Registry No. $\mathrm{Ru(bpy)_3^{2+}}$, 15158-62-0; $\mathrm{Ru(bpy\text{-}}d_8\mathrm{)_3^{2+}}$, 67573-02-8.

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Photosubstitution Reactivity of a Series of Tetracarbonylbis(substituted pyridine)tungsten(0) Complexes Having Ligand Field or Charge-Transfer Lowest Excited States

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Electronic absorption and emission spectra and photosubstitution efficiencies are reported for *cis*-$\mathrm{W(CO)_4X_2}$ (X = 3,4-dimethylpyridine, 4-ethylpyridine, pyridine, 3-benzoylpyridine, 4-phenylpyridine, 3,5-dichloropyridine, 3,5-dibromopyridine, 4-benzoylpyridine, 4-cyanopyridine, 4-formylpyridine). The spectral data show that the tungsten → pyridine charge-transfer (CT) state moves smoothly to lower energy with more electron-withdrawing substituents on the pyridine, while the ligand field (LF) states are essentially insensitive to these changes. Photosubstitution of X occurs in all cases upon irradiation into the lowest energy absorption system, but the quantum efficiency for the substitution is very dependent on whether the lowest energy excited state is LF or W → XCT in character. The W → XCT state is virtually unreactive; e.g., *cis*-$\mathrm{W(CO)_4(4\text{-}form\text{-}py)_2}$ undergoes photosubstitution with a 436-nm quantum yield of ~0.0007. Complexes having LF lowest excited states are very photosubstitution labile; e.g., for X = 3,4-dimethylpyridine, 4-ethylpyridine, or pyridine the photosubstitution of X in *cis*-$\mathrm{W(CO)_4X_2}$ occurs with a 436-nm quantum yield of ~0.4.

A large amount of work has been done to increase the understanding of the electronic structure and photochemistry of metal carbonyls[2] and particularly simply substituted d^6 metal carbonyl complexes. Studies of $\mathrm{W(CO)_5X}$ (X = substituted pyridine) have shown that when the lowest excited state is ligand field (LF) in character, photosubstitution of both CO and X is found in fluid solution at room temperature.[3-6] The quantum yield for X dissociation is generally ≥0.5 in these cases,[3,4] and although the efficiency for CO substitution increases as the energy of irradiation increases, the predominant reaction remains loss of X. This is consistent with a substantial amount of reaction from the lowest excited state, even when upper excited states are directly populated. When the lowest excited state is clearly metal to ligand charge transfer (W → XCT) in character,[4] the quantum yield for substitution of X is several orders of magnitude smaller than the quantum yield associated with LF lowest excited states.

The red shift in the energetic position of the W → XCT absorption with the introduction of electron-withdrawing substituents onto the pyridine ring, which was used to elucidate the photosubstitution behavior of $\mathrm{W(CO)_5X}$,[4] has also been found to occur in complexes of the type $\mathrm{Ru(NH_3)_5X^{2+}}$,[7] $(\eta^5\text{-}\mathrm{C_5H_5})\mathrm{M(CO)_2X}$ (M = Mn, Re),[8] and $\mathrm{Fe(CN)_5X^{3-}}$.[9] In $\mathrm{Ru(NH_3)_5X^{2+}}$, $(\eta^5\text{-}\mathrm{C_5H_5})\mathrm{Re(CO)_2X}$, and $\mathrm{Fe(CN)_5X^{3-}}$ complexes the photosubstitution results parallel those for $\mathrm{W(CO)_5X}$; i.e., when the M → XCT excited state is higher than the LF state, efficient photosubstitution of X obtains, and when the M → XCT is the lowest excited state, the quantum yield for photosubstitution is greatly reduced.

In this paper we wish to report an electronic spectral and photochemical study for complexes of the general formula *cis*-$\mathrm{W(CO)_4X_2}$ (X = pyridine or a substituted pyridine). Aside from elaborating the number of systems for which photosubstitution lability can be manipulated by simple variation in X, the data allow a direct comparison of the relative LF and W → XCT positions in $\mathrm{W(CO)_5X}$ and *cis*-$\mathrm{W(CO)_4X_2}$.

