Photosubstitution Reactions of $M(CO)_4$(1,10-phenanthroline) (M = Mo, W). Influence of Entering Ligand, Irradiation Wavelength, and Pressure

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The influence of the entering nucleophile, irradiation wavelength, and pressure on the quantum yield for the photosubstitution of $M(CO)_4$phen (M = Mo, W) to produce $M(CO)_3$(L)phen (L = PMe_3, PPh_3) was investigated in toluene at 298 K. From the pressure dependence of the quantum yield apparent volumes of activation could be determined as a function of irradiation wavelength. These could be analyzed in terms of contributions arising from dissociative ligand field excitation and associative metal-to-ligand charge transfer excitation. The influence of steric hindrance on the entering ligand (PPh_3 > PEt_3 > PMe_3) controls the contribution of the associative charge-transfer photosubstitution reaction. An overall mechanistic picture is presented and discussed in reference to available literature data.

Introduction

The apparent volume of activation, $\Delta V_\phi^\ddagger$, obtained from the pressure dependence of the quantum yield for a photochemical reaction has become an interesting parameter for the elucidation of the intimate mechanism of photoinduced reactions of inorganic and organometallic complexes.[1−7] In an earlier study on the photosubstitution reactions of $M(CO)_4$phen (M = Mo, W; phen = 1,10-phenanthroline) with PEt_3, the values of $\Delta V_\phi^\ddagger$ pointed to a dissociative mechanism for ligand field (LF) excitation as compared to an associative mechanism for metal-to-ligand charge-transfer (MLCT) excitation.[2,8] These measurements were performed under limiting wavelength conditions, during which either LF or MLCT photochemistry was observed. Little is known about the fine tuning of such processes as controlled by the irradiation wavelength, the nature and concentration of the entering nucleophile (PR_3), the central metal atom (Cr, Mo, W), and the applied pressure. A systematic variation of these variables should enable a control over the nature of the photosubstitution mechanism. In this respect the pressure variable can provide crucial information on the intimate nature of the photochemical mechanism,[1−8] as has been the case for many related thermal processes.[9,10] A similar detailed study was recently performed on the photosubstitution reaction of $Cr(CO)_4$phen with PMe_3 and PPh_3.[11] It could be shown that LF excitation resulted in a dissociative (D) substitution mechanism, whereas MLCT excitation resulted in a dissociative interchange (I_d) substitution mechanism. Steric hindrance on the entering nucleophile (PR_3) had no influence on the nature of the substitution mechanism. The latter was only controlled by the excitation wavelength.

We have now undertaken a detailed study of the photosubstitution behavior of $Mo(CO)_4$phen and $W(CO)_4$phen as a function of irradiation wavelength for PMe_3 and PPh_3 as entering ligands. The nucleophile concentration and pressure dependences of these reactions clearly demonstrate the sensitivity of the underlying substitution mechanism to the size of the central metal atom and the entering ligand, as controlled by the population of LF and MLCT excited states.

Experimental Section

$M(CO)_4$phen (M = Mo, W) were synthesized photochemically under an argon atmosphere as previously described[12−17] and recrystallized from isooctane/dichloromethane.[18] Their UV−vis absorption spectra were found to be in good agreement with those cited in the literature.[8,19] $M(CO)_6$ (M = Mo, W) and 1.0 M PMe_3 solution in toluene were purchased from Aldrich and used without further purification. Triphenylphosphine (PPh_3, Merck) was recrystallized twice from ethanol. Elemental analyses were performed by Beller Analytical Laboratory (Göttingen, Germany). Anal. Found for PPh_3: C, 82.17; H, 6.19; P, 11,74. Found for $Mo(CO)_4$phen: C, 49.51; H, 2.23; N, 6.59. Found for $W(CO)_4$phen: C, 40.01; H, 1.83; N, 5.87.

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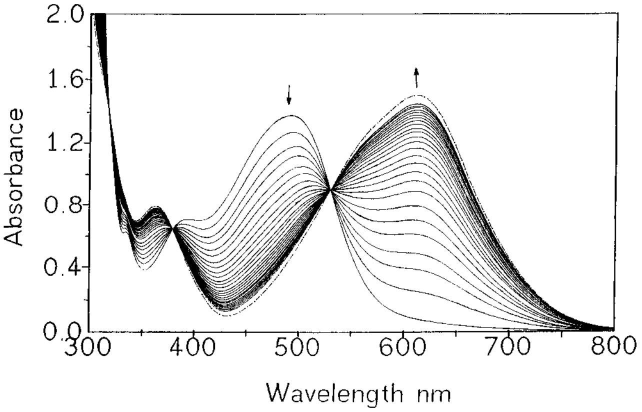

Figure 1. UV−vis absorption spectra recorded during the irradiation of 2.6 × 10^{-4} M Mo(CO)$_4$phen and 0.3 M PMe$_3$ in toluene at 546 nm and 298 K. The dot-dash line represents the absorption spectrum of Mo(CO)$_3$(PMe$_3$)phen.

Toluene (Aldrich spectroscopic grade) was distilled over sodium under an Ar atmosphere and saturated with high-purity Ar prior to use.

Photochemical measurements were performed in a thermostated (±0.1 °C) high-pressure cell[20] that was equipped with two windows and a calibrated photodiode mounted on the rear window, situated inside a black metal compartment and placed on top of a magnetic stirrer on an optical rail. Test solutions were transferred under an Ar atmosphere into a "pillbox" optical cell[21] and stirred with a Teflon-coated magnetic bar, using a combination of Schlenk and double-tip-needle techniques and a specially designed filling system.[22] The pillbox was then placed into the high-pressure cell, which was filled with *n*-heptane as the pressure-transmitting medium.

