Photosubstitution Reactivity of a Series of Pentacarbonylpyridinotungsten(0) Complexes Having Ligand Field or Charge-Transfer Lowest Excited States

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Abstract: Emission, electronic absorption, and photosubstitution efficiencies are reported for $W(CO)_5X$ (X = 3,4-dimethylpyridine, 4-methylpyridine, pyridine, 3-bromopyridine, 3-acetylpyridine, 3-benzoylpyridine, 3,5-dibromopyridine, 4-cyanopyridine, 4-acetylpyridine, 4-benzoylpyridine, and 4-formylpyridine). The spectral data show that the W → pyridyl charge transfer (CT) state moves smoothly to the red with more electron-withdrawing substituents. Using $W(CO)_5$(piperidine) as a comparison, the ligand field (LF) absorptions remain constant in energy for all X used here. Photosubstitution of X occurs in all cases upon irradiation into the lowest energy absorption system, but the quantum efficiency is a dramatic function of whether the lowest energy absorption is LF or W → X CT. The CT state is virtually unreactive [$W(CO)_5$(4-formylpyridine) yields substitution of 4-formylpyridine at 514 nm with a quantum efficiency of 0.002], while the LF state gives X substitution with a quantum efficiency of ~0.60 for complexes where the LF state is the lowest energy excited state.

The aim of this paper is to report the results of an investigation of the absorption and emission spectroscopy and photosubstitution reactivity of $W(CO)_5X$, where X is a substituted pyridine. We have attempted to vary the nature of the lowest electronic excited state in $W(CO)_5X$ by simple variation in the substituents on pyridine, in order to gain insight into the substitution reactivity of certain types of electronic states in a situation where the essential components of the coordination sphere are constant.

Quite a great deal of work has already been undertaken toward understanding the photochemistry and spectroscopy of metal carbonyls[2] and particularly of $W(CO)_5X$ complexes. For X = *n*-electron donor, the lowest absorption bands were assigned[3] as ligand field (LF) $^1A_1(e^4b_2^2) \rightarrow {}^{1,3}E(e^3b_2^2a_1^1)$, and it was found[3-5] that emission from the ^3E state occurs at low temperatures. Photosubstitution of both X and CO are found in $W(CO)_5X$[5-8] in solution at room temperature. The dominant reaction is efficient dissociation of X for X = pyridine or aliphatic amine when the irradiation is into the lowest LF absorption band system.[5,6] The quantum efficiency for W–X dissociation is generally ≥0.5 for the cases investigated,[5,6] and though the efficiency for CO substitution increases with increasing excitation energy the dominant reaction remains loss of X, which is consistent with a substantial amount of reaction from the lowest excited state even when upper excited states are directly populated. Dissociative loss of X is consistent with the directed σ-antibonding nature of the d_{z^2} orbital, which is populated in the lowest LF excited states.

