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# Photoacoustic Calorimetry and Quantum Yields of $Mo(CO)_6$ Ligand Exchange in Linear Alkanes: Determination of Volume of Reaction, Energetics, and Kinetics of Nucleophile Displacement of Alkane from $Mo(CO)_5$(Alkane)

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**Abstract:** Photoacoustic calorimetry (PAC) and actinometry studies were used to determine the enthalpies and volumes of reaction for the production of a transient intermediate, $Mo(CO)_5$-alkane, and for its subsequent reaction with tetrahydrofuran (THF). Both the enthalpy and the volume of reaction contribute to the photoacoustic signal and have been resolved by changing the solvent thermal expansion properties with a series of linear alkanes. The enthalpies for substitution of CO on $Mo(CO)_6$ by an alkane and of coordinated alkane on $Mo(CO)_5$(alkane) by THF are 30 and −14 kcal/mol, respectively. Likewise, the volumes of reaction are 18 and −1 mL/mol. From available data for the Mo−CO bond energy, these results allow the calculation of the Mo-alkane and Mo-THF bond energies (11 and 25 kcal/mol, respectively). The Mo-alkane result is 7 kcal/mol less than that from our previous PAC study, which ignored the volume of reaction, and is in better agreement with the results of kinetic studies. The large absolute difference in the reaction volumes for each step is partially attributed to a void volume created during the formation of the Mo−THF bond. In general, the volume of reaction cannot be neglected in the calculation of enthalpies of ligand substitution from PAC studies. The quantum yields for photosubstitution of $Mo(CO)_6$, in contrast to $Cr(CO)_6$, were found to be insensitive to the chain length of the alkane solvent.

## Introduction

It has been reported that transition metals can form σ-complexes with alkanes in complexes such as $M(CO)_5$(alkane) (eq 1, M = Cr, Mo, and W) and more recently in an iron porphyrin−alkane and ($\eta^5$-$C_5H_5$)$Re(CO)_2$(alkane).[1] In addition, flash photolysis studies have also shown that metal−alkane σ-complexes are important intermediates on the path to alkane CH activation.[2] Metal−alkane σ-complexes do form without CH activation (e.g., during ligand substitution), but the significance of these metal−alkane interactions is not always clear since the σ-complex may be in equilibrium with a reaction intermediate (such as a truly coordinatively unsaturated complex) but not on the pathway to the product. These metal−alkane interactions would be better understood if the bond strengths relative to those for better ligands were known. Such information can be obtained from the enthalpies of alkane displacement by common nucleophiles ($\Delta H_2$, eq 2). For example, the difference in the M−L bond energy and $\Delta H_2$ provides the M−alkane bond strength. The kinetics of solvent displacement by various nucleophiles can also provide information about the transition state and whether metal−solvent coordination occurs in the transition state. Both dissociative and associative mechanisms have been proposed recently for solvent displacement by nucleophiles depending on the solvent, nucleophile, and metal center.[3]

$$M(CO)_6 + \text{alkane} \xrightarrow{h\nu} M(CO)_5(\text{alkane}) + CO$$

$$M(CO)_5(\text{alkane}) + L \rightarrow M(CO)_5L + \text{alkane}$$

We previously reported the energetics of CO substitution by heptane (eq 1, M = Mo, alkane = heptane) and heptane substitution by piperidine (eq 2, M = Mo, L = piperidine) using photoacoustic calorimetry (PAC).[4] The enthalpy for substitution ($\Delta H_1 + \Delta H_2$) agreed with a published result,[5] but a surprisingly large value for the enthalpy of interaction between $Mo(CO)_5$ and heptane was reported (17 kcal/mol). We suggested that the volume of reaction might contribute to the observed PAC signals and result in the calculation of incorrect bond enthalpies.[6] In fact, we recently found that reaction volumes for each step of the photosubstitution of $Cr(CO)_6$ with acetonitrile in heptane were quite large.[7] By using various pressures, the volume of

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[6] The volume of reaction should not be confused with activation volume, which suffers from the uncertainty of the structure of the transition state and the incumbent ambiguity of interpretation.

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reaction was determined from the dependence of the PAC signals on solvent expansivity. The results showed that the volume of reaction significantly affects the calculation of reaction enthalpies for heptane displacement of CO and subsequent heptane displacement by acetonitrile.

High-pressure PAC experiments are complicated, and we are examining complementary methods of changing solvent expansivity. One method uses a series of linear alkanes to determine the volume and enthalpy of reaction as demonstrated for the photolysis of diphenylcyclopropenone.[8] We have used this method to examine the photosubstitution of $Mo(CO)_6$ with tetrahydrofuran (THF) with the caution that the linear alkanes, although very similar, are not chemically identical. THF was chosen because it is expected to form a weaker bond with molybdenum than acetonitrile and have a smaller absolute volume of reaction during bond formation.