Monochromatic light at 313, 336, 366, 403, 436, 486, and 546 nm was selected from a high-pressure mercury lamp (Osram HBO 100/2) using Oriel interference filters. It was necessary to stir the solution effectively during the irradiation. The incident light intensity was determined by ferrioxalate actinometry[23−25] for irradiation at 313−436 nm, whereas actinochrome N 475/610 (Amko)[26,27] was used for irradiation at 486 and 546 nm. In all the photolysis experiments the concentration of reactants and products was monitored by UV−visible spectroscopy using a Cary 1 spectrophotometer. The photosubstitution quantum yields were corrected for inner filter effects.

Results and Discussion

Spectral Characterization. Absorption spectra were recorded during the photoinduced substitution reaction of M(CO)$_4$phen (M = Mo, W) with PMe$_3$ and PPh$_3$. Figure 1 illustrates a typical observed spectral sequence following irradiation (546 nm) of Mo(CO)$_4$phen in a toluene solution containing the PMe$_3$ nucleophile. The characteristic MLCT bands (see ref 8 and literature cited therein) of both Mo(CO)$_4$phen and Mo(CO)$_3$(PMe$_3$)phen appear at 495 and 616 nm, respectively, and the presence of clear isosbestic points at 383 and 532 nm indicates that the reaction does not seem to be complicated by subsequent substitution processes. This is in agreement with the tendency of M(CO)$_4$phen complexes to undergo photosubstitution according to reaction 1.[8]

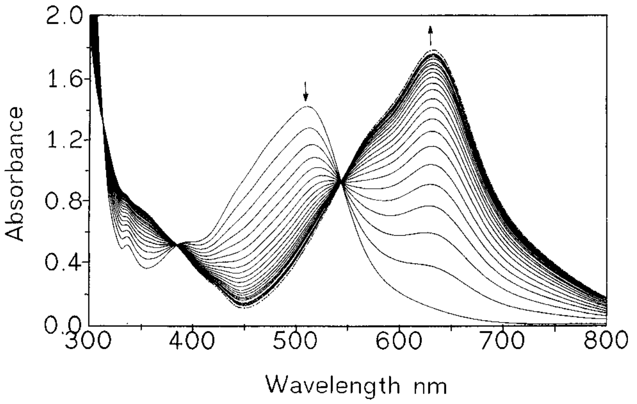

Figure 2. UV−vis absorption spectra recorded during the irradiation of 1.9 × 10^{-4} M W(CO)$_4$phen and 0.3 M PMe$_3$ in toluene at 546 nm and 298 K. The dot-dash line represents the absorption spectrum of W(CO)$_3$(PMe$_3$)phen.

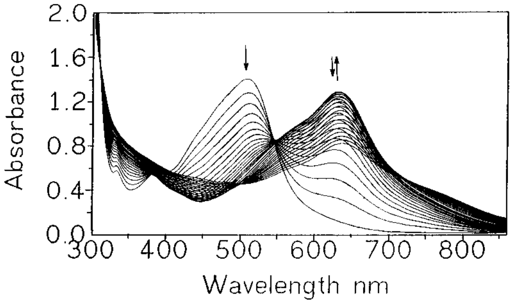

Figure 3. UV−vis absorption spectra recorded during the irradiation of 1.8 × 10^{-4} M W(CO)$_4$phen and 0.3 M PMe$_3$ in toluene at 313 nm and 298 K.

$$\mathrm{M(CO)_4phen + PR_3} \xrightarrow{h\nu} fac\text{-}\mathrm{M(CO)_3(PR_3)phen + CO} \quad (1)$$

$$\mathrm{M = Mo, W;\ R = Me, Ph}$$

Similar spectral changes were observed during the photolysis of W(CO)$_4$phen in the presence of PMe$_3$ (see Figure 2), and the clean isosbestic points once again demonstrate that the formation of W(CO)$_3$(PMe$_3$)phen is not affected by subsequent reactions or the apparent buildup of any intermediate species.

In the case of photolysis in the LF band at $\lambda < 350$ nm (see ref 8 and literature cited therein), the primary formation of M(CO)$_3$(PR$_3$)phen is followed by the subsequent formation of M(CO)$_2$(PR$_3$)$_2$phen according to reaction 2 (see Figures 3 and 4), for which a second series of clean isosbestic points are observed. Figure 4 illustrates the steric effect of the entering ligand on the subsequent photoreaction at 366 nm photolysis. Formation of Mo(CO)$_2$(PPh$_3$)$_2$phen seems to occur easily in a subsequent reaction, due to the labilization of CO by PPh$_3$ on Mo(CO)$_3$(PPh$_3$)phen during LF excitation,

$$\mathrm{M(CO)_3(PR_3)phen + PR_3} \xrightarrow{h\nu} cis\text{-}\mathrm{M(CO)_2(PR_3)_2phen + CO} \quad (2)$$

$$\mathrm{M = Mo, W;\ R = Me, Ph}$$

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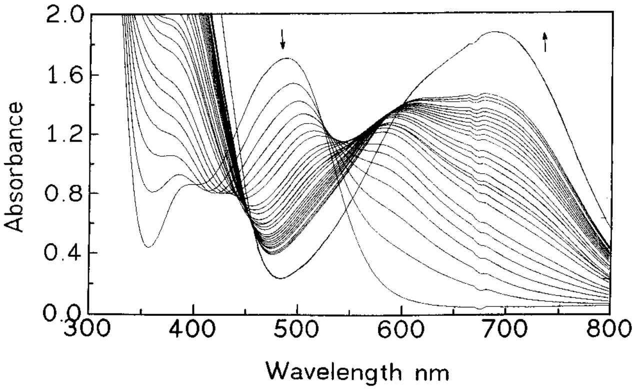

Figure 4. UV–vis absorption spectra recorded during the irradiation of 2.8 × 10^{-4} M $Mo(CO)_4phen$ and 0.2 M PPh_3 in toluene at 366 nm and 298 K.