For X = pyridine, but not aliphatic amine, one expects a relatively low lying W → X charge-transfer (CT) absorption because the complex is low valent and there are accessible π^* pyridine levels. Such a transition has not been identified in the absorption spectrum of $W(CO)_5$(py) (py = pyridine), but we have recently encountered spectral differences in $W(CO)_5$(pip) (pip = piperidine) and $W(CO)_5$(py), which point to the presence of such a transition to the blue of the lowest LF absorption system. With variation in the substituents on pyridine the W → pyridine CT should vary in energy. Complexes $Ru(NH_3)_5X^{2+}$ (X = substituted pyridine) are also C_{4v}, low-spin d^6 systems having low lying Ru → X CT.[9] The position of the Ru → X CT absorption band in H_2O varies from 398 nm for X = 4-methylpyridine to 545 nm for X = 4-formylpyridine.[9] The photochemistry of $Ru(NH_3)_5(py)^{2+}$ in H_2O has been investigated for irradiations corresponding to Ru → pyridine CT.[10] Both NH_3 and pyridine are photoaquated with modest quantum efficiency. There is little selectivity for substitution of *cis*- or *trans*-NH_3 or the pyridine, and one might be thus tempted to ascribe the reactivity to some LF character of the lowest excited state. Since the $Ru(NH_3)_5(py)^{2+}$ complex has essentially an O_h field, it is appropriate to consider the lowest LF state to be nearly the same as in $Ru(en)_3^{2+}$ (en = ethylenediamine), which has no low-lying CT absorption. The LF $^1A_{1g}(t_{2g}^6) \rightarrow {}^1T_{1g}(t_{2g}^5e_g^1)$ transition in $Ru(en)_3^{2+}$ falls at 370 nm (ϵ 40 l. mol^{-1} cm^{-1}),[11] which is comparable energetically to the position of the Ru → pyridine CT absorption in $Ru(NH_3)_5(py)^{2+}$ [9] (407 nm, ϵ 7762 l. mol^{-1} cm^{-1}). Accepting the notion that the Ru → pyridine CT state can be viewed as a Ru(III) complex of the radical anion of pyridine, there is no compelling reason to expect such a state to have vastly enhanced substitution rates. Given that the excited state lifetimes are very short (likely less than 10^{-9} s), it is likely that the excited states responsible for substitution must have substitution rate constants which are perhaps 10 to 20 orders of magnitude larger than those for the ground electronic state. The thermal substitution *stability* of both Ru(II) and Ru(III) amine complexes[12] is seemingly inconsistent with a strong labilization from a Ru → pyridine CT state. By way of contrast, the LF states should be strongly labilizing.[13] Recently, convincing evidence has been reported[14] showing that the Ru → pyridine CT state *is not* likely the substitutionally reactive state. The convincing result[14] is that complexes of substituted pyridine having very low energy CT absorption, such as $Ru(NH_3)_5$(4-formyl-py)$^{2+}$, have very inefficient photosubstitution processes. These results are consistent with a reactive LF state.[10a,14]

Among metal carbonyls, the only mononuclear complexes which have been investigated which unequivocally have a M → ligand CT lowest excited state are $W(CO)_4L$ (L = 1,10-phenanthroline and related ligands).[15] For these complexes the W → L CT transition yielded no detectable CO substitution, though direct absorption into upper excited states (LF?) yielded modest CO dissociation quantum yields. In substitution-inert metal carbonyls, the M → L CT states might yield substitution lability with respect to CO dissociation due to the "oxidation" by one unit of the central metal, since stable CO complexes are generally found for the lower oxidation state metals. Similar reasoning[16] leads to the conclusion that the σ-donor ligands will tend to be more substitutionally inert in the higher oxidation state.

Results and Discussion

a. Synthesis of $W(CO)_5X$. Preparation of $W(CO)_5X$ was by

Table I. Carbonyl Infrared Stretching Bands for $W(CO)_5X$

X	Bands, cm^{-1} [a]		
3,4-Dimethylpyridine	2070 (w)	1928 (s)	1914 (m)
4-Methylpyridine	2071 (w)	1929 (s)	1917 (m)
Pyridine	2071 (w)	1930 (s)	1918 (m)
3-Bromopyridine	2072 (w)	1932 (s)	1923 (sh)
3,5-Dibromopyridine	2073 (w)	1933 (s)	1927 (sh)
Piperidine	2070 (w)	1926 (s)	1915 (m)
4-Acetylpyridine	2071 (w)	1932 (s)	1923 (sh)
4-Benzoylpyridine	2071 (w)	1930 (s)	1921 (sh)
4-Cyanopyridine	2071 (w)	1931 (s)	1927 (sh)
4-Formylpyridine	2071 (w)	1935 (s)	1927 (sh)
3-Benzoylpyridine	2071 (w)	1928 (s)	1920 (sh)
3-Acetylpyridine	2072 (w)	1930 (s)	1921 (sh)

[a] 298 K in isooctane; (w) = weak; (m) = medium; (s) = strong; and (sh) = shoulder.

