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Electronic and Steric Effects in Ligand Substitution at a Transient Organometallic Species: The Reaction of $W(CO)_5$(Cyclohexane) with $(CH_3)_n$THF and $(CH_3)_n$Furan ($n = 1, 2$)

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Time-resolved infrared absorption spectroscopy is used to study the reactions of the solvated transient intermediate $W(CO)_5$(cyclohexane) with the molecules (L) 2-methyltetrahydrofuran (MeTHF), 2,5-dimethyltetrahydrofuran (Me_2THF), 2-methylfuran (MeFur), and 2,5-dimethylfuran (Me_2Fur). In all four cases, the only reaction observed on the microsecond to millisecond time scale is substitution of the cyclohexane molecule to form $W(CO)_5$(L). From the temperature dependence of the reaction rate constant, measured over the range 15−60 °C, we determine the following activation parameters: for L = MeTHF, $\Delta H^{\ddagger} = 4.0 \pm 0.3$ kcal mol^{-1}, $\Delta S^{\ddagger} = -14.1 \pm 1.0$ eu; for L = Me_2THF, $\Delta H^{\ddagger} = 4.3 \pm 0.3$ kcal mol^{-1}, $\Delta S^{\ddagger} = -14.8 \pm 1.2$ eu; for L = MeFur, $\Delta H^{\ddagger} = 6.0 \pm 0.2$ kcal mol^{-1}, $\Delta S^{\ddagger} = -10.2 \pm 1.2$ eu; and for L = Me_2Fur, $\Delta H^{\ddagger} = 6.3 \pm 0.4$ kcal mol^{-1}, $\Delta S^{\ddagger} = -9.8 \pm 1.0$ eu. We find that the relative rates of reaction of MeTHF and Me_2THF can be explained solely in terms of a steric effect, while for MeFur and Me_2Fur, the inductive effect of the electron-donating substituents leads to an electronic effect that competes with the steric effect.

Introduction

Because of their importance in many catalytic reaction cycles, "coordinatively unsaturated" transition metal intermediates and their chemistry have been of considerable interest. It is now generally accepted that in solution such intermediates, formally missing a ligand, in fact have a weakly bound[1] (by ca. 10−15 kcal mol^{-1}) solvent molecule as a "token" ligand in place of the nominally empty coordination site. Picosecond spectroscopy has been used to study the solvation process itself,[2] while the bimolecular reactions of solvated intermediates, which typically take place on a microsecond time scale, have been studied by a variety of methods such as photoacoustic calorimetry (PAC),[1,3] time-resolved UV−visible spectroscopy (TRUVVIS),[4] and time-resolved infrared absorption spectroscopy (TRIR).[5] These reactions are analogous to steps in homogeneous catalytic processes in which a substrate molecule binds to a "coordinatively unsaturated" catalytic intermediate.[6]

Although it is well known that even subtle changes in an organometallic system can lead to significant changes in reactivity,[7] relatively few systematic studies of how such changes affect reactivity at organometallic transient intermediates have been performed. Yang et al.[8] performed a PAC study of the reaction of $Cr(CO)_5$-(n-heptane) interacting with a variety of ligands and found that the reaction rates for pyridine, 2-picoline, and 2,6-lutidine decreased in that order, apparently due to increasing steric congestion. More recently, Dobson and Zhang[9] used TRUVVIS to extend that work to a variety of other reactant molecules including inter alia THF,

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acetonitrile, and 1-hexene. While their study did not reveal any clear relationship between the structure of the substrate molecule and the overall reactivity, Dobson and Zhang did observe an overall correlation between $\Delta H^\ddagger$ and $\Delta S^\ddagger$ for the various ligand substitution reactions they investigated. In contrast to these experiments that investigated reactivity as a function of the attacking ligand, Breheny et al.[10] measured the recombination of $M(CO)_5$(solvent) (M = Cr, Mo, W) and of (η^6-arene)$Mo(CO)_2$(solvent) with CO as a function of the alkane solvent and found that the differences in reaction rate were controlled primarily by changes in $\Delta S^\ddagger$.

In our laboratory, we have taken a slightly different approach to the problem. In order better to understand the nature of the ligand exchange process at a transition metal center, we have been investigating ligand exchange at an alkane-solvated intermediate as a function of the attacking ligand for series of similar ligands. By minimizing the changes in the ligands, we can better focus on which specific properties lead to which specific differences in behavior. In a preliminary study,[11] we observed that the second-order rate constant for the ligand exchange reaction at $W(CO)_5(CyH)$ (CyH = cyclohexane), reaction 1,

$$W(CO)_5(CyH) + L \rightarrow W(CO)_5L \tag{1}$$

with $L = C_4H_nE$ (E = O, NH; n = 4, 6, 8), correlates with the C−O stretching frequencies of the product complex $W(CO)_5L$, consistent with an associative mechanism for the reaction. More detailed studies[12,13] have focused on the behavior of five-membered heterocyclic ligands L of the type C_4H_nO (n = 4, 6, 8) in reaction 1. Our assumption was that any differences in the kinetics among these reactants would be due primarily to electronic effects. We observed for this series of ligands that $\Delta H^\ddagger$ for reaction 1 is much less than the $(CO)_5W-CyH$ bond strength and that $\Delta S^\ddagger < 0$, once again consistent with an associative reaction. Furthermore, as L becomes more electron-withdrawing (as indicated by k_{CO}^{trans}, the C−O stretching force constant in $W(CO)_5L$ for the carbonyl *trans* to L), $\Delta H^\ddagger$ and $\Delta S^\ddagger$ both increase, once again consistent with an associative reaction.[13]

Here, we extend these investigations to include 2-methyl- and 2,5-dimethyl-substituted ligands. On one hand, increasing the substitution near the heteroatom should increase the steric hindrance and hence raise the barrier to reaction. On the other hand, the inductive effect of the methyl groups should make the substituted ligand a better electron donor than its unsubstituted counterpart. According to the considerations discussed in the previous paragraph, this effect should lead to a lower barrier to reaction. The present study was undertaken in order to try to unravel the relative importance of these two competing effects in the kinetics of reaction 1.

Experimental Section

The apparatus upon which these experiments were performed has been described in detail previously,[12] so only a brief description will be given here. Reaction takes place in a 0.5 mm pathlength 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 approximately 0.5×10^{-3} mol L^{-1} $W(CO)_6$ and at least a 10-fold excess of the reactant ligand L flows continuously through the cell with a reservoir of reactant solution remaining under Ar in a constant-temperature bath.