The quantum yields for eq 1 and 2 in each solvent are required for the calculation of enthalpies from PAC data. We found that the substitution quantum yields for $Mo(CO)_6$, unlike those for $Cr(CO)_6$,[9] were solvent independent (vide infra); therefore we chose to study $Mo(CO)_6$ to minimize the uncertainties in the calculations. The results allow the calculation of enthalpy of ligand substitution as well as bond energies. In addition, the rate constant for the displacement of heptane by THF is reported. Taken together, these data provide insight into the nature of solvent and ligand coordination and the mechanism of their interchange.

## Experimental Section

**Materials.** All reagents and solvents were obtained from Aldrich unless otherwise noted. Toluene was distilled over sodium. $Mo(CO)_6$ (Strem) was sublimed under vacuum and stored under argon until used. Pentane and heptane were HPLC grade, hexane, decane, and dodecane were 99+% grade. Heptane and dodecane were distilled from sodium under argon after refluxing 6 h or longer. Tetrahydrofuran (THF, Fisher certified), piperidine (pip, Eastman), pentane and hexane were likewise treated with potassium. Decane (2.4 L previously used in PAC experiments with ferrocene and $Cr(CO)_6$) was stirred 3 days with 50 mL of concentrated $H_2SO_4$. The decane was separated and stirred an additional 6 h with 50 mL of concentrated $H_2SO_4$. After separation, the decane was washed with saturated aqueous $Na_2CO_3$, dried with $MgSO_4$, passed through a 25 mm × 300 mm column of alumina, and distilled from NaK alloy under argon after refluxing for 3 h. The 337 nm absorbances of distilled alkane solvents were the same as heptane or hexane obtained directly from Aldrich ($\Delta OD = 0.001$). Ferrocene (Ethyl Corporation) was sublimed under vacuum. The preparation of $Mo(CO)_5pip$ was described previously.[4] The purity of $Mo(CO)_5pip$ and THF was 99% or better as determined by IR and NMR, respectively. Fulgide ((*E*)-2[1-(2,5-dimethyl-3-furanyl)ethylidene]-3-(1-methylethylidene)succinic anhydride, Aberchromics, Ltd., Cardiff) was stored at −20 °C until used. Azobenzene was recrystallized from hot methanol. Gases (Air Products) were Zero Grade or better.

In general, airless procedures were used for actinometry and PAC experiments. Syringes and cannulas were used for transfers between septum-sealed argon-purged flasks or cuvettes. Septa (Aldrich, white) were washed with heptane and dried before use. All errors in the significant digit(s) are reported in parentheses as one $\sigma$.

**Actinometry**. The quantum yield for substitution of $Mo(CO)_6$ with piperidine was determined by measuring the appearance of $Mo(CO)_5pip$. The procedures have been described previously.[4,10] All quantum yields ($\Phi$) were determined for photolysis at 337 nm. Fulgide was the actinometer used for studies with heptane, benzene, and perfluorohexane, while azobenzene was used for the comparison of the alkane solvents. Volumes of solutions transferred to cuvettes were determined by weight.

**Photoacoustic Calorimetry**. The apparatus and methods have been described in detail previously and are discussed briefly to define terms.[10,11] Flash photolysis of a sample solution generates acoustic signals that depend on the heats, volumes, and rates of reactions. The amplitude of a signal from a sample solution is expressed as a fraction ($\phi$) of the amplitude of a signal from a reference solution. For a 1 MHz transducer, fast reactions ($k > 10^7$ s$^{-1}$) produce signals without phase shifts relative to the reference solution signal. Signals from such reactions cannot be resolved from each other. Only a single amplitude ($\phi_1$) and an upper limit for the lifetimes ($\tau_1 <$ ca. $10^{-7}$ s) of all the fast processes can be assigned. On the other hand, reactions whose lifetimes are similar to that of the transducer response time ($10^{-7}$ s $< \tau < 10^{-5}$ s) produce phase-shifted signals. The sample signal is deconvoluted with the signal from a reference solution (which provides an instrument response function) yielding the amplitude ($\phi_1$) of the fast signal in addition to the amplitude ($\phi_2$) and lifetime ($10^{-7}$ s $< \tau_2 < 10^{-5}$ s) of the slower signal, if one is present.[12] Signals with lifetimes much longer than the transducer response time ($\tau_2 > 10^{-5}$ s) are not detected.

