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Photochemistry of (η^6-arene)Mo(CO)$_3$ and the Role of Alkane Solvents in Modifying the Reactions of Coordinatively Unsaturated Metal Carbonyl Fragments

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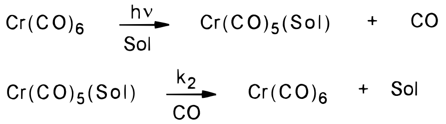
The reactions of (η^6-arene)Mo(CO)$_2$(Sol) and M(CO)$_5$(Sol) with CO have been studied in a range of alkane solvents (Sol), and the kinetic and activation parameters have been determined (M = Cr, Mo, or W). For M = Cr the $\Delta H^\ddagger$ is constant (22 ± 2 kJ mol^{-1}), while the $\Delta S^\ddagger$ term becomes less negative as the alkane chain length increases. For the larger metals the variation in kinetic and activation parameters is less significant. Solvent displacement by CO involves an interchange mechanism for the Cr system, while for Mo or W complexes the mechanism is more associative in character. The photochemistry of (η^6-arene)Mo(CO)$_3$ (arene = benzene, mesitylene, *p*-xylene, or hexamethylbenzene) compounds was investigated by laser flash photolysis, supported by matrix isolation and time-resolved infrared spectroscopy (TRIR). In contrast to the behavior to the analogous (η^6-arene)Cr(CO)$_3$, it is found that the efficiency for photochemical expulsion of CO from (η^6-mesitylene)Mo(CO)$_3$ is markedly wavelength dependent (Φ_{CO} = 0.587, 0.120, and 0.053 at 266, 313, and 334 nm, respectively).

Introduction

It has been known for some years that the reaction of 16-electron coordinatively unsaturated intermediates such as Cr(CO)$_5$ with CO is affected by alkane solvents.[2] For instance the second-order rate constant (k_2 in Scheme 1) in *n*-heptane is more than twice that measured in cyclohexane. In these systems the solvent molecule has been described as a "token ligand",[3] and the interaction between the "token ligand" and the metal center is described in terms of a two-electron three-center bond (M−H−C).[4] Obviously it is important to understand what influence these "token ligands" exert on reactivity, since coordinatively unsaturated species are implicated in a range of catalytic systems.[5] These two-electron three-center interactions have been structurally characterized by Kubas and co-workers,[6] and the molecular structure of Cr(CO)$_3$(P(cyclohexyl)$_3$)$_2$ has been determined by X-ray diffraction. This complex is formally coordinatively unsaturated. However, a hydrogen atom on the α-carbon of a cyclohexyl ligand occupies the sixth coordination site on the metal. While a comparison of the reactivity of M(CO)$_5$ species in alkane[7] and aromatic solvents has been reported,[8] no systematic investigation of the reactivity toward CO in a range of alkane solvents has been published to date. Arrhenius parameters for the CO-for-ethylene dissociative substitution of Cr(CO)$_5$(C$_2$H$_4$) have been evaluated in the gas phase in which the large preexponential factor is explained in terms of a loosening of the incipient translational and rotational degrees of freedom as the metal−olefin bond breaks.[9] It is likely that this phenomenon will be more significant in condensed phase reactions.

Scheme 1



Investigations into the (η^6-arene)Cr(CO)$_3$ systems showed that the reactivity of the primary photoproduct (η^6-arene)Cr(CO)$_2$(Sol) toward CO was also affected by the nature of the alkane solvent.[10] As with Cr(CO)$_5$, (η^6-arene)Cr(CO)$_2$(Sol) reacts with CO more than twice as fast in *n*-heptane as it does in cyclohexane.[11] Furthermore, (η^6-arene)M(CO)$_3$ systems allow a greater degree of steric control over the 16-electron intermediates by changes in the number and size of alkyl

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Table 1. Wavelength Dependence of Quantum Yield for CO Expulsion (Φ_{CO}) from (η^6-mesitylene)Mo(CO)$_3$

compd	λ_{exc} (nm)	Φ_{CO}
(η^6-mesitylene)Mo(CO)$_3$	266	0.587
(η^6-mesitylene)Mo(CO)$_3$	313	0.120
(η^6-mesitylene)Mo(CO)$_3$	334	0.053

substituents on the arene ligand. This work demonstrated the importance of the entropy term ($\Delta S^\ddagger$) in determining the magnitude of the second-order rate constants for the reactions of these 16-electron intermediates. No variation in the enthalpy of activation ($\Delta H^\ddagger$) was observed, irrespective of the substituents on the arene ring or the nature of the alkane solvent. The magnitude of the $\Delta H^\ddagger$ term for these reactions was approximately half that of ΔH_{M-Sol} in Cr(CO)$_5$(Sol) (24 ± 2 kJ mol^{-1} compared to 50 ± 5 kJ mol^{-1}).[12] The $\Delta S^\ddagger$ values for these systems are small and negative, and consequently, an interchange mechanism was proposed for the displacement of solvent by CO.