Reaction is initiated by the pulse of a XeCl excimer laser operating at 4 Hz (308 nm, ~20 ns/pulse, typically 30−60 mJ/pulse), which photolyzes the $W(CO)_6$ to $W(CO)_5$ + CO; solvation of $W(CO)_5$ to $W(CO)_5(CyH)$ occurs within 100 ps of the loss of the carbonyl ligand.[2] The progress of reaction 1 is monitored by measuring the time evolution of the IR absorption 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 typically at 4 cm^{-1} resolution) 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. Measurement of the time-dependent IR signal was performed by using either an InSb (~50 ns rise time) or an MCT (~20 ns rise time) detector.

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, k_{obs}, is determined from a linear fit to $\ln|\Delta A_0 - \Delta A_\infty|$ as a function of time. Pseudo-first-order rate constants reported here represent the averages of at least two independent data sets and usually represent averages of transient absorptions corresponding both to decay of the absorbance of the intermediate and to the growth of the product absorbance. Because of the weaker absorptions of the product complexes and the weaker output of our diode laser at their absorption frequencies, 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%.

$W(CO)_6$ was obtained from Strem (98% purity) and used without further purification. The ligands L [THF, 2-methyltetrahydrofuran (MeTHF), 2,5-dimethyltetrahydrofuran (Me_2THF), furan, 2-methylfuran (MeFur), and 2,5-dimethylfuran (Me_2Fur)] were obtained from commercial suppliers in >97% purity, Me_2THF as a ~50:50 mixture of the *cis* and *trans* isomers, and then further purified by distillation from an appropriate drying agent. For MeFur and Me_2Fur, this step was preceded by stirring over KOH. All purities were confirmed by ^{1}H NMR spectroscopy. Cyclohexane was obtained in HPLC or spectrophotometric grade (>99% purity) and distilled from Na/benzophenone under N_2 to remove remaining traces of water.

Results

General Observations. Upon photolysis, the reaction solution's IR absorption spectrum shows a bleach

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Table 1. C−O Stretching Frequencies and Force Constants[c] for $W(CO)_5L$

	ν_{CO} (cm^{-1})			force constant (mdyn/Å)		
ligand	$A_1(1)$	E	$A_1(2)$	k_{trans}	k_{cis}	k_i
THF[a]	2074	1933	1911	14.980	15.778	0.342
MeTHF	2074	1932	1910	14.967	15.768	0.345
Me_2THF	2073	1930	1909	14.953	15.741	0.347
furan[b]	2078	1949	1936	15.350	15.974	0.315
MeFur	2077	1947[d]	1931	15.274	15.947	0.317
Me_2Fur	2075	1941	1927	15.217	15.871	0.326

[a] Ref 12. [b] Ref 13. [c] k_{cis}, carbonyl *cis* to L; k_{trans}, carbonyl *trans* to L; k_i, interaction force constant.[15] [d] Weighted average of the two peaks into which the doubly degenerate E peak is split; see the text.

at 1981 cm^{-1}, corresponding to the photolysis of the parent $W(CO)_6$. Within the rise time of the detector, three peaks appear, at 1928, 1954, and 2087 cm^{-1}, corresponding to the C−O stretches of $W(CO)_5(CyH)$.[12,14] In the presence of a reactant ligand L, these absorbances decay with time, and simultaneously, three new peaks appear, indicating conversion of $W(CO)_5(CyH)$ to $W(CO)_5L$. IR spectral data and C−O stretching force constants (determined by using the Cotton−Kraihanzel method[15]) are given in Table 1. The product absorbances do not decay during the time period of these measurements, showing that the products of reaction 1 do not undergo any further reaction during the course of the experiment.

$W(CO)_5(CyH)$ + 2-Methyltetrahydrofuran and 2,5-Dimethyltetrahydrofuran. The new complexes formed by reaction of $W(CO)_5(CyH)$ with MeTHF and Me_2THF have IR absorbances similar to those of $W(CO)_5(THF)$, although the E and $A_1(2)$ stretches are shifted to slightly lower energy, Table 1. Figure 1 shows the pseudo-first-order rate constant k_{obs} as a function of [MeTHF]. As can be seen from the figure, the pseudo-first-order rate constant is a linear function of [MeTHF] over the entire concentration range studied, 0.03−0.8 mol L^{-1} for $T \leq 30$ °C, 0.03−0.4 mol L^{-1} for $T = 40$ and 50 °C, and 0.03−0.36 mol L^{-1} for $T = 60$ °C; the upper limit of the concentration decreases with increasing temperature as the reaction becomes too fast ($k_{obs} >$ ca. 6×10^6 s^{-1}) for us to measure accurately.

For reaction with Me_2THF, k_{obs} is a linear function of [L] as well; the concentration range over which measurements were performed in this case was 0.03−1.01 mol L^{-1} for $T \leq 50$ °C and 0.03−0.8 mol L^{-1} for $T = 60$ °C. Plots of k_{obs} as a function of [Me_2THF] are given as Figure S1 in the Supporting Information. Although the Me_2THF we used was an approximately 1:1 mixture of the *cis* and *trans* isomers, we did not see any kinetic or spectroscopic evidence for any difference in the reactivities of the two isomers; this observation is discussed in more detail below.

$W(CO)_5(CyH)$ + 2-Methylfuran and 2,5-Dimethylfuran. Reaction of $W(CO)_5(CyH)$ with MeFur and Me_2Fur results in the formation of $W(CO)_5(MeFur)$ and $W(CO)_5(Me_2Fur)$, the IR absorbances of which are given in Table 1. As can be seen from the table, the frequencies of the E and $A_1(2)$ C−O stretching modes for the MeFur and Me_2Fur complexes are higher than those for the MeTHF and Me_2THF complexes.