The theory for solvent-dependent PAC also has been described previously.[8,13] The $\phi_1$ is dependent on the energy of absorbed light ($h\nu$), the expansivity of the solvent ($\chi = \beta/C_p\rho$, thermal expansion, heat capacity, and density, respectively), the quantum yield for substitution ($\Phi$), the enthalpy of reaction ($\Delta H_1$), and the volume of reaction ($\Delta V_1$) and leads to the expression in eq 3.[14] For processes occurring on the transducer time scale, a similar relationship (eq 4) holds for $\phi_2$ except for no direct contribution from the laser pulse. The second-order rate constants corresponding to $\phi_2$ (and therefore $\Delta H_2$ and $\Delta V_2$) are obtained from eq 5 where $1/\tau_2$ is the observed rate constant.

$$\frac{h\nu(1-\phi_1)\chi}{\Phi} = \Delta H_1\chi - \Delta V_1 \tag{3}$$

$$\frac{-h\nu\phi_2\chi}{\Phi} = \Delta H_2\chi - \Delta V_2 \tag{4}$$

$$1/\tau_2 = k_0 + k_2[\mathrm{THF}] \tag{5}$$

In a typical experiment, $Mo(CO)_6$ (8.5 mg) was transferred to a 500 -mL volumetric flask fitted with a septum. The flask was evacuated and filled with argon, followed by 350 mL of heptane, covered with aluminum foil, and agitated until the $Mo(CO)_6$ was dissolved. Ferrocene (57 mg) was dissolved in 100 mL of heptane. The absorbances of $Mo(CO)_6$ and ferrocene solutions were about 0.1. Solutions of ferrocene (100 mL), $Mo(CO)_6$ (50 mL), and heptane (100 mL) were transferred to their respective reservoirs that were connected to the PAC flow cuvette via a glass manifold with Teflon stopcocks. The $Mo(CO)_6$ solution was cannulated to its septum-sealed reservoir that was previously purged with helium. THF was added with a microliter syringe to the reservoirs containing $Mo(CO)_6$ and ferrocene. Helium purging provided mixing.

All PAC experiments were performed with ferrocene as the reference at 24(1) °C in a dark room with a Thomas safety light.[15] Samples were irradiated in a flow cuvette (1 cm × 1 cm × 3 cm) at 337.1 nm (800 ps, 20−30 $\mu$J/pulse at 1 Hz, 1 × 1 mm beam at the sample). The flow rate for $Mo(CO)_6$ solutions (>6 mL/min) was maintained so that only fresh sample was irradiated. A measurement included signals

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**Table 1.** Quantum Yields for Ligand Substitution of $Mo(CO)_6$ at 337 nm in Various Solvents

| solvent | $\Phi$ |
|---|---|
| pentane | 0.93 (3) |
| heptane | 0.89 (2), 0.91 (2)[4] |
| dodecane | 0.89 (2) |
| perfluorohexane | 0.77 (1) |
| benzene | 0.90 (1) |

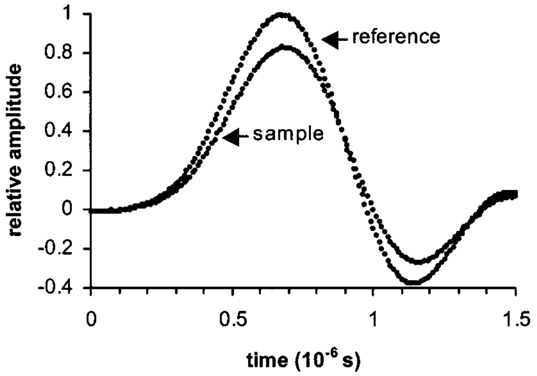

**Figure 1.** Photoacoustic signals following 337.1 nm laser photolysis of $Mo(CO)_6$ and ferrocene with tetrahydrofuran in decane: the reference is 2.7 mM ferrocene with 30 mM THF, and the sample is 0.08 mM $Mo(CO)_6$ also with 30 mM THF (simulation waveform best fit may be inspected in Supporting Information).

averaged from 16 to 32 acceptable laser pulses. Prior to each measurement, pulses were recorded until 4−8 pulses were obtained that did not deviate more than 10% from their average energy. For the subsequent measurement, this average energy was used to reject signals with pulse energies deviating more than 5% from the average. For each THF concentration, three to six measurements were obtained. Signals for ferrocene solutions were measured before and after the measurement of signals for each $Mo(CO)_6$ solution, and signals for solvent were measured before the first and after the last measurements of signals for ferrocene solutions. Signal amplitudes were corrected for differences in pulse energies and solution absorbances. MQ or Sound Analysis programs (Quantum Northwest, Spokane, WA) were used to deconvolute the signals for $Mo(CO)_6$ solutions with that for ferrocene solutions.[12] The deconvolution programs provide $\phi_1$, $\phi_2$, $\tau_2$, and $X^2$ (sum of the squares of residuals). Goodness of fit was determined from $X^2$.