Table 1. Quantum Yield for Reaction 1 as a Function of [PMe_3] and Irradiation Wavelength at Ambient Pressure

[PMe_3], M	λ_{irr} = 366 nm $\phi_d \times 10^2$	λ_{irr} = 366 nm $\phi_p \times 10^2$	λ_{irr} = 436 nm $\phi_d \times 10^3$	λ_{irr} = 436 nm $\phi_p \times 10^3$
	$Mo(CO)_4phen^a$			
0.0010	3.83 ± 0.05	3.09 ± 0.12		
0.0015	3.79 ± 0.06	3.29 ± 0.05	1.92 ± 0.01	1.34 ± 0.11
0.0020	3.73 ± 0.01	3.41 ± 0.17		
0.0030	3.63 ± 0.01	3.62 ± 0.02	2.57 ± 0.15	2.06 ± 0.03
0.0050	4.03 ± 0.03	3.89 ± 0.04		
0.0060	4.16 ± 0.08	3.93 ± 0.05	3.67 ± 0.15	3.23 ± 0.02
0.010	4.19 ± 0.24	4.08 ± 0.02	5.10 ± 0.00	4.90 ± 0.19
0.020	4.60 ± 0.13	4.74 ± 0.13	10.15 ± 0.12	9.30 ± 0.15
0.030	5.41 ± 0.36	5.48 ± 0.34	14.39 ± 1.00	14.37 ± 0.48
	$W(CO)_4phen^b$			
0.0015	1.57 ± 0.10	0.77 ± 0.02	0.54 ± 0.03	0.21 ± 0.05
0.0030	1.51 ± 0.06	0.91 ± 0.06	0.73 ± 0.03	0.43 ± 0.03
0.0060	1.42 ± 0.10	1.05 ± 0.05	1.09 ± 0.08	0.79 ± 0.04
0.010	1.39 ± 0.05	1.20 ± 0.03	1.64 ± 0.07	1.37 ± 0.03
0.020	1.42 ± 0.01	1.47 ± 0.01	2.84 ± 0.06	2.95 ± 0.04
0.030	1.55 ± 0.02	1.52 ± 0.02	4.09 ± 0.03	4.42 ± 0.09

[a] [$Mo(CO)_4phen$] = 2.48 × 10^{-4} M; ϕ_d, disappearance of $Mo(CO)_4phen$; ϕ_p, formation of $Mo(CO)_3(PMe_3)phen$. [b] [$W(CO)_4phen$] = 2.42 × 10^{-4} M; ϕ_d, disappearance of $W(CO)_4phen$; ϕ_p, formation of $W(CO)_3(PMe_3)phen$.

which is very similar to that found for the photosubstitution reaction of $Cr(CO)_4phen$.[11] During this photolysis, the color of the solution clearly changes from red to violet and then to green.[28,29] This reaction can be prevented by using shorter irradiation times during LF excitation. Due to the significantly lower quantum yield and the different nature of the photosubstitution mechanism in the case of MLCT excitation (see below), significant interference of the subsequent reaction (2) is not observed under such conditions.

Concentration Dependence of Quantum Yield. The quantum yields for the LF and MLCT photosubstitution reactions, on the basis of available literature data,[8,19,30] are expected to exhibit characteristic concentration dependences. The overall quantum yield for reaction 1, $\phi_{tot} = \phi_{LF} + \phi_{MLCT}$, was therefore measured as a function of [PMe_3] and irradiation wavelength. Preliminary measurements, summarized in Table 1, indicated that at low [PMe_3] the quantum yield for the disappearence of $M(CO)_4phen$ was higher than that for the formation of $M(CO)_3(PMe_3)phen$. This was ascribed to a small contribution of a decomposition process in the absence of excess PMe_3. Plots of ϕ_{tot} (based on the formation of $M(CO)_3(PMe_3)phen$) as a function of [PMe_3] and irradiation wavelength are summarized for M = Mo in Figure 5, whereas the corresponding data for M = W are summarized in Table 2. The plots clearly show the deviation from linear behavior at low [PMe_3] due to the participation of side reactions under such conditions as discussed above. The data show that ϕ_{tot} increases with increasing [PMe_3], and the contribution of the intercept increases with increasing excitation energy, i.e. decreasing irradiation wavelength. These trends are typical

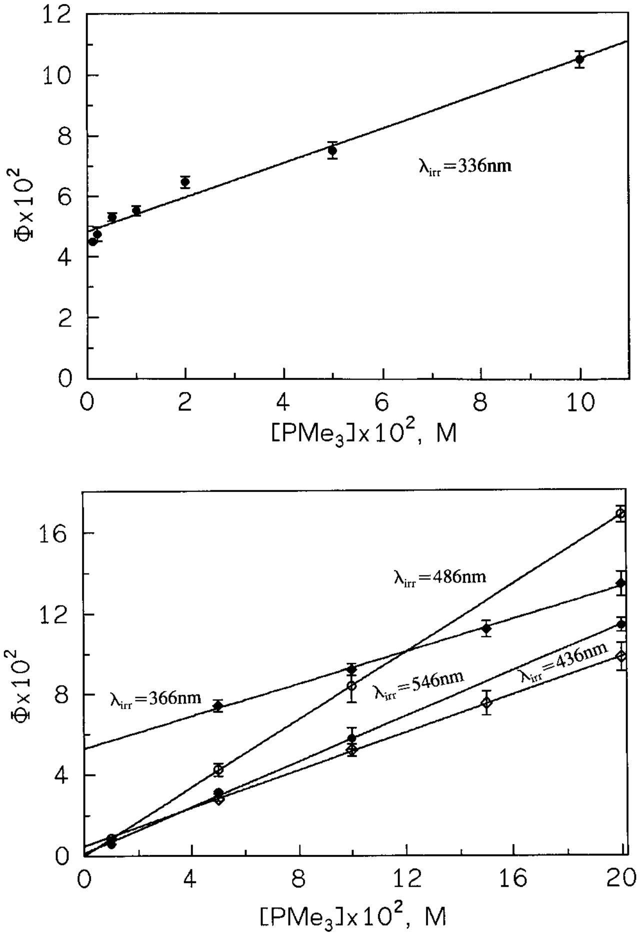

Figure 5. ϕ_{tot} as a function of [PMe_3] and irradiation wavelength for the photosubstitution of $Mo(CO)_4phen$ at 298 K.