To assist with a fuller understanding of the mechanistic pathways available to these complexes, a systematic investigation of these systems was undertaken and the activation parameters associated with the reactions of M(CO)$_5$(Sol) with CO (M = Cr, Mo, or W) in a range of alkane solvents were measured. The investigation was extended to include the photochemistry of (η^6-arene)Mo(CO)$_3$ for comparison with the published data on the chromium system.[11] It was thought that the larger Mo and W compounds could access more associative mechanisms. However, it became apparent that the photochemistry of (η^6-arene)Mo(CO)$_3$ has not received a great deal of attention,[13] and preliminary experiments were required to identify the primary photoproduct and the efficiency with which it is produced. Matrix isolation and flash photolysis in combination with time-resolved infrared spectroscopy studies were undertaken. UV/vis flash photolysis was then used to measure the kinetic and activation parameters for the reactions of the photoproducts with CO. This work reveals for the first time a wavelength dependency for the efficiency of CO photoexpulsion from (η^6-arene)Mo(CO)$_3$, in marked contrast to the analogous chromium system.

Results

Quantum Yield Measurements. Quantum yield measurements for the photosubstitution of CO by L (L = pyridine or (*Z*)-cyclooctene (*z*-co)) in (η^6-mesitylene)-Mo(CO)$_3$ were performed in cyclohexane solution containing excess L using monochromatic irradiation (λ_{exc} = 266 nm (L = *z*-co) and λ_{exc} = 313 and 334 nm (L = pyridine)). Under these conditions the reactions proceed smoothly, and conversions of the starting material were driven to a maximum of 10% to minimize the effect of product absorption at the excitation wavelengths. The results are displayed in Table 1.

Matrix Isolation Studies. The CO stretching region of the IR spectrum of (η^6-mesitylene)Mo(CO)$_3$ in a methane matrix at 12 K consists of two bands at 1973 and 1900 cm^{-1}. Photolysis at λ_{exc} = 313 nm revealed the formation of two new bands at 1914 and 1861 cm^{-1}. This represents a respective shift of 59 and 39 cm^{-1} for the high- and low-energy bands relative to the parent ν_{CO} bands. These shifts are comparable to those observed following photolysis of (η^6-benzene)Cr(CO)$_3$ (57 and 43 cm^{-1}) in a similar matrix.[14] Furthermore evidence for free CO was observed at 2137 cm^{-1}. The bands at 1914 and 1861 cm^{-1} were assigned to the CO-loss fragment (η^6-mesitylene)Mo(CO)$_2$.

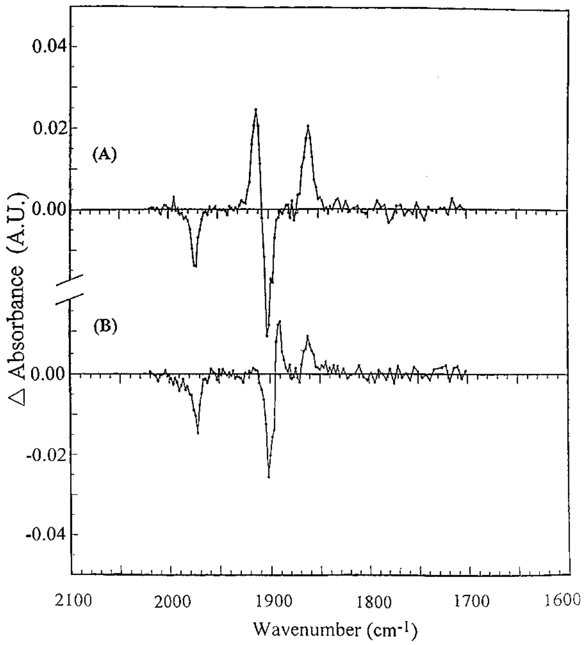

Figure 1. IR difference spectrum of a CO (9.0 mM) saturated cyclohexane solution of (η^6-mesitylene)Mo(CO)$_3$ (0.75 mM) recorded (A) 2 μs and (B) 180 μs after laser flash photolysis (λ_{exc} = 308 nm).

