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Contribution from the Institute for Physical and Theoretical Chemistry, University of Frankfurt,
Niederurseler Hang, 6000 Frankfurt 50, FRG, Institute for Inorganic Chemistry, University of Witten/Herdecke,
Stockumer Strasse 10, 5810 Witten, FRG, and Department of Chemistry and Quantum Institute,
University of California, Santa Barbara, California 93106

Mechanistic Interpretation of High-Pressure Effects on the Photosubstitution of Pyridine and 4-Substituted Pyridine in Complexes of Tungsten Pentacarbonyl

S. Wieland,[1a] R. van Eldik,*[,1b] D. R. Crane,[1c] and P. C. Ford*[,1c]

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Volumes of activation for the photosubstitution of the nitrogen donor ligand by triethyl phosphite in $W(CO)_5$(pyridine), $W(CO)_5$(4-cyanopyridine), and $W(CO)_5$(4-acetylpyridine) were determined in toluene as solvent and have the values 5.7, 6.3, and 9.9 $cm^3\ mol^{-1}$, respectively. The effect of pressure on the luminescence lifetimes of the two latter complexes, for which the lowest energy electronic excited states are metal-to-ligand charge transfer, was also studied. The larger volumes of activation for photosubstitution of these compounds are interpreted in terms of the volume increase during the dissociative reaction of the ligand field excited state and the difference in volume between this state and the lowest exicted CT state.

Introduction

Pressure effects on reaction rates and quantum yields and the volumes of activation $\Delta V^{\ddagger}$ estimated from these constitute important phenomena that help to complete our comprehension of thermal and photochemical mechanisms.[2-4] The photosubstitution reactions resulting from the ligand field (LF) excitations of d^3 and d^6 Werner-type transition-metal complexes were the first for which systematic studies on the pressure effects were conducted. We performed a series of detailed investigations on the mechanisms of excited-state reactions of rhodium(III) ammine complex ions and were able to estimate volumes of activation for photochemical reaction steps by combining quantum yield and luminescence lifetime measurements, using high-pressure techniques.[5-8] It is evident that the experimentally determined activation volumes are composites of contributions originating from the displacement of atoms at the activation site (the intrinsic component) and from changes in electrostriction in forming the activated state. The solvational contributions play an important role when net charge creation or neutralization is involved, i.e. when charged complexes with charged ligands and/or charged entering ligands participate in the activated complex. Although the electrostrictional effects can be accounted for qualitatively, they complicate the interpretation of the data and sometimes prevent a clear mechanistic conclusion. We have therefore undertaken a series of high-pressure studies on the photochemical reactions of metal complexes in a low oxidation state and with neutral ligands.

A number of aspects should be considered in the selection of suitable systems. First, to avoid changes in charge or dipole moment during the reaction the complexes, leaving and entering ligands should be neutral. Second, it is desirable to use nonpolar solvents in order to minimize solvational contributions to the observed pressure effect. Third, the excited states of the complexes should be emissive so that lifetime measurements can be performed, since the combination of photochemical and photophysical measurements can provide valuable information on the excited-state kinetics. In general, these requirements are well met by group 6 metal carbonyl complexes that include other neutral ligands such as phosphines, phosphites, and amines.

The reactions and quantum yields at ambient pressure have been previously characterized.[9] More recent studies have focused on the reactivity of complexes with a metal-to-ligand charge-transfer (MLCT) state as the lowest electronic excited state (LEES) including the tungsten carbonyl complexes $W(CO)_5L$ with 4-acetyl- (4-Ac-py), 4-benzoyl-, 4-cyano- (4-NC-py), 4-formylpyridine as L[10,11] and the corresponding chromium and molybdenum complexes[12,13] In addition to the photosubstitution observed for $W(CO)_5$(4-Ac-py), irradiation in nonnucleophilic, nonpolar solvents in the absence of potential ligands results in photodisproportionation.[14]

The present study deals with the effect of pressure on the photosubstitution of pyridine and substituted pyridines in tungsten pentacarbonyl complexes by triethyl phosphite (eq 1). Photo-

$$W(CO)_5(4\text{-}X\text{-}py) + P(OC_2H_5)_3 \xrightarrow[\text{toluene}]{h\nu,\ 436\ \text{nm}} W(CO)_5[P(OC_2H_5)_3] + 4\text{-}X\text{-}py \quad (1)$$

$$X = H, Ac, NC$$

physical measurements on the complexes with lowest excited MLCT states were also performed as a function of pressure, and the results are discussed in terms of a proposed excited state reaction scheme.

