

# Systematic Tuning of the Photosubstitution Mechanism of $M(\text{CO})_4(1,10\text{-phenanthroline})$ by Variation of the Metal, Entering Nucleophile, Excitation Wavelength, and Pressure

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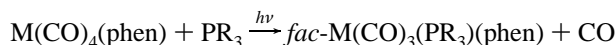
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The photosubstitution reactions of  $M(\text{CO})_4(\text{phen})$  ( $M = \text{Cr, Mo, W}$ ; phen = 1,10-phenanthroline) with  $\text{PR}_3$  ( $R = \text{Me, Bu}^n, \text{Ph}$ ) to form  $M(\text{CO})_3(\text{PR}_3)(\text{phen})$  were studied as a function of excitation wavelength, entering nucleophile concentration, and pressure. Ligand field photolysis in general results in a dissociative substitution mechanism, whereas charge-transfer photolysis can, depending on the nature of  $M$  and  $\text{PR}_3$ , proceed according to an associative mechanism. The chemical and physical variables studied result in a systematic tuning of the photosubstitution mechanism. Nucleophile concentration, excitation wavelength, and pressure dependencies reveal unique mechanistic information. The results are discussed in reference to available literature data, and a complete mechanistic analysis is presented.

## Introduction

The series of complexes  $M(\text{CO})_4(\text{phen})$  ( $M = \text{Cr, Mo, W}$ ; phen = 1,10-phenanthroline) provide the unique possibility to tune the nature of their photosubstitution mechanism for reaction 1 through a systematic variation of the central metal, entering



nucleophile, excitation wavelength, and pressure. This possibility originates from the exceptional character of the ligand field and charge-transfer excited states; viz., the latter occur at a significantly lower energy than the ligand field states.<sup>1–3</sup> This in principle allows different substitution mechanisms to operate from the excited states as a result of the intrinsic character of these states. Thus a systematic tuning of the photosubstitution mechanism is possible via a careful variation of the nature of the metal center and the nature and concentration of the entering nucleophile  $\text{PR}_3$ . In addition, the population of these excited states will strongly depend on the excitation wavelength, which adds another variable to the tuning concept. Finally, since ligand substitution reactions in general exhibit very characteristic pressure dependences that are governed by bond formation and bond breakage processes, different photosubstitution mechanisms will exhibit different pressure dependences. Thus a further (physical) variable can be added to the systematic tuning of photosubstitution mechanisms.

We and other groups have been involved in the study of the systems described by reaction 1,<sup>4–10</sup> and a wealth of information

is presently available. It is only during the last few years that the mechanistic differences between ligand field and charge-transfer photochemistry of these systems have become clear,<sup>11–12</sup> and it is only recently that the different dependences have been studied in detail.<sup>13,14</sup> We are now in the position to report data on a complete series of systems, including all the variables mentioned above, and to present a complete mechanistic analysis for these reactions. It will become clear from our presentation how the photosubstitution mechanism of these and related complexes can be systematically tuned through the variation of various chemical and physical parameters.<sup>15,16</sup> These results have important consequences for the photochemical behaviour of related complexes and add a new dimension to the understanding of and control over photochemical processes.

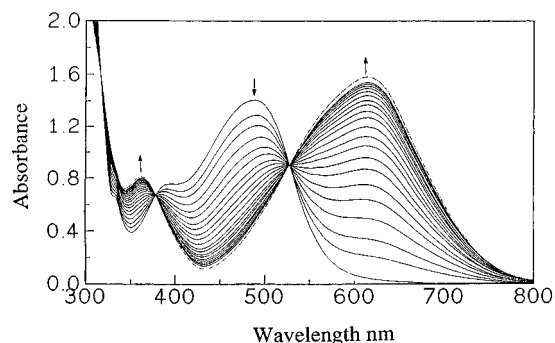
## Experimental Section

**Preparative Procedures.** Chromium hexacarbonyl, molybdenum hexacarbonyl, tungsten hexacarbonyl, and 1,10-phenanthroline (phen) were obtained from Aldrich Chemicals.  $M(\text{CO})_4\text{phen}$  ( $M = \text{Cr, Mo, W}$ ) complexes were prepared photochemically under an argon atmosphere according to published procedures and recrystallized from isooctane–dichloromethane.<sup>17–21</sup> The elemental analyses of the complexes were performed by Beller Analytical Laboratory (Göttingen, FRG), and the results are in good agreement with the theoretically

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- (1) Balk, R. W.; Snoeck, T.; Stufkens, D. J.; Oskam, A. *Inorg. Chem.* **1980**, *19*, 3015.
- (2) Virrels, I. G.; George, M. W.; Turner, J. J.; Peters, J.; Vlček, A., Jr. *Organometallics* **1996**, *15*, 4089.
- (3) Lees, A. J. *Chem. Rev.* **1987**, *87*, 711.
- (4) Wrighton, M. S.; Morse, D. L. *J. Organomet. Chem.* **1975**, *97*, 405.
- (5) Wrighton, M. *Chem. Rev.* **1974**, *4*, 401.

- (6) Wieland, S.; van Eldik, R. *Coord. Chem. Rev.* **1990**, *97*, 155.
- (7) Stufkens, D. J. *Coord. Chem. Rev.* **1990**, *104*, 39.
- (8) Lindsay, E.; Vlček, A., Jr.; Langford, C. H. *Inorg. Chem.* **1993**, *32*, 2269.
- (9) Manuta, D. M.; Lees, A. J. *Inorg. Chem.* **1983**, *22*, 572.
- (10) Manuta, D. M.; Lees, A. J. *Inorg. Chem.* **1983**, *22*, 3825.
- (11) Wieland, S.; van Eldik, R. *J. Chem. Soc., Chem. Commun.* **1989**, 367.
- (12) Wieland, S.; Bal Reddy, K.; van Eldik, R. *Organometallics* **1990**, *9*, 1802.
- (13) Fu, W. F.; van Eldik, R. *Inorg. Chim. Acta* **1996**, *251*, 341.
- (14) Fu, W. F.; van Eldik, R. *Organometallics* **1997**, *16*, 572.
- (15) Fu, W. F.; Kisch, H.; van Eldik, R. *Organometallics* **1997**, *16*, 3439.
- (16) Wieland, S.; van Eldik, R. *J. Phys. Chem.* **1990**, *94*, 5865.
- (17) Bock, H.; tom Diek, H. *Angew. Chem.* **1966**, *78*, 549.
- (18) Bock, H.; tom Diek, H. *Chem. Ber.* **1967**, *100*, 228.
- (19) Brunner, H.; Herrmann, W. A. *Chem. Ber.* **1972**, *105*, 770.
- (20) Schadt, M. J.; Lees, A. J. *Inorg. Chem.* **1986**, *25*, 672.
- (21) Marx, D. E.; Lees, A. J. *Inorg. Chem.* **1987**, *26*, 620.