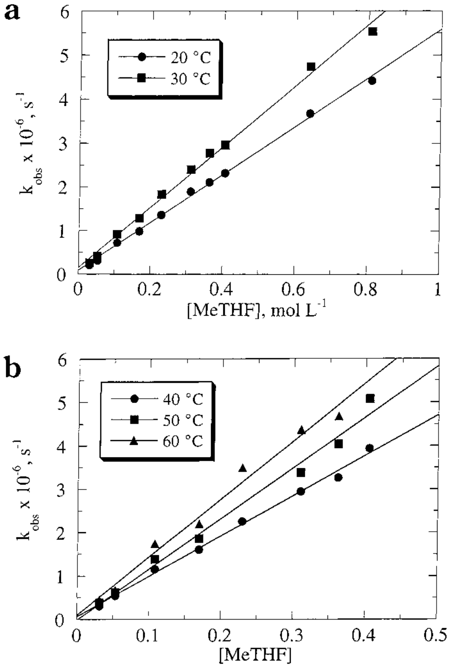

Figure 1. Pseudo-first-order rate constant k_{obs} as a function of [L] for reaction 1 with L = MeTHF. Part a shows results for reaction at 20 °C (●) and 30 °C (■). Part b shows results for reaction at 40 °C (●), 50 °C (■), and 60 °C (▲). The solid lines represent least squares linear fits to the data.

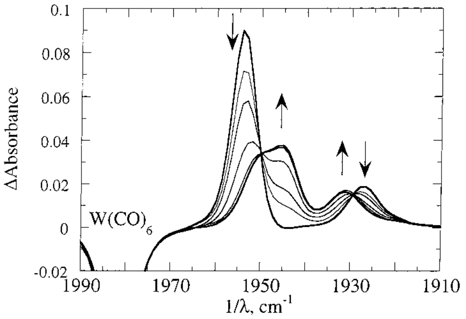

Figure 2. Time-resolved S^2FTIR spectra for the reaction of $W(CO)_5(CyH)$ with 0.4 mol L^{-1} MeFur. Shown are spectra obtained at time intervals of 0, 0.4, 1, 2, 4, and 7 μs following the photolysis flash. The peaks at 1954 and 1928 cm^{-1} that disappear with time are due to absorptions of $W(CO)_5(CyH)$, while the peaks at 1945/1951 and 1931 cm^{-1} that grow in with time are due to absorptions of $W(CO)_5(MeFur)$.

Typical S^2FTIR results for reaction 1 with L = MeFur are shown in Figure 2. Unlike the other product complexes in this study, the E peak of $W(CO)_5(MeFur)$ appears to be split into two components at 1951 and 1945 cm^{-1}. FTIR spectra taken of a CyH solution of $W(CO)_6$ photolyzed in the presence of excess MeFur also show this splitting, indicating that the product that appears within tens of microseconds persists at least for several minutes. Apparently, the lowering of the symmetry of the $W(CO)_5(MeFur)$ from C_{4v} is sufficiently significant to remove the degeneracy of the E C−O stretch. Such splitting of the E symmetry C−O stretch has been noted in other $W(CO)_5L$ complexes with asymmetrical ligands.[16]

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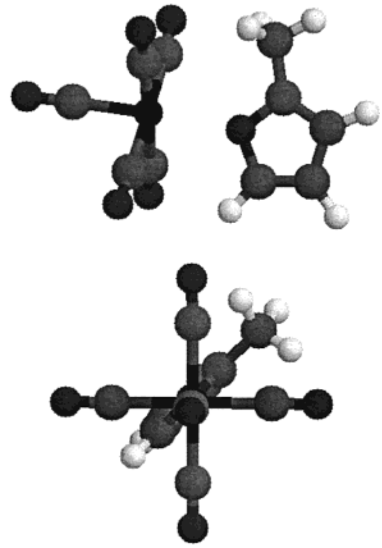

Figure 3. Two views of the structure of $W(CO)_5$(MeFur) as determined by a DFT calculation.

Table 2. Geometrical Parameters of $W(CO)_5$(MeFur) as Calculated by DFT[a]

bond	bond length, Å	atoms ABC	bond angle, deg
W−O	2.45	$C_{cis}-W-C_{trans}$	88.2
$W-C_{cis}$	2.08	$C_{cis}-W-C_{cis}$	178.8
$W-C_{trans}$	1.88	$W-C_{trans}-O_{trans}$	180.0
carbonyl C−O	*cis* 1.19; *trans* 1.18	$W-C_{cis}-O_{cis}$	177.3
$O-C_2$	1.40	$W-O_{Fur}-C_2$	133.0
$O-C_5$	1.39	$W-O_{Fur}-C_5$	119.6
C_2-C_{Me}	1.50	$O-C_2-C_3$	108.7
C_2-C_3	1.38	$C_2-C_3-C_4$	107.5
C_3-C_4	1.45	$C_3-C_4-C_5$	106.4
C_4-C_5	1.37	C_5-O-C_2	107.4
$C_{ring}-H$	1.09	$O-C_2-C_{Me}$	119.2
$C_{Me}-H$	1.10	$H_{Me}-C_{Me}-H_{Me}$	108.1

[a] C_{cis} and C_{trans} refer to the carbonyl carbon atoms relative to the MeFur ligand; carbon atoms of the furan ring are numbered sequentially, with C_2 being the methyl-substituted atom.

To understand the structure and spectrum of $W(CO)_5$(MeFur), a DFT calculation[17] at the B31LYP/CEP31G* level was performed. The calculated structure is shown in Figure 3, and calculated geometrical parameters are given in Table 2. The calculation took an unusually long time to converge, indicating that the potential near the minimum is relatively flat or that there are several different structures with similar energies. The DFT calculation predicts that the minimum energy structure has the MeFur ligand bound η^1 to the W atom with the methyl group between two carbonyl ligands (the $C_{cis}-W-O_{fur}-C_2$ dihedral angle is 45.4°). The *cis* carbonyl ligands are bent back slightly (the $O_{cis}-C_{cis}-W-C_{cis}$ dihedral angle is 1.4°), while the furan ring remains essentially planar (dihedral angles <1°). There is no ligand C−H bond lengthening typical of "agostic" W−C−H three-center interactions seen, for example, in $W(CO)_5$(alkane) complexes.[12] While DFT calculations typically only predict vibrational frequencies to within a few percent,[17b] they do indicate that the E symmetry CO stretch in $W(CO)_5$(MeFur) is somewhat more split than in other $W(CO)_5L$ complexes (~0.5 cm^{-1} for MeFur vs ~0.1 cm^{-1} for ligands such as CyH[12]), showing, qualitatively at least, that the MeFur−$W(CO)_5$ interaction is stronger than in other similar complexes, leading to an effective lowering of the symmetry.