## Results

Photolysis of $Mo(CO)_6$ with piperidine produced $Mo(CO)_5$pip. At low conversions of $Mo(CO)_6$ (2−10% where secondary photolysis is avoided) new IR bands are observed only for $Mo(CO)_5$pip.[4] The quantum yields for formation of $Mo(CO)_5$pip are reported in Table 1, and the extinction coefficients are available in the Supporting Information.[16]

For $Mo(CO)_6$ in the presence of THF, a phase shift can be detected in the photoacoustic signal as shown in Figure 1. Deconvolution of the $Mo(CO)_6$ signal with a ferrocene signal gives a good fit by using two lifetimes ($\tau_1$ fixed at 1 ns). As an example, $\tau_2$ decreases from 1.0 to 0.11 $\mu$s as THF increased from 3 to 60 mM in decane, thus the observed rate constant for $\phi_2$ ($k_{obs} = 1/\tau_2$) increases with the THF concentration (Figure 2). Second-order rate constants were obtained from the slopes of plots of $1/\tau_2$ versus THF concentration. The $\phi_1$ was found to be independent of THF concentration while $\phi_2$ was independent only above 14 mM THF (Figure 3). These PAC results are consistent with those previously reported for piperidine in heptane,[4] although different nucleophile concentrations were used. For decane, an average $\phi_1$ was calculated from the results for all concentrations, but for $\phi_2$ only the results from concentrations above 14 mM THF were used. The results for other solvents were similarly treated and are summarized in Table 2. A plot of $h\nu(1 - \phi_1)\chi/\Phi$ versus $\chi$ (Figure 4) is linear, yielding a $\Delta H_1$ of 29.7(17) kcal/mol from the slope and a $\Delta V_1$ of 18(6) mL/mol from the intercept. Likewise, a plot of $-h\nu\phi_2\chi/\Phi$ versus $\chi$ (Figure 5) yields a $\Delta H_2$ of −13.8(14) kcal/mol and a $\Delta V_2$ of −0.6(49) mL/mol.

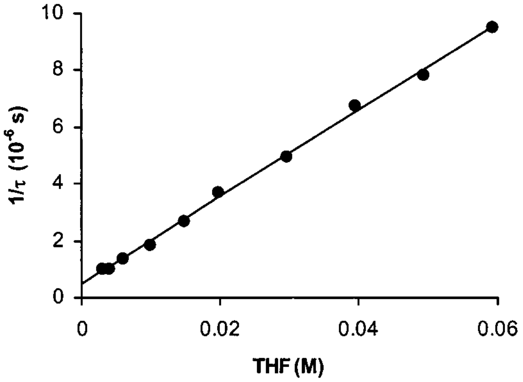

**Figure 2.** Plot of observed rate constants ($k_{obs} = 1/\tau_2$) for the slow component of the photoacoustic signal for $Mo(CO)_6$ with THF in *n*-decane. Intercept = 4.9(7) × $10^5$ $s^{-1}$, slope = 1.53(2) × $10^8$ $M^{-1}$ $s^{-1}$, $r$ = 0.999.

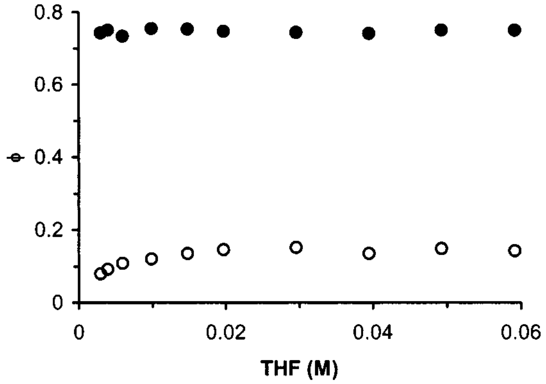

**Figure 3.** Plots of fractional amplitudes for the fast ($\phi_1$) and slow ($\phi_2$) components of the photoacoustic signal versus THF concentration for $Mo(CO)_6$ in *n*-decane: $\phi_1$ = solid circles, $\phi_2$ = open circles.