Results and Discussion

a. Preparation of *cis*-$\mathbf{W(CO)_4X_2}$. Synthesis of *cis*-$\mathrm{W(CO)_4X_2}$ was by one of the two routes indicated in eq 1 or 2.

$$\mathrm{W(CO)_6} \xrightarrow[\mathrm{X}]{h\nu} \mathrm{W(CO)_5X\ (+CO)} \xrightarrow[\mathrm{X}]{h\nu} cis\text{-}\mathrm{W(CO)_4X_2\ (+CO)} \tag{1}$$

$$cis\text{-}\mathrm{W(CO)_4(pip)_2} \xrightarrow[\mathrm{C_6H_6\ or\ CH_2Cl_2}]{\text{excess X}} cis\text{-}\mathrm{W(CO)_4X_2} + 2\mathrm{pip} \tag{2}$$

Both routes have some precedence[3,10] even though only a few of the *cis*-$\mathrm{W(CO)_4X_2}$ complexes studied have actually been reported. The major impurities are $\mathrm{W(CO)_5X}$ and free ligand, and these can be separated from the desired product by chromatography on alumina and/or recrystallization. Four infrared band maxima, Table I, in the CO stretching region are consistent with the formulation of these compounds as C_{2v},

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Table I. Carbonyl Infrared Stretching Bands for *cis*-$W(CO)_4X_2$

X	Bands, cm^{-1} (ϵ, M^{-1})[a]				
3,4 Me_2-py	2004 (2200)	1875 (5660)	1865 (6410)	1839 (5290)	
4-Et-py	2005 (2450)	1876 (5980)	1866 (6700)	1841 (4930)	
py	2006 (2650)	1879 (6000)	1869 (7050)	1844 (4940)	
3-Bz-py	2008 (2600)	1884 (5100)	1873 (5700)	1848 (4000)	1669 (1200)[b]
4-Ph-py	2005 (2650)	1878 (5130)	1869 (5950)	1843 (4230)	
3,5-Cl_2-py	2012 (*5.0*)	1892 (*9.0*)	1879 (*10.0*)	1857 (*6.5*)	
3,5-Br_2-py	2011 (*5.1*)	1892 (*9.1*)	1878 (*10.0*)	1856 (*6.9*)	
4-Bz-py	2007 (2650)	1884 (4600)	1875 (5020)	1850 (3650)	1670 (974)[b]
4-CN-py	2006 (3650)	1890 (5630)	1878 (6280)	1860 (4990)	
4-form-py	2005 (*5.3*)	1886 (*8.3*)	1875 (*10.0*)	1853 (*6.8*)	1715 (*3.7*)[b]
TMEDA=X_2[c]	2007 (1500)	1872 (sh)	1863 (8080)	1836 (5530)	
cis-$Ph_2PCH=CHPPh_2=X_2$	2023 (3490)	1923 (4070)	1909 (6530)	1894 (4820)	

[a] In C_6H_6 at 298 K; italic values are relative intensities. [b] Due to pyridine ligand ketone stretch. [c] TMEDA = *N,N,N′,N′*-tetramethylethylenediamine.

Table II. Electronic Absorption Spectral Features for *cis*-$W(CO)_4X_2$ Complexes[a]

X	abs max, nm (ϵ, M^{-1} cm^{-1})[b]		
3,4-Me_2-py	356 (7280)	403 (7855)	455 (sh)
4-Et-py	360 (6880)	408 (7600)	457 (sh)
py	367 (6470)	413 (7940)	460 (sh)
3-Bz-py	372 (sh)	412 (7020)	470 (sh)
4-Ph-py	380 (sh)	434 (9330)	475 (sh)
3,5-Cl_2-py	382 (sh)	440 (8250)	485 (sh)
3,5-Br_2-py	382 (sh)	442 (10500)	485 (sh)
4-Bz-py	387 (sh)	492 (9520)	555 (sh)
4-CN-py	390 (sh)	489 (7980)	560 (sh)
4-form-py	398 (sh)	514 (7400)	580 (sh)
TMEDA=X_2[c]	300 (11250)	402 (1420)	450 (sh)

[a] In benzene solution at 298 K. [b] sh = shoulder. [c] TMEDA = *N,N,N′,N′*-tetramethylethylenediamine.

