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Reaction of the Transient Species W(CO)$_5$(Cyclohexane) with Cyclo-C$_4$H$_n$O (n = 4, 6, 8) Studied by Time-Resolved Infrared Absorption Spectroscopy[†]

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Time- and temperature-resolved infrared absorption spectroscopy is used to monitor the ligand substitution reaction of W(CO)$_5$(cyclohexane) with a series of ligands L of the form cyclo-C$_4$H$_n$O ($n = 4, 6, 8$). Second-order rate constants for the formation of W(CO)$_5$(L) are obtained over the temperature range 20−60 °C, and from these temperature-dependent rate constants, activation parameters for the ligand substitution reaction are obtained. We find that for L = furan, $\Delta H^‡ = 7.1 \pm 0.7$ kcal mol^{-1} and $\Delta S^‡ = -7.1 \pm 5.1$ eu; for L = 2,3-dihydrofuran, $\Delta H^‡ = 5.9 \pm 0.5$ kcal mol^{-1} and $\Delta S^‡ = -8.9 \pm 7.3$ eu; and for L = 2,5-dihydrofuran, $\Delta H^‡ = 3.8 \pm 0.2$ kcal mol^{-1} and $\Delta S^‡ = -14.0 \pm 3.5$ e.u. We find that as L becomes less strongly electron-donating, as determined by the trans C−O stretching force constant of W(CO)$_5$L, $\Delta H^‡$ rises and $\Delta S^‡$ becomes less negative. The correlation of the activation enthalpy with the properties of the products and the low activation enthalpies relative to the (CO)$_5$W-cyclohexane bond dissociation energy are consistent with an associative interchange (**I$_a$**) mechanism for the ligand exchange.

1. Introduction

Because of the significance of transition-metal (TM) chemistry to modern synthesis and catalysis, reaction intermediates containing TMs have been the subject of considerable study over the past 15 years.[1] In particular, because of possible relevance to such chemical problems as TM-mediated alkane activation, the properties of transient complexes in which an alkane molecule is weakly bound to a TM center have received much attention from a variety of experimental[2−5] and theoretical[6] techniques. Such studies have investigated the behavior of such species down to the picosecond time scale,[7] and fast spectroscopic techniques applied to TM intermediates have proved invaluable in aiding our understanding of many interesting and important chemical processes.[8−10] Most of the work on TM-alkane complexes in solution has been aimed at trying to understand the simplest possible reaction of such a species, namely, ligand exchange of a weakly bound alkane solvent molecule (solv) at a TM center [M], reaction 1,

$$[\mathrm{M}]\text{−solv} + \mathrm{L} \rightarrow [\mathrm{M}]\text{−L} \qquad (1)$$

to form the stable product complex [M]−L.[11]

While the room-temperature spectroscopy and kinetics of reaction 1 have received considerable attention, measurement of activation parameters for the reaction in alkane solvent have been quite infrequent, and *systematic* studies of reaction 1, that is, studies in which the behavior of the reaction is studied as a function of systematic changes in one or more of the components of the reaction system, are rarer still; to our knowledge, there have only been four such studies performed on solution systems to date.

Two reports have considered the effect of changing the alkane on the course of reaction 1. Long and co-workers[12] examined the effect of changing the alkane solvent on the recombination reaction (L = CO) of a number of group 6 [M]−alkane intermediates. They observed that changing the alkane tends to affect $\Delta S^‡$, while having much less of an effect on $\Delta H^‡$, for the ligand substitution. A more recent study[13] was primarily aimed at understanding the effect of the alkane on alkane C−H bond activation by photolytically generated Cp*Rh(CO)Kr (Cp* = cyclo-C$_5$(CH$_3$)$_5$) in liquid Kr solution. The initial step of the activation reaction is believed to be formation of the [Rh]−alkane complex, essentially the reverse of reaction 1. In the case of reaction of a variety of alkanes with Cp*Rh(CO)Kr, the binding of the alkane was observed to become stronger as the size of the alkane increases, although it was not clear to what extent electronic, steric, and conformational factors contribute to the observed differences in the binding.

Two studies have considered the effects of changing the *ligand* on the behavior of the reaction system. Yang et al.[3a] performed a photoacoustic calorimetry study of the reaction 1 at the Cr(CO)$_5$(heptane) intermediate for a variety of incoming ligands L. They found that the overall exothermicity for the series pyridine/2-picoline/2,6-lutidine decreases as the steric hindrance at the ligand N atom increases, and that $\Delta H^‡$ and $\Delta S^‡$ are both greater for reaction with 2-picoline than for reaction with pyridine. More recently, Dobson and Zhang[14] used time-resolved UV−vis absorption spectroscopy to measure the activation parameters for reaction of the same intermediate with a number of incoming ligands. They discovered that, apparently, the correlation between $\Delta H^‡$ and $\Delta S^‡$ for reaction 1 by Yang et al. is more general, and can be applied to a variety of different ligands. Dobson and Zhang also discovered that the correlation between $\Delta H^‡$ and the room-temperature second-order rate constant is much poorer. They interpreted the results in terms of competition between associative and dissociative reaction pathways in which the overall rate constant will depend on the ability of the incoming ligand to compete with a molecule of

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the solvent for the vacant site of a "naked" $Cr(CO)_5$ intermediate produced in a dissociative pathway.