For ligands such as THF and substituted THFs there is only one possible site of interaction between the metal and ligand, namely, through a lone pair on the ligand heteroatom. For furan and substituted furans, however, there are three reasonable bonding geometries: η^1 through a lone pair on the O atom, η^2 through a pair of adjacent carbon atoms, or η^5 with the metal face-on to the ring. In the case of the complexes observed in our experiment, the most reasonable structure is the η^1-*O*-bound. We base this conclusion on several factors: the similarity of the IR spectra of $W(CO)_5$(MeFur) and $W(CO)_5(Me_2Fur)$ to that of $W(CO)_5$(furan) and of those of $W(CO)_5$(MeTHF) and $W(CO)_5(Me_2THF)$ to that of $W(CO)_5$(THF); the structure predicted by the DFT calculation; and the observation that the C−O stretches of $W(CO)_5$(MeFur) and $W(CO)_5(Me_2Fur)$ are significantly lower than those typically found in $W(CO)_5$(olefin) complexes.[18]

Unlike the other products of reaction 1 studied here, which are stable at least for minutes, $W(CO)_5(Me_2Fur)$ has a lifetime on the order of only ~1 s. The absorbances attributed to this complex disappear with a rate that appears to be *independent* of $[Me_2Fur]$, while simultaneously new absorbances appear at 1957, 1991, 2030, and 2097 cm^{-1}. While this new complex has not been definitively identified, the data are consistent with loss of a second CO ligand to form $W(CO)_4(\eta^4\text{-}Me_2Fur)$. Intramolecular substitution of a second CO at $W(CO)_5L$ occurring on this time scale has been observed for L = bipyridyl-type ligands[19] and thiouracil;[20] intramolecular $\eta^1 \rightarrow \eta^2$ linkage isomerization in group 6 $M(CO)_5$(dihydrofuran) complexes also typically occurs on a time scale of 0.1−1 s.[21] Further work is underway to provide a more detailed understanding of the process(es) taking place in the present system.[22] Since this further reaction of the $W(CO)_5(Me_2Fur)$ complex initially formed in reaction 1 is much slower than reaction 1 itself, this reaction is not further considered in our analyses of the reactivity of $W(CO)_5$(CyH) with Me_2Fur.

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(19) (a) Bal Reddy, K.; Hoffman, R.; Konya, G.; van Eldik, R.; Eyring, E. M. *Organometallics* **1992**, *11*, 2319. (b) Ji, Q.; Lloyd, C. R.; Eyring, E. M.; van Eldik, R. *J. Phys. Chem. A* **1997**, *101*, 243.

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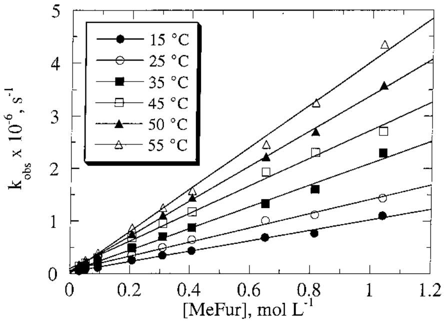

Figure 4. Pseudo-first-order rate constant k_{obs} as a function of [L] for reaction 1 with L = MeFur at 15 °C (●), 25 °C (○), 35 °C (■), 45 °C (□), 50 °C (▲), and 55 °C (△). The solid lines represent least squares linear fits to the data.

Reaction with MeFur was monitored over a concentration range of 0.031−1.039 mol L^{-1}. For this ligand, kinetic measurements were made over a temperature range extending only to 55 °C. Previously,[13] we found that results for reaction of furan were not reproducible at 60 °C and attributed this difficulty to the volatility of furan (bp 32 °C). Since the boiling point of MeFur is only 63 °C, approximately 20° lower than the other ligands studied here, we decided not to attempt kinetic experiments at 60 °C. For Me_2Fur, the concentration range over which the measurements were made was 0.1−1.2 mol L^{-1} for T = 20−60 °C. Plots of k_{obs} as a function of [MeFur] at different temperatures are given in Figure 4; similar plots for [Me_2Fur] are given in the Supporting Information as Figure S2.

$W(CO)_5(CyH)$ + 2,2,5,5-Tetramethyltetrahydrofuran. We also attempted to measure the kinetics of the reaction of $W(CO)_5(CyH)$ with Me_4THF. A preliminary S^2FTIR experiment revealed that even at [Me_4THF] = 0.11 mol L^{-1} reaction 1 was much slower than it was for the other ligands, so much so that no product peaks unambiguously assignable to $W(CO)_5(Me_4THF)$ could be observed. Instead, several peaks appeared, some consistent with formation of $W(CO)_5(H_2O)$[14] and others that could not be assigned to any known complexes. As discussed below, the rate constant for reaction with Me_4THF is sufficiently small that under these experimental conditions even species present in very low concentrations, such as unphotolyzed $W(CO)_6$ molecules, trace amounts of H_2O remaining in the CyH, or even impurities in the Me_4THF itself (~1%), can compete with Me_4THF for the $W(CO)_5(CyH)$ intermediate. Because we could not find any clear evidence for formation of $W(CO)_5(Me_4THF)$ or any way of isolating the kinetics of its formation from the other reactions, no detailed kinetic studies of this reaction were performed.

Discussion

Mechanism of Reaction 1 for Substituted Furan and THF. To be able to draw any conclusions about the influence of the structure of the attacking ligand on the course of reaction 1, we must first have a reasonably well-grounded understanding of the reaction mechanism. Prior studies in our laboratory have indicated that reaction 1 with L = C_4H_nO ligands appears to proceed via an associative interchange (**I_a**) mechanism.[12,13] This conclusion was based primarily on the low $\Delta H^‡$ relative to the $(CO)_5W{-}CyH$ bond strength, the negative $\Delta S^‡$, and the strong correlation between the reaction's activation parameters and the electron-donating ability of the incoming ligand. We can use similar tests to interpret the mechanism of reaction 1 for L = substituted ligands as well. Values of the second-order rate constants for reaction 1, determined from linear fits of k_{obs} as a function of [L], are given in Table 3. Eyring analyses of these second-order rate constants are shown graphically in Figure 5, and the results of these analyses are given numerically in Table 4. For all four ligands studied here, $\Delta H^‡$ is significantly less than the $(CO)_5W{-}CyH$ bond strength, estimated to be 10−15 kcal mol^{-1}.[3,23] Furthermore, $\Delta S^‡$ remains significantly negative for all four reactions, implying a transition state more ordered than the reactants, i.e., an associative reaction. Finally, the reaction's activation parameters and the properties of the product complex are strongly correlated, as discussed in detail below. While the kinetic behavior is consistent with associative reaction, we have not explicitly observed a seven-coordinate intermediate, and therefore conclude that reaction 1 proceeds via an **I_a** mechanism for substitution by the four ligands studied here.