Time-Resolved Infrared Spectroscopy (TRIR). Reactions of (η^6-mesitylene)Mo(CO)$_2$(Sol) with CO. Flash photolysis experiments in combination with time-resolved IR spectroscopy in cyclohexane solution were carried out to identify the primary photoproduct of (η^6-mesitylene)Mo(CO)$_3$ in solution at ambient temperature. The transient difference spectrum recorded 2 μs after flash excitation (λ_{exc} = 308 nm) of (η^6-mesitylene)Mo-(CO)$_3$ (0.75 mM) in CO-saturated cyclohexane ([CO] = 9.0 mM) shows two strong positive absorptions at 1914 and 1860 cm^{-1} in addition to the depletion bands of the starting material at 1973 and 1900 cm^{-1} (Figure 1 and Table 2). These new features are readily assigned to the CO-loss product (η^6-mesitylene)Mo(CO)$_2$(Sol) (Sol = cyclohexane) by comparison with the respective low-temperature matrix data (Table 2). These bands decay within ca. 100 μs with concomitant formation of a new species attributed to a dinuclear compound of the type (η^6-arene)$_2$Mo$_2$(CO)$_5$ (for band positions see Table 2). However no bands in the bridging region (down to 1650 cm^{-1}) of the spectrum could be detected for this species presumably because of their low extinction coefficients. Similar dinuclear species have been reported following photolysis of other group 5,[15] 6,[16]and 7[17]carbonyl com-

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Table 2. Infrared and UV/Vis Spectroscopic Parameters for the Compounds in this Study

compd	ν_{CO}[a] (cm^{-1})	λ_{max} (nm)	ϵ (λ)[b]
$Cr(CO)_6$	1985	250	203 (355)
$Mo(CO)_6$	1985	298	266 (355)
$W(CO)_6$	1981	298	856 (355)
(η^6-benzene)$Mo(CO)_3$	1987, 1916	318	2180 (266)
(η^6-*p*-xylene)$Mo(CO)_3$	1976, 1905	328	2260 (266)
(η^6-mesitylene)$Mo(CO)_3$	1973, 1901	320	2908 (266)
(η^6-hexamethylbenzene)$Mo(CO)_3$	1959, 1884	330	3469 (266)
(η^6-mesitylene)$Mo(CO)_3$[c]	1973, 1900		
(η^6-mesitylene)$Mo(CO)_2(CH_4)$[c]	1914, 1861		
(η^6-mesitylene)$Mo(CO)_2(C_6H_{12})$[d]	1914, 1860		
(η^6-*p*-xylene)$Mo(CO)_2(C_6H_{12})$[d]	1916,1864		
(η^6-mesitylene)$_2Mo_2(CO)_5$[d]	1892, 1862, 1840(w)[e]		
(η^6-mesitylene)$Mo(CO)_2$(η^2-*z*-co)	1915, 1861		
(η^6-mesitylene)$Mo(CO)_2(P(OMe)_3)$	1907, 1854		

[a] Cyclohexane solution, ±1 cm^{-1}. [b] L mol^{-1} cm^{-1} ± 5%. [c] In a methane matrix at 12 K. [d] From TRIR experiments. [e] This band is observed only in the absence of added CO.

pounds. Concurrent with the formation of the dinuclear species the depleted parent absorptions recover to approximately 30% of their initial intensity. Thus unlike the chromium system, this system is not fully reversible on this time scale. However, the parent complex is regenerated fully with accompanying complete decay of the proposed dinuclear species on observing the spectral changes over a longer time scale (1.8 s). This was confirmed by the time dependence of the parent absorption at 1970 cm^{-1} when monitored on this time scale.

Reactions of (η^6-mesitylene)$Mo(CO)_2$(Sol) with the Parent Tricarbonyl and CO. Under similar conditions as above but under argon atmosphere, the parent bands similarly suffer depletion following excitation, followed by a slow regeneration over 300 μs. The two primary photoproduct bands were again observed, and these decayed on a time scale of 300 μs with the appearance of the IR bands assigned to the dinuclear species, albeit with a higher yield than that observed in the presence of CO. On observation of the changes over a longer time scale (1.8 s), the ν_{CO} bands of the dinuclear compound decline to ca. 50% of their maximum intensity with parallel regeneration of the starting material also by ca. 50%. In the presence of 9.0 mM CO the initial parent absorptions are regenerated over a 4 s time scale. The parent material is regenerated both by recombination of the primary photoproduct (η^6-mesitylene)$Mo(CO)_2$(Sol) with added CO and also by the decay of the dinuclear species.