Experimental Section

Materials. The complexes $W(CO)_5$(py), $W(CO)_5$(4-Ac-py), and $W(CO)_5$(4-NC-py) were prepared and purified according to published procedures.[11,15] The synthesized compounds were characterized by their UV/vis and IR spectra; the spectral data were in good agreement with earlier published data. Elemental analysis were performed by Beller Analytical Laboratory (Göttingen, FRG) and gave the following results (values in percent, theoretical values in parenthesis). $W(CO)_5$(py): C, 30.39 (29.80); H, 1.27 (1.25); N, 3.43 (3.48). $W(CO)_5$(4-Ac-py): C, 32.62 (32.38); H, 1.63 (1.59); N, 3.16 (3.15). $W(CO)_5$(4-NC-py): C, 31.10 (30.87); H, 1.13 (0.94); N, 6.47 (6.55).

The solvent toluene was of spectrophotometrical grade (Merck, Uvasol) and was degassed by freeze-pump-thaw cycles and then saturated with high-purity Ar. The triethyl phosphite (EGA, 97%) was vacuum distilled over sodium prior to use.

Photoreaction Instrumentation and Procedures. Photolyses were carried out in a thermostated (25.0 ± 0.2 °C) high-pressure cell compartment[16] positioned on top of a magnetic stirrer. The solutions were irradiated in a pillbox[17] spectrophotometer cell (2.8 cm^3 volume at ambient pressure) and stirred during irradiation with a Teflon-coated magnetic bar (2 × 6 mm). A high-pressure mercury lamp (Osram HBO 100/2) was used for the photolyses, and light at 436 nm was selected by using an Oriel interference filter (bandwidth 10 nm). The light intensity was

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(1) (a) University of Frankfurt. (b) University of Witten/Herdecke. (c) University of California, Santa Barbara.
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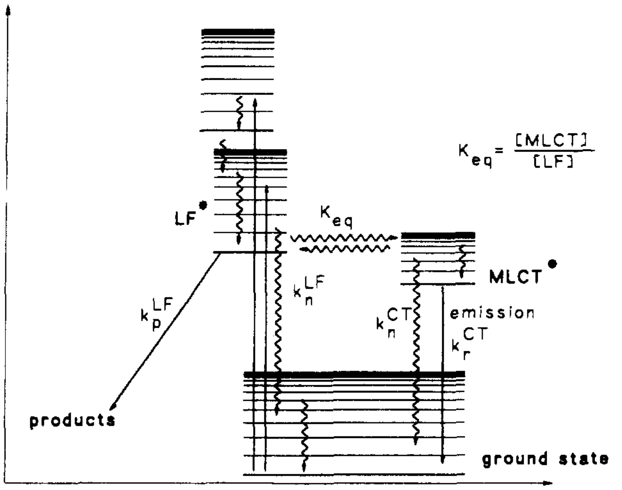

Figure 1. Schematic diagram representing the various reaction routes of $W(CO)_5L$ complexes. Absorption results in the population of electronic excited states and rapid interconversion populates the lowest LF* and MLCT* excited states. These are deactivated through radiative (k_r), nonradiative (k_n) and photochemical (k_p) deactivation. The LF* and MLCT* states are in the equilibrium described by K_{eq}.

measured with the aid of a calibrated photodiode. The complete apparatus has been described before.[8] The solutions were always handled under argon atmosphere. The transfer into the pillbox cell was achieved by using a combination of Schlenk and double-tip-needle techniques. The procedure and the specially designed apparatus is described elsewhere.[18]

Calculation of Quantum Yields. Photolysis experiments were performed at nine different pressures ranging from 0.1 to 200 MPa. The photochemical conversion was determined spectrophotometrically by following the decrease of the long wavelength absorbance as a function of irradiation time. The assumption was made that product absorption at the irradiation and the observation wavelengths is near zero. Each quantum yield determination at one pressure is the mean of 5–10 independent measurements.