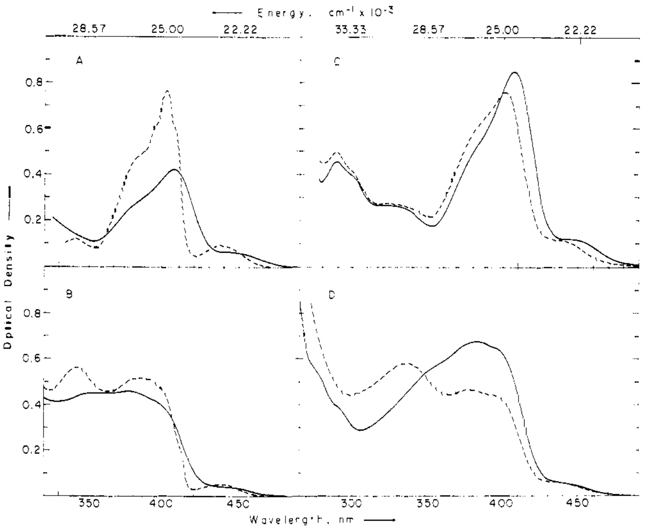

Figure 1. Comparison of temperature and solvent effects on absorption of $W(CO)_5(pip)$ and $W(CO)_5(py)$. Curves A and C are for the piperidine complex and curves B and D are for the pyridine complex. For A and B the solvent is 1-pentene and the solid curve is the spectrum at 298 K and the dashed curve is at 77 K (uncorrected for solvent correction). Curves C and D are for 298 K spectra in isooctane (—) and at the same concentration isooctane/EtOH (1:1 by volume) (- - -).

$$W(CO)_6 \xrightarrow[\substack{X \\ N_2\ \text{purge} \\ \text{isooctane} \\ \text{solvent}}]{h\nu} W(CO)_5X + CO \qquad (1)$$

$$W(CO)_6 \xrightarrow[THF]{h\nu} \underset{\substack{+ \\ CO}}{W(CO)_5THF} \xrightarrow[\Delta]{X} W(CO)_5X + THF \qquad (2)$$

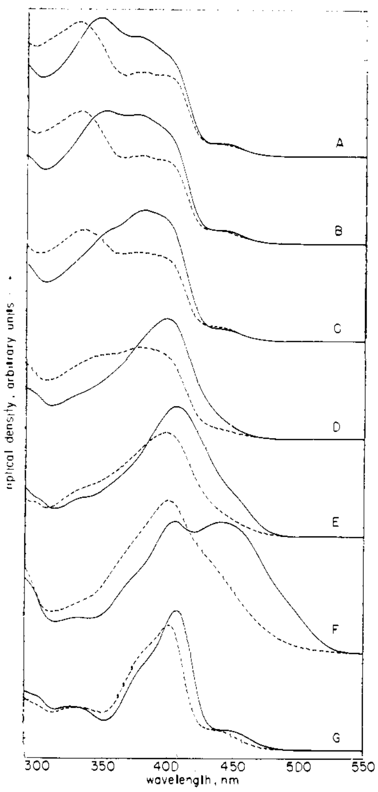

Figure 2. Absorption spectra at 298 K in isooctane (—) and isooctane/EtOH (1:1 volume) (- - -) for $W(CO)_5X$ at the same concentration for both solvents. A = $W(CO)_5(3,4\text{-diMe-py})$; B = $W(CO)_5(4\text{-Me-py})$; C = $W(CO)_5(py)$; D = $W(CO)_5(3\text{-Br-py})$; E = $W(CO)_5(3,5\text{-diBr-py})$; F = $W(CO)_5(4\text{-acetyl-py})$; G = $W(CO)_5(pip)$.