Because there are many variables at work in these systems, we have taken a slightly different approach in our laboratory. While Dobson and Zhang chose to measure the kinetics of reaction 1 for a variety of types of ligands, we decided to concentrate on a series of similar ligands to see if there were any particular ligand properties that would correlate with the reaction's rate or activation parameters. To that end, we chose to investigate reaction 1 by using time-resolved Step-Scan Fourier Transform IR (S^2FTIR) spectroscopy, using for the intermediate the cyclohexane (CyH) solvated intermediate $W(CO)_5(CyH)$ and for L a series of five-membered N- and O-containing heterocyclic ligands.[15] In that study, we found that the as the C−O stretching frequencies of the *product* $W(CO)_5L$ complex decrease, the room-temperature second-order rate constant increases. We interpreted this correlation between the rate constant and the properties of the product as indicating that the reaction proceeds with a late transition state (i.e., "associative"-like reaction).

In an effort to better understand the details of the reaction, we have recently completed a study of reaction 1 for the reaction of $W(CO)_5(CyH)$ with THF.[16] That study provided further evidence for a late transition state for reaction 1 in CyH: not only is $\Delta H^{\ddagger}$ considerably lower than the $(CO)_5W{-}CyH$ bond dissociation energy,[3,17] but the reaction proceeds more slowly in C_6D_{12} over the temperature range studied (20−60 °C) even though $\Delta H^{\ddagger}$ is lower in C_6D_{12} than it is in C_6H_{12}, indicating that the solvent makes a large entropic contribution to the reaction energetics, presumably from low-frequency $(CO)_5W-$alkane hindered rotations.

We undertook the present study in order to expand upon our observations in our prior work. In particular, we have chosen to measure the activation parameters for reaction 1 for $W(CO)_5(CyH)$ reacting with the series of ligands furan, 2,3-dihydrofuran (DHF), and 2,5-DHF, and to compare these results with the results of the study on the reaction of $W(CO)_5(CyH)$ with THF. We assume that for this series of ligands, the primary effects on the reaction will be electronic rather than steric, and so the primary goal of this study was to determine whether there is any correlation between the electronic properties of a series of related ligands and the activation parameters for these ligands displacing an alkane solvent molecule at the $W(CO)_5$ center.

2. Experimental Section

The apparatus upon which these experiments were performed has been described in detail previously,[16] so only a brief description will be given here. Reaction takes place in an 0.5 mm path length CaF_2 IR cell, whose temperature has previously been set to within 1 °C of the nominal reaction temperature. A reaction mixture consisting of an Ar-degassed CyH solution containing $0.5{-}1.0 \times 10^{-3}$ mol L^{-1} $W(CO)_6$ and at least a 10-fold excess of the reactant ligand L flows continuously through the cell. The continuous flow is maintained so that each photolysis pulse irradiates fresh solution. The reservoir of reactant solution is held under Ar in a constant-temperature bath.

Reaction is initiated by the pulse of a XeCl excimer laser operating at 2−5 Hz (308 nm, ∼20 ns/pulse, typically 30−60 mJ/pulse). The UV flash photolyzes $W(CO)_6$ to $W(CO)_5 + CO$, which solvates within the laser flash[7] to form the transient species $W(CO)_5(CyH)$. The progress of reaction 1 is monitored through measurement of the time evolution of the IR absorption spectrum (measured in the C−O stretching region) of the reactant solution. For determination of the locations of the absorption peaks of interest, Step-Scan FTIR (S^2FTIR, using a Bruker Equinox 55 instrument) is used. Once the absorptions of interest have been identified, detailed kinetic studies are performed with the use of a continuous-wave Pb−salt diode laser tuned to a wavelength corresponding to an absorption of the $W(CO)_5(CyH)$ intermediate or of the $W(CO)_5L$ product. The laser output is collimated to a 5 mm diameter beam which passes through the reaction cell collinear with (and completely overlapped by) the UV photolysis pulse, after which it impinges on an InSb detector (50 ns response time).

The time-dependent detector output is passed to a digital oscilloscope for digitization and storage. The raw signal is converted to the change in absorbance (ΔA), and the pseudo-first-order rate constant determined from a linear fit to $\ln|\Delta A_0 - \Delta A_\infty|$. Pseudo-first-order rate constants reported here represent the averages of at least two independent data sets, and usually represent data collected for decay of the absorbance of the intermediate and for the growth of the product absorbance. Because of the weaker extinction coefficient of the product absorptions and the stronger output of our diode laser at the absorption of the intermediate at 1954 cm^{-1} compared with its output at the absorptions of the products, however, occasionally (especially at high [L]), the product absorption did not give a transient of sufficiently high quality to provide a reproducible value of the rate constant. In such cases, the reported rate constant is from the decay of the intermediate alone. In all cases, however, the rate of growth of the product was consistent with the rate constant obtained from the disappearance of the absorption due to the intermediate. On the basis of run-to-run reproducibility and the uncertainties in the temperature and concentrations, we estimate that the pseudo-first-order rate constants are accurate to within 10−15%.

