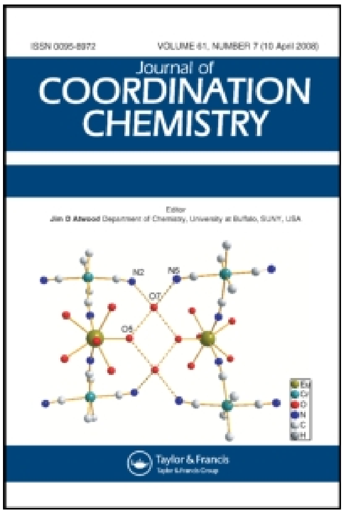

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ALKANE COORDINATION BY MOLYBDENUM AND CHROMIUM PENTACARBONYLS: AN EXAMINATION OF THE ENERGETICS OF INTERMOLECULAR AGOSTIC BONDING

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The photochemistry of $Mo(CO)_6$ in heptane has been investigated using actinometry and photoacoustic calorimetry. The quantum yield for CO substitution on $Mo(CO)_6$ by piperidine in heptane was found to be 0.93 for 337 nm irradiation at 25°C. This was clearly different than the quantum yield found for CO substitution on $Cr(CO)_6$ by piperidine (0.75). Two heat decays were observed following flash photolysis of $Mo(CO)_6$ in the presence of piperidine. The first heat decay is independent of piperidine concentration (8-80 mM), while the lifetime (τ_2) of the second heat decay decreases with increasing piperidine concentration. A plot of $1/\tau_2$ shows a first-order dependence on piperidine concentration. The first heat decay has been assigned to the displacement of CO on $Mo(CO)_6$ by heptane and the second, to the displacement of heptane on $Mo(CO)_5$(heptane) by piperidine. The second-order rate constant for heptane displacement is 4.8×10^7 $M^{-1}s^{-1}$. The enthalpies of CO displacement by heptane (ΔH_1) and heptane displacement by piperidine (ΔH_2) are estimated as 24 and -17 kcal/mol, respectively. This yields an enthalpy of CO substitution by piperidine ($\Delta H_1 + \Delta H_2$) of 6.3 kcal/mol in agreement with literature results. The $Mo(CO)_5$,(heptane) and $Mo(CO)_5$ (piperidine) bond dissociation energies are estimated to be 17 and 34 kcal/mol, respectively. The former value is more likely to be affected by corrections for reaction volume changes and should be treated as an upper limit.

KEYWORDS: photoacoustic calorimetry, molybdenum hexacarbonyl, kinetics, agostic bonding, quantum yields

INTRODUCTION

Coordinatively-unsaturated metal centers are proposed intermediates for many organometallic reactions.[1] It is increasingly clear that these intermediates are in equilibrium with solvent coordinated species even if the solvent is an alkane.[2,3] By strict definition, the interaction between the metal and alkane is an intermolecular agostic bond,[4] and a key to understanding the importance of these interactions is the bond strength. The first value reported for an agostic bond was about 10 kcal/mol for $Cr(CO)_5$(heptane).[5,6] Since other metal complexes have not been studied in detail it was not clear whether this value was typical. Thus, we have undertaken studies of $Mo(CO)_5$(heptane) and other metal complexes.

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Previous studies give conflicting results for the strength of the agostic interaction between $Mo(CO)_5$ and alkane solvents. Early results obtained by photoacoustic calorimetry (PAC) indicated a bond dissociation energy (BDE) of 0 kcal/mol for $Mo(CO)_5$-(cyclohexane).[7] However, the results also suggested that the Mo-solvent interaction was the same for cyclohexane and ethanol. This was clearly incorrect since the strength of the Mo-O bond will be greater than the Mo-CH agostic bond. An examination of PAC calculations and experiments indicates where corrections might be required. The enthalpy of ligand substitution is the difference between the bond dissociation energies broken and formed if the difference in solvation of reactants and products is negligible. This has been shown to be the case for organometallic reactions in organic solvents.[8] If the enthalpy for CO displacement by a solvent molecule (eq 1, S = solvent) can be determined by PAC and the $Mo(CO)_5$-CO BDE is known, then the $Mo(CO)_5$-(S) BDE can be calculated. One source of error for S = ethanol may be the contribution of hydrogen bonding to observed heats of reaction.