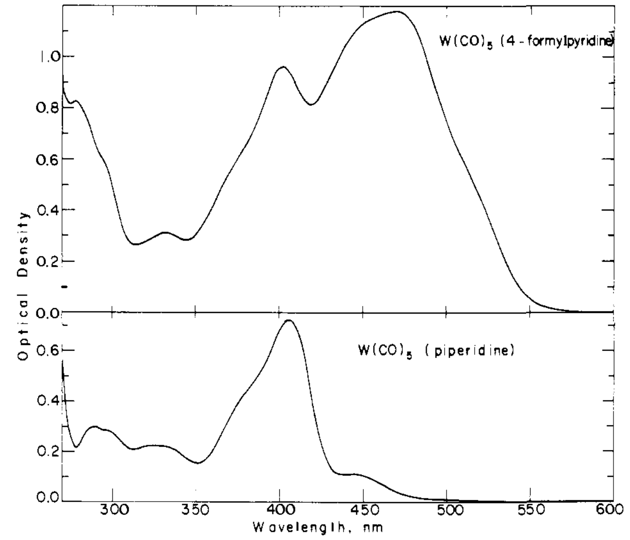

Figure 3. Comparison of the absorption spectra of $W(CO)_5(pip)$ and $W(CO)_5(4\text{-formyl-py})$ at 298 K in isooctane. Note that all of the bands present in $W(CO)_5(pip)$ are present in $W(CO)_5(4\text{-formyl-py})$ at very nearly the same position and relative intensity.

one of the two routes indicated in the reactions 1 or 2. Both routes have considerable precedence,[2,17] even though only a few of the $W(CO)_5X$ complexes studied have actually been reported. Usually, the major impurity (aside from unreacted starting materials) from the synthetic procedures used is $W(CO)_4X_2$. Generally, purification can be achieved by chromatography on alumina. Ir band maxima (Table I) for the $W(CO)_5X$ complexes are consistent with the C_{4v} arrangement of the five CO's, and, importantly, the similarity of all the complexes is consistent with bonding of the pyridine through the pyridine ring nitrogen atom. Specifically, the 4-cyanopyridine complex is likely bound through the pyridine nitrogen atom based on both the position of the C≡N stretch of the complex (2236 cm^{-1}) compared to the free ligand (2236 cm^{-1}) and the similarity of the CO stretching bands to those for the pyridine complex.

b. Electronic Absorption Spectra. Electronic spectra for the $W(CO)_5X$ complexes have been recorded in solution. Some spectra are shown in Figures 1–3 and data are summarized in Table II. First, spectra of $W(CO)_5(py)$ and $W(CO)_5(pip)$ are compared in Figure 1. Each complex exhibits a low energy band near 440 nm (ϵ 500 l. mol^{-1} cm^{-1}), which is the one previously associated[2-6] with the LF $^1A_1(e^4b_2^2) \rightarrow {}^3E(e^3b_2^2a_1^1)$ transition. The corresponding singlet-singlet LF

Table II. Spectral Band Maxima and Assignments for $W(CO)_5X$ Complexes[a]

X[b]	Abs. max, nm (ε)[c]	${}^1A_1(e^4b_2^2) \to {}^3E(e^3b_2^2a_1^1)$,[d] nm (ε)	${}^1A_1(e^4b_2^2) \to {}^1E(e^3b_2^2a_1^1)$, nm (ε)	W → X CT, nm (ε)
Piperidine	407 (3960)	443 (560)	407 (3960)	None
3,4-DiMe-py	347 (6580)	435 (615)	~390	347 (6580)
4-Me-py	351 (6960), 375 (6730)	437 (655)	~390	351 (6960)
Py	382 (7480)	440 (615)	~390	355 (~6800)
3-Br-py	399 (9670)		Overlapping CT and LF[e]	
3-Acetyl-py	398 (7550)		Overlapping CT and LF[e]	
3-Benzoyl-py	400 (5700)		Overlapping CT and LF[e]	
3,5-DiBr-py	407 (9410)		Overlapping CT and LF[e]	
4-Benzoyl-py	405 (7410), 435 (6600)	*f*	405 (7410)	435 (6600)
4-Acetyl-py	404 (8400), 440 (8200)	*f*	404 (8400)	440 (8200)
4-CN-py	404 (5530), 455 (7060)	*f*	404 (5530)	455 (7060)
4-Formyl-py	402 (5300), 470 (6470)	~445	402 (5300)	470 (6470)

[a] Isooctane solutions at 298 K. [b] py = pyridine. [c] Only actual band maxima are given here. [d] Generally, this band is only a shoulder. [e] For example, cf. curves D and E in Figure 2. [f] Obscured by W → X CT absorption.