Emission Lifetime Measurements at High Pressure. Toluene solutions of the complexes $W(CO)_5(4\text{-Ac-py})$ and $W(CO)_5(4\text{-NC-py})$ were deaerated by bubbling with dinitrogen in a glovebox. These solutions were loaded by syringe into a small glass capsule (25 mm × 8 mm), which was subsequently capped with a Teflon piston with two Viton O-rings. (The capsule/piston combination transmits applied pressure without exchanging solution with the surrounding medium.) The capsule was placed into a modified Nova-Swiss four-window, 400-MPa (4-kbar) high-pressure spectroscopic cell, which was then filled with deaerated pressure-transmitting fluid (toluene) and sealed. The high-pressure cell was attached to an Enerpac hand pump and gauge used to generate and measure the applied pressures. The apparatus used for lifetime measurements was based on a Quanta Ray DCR-1A Nd/YAG pulse laser with harmonic generator operating at 355 or 532 nm as the excitation source. The emission was monitored at right angles at 640 nm with an EMI 9816A photomultiplier tube through a Spex double monochromator. The signal from the photomultiplier tube was processed by a Tektronix 7912 AD transient digitizer and a Tektronix 4052 microcomputer.[5,6]

Lifetime measurements at 25.0 ± 0.5 °C required signals averaging over a number of laser pulses (generally 64) in order to obtain reproducible decay rates from these relatively weak emitters under these conditions. Unfortunately, when the above solutions were subjected to the laster photolysis in the high-pressure cell (capsule volume 0.25 mL) decomposition of the sample became evident owing to the photoreactivity of the complexes. Consequently, it was not possible to carry out standard pressure/lifetime runs where a single sample is studied at a series of pressures ranging from ambient to the limit of the system. Instead, lifetimes were determined at low pressure (0.1 MPa), then at 300 MPa, then at an intermediate pressure, then again at 0.1 MPa to demonstrate that the sample had not undergone substantial photodecomposition.

Results and Discussion

The photoreactions of $W(CO)_5L$ have been interpreted in terms of a model such as described in Figure 1.[9] Initial excitation is followed by rapid internal conversion/intersystem crossing to the lowest energy excited states from which most chemical reaction occurs. For complexes such as $W(CO)_5(py)$, the LEES is a substitution-labile ligand field (LF) state, and photosubstitution reactions occur with high quantum yields ϕ_p. However, for the complexes $W(CO)_5(X\text{-py})$, where X is a strongly electron-withdrawing substitution such as 4-cyano or 4-acetyl, a much less reactive metal-to-ligand charge-transfer (MLCT) state is the LEES. Hence, for these complexes, photosubstitution quantum yields are much smaller; indeed, the model suggests that most of the observed photochemistry occurs via back-population from the MLCT LEES to the more labile LF state. A similar model was proposed to explain the photosubstitution reactions of the ruthenium(II) pentaammine complexes $Ru(NH_3)_5(X\text{-py})^{2+}$.[19-21]