$$Mo(CO)_6 + S \xrightarrow{\Delta H_1} Mo(CO)_5S + CO \tag{1}$$

$$Mo(CO)_5S + L \xrightarrow{\Delta H_2} Mo(CO)_5L + S \tag{2}$$

It should also be noted that the quantum yield for $Mo(CO)_6$ photosubstitution in solution, which is required for the PAC calculation, was not available and had been assumed to be 1 for both ethanol and cyclohexane. Another potential source of error is the value used for $Mo(CO)_5$-CO BDE. The authors used a value that is substantially less than the currently accepted value of 40.5 (20) kcal/mol.[9,10] By using this value, 7 (5) kcal/mol is obtained for the $Mo(CO)_5$-(cyclohexane) BDE. We subsequently reported a value of 9 (3) kcal/mol for $Mo(CO)_5$-(heptane), which was also similar to the value reported for $Cr(CO)_5$-(heptane).[5] This result was based on the assumption that the quantum yield for $Mo(CO)_6$ was the same as that for $Cr(CO)_6$ (0.67 in cyclohexane); however, Wieland and van Eldik later reported that the values for $Cr(CO)_6$ (0.73, (1)) and $Mo(CO)_6$ (0.93 (1)) in heptane were significantly higher.[11] This would increase the Cr-heptane and Mo-heptane BDE to 12 and 15 kcal/mol, respectively. These results suggest that the agostic bond is stronger for Mo than for Cr and could have important mechanistic implications. It is therefore important to establish these results with a greater certainty.

In this study, improved PAC methods have been used to examine the reactions initiated by photolysis of $Mo(CO)_6$. We have studied the energetics of CO substitution by heptane (eq 1) and the kinetics and energetics of heptane displacement by piperidine (eq 2) by deconvolution of PAC signals. With these results, the enthalpy of CO substitution by heptane (ΔH_1) and by piperidine ($\Delta H_1 + \Delta H_2$) have been calculated. Furthermore, the Mo-heptane and Mo-piperidine BDE's have been estimated. In addition, we have re-determined the quantum yields for CO substitution on $Cr(CO)_6$ and $Mo(CO)_6$ in heptane.

EXPERIMENTAL SECTION

Materials

Heptane(Aldrich HPLC grade) was refluxed overnight with sodium, under argon, prior to distillation. Toluene was distilled before use. $Cr(CO)_6$ (Aldrich) and

$Mo(CO)_6$ (Strem) were sublimed twice under vacuum and stored under argon until used. Piperidine (pip) was distilled after refluxing it under argon for at least 6 h with CaH_2. 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. $Mo(CO)_5(pip)$ was synthesized by an established procedure except that an immersion-well reactor (similar to Lurex LX6122) was used.[12] $Mo(CO)_6$(4 g, 15 mmol) and piperidine (12 mL, 121 mmol) were dissolved in 120 mL of cyclohexane and photolyzed for 4 hours with a Hanovia 150-W high-pressure xenon lamp. The solvent was evaporated, and the product was recrystallized consecutively from cyclohexane (ambient temperature) and *n*-hexane (−80°C). Traces of $Mo(CO)_6$ were removed by sublimation at room temperature. In a subsequent sublimation at 50°C, product was collected from the cold finger, and stored under argon at -20°C until used. IR(heptane): 2071, 1937, 1919 cm^{-1}. Lit[12] (hexane): 2073, 1939, 1921 cm^{-1}.

In general, air-less 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. Solution volumes that were transferred to cuvettes were determined by weight.

Quantum Yield Determinations

The quantum yield for ligand substitution of $Mo(CO)_6$ with piperidine (Φ) was determined by following the formation of $Mo(CO)_5pip$ at 397.5 nm. The following procedure was typical for determining an accurate extinction coefficient for $Mo(CO)_5(pip)$. A piperidine solution was prepared by adding piperidine (200 μL, 2 mmol) to a septum-sealed, argon-purged, 100-mL reservoir of heptane. $Mo(CO)_5(pip)$ (1–2 mg, 3–6 μmol) was placed in a 25-mL flask. The flask was evacuated, filled with argon, and shaken to dissolve the complex as it was filled to the mark with the piperidine solution. Aliquots (volumes determined by weight) were transferred to three septum-sealed, argon-purged, 10-mL flasks and diluted to the mark with the piperidine solution. Each dilution was repeated in triplicate. About 2 mL of each solution was transferred to a cuvette thermostated at 25°C. A similarly prepared solution without $Mo(CO)_5(pip)$ was used to correct for background absorption.