**Figure 1.** Spectral changes during 436 nm photolysis of  $2.6 \times 10^{-4}$  M  $\text{Mo}(\text{CO})_4(\text{phen})$  and 1.1 M  $\text{PBu}^t_3$  in toluene solution at 298 K, where - - - represents the spectrum of  $\text{Mo}(\text{CO})_3(\text{PBu}^t_3)(\text{phen})$  after complete conversion.

expected values. Tributylphosphine (Aldrich) was distilled twice under an argon atmosphere under reduced pressure. Toluene (Aldrich spectroscopic grade) used in the photolysis was distilled over Na under an argon atmosphere and saturated with high purity argon prior to use.

**Equipment and Procedure.** UV-vis absorption spectra during irradiation were recorded on a Shimadzu UV-250 spectrophotometer. Test solutions were transferred under an argon atmosphere into a pillbox quartz cell (containing a Teflon-coated magnetic bar) by using a combination of Schlenk and double-tip-needle techniques and a specially designed filling system.<sup>22,23</sup> The pillbox was then placed inside a two-window high-pressure cell which was filled with additional solvent as the pressure-transmitting medium, equipped with a calibrated photodiode mounted on the rear window and placed on top of a magnetic stirrer.<sup>24</sup> A model 101 C transimpedance amplifier connected to the photodiode and a model 561 recorder were used to monitor the intensity variation of the light flux reaching the test solution. The temperature of the solution in the cell was controlled to  $\pm 0.1$  °C by circulating thermostated water. Samples were irradiated at four different pressures between 0.1 and 150 MPa by monochromatic light that was selected from a high-pressure mercury lamp (Osram HBO 100/2) using Oriel interference filters. The light intensities entering the photolysis cell were kept in the range  $10^{-9}$ – $10^{-8}$  einstein  $\text{s}^{-1}$  and determined by ferrioxalate (313, 366, 403, and 436 nm)<sup>25,26</sup> or actinochrome N475/610 (AMKO) (486, 546 nm) actinometry.<sup>27,28</sup> The concentration of reactant  $M(\text{CO})_4(\text{phen})$  before and after irradiation was measured spectrophotometrically by following the UV-vis spectra as a function of irradiation time. The extent of product formation was limited to a photoconversion of less than 12%. Quantum yields that were corrected for inner filter effects were obtained for the disappearance of the reactant and appearance of the product.

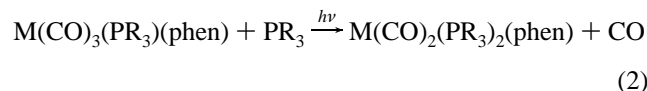
## Results and Discussion

**Electronic Absorption Spectra.** When toluene solutions of  $M(\text{CO})_4(\text{phen})$  ( $M = \text{Cr}, \text{Mo}, \text{W}$ ) complexes are irradiated at different wavelengths in the presence of excess  $\text{PBu}^t_3$ , the UV-vis spectral changes that accompany the photosubstitution of CO by  $\text{PBu}^t_3$  according to reaction 1 are shown in Figure 1 and Supporting Information Figures S1 and S2. The MLCT band around 500 nm shifts to lower energy in accordance with the photosubstitution of an electron-withdrawing CO group by the nucleophilic  $\text{PBu}^t_3$  ligand. The changes in  $\lambda_{\text{max}}$  for the Cr, Mo, and W complexes are from 524, 495, and 514 nm to 670,

620, and 640 nm, respectively. The position of the lowest energy absorption for  $M(\text{CO})_3(\text{PR}_3)(\text{phen})$  depends on the nature of  $\text{PR}_3$ . As the steric effect of R changes, the lowest energy features for  $\text{PMe}_3$  and  $\text{PPh}_3$  shift to 665, 616, 634 nm and 630, 578, 600 nm, respectively. A comparison of these MLCT bands indicates that the donor ability of the attacking nucleophile is arranged in the order  $\text{PBu}^t_3 > \text{PMe}_3 > \text{PPh}_3$ ,<sup>29–31</sup> whereas, for any particular ligand, the energy of the MLCT absorption follows the order  $\text{Mo} > \text{W} > \text{Cr}$ . These observations are in good agreement with those reported before.<sup>1,32</sup>

The photochemical conversion of  $M(\text{CO})_4(\text{phen})$  to  $M(\text{CO})_3(\text{PR}_3)(\text{phen})$  is accompanied by characteristic spectral changes that demonstrate a clear progression to those of  $M(\text{CO})_3(\text{PBu}^t_3)(\text{phen})$  (see typical example for  $M = \text{Mo}$  in Figure 1 and for  $M = \text{Cr}$  and  $\text{W}$  in Supporting Information Figures S1 and S2). The observed spectral changes are independent of the selected experimental conditions, viz. nucleophile concentration, irradiation wavelength, and pressure, and indicate that *fac*- $M(\text{CO})_3(\text{PR}_3)(\text{phen})$  is formed under all conditions.<sup>1,2,12–14</sup>

On longer irradiation of  $\text{Mo}(\text{CO})_4(\text{phen})$  at 366 nm, the isosbestic points change from 385 and 530 nm to 490 and 658 nm, which illustrates the formation and subsequent disappearance of the initially produced  $\text{Mo}(\text{CO})_3(\text{PBu}^t_3)(\text{phen})$  to form  $\text{Mo}(\text{CO})_2(\text{PBu}^t_3)_2(\text{phen})$ .<sup>33</sup> In comparing the absorption positions of the complexes, we find that the lowest energy band shifts to longer wavelength when a second carbonyl ligand is displaced by a stronger donor ligand  $\text{PBu}^t_3$ . However, the rate of the photosubstitution reaction 2 is much smaller than that of



(1); the conversion according to reaction 3 can only be accomplished after extended irradiation, and the clean isosbestic points demonstrate that the subsequent substitution reaction 2 is uncomplicated by side or further substitution processes. It follows that reaction 1 is a well-behaved photosubstitution process and the selected systems are appropriate for the detailed studies undertaken here.

**Nucleophile Concentration Dependence.** The quantum yield for reaction 1 in toluene was measured in this study for  $R = \text{Bu}^t$  as a function of excitation wavelength and concentration of the entering nucleophile  $\text{PBu}^t_3$ . The results are reported in Figures 2 and 3 (and Supporting Information Figure S3) for  $M = \text{Cr}, \text{Mo},$  and  $\text{W}$ , respectively. It can be seen from Figure 2 that the quantum efficiency exhibits within the experimental error limits no dependence on  $[\text{PR}_3]$  at the different irradiation wavelengths for  $[\text{PBu}^t_3] \geq 0.005$  M. The quantum yield decreases sharply in going from LF to MLCT excitation, clearly reflected by the decrease in the limiting values reached in the plots in Figure 2. These dependences for the larger metal centers (Mo and W) in Figures 3 and S3 demonstrate a strong decrease in the intercept but almost no change in the slope of the plots on increasing the excitation wavelength from 366 to 546 nm.

In general ligand field excitation leads to population of  $\sigma^*$  antibonding orbitals, i.e. a nonbonded state, which in the

(22) le Noble, W. J.; Schlott, R. *Rev. Sci. Instrum.* **1976**, *47*, 770.