CyH was obtained in HPLC or spectrophotometric grade (>99% purity) and distilled from Na/benzophenone under N_2 to remove remaining traces of water. The ligands L were obtained from commercial sources in >97% purity (confirmed by NMR), distilled from an appropriate drying agent under N_2 or Ar, and stored over a drying agent (molecular sieves or Na). $W(CO)_6$ was obtained from Strem (98% purity) and used without further purification.

3. Results

3.1. $W(CO)_5(CyH)$ + 2,5-DHF and 2,3-DHF. Upon photolysis of a CyH solution of $W(CO)_6$, the C−O stretching region of the IR spectrum shows a bleach at 1981 cm^{-1}, corresponding to photolysis of the parent $W(CO)_6$. Simultaneously (i.e., within the 50 ns rise time of the detector), three new peaks appear, relatively strong ones at 1954 and 1928 cm^{-1}, and a very weak one at 2087 cm^{-1}. We attribute these peaks to the E, $A_1(2)$, and $A_1(1)$ C−O stretches of the solvated $W(CO)_5(CyH)$ intermediate,[18] which is formed within tens of picoseconds of the photolysis.[7] These absorptions disappear over time, while three new peaks, corresponding to formation of $W(CO)_5(L)$, reaction 1, appear with the same (exponential) time dependence. The positions of these new peaks are given in Table 1 for the four ligands L used in this study. A typical set of time-resolved S^2FTIR spectra for reaction of $W(CO)_5(CyH)$ with 2,5-DHF is shown in Figure 1.

For ligands such as THF, there is only one possible site of interaction between the metal and ligand, namely, through a lone pair on the ligand heteroatom. For the two isomers of DHF, however, there are two possible sites of interaction, either via a lone pair of electrons on the heteroatom or via the double bond. On the time scale of the experiments discussed here, only

TABLE 1: Frequencies (cm^{-1}) and Force Constants (mdyn Å^{-1})[a] for $W(CO)_5L$ Complexes

complex	ν_{CO} $A_1(1)$	ν_{CO} E	ν_{CO} $A_1(2)$	k_1	k_2	k_i
$W(CO)_5$(CyH)	2087	1954	1928	15.233	16.075	0.326
$W(CO)_5$(THF)	2074	1933	1911	14.980	15.778	0.342
$W(CO)_5$(2,5-DHF)[b]	2075	1934	1913	15.011	15.794	0.343
$W(CO)_5$(2,3-DHF)[b]	2077	1936	1914	15.027	15.826	0.343
$W(CO)_5$(furan)	2078	1949	1936	15.350	15.974	0.315

[a] Cotton−Kraihanzel method (ref 31). k_1 = force constant for C−O trans to L, k_2 = force constant for C−O cis to L, k_i = force constant for interaction of mutually cis CO groups. [b] Kinetic product, see text.

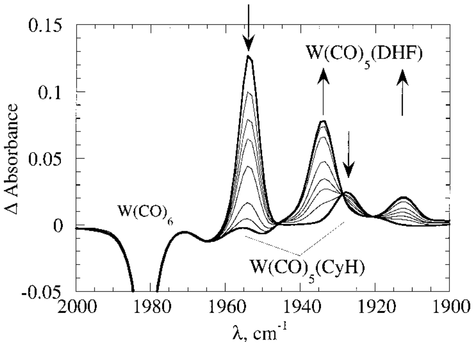


Figure 1. Time-resolved S^2FTIR spectra for the reaction of $W(CO)_5$(CyH) with 2,5-DHF. Shown are spectra obtained 0, 1, 2, 3, 5, 10, 15, and 25 μs following the photolysis flash. The peaks at 1954 and 1928 cm^{-1} that disappear with time are due to absorptions of $W(CO)_5$(CyH), while the peaks at 1934 and 1913 cm^{-1} that grow in with time are due to absorptions of $W(CO)_5$(2,5-DHF).

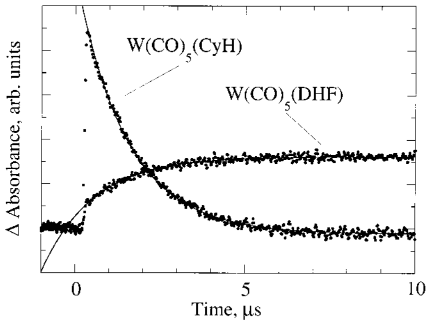


Figure 2. Typical experimental traces. Shown are the time-resolved IR absorbances at 1956 cm^{-1}, corresponding to $W(CO)_5$(CyH), and at 1934 cm^{-1}, corresponding to $W(CO)_5$(2,5-DHF), following photolysis of a $W(CO)_6$ solution containing 0.04 mol L^{-1} 2,5-DHF at 50 °C. The solid lines are single-exponential fits to the data with $k_{obs} = 6.58 \times 10^5$ s^{-1}. The nonzero absorption at time = 0 at 1934 cm^{-1} is due to a small amount of overlap with the $W(CO)_5$(CyH) peak at 1928 cm^{-1}.