Samples for photolysis were prepared in a similar manner. A flask containing $Mo(CO)_6$(25 mg, 95 μmol) was septum-sealed, evacuated, and filled with argon. Piperidine (100–200 μL, 1–2 mmol) was transferred to the flask along with 20 mL heptane. After the $Mo(CO)_6$ was dissolved, the solution was purged with argon for 10 min, and 2 mL (determined by weight) was transferred to a cuvette for photolysis.

The photolysis apparatus, light intensity determination, and quantum yield calculations have been described previously.[13] During photolysis and absorbance measurements the cuvettes were maintained at 25.0°C. The extinction coefficient at 397.5 nm for $MoCO)_5(pip)$ is 4614 (51) $cm^{-1}M^{-1}$. In all experiments, conversion to product was less than 5%, nevertheless, ε_{337} for $MoCO)_5(pip)$ (2060 (100) $cm^{-1}M^{-1}$) is greater than that for $Mo(CO)_6$ (1080 (100) $cm^{-1}M^{-1}$), and the quantum yield required correction for inner-filter effects.[16]

Light intensities were determined using a fulgide solution.[14] The fulgide (3–4 mg, 4–5 mmol) was dissolved with 2.2 mL of toluene in a cuvette. A fulgide sample was photolyzed before and after the photolysis of each $Mo(CO)_6$ solution and used repeatedly by photo reversing with visible light from 50-W incandescent lamps. Contrary to a recent report, we found no degradation of the fulgide solution after 10 or more cycles.[15] On the other hand, degradation of fulgide obtained from Aldrich (rather than Aberchromics) was observed even if purified by sublimation. We found that the conversion of this source of fulgide to product decreased with successive cycles compared to samples not previously irradiated; furthermore, photo reversing was less than 100% effective. The reliability of the fulgide method is supported by the excellent agreement between our results and literature data[11,16,17] for $Cr(CO)_6$ and $Mo(CO)_6$ (also see RESULTS).

Optical differences between cuvettes used for $Mo(CO)_6$ and fulgide photolysis were determined by comparing the results of photolysis of the same fulgide solution in each cuvette. Light intensities were calculated from eq 3 where ΔA is the absorbance difference at 494 nm before and after photolysis of the fulgide solution, V is the volume of irradiated solution, ε_{494} is the molar extinction coefficient of fulgide photolysis product in toluene (8200 cm^{-1}), t is the duration of irradiation

$$I = (\Delta AV/\varepsilon_{494} dt\Phi) \qquad (3)$$

in sec, d is the cuvette path length (1 cm), and Φ is the quantum yield of the fulgide reaction (0.20).[14] Light intensities were 4-6 × 10^{-10} Einstein s^{-1}, and irradiation times were 8-12 min.

Experiments with $Cr(CO)_6$ are identical to those described previously for cyclohexane.[17] The extinction coefficient for $Cr(CO)_5(pip)$ in heptane at 420 nm is 3489 (10) cm^{-1} M^{-1}. The extinction coefficients for $Cr(CO)_5(pip)$ and $Cr(CO)_6$ in heptane at 337 nm are 780 (40) cm^{-1}, M^{-1} and 1060 (34) cm^{-1} M^{-1}, respectively. For photolysis, the piperidine and $Cr(CO)_6$ concentrations were 51 and 2.6 mM, respectively.

Photoacoustic Calorimetry

The apparatus and methods have been described in detail previously.[13] A light pulse from a laser was weakly focused on a sample cuvette. The absorbed light initiates chemical and physical processes that liberate heat and generate an acoustic wave which is detected with an ultrasonic transducer clamped to the side of the cuvette. The transducer responds to processes that generate heat faster or near the transducer frequency response; therefore, fast heat decays can be resolved from slow ones. The calorimeter is standardized with a compound that deposits all light energy (as heat) faster than the frequency response of the transducer (1 Mhz). In all experiments, ferrocene was used as the standard.[18] The observed heat from a sample is expressed as a fraction, ϕ, of the heat released by the reference solution. While fast reactions ($k > 10^7 s^{-1}$) produce transducer signal amplitudes directly proportional to the amount of heat liberated, heat from reactions whose rates are similar to that of the transducer frequency response (10^7 $s^{-1} > k > 10^5$ s^{-1}) produce phase-shifted signals with reduced amplitudes. These signals are deconvoluted with the signal from the reference solution (which provides an instrument-response function) yielding the magnitudes and lifetimes of the heat decays.[19] Processes much faster than the transducer response cannot be distinguished and produce signals without phase shifts relative to the reference solution signal. Only a single heat (ϕ_1) and an upper limit for the lifetime ($\tau_1 < ca. 10^{-7}$s) for these processes can be assigned. Both a heat (ϕ_2) and a lifetime (τ_2) can be assigned for processes having lifetimes on the same time scale as the transducer.

