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Photosubstitution Behavior of Dicarbonyl(η^5-cyclopentadienyl)pyridinomanganese and -rhenium and Related Complexes

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Received July 26, 1976 AIC60545B

Electronic spectra and photosubstitution reactions of $(\eta^5\text{-}C_5H_5)M(CO)_2X$ (M = Mn, Re; X = CO, aliphatic amine, pyridine, or a substituted pyridine) have been investigated. The low-energy region of the electronic absorption spectra of the pyridine and substituted pyridine complexes is dominated by a $M \rightarrow \pi^*$ X CT absorption ($\epsilon \approx 5 \times 10^3$ l. mol^{-1} cm^{-1}). The $M \rightarrow \pi^*$ X CT absorption blue shifts in more polar or polarizable media, and the band position for a given M and solvent red shifts smoothly with increasing electron withdrawing power of the substituent(s) on the pyridine ring. For example, in isooctane at 25 °C the $Mn \rightarrow \pi^*$ X CT maximum is at 385 nm for X = 3,4-dimethylpyridine and at 555 nm for X = 4-formylpyridine. For all complexes the exclusive photosubstitution is dissociative loss of X for irradiation into the lowest absorption band. However, the quantum yield is a function of M and X and spans a range of approximately four orders of magnitude. For M = Mn all of the complexes are quite photosensitive with efficiencies in the range of 0.2–0.4, whereas for M = Re only those complexes *not* having low energy Re → X CT bands are reactive. The crucial fact is that for several Re complexes the relaxed M → X CT excited state is lowest in energy, and the complexes are photosubstitution inert ($\Phi < 10^{-4}$). A correlation of the spectroscopic results and the quantum efficiencies suggests that the CT state is unreactive with respect to ligand substitution, and the data are consistent with a substitutionally reactive ligand field excited state.

Irradiation of (arene)$M(CO)_3$ complexes is known[2] to result in photosubstitution of CO to yield substituted derivatives in the presence of an entering nucleophilic group, X, or oxidative addition substrate, Y–Z, to yield (arene)$M(CO)_2X$ or (arene)$M(CO)_2(Y)(Z)$, respectively. The range of arene groups and metals is quite large; virtually any nucleophile, X, can be used, and chemical yields of products can be quite high. But aside from these qualitative features, little is known about the excited state chemistry in any of the systems. In particular, little can be said concerning the nature of the excited state responsible for the reaction. Moreover, there have been no studies of the photochemistry of the substituted complexes. Such studies are seemingly crucial to a general understanding of ligand photosubstitution processes.

In this paper we wish to report the results of a study of the electronic spectra and photochemistry of $(\eta^5\text{-}C_5H_5)M(CO)_2X$ (M = Mn, Re; X = CO, aliphatic amine, pyridine, or a substituted pyridine). We were prompted to investigate the pyridine complexes by our recent work[3] on $W(CO)_5X$ (X = pyridine or a substituted pyridine) where we found that a low-lying $W \rightarrow \pi^*$ X CT absorption could be identified. Paralleling results for $Ru(NH_3)_5X^{2+}$ complexes,[4,5] the energetic position of the $M \rightarrow \pi^*$ X CT absorption band red shifts with the introduction of electron-withdrawing substituents in the pyridine ring. Shifts of the order of 7000 cm^{-1} have been observed in each system. In contrast to the $Ru(NH_3)_5X^{2+}$ case, the $W(CO)_5X$ series has ligand field (LF) absorptions that are easily observable. By comparing the spectra of $W(CO)_5X$ with $W(CO)_5$(piperidine), which has no low-lying CT absorption, it was found that the position of the LF bands is constant for all of the $W(CO)_5X$ complexes studied. For both $Ru(NH_3)_5X^{2+}$ [5] and $W(CO)_5X$[3] it has been possible to move the $M \rightarrow \pi^*$ X CT absorption from a position comparable to the LF band system to one well below. The photosubstitution efficiency is very small when the CT state is lowest and reasonably large when the LF state is lowest in energy. The pyridine derivatives of metal carbonyls should generally exhibit low-energy CT absorptions owing to the low oxidation states of the metal. Thus, it should be possible to provide generalizations concerning photosubstitution for other symmetries and d^n configurations. Not incidentally, we are curious as to the generality of the extraordinary shifts in CT position found in $Ru(NH_3)_5X^{2+}$ and $W(CO)_5X$ with simple variation in the substituents in the pyridine, X.

The qualitative aspects of the photochemistry of $(\eta^5\text{-}C_5H_5)Mn(CO)_3$ are well known. In particular, reaction 1 is believed to occur with a quantum efficiency of unity.[6]

$$(\eta^5\text{-}C_5H_5)Mn(CO)_3 \xrightarrow[X]{h\nu} (\eta^5\text{-}C_5H_5)Mn(CO)_2X + CO \qquad (1)$$

X = almost any nucleophile

Reaction 2 has also been reported.[7] The photochemistry of

$$(\eta^5\text{-}C_5H_5)Mn(CO)_3 \xrightarrow[HSiCl_3]{h\nu} (\eta^5\text{-}C_5H_5)Mn(CO)_2(H)(SiCl_3) + CO \qquad (2)$$

$(\eta^5\text{-}C_5H_5)Re(CO)_3$ is much less well studied, but reaction 3

$$(\eta^5\text{-}C_5H_5)Re(CO)_3 \xrightarrow[\text{hexane, } N_2]{h\nu} (\eta^5\text{-}C_5H_5)_2Re_2(CO)_5 + CO \qquad (3)$$

has been reported.[8] Thus, all of the known photochemistry is consistent with dissociative loss of CO as the principal result of electronic excitation. The $(\eta^5\text{-}C_5H_5)Re(CO)_2X$ species do not seem to be common but should be accessible. The photochemisry of the $(\eta^5\text{-}C_5H_5)Mn(CO)_2X$ complexes has not been investigated per se, but the photoproduction of $(\eta^5\text{-}C_5H_5)Mn(CO)X_2$, namely *disubstituted* products, from $(\eta^5\text{-}C_5H_5)Mn(CO)_3$[9] is logically a result of irradiation of $(\eta^5\text{-}C_5H_5)Mn(CO)_2X$ in the presence of excess entering group, X. We now report the first detailed studies of the photochemistry of the $(\eta^5\text{-}C_5H_5)M(CO)_2X$ complexes.

Results

(a) Preparation and Characterization of the Complexes. The details of the preparation of the complexes are given in the Experimental Section, but here it is appropriate to point out that all of the substituted $(\eta^5\text{-}C_5H_5)M(CO)_3$ complexes can be prepared by the irradiation of either the $(\eta^5\text{-}C_5H_5)M(CO)_3$ itself or by irradiation of the $(\eta^5\text{-}C_5H_5)M(CO)_2$(py). The direct, thermal substitution of CO in $(\eta^5\text{-}C_5H_5)M(CO)_3$ is apparently not possible,[10] but we have found that $(\eta^5\text{-}C_5H_5)M(CO)_2X$ can be prepared by the 25 °C thermal substitution of ether in $(\eta^5\text{-}C_5H_5)M(CO)_2$(ether). The $(\eta^5\text{-}C_5H_5)M(CO)_2$(ether) can be prepared in ether solution by irradiation of $(\eta^5\text{-}C_5H_5)M(CO)_3$. Preparation of complexes of the near-uv-absorbing pyridyl ketones is best accomplished via the thermal exchange of the ether complex or by the visible light irradiation of the pyridine complex. Extensive degradation and slow conversion typify attempts to prepare complexes of the absorbing ligands by photolysis of the $(\eta^5\text{-}C_5H_5)Re(CO)_3$, since the $(\eta^5\text{-}C_5H_5)Re(CO)_3$ does not absorb substantially in the visible or near uv.