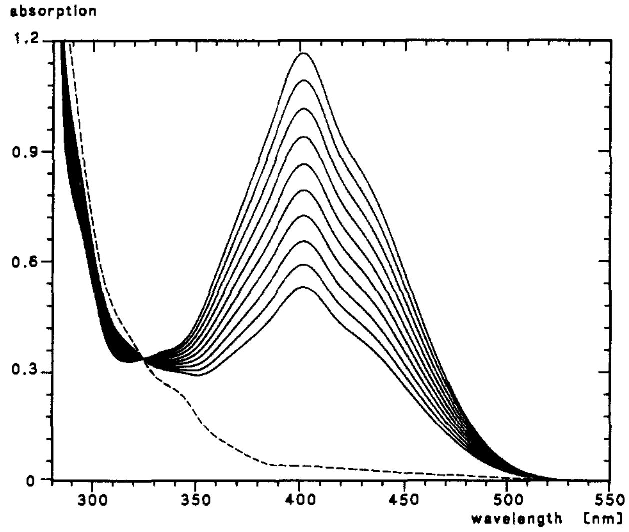

Figure 2. Spectral changes observed during the substitution of 4-acetylpyridine by triethyl phosphite in $W(CO)_5(4\text{-Ac-py})$. Solvent = toluene; irradiation wavelength = 436 nm; Δt = 4 min; photon flux = 5.6×10^{-8} einstein min^{-1}; -- = final spectrum after complete conversion. The absorption changes in the visible region are characteristic for the substitution reaction of tungsten carbonyl complexes with a long-wavelength MLCT absorption by a ligand that does not have energetically low-lying unoccupied π^* orbitals.

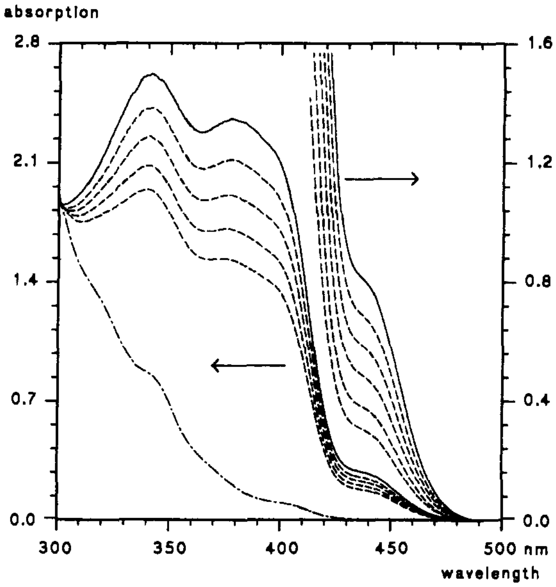

Figure 3. Changes in absorption in the visible spectral region during the substitution of pyridine by $P(OC_2H_5)_3$ in $W(CO)_5(py)$: (—) $W(CO)_5(py)$; (-·-) final product spectrum. Solvent = toluene; irradiation wavelength = 436 nm.

Reaction 1 is accompanied by a disappearance of the MLCT absorption band and a blue shift of the longest wavelength LF

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Table I. Quantum Yield as a Function of Pressure for the Photosubstitution of Pyridine and Substituted Pyridine in Tungsten Pentacarbonyl Complexes by $P(OC_2H_5)_3$ in Toluene[a]

pressure, MPa	ϕ	10ϕ	
	$W(CO)_5(py)$	$W(CO)_5(4\text{-Ac-py})$	$W(CO)_5(4\text{-NC-py})$
5	0.530 ± 0.027	0.724 ± 0.004	1.02 ± 0.04
25	0.518 ± 0.005	0.676 ± 0.016	0.91 ± 0.10
50	0.507 ± 0.007	0.590 ± 0.044	0.82 ± 0.09
75	0.477 ± 0.008	0.555 ± 0.003	0.82 ± 0.03
100	0.469 ± 0.005	0.487 ± 0.016	0.81 ± 0.03
125	0.467 ± 0.004	0.436 ± 0.010	0.76 ± 0.03
150	0.440 ± 0.004	0.400 ± 0.014	0.677 ± 0.009
175	0.432 ± 0.006	0.365 ± 0.015	0.627 ± 0.005
200	0.419 ± 0.004	0.338 ± 0.016	0.589 ± 0.012
10^4[W], M	12.0	1.1	1.0
10^2[L], M	2.34	1.17	1.17

[a] Irradiation wavelength 436 nm; [W] = tungsten complex concentration; [L] = ligand concentration.

Table II. Emission Lifetime as a Function of Solvent[a] for $W(CO)_5(X\text{-py})$

X	lifetime, τ, ns				
	MCH[b]	*n*-hexane	isooctane	toluene	benzene
4-NC	360	311 ± 10	297	205 ± 5	202; 198 ± 5
4-Ac	428	395 ± 10	390	226 ± 5	197; 213 ± 5

[a] Values with experimental error limits were determined in this study (observation wavelength 530–650 nm); values without error limits were taken from the literature;[11] excitation wavelength 353 nm; all solutions were handled under Ar atmosphere. [b] Methylcyclohexane.