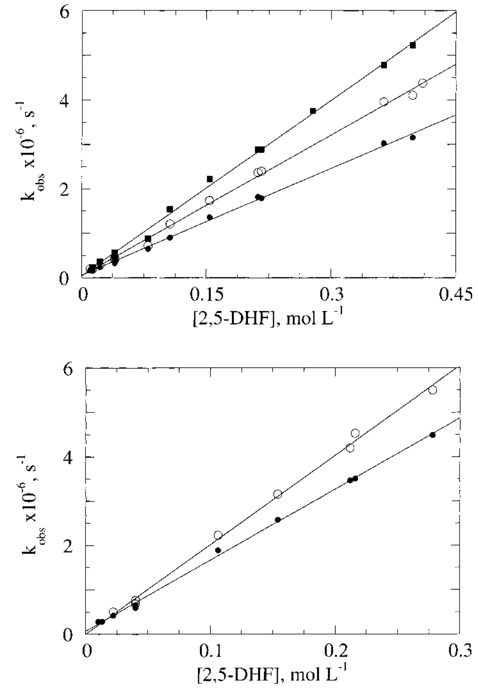


Figure 3. Pseudo-first-order rate constant $k_{obs} \times 10^{-6}$ (s^{-1}) as a function of [2,5-DHF] for reaction 1. Figure 3a shows results for reaction at (●) 20 °C, (○) 30 °C, and (■) 40 °C. Figure 3b shows results for reaction at (●) 50 °C and (○) 60 °C. The solid lines represent least-squares linear fits to the data. Similar plots for reaction with 2,3-DHF and with furan are given in the Supporting Information.

a single product is seen for the reaction, to which we attribute the O-bound structure. Our assignment is due primarily to the similarity of the IR spectra of $W(CO)_5$(THF), $W(CO)_5$(2,5-DHF), and $W(CO)_5$(2,3-DHF), Table 1, in contrast to C−O stretching frequencies for $W(CO)_5$(alkene) complexes, which are significantly higher in energy.[15,19] Furthermore, k_1, the force constant for the C−O stretch of the carbonyl trans to L, is lower in the DHF complexes than it is in the CyH complex, implying that both isomers of DHF are stronger σ-donors than CyH. Strong σ-donation also implies the η^1-*O* bound structure rather than the η^2 structure.

In addition, we have recently discovered[20] that on a much longer time scale (0.1−1 s) than that observed here, the $W(CO)_5$ complexes of 2,5-DHF and 2,3-DHF undergo an intramolecular isomerization reaction to a form species with significantly higher C−O stretching frequencies; these thermodynamic products are assigned the η^2-bound complex, both on the basis of the IR spectra and from ^{1}H NMR spectra of $W(CO)_5$(DHF) which we were able to obtain for both DHF isomers.[21] Since the isomerization is so much slower than the kinetic processes observed here, we do not further consider it in the present discussion, and all references to "$W(CO)_5$(2,5-DHF)" and "$W(CO)_5$(2,3-DHF)" are to the O-bound kinetic product that is formed on the μs time scale.

Having determined the locations of the product absorbances from S^2FTIR, we then measured the time-dependent absorptions of the intermediate and product. Typical traces are shown in Figure 2. These traces are then converted to pseudo-first-order reaction rate constants (k_{obs}) as described above. Figure 3 shows k_{obs} as a function of concentration for reaction with 2,5-DHF at five different temperatures. As can be seen from the plot, the pseudo-first-order rate constant is a linear function of [2,5-DHF] over the entire concentration range studied (0.01−0.4 mol L^{-1} for $T < 40$ °C, 0.01−0.28 mol L^{-1} for $T \geq 40$ °C; the upper limit of the concentration decreases with increasing temperature because the reaction becomes too fast ($k_{obs} >$ ca. 5×10^6 s^{-1}) for us to measure accurately). Similarly, k_{obs} is a linear function of [L] for reaction with 2,3-DHF as well; for this ligand, the concentration range over which measurements were made was 0.02−1.08 mol L^{-1} for $T < 40$ °C, 0.02−1.02 mol L^{-1} for $T = 40$ °C, and 0.02−0.6 mol L^{-1} for $T > 40$ °C. Plots of k_{obs} as a function of [2,3-DHF] are given as Figure S1 in the Supporting Information.