Infrared spectra in the CO stretching region for the $(\eta^5\text{-}C_5H_5)M(CO)_2X$ complexes have been recorded, and as expected, two absorptions are found in each case. The band

Table I. Infrared Carbonyl Stretching Frequencies for Complexes Studied[a]

X	$(\eta^5\text{-}C_5H_5)\text{-}Re(CO)_2X$	$(\eta^5\text{-}C_5H_5)\text{-}Mn(CO)_2X$	$(\eta^5\text{-}C_5H_4CH_3)\text{-}Mn(CO)_2X$
CO	2028; 1938	2025; 1942	2024; 1938
1-Pentene	1973; 1902	1966; 1907	
3,4-DiMe-py	1919; 1854	1931; 1863	1927; 1860
4-Me-py	1921; 1855	1933; 1863	1927; 1860
py	1921; 1857	1933; 1865	1929; 1863
3-Br-py	1925; 1860		
3,5-DiCl-py	1929; 1867	1938; 1874	1935; 1870
3-Acetyl-py	1928; 1863		
3-Benzoyl-py	1926; 1861		
4-Acetyl-py	1927; 1865	1937; 1873	1933; 1869
4-Benzoyl-py	1928; 1866	1936; 1872	1936; 1872
4-Formyl-py	1929; 1867	1938; 1874	1937; 1872
4-Ph-py	1925; 1860		
Piperidine	1915; 1846	1926; 1855	1923; 1938
NH_3[b]	1900; 1820		
THF[c]		1921; 1850	

[a] Spectra recorded in isooctane solution (unless otherwise noted) at 25 °C using a Perkin-Elmer 567 instrument; py = pyridine; Me = methyl; Ph = phenyl. The two bands for each complex are of similar intensity, and in all cases the bands are strong. [b] Recorded in CH_2Cl_2 solution. [c] Recorded in THF solution.

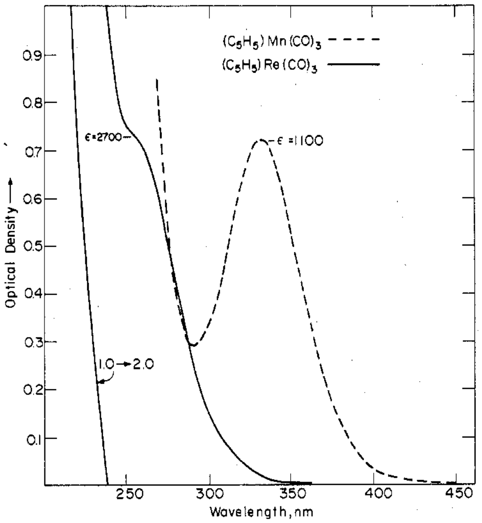


Figure 1. Electronic absorption spectra of $(C_5H_5)Re(CO)_3$ (–), 2.63×10^{-4} M, and $(C_5H_5)Mn(CO)_3$ (- - -), 6.67×10^{-4} M, in isooctane solution at 298 K. The path length is 1.00 cm.

maxima are listed in Table I. A general trend in the positions of the bands is observed; more electron-withdrawing substituents on pyridine results in a complex having higher energy CO stretching bands. Paralleling this result, electron-withdrawing substituents in the arene group in (arene)$Cr(CO)_3$ also give higher energy CO stretching bands.[11]

(b) Electronic Spectral Studies. Complexes $(\eta^5\text{-}C_5H_5)\text{-}M(CO)_2X$ typically have significant absorption in the optical region, and the objective in studying the electronic spectra is to aid in establishing a reasonable rationale for the chemistry associated with the lowest excited states. Generally, the substitution of CO by nitrogen donors in $(\eta^5\text{-}C_5H_5)M(CO)_3$ leads to lower energy absorptions. The yellow $(\eta^5\text{-}C_5H_5)\text{-}Mn(CO)_3$ has a well-defined ultraviolet transition maximizing near 330 nm, ε 1100 l. mol^{-1} cm^{-1}, with an onset well below 400 nm. But the pristine white $(\eta^5\text{-}C_5H_5)Re(CO)_3$ has no such low-lying transition and its first absorption appears only as a shoulder in the vicinity of 255 nm (ε 2700 l. mol^{-1} cm^{-1}). The 298 °K spectra of $(\eta^5\text{-}C_5H_5)M(CO)_3$ (M = Mn, Re) are given in Figure 1. We have also examined the spectral changes accompanying cooling EPA solutions of these complexes to 77 °K. Aside from band sharpening little change is noted. For neither Mn nor Re have we been able to resolve any bands other than those shown in Figure 1.

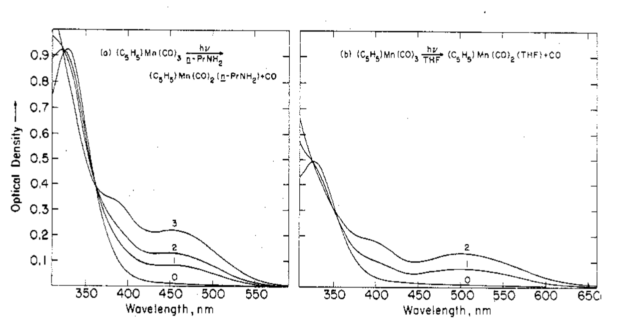


Figure 2. (a) Initial electronic spectral changes accompanying the photoconversion of $(C_5H_5)Mn(CO)_3$ (8.5×10^{-4} M) to $(C_5H_5)Mn(CO)_2$ (n-$PrNH_2$) in an N_2 deoxygenated 3.0 ml isooctane solution of 0.05 M n-$PrNH_2$. Curves 0, 1, 2, and 3 correspond to 0, 25, 50, and 200 s irradiation times using a GE black light. Curve 3 corresponds to ~32% conversion. Note the two low-energy bands at 455 and 380 nm for the n-$PrNH_2$ complex. (b) Initial electronic spectral changes accompanying the photoconversion of $(C_5H_5)Mn(CO)_3$ (4.45×10^{-4} M) to $(C_5H_5)Mn(CO)_2THF$ in 3.0 ml of N_2 deoxygenated THF. Curves 0, 1, and 2 correspond to 0, 25, and 100 s irradiation times using the GE black light. Curve 2 corresponds to ~27% conversion. Note the two low-energy bands for the THF complex.