transition is associated with the absorption band near 400 nm (ε 5000–7000 l. mol^{-1} cm^{-1}). In the region near 340 nm (in 1:1, isooctane/EtOH, v/v) the $W(CO)_5(py)$ has an absorption band which is apparently not present in the $W(CO)_5(pip)$. Moreover, the position of this band is extraordinarily sensitive to the solvent compared to the 440 or 400 nm band in either the pyridine or piperidine complex. The band appears to blue shift in more polar media just as does the W → phenanthroline CT band in $W(CO)_4(phen)$[18] (phen = 1,10-phenanthroline). The band is clearly present in the 77 K spectrum of $W(CO)_5(py)$, but *not* in $W(CO)_5(pip)$. These results are enough for us to tentatively ascribe the 340 nm band in $W(CO)_5(py)$ to a W → pyridine CT transition. In Figure 2 and Table II spectroscopic data are given for several complexes of various substituted pyridines. Generally, the more electron-withdrawing substituent yields a lower energy W → X CT absorption. But it is not until one gets to the 4-acetyl, 4-cyano, 4-benzoyl, and 4-formyl derivatives that the CT band moves markedly below the LF ${}^1A_1 \to {}^{1,3}E$ bands. The shift of the W → X CT band in isooctane is ~ 6600 cm^{-1} from X = 4-methylpyridine to 4-acetylpyridine, and this is quite comparable to the shift of the Ru → X CT in $Ru(NH_3)_5X^{2+}$ for the same two X's.[14] The solvent effect on the W → X CT is uniformly a large blue shift with the more polar medium. Importantly, from the 4-substituted pyridines with strongly electron-withdrawing substituents we see that the band at 400 nm, ascribed to the ${}^1A_1 \to {}^1E$ LF absorption, is still present as a prominent feature of the spectrum. A remarkable comparison of $W(CO)_5(pip)$ and $W(CO)_5(4\text{-formyl-py})$ is shown in Figure 3, which clearly reveals that all of the bands present in the piperidine complex are present in the 4-formylpyridine complex at nearly the same energies. We thus feel the state diagrams indicated in Scheme I are appropriate in absorption. The data show, beyond reasonable doubt, that in absorption the position of the W → X CT can be changed rather dramatically by tampering with the electronic nature of X, while the LF absorptions are essentially not affected. The LF bands are unobservably weak in $Ru(NH_3)_5X^{2+}$, but it was *assumed* that they are not shifted by changes in the various pyridines, X.[14] The invariance of the bands at ~400 nm is consistent with their LF character in that the changes in the CT properties have been brought about without changing the set of donor atoms coordinated to the central metal. Similarly, the LF bands present in $W(CO)_4(en)$[19] are present in about the same position in $W(CO)_4(phen)$,[19] which has W → 1,10-phenanthroline CT at lower energy. We outline below results on radiative decay and photosubstitution of X in $W(CO)_5X$ which show that the state diagrams shown in Scheme I are still appropriate for the relaxed excited states.

Scheme I

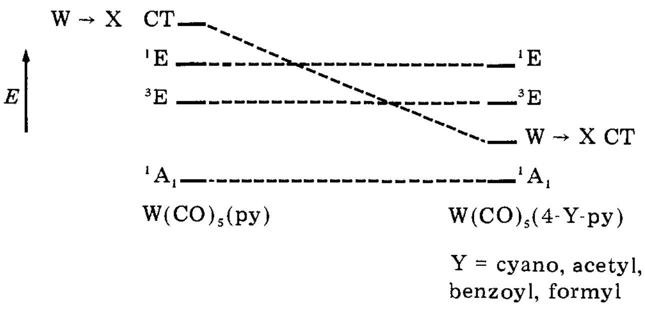

Table III. Emission Data for $W(CO)_5X$ in EPA at 77 K

X	Emission max,[a] kK	Emission half-width,[b] kK	Emission lifetime × 10^6
3,4-Dimethylpyridine	19.7	3.1	0.96
4-Methylpyridine	19.6	3.1	1.07
Pyridine	19.1	4.0	0.86
3-Bromopyridine	18.9	4.1	1.00
3-Acetylpyridine	18.7	4.4	1.17
3-Benzoylpyridine	18.5	4.4	1.25
3,5-Dibromopyridine	18.1	2.9	1.25
4-Cyanopyridine	16.6	4.1	33.0
4-Acetylpyridine	17.0	4.5	38.3
4-Benzoylpyridine	16.8	4.2	29.5
4-Formylpyridine	15.2	4.0	15.0
Piperidine	18.3	4.1	0.82

