

Competing Thermal and Photochemical Ligand Substitution Reactions of the Dimetallacycle $(\text{CO})_4\text{Mo}(\mu\text{-PMD})_2\text{Mo}(\text{CO})_4$ (PMD = Pentamethylenediazine). Mechanistic Information from Entering Nucleophile and Pressure Dependences

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Photolysis of the dimetallacycle $(\text{CO})_4\text{Mo}(\mu\text{-PMD})_2\text{Mo}(\text{CO})_4$ (PMD = pentamethylenediazine) in toluene solutions containing a series of diimine ligands (2,2'-bipyridine, 1,10-phenanthroline, and 1,2-bis(diphenylphosphino)ethane) on MC and MLCT excitation has been investigated as a function of entering ligand concentration and pressure. Separation of the volumes of activation for competing ligand substitution reactions in the excited and ground states has been achieved. The results obtained for MC photolysis clearly reveal that photochemical and thermal ligand substitution proceed according to different reaction routes, viz. dissociative (D) and associative (A), respectively. The thermal and photochemical reactions give different products whenever 1,2-bis(diphenylphosphino)ethane is used as nucleophile. Significant interference of the thermal reaction during photolysis is observed throughout. Evidence for an associatively activated ligand substitution reaction upon MLCT excitation is reported.

Introduction

It is well-known that the photochemical reaction path can differ distinctly from that for the thermal reaction, particularly where the products are also different for such reactions.^{1,2} Kinetic investigations on photochemical and thermal ligand substitution reactions of complexes such as $\text{M}(\text{CO})_4(\text{diimine})$,^{3–9} $(\text{CO})_4\text{M}(\mu\text{-PMD})_2\text{M}(\text{CO})_4$,^{10,11} and $\text{M}(\text{CO})_5\text{L}$ ^{12–15} (M = Cr, Mo, W; L is a derivative of pyridine; $\mu\text{-PMD}$ = 3,3-pentamethylenediazine), which all possess the characteristics of a higher energy ligand field (LF) excited state and a lower lying metal to ligand charge to transfer (MLCT) state, have been the subject of numerous studies in organo-

metallic chemistry. The results of these studies have shown that LF excitation results primarily in breakage of the M–CO bond in $\text{M}(\text{CO})_4(\text{diimine})$ complexes. This differs significantly from MLCT excitation, which gives rise to a bimolecular associative process.^{16,17} Our recent studies demonstrated that ligand substitution of excited molecules in LF and MLCT states proceeds according to different reaction routes operating in parallel.^{18,19} In some cases thermal substitution reactions also proceed according to parallel reaction paths that depend on the structure, stability, and reactivity of the metal centers and nature of the entering nucleophile.^{20,21} In these studies volumes of activation, ΔV^\ddagger , obtained from the pressure dependence of quantum yields and rate constants, form an important kinetic parameter that can improve our mechanistic understanding, as has been established for various chemical reactions.^{22–29}

In the systems referred to above, MLCT excitation resulted in unique mechanistic behavior. A gradual changeover from a dissociative to an associative reaction

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mechanism on going from LF to MLCT excitation could be observed^{16–19} for the resulting ligand substitution process. In a recent series of studies^{10,11} on photosubstitution reactions of dimetallaheterocycles of the type $(\text{CO})_4\text{M}(\mu\text{-PMD})_2\text{M}(\text{CO})_4$ ($\text{M} = \text{Cr}, \text{Mo},$ and W), it was shown that these complexes exhibit clearly separated lower energy MLCT and higher energy MC (metal-centered) states. Irradiation in the presence of bidentate nitrogen ligands (N-N) led to the formation of $\text{M}(\text{CO})_4(\text{N-N})$ and PMD by cleavage of the metal–diazirine bonds. Irradiation of the chromium complex in the presence of the bidentate phosphorus ligand dppe, 1,2-bis(diphenylphosphino)ethane, afforded $(\text{CO})_3\text{Cr}(\mu\text{-PMD})_2(\mu\text{-dppe})\text{Cr}(\text{CO})_3$ via substitution of coordinated CO .¹⁰

The present study was undertaken in order to elucidate the nature of the photosubstitution mechanism associated with MC and MLCT excitation as a function of entering ligand. We selected the Mo complex for our measurements, since Mo is known from our earlier work^{16–19} to be a suitable candidate for possible mechanistic variations depending on the nature of the excited state. We detected a significant interference of parallel thermal reactions under all conditions and therefore performed a detailed study of both the photochemical and thermal ligand substitution reactions. The reactions were studied as a function of entering ligand concentration, irradiation wavelength, and pressure. The results enable us to determine the intimate nature of both the thermal and photochemical substitution mechanisms and to discuss these in reference to available literature data.

Experimental Section

$(\text{CO})_4\text{Mo}(\mu\text{-PMD})_2\text{Mo}(\text{CO})_4$ was synthesized under an argon atmosphere as previously described^{30,31} and purified according to the literature. 2,2'-Bipyridine (bpy), 1,10-phenanthroline (phen), and dppe (Aldrich) were used as purchased without further purification. Toluene (Aldrich spectroscopic grade) was distilled over sodium under an argon atmosphere and saturated with high-purity argon prior to use.

Photochemical measurements were performed in a thermostated (± 0.1 °C) high-pressure cell,³² which was equipped with two windows and a calibrated photodiode mounted on the rear window. This cell is inside a black metal compartment and is placed on top of a magnetic stirrer on an optical rail. The sample solutions for photolysis and thermal reaction were prepared under an argon atmosphere in the dark and transferred into a "pillbox" optical cell,³³ stirred with a Teflon-coated magnetic bar, by using a combination of Schlenk and double-tip-needle techniques using a specially designed filling system.³⁴ The pillbox was then placed in the high-pressure cell, which was filled with *n*-heptane as the pressure-transmitting medium. Identical procedures were used for measurements in the absence and presence of light.