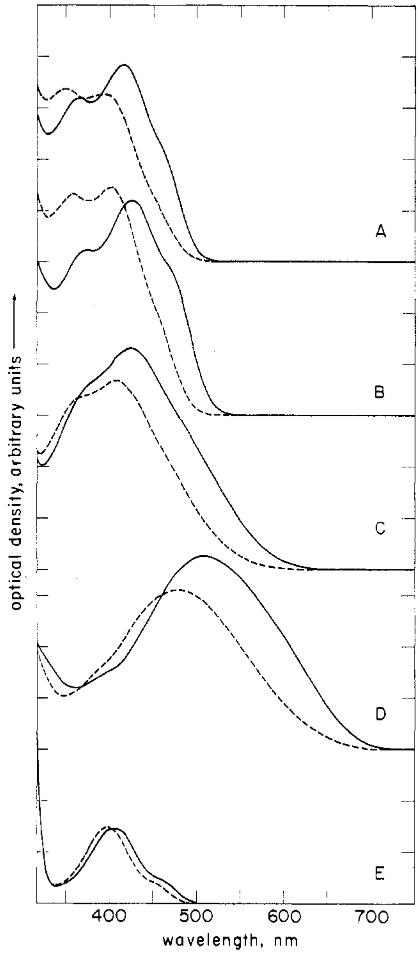

Figure 1. Electronic absorption spectra at 298 K in benzene/isooctane (1:4 volume) (—) and benzene/isooctane/EtOH (1:4:5 volume) (- - -) for *cis*-$W(CO)_4X_2$ at the same concentration for both solvents. X is 3,4-dimethylpyridine, pyridine, 3-benzoylpyridine, 4-benzoylpyridine, and TMEDA for A, B, C, D, and E, respectively. Cf. Table II for band positions and absorptivities.

cis-$W(CO)_4X_2$ complexes. Representative elemental analyses (cf. Experimental Section) are satisfactory.

b. Electronic Absorption Spectra. Electronic absorption spectra for the *cis*-$W(CO)_4X_2$ complexes have been recorded in solution. Some representative spectra are shown in Figure 1 and the data for all complexes studied are set out in Table II. Each of the complexes exhibits absorption in the visible and near-UV; the position of the lowest energy absorption maximum depends on the nature of X in a manner as previously established for $W(CO)_5X$.[4] Consequently, some fraction of the lowest absorption system can be attributed to a W → XCT transition. The lowest absorption system is quite solvent sensitive, Figure 1; more polar or polarizable solvents give rise to the higher energy W → XCT absorption, as found for other metal carbonyl derivatives exhibiting M → LCT absorptions.[4,8,10,11]

In order to compare the LF absorptions and their intensity for the *cis*-$W(CO)_4(N\text{-donor})_2$ complexes, we have included data for the $W(CO)_4$(TMEDA) (TMEDA = *N,N,N′,N′*-tetramethylethylenediamine) which should exhibit no low lying W → LCT absorptions. Our data for the TMEDA complex are very similar to previously published data for the ethylenediamine complex[10,11] and other *cis*-$W(CO)_4$(bis saturated amine) species.[10] The absorption features at ~450 nm (sh) and 402 nm ($\epsilon \approx 1400$ M^{-1} cm^{-1}) have been attributed to the first singlet → triplet and singlet → singlet LF transition, respectively.[10] Note that these absorptions are relatively weak compared to the absorptions for the pyridine complexes. Consequently, the LF absorptions in *cis*-$W(CO)_4X_2$ are obscured by the more intense W → XCT absorption. But since the immediate coordination sphere is the same for all complexes, we will assume that the LF states are at nearly the same energy in every case.