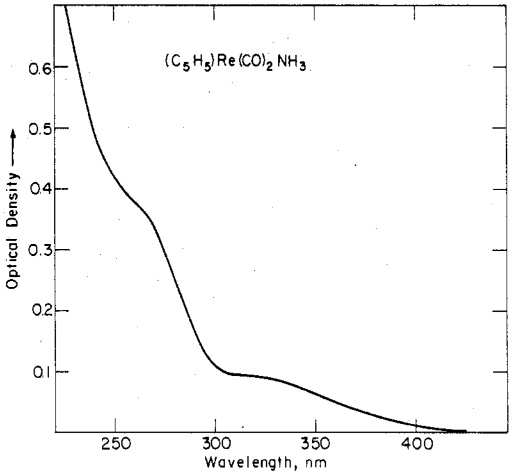


Figure 3. Electronic spectrum of 8.0×10^{-5} M $(C_5H_5)Re(CO)_2NH_3$ in deoxygenated EtOH solution using a 1.00 cm path length.

The complexes $(\eta^5\text{-}C_5H_5)M(CO)_2(THF)$ or $(\eta^5\text{-}C_5H_5)\text{-}M(CO)_2$(aliphatic amine) have fairly low intensity (ε 1000 l. mol^{-1} cm^{-1}) and relatively low energy electronic absorptions, Figures 2 and 3. The bands for these complexes fall substantially to the red of the first absorptions in the parent $(\eta^5\text{-}C_5H_5)M(CO)_3$ species. By way of contrast, the $(\eta^5\text{-}C_5H_5)M(CO)_2X$ (X = pyridine or substituted pyridine) species all have fairly intense visible absorption bands whose maxima depend dramatically on the nature of the substituent on the pyridine ring. Spectra of several of the pyridine complexes of the Re and Mn species are given in Figure 4 and spectral band maxima for all relevant complexes are listed in Table II. The lowest energy band in the pyridine complexes is uniformly composed of two components, with the lowest energy component generally appearing as just a shoulder at ~3000 cm^{-1} to the red of the actual maximum. The splitting is largely independent of whether M = Re or Mn and the particular pyridine (cf. Figure 4).

As can be seen from the data in Figure 4 and Table II, the position of the first absorption maxima depends significantly on the nature of the substituents in the pyridine ring. This occurs despite the fact that atoms of the ligands directly bonded to the central metal are invariant. The position of the

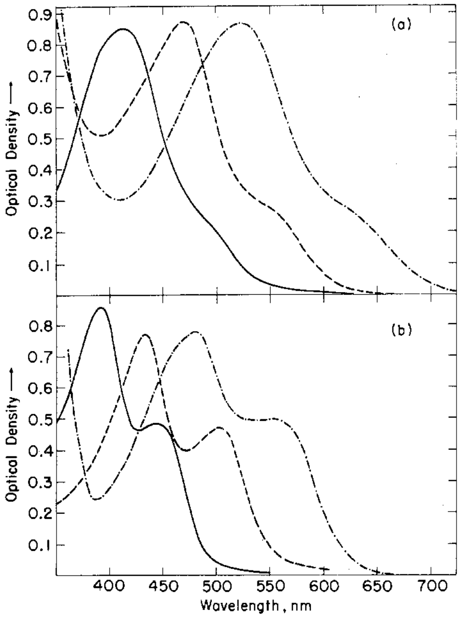


Figure 4. Electronic spectra of (C$_5$H$_5$)M(CO)$_2$X (~10^{-4} M) in isooctane solution at 298 K using 1.00 cm path length cells for M = Mn (a) and M = Re (b) and X = pyridine (—), 3,5-dichloropyridine (- - -), and 4-acetylpyridine (- · -). Band maxima and molar absorptivity are given in Table II.

first absorption maxima for the pyridine complexes can be seen to correlate nicely with the electron-withdrawing power of the substituent, and the ordering of band positions for the various pyridine complexes follows that reported for Ru(NH$_3$)$_5$X^{2+} [5] and W(CO)$_5$X (X = pyridine or substituted pyridine). The most electron-releasing substituents (CH$_3$) yield complexes having the highest energy absorption whereas the most electron-withdrawing substituent (CHO) yields a complex having the lowest energy absorption maximum. The position of the substituent-sensitive band varies by ~8000 cm^{-1}, and it is interesting that this value is comparable to the change in band position for the Ru(NH$_3$)$_5$X^{2+} [5] and W(CO)$_5$X[3] complexes with variation in X.

Absorption maxima for (η^5-C$_5$H$_4$(CH$_3$))Mn(CO)$_2$X are included in Table II, and it is seen that the band maxima are red shifted a small, but consistent, amount from the position of the band maxima for the (η^5-C$_5$H$_5$)Mn(CO)$_2$X species for X = pyridine or substituted pyridine. However, for X = piperidine the position of the lowest absorptions is the same for both the methylcyclopentadienyl and cyclopentadienyl complexes. It is noteworthy that the position of all of the bands for M = Re compared to M = Mn is generally higher in energy. Though the differences are sometimes small, this statement is even true for the low-energy intense transitions associated with X = pyridine or substituted pyridine. For the Re complexes (X = CO, THF, amine) the bands are significantly above those for the analogous Mn complexes.

One final trend is worth noting at this point. Low-energy transitions for the pyridine complexes are solvent dependent, and we find that the more polar or polarizable solvents yield the highest energy absorption maxima. Solvent dependence of the bands is typified by the data given in Table III for (η^5-C$_5$H$_5$)M(CO)$_2$(py). Importantly, the solvent shifts do not correspond to any net chemical reaction as evidenced by (1) the lack of an isosbestic point in smoothly changing the composition of the solvent from 100% isooctane to 100% EtOH at a constant complex concentration and (2) the ability to recover the complex unchanged from several different solvents.

(c) Photochemistry of (η^5-C$_5$H$_5$)M(CO)$_2$X. For all complexes investigated the photochemistry is dominated by substitution of X upon irradiation into the lowest absorption band systems. In all cases the photosubstitution has been found to occur essentially as indicated in reaction 4. Figures 5–7 show representative electronic spectral changes accompanying

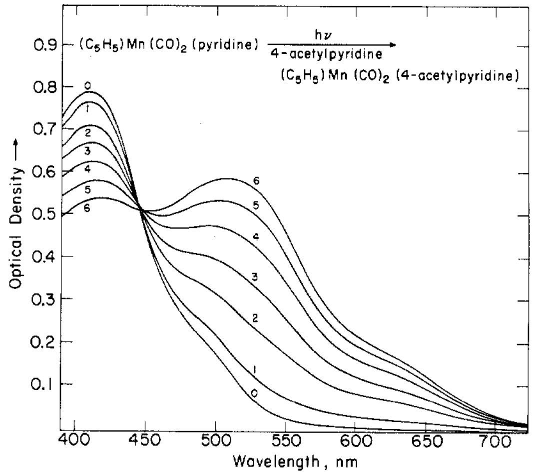


Figure 5. Spectral changes accompanying 436 nm irradiation of (C$_5$H$_5$)Mn(CO)$_2$(py) (1.50 × 10^{-4} M) in a degassed 3.0 ml isooctane solution 0.25 M in 4-acetylpyridine. Curves 0, 1, 2, 3, etc., represent the initial spectrum (0) and increasing irradiation times. Curve 6 represents ~56% conversion. The initial quantum yield is 0.35.