3.2. $W(CO)_5$(CyH) + Furan. Reaction of $W(CO)_5$(CyH) with L = furan follows essentially the same course as it does for reaction with the two isomers of DHF. Two complications arose, however, in this experiment. The first difficulty was that we were unable to obtain reproducible results for this ligand for reaction at 60 °C. The most likely explanation is the much greater volatility of furan (bp 32 °C) relative to the other ligands

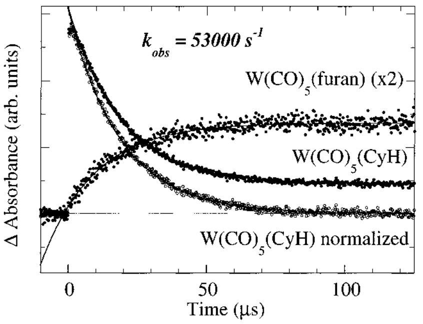


Figure 4. Transient time-resolved absorptions for reaction of W(CO)$_5$(CyH) with 0.0148 mol L^{-1} furan at 30 °C. Shown are the time-dependent absorptions of the intermediate (measured at 1956 cm^{-1}) and product (measured at 1950 cm^{-1}), and the difference obtained from subtracting the latter (normalized to the same ΔA_∞) from the former. The solid lines are exponential fits to the data sets with $k_{obs} = 5.3 \times 10^4$ s^{-1}.

(bp 55−65 °C). While expansion of the CyH as it is heated will introduce an uncertainty in the concentration of at most a few percent,[22] it is not inconceivable that if the temperature is raised sufficiently high, enough furan will evaporate to significantly affect its concentration in the solution; the extent to which this will occur will depend on poorly reproducible experimental conditions such as the length of time the solution remains at elevated temperatures and the quality of the seal made by the septum enclosing the flask. We therefore only report results for the temperature range 20−50 °C for the reaction with furan.

Unlike the results obtained for the other ligands, the absorption at 1954 cm^{-1} does not return to baseline due to overlap with an absorbance of the product complex, Table 1. If the product observed is being formed from the intermediate whose concentration we are monitoring, the time *dependence* of the decay will be unaffected (except, of course, at the isosbestic point). To double-check that this was indeed the case, we initially determined the rate constant from ΔA itself. We then subtracted out the growth in ΔA of the product, normalized to bring ΔA_∞ for the intermediate to zero, and determined the rate constant of the resulting "corrected" intermediate absorption. As shown in Figure 4, k_{obs} does not change when such a subtraction is done; we therefore determined k_{obs} from linear fits to $\ln|A_0 - A_\infty|$ as described above. As with the reactions of DHF, k_{obs} for reaction with furan is a linear function of [furan] over the entire concentration range studied, which in this case was 0.0148−2.14 mol L^{-1} for $T < 50$ °C, and 0.0148−1.61 mol L^{-1} at $T = 50$ °C. Plots of k_{obs} vs [furan] are given as Figure S2 in the Supporting Information.

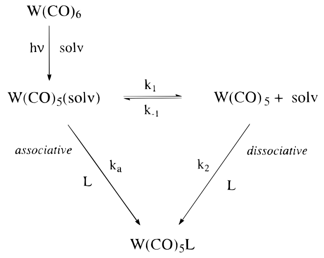
Unlike the cases of the other three ligands used here, the structure of W(CO)$_5$(furan) is subject to some ambiguity, as it is not immediately apparent whether the ligand binds η^1-*O*, η^2 through a pair of adjacent C atoms, or η^5 with the metal face-on to the ring. In contrast to the behavior of the DHF complexes, the IR spectrum of W(CO)$_5$(furan) is the same after several minutes as it is on the time scale of this experiment. Unfortunately, we have not yet succeeded in preparing a solution of this complex that is simultaneously sufficiently concentrated and free of paramagnetic side products to be amenable to NMR analysis to prove unambiguously the structure of W(CO)$_5$(furan). The IR spectra and transient kinetics of the reaction of W(CO)$_5$(CyH) with furan are consistent with an η^1-O bound structure for this complex, however. Although the C−O stretches of W(CO)$_5$(furan) are higher than those of the other ligands, they are significantly lower than those typically found in W(CO)$_5$(alkene) complexes.[15,19] Stolz et al.[23] observed that photolysis of W(CO)$_6$ in the presence of furan at −180 °C in a 1:4 mixture of isopentane and methylcyclohexane produced a complex with IR C−O stretching frequencies of 2090, 1949, and 1919 cm^{-1}, which upon warming formed irreversibly a second complex with IR C−O stretching frequencies of 2083, 1950, and 1935 cm^{-1}. They proposed that the former was bound to the furan ring face-on, while the latter was the η^1-O bound complex. From the similarity of the IR spectrum we observe here (Table 1) to that observed by Stolz et al., from its dissimilarity to the IR spectra of known (CO)$_5$W−alkene complexes, and from the observation that the kinetic product of reaction with DHF is the η^1 structure, we conclude that the most likely structure for W(CO)$_5$(furan) observed in our experiment is as the η^1−O bound complex.[23]

TABLE 2: Second-Order Rate Constants for Reaction 1 (10^6 L mol^{-1} s^{-1})[a]

temperature (°C)	rate constant 2,5-DHF	 2,3-DHF	 furan
20	7.95 (0.12)	2.62 (0.05)	0.860 (0.014)
30	10.58 (0.17)	4.00 (0.06)	1.41 (0.030)
40	13.13 (0.21)	5.38 (0.20)	1.98 (0.022)
50	16.20 (0.23)	7.87 (0.19)	3.11 (0.084)
60	20.18 (0.45)	9.46 (0.39)	

[a] 1σ uncertainties to the linear fits of k_{obs} vs [L] are given in parentheses.