[a] Corrected for variation in detector response as a function of wavelength. [b] Width of emission band at half-height.

c. Emission of $W(CO)_5X$. All of the $W(CO)_5X$ complexes investigated here undergo radiative decay subsequent to electronic excitation at 77 K in EPA solution. Corrected emission spectra have been measured for all of the complexes. The corrected emission maximum, the width of the emission peak at half-height, and the emission lifetimes for all of the complexes are listed in Table III and corrected spectra are shown for several complexes in Figure 4. The spectral distribution and efficiency of the emission are insensitive to the excitation wavelengths longer than 300 nm. Several points are

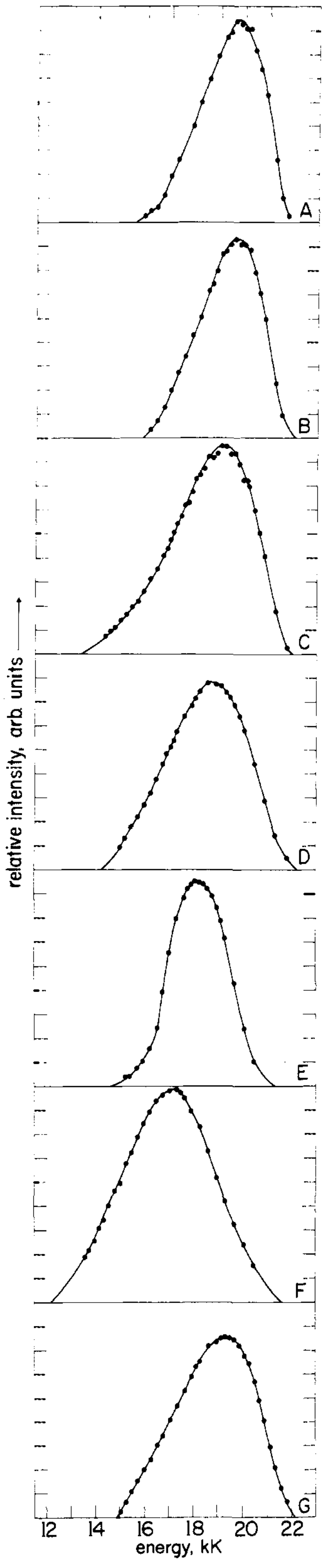

Figure 4. Corrected emission spectra in EPA at 77 K for $W(CO)_5X$. A-G are the same as in Figure 2. The excitation wavelength is 351, 364 nm.

Table IV. Photosubstitution of X in $W(CO)_5X$[a]

X	$\Phi \pm 10\%$		Lowest excited state
	436 nm	514 nm[b]	
3,4-Dimethylpyridine	0.53		LF
4-Methylpyridine	0.55		LF
Pyridine	0.62		LF
3-Bromopyridine	0.66		LF
3-Acetylpyridine	0.75		LF
3-Benzoylpyridine	0.73		LF
3,5-Dibromopyridine	0.82		LF
4-Benzoylpyridine	0.12	0.02	W → X CT
4-Cyanopyridine	0.12	0.02	W → X CT
4-Acetylpyridine	0.15	0.02	W → X CT
4-Formylpyridine	0.05	0.002	W → X CT
Piperidine	0.58		LF

[a] Irradiation carried out at 298 K in isooctane/1-pentene (2/1 by volume). The only photoproduct is $W(CO)_5$(1-pentene). [b] Data at 514 nm are given only for those complexes that absorb sufficiently to give accurate quantum yields.

worth noting. First, there appears to be a sharp break in emission lifetimes from ~1 to 15–30 μs for complexes having LF and CT lowest energy absorptions, respectively. Second, while there is a general trend to lower energy emission maxima with increasing electron-withdrawing power of X, there is a sharp decline in emission energy for those complexes having lowest W → X CT absorptions. The general decline in emission energy with a more electron-withdrawing substituent on pyridine likely reflects an increasing admixture of CT character to the lowest excited state as the emitting CT and LF states become closer energetically, and finally the CT crosses below the LF level for the 4-Y-pyridines for Y = cyano, acetyl, benzoyl, and formyl.