Monochromatic light at 366, 403, 436, and 486 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 reaction. The incident light intensity was determined by ferrioxalate actinometry^{35–37} for

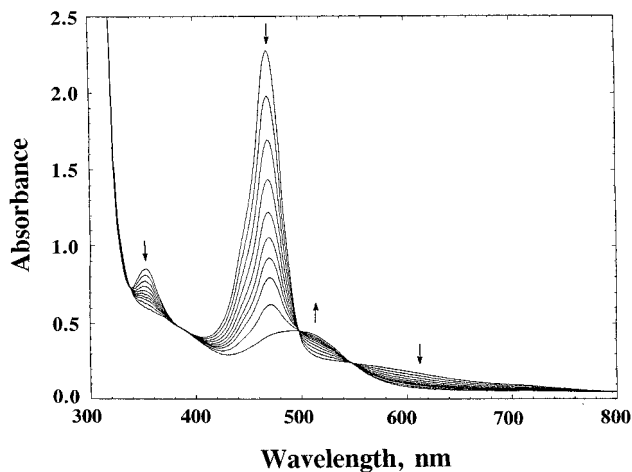
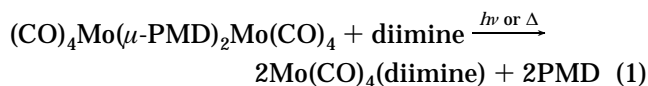


Figure 1. UV–vis absorption spectra recorded during the irradiation of 4.02×10^{-5} M $\text{Mo}_2(\mu\text{-PMD})_2(\text{CO})_8$ and 0.05 M bpy in toluene at 486 nm and 293 K.

irradiation at 366 and 436 nm. In all the experiments the concentration of reactants and products was monitored by UV–visible spectroscopy using Cary 1 and Shimadzu CPS-260 spectrophotometers. The disappearance of the starting material during photolysis was monitored to less than 15% of reaction such that interference of subsequent photochemical reactions can be eliminated. A constant reaction/irradiation time and incident light intensity were selected for a particular irradiation wavelength in order that the thermal component of the observed quantum yield contributes linearly and does not overrule the latter. The photosubstitution quantum yields were corrected for inner filter effects,³⁸ and the value of ΔV_ϕ^\ddagger was determined from the plot of $\ln \phi$ vs pressure according to the equation $(\delta \ln \phi / \delta p)_T = -\Delta V_\phi^\ddagger / RT$. The thermal substitution reaction was studied in parallel under the same conditions as described in this section, except that the reaction was carried out in the dark.

Results and Discussion

Spectral Characterization. We found direct evidence for competitive photochemical and thermal substitution reactions of $(\text{CO})_4\text{M}(\mu\text{-PMD})_2\text{M}(\text{CO})_4$ ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$) at ambient temperature, in particular at high nucleophile concentration and during MLCT excitation. Detailed spectral studies were undertaken on substitution reactions of $(\text{CO})_4\text{Mo}(\mu\text{-PMD})_2\text{Mo}(\text{CO})_4$ in toluene containing bpy and phen, during photolysis at 366, 403, and 486 nm and at 293 K. The overall substitution reaction can be summarized as shown in (1).¹⁰ The



diimine = bpy, phen

starting material shows a strong MLCT band at 469 nm and a weak MC band at 354 nm. Irradiation at 486 nm in the presence of 0.05 M bpy affords a spectrum with isosbestic points at 338, 385, 499, and 548 nm (see Figure 1) and a new band at 494 nm due to $\text{Mo}(\text{CO})_4\text{bpy}$. This reaction is accompanied by a color change from brown-yellow to pale red. During irradiation at higher

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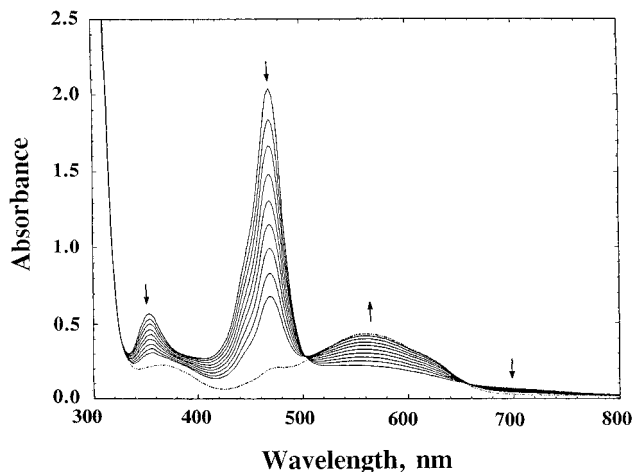
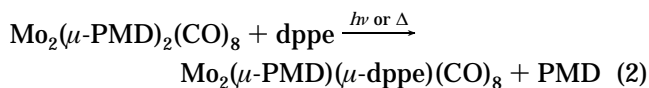


Figure 2. UV-vis absorption spectra recorded during the irradiation of 3.90×10^{-5} M $\text{Mo}_2(\mu\text{-PMD})_2(\text{CO})_8$ and 0.009 M dppe in toluene at 486 nm and 293 K.

energy (403 and 366 nm), isosbestic points evident early in the reaction are lost during subsequent irradiation, indicating that MC excitation is complicated by subsequent reactions. Similar measurements in 0.009 M phen showed clean isosbestic points for all three excitation wavelengths. Thus, ligand substitution by phen is affected little by subsequent reactions, even during longer irradiation time at 366 nm. The overall spectral changes are very similar to those found for bpy as entering ligand. This result is not surprising, since monodentate phen complexes will chelate more rapidly than bpy complexes.^{39,40}

Typical spectral changes observed during the irradiation of $(\text{CO})_4\text{Mo}(\mu\text{-PMD})_2\text{Mo}(\text{CO})_4$ in the presence of dppe at 486 nm are shown in Figure 2. Similar results were obtained during irradiation at 366 and 403 nm. The MLCT band shifts from 470 to 560 nm, the solution color changes to purple, and some evidence for the onset of secondary reactions is observed during extensive irradiation. The last effect shows up more clearly during irradiation at 366 nm. An identical final spectrum is also obtained when the reaction is conducted thermally under identical conditions. The observed spectral changes and subsequent decomposition can, on the basis of what has been reported for the corresponding Cr-dppm complex (dppm = 1,2-bis(diphenylphosphino)methane), be assigned to the displacement of one bridging PMD ligand as shown in (2).^{11,41,42} A number



of experiments were performed on an equimolar ($\sim 10^{-3}$ M) mixture of $\text{Mo}_2(\mu\text{-PMD})_2(\text{CO})_8$ and dppe. Under these conditions new bands appeared at 486 and 509 nm, which can be assigned to the intermediate formation of $\text{Mo}_2(\mu\text{-PMD})_2(\text{dppe})(\text{CO})_7$ by comparison with the analogous Cr compound.¹⁰ Further decomposition can

produce $\text{Mo}(\text{CO})_4(\text{dppe})$.^{43,44} These species may participate as intermediates and/or account for the secondary reactions under the conditions selected for all subsequent measurements, i.e. those adopted in Figure 2.