(23) Wieland, S.; van Eldik, R. *Rev. Sci. Instrum.* **1989**, *60*, 955.

(24) Fleischmann, F. K.; Conze, E. G.; Kelm, H.; Stranks, D. R. *Rev. Sci. Instrum.* **1974**, *45*, 1427.

(25) Lee, J.; Seliger, H. H. *J. Chem. Phys.* **1964**, *40*, 519.

(26) Bowman, W. D.; Demas, J. N. *J. Phys. Chem.* **1976**, *80*, 2434.

(27) Brauer, H. D.; Schmidt, R.; Gauglitz, G.; Hubig, S. *Photochem. Photobiol.* **1983**, *37*, 595.

(28) Schmidt, S.; Drews, W.; Brauer, H. D. *J. Am. Chem. Soc.* **1980**, *102*, 2791.

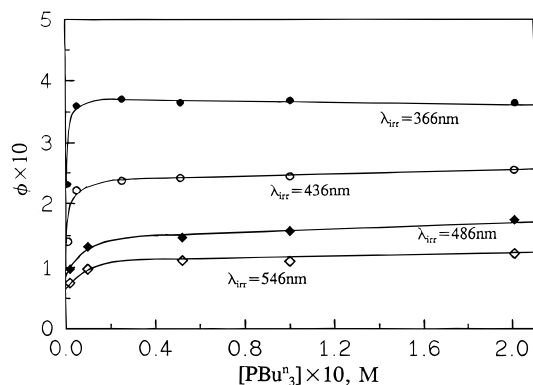
(29) Bursten, B. E.; Darensbourg, D. J.; Kellogg, G. E.; Lichtenberger, D. L. *Inorg. Chem.* **1984**, *23*, 4361.

(30) Alyea, E. C.; Lenkinski, R. E.; Somogyvari, A. *Polyhedron* **1982**, *1*, 130.

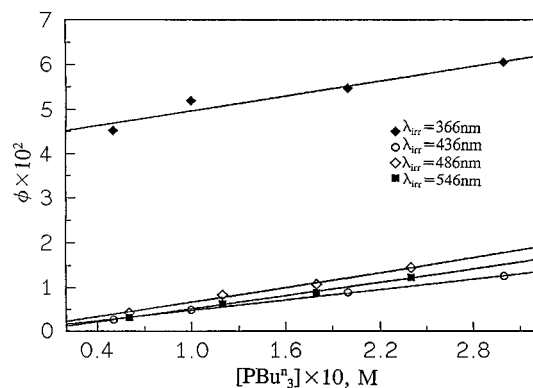
(31) Diaz, C.; Yutronic, N. *Polyhedron* **1989**, *8*, 1099.

(32) Chun, S.; Getty, E. E.; Lees, A. J. *Inorg. Chem.* **1984**, *23*, 2155.

(33) Houk, L. W.; Dobson, G. R. *Inorg. Chem.* **1966**, *5*, 2119.

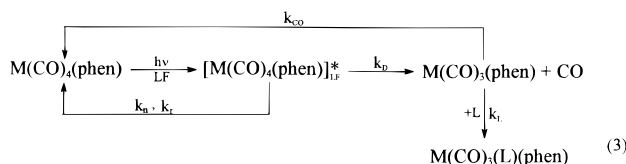


**Figure 2.** Relationship between the quantum yield and the ligand concentration for the photosubstitution reaction 1 ( $M = \text{Cr}$ ;  $R = \text{Bu}^n$ ) in toluene at 298 K.



**Figure 3.** Relationship between the quantum yield and the ligand concentration for the photosubstitution reaction 1 ( $M = \text{Mo}$ ;  $R = \text{Bu}^n$ ) in toluene at 298 K.

reactions studied leads to  $M\text{--CO}$  bond cleavage. The reaction sequence outlined in (3) indicates that the excited LF state can



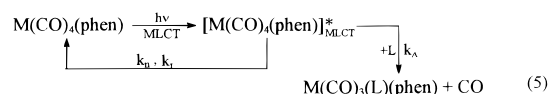
return to the ground state via radiative ( $k_r$ ) and nonradiative ( $k_{nr}$ ) deactivation or undergo  $M\text{--CO}$  cleavage ( $k_D$ ) following a dissociative (D) mechanism. The five-coordinate  $\text{M(CO)}_3(\text{phen})$  complex produced can either recombine with  $\text{CO}$  ( $k_{\text{CO}}$ ) or react indirectly (via the coordination of a solvent molecule) or directly ( $k_L$ ) with the entering nucleophile (L) to produce the photochemical product  $\text{M(CO)}_3(\text{L})(\text{phen})$ .<sup>34,35</sup> For the sequence outlined in (3), a simplified expression for the quantum yield ( $\phi_{\text{LF}}$ ) is given in (4), in which intersystem crossing between

$$\phi_{\text{LF}} = \left( \frac{k_D}{k_D + k_n + k_t} \right) \left( \frac{k_L[\text{L}]}{k_L[\text{L}] + k_{\text{CO}}[\text{CO}]} \right) = \frac{k_{\text{LF}}k_L[\text{L}]}{k_L[\text{L}] + k_{\text{CO}}[\text{CO}]} \approx k_{\text{LF}} \quad (4)$$

different LF excited states (usually from a singlet to a lower lying triplet state) is not taken into account. In this expression

$k_{\text{LF}}$  represents the efficiency of the bond cleavage process. It follows from (4) that under conditions where competition between  $\text{CO}$  and  $\text{L}$  for scavenging the  $\text{M(CO)}_3(\text{phen})$  intermediate exists,  $\phi_{\text{LF}}$  will increase with increasing  $[\text{L}]$  and reach a saturation under conditions where  $k_L[\text{L}] \gg k_{\text{CO}}[\text{CO}]$ ; i.e.,  $\phi_{\text{LF}} = k_{\text{LF}}$  and independent of  $[\text{L}]$ . This behavior is clearly seen for the irradiation of  $\text{Cr(CO)}_4(\text{phen})$  in Figure 2. The other complexes ( $M = \text{Mo}, \text{W}$ ) only exhibit a clear intercept (Figures 3 and S3) at low  $[\text{L}]$  during LF excitation, which corresponds to the situation  $\phi_{\text{LF}} = k_{\text{LF}}$ .

In general MLCT excitation leads to a bound excited state in which electron density from the metal is placed on the  $\pi^*$  antibonding orbital of the diimine ligand. This process results in an electron deficiency on the metal center and promotes an associative (A) attack by the entering nucleophile. The latter must result in an increase in quantum yield with increasing  $[\text{L}]$ .<sup>8,14,36,37</sup> This reaction sequence is outlined in (5), and the



corresponding expression for the quantum yield ( $\phi_{\text{MLCT}}$ ), again under exclusion of possible intersystem crossing (within the MLCT states and between the MLCT and LF states), is given in (6). The  $[\text{L}]$  dependences observed in Figures 3 and S3

$$\phi_{\text{MLCT}} = \frac{k_A[\text{L}]}{k_A[\text{L}] + k_n + k_t} \approx \frac{k_A[\text{L}]}{k_n + k_t} = k_{\text{MLCT}}[\text{L}] \quad (6)$$

demonstrate a linear increase in  $\phi$  with increasing  $[\text{L}]$ , and the absence of a saturation of  $\phi$  at high  $[\text{L}]$  justifies the approximation shown in (6).

