF emission. Furthermore, the emission energies for any particular ligand typically follow the Mo > W > Cr order that is seen for the MLCT absorption maxima.

Fluid solution luminescence was not observed from the 5-NO$_2$-phen derivations (see Table V) despite the MLCT excited state being lowest lying and low quantum yields for photosubstitution.[110] Moreover, it is noticeable that emission from these complexes has not been observed at low temperature either.[94] The presence of a nitro substituent on phen apparently provides an efficient vibrational relaxation route; this may involve M–N bond breaking as the 5-NO$_2$-phen ligand is the weakest base of the 5-substituted phen series.[128,129]

Solvent dependence of the higher energy emission band of Mo(CO)$_4$(4-Me-phen) is illustrated in Table VI. This solvent sensitivity is typical of the M(CO)$_4$L (L = bpy or phen) series. The variations in half-width and quantum yield data have been attributed to differences in the degree of overlap of the two MLCT bands; in a more polar solvent the lower energy MLCT component overlaps substantially with its higher energy counterpart. It may also be noted that the M(CO)$_4$(en) complexes exhibit $^1A_1 \rightarrow {}^1E$ or $^1A \rightarrow {}^3E$ LF states at approximately the same energies as the M(CO)$_4$(α-diimine) complexes[98,99] but they do not possess low-energy MLCT excited states or give rise to room temperature luminescence following $^1A \rightarrow {}^1E$ excitation. Additionally, the large differences in energy between the two emission maxima indicate that the lowest lying MLCT excited state is much more distorted with respect to the ground state than the other MLCT component.

Emission lifetimes have been determined to be ~350 ± 35 ns for both the high- and low-energy MLCT excited states of Mo(CO)$_4$(4-Me-phen) in benzene at 293 K, and it has been concluded that the two MLCT states possess considerable triplet character.[110] Previous reports of emission from these M(CO)$_4$(α-diimine) complexes in rigid media have placed the emission maxima in the 14 400-15 660-cm^{-1} range (see Table IV). These maxima are believed to correspond with the low-energy emission components determined at room temperature, concordant with observations made from other substituted group 6 metal carbonyl complexes.[80,97] This energy shift upon cooling was first noted for a series of ClRe(CO)$_3$L (L = bpy, phen, or a related derivative ligand) complexes (vide infra) and has been referred to as "luminescence rigidochromism".[130] The exact cause of this effect is not clearly understood at the present time.
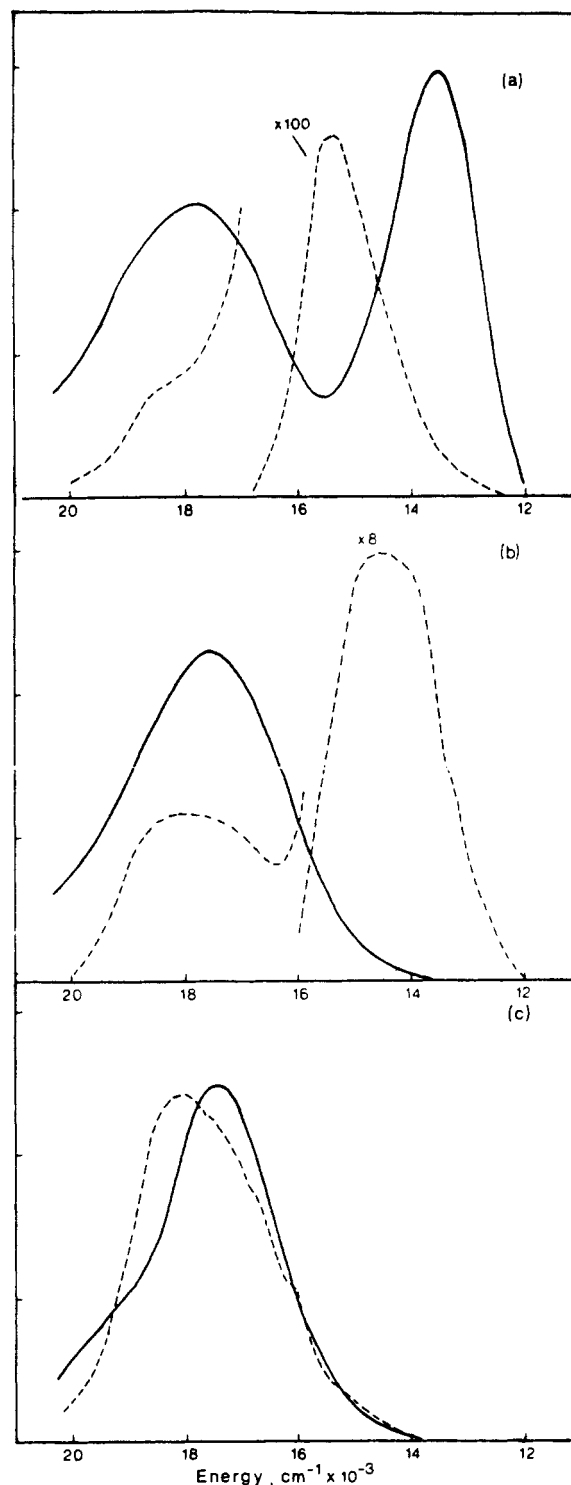
Figure 12. Luminescence spectra at 293 K in C$_6$H$_6$ (—) and at 80 K in 2-Me-THF (- - -) of (a) W(CO)$_4$(4,7-Ph$_2$-phen), (b) W(CO)$_4$(i-Pr-pyca), and (c) W(CO)$_4$(i-Pr-dab). The excitation wavelength is 488 nm. Reproduced with permission from ref 111. Copyright 1986 American Chemical Society.

In contrast to the above bpy and phen complexes, photophysical measurements of W(CO)$_4$(R-dab) and W(CO)$_4$(R-pyca) (R-dab = 1,4-diaza-1,3-butadiene; R-pyca = pyridine-2-carbaldehyde imine) complexes

R-dab   R-pyca
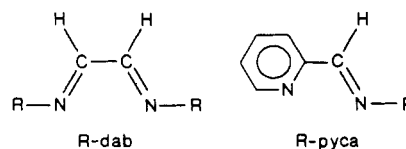
have shown only a single emission feature in room temperature solution.[111] Figure 12 illustrates a comparison of the luminescence spectra obtained from $W(CO)_4L$ complexes, where L = 4,7-Ph_2-phen, i-Pr-pyca, and i-Pr-dab, in benzene at 293 K and in 2-Me-THF at 80 K. The emission spectra of the pyca and dab complexes were observed to be dependent on the excitation wavelength, indicating the presence of two emitting states under these apparently single emission bands. These emission features are solvent sensitive and can be assigned to MLCT transitions analogous to the corresponding $W(CO)_4$(bpy) and $W(CO)_4$(phen) compounds. When the temperature is lowered to 80 K, the emission spectrum of the $W(CO)_4$(i-Pr-pyca) complex exhibits a low-energy component, resembling that of the bpy and phen complexes. On the other hand, the emission spectrum of the $W(CO)_4$(i-Pr-dab) complex undergoes relatively minor alternation on cooling. It may be concluded that the emission spectra of these $W(CO)_4$(α-diimine) complexes are strongly influenced by the MLCT character of the z-polarized transition; the mixing of metal d_{yz} and ligand π^* orbitals is much stronger for the dab complexes than in the bpy or phen complexes.[111,131] The MLCT character of the pyca complexes lies in between the dab and phen derivatives. The varying degree of MLCT characters are also shown to be reflected in the solvatochromism and photochemical properties of these and other closely related complexes.[100-104,106,132-134] A very weak third emission feature has been noted for several of the α-diimine complexes at room temperature and has been associated with a ^{3}LF excited state.[110,111]

The nature of the $b_2 \rightarrow b_2^*$ transition is the key to understanding the photophysical properties of these molecules. Resonance Raman excitation profiles have illustrated that MLCT $b_2 \rightarrow b_2^*$ excitation mainly affects the metal–ligand skeletal vibrations of the R-dab complexes, whereas the internal vibrations of the α-diimine ligands are affected in the bpy or phen derivatives. The R-dab complexes are considered to undergo efficient nonradiative decay (hence the absence of the low-energy emission feature) because these metal–ligand skeletal vibrations most strongly influence the electronic integral and therefore the matrix element connecting the ground and excited states.[135] Resonance Raman spectra of the $W(CO)_4$(R-pyca) complexes indicate that the z-polarized $b_2 \rightarrow b_2^*$ transition has some MLCT character and, thus, the R-pyca complexes behave photophysically like the R-dab complexes at room temperature. However, in a rigid environment at low temperature the radiationless deactivation processes of these molecules are reduced and the emission spectra are more like the bpy or phen derivatives.[111]

Luminescence excitation spectra have been reported for the low-energy emission feature of $W(CO)_4$(4,7-Ph_2-phen) at room temperature (see Figure 13).[111] This result has indicated that the z-polarized $b_2 \rightarrow b_2^*$ and x-polarized $a_2 \rightarrow a_2^*$ transitions (at 530 and 470 nm, respectively) contribute substantially to the low-energy emission feature. Moreover, solvent dependence studies of the excitation spectra further illustrate the highly solvatochromic nature of the z-polarized $b_2 \rightarrow b_2^*$ transition.
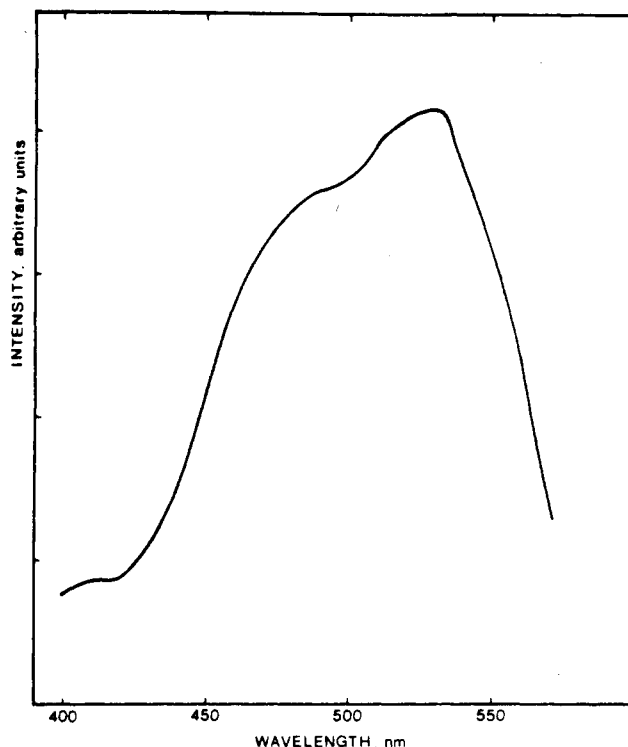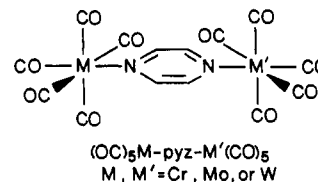

Figure 13. Luminescence excitation spectrum of $W(CO)_4$(4,7-Ph_2-phen) in C_6H_6. Luminescence monitored at 730 nm. Reproduced with permission from ref 111. Copyright 1986 American Chemical Society.

Room temperature luminescence spectra have been recorded from a series of binuclear $(OC)_5M$(pyz)M'-$(CO)_5$ complexes, where M and M′ = Cr, Mo, or W and

(OC)$_5$M-pyz-M′(CO)$_5$
M, M′=Cr, Mo, or W

pyz = pyrazine.[136,137] These complexes exhibit $^1A_1(e^4b_2{}^2)$ $\rightarrow$ $^1E(e^3b_2{}^2a_1{}^1)$ LF, $^1A_1(e^4b_2{}^2)$ $\rightarrow$ $^3E(e^3b_2{}^2a_1{}^1)$ LF, and M $\rightarrow$ π^*(pyz) charge-transfer states in the visible spectral region and are particularly noteworthy as the MLCT transitions are far removed from higher energy LF excited states. The onset of the emission in the 550–660-nm region and the 675–722-nm position of the emission maxima have led to an unequivocal MLCT assignment. The emission features of these binuclear compounds are broad (half-widths 2900–3900 cm^{-1}) and fairly weak (ϕ_e = 0.7 × 10^{-4} to 6.2 × 10^{-4}) following MLCT excitation. It is also noted that all of these binuclear complexes, including the Cr derivatives, emit in fluid solution. Emission yields are, however, greater for the heavier metal complexes, consistent with enhancement of a triplet–singlet radiative deactivation mechanism.[137,138]

Metal–metal-bonded $[(Cp)M(CO)_3]_2$ (M = Mo or W and Cp = C_5H_5) complexes have been found to exhibit two weak emission features in room temperature cyclohexane solutions following excitation at 354 nm with a 9-ps pulse.[139] The lowest energy absorption band of these complexes is very similar to $Mn_2(CO)_{10}$, which has been assigned from polarized absorption studies[140] and semiempirical MO calculations[141] to comprise $^1A_1 \rightarrow {}^1E_1$ (d$\pi \rightarrow \sigma^*$) and $^1A_1 \rightarrow {}^1B_2$ ($\sigma \rightarrow \sigma^*$) M–M localized

transitions. There are also strong parallels between the homolytic photochemistries of $[(Cp)M(CO)_3]_2$ and $Mn_2(CO)_{10}$.[142] However, an excitation wavelength dependence of the short-wavelength emission bands of the $[(Cp)W(CO)_3]_2$ and $[(Cp)Mo(CO)_3]_2$ complexes has prompted the suggestion that the near-UV absorption bands include a component involving transitions to the cyclopentadienyl π^*-orbitals. Moreover, the $Mn_2(CO)_{10}$ complex has been shown to not be emissive under identical experimental conditions, which were sensitive to detection of 10^{-6} emission quantum yields. The lifetimes of the short- and long-wavelength emission features are ~10 ps (an upper limit) and 4–5 ns, respectively, and are consistent with spin-allowed and spin-forbidden radiative decay from the metal–cyclopentadienyl excited states.[139]

Recently emission in fluid solution has been reported from an organometallic complex containing a metal–carbon multiple bond, the complex having the general formula $[XW(CO)_2L_2(CR)]$, where X = halide, L = a donor ligand, and R = phenyl.[143] For example, $[BrW(CO)_2(TMEDA)(CPh)]$, where TMEDA = tetramethylethylenediamine, emits with an excited-state lifetime of 180 ns and an emission quantum yield of 5.3 $\times 10^{-4}$. The emission spectra of these complexes exhibit maxima in the $15\,630$–$16\,000$-cm^{-1} region, and the radiative process has been associated with a lowest lying metal $d\pi \rightarrow \pi^*$ (alkylidyne) charge-transfer state in which the π-conjugation extends into the phenyl π^* system.[144,145] This hypothesis is supported by the observation that the emission properties are greatly dependent on the nature of both the R group and L ligand. If the phenyl group is replaced by a $tert$-butyl group, the complexes are not observed to emit under fluid conditions; this can be attributed to the loss of π-conjugation between the alkylidyne linkage and the phenyl π^* system. Also, replacing L by bpy involves further coupling of the metal $d\pi \rightarrow \pi^*$ (alkylidyne) excited state with a metal $d\pi \rightarrow \pi^*$ (bpy) state, and it is believed that the latter state may effectively quench the former one.[143] In view of the luminescence properties observed for $W(CO)_4$(bpy) (vide supra) it may be anticipated that these $[XW(CO)_2(bpy)(CR)]$ complexes are emissive, albeit weakly.

3. Manganese and Rhenium Complexes

Luminescence has been observed from solid $XRe(CO)_5$ (X = Cl, Br, I) compounds at 25 K (see Figure 14).[146] On the basis of this emission the lowest absorption bands in these complexes have been attributed to ligand field (LF) $^1A_1(e^4b_2^2) \rightarrow {}^1E(e^3b_2^2a_1^1)$ and $^1A_1(e^4b_2^2) \rightarrow {}^3E(e^3b_2^2a_1^1)$ transitions, in accordance with the assignments previously made for the lowest excited states of a wide range of low-spin d^6 complexes.[23,25,147-153] Importantly, the corresponding first-row $XMn(CO)_5$ complexes were not observed to emit as pure solids at 25 K, and thus the emission of the Re complexes has been associated with a spin-forbidden $^3E \rightarrow {}^1A$ transition. These observations are analogous to those made for the anionic $M(CO)_6^-$ (M = V, Nb, Ta) complexes (vide supra).[25]

Although the emission spectral distribution of $XRe(CO)_5$ is not sensitive to temperature, the emission quantum yield (ϕ_e) and lifetime (τ) are reduced substantially as the temperature is raised. Plots of ϕ_e and
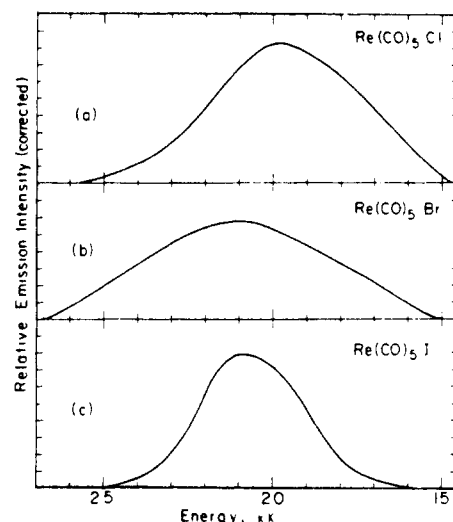

Figure 14. Corrected emission spectra of pure powdered $XRe(CO)_5$ at 25 K. Excitation wavelength is 370 nm. Reproduced with permission from ref 146. Copyright 1976 American Chemical Society.

τ over a 25–90 K range indicate that these parameters have parallel temperature dependencies; this behavior is again analogous to the previous measurements on $Ta(CO)_6^-$ [25] and illustrate that k_r does not vary significantly over this temperature range. This conclusion is, however, not consistent[146] with the spin-orbit coupling model for the $^3E(e^3b_2^2a_1^1)$ excited state previously proposed for isoelectronic Co(III) and Ru(II) complexes,[28,154,155] which should split this Re(I) state into E, A_1, A_2, B_1, and B_2 components of varying radiative decay properties.[146]

The emission bands of the $XRe(CO)_5$ complexes are especially broad (see Figure 14), suggesting that there is a large geometrical distortion of the ^3E excited state with respect to the $^1A_1$ ground state in this system. This distortion is thought to arise from an elongation of the X–Re–CO axis upon excitation to the $d_z^2(a_1)$ orbital which has σ^* character.[22] It may be noted that the emission band of $XRe(CO)_5$ is much broader and more red shifted from the $^1A_1 \rightarrow {}^3E$ absorption than in the isoelectronic d^6 $W(CO)_5$(amine) complexes (e.g., see Figure 4). This can be rationalized by assuming a greater weakening of the axial Re–C bond on excitation, in comparison to that of the W–N bond.[146]

Emission has been reported from $ClRe(CO)_3L$ (L = bpy, phen, or a related ligand derivative) complexes in EPA glasses at 77 K or in room temperature solution.[130] Absorption and emission spectra obtained from $ClRe(CO)_3$(phen) are depicted in Figure 15, and the emission data reported from this series are illustrated in Table VII. The emission energy position depends substantially on the nature of L, and in each case the emission has been associated with the lowest lying M $\rightarrow \pi^*(L)$ absorption band. The emissive state is thought to possess substantial triplet character on the basis that emission was not detected from the corresponding Mn complexes.

The luminescence characteristics of these $ClRe(CO)_3$(phen) complexes depend significantly on the environment; longer lived and more intense emission has been observed in rigid polyester resins or in EPA glasses at 77 K as compared to that in room temperature fluid solution (see Tables VII and VIII).[130] This

TABLE VII.[a] **Luminescence Characteristics for ClRe(CO)₃L Complexes**[b]

L	emission max, 10^{-3} cm^{-1} 298 K	77 K	lifetime, μs 298 K	77 K	ϕ_e ($\pm 15\%$)[c] at 298 K	ϕ_e ($\pm 15\%$) at 77 K
phen	17.33	18.94	0.3	9.6	0.036	0.33
bpy		18.87	0.6	3.8		
5-Me-phen	17.01	18.83	<0.65	5.0	0.030	0.33
4,7-Ph₂-phen	17.24	18.18	0.4	11.25		
5-Cl-phen	17.12	18.69	<0.65	6.25		
5-Br-phen	17.12	18.69	<0.65	7.6	0.020	0.20
5-NO₂-phen	d	18.28		11.8		0.033
phen-5,6-dione	d	18.45		2.5		
biquin[e]	d	14.58				

[a] Reprinted with permission from ref 130. Copyright 1974 American Chemical Society. [b] Measurements in EPA at 77 K or in CH₂Cl₂ at 298 K. [c] Quantum yields determined in benzene at 298 K. [d] Luminescence is not detectable from these complexes in solution at 298 K. [e] biquin = 2,2′-biquinoline.
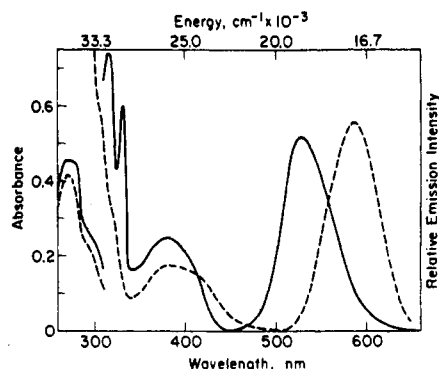

Figure 15. Electronic absorption (left) and emission (right) spectra of ClRe(CO)₃(phen) in EPA at 77 K (—) and 298 K (- - -). Room temperature absorption maxima are at 26 100 cm⁻¹ (ϵ 4000) and 37 030 cm⁻¹ (ϵ 30 600). The low-temperature spectrum is uncorrected for solvent contraction, and the emissions at 77 and 298 K were not recorded at the same sensitivity. Reproduced with permission from ref 130. Copyright 1974 American Chemical Society.

TABLE VIII.[a] **Environmental Effects on Absorption and Emission Maxima of ClRe(CO)₃L Complexes**

L	environment, (T, K)	first absorption max, 10^{-3} cm^{-1}	emission max, 10^{-3} cm^{-1} (τ, μs)
phen	CH₂Cl₂ (298)	26.53	17.33 (0.3)
	polyester resin (298)		18.52 (3.67)
	EPA (77)		18.94 (9.6)
5-Me-phen	benzene (298)	25.65	17.00 ($\leq$0.65)
	CH₂Cl₂ (298)	26.32	17.01
	CH₃OH (298)	27.05	17.00
	pure solid (298)		18.42
	polyester resin (298)		18.48 (3.5)
	EPA (77)		18.83 (5.0)
5-Br-phen	benzene (298)	25.32	17.15 ($\leq$0.65)
	CH₂Cl₂ (298)	25.84	17.12
	CH₃OH (298)	26.88	17.04
	pure solid (298)		17.83
	polyester resin (298)		18.32 (2.2)
	EPA (77)		18.69 (7.6)
5-Cl-phen	CH₂Cl₂ (298)	25.91	17.12
	pure solid (298)		17.99
	EPA (77)		18.69 (6.25)

[a] Reprinted with permission from ref 130. Copyright 1974 American Chemical Society.

is consistent with a decrease in the rate of nonradiative deactivation in the rigid media. It is surprising that the emission energies are not particularly solvent sensitive (see Table VIII) despite a ~1500-cm⁻¹ shift in the M → π*(L) absorption band. This effect was also noticeable for W(CO)₅L complexes (vide supra) and appears to be a general one for metal carbonyl complexes; the implication is that while solvent may energy shift the excited-state potential well it need not necessarily affect the potential minimum.[130] An alternative explanation is that the thermally equilibrated MLCT excited states of these types of complexes may undergo varying degrees of distortion depending on solvation effects.[156] More work clearly needs to be done to fully understand the influence of solvent on excited-state properties.