**Table 2.** Rate Constants and Normalized Photoacoustic Signal Amplitudes for $Mo(CO)_6$ with Tetrahydrofuran in Linear Alkanes

| solvent ([THF] mM) | $n^a$ | $k_2$ ($10^8$ $M^{-1}$ $s^{-1}$) | $k_0$ ($10^5$ $s^{-1}$) | $\phi_1$ | $\phi_2$ |
|---|---|---|---|---|---|
| pentane (7.8−78) | 8 | 1.4(1) | 1.0(5) | 0.728(23) | 0.148(23) |
| hexane (3−39) | 10 | 2.04(5) | −0.5(15) | 0.728(9) | 0.141(21) |
| heptane (8−98) | 9 | 1.68(8) | 9(4) | 0.751(11) | 0.134(15) |
| decane (3−59) | 10 | 1.53(2) | 4.8(7) | 0.747(7) | 0.143(8) |
| dodecane (7.8−78) | 8 | 1.33(10) | 12(5) | 0.768(5) | 0.152(10) |

[a] $n$ = number of experiments with different concentrations of THF.

## Discussion

**Quantum Yield Dependence on Solvent.** The quantum yields for substitution are independent of the piperidine concentration when it is in large excess over $Mo(CO)_6$. This indicates that $Mo(CO)_5$(alkane) reacts completely with piperidine and that the quantum yield for $Mo(CO)_5$(alkane) formation is the same as that for $Mo(CO)_5$pip. The quantum yields were determined for substitution with piperidine instead of THF

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(16) The $\Phi$ reported previously has been corrected for an error in the determination of the $\epsilon$ for $Mo(CO)_5$(pip) at 337 nm. We found it to be 937 $cm^{-1}$ $M^{-1}$ instead of 2060 $cm^{-1}$ $M^{-1}$.

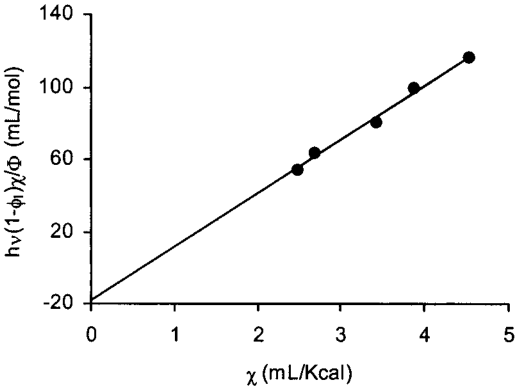


**Figure 4.** Dependence of the fast component of photoacoustic signal ($\phi_1$) on solvent expansivity ($\chi$) following photolysis of Mo(CO)$_6$ with THF in linear alkanes.

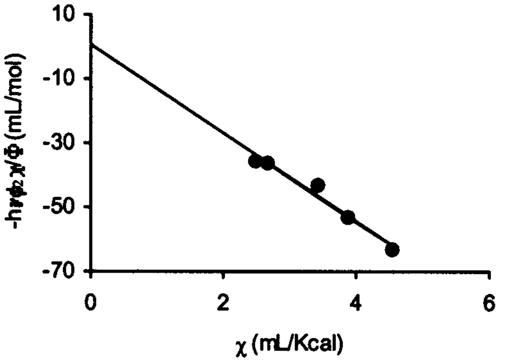


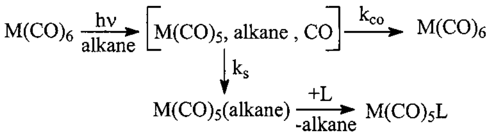
**Figure 5.** Dependence of the slow component of photoacoustic signal ($\phi_2$) on solvent expansivity ($\chi$) following photolysis of Mo(CO)$_6$ with THF in linear alkanes.

because Mo(CO)$_5$THF is not as stable and not as easily measured. Nevertheless, the initial yield should be the same for each ligand substitution since each ligand was present in large excess.

The solvent dependence of the quantum yields for photosubstitution of Mo(CO)$_6$ differs from that observed for Cr(CO)$_6$. For some time it has been known that the ligand substitution quantum yields for Cr(CO)$_6$ in alkane solvents change with the alkane chain length.[17] For example, the yields are 0.72 and 0.58 for pentane and dodecane, respectively.[9] Our results show, within experimental error, that the quantum yield for Mo(CO)$_6$ does not change in these alkane solvents and is greater than that observed in any solvent for Cr(CO)$_6$. The only solvent dependence observed for Mo(CO)$_6$ is a lower quantum yield in perfluorohexane.