In comparing the absorption position of the TMEDA complex with the pyridine complexes we find that in all cases there appears to be substantial W → XCT absorption at a position lower than the LF singlet → triplet absorption. This is in contrast to the C_{4v} $W(CO)_5X$ case where for certain X the LF singlet → triplet was well below any W → XCT absorption. This finding allows the conclusion that in going from $W(CO)_5X$ to *cis*-$W(CO)_4X_2$ the W → XCT state moves to lower energy by a greater amount than do the LF states.

c. Emission Spectra. Emission spectral studies for the *cis*-$W(CO)_4X_2$ confirm the essence of the conclusion drawn from the absorption spectra. Except for *cis*-$W(CO)_4(4\text{-form-py})_2$ (4-form-py = 4-formylpyridine), all of the electronic excited *cis*-$W(CO)_4X_2$ complexes studied here undergo ra-

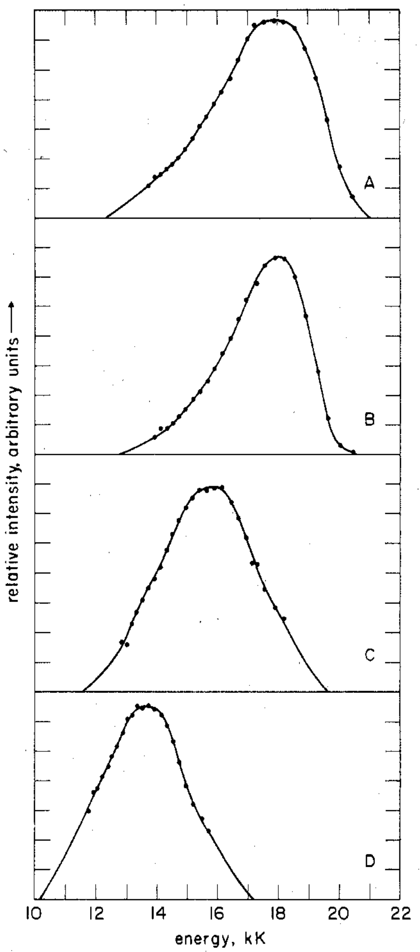

Figure 2. Corrected emission spectra in EPA at 77 K for *cis*-W-$(CO)_4X_2$. A–D are the same as in Figure 1. The excitation wavelength is 450 nm. Cf. Table III for band maxima and emission lifetimes.

Table III. Emission Data for $W(CO)_4X_2$ Complexes

X	emission max (FWHM),[a] $cm^{-1} \times 10^3$ 77 K glass[b]	emission lifetime, s × 10^6 77 K glass[b]
3,4-Me_2-py	18.0 (4.1)	7.3
4-Et-py	18.0 (3.6)	19.2
py	17.9 (3.1)	24.0
3-Bz-py	15.8 (4.0)	6.8
4-Ph-py	16.7 (3.3)	18.5
3,5-Cl_2-py	15.7 (3.5)	9.2
3,5-Br_2-py	15.7 (3.4)	8.3
4-Bz-py	13.6 (3.3)	15.3
4-CN-py	14.5 (3.5)[c]	6.2[c]
4-form-py	d	d
pip[e]	18.35 (-)	28.5

[a] Corrected for variation in detector output as a function of wavelength; FWHM = full width at half maximum. [b] EPA solvent unless otherwise noted. [c] In 1:1 toluene/methylcyclohexane. [d] Emission not observed. [e] Data from ref 10.

diative decay at 77 K in a glassy solvent. Some representative emission spectra are shown in Figure 2, and the data for all complexes are summarized in Table III. The spectral distribution and efficiency of the emission are independent of the excitation wavelength for wavelengths longer than 300 nm. Thus, these complexes likely emit from the lowest excited state. Emission lifetimes are included in Table III and the ~10^{-5} s values likely reflect an emitting state which has considerable triplet character.

For X = 3,4-dimethylpyridine, 4-ethylpyridine, and pyridine the emission maximum is near 18 000 cm^{-1}. These complexes emit at an energy very nearly equal to that previously reported for *cis*-$W(CO)_4(pip)_2$ (pip = piperidine) which emits from a LF triplet state.[10] Consequently, the LF state is likely the lowest excited state in the *cis*-$W(CO)_4X_2$ complexes where X = 3,4-dimethylpyridine, 4-ethylpyridine, and pyridine. For the remaining pyridine complexes the emission is substantially to the red of that for the LF emitter. Thus, for X = 3- and 4-benzoylpyridine, 4-phenylpyridine, 3,5-dihalopyridine, 4-cyanopyridine, and 4-formylpyridine, the W → XCT state is lower in energy than the lowest LF state in *cis*-$W(CO)_4X_2$. By way of contrast, the lowest excited state for $W(CO)_5X$ is LF for either X = 3,5-dihalopyridine or 3-benzoylpyridine. These facts support the conclusion that the W → XCT state moves to a lower energy by an amount greater than for the LF state in going from $W(CO)_5X$ to *cis*-$W(CO)_4X_2$[4]