SCHEME 1



3.3. W(CO)$_5$(CyH) + THF. We have recently performed a detailed study of this reaction.[16] For comparison, we mention here the results of that study to enable ready comparison with the reactions of the other three ligands. For reaction with THF, the kinetics were measured over the temperature range 20−60 °C and from the kinetic results, values of $\Delta H^\ddagger = 3.6 \pm 0.2$ kcal mol^{-1} and $\Delta S^\ddagger = -13.7 \pm 2.5$ eu were determined. To provide a basis for understanding the structures and NMR spectra of the DHF complexes, for the present study, we measured the ^{1}H NMR spectrum of W(CO)$_5$(THF) as well;[26] although W(CO)$_5$(THF) is a very common reagent for the synthesis of tungsten complexes, to our knowledge, its NMR spectrum has not been reported previously.

4. Discussion

4.1. Activation Parameters and Reaction Mechanism. Second-order rate constants k_{second} derived from linear fits to k_{obs} vs [L] are summarized in Table 2. The physical meaning of these rate constants will, of course, depend on the mechanism of the reaction. We can consider two limiting cases for the mechanism, shown in Scheme 1: an *associative* pathway in which binding of L and loss of solvent are simultaneous, and a *dissociative* pathway in which L does not bind to the metal center until the solvent molecule has left. In the case of a purely associative mechanism, $k_{second} = k_a$, the rate constant for association of L, while in the case of a purely dissociative mechanism, $k_{second} = k_1k_2[L]/(k_{-1}[solv] + k_2[L])$. Under our experimental conditions, [solv] ≫ [L]; with the not unreasonable assumption that $k_{-1} \approx k_2$,[7,27] i.e., a "naked" W(CO)$_5$ will not discriminate very strongly between possible reaction partners,

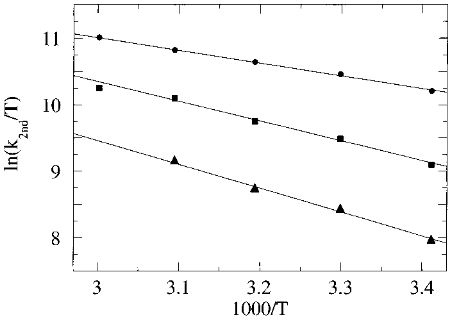


Figure 5. Eyring analyses of k_{second} for reaction of $W(CO)_5(CyH)$ + (●) 2,5-DHF, (■) 2,3-DHF, and (▲) furan. The solid lines are least-squares linear fits to the rate constants weighted by the relative uncertainties given in Table 2.

TABLE 3: Activation Parameters for Reaction 1[a]

ligand L	$\Delta H^\ddagger$, kcal mol^{-1}	$\Delta S^\ddagger$, eu
THF[b]	3.6 ± 0.2	−13.7 ± 2.5
2,5-DHF	3.8 ± 0.2	−14.0 ± 3.5
2,3-DHF	5.9 ± 0.5	−8.9 ± 7.3
furan	7.1 ± 0.7	−7.1 ± 5.1

[a] Cited uncertainties are 90% confidence limits to the slope and intercept of an Eyring analysis of the second-order rate constants, weighted by their relative uncertainties, as given in Table 2 (cf. Figure 5). [b] Reference 16.

in our system, a dissociative reaction will yield $k_{second} \approx k_1k_2/(k_{-1}[\text{solv}])$. Eyring analyses of the temperature dependence of k_{second} are shown in Figure 5, and the derived values of $\Delta H^\ddagger$ and $\Delta S^\ddagger$ given in Table 3.