A theory of M(CO)$_6$ photosubstitution has been described previously and, with minor modification, accounts for the different solvent dependence of quantum yields.[9,18,19] The theory predicts that the quantum yield depends on the competition between solvent addition and geminate CO recombination with M(CO)$_5$ (Scheme 1 and eq 6). This will be true if M(CO)$_6$ and M(CO)$_5$(alkane) are formed irreversibly and M(CO)$_5$(alkane) exclusively forms M(CO)$_5$L. Indeed subsequent studies demonstrated that the formation of M(CO)$_5$(alkane) and M(CO)$_6$ is irreversible on the picosecond time scale.[20,21] Since the displacement of coordinated alkane by CO is slow ($k = 10^7$ M$^{-1}$ s$^{-1}$)[3b,22] relative to CO cage escape, the formation of M(CO)$_5$(alkane) leads only to M(CO)$_5$L when L is in excess of the CO generated from photolyzed M(CO)$_6$. Clearly the quantum yield for formation of M(CO)$_5$L will be equal to that for the formation of Mo(CO)$_5$(alkane). In contrast, perfluorocarbons interact with M(CO)$_5$ more weakly than alkanes and do not compete for Mo(CO)$_5$ as effectively as alkanes.[1b] Therefore it was previously proposed that the quantum yield in a perfluorocarbon may be expected to be less than that in an alkane.[18,23]

**Scheme 1**



$$\Phi = \frac{k_s}{k_s + k_{CO}} \tag{6}$$

The larger quantum yield for Mo(CO)$_6$ and its insensitivity to alkane chain length compared to that for Cr(CO)$_6$ might be attributed to a steric effect. The larger molybdenum may bind methyl and methylenes similarly while the smaller chromium binds methylenes more poorly than methyls.[24] Since the effective concentration of methyl groups decreases with longer alkane solvents, the trapping of chromium by alkane would decrease leading to more CO recombination and a lower quantum yield. Therefore alkanes of different chain length react equally well with Mo(CO)$_5$ but not with Cr(CO)$_5$ (i.e., $k_s$ decreases significantly with alkane chain length for Cr(CO)$_5$ but not for Mo(CO)$_5$).[18]

**Assignment of PAC Data.** The results of this and previous studies allow the assignment of $\phi_1$ and $\phi_2$ to specific processes. The Mo(CO)$_5$(alkane), generated following photolysis of Mo(CO)$_6$ in alkane solvents (eq 1), is thermally equilibrated in less than a nanosecond.[20,25] In the absence of added THF, Mo(CO)$_5$(alkane) is stable for several milliseconds.[26] The lifetime of $\phi_1$ could not be determined with a 1 MHz transducer and therefore has a lifetime less than $10^{-7}$ s. Furthermore, $\phi_1$ is not affected by THF, as demonstrated by its independence of ligand structure (same $\phi_1$ for pip[4]), and is independent of THF concentration up to 80−100 mM (Figure 3).[27] On the other hand, $\phi_1$ does change with solvent (Table 2). We conclude that $\phi_1$ (and likewise $\Delta H_1$ and $\Delta V_1$) should be assigned to those processes leading to the formation of Mo(CO)$_5$(alkane).

Once Mo(CO)$_5$(alkane) is formed, it can react with CO dispersed in solution, unphotolyzed Mo(CO)$_6$, or THF. The concentration of THF was greater than 1 mM, while the experimental conditions dictate that the concentration of CO generated for each laser pulse is about $1 \times 10^{-6}$ M and the concentration of unphotolyzed Mo(CO)$_6$ is about $10^{-4}$ M. Nucleophiles at millimolar concentrations displace coordinated

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(24) We would like to thank a reviewer for suggesting this distinction.

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(27) At this concentration the reaction with THF is so fast that it begins to contribute to $\phi_1$.

alkane solvents on a microsecond time scale (eq 2).[3,4,28] As a result, $Mo(CO)_5$(alkane) will be scavenged preferentially by THF on this time scale. Since a $\tau_2$ was observed in the microsecond range, we assign the $\tau_2$ observed for $\phi_2$ to eq 2 (see Results and Supporting Information). Furthermore, the assignment of $\tau_2$ and $\phi_2$ (and the corresponding $k_2$, $\Delta H_2$, and $\Delta V_2$) to eq 2 is consistent with $\tau_2$ decreasing with increasing concentration of THF and the fact that $k_2$ and $\phi_2$ are different from those for piperidine.[4]

The intercept is not zero in Figure 2 and inspection of Table 2 shows that for pentane, decane, and dodecane the intercepts are not within experimental error of zero for plots of observed rate constants versus THF concentration. In these cases, a side reaction is occurring, most likely with an impurity. The effect of the impurity can be seen in the plot of $\phi_2$ in Figure 3. At low THF concentration, $\phi_2$ decreases because the reaction with the impurity becomes significant, and the impurity forms either a weaker bond than THF or has a negative volume of reaction (or both). The impurity is not likely to be water since the solvents were carefully dried. Another candidate is an alkene since we have observed a smaller $\phi_2$ for *n*-hexene in heptane.[29] A solvent effect is not responsible for the variation of $\phi_2$ with THF concentration, otherwise $\phi_1$ would behave similarly at low THF concentration. For the calculation of $\Delta H_2$, only $\phi_2$ values that were independent of THF concentration were used.