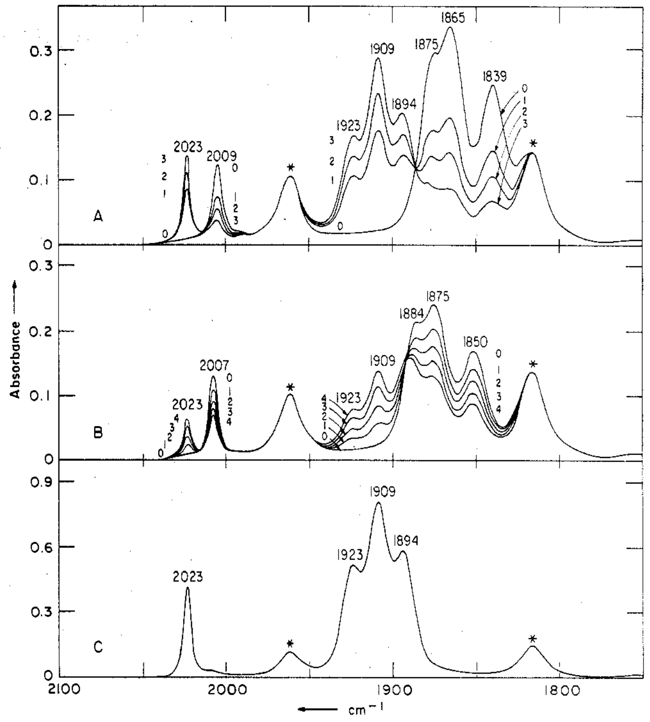

Figure 3. Infrared absorption spectral changes accompanying the 436-nm irradiation of A, *cis*-$W(CO)_4(3,4\text{-}Me_2\text{-}py)_2$ and B, *cis*-W-$(CO)_4(4\text{-}Bz\text{-}py)_2$ in benzene containing 0.01 M *cis*-$Ph_2PCH{=}CHPPh_2$ at 298 K. The photoproduct in each case is $W(CO)_4$(*cis*-$Ph_2PCH{=}CHPPh_2$), the infrared spectrum of which in benzene is shown in C. Bands marked with * are solvent absorptions from a slight mismatch of the IR cells.

d. Photosubstitution Behavior of *cis*-$W(CO)_4X_2$. Irradiation of *cis*-$W(CO)_4X_2$ results in substitution of X as the dominant chemical reaction in solution. The quantum efficiency for reaction 3 was measured as a function of X under a constant

$$cis\text{-}W(CO)_4X_2 \xrightarrow[L,\ C_6H_6]{436\ \text{nm}} W(CO)_4L + 2X \qquad (3)$$

$$L = cis\text{-}Ph_2PCH{=}CHPPh_2$$

set of conditions using 436-nm irradiation. Figure 3 shows representative infrared spectral changes accompanying the photoconversion of *cis*-$W(CO)_4X_2$ to $W(CO)_4L$. The chemical yield of $W(CO)_4L$ is virtually quantitative in all cases, but the quantum efficiency depends markedly on X, Table IV.

cis-$Ph_2PCH{=}CHPPh_2$ as an entering group was chosen for convenience in identifying and monitoring the photoreaction, since each *cis*-$W(CO)_4X_2$ gives the same product. However, reaction 3 proceeds via dissociative loss of X as in reaction 4.

$$cis\text{-}W(CO)_4X_2 \xrightarrow{436\ \text{nm}} W(CO)_4X + X \qquad (4)$$

The coordinatively unsaturated species $W(CO)_4X$ then reacts

Table IV. Photosubstitution of X in *cis*-$W(CO)_4X_2$[a]