In the limit of an associative reaction, the activation parameters derived from k_{second} are those for the reaction itself, while in the limit of a dissociative reaction, $\Delta H^\ddagger \approx \Delta H^\ddagger_1 + \Delta H^\ddagger_2 - \Delta H^\ddagger_{-1}$, and $\Delta S^\ddagger \approx \Delta S^\ddagger_1 + \Delta S^\ddagger_2 - \Delta S^\ddagger_{-1}$. It is important to emphasize that the failure to observe saturation kinetics is in and of itself *not* sufficient to disprove a dissociative mechanism even at high concentrations of [L]; if $k_{-1} \approx k_2$, a linear relationship between k_{obs} and [L] may be seen even in the case of a purely dissociative reaction because [solv] is not independent of [L].[28] Nonetheless, reaction 1 is almost certainly not dissociative for this reaction system. One important piece of evidence for this conclusion is the low values of $\Delta H^\ddagger$ relative to the $(CO)_5W-CyH$ bond strength, which is believed to be approximately 15 kcal/mol.[3,17] Since the "naked" carbonyl $W(CO)_5$ is known to solvate within tens of ps in widely differing solvents (e.g., alkanes or alcohols),[7] it is extremely unlikely that k_{-1} and k_2 should be very different; and the rapidity of the solvation reaction implies that it is essentially unactivated (i.e., $\Delta H^\ddagger_2$ and $\Delta H^\ddagger_{-1}$ are both small and $\Delta H^\ddagger_2 - \Delta H^\ddagger_{-1} \approx 0$). Thus, in a dissociative reaction, we expect that $\Delta H^\ddagger \approx \Delta H^\ddagger_1$, the bond dissociation energy for the metal−solvent bond. This approximate equality has been observed in dissociative ligand exchange reactions of $CpMn(CO)_2(THF)$, for example.[29] Our observation of a much lower activation enthalpy implies that the rate-determining step is *not* solvent dissocation. Furthermore, our observation of significantly negative activation *entropies* is also consistent with a more associative (or more precisely, lacking direct evidence for an intermediate of increased coordination number, "associative interchange," $\mathbf{I_a}$) behavior. Thus, the activation parameters summarized in Table 3 may be considered those for k_a, that is, those for the reaction itself.

4.2. Correlation of Activation Parameters to Product C−O Stretching Force Constants. Further insight into the reaction can be obtained from consideration of the relationship between the activation parameters and the properties of the ligands. In our previous study,[15] we noticed an inverse correlation between k_{second} and the average of the E and $A_1(2)$[30] C−O stretching frequencies. Since that time, we have improved our instrumental sensitivity to the point where we can observe the weak $A_1(1)$ C−O stretch for the intermediate and products, enabling us to calculate C−O stretching force constants by the Cotton−Kraihanzel method.[31]

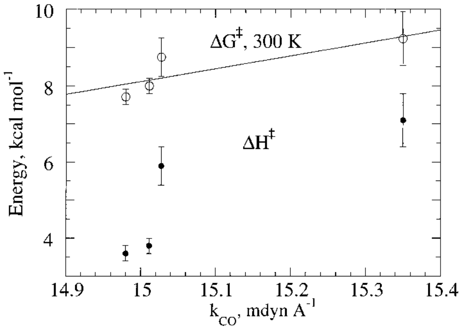


Figure 6. (●) $\Delta H^\ddagger$ and (○) $\Delta G^\ddagger$ (300 K) for reaction 1 as a function of k_{CO}^{trans} of the product complex $W(CO)_5L$ (Table 1) for L = cyclo-C_4H_nO. The solid line is a least-squares linear fit to $\Delta G^\ddagger$ as a function of k_{CO}^{trans}.

According to the Chatt−Dewar−Duncanson CDD "backbonding" model of bonding in organometallic complexes,[32] the CO ligand is primarily a π-acceptor that binds to the metal center by accepting electron density into its π^* LUMO from a metal d orbital of appropriate symmetry. It also acts as a σ-donor from the 5σ HOMO into an empty metal d orbital, but for most carbonyl compounds, this component of the backbonding is much less significant.[33] Since in $W(CO)_5L$ the carbonyl ligand trans to the L ligand shares both the metal d_σ and d_π orbitals, according to the CDD model, the C−O stretching force constant of this carbonyl should strongly depend on the nature of L; as L becomes less strongly electron donating (or more strongly electron withdrawing), there should be less electron density in the CO π^* orbital, and the C−O bond order and stretching force constant will increase. As can be seen in Table 1, the trans C−O stretching force constant does increase as L moves from the strongly electron donating THF to the much more weakly donating ligand furan.

In our previous study, we observed that k_{second} (i.e., $\Delta G^\ddagger$) for reaction 1 correlates very well with the C−O stretching frequencies in $W(CO)_5L$ for L = cyclo-C_4H_nE (E = NH or O). Here, we consider the correlation of the physically more significant trans C−O stretching force constant k_{CO}^{trans} ("k_1" of Table 1) with the activation parameters for the O-containing heterocyclic ligands. If reaction 1 is "associative" with a late transition state, then we expect that not only $\Delta G^\ddagger$ should correlate with properties of the product complex, but $\Delta H^\ddagger$ as well. Figure 6 shows $\Delta H^\ddagger$ and $\Delta G^\ddagger$ (300 K) plotted as a function of k_{CO}^{trans}. We can see that, as expected, there clearly is a general trend in which $\Delta H^\ddagger$ increases with increasing k_{CO}^{trans}. The explanation for such a correlation in terms of an associative mechanism is straightforward: as the ligand becomes less able to donate electron density to the complex, it becomes less able to stabilize the transition state at the nominally electron-deficient metal center, and the enthalpy of activation increases. This behavior is in contrast to dissociative reaction, in which there should be little if any dependence of $\Delta H^\ddagger$ on the C−O stretching force constants, as the transition state occurs before there is any significant amount of M−L bonding. Indeed, we have observed that, in reaction 1 with [M]−solv = $CpMn(CO)_2(CyH)$ and L = a series of heterocyclic ligands, there is no obvious correlation between the C−O stretching force constant and $\Delta H^\ddagger$.[28]