In a typical experiment, $Mo(CO)_6$ (8.5 mg) was transferred to a 500 mL, aluminum-foil covered volumetric flask fitted with a septum. The flask was evacuated, filled with argon. Heptane (350 mL) was transferred by cannula and then agitated until the $Mo(CO)_6$ was dissolved. In a pair of 100 mL flasks, ferrocene (57 mg each, 117 μmol) was dissolved with heptane filled to the marks. The absorbances of $Mo(CO)_6$ and ferrocene solutions at 337 nm were about 0.1. Solutions of ferrocene (100 mL), $Mo(CO)_6$ (50 mL) and heptane (100 mL) were transferred to three reservoirs connected to the PAC flow cuvette *via* a glass manifold (Teflon stopcocks). Prior to addition of a $Mo(CO)_6$ solution with a cannula, the reservoir was septum-sealed and purged with helium. Piperidine was added with a microliter syringe to the reservoirs containing $Mo(CO)_6$ and ferrocene, while helium purging provided mixing.

All PAC experiments were performed at 23 (1)°C in a dark room using a Thomas safety light. Samples were irradiated with a nitrogen laser (337.1nm, 800 ps, 20–30 μJ/pulse at 1 Hz, 1 x 3 mm beam at the sample.) The flow rate for metal carbonyl solutions through the sample cuvette was increased until the results were independent of the flow rate (10–15 mL/min). Prior to each measurement, the solution in the sample cell was pulsed with ten laser shots. The results were averaged and subsequently used to reject signals for laser pulses that deviate more than 5% from the average. For each measurement, transducer signals are captured on a digital oscilloscope and transferred to a PC until 32 signals of acceptable shots are obtained. For each ligand concentration, three $Mo(CO)_6$ measurements were obtained. Ferrocene was measured before and after each $Mo(CO)_6$ measurement, and solvent was measured before the first and after the last measurement of ferrocene.

The MQ program was used to deconvolute the signal for $Mo(CO)_6$ solutions with that for ferrocene solutions.[19] Up to three heat decays can be deconvoluted, and goodness-of-fit was determined from the sum of the squares of residuals (χ^2).[20] Observed signals were corrected for differences in pulse energies and solution absorbances. MQ provided ϕ_1, ϕ_2, τ_2, and χ^2. The corresponding enthalpies of reaction are obtained by using eq 4 and 5 where E_{hv} is the photon energy (84.8 kcal/mol).[21] The second-order rate constant (k_2) for reaction 2 can be obtained from the slope a plot of the observed rate constant ($1/\tau_2$) *vs.* [L] (eq 6). All errors listed in parentheses are one σ and are the errors in the last digit(s).

$$\Delta H_1 = E_{hv}(1 - \phi_1)/\Phi \qquad (4)$$

$$\Delta H_2 = -E_{hv}\phi_2/\Phi \qquad (5)$$

$$1/\tau_2 = k_o + k_2[L] \qquad (6)$$

RESULTS

The photosubstitution chemistry of $Mo(CO)_6$ in heptane at 25°C was investigated for pip and acetonitrile. When secondary photolysis is avoided in each case, only the monosubstituted product was observed by IR spectroscopy for 337 nm irradiation (for example, see Figure 1). $Mo(CO)_5(pip)$ formation was determined quantitatively by optical spectroscopy. The quantum yield for $Mo(CO)_5(pip)$ formation in heptane was found to be independent of a ten-fold change in pip concentration (Table 1). The average value for the quantum yield was 0.933 (7). Similar experiments were undertaken with $Cr(CO)_6$ where the average value for the quantum yield was 0.75 (3).