Reactions of (η^6-mesitylene)$Mo(CO)_2$(Sol) in the Presence of Trapping Agents. In the presence of excess *z*-co (50 mM) under CO (9.0 mM) atmosphere, the photolysis of (η^6-mesitylene)$Mo(CO)_3$ (0.75 mM) resulted in the depletion of the parent tricarbonyl bands. Under these conditions no evidence for either further depletion or recovery of the parent compound was observed on the time scale of 200 μs. In these experiments the formation of the dinuclear species was completely suppressed, but the two bands assigned to the (η^6-arene)$Mo(CO)_2$(Sol) exhibited only a marginal reduction in their absorbances. These observations are explained by an efficient trapping of the dicarbonyl species by the *z*-co (reaction 1). Unfortunately, the ν_{CO} bands for the (η^6-arene)$Mo(CO)_2$(η^2-*z*-co) coincide with those of the (η^6-arene)$Mo(CO)_2$(Sol) bands (Figure 2, Table 2).

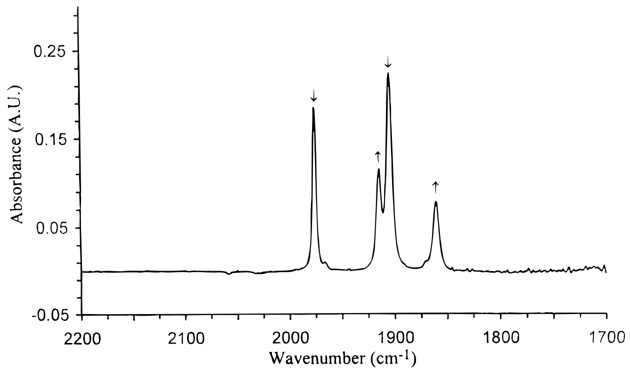

Figure 2. CO stretching vibrational spectrum of (η^6-mesitylene)$Mo(CO)_3$ following steady-state photolysis in the presence of excess *z*-co.

$$(\eta^6\text{-arene})Mo(CO)_2(Sol) \xrightarrow[L]{\Delta} (\eta^6\text{-arene})Mo(CO)_2(L) + Sol \quad (1)$$

In the presence of trimethyl phosphite ($P(OMe)_3$) in high concentration (30 mM) under conditions similar to those above, the photogenerated (η^6-mesitylene)$Mo(CO)_2$(Sol) is detected as a short-lived (15 μs) species. Its reaction with parent (η^6-mesitylene)$Mo(CO)_3$, leading to the formation of the dinuclear compound, is suppressed in favor of the trapping by the $P(OMe)_3$ ligand to give the persisting IR bands of the dicarbonyl product (Table 2).

TRIR Kinetic Experiments. Kinetic analysis of the signals obtained in the TRIR experiments yielded the second-order rate constant for the reaction of (η^6-mesitylene)$Mo(CO)_2$(Sol) with CO (2.1×10^6 M^{-1} s^{-1} at 298 K; Sol = cyclohexane; Table 3). The rate data obtained in this manner can be used to correlate the results of both the TRIR and the UV/vis flash photolysis experiments. UV/vis flash photolysis was subsequently used to evaluate both the kinetic and activation parameters associated with the reactions of the (η^6-arene)$Mo(CO)_2$(Sol) species.

UV/Vis Flash Photolysis Experiments. Determination of Activation Parameters for the Reaction of (η^6-arene)$Mo(CO)_2$(Sol) with CO. For these investigations an excitation wavelength of 266 nm was used because of the low quantum efficiency of CO loss following irradiation at 355 nm. The kinetic information was obtained from the recovery of the depleted parent absorption at 330 nm because the (η^6-arene)$Mo(CO)_2$(Sol) species do not absorb strongly in the visible region of the spectrum. Pseudo-first-order conditions were maintained as ([CO] ≫ (η^6-arene)$Mo(CO)_2$(Sol)), and k_{obs} were obtained from the slope of plots of $\ln(A_\infty - A_0)/(A_\infty - A_t)$ vs time as previously described.[11] A typical transient signal and first-order analysis are presented in Figure 3. The second-order rate constants (k_2) were calculated by plotting k_{obs} vs [CO]. Eyring plots were constructed using k_2 over a temperature