d. Photosubstitution of X in $W(CO)_5X$. Photoinduced substitution of X occurs in $W(CO)_5X$ upon excitation into the lowest energy absorption. We have investigated the quantum efficiency for the reaction

$$W(CO)_5X \xrightarrow[\text{1-pentene}]{436\text{ nm}} W(CO)_5(\text{1-pentene}) + X \qquad (3)$$

under a constant set of conditions. In all cases, the reaction is essentially quantitative with little contribution from reaction 4 ($\phi \leq 0.01$).

$$W(CO)_5X \xrightarrow[\text{1-pentene}]{436\text{ nm}} W(CO)_4(X)(\text{1-pentene}) + CO \qquad (4)$$

Quantum yields determined for reaction 3 are summarized in Table IV, and typical electronic absorption spectral changes accompanying the reaction are depicted in Figure 5 for $W(CO)_5$(3,4-diMe-py) and $W(CO)_5$(4-formyl-py). Quantum yields for several complexes are also shown for 514-nm photolysis. The data show that for the complexes where a W → X CT absorption is the lowest energy absorption, there is a relatively low quantum yield for substitution. The complexes showing low substitution quantum yields are just those which show the lowest energy emission and have the longest emission lifetimes. It is *unlikely* that the differences in substitution yields are due to the "bulk" of the substituent, since for X = 3-benzoylpyridine or 3-acetylpyridine quantum yields typical of a LF lowest excited state are obtained, consistent with the absorption and emission data. Therefore, *we conclude that the W → X CT state is unequivocally and significantly less reactive than the lowest LF states with respect to substitution of X.* This conclusion is in accord with that for $Ru(NH_3)_5X^{2+}$.[14]

Aside from our conclusion that the W → X CT state is relatively unreactive with respect to dissociative loss of X, we can comment intelligently on the consequences of W → ligand CT with respect to loss of CO. Obviously, the complexes studied here do not undergo efficient dissociative loss of CO from the lowest excited state. Consequently, we must conclude that depopulation of π-d orbitals, which are π bonding with respect to the W-CO interaction, does not labilize CO to an extent which allows dissociation within the lifetime of the excited state. This obtains despite the fact that the W → X CT tran-

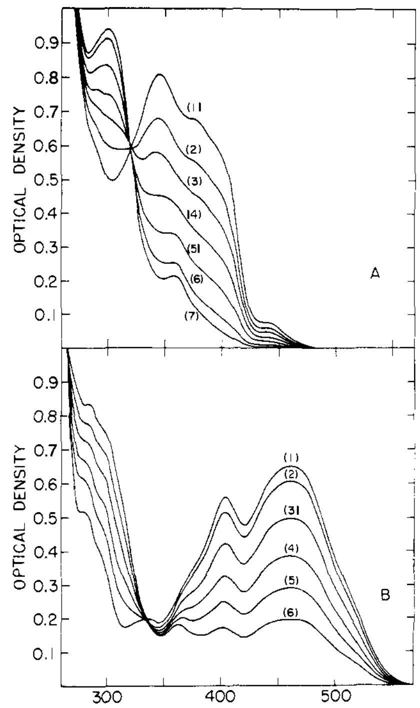

Figure 5. Electronic absorption spectral changes accompanying the 436 nm irradiation of A, $W(CO)_5(3,4\text{-diMe-py})$ and B, $W(CO)_5(4\text{-formyl-py})$ in isooctane/1-pentene (2:1 by volume) at 298 K. The photoproduct in each case is $W(CO)_5$(1-pentene).

sition can be viewed as a central metal oxidation which should a priori labilize the W–CO bond. Our results here argue against the possibility of an M → CO CT reactive state in $M(CO)_6$ (M = Cr, Mo, W). The notion[5] that the reactive excited states are just those of the LF $t_{2g} \rightarrow e_g$ type remains secure.