Two heat decays (ϕ_1 and ϕ_2) were observed after photolysis of $Mo(CO)_6$ solutions containing 8-80 mM pip. The ϕ and ϕ_2 values are plotted *vs.* [pip] in Figure 2. The intercepts are 0.728 (6) and 0.189 (30), and the slopes are 0.29 (11) and 0.02 (22), respectively. The averages for ϕ_1 and ϕ_2 are 0.740 (10) and 0.190 (14), respectively. The intercepts are within experimental error of the averages, and the slopes are within experimental error of zero. We conclude that ϕ_1 and ϕ_2 are independent of pip concentration over the range reported. At higher concentrations of pip, only a single heat decay is observed, and it is larger than ϕ_1 at 8–80 mM pip. On the other hand, for pip concentrations lower than 8–80 mM, only a single heat decay is observed, and it is the same as that observed for ϕ_1 at 8–80 mM pip. These results are consistent with the rate of reaction 2 being comparable with the frequency response of the transducer for 8–80 mM pip but faster at higher concentrations and slower at lower concentrations. This is supported by the concentration dependence observed for the lifetimes (τ_2) corresponding to ϕ_2. A plot of the pseudo first-order rate constants ($1/\tau_2$) *vs.* [pip] is shown in Figure 3. The slope (k_2) is $6.0\ (3) \times 10^7\ M^{-1}s^{-1}$, and the intercept is $4.8\ (14) \times 10^5\ M^{-1}s^{-1}$ ($r = 0.993$).

DISCUSSION

The quantum yields for photosubstitution of $Cr(CO)_6$ and Mo $(CO)_6$ in heptane are in excellent agreement with the values reported by Wieland and van Eldik.[11] We concur with these investigators that the quantum yields for $M(CO)_6$ ($M = Cr$ and Mo)[11,17] are different for each M and can vary significantly for different alkane solvents. In general, we caution that quantum yields may change upon the simplest change in the solvent structure.

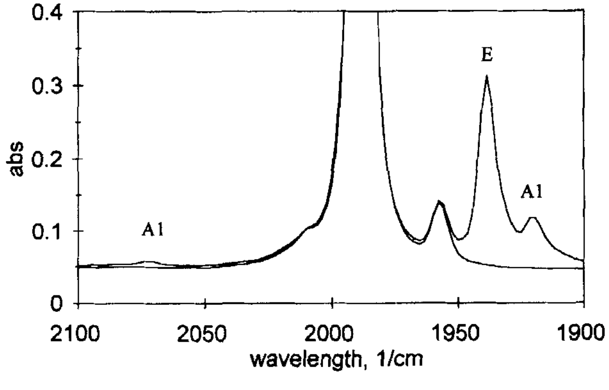

Figure 1 3.78mM $Mo(CO)_6$ and 0.05 M piperidine in heptane before (lower spectrum) and after (upper spectrum)10 min photolysis at 337 nm. Peaks due to $Mo(CO)_5pip$ are labeled A1 and E.

Table 1 Quantum yields for photosubstitution of $Mo(CO)_6$ in heptane with 337 nm light at 25°C.

$[Mo(CO)_6]$	[pip]	Φ
(mM)	(M)	
3.01	0.005	0.940(4)
4.53	0.01	0.937(10)
4.72	0.01	0.938(16)
4.60	0.015	0.925(20)
4.55	0.015	0.942(17)
4.86	0.05	0.0926(7)
2.63	0.05	0.927(7)

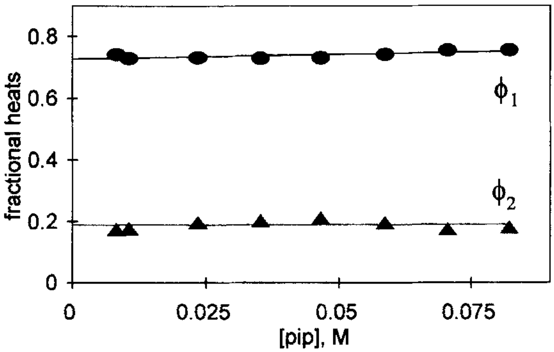

Figure 2 Observed heats following photolysis of $Mo(CO)_6$ in heptane. Fractional amplitudes of heat decays, ϕ_1 and ϕ_2, are plotted *vs.* piperidine concentration.