X	Φ ± 15%	X	Φ ± 15%
3,4-Me_2-py	0.37	3,5-Cl_2-py	<0.02[b]
4-Et-py	0.42	3,5-Br_2-py	<0.06[b]
py	0.31	4-Bz-py	0.002
3-Bz-py	0.004	4-CN-py	0.01
4-Ph-py	0.002	4-form-py	0.0007

[a] Irradiation carried out at 298 K in benzene solution of ~10^{-3} M *cis*-$W(CO)_4X_2$ containing 10^{-2} M *cis*-$Ph_2PCH{=}CHPPh_2$ at a wavelength of 436 nm. Data are corrected for the thermal component of the substitution. [b] A large thermal component of reaction prevented accurate determination of Φ.

with the chelate ligand L to extrude a second molecule of X resulting in the formation of $W(CO)_4L$, reaction 5. A similar

$$W(CO)_4X \xrightarrow[\Delta]{L} W(CO)_4L + X \qquad (5)$$

assumption was made previously in studies where 1,10-phenanthroline was used as an entering group.[10] To establish that reaction 4 is the primary photoprocess, *cis*-$W(CO)_4(py)_2$ and *cis*-$W(CO)_4(3\text{-Bz-py})_2$ were irradiated in the presence of PPh_3 as an entering group. The observed primary photoproduct is *cis*-$W(CO)_4(PPh_3)X$, reaction 6. For the two

$$cis\text{-}W(CO)_4X_2 \xrightarrow[PPh_3]{h\nu} cis\text{-}W(CO)_4(PPh_3)X + X \qquad (6)$$

species investigated the 436-nm quantum yield for reaction 6 was the same as that found for reaction 3.

Finally, with respect to the photochemistry, we do not find any evidence for any competitive formation of $W(CO)_3XL$; i.e., when L enters the coordination sphere it always displaces an X from $W(CO)_4X$ and not CO. This result also shows that CO loss is not an important photoreaction at 436 nm.

The quantum yield variation upon changes in X are in accord with the interpretation that the LF state is lowest for X = 3,4-dimethylpyridine, 4-ethylpyridine, and pyridine. For the other pyridine complexes studied here the W → XCT state is the lowest excited state and this state is not reactive with respect to loss of either CO or X. The complexes having lowest LF excited states are very photosensitive and give exclusively dissociative loss of X. The crossover to a W → XCT lowest excited state parallels the findings from the electronic spectra. By comparison to $W(CO)_5X$, the W → XCT in *cis*-$W(CO)_4X_2$ is somewhat lower in energy relative to the lowest LF state and the break in photoreactivity occurs for pyridine substituents which are less electron withdrawing.[4]

Experimental Section

Materials. All substituted pyridines used are commercially available and were used without purification. $W(CO)_6$ was obtained from Strem Chemicals or Pressure Chemical Co. The *cis*-1,2-bis(diphenylphosphino)ethylene was obtained from Strem. Commercially available PPh_3 was recrystallized prior to use. Benzene was reagent grade and distilled from Na/K alloy. All other solvents were reagent grade, except isooctane which was spectroscopic grade.

Synthesis of *cis*-$W(CO)_4X_2$ (X = pyridine or substituted pyridine). The complexes *cis*-$W(CO)_4X_2$ were prepared either (1) by irradiation of $W(CO)_6$ in the presence of excess X in N_2 purged alkane solution or (2) by thermally reacting *cis*-$W(CO)_4(pip)_2$ with X in N_2-purged CH_2Cl or C_6H_6. In the first case $W(CO)_5X$ was the initial product, which undergoes further photosubstitution in solution to produce *cis*-$W(CO)_4X_2$ which precipitates out of solution, being insoluble in alkane solvents. Purification consisted of washing the solid with alkane solvent to remove $W(CO)_6$, $W(CO)_5X$, and free X, followed by recrystallization from CH_2Cl_2/alkane or C_6H_6/alkane mixtures. In some cases column chromatography on alumina was necessary to obtain pure samples.