**Reaction Enthalpies**. It is assumed that $\Delta H_1$ is independent of alkane chain length (see **Volumes of Reaction** and **Mo−Alkane Bond Strengths**). The $\Delta H_1$ is endothermic and its assignment to CO substitution by alkane is consistent with the fact that a weaker Mo−alkane bond replaces the much stronger Mo−CO bond. Likewise, $\Delta H_2$ is exothermic and its assignment to alkane substitution by THF is consistent with a stronger Mo−THF bond replacing a weaker Mo−alkane bond. The sum of the enthalpies of the two steps (16 kcal/mol) is equal to the enthalpy of CO substitution by THF and demonstrates that the Mo−THF bond is much weaker than the Mo−CO bond. If the volumes of reaction had been assumed to be negligible and had the experiments been performed in only a single solvent such as heptane, then the calculated $\Delta H_1$ and $\Delta H_2$ would have been 23.5 and −12.6 kcal/mol, respectively. So errors of 6.5 and 1.5 kcal/mol would have resulted (the latter not being significant).

**Volumes of Reaction**. The volume of reaction may be considered formally to have two contributions: (1) the difference in volumes of the reactants and products and (2) changes in solvent interactions with the reactants and products. The derivation of eqs 3 and 4 assumes that linear alkanes do not differ significantly in their interactions with reactants and products. This is reasonable considering the structural similarity of the linear alkanes. They each have methyl and methylene groups that can provide the same van der Waals interactions (enthalpy of solvation) and can be equally excluded from the space (void and molecular volume) taken up by the reactants and products. The volume of CO substitution by alkane for $Mo(CO)_6$ is within experimental error of that recently reported for $Cr(CO)_6$ (21 ± 2 mL/mol) in heptane at high pressures.[7] We believe the agreement of these results from divergent methodology is a good test of their reliability.

In contrast, the volume for THF substitution by alkane (reverse of eq 2) is within experimental error of zero. The Mo−THF bond is weaker than the Mo−CO bond (vide supra) and probably undergoes less compression during formation than the Mo−CO bond. Hence a smaller (but not zero) volume change was anticipated for the THF bond formation. The negligible volume change may be attributed to an excluded volume that the solvent must vacate as the Mo−THF bond is formed. In other words, there is a void between the THF α-methylenes and the $Mo(CO)_5$ fragment that is too small for the solvent to occupy. This extra void volume tends to cancel the volume decrease that accompanies the Mo−THF bond formation. In the study of acetonitrile substitution with $Cr(CO)_6$, the volume of heptane substitution by acetonitrile was found to be only 4 mL/mol (17 mL/mol) less than that for heptane substitution by CO.[7] The difference was attributed mostly to differences in bond lengths since the creation of void volumes is not going to be appreciably different for CO and acetonitrile ligands.

**Mo−Alkane Bond Strengths**. The value for $\Delta H_1$ can be used to estimate the strength of the Mo−alkane bond. For organometallic reactions in hydrocarbon solvents the difference in solvation enthalpies of reactants and products is small, on the order of 1−2 kcal/mol.[30] Thus $\Delta H_1$ will be the difference between the bond energies broken and formed, and a value for the Mo−CO bond energy will allow the calculation of the Mo−heptane bond energy. Several experimental results support an assignment of about 30 kcal/mol for the Mo−CO bond energy (vide infra), and the difference between this value and $\Delta H_1$ yields about 0 kcal/mol for the Mo−heptane bond energy. Since the rate constant for alkane displacement by several ligands is not even the diffusion-controlled limit, it seems unlikely that the Mo−alkane bond energy is near 0 kcal/mol.[31]

An Mo−CO bond strength of 30 kcal/mol is based on activation enthalpies for CO dissociation, and there are reasons to suspect this value. For the gas-phase substitution of $Mo(CO)_6$ with $^{14}CO$, the kinetics were unimolecular with an activation enthalpy of 30.2 kcal/mol.[32] Similar results were reported for the unimolecular substitution of CO by tri-*n*-butylphosphine in Decalin (31.7 kcal/mol), by triphenylphosphine in *n*-decane-cyclohexane (30.2 kcal/mol), and by triazine in *n*-decane-cyclohexane (30.8 kcal/mol).[33,34] Since these reactions are first order only in $Mo(CO)_6$, it might be expected that the reaction is a simple dissociative process with CO dissociation as the rate-determining step. However, in each case the activation entropies are much less than what is expected for purely dissociative processes: −0.4 (CO), 6.7 (tri-*n*-butylphosphine), 2.7 (triphenylphosphine), and 4.3 eu (triazine). Although the latter three values are too positive for highly associative processes, they are reasonable for an interchange mechanism involving solvent (or an interchange mechanism with the solvent that competes with a purely dissociative mechanism).[35] In contrast, the CO substitution by benzylamine in Decalin is also unimolecular, but the activation enthalpy and entropy are significantly larger than that observed in the other cases (36.0 kcal/mol and 19.1 eu, respectively).[36] The larger entropy suggests a greater contribu-

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[31] For example, the rate constant for reaction of $Mo(CO)_5$(heptane) with 1-hexene is $1.58(1) \times 10^7$ $M^{-1}$ $s^{-1}$, see ref 3a.