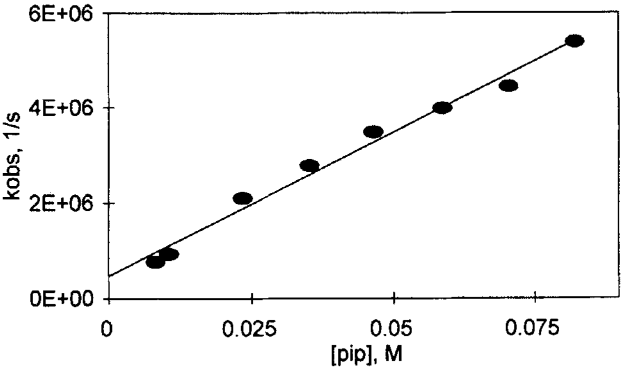

Figure 3 Plot of the pseudo first-order rate constant for the second heat decay (ϕ_2) observed following photolysis of $Mo(CO)_6$ in heptane *vs.* piperidine concentration.

Picosecond flash photolysis studies of $Mo(CO)_6$ show that $Mo(CO)_5$(alkane) is formed and thermally relaxed on a 100 ps time scale.[22] The concentration of piperidine is too low for a signficant amount to be in the solvent cage when $Mo(CO)_6$ is photolyzed. Thus $Mo(CO)_5$(pip) must be formed from $Mo(CO)_5$(heptane). In our experiments, subsequent displacement of heptane by dispersed CO must compete with piperidine. The concentration of CO is at least ten-fold less than piperidine since no more than 10% of $Mo(CO)_6$ was photolyzed. The independence of the quantum yield for $Mo(CO)_5$(pip) formation on the piperidine concentration indicates that all $Mo(CO)_5$(heptane) is scavenged by the piperidine and that the quantum yield for $Mo(CO)_5$(heptane) formation is the same as that for $Mo(CO)_5$(pip).

Since the formation of $Mo(CO)_5$(alkane) is much faster than the frequency response of our 1 MHz transducer (*vide supra*) the heat for reaction 1 must contribute to the first heat decay (ϕ_1). Between 8 and 80 mM piperidine, ϕ_2 depends on piperidine since the observed rate constant associated with ϕ_2 increases with piperidine concentration. We therefore assign ϕ_1 to reaction 1 and ϕ_2 to reaction 2. From eq 4 and 5 and the average values of ϕ_1 and ϕ_2, ΔH_1 (23.6(9)) and ΔH_2(-17.3(13)) may be calculated. In contrast to studies of $Cr(CO)_6$ with various aliphatic amines,[5] no PAC evidence of hydrogen bonding between the product and free amine was observed. This is expected since the equilibrium constant for hydrogen bond formation is about 1,[5] and we are using piperidine concentrations 10 to 100-fold less than in the previous study.

The enthalpy of CO substitution by piperidine (ΔH_1 + ΔH_2) is 6.3 (16) kcal/mol, and is within experimental error of 4.6 (1) kcal/mol reported by Nakashima and Adamson.[23,24] This is better agreement than for piperidine substitution with $Cr(CO)_6$ where the PAC value was 8.3 kcal/mol more endothermic than that reported by these investigators.[23] The discrepancy is likely caused by the high piperidine concentrations used in the previous PAC experiments (near 1 M). Specifically, there may be a solvent effect on the quantum yield for substitution of $Cr(CO)_6$ since the quantum yield has been shown to change significantly even when the solvent is changed from heptane to cyclohexane (*vide supra*).[11,17] Thus a PAC study of $Cr(CO)_6$ at lower piperidine concentrations is warranted.