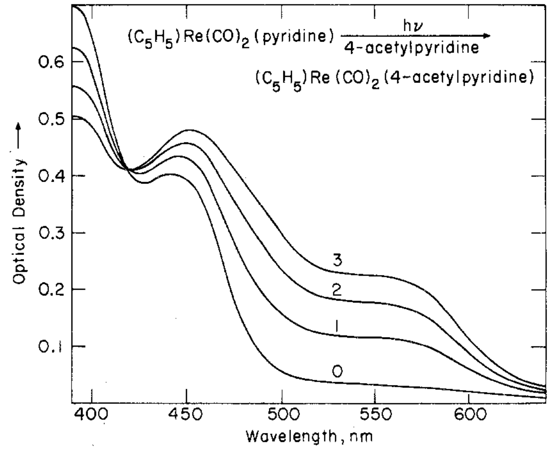


Figure 6. Spectral changes accompanying 436 nm irradiation of (C$_5$H$_5$)Re(CO)$_2$(py) (2 × 10^{-4} M) in a degassed 3.0 ml isooctane solution 0.25 M in 4-acetylpyridine. Curve 0 is the initial spectrum and curve 3 represents ~50% conversion, and the initial quantum yield is 0.09.

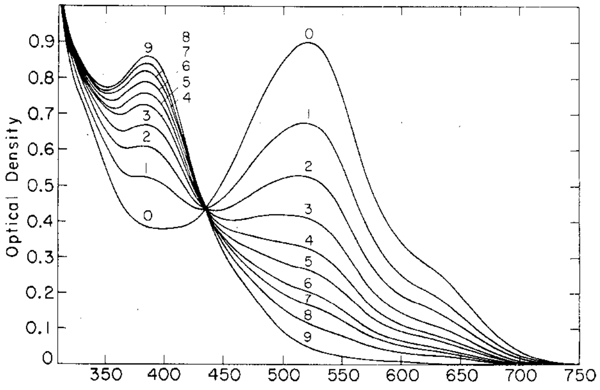


Figure 7. Spectral changes accompanying the 633 nm irradiation of (C$_5$H$_5$)Mn(CO)$_2$(4-acetyl-py) (1.4 × 10^{-4} M) in a 3.0 ml degassed isooctane solution 0.25 M in 3,4-dimethylpyridine. Curve 0 is the initial spectrum and curve 9 represents ~100% conversion, and the initial quantum yield is 0.25.

Table II. Electronic Absorption Spectral Band Maxima in Low-Energy Region for Complexes Studied[a]

X	$(\eta^5\text{-}C_5H_5)Re(CO)_2X$ Band max, nm (ϵ)	$(\eta^5\text{-}C_5H_5)Mn(CO)_2X$ Band max, nm (ϵ)	$(\eta^5\text{-}C_5H_4CH_3)Mn(CO)_2X$ Band max, nm
CO	255 (2700)	330 (1100)	330
3,4-DiMe-py	425 (2740); 375 (4740)	470 (1160); 385 (5430)	480; 395
4-Me-py	430 (2780); 380 (4800)	485 (1250); 390 (5800)	490; 400
py	445 (2880); 393 (5000)	495 (1280); 412 (5100)	505; 420
3-Br-py	475 (3040); 415 (5260)		
4-Ph-py	475 (3600); 417 (5570)		
3,5-DiCl-py	505 (2950); 435 (5180)	555 (1880); 470 (5610)	560; 477
3-Acetyl-py	510 (1860); 410 (4650)		
3-Benzoyl-py	510 (1950); 410 (4780)		
4-Acetyl-py	555 (3000); 480 (5310)	640 (1990); 525 (6790)	650; 535
4-Benzoyl-py	555 (3070); 480 (4870)	640 (1760); 525 (6380)	
4-Formyl-py	585 (3100); 495 (5180)	670 (2240); 555 (6530)	680; 565
n-PrNH$_2$	320	455 (825); 380 (1300)	
Piperidine	320	455; 380	455; 380
THF	335	510 (990); 400 (1400)[b]	
NH$_3$	320 (1000); 260 (4000)[c]	455	

[a] All spectra recorded in isooctane solution (unless noted otherwise) at 25 °C using a Cary 17 instrument; py = pyridine; Me = methyl; Pr = propyl. [b] Recorded in THF solution. [c] Recorded in EtOH solution.

Table III. Solvent Dependence of First Absorption Band System in $(\eta^5\text{-}C_5H_5)M(CO)_2(py)$[a]

Solvent	Absorbance max, nm (ϵ) M = Mn	M = Re
Isooctane	412 (5100)	393 (5000)
C_6H_6	388 (4970)	
$(C_2H_5)_2O$	388 (4910)	370
$CHCl_3$	380 (4670)	
THF	380 (4970)	360
CH_2Cl_2	378 (5850)	
C_2H_5OH	378 (5150)	
Acetone	370 (5980)	
CH_3CN	365 (5600)	345

[a] Data reported for 25 °C solutions.

Table IV. Quantum Yields for $(\eta^5\text{-}C_5H_5)Mn(CO)_2X + Y$ to $(\eta^5\text{-}C_5H_5)Mn(CO)_2Y + X$ Ligand Substitution[a]

X	Y	Irradiation, λ, nm	Φ ± (0.15Φ)
CO	py	313	0.65
Piperidine	4-Acetyl-py	436	0.14
	1-Pentene	436	0.16
py	4-Acetyl-py	405	0.35
	1-Pentene	405	0.37
3,5-DiCl-py	Piperidine	436	0.42
	1-Pentene	436	0.40
	3,4-DiMe-py	436	0.38
4-Acetyl-py	1-Pentene	550	0.25
	Piperidine	550	0.24
	3,4-DiMe-py	550	0.25
	4-Me-py	550	0.23
	py	550	0.25
4-Formyl-py	3,4-DiMe-py	550	0.25
	4-Me-py	550	0.25
	Py	550	0.25
	3,4-DiMe-py	633	0.25
	4-Me-py	633	0.25
	py	633	0.25

[a] All photoreactions in isooctane solutions of 0.25 M Y at 25 °C; py = pyridine; Me = methyl.

$$(\eta^5\text{-}C_5H_5)M(CO)_2X + Y \xrightarrow{h\nu} (\eta^5\text{-}C_5H_5)M(CO)_2Y + X \qquad (4)$$
$$Y = \text{nucleophile};\ M = \text{Mn, Re}$$

photosubstitution of various $(\eta^5\text{-}C_5H_5)M(CO)_2X$ complexes. As shown these reactions occur quite smoothly and isosbestic points (when they occur) are preserved even at very high conversion. The photoproducts have been identified both by the infrared carbonyl stretching bands and by the electronic spectra.