On variation of the excitation wavelength from 366 to 546 nm, a gradual changeover in the population of the LF and MLCT states occurs. This accounts for the significant decrease in the intercept of the plots in Figures 3 and S3, on increasing the irradiation wavelength, since the lower energy does not allow population of the higher lying LF states under such conditions. Population of the MLCT state will cause an increase in  $\phi$  with increasing  $[\text{L}]$  (see Figures 3 and S3), such that the combined effect of LF and MLCT excitation can be expressed as shown in eq 7. In this equation  $k_{\text{LF}}$  and  $k_{\text{MLCT}}$  are wavelength-

$$\phi_{\text{tot}} = \phi_{\text{LF}} + \phi_{\text{MLCT}} = k_{\text{LF}} + k_{\text{MLCT}}[\text{L}] \quad (7)$$

dependent quantities and represent the contribution from the intercept and the slope of the plots in Figures 2, 3, and S3, respectively. In the case of  $M = \text{Mo}$  and  $\text{W}$  (Figures 3 and S3), LF irradiation at 366 nm also exhibits a significant  $[\text{L}]$  dependence of  $\phi$ . This can be ascribed to a partial delocalization of the electron density from the  $\sigma^*$  (LF excitation) to the lower lying  $\pi^*$  orbital (MLCT excitation), such that a significant contribution from a parallel associative reaction path is observed (see further Discussion).

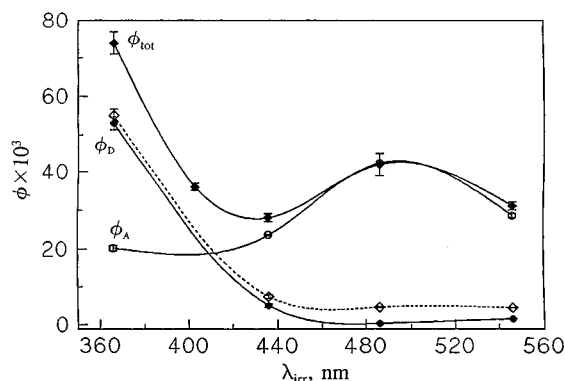
As pointed out by a reviewer, a crucial aspect not addressed by the reaction schemes presented in (3) and (5) above concerns the time scale of the processes and the possible participation of solvent intermediates. It is well-known from earlier studies<sup>2,8</sup> that, during LF and MLCT irradiation of  $\text{Cr(CO)}_4(\text{bpy})$ ,  $\text{bpy} = 2,2'$ -bipyridine, in  $\text{CH}_2\text{Cl}_2$  as solvent, *fac*- $\text{Cr(CO)}_3(\text{CH}_2\text{Cl}_2)(\text{bpy})$

(34) Geoffroy, G. L.; Wrighton, M. S. *Organometallic photochemistry*; Academic: New York, 1979.

(35) Schneider, K. J.; van Eldik, R. *Organometallics* **1990**, *9*, 92; **1990**, *9*, 1235.

(36) van Dijk, H. K.; Servaas, P. C.; Stufkens, D. J.; Oskam, A. *Inorg. Chim. Acta* **1985**, *104*, 179.

(37) Strouse, G. F.; Schoonover, J. R.; Duesing, R.; Boyde, S.; Jones, W. E., Jr.; Meyer, T. J. *Inorg. Chem.* **1995**, *34*, 473.



**Figure 4.** Quantum yield as a function of irradiation wavelength for the reaction 1 ( $M = \text{Mo}$ ;  $R = \text{Me}$ ) at a fixed  $\text{PMe}_3$  concentration in toluene at 298 K:  $\phi_{\text{tot}}$  ( $\blacklozenge$ ),  $\phi_A$  ( $\circ$ )  $\phi_D$  ( $\bullet$ ),  $[\text{PMe}_3] = 0.0506 \text{ M}$ ;  $\phi_{\text{tot}}$  ( $\diamond$ ),  $[\text{PMe}_3] = 0.0051 \text{ M}$ .

is formed on a ps/sub-ps time scale. This solvento intermediate reacts rapidly with  $\text{PPh}_3$  ( $1 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ )<sup>2</sup> to produce *fac*- $\text{Cr}(\text{CO})_3(\text{PPh}_3)(\text{bpy})$ . Although the effective participation of such solvento intermediates will strongly depend on the donor property of the selected solvent, it remains realistic to consider the participation of  $\text{M}(\text{CO})_3(\text{Sol})(\text{phen})$  species in the present study. The formation of  $\text{M}(\text{CO})_3(\text{PR}_3)(\text{phen})$  can compete with the formation of  $\text{M}(\text{CO})_3(\text{Sol})(\text{phen})$  on a ps/sub-ps time scale when  $\text{PR}_3$  is present as an encounter partner prior to excitation. Alternatively,  $\text{PR}_3$  can in a subsequent non-photochemical reaction rapidly displace the weakly coordinated solvent molecule. Both these routes will lead to a dependence of the quantum yield on the concentration of  $\text{PR}_3$ , similar to that expressed in eq 6 for the reaction scheme in (5) involving direct attack of  $\text{PR}_3$  on the MLCT state. However, the exclusive formation of solvento intermediates following the excitation process cannot account for the totally different concentration dependences (and pressure dependences; see further Discussion) of the quantum yield observed for different excitation wavelengths. Solvent displacement itself is a subsequent thermal process independent of the nature of the excited state from which the solvento complex originates. Thus the observed concentration (and pressure) dependences must arise from a competition between solvent and  $\text{PR}_3$  in the excited state of the  $\text{M}(\text{CO})_4(\text{phen})$  species. The LF and MLCT excited states can discriminate between the solvent and  $\text{PR}_3$  molecules as entering nucleophiles following a dissociative or associative substitution mechanism, respectively.  $\text{M}(\text{CO})_3(\text{Sol})(\text{phen})$  species produced in such a way will undergo rapid thermal substitution to produce  $\text{M}(\text{CO})_3(\text{PR}_3)(\text{phen})$  as discussed above.