absorption (Figures 2 and 3). The measured quantum yields under different pressures and the selected experimental conditions are summarized in Table I. The results at low pressure are in good agreement with those reported in the literature at ambient pressure. The high quantum yield of 0.53 ± 0.03 for the reaction of $W(CO)_5(py)$ is a strong indication for a reaction from a very effectively populated LF state. Dahlgren reported a ϕ_p of 0.58 for the photosubstitution of piperidine in $W(CO)_5$(piperidine) by pyridine (λ_{irr} = 436 nm).[22] A slightly higher value was reported for the photosubstitution of pyridine in $W(CO)_5(py)$ by 1-pentene.[9] For the low-efficiency substitution of 4-acetyl- and 4-cyanopyridine, Wrighton[9] reported ϕ_p's very similar to each other, whereas Lees et al.[11] found a clear reactivity difference for these complexes. The 4-acetylpyridine complex exhibits a smaller quantum yield than the 4-cyanopyridine complex. This trend is in agreement with our own measurements (Table I).

In fluid solution, all three tungsten complexes exhibit emission following electronic excitation. The luminescence of the pyridine complex has been assigned to the $^3E \rightarrow {}^1A_1$ ligand field transition (see for example ref 23), and the lifetime is very short in solution at room temperature (<10 ns; lifetimes were immeasurable with a 20-ns laser pulse[11]). The 4-acetylpyridine and 4-cyanopyridine complexes exhibit relatively longlived MLCT $\rightarrow {}^1A_1$ emissions with exponential decay rates (Table II). Since these emissions originate from the MLCT states, the spectra and lifetimes depend strongly on the nature of the solvent.[24] The pressure effect on the MLCT emission lifetimes of the two substituted-pyridine complexes in ambient-temperature toluene solutions was determined to be reproducibly very small. The lifetimes (number of independent measurements in parentheses) for $W(CO)_5(4\text{-Ac-py})$ at 0.1 and 300 MPa were found to be, respectively, 226 ± 5 (10) and 230 ± 2 ns (6) and those for $W(CO)_5(4\text{-NC-py})$ at 0.1 and 300 MPa were found to be, respectively, 205 ± 5 (6) and 237 ± 2 ns (5) and were independent of the excitation wavelength (532 or 355 nm). On the basis of the definition

$$(\Delta V^*)\tau^{-1} = -RT\left(\frac{\delta \ln \tau^{-1}}{\delta P}\right)_T \qquad (2)$$

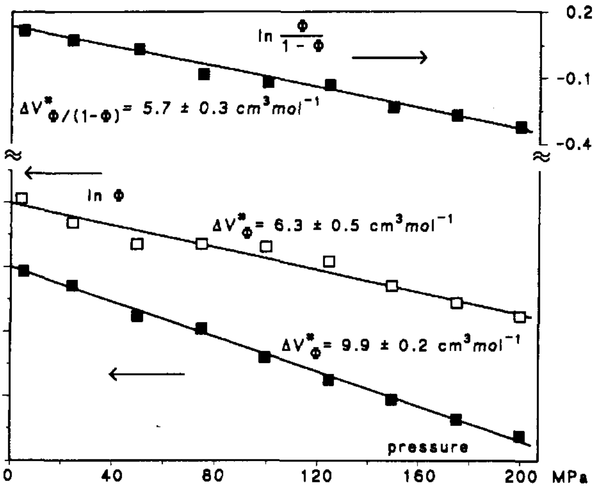

Figure 4. Plots of ln ϕ and ln ($\phi/(1-\phi)$) versus pressure for the photolysis of $W(CO)_5(py)$ (■, upper half), $W(CO)_5(4\text{-NC-py})$ (□), and $W(CO)_5(4\text{-Ac-py})$ (■, lower half) in toluene. The standard deviation for each experimental point is within the size of the employed symbols. Irradiation wavelength = 436 nm; entering ligand = $P(OC_2H_5)_3$; overall reaction is $W(CO)_5(4\text{-X-py}) + L \rightarrow W(CO)_5L + 4\text{-X-py}$ (X = H, Ac, NC).

the ΔV^* value for the total decay rate (τ^{-1}) of MLCT emission from the 4-acetylpyridine complex was determined to be approximately zero (+0.1 ± 0.3 $cm^3\ mol^{-1}$) and that from the 4-cyanopyridine analogue to be +1.2 ± 0.3 $cm^3\ mol^{-1}$.

For the model indicated by Figure 1, quantum yields and lifetimes are related to the excited-state rate constants as follows:

$$\phi_p = k_p^{LF}/(k_p^{LF} + k_n^{LF} + K_{eq}(k_n^{CT} + k_r^{CT})) \qquad (3)$$

$$\tau = (1 + K_{eq})/(k_p^{LF} + k_n^{LF} + K_{eq}(k_n^{CT} + k_r^{CT})) \qquad (4)$$

where K_{eq} = [MLCT]/[LF]. This model assumes that no significant decay occurs via emission from the LF state and that chemical reaction directly form the MLCT state is (at most) a minor component of the photosubstitution mechanism. Given that the room temperature emissions from all three complexes are weak, eq 3 and 4 can be further simplified by making the approximation

$$k_r^{CT} + k_n^{Ct} \approx k_n^{CT}$$

For $W(CO)_5(py)$, the LF state is the LEES; thus, $K_{eq} \ll 1$. Furthermore, since the lifetime of this derivative is dramatically shorter than those of the 4-acetyl- and 4-cyanopyridine complexes, one may conclude that the rate constants for reactive and nonradiative deactivation from the LF state (k_p^{LF} and k_n^{LF}) are considerably larger than k_n^{CT}. Similar conclusions have been drawn for other d^6 complexes showing evidence of LF and MLCT lowest energy states in thermal equilibrium with each other.[25] Thus, for this case, eq 3 may be simplified to

$$\phi_p = k_p^{LF}/(k_p^{LF} + k_n^{LF}) \qquad (5)$$

Given that τ for this complex was too short to measure, the pressure dependence of the individual rate constants can only be estimated from the pressure dependence of ϕ_p by assuming that the nonradiative rate constant is relatively pressure insensitive, as is often observed.[26,27] In that case, the activation volume for the reaction pathway is given by eq 6.[7] The plot of ln (ϕ_p/(1

$$\Delta V^*(k_p^{LF}) = -RT\left(\frac{\delta \ln (\phi_p/(1-\phi_p))}{\delta P}\right)_T \qquad (6)$$

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$- \phi_p))$ vs P (Figure 4) gives the positive $\Delta V^{\ddagger}(k_p{}^{LF})$ value +5.7 ± 0.3 cm^3 mol^{-1}, a result that suggests a substantially dissociative character of the mechanism for pyridine labilization from the W(CO)$_5$(py) LF excited state.[31]

The interpretation of the pressure effect on the ϕ_p and τ values for the 4-acetyl- and 4-cyanopyridine complexes is further complicated by the fact that the MLCT is the LEES; thus, according to the model in Figure 1, ligand substitution requires back-population to the higher energy LF state. If $K_{eq} \gg 1$, eq 3 can be simplified to

$$\phi_p = k_p{}^{LF}(K_{eq}{}^{-1})\tau \tag{7}$$

giving the relationship

$$\Delta V^{\ddagger}{}_{\phi} = \Delta V^{\ddagger}(k_p{}^{LF}) - \Delta \bar{V}(K_{eq}) - \Delta V^{\ddagger}(\tau^{-1}) \tag{8}$$

The values of $\Delta V^{\ddagger}{}_{\phi}$ determined by plotting ln ϕ_p vs P (Figure 4) were +9.9 and +6.3 cm^3 mol^{-1} for W(CO)$_5$(4-Ac-py) and W(CO)$_5$(4-NC-py), respectively. If it is assumed that $\Delta V^{\ddagger}(k_p{}^{LF})$ is insensitive to the pyridine substituents (i.e., equals +5.7 cm^3 mol^{-1} in each case), it follows that $\Delta \bar{V}(K_{eq})$ can be calculated from the measured values of $\Delta V^{\ddagger}{}_{\phi}$ and $\Delta V^{\ddagger}(\tau^{-1})$ plus the estimate for $\Delta V^{\ddagger}(k_p{}^{LF})$. The resulting values of $\Delta V(K_{eq})$ are −4.3 and −1.8 cm^3 mol^{-1} for the 4-acetylpyridine and 4-cyanopyridine complexes, respectively. These are consistent with the volume differences one might expect between the LF and MLCT excited states. For comparison a $\Delta \bar{V}(K_{eq})$ value of about −4 cm^3 mol^{-1} was reported for the analogous equilibrium between the LF and MLCT excited states of the complex ion Ir(Mephen)$_2$Cl$_2{}^+$ (Mephen = 5,6-dimethyl-1,10-phenanthroline) in DMF solution.[25,28]