Differences in the 514-nm and the 436-nm quantum yields deserve some comment. For the complexes where 514-nm irradiations are possible the W → X CT state gives rise to the lowest energy absorption band. When the lowest absorption band corresponds to the LF $^1A \rightarrow {}^3E$ or to a mixture of the LF and CT transitions, the molar absorptivity is not great enough at 514 nm to allow accurate determinations of photosubstitution efficiency. The differences that do obtain likely reflect the fact that the LF state can yield substitution at a rate which is very competitive with internal conversion to the lowest CT state. Similarly, strongly wavelength-dependent CO photosubstitution was found in $W(CO)_4$(phen) and related complexes where a W → 1,10-phenanthroline CT transition is lowest in energy.[15]

Experimental Section

Materials. All substituted pyridines and solvents used are commercially available and were used without purification. Tungsten carbonyl was obtained from Pressure Chemical Co. The isooctane used was spectroscopic grade, and the 1-pentene was obtained from Chemical Samples Co. (>99% pure).

Synthesis of $W(CO)_5X$ (X = Pyridine or Substituted Pyridine). Preparation of $W(CO)_5X$ was either (1) by irradiation of $W(CO)_6$ in the presence of X in N_2 purged isooctane solution or (2) by thermally reacting photogenerated $W(CO)_5$(THF) with X in N_2 purged THF solution. In either case the $W(CO)_5X$ was recovered by first evaporating the solvent followed by chromatography on alumina. Elution first with isooctane removed $W(CO)_6$ and elution with Et_2O typically moved the $W(CO)_5X$. The Et_2O was then removed by rotary evaporation. Purity was established spectroscopically. In all cases photosubstitution of X by 1-pentene yielded $W(CO)_5$(1-pentene) in the correct stoichiometric amount consistent with the fact that all $W(CO)_5X$ were pure. Typically, the major difficulty in purity was the presence of free ligand. In some cases, repeated chromatography was required to achieve pure $W(CO)_5X$. The synthetic procedures are well established.[2,6,17]

Spectra. Infrared spectra were recorded using a Perkin-Elmer Model 521 spectrometer. Uv-vis absorption spectra were obtained with a Cary 17 spectrophotometer. Low-temperature absorption spectra were obtained using an all quartz liquid N_2 Dewar fitted with optical quality quartz flats for windows. Emission spectra were typically obtained using the detection optics of the Cary 17. The sample was placed at the source position of the Cary 17 and the emission was excited with an argon ion laser tuned to the 351, 364 nm doublet. The maximum power of the Spectra Physics Model 164 laser operated in this manner was approximately 20 mW. The emission spectra were constant in time, evidencing no photoreaction by the excitation light. A 77 K Dewar, typically used with an Aminco-Bowman emission spectrophotofluorometer, was used for the Cary 17 emission studies. Emission spectra were corrected using the procedure and equipment described previously.[20] Excitation spectra for the emission were obtained using an Aminco-Bowman SPF-2 spectrophotofluorometer. Emission lifetimes were determined using the procedures and equipment described previously.[20] Since there existed the possibility of multiple emissions (LF and CT), we were careful to look for nonexponential plots of log (emission intensity) vs. time. No evidence for multiple emissions was obtained at 77 K in EPA solutions.

Irradiation Procedures. All irradiations were carried out using merry-go-rounds to expose 3.0-ml aliquots of $W(CO)_5X$ in isooctane/1-pentene (2:1 by volume) in hermetically sealed 13 × 100 mm Pyrex test tubes. The solutions were typically degassed by three freeze-pump-thaw cycles prior to being sealed. The 436-nm irradiations were carried out using a Hanovia 450-W medium pressure Hg lamp filtered with Corning glass filters to isolate the 436 nm emission. Irradiations at 514 nm were carried out using the argon ion laser with a 6X beam expander. Light intensity was determined by ferrioxalate actinometry[21] (436 nm) or Reinecke's salt actinometry[22] (514 nm). The photoproduct of $W(CO)_5X$ is $W(CO)_5$(1-pentene) by ir (2080(w), 1965(s), 1952(s) cm^{-1}) and uv-vis spectra. The large difference in the absorption spectra of $W(CO)_5X$ and $W(CO)_5$(1-pentene) allowed quantitative determination of the extent of reaction by measuring the optical density as a function of irradiation time; cf. Figure 5.

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