Effect of Concentration on Quantum Yields. In the absence of light a slow thermal reaction occurred, and we therefore had to separate the contributions of the photochemical and thermal reactions to the overall reaction.

The dependence of the quantum yield for a photosubstitution reaction on the concentration of the entering ligand was shown to be crucial in distinguishing between the mechanisms of LF and MLCT photochemistry.^{18,19,45-47} We have therefore measured this dependence also in the present system by following both MC and MLCT excitation at 366 and 436 nm, respectively. The results for reaction (1) are summarized in Tables 1 and 2, for which the overall apparent quantum yields were measured by irradiation with typical light intensities in the range of 10^{-6} – 10^{-7} einstein min^{-1} . The reaction of $\text{Mo}_2(\mu\text{-PMD})_2(\text{CO})_8$ with bpy demonstrates that the main photochemical changes are accompanied by a thermal reaction that becomes important at higher concentrations of bpy and during MLCT excitation (see Table 1 and Figure 3). The intercept in Figure 3 illustrates the contribution arising from a dissociative "D" photochemical reaction, whereas both ϕ and Δ_{therm} (the contribution of the thermal component to quantum yield observed is measured as a function of reaction time, incident light intensity, and pressure applied) depend linearly on the bpy concentration. The observed slight increase in ϕ with increasing [bpy] results from the partial MC \rightarrow MLCT conversion, i.e. the population of the MLCT state. As the excitation enters into the range of the MLCT band at 436 nm, ϕ shows a stronger [bpy] dependence which indicates the importance of an associative mechanism in going from MC to MLCT excitation (see Table 1). No significant intercept is observed, since MC excitation is suppressed under these conditions.

For the reaction of $\text{Mo}_2(\mu\text{-PMD})_2(\text{CO})_8$ with phen and dppe, the plots of ϕ_{app} and ϕ versus nucleophile concentration are given in Figures 4–6, respectively, from which it can be seen that the plots are linear over the investigated concentration range. Similar results for the reaction with phen and with dppe, compared to those for bpy, were obtained during irradiation at 366 nm; i.e., a significant intercept and a linear dependence on the entering ligand concentration (Figures 3 and 5) were obtained. All reactions investigated exhibited a substantial increase in ϕ with increasing ligand concentration and no significant intercept during excitation at 436 nm (see Figures 4 and 6). Thus, MLCT excitation at 436 nm favors an associative substitution process as compared to a dissociative substitution reaction upon MC excitation.

The dependence of the measured photosubstitution quantum yield on [L] is expected to follow eq 3 for MC

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(42) This assignment is based on the large, full half-width of the MLCT band (4300 cm^{-1} at 562 nm^{41}). In contrast to this, the alternative product $\text{Mo}_2(\mu\text{-PMD})_2(\mu\text{-dppe})(\text{CO})_6$ has only a full half-width of 1800 cm^{-1} at 552 nm^{41} .

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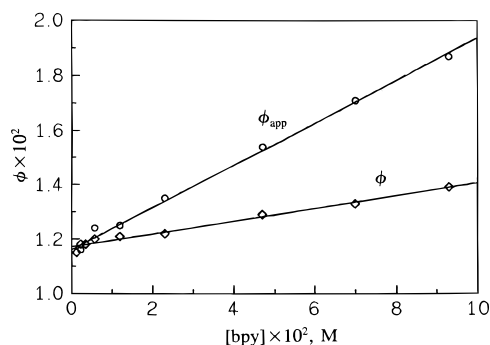
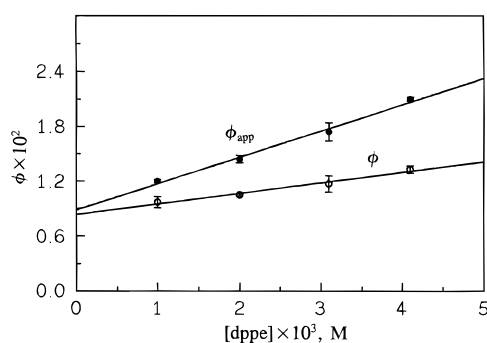
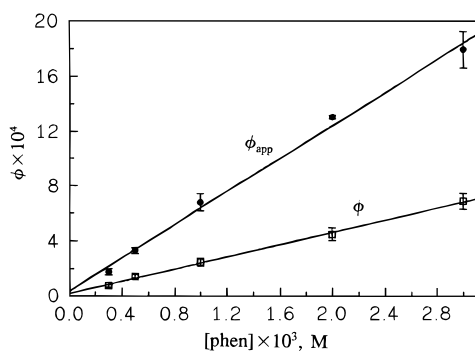
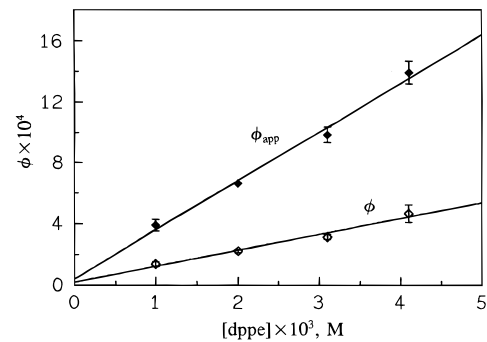
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Table 1. Concentration Dependence of the Quantum Yield for the Disappearance of Reactant during the Reaction of $\text{Mo}_2(\mu\text{-PMD})_2(\text{CO})_8$ with 2,2'-Bipyridine in Toluene at 288 K^a