It is clear that the above estimates are subject to considerable uncertainties, a key one being whether $\Delta V^{\ddagger}(k_p{}^{LF})$ is truly independent of the ligand substituents. Nonetheless, this point is not essential to the qualitative conclusion that the larger activation volumes in the case of the substituted-pyridine complexes originate from a positive $\Delta V^{\ddagger}$ and a moderate volume difference $\Delta \bar{V}(K_{eq})$ between the LF and MLCT states. From the minor pressure dependence of τ, it follows that the minimum $\Delta V^{\ddagger}$ for ligand dissociation from the LF state must fall in the range +3 to +6 cm^3 mol^{-1}, similar to values reported for the photolabilization of neutral ligands such as NH$_3$ from Rh(III) complexes.[5,6] Interpretation of the pressure effects measured on emission lifetimes of the substituted-pyridine complexes is further complicated given that even if $K_{eq} \gg 1$ and $k_r{}^{CT} \ll k_n{}^{CT}$, the overall decay rate remains a sum, not a product of significant terms:

$$\tau^{-1} = k_n{}^{CT} + K_{eq}{}^{-1}(k_n{}^{LF} + k_p{}^{LF}) \tag{9}$$

If one assumes that for these complexes the reactions and nonradiative decay pathways directly from the LF state partition in the manner they do in W(CO)$_5$(py) (i.e., $k_n{}^{LF} \approx k_p{}^{LF}$), then the second term in eq 9 should contribute only about 10–20% to the total deactivation. This contribution to $\Delta V^{\ddagger}(\tau^{-1})$ should be positive given that the LF state has a greater partial molar volume than the MLCT state and that $\Delta V^{\ddagger}(k_p)$ is positive, and it is likely that $\Delta V^{\ddagger}(k_n{}^{LF})$ is positive.[31] Consequently, the observation that $\Delta V^{\ddagger}(\tau^{-1})$ has a small positive value in the case of W(CO)$_5$(4-NC-py) and is nearly zero in the case of W(CO)$_5$(4-Ac-py) strongly suggests that $\Delta V^{\ddagger}(k_n{}^{CT})$ must have a value near zero or is slightly negative to compensate for the expected opposite effect of pressure on the second term. Although the contribution of this second term to the overall decay is small (10–20%), it may dominate the observed pressure effect. A small negative value would be consistent with that expected for a MLCT state decaying nonradiatively via a weak-coupling mechanism.[29,30]

In summary, we conclude that the observed pressure effects on the photoreaction quantum yields and the estimated values of activation volumes for the individual steps are consistent with the model shown in Figure 1 where photosubstitution occurs largely from the LF excited state. The interpretation of these effects is simplified by the fact that both the complexes and the photolabilized ligands are uncharged; thus, solvational contributions are minimized.

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(31) The complete form of eq 6 is

$$\Delta V^{\ddagger}(k_p{}^{LF}) = -RT\left(\frac{\delta \ln (\phi_p/(1-\phi_p))}{\delta P}\right)_T + \Delta V^{\ddagger}(k_n{}^{LF})$$

For other d^6 complexes, the pressure dependence of the nonradiative deactivation rate has been shown to parallel that of the principal photoreaction pathway.[5,8,26] Thus $\Delta V^{\ddagger}(k_n)$ and $\Delta V^{\ddagger}(k_p)$ would be expected to have the same sign, and one is led to conclude that estimation of $\Delta V^{\ddagger}(k_p{}^{LF})$ by eq 6 gives but a lower limit for this term.