Table V. Entering Group Concentration Effect on Photosubstitution Quantum Yield in $(\eta^5\text{-}C_5H_5)Mn(CO)_2(4\text{-acetyl-py})$[a]

Entering group (M)	Φ at 550 nm ± 10% Φ
Pyridine (0.025)	0.24
Pyridine (0.10)	0.25
Pyridine (0.25)	0.23
Pyridine (0.50)	0.25
Pyridine (1.00)	0.23

[a] Product in each case is $(\eta^5\text{-}C_5H_5)Mn(CO)_2(py)$. Irradiations were carried out at 25 °C in degassed isooctane solutions of $(\eta^5\text{-}C_5H_5)Mn(CO)_2(4\text{-acetyl-py})$ (5×10^{-4} M).

Table VI. Quantum Yields for $(\eta^5\text{-}C_5H_5)Re(CO)_2X + Y$ to $(\eta^5\text{-}C_5H_5)Re(CO)_2Y + X$ Ligand Substitution[a]

X	Y	Irradiation, λ, nm	Φ ± (0.15Φ)
CO	py	313	0.30
NH$_3$	py	313	0.34
	3,5-DiCl-py	313	0.28
4-Me-py	4-Acetyl-py	436	0.28
4-Me-py	1-Pentene	436	0.30
py	4-Acetyl-py	436	0.09
	1-Pentene	436	0.11
3-Br-py	1-Pentene	436	0.013
	3,4-DiMe-py	436	0.013
	4-Me-py	436	0.013
3,5-DiCl-py	1-Pentene	436	0.005
	3,4-DiMe-py	436	0.005
	4-Me-py	436	0.005
3-Acetyl-py	1-Pentene	436	0.005
3-Benzoyl-py	1-Pentene	436	0.005
4-Acetyl-py	3,4-DiMe-py	436 or 550	$<10^{-4}$
	4-Me-py	436 or 550	$<10^{-4}$
	py	436 or 550	$<10^{-4}$
4-Benzoyl-py	3,4-DiMe	436 or 550	$<10^{-4}$

[a] All photoreactions in isooctane solution of 0.25 M Y at 25 °C; py ≡ pyridine; Me ≡ methyl.

The initial quantum yield for reaction 4 as a function of irradiation wavelength and M, X, Y, and Y concentration has been measured and the crucial data are summarized in Tables IV–VI. First, consider the Mn complexes. The quantum efficiency for photosubstitution is high (0.65–0.14), and note that for every pyridine or substituted pyridine complex the quantum efficiency is very comparable, spanning a range of only 0.42–0.23. The quantum efficiency is independent of the entering group (Table IV). Table V gives some representative data showing that, for a given X, the quantum yield is independent of the concentration of the entering group. Similar data were obtained for the other combinations of X and Y indicated in Table IV. Within the lowest absorption system the quantum yield for the pyridine complexes is independent of whether the irradiation is into the low- or high-energy region of the band. Additionally, several photosubstitution experiments were carried out with $(\eta^5\text{-C}_5\text{H}_4(\text{CH}_3))\text{Mn(CO)}_2\text{X}$ and the results are qualitatively similar. In particular, we note that irradiation into the low-energy portion of the first absorption band of $(\eta^5\text{-C}_5\text{H}_4(\text{CH}_3))\text{Mn(CO)}_2$(4-formyl-py) yields very efficient photosubstitution ($\Phi = 0.25$).

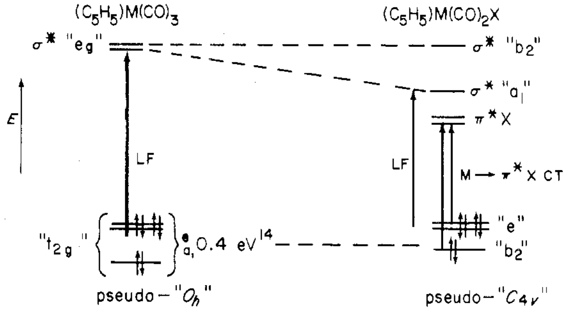
By way of contrast, consider similar investigations for the $(\eta^5\text{-C}_5\text{H}_5)\text{Re(CO)}_2\text{X}$ complexes, Table VI. For a given X, the quantum yields again are insensitive to entering group. Quantum yields for substitution are independent of the entering group concentration for the X and Y combinations indicated in Table VI. For variations in entering group concentrations of 0.05–1.0 M the relative quantum yields were constant within 5%. Photosubstitution efficiency is remarkably sensitive to the nature of the leaving group X. For the pyridine complexes of Re the quantum yields span a range of at least four orders of magnitude. As seen in Table VI, the general trend is that the lowest quantum yields are found for the complexes of substituted pyridines having strongly electron-withdrawing groups which are just the complexes having the lowest energy absorptions.

Discussion

The electronic spectral data reported here for these d^6 $(\eta^5\text{-C}_5\text{H}_5)\text{M(CO)}_2\text{X}$ (X = pyridine or a substituted pyridine) complexes strongly support the assignment of the lowest absorption maximum in these complexes as $\text{M} \rightarrow \pi^*$ X CT. The substituent effects on the position of the band and the direction of the band shift with variation in the pyridine substituent confirm both the CT assignment and its direction as M → X. The red-shifted maxima in $(\eta^5\text{-C}_5\text{H}_4(\text{CH}_3))\text{Mn(CO)}_2\text{X}$ compared to $(\eta^5\text{-C}_5\text{H}_5)\text{Mn(CO)}_2\text{X}$ are consistent with the electron-releasing nature of CH_3 which places more negative charge on Mn to lower the energy required for the Mn → X CT transition. Finally, consistent with the M → X CT assignment, the bands are very sensitive to the solvent just as they are in other metal carbonyls where the M → ligand CT assignment has been adopted, as in $\text{W(CO)}_5\text{X}$ (X = pyridine or substituted pyridine),[3] $\text{ClRe(CO)}_3\text{L}$ (L = 1,10-phenanthroline and related ligands),[12] and $\text{M(CO)}_4\text{L}$ (M = Cr, Mo, W; L = 1,10-phenanthroline and related ligands).[13]