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Table 3. Kinetic and Activation Parameters for the Reaction of CO-Loss Intermediates with CO

intermediate	method	k_2[a]	$\Delta H^{\ddagger}$[b]	$\Delta S^{\ddagger}$[c]	Sol
Cr(CO)$_5$(Sol)	UV/vis	2.3	22	−46	cyclohexane
	UV/vis	3.5	24	−40	methylcyclohexane
	UV/vis	9.3	21	−42	*n*-heptane
	UV/vis	12	23	−29	*n*-decane
	UV/vis	24	24	−24	*n*-dodecane
Mo(CO)$_5$(Sol)	UV/vis	4.7	21	−48	cyclohexane
	UV/vis	7.8	21	−41	*n*-heptane
	UV/vis	8.8	21	−42	*n*-decane
W(CO)$_5$(Sol)	UV/vis	0.5	23	−60	cyclohexane
	UV/vis	1.8	20	−58	*n*-heptane
	UV/vis	1.1	21	−59	*n*-decane
(η^6-benzene)Mo(CO)$_2$(Sol)	UV/vis	1.5	24	−46	cyclohexane
(η^6-*p*-xylene)Mo(CO)$_2$(Sol)	UV/vis	1.6	23	−47	cyclohexane
(η^6-mesitylene)Mo(CO)$_2$(Sol)	UV/vis	1.8	23	−46	cyclohexane
(η^6-mesitylene)Mo(CO)$_2$(Sol)	TRIR	2.1[d]			cyclohexane
(η^6-mesitylene)Mo(CO)$_2$(Sol)	UV/vis	2.0	23	−46	*n*-heptane
(η^6-mesitylene)Mo(CO)$_2$(Sol)	UV/vis	2.5	25	−39	*n*-decane
(η^6-hexamethylbenzene)Mo(CO)$_2$(Sol)	UV/vis	2.1	23	−48	cyclohexane
(η^6-benzene)Cr(CO)$_2$(Sol)[e]	UV/vis	9.8	22	−37	cyclohexane
(η^6-benzene)Cr(CO)$_2$(Sol)[e]	UV/vis	28	26	−12	*n*-decane
(η^6-hexamethylbenzene)Cr(CO)$_2$(Sol)[e]	UV/vis	15	25	−26	cyclohexane

[a] $\times 10^{-6} \pm 10\%$ M^{-1} s^{-1} at 298 ± 2 K. [b] ±2 kJ mol^{-1}. [c] ±5 J mol^{-1} K^{-1}. [d] It should be noted that, under these conditions, formation of the dinuclear species is not fully suppressed and this rate constant is therefore a slight overestimate. [e] From ref 11.

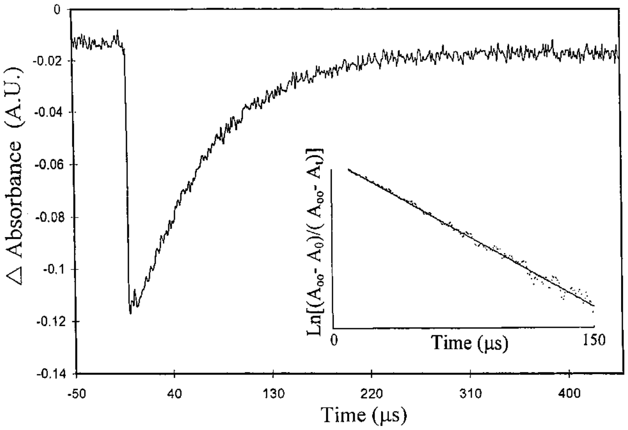

Figure 3. Typical transient signal showing the rapid depletion of the parent absorption monitored at 330 nm following laser pulse photolysis (λ_{exc} = 266 nm) of a cyclohexane solution of (η^6-hexamethylbenzene)Mo(CO)$_3$ (0.17 mM) and its subsequent recovery ([CO] = 7.0 mM). Inset: first-order analysis of the transient signal.

range 283−313 K depending on the solvent, providing the $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ terms for reaction 2 (Table 3).

$$(\eta^6\text{-arene})\text{Mo(CO)}_2\text{(Sol)} + \text{CO} \rightarrow (\eta^6\text{-arene})\text{Mo(CO)}_3 + \text{Sol} \quad (2)$$