MeTHF and Me_2THF: Steric Effect on Reaction 1. We consider first reaction 1 for the two substituted THF ligands. As shown in Table 1, the C−O stretching force constant for the carbonyl *trans* to L, k_{CO}^{trans}, decreases in the order THF > MeTHF > Me_2THF; that is, the ligand becomes a stronger electron donor with increasing methyl substitution.

In our previous studies of the ligand substitution reactions of $W(CO)_5(CyH)$ + C_4H_nO, we observed that as L becomes more strongly electron-donating, both $\Delta G^‡$ and $\Delta H^‡$ decrease. We were able to explain this behavior as being the result of an electronic effect: as the incoming ligand becomes more electron-donating, it is better able to stabilize an associative transition state, lowering the barrier to reaction. As can be seen from Figure 6, the series THF, MeTHF, Me_2THF behaves exactly the opposite of what would have been predicted from the electronic properties of the ligands. The obvious explanation for this trend is that the primary effect controlling the reactivity of Me_nTHF is steric hindrance, which would tend to slow the rate of reaction 1 as the number of methyl groups near the O atom increases.

The relative activation energies derived from the experimentally measured rate constants ($\Delta G^‡_{obs}$) provide more quantitative insight into the steric effect on reaction 1. At 20 °C, $\Delta G^‡_{obs}$ for MeTHF (8.11 ± 0.02 kcal mol^{-1}) and Me_2THF (8.57 ± 0.03 kcal mol^{-1}) are respectively approximately 0.5 and 1.0 kcal mol^{-1} higher than that of THF (7.65 ± 0.02 kcal mol^{-1}). Thus, we can see that each additional methyl group raises the activation energy by ~0.5 kcal mol^{-1}, Scheme 1. We can also deduce the existence of this primarily steric effect by measuring deviations from the expected electronic effect. In our previous work, we showed that for cyclo-C_4H_nO ligands (n = 4, 6, or 8) there is a linear relationship between $\Delta G^‡_{obs}$ of reaction 1 and k_{CO}^{trans} of the product $W(CO)_5L$ complex.[13] If we adopt this rela-

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[23] (a) Burkey, T. J. Personal communication. (b) Brown, C. W.; Ishikawa, Y.; Hackett, P. A.; Rayner, D. A. *J. Am. Chem. Soc.* **1990**, *112*, 2530. (c) Weitz, E. *J. Phys. Chem.* **1994**, *98*, 11256.

Table 3. Second-Order Rate Constants[a] for Reaction 1 (10^6 L mol^{-1} s^{-1})

T, °C	THF[b]	MeTHF	Me$_2$THF	furan[c]	MeFur	Me$_2$Fur
15					0.99 (0.04)	
20	12.1 (0.3)	5.48 (0.12)	2.46 (0.08)	0.86 (0.01)		0.83 (0.06)
25					1.35 (0.05)	
30	15.6 (0.9)	6.92 (0.23)	3.03 (0.08)	1.41 (0.03)		1.22 (0.07)
35					2.07 (0.10)	
40	19.8 (0.5)	9.29 (0.35)	3.92 (0.12)	1.98 (0.02)		1.68 (0.12)
45					2.64 (0.11)	
50	24.3 (1.1)	11.7 (0.6)	5.28 (0.17)	3.11 (0.08)	3.35 (0.05)	2.39 (0.16)
55					4.03 (0.13)	
60	28.5 (1.2)	13.4 (1.1)	6.52 (0.12)			3.59 (0.25)

[a] 1σ uncertainties to linear fits of ln(k_{obs}) vs [L] are given in parentheses. [b] Ref 12. [c] Ref 13.

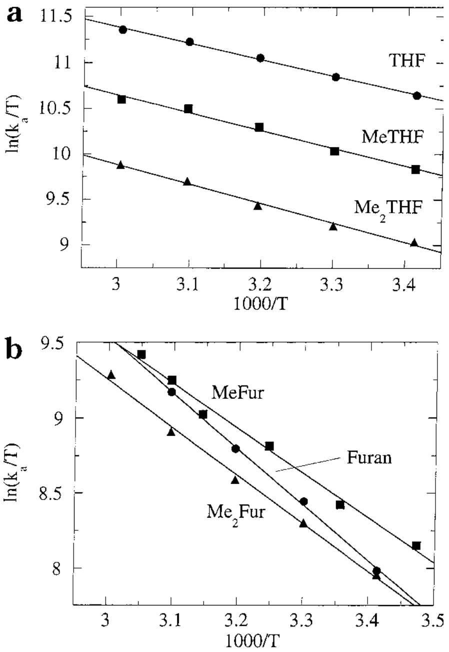


Figure 5. Eyring analyses of the second-order rate constant k_a for reaction 1. Figure 5a shows results for reaction of W(CO)$_5$(CyH) + THF (●), MeTHF (■), and Me$_2$-THF (▲). Figure 5b shows results for reaction of W(CO)$_5$-(CyH) + furan (●), MeFur (■), and Me$_2$Fur (▲). The lines are least squares linear fits to the rate constants weighted by the relative uncertainties given in Table 3.

Table 4. Activation Parameters for Reaction 1[a]

L	$\Delta H^‡$, kcal mol^{-1}	$\Delta S^‡$, cal mol K^{-1}
THF[b]	3.6 ± 0.2	−13.7 ± 0.7
MeTHF	4.0 ± 0.2	−14.1 ± 1.0
Me$_2$THF	4.3 ± 0.2	−14.8 ± 1.2
furan[c]	7.1 ± 0.4	−7.1 ± 2.7
MeFur	6.0 ± 0.2	−10.2 ± 1.2
Me$_2$Fur	6.3 ± 0.3	−9.8 ± 1.0
2,5-DHF[c]	3.8 ± 0.1	−14.0 ± 1.0
2,3-DHF[c]	5.9 ± 0.3	−8.9 ± 2.1

[a] 1σ uncertainties. [b] Ref 12. [c] Ref 13.