[bpy], M	$\lambda_{\text{irr}} = 366 \text{ nm}$			$\lambda_{\text{irr}} = 436 \text{ nm}$		
	$10^2\phi_{\text{app}}$	$10^2\phi$	$10^2\Delta_{\text{therm}}$	$10^4\phi_{\text{app}}$	$10^4\phi$	$10^4\Delta_{\text{therm}}$
0.0012	1.15 ± 0.05	1.15 ± 0.02	0.00 ± 0.03			
0.0023	1.16 ± 0.10	1.18 ± 0.01	-0.02 ± 0.09			
0.0035	1.18 ± 0.03	1.18 ± 0.05	0.00 ± 0.02			
0.0058	1.24 ± 0.00	1.20 ± 0.02	0.04 ± 0.02	1.03 ± 0.03	0.53 ± 0.01	0.50 ± 0.04
0.012	1.25 ± 0.08	1.21 ± 0.08	0.04 ± 0.00	1.58 ± 0.03	0.84 ± 0.10	0.74 ± 0.07
0.023	1.35 ± 0.00	1.22 ± 0.01	0.13 ± 0.01	3.08 ± 0.15	1.52 ± 0.07	1.56 ± 0.08
0.047	1.54 ± 0.10	1.29 ± 0.03	0.25 ± 0.07	5.93 ± 0.16	2.67 ± 0.20	3.26 ± 0.36
0.070	1.71 ± 0.02	1.33 ± 0.02	0.38 ± 0.04	8.56 ± 0.43	3.83 ± 0.27	4.73 ± 0.16
0.093	1.87 ± 0.01	1.39 ± 0.04	0.48 ± 0.03	11.29 ± 0.16	5.12 ± 0.03	6.17 ± 0.19

^a $[\text{Mo}_2(\mu\text{-PMD})_2(\text{CO})_8] = 4.15 \times 10^{-5} \text{ M}$.**Table 2. Concentration Dependence of the Quantum Yield for the Disappearance of Reactant during the Reaction of $\text{Mo}_2(\mu\text{-PMD})_2(\text{CO})_8$ with 1,10-Phenanthroline in Toluene at 288 K^a**

[phen], M	$\lambda_{\text{irr}} = 366 \text{ nm}$			$\lambda_{\text{irr}} = 436 \text{ nm}$		
	$10^2\phi_{\text{app}}$	$10^2\phi$	$10^2\Delta_{\text{therm}}$	$10^4\phi_{\text{app}}$	$10^4\phi$	$10^4\Delta_{\text{therm}}$
0.0003	1.12 ± 0.06	1.03 ± 0.04	0.09 ± 0.02	1.76 ± 0.22	0.76 ± 0.10	1.00 ± 0.12
0.0005	1.35 ± 0.05	1.22 ± 0.07	0.13 ± 0.02	3.29 ± 0.21	1.44 ± 0.13	1.85 ± 0.08
0.001	1.65 ± 0.03	1.31 ± 0.01	0.34 ± 0.04	6.79 ± 0.63	2.47 ± 0.27	4.32 ± 0.36
0.002	1.94 ± 0.11	1.36 ± 0.10	0.58 ± 0.01	13.04 ± 0.12	4.48 ± 0.46	8.56 ± 0.58
0.003	2.34 ± 0.04	1.37 ± 0.07	0.97 ± 0.11	17.94 ± 1.32	6.89 ± 0.57	11.05 ± 0.75

^a $[\text{Mo}_2(\mu\text{-PMD})_2(\text{CO})_8] = 3.96 \times 10^{-5} \text{ M}$.**Figure 3.** ϕ_{app} and ϕ as a function of [bpy] for the photosubstitution of $\text{Mo}_2(\mu\text{-PMD})_2(\text{CO})_8$ at 366 nm and 288 K.**Figure 5.** ϕ_{app} and ϕ as a function of [dppe] for the photosubstitution of $\text{Mo}_2(\mu\text{-PMD})_2(\text{CO})_8$ at 366 nm and 288 K.**Figure 4.** ϕ_{app} and ϕ as a function of [phen] for the photosubstitution of $\text{Mo}_2(\mu\text{-PMD})_2(\text{CO})_8$ at 436 nm and 288 K.**Figure 6.** ϕ_{app} and ϕ as a function of [dppe] for the photosubstitution of $\text{Mo}_2(\mu\text{-PMD})_2(\text{CO})_8$ at 436 nm and 288 K.

excitation, where ϕ (MC) is the quantum yield resulting

$$\begin{aligned} \phi_{\text{app}}(\text{MC}) &= \Delta_{\text{therm}} + \phi \\ &= \Delta_{\text{therm}} + \phi(\text{MC}) + P_{\text{MC-MLCT}}[\text{L}] \end{aligned} \quad (3)$$

from the dissociative contribution, i.e. the intercept of the plots, L is the entering ligand (bpy, phen, and dppe), and $P_{\text{MC-MLCT}}$ is the contribution of the population of MLCT to $\phi_{\text{app}}(\text{MC})$, i.e. the slope of the plots. Upon

MLCT excitation, the total observed quantum yield is given by eq 4, where the proportionality factor B_{MLCT}

$$\begin{aligned} \phi_{\text{app}}(\text{MLCT}) &= \Delta_{\text{therm}} + \phi \\ &= \Delta_{\text{therm}} + B_{\text{MLCT}}[\text{L}] \end{aligned} \quad (4)$$

relates quantum yield to the nucleophile concentration and represents the slope of the plots in Figures 4 and 6. It should be kept in mind throughout that the