The term "luminescence rigidochromism" has been used to describe the substantial dependence of the emission maxima on environmental rigidity. These complexes exhibit a shift of up to ~1500 cm⁻¹, depending on the medium rigidity, giving rise to yellow–green emission in a rigid medium and red–orange emission in fluid solution (see Table VIII). The cause of this effect is not fully understood, although with more complexes recently established as being emissive under fluid solution conditions, further environmental comparisons indicate that it is not uncommon. This effect may also reflect changes in the shape of the excited-state potential well.

Although the heavy metal nature of these complexes precludes describing the lowest energy excited states of this system as "pure" triplets,[157] in as far as energy-transfer phenomena are concerned these complexes behave like organic triplet donors. The ClRe(CO)₃L complexes are quenched by both anthracene (E_T = 14 700 cm⁻¹)[83] and trans-stilbene (E_T = 17 500 cm⁻¹)[158] according to Stern–Volmer kinetics. Accompanying the ClRe(CO)₃L quenching is trans- → cis-stilbene isomerization, illustrating that it is the triplet excited state of trans-stilbene which is involved in the energy-transfer process.[159] In fact, the obtained trans- → cis-stilbene isomerization yields are the same within experimental error as in the benzophenone sensitization of trans-stilbene,[158] indicating that the intersystem crossing efficiency is unity[160] for these Re compounds.

Time-resolved resonance Raman spectra have been obtained from fac-XRe(CO)₃(bpy) (X = Cl or Br), and these strongly support the Re → π*(bpy) CT assignment for the lowest energy excited state.[161] Intense excited-state Raman signals have been observed that may be associated with the bpy radical anion and, additionally, the amount of charge transferred from Re to bpy π* has been estimated to be 0.84 in the lowest excited state of the ClRe(CO)₃(bpy) molecule.[162]
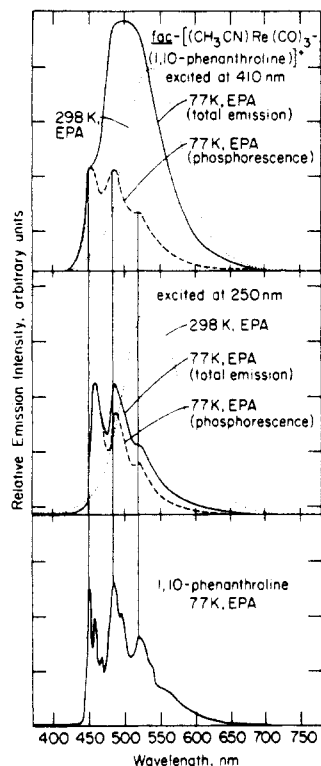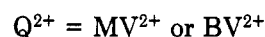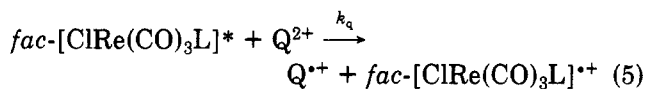
Figure 16. Emission spectra excited at 410 nm (top) and 250 nm (middle) for $\sim 10^{-4}$ M fac-[(CH$_3$CN)Re(CO)$_3$(phen)](CF$_3$SO$_3$) in EPA. The total emission of phen (bottom) is shown for comparison. The spectra are not shown at the same sensitivity. All spectra are total emission spectra except the two marked "phosphorescence", which were recorded with the phosphoroscope attachment in place. The phosphoroscope allows only the detection of emissions longer than ~ 50 μs. Reproduced with permission from ref 163. Copyright 1979 American Chemical Society.

A series of fac-[SRe(CO)$_3$L]$^+$ complexes, where S = CH$_3$CN, PhCN, pyridine (py), or piperidine (pip) and L = 1,10-phenanthroline (phen) or 2,2'-biquinoline (biquin), are known to exhibit multiple emission characteristics.[163] The emission spectra obtained for fac-[(CH$_3$CN)Re(CO)$_3$(phen)]$^+$ at 77 K and 298 K are representative of these Re(I) complexes and are depicted in Figure 16. The total emission band envelope at 77 K comprises two emission features; these have been assigned to Re $\rightarrow$ π*(phen) CT and $\pi \rightarrow$ π*(phen) IL excited states. Emission lifetimes at 77 K for these states are 11 and 75 μs, respectively. Use of a phosphoroscope that allows detection of only the long-lived (>50 μs) component clearly illustrates the spectral features of the IL emission (see Figure 16), and this is attributable to a perturbed $^3(\pi \rightarrow \pi)$ state on the phen ligand. The total emission spectrum is, however, dominated by the MLCT emission, and at 298 K the observed emission appears to be exclusively Re $\rightarrow$ π*-(phen) character with a lifetime of 0.80 μs. In accordance with the MLCT assignment, the emission maxima depend on S in the order CH$_3$CN > PhCN > py > pip; i.e., complexes exhibiting the lowest electron density on Re have the highest energy MLCT state.

The relative intensities of the Re $\rightarrow$ π* CT and $^3(\pi \rightarrow \pi$*) IL emissions are largely dependent on the energetic separation of these two excited states. Internal conversion between these two states will be controlled by the degree of electronic and vibronic coupling, but apparently this is slow in the fac-[SRe(CO)$_3$L]$^+$ system

even when the Re $\rightarrow$ π* and $^3(\pi \rightarrow \pi$*) states are close in energy. The large difference in geometry of these two excited states is probably the major factor contributing to this slow interconversion rate. When the energy gap between the Re $\rightarrow$ π* and $^3(\pi \rightarrow \pi$*) states is increased, the vibronic coupling is strengthened and only the MLCT emission is observable.[163]
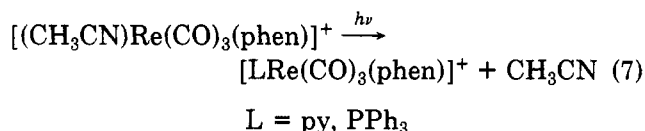
A number of studies have been concerned with the excited-state properties of these exceptionally long-lived and intensely emissive fac-XRe(CO)$_3$L complexes in solution. It has been established that the lowest energy MLCT state of fac-ClRe(CO)$_3$L (L = bpy, phen, 4,7-Ph$_2$-phen) undergoes electron transfer to N,N'-dimethyl-4,4'-bipyridinium (MV^{2+}) or N,N'-dibenzyl-4,4'-bipyridinium (BV^{2+}) and forms MV$^+$ or BV$^+$ (eq 5) as detected by transient absorption[164] or transient

$$\text{fac-[ClRe(CO)}_3\text{L]}^* + Q^{2+} \xrightarrow{k_q}$$
$$Q^{\bullet +} + \text{fac-[ClRe(CO)}_3\text{L]}^{\bullet +} \quad (5)$$

$$Q^{2+} = MV^{2+} \text{ or } BV^{2+}$$

Raman[165] spectroscopic techniques. Luminescence quenching measurements have yielded linear Stern–Volmer plots with bimolecular quenching constants at the diffusion-controlled limit for these electron-transfer processes.[164] Moreover, the thermal back reaction (eq 6) is also apparently diffusion controlled.

$$Q^{\bullet +} + \text{fac-[ClRe(CO)}_3\text{L]}^{\bullet +} \rightarrow$$
$$Q^{2+} + \text{fac-[ClRe(CO)}_3\text{L]} \quad (6)$$
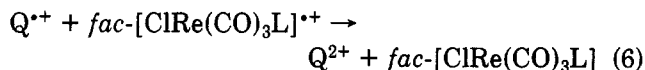
These spectroscopic results have illustrated that the excited-state electron-transfer process is essentially the same as in photoexcited Ru(bpy)$_3^{2+}$/MV^{2+} solutions.[166] Furthermore, luminescence quenching measurements show that fac-[(CH$_3$CN)Re(CO)$_3$(phen)]$^+$ on photoexcitation undergoes a most unusual electron-transfer mechanism that results in substitution of CH$_3$CN (see eq 7).[167]

$$[(\text{CH}_3\text{CN})\text{Re(CO)}_3(\text{phen})]^+ \xrightarrow{h\nu}$$
$$[\text{LRe(CO)}_3(\text{phen})]^+ + \text{CH}_3\text{CN} \quad (7)$$

$$L = py, PPh_3$$

The quantum yields for this excited-state electron-transfer process far exceed unity, and the substitution reaction proceeds via a 19-electron [(CH$_3$CN)Re-(CO)$_3$(phen)]^0 intermediate.

In a related study, luminescence quenching experiments on a BrRe(CO)$_3$(bpy)/ethanolamine/dimethylformamide system have implied that a 19-electron [BrRe(CO)$_3$(bpy)]$^-$ intermediate is involved in the photochemical reduction of CO$_2$.[168] Transient absorption spectra for the production and decay of this intermediate have illustrated that it may be observed in the nano- to microsecond timescale and that it reacts directly with CO$_2$. This system is specific for the photoinduced reduction of CO$_2$ to CO and is efficient with quantum yields reaching 0.15.

Effects of pressure and freezing on the radiative and nonradiative decay rates have been studied for ClRe(CO)$_3$(phen) and ClRe(CO)$_3$(4,7-Ph$_2$-phen) in solvents of varying polarity.[169] The radiative (k_r) and nonradiative (k_{nr}) decay rates have been obtained from emission quantum yield (ϕ_e) and lifetime (τ) data, ac-
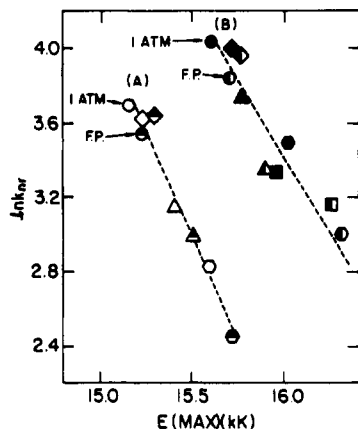
Figure 17. Plot of ln k_{nr} vs. energy of emission band maxima for (A) ClRe(CO)$_3$(4,7-Ph$_2$-phen) and (B) ClRe(CO)$_3$(phen) in various solvents (O DMF, $\Diamond$ CH$_3$CN, $\triangle$ heptanol, O m-xylene) in the liquid phase. F.P. represents value immediately before freezing. Open and solid symbols represent 1-atm data; half-filled symbols represent data just before freezing. Reproduced with permission from ref 169. Copyright 1982 American Institute of Physics.

cording to eq 8 and 9. Here ϕ_e has been corrected for solvent compressibility.

$$k_r = \phi_e / \tau \tag{8}$$

$$k_{nr} = (1 - \phi_e)/\tau \tag{9}$$

Radiative decay rates correlate substantially with the solvent dielectric constant (ϵ) over a 10-kbar pressure range, and this correlation is particularly evident at the phase transition of the solvent. In nonpolar solvents k_r and ϵ are only slightly changed at the solvent freezing point, whereas in polar solvents k_r and ϵ drop discontinuously. This large drop in ϵ for the polar solvents on freezing is due to the great reduction in the orientational polarizability of the solvent molecules. From these results it can be inferred that the transition moment is affected in a similar manner.

Nonradiative decay rates in both the liquid and the solid form depend primarily on the energy of the emission peak, with k_{nr} decreasing as the band maxima blue shift; the data for ClRe(CO)$_3$L in several solvents are shown in Figure 17. This exponential dependence of k_{nr} on the energy gap between the ground and excited states is in agreement with proposed theory (eq 10) that

$$\log F(E) = \log F(E_0) - [(E - E_0)/\eta]f; \quad E > E_0 \tag{10}$$

relates the radiationless Franck–Condon factor to the triplet excited-state energy,[170] where F is the Franck–Condon factor, E is the triplet ground-state energy, and E_0, η, and f are molecular constants.[169,170] As the emission maxima move to higher energy, F and therefore k_{nr} decrease.

As the pressure is increased, the orientational polarizability and consequently the solvent polarity of the solvent molecules are increased[171] and a blue shift is observed in the emission maxima from either the liquid or solid phases.[169] Accompanying this pressure increase is a decrease in k_{nr}, in accordance with the energy gap expression (eq 10). However, at the phase transition on freezing, k_{nr} actually rises dramatically despite a blue shift in the emission band. This seemingly anomalous effect may be interpreted on a potential diagram in which the ground-state potential well becomes narrower on solidification (see Figure 18). Evidence for this has
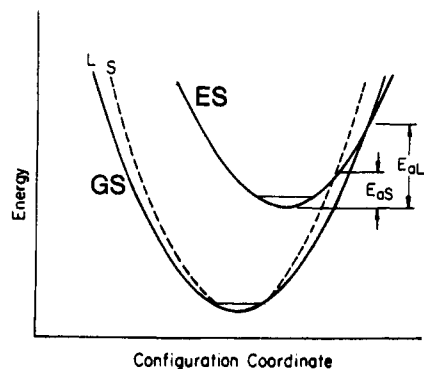

Configuration Coordinate

Figure 18. Potential-energy diagram for ground state (GS) and excited state (ES) of ClRe(CO)$_3$(phen) complexes in liquid (L) and solid (S) phases. E_a is the energy barrier between the intersection of the ground- and excited-state surfaces. Reproduced with permission from ref 169. Copyright 1982 American Institute of Physics.

been obtained experimentally as the emission band half-widths are greater for the complexes in the solid phase than in liquid form. In this description the excited-state potential well crosses the ground-state well at a higher energy for the liquid than for the solid. The radiationless transition probability W can be related to the energy barrier by the following equations.[172,173]

$$W = \frac{C^2(2\pi)^{1/2}}{h(E_M k_B T^*)^{1/2}} \exp(-E_a/k_B T^*) \tag{11}$$

$$k_B T^* = \tfrac{1}{2} h \langle \omega \rangle \coth (h \langle \omega \rangle 2 k_B T) \tag{12}$$

Here C^2 is a constant representing energy parameters for internal conversion and intersystem crossing, h is Planck's constant, k_B is the Boltzmann constant, $\langle \omega \rangle$ is the mean vibrational frequency, $2E_M$ is the Stokes shift, and E_a is the energy barrier between the intersection of the ground- and excited-state potential energy surfaces. A narrowing of the ground-state potential well will result in an increase of W and hence k_{nr}.

Studies of the energy gap law have been applied to the MLCT excited state for a series of fac-[LRe(CO)$_3$(bpy)](PF$_6$) compounds.[174] Luminescence data and the derived radiative and nonradiative decay parameters are listed in Table IX. In this series the emission energies (E_{em}) systematically depend on the σ-donor and π-acceptor properties of the nonchromophoric ligand L. From theory by Englman, Jortner, and Freed[172,173] a relationship has been determined between the nonradiative rate constant (k_{nr}) and the emission energy (E_{em}) (see eq 13–16).[174] Here, ω_M is the angular

$$\ln k_{nr} = \ln \beta_0 - S_M - \left[\frac{\gamma_0 E_{em}}{h\omega_M} \right] + \left[\frac{b\chi_0}{h\omega_M} \right] + \left[S_L \left(\frac{\omega_L}{\omega_M} \right) (\gamma_0 + 1) \right] \tag{13}$$

$$\beta_0 = C^2 \omega_k \left[\frac{\pi}{2h\omega_M E_{em}} \right]^{1/2} \tag{14}$$

$$\gamma_0 = \ln \left[\frac{E_{em}}{S_M h\omega_M} \right] - 1; \quad b = (k_B T/h\omega_M)(\gamma_0 + 1)^2 \tag{15}$$

$$\omega_M = 2\pi\nu_M; \quad S_M = 1/2\Delta_M^2; \\ \chi_0 = S_0 h \langle \omega_0 \rangle \tag{16}$$

TABLE IX.[a] **Excited-State Decay Parameters for the MLCT Excited States of *fac*-[LRe(CO)$_3$(bpy)](PF$_6$) Complexes in Deoxygenated Methylene Chloride Solution at 296 K**

L	E_{em}, 10^{-3} cm^{-1}	ϕ_e	τ, ns	k_r, s^{-1}	k_{nr}, s^{-1}
Cl$^-$	16.08	0.005	51	9.79×10^4	1.95×10^7
4-(N,N-dimethylamino)pyridine	16.39	0.017	95	1.78×10^5	1.03×10^7
4-aminopyridine	16.75	0.052	129	4.06×10^5	7.34×10^6
N-methylimidazole	16.98	0.058	161	3.59×10^5	5.85×10^6
4-ethylpyridine	17.64	0.18	604	2.96×10^5	1.36×10^6
pyridine	17.92	0.16	669	2.36×10^5	1.26×10^6
P(CH$_3$)$_3$	18.38	0.27	1169	2.32×10^5	6.23×10^5
CH$_3$CN	18.66	0.41	1201	3.43×10^5	4.90×10^5

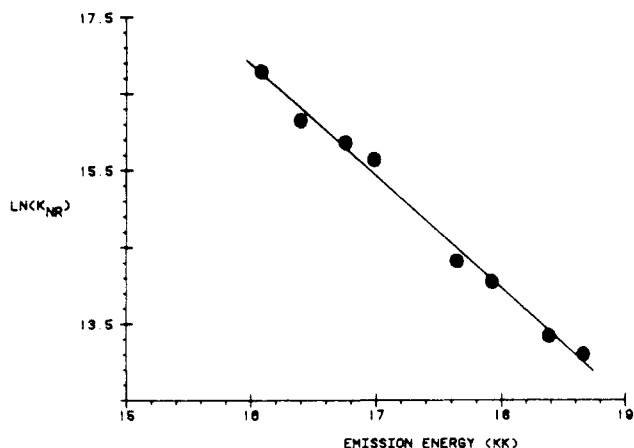[a] Reproduced with permission from ref 174. Copyright 1983 American Chemical Society.

Figure 19. Plot of ln k_{nr} vs. E_{em} for the MLCT excited states of the series of complexes *fac*-[LRe(CO)$_3$(bpy)](PF$_6$) at 296 K in methylene chloride solution. Reproduced with permission from ref 174. Copyright 1983 American Chemical Society.

Figure 20. Emission spectra of 1.5×10^{-4} M ClRe(CO)$_3$(4,7-Ph$_2$-phen) in decalin in the presence of (a) 0 M, (b) 8×10^{-4} M, (c) 2×10^{-3} M, and (d) 8×10^{-3} M DMA. Reproduced with permission from ref 175. Copyright 1980 Elsevier Sequoia S.A.

frequency of the ground-state acceptor vibration, h is Planck's constant, k_B is the Boltzmann constant, T is temperature, C^2 is the nuclear momentum matrix element for the promoting vibration (or vibrations) of angular frequency ω_k that lead to the transition between states, S_M is a measure of the distortion of ω_M in the MLCT excited state, Δ_M is the fractional displacement in vibration ω_M between the thermally equilibrated ground and excited states, S_L and ω_L are the low-frequency vibration equivalents of S_M and ω_M, $S_0 = 1/2\Delta_0{}^2$, a measure of the average solvent vibrational distortion in the MLCT excited state, and $\langle\omega_0\rangle$ is mean frequency for the collective trapping vibrations of the solvent.[172-174] Equation 13 predicts that for this series of complexes with closely related chromophores (hence $C^2\omega_k$ and $S_L\omega_L$ remain relatively constant) ln k_{nr} should reduce linearly with increasing emission energy (E_{em}). This relationship is indeed observed experimentally (see Figure 19).

An emitting charge-transfer (CT) exciplex has been reported to be formed between *fac*-ClRe(CO)$_3$(4,7-Ph$_2$-phen) as electron acceptor and N,N-dimethylaniline (DMA) as electron donor.[175] Emission spectra obtained from *fac*-ClRe(CO)$_3$(4,7-Ph$_2$-phen) in decalin with various concentrations of DMA are shown in Figure 20. Importantly, the emission does not appear to be quenched by addition of DMA to the decalin solution, but it is quenched according to Stern–Volmer kinetics by adding DMA in acetonitrile. The lack of emission in acetonitrile solution is consistent with the quenching of a CT exciplex in a polar solvent because of its dissociation into ions, as previously noted for
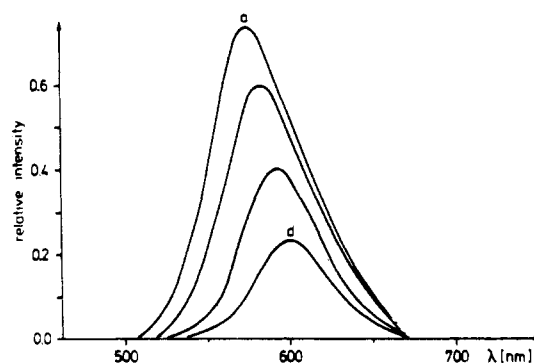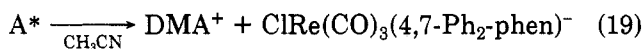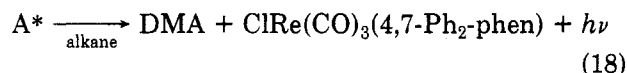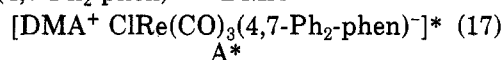
organic compounds.[176,177] These results can be expressed in eq 17–19. The enthalpy of this CT exciplex

$$\text{ClRe(CO)}_3\text{(4,7-Ph}_2\text{-phen)}^* + \text{DMA} \rightarrow$$
$$[\text{DMA}^+ \ \text{ClRe(CO)}_3\text{(4,7-Ph}_2\text{-phen)}^-]^* \quad (17)$$
$$A^*$$

$$A^* \xrightarrow{\text{alkane}} \text{DMA} + \text{ClRe(CO)}_3\text{(4,7-Ph}_2\text{-phen)} + h\nu \quad (18)$$

$$A^* \xrightarrow{\text{CH}_3\text{CN}} \text{DMA}^+ + \text{ClRe(CO)}_3\text{(4,7-Ph}_2\text{-phen)}^- \quad (19)$$

formation has been determined to be -5.7 kcal mol^{-1} and the energy of A* estimated to be ~48 kcal. This compares to a value of 51 kcal that has been calculated for A* from the redox potentials of *fac*-ClRe(CO)$_3$-(4,7-phen) and DMA.[175,178,179] Exciplex formation was also observed with other amines as electron donors but not with any electron acceptors.

Excited-state lifetimes have been measured for a series of *fac*-[LRe(CO)$_3$(bpy)]$^+$ (L = NC(CH$_2$)$_n$CH$_3$, n = 0, 2, 5, 6, 7, 9, 10, 13, 17) species in room temperature solution.[180] Although the emission is of d → π^*(bpy) character and thus the alkyl chain is electronically passive in this system, the emission lifetimes of these complexes depend substantially on the nitrile chain length. The lifetime τ is essentially invariant for n = 0–5, but rises steeply over the n = 6–13 range and then remains constant for n > 13. This overall increase in lifetime may exceed a factor of 3 in some solvents; clearly the MLCT excited-state properties in this series are greatly perturbed by the length of the nitrile chain. The lifetime dependence may be interpreted in terms of changes in the environment about the MLCT excited state where the longer alkyl groups are able to undergo a foldback of the chain onto a face of the bpy ligand. This results in displacement of the solvent, and the
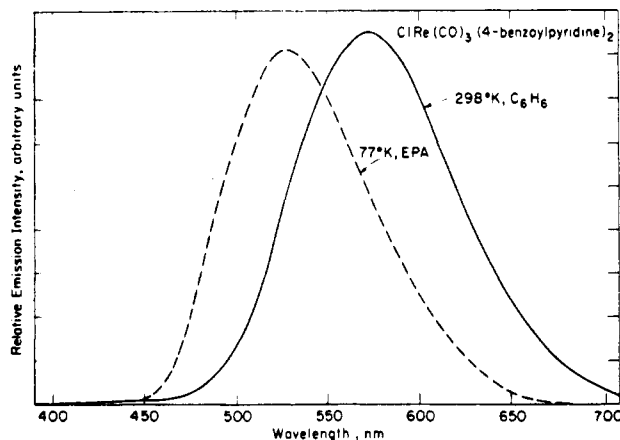
Figure 21. Total corrected emission spectra of ~10^{-4} M ClRe-$(CO)_3(4\text{-BN-py})_2$ in solution following excitation at 330 nm. The 298 and 77 K emission spectra are not shown at the same sensitivity. Reproduced with permission from ref 181. Copyright 1978 American Chemical Society.

varying solvent contact significantly influences the rates of nonradiative decay from the MLCT excited state. Short chains ($n \leqslant 5$) are unable to fold back, medium chains ($6 \leqslant n \leqslant 13$) are able to interact with the bpy ligand, and long chains ($n > 13$) can completely cover one bpy face. It has been estimated, with the use of space-filling molecular models, that when $n = 9$ approximately 50% of the bpy face is shielded from solvent contact, whereas when $n = 13$ almost all of a bpy face is solvent shielded.[180]

Luminescence properties of the closely related *fac*-XRe$(CO)_3L_2$ (X = Cl, Br, or I and L = a pyridine derivative) complexes depend substantially on the nature of the coordinated ligand L.[181,182] A comparison of the emission spectra of *fac*-ClRe$(CO)_3L_2$, where L = 4-benzoylpyridine (4-BN-py) and 3-benzoylpyridine (3-BN-py), is illustrated by Figures 21 and 22.[181] As in the previously discussed *fac*-[SRe$(CO)_3L]^+$ complexes, these room temperature emissions are broad and unstructured and are typical of those from a Re → π^*(L) excited state. The lifetimes of ~0.5 μs at 298 K are consistent with this MLCT assignment. These complexes differ greatly, however, in their emission characteristics at 77 K. When L = 4-BN-py, the emission feature remains unstructured, but intensifies and substantially blue shifts (see Figure 21); this appears to be another example of the luminescence rigidochromism effect on the MLCT state. The emission lifetime of this compound at 77 K is 39 μs. In contrast, when L = 3-BN-py, the emission becomes much more structured on cooling to 77 K and exhibits features resembling those of the free ligand (see Figure 22). Hence, the total emission spectrum at 77 K may be attributed to consist of Re → π^*(L) and ^{3}(n → π^*) IL excited states. The lifetimes of these emission components at 77 K are 18 and 1400 μs, respectively, in support of the above assignments. The similarity of the IL and free ligand spectral features (see Figure 22) indicates that the ^{3}(n → π^*) IL state is only slightly perturbed from that of the corresponding state in the free ligand. Multiple emission from the 3-BN-py complex illustrates that the MLCT and IL excited states are not thermally equilibrated at low temperature, even though they have been determined to be close in energy. When the energy gap between these states is increased (i.e., when L = 4-BN-

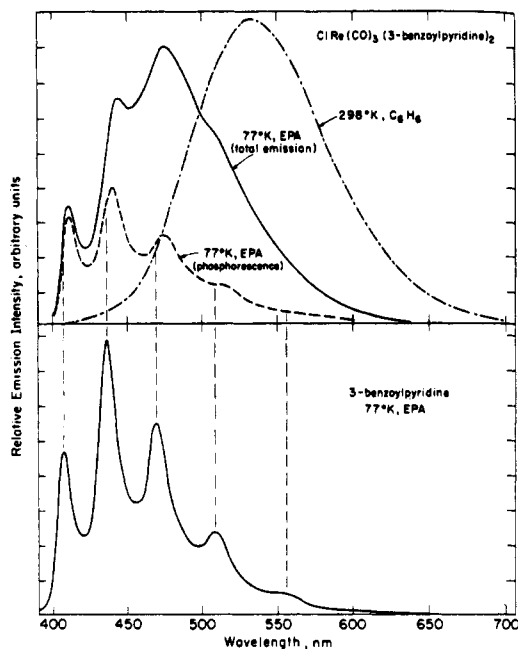**Figure 22.** Corrected emission spectra of ~10^{-4} M ClRe-$(CO)_3(3\text{-BN-py})_2$ and ~10^{-4} M 3-BN-py following excitation at 330 nm. The spectra are not shown at the same sensitivity. All spectra are total emission spectra except the one marked "phosphorescence", which was recorded with a phosphoroscope in place during spectral acquisition. The phosphoroscope allows only the detection of emission longer than ~1.0 ms. Reproduced with permission from ref 181. Copyright 1978 American Chemical Society.

py), the vibronic coupling is strengthened and only MLCT emission is observed.[163,181]

Similarly, a variable mixture of Re → π^*(L) CT and ^{3}(π → π^*) IL characters have been assigned to the emissive states of *fac*-XRe$(CO)_3L_2$ complexes, where X = Cl, Br, or I and L = 4-phenylpyridine (4-Ph-py) or 4,4'-bipyridine (4,4'-bpy).[182] The L = 4,4'-bpy complexes may be described as "pure" MLCT emitters, whereas the L = 4-Ph-py complexes have considerable mixing of IL character in the lowest energy excited state. A further interesting aspect of the emission from the L = 4-Ph-py complex is that despite the MLCT and IL assignment only one lifetime has been recorded at 77 K, in contrast to the above L = 3-BN-py complex. This has been attributed to substantial mixing of the Re(dπ) → π^*(L) and π → π^* states in the former complex, whereas in the latter compound the Re(dπ) → π^*(L) state may not be greatly perturbed by the n → π^* IL state.

Mixing of the MLCT and IL excited states in the *fac*-ClRe$(CO)_3(4\text{-Ph-py})_2$ complex is also reflected in the reported radiative (k_r) and nonradiative (k_{nr}) decay constants. For this complex in EPA from 298 to 50 K, k_r decreases from 6700 to 2100 s^{-1}, and k_{nr} decreases from 6.6×10^5 to 2.1×10^2 s^{-1}.[180] These results are in contrast to those observed for Ta$(CO)_6^{-}$ [25] and XRe-$(CO)_5$[146] in which k_r was invariant with changes in temperature and the luminescence was assigned to a single excited state (vide supra).

The protonated form of the above *fac*-ClRe$(CO)_3L_2$ complexes are notably not emissive under room temperature solution conditions.[182] The absence of solution emission from the protonated complex may either be due to increased vibrational relaxation or because of an electron-transfer mechanism to the attached proton.
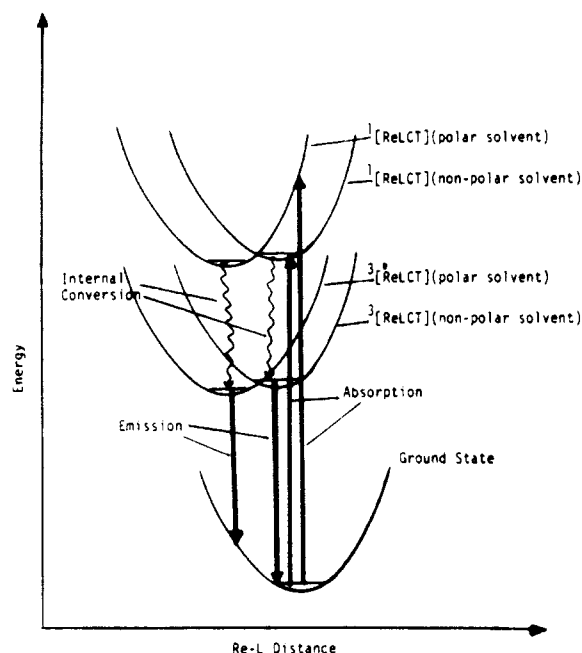
Figure 23. Representation of solvent dependencies of state geometries and transition energies relative to the ground state in fac-XRe(CO)₃L₂ complexes. Reproduced with permission from ref 182. Copyright 1979 American Chemical Society.

Unusual solvent effects have been reported for the luminescence of fac-XRe(CO)₃L₂ (L = 4-Ph-py, 4,4'-bpy) complexes. Emission maxima of these compounds are blue shifted between 500 and 1000 cm⁻¹ in benzene compared to acetonitrile, despite a >2000-cm⁻¹ shift to the red for the Re → π*(L) absorption band in the same solvents. This apparent contradiction may be reasoned on a potential-energy diagram (see Figure 23) in which solvation effects on equilibrium geometry of the ¹MLCT and ³MLCT excited states are described with respect to the ground state.[182] In this qualitative scheme the excited state is shown to undergo a compression of the Re–L bond concordant with the induced dipole produced on MLCT excitation. The absorption and emission energies are thus solvent shifted in opposite directions. It should be recognized, however, that a potential-energy description involving the formation of a longer Re–L bond in the MLCT excited states would equally account for the observed absorption and emission solvent dependencies.

Luminescence measurements of fac-XRe(CO)₃L₂ (X = Cl or I and L = 4-BN-py or 4-AC-py) complexes have illustrated that the lowest lying MLCT excited state may be quenched via an electron-transfer process.[183] The mechanism of reaction is similar to that discussed above for the closely related fac-XRe(CO)₃L (L = bpy or phen) compounds. A significant feature of this reaction is that the coordinated ligand is able to undergo a redox process and these excited complexes can be used to efficiently sensitize the photoreduction of ketones to alcohols.

A series of Re(I) complexes of the general formula [Re(CO)₂(bpy)L₂](PF₆), where L is a tertiary phosphine, have also been reported to luminescence strongly in fluid media.[184] The emission maxima of the complexes correlate well with the quantity $\Delta E_{1/2}$, where $\Delta E_{1/2}$ is the difference between the reduction potential for the Re(II)/Re(I) couple and the ligand-based (0)/(1−) reduction. Correlations of this type have also appeared

in the literature for classical coordination systems.[185]

Recently luminescence has been observed for a number of (C₅H₄R)M(CO)₂L (M = Mn or Re, R = H or CH₃, and L = a series of pyridine derivatives) complexes in room temperature solution.[186] This finding is unusual as it represents the first determination of radiative decay from a Mn carbonyl complex under fluid conditions. For each complex the emission has been associated with the lowest lying M → π*(L) absorption system.[186,187]

Metal–metal-bonded Re₂(CO)₈(phen) has been determined to emit at λ_em ~650 nm in EPA at 77 K.[188] The lowest energy absorption band has been assigned to a (M–M)σ_b → π*(L) CT transition and not to σ_b → σ* or dπ → σ* transitions as this band is sensitive to changes in the nature of ligand, solvent, and temperature. The 95-μs emission lifetime and ~10⁻² emission quantum yield strongly support this MLCT assignment and suggest that the emitting state has considerable triplet character. Emission has also been observed from the pure solid complexes but not from the corresponding Mn complexes under comparable experimental conditions.

Emission properties of the closely related metal–metal-bonded Ph₃GeRe(CO)₃(phen) and Ph₃SnRe(CO)₃(phen) complexes have been investigated.[189,190] As in the above system, these complexes exhibit emission from low-lying metal–metal σ_b → π*(L) excited states; however, in this case the emission is detectable under room temperature solution conditions. Although these complexes undergo efficient photodissociation at 298 K (φ ~0.25), the obtained emission quantum yields and lifetimes are ~10⁻³ and ~2 μs, respectively. Quenching experiments have established that photoreaction (Re–Ge or Re–Sn bond breaking) and emission both occur from the metal–metal σ_b → π*(L) excited state. Rate constants ($k*_{diss}$) for conversion of this excited state to photoproduct have been calculated from the emission lifetimes and reaction quantum yields and are 1.0 × 10⁵ and 1.3 × 10⁵ s⁻¹ for the Ge and Sn compounds, respectively. It has been estimated that this represents at least a 10¹¹ enhancement in the excited-state reaction rate for the dissociation of Re–Ge or Re–Sn bonds as compared to the ground-state reaction for these complexes.[189] The corresponding Mn complexes have also been determined to emit, but only in 77 K EPA solutions; emission yields and lifetimes are ~6 × 10⁻⁴ and ~0.4 μs, substantially lower than those for the Re analogues.[190] These Mn complexes emit at higher energies than the Re derivatives, and they strongly overlap with the lowest energy absorption. These observations have led to the suggestion that the emission from the Mn complexes may arise from the lowest lying metal–metal σ_b → π*(L) charge-transfer singlet state.

Emission has been characterized from the mixed-valence [Cl(OC)₃Re(bpym)Ru(bpy)₂](PF₆) (bpym = 2,2'-bipyrimidine) dimer complex as a solid at 77 K, but is notably absent from the solid [Cl(OC)₃Re(bpym)-Re(CO)₃Cl] dimer, even as low as 4 K.[191] The lack of emission from the latter complex is unexpected as the corresponding monomeric species ClRe(CO)₃(bpym) exhibits an intense MLCT emission (λ_em = 567 nm) in room temperature solution, and other bridged structures such as (OC)₅W(pyz)W(CO)₅[136,137] or (bpy)₂Re-(bpym)Ru(bpy)₂⁴⁺[192] complexes emit from their lowest

TABLE X.[a] **Emission Properties of Polynuclear Rhenium Carbonyl Hydrides**

complex	solvent conditions (T, K)	E_{em},[b] cm^{-1}	$\Delta\nu_{1/2}$,[c] cm^{-1}	ϕ_e[d]	τ,[d] μs
$H_4Re(CO)_{12}$	pure solid (298)	13 700	2000		1.02
	pure solid (77)	14 600	1700		7.09
	3-methylpentane (298)	13 800	2100	0.0034	<0.02
	3-methylpentane (77)	14 600	1700	0.25	12.11
	toluene (298)	13 800	2100	0.032	0.096
$D_4Re_4(CO)_{12}$	pure solid (298)	13 700	2100		1.30
	pure solid (77)	14 600	1700		8.65
	3-methylpentane (298)	13 700	2200	0.0039	<0.02
	3-methylpentane (77)	14 600	1700	0.33	15.97
	toluene (298)	13 700	2200	0.037	0.111
$[n\text{-}Bu_4N]_2[H_6Re_4(CO)_{12}]$	pure solid (77)	17 900	3600		1.64
	2-Me-THF (77)	17 900	3500	0.012	2.16
$[n\text{-}Bu_4N]_2[D_6Re_4(CO)_{12}]$	pure solid (77)	17 900	3600		2.35
	2-Me-THF (77)	17 800	3600	0.020	3.42

[a] Reprinted with permission from ref 195. Copyright 1981 American Chemical Society. [b] Error limits are ±100 cm^{-1}. [c] $\Delta\nu_{1/2}$ is the full width at half-height of the emission band; limits are ±100 cm^{-1}. [d] Error limits of ϕ_e and τ are ±10%.

energy M → π^*(bridging-L) excited states. It has been suggested that a Re(I) → Re(I) charge-transfer (MMCT) excited state may be lowest lying in this system and that this state may effectively quench the MLCT emission. On the other hand, the Re(I)–L–Ru(II) dimer at 77 K yields emission at λ_{em} = 774 nm, which has been associated with a Ru(II) → π^*(bpym) CT state. It has been shown that the emission from this mixed valence complex is obtained following either direct excitation to the Ru(II) → π^*(bpym) CT state or via an intramolecular electron-transfer process[193,194] after initial population of the higher lying Re(I) → π^*(bpym) CT excited state.

Excited-state properties of polynuclear rhenium carbonyl hydrides have been investigated following observation of emission from $H_4Re_4(CO)_{12}$ and [n-$Bu_4N]_2[H_6Re_4(CO)_{12}]$.[195] The lowest energy excited state of these clusters has been identified as metal centered involving metal–metal bonding orbitals that are delocalized over the core of metal atoms and perturbed by the interaction with the H+ atoms.[195,196] Emission from the $H_4Re_4(CO)_{12}$ complex has been recorded from the solid form or from hydrocarbon solutions at 77 or 298 K, but the $[H_6Re_4(CO)_{12}]^{2-}$ cluster has only been observed to emit at 77 K. Typical emission spectra of these hydrides are depicted in Figures 24 and 25, and the emission spectral features recorded in a variety of experimental conditions are summarized in Table X. In each case the emission features are associated with the lowest energy delocalized metal–metal-centered state; from the lifetime values this state is thought to be predominantly of triplet character.

Replacement of ^{1}H by ^{2}H significantly affects the excited-state properties, increasing the emission quantum yield and lifetime by 20–30% for the neutral polynuclear carbonyl and by ~50% for the anionic complex (see Table X). Calculated radiative and nonradiative decay parameters illustrate that k_{nr} is decreased on deuteriation while k_r remains relatively constant. This effect can be identified as an intramolecular one because deuteriation of the solvent does not affect the experimentally determined parameters. It has been suggested[195] that the greater influence of perdeuteriation on the excited-state properties of $[H_6Re_4(CO)_{12}]^{2-}$ may pertain to the edge-bridging nature of the H atoms in this complex,[197] whereas in
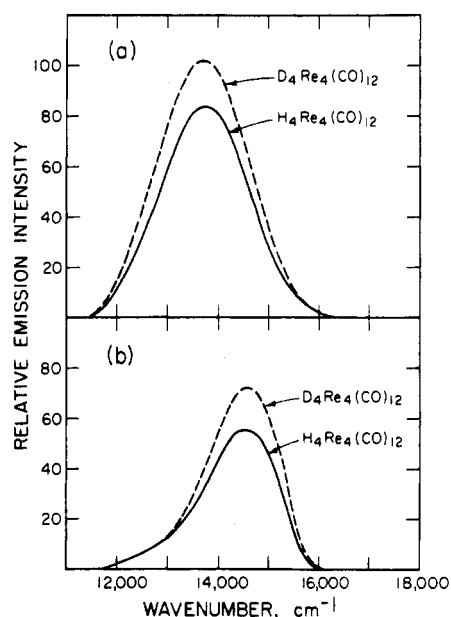

Figure 24. Corrected emission spectra for $H_4Re_4(CO)_{12}$ (—) and $D_4Re_4(CO)_{12}$ (- - -) in 3-methylpentane at (a) 298 K and (b) 77 K. The excitation wavelength is 470 nm. The spectra in (a) were recorded at ~1000 times the sensitivity as those in (b). Reproduced with permission from ref 195. Copyright 1981 American Chemical Society.
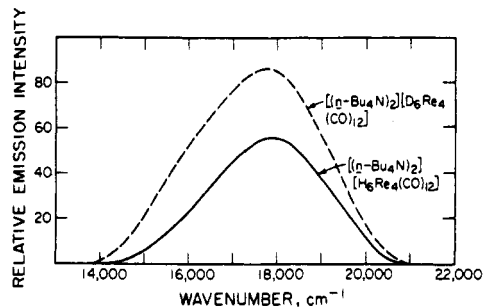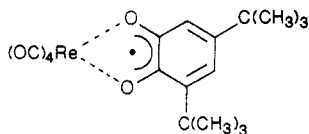

Figure 25. Corrected emission spectra for [n-$Bu_4N]_2[H_6Re_4(CO)_{12}]$ (—) and [n-$Bu_4N]_2[D_6Re_4(CO)_{12}]$ (- - -) in 2-methyltetrahydrofuran at 77 K. The excitation wavelength is 375 nm. Reproduced with permission from ref 195. Copyright 1981 American Chemical Society.

$H_4Re_4(CO)_{12}$ the H atoms are of face-bridging nature.[198,199] In the former complex the Re–H stretching frequency is at greater energy, and this will tend to increase the rate of nonradiative decay.[195] Alternatively,

this isotope effect on k_{nr} may be related to the energy gap law (vide supra), as it is noted that the emitting state of $[H_6Re_4(CO)_{12}]^{2-}$ is at higher energy than that of the $H_4Re_4(CO)_{12}$ complex. Finally, luminescence quenching experiments on $H_4Re_4(CO)_{12}$ indicate that energy transfer occurs from the lowest excited state at rates close to the diffusion-controlled limit, and these are consistent with a triplet assignment in this compound. The energy of this excited state has been estimated to be at ~46 kcal mol^{-1}.[195]

An emission spectrum of a Re(CO)$_4$(DTBQ)$^{\bullet}$ (DTBQ = 3,5-di-*tert*-butyl-*o*-benzoquinone) radical complex has been obtained in benzene solution at room temperature.[200] This constitutes the first report of lumines-

cence from a transition-metal organometallic radical complex. The observed emission spectrum has band centers at 345 and 705 nm and closely mirrors the absorption spectrum, suggesting that the quinone group is still planar in the radical species.

4. Iron, Ruthenium, and Osmium Complexes

There are a number of reports concerning luminescence of porphyrins that contain carbonyl ligands. Both fluorescence (λ_{em} = 556 nm) and phosphorescence (λ_{em} = 658 nm) have been determined from carbonyloctaethylporphyrinpyridineruthenium(II), Ru(OEP)(CO)-(py).[201,202] The high-energy emission component of this ruthenium porphyrin carbonyl is not observable at temperatures below −10 °C and has, therefore, been attributed to thermally activated ("E-type") delayed fluorescence.[202] Carbonylpiperidinetetraphenyl-porphyrinruthenium(II), Ru(TPP)(CO)(pip), gives rise to typical porphyrin π,π^* luminescence.[203,204] The LF state is believed to be higher in energy than the lowest porphyrin triplet state in this molecule. Replacement of Ru by the lighter Fe atom reduces the LF splitting and the Fe(TPP)(CO)(pip) complex does not exhibit the characteristic porphyrin phosphorescence, but an emission assigned to the lowest energy LF state.[203] It is not possible to directly observe the LF bands of these compounds as they are hidden under the intense spin-allowed π,π^* porphyrin absorptions.[205] However, this suggestion of a lowest lying LF state is in accordance with previous studies on porphyrin emission spectra which have established that excited states at lower energy than the porphyrin triplet effectively quench the porphyrin phosphorescence.[206,207]

A comparative study of the emission properties of Ru(OEP)(CO)(py) and Os(OEP)(CO)(py) complexes has also revealed emitting states of different excited-state character.[208] The Ru(OEP)(CO)(py) compound gives rise to phosphorescence from a porphyrin π,π^* triplet with a sharp O–O origin at 653 nm; emission quantum yields and lifetimes at 77 K are ~0.06 and 405 μs, respectively. The $^3(\pi,\pi^*)$ phosphorescence is observable at room temperature, but no evidence has been found for delayed fluorescence from Ru(OEP)(CO)(py) in this work.[208] Emission from the Os(OEP)(CO)(py) complex is contrastingly broad (720–780-nm region), weak (ϕ_e ~6 × 10^{-4}), and short-lived (τ <6 μs).

TABLE XI.[a] **Emission Band Maxima and Decay Lifetimes for Monomer and Ligand-Bridged Dimer Dimer Os(II) Complexes in Ethanol–Methanol (4:1 v/v) Solution at 77 K**[b]

compound	λ_{em}, nm	τ,[c] ns
[(bpy)$_2$(OC)Os(4,4'-bpy)][PF$_6$]$_2$	546	5260
[(bpy)$_2$(OC)Os(4,4'-bpy)Os(Cl)(phen)(dppe)]-[PF$_6$]$_3$[e]	550	<10[d]
	625	3930
[(bpy)$_2$(OC)Os(bpa)][PF$_6$]$_2$	550	5430
[(bpy)$_2$(OC)Os(bpa)Os(Cl)(phen)(dppe)][PF$_6$]$_3$[e]	550	45
	640	3740

[a] Reprinted with permission from ref 194. Copyright 1985 American Chemical Society. [b] 4,4'-bpy = 4,4'-bipyridine; bpa = 1,2-bis(4-pyridyl)ethane; dppe = *trans*-1,2-bis(diphenylphosphino)-ethylene. [c] Error <5% in lifetimes. [d] Lifetime too short to be resolved. [e] Dual emissions are observed for the dimers: an intense component (>90% of total emission) centered at λ = 625 nm (L = 4,4'-bpy) or 640 nm (L = bpa) with a weak band on the high-energy side.

Moreover, this emission is substantially red shifted from the $^3(\pi,\pi^*)$ emission of the analogous Ru complex, even though the absorption band of the Os(II) species is blue shifted from the Ru complex. As a consequence, the emission of the Os(OEP)(CO)(py) complex can be assigned to a $^3(d,\pi^*)$ MLCT excited state.[208]
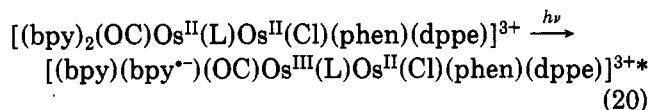
A series of para-substituted (tetraphenylporphine)-ruthenium(II) carbonyl complexes, Ru(p-XTPP)(CO), where X = MeO, Me, H, F, Br, and Cl, have been observed to display porphyrin-ring $^3(\pi,\pi^*)$ luminescence in room-temperature solution.[209] The emission of these compounds is centered at 730 ± 10 nm with an excited-state lifetime of 30 ± 10 μs, but these parameters depend on the substituent attached to the phenyl ring. Emission maxima shift to longer wavelengths and the lifetimes become longer as the electron-donor ability of the substituent increases. The emission data of this system correlate well with the Hammett substituent constant, σ_p.[209]

Also relevant are the closely related Os(TTP)(CO)L complexes, where TTP = *meso*-tetra-*p*-tolylporphyrin and L = CH$_3$OH or py, which exhibit luminescence at 653 and 651 nm, respectively.[210] The short-lived emission (τ ~10 ns) is fairly intense, even at room temperature, and has been assigned to π,π^* phosphorescence from the T$_1$(0,0) state of the porphyrin ring. This result contrasts with the above (d,π^*) MLCT assignment for the corresponding Os(OEP)(CO)(py) complex.[208]
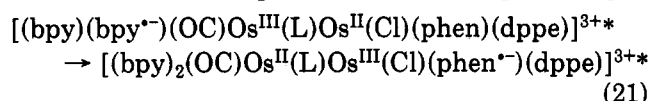
Emission properties of *cis*-[ClOs(CO)L$_2$](PF$_6$) (L = bpy or phen) complexes have been studied as part of an extensive Os(II) polypyridyl series.[211] Both bpy and phen complex cations have been reported to emit at 700 nm with emission quantum yields of 1.68 × 10^{-3} and 6.84 × 10^{-3}, respectively.

A study of the emission maxima and lifetimes of a series of monomer and ligand-bridged dimer complexes of Os(II) has indicated that the photochemically produced mixed-valence dimers undergo deactivation via an intramolecular electron-transfer mechanism.[194] Emission data obtained from these compounds in ethanol:methanol (4:1 v/v) glasses at 77 K are shown in Table XI; the emission bands centered at ~550 and 625–640 nm are associated with the Os $\rightarrow$ π^*(bpy) and Os $\rightarrow$ π^*(phen) excited states, respectively. Here L = 4,4'-bipyridine (4,4'-bpy) or 1,2-bis(4-pyridyl)ethane (bpa), and dppe = *trans*-1,2-bis(diphenylphosphino)-ethylene. In the dimer complexes it is noticeable that
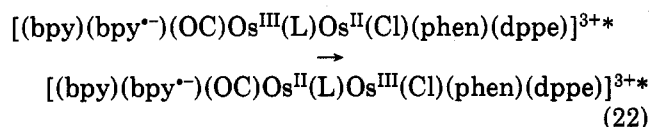
the emission from the Os(III)(phen$^{\cdot-}$) state is much more intense and longer lived than the emission of the Os(III)(bpy$^{\cdot-}$) state and that the latter emission is considerably quenched in comparison to the related monomers. Apparently electronic coupling is weak in these dimer systems as reflected in their absorption spectral features which are similar to those of the monomers. Thus, excitation into the higher lying Os(II) $\rightarrow \pi^*$(bpy) state produces a mixed-valence dimer (see eq 20). Importantly, excitation spectra illustrate that

$$[(bpy)_2(OC)Os^{II}(L)Os^{II}(Cl)(phen)(dppe)]^{3+} \xrightarrow{h\nu}$$
$$[(bpy)(bpy^{\cdot-})(OC)Os^{III}(L)Os^{II}(Cl)(phen)(dppe)]^{3+*}$$
$$(20)$$

Os(II) $\rightarrow \pi^*$(bpy) excitation does not give rise to emission from the Os(III)(phen$^{\cdot-}$) state and, therefore, the short Os(III)(bpy$^{\cdot-}$) excited-state lifetime cannot be reasoned by invoking energy transfer between these two excited states (see eq 21). Instead, the quenching of

$$[(bpy)(bpy^{\cdot-})(OC)Os^{III}(L)Os^{II}(Cl)(phen)(dppe)]^{3+*}$$
$$\rightarrow [(bpy)_2(OC)Os^{II}(L)Os^{III}(Cl)(phen^{\cdot-})(dppe)]^{3+*}$$
$$(21)$$

the Os(III)(bpy$^{\cdot-}$) state has been attributed to an intramolecular electron-transfer mechanism (see eq 22).

$$[(bpy)(bpy^{\cdot-})(OC)Os^{III}(L)Os^{II}(Cl)(phen)(dppe)]^{3+*}$$
$$\rightarrow$$
$$[(bpy)(bpy^{\cdot-})(OC)Os^{II}(L)Os^{III}(Cl)(phen)(dppe)]^{3+*}$$
$$(22)$$

Electrochemical measurements have shown that this process is an exothermic one.[194]

5. Rhodium and Iridium Complexes

A series of d^8 complexes of the general formula [MLL′(mnt)]$^-$ (M = Rh or Ir, L = CO, L′ = CO, PPh$_3$, or CN$^-$, and mnt = maleonitriledithiolate) have recently been reported to luminesce.[212] All of the organometallic Ir(I) complexes emit at room temperature in the solid state and in frozen EPA solutions at 77 K, whereas the Rh(I) complexes have been observed to only emit at the lower temperature. Excitation and emission spectra recorded at 77 K from the solid state are highly structured; the spectra recorded for (PPN)[Ir(CO)(PPh$_3$)-(mnt)] (PPN = bis(triphenylphosphine)iminium) are typical of this d^8 system and are shown in Figure 26. In most cases a small Stokes shift of <400 cm^{-1} may be observed, which indicates that the emitting state is essentially undistorted from the planar ground-state geometry. Moreover, the emission and excitation spectra mirror each other, indicating that these spectra arise from the same electronic transition. First emission maxima at 77 K range from 15110 to 18060 cm^{-1} and are affected by both the nature of the metal and the electron-donor ability of the ligand; the emission is associated with the M $\rightarrow \pi^*$(mnt) MLCT absorption in all of the complexes. Emission lifetimes at 77 K for the Rh(I) complexes range from 99 to 389 μs and are 8–105 μs for the Ir(I) complexes. The shorter lifetimes for the heavier metal complexes imply that this emission has substantial spin-forbidden character. Vibrational progressions in the emission and excitation spectra are attributed to vibrations within the metal–mnt moiety; the dominant vibrational spacing in this emission spectra is typically at ~1400 cm^{-1} and corre-
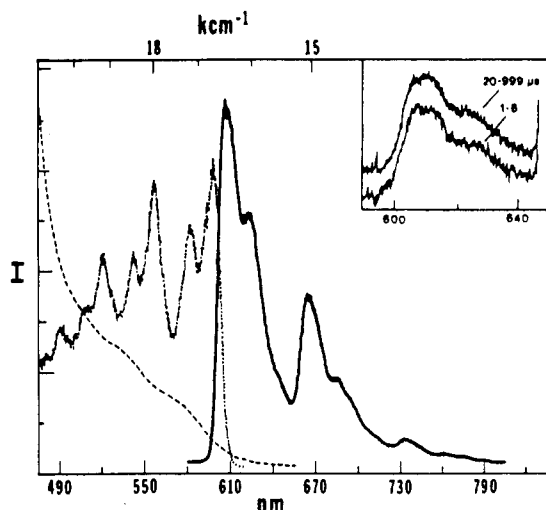

Figure 26. Emission (—, solid state at 77 K), excitation (···, solid state at 77 K), and absorption (- - -, CH$_3$CN solution at 298 K) spectra of (PPN)[Ir(CO)(PPh$_3$)(mnt)]. The inset shows emission spectra at different time intervals following pulsed-laser excitation, indicating that the emissions decay uniformly. Reproduced with permission from ref 212. Copyright 1983 American Chemical Society.

sponds to the mnt C=C stretch in the ground-state molecule. As a comparison, the $\nu_{C=C}$ stretch in the infrared spectrum of K[Ir(CO)$_2$(mnt)] is reported at 1476 cm^{-1}. The vibrational spacing at ~1250 cm^{-1} in the excitation spectra has been attributed to the mnt C=C stretch in the π^*(mnt) excited state, which is C=C antibonding and therefore undergoes a slight reduction in the bond order.

A series of binuclear d^8 dimers of the general formula [ClM(CO)L]$_2$, where M = Rh or Ir and L = bis(diphenylarsino)methane (dam) or bis(diphenylphosphino)methane (dppm), have been reported to luminesce at 77 K and at room temperature.[213] The complexes exhibit two emission bands that, on the basis of spectral position, temperature dependence, and lifetimes, have been assigned to fluorescence and phosphorescence $np_z \rightarrow (n - 1)d_{z^2}$ transitions (n = 5 for Rh, n = 6 for Ir). At 77 K lifetimes of these spin-allowed and spin-forbidden emissions are ~20 ns and ~1 μs, respectively. The higher energy emission is relatively weak for the Ir complexes, consistent with an enhancement of the intersystem crossing rates for the heavy metal compounds which have large spin–orbit coupling parameters.

B. Metallocenes

A large number of photochemical studies have been carried out on this important class of organometallic compounds,[14,20,22] but reports of luminescence are very scarce.

1. Ferrocene

The electronic structure of ferrocene has been much discussed in the literature and has been shown to consist of LF, LMCT, and MLCT transitions.[214-221] A MSCT band has also been identified in the spectrum of ferrocene in halocarbon solvents in halocarbon solvents.[222,223] The lowest energy absorption bands have been resolved into three spin-allowed $^1A_{1g} \rightarrow a^1E_{1g}$, $^1A_{1g} \rightarrow {}^1E_{2g}$, and $^1A_{1g} \rightarrow b^1E_{1g}$ LF transitions.[218,221] A detailed study of ferrocene crystals at 4.2 K has reported
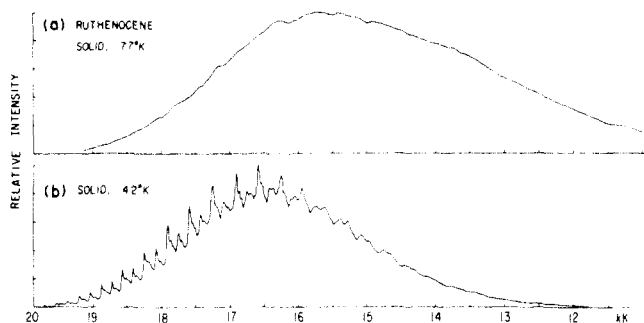
Figure 27. Corrected emission spectra of solid ruthenocene at (a) 77 K and (b) 4.2 K. Reproduced with permission from ref 234. Copyright 1974 Elsevier Science Publishers, B.V.
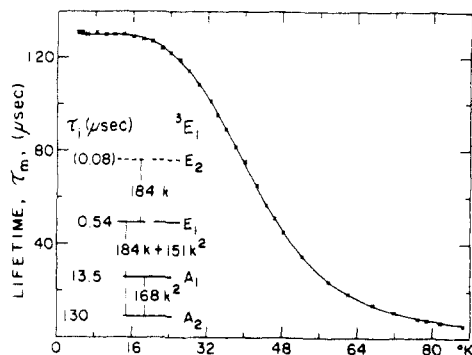
Figure 28. Measured decay times of solid ruthenocene as a function of temperature; (×) data points; (—) computer fit. Splittings are given in cm^{-1} ($k = 0.7$). Reproduced with permission from ref 234. Copyright 1974 Elsevier Science Publishers, B.V.

that the lowest lying triplet level is at 18 600 cm^{-1},[218] and SCF-Xα calculations have estimated this state to be at approximately 18 900 cm^{-1}.[221] On the other hand, ferrocene is known to be an efficient quencher of triplet excited states, and these studies have placed the lowest lying triplet state at about 15 000 cm^{-1}.[224-229]

A phosphorescence band in the ~15 000–20 000-cm^{-1} region with a lifetime of ~2 s has been reported from ferrocene in 3-methylpentane or EPA glasses at 77 K.[215] This feature was only observed following excitation at 324 nm but not on excitation in the 420–440-nm region; these results have been discussed in terms of emission from a higher lying triplet state, and the analogy has been drawn[215] to the S$_2$ → S$_0$ process established for azulene.[55,230,231] A weak emission feature has also been observed from ferrocene isolated in inert gas matrices at 20 K and was similarly assigned to a T → S transition.[232] Once again, the phosphorescence was only detected following excitation into a higher energy state at 310–350 nm. The reported emission lifetimes vary between 1 and 4 s depending on the matrix material.

Other studies have questioned the existence of phosphorescence in this molecule and have attributed the earlier reports to be due to sample impurity, solvent impurity, or to photolysis decomposition products.[216,233] Moreover, it has been convincingly argued that the long-lived emission with a spin-forbidden radiative rate constant of k_p = 0.5 s^{-1} would not compete effectively with S$_2$ ⤳ S$_1$, S$_2$ ⤳ S$_0$, and S$_2$ ⤳ T radiationless tunneling processes.[216]

2. Ruthenocene

Ruthenocene has been observed to emit as a solid at 4.2–77 K or in an EPA glass at 77 K.[227,234] Below 40 K the orange–yellow luminescence becomes much more intense and is highly structured (see Figure 27). Emission lifetimes of ruthenocene increase as the temperature is lowered but are constant below 20 K; this behavior may be interpreted with the use of a spin–orbit coupling description in which the lowest excited Russell–Saunders LF $^3E_1$ term[218] is split into A$_2$, A$_1$, E$_1$, and E$_2$ levels.[234] It can be assumed that emission then occurs from each of these four states in which there is rapid Boltzmann relaxation among the levels compared with the excited-state to ground-state relaxation. The experimentally determined decay times and a computer-generated curve fit based on this Boltzmann equilibration model are shown in Figure 28. At 4.2 K the emission may be assigned to arise from the A$_2$ level, which is the lowest energy component of the $^3E_1$ term.[234] Calculated energy splittings above the A$_2$ level are also

included in Figure 27. A later study has illustrated that the emission quantum yields of ruthenocene and 1,1'-diacetylruthenocene also exhibit similar temperature dependencies over the 20–100 K range, and it can be concluded that k_r is essentially invariant over these temperatures.[227] In this work the authors concur with the essential features of the earlier spin–orbit coupling model[234] but note that the data could also be fitted to a one-level scheme in which temperature-dependent k_{nr} values account for the increases in decay constants at the higher energy levels.

The emission spectrum of ruthenocene is unusually broad and is red shifted by ~9,000 cm^{-1} from the lowest energy $^1A_{1g}$ → $^3E_{1g}$ absorption maximum. These features indicate that there is an exceptionally large distortion in the excited state of this molecule. The spectrum at 4.2 K exhibits two main vibrational progressions, each spaced at 330 (±5) cm^{-1}. The well-defined nonconverging progression suggests that the D$_5$ ground-state symmetry is largely retained in the excited state but the geometry is substantially altered on excitation. Both vibrational progressions have been assigned to the Ru–cp ring a$_1$ stretching frequency, observed at 333 cm^{-1} in both infrared and Raman spectra;[235,236] the excited-state distortion is thought to be a symmetrical expansion of the molecule about the Re–cp bonds. A Franck–Condon factor analysis of the emission band structure has demonstrated that the Re–cp distance is increased in the A$_2$($^3E_1$) excited state by about 0.14 Å compared to the distance in the ground state.[234]

C. Metal Isocyanides

Isocyanide ligands are both good σ-donors and good π-acceptors, and like CO they lie high in the spectrochemical series. Although a wide range of metal isocyanide complexes have been characterized,[237-242] only a few luminescence studies have been carried out. However, the nature of the excited states and deactivation processes of metal complexes containing these ligands provides a useful comparison to the more extensively studied metal carbonyls. Typically, metal isocyanides exhibit very low lying metal to isocyanide charge-transfer (MLCT) transitions; this is particularly so for aryl isocyanides because of conjugation of one of the CN π^* orbitals with the arene π^* orbital.[243] Thus, the MLCT band is blue shifted for alkyl isocyanide complexes compared to that of the corresponding aryl derivatives.
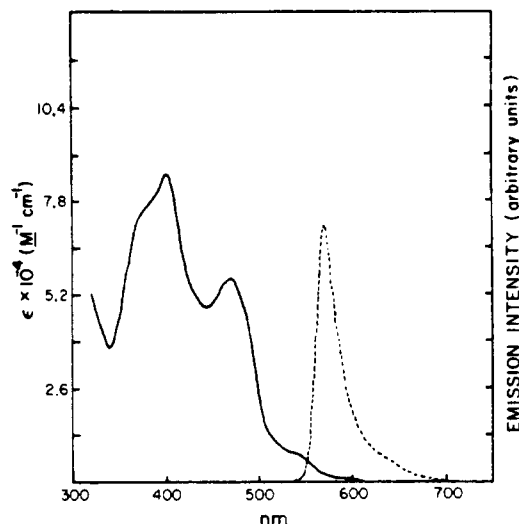
Figure 29. Electronic absorption and emission spectra of W-(CNPh)$_6$ in 2-Me-THF at 77 K. Reproduced with permission from ref 245. Copyright 1977 American Chemical Society.

1. Chromium, Molybdenum, and Tungsten Complexes

Absorption spectra obtained from octahedral M-(CNPh)$_6$ complexes, where M = Cr, Mo, and W, have identified d$\pi \rightarrow \pi_v$* (CNPh) and d$\pi \rightarrow \pi_h$* (CNPh) MLCT transitions as lowest lying and $\pi \rightarrow \pi$* ligand-localized IL transitions at higher energies.[244] It is also assumed that d $\rightarrow$ d transitions are present in these complexes and that they lie in between the MLCT and IL states, but they are weak and have not been directly observed. The d$\pi \rightarrow \pi_v$* (CNPh) states have been shown to be lower in energy than the d$\pi \rightarrow \pi$* (CO) states of the corresponding hexacarbonyls because of the stabilization of the π_v* (CN) orbital by conjugation with the π* (C$_6$H$_5$) system and the increased σ-donation by the more basic CNPh ligands.[243,244]

Luminescence has been observed from the lowest energy d$\pi \rightarrow \pi$*(L) states of M(CNPh)$_6$ and M(CNIph)$_6$ (M = Cr, Mo, or W and Iph = 2,6-diisopropylphenyl) complexes in 2-methyltetrahydrofuran (2-Me-THF) glasses at 77 K and in room temperature solutions.[245] Absorption and emission spectra obtained for W-(CNPh)$_6$ in 2-Me-THF at 77 K are representative of these complexes and are shown in Figure 29. Emission from the Cr(0) compounds is much weaker than that observed from the corresponding Mo(0) and W(0) species. Emission lifetimes reported from the M-(CNIph)$_6$ complexes in 2-methylpentane at 77 K are <10 ns (Cr), 40.2 ± 0.5 μs (Mo), and 7.6 μs (W) and at 298 K are 43 ± 2 ns (Mo) and 83 ± 2 nsec (W). These lifetimes indicate a greater degree of spin-forbidden character in the emitting excited states of the Mo and W isocyanides than in the Cr complexes. Thus, the emission properties of these isocyanides are very similar to those of metal carbonyl complexes with low-lying MLCT states. In this context, a number of these metal isocyanide complexes also appear to exhibit the luminescence rigidochromic effect as their emission bands are substantially blue shifted and sharpened on going from 298 K solution to a 77 K glass.

The lowest energy d$\pi \rightarrow \pi_v$* (CNR) excited states of these group 6 isocyanide complexes also give rise to a rich photochemistry, including redox processes, and associative or dissociative photosubstitution reactions.[245,246]

2. Rhodium Complexes

Square planar rhodium(I) isocyanide complexes have been shown to aggregate in solution,[247] and emission (λ_{em} = 697 nm, ϕ_e = 0.0065, τ < 2 ns) has been determined from concentrated acetonitrile solutions of [Rh(tol)$_4$](PF$_6$) (tol = p-methylphenyl isocyanide) at room temperature following excitation into the dimer absorption band.[248] A [Rh$_2$(bridge)$_4$](BPh$_4$)$_2$ (bridge = 1,3-diisocyanopropane) complex has been prepared and this complex is highly emissive (λ_{em} = 656 nm, ϕ_e = 0.056, τ = 1.1 ns).[248,249] For each Rh(I) dimer the emission has been associated with a ^{1}A$_{2u} \rightarrow$ ^{1}A$_{1g}$ (2a$_{1g}$ $\rightarrow$ 1a$_{2u}$) spin-allowed transition derived from the (dσ)^2(dσ*)^1(pσ)^1 electronic configuration. Later work has shown that the lowest excited states of Rh$_2$-(bridge)$_4$$^{2+}$ and Rh$_2$(TMB)$_4$$^{2+}$ (TMB = 2,5-dimethyl-2,5-diisocyanohexane) are the corresponding ^{3}A$_{2u}$ triplets; emission lifetimes obtained from the 770–800-nm region for these compounds in acetonitrile at 294 K are 8.5 ± 0.5 μs and 25 ± 5 ns, respectively.[250] The emissive ^{3}A$_{2u}$ state is therefore strongly metal–metal bonding,[251-254] and it is also known to undergo reversible electron-transfer processes with various donors and acceptors.[250,255,256]

Temperature-dependence studies of Rh$_2$(TMB)$_4$$^{2+}$ have shown that the dσ* $\rightarrow$ pσ triplet (^{3}A$_{2u}$) lifetimes are increased considerably on cooling (25 ns at 300 K to 20 μs at 77 K), whereas those of Rh$_2$(bridge)$_4$$^{2+}$ are comparatively unaffected (9 μs at 294 K to 16 μs at 77 K).[249] The activation energy for the former binuclear cation has been calculated from the emission dependence to be 2250 cm^{-1}. As the emission yields and lifetimes follow the same trend, the excited-state deactivation apparently proceeds via a temperature-dependent radiationless mechanism. It has been suggested that the ^{3}(dσ* $\rightarrow$ pσ) excited state is thermally activated to a d $\rightarrow$ d state that is D$_{2d}$ distorted (i.e., toward a tetrahedral geometry) about the Rh(I) center and that this state undergoes rapid nonradiative decay.[249] This d $\rightarrow$ d state may not be easily reached in the Rh$_2$(bridge)$_4$$^{2+}$ complex, as it is held in a square planar geometry and would be less able to distort (and deactivate) in this fashion.

D. Alkenes

Photochemical studies of alkene complexes have illustrated that these complexes display a wide range of reactions, including alkene or ligand substitution, isomerization, and skeletal rearrangement.[14,257] Actually there is relatively little detailed information presently available about the excited states of alkene complexes that give rise to these processes. Only in a few cases have luminescence techniques been effectively used to characterize the nature of their low-energy states.

1. Rhodium and Iridium Complexes

Emission spectra and lifetimes have been determined for a series of [ML(diene)]$^+$ complexes, where M = Rh(I) or Ir(I), L = en, bpy, phen, 4,7-Ph$_2$-phen, or 2,2'-bipyrazine (bpz), and diene = 1,5-cyclooctadiene (cod), 2,5-norbornadiene (nbd), or 1,5-hexadiene (hex).[258] Emission data have been recorded at 77 K from these compounds as solids or in an ethanol-methanol–dichloromethane (16:4:1 v/v) glass. When
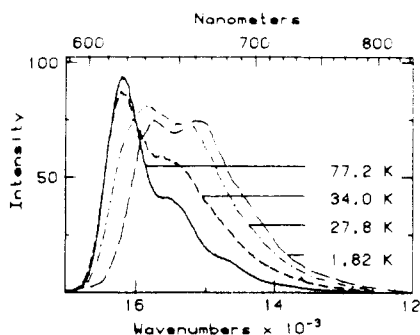
Figure 30. Emission spectra of [Ir(2=phos)(cod)]PF$_6$ in ethanol–methanol–dichloromethane (16:4:1 v/v) glasses at the indicated temperatures. Relative intensities between spectra are arbitrary. Reproduced with permission from ref 261. Copyright 1982 American Chemical Society.

L = en, the lowest energy absorption feature is a mixture of metal to diene charge-transfer (^{1}A → diene ^{1,3}CT) and nd_{z^2} → (n + 1)p$_z$ transitions.[258,259] Emission was not observed from the [Rh(en)(cod)]ClO$_4$ complex, but two bands have been detected from [Ir(en)(cod)]-ClO$_4$ at λ_{em} = 488 and 508 nm. The emission from the latter complex exhibits a small Stokes shift and has been tentatively assigned to a metal to olefin CT excited state. When L = bpy, phen, 4,7-Ph$_2$-phen, and bpz, the lowest energy absorption is clearly of metal to N-ligand charge-transfer (^{1}A$_1$ → π*(L) CT) character, and emission spectra (λ_{em} = 630–810 nm) and lifetimes (0.5–4.4 μs) obtained from these complexes are consistent with a ^{3}B → ^{1}A$_1$(2b$_1$ → 2a$_1$) radiative assignment that has been derived from a mixing of the π*(L) orbital with the (n + 1)p$_z$ orbital. Complexes containing the hex ligand exhibit comparatively weak luminescence features and have large Stokes shifts; this may be due to the particularly flexible nature of this alkene,[260] giving rise to substantial excited-state distortion and an enhancement of the radiationless decay mechanisms.[258]

Emission lifetimes of [M(bpy)(cod)]ClO$_4$ (M = Rh, Ir) complexes have been obtained over the 2–100 K range, and the results indicate that two states are emitting.[258] The emitting ^{3}B$_1$ term is apparently spin–orbit split into A$_1$ and B$_2$ (both dipole-allowed) and A$_2$ (dipole-forbidden) states which are in rapid Boltzmann equilibrium. In support of this interpretation, computer-generated fits of the emission decay curves have resolved two lifetimes in this system, a fast decay (0.11–1.00 μs) from the state at higher energy and a slow decay (4.53–103 μs) from the lowest energy state.

Further evidence for spin–orbit splitting of emitting states and Boltzmann equilibrium among two levels has been obtained from an emission study of the closely related [ML(cod)]$^+$ complexes, where L = Ph$_2$PCH$_2$CH$_2$PPh$_2$, 1,2-bis(diphenylphosphino)ethane (diphos), Ph$_2$PCHCHPPh$_2$, cis-1,2-bis(diphenylphosphino)ethylene (2=phos), and Ph$_2$PC$_6$H$_4$PPh$_2$, 1,2-bis(diphenylphosphino)benzene (dpbe).[261] Figure 30 illustrates the emission spectra recorded from [Ir(2=phos)(cod)]PF$_6$ in an ethanol–methanol–dichloromethane (16:4:1 v/v) glass at several temperatures. This spectral change can be analyzed according to eq 23,[261,262] where I_1 and I_2 are the integrated emission

$$\ln (I_2/I_1) = -\Delta\epsilon/k_B T + \ln (2k_{2r}/k_{1r}) \qquad (23)$$

intensities from energy levels 1 (lower) and 2 (upper), respectively, $\Delta\epsilon$ is the energy gap between these levels,
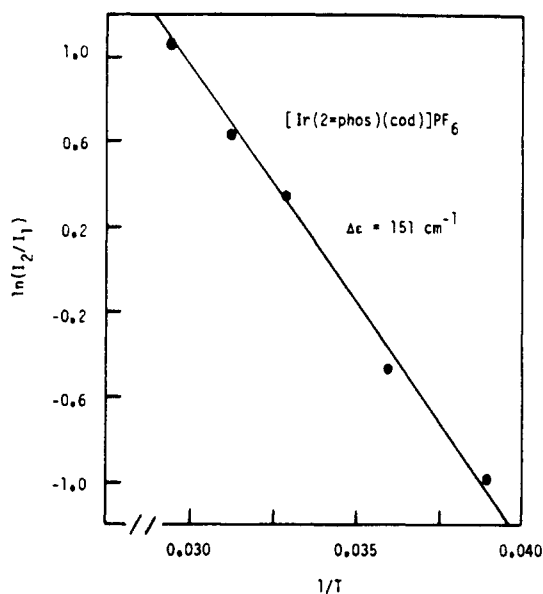

Figure 31. Temperature dependence of the logarithm of the ratio of the intensity of the high-temperature emission spectrum to the low-temperature emission spectrum of [Ir(2=phos)(cod)]PF$_6$. Reproduced with permission from ref 261. Copyright 1982 American Chemical Society.

k_B is Boltzmann's constant, T is temperature, and k_{1r} and $2k_{2r}$ are the radiative rate constants for decay from levels 1 and 2, respectively. Assuming temperature-independent k_{1r} and k_{2r} values, a plot of ln (I_2/I_1) vs. $1/T$ should yield a straight line, with slope $\Delta\epsilon$. This behavior was indeed observed experimentally (see Figure 31), and the value obtained for $\Delta\epsilon$ was 151 cm^{-1}.

A lifetime treatment may also be applied to this system based on eq 24.[261] The value of $\Delta\epsilon$ obtained in

$$\tau(T) = [1 + 2 \exp(-\Delta\epsilon/k_B T)]/[k_1 + 2k_2 \exp(-\Delta\epsilon/k_B T)] \qquad (24)$$

a least-squares curve-fitting analysis of the lifetime data was 140 cm^{-1}, in good agreement with that obtained from the emission spectral analysis.

It may be concluded that emission from the upper level is a partially allowed transition, whereas the emission from the lower level is forbidden. An ^{3}A$_{2u}$ → ^{1}A$_{1g}$ (a$_{2u}$ → a$_{1g}$) assignment can be adopted for the phosphorescence bands of these Rh(I) and Ir(I) complexes; both spin–orbit terms, the shorter lived upper level assigned to an E$_u$ component and the longer lived lower level assigned to an A$_{1u}$ component, are derived from the ^{3}A$_{2u}$ term.[261]

Recently pyrazoyl-bridged iridium(I) complexes, [Ir(μ-pz)(cod)]$_2$ (pz = pyrazoyl), have been reported to emit in room temperature solution.[263] These complexes have been shown to have an "open-book" type of geometry. Both fluorescence and phosphorescence features have been observed and are assigned to singlet (^{1}B$_1$) and triplet (^{3}B$_2$) components of the dσ* → pσ transition, analogous to the "face-to-face" binuclear rhenium diisocyanide complexes (vide supra). Emission parameters obtained in acetonitrile solutions at 295 K are fluorescence λ_{em} = 564 nm, ϕ_e = 1 × 10^{-4}, and τ < 100 ps and phosphorescence λ_{em} = 687 nm, ϕ_e = 7.8 × 10^{-3}, τ = 250 ns. The emission quantum yield and lifetime values for the spin-forbidden process increase greatly on cooling to liquid N$_2$ temperatures (τ = 2.68 μs at 77 K), and this is thought to be mainly due to

variations in k_{nr}. The temperature dependence of the observed phosphorescence lifetimes (τ_{obsd}) may be fitted to the two-term expression shown in eq 25.[263] Here it

$$1/\tau_{obsd} = k_0 + k_1 e^{-E_a/RT} \qquad (25)$$

is assumed that $1/\tau_{obsd}$ is approximately equal to k_{nr} as $\phi_e < 0.1$ at room temperature. The calculated activation energy (E_a) is 2600 cm^{-1} for the $^3B_2(d\sigma^* \rightarrow p\sigma)$ state of $[Ir(\mu\text{-pz})(cod)]_2$, and similar values were obtained for a number of substituted pyrazoyl complexes. The excited-state deactivation mechanism of these Ir(I) dimers is, thus, analogous to that discussed for the D_{4h} d^8–d^8 Rh$_2$(TMB)$_4$$^{2+}$ complex.[249]

Further studies of binuclear complexes of the form $[Ir(\mu\text{-L})(cod)]_2$, where L = 2-hydroxypyridinate (hp) or 6-methyl-2-hydroxypyridinate (mhp), have also reported emission from a d$\sigma^* \rightarrow$ pσ state.[264] These molecules have been shown to have the Ir(I) square planes orientated so that the plane normals are not aligned but directed toward an olefinic carbon atom of the opposite metal. This geometry is in contrast to the face-to-face geometry exhibited by Rh$_2$L$_4$$^{2+}$ (L = bridging diisocyanide) or the open-book geometry known for $[Ir(\mu\text{-pz})(cod)]_2$ (vide supra). However, the emission is characteristic of the weakly interacting d^8–d^8 metal dimers; at 77 K both spin-allowed (λ_{em} = 598 nm) and spin-forbidden (λ_{em} = 723 nm) spectral features are observed. At room temperature the emission intensity of the long-wavelength band is decreased by a factor of 400, consistent with the spin-forbidden assignment.
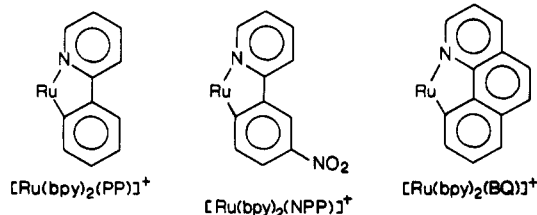
2. Platinum Complexes

The well-known and historically important Zeise's square planar Pt(II) salt, Pt(C$_2$H$_4$)Cl$_3$$^-$, has been observed to emit both in the solid form and in a 50% aqueous ethylene glycol glass at 77 K.[265] Emission of this complex is centered at λ_{em} = 700 nm with a weaker component at λ_{em} = 875 nm and has been attributed to result from a $^3T_1$^{0} excited state that is substantially distorted from the ground-state geometry.

E. Ortho-Metalated Complexes

Very recently a number of examples belonging to this class of organometallic complexes have been shown to luminesce in glasses at 77 K or in room temperature solutions.

1. Ruthenium Complexes

A useful photophysical comparison to Ru(bpy)$_3$$^{2+}$ has been reported for a series of cyclometalated Ru(II) complexes, [Ru(bpy)$_2$L]$^+$, where L = 2-phenylpyridine (PP), 2-(3-nitrophenyl)pyridine (NPP), and benzo[h]-quinoline (BQ).[266,267] The coordination of these ligands to the Ru(II) center is shown below. The [Ru(bpy)$_2$-

[Ru(bpy)$_2$(PP)]$^+$ [Ru(bpy)$_2$(NPP)]$^+$ [Ru(bpy)$_2$(BQ)]$^+$

(NPP)]$^+$ complex emits at λ_{em} = 682 nm in an ethanol–methanol (4:1 v/v) glass at 77 K; this compares to the 583-nm emission from Ru(bpy)$_3$$^{2+}$ under the same

experimental conditions. The red shift in emission (2490 cm^{-1}) for the cyclometalated complex is approximately equivalent to that observed in absorption (1922 cm^{-1}), and the emission has, therefore, been assigned to the Ru(t$_{2g}$) $\rightarrow$ π*(bpy) MLCT band. Furthermore, the emission spectrum of [Ru(bpy)$_2$(NPP)]$^+$ exhibits the fine structure associated with Ru $\rightarrow$ π*(bpy) MLCT emission.[268–270] The red shift of the emission from the cyclometalated derivative is understood to be due to a raising of the metal-centered t$_{2g}$ orbital, as evidenced by a substantial increase in oxidation potential of this complex in comparison to Ru(bpy)$_3$$^{2+}$.[266]

Luminescence quantum yields and lifetimes of [Ru(bpy)$_2$(NPP)]$^+$ at 77 K are 0.038 and 878 ns, respectively. However, these values decrease dramatically as the temperature is raised. When a treatment analogous to that described above for several of the metal diisocyanides and alkene complexes (also see eq 25) is used, the emission temperature dependence can be characterized by a two-state scheme, in which the MLCT emitting state is able to thermally populate a higher lying triplet MLCT state that contains a significant amount of singlet character as a result of spin-orbit coupling.[271] This higher lying state is thought not to be a LF state as the energy gap between the LF and ^{3}MLCT states in Ru(bpy)$_3$$^{2+}$ has been determined to be 3560–4000 cm^{-1},[272–274] and the LF state would be expected to be at higher energy in the cyclometalated complex because a carbanion-donor ligand is much higher in the spectrochemical series than a N donor. Moreover, as noted above, the absorption and emission MLCT maxima are red shifted for the cyclometalated species. Emission has been detected from the [Ru(bpy)$_2$(PP)]$^+$ and [Ru(bpy)$_2$(BQ)]$^+$ complexes, but it is comparatively weak and only observable below 140 K. It is thought that the activation energy for population of the upper ^{3}MLCT state is very small in these compounds.

2. Rhodium and Iridium Complexes

Electronic data obtained from [Ir(bpy)$_2$(H$_2$O)(bpy)]$^{3+}$ have indicated that this cation has distinct absorption and emission spectral characteristics, as well as different photophysical properties[275–277] from the [Ir(bpy)$_3$]$^{3+}$ species.[278] Additionally, NMR[279–281] and crystal structure[282,283] evidence has confirmed that the [Ir(bpy)$_2$-(H$_2$O)(bpy)]$^{3+}$ complex does indeed contain three chelated bpy ligands but that one of these has a single carbon atom bonded to the metal center which replaces one of the nitrogen coordination sites. The 450–625-nm emission of [Ir(bpy)$_3$]$^{3+}$ at 77 K (τ ~80 μs) has been assigned to a $^3(\pi,\pi^*)$ IL transition on the bpy ligand,[278] whereas the 450–650-nm emission at 77 K (τ = 15.6 μs) of [Ir(bpy)$_2$(H$_2$O)(bpy)]$^{3+}$ may originate from an Ir $\rightarrow$ π*(bpy) MLCT state that is partially mixed with bpy IL states.[275] Even in room temperature solution, the emission of the [Ir(bpy)$_2$(H$_2$O)(bpy)]$^{3+}$ complex is very long lived (τ = 12.2 μs) and intense (ϕ_e = 0.3).

Recently, the ortho-metalated [Ir(bpy)$_2$(bpy)]$^{2+}$ complex (one bpy is coordinated as a C^3, N′ isomer) has been shown to sensitize the valence photoisomerization of norbornadiene to quadricyclene (eq 26).[284,285]

(26)
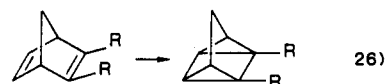
Figure 32. Absorption (—) and emission (- - -) spectra of Rh(III) dichloro-bridged dimers of 2-phenylpyridine (PP) and benzo-[h]quinoline (BQ). Absorption measured at 295 K in dichloromethane, and emission at 77 K in ethanol–methanol–dichloromethane glass (4:1:1 v/v) of (a) [Rh(BQ)$_2$Cl]$_2$ and (b) [Rh(PP)$_2$Cl]$_2$. Reproduced with permission from ref 286. Copyright 1984 American Chemical Society.
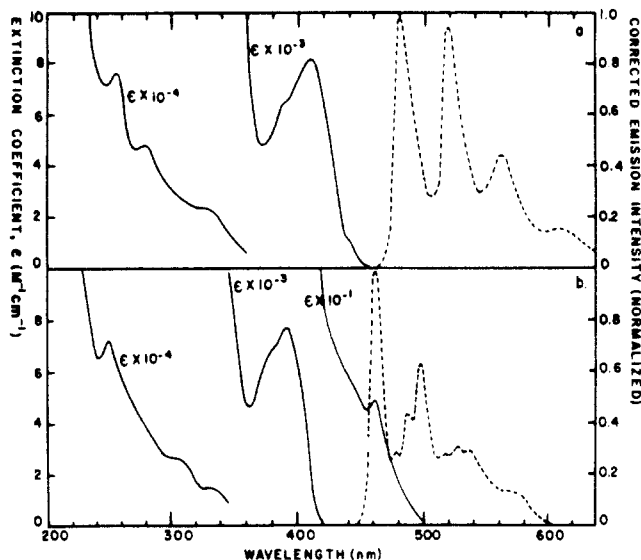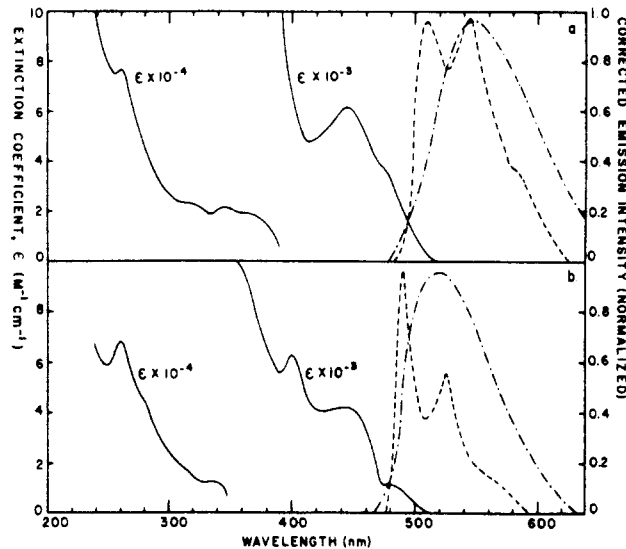

Figure 33. Absorption (—) and emission (- - -) spectra of Ir(III) dichloro-bridged dimers of 2-phenylpyridine (PP) and benzo-[h]quinoline (BQ). Absorption measured at 295 K in dichloromethane, and emission at 77 K in ethanol–methanol–dichloromethane glass (4:1:1 v/v) of (a) [Ir(BQ)$_2$Cl]$_2$ and (b) [Ir(PP)$_2$Cl]$_2$. Reproduced with permission from ref 286. Copyright 1984 American Chemical Society.

TABLE XII.^{a} Emission Lifetimes of Dichloro-Bridged Rh(III) and Ir(III) Dimers of 2-Phenylpyridine (PP) and Benzo[h]quinoline (BQ)

	emission lifetime	
complex	77 K^b	295 K^c
[Rh(BQ)$_2$Cl]$_2$	2.7 ms	d
[Rh(PP)$_2$Cl]$_2$	93.0 μs	d
[Ir(BQ)$_2$Cl]$_2$	30.0 μs	1.4 μs
[Ir(PP)$_2$Cl]$_2$	4.8 μs	0.14 μs

^{a} Reproduced with permission from ref 286. Copyright 1984 American Chemical Society. ^{b} Measured in ethanol–methanol–dichloromethane glass (4:1:1 v/v). ^{c} Measured in nitrogen-purged dichloromethane. ^{d} No luminescence observed.

Accompanying this conversion is a quenching of the luminescence of the Ir(III) complex (λ_{em} = 462 and 491 nm and τ = 10.2 μs in acetonitrile at 298 K) according to Stern–Volmer kinetics with k_q = 1.4 × 10^8 M^{-1} s^{-1} and a limiting sensitization efficiency of 0.72 ± 0.05. However, this result is an unusual one, as the lowest energy excited state of the ortho-metalated Ir(III) complex lies considerably below the reactive triplet excited state of norbornadiene. It is believed that the excited metal complex initially forms an encounter complex with norbornadiene that may undergo collisional energy transfer or produce a charge-transfer-stabilized species before deactivation to ground-state products.[285]

A series of dichloro-bridged dimers of the formula [ML$_2$Cl]$_2$, where M = Rh(III) or Ir(III) and L = 2-phenylpyridine (PP) or benzo[h]quinoline [BQ] (ligand structures were depicted above), have been shown to luminesce.[286] All four of these ortho-metalated complexes emit in glasses at 77 K, and the Ir(III) dimers have been reported to emit in deoxygenated dichloromethane solutions at 295 K. Emission spectra of these complexes are shown in Figures 32 and 33. Lifetimes for these complexes at both temperatures are listed in Table XII. On the basis of these emission spectral features and lifetimes, a $^3(\pi \rightarrow \pi^*)$ IL assignment has been adopted for the Rh(III) dimers, but a MLCT d $\rightarrow$

π^*(L) assignment has been chosen for the Ir(III) dimers. In support of this assignment the emission energies are solvent sensitive for the Ir complexes but not in the case of the Rh complexes. Overall the emission results are consistent with the notion that the PP and BQ ligands are strong σ-donors and excellent π-acceptors. Thus, in comparison with the Ru(diimine)$_3^{2+}$ and Ir(diimine)$_3^{2+}$ (diimine = bpy or phen) complexes these cyclometalated compounds have relatively high-energy LF excited states but still exhibit low-energy MLCT transitions.

Recently, the luminescence properties of a triply ortho-metalated Ir(III) complex, fac-Ir(PP)$_3$, have been studied.[287] This complex emits in an ethanol–methanol glass (4:1 v/v) at 77 K or in room temperature solution; determined lifetimes are 5 μs at 77 K and ~2 μs in deoxygenated toluene or acetonitrile at 295 K. An emission quantum yield of 0.4 ± 0.1 was obtained in room temperature toluene, indicating a radiative lifetime of ~5 μs at this temperature. This long-lived emitting state has been assigned to a MLCT state. The agreement of the radiative lifetime in room temperature toluene and the observed lifetime in the 77 K glass (both being 5 μs) implies that the luminescence quantum yield is close to unity at the lower temperature.

In deoxygenated methylene chloride at room temperature, however, the emission lifetime of this complex is only 100 ns, and substantial photoreactivity was observed in this and other halocarbon solvents. A series of oxidative quenchers have been demonstrated to quench the luminescence lifetime of fac-Ir(PP)$_3$ at approximately the diffusion-controlled limit. However, there is a sharp lowering in the quenching constants (k_q) caused by acceptors with reduction potentials below −1.8 V. It has been concluded that the quenching is due to outer-sphere electron transfer from the excited state of the complex to the acceptor molecule.[287,288] The obtained k_q values provide a rough estimate of −1.8 V vs. SCE for the reduction potential of the oxidized ground state|excited state couple, fac-Ir(PP)$_3^+$|fac-Ir-

TABLE XIII.[a] **Emission Data Obtained from Pd(II) Complexes Containing an Ortho-Metalated Azobenzene Derivative**

complex[b]	excitation λ, nm	λ_{em},[c] nm	τ, ps
Pd(azb)Br(L)	540	639	d
Pd(azb)Br(L')	560	638	63[e]
Pd(azb)(diphos)$^+$	560	632	64[e]
Pd(azb')Br(L')	400, 500	550	f

[a] Reprinted with permission from ref 290. Copyright 1986 American Chemical Society. [b] azb = ortho-metalated 4-nitro-4'-(dimethylamino)azobenzene; azb' = ortho-metalated 4-methoxyazobenzene; L = cis-4-stilbazole; L' = trans-4-stilbazole; diphos = 1,2-bis(diphenylphosphino)ethane. [c] Emission maximum in CH_2Cl_2 at 298 K. [d] Not determined. [e] Sample excited at 585 nm and emission monitored at 630 nm. [f] Emission intensity unaffected after bubbling sample solution with O_2.

$(PP)_3^*$. Furthermore, the strong reducing properties of this excited cyclometalated complex contrast with the strong oxidizing properties known for the excited state of the N-bonded fac-Ir(bpy)$_3^{3+}$ complex.[289]

3. Palladium and Platinum Complexes

Lately, the excited-state pathways of several ortho-metalated azobenzenepalladium(II) complexes have been investigated.[290] Emission has been observed from
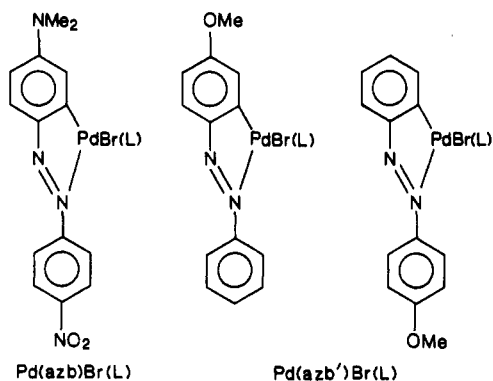
Pd(azb)Br(L)   Pd(azb')Br(L)

several complexes and the data are summarized in Table XIII. The short-lived room temperature emission of the Pd(azb)Br(L), Pd(azb)Br(L'), and Pd-

(azb)(diphos)$^+$ complexes (L = cis-4-stilbazole, L' = $trans$-4-stilbazole) was assigned to a ligand-localized (IL) π,π^* fluorescence, and from the absorption and emission spectral overlap the 0–0 band has been estimated to be at 47–48 kcal for the Pd(azb)Br(L') compound. The higher energy emission of Pd(azb')Br(L') has been tentatively attributed to a n,π^* fluorescence and is not noticeably quenched by O_2. Neither of the two free azobenzene ligands emits under these room temperature conditions; it is thought that the metalation by Pd imparts rigidity to the azo linkage, which in turn reduces the nonradiative processes and increases the emission efficiency.

A series of ortho-metalated Pt(II) complexes have been studied following the initial observation of emission from solid Pt(PP)$_2$.[291-293] Emission spectra and lifetimes have been obtained for PtL$_2$ complexes, where L are the C-deprotonated forms of 2-phenylpyridine (PP), 2-(2-thienyl)pyridine (TP), and benzo[h]quinoline (BQ).[293] Examples of the coordination of the PP and BQ ligands were shown above for cyclometalated Ru(II) complexes; the Pt(TP)$_2$ complex is shown below. Each

Pt(TP)$_2$
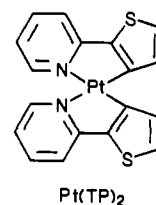
of these PtL$_2$ complexes emits in nitrile (propionitrile–butyronitrile in a 4:5 v/v mixture) and methylcyclohexane glasses at 77 K; these spectra are illustrated in Figure 34. Limited work has been carried out in room temperature solution as only the Pt(TP)$_2$ complex emits under these conditions. Emission data of these complexes are summarized in Table XIV. In each case the emission of these ortho-metalated Pt(II) complexes may be assigned to a MLCT excited state, and it is observed to be slightly solvent dependent in accordance with the MLCT absorption system. Moreover, the emission spectra and lifetimes of the free

TABLE XIV.[a] **Emission Data of Ortho-Metalated Pt(II)[a] and Pt(IV)[b] Complexes**

		emission				
		77 K		293 K		
	solvent	λ_{em},[c] nm	τ,[d] μs	λ_{em}, nm	τ,[d] μs	ϕ_e[e]
Pt(PP)$_2$	nitrile	491	4.0			
	methylcyclohexane	505	4.4			
Pt(TP)$_2$	nitrile	570	12	578	2.2	0.30
	methylcyclohexane	580	10	585	3.2	0.36
Pt(BQ)$_2$	nitrile	492	6.5			
Pt(PP)$_2$(CH$_2$Cl)Cl	nitrile	444	300			
	methylene chloride			447	150	0.15
Pt(PP)$_2$(CHCl$_2$)Cl	nitrile	444	360			
	methylene chloride			446	100	0.10
Pt(TP)$_2$(CH$_2$Cl)Cl	nitrile	507	340			
	methylene chloride			513	200	0.05
Pt(TP)$_2$(CHCl$_2$)Cl	nitrile	507	430			
	methylene chloride			513	270	0.05

[a] Reprinted with permission from ref 293. Copyright 1985 Elsevier Science Publishers B.V. [b] Reprinted with permission from ref 294. Copyright 1986 American Chemical Society. [c] λ_{em} is the high-energy feature of the phosphorescence emission. [d] Emission lifetime from deaerated solution; estimated error ±10%. [e] Quantum yield relative to value of 0.028 reported for Ru(bpy)$_3^{2+}$ in water at room temperature (see ref 295); estimated error ±20%.
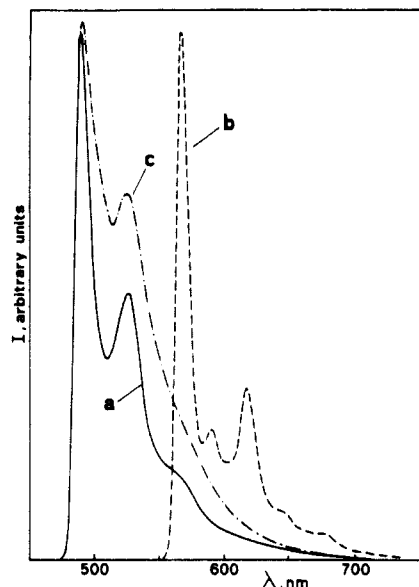
Figure 34. Emission spectra of (a) Pt(PP)$_2$, (b) Pt(TP)$_2$, and (c) Pt(BQ)$_2$ in propionitrile–butyronitrile solution (4:5 v/v) at 77 K. Reproduced with permission from ref 293. Copyright 1985 Elsevier Science Publishers B.V.

ligands are distinct from the emission of the complexes. The radiative lifetime of Pt(TP)$_2$ has been estimated from the emission quantum yield and lifetime data to be 10 μs in nitrile solution at 293 K; this value is consistent with the MLCT assignment and, in fact, is quite close to that reported for the fac-Ir(PP)$_3$ complex discussed above.

Most recently a number of Pt(IV) organometallic complexes have been reported to strongly luminesce either in glasses at 77 K or in room temperature solution.[294] These ortho-metalated Pt(IV) complexes have been prepared by photooxidative addition from the above PtL$_2$ complexes, and their emission parameters are listed in Table XIV. The exceptionally long-lived emission lifetimes of these compounds suggest that the luminescent state is the lowest triplet ligand-centered (IL) excited state. Emission spectra of the C-protonated free PP ligand and the Pt(PP)$_2$(CH$_2$Cl)Cl complex in nitrile solution at 77 K are fairly close in energy and exhibit similar vibrational structure (see Figure 35). This similarity further indicates that the emitting state is an IL state in which the PP orbitals are slightly perturbed by metalation.

F. Dinitrogen Complexes

A brief report of luminescence from trans-[W(N$_2$)$_2$-(diphos)$_2$], where diphos = 1,2-bis(diphenyl-phosphino)ethane, has appeared.[296] The emission (λ_{em} = 565 nm, ϕ_e = 0.08 ± 0.02, τ = 19 μs) is similar to that observed from trans-[W(CO)$_2$(diphos)$_2$] (λ_{em} = 568 nm, ϕ_e = 0.14, τ = 23 μs) and for both species is thought to contain some d → π^* CT character.

III. Chemiluminescence

Chemiluminescence has been determined in the reactions of gas-phase Cr(CO)$_6$, Mo(CO)$_6$, W(CO)$_6$, Fe-(CO)$_5$, Ni(CO)$_4$, Mn$_2$(CO)$_{10}$, and Co(CO)$_3$(NO) with N, H, O, He, Ar, and Ne atoms.[297-300] The bright blue chemiluminescence from the interaction of nitrogen atoms with metal carbonyls is thought to be caused by
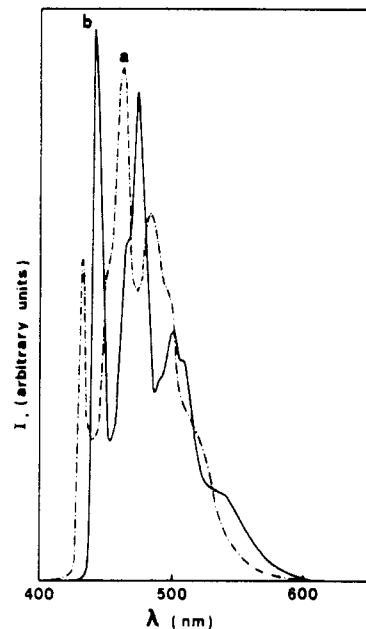

Figure 35. Emission spectra of (a) C-protonated PP and (b) Pt(PP)$_2$(CH$_2$Cl)Cl in propionitrile–butyronitrile (4:5 v/v) solution at 77 K. Reproduced with permission from ref 294. Copyright 1986 American Chemical Society.

collisions of metal atoms with metastable A$^3\Sigma$ nitrogen molecules.[297] The chemiluminescence spectra have been shown to be comprised of lines that are exclusively from the emission of neutral metal atoms. It has been suggested that the chemiluminescence excitation mechanism in the reaction with N atoms involves formation of metal atoms by stepwise degradation of the metal complex (see eq 27–29). The M* species are very

$$M(CO)_n + N \rightarrow M(CO)_{n-1} + NCO \quad (27)$$

$$M + N_2^* \rightarrow M^* + N_2 \quad (28)$$

$$M^* \rightarrow M + h\nu \quad (29)$$
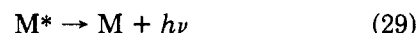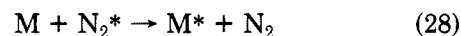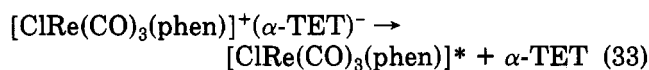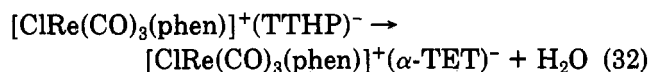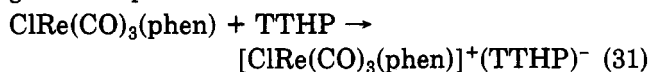
short-lived and deactivate rapidly on the reactor walls.

A closely related study has attributed chemiluminescence produced in the reaction of Cr(CO)$_6$, Mo(CO)$_6$, W(CO)$_6$, Fe(CO)$_5$, and Ni(CO)$_4$ with oxygen atoms to emission from MCO*, MO*, and M* species.[298] A stepwise degradation mechanism analogous to that shown above has been suggested, and the MO* species are thought to be formed by reaction of the naked metal atoms with the oxygen atoms. In the reaction of Mo(CO)$_6$ with hydrogen or nitrogen atoms chemiluminescence has been observed at λ_{em} = 520 nm and has been attributed to be from Mo$_2$*. For each complex, reaction with oxygen atoms produces a chemiluminescence continuum that, on the basis of kinetic and spectroscopic results, has been assigned to MCO*.[298]

Intense chemiluminescence has been reported from the reactions of Fe(CO)$_5$ and Ni(CO)$_4$ with metastable He(2^{3}S), Ne(3P$_2$), and Ar*(3P$_2$) atoms produced in a hollow-cathode flowing afterglow apparatus.[299,300] Again the emission is attributable to the neutral metal atoms. Kinetic results have illustrated that the formation of the excited molecules is dependent on the concentration of the metastable atoms (A) and the metal carbonyl pressure, thus indicating a bimolecular reaction (see eq 30).
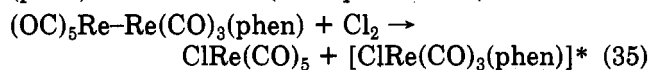
$$M(CO)_n + A^* \rightarrow M^* + A + nCO \quad (30)$$
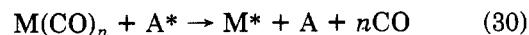
Also, a preliminary report of redox chemiluminescence from a number of organometallic complexes in solution has recently appeared.[301]

A bright chemiluminescence with λ_{em} = 580 nm has been reported from ClRe(CO)$_3$(phen) during the catalytic decomposition of tetralinyl hydroperoxide (TTHP) in forming α-tetralone (α-TET) and water.[302] The proposed reaction mechanism shown below is analogous to that known for the peroxide decomposition by organic compounds.[302,303]

$$\text{ClRe(CO)}_3\text{(phen)} + \text{TTHP} \rightarrow$$
$$[\text{ClRe(CO)}_3\text{(phen)}]^+\text{(TTHP)}^- \quad (31)$$

$$[\text{ClRe(CO)}_3\text{(phen)}]^+\text{(TTHP)}^- \rightarrow$$
$$[\text{ClRe(CO)}_3\text{(phen)}]^+\text{(}\alpha\text{-TET)}^- + \text{H}_2\text{O} \quad (32)$$

$$[\text{ClRe(CO)}_3\text{(phen)}]^+\text{(}\alpha\text{-TET)}^- \rightarrow$$
$$[\text{ClRe(CO)}_3\text{(phen)}]^* + \alpha\text{-TET} \quad (33)$$

$$[\text{ClRe(CO)}_3\text{(phen)}]^* \rightarrow \text{ClRe(CO)}_3\text{(phen)} + h\nu \quad (34)$$

Chemiluminescence of ClRe(CO)$_3$(phen) has also been recorded following the oxidation of Re$_2$(CO)$_8$-(phen) with chlorine (see eq 35 and 36).[304]

$$\text{(OC)}_5\text{Re–Re(CO)}_3\text{(phen)} + \text{Cl}_2 \rightarrow$$
$$\text{ClRe(CO)}_5 + [\text{ClRe(CO)}_3\text{(phen)}]^* \quad (35)$$

$$[\text{ClRe(CO)}_3\text{(phen)}]^* \rightarrow \text{ClRe(CO)}_3\text{(phen)} + h\nu \quad (36)$$

Thus, chemiluminescence has been established from only a few complexes, but these reactions serve to indicate that the field of transition-metal organometallic chemiluminescence is in its infancy and certainly it is one that is attractive to further investigation.

IV. Electrogenerated Chemiluminescence

A special case of chemiluminescence exists when one or both of the reactant species is or are formed electrochemically. This type of radiative process has been termed electrogenerated chemiluminescence or ecl,[305] and at the present it has been characterized for only two organometallic systems.

Cyclic voltammetry measurements on fac-ClRe-(CO)$_3$L (L = phen or 4,7-Ph$_2$-phen) have shown that the [fac-ClRe(CO)$_3$L]^0/[fac-ClRe(CO)$_3$L]$^{\bullet-}$ and [fac-ClRe-(CO)$_3$L]$^{\bullet+}$/[fac-ClRe(CO)$_3$L]^0 couples (L = phen or 4,7-Ph$_2$-phen) differ by approximately 2.6 V.[164] Thus the recombination reaction of the one-electron-oxidized and one-electron-reduced species yields enough energy to electronically excite one of the neutral metal complexes (see eq 37 and 38). This is evidenced by the fact

$$[fac\text{-ClRe(CO)}_3\text{L}]^{\bullet+} + [fac\text{-ClRe(CO)}_3\text{L}]^{\bullet-} \rightarrow$$
$$[fac\text{-ClRe(CO)}_3\text{L}]^0 + [fac\text{-ClRe(CO)}_3\text{L}]^{0*} \quad (37)$$

$$[fac\text{-ClReCO)}_3\text{L}]^* \rightarrow fac\text{-ClRe(CO)}_3\text{L} + h\nu \quad (38)$$
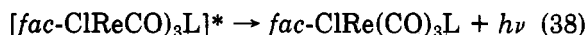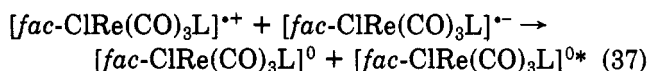
that the emission maximum of fac-ClRe(CO)$_3$L in the electrolyte solution is ~2.0 eV. Chemiluminescence has been observed in this system by cyclic stepping of the potential of a Pt electrode from -1.3 to +1.3 V vs. SCE, and its spectral distribution is coincident with that obtained on photoexcitation.[164] The electrogenerated chemiluminescence and photoluminescence spectra obtained for ClRe(CO)$_3$(phen) are depicted in Figure 36, and similar results have been observed for the ClRe(CO)$_3$(4,7-phen) complex.

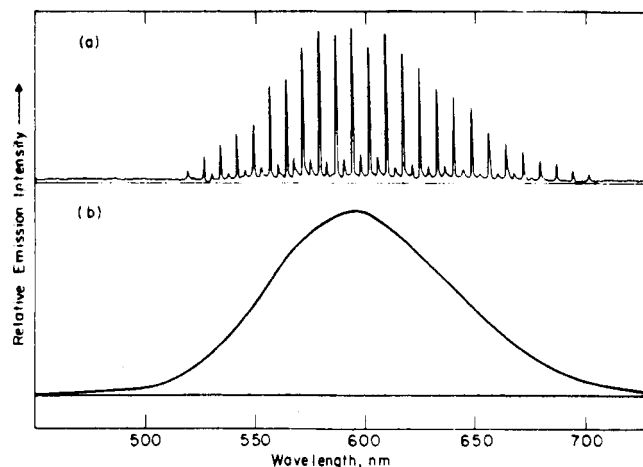Electrogenerated chemiluminescence has recently been determined from the ortho-metalated Pt(TP)$_2$

Figure 36. (a) Electrogenerated chemiluminescence from a 0.1 M (n-Bu$_4$N)ClO$_4$ CH$_3$CN solution of fac-ClRe(CO)$_3$(phen). The potential of the working Pt electrode was stepped from +1.6 to -1.6 V (vs. Ag wire) at a frequency of 0.2 Hz. (b) Optically (420 nm) excited luminescence from solution in (a). Figure reproduced with permission from ref 164. Copyright 1978 American Chemical Society.
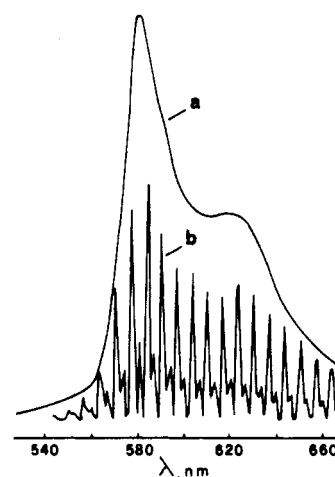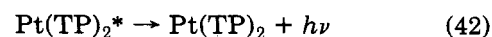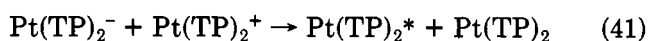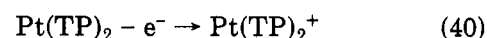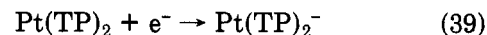

Figure 37. Photoluminescence (a) and electrochemiluminescence (b) spectra of 1.0 × 10^{-4} M Pt(TP)$_2$ in DMF solution. The photoluminescence spectrum was obtained by 420-nm excitation, and the ecl spectrum was obtained by stepping the potential between +0.85 and -1.80 V, with a pulse duration of 2 s. Figure reproduced with permission from ref 306. Copyright 1986 American Chemical Society.

complex in DMF solution.[306] This ecl emission closely matches the photoluminescence spectrum (see Figure 37) and has, therefore, been attributed to the lowest energy triplet MLCT excited state of Pt(TP)$_2$. The mechanism of electrochemical luminescence production is shown by eq 39–42.

$$\text{Pt(TP)}_2 + \text{e}^- \rightarrow \text{Pt(TP)}_2^- \quad (39)$$

$$\text{Pt(TP)}_2 - \text{e}^- \rightarrow \text{Pt(TP)}_2^+ \quad (40)$$

$$\text{Pt(TP)}_2^- + \text{Pt(TP)}_2^+ \rightarrow \text{Pt(TP)}_2^* + \text{Pt(TP)}_2 \quad (41)$$

$$\text{Pt(TP)}_2^* \rightarrow \text{Pt(TP)}_2 + h\nu \quad (42)$$

An ecl coulombic efficiency (ϕ_{ecl}) may be defined as approximately equal to the number of photons produced per electron-transfer event, and it has been estimated to be 5 × 10^{-3} for this complex. Furthermore, generation of a chemiluminescence signal has also been shown to yield valuable information on the mechanism of reaction of Pt(TP)$_2$ and other redox species in elec-

trochemical experiments.[306] It may be expected that ecl determination will become an important physical method that will enable further advances in characterizing organometallic redox processes.

V. Closing Remarks

The examples discussed above illustrate the rich variety of excited states and photophysical behavior exhibited by transition-metal complexes. A great deal has been learned about the excited states of these systems from their luminescence properties. In many cases, detailed studies of the electronic absorption and emission data have enabled specific excited-state assignments to be made.

It is apparent that a wide range of organometallic compounds have been established to luminesce in a rigid low-temperature environment or, more recently, in solution at room temperature. Indeed the fairly large number of examples can be rationalized by recognizing that the LF splittings of these complexes are relatively high, placing these normally photoreactive states above other emitting states. Low-lying MLCT excited states are often observed because of the low-valent metal centers and vacant low-energy ligand acceptor orbitals in many organometallic complexes. Reported luminescence data are perhaps most extensive for metal carbonyl complexes, and this has clearly demonstrated the relationships that exist between the energy ordering of the excited-state levels and the observed photophysical and photochemical properties. The great majority of examples of room temperature emission have been attributed to MLCT excited states that lie below IL or LF levels. On the other hand, complexes with low-lying LF states are typically highly photoreactive at room temperature and have only been observed to exhibit luminescence in rigid low-temperature media.

In numerous instances emission has been observed from second- and third-row-metal complexes but is absent from their first-row analogues. This suggests that the emissions of these complexes comprise a significant degree of spin-forbidden character. Moreover, energy-transfer experiments support this interpretation; the luminescence and quencher properties of a number of systems illustrate that they behave much like organic triplet donors and acceptors. It should be noted, however, that the spin–orbit coupling of the heavy metal precludes a pure triplet description of these emissions, and in many of the described examples the observed absorption and emission spectra indicate that this influence is extensive.

Several complexes have been recognized to display multiple-emission properties either in fluid solution (see $W(CO)_4(\alpha\text{-diimine})$ complexes) or in a low-temperature glass environment (see, for e.g., $fac\text{-XRe(CO)}_3L_2$ complexes). In the former example the emitting states have been assigned to be of MLCT character, and they are apparently rapidly thermally equilibrated, whereas in the latter complexes the emissions are attributed to IL and MLCT states that are unable to interconvert at low temperature. A great deal, though, remains to be understood about the detailed photophysics of multiple-luminescence systems.

Studies of the temperature dependence of luminescence spectra and lifetimes have yielded valuable information on the nature of the excited states involved

in the radiative decay. Models have been developed for a number of systems that picture the lowest excited state as being split by spin–orbit coupling into several levels. Emission may then be described as arising from each of these levels in which there is rapid Boltzmann relaxation compared with the excited-state to ground-state degradation.

Luminescence measurements have shown that the MLCT excited state may be exceptionally long-lived and one that is capable of undergoing outer sphere electron transfer to acceptor molecules. In this manner photoexcited organometallic complexes have been demonstrated to sensitize photoreduction process, e.g., CO_2 to CO and ketones to alcohols. Intramolecular electron-transfer mechanisms have also been invoked in the deactivation processes of organometallic complexes.

In conclusion, the literature reviewed here has clearly demonstrated the usefulness of luminescence data in understanding the photophysical and photochemical properties of organometallic compounds. This field has enjoyed rapid progress, and it promises to yield further significant developments.

VI. Acknowledgments

VII. References

(1) Balzani, V.; Carassiti, V. Photochemistry of Coordination Compounds; Academic: London, 1970.
(2) Adamson, A. W.; Waltz, W. L.; Zinato, E.; Watts, D. W.; Fleischauer, P. D.; Lindholm, R. D. Chem. Rev. 1968, 68, 541.
(3) Fleischauer, P. D.; Fleischauer, P. Chem. Rev. 1970, 70, 199.
(4) Concepts of Inorganic Photochemistry; Adamson, A. W., Fleischauer, P. D., Eds.; Wiley: New York, 1975.
(5) Wehry, E. L. Q. Rev., Chem. Soc. (London) 1967, 21, 213.
(6) Balzani, V.; Moggi, L.; Scandola, F.; Carassiti, V. Inorg. Chim. Acta Rev. 1967, 1, 7.
(7) Wrighton, M. S. Top. Curr. Chem. 1976, 65, 37.
(8) Inorganic and Organometallic Photochemistry; Wrighton, M. S., Ed.; Advances in Chemistry Series 168; American Chemical Society: Washington, DC, 1978.
(9) Ford, P. C. Rev. Chem. Intermed. 1979, 2, 267.
(10) Adamson, A. W. Comments Inorg. Chem. 1981, 1, 33.
(11) A symposium titled "Inorganic Photochemistry—State of the Art" was recently held and this has been summarized in: J. Chem. Educ. 1983, 60, 784.
(12) Strohmeier, W. Angew. Chem., Int. Ed. Engl. 1964, 3, 730.
(13) Strohmeier, W. Fortschr. Chem. Forsch. 1968, 10, 306.
(14) Koerner von Gustorf, E.; Grevels, F.-W. Fortschr. Chem. Frosch. 1969, 13, 366.
(15) Dobson, G. R.; Stolz, I. W.; Sheline, R. K. Adv. Inorg. Chem. Radiochem. 1966, 8, 1.
(16) Reference 2, p 556.
(17) Volger, A., in ref 4, p 269.
(18) Wrighton, M. Chem. Rev. 1974, 74, 401.
(19) Turner, J. J. Angew. Chem., Int. Ed. Engl. 1975, 14, 304.
(20) Bock, C. R.; Koerner von Gustorf, E. A. Adv. Photochem. 1977, 10, 221.
(21) Reference 7, pp 59–90.
(22) Geoffroy, G. L.; Wrighton, M. S. Organometallic Photochemistry; Academic: New York, 1979.
(23) Beach, N. A.; Gray, H. B. J. Am. Chem. Soc. 1968, 90, 5713.
(24) Jorgensen, C. K. Absorption Spectra and Chemical Bonding in Complexes; Pergamon: New York, 1962.

(25) Wrighton, M. S.; Handeli, D. I.; Morse, D. L. *Inorg. Chem.* **1976**, *15*, 434.
(26) Wrighton, M. S.; Ginley, D. S.; Morse, D. L. *J. Phys. Chem.* **1974**, *78*, 2229.
(27) Mingardi, M.; Porter, G. B. *J. Chem. Phys.* **1966**, *44*, 4354.
(28) Hipps, K. W.; Crosby, G. A. *Inorg. Chem.* **1974**, *13*, 1543.
(29) Rest, A. J.; Sodeau, J. R. *J. Chem. Soc., Faraday Trans. 2* **1977**, *73*, 1691.
(30) McHugh, T. M.; Narayanaswamy, R.; Rest, A. J.; Salisbury, K. *J. Chem. Soc., Chem. Commun.* **1979**, 208.
(31) Mitteilung, K. *Z. Phys. Chem. (Munich)* **1961**, *27*, 439.
(32) Dobson, G. R. *J. Phys. Chem.* **1965**, *69*, 677.
(33) Darensbourg, D. J.; Brown, T. L. *Inorg. Chem.* **1968**, *7*, 959.
(34) Herberhold, M. *Angew. Chem., Int. Ed. Engl.* **1968**, *7*, 305.
(35) Braterman, P. S.; Walker, A. P. *Discuss. Faraday Soc.* **1969**, *47*, 121.
(36) Darensbourg, M. Y.; Darensbourg, D. J. *Inorg. Chem.* **1970**, *9*, 32.
(37) Graham, M. A.; Rest, A. J.; Turner, J. J. *J. Organomet. Chem.* **1970**, *24*, C54.
(38) Graham, M. A.; Poliakoff, M.; Turner, J. J. *J. Chem. Soc. A* **1971**, 2939.
(39) Casey, C. P.; Burkhardt, T. J. *J. Am. Chem. Soc.* **1973**, *95*, 5833.
(40) Wrighton, M.; Hammond, G. S.; Gray, H. B. *J. Organomet. Chem.* **1974**, *70*, 283.
(41) Wrighton, M. *Inorg. Chem.* **1974**, *13*, 905.
(42) Burdett, J. K.; Perutz, R. N.; Poliakoff, M.; Turner, J. J. *J. Chem. Soc., Chem. Commun.* **1975**, 157.
(43) Perutz, R. N.; Turner, J. J. *J. Am. Chem. Soc.* **1975**, *97*, 4791.
(44) Turner, J. J.; Burdett, J. K.; Perutz, R. N.; Poliakoff, M. *Pure Appl. Chem.* **1977**, *49*, 271.
(45) Wensky, D. A.; Wensky, A. K. *Spectrochim. Acta, Part A* **1975**, *31*, 23.
(46) Darensbourg, D. J.; Murphy, M. A. *J. Am. Chem. Soc.* **1978**, *100*, 463.
(47) Dahlgren, R. M.; Zink, J. I. *Inorg. Chem.* **1977**, *16*, 3154.
(48) Dahlgren, R. M.; Zink, J. I. *J. Am. Chem. Soc.* **1979**, *101*, 1448.
(49) Dahlgren, R. M.; Zink, J. I. *Inorg. Chem.* **1979**, *18*, 597.
(50) Wrighton, M.; Hammond, G. S.; Gray, H. B. *J. Am. Chem. Soc.* **1971**, *93*, 4336.
(51) Wrighton, M.; Hammond, G. S.; Gray, H. B. *Inorg. Chem.* **1972**, *11*, 3122.
(52) Ryskin, A. I.; Tkachuk, A. M.; Tolstoi, N. A. *Opt. Spektrosk.* **1965**, *18*, 238.
(53) Demas, J. N.; Crosby, G. A. *J. Am. Chem. Soc.* **1970**, *92*, 7262.
(54) Watts, R. J.; Crosby, G. A. *J. Am. Chem. Soc.* **1972**, *94*, 2606.
(55) Robinson, G. W.; Frosch, R. P. *J. Chem. Phys.* **1962**, *37*, 1962.
(56) O'Sullivan, M.; Testa, A. C. *J. Am. Chem. Soc.* **1970**, *92*, 5842.
(57) O'Sullivan, M.; Testa, A. C. *J. Am. Chem. Soc.* **1970**, *92*, 258.
(58) Wrighton, M.; Hammond, G. S.; Gray, H. B. *Mol. Photochem.* **1973**, *5*, 179.
(59) Wrighton, M. S.; Abrahamson, H. B.; Morse, D. L. *J. Am. Chem. Soc.* **1976**, *98*, 4105.
(60) Frazier, C. C.; Kisch, H. *Inorg. Chem.* **1978**, *17*, 2736.
(61) Hay, P. J. *J. Am. Chem. Soc.* **1978**, *100*, 2411.
(62) Boxhoorn, G.; Schoemaker, G. C.; Stufkens, D. J.; Oskam, A.; Rest, A. J.; Darensbourg, D. J. *Inorg. Chem.* **1980**, *19*, 3455.
(63) Boxhoorn, G.; Oskam, A.; Gibson, E. P.; Narayanaswamy, R.; Rest, A. J. *Inorg. Chem.* **1981**, *20*, 783.
(64) Parker, C. A. *Photoluminescence of Solutions*; Elsevier: Amsterdam, 1968; p 22.
(65) Birks, J. B. *Photophysics of Aromatic Molecules*; Wiley: London, 1970; p 120.
(66) Wright, M. R.; Frosch, R. P.; Robinson, G. W. *J. Chem. Phys.* **1960**, *33*, 934.
(67) Robinson, G. W. *J. Mol. Spectrosc.* **1961**, *6*, 58.
(68) Gibson, E. P.; Rest, A. J. *J. Chem. Soc., Faraday Trans. 2* **1981**, *77*, 109.
(69) Tutt, L.; Tannor, D.; Heller, E. J.; Zink, J. I. *Inorg. Chem.* **1982**, *21*, 3858.
(70) Tutt, L.; Tannor, D.; Schindler, J.; Heller, E. J.; Zink, J. I. *J. Phys. Chem.* **1983**, *87*, 3017.
(71) Brown, R. A.; Dobson, G. R. *Inorg. Chim. Acta* **1972**, *6*, 65.
(72) English, A. M.; Plowman, K. R.; Butler, I. S. *Inorg. Chem.* **1981**, *20*, 2553.
(73) Heller, E. J. *J. Chem. Phys.* **1978**, *68*, 3891.
(74) Heller, E. J.; Gelbart, W. M. *J. Chem. Phys.* **1980**, *73*, 626.
(75) Heller, E. J. In *Potential Energy Surface and Dynamic Calculations*; Truhlar, D. G., Ed.; Plenum: New York, 1981.
(76) Heller, E. J. *Acc. Chem. Res.* **1981**, *14*, 368.
(77) Yersin, H.; Otto, H.; Zink, J. I.; Gliemann, G. *J. Am. Chem. Soc.* **1980**, *102*, 951. Eyring, G.; Schmidtke, H.-H. *Ber. Bunsen-Ges. Phys. Chem.* **1981**, *85*, 597.
(78) Dillinger, R.; Gliemann, G. *Chem. Phys. Lett.* **1985**, *122*, 66. Dillinger, R.; Gliemann, G. *Z. Naturforsch.* **1986**, *41a*, 1071. Gliemann, G. *Comments Inorg. Chem.* **1986**, *5*, 263.
(79) Lees, A. J.; Adamson, A. W. *J. Am. Chem. Soc.* **1980**, *102*, 6874.

(80) Lees, A. J.; Adamson, A. W. *J. Am. Chem. Soc.* **1982**, *104*, 3804.
(81) Lees, A. J. *J. Am. Chem. Soc.* **1982**, *104*, 2038.
(82) Kolodziej, R. M.; Lees, A. J. *Organometallics* **1986**, *5*, 450.
(83) Reference 65, p 182.
(84) Fang, T.-S.; Singer, L. A. *J. Am. Chem. Soc.* **1978**, *100*, 6276.
(85) Ford, P.; Rudd, D. P.; Gaunder, R.; Taube, H. *J. Am. Chem. Soc.* **1968**, *90*, 1187.
(86) Ford, P. C.; Stuermer, D. H.; McDonald, D. P. *J. Am. Chem. Soc.* **1969**, *91*, 6209.
(87) Chaisson, D. A.; Hintze, R. E.; Stuermer, D. H.; Petersen, J. D.; McDonald, D. P.; Ford, P. C. *J. Am. Chem. Soc.* **1972**, *94*, 6665.
(88) Malouf, G.; Ford, P. C. *J. Am. Chem. Soc.* **1974**, *96*, 601.
(89) Hintze, R. E.; Ford, P. C. *Inorg. Chem.* **1975**, *14*, 1211.
(90) Malouf, G.; Ford, P. C. *J. Am. Chem. Soc.* **1977**, *99*, 7213.
(91) Matsubara, T.; Ford, P. C. *Inorg. Chem.* **1978**, *17*, 1747.
(92) Figard, J. E.; Petersen, J. D. *Inorg. Chem.* **1978**, *17*, 1059.
(93) Abrahamson, H. B.; Wrighton, M. S. *Inorg. Chem.* **1978**, *17*, 3385.
(94) Wrighton, M. S.; Morse, D. L. *J. Organomet. Chem.* **1975**, *97*, 405.
(95) Pdungsap, L.; Wrighton, M. S. *J. Organomet. Chem.* **1977**, *127*, 337.
(96) Chun, S.; Lees, A. J. *Inorg. Chim. Acta* **1982**, *65*, L167.
(97) Chun, S.; Getty, E. E.; Lees, A. J. *Inorg. Chem.* **1984**, *23*, 2155.
(98) Saito, H.; Fujita, J.; Saito, K. *Bull. Chem. Soc. Jpn.* **1968**, *41*, 359.
(99) Saito, H.; Fujita, J.; Saito, K. *Bull. Chem. Soc. Jpn.* **1968**, *41*, 863.
(100) Staal, L. H.; Stufkens, D. J.; Oskam, A. *Inorg. Chim. Acta* **1978**, *26*, 255.
(101) Balk, R. W.; Stufkens, D. J.; Oskam, A. *Inorg. Chim. Acta* **1978**, *28*, 133.
(102) Balk, R. W.; Stufkens, D. J.; Oskam, A. *J. Chem. Soc., Chem. Commun.* **1978**, 1016.
(103) Staal, L. H.; Terpstra, A.; Stufkens, D. J. *Inorg. Chim. Acta* **1979**, *34*, 97.
(104) Balk, R. W.; Stufkens, D. J.; Oskam, A. *Inorg. Chim. Acta* **1979**, *34*, 267.
(105) Balk, R. W.; Stufkens, D. J.; Oskam, A. *J. Chem. Soc., Chem. Commun.* **1979**, 604.
(106) Balk, R. W.; Snoeck, T.; Stufkens, D. J.; Oskam, A. *Inorg. Chem.* **1980**, *19*, 3015.
(107) Kaizu, Y.; Fujita, I.; Kobayashi, H. *Z. Phys. Chem. (Munich)* **1972**, *79*, 298.
(108) Fujita, I.; Kobayashi, H. *Z. Phys. Chem. (Munich)* **1972**, *79*, 309.
(109) Manuta, D. M.; Lees, A. J. *Inorg. Chem.* **1983**, *22*, 572.
(110) Manuta, D. M.; Lees, A. J. *Inorg. Chem.* **1986**, *25*, 1354.
(111) Servaas, P. C.; van Dijk, H. K.; Snoeck, T. L.; Stufkens, D. J.; Oskam, A. *Inorg. Chem.* **1985**, *24*, 4494.
(112) For a review of literature appearing up to 1980 see: DeArmond, M. K.; Carlin, C. M. *Coord. Chem. Rev.* **1981**, *36*, 325.
(113) Halper, W.; DeArmond, M. K. *J. Lumin.* **1972**, *5*, 225.
(114) Merrill, J. T.; DeArmond, M. K. *J. Am. Chem. Soc.* **1979**, *101*, 2045.
(115) Sullivan, B. P.; Abruna, H.; Finklea, H. O.; Salmon, D. J.; Nagle, J. K.; Meyer, T. J.; Sprintschnik, H. *Chem. Phys. Lett.* **1978**, *58*, 389.
(116) Kirk, A. D.; Porter, G. B. *J. Phys. Chem.* **1980**, *84*, 887.
(117) Breddels, P. A.; Berdowski, P. A. M.; Blasse, G. *J. Chem. Soc., Faraday Trans. 2* **1982**, *78*, 595.
(118) Rader, R. A.; McMillin, D. R.; Buckner, M. T.; Matthews, T. G.; Casadonte, D. J.; Lengel, R. K.; Whittaker, S. B.; Darmon, L. M.; Lytle, F. E. *J. Am. Chem. Soc.* **1981**, *103*, 5906.
(119) Kirchhoff, J. R.; Gamache, R. E.; Blaskie, M. W.; Del Paggio, A. A.; Lengel, R. K.; McMillin, D. R. *Inorg. Chem.* **1983**, *22*, 2380.
(120) Sexton, D. A.; Ford, P. C.; Magde, D. *J. Phys. Chem.* **1983**, *87*, 197.
(121) Martin, M.; Krogh-Jespersen, M.-B.; Hsu, M.; Tewksbury, J.; Laurent, M.; Viswanath, K.; Patterson, H. *Inorg. Chem.* **1983**, *22*, 647.
(122) Segers, D. P.; DeArmond, M. K.; Grutsch, P. A.; Kutal, C. *Inorg. Chem.* **1984**, *23*, 2874.
(123) Nishizawa, M.; Suzuki, T. M.; Sprouse, S.; Watts, R. J.; Ford, P. C. *Inorg. Chem.* **1984**, *23*, 1837.
(124) Belser, P.; von Zelewsky, A.; Juris, A.; Barigelletti, F.; Balzani, V. *Chem. Phys. Lett.* **1984**, *104*, 100.
(125) Casadonte, D. J.; McMillin, D. R. *J. Am. Chem. Soc.* **1987**, *109*, 331.
(126) Manuta, D. M.; Lees, A. J. *Inorg. Chem.* **1983**, *22*, 3825.
(127) Manuta, D. M.; Lees, A. J. *Inorg. Chem.* **1986**, *25*, 3212.
(128) Brandt, W. W.; Gullstrom, D. K. *J. Am. Chem. Soc.* **1952**, *74*, 3532.
(129) Annibale, G.; Natile, G.; Cattalini, L. *J. Chem. Soc., Dalton Trans.* **1976**, 285.
(130) Wrighton, M.; Morse, D. L. *J. Am. Chem. Soc.* **1974**, *96*, 998.