tionship (see Figure 6) as our baseline (in a manner not dissimilar to Hammett analyses familiar from physical organic chemistry[24]), then we can predict $\Delta G^‡$ for a given k_{CO}^{trans} on the assumption that it depends only on the electron-donating ability of L. In Scheme 1, $\Delta G^‡{}_{obs}$, the value of $\Delta G^‡$ determined from the experimentally measured rate constant, is also shown in terms of the value calculated from this correlation. We find that for

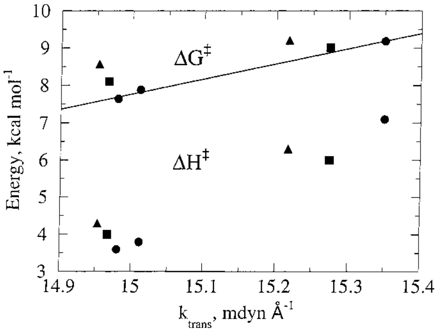
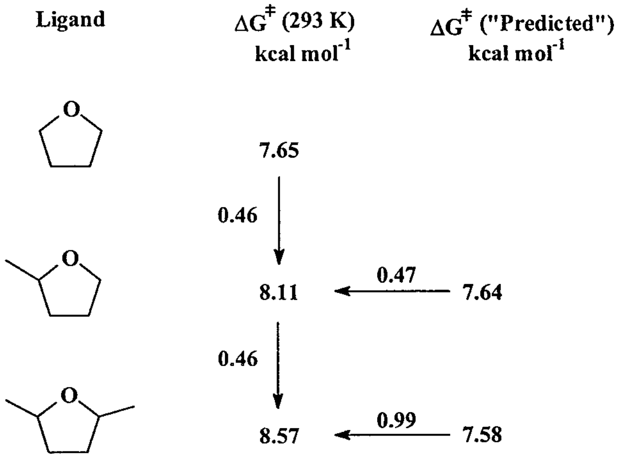


Figure 6. $\Delta H^‡$ and $\Delta G^‡$ (293 K) for reaction 1 as a function of the *trans* C−O stretching force constant k_{CO}^{trans} in the product complex W(CO)$_5$L, where L = C$_4$H$_n$O (●), MeC$_4$H$_{n-1}$O (■), and Me$_2$C$_4$H$_{n-2}$O (▲). The solid line is a least squares fit to the values of $\Delta G^‡$ (293 K) for reaction 1 as a function of k_{CO}^{trans} in W(CO)$_5$(C$_4$H$_n$O).[13]

Scheme 1



MeTHF, $\Delta G^‡{}_{obs}$ is once again ~0.5 kcal mol^{-1} higher than predicted from the behavior of C$_4$H$_n$O, while for Me$_2$THF, it is ~1.0 kcal mol^{-1} higher than predicted. Since the difference per methyl group between $\Delta G^‡{}_{obs}$ and the value of $\Delta G^‡$ predicted on the assumption of a purely electronic effect is constant, we conclude that the relative reactivity of Me$_n$THF (n = 0, 1, 2) in reaction 1 is determined purely by a steric effect.

This steric effect can also explain our failure to see any significant reactivity between W(CO)$_5$(CyH) and Me$_4$THF in the S^{2}FTIR experiment described above. If we use the assumption that $\Delta G^‡$ at 293 K for reaction of Me$_n$THF increases by ~0.5 kcal mol^{-1} for each additional methyl group, then the room-temperature second-order rate constant k_a for reaction of Me$_4$THF should be approximately 4 × 10^5 L mol^{-1} s^{-1}. At

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[24] Lowry, T. H.; Richardson, K. S. *Mechanism and Theory in Organic Chemistry*, 3rd ed.; Harper and Row: New York, 1987; Chapter 2.

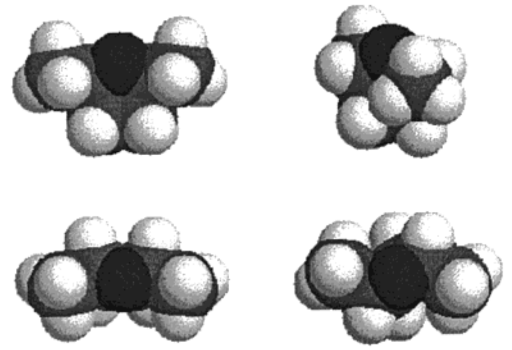
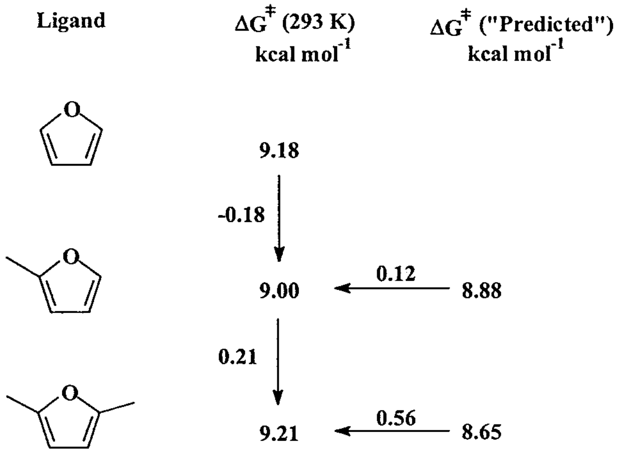


Figure 7. Space-filling diagrams for the *cis* (left) and *trans* (right) isomers of Me_2THF, as calculated by DFT. Shown are top and side views of the ring.

Scheme 2



$[Me_4THF] = 0.1$ mol L^{-1}, the resulting pseudo-first-order rate constant k_{obs} should thus be about 4×10^4 s^{-1}. In the absence of any added ligand, the $W(CO)_5(CyH)$ intermediate disappears with a rate constant on the order of 10^4 s^{-1},[12,14] consistent with the results of the S^2FTIR experiment in which the formation of products from H_2O and other impurities competes with the formation of $W(CO)_5(Me_4THF)$.

It is neither unreasonable nor particularly unexpected that the primary effect for Me_nTHF should be steric. While the additional methyl group does make the ligand a slightly stronger electron donor, the differences are not great (Table 1). Since these ligands are aliphatic, there is little conjugation between the methyl groups and the O atom, leading to only a modest electronic effect. On the other hand, the presence of the methyl groups will restrict the geometry by which the ligand can approach the $W(CO)_5(CyH)$ complex, leading to the observed steric effect.