We note that the correlation between k_{CO}^{trans} and $\Delta H^‡$ is not linear in that $\Delta H^‡$ for reaction of 2,3-DHF seems to be higher than would be predicted from the values of $\Delta H^‡$ for the other three ligands, which do show a linear dependence on k_{CO}^{trans}. There is of course no reason to believe a priori that the relationship between $\Delta H^‡$ and k_{CO}^{trans} should necessarily be linear. Indeed, it is more reasonable to assume that $\Delta H^‡$ asymptotically approaches the $(CO)_5W-CyH$ bond dissociation energy as k_{CO}^{trans} increases; that is, at some point, the incoming ligand becomes strongly enough electron-withdrawing that it is incapable of stabilizing an associative transition state relative to $(CO)_5W-CyH$ dissociation, and the reaction becomes dissociative. The possibility of such competition between associative and dissociative mechanisms has been commented on previously.[14,34] In any case, while it is dangerous to overinterpret data, the apparently anomalously high $\Delta H^‡$ for reaction with 2,3-DHF may be due to a difference in its behavior as a free molecule and as a bound ligand. In the free molecule, there is a resonance structure that places positive charge on the O atom of 2,3-DHF (unlike the other three ligands considered here); contribution from this resonance structure would make 2,3-DHF a poorer electron donor as it enters the vicinity of the intermediate. If upon binding, the contribution of this resonance structure is less significant due to the polarization induced by the electropositive metal center, then ligated 2,3-DHF (whose influence on k_{CO}^{trans} is what we measure) will be a better electron donor than free 2,3-DHF (which actually does the ligand substitution), and $\Delta H^‡$ will be higher than the simple model outlined above would predict.

Finally, we consider the relation between $\Delta H^‡$ and $\Delta S^‡$. As can be seen from Table 3, as $\Delta H^‡$ increases, $\Delta S^‡$ increases (becomes less negative) as well; in fact, the relation between the two is nearly linear. The correlation between $\Delta H^‡$ and $\Delta S^‡$ is also easy to rationalize in terms of an $\mathbf{I_a}$ mechanism. The ordering of an "associative" ligand exchange transition state will depend on the ability of the incoming ligand to stabilize it. That is, as shown above, as L becomes a poorer electron donor, and hence less able to stabilize the transition state, the transition state becomes more "dissociative" in nature, with the outgoing solvent and incoming L molecules more loosely bound. Thus, as $\Delta H^‡$ increases, $\Delta S^‡$ increases as well. Indeed, this "compensation" of $\Delta H^‡$ and $\Delta S^‡$ leads to a linear dependence of $\Delta G^‡$ on k_{CO}^{trans}.

5. Summary

We have used time-resolved IR absorption spectroscopy to observe the reaction of the transient species $W(CO)_5(CyH)$ with 2,3-DHF, 2,5-DHF, and furan. We have obtained activation parameters for these reactions of $\Delta H^‡ = 5.9 \pm 0.5$ kcal mol^{-1} and $\Delta S^‡ = -8.9 \pm 7.3$ eu for reaction with 2,3-DHF; $\Delta H^‡ = 3.8 \pm 0.2$ kcal mol^{-1}, $\Delta S^‡ = -14.0 \pm 3.5$ eu for reaction with 2,5-DHF; and $\Delta H^‡ = 7.1 \pm 0.7$ kcal mol^{-1}, $\Delta S^‡ = -7.1 \pm 5.1$ eu for reaction with furan. For the series of ligands of the form cyclo-C_4H_nO ($n = 4, 6, 8$), we find that the activation parameters correlate with the electronic effects of the ligand in the *product* complex, as both $\Delta H^‡$ and $\Delta S^‡$ increase as the ligand becomes less strongly electron-donating. These results, combined with the low activation energies for the reaction relative to the metal−CyH bond dissociation energy, are consistent with an associative interchange mechanism for the process.

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Supporting Information Available: Tables of pseudo-first-order rate constants for reaction 1, plots of k_{obs} vs [L] for L = 2,3-DHF and furan, and tabulated results for the DFT calculations of the structure of $W(CO)_5$(furan). This material is available free of charge via the Internet at http://pubs.acs.org.

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(21) NMR Data for $W(CO)_5(\eta^2$-DHF): $\mathbf{W(CO)_5}$**(2,3-DHF)** (300 MHz, C_6D_{12}): δ 7.36 (s, 1H); 4.40 (m, 1H); 4.2 (br m); 2.99 (m, 1H); 2.73 (m, 1H). Because of overlap from a resonance of 2,3-DHF, integration of the peak at δ 4.2 was not possible. $\mathbf{W(CO)_5}$**(2,5-DHF)** (600 MHz, C_6D_{12}): δ 4.75 (s, 2H); 4.54 and 4.59 (AB q, $J = 9.5$ Hz, 2H each). Note that for both complexes, CH_2 protons are diastereotopic, indicating that the symmetry of the ring is broken by binding to the $W(CO)_5$ fragment.

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