Determination of Activation Parameters for the Reaction of M(CO)$_5$(Sol) with CO. The observed rate constants for the reaction of M(CO)$_5$ with CO was measured by analysis of the transient absorptions at 500, 420, or 450 nm corresponding to the λ_{max} of the appropriate M(CO)$_5$(Sol) (M = Cr, Mo, or W) species, following excitation at 355 nm.[16,18] Again pseudo-first-order conditions were maintained and the kinetic and activation parameters for reaction 3 were obtained in a manner similar to that of the (η^6-arene)Mo(CO)$_2$(Sol) system. The results are presented in Table 3.

$$\text{M(CO)}_5\text{(Sol)} + \text{CO} \rightarrow \text{M(CO)}_6 + \text{Sol} \qquad (3)$$

Discussion

Photochemical Studies. It is clear from matrix isolation and time-resolved IR experiments that CO loss is a primary photoprocess for (η^6-arene)Mo(CO)$_3$ compounds. The variation in the quantum yield for CO loss (Φ_{CO}) for this system (Table 1) contrasts to the behavior of (η^6-arene)Cr(CO)$_3$, in which the Φ_{CO} is constant at 0.7 ± 0.1 for excitation wavelengths between 436 and 313 nm (arene = benzene or mesitylene).[19,20] It is accepted that the absorption of these materials is dominated by metal-to-ligand charge transfer (MLCT) transitions.[21] Figure 4 contains the UV/vis ground-state absorption spectra of (η^6-mesitylene)W(CO)$_3$, (η^6-mesitylene)Mo(CO)$_3$, and (η^6-mesitylene)Cr(CO)$_3$ for comparison. In the spectra of both the Mo and W compounds a feature is observed on the low-energy side of the lowest energy absorption maximum at 320 nm (marked with an asterisk) while this feature is unresolved in the case of the chromium compound. The width at half-height of the 320 nm band for the W compound is approximately 24 nm compared to 40 nm in the case of the chromium analogue. This would indicate a greater degree of overlap of the individual transitions which comprise this band in the chromium compound which in turn may explain the differences in the photochemical behavior in going down the triad. The photochemistry of the molybdenum compound represents an intermediate stage in moving from a high Φ_{CO} for chromium to a low or zero Φ_{CO} for the tungsten compounds.

Until recently it has been assumed that CO loss occurs via a ligand field (LF) excited state;[22] however, recent calculations on Cr(CO)$_6$ indicate that CO loss follows MLCT excitation.[23] Evidence has also been presented which indicates that excited states resulting

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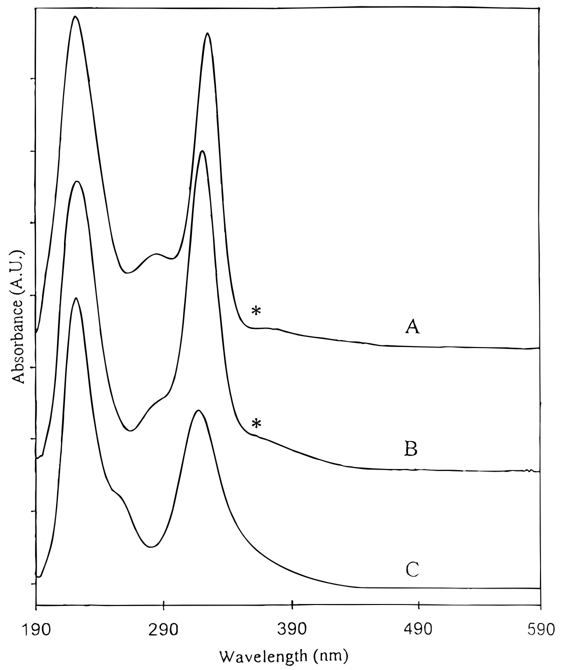

Figure 4. UV/vis spectra of (η^6-mesitylene)W(CO)$_3$ (A), (η^6-mesitylene)Mo(CO)$_3$ (B), and (η^6-mesitylene)Cr(CO)$_3$ (C) in cyclohexane. (Each division represents 0.5 AU.)

from MLCT excitation can undergo ligand exchange by associative mechanisms, whereas usually LF excited states react by way of dissociative processes.[24] While it may be possible that such an explanation may account for the variation in quantum yield for CO loss in the (η^6-arene)Mo(CO)$_3$ system, we believe that a more likely explanation for this observation is that two excited states, each with its own resultant photochemistry, are accessible for these systems similar to that observed for (η^6-pyridine)Cr(CO)$_3$.[25] In this system long-wavelength photolysis resulted in a ring slip process while short-wavelength photolysis was required to induce CO loss. In the case of (η^6-arene)Mo(CO)$_3$ compounds the photoinduced change in the arene hapticity is followed by a very rapid thermal reversal to the parent. However, an authoritative explanation for the behavior of the (η^6-arene)Mo(CO)$_3$ system with respect to CO loss must await accurate calculations on the excited-state dynamics of this system. Our results would suggest that there is either inefficient or no CO loss from the lowest energy excited state, and the higher excited states must be populated to induce expulsion of a carbonyl ligand.