The good agreement between our data for $Mo(CO)_6$ and the literature results gives us confidence that the PAC results in general are free of significant experimental errors and may be applied to other calculations. The $Mo(CO)_5$-pip BDE may be estimated as 34.2 kcal/mol from $\Delta H_1 + \Delta H_2$ and the gas-phase $Mo(CO)_5$-CO BDE. For comparison, the activation enthalpy for thermal decomposition of $Mo(CO)_5$(pip) in hexane is 23.1 (11) kcal/mol.[12] This activation enthalpy presumably corresponds to the dissociation of piperidine and indicates that the transition state is 11.1 kcal/mol lower in energy than dissociated piperidine and $Mo(CO)_5$ (without agostic bonding). A possible explanation for the low transition-state energy is stabilization of the transition state by agostic bonding with the solvent. If this is the case, then agostic bonding in the intermediate, $Mo(CO)_5$(hexane), might be expected to be even stronger. Consistent with this, the $Mo(CO)_5$-heptane BDE calculated from ΔH_1 is 16.9 kcal/mol. For comparison, the $Cr(CO)_5$-cyclohexane BDE is 12.6 kcal/mol when calculated from the Cr-CO BDE (36.8 (20) kcal/mol)[9] and ΔH_1 in cyclohexane (24.3 (8) kcal/mol).[17] Using 0.73 for the quantum yield for $Cr(CO)_6$ photosubstitution in heptane, the previous PAC calculation for this solvent may be corrected.[5,6,25] This gives 24.8 (12) kcal/mol for

ΔH_1 in heptane and 12.0 for the $Cr(CO)_5$-heptane BDE. Within experimental errors, these results indicate that the agostic bond strengths for cyclohexane and heptane to $Cr(CO)_5$ are the same but smaller by 4–5 kcal/mol than the $Mo(CO)_5$-heptane BDE.

A comparison with activation enthalpies for solvent displacement is revealing. An activation enthalpy of 12.5 (1) kcal/mol for unimolecular benzene displacement from $Mo(CO)_5$(benzene) has been reported by Zhang and Dobson.[26] They proposed this value as a good estimate of the Mo-benzene bond energy. Since benzene is presumably a better Lewis base and π-acid than heptane, it is anticipated that the Mo-benzene bond is stronger than the corresponding Mo-heptane bond. If 12.5 kcal/mol is the bond dissociation energy for benzene, then 16.9 kcal/mol clearly is too large for heptane. On the other hand, the activation entropy for benzene dissociation is surprisingly small (4.1 (2) eu) for a purely dissociative process. For example, the activation entropy for unimolecular CO substitution by benzylamine in decalin is 19.1 (92) eu,[27] and the corresponding activation enthalpy is 36.0 (29) kcal/mol, which is only about 4 kcal/mol less than the gas-phase value for the $Mo(CO)_5$-CO BDE. It might be postulated that since decalin is bulky it does not readily stabilize the transition state; thus little association occurs to reduce the activation entropy or enthalpy. For benzene, the low activation entropy suggests there may be residual bonding to benzene in the transition state, and the activation enthalpy is a lower limit to the Mo-benzene bond strength.

It must be cautioned that volume changes that occur during a reaction can also contribute to observed PAC signals. Unfortunately, partial molar volumes are not readily obtained for $Mo(CO)_6$, $Mo(CO)_5$(pip), and certainly not for $Mo(CO)_5$(heptane). While it is true that reaction 1 involves dissociation of CO, requiring an increase in volume, the reaction also involves the association of heptane, requiring a decrease in volume. The volume changes of the two processes will tend to cancel. It has been argued that reaction volume changes are not significant for reactions in organic solvent where coefficients of thermal expansions are very large.[25,28] This may be reasonable for well-defined reactants and products where one strong bond has replaced another, but is not clear for a process involving a weakly-bound solvent molecule. It has been shown that processes that involve the homolysis of a C-C bond generate a volume change of 10 mL/mol in forming the transition state.[29] In general, we would predict a positive volume change for the replacement of a strong metal-ligand bond by a weak metal-solvent bond. This leads to the prediction that ΔH_1 will appear too exothermic when calculated from PAC signals without correction for reaction volume changes. Likewise, ΔH_2 will be too endothermic. On the other hand, the same solvent molecule is involved for the calculation of ΔH_1 and ΔH_2, so the volume changes associated with the solvent will cancel. We therefore predict the results for the enthalpy of ligand exchange ($\Delta H_1 + \Delta H_2$) to be more accurate than ΔH_1 and ΔH_2 individually.

We conclude that our estimate for the $Mo(CO)_5$-heptane BDE is an upper limit. More importantly, it is reasonable to expect that the volume changes for formation of $Cr(CO)_5$(heptane) and $Mo(CO)_5$(heptane) will be very similar. If this is the case, the PAC results demonstrate that the Cr-heptane bond is 4-5 kcal/mol weaker than the Mo-heptane bond. We are currently, developing a high-pressure PAC apparatus to detemine the contribution of reaction volume changes to PAC signals.

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