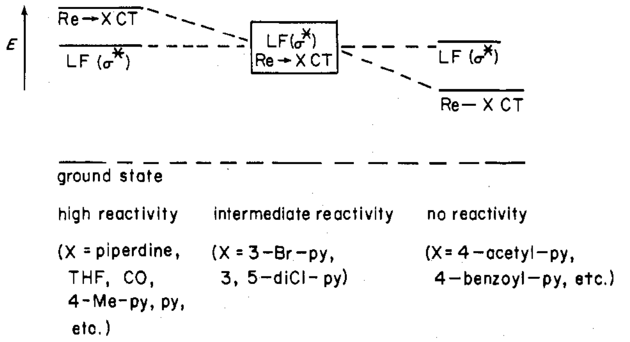
To interpret the splitting of the M → X CT absorption band and to understand the spectra of the THF and aliphatic amine complexes, we will adopt the notion that $(\eta^5\text{-C}_5\text{H}_5)\text{M(CO)}_2\text{X}$ species can be viewed as perturbed C_{4v} $\text{M}'\text{(CO)}_5\text{X}$ (M′ = Cr, Mo, W) species caused by substituting three carbon donor carbonyls for a cyclopentadienyl and changing the central metal. This approximation was adopted recently in discussing the photoelectron spectra (PES) of $(\eta^5\text{-C}_5\text{H}_5)\text{Fe(CO)}_2\text{X}$ (X = Cl, Br, I, CH_3) complexes.[14] We also have at our disposal the PES[14] of the parent $(\eta^5\text{-C}_5\text{H}_5)\text{M(CO)}_3$ (M = Mn, Re) complexes which we could now call "pseudo-O_h". We note that the typical splitting of the M → X CT band is of the order of 3000 cm^{-1} (independent of M). This splitting is very close to the splitting observed in the lowest energy PES band corresponding to ionization of the electrons from the filled e and a_1 orbitals in $(\eta^5\text{-C}_5\text{H}_5)\text{M(CO)}_3$. Splittings of the first ionization for Mn and Re are comparable in the PES, but as a consequence of spin–orbit coupling the first ionization band in the Re complex has more structure and is better resolved than for the Mn species. We note that the two components of the Re → X CT band are more clearly resolved than are those for the Mn → X CT (Figure 4). To the extent that the CT transition can be viewed as a sort of "internal ionization" we ascribe the better resolution of the bands in the Re complexes to spin–orbit coupling. The interpretation of the splitting of the M → X CT bands that we offer is shown in Scheme I. Our interpretation is consistent with the approximate value of the splitting of the highest occupied orbitals in the $(\text{C}_5\text{H}_5)\text{M(CO)}_3$ species,[14] and in the $(\text{C}_5\text{H}_5)\text{M(CO)}_2\text{X}$ species these splittings should be similar. Further, the interpretation is not only consistent with a splitting independent of M but also one independent of the particular pyridine. Finally, the acceptor π^* orbital(s) in pyridine itself is (are) virtually doubly degenerate[15] and the splitting should not increase upon coordination.

Scheme I. Orbital Scheme for $(\text{C}_5\text{H}_5)\text{M(CO)}_3$ and $(\text{C}_5\text{H}_5)\text{M(CO)}_2\text{X}$



With the data at hand we are really in no position to make a detailed electronic spectral assignment for the complexes where X *is not* a pyridine or substituted pyridine. However, some reasonable deductions and observations can be made for simple ligands like THF or aliphatic amine. We regard these as "simple" since they have no low-lying electronic excited states, and, consequently, should not yield $(\eta^5\text{-C}_5\text{H}_5)\text{M(CO)}_2\text{X}$ complexes having low-lying M → X CT excited states. These simple ligands bind to the central metal atom only via σ interactions. The low-energy absorptions in the THF and piperidine complexes are substantially weaker than for the pyridine and related complexes. But we do find that the band positions for the THF and amine complexes are comparable to the positions found for the higher energy-absorbing pyridine complexes (X = 3,4-diMe-py, py, 4-Me-py). It is logical to assume that the bands observed for the amine complexes are also present in the pyridine complexes, but that they are too weak to be observed in view of the high absorptivities which obtain for the M → X CT absorptions. The reasonableness of this assumption rests in the fact that the same donor atoms are involved in all cases. This same assumption has been made for the $\text{Ru(NH}_3)_5\text{X}^{2+}$ [4] complexes, and it was experimentally verified for the $\text{W(CO)}_5\text{X}^{2+}$ species.[3] We adopt the notion that the weaker, low-energy electronic absorptions in the amine and THF complexes are LF bands associated with "d–d" transitions. The assignment of these bands as LF is reasonable on the basis of their intensity and the fact that the introduction of σ-donor (O or N donor) ligands gives a weaker LF than in the parent $(\eta^5\text{-C}_5\text{H}_5)\text{M(CO)}_3$ complexes. The fact that these LF bands are substantially higher in energy for M = Re than for M = Mn is also consistent with the LF assignment. A similar trend was found[16] for $\text{M(CO)}_5\text{X}$ (M = Mn, Re; X = Cl, Br, I) where the LF assignment is appropriate. For the complexes $(\eta^5\text{-C}_5\text{H}_5)\text{M(CO)}_2\text{X}$ (X = σ donor) we expect a substantial lowering in energy of the lowest virtual orbital consistent with the low-energy absortions. First band positions in the amine and THF complexes are shifted of the order of ~10 000 cm^{-1} from the first band in $(\eta^5\text{-C}_5\text{H}_5)\text{M(CO)}_3$ which is analogous to the shift in going from M(CO)_6 to M(CO)_5(amine).[16a] The LF transitions are included in Scheme I. The orbital populated in the LF transitions is likely one which is strongly antibonding with respect to the M–X bond, and indeed, turning to the C_{4v} W(CO)_5(amine) analogues this assignment seems most appropriate (vide infra).

Scheme II. Relaxed Excited State Energy and Photoreactivity for $(\eta^5\text{-}C_5H_5)Re(CO)_2X$



We turn now to a consideration of the excited state phenomena. For all of the complexes studied we find only loss of X. This result is reminiscent of the result obtained for analogous $W(CO)_5X$ complexes upon excitation into the lowest absorption.[3] In the C_{4v} case the lowest LF states involve population of σ^* states directed along the C–W–X axis for X $\ll$ CO in LF strength.[3,17] The similarity of the specificity of ligand photosubstitution in $(\eta^5\text{-}C_5H_5)M(CO)_2X$ and $W(CO)_5X$ implicates directed σ^* excited states. This would account for the reactions of the amine and THF complexes. Disubstituted complexes $(\eta^5\text{-}C_5H_5)M(CO)X_2$ only seem[2] to result from the irradiation of $(\eta^5\text{-}C_5H_5)M(CO)_2X$ when X is a reasonable π-acceptor ligand, i.e., dissociative loss of CO from the substituted complexes occurs when the group X is similar to CO in its bonding capabilities. This again parallels the situation for $W(CO)_5X$.[2]

For the pyridine and substituted pyridine complexes which are photosensitive, we only find substitution of the N donor, and the question is: which is the reactive excited state, the LF or M → X CT state. In the absence of a wavelength effect, one generally assumes that the reactive excited state is the lowest energy, *relaxed* excited state. For the Re complexes we find that some complexes are reactive and others are not. The reactive complexes have Re → X CT absorptions energetically comparable to those for the amine and THF complexes, whereas the nonreactive complexes exhibit Re → X CT absorption substantially below the LF bands. This is the same pattern found for $W(CO)_5X$[3] and $Ru(NH_3)_5X^{2+}$.[4] Thus, we conclude that the Re → X CT state is unreactive and the LF type states are responsibe for substitution. The state situation for reactive and nonreactive Re complexes is shown in Scheme II. The parallels in the photochemistry of these pseudo-C_{4v} systems and the actual C_{4v} case are again very striking.