Table 2. ϕ_{tot} for Reaction 1 as a Function of [PMe_3] and Irradiation Wavelength for M = W[a] at 298 K

[PMe_3], M	$\phi \times 10^2$ λ_{irr} = 366 nm	λ_{irr} = 436 nm	λ_{irr} = 486 nm	λ_{irr} = 546 nm
0.010	1.20 ± 0.03	0.14 ± 0.03	0.23 ± 0.02	0.19 ± 0.01
0.020	1.47 ± 0.01	0.30 ± 0.04		
0.050	2.23 ± 0.12	0.79 ± 0.03	0.94 ± 0.05	0.94 ± 0.04
0.10	2.98 ± 0.19	1.42 ± 0.01	1.86 ± 0.03	1.89 ± 0.07
0.15	3.59 ± 0.05	2.18 ± 0.01		
0.20	4.04 ± 0.08	2.77 ± 0.05	3.40 ± 0.15	3.14 ± 0.04
0.30			4.34 ± 0.38	4.39 ± 0.04
$\phi_{LF} \times 10^2$	1.27 ± 0.15	0.04 ± 0.03	0.26 ± 0.18	0.23 ± 0.13
$b \times 10$	1.49 ± 0.13	1.39 ± 0.03	1.43 ± 0.10	1.42 ± 0.08

[a] Conditions: [$W(CO)_4phen$] = 2.42 × 10^{-4} M, λ_{irr} = 366 nm, λ_{irr} = 436 nm; [$W(CO)_4phen$] = 2.20 × 10^{-4} M, λ_{irr} = 486 nm, λ_{irr} = 546 nm.

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for parallel reaction pathways, viz. a concentration-independent LF and concentration-dependent MLCT reaction, and can be considered as an important piece of information regarding the nature of the photosubstitution mechanism. This observation is of fundamental importance in the interpretation of the wavelength dependence of photosubstitution reactions usually measured at a fixed ligand concentration. The difference in the concentration dependences of LF and MLCT photosubstitution reactions can lead to an unexpected increase in quantum yield on increasing the excitation wavelength due to a concentration-independent process going to a concentration-dependent process and can lead to a wrong interpretation in terms of excited-state effects only.[31] The competition between a concentration-independent and a concentration-dependent pathway requires that wavelength dependence should be studied as a function of entering ligand concentration.

The dependence of ϕ_{tot} on [PR$_3$] can be expressed by eq (3), where ϕ_{LF} represents the intercept and b the slope of the plots. The values of ϕ_{LF} and b strongly

$$\begin{aligned}\phi_{tot} &= \phi_{LF} + \phi_{MLCT} \\ &= \phi_{LF} + b[PR_3] \qquad (3)\end{aligned}$$

depend on the irradiation wavelength, as shown in Table 2. Similar experiments were performed for the bulkier PPh$_3$ ligand. Typical plots of ϕ_{tot} versus [PPh$_3$] as a function of irradiation wavelength are shown in Figure 6, which clearly demonstrate that ϕ decreases with increasing irradiation wavelength, in good agreement with results reported before.[2,8,11] The ligand concentration independence of ϕ is typical for dissociative LF photochemistry. Even for the excitation at 436 nm for M = Mo no meaningful dependence of ϕ on [PPh$_3$] was observed.[19] This indicates that MLCT excitation presumably also results in a dissociative substitution process, in contrast to that reported above for the significantly smaller entering nucleophile PMe$_3$. In the case of M = W, the plot of ϕ_{tot} versus [PPh$_3$] shown in Figure 6b clearly indicates the contribution of an associative reaction path during MLCT excitation at 546 nm.[31] In an effort to obtain further mechanistic insight, the pressure dependence of these reactions was studied at different excitation wavelengths.

Pressure Dependence of Quantum Yield. In order to investigate the effect of pressure on this photosubstitution reaction, it is essential to separate the pressure dependence of ϕ_{LF} and ϕ_{MLCT}. ϕ_{LF} makes a significant contribution at short irradiation wavelengths such that the pressure dependence of ϕ_{tot} must be studied as a function of [PR$_3$] in order to separate the contribution of ϕ_{LF} and ϕ_{MLCT}. A typical example is shown in Figure 7, from which it follows that the intercept decreases and the slope increases with increasing pressure. The values of ϕ_{LF} and b (according to eq 3) are summarized as a function of pressure in Table 3. The results clearly show that ϕ_{LF} is characterized by a strongly positive apparent volume of activation, whereas b is characterized by significantly negative volumes of activation. In the case of M = Mo, the latter value is even more negative than those observed for M = W. These data clearly demonstrate that, for the photosubstitution of CO by PMe$_3$, LF excitation strongly favors a dissociative reaction path whereas MLCT excitation favors an associative reaction path.

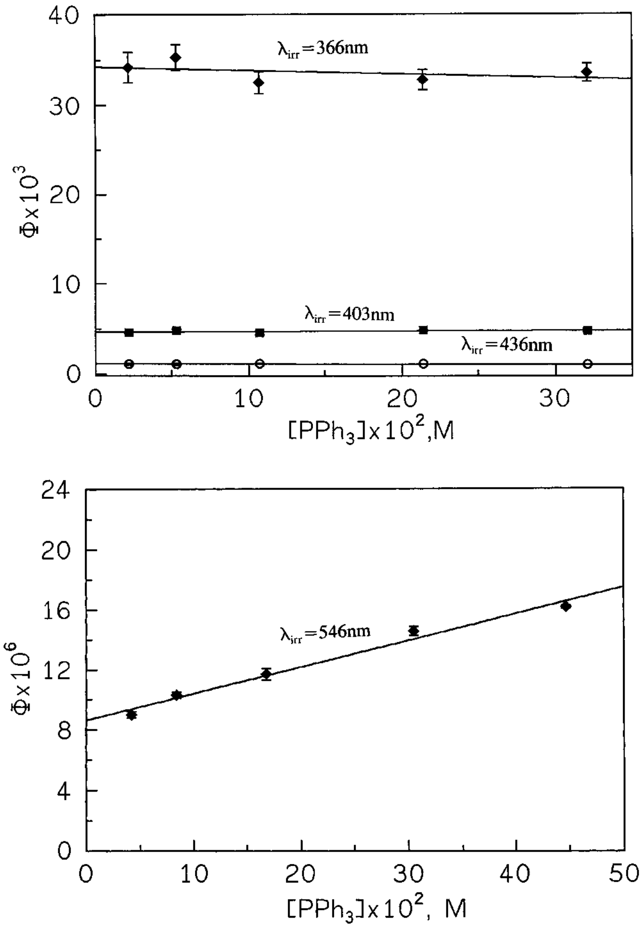

Figure 6. ϕ_{tot} as a function of [PPh$_3$] and irradiation wavelength for the photosubstitution of M(CO)$_4$phen at 298 K: (a, top) M = Mo; (b, bottom) M = W.

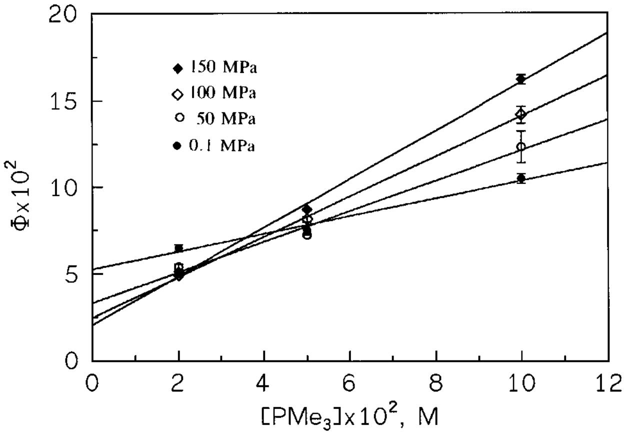

Figure 7. ϕ_{tot} as a function of [PMe$_3$] and pressure for the photosubstitution of Mo(CO)$_4$phen at 336 nm and 298 K.

This mechanistic changeover can also be seen in an overall manner when the pressure dependence of these substitution reactions is studied at various irradiation wavelengths and [PMe$_3$], for which some typical data are reported in Table 4. The typical plots of ln ϕ versus pressure in Figure 8 show how the pressure dependence of ϕ changes as a function of irradiation wavelength. According to Table 4 the pressure dependence of ϕ_{tot}

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Table 3. Summary of ϕ_{LF} and *b* as a Function of Irradiation Wavelength, Metal, and Pressure for the Reaction

$$\mathrm{M(CO)_4phen + PMe_3 \xrightarrow{h\nu} M(CO)_3(PMe_3)phen + CO}$$

	λ_{irr} = 336 nm		λ_{irr} = 366 nm	
pressure, MPa	$\phi_{LF} \times 10^2$	b × 10	$\phi_{LF} \times 10^2$	b × 10
		Mo(CO)$_4$phen[a]		
0.1	5.26 ± 0.42	5.12 ± 0.65	4.08 ± 0.92	5.34 ± 1.40
50	3.33 ± 0.70	8.82 ± 1.07	2.99 ± 0.83	8.38 ± 1.26
100	2.48 ± 0.23	11.64 ± 0.35	3.16 ± 1.28	9.47 ± 1.94
150	2.06 ± 0.53	14.02 ± 0.81	1.93 ± 1.47	13.53 ± 2.24
$\Delta V^‡$, (cm^3 mol^{-1})	+15.4 ± 2.1	−16.4 ± 2.9	+10.9 ± 3.5	−14.4 ± 2.1
		W(CO)$_4$phen[b]		
0.1	1.18 ± 0.18	1.85 ± 0.27	4.17 ± 7.07	1.40 ± 0.11
50	1.00 ± 0.14	2.07 ± 0.21	3.06 ± 12.5	1.92 ± 0.19
100	0.80 ± 0.09	2.46 ± 0.14	2.62 ± 7.99	2.29 ± 0.12
150	0.61 ± 0.01	2.85 ± 0.02	1.95 ± 6.61	2.65 ± 0.10
$\Delta V^‡$, (cm^3 mol^{-1})	+10.9 ± 0.8	−7.3 ± 0.4	+12.1 ± 1.0	−10.4 ± 1.4

[a] Conditions: [M] = 2.48 × 10^{-4} M; solvent toluene; *T* = 298 K. [b] Conditions: [M] = 2.42 × 10^{-4} M; solvent toluene; T = 298 K.

Table 4. ϕ_{tot} (×10^2) as a Function of [PMe$_3$], Irradiation Wavelength, and Pressure for Photosubstitution of M(CO)$_4$phen Complexes in Toluene at 298 K

			pressure, MPa				
λ_{irr}, nm	[M] × 10^4, M	[PMe$_3$], M	0.1	50	100	150	$\Delta V^‡_\phi$, cm^3 mol^{-1}
				Mo(CO)$_4$phen			
336	2.48	0.02	6.47 ± 0.19	5.40 ± 0.16	4.91 ± 0.04	5.10 ± 0.16	+4.0 ± 1.7
336	2.48	0.05	7.52 ± 0.27	7.24 ± 0.02	8.14 ± 0.15	8.70 ± 0.05	−2.8 ± 1.1
336	2.48	0.10	10.49 ± 0.27	12.33 ± 0.91	14.18 ± 0.49	16.22 ± 0.27	−7.2 ± 0.2
366	2.48	0.02	4.74 ± 0.13	4.30 ± 0.04	4.49 ± 0.10	3.99 ± 0.17	+2.4 ± 1.1
366	2.48	0.05	7.39 ± 0.32	7.76 ± 0.38	8.79 ± 0.29	9.73 ± 0.24	−4.7 ± 0.5
366	2.48	0.10	9.17 ± 0.28	11.15 ± 0.11	12.29 ± 0.78	15.08 ± 1.66	−7.9 ± 0.7
				W(CO)$_4$phen			
366	2.42	0.02	1.47 ± 0.01	1.35 ± 0.02	1.25 ± 0.08	1.19 ± 0.11	+3.5 ± 0.3
366	2.42	0.05	2.23 ± 0.12	2.13 ± 0.06	2.09 ± 0.10	2.03 ± 0.12	+1.5 ± 0.2
366	2.42	0.10	2.98 ± 0.19	3.03 ± 0.04	3.23 ± 0.01	3.47 ± 0.01	−2.6 ± 0.5
436	2.42	0.02	0.29 ± 0.02	0.36 ± 0.01	0.45 ± 0.04	0.52 ± 0.02	−9.8 ± 0.6
436	2.42	0.05	0.79 ± 0.03	1.08 ± 0.05	1.23 ± 0.05	1.39 ± 0.08	−9.1 ± 1.6
436	2.42	0.10	1.42 ± 0.00	1.92 ± 0.02	2.30 ± 0.10	2.65 ± 0.10	−10.2 ± 1.3

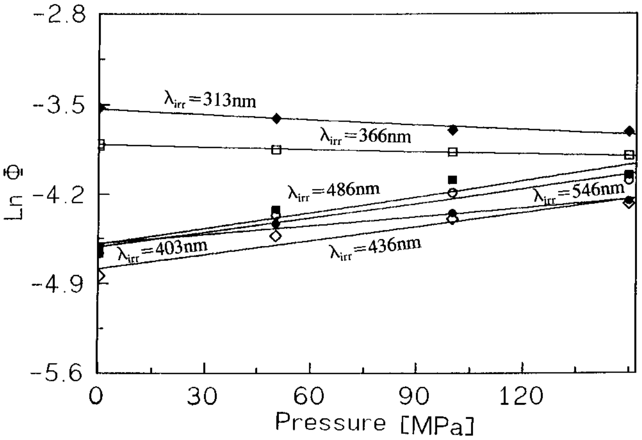


Figure 8. Plots of ln ϕ_{tot} versus pressure as a function of irradiation wavelength for the reaction

$$\mathrm{W(CO)_4phen + PMe_3 \xrightarrow{h\nu} W(CO)_3(PMe_3)phen + CO}$$

Experimental conditions: [W(CO)$_4$phen] = 2.1 × 10^{-4} M; [PMe$_3$] = 0.05 M; *T* = 298 K; toluene solvent.

exhibits an overall trend from slightly positive to significantly negative volumes of activation on increasing both the irradiation wavelength and the concentration of PMe$_3$. This is a logical consequence of the [PMe$_3$] dependence of ϕ_{tot} as expressed by eq 3. It follows that the reported $\Delta V^‡$ values for ϕ_{LF} and *b* (representing ϕ_{MLCT}) in Table 3 characterize the dissociative and associative nature of the photosubstitution process, respectively.

In the case of PPh$_3$ as entering nucleophile, typical plots of ln ϕ versus pressure are shown in Figure 9 and the corresponding apparent volumes of activation are summarized in Table 5. It follows from these data that substitution of CO by PPh$_3$ on Mo(CO)$_4$phen follows a dissociatively activated process at all irradiation wavelengths. The trend in $\Delta V_\phi^‡$ to smaller values at 546 nm irradiation for M = Mo suggests a possible changeover

Table 5. Volumes of Activation for Photosubstitution of CO in M(CO)$_4$(phen) Complexes by the Ligand PR$_3$ at Different Excitation Wavelengths[a]

	$\Delta V^‡_\phi$, cm^3 mol^{-1}			
	Mo(CO)$_4$phen		W(CO)$_4$phen	
λ_{irr}, nm	PMe$_3$	PPh$_3$	PMe$_3$	PPh$_3$
313	+14.4 ± 3.1		+3.2 ± 0.6	
336	−2.8 ± 1.1			
366	−4.7 ± 0.5	+7.6 ± 1.3	+1.5 ± 0.2	+10.9 ± 0.6
403	−12.3 ± 0.1	+6.7 ± 1.5	−5.8 ± 0.8	+13.9 ± 1.5
436	−13.3 ± 0.9	+11.0 ± 1.6	−9.1 ± 1.6	+8.1 ± 1.5
486	−13.3 ± 3.2		−10.3 ± 2.5	
546	−10.7 ± 2.5	+3.4 ± 1.6[b]	−9.6 ± 1.6	−8.2 ± 0.8[c]

[a] Experimental conditions: [M] = (1.90−2.48) × 10^{-4} M; [PMe$_3$] = 0.0506 M, [PPh$_3$] = 0.100 M; solvent toluene; *T* = 298 K. [b] [PPh$_3$] = 0.320 M. [c] [PPh$_3$] = 0.305 M.

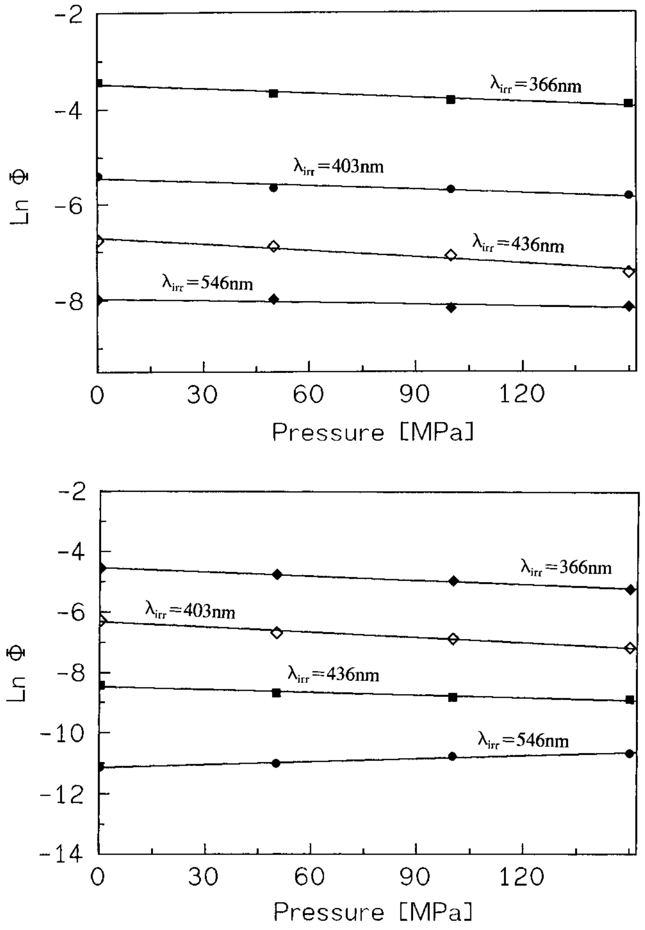


Figure 9. Plots of ln ϕ_{tot} versus pressure as a function of irradiation wavelength for the reaction

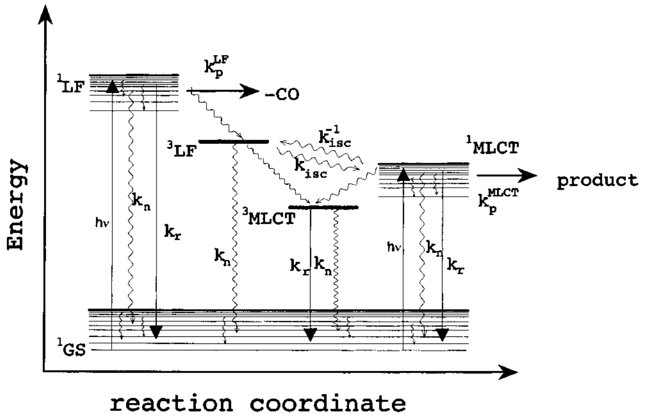
$$M(CO)_4phen + PPh_3 \xrightarrow{h\nu} M(CO)_3(PPh_3)phen + CO$$

(a, top) M = Mo; (b, bottom) M = W. Experimental conditions: $[Mo(CO)_4phen] = 1.80 \times 10^{-4}$ M; $[W(CO)_4phen] = 1.98 \times 10^{-4}$ M; λ_{irr} = 366, 403 and 436 nm, $[PPh_3] = 0.100$ M; λ_{irr} = 546 nm, M = Mo, $[PPh_3] = 0.320$ M; λ_{irr} = 546 nm, M = W, $[PPh_3] = 0.305$ M; T = 298 K; toluene solvent.

to an interchange (I_d) photosubstitution mechanism during MLCT excitation. Although the MLCT state obviously favors an associative reaction path for the smaller ligands (PMe_3 and PEt_3[8]), the bulkier PPh_3 nucleophile forces the systems to follow an I_d reaction route. In a similar way, MLCT excitation also induces an I_d mechanism for the reaction of $Cr(CO)_4phen$ with the smaller PMe_3 nucleophile, which is due to the smaller metal center in the chromium complex. For the photosubstitution of CO by PPh_3 on $W(CO)_4phen$, the results in Table 5 and Figure 9b clearly show a changeover from a dissociative process at low-wavelength irradiation to an associative process at high-wavelength irradiation. A comparison of the data for M = Mo and W indicates a significant difference in these systems during MLCT excitation at 546 nm. The W complex does exhibit an associative substitution mode under these conditions, which is in line with the $[PPh_3]$ dependence reported in Figure 6b. Thus, steric congestion as determined by the size of the central metal and the entering nucleophile controls the intimate nature of the photosubstitution mechanism.

Overall Comparison. The interpretation outlined above is based on the apparent volumes of activation determined from the effect of pressure on the overall photosubstitution quantum yield. Since quantum yield is a composite quantity, its pressure dependence may also be influenced by the effect of pressure on various photophysical processes that contribute to its value.[1-3] For that reason it is necessary to analyze the above interpretation in more detail. Photoexcitation of $M(CO)_4phen$ leads to the population of LF and MLCT excited states, depending on the irradiation wavelength.[8,30,31] Detailed studies have resulted in different energy diagrams that represent the relative location of singlet and triplet states, as well as possible intersystem crossings (isc).[18,31,32] An overall summary of possible activation and deactivation routes is presented in Scheme 1. It is generally known that radiative deactivation (k_r) is slow, since these complexes exhibit almost no emission.[19,33] Decay of the excited state can occur via nonradiative deactivation (k_n) and photochemical conversion ($k_p{}^{LF}$ and $k_p{}^{MLCT}$), and photochemistry is suggested to occur from the spin-singlet states. We could clearly demonstrate in our earlier work that the LF and MLCT excited states exhibit their own characteristic photosubstitution mechanism.[2,8] In general LF excitation results in the activation of the M−CO bonds and leads to dissociative ligand substitution reactions. 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 π^*(diimine) orbital, occupied in the MLCT state, to the $\sigma^*(M-C_{ax})$ orbital may occur via vibronic mixing.[12] This will in turn result in the dissociation of the axial CO ligand. 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. The latter will induce an associative attack of a nucleophile on the metal center and result in a nucleophile concentration dependence of ϕ. Thus, both dissociative and associative reaction modes are feasible in the case of pure MLCT excitation. According to Scheme 1, a back-population from MLCT to LF is not ruled out and will be included in the observed concentration-independent ϕ_{LF}.

Scheme 1



In general, the observed quantum yield for reaction 1 will be the sum of the contributions resulting from

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LF and MLCT excitation. Expressions for the wavelength-dependent ϕ_{LF} and ϕ_{MLCT} in terms of [L], k_n, and k_p have been dealt with in the past.[8] Crucial for the present study is the dependence of ϕ_p^{MLCT} on the concentration and nucleophilicity of the entering ligand L. In the case of relatively low quantum yields, $k_n \gg k_p$ and eq 4 applies. This is in good agreement with the

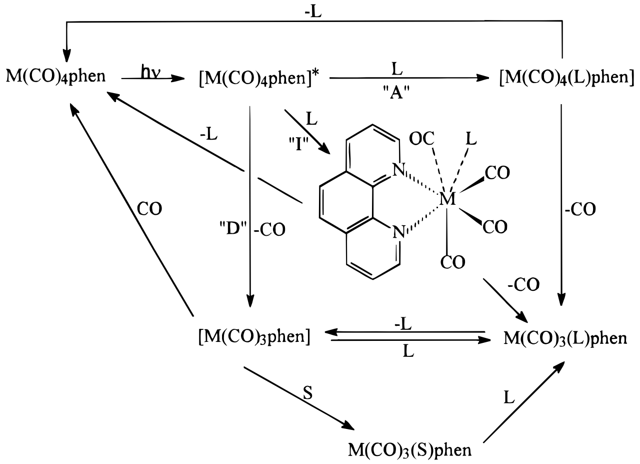
$$\phi_{tot} = \phi_{LF} + \phi_{MLCT} = (k_p^{LF}/k_n^{LF}) + (k_p^{MLCT}[L]/k_n^{MLCT}) \quad (4)$$

empirically found relationship in (3). The dependence of ϕ_{MLCT} on [L] will depend on the role of the associative reaction pathway. On the assumption that nonradiative deactivation is not very pressure sensitive, which has been shown to be the case in systems where it was possible to measure the effect of pressure on the lifetime of the excited state,[1-3,34,35] the pressure dependence of ϕ_{LF} and ϕ_{MLCT} will represent that of the photochemical rate constants k_p^{LF} and k_p^{MLCT}, respectively. In the case of a dissociative mechanism operating for both LF and MLCT excitation, this will result in a concentration-independent ϕ_{tot}. Alternatively, if MLCT excitation results in an associative ligand substitution mechanism, ϕ_{tot} will exhibit a linear dependence on [L] as found in the present study for L = PMe_3. It is important to note that in considering the contributions of ϕ_{LF} and ϕ_{MLCT} in eq 4, the MLCT state can be considered as a bound state but the LF state cannot, which leads to a wavelength-dependent contribution from ϕ_{LF} . On the other hand, as indicated above, it is the contribution from ϕ_{MLCT} that will depend on the ligand concentration, such that ϕ_{tot} can exhibit rather complicated or unexpected wavelength dependences at a fixed ligand concentration.[31] It follows that the wavelength dependence of ϕ_{tot} should always be studied as a function of ligand concentration in such systems.

In the case of the W complex, irradiation at 366 nm (Figure 5) also exhibits a meaningful ligand concentration dependence and factor *b* (Table 2) remains practically constant on increasing the irradiation wavelength to 546 nm. This can be considered as clear evidence for the nonradiative population of the ^{3}MLCT state (Scheme 1), from which the associative substitution reaction occurs. Thus, the associative photosubstitution reactions occur from the lowest, presumably triplet MLCT state as suggested in the literature.[31] The data in Table 2 furthermore demonstrate that ϕ_{LF} reduces to practically zero within the experimental error limits at higher irradiation wavelength where only the MLCT state is populated.

No dependence of ϕ_{tot} on [L] was found for excitation in the region from LF to MLCT in the case of L = PPh_3 and M = Mo. The cone angles of PMe_3 and PPh_3 are 118 and 145°, respectively,[36] such that steric crowding caused by the PPh_3 nucleophile can prevent an associative ligand substitution process. In fact a cone angle of 145° seems to be critical in controlling the nature of addition of nucleophiles to a metal center, as recently demonstrated for addition to the $H_2Os_3(CO)_{10}$ cluster.[37] The steric crowding can also account for the operation of a dissociative interchange mechanism during the displacement of CO by PPh_3 on MLCT excitation, where bond cleavage (Mo−CO) will be the controlling factor (Scheme 2). On the basis of these results we cannot distinguish whether the dissociative nature arises from the MLCT state itself or from the thermal promotion of MLCT to LF states. In the case of MLCT excitation of $W(CO)_4$phen, the quantum yield does increase with increasing [PPh_3] and the corresponding volume of activation also supports the operation of an associative mechanism. Thus, there is a significant difference between $Mo(CO)_4$phen and $W(CO)_4$phen in their ability to bind PPh_3 during MLCT excitation. This trend can only be related to steric effects associated with the metal complex in the excited state and the entering nucleophile.

Scheme 2



The results of this study have clearly demonstrated that the intimate nature of the photosubstitution mechanism can be controlled by the nature of the metal center, the nature and concentration of the entering nucleophile, the irradiation wavelength, and the applied pressure. It is in particular the entering nucleophile concentration dependence and the associated pressure dependence that reveal the intimate nature of the photosubstitution mechanism. The variables mentioned enable a systematic "tuning" of the selected photosubstitution route.

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