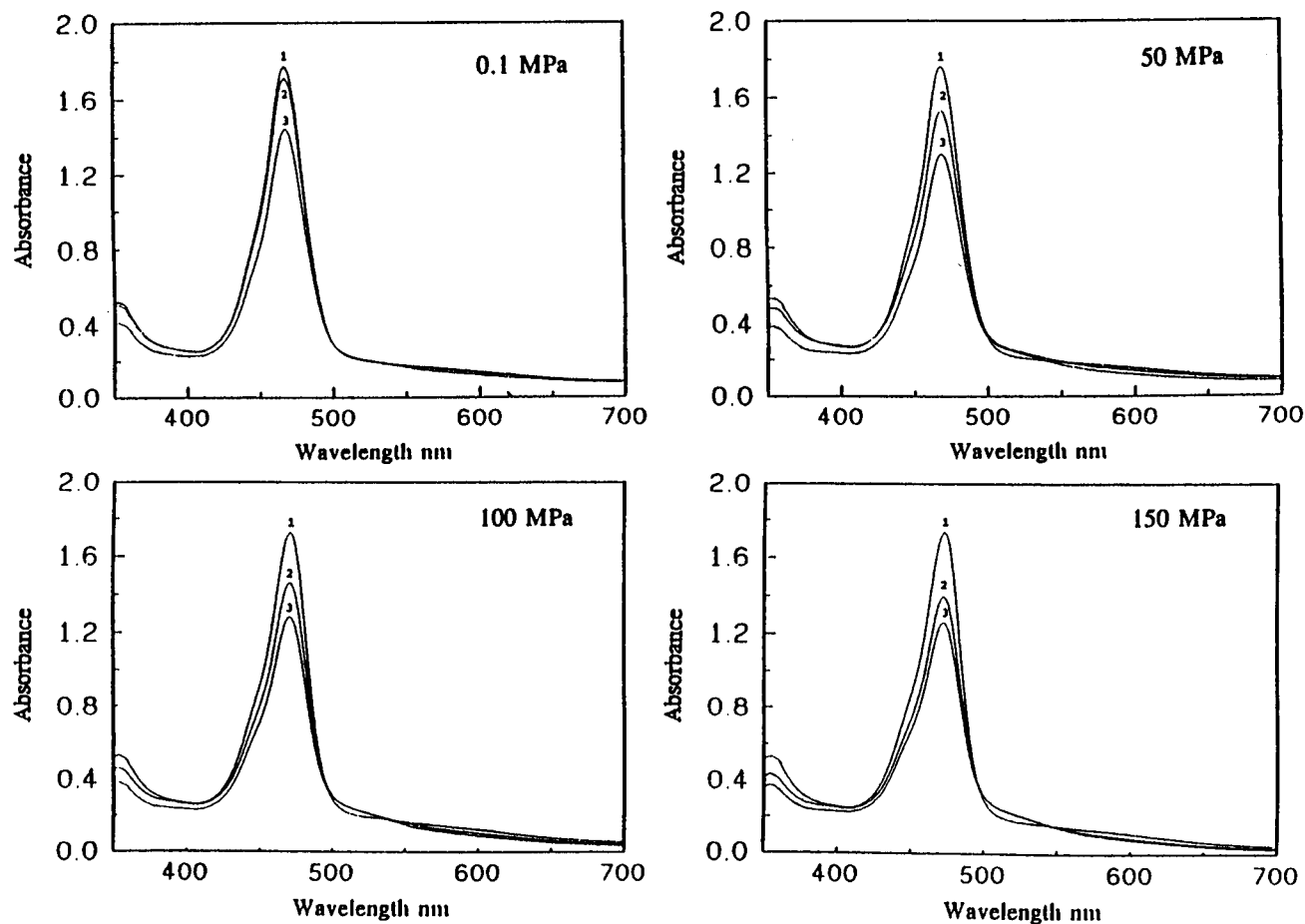


Figure 7. Spectral changes accompanying the photochemical and thermal reactions of $\text{Mo}_2(\mu\text{-PMD})_2(\text{CO})_8$ in toluene containing 0.002 M phen at 288 K as a function of pressure: (curve 1) initial spectrum; (curve 2) spectrum recorded after thermal reaction only; (curve 3) spectrum recorded after 5 min photolysis at 366 nm.

thermal contribution, Δ_{therm} , also exhibits a linear concentration dependence under all conditions.

It follows that the quantum yield for parallel reaction pathways of competing dissociative and associative reactions resulting from MC and MLCT excitation is given by eq 5. In order to obtain more detailed informa-

$$\begin{aligned} \phi_{\text{app}} &= \phi_{\text{app}}(\text{MC}) + \phi_{\text{app}}(\text{MLCT}) \\ &= \Delta_{\text{therm}} + \phi(\text{MC}) + P_{\text{MC} \rightarrow \text{MLCT}}[\text{L}] + B_{\text{MLCT}}[\text{L}] \quad (5) \end{aligned}$$

tion on the nature of the primary photosubstitution process, the dependence of the quantum yields, ϕ , on applied pressure was investigated for the reaction systems. The sign and magnitude of the activation volume, ΔV^\ddagger , are more likely to reveal the nature of the ligand substitution mechanism.^{48–52}

Pressure Dependence of Quantum Yield. The photosubstitution reactions (1) and (2) were studied as a function of pressure at temperatures where the thermal component can be separated and correction made for it. In general, a series of parallel dark reactions were performed under conditions identical

with those selected for the photochemical reactions. A typical series of spectra recorded for the reaction of $\text{Mo}_2(\mu\text{-PMD})_2(\text{CO})_8$ with phen in toluene as a function of pressure is reported in Figure 7. The spectra clearly show that the thermal component increases with increasing pressure, whereas the photochemical component (irradiation at 366 nm) clearly decreases with increasing pressure. Thus, the competition between thermal and photochemical reactions becomes more severe at higher pressure. Similar results were found for the reactions with bpy and dppe during the irradiation at 366 nm. A typical example of the relative absorbance changes as a function of pressure for the reaction of $\text{Mo}_2(\mu\text{-PMD})_2(\text{CO})_8$ with bpy is given in Figure 8. The general trend of pressure acceleration of the thermal reaction and pressure deceleration of the photochemical reaction shown in Figures 7 and 8 suggests that the thermal substitution process follows an associative reaction mode, whereas the photochemical reaction follows a dissociative reaction mode.

A more detailed analysis of the data can be obtained from the calculated quantum yields ϕ_{app} and ϕ , summarized as a function of pressure in Tables 3 and 4. Typical plots of $\ln \phi$ versus pressure for the reaction with dppe under similar conditions (irradiation at 366 nm) are reported in Figure 9, from which it follows that such plots are linear within the experimental error limits. The calculated apparent volumes of activation are included in Tables 3 and 4 and summarized for all experimental conditions employed in Table 5. MC

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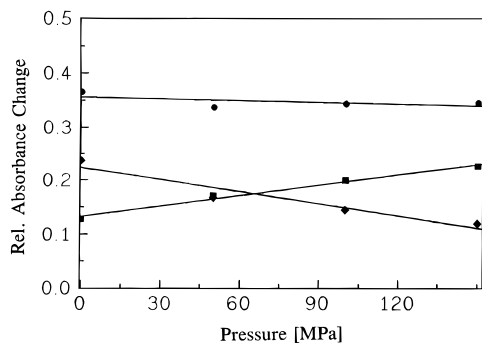


Figure 8. Plots of relative absorbance changes for the photolysis of $\text{Mo}_2(\mu\text{-PMD})_2(\text{CO})_8$ in toluene containing 0.07 M bpy at 366 nm and 288 K as a function of pressure: (filled circle) total reaction; (filled square) thermal reaction; (filled diamond) photoreaction, irradiation 4 min.

Table 3. Disappearance Quantum Yield for the Reaction of $\text{Mo}_2(\mu\text{-PMD})_2(\text{CO})_8$ with 1,10-Phenanthroline as a Function of Pressure in Toluene at 366 nm and 288 K

pressure, MPa	[phen] = 0.0005 M ^a		[phen] = 0.002 M ^b	
	$10^2\phi_{\text{app}}$	$10^2\phi$	$10^2\phi_{\text{app}}$	$10^2\phi$
0.1	1.35 ± 0.07	1.22 ± 0.07	1.94 ± 0.11	1.36 ± 0.10
50	1.25 ± 0.06	0.87 ± 0.06	2.42 ± 0.14	1.15 ± 0.07
100	1.18 ± 0.06	0.78 ± 0.05	2.34 ± 0.16	0.91 ± 0.03
150	0.93 ± 0.05	0.57 ± 0.04	2.50 ± 0.10	0.69 ± 0.05
$\Delta V_{\phi}^{\ddagger}$, $\text{cm}^3 \text{mol}^{-1}$	+5.6 ± 1.4	+11.5 ± 1.5	-3.5 ± 1.7	+10.9 ± 0.8

^a $[\text{Mo}_2(\mu\text{-PMD})_2(\text{CO})_8] = 3.32 \times 10^{-5} \text{ M}$. ^b $[\text{Mo}_2(\mu\text{-PMD})_2(\text{CO})_8] = 3.11 \times 10^{-5} \text{ M}$.

Table 4. Disappearance Quantum Yield for the Reaction of $\text{Mo}_2(\mu\text{-PMD})_2(\text{CO})_8$ with 2,2'-Bipyridine as a Function of Pressure in Toluene at 366 nm and 288 K^a

pressure, MPa	[bpy] = 0.0012		[bpy] = 0.070	
	$10^2\phi_{\text{app}}$	$10^2\phi$	$10^2\phi_{\text{app}}$	$10^2\phi$
0.1	1.15 ± 0.05	1.15 ± 0.02	1.71 ± 0.02	1.33 ± 0.02
50	0.83 ± 0.01	0.83 ± 0.01	1.58 ± 0.03	0.93 ± 0.00
100	0.64 ± 0.01	0.63 ± 0.01	1.60 ± 0.08	0.81 ± 0.03
150	0.55 ± 0.01	0.53 ± 0.01	1.59 ± 0.01	0.66 ± 0.02
$\Delta V_{\phi}^{\ddagger}$, $\text{cm}^3 \text{mol}^{-1}$	+11.9 ± 1.3	+12.5 ± 1.2	+1.0 ± 0.7	+10.7 ± 1.5

^a $[\text{Mo}_2(\mu\text{-PMD})_2(\text{CO})_8] = 3.48 \times 10^{-5} \text{ M}$.

irradiation (366 nm) results in significantly positive $\Delta V_{\text{photo}}^{\ddagger}$ values of $+11.5 \pm 1.5$ and $+10.9 \pm 0.8 \text{ cm}^3 \text{mol}^{-1}$ for the substitution of $\text{Mo}_2(\mu\text{-PMD})_2(\text{CO})_8$ by phen according to reaction 1 (see Table 3), independent of the selected [phen]. At the lower concentration of phen less interference of the thermal reaction is observed (see Tables 2 and 3), whereas at the higher concentration the thermal reaction contributes to such an extent that ϕ_{app} exhibits an overall negative volume of activation. From the difference $\phi_{\text{app}} - \phi$, the pressure dependence of Δ_{therm} can be calculated, which results in ΔV^{\ddagger} values of ca. $-15 \pm 5 \text{ cm}^3 \text{mol}^{-1}$. The data for bpy as entering ligand (Table 4) exhibit similar trends. At low [bpy], ϕ_{app} and ϕ exhibit a similar pressure dependence because only a minor thermal component is observed under such conditions. However, at higher [bpy], ϕ exhibits a pressure dependence similar to that at low [bpy], but ϕ_{app} exhibits almost no pressure dependence. This means that the pressure acceleration of the thermal component almost compensates the pressure de-

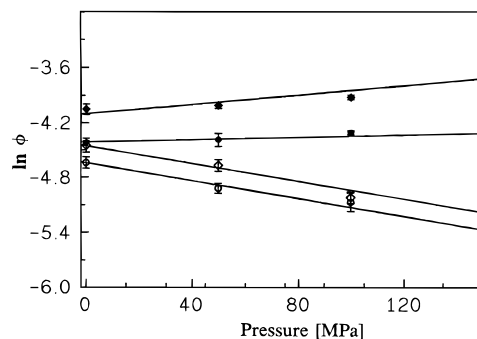


Figure 9. Plots of $\ln \phi_{\text{app}}$ and $\ln \phi$ versus pressure as a function of [dppe] for photolysis of $\text{Mo}_2(\mu\text{-PMD})_2(\text{CO})_8$ in toluene at 366 nm and 288 K: (filled circle) total reaction; (open circle) photoreaction, [dppe] = 0.001 M; (filled diamond) total reaction; (open diamond) photoreaction, [dppe] = 0.003 M.

Table 5. Volumes of Activation for Photosubstitution of the $\text{Mo}_2(\mu\text{-PMD})_2(\text{CO})_8$ Complex by the Bidentate L-L in Toluene at Different Excitation Wavelengths

λ_{irr} , nm	L-L	[L-L], M	$10^5[\text{M}]$, M	$\Delta V_{\text{app}}^{\ddagger}$, $\text{cm}^3 \text{mol}^{-1}$	$\Delta V_{\text{photo}}^{\ddagger}$, $\text{cm}^3 \text{mol}^{-1}$
366 ^a	bpy	0.0012	3.48	+11.9 ± 1.3	+12.5 ± 1.2
		0.070	3.48	+1.0 ± 0.7	+10.7 ± 1.5
		0.00050	3.32	+5.6 ± 1.4	+11.5 ± 1.5
	phen	0.0020	3.31	-3.5 ± 1.7	+10.9 ± 0.8
		0.0010	3.69	-1.6 ± 0.8	+11.8 ± 1.2
		0.0030	3.21	-6.0 ± 1.6	+11.5 ± 1.5
436 ^b	bpy	0.070	3.48	-12.0 ± 1.6	-3.4 ± 2.0
	phen	0.0020	3.48	-11.4 ± 1.4	-6.3 ± 0.9

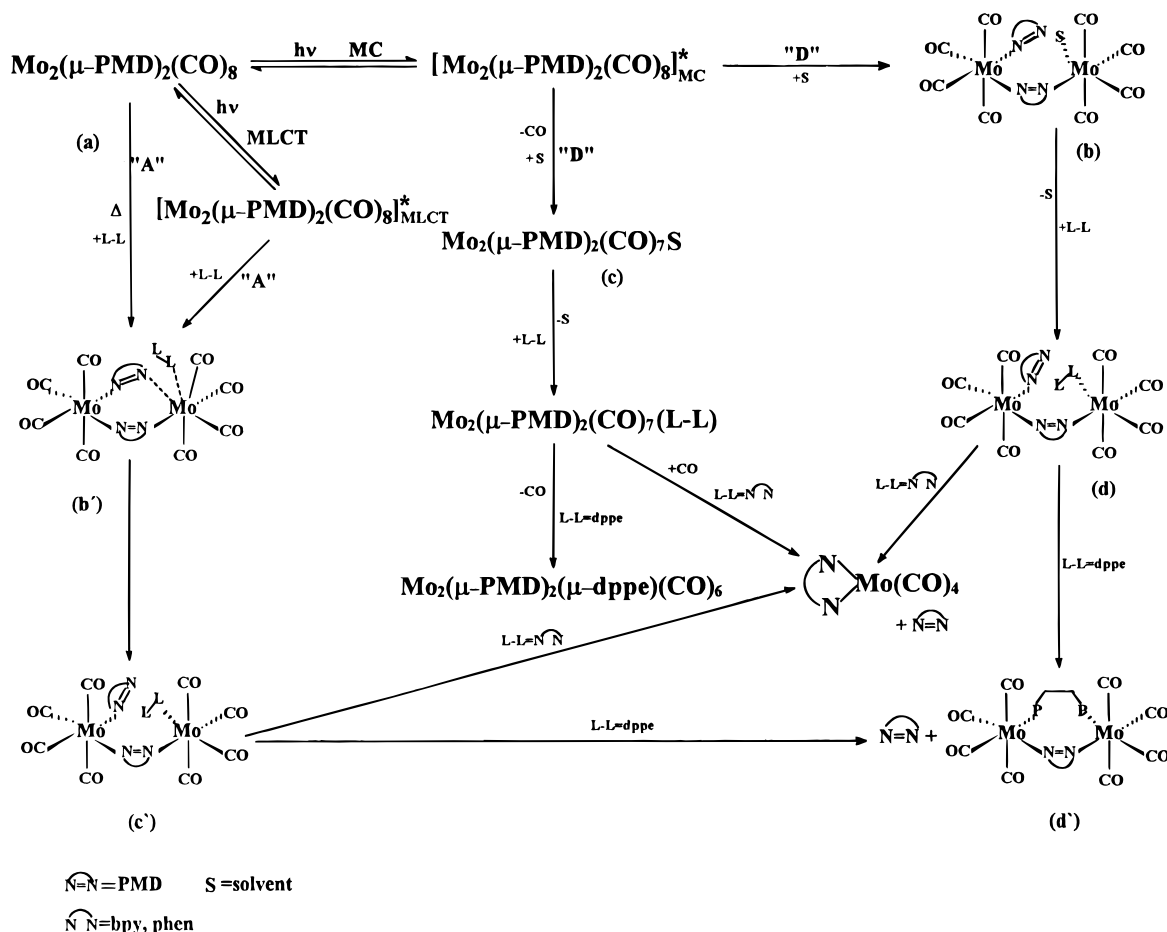
^a $T = 288 \text{ K}$. ^b $T = 278 \text{ K}$.

celeration of the photochemical component under such conditions. The resulting ΔV^{\ddagger} value for Δ_{therm} is $-13.8 \pm 3.0 \text{ cm}^3 \text{mol}^{-1}$. In a separate series of experiments the thermal substitution reactions (1) were studied and spectral changes similar to those reported for the photochemical reactions were observed. The first-order observed rate constants as a function of pressure are summarized in Table 6. The corresponding volumes of activation, viz -12.4 ± 1.0 and $-14.5 \pm 0.6 \text{ cm}^3 \text{mol}^{-1}$ for substitution by phen and bpy, respectively, could be determined more accurately and are in close agreement with those obtained in the indirect manner as outlined above. These values clearly underline our earlier qualitative interpretation, viz. the thermal substitution reaction (1) follows an associative mechanism, whereas the photochemical reaction exhibits an apparent dissociative character (see below).

Similar results were found for reaction 2, as shown in Table 5 for irradiation at 366 nm. The positive $\Delta V_{\text{photo}}^{\ddagger}$ values are very similar to those reported above for reaction 1, whereas the overall negative values for $\Delta V_{\text{app}}^{\ddagger}$ (especially at higher [dppe]) indicate a strong negative contribution from $\Delta V_{\text{therm}}^{\ddagger}$ amounting to ca. $-20 \pm 5 \text{ cm}^3 \text{mol}^{-1}$. The direct measurement of the thermal reaction (Table 6) resulted in a $\Delta V_{\text{therm}}^{\ddagger}$ value of $-18.4 \pm 0.8 \text{ cm}^3 \text{mol}^{-1}$, which is in good agreement with the indirectly determined value given above. These values are more negative than those found for reaction 1, which must be due to the increased bulk (i.e. partial molar volume) of dppe as compared with bpy and phen. It follows that the results for MC excitation of all three systems, summarized in Table 5, are indeed

Table 6. First-Order Rate Constants ($\times 10^4, \text{s}^{-1}$) for the Thermal Substitution Reaction (1) Measured as a Function of Pressure at 298 K

L	[L], M	pressure, MPa				$\Delta V^\ddagger, \text{cm}^3 \text{mol}^{-1}$
		0.1	50	100	150	
bpy	0.101	3.61 ± 0.01	5.05 ± 0.01	6.75 ± 0.01	8.70 ± 0.01	-14.5 ± 0.6
phen	0.0021	2.96 ± 0.01	4.12 ± 0.01	5.11 ± 0.03	6.33 ± 0.06	-12.4 ± 1.0
dppe	0.0021	1.75 ± 0.01	2.65 ± 0.01	3.86 ± 0.01	5.30 ± 0.01	-18.4 ± 0.8

Scheme 1

very similar and reveal the same mechanistic information for both reactions 1 and 2.

It is in general more complicated to perform similar measurements for MLCT excitation due to the significantly lower quantum yield and as a result of the more marked interference by the parallel thermal substitution process. The reactions were therefore performed at 278 K instead of 288 K, and the results for reaction 1 are included in Table 5. For both bpy and phen the values of $\Delta V^\ddagger_{\text{photo}}$ are significantly negative, in contrast to the positive values found for MC excitation. This suggests that MLCT excitation can result in an associative substitution reaction, which is in agreement with the concentration dependences observed under such conditions (see Tables 1 and 2 and Figures 4 and 6) and earlier findings on MLCT photostitution of molybdenum carbonyl complexes.^{16–19} The thermal reactions under such conditions contribute in a way similar to that during MC excitation such that $\Delta V^\ddagger_{\text{app}}$ becomes as negative as -12.5 ± 1.6 and $-14.3 \pm 1.6 \text{ cm}^3 \text{mol}^{-1}$ for phen and bpy, respectively, which mainly represent the strong thermal contributions under such conditions. The results for MLCT excitation suggest that the photosub-

stitution reactions follow an associative mechanism similar to that for the parallel thermal substitution reaction.

Mechanism of Ligand Substitution. The reported results demonstrate how the effect of entering ligand concentration and pressure can be employed to differentiate between the mechanism of thermal and photochemical substitution reactions of the studied dimetallacycle. It is not surprising that MC excitation leads to a weakening of the metal–ligand bonds, i.e. Mo–CO and Mo–N=N, and favors a dissociative mechanism. The significant intercept of the plots of quantum yield versus nucleophile concentration and the positive volumes of activation found under such conditions indicate the operation of a dissociative mechanism. The volumes of activation reported for ϕ under such conditions are in good agreement with those reported earlier for related processes.^{16–19} The details of this reaction route, via the release of PMD to produce $\text{Mo}(\text{CO})_4(\text{L-L})$ (L-L = bpy, phen) or via the release of CO to produce $\text{Mo}_2(\mu\text{-PMD})_2(\mu\text{-dppe})(\text{CO})_6$ and via the substitution of PMD to produce $\text{Mo}_2(\mu\text{-PMD})_2(\mu\text{-dppe})(\text{CO})_8$, are shown in Scheme 1. The initial dissociation of CO or PMD

must be rate-determining to account for the positive volume of activation. This is then followed by a series of fast subsequent reactions, leading to the detected products.

The increase of reaction efficiency with increasing nucleophile concentration observed throughout for the thermal reaction, to a minor degree for MC excitation, but to a larger degree for MLCT excitation, can be interpreted in terms of strong evidence for an associative substitution mechanism for both the thermal and MLCT substitution processes. In addition, the activation volumes for these processes are all significantly negative and further underline the validity of this conclusion. The fact that $\Delta V_{\text{therm}}^\ddagger$ is more negative for the reaction with dppe, as compared with the values for bpy and phen, further underlines the associative character. During MC excitation at higher nucleophile concentrations, population of the lower lying MLCT state can occur, which can account for the increase in quantum yield with increasing concentration of entering nucleophile. There are numerous examples known where molybdenum carbonyl complexes can undergo associative thermal and MLCT photochemical ligand substitution reactions.^{16–21} The suggested reaction paths to account for these observations are included in Scheme 1. Associative substitution leads to the formation of b', which via c' can lead to the reaction products depending on the nature of L-L. By way of comparison, dissociative substitution leads to b or c, which can react directly or indirectly with L-L to produce the same reaction products.

During MLCT excitation, electron density from the metal center is placed on the PMD ligand, such that the deficient electron density on the metal center will enable an associative nucleophilic attack to occur.^{53,54} Naturally, the possibility will be controlled by the

nature of the metal center, and it is to be expected that MLCT excitation in the case of the corresponding Cr complex will not lead to an associative reaction mode, on the basis of results reported for related systems.^{16–19}

The results of this study have been interpreted in terms of associative and dissociative substitution mechanisms, and no reference to the possible participation of interchange mechanisms was made. No evidence for the operation of an interchange mechanism was revealed by the studied concentration dependences. Furthermore, the absolute magnitude of the activation volumes is such that it supports the operation of limiting associative and dissociative mechanisms rather than interchange mechanisms.^{51,52}

We conclude that the nature of the competitive substitution mechanisms for photochemical (MC and MLCT excitation) and thermal activation of $\text{Mo}_2(\mu\text{-PMD})_2(\text{CO})_8$ in the presence of bpy, phen, and dppe can be unambiguously determined from a combination of incoming ligand concentration and pressure dependence data. Excitation of the higher energy MC state causes the substitution reaction to follow a dissociative reaction mode, in contrast to the associative reaction mode found for the thermal reaction and for excitation of the low-energy MLCT state.

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