The nature of eq 7 is such that experiments performed at a fixed value of  $[\text{L}]$  as a function of irradiation wavelength can be misleading due to the composite nature of  $\phi_{\text{tot}}$ . This can be clearly seen from the typical examples presented in Figure 4, where the contribution of  $\phi_D (= \phi_{\text{LF}})$  decreases and the contribution of  $\phi_A (= \phi_{\text{MLCT}})$  increases with increasing irradiation wavelength, respectively. A summary of the ratio  $k_{\text{MLCT}}/k_{\text{LF}}$  for the photosubstitution of  $\text{M}(\text{CO})_4(\text{phen})$  by  $\text{PMe}_3$  and  $\text{PBU}^n_3$  as a function of irradiation wavelength is given in Table 1. There is a steady increase in the ratio  $k_{\text{MLCT}}/k_{\text{LF}}$  on increasing irradiation wavelength, clearly demonstrating the more important role of the associative reaction route on population of the MLCT state. In the case of the chromium complex the associative contribution remains relatively small (as compared to Mo and W), but the stronger  $\sigma$ -donor ligand  $\text{PBU}^n_3$  does exhibit a more definite contribution than  $\text{PMe}_3$  and  $\text{PPh}_3$ . In the case of the bulky  $\text{PPh}_3$  nucleophile, little evidence for an associative

**Table 1.** Values of  $k_{\text{MLCT}}/k_{\text{LF}}$  for Associative and Dissociative Contributions to Total Quantum Yield as a Function of Excitation Wavelength for the Photosubstitution Reaction at 298 K

$$\text{M}(\text{CO})_4(\text{phen}) + \text{PR}_3 \xrightarrow{h\nu} \text{M}(\text{CO})_3(\text{PR}_3)(\text{phen}) + \text{CO}$$

M	PR <sub>3</sub>	366 nm	436 nm	486 nm	546 nm
Cr	PMe <sub>3</sub>	0.0034	0.18	0.17	0.76
	PBU <sup>n</sup> <sub>3</sub>	0.016	0.64	1.64	1.16
Mo	PMe <sub>3</sub>	7.5	93	312	370
	PBU <sup>n</sup> <sub>3</sub>	1.3	46	48	278
W	PMe <sub>3</sub>	11.7		154	101
	PBU <sup>n</sup> <sub>3</sub>	1.25	49	156	263

reaction path as characterized by a dependence of  $\phi$  on  $[\text{PPh}_3]$  could be found.<sup>14</sup> The results for  $\text{PMe}_3$  and  $\text{PBU}^n_3$  are very similar in the case of  $M = \text{W}$ , whereas the ratio  $k_{\text{MLCT}}/k_{\text{LF}}$  is significantly larger for  $\text{PMe}_3$  than for  $\text{PBU}^n_3$  in the case of  $M = \text{Mo}$ . Thus the associative contribution for  $\text{PBU}^n_3$  follows the sequence  $\text{Mo} \sim \text{W} > \text{Cr}$ , compared to  $\text{Mo} > \text{W} > \text{Cr}$  for  $\text{PMe}_3$ .

**Pressure Dependence.** Earlier work from our laboratories for reaction 1 with  $\text{PMe}_3$  and  $\text{PPh}_3$  has demonstrated that the effect of pressure on the observed quantum yield can be of significant diagnostic value.<sup>13,14</sup> This is based on the fundamental principle that bond formation can be accelerated and bond breakage can be decelerated by pressure. Thus  $k_{\text{MLCT}}$  is expected to increase and  $k_{\text{LF}}$  is expected to decrease with increasing pressure. Such effects can help us to understand further the nature of the photosubstitution mechanism of LF and MLCT excited-state species.

In general the deactivation of excited states may follow different pathways as indicated by  $k_n$ ,  $k_r$ ,  $k_D$ , and  $k_A$  in reactions 3 and 5, and these rate constants can, in principle, all be affected by pressure.<sup>38–41</sup> The chemical and physical processes of interest that take place in electronically excited states occur on a time scale that allows application of the transition state theory. Thus the pressure dependence of the different deactivation processes can be ascribed in terms of volumes of activation that represent the volume changes associated with the transition state of the deactivation (physical and chemical) pathway.<sup>42</sup>

The pressure dependence of  $\phi$  for photosubstitution of  $\text{M}(\text{CO})_4(\text{phen})$  by  $\text{PBU}^n_3$  was studied as a function of excitation wavelength, and the results are summarized in Table 2 ( $M = \text{W}$ ), Supporting Information Figure S4, and Figure 5 ( $M = \text{Cr}$  and  $\text{Mo}$ , respectively). The results in Figure S4 clearly show that under all conditions  $\phi$  decreases with increasing pressure. However, in the case of  $M = \text{W}$  and  $\text{Mo}$ , the data clearly show a decrease in  $\phi$  with increasing pressure during LF excitation but an increase in  $\phi$  with increasing pressure during MLCT excitation. The trends can be converted into an apparent volume of activation, defined in (8), and the results are summarized in Tables 2 and 3, where the latter also include results available for photosubstitution by  $\text{PMe}_3$  and  $\text{PPh}_3$ .

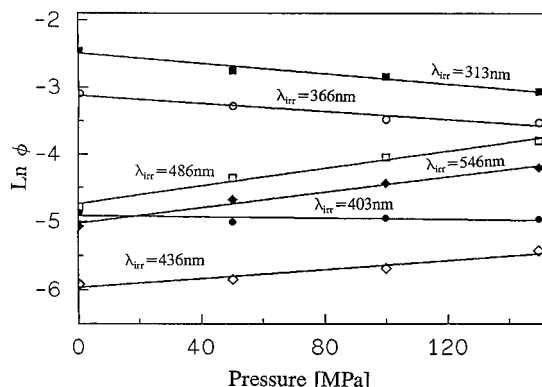
$$\left(\frac{\partial \ln \phi}{\partial P}\right)_T = -\frac{\Delta V_{\phi}^{\ddagger}}{RT} \quad (8)$$

The results in Table 2 ( $M = \text{W}$ ) demonstrate that  $\Delta V_{\phi}^{\ddagger}$ , obtained from the slope of  $\ln \phi$  versus pressure, changes from

- (38) Endicott, J. F.; Ramasami, T.; Tamilarasan, R.; Lessard, R. B.; Ryu, C. K. *Coord. Chem. Rev.* **1987**, *77*, 1.  
 (39) Dibenedetto, J.; Ford, P. C. *Coord. Chem. Rev.* **1985**, *64*, 361.  
 (40) Kirk, A. D.; Porter, G. B. *J. Phys. Chem.* **1980**, *84*, 2998.  
 (41) Lang, J. M.; Dreger, Z. A.; Drickamer, H. G. *J. Phys. Chem.* **1990**, *94*, 5865.  
 (42) Endicott, J. F.; Ryu, C. K. *Comments Inorg. Chem.* **1987**, *6*, 91.