The above analysis is based in part on our observation that there is no evidence for any significant difference in the reactivities of the two isomers of Me_2THF. We see no evidence for formation of a second product on the time scale corresponding to disappearance of the intermediate (~1−100 μs). Furthermore, the IR spectrum obtained after photolyzing a CyH solution of $W(CO)_6$ and a large excess of Me_2THF (~300 laser shots irradiating 25 mL of solution) is indistinguishable from the S^2FTIR spectrum obtained at the completion of the microsecond ligand exchange process, indicating that the product of reaction 1 is stable at least for minutes.

As a further test of the intuitive notion that there might be significant differences in the steric hindrance of the two isomers, we performed a DFT calculation of the structures of the two isomers of Me_2THF. The results of this calculation are shown in Figure 7. As can be seen in the figure, access to the oxygen atom in the equilibrium structure is similar for the two isomers. Furthermore, pseudorotation is known to be a very low-energy process for five-membered rings; for THF, the barrier to pseudorotation has been measured to be 0.163 kcal mol^{-1}.[25] In the limiting case that only one isomer reacts, then our kinetic analysis that assumes that all of the Me_2THF added is reacting would overestimate its concentration by a factor of 2. If this were occurring, then the "reactive" isomer would be about as reactive as MeTHF, which contradicts the assumption that steric hindrance from the second methyl group inhibits the reactivity of Me_2THF. We therefore conclude that it is reasonable to treat the two isomers of Me_2THF as being equally reactive in reaction 1.

MeFur and Me_2Fur: Competing Electronic and Steric Effects on Reaction 1. For the substituted furan ligands, the kinetic behavior upon substitution is somewhat more complex than the simple monotonic increase in $\Delta H^‡$ and $\Delta G^‡$ seen with the Me_nTHF ligands. In fact, $\Delta H^‡$ for substitution by MeFur is actually *lower* than that for furan, while upon addition of the second methyl group, $\Delta H^‡$ increases, as shown in Table 4 and Figure 6. This behavior can be explained by an electronic effect that dominates the behavior of MeFur and competes with the steric effect in Me_2Fur. Note that, as expected, MeFur and Me_2Fur are stronger electron donors than furan itself, Table 1. In this case, however, because of the possibility of conjugation to the aromatic ring, methyl substitution has a much stronger effect on the electron-donating properties of furan than it does upon those of THF.

As shown in Scheme 2, at 293 K, $\Delta G^‡_{obs}$ for reaction 1 with L = MeFur is ~0.2 kcal mol^{-1} lower than it is when L = furan. This behavior is consistent with the electronic effect expected upon methyl substitution. Indeed, $\Delta G^‡_{obs}$ for L = MeFur is very nearly (to within about 0.1 kcal mol^{-1}) what would be expected if the electronic effect seen with the unsubstituted ligands were the only effect in operation, and MeFur seems to behave as an electron-rich furan rather than as a sterically hindered one. This lack of steric hindrance, in contrast to what was observed for MeTHF, is presumably a consequence of the aromaticity and planarity of the furan ring. Since the ring itself can provide electron density to the metal center,[26] furan ligands are not restricted to attack via the heteroatom, while in the case of MeTHF, attack must occur via the lone pair on the O atom, and even a single methyl substituent will cause significant steric hindrance.

As can be seen in Figure 6 and Scheme 2, $\Delta H^‡$ and $\Delta G^‡_{obs}$ are higher for reaction with Me_2Fur than for reaction with MeFur even though Me_2Fur is the better electron donor. In this case, it appears that addition of

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(25) Engherholm, G. G.; Luntz, A. C.; Gwinn, W. D.; Harris, D. O. *J. Chem. Phys.* **1972**, *56*, 1440.

(26) Stolz, I. W.; Haas, H.; Sheline, R. K. *J. Am. Chem. Soc.* **1965**, *87*, 716.

the second methyl substituent does lead to steric interference in the substitution reaction. Presumably, the presence of a second methyl group restricts the attack by the Me_2Fur ligand to angles that place it fairly close to its equilibrium geometry in $W(CO)_5$(Me_2Fur), whereas for MeFur, geometries in which the metal could interact with the aromatic system could eventually lead to reaction. This kinetic effect would then compete with the electronic effect that would favor reaction with Me_2Fur thermodynamically.[27] Thus, the transition state is less stabilized by Me_2Fur than by MeFur, and $\Delta H^‡$ and $\Delta G^‡$ are higher for Me_2Fur than for MeFur. Further support for the idea of a steric effect from the second methyl substituent can be seen from the observed $\Delta G^‡$, which is approximately 0.5 kcal mol^{-1} higher for reaction of Me_2Fur than would be predicted based on a purely electronic effect. As was discussed above, 0.5 kcal mol^{-1} is the amount by which the steric hindrance of a single methyl substituent increases the reaction barrier. Thus, while MeFur behaves like an electron-rich furan, Me_2Fur behaves like an electron-rich furan with an extra methyl substituent; that is, for Me_2Fur, the electronic effect that dominates the reactivity of MeFur in reaction 1 competes with steric hindrance.

Relationships among the Activation Parameters. In addition to the comparisons discussed above, we can gain some insight into the dynamics of reaction 1 by considering relationships among the kinetic parameters from a more general point of view. One relatively frequent observation is that for a series of related reactions $\Delta S^‡$ and $\Delta H^‡$ tend to be correlated.[24] These compensation effects, the conditions under which they can accurately be described as "isokinetic relationships," and their uses and abuses in mechanistic chemistry have been extensively reviewed.[28] While linear free-energy relationships in ligand substitution reactions at kinetically stable transition metal complexes have been extensively studied,[29] there are practically no such investigations reported in the literature for reactions of transition metal *intermediates*. In their study of ligand substitution at the $Cr(CO)_5$(heptane) intermediate, Dobson and Zhang[9] reported a positive correlation between $\Delta H^‡$ and $\Delta S^‡$ and attributed it to an increasingly dissociative transition state as $\Delta H^‡$ increases. We also observed such a correlation in our studies of reaction 1 for $L = C_4H_nO$, as can be seen from the data presented in Table 4. In these ligand substitution reactions, it is not difficult to rationalize such a trend. As the incoming ligand becomes less able to donate electron density to the electron-poor intermediate, it becomes less able to stabilize an associative transition state, the transition state becomes earlier and looser (i.e., more dissociative-like), and both $\Delta H^‡$ and $\Delta S^‡$ increase.