The complexes are reasonably stable in the solid form and were stored at 0 °C in the dark. Solutions of the complexes exhibited varying degrees of thermal reactivity with *cis*-$W(CO)_4(3,5\text{-}X_2\text{-py})_2$ exhibiting the fastest decomposition. Elemental analyses were obtained for some key representative compounds. Calcd for $W(CO)_4(3,4\text{-}Me_2\text{-py})_2$: C, 42.38; H, 3.56; N, 5.49. Found: C, 42.23; H, 3.46; N, 5.39. Calcd for $W(CO)_4py_2$: C, 37.03; H, 2.22; N, 6.17. Found: C, 37.10; H, 2.26; N, 6.02. Calcd for $W(CO)_4(4\text{-Bz-py})_2$: C, 50.78; H, 2.74; N, 4.23. Found: C, 50.56; H, 2.79; N, 4.08. The analyses were performed by Alfred Bernhardt, West Germany.

Irradiation Procedures. All irradiations were carried out using merry-go-rounds to expose 3.0-mL aliquots of ~10^{-3} M *cis*-$W(CO)_4X_2$ in benzene solution containing 1.0×10^{-2} M *cis*-$Ph_2PCH{=}CHPPh_2$ in hermetically sealed 13 × 100 mm Pyrex test tubes. The solutions were typically degassed by four 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. Light intensity was determined by ferrioxalate actinometry.[12] The extent of reaction was quantitatively determined by measuring the decline in optical density of *cis*-$W(CO)_4X_2$ in a region where the photoproduct $W(CO)_4(Ph_2PCH{=}CHPPh_2)$ does not absorb.

For the irradiations using PPh_3 as the entering ligand, samples were dissolved in the appropriate solutions and were degassed by an argon purge. The solution was then used to fill an amalgam sealed infrared cell with the exclusion of air. The cell was irradiated, and the changes in solution were monitored by infrared spectroscopy. Light intensity was determined by monitoring the progress of the reaction of *cis*-$W(CO)_4(3,4\text{-}Me_2\text{-py})_2$ with 10^{-2} M *cis*-$Ph_2PCH{=}CHPPh_2$ under the same conditions. The extent of reaction was quantitatively determined by measuring the decline in optical density of the lowest energy band of $W(CO)_4X_2$. Isosbestic points were obtained for low (<25%) conversions. The primary photoproduct was *cis*-$W(CO)_4(PPh_3)X$.[13] Some *cis*-$W(CO)_4(PPh_3)_2$ was formed with long irradiation times.

Spectra. Infrared spectra were recorded on a Perkin-Elmer Model 180 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 obtained either by using a Hitachi-Perkin-Elmer MPF-44 instrument equipped with a Hammamatsu R777 PMT or by using an Aminco-Bowman SPF-2 spectrophotofluorometer with a grating blazed at 750 nm and a dry ice cooled RCA 7102 PMT for detection of lower energy emission. Emission lifetimes were determined and emission spectra were corrected using the procedures and equipment described previously.[14]

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Registry No. *cis*-$W(CO)_4(3,4\text{-}Me_2\text{-py})_2$, 67921-70-4; *cis*-$W(CO)_4(4\text{-Et-py})_2$, 67951-65-9; *cis*-$W(CO)_4(py)_2$, 16743-01-4; *cis*-$W(CO)_4(3\text{-Bz-py})_2$, 67951-64-8; *cis*-$W(CO)_4(4\text{-Ph-py})_2$, 67921-71-5; *cis*-$W(CO)_4(3,5\text{-}Cl_2\text{-py})_2$, 67921-72-6; *cis*-$W(CO)_4(3,5\text{-}Br_2\text{-py})_2$, 67921-73-7; *cis*-$W(CO)_4(4\text{-Bz-py})_2$, 67921-74-8; *cis*-$W(CO)_4(4\text{-CN-py})_2$, 67921-75-9; *cis*-$W(CO)_4(4\text{-form-py})_2$, 67921-76-0; $W(CO)_4(TMEDA)$, 15024-58-5; $W(CO)_4$(*cis*-$Ph_2PCH{=}CHPPh_2$), 21044-39-3; $W(CO)_6$, 14040-11-0; *cis*-$W(CO)_4(pip)_2$, 56083-13-7.

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