**Table 2.** Quantum Yield ( $\times 10^3$ ) as a Function of Pressure and Excitation Wavelength for the Photochemical Reaction in Toluene at 298K
$$\text{W}(\text{CO})_4(\text{phen}) + \text{PBU}^n_3 \xrightarrow{h\nu} \text{W}(\text{CO})_3(\text{PBU}^n_3)(\text{phen}) + \text{CO}$$

$\lambda_{\text{irr}}$ , nm	$10^4[\text{M}]$ , M	[L], M	P, MPa				$\Delta V_{\phi}^{\ddagger}$ , $\text{cm}^3 \text{mol}^{-1}$
			0.1	50	100	150	
313	2.25	0.0506	$26.6 \pm 1.2$	$19.87 \pm 0.05$	$16.5 \pm 0.5$	$13.9 \pm 0.4$	$+10.5 \pm 1.0$
366	2.09	0.0506	$13.9 \pm 0.6$	$11.9 \pm 0.8$	$9.7 \pm 0.6$	$8.6 \pm 0.4$	$+8.2 \pm 0.6$
403	2.13	0.0506	$3.19 \pm 0.09$	$3.16 \pm 0.05$	$3.3 \pm 0.1$	$3.3 \pm 0.2$	$-0.6 \pm 0.4$
436	2.13	0.0506	$1.42 \pm 0.08$	$1.79 \pm 0.07$	$2.3 \pm 0.1$	$2.59 \pm 0.08$	$-10.2 \pm 1.0$
486	2.10	0.154	$3.45 \pm 0.07$	$5.16 \pm 0.01$	$6.26 \pm 0.07$	$7.6 \pm 0.2$	$-12.7 \pm 1.8$
546	2.10	0.154	$3.72 \pm 0.08$	$4.63 \pm 0.08$	$6.5 \pm 0.1$	$7.4 \pm 0.2$	$-12.0 \pm 1.4$

**Figure 5.** Pressure dependence of the quantum yield for the photochemical reaction 1 ( $\text{M} = \text{Mo}$ ;  $\text{R} = \text{Bu}^n$ ) as a function of irradiation wavelength in toluene at 298 K:  $\lambda_{\text{irr}} = 313, 366, 403$  and  $436$  nm,  $[\text{PBU}^n_3] = 0.0506$  M;  $\lambda_{\text{irr}} = 486$  and  $546$  nm,  $[\text{PBU}^n_3] = 0.1204$  M.

$+10$  to  $-12 \text{ cm}^3 \text{mol}^{-1}$  on increasing the irradiation wavelength from 313 to 546 nm. Very similar results are reported for  $\text{M} = \text{Mo}$  in Table 3 (data taken from Figure 5). These results show a clear changeover in the photosubstitution mechanism from dissociative (LF) to associative (MLCT) on increasing the irradiation wavelength. In the case of  $\text{M} = \text{Cr}$  (Table 3, data from Figure S4) the value of  $\Delta V_{\phi}^{\ddagger}$  remains almost constant within the experimental error limits and no changeover in the nature of the photosubstitution mechanism can be observed.

Table 3 allows us to see the influence of R (Me,  $\text{Bu}^n$ , Ph) on the value of  $\Delta V_{\phi}^{\ddagger}$  and the associated photosubstitution mechanism. In the case of  $\text{M} = \text{Cr}$ , a decrease in steric hindrance on  $\text{PR}_3$  causes a trend in  $\Delta V_{\phi}^{\ddagger}$  going to smaller positive values on increasing the excitation wavelength. This has been interpreted in terms of a possible changeover from dissociative (D) to interchange dissociative ( $\text{I}_d$ ) on going from LF to MLCT excitation for the smallest entering nucleophile.<sup>13</sup> However, such a trend is not observed in the case of  $\text{R} = \text{Bu}^n$ , investigated in the present study. In the case of  $\text{M} = \text{Mo}$  and  $\text{W}$ , the overall trend in  $\Delta V_{\phi}^{\ddagger}$  from more positive to more negative values on increasing the excitation wavelength does depend on the nature of R. The changeover from positive to negative values occurs sooner for  $\text{R} = \text{Me}$  as compared to  $\text{R} = \text{Bu}^n$  and does not occur at all for  $\text{R} = \text{Ph}$ . Thus the size of the entering nucleophile clearly controls the associative character of the photosubstitution mechanism.

The reported results demonstrate the substantial effect of steric properties of the ligand on the reaction pathway when for instance  $\text{PMe}_3$  was chosen as entering group. In this respect it is interesting to note a large difference in the magnitudes of  $\Delta V_{\phi}^{\ddagger}$  for Mo and W complexes on LF excitation. The smaller positive  $\Delta V_{\phi}^{\ddagger}$  values for the reaction of  $\text{W}(\text{CO})_4(\text{phen})$  with  $\text{PMe}_3$  suggest that ligand substitution in the LF excited state proceeds via a dissociative interchange ( $\text{I}_d$ ) mechanism ( $\Delta V_{\phi}^{\ddagger}$

$= 3.2 \text{ cm}^3 \text{mol}^{-1}$ , at 313 nm) in which bond breakage is partially cancelled by bond formation. In contrast to  $\text{W}(\text{CO})_4(\text{phen})$ , the markedly negative  $\Delta V_{\phi}^{\ddagger}$  value for  $\text{Mo}(\text{CO})_4(\text{phen})$  suggests that photosubstitution follows an  $\text{I}_a$  mechanism upon irradiation at 366 nm ( $\Delta V_{\phi}^{\ddagger} = -4.7 \text{ cm}^3 \text{mol}^{-1}$ ), which could result from the blue shift of 19 nm for the MLCT maximum absorption bands compared with those of  $\text{W}(\text{CO})_4(\text{phen})$ . In general, a shift in the MLCT band can cause a more efficient crossing from the LF to the MLCT states and so affect the overall value of  $\Delta V_{\phi}^{\ddagger}$ . Steric effects of the entering ligands on the reaction of the Cr complex on LF excitation at 366 nm seem not to be important since the magnitude of the activation volume indicates that photosubstitution of CO in  $\text{Cr}(\text{CO})_4(\text{phen})$  proceeds via a dissociative (D) mode due to the smaller size of the Cr metal center. Even if a much stronger  $\sigma$ -donor ( $\text{PBU}^n_3$ ) and smaller nucleophile ( $\text{PMe}_3$ ) are used, it is not possible to cause a changeover to a more associative mechanism as found for the larger metal centers Mo and W. The  $\Delta V_{\phi}^{\ddagger}$  values for the  $\text{Cr}(\text{CO})_4(\text{phen})$  reactions with  $\text{PMe}_3$  show only a small change from dissociative (D) to dissociative interchange ( $\text{I}_d$ ) in going from LF to MLCT excitation. In the case of the larger Mo and W metal centers, associative processes were found for ligands that are known to be good electron-pair donors, with the decreasing size of the nucleophile resulting in significant effects on the mechanism of ligand substitution when the excitation was gradually changed from LF to MLCT. Ligand substitution reactions between  $\text{Mo}(\text{CO})_4(\text{phen})$  and  $\text{PBU}^n_3$  were examined with irradiation at 403, 436, 486, and 546 nm, and the  $\Delta V_{\phi}^{\ddagger}$  values of 1.1,  $-7.9$ ,  $-16.4$ , and  $-14.1 \text{ cm}^3 \text{mol}^{-1}$ , respectively, are in accord with a trend toward increasing associative character.