As has been pointed out before, it is very easy to overinterpret these kinds of relationships.[28] In particular, because analyses of Eyring plots derive $\Delta S^‡$ as the intercept of a line constructed from data points that do not have a large span, the uncertainties in the values of $\Delta S^‡$ are often much too large to draw any absolute conclusions about the existence or nonexistence of correlations between $\Delta S^‡$ and other kinetic parameters. To some extent, this is the case with the present results as well. Although we are currently undertaking volume of activation measurements in order to resolve some of the remaining ambiguities in the data,[30] we can draw qualitative conclusions from the results reported here. The data presented in Figure 5 clearly indicate that for these reactions there *cannot* be an isokinetic effect; that is, from the Eyring analyses presented in the figure, there is no single temperature at which all of the reactions proceed at the same rate.

In fact, for the series of ligands THF, MeTHF, Me_2-THF, it appears that not only is there no isokinetic effect but there is no compensation effect either; that is, $\Delta H^‡$ and $\Delta S^‡$ are *anticorrelated*. To our knowledge, this is the first time that a series of ligand substitution reactions at a transition metal intermediate has failed to show an obvious compensation effect. While, as discussed above, the uncertainties in $\Delta S^‡$ are too large to make any definitive statements, the lack of a compensation effect for reaction of these ligands is consistent with our proposal that their relative reactivities are controlled by steric rather than the electronic factors that appear to control the reactivities of the other ligands.

In our prior work,[13] we noted a qualitative correlation between $\Delta H^‡$ for reaction 1 and k_{CO}^{trans} of the product complex $W(CO)_5L$. For the substituted THF ligands, this correlation appears not to exist. On the other hand, $\Delta S^‡$ *does* correlate with k_{CO}^{trans} for all of the ligands studied, whether substituted or unsubstituted, and whether derived from furan or from THF, Figure 8, with the exception of 2,3-DHF, whose anomalous behavior we have discussed previously.[13] This correlation, while presumably related to the general correlation of k_{obs} (a function of $\Delta G^‡$) with k_{CO}^{trans} of $W(CO)_5L$, is actually stronger than that observed for $\Delta H^‡$ with k_{CO}^{trans}. It thus appears that $\Delta S^‡$ is more sensitive to the electron-donating ability of the ligand than is $\Delta H^‡$ and much less dependent on possible steric effects. While this conclu-

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(27) A MNDO calculation has been reported that predicts that the relative stability of binding to Li^+ follows the order $Me_2THF > MeTHF > THF$ (Pinchuk, V. M.; Plakhotnik, A. V.; Pinchuk, T. V. *Zh. Strukt. Khim.* **1994**, *35*, 134; *Chem. Abstr.* 121:92161). Similarly, Benson and Angelici have observed that for complexes of $Cp(CO)_2Ru(Me_n$-thiophene$)^+$ the stability of the complex increases with increasing methyl substitution on the thiophene ligand: Benson, J. W.; Angelici, R. J. *Organometallics* **1993**, *12*, 680.

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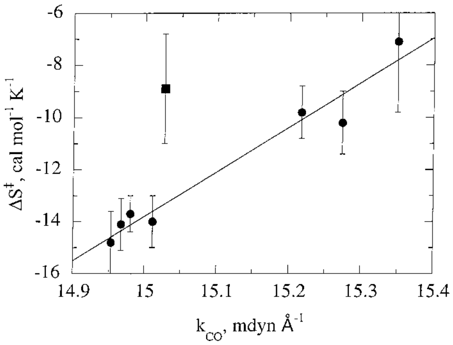

Figure 8. Entropy of activation $\Delta S^‡$ for reaction 1 as a function of the *trans* C−O stretching force constant k_{CO}^{trans} of the product complex $W(CO)_5L$ for L = C_4H_nO, Me$_n$THF, and Me$_n$Fur. Data for the C_4H_nO systems are taken from refs 12 and 13. The solid square represents results for L = 2,3-DHF; the solid line is a least squares fit to the results for the remaining ligands.

sion may seem counterintuitive—steric interference might be expected to lead to a looser transition state and hence a *larger* value of $\Delta S^‡$—it is not unreasonable, as consideration of an associative ligand exchange transition state will show. As we have seen, the relative energy of the transition state is determined primarily by the relative ability of L to stabilize it by donating electron density. Methyl group substitution at THF makes the ligand more electron donating and therefore capable of stronger binding to the metal center. A methyl-substituted ligand will thus be able to approach the metal atom more closely than an unsubstituted one, lowering $\Delta V^‡$ and hence $\Delta S^‡$.[31] Increased steric strain in complexes of substituted ligands could contribute to an increase in the overall internal energy of the transition state, leading to an increase in $\Delta H^‡$ and $\Delta G^‡$. These constraints may also lead to further loss of entropy at the transition state, due to the increase in the frequencies of the ring−methyl bending vibrational modes. The importance of the contribution of low-frequency vibrational modes to the activation entropy has been observed previously.[10,13] Further studies are underway to further probe the details of this competition between steric and electronic effects in ligand substitution reactions of transition metal intermediates and of enthalpic and entropic contributions to the reaction activation energy.[22,30]

Summary and Conclusions

Time-resolved infrared spectroscopy has been used to study the ligand displacement reaction of $W(CO)_5(CyH)$ with 2- and 2,5-substituted molecules MeTHF, Me$_2$THF, MeFur, and Me$_2$Fur. The low values of $\Delta H^‡$ measured here relative to the $(CO)_5W$−CyH bond dissociation energy, negative $\Delta S^‡$, and strong dependence of the reaction rates with the properties of the incoming ligand indicate that, as with the analogous unsubstituted ligands, the reaction proceeds through an associative interchange (**I$_a$**) mechanism.

We find that the reactivity of MeTHF and Me$_2$THF with $W(CO)_5(CyH)$ is controlled primarily by steric hindrance imposed by the substituent methyl group(s), with each additional methyl group adding ca. 0.5 kcal mol^{-1} to $\Delta G^‡$. For MeFur and Me$_2$Fur, however, an electronic effect in which the electron-donating methyl groups tend to *lower* $\Delta G^‡$ competes with the steric effect. We observe that while $\Delta H^‡$ for these reactions is primarily sensitive to *steric* effects, $\Delta S^‡$ is more sensitive to *electronic* effects. These differences appear to be related to competing demands on the nature of the incoming ