THE NATURE OF THE LOWEST EXCITED STATE AND PHOTOSUBSTITUTION REACTIVITY OF TETRACARBONYL-1,10-PHENANTHROLINETUNGSTEN(0) AND RELATED COMPLEXES

MARK S. WRIGHTON* and DAVID L. MORSE

Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139 (U.S.A.)

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Summary

Absorption and emission spectral studies of $M(CO)_4L$ complexes (M = Cr Mo, W; L = 2,2'-bipyridine, 1,10-phenanthroline, 5-CH_3-, 5-Cl-, 5-Br-, 5-NO_2-1,10-phenanthroline) have been carried out and reveal that the lowest excited state in every case is charge-transfer (CT) in character, M→L CT in absorption, and in no case do the ligand field (LF) excited states cross below the CT state. Minimum energies of the LF states have been established by the spectroscopic study of *cis*-bis(pyridine)- and *cis*-bis(aliphatic amine)-tetracarbonylmetal(0) complexes which all have LF lowest excited states for M = Mo, W. For the $M(CO)_4L$ complexes emission is detectable for M = Mo or W and occurs in the range 14.40-15.66 kK with lifetimes of 7.9-13.3 μsec and quantum yields of 0.02-0.09 all in EPA solution at 77 K. For the bis-pyridine and -aliphatic amine complexes emission occurs only from the W complexes and is of the order of 3.0-4.0 kK higher in energy than for the $M(CO)_4L$ complexes. Photosubstitution of pyridine is efficient in *cis*-$W(CO)_4(py)_2$ (py = pyridine): $\Phi_{436nm} = 0.23$; $\Phi_{405nm} = 0.27$; and $\Phi_{366nm} = 0.23$. The $M(CO)_4L$ complexes have strongly wavelength dependent, but modest, quantum yields for CO substitution and show that the lowest CT state is unreactive. Typical values for CO substitution for M = W and L = 1,10-phenanthroline are: $\Phi_{436nm} = 1.6 \times 10^{-4}$; $\Phi_{405nm} = 1.2 \times 10^{-3}$; $\Phi_{366nm} = 9.2 \times 10^{-3}$; and $\Phi_{313nm} = 2.2 \times 10^{-2}$.

The photochemistry of metal carbonyls has usually concerned complexes where the lowest excited state has been of the ligand field (LF) type [1]. General rationalizations for the substitutional reactivity of such excited states have been outlined [2,3]. Surprisingly, no work has been reported for metal carbonyls in which the lowest excited states (at least in absorption) are unambiguously

charge-transfer (CT) in character. Complexes which are appropriate for some initial studies are those of the general formula $M(CO)_4L$ (M = Cr, Mo, W) where L is a bidentate nitrogen donor chelate such as 2,2'-bipyridine (bipy) or 1,10-phenanthroline (1,10-phen) or their derivatives. Such species are well known, well characterized [4,5] substances whose thermal substitution chemistry has been studied [5]. Electronic spectral studies have been previously carried out [6,7], and the lowest absorptions in these molecules are definitively due to M→L CT transitions. A qualitative report [8] of the electronic emission of the bipy and several methyl-substituted bipy complexes suggests that the lowest excited state in emission is also CT in character.

In addition to describing the photosubstitution reactivity of $M(CO)_4L$ we report herein some new electronic absorption and emission spectral measurements of $M(CO)_4L$ complexes in order to (1) assess the parameters influencing changes in the energetic position of the M→L CT absorption band and (2) determine generally whether the CT excited state is still the lowest excited state when the excited molecule relaxes or whether the LF excited state cross below the CT state. The LF excited states are at slightly higher energies than the M→L CT in absorption for the $M(CO)_4L$ complexes. For the $M(CO)_4(en)$ (M = Cr, Mo, W; en = ethylenediamine) complexes there is no possibility of low energy CT absorption involving the nitrogen donor ligands, and consequently, in these systems the lowest energy absorptions were associated with LF transitions [6]. For the purposes of comparison we have also carried out some luminescence measurements on these aliphatic bis-nitrogen donor complexes and some non-chelated analogues.

Results and discussion

Electronic spectra

The electronic absorption spectra of a number of $M(CO)_4L$ complexes have been recorded, and the large number of derivatives measured for each metal (Cr, Mo and W) allow generalizations to be made. First, Table 1 lists the lowest energy absorption maxima of the complexes at 25°C in CH_2Cl_2. For a given L the lowest energy absorption maximum is generally ordered energetically Mo > W > Cr, and for a given M the band is generally ordered 1,10-phen > 2,2'-bipy > 5-CH_3- > 5-Cl- ≈ 5-Br- > 5-NO_2-phenanthroline. The variations in band position are not large (<2000 cm^{-1}) in any case, but are measurable, and the substituents Cl, Br, NO_2, which are electron-withdrawing, yield the lowest energy absorption maxima as expected for the M→L direction of the CT. The variation in the position of the M→L CT absorption with changes in solvent can be exceptionally large and has already been extensively investigated [7] for L = 2,2'-bipy and 1,10-phen. More polar solvents yield the highest energy absorption maximum and variations of the order of 4000 cm^{-1} can be seen in changing the solvent from CH_3CN to cyclohexane for $W(CO)_4(1,10-phen)$ [7]. In no case, however, does the M→L CT absorption maximum shift to higher energy than the LF absorption found in the corresponding $M(CO)_4(en)$ complex.

The low energy region of the electronic absorption spectra of the $M(CO)_4L$ complexes changes markedly upon cooling from 298 to 77 K in solution. The

TABLE 1

M→L CT ABSORPTION MAXIMA IN M(CO)$_4$L COMPLEXES

M	L	Lowest energy abs. max., kK (ϵ)	
		298 K, CH$_2$Cl$_2$	77 K, EPA
Cr	2,2'-bipy	20.11 (3715)	
	1,10-phen	20.20 (1430)	
	5-CH$_3$-1,10-phen	20.00 (1460)	
	5-Cl-1,10-phen	19.68 (1470)	
	5-Br-1,10-phen	19.53 (3260)	
	5-NO$_2$-1,10-phen	18.69	
Mo	2,2'-bipy	21.60 (4790)	
	1,10-phen	21.74 (3550)	21.74, 22.57
	5-CH$_3$-1,10-phen	21.28 (4560)	21.64, 22.62
	5-Cl-1,10-phen	20.79 (3530)	20.92; 22.12
	5-Br-1,10-phen	20.62 (8180)	
	5-NO$_2$-1,10-phen	19.88 (7330)	20.00, 21.50
W [a]	2,2'-bipy	20.53 (5130)	
	1,10-phen	20.83 (5020)	21.01, 22.42
	5-CH$_3$-1,10-phen	20.62 (3390)	20.92, 22.03
	5-Cl-1,10-phen	19.96 (5390)	20.37, 22.47
	5-Br-1,10-phen	19.96 (4170)	20.41, 22.37

[a] A shoulder to the red of the lowest absorption maximum is revealed in the 77 K spectra in EPA, cf. Fig. 1 and text.

typical sharpening and blue-shift of the M→L CT band in EPA accompanying the change from 298 to 77 K is shown in Fig. 1. The M→L CT band is observed to be resolved into two components at low temperature. Band maxima for the M→L CT absorption system at 77 K in EPA are given in Table 1 for several complexes. Importantly, the relative band maxima at 77 K do have nearly the same energetic ordering as a function of ligand and metal as found at 298 K in CH$_2$Cl$_2$. The absorption spectra at 77 K (Fig. 1) reveal a low energy absorption shoulder in the tungsten complexes which is not present in the chromium or molybdenum analogues. For the M(CO)$_6$ and M(CO)$_5$X (X = n-electron donor) complexes the low energy absorption shoulder present only for M = W has been ascribed to a spin-forbidden LF transition [9]. We assign the low energy shoulder in the W(CO)$_4$L complexes to a singlet→triplet M→L CT absorption.

Optical emission has been detected from the M(CO)$_4$L complexes for M = Mo or W, but not for M = Cr, either as the pure solids at 298 K or in EPA solution at 77 K. The first set of emission data was collected for the pure solids at 298 K by using a Raman spectrometer equipped with a He—Ne laser excitation source (632.8 nm, 15803 cm^{-1}). The observation of emission at 298 K itself is significant in that the W(CO)$_5$X (X = n-electron donor) complexes which exhibit LF luminescence only emit at low temperature [9]. In fact, ClRe(CO)$_3$(1,10-phen) and related complexes [10] are the only metal carbonyls known to luminescence at room temperature, and these complexes emit from CT states (Re→1,10-phen in absorption). Emission from the Mo(CO)$_4$L complexes is also in contrast to the M(CO)$_5$X series since for the C_{4v} complexes only the W com-
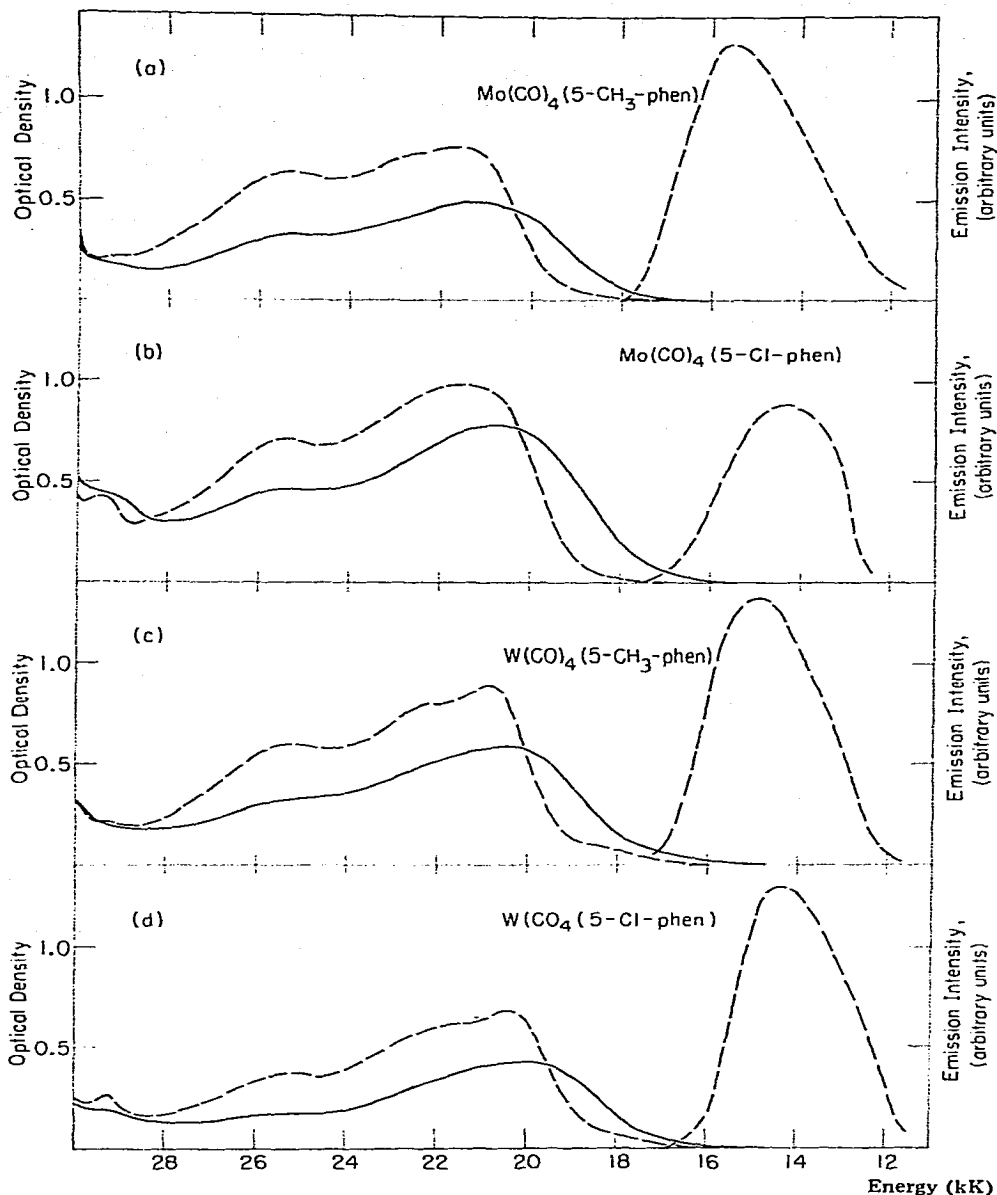
Fig. 1. Absorption (left) and emission (right) at 298 K (———) and 77 K (— — —) in EPA solution. The spectral changes accompanying cooling from 298 to 77 K are not corrected for solvent contraction. The emission spectra are corrected, and the excitation source is the 351, 364 nm emission of an argon ion laser.

plexes are luminescent [9]. The $M(CO)_4L$ emission maxima, from 632.8 nm excited emission spectra, uncorrected for variation in detector response as a function of wavelength, are given in Table 2. Overlap of the absorption and emission of the $M(CO)_4L$ complexes is evidenced by the small red-shift of the emission maxima from the He—Ne laser excitation line. In fact, the overlap of the emission and the excitation line is such that the high energy region of the

TABLE 2

EMISSION MAXIMA OF PURE SOLID M(CO)$_4$L COMPLEXES AT 298 K [a]

M	L	Emission max. (kK)
Mo	2,2'-bipy	14.95
	1,10-phen	15.45
	5-CH$_3$-1,10-phen	15.16
	5-Cl-1,10-phen	14.66
	5-Br-1,10-phen	14.61
W	2,2'-bipy	14.70
	1,10-phen	14.84
	5-CH$_3$-1,10-phen	14.93
	5-Cl-1,10-phen	14.83
	5-Br-1,10-phen	14.23

[a] Excited at 632.8 nm at room temperature; these are maxima from uncorrected spectra to illustrate the trend in emission maximum as a function of M and L.

emission is obscured by the He—Ne laser excitation line. The emission maxima, however, are quite clear, and the energetic position of the band is again related generally to the nature of L; the more electron-withdrawing group tends to yield the lowest energy emission maximum. Additionally, as in absorption, the higher energy bands are found for M = Mo for a given L.

Since absorption data were not obtained for the pure solids it would be more appropriate to relate emission maxima taken under conditions comparable to those for absorption. Unfortunately, no emission could be detected from the M(CO)$_4$L complexes in solution at room temperature. However, emission is easily detectable from M(CO)$_4$L at 77 K in EPA, and corrected emission maxima, emission lifetimes, and emission quantum yields are set out in Table 3. We have determined that the excitation spectra are the same as the absorption spectra below 33.0 kK in energy. Typical emission spectra are included in Fig.

TABLE 3

EMISSION DATA FOR M(CO)$_4$L AT 77 K IN EPA SOLUTION

M	L	Em. max, [a] (kK ± 0.05)	Em. ½ width, [a] (cm^{-1} ±50)	Em. τ, (µsec ± 10%)	Em. Φ [b] (±20%)
Mo	2,2'-bipy	15.25	3440		
	1,10-phen	15.66	3150	11.6	0.09
	5-CH$_3$-1,10-phen	15.55	3260	13.2	0.08
	5-Cl-1,10-phen	14.40	2940	13.3	0.04
	5-Br-1,10-phen	14.90	3325	9.5	
W	2,2'-bipy	15.10	3500		
	1,10-phen	15.30	3210	11.6	0.05
	5-CH$_3$-1,10-phen	14.90	3200	12.5	0.04
	5-Cl-1,10-phen	14.40	2950	7.9	0.02
	5-Br-1,10-phen	14.40	3340	7.9	

[a] From corrected emission spectra (cf. Experimental); emission half width is the width of the emission band at half height; excitation wavelength is 351.1, 363.4 nm from an argon ion laser. [b] Relative to rhodamine B, cf. Experimental.

TABLE 4

ELECTRONIC SPECTRAL FEATURES OF BIS(AMINE)- AND BIS(PYRIDINE)TETRACARBONYL-METAL(0) COMPLEXES [a]

Complex	Absorption max., kK (ϵ)			Em. max., (kK)	Em. τ, (μsec)
	LF, S→T	LF, S→S	M→π* CO		
Mo(CO)$_4$(en)	Not observed	24.88 (1700) [b]	32.68 (10000) [b, c]	Not observed	
cis-Mo(CO)$_4$(py)$_2$	Not observed	25.32 [d]	33.0 [d]	Not observed	
W(CO)$_4$(en)	22.42 (400) [b]	24.57 (1400) [b]	33.67 (8300) [b, c]	18.32	23.5
cis-W(CO)$_4$(n-PrNH$_2$)$_2$	22.22	24.27	33.67	18.52	0.9
cis-W(CO)$_4$(pip)$_2$	22.47	24.63	33.90	18.35	28.5
cis-W(CO)$_4$(py)$_2$	22.12 (4700) [c]	24.39 (9400) [e]	33.0	18.31	48.3

[a] All data for EPA solutions at 77 K except where noted otherwise; abbreviations are: en = ethylenediamine; py = pyridine; pip = piperidine; n-PrNH$_2$ = n-propylamine; for assignments see text. [b] Extinction coefficient is from ref. 6. [c] Absorption maximum in EPA at 298 K. [d] Benzene solution, 298 K. [e] Extinction coefficients are for benzene solution, 298 K.

1. These data show more convincingly that it is reasonable to associate the emitting state with the M→L CT state in absorption. For nearly every M(CO)$_4$L examined the same orderings of emission maxima and M→L CT absorption maxima are found. The spin multiplicity of the emitting CT state is logically assigned as triplet, but this label should be used with caution as the extent of spin—orbit coupling is so large as to preclude discrete singlet and triplet excited states [11].

In order to determine the approximate position of the lowest LF states in M(CO)$_4$L we have examined the spectra of several bis-nitrogen donor complexes for which M→L CT is not likely. Only the absorption spectra of M(CO)$_4$-(en) (M = Cr, Mo, W) have been measured previously [6], and no emission has been reported. New absorption spectral data have been acquired for the complexes cis-Mo(CO)$_4$(py)$_2$, cis-W(CO)$_4$(X)$_2$ (X = piperidine (pip), n-PrNH$_2$, py), Mo(CO)$_4$(en), and W(CO)$_4$(en). The cis-W(CO)$_4$(pip)$_2$ and cis-W(CO)$_4$(n-PrNH$_2$)$_2$ are too substition labile in solution to obtain accurate molar extinction coefficients, but it can be said that their spectra are, as expected, nearly the same as for W(CO)$_4$(en) in the number of bands, their relative and absolute intensities, and the band positions. The absorption data are summarized in Table 4. The 77 K spectra in EPA of W(CO)$_4$(en) and Mo(CO)$_4$(en) (Fig. 2) show more clearly the difference in the low energy region of the first absorption system: the W species shows a pronounced shoulder not present in the Mo complex. Further, at 77 K in EPA the W, but not the Mo, bis-amine complexes exhibit luminescence subsequent to electronic excitation as shown in Fig. 2 for W(CO)$_4$-(en). These results substantially parallel earlier results for W(CO)$_5$(amine) and Mo(CO)$_5$(amine) [9].

We adopt the earlier LF [6] assignment for the lowest absorption band system in the cis-M(CO)$_4$-bis(aliphatic amine) species. The strong spectral similarity of the bis-pip and bis-n-PrNH$_2$ complexes to the ethylenediamine complexes support this general assignment. Additionally, the bands for the C_{2v} complexes are modestly red-shifted from those [9] of the C_{4v} M(CO)$_5$(amine), as expected
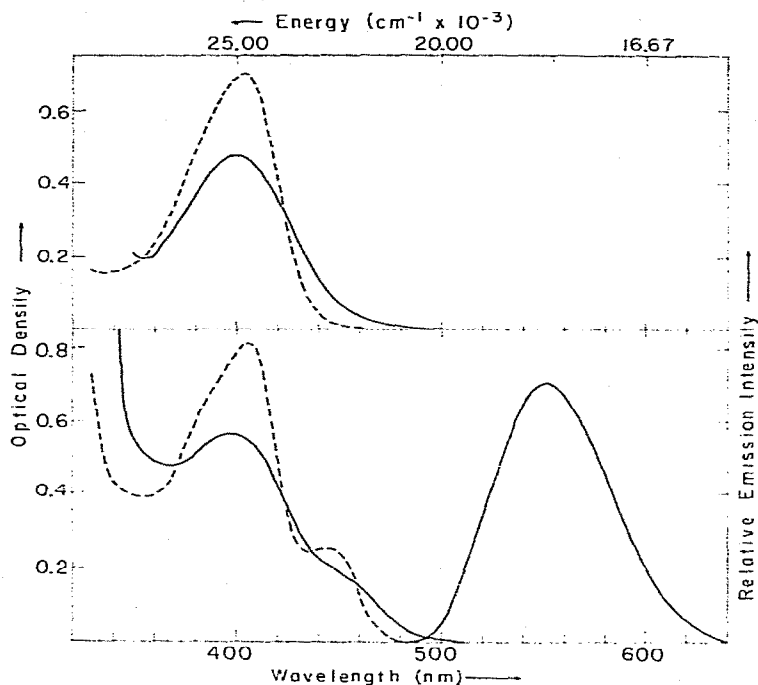
Fig. 2. Absorption (left curves) at 298 K (————) and 77 K (— — —) in EPA for Mo(CO)$_4$(en) (3 X 10^{-4} M and 1.00 cm path length) (upper curves) and W(CO)$_4$(en) (at 4 X 10^{-4} M and 1.00 cm path length) (lower curves). Emission of W(CO)$_4$(en) (right, lower curve) in EPA at 77 K.

for LF bands in the $C_{4v} \rightarrow C_{2v}$ descent in symmetry. The new low temperature absorption and emission data now allow us to assign the lowest energy shoulder in the W complexes as a LF singlet→triplet absorption but again with the realization that spin—orbit coupling is large. The emission from the cis-W(CO)$_4$-bis-(aliphatic amine) complexes is logically associated with the state achieved by the lowest energy absorption shoulder. Though a more thorough study of the electronic structure of these C_{2v} complexes will yield valuable new information, the essential nature of their lowest excited states is LF and likely involves population of orbitals which are strongly σ-antibonding with respect to the C—M—N axes. Moreover, it is certain that the energies of these states, even when relaxed, are substantially higher than for the relaxed CT excited states in the M(CO)$_4$L complexes. From these studies we can expect the LF states in M(CO)$_4$L to be ⩾22.5 kK in absorption and will therefore be upper excited states in the M(CO)$_4$L species.

The cis-M(CO)$_4$(py)$_2$ complexes likely have lowest excited states which are substantially LF in character, though some M→py CT character is evidenced by the large extinction coefficients found in cis-W(CO)$_4$(py)$_2$. Similarity in the lowest absorption and in the emission band positions of cis-W(CO)$_4$(py)$_2$ compared to W(CO)$_4$(en) is the main line of evidence supporting a strong contribution from a state essentially LF in character for both complexes. In W(CO)$_5$(py) a definite W→py CT absorption is observed [12], but it is substantially higher in energy than the LF absorptions. Figure 3 shows the low energy region of the
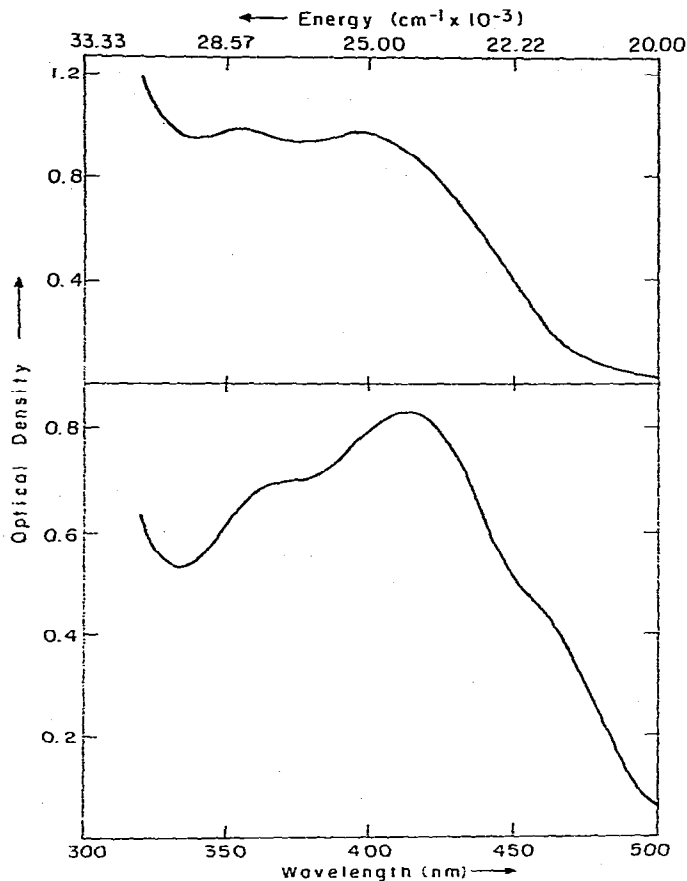
Fig. 3. Absorption of *cis*-M(CO)₄(py)₂ in benzene at 298 K for M = Mo (upper curve) and M = W (lower curve) at 1.0 × 10⁻⁴ *M* and 0.9 × 10⁻⁴ *M*, respectively, in 1.00 cm path length cells.

absorption spectra of *cis*-M(CO)$_4$(py)$_2$, and a band is observed near 370 nm which is not present in M(CO)$_4$(en), Fig. 2. We ascribe the band near 370 nm to the M→py CT transition and the lower band system to the LF transitions in *cis*-M(CO)$_4$(py)$_2$ (M = Mo, W). For W(CO)$_5$(py) and W(CO)$_5$(pip) excited state decay phenomena, including emission maxima [9] and photosubstitution [13] quantum yields involving W—N cleavage, are very similar, and we thus expect analogous results for the bis-nitrogen donor complexes. A full characterization [12] of the lowest excited LF and CT states in M(CO)$_5$(py) and *cis*-M(CO)$_4$(py)$_2$ supports the tentative conclusions outlined here concerning relative energetic ordering of LF and CT states in absorption.

Photosubstitution chemistry

Establishing the essential nature of the *cis*-W(CO)$_4$(py)$_2$ lowest excited state as LF allows us to use this molecule as a model of LF reactivity for the C_{2v} bis-nitrogen donor system. First, we have investigated the efficiency of W—C dissociation by irradiating *cis*-W(CO)$_4$(py)$_2$ in benzene solutions of pyridine.

TABLE 5

PHOTOSUBSTITUTION OF *cis*-W(CO)$_4$(py)$_2$ ^{a}

Irradiation λ (nm)	Φ ± 10%
436	0.23
405	0.27
366	0.23

^{a} Reaction is *cis*-W(CO)$_4$(py)$_2$ $\xrightarrow{h\nu}$ W(CO)$_4$(1,10-phen) at 25°C in benzene; 1,10-phenanthroline is 0.1 *M*.

The expected reaction is indicated in eqn. 1, but we have found that this con-

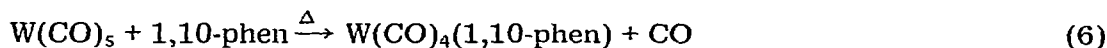$$cis\text{-W(CO)}_4\text{(py)}_2 \xrightarrow[\text{py}]{h\nu} fac\text{-W(CO)}_3\text{(py)}_3 + \text{CO} \tag{1}$$
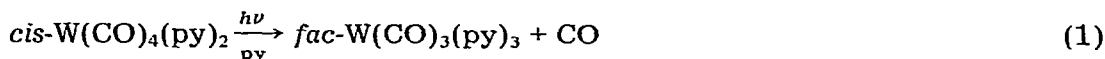
version upon near UV irradiation (313, 366 nm) has a quantum efficiency of ≈10^{-3}. It has also been found [13b] that *cis*-M(CO)$_4$-bis(aliphatic amine) (M = Mo, W; amine = pip or n-PrNH$_2$) for M—C cleavage are essentially non-photosensitive at 366, 405, or 436 nm. Efficiency for M—N cleavage in *cis*-W(CO)$_4$(py)$_2$ is, however, quite substantial. The reaction actually measured is reaction 2 which occurs with the quantum efficiencies in Table 5. Quantum efficiency is essentially

$$cis\text{-W(CO)}_4\text{(py)}_2 \xrightarrow[\text{1,10-phen}]{h\nu} \text{W(CO)}_4\text{(1,10-phen)} + 2 \text{ py} \tag{2}$$
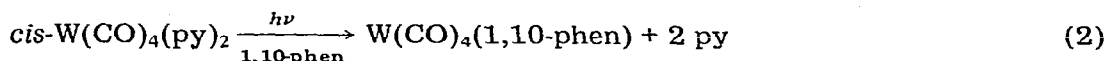
invariant for the three excitation wavelengths used which all lead to population of the low lying LF excited states. The thermal substitution lability of the bis-aliphatic amine complexes precludes quantitative photosubstitution measurements, but we have established that for W(CO)$_4$(en) the W—N photosubstitution efficiency is very similar to that for the *cis*-W(CO)$_4$(py)$_2$. The reaction of *cis*-W-(CO)$_4$(py)$_2$ in the presence of 1,10-phen likely proceeds as indicated in eqns. 3 and 4. The loss of both pyridine groups is similar to the production of W(CO)$_4$-(1,10-phen) by irradiation of W(CO)$_6$, reactions 5 and 6 [12]. It is interesting

$$cis\text{-W(CO)}_4\text{(py)}_2 \xrightarrow{h\nu} \text{W(CO)}_4\text{(py)} + \text{py} \tag{3}$$

$$\text{W(CO)}_4\text{(py)} + \text{1,10-phen} \xrightarrow{\Delta} \text{W(CO)}_4\text{(1,10-phen)} + \text{py} \tag{4}$$
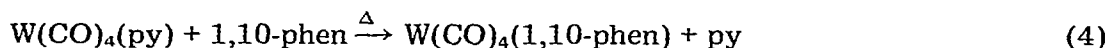
to note that the interaction of 1,10-phen with coordinatively unsaturated W(CO)$_4$-

$$\text{W(CO)}_6 \xrightarrow{h\nu} \text{W(CO)}_5 + \text{CO} \tag{5}$$

$$\text{W(CO)}_5 + \text{1,10-phen} \xrightarrow{\Delta} \text{W(CO)}_4\text{(1,10-phen)} + \text{CO} \tag{6}$$

(py) apparently yields only W(CO)$_4$(1,10-phen) and no W(CO)$_3$(py)(1,10-phen), which is a photosubstitution product of W(CO)$_4$(1,10-phen) (vide infra).

The overwhelming M—N lability in the excited state compared to M—C lability for these bis-nitrogen donor complexes is similar to the situation for the M(CO)$_5$(amine) and M(CO)$_5$(py) complexes [13]. As with the C_{4v} complexes,
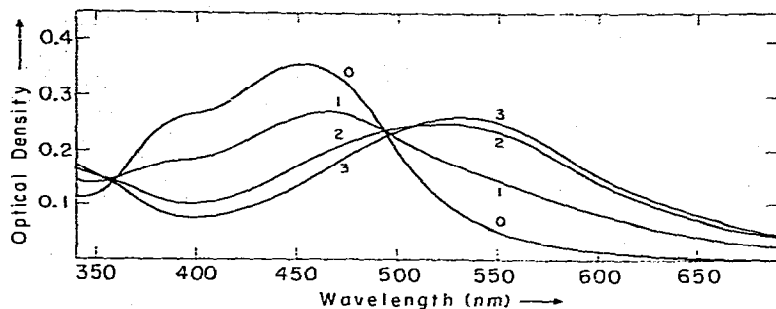
Fig. 4. Absorption spectral changes upon near UV irradiation of W(CO)₄(1,10-phen) initially at 0.7 X 10⁻⁴ M in degassed CH₃CN at 298 K. Curve 0 is the initial spectrum and curve 3 represents the final spectrum of (CH₃CN)W(CO)₃(1,10-phen). Spectra are measured in 1.00 cm path length cells.

one is tempted to rationalize this behavior by invoking lowest LF states which are σ-antibonding for the C—M—N axis. Both M—C and M—N lability are strongly enhanced in the excited state compared to the ground state, but essentially only M—N excited state dissociation is found since the M—N bond is much more labile in the ground state.

Turning now to the $M(CO)_4L$ complexes having lowest M→L CT states we have investigated reaction 7 for several L and X. Photosubstitution according to reaction 7 is very clean and typical UV-visible spectral changes accompanying

$$W(CO)_4L \xrightarrow[X]{h\nu} XW(CO)_3L + CO \tag{7}$$

the reaction are depicted in Fig. 4. Generally, an isosbestic point in the UV-visible is obtained, and the lowest absorption maximum of the $XW(CO)_3L$ complex is to the red to that for the starting $W(CO)_4L$ complex. The position of the isosbestic point and the lowest absorption maximum of the products are given in Table 6. Thermal reaction at 298 K does not occur on the same time scale as the irradiation times used to induce reaction 7. However, the products obtained are those expected for thermal CO substitution in $M(CO)_4L$ [5]. In no case have we found evidence for substitution of L.

TABLE 6

ABSORPTION MAXIMA FOR $XW(CO)_3L$ AND ISOSBESTIC POINTS IN THE PHOTOINDUCED $W(CO)_4L \xrightarrow{X} XW(CO)_3L$ CONVERSION

L	X	Solvent	Isosbestic Point (kK)	$XW(CO)_3L$, Abs. max., kK (ϵ)
1,10-phen	PPh₃	benzene	17.95	16.61 (2040)
1,10-phen	py	benzene	18.10	14.92 (5340)
1,10-phen	CH₃CN	CH₃CN	20.24	18.94 (3200)
1,10-phen	t-4-styryl-pyridine	benzene	18.10	17.80 (11, 100) and 15.15 (9130)
5-Br-1,10-phen	CH₃CN	CH₃CN	19.50	18.18 (2320)
5-CH₃-1,10-phen	CH₃CN	CH₃CN	20.50	18.94 (2900)
2,2'-bipy	CH₃CN	CH₃CN	20.00	18.62 (3600)

While the chemical yield of XW(CO)$_3$L is typically quantitative the quantum efficiency is very modest, but, importantly, the quantum efficiency for reaction 7 is very wavelength dependent. Quantum yield data are summarized in Table 7. Quantum yields for XW(CO)$_3$L formation are equal to W(CO)$_4$L disappearance values. Determinations of the quantum yields have been made by measuring either the decline of absorbance due to W(CO)$_4$L or the increase in absorbance for the product. Typical plots of such absorbances as a function of irradiation time are given in Fig. 5.

Chemical reaction involving CO substitution from the W→L CT state in W(CO)$_4$L apparently does not occur with measurable efficiency. The lack of reaction in the CT state allows two fundamental conclusions: (1) since the CT excited state lies higher in energy above the ground state than the typical thermal activation energy for ground state substitution, we conclude that the CT state does not decay via the transition state for the thermal substitution; (2) the CT
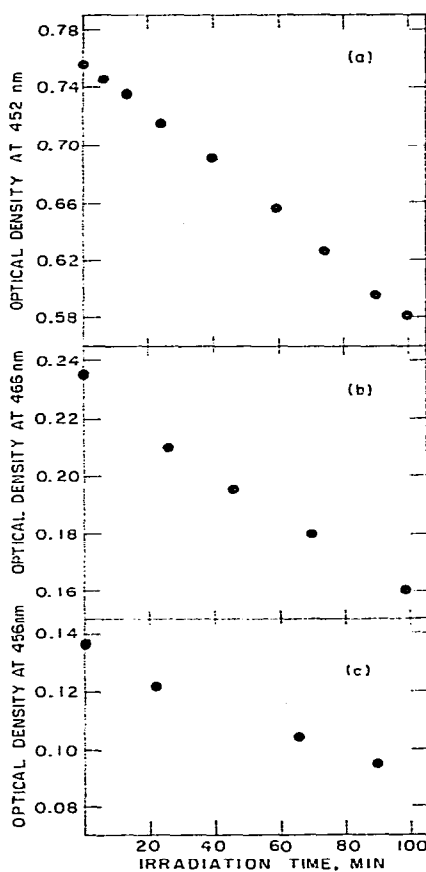

Fig. 5. Decline in absorbance of low energy absorption maximum of W(CO)$_4$L complexes upon 313 nm photolysis in neat CH$_3$CN solutions: (a) 3.0 ml of W(CO)$_4$(1,10-phen) initially 1.2 X 10^{-4} M photolyzed at 7.1 X 10^{-8} ein min^{-1} (100% absorbed) and the monitoring wavelength is 452 nm; (b) 3.0 ml of W(CO)$_5$(5-Br-1,10-phen) initially 3.7 X 10^{-5} M photolyzed at 6.6 X 10^{-8} ein min^{-1} (60% absorbed) and the monitoring wavelength is 456 nm; (c) 3.0 ml of W(CO)$_5$(5-CH$_3$1,10-phen) initially 3.3 X 10^{-5} M photolyzed at 6.5 X 10^{-8} ein min^{-1} (54% absorbed) and the monitoring wavelength is 456 nm.

TABLE 7

PHOTOSUBSTITUTION OF W(CO)$_4$L COMPLEXES TO YIELD W(CO)$_3$LX COMPLEXES [a]

L	X (M)	Solvent	Φ_{436nm}	Φ_{405nm}	Φ_{366nm}	Φ_{313nm}
1,10-phen	CH$_3$CN (neat)	CH$_3$CN	1.6 × 10^{-4}	1.2 × 10^{-3}	9.2 × 10^{-3}	2.2 × 10^{-2}
2,2'-bipy	CH$_3$CN (neat)	CH$_3$CN	5.3 × 10^{-5}			2.1 × 10^{-2}
5-CH$_3$-1,10-phen	CH$_3$CN (neat)	CH$_3$CN	1.5 × 10^{-5}			2.0 × 10^{-2}
5-Br-1,10-phen	CH$_3$CN (neat)	CH$_3$CN	1.2 × 10^{-4}			2.4 × 10^{-2}
1,10-phen	pyridine (0.02)	benzene	0.9 × 10^{-4}	1.5 × 10^{-3}		1.0 × 10^{-2}
1,10-phen	t-4-styrylpyri-dine (0.02)	benzene		1.4 × 10^{-3}		

[a] All quantum yields are ±10%; 298 K.

excited state is achieved by a one-electron depopulation of π—d orbitals which are π-bonding with respect to the CO's and results in an "oxidized central metal, M(O)→M(I)", but we must conclude that this simply does not labilize the M—C bonds enough to allow M—C dissociation prior to relaxation of the CT excited state to ground state. Interestingly, Ru→py CT in low-spin d^6 Ru(NH$_3$)$_5$(py)$^{2+}$ and related complexes does not lead to observed substitution via the CT state but rather via LF states [14].

Increasing CO substitution quantum yields with increasing excitation energy shows that an upper electronically excited state is responsible for the observed chemistry. The CO substitution yields for M(CO)$_4$L are about the same order of magnitude as for the cis-W(CO)$_4$(py)$_2$. Thus, one is tempted to conclude that the LF states are responsible for the CO substitution. But, though the CO substitution efficiency is very small, it should be kept in mind that the major fraction of the LF states likely relax to the lowest CT state, as evidenced by the resemblance of the excitation spectrum to the absorption spectrum for M(CO)$_4$L. Thus, the small efficiencies for M—C dissociation actually represent substantial reactivity for an upper-excited state. The remaining unanswered question here is whether the relative M—N and M—C labilizations are similar to those for, say, cis-W(CO)$_4$(py)$_2$. The major difference is likely to rest with the chelate effect, but for complexes of 2,2'-bipy reaction 8 is conceivable while a

$$(8)$$
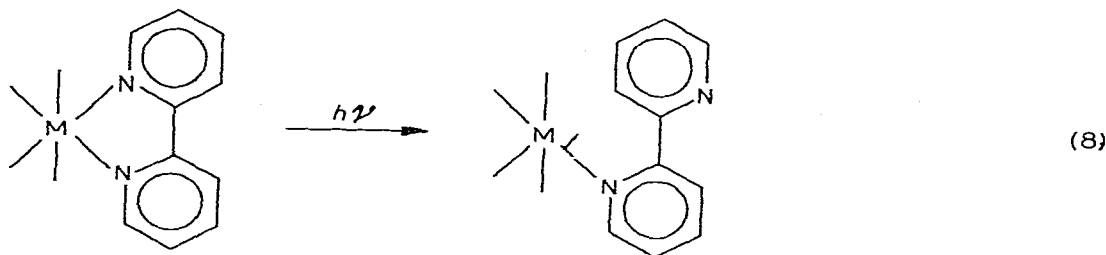
similar decay path for a 1,10-phen is unlikely. Data in Table 7 show similar CO photosubstitution yields for the 1,10-phen and 2,2'-bipy complexes and therefore either reaction 8 is unimportant or M—N labilization is not coupled to M—C labilization. A more definitive conclusion is likely to result from studies in progress on metal carbonyls containing non-chelating charge acceptor ligands.

Experimental

Spectra

All UV-visible electronic absorption spectra were measured with a Cary 17 spectrophotometer. Spectra for samples at 77 K were taken using an all quartz Dewar with optical-quality quartz flats for windows. Changes in absorption spectra upon cooling to 77 K shown in Figs. 1 and 2 are not corrected for solvent contraction. Low-temperature emission spectra were recorded using (*1*) an Aminco— Bowman spectrophotofluorometer equipped with either a 1P21 photomultiplier tube detector or a dry-ice cooled RCA 7102 photomultiplier tube for measurements in the red and near infrared region or (2), a Cary 17 with the sample positioned at the source position and using the 351, 364 nm lines of an argon ion laser (Spectra-Physics Model 164) as the excitation source. Corrected spectra were obtained using the equipment and procedure recently reported [15]. Room temperature emission spectra of the pure solids were measured using a Cary 81 Raman instrument equipped with an He—Ne laser (632.8 nm) exciting source. IR spectra were recorded on a Perkin—Elmer 237 or 521 spectrometer.

Synthesis of complexes

The $M(CO)_4L$ complexes were prepared by irradiation at 25°C of the corresponding $M(CO)_6$ (from Pressure Chemical Co.) in the presence of the appropriate ligand in continuously N_2-purged isooctane solution [4,5]. The $M(CO)_4L$ complexes are sparingly soluble in isooctane and precipitated almost immediately. The precipitate was collected and recrystallized from CH_2Cl_2 by addition of n-pentane. IR spectra [4,5] confirmed product purity and served to identify the previously known $\approx C_{2v}$ complexes: a weak band at 2010 ± 10^{-1}, a very strong band at 1910 ± 10 cm^{-1}, and two strong bands at 1880 ± 10 cm^{-1} and 1830 ± 10 cm^{-1}. The *cis*-$M(CO)_4$-bis(amine) complexes were prepared by irradiation of $M(CO)_6$ in the presence of the amine in N_2-purged isooctane solution [13b]. The product precipitated from solution and was collected and washed repeatedly with isooctane in which $M(CO)_5X$, $M(CO)_6$ and free amine are soluble. IR and UV-visible absorption spectra confirmed the product purity. All ligands used are commercially available.

Luminescence lifetimes

Emission lifetimes were measured using a TRW Model 75A Decay Time Fluorometer equipped with a Xenon Corporation Model 437 Nanopulser exciting source filtered with a Corning # 7-51 glass filter to pass near UV excitation. On the detection side a Corning # 3-73 glass filter was employed to absorb the UV excitation pulse and transmit the visible emission of the samples. The RCA 931A or the RCA 31025C PMT detector was powered by a Kepco Model ABC 2500 regulated high voltage power supply. The output of the PMT was monitored using a Tektronix 453 oscilloscope and recorded with a Polaroid camera. Plots of log(emission intensity) against time were linear in each case over two emission lifetimes. The lifetime was taken to be the time required for the emission intensity to decay to (1/*e*) of its original value.

Luminescence quantum yields

Absolute luminescence quantum yields were measured relative to rhodamine

B in ethanol having a luminescence yield of 0.69 [16]. In each case the optical density of the standard (at 298 K) and the sample (at 77 K) were matched at the excitation wavelength and emission spectra were recorded under identical conditions except that the metal complexes were measured in EPA at 77 K and the standards were measured at 298 K. Since the same number of photons is incident on the sample and standard and the absorbance in each is matched (OD 0.1 in a 2 mm path length round tube) the emission quantum yield of the complex is the ratio of area under the complex emission curve (plotted in energy units) to the area under the rhodamine B emission curve. The excitation wavelength was 490 nm and the PMT was the RCA 7102. The differences in solvent and temperature in the sample and standard introduce relatively large errors and we thus estimate the yields to be ±20%.

Substitution quantum yields

Substitution quantum yields were measured by irradiation in merry-go-rounds [17] equipped with either 450 or 550W medium pressure Hg Hanovia lamps with appropriate filters to isolate the 313, 366, 405 and 436 nm Hg lines. Light intensities were measured by ferrioxalate actinometry [18] and typical light intensities were in the range 10^{-7}-10^{-8} ein min^{-1}. Three ml samples in 13 × 100 mm Pyrex tubes of the $W(CO)_4L$ ($\approx 10^{-4}$ M) in either benzene or cyclohexane solutions of pyridine (0.02 M) or *trans*-4-styrylpyridine (0.02 M) or in pure CH_3CN were freeze-pump-thaw degassed in three cycles and hermetically sealed. Analysis of the reaction was by UV-visible absorption spectral changes which are linear in irradiation time for small conversion (cf. Figs. 4 and 5). Quantum yields were the same for formation of the product and disappearance of the starting material. The $XW(CO)_3L$ product was identified spectroscopically e.g., $PPh_3W(CO)_3(1,10$-phen) has three bands at 1910, 1820, and 1780 cm^{-1} in the CO stretching region of the IR as expected [4,5]. Quantum yields for CO substitution in *cis*-$W(CO)_4(py)_2$ were measured by monitoring the decline in absorption due to *cis*-$W(CO)_4(py)_2$ upon irradiation in the presence of pyridine. Study of the photosubstitution of pyridine in *cis*-$W(CO)_4$-$(py)_2$ was carried out by irradiation in the presence of 1,10-phen which leads to $W(CO)_4(1.10$-phen). The reaction was carried out to a small enough conversion to prevent competitive light absorption by the $W(CO)_4(1,10$-phen) product. In cases where the samples absorbed less than 100% of the incident light appropriate corrections were applied. All quantum yields reported here are the initial quantum yields.

Acknowledgement

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