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tion of a dissociative process (or an interchange process becoming more dissociative in nature) and less stabilization by solvent coordination; therefore the activation enthalpy is expected to be larger. The interchange mechanism for ligand substitution has been observed previously for $Mo(CO)_6$ in solution,[33] and given the fact that several studies indicate that the metal−alkane bond strength is significant,[1] it is possible that the transition state for CO dissociation is stabilized by metal−alkane bonding. This being the case, the activation enthalpy for CO displacement in many instances would correspond to a kinetically dissociative process, but microscopically it would involve an interchange process with the solvent that is kinetically undetected since the solvent dependence is usually not probed.[37] We conclude that the Mo−CO bond energy is substantially larger than the activation enthalpies observed for unimolecular substitution of CO.[38]

More recent gas-phase studies report values of 40.5(20) and 35(5) kcal/mol for the $Mo(CO)_5$−CO bond energy.[39,40] The former is highly cited[41] and is supported by a theoretical study that predicts an Mo−CO bond energy of 40.3 kcal/mol.[42] Using 40.5 kcal/mol leads to an Mo−alkane bond energy of 10.8(26) kcal/mol. The only example for comparison is an activation enthalpy of 12.5(1) kcal/mol for unimolecular benzene displacement by 1-hexene from $Mo(CO)_5$(benzene), which has been used as an estimate of the Mo−benzene bond strength.[37]

We have assumed that the enthalpy of reaction is also independent of the alkane, that is, the metal−solvent bond energy does not change. This assumption is supported by the lack of significant variation in the rate constant for solvent displacement (see $k_2$ in Table 2). Nevertheless, previous investigations indicate that metal−alkane bonds strengths do change and are dependent on alkane ionization potentials and polarizabilities. For example, the $W(CO)_5$−(alkane) bonds were found to increase from 7.4 (ethane) to 10.6 kcal/mol (*n*-hexane),[43] but it is worth noting that the result for *n*-pentane was within experimental error of that for *n*-hexane. Furthermore, studies of alkane $\sigma$ complexes with $Cp^*Rh(CO)_2$ suggest that beyond *n*-hexane the metal−alkane bond is not very sensitive to an increase in chain length.[2] This result might be expected since ionization potentials of linear alkanes rapidly reach an upper limit.[44] Using the literature results, we can estimate how the Mo−alkane bond might vary. The W−alkane bond energy changes by 3.2 kcal/mol for a 1.39 eV change in alkane ionization energy (ethane to hexane). If a similar relation holds for Mo−alkane bonds, then the difference between the Mo−pentane and Mo−dodecane bonds for our study would be 2.0 kcal/mol. Assuming 10.8 kcal/mol represents the median Mo−alkane bond energy then the Mo−pentane and Mo−dodecane bonds are 9.8 and 11.8 kcal/mol, respectively. Notwithstanding that these values are within experimental error of each other, calculations with eq 3 require that the corresponding volumes of reaction change to −23 and −17 mL/mol, respectively. While we suspect that the volume of reaction does not vary this much, these values do not materially change any of our conclusions.

## Conclusions

Unlike the substitution of CO by acetonitrile on $Cr(CO)_6$, the volume of reaction has a large effect on the determination of the enthalpy of CO substitution by THF on $Mo(CO)_6$. Examination of the individual steps of the substitution reveals that the volume of alkane substitution on $Mo(CO)_5$−alkane is much smaller for THF than that for CO. This is attributed to the weaker metal−ligand bond for THF and steric effects. It is clear that the volume increase associated with ligand dissociation is not always canceled by the decrease in associated solvent addition to the metal or another ligand. Unless the volume of reaction is taken into account, PAC cannot be used to determine enthalpies of reaction. Systematic studies of other ligands will provide a greater understanding of the relationship between structure and volume of reaction. The studies to date indicate that metal−alkane bond energies for typical alkanes do not significantly exceed 10 kcal/mol.[2,7]

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**Supporting Information Available:** A listing of the derivation of eqs 3−5, optical data, $\phi_1$, $\phi_2$, and $\tau_2$ at various THF concentrations, alkane ionization potentials, and $\chi$ values (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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