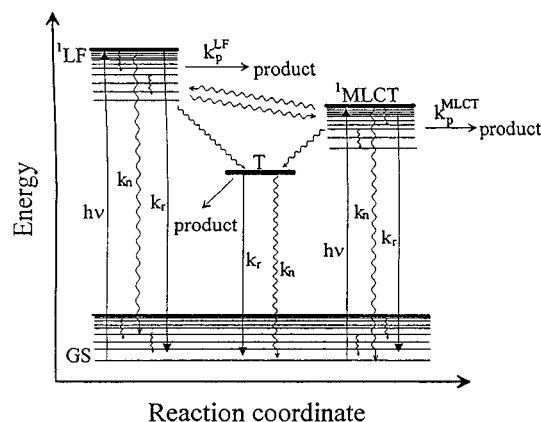
In addition, we notice from the data that the smallest nucleophile  $\text{PMe}_3$  makes the substitution of CO in  $\text{M}(\text{CO})_4(\text{phen})$  ( $\text{M} = \text{Mo}, \text{W}$ ) more associative in comparison to  $\text{PBU}^n_3$  on excitation at 403 nm as demonstrated by the more negative  $\Delta V_{\phi}^{\ddagger}$  value. Pure associative behavior is observed for excitation into the MLCT band at 436 nm. The significantly negative  $\Delta V_{\phi}^{\ddagger}$  value of  $-12.3 \text{ cm}^3 \text{mol}^{-1}$  found for substitution of CO in  $\text{Mo}(\text{CO})_4(\text{phen})$  by  $\text{PMe}_3$  during excitation at a wavelength as low as 403 nm demonstrates that the associative reaction mode can even be favored under such conditions.

**Mechanistic Interpretation.** The mechanistic trends presented above are based on the apparent pressure dependence of the photosubstitution quantum yield, expressed as  $\Delta V_{\phi}^{\ddagger}$ , and require a more careful analysis due to the composite nature of the quantum yield as indicated in eqs 4, 6, and 7. The photophysical aspects of such photosubstitution reactions have been treated in detail before,<sup>43–46</sup> and an overall summary of possible excitation and deactivation routes is presented in

(43) Manuta, D. M.; Lees, A. J. *Inorg. Chem.* **1986**, *25*, 1354.(44) Vichová, J.; Hartl, F.; Vlček, A., Jr. *J. Am. Chem. Soc.* **1992**, *114*, 10903.

**Table 3.** Volumes of Activation for Photosubstitution of CO in  $M(\text{CO})_4(\text{phen})$  Complexes by Ligand L at Different Excitation Wavelengths

M	L	$\Delta V_{\phi}^{\ddagger}$ , $\text{cm}^3 \text{mol}^{-1}$					
		313 nm	366 nm	403 nm	436 nm	486 nm	546 nm
Cr	$\text{PMe}_3$		$6.8 \pm 1.3$	$4.7 \pm 1.0$	$-0.2 \pm 0.8$	$1.3 \pm 0.6$	$1.9 \pm 0.7$
	$\text{PBu}^n_3$		$4.2 \pm 0.7$	$4.5 \pm 0.9$	$2.7 \pm 0.7$	$3.0 \pm 0.5$	$4.1 \pm 0.6$
	$\text{PPh}_3$		$6.4 \pm 0.3$	$5.0 \pm 0.8$	$2.9 \pm 0.1$	$2.8 \pm 0.7$	$2.7 \pm 0.8$
Mo	$\text{PMe}_3$	$14.4 \pm 3.1$	$-4.7 \pm 0.6$	$-12.3 \pm 0.1$	$-13.3 \pm 0.9$	$-13.3 \pm 3.2$	$-10.7 \pm 2.5$
	$\text{PBu}^n_3$	$9.6 \pm 1.4$	$7.4 \pm 1.2$	$1.1 \pm 1.3$	$-7.9 \pm 1.2$	$-16.4 \pm 1.4$	$-14.1 \pm 1.3$
	$\text{PPh}_3$		$7.6 \pm 1.3$	$6.7 \pm 1.5$	$11.0 \pm 1.6$		$3.4 \pm 1.6$
W	$\text{PMe}_3$	$3.2 \pm 0.6$	$1.5 \pm 0.2$	$-5.8 \pm 0.8$	$-9.1 \pm 1.6$	$-10.3 \pm 2.5$	$-9.6 \pm 1.6$
	$\text{PBu}^n_3$	$10.5 \pm 1.0$	$8.2 \pm 0.6$	$-0.6 \pm 0.4$	$-10.2 \pm 1.0$	$-12.7 \pm 1.8$	$-12.0 \pm 1.4$
	$\text{PPh}_3$		$10.9 \pm 0.6$	$13.9 \pm 1.5$	$8.1 \pm 1.5$		$-8.2 \pm 0.8$

**Scheme 1<sup>a</sup>**

<sup>a</sup> T =  ${}^3\text{LF}/{}^3\text{MLCT}$ .

Scheme 1. In general, LF excitation results in the activation of the M–CO bonds and leads to a dissociative ligand substitution mechanism. In the case of MLCT excitation, the nature of the excited state will determine the nature of the ligand substitution mechanism. Partial delocalization of the electron density from the  $\pi^*$  (diimine) orbital to the  $\sigma^*$  (M–C<sub>ax</sub>) orbital may occur via vibronic mixing.<sup>47</sup> This will in turn result in the dissociation of the axial CO ligand and promote a dissociative substitution mechanism. Alternatively, delocalization on the phen ligand will cause a decrease in the electron density on the metal center (formally then a 17-electron species) and an increase in electrophilicity, which will induce an associative nucleophilic substitution mechanism. In this respect it is interesting to note that a series of theoretical studies on metal carbonyl complexes has recently revealed a new aspect of excited state reactivity with regards to the role of the MLCT state.<sup>48–50</sup> It follows from these studies that it is possible that the nonreactive MLCT state crosses the reactive LF state (i.e. delocalization of electron density from  $\pi^*$  to  $\sigma^*$ ) only at longer M–CO distances. M–CO bond lengthening can cause the crossing of a nonreactive MLCT state with the rapidly descending LF state and release of CO. Such a situation is likely to occur upon the formation of a seven-coordinate exciplex in the MLCT excited state.

According to 7 the observed quantum yield will be the sum of the contributions resulting from LF and MLCT excitation.

(45) Servaas, P. C.; van Dijk, H. K.; Snoeck, T. L.; Stufkens, D. J.; Oskam, A. *Inorg. Chem.* **1985**, *24*, 4494.

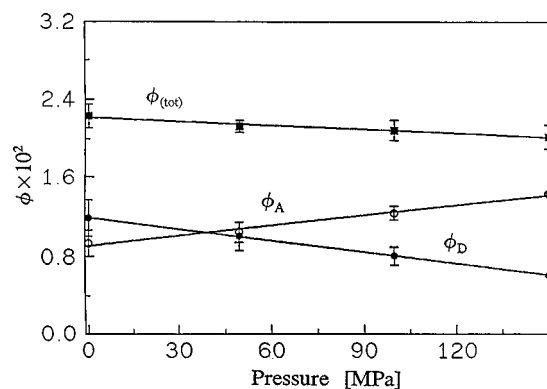
(46) Rawlins, K. A.; Lees, A. J. *Inorg. Chem.* **1989**, *28*, 2154.