(131) Van Dijk, H. K.; Servaas, P. C.; Stufkens, D. J.; Oskam, A. *Inorg. Chim. Acta* **1985**, *104*, 179.
(132) Ernst, S.; Kaim, W. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 430.
(133) Ernst, S.; Kurth, Y.; Kaim, W. *J. Organomet. Chem.* **1986**, *302*, 211.
(134) Kaim, W.; Kohlmann, S. *Inorg. Chem.* **1986**, *25*, 3306.
(135) Robbins, D. J.; Thomson, A. *J. Mol. Phys.* **1973**, *25*, 1103.
(136) Chun, S.; Palmer, D. C.; Mattimore, E. F.; Lees, A. J. *Inorg. Chim. Acta* **1983**, *77*, L119.
(137) Lees, A. J.; Fobare, J. M.; Mattimore, E. F. *Inorg. Chem.* **1984**, *23*, 2709.
(138) Zulu, M. M.; Lees, A. J., to be submitted for publication.
(139) Morgante, C. G.; Struve, W. S. *Chem. Phys. Lett.* **1980**, *69*, 56.
(140) Levenson, R. A.; Gray, H. B.; Ceasar, G. P. *J. Am. Chem. Soc.* **1970**, *92*, 3653.
(141) Levenson, R. A.; Gray, H. B. *J. Am. Chem. Soc.* **1975**, *97*, 6042.
(142) Wrighton, M. S.; Ginley, D. S. *J. Am. Chem. Soc.* **1975**, *97*, 4246.
(143) Bocarsly, A. B.; Cameron, R. E.; Rubin, H.-D.; McDermott, G. A.; Wolff, C. R.; Mayr, A. *Inorg. Chem.* **1985**, *24*, 3976.
(144) Kostic, N. M.; Fenske, R. F. *Organometallics* **1982**, *1*, 489.
(145) Vogler, A.; Kisslinger, J.; Roper, W. R. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1983**, *38*, 1506.
(146) Wrighton, M. S.; Morse, D. L.; Gray, H. B.; Ottersen, D. K. *J. Am. Chem. Soc.* **1976**, *98*, 1111.
(147) McLean, R. A. N. *J. Chem. Soc., Dalton Trans.* **1974**, 1568.
(148) Yamada, S.; Nakahara, A.; Shimura, Y.; Tsuchida, R. *Bull. Chem. Soc. Jpn.* **1955**, *28*, 222.
(149) Wentworth, R. A. D.; Piper, T. S. *Inorg. Chem.* **1965**, *4*, 709.
(150) Schmidtke, H.-H. *Z. Phys. Chem. (Munich)* **1965**, *45*, 305.
(151) Schmidtke, H.-H. *Inorg. Chem.* **1966**, *5*, 1682.
(152) Gutterman, D. F.; Gray, H. B. *J. Am. Chem. Soc.* **1971**, *93*, 3364.
(153) Geoffroy, G. L.; Wrighton, M. S.; Hammond, G. S.; Gray, H. B. *Inorg. Chem.* **1974**, *13*, 430.
(154) Harrigan, R. W.; Hager, G. D.; Crosby, G. A. *Chem. Phys. Lett.* **1973**, *21*, 487.
(155) Harrigan, R. W.; Crosby, G. A. *J. Chem. Phys.* **1973**, *59*, 3468.
(156) Lees, A. J., unpublished observations.
(157) Crosby, G. A.; Hipps, K. W.; Elfring, W. H. *J. Am. Chem. Soc.* **1974**, *96*, 629.
(158) Saltiel, J.; D'Agostino, J.; Megarity, E. D.; Metts, L.; Neuberger, K. R.; Wrighton, M.; Zafiriou, O. C. *Org. Photochem.* **1973**, *3*, 1.
(159) Fischer, G.; Muszkat, K. A.; Fischer, E. *J. Chem. Soc. B* **1968**, 1156.
(160) Turro, N. J. *Modern Molecular Photochemistry*; Benjamin-Cummings: Menlo Park, CA, 1978; p 179.
(161) Smothers, W. K.; Wrighton, M. S. *J. Am. Chem. Soc.* **1983**, *105*, 1067.
(162) Caspar, J. V.; Westmoreland, T. D.; Allen, G. H.; Bradley, P. G.; Meyer, T. J.; Woodruff, W. H. *J. Am. Chem. Soc.* **1984**, *106*, 3492.
(163) Fredericks, S. M.; Luong, J. C.; Wrighton, M. S. *J. Am. Chem. Soc.* **1979**, *101*, 7415.
(164) Luong, J. C.; Nadjo, L.; Wrighton, M. S. *J. Am. Chem. Soc.* **1978**, *100*, 5790.
(165) Mabrouk, P. A.; Wrighton, M. S. *Chem. Phys. Lett.* **1984**, *103*, 332.
(166) Forster, M.; Hester, R. E. *Chem. Phys. Lett.* **1982**, *85*, 287.
(167) Summers, D. P.; Luong, J. C.; Wrighton, M. S. *J. Am. Chem. Soc.* **1981**, *103*, 5238.
(168) Kutal, C.; Weber, M. A.; Ferraudi, G.; Geiger, D. *Organometallics* **1985**, *4*, 2161.
(169) Salman, O. A.; Drickamer, H. G. *J. Chem. Phys.* **1982**, *77*, 3337.
(170) Siebrand, W. *J. Chem. Phys.* **1967**, *47*, 2411.
(171) Macholdt, H.-T.; Van Eldik, R.; Kelm, H.; Elias, H. *Inorg. Chim. Acta* **1985**, *104*, 115.
(172) Englman, R.; Jortner, J. *Mol. Phys.* **1970**, *18*, 145.
(173) Freed, K. F.; Jortner, J. *J. Chem. Phys.* **1970**, *52*, 6272.
(174) Caspar, J. V.; Meyer, T. J. *J. Phys. Chem.* **1983**, *87*, 952.
(175) Vogler, A.; Kunkely, H. *Inorg. Chim. Acta* **1980**, *45*, L265.
(176) Stevens, B. *Adv. Photochem.* **1971**, *8*, 161.
(177) Beens, H.; Weller, A. In *Organic Molecular Photophysics*; Birks, J. B., Ed.; Wiley: New York, 1975; Vol. 2, p 159.
(178) Knibbe, H.; Rehm, D.; Weller, A. *Ber. Bunsen-Ges. Phys. Chem.* **1969**, *73*, 839.
(179) Rehm, D.; Weller, A. *Z. Phys. Chem. (Munich)* **1970**, *69*, 183.
(180) Reitz, G. A.; Dressick, W. J.; Demas, J. N.; DeGraff, B. A. *J. Am. Chem. Soc.* **1986**, *108*, 5344.
(181) Giordano, P. J.; Fredericks, S. M.; Wrighton, M. S.; Morse, D. L. *J. Am. Chem. Soc.* **1978**, *100*, 2257.
(182) Giordano, P. J.; Wrighton, M. S. *J. Am. Chem. Soc.* **1979**, *101*, 2888.
(183) Fredericks, S. M.; Wrighton, M. S. *J. Am. Chem. Soc.* **1980**, *102*, 6166.

(184) Caspar, J. V.; Sullivan, C. B.; Meyer, T. J. *Inorg. Chem.* **1984**, *23*, 2104.
(185) E.g., correlations for an Os(III)/Os(II) couple have been reported: Kober, E. M.; Marshall, J. L.; Dressick, W. J.; Sullivan, B. P.; Caspar, J. V.; Meyer, T. J. *Inorg. Chem.* **1985**, *24*, 2755.
(186) Glezen, M. M.; Lees, A. J., to be submitted for publication.
(187) Giordano, P. J.; Wrighton, M. S. *Inorg. Chem.* **1977**, *16*, 160.
(188) Morse, D. L.; Wrighton, M. S. *J. Am. Chem. Soc.* **1976**, *98*, 3931.
(189) Luong, J. C.; Faltynek, R. A.; Wrighton, M. S. *J. Am. Chem. Soc.* **1979**, *101*, 1597.
(190) Luong, J. C.; Faltynek, R. A.; Wrighton, M. S. *J. Am. Chem. Soc.* **1980**, *102*, 7892.
(191) Vogler, A.; Kisslinger, J. *Inorg. Chim. Acta* **1986**, *115*, 193.
(192) Hunziker, M.; Ludi, A. *J. Am. Chem. Soc.* **1977**, *99*, 7370.
(193) Bignozzi, C. A.; Roffia, S.; Scandola, F. *J. Am. Chem. Soc.* **1985**, *107*, 1644.
(194) Schanze, K. S.; Meyer, T. J. *Inorg. Chem.* **1985**, *24*, 2121.
(195) Graff, J. L.; Wrighton, M. S. *J. Am. Chem. Soc.* **1981**, *103*, 2225.
(196) Hoffmann, R.; Schilling, B. E. R.; Bau, R.; Kaesz, H. D.; Mingos, D. M. P. *J. Am. Chem. Soc.* **1978**, *100*, 6088.
(197) Kaesz, H. D.; Fontal, B.; Bau, R.; Kirtley, S. W.; Churchill, M. R. *J. Am. Chem. Soc.* **1969**, *91*, 1021.
(198) Saillant, R.; Barcelo, G.; Kaesz, H. *J. Am. Chem. Soc.* **1970**, *92*, 5739.
(199) Wilson, R. D.; Bau, R. *J. Am. Chem. Soc.* **1976**, *98*, 4687.
(200) Creber, K. A. M.; Wan, J. K. S. *J. Am. Chem. Soc.* **1981**, *103*, 2101.
(201) Sovocool, G. W.; Hopf, F. R.; Whitten, D. G. *J. Am. Chem. Soc.* **1972**, *94*, 4350.
(202) Hopf, F. R.; O'Brien, T. P.; Scheidt, W. R.; Whitten, D. G. *J. Am. Chem. Soc.* **1975**, *97*, 277.
(203) Vogler, A.; Kunkely, H. *Ber. Bunsen-Ges. Phys. Chem.* **1976**, *80*, 425.
(204) Hopf, F. R.; Whitten, D. G. In *Porphyrins Metalloporphyrins*; 1975; Chapter 16.
(205) Zerner, M.; Gouterman, M.; Kobayashi, H. *Theor. Chim. Acta* **1966**, *6*, 363.
(206) Eastwood, D.; Gouterman, M. *J. Mol. Spectrosc.* **1970**, *35*, 359.
(207) Kachura, T. F.; Sevchenko, A. N.; Solovev, K. N.; Tsivrko, M. P. *Dokl. Akad. Nauk SSSR* **1974**, *217*, 1121.
(208) Antipas, A.; Buchler, J. W.; Gouterman, M.; Smith, P. D. *J. Am. Chem. Soc.* **1978**, *100*, 3015.
(209) Rillema, D. P.; Nagle, J. K.; Barringer, L. F.; Meyer, T. J. *J. Am. Chem. Soc.* **1981**, *103*, 56.
(210) Vogler, A.; Kisslinger, J.; Buchler, J. W. In *Optical Properties and Structure of Tetrapyrroles*; Blauer, G., Sund, H., Eds.; Walter de Gruyter: Berlin, 1985; p 107.
(211) Caspar, J. V.; Kober, E. M.; Sullivan, B. P.; Meyer, T. J. *J. Am. Chem. Soc.* **1982**, *104*, 630.
(212) Johnson, C. E.; Eisenberg, R.; Evans, T. R.; Burberry, M. S. *J. Am. Chem. Soc.* **1983**, *105*, 1795.
(213) Kenney, M. I. S.; Kenney, J. W.; Crosby, G. A. *Organometallics* **1986**, *5*, 230.
(214) Nesmeyanov, A. N.; Perevalova, E. G.; Nesmeyanova, O. A. *Dokl. Akad. Nauk SSSR* **1955**, *100*, 1099.
(215) Scott, D. R.; Becker, R. S. *J. Chem. Phys.* **1961**, *35*, 516.
(216) Armstrong, A. T.; Smith, F.; Elder, E.; McGlynn, S. P. *J. Chem. Phys.* **1967**, *46*, 4321.
(217) Armstrong, A. T.; Carroll, D. G.; McGlynn, S. P. *J. Chem. Phys.* **1967**, *47*, 1104.
(218) Sohn, Y. S.; Hendrickson, D. N.; Gray, H. B. *J. Am. Chem. Soc.* **1971**, *93*, 3603.
(219) Evans, S.; Green, M. L. H.; Jewitt, B.; Orchard, A. F.; Pygall, C. F. *J. Chem. Soc., Faraday Trans. 2* **1972**, *68*, 1847.
(220) Rabalais, J. W.; Werme, L. O.; Bergmark, T.; Karlsson, L.; Hussain, M.; Siegbahn, K. *J. Chem. Phys.* **1972**, *57*, 1185.
(221) Rosch, N.; Johnson, K. H. *Chem. Phys. Lett.* **1974**, *24*, 179.
(222) Brand, J. C. D.; Snedden, W. *Trans. Faraday Soc.* **1957**, *53*, 894.
(223) Traverso, O.; Scandola, F. *Inorg. Chim. Acta* **1970**, *4*, 493.
(224) Gilbert, A.; Kelly, J. M.; Koerner von Gustorf, E. *Mol. Photochem.* **1974**, *6*, 225.
(225) Kikuchi, M.; Kikuchi, K.; Kokubun, H. *Bull. Chem. Soc. Jpn.* **1974**, *47*, 1331.
(226) Kikuchi, K.; Kokubun, H.; Kikuchi, M. *Bull. Chem. Soc. Jpn.* **1975**, *48*, 1378.
(227) Wrighton, M. S.; Pdungsap, L.; Morse, D. L. *J. Phys. Chem.* **1975**, *79*, 66.
(228) Herkstroeter, W. G. *J. Am. Chem. Soc.* **1975**, *97*, 4161.
(229) Balzani, V.; Bolletta, F.; Scandola, F. *J. Am. Chem. Soc.* **1980**, *102*, 2152.
(230) Hunt, G. R.; McCoy, E. F.; Ross, I. G. *Aust. J. Chem.* **1962**, *15*, 591.
(231) Byrne, J. P.; McCoy, E. F.; Ross, I. G. *Aust. J. Chem.* **1965**, *18*, 1589.
(232) Smith, J. J.; Meyer, B. *J. Chem. Phys.* **1968**, *48*, 5436.

(233) Muller-Goldegg, A.; Voitlander, J. Z. Naturforsch., A: Astrophys., Phys. Phys. Chem. **1968**, 23, 1236.

(234) Crosby, G. A.; Hager, G. D.; Hipps, K. W.; Stone, M. L. Chem. Phys. Lett. **1974**, 28, 497. Hipps, K. W.; Francis, A. H. J. Phys. Chem. **1979**, 83, 1879.

(235) Lippincott, E. R.; Nelson, R. D. Spectrochim. Acta **1958**, 10, 307.

(236) Adams, D. M.; Fernando, W. S. J. Chem. Soc., Dalton Trans. **1972**, 2507.

(237) Malatesta, L.; Bonati, F. In Isocyanide Complexes of Metals; Wiley: New York, 1969.

(238) Sarapu, A. C.; Fenske, R. F. Inorg. Chem. **1972**, 11, 3021.

(239) Treichel, P. M. Adv. Organomet. Chem. **1973**, 11, 21.

(240) Bonati, F.; Minghetti, G. Inorg. Chim. Acta **1974**, 9, 95.

(241) Fantucci, P.; Naldini, L.; Cariati, F.; Valenti, V.; Bussetto, C. J. Organomet. Chem. **1974**, 64, 109.

(242) Sarapu, A. C.; Fenske, R. F. Inorg. Chem. **1975**, 14, 247.

(243) Bursten, B. E.; Fenske, R. F. Inorg. Chem. **1977**, 16, 963.

(244) Mann, K. R.; Cimolino, M.; Geoffroy, G. L.; Hammond, G. S.; Orio, A. A.; Albertin, G. Inorg. Chim. Acta **1976**, 16, 97.

(245) Mann, K. R.; Gray, H. B.; Hammond, G. S. J. Am. Chem. Soc. **1977**, 99, 306.

(246) Gray, H. B.; Mann, K. R.; Lewis, N. S.; Thich, J. A.; Richman, R. M. In ref 8, p 44.

(247) Mann, K. R.; Gordon, J. G.; Gray, H. B. J. Am. Chem. Soc. **1975**, 97, 3553.

(248) Miskowski, V. M.; Nobinger, G. L.; Kliger, D. S.; Hammond, G. S.; Lewis, N. S.; Mann, K. R.; Gray, H. B. J. Am. Chem. Soc. **1978**, 100, 485.

(249) Rice, S. F.; Milder, S. J.; Gray, H. B.; Goldbeck, R. A.; Kliger, D. S. Coord. Chem. Rev. **1982**, 43, 349.

(250) Milder, S. J.; Goldbeck, R. A.; Kliger, D. S.; Gray, H. B. J. Am. Chem. Soc. **1980**, 102, 6761.

(251) Rice, S. F.; Gray, H. B. J. Am. Chem. Soc. **1981**, 103, 1593.

(252) Dallinger, R. F.; Miskowski, V. M.; Gray, H. B.; Woodruff, W. H. J. Am. Chem. Soc. **1981**, 103, 1595.

(253) Rice, S. F.; Gray, H. B. J. Am. Chem. Soc. **1983**, 105, 4571.

(254) Che, C.-M.; Butler, L. G.; Gray, H. B.; Crooks, R. M.; Woodruff, W. H. J. Am. Chem. Soc. **1983**, 105, 5492.

(255) Che, C.-M.; Butler, L. G.; Gray, H. B. J. Am. Chem. Soc. **1981**, 103, 7796.

(256) Fukuzumi, S.; Hironaka, K.; Nishizawa, N.; Tanaka, T. Bull. Chem. Soc. Jpn. **1983**, 56, 2220.

(257) Reference 22, Chapter 3, and references therein.

(258) Fordyce, W. A.; Crosby, G. A. Inorg. Chem. **1982**, 21, 1023.

(259) Epstein, R. A.; Geoffroy, G. L.; Keeney, M. E.; Mason, W. R. Inorg. Chem. **1979**, 18, 478.

(260) Mestroni, G.; Zassinovich, G.; Camus, A. J. Organomet. Chem. **1977**, 140, 63.

(261) Fordyce, W. A.; Crosby, G. A. Inorg. Chem. **1982**, 21, 1455.

(262) Fordyce, W. A.; Rau, H.; Stone, M. L.; Crosby, G. A. Chem. Phys. Lett. **1981**, 77, 405.

(263) Marshall, J. L.; Stobart, S. R.; Gray, H. B. J. Am. Chem. Soc. **1984**, 106, 3027.

(264) Rodman, G. S.; Mann, K. R. Inorg. Chem. **1985**, 24, 3507.

(265) Natarajan, P.; Adamson, A. W. J. Am. Chem. Soc. **1971**, 93, 5599.

(266) Reveco, P.; Schmehl, R. H.; Cherry, W. R.; Fronczek, F. R.; Selbin, J. Inorg. Chem. **1985**, 24, 4078.

(267) Reveco, P.; Cherry, W. R.; Medley, J.; Garber, A.; Gale, R. J.; Selbin, J. Inorg. Chem. **1986**, 25, 1842.

(268) Anderson, S.; Seddon, K. R.; Wright, R. D.; Cocks, A. T. Chem. Phys. Lett. **1980**, 71, 220.

(269) Klassen, D. M. Chem. Phys. Lett. **1982**, 93, 383.

(270) Barigelletti, F.; Juris, A.; Balzani, V.; Belzer, P.; von Zelewsky, A. A. Inorg. Chem. **1983**, 22, 3335.

(271) Allen, G. H.; White, R. P.; Rillema, D. P.; Meyer, T. J. J. Am. Chem. Soc. **1984**, 106, 2613.

(272) Van Houten, J.; Watts, R. J. J. Am. Chem. Soc. **1976**, 98, 4853.

(273) Allsopp, S. R.; Cox, A.; Kemp, T. J.; Reed, W. J. J. Chem. Soc., Faraday Trans. 1 **1978**, 74, 1275.

(274) Durham, B.; Caspar, J. V.; Nagle, J. K.; Meyer, T. J. J. Am. Chem. Soc. **1982**, 104, 4803.

(275) Watts, R. J.; Harrington, J. S.; Van Houten, J. J. Am. Chem. Soc. **1977**, 99, 2179.

(276) Watts, R. J.; Bergeron, S. F. J. Phys. Chem. **1979**, 83, 424.

(277) Kahl, J. L.; Hanck, K.; DeArmond, K. J. Inorg. Nucl. Chem. **1979**, 41, 495.

(278) Flynn, C. M.; Demas, J. N. J. Am. Chem. Soc. **1974**, 96, 1959.

(279) Gillard, R. D.; Lancashire, R. J.; Williams, P. A. J. Chem. Soc., Dalton Trans. **1979**, 190.

(280) Spellane, P. J.; Watts, R. J. Inorg. Chem. **1981**, 20, 3561.

(281) Spellane, P. J.; Watts, R. J.; Curtis, C. J. Inorg. Chem. **1983**, 22, 4060.

(282) Wickramasinghe, W. A.; Bird, P. H.; Serpone, N. J. Chem. Soc., Chem. Comm. **1981**, 1284.

(283) Nord, G.; Hazell, A. C.; Hazell, R. G.; Farver, O. Inorg. Chem. **1983**, 22, 3429.

(284) Kutal, C. Adv. Chem. Ser. **1978**, 168, 158.

(285) Grutsch, P. A.; Kutal, C. J. Am. Chem. Soc. **1986**, 108, 3108.

(286) Sprouse, S.; King, K. A.; Spellane, P. J.; Watts, R. J. J. Am. Chem. Soc. **1984**, 106, 6647.

(287) King, K. A.; Spellane, P. J.; Watts, R. J. J. Am. Chem. Soc. **1985**, 107, 1431.

(288) Balzani, V.; Scandola, F. In Photochemical Conversion and Storage of Solar Energy; Connolly, J. S., Ed.; Academic: New York, 1981; p 97.

(289) Bergeron, S. F.; Watts, R. J. J. Am. Chem. Soc. **1979**, 101, 3151.

(290) Wakatsuki, Y.; Yamazaki, H.; Grutsch, P. A.; Santhanam, M.; Kutal, C. J. Am. Chem. Soc. **1985**, 107, 8153.

(291) Chassot, L.; Muller, E.; von Zelewsky, A. Inorg. Chem. **1984**, 23, 4249.

(292) Bar, L.; Gliemann, G.; Chassot, L.; von Zelewsky, A. Chem. Phys. Lett. **1986**, 123, 264.

(293) Maestri, M.; Sandrini, D.; Balzani, V.; Chassot, L.; Jolliet, P.; von Zelewsky, A. Chem. Phys. Lett. **1985**, 122, 375.

(294) Chassot, L.; von Zelewsky, A.; Sandrini, D.; Maestri, M.; Balzani, V. J. Am. Chem. Soc. **1986**, 108, 6084.

(295) Nakamuru, K. Bull. Chem. Soc. Jpn. **1982**, 55, 2697.

(296) Caruana, A.; Kisch, H. Angew. Chem., Int. Ed. Eng. **1979**, 18, 328.

(297) Brennen, W. R.; Kistiakowsky, G. B. J. Chem. Phys. **1966**, 44, 2695.

(298) Becker, K. H.; Schurgers, M. Angew. Chem., Int. Ed. Eng. **1971**, 10, 934.

(299) Hartman, D. C.; Winn, J. S. J. Chem. Phys. **1978**, 68, 2990.

(300) Hartman, D. C.; Hollingsworth, W. E.; Winn, J. S. J. Chem. Phys. **1980**, 72, 833.

(301) Bulgakov, R. G.; Maistrenko, G. Y.; Yakovlev, V. N.; Kuleshov, S. P.; Tolstikov, G. A.; Kazakov, V. P. Dokl. Akad. Nauk SSSR **1985**, 282, 1385.

(302) Vogler, A.; Kunkely, H. Ang. Chem., Int. Ed. Eng. **1981**, 20, 469.

(303) Schuster, G. B. Acc. Chem. Res. **1979**, 12, 366.

(304) Vogler, A.; El-Sayed, L.; Jones, R. G.; Namnath, J.; Adamson, A. W. Inorg. Chim. Acta **1981**, 53, L35.

(305) Faulkner, L. R.; Bard, A. J. In Electroanalytical Chemistry; Bard, A. J., Ed.; Dekker: New York, 1977; Vol. 10, p 1.

(306) Bonafede, S.; Ciano, M.; Bolletta, F.; Balzani, V.; Chassot, L.; von Zelewsky, A. J. Phys. Chem. **1986**, 90, 3836.