Now it must be realized that we are correlating the spectroscopically observed states in absorption with the photosubstitution behavior and the relative position of relaxed states. Difficulties will naturally be encountered in such a correlation, especially in the region where "intermediate reactivity" obtains. A case in point is with $(\eta^5\text{-}C_5H_5)Re(CO)_3$(3-acetyl-py) where the M → X CT absorption maximum dictates a higher photoreactivity than reflected in its substitution quantum yields. The relatively low yields can be rationalized by a greater change in the position of the CT state upon relaxation subsequent to vertical excitation. Further, merely by examining LF and Re → X CT absorption energies upon changes in ligands one cannot predict the relative nonchemical, nonradiative decay rates. Despite these qualifications, though, the correlation of photosubstitution efficiency and the position of the absorptions in the $(\eta^5\text{-}C_5H_5)Re(CO)_2X$ complexes is very good, and the Re → X CT band position is apparently a good predictor of photochemical reactivity.

The results that we have obtained for the $(\eta^5\text{-}C_5H_5)Mn(CO)_2X$ complexes are surprising in view of the above rationale for the reactivity of the Re complexes. For all X, even 4-formylpyridine, we find very efficient photosubstitution of X for the Mn species. Assuming that the explanation for $(\eta^5\text{-}C_5H_5)Re(CO)_2X$, $W(CO)_5X$,[3] and $Ru(NH_3)_5X^{2+}$ [4] is correct, we can only conclude that for the Mn complexes the relaxed excited state is *not* the CT state. Despite the observation of very low-lying Mn → X CT *absorption*, the excited state reactivity is consistent with a LF lowest excited state. We do see from the absorption spectral data that the LF bands are relatively (compared to M → L CT) lower lying in the Mn complexes than in the Re complexes. Additionally, in the Re complexes it is not unreasonable to assume that the observable absorptions include substantial singlet → triplet character whereas the Mn species do not. This is certainly true in $Re(CO)_5X$ compared to $Mn(CO)_5X$[16] and likewise in $W(CO)_5X$ and $Cr(CO)_5X$.[17] *If the triplet states are the reactive excited states*, then the absorption band positions in the Mn species are even less useful as an indicator of reactive state positions. One interesting point concerning the Mn complexes studied here is that the chromophore is the M → X CT having high visible absorptivity, whereas the reaction apparently occurs from a spectroscopically nondetectable state. Such a situation parallels that for organic molecules where singlet excited states are achieved by direct excitation, whereas reaction often occurs from a nonobservable triplet state.[18]

Experimental Section

Materials. Pyridine and substituted pyridine ligands used in this study are all commercially available. Isooctane solvent was generally used for spectroscopic and photochemical studies and was used as commercially available in spectroscopic grade. The $(\eta^5\text{-}C_5H_5)Mn(CO)_3$ was obtained from Ethyl Corp. and was sublimed before use, mp 77 °C (lit.[19] mp 76.8–77.1 °C). The $(\eta^5\text{-}C_5H_4(CH_3))Mn(CO)_3$ was purchased from Pressure Chemical Co. and was purified prior to use by chromatography on alumina. Synthesis of $(\eta^5\text{-}C_5H_5)Re(CO)_3$ was by a literature procedure[20] and final purification by chromatography on alumina yielded a white solid with mp 103–105 °C (lit.[20] 104–105 °C).

Synthesis of $(\eta^5\text{-}C_5H_5)Mn(CO)_2(py)$. The preparation of $(\eta^5\text{-}C_5H_5)Mn(CO)_2(py)$ was achieved essentially according to the procedure reported in the literature.[21] The $(\eta^5\text{-}C_5H_5)Mn(CO)_3$ and pyridine were dissolved in isooctane in a 1:10 mol ratio and irradiated several hours with a broad band ultraviolet light source. The solvent was rotary evaporated to dryness yielding a yellow-orange solid. The solid was fractionally sublimed removing unreacted $(\eta^5\text{-}C_5H_5)Mn(CO)_3$ at ~50 °C, and then slightly higher temperatures up to ~90 °C yielded sublimation of the $(\eta^5\text{-}C_5H_5)Mn(CO)_2(py)$. The yellow crystals melt at 112–114 °C in accord with the literature value of 114 °C.[21]

Synthesis of $(\eta^5\text{-}C_5H_5)Mn(CO)_2X$. All complexes of the formula $(\eta^5\text{-}C_5H_5)Mn(CO)_2X$ were prepared at room temperature by ultraviolet irradiation of *either* $(\eta^5\text{-}C_5H_5)Mn(CO)_2(py)$ or $(\eta^5\text{-}C_5H_5)Mn(CO)_3$ in degassed isooctane solutions of X. In most cases the $(\eta^5\text{-}C_5H_5)Mn(CO)_2X$ complexes were not isolated from solution but were used as photogenerated. For determination of the extinction coefficient of the $(\eta^5\text{-}C_5H_5)Mn(CO)_2X$ complexes in solution, we showed that the conversion of $(\eta^5\text{-}C_5H_5)Mn(CO)_2(py)$ is complete by infrared. The test that ensured purity of the $(\eta^5\text{-}C_5H_5)Mn(CO)_2X$ compound was the fact that the $(\eta^5\text{-}C_5H_5)Mn(CO)_2(py)$ is *quantitatively regenerated* by the irradiation of $(\eta^5\text{-}C_5H_5)Mn(CO)_2X$ subsequent to adding an excess of pyridine to the solution. That is, we can first quantitatively convert either $(\eta^5\text{-}C_5H_5)Mn(CO)_3$ or $(\eta^5\text{-}C_5H_5)Mn(CO)_2(py)$ to the photosubstitution product $(\eta^5\text{-}C_5H_5)Mn(CO)_2X$ and then quantitatively regenerate the pyridine complex. Thus, the readily reversible chemistry monitored simultaneously by infrared and uv–visible spectral changes confirms product purity.

Synthesis of $(\eta^5\text{-}C_5H_5)Re(CO)_2(py)$. $(\eta^5\text{-}C_5H_5)Re(CO)_3$ (0.2 g) was dissolved in continuously Ar-purged Et_2O in a Vycor tube. The Ar-purged solution was irradiated at 254 nm with a UV Products, Inc., 254-nm light source to yield $(\eta^5\text{-}C_5H_5)Re(CO)_2(Et_2O)$ (not isolated). Pyridine was added to the solution in a fourfold excess. The solution was simply allowed to evaporate under vigorous Ar purge and a brown solid remained. Chromatography on neutral alumina and recrystallization from Et_2O/hexane at −78 °C yielded bright yellow crystals, mp 143–145 °C dec. Elemental analysis (Alfred Bernhardt) was satisfactory. Calcd: C, 37.20; H, 2.60; N, 3.60. Found: C, 37.45; H, 2.71; N, 3.53.

Synthesis of $(\eta^5$-$C_5H_5)Re(CO)_2$(4-benzoyl-py). Since many of the $(\eta^5$-$C_5H_5)Re(CO)_2X$ are not photosubstitution labile, we cannot prove their purity by photoregeneration of the $(\eta^5$-$C_5H_5)Re(CO)_2$(py) from which they can be made. Thus, we have isolated and characterized our $(\eta^5$-$C_5H_5)Re(CO)_2$(4-benzoyl-py) as representative of these complexes. Others were synthesized in a manner analogous to that which follows or by irradiation of $(\eta^5$-$C_5H_5)Re(CO)_2$(py) in the presence of X in degassed solution.