Kinetic and Activation Parameters. Originally it was thought that the different reactivity in cyclic as opposed to linear alkanes was a reflection of a different interaction energy ($\Delta H_{\mathrm{M-Sol}}$) between the metal center and the solvent molecule.[26] A variety of methods have been used to estimate $\Delta H_{\mathrm{M-Sol}}$ for M(CO)$_5$(Sol) (M = Cr or W; Sol = alkane). These include equilibrium studies in the gas phase (M = W)[27] and time-resolved photoacoustic calorimetry (PAC) in condensed phases (M = Cr).[28] The former technique gave a value of 40 kJ mol^{-1} for $\Delta H_{\mathrm{M-Sol}}$ while the latter showed an apparent difference in $\Delta H_{\mathrm{M-Sol}}$ depending on the alkane. However, the quantitative results of the PAC experiments depend on an accurate estimate for the quantum yield (Φ_{CO}) of the photochemical process and the original assumption that Φ_{CO} was independent of the alkane solvent was subsequently found to be invalid.[12,28] The apparent variation in $\Delta H_{\mathrm{M-Sol}}$ was therefore the result of variations in the quantum yield of CO expulsion from the parent hexacarbonyl. The corrected values of Φ yield 50 ± 5 kJ mol^{-1} for $\Delta H_{\mathrm{Cr-Sol}}$. We have measured Φ_{CO} for the Cr(CO)$_6$ system in a range of alkane solvents. A value of 0.72 for linear alkanes compares to the published value of 0.67 for cyclohexane.[29]

Further insight into the mechanisms of solvent displacement reactions can be obtained from the kinetic and activation parameters derived from time-resolved experiments. The kinetic data presented in Table 3 demonstrates that a significant variation in k_2 is observed mainly for the chromium systems. Also the $\Delta H^{\ddagger}$ values are approximately half $\Delta H_{\mathrm{M-Sol}}$ as determined by time-resolved photoacoustic calorimetry. If the mechanism of the replacement of solvent molecule by CO were to be dissociative in character, then the $\Delta H^{\ddagger}$ term should approximate $\Delta H_{\mathrm{M-Sol}}$. This is because the rates of the reactions of M(CO)$_5$ with alkanes are essentially at the diffusion-controlled limit.[18] A dissociative mechanism is therefore precluded. In the chromium system, an associative mechanism is unlikely on steric grounds and would also be inconsistent with the published $\Delta V^{\ddagger}$ data for these reactions.[3] Also, such a mechanism could not discriminate between different alkane solvents. Consequently, we propose that an interchange mechanism best describes this reaction. The variation in k_2 observed on changing the solvent results from a difference in the $\Delta S^{\ddagger}$ term in the free energy expression. When an alkane solvent occupies the sixth coordination site on the metal, its motional freedom is restricted. This restriction is removed upon displacement by CO, increasing the $\Delta S^{\ddagger}$ term. This effect is greatest for the longer chain alkanes; thus, k_2 is larger in such solvents.

The effect of solvent on k_2 is less significant for the Mo or W systems. Here the $\Delta S^{\ddagger}$ terms are more negative than for the chromium systems, and this can be explained by a more associative character at the transition state. Consequently the breaking of the M−Sol interaction influences the kinetics to a lesser extent, while the M−CO bond formation becomes more important.

Concluding Remarks. The variation in the quantum yield of CO loss from (η^6-arene)Mo(CO)$_3$ complexes provides the clearest evidence that more than one excited state is accessible to these compounds. It is tempting to speculate that long-wavelength irradiation populates a MLCT state responsible for arene loss, while a LF state is populated following short-wavelength photolysis and results in efficient CO loss although this must await further theoretical calculations. Recent studies on the photochemistry of (η^6-pyridine)Cr(CO)$_3$

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and related compounds indicate that haptotropic shifts (η^6 to η^1) result from population of low-energy excited states.[25] Consequently we feel that it is appropriate to review the proposal that photoinduced arene exchange in (η^6-arene)M(CO)$_3$ systems is achieved via the CO loss intermediate, particularly in view of the greater quantum efficiency of photoinduced arene exchange in the Mo when compared to the Cr system.[13]

The systematic investigation of the activation parameters associated with the displacement of solvent molecules from the CO loss intermediates by CO supports an associative mechanism except for the chromium systems, which are best described in terms of an interchange mechanism. For the interchange mechanism both the enthalpic and entropic component of the M−Sol breaking are important in determining the reaction kinetics. Unlike the gas-phase studies[9] the enthalpic term is significantly less than the proposed M−Sol interaction energy, and this precludes a purely dissociative mechanism for solvent−CO exchange. However, an associative mechanism would not discriminate between different solvents as is observed for the Mo and W systems.