(47) Vlček, A., Jr.; Vichová, J.; Hartl, F. *Coord. Chem. Rev.* **1994**, *132*, 167.

(48) Pierloot, K.; Tsokos, E.; Vanquickenborne, L. G. *J. Phys. Chem.* **1996**, *100*, 16545.

(49) Rosa, A.; Ricciardi, G.; Baerends, E. J.; Stufkens, D. J. *Inorg. Chem.* **1996**, *35*, 2886.

(50) Wilms, M. P.; Baerends, E. J.; Rosa, A.; Stufkens, D. J. *Inorg. Chem.* **1997**, *36*, 1541.



**Figure 6.** Effect of pressure on  $\phi_{\text{tot}}$ ,  $\phi_A$ , and  $\phi_D$  for the photosubstitution reaction 1 (M = W; R = Me):  $\lambda_{\text{in}} = 366 \text{ nm}$ ;  $[\text{PMe}_3] = 0.0506 \text{ M}$ ; 298 K.

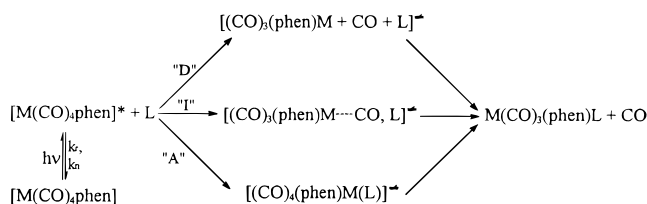
Along the arguments presented before,<sup>12,14</sup> it was shown that since  $k_n \gg k_p \gg k_r$  ( $k_p = k_D$  or  $k_A[\text{L}]$  in eqs 4 and 6, respectively) and nonradiative deactivation in general is hardly pressure sensitive,<sup>39,40,51,52</sup> the effect of pressure on  $\phi_{\text{tot}}$  can be related to the pressure dependence of  $k_D$  and  $k_A$ , which control the values of  $\phi_{\text{LF}}$  and  $\phi_{\text{MLCT}}$ , respectively. It follows that the effect of pressure on the nature of the plots of  $\phi_{\text{tot}}$  versus  $[\text{L}]$  can be related to the pressure dependence of  $k_D$  (from the intercept) and  $k_A$  (from the slope).<sup>14</sup> Thus, an increase in the concentration of the entering nucleophile gradually shifts the importance of the contribution of  $\phi_{\text{LF}}$  and  $\phi_{\text{MLCT}}$ , depending on the irradiation wavelength used. The trends reported in Table 3 are very clear and demonstrate how the nature of the photosubstitution mechanism can be tuned by selecting various M, L, and irradiation wavelength. The results in Figure 5 typically show the mechanistic changeover observed for a particular M and L as a function of irradiation wavelength. For a particular set of selected experimental conditions,  $\phi_{\text{tot}}$  may exhibit almost no meaningful pressure dependence (see Figure 6), although the components  $\phi_A$  and  $\phi_D$  exhibit significant and opposite pressure dependences. The resulting average  $\Delta V_{\phi}^{\ddagger}$  value is close to zero over the applied pressure range.

In terms of the excitation and deactivation pathways included in Scheme 1, it can be stated that intersystem crossing can lead to the population of the  ${}^1\text{MLCT}$  and  ${}^3\text{MLCT}$  states from the higher energy LF states, which will result in an associative component (characterized by an increase in  $\phi$  with increasing  $[\text{L}]$ ) during LF excitation. Similarly, MLCT excitation can via thermal back-population lead to the population of  ${}^3\text{LF}$  and so result in a dissociative component (characterized by an independence of  $\phi$  on  $[\text{L}]$ ) during MLCT excitation. However, for the photosubstitution of  $\text{W}(\text{CO})_4\text{phen}$  by  $\text{PMe}_3$ , the quantum

(51) Weber, W.; van Eldik, R.; Kelm, H.; Dibenedetto, J.; Ducommun, Y.; Offen, H.; Ford, P. C. *Inorg. Chem.* **1983**, *22*, 623.

(52) Fetterolf, M. L.; Offen, H. W. *J. Phys. Chem.* **1986**, *90*, 1828.

## Scheme 2



yield at 546 nm irradiation exhibits no dependence on the temperature (298, 318, and 338 K), indicating that thermal back-population from MLCT to LF excited states cannot play a significant role. In general it is expected that the photosubstitution reaction will occur from the lower lying  $^3LF$  and  $^3MLCT$  states.

The results of the present study can be summarized with the overall reaction mechanism presented in Scheme 2, in which the possible participation of intermediate solvento species has not been included. Here the dissociative (D), interchange (I), and associative (A) pathways are presented, and the preferred route will depend on the nature of the excited state (as controlled by the irradiation wavelength), the size of M, the nucleophilicity and steric hindrance of L, and the concentration of L. These variables will control the nature of the substitution mechanism, which in turn can be characterized from the observed pressure dependence. In the case of the smaller Cr center there is some evidence for a changeover from D to  $I_d$  for the substitution of CO by a small nucleophile such as  $PMe_3$ , on increasing the irradiation wavelength. In the case of the larger Mo and W centers there is clear evidence for a changeover from D to A on increasing the irradiation wavelength from LF to MLCT excitation for  $PMe_3$  and  $PBu^t_3$  as entering nucleophiles. Even

in the latter case this changeover does not occur for the very bulky  $PPh_3$  nucleophile. It follows that the size of both M and L and the irradiation wavelength control the nature of the photosubstitution mechanism of complexes of the type  $M(CO)_4(phen)$ .<sup>53</sup> Since pressure will accelerate associative and decelerate dissociative reactions, this parameter introduces a further tuning possibility especially under conditions where parallel associative and dissociative reactions may occur. Such a situation exists for instance for the substitution of  $W(CO)_4(phen)$  by  $PBu^t_3$  (Table 2) during irradiation in the range 380 to 420 nm where a sudden changeover in the importance of the associative and dissociative pathways occurs. It is therefore appropriate to conclude that the photosubstitution mechanism of  $M(CO)_4(phen)$  can be systematically tuned by variation of the metal, entering nucleophile, nucleophile concentration, excitation wavelength, and applied pressure.

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**Supporting Information Available:** Figures showing spectral changes observed during the photosubstitution of  $Cr(CO)_4(phen)$  and  $W(CO)_4(phen)$  by  $PBu^t_3$ , effect of nucleophile concentration on the quantum yield for the photosubstitution reaction of  $W(CO)_4(phen)$ , and pressure dependence of the quantum yield for the photosubstitution reaction of  $Cr(CO)_4(phen)$  as a function of irradiation wavelength (5 pages). Ordering information is given on any current masthead page.

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(53) Cao, S.; Reddy, K. B.; Eyring, E. M.; van Eldik, R. *Organometallics* **1994**, *13*, 91.