$(\eta^5$-$C_5H_5)Re(CO)_3$ (0.2 g) was dissolved in continuously Ar-purged Et_2O in a Vycor tube. Irradiation for 1 h with an Ar purge yielded $(\eta^5$-$C_5H_5)Re(CO)_2(Et_2O)$ (not isolated). Excess 4-benzoylpyridine was added and the solution was allowed to evaporate to dryness under vigorous Ar purge, yielding a red powder. The red powder was chromatographed on grade No. 3 alumina, eluting with Et_2O. Rotary evaporation yielded a red solid which was recrystallized from Et_2O/hexane at −78 °C. The solid decomposes without melting at ~50 °C. The elemental analysis (Alfred Bernhardt) was satisfactory. Calcd: C, 46.50; H, 2.85; N, 2.85. Found: C, 46.25; H, 2.97; N, 2.88.

Spectra. All infrared spectra were recorded using either a Perkin-Elmer 337, 567, or 521 instrument with either 0.1 or 1.0 mm path length matched cells. All electronic spectra were recorded using a Cary 17, and low-temperature spectra were obtained using an all quartz liquid N_2 Dewar equipped with optical quality flats for windows. Owing to the air sensitivity of the complexes in solution (other than $(\eta^5$-$C_5H_5)M(CO)_3$), the molar absorptivities were always determined for deaerated samples.

Irradiation Procedures. Samples to be irradiated were freeze–pump–thaw degassed in at least three cycles in 3.0-ml aliquots using ampules prepared from 13 × 100 mm Pyrex test tubes. After degassing the samples were hermetically sealed. Irradiations were carried out using merry-go-rounds[22] equipped with 550 and 450 W Hanovia Hg lamps filtered to isolate the 313, 436, or 550 Hg emission. For the 633-nm irradiations a 6X beam expanded He–Ne laser was used providing $\sim 10^{-6}$ einstein/min/cm^2 intensity. Ferrioxalate actinometry[23] was used for 313- and 436-nm irradiations, and Reinecke's salt actinometry[24] was used for 550- or 633-nm irradiations. Photoproducts were identified by infrared and uv–visible spectra by comparison with spectra for authentic samples. Quantitative analyses were made by monitoring electronic spectral changes, and it was determined that the quantum yield for appearance of product is equal to that for the disappearance of starting material, consistent with the stoichiometry indicated in eq 4. Quantum yields were determined from initial spectral changes where optical density changes were linear with irradiation time. The values given in Tables IV–VI are for conversion of <20%. Yields given in the tables are the average of at least duplicate, and often triplicate, determinations.

Acknowledgment. We thank the National Science Foundation for support of this work. Support from the Cabot Solar Energy Research Fund of M.I.T. is also gratefully acknowledged.

Registry No. $(\eta^5$-$C_5H_5)Re(CO)_3$, 12079-73-1; $(\eta^5$-$C_5H_5)Re(CO)_2$(1-pentene), 60706-11-8; $(\eta^5$-$C_5H_5)Re(CO)_2$(3,4-DiMe-py), 60706-12-9; $(\eta^5$-$C_5H_5)Re(CO)_2$(4-Me-py), 60706-13-0; $(\eta^5$-$C_5H_5)Re(CO)_2$py, 59423-85-7; $(\eta^5$-$C_5H_5)Re(CO_2)_2$(3-Br-py), 60706-15-2; $(\eta^5$-$C_5H_5)Re(CO_2)_2$(3,5-DiCl-py), 60706-16-3; $(\eta^5$-$C_5H_5)Re(CO)_2$(3-acetyl-py), 60706-17-4; $(\eta^5$-$C_5H_5)Re(CO)_2$(3-benzoyl-py), 60718-60-7; $(\eta^5$-$C_5H_5)Re(CO)_2$(4-acetyl-py), 60718-61-8; $(\eta^5$-$C_5H_5)Re(CO)_2$(4-benzoyl-py), 60718-62-9; $(\eta^5$-$C_5H_5)Re(CO)_2$(4-formyl-py), 60718-63-0; $(\eta^5$-$C_5H_5)Re(CO)_2$(4-Ph-py), 60718-64-1; $(\eta^5$-$C_5H_5)Re(CO)_2$(piperidine), 60718-65-2; $(\eta^5$-$C_5H_5)Re(CO)_2NH_3$, 60718-66-3; $(\eta^5$-$C_5H_5)Re(CO)_2$THF, 59423-86-8; $(\eta^5$-$C_5H_5)Mn(CO)_3$, 12079-65-1; $(\eta^5$-$C_5H_5)Mn(CO)_2$(1-pentene), 60718-67-4; $(\eta^5$-$C_5H_5)Mn(CO)_2$(3,4-DiMe-py), 60718-68-5; $(\eta^5$-$C_5H_5)Mn(CO)_2$(4-Me-py), 60718-69-6; $(\eta^5$-$C_5H_5)Mn(CO)_2$py, 12088-91-4; $(\eta^5$-$C_5H_5)Mn(CO)_2$(3,5-DiCl-py), 60718-70-9; $(\eta^5$-$C_5H_5)Mn(CO)_2$(4-acetyl-py), 60718-71-0; $(\eta^5$-$C_5H_5)Mn(CO)_2$(4-benzoyl-py), 60718-72-1; $(\eta^5$-$C_5H_5)Mn(CO)_2$(4-formyl-py), 60718-73-2; $(\eta^5$-$C_5H_5)Mn(CO)_2$piperidine, 38497-86-8; $(\eta^5$-$C_5H_5)Mn(CO)_2$THF, 12093-26-4; $(\eta^5$-$C_5H_4CH_3)Mn(CO)_3$, 12108-13-3; $(\eta^5$-$C_5H_4CH_3)Mn(CO)_2$(3,4-DiMe-py), 60718-80-1; $(\eta^5$-$C_5H_4CH_3)Mn(CO)_2$(4-Me-py), 60718-81-2; $(\eta^5$-$C_5H_4CH_3)Mn(CO)_2$py, 60718-82-3; $(\eta^5$-$C_5H_4CH_3)Mn(CO)_2$(3,5-DiCl-py), 60718-83-4; $(\eta^5$-$C_5H_4CH_3)Mn(CO)_2$(4-acetyl-py), 60718-84-5; $(\eta^5$-$C_5H_4CH_3)Mn(CO)_2$(4-benzoyl-py), 60718-85-6; $(\eta^5$-$C_5H_4CH_3)Mn(CO)_2$(4-formyl-py), 60734-26-1; $(\eta^5$-$C_5H_4CH_3)Mn(CO)_2$piperidine, 60718-86-7; $(\eta^5$-$C_5H_5)Re(CO)_2(n$-$PrNH_2)$, 60718-87-8; $(\eta^5$-$C_5H_5)Mn(CO)_2(n$-$PrNH_2)$, 60718-88-9; $(\eta^5$-$C_5H_5)Mn(CO)_2NH_3$, 40687-07-8.

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