Experimental Section

Materials. All operations were performed under inert gas atmospheres, and purities of all isolated products were verified by microanalysis. Metal hexacarbonyl compounds (Aldrich) were used as obtained as were cyclohexane, *n*-heptane, *n*-decane, *n*-dodecane (Aldrich spectroscopic grade), *z*-co, trimethyl phosphite, *p*-xylene, and mesitylene (Merck, synthetic grade). The matrix gas ($CH_4 \geq 99.99\%$, Messer Griesheim) was used as received.

Apparatus. Spectra were recorded on the following instruments: IR, Perkin-Elmer 1600 or 2000 FT-IR (2 cm^{-1} resolution); UV/vis, Hewlett-Packard 8452A; NMR, Bruker AC 400.

The laser flash photolysis apparatus has been described previously,[11] and for this work both the 266 and the 355 nm lines of a pulsed Nd:YAG laser were used (energy approximately 40 and 35 mJ per pulse, respectively; system response 20 ns). Solutions for analysis were placed in a fluorescence cuvette ($d = 1$ cm) attached to a degassing bulb and were degassed by 3 cycles of freeze−pump−thaw to 10^{-2} Torr, followed by a substantial liquid pumping to remove traces of water and carbon dioxide (this typically removed half the original volume of solvent except for the highest boiling alkanes). The UV/vis spectrum of the sample solution was monitored throughout the experiments to verify sample stability. The absorbance of the solution at the excitation wavelength was adjusted to lie in the range 0.3−1.5 AU. The concentration of CO was determined by the pressure of CO admitted to the cell. The solubilities of CO in *n*-heptane, *n*-decane, *n*-dodecane, and cyclohexane are 1.2×10^{-2}, 8.5×10^{-3}, 6.8×10^{-3}, and 9.0×10^{-3} M, respectively, under 1 atm of CO at 298 K.[30]

The instrumentation for TRIR laser flash photolysis[31] and matrix isolation apparatus has been described previously.[32]

Preparation of (η^6-arene)Mo(CO)$_3$ Complexes (Arene = Benzene, *p*-Xylene, or Mesitylene). Mo(CO)$_6$ (1 g, 3.7 mmol) was dissolved in 40 mL of the appropriate arene, and the solution was brought to its reflux temperature for 3 h under an Ar atmosphere. The excess arene was removed under reduced pressure and the crude produce recrystallized from chloroform/*n*-hexane mixtures.

Preparation of (η^6-hexamethylbenzene)Mo(CO)$_3$. (η^6-hexamethylbenzene)Mo(CO)$_3$ was prepared by the method of Pidcock and Smith,[33] which involves heating Mo(CO)$_6$ (1.5 g, 5 mmol) with hexamethylbenzene (3 g, 22.5 mmol) in *n*-heptane (80 mL) at its reflux temperature for 10 h under an Ar atmosphere. The product was isolated by removal of the solvent under reduced pressure and purified by recrystallization from isopropyl ether.

Quantum Yield Determinations. Quantum yield measurements were performed according to the method described by Rabek.[34] Potassium ferrioxalate was used for actinometer measurements. Irradiations of 4.0 mL aliquots of a stock solution of (η^6-mesitylene)Mo(CO)$_3$ in degassed, argon-saturated cyclohexane/*z*-co or argon-saturated cyclohexane/pyridine solution were performed at ambient temperature in a quartz cuvette ($d = 1$ cm), using a Oriel 100 W Hg lamp in conjunction with solution filters. The concentrations of (η^6-mesitylene)Mo(CO)$_3$, (η^6-mesitylene)Mo(CO)$_2$(*z*-co), and (η^6-mesitylene)Mo(CO)$_2$(pyridine) were determined by means of quantitative UV spectroscopy.

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Supporting Information Available: Tables of pseudo-first-order kinetic information (8 pages). Ordering information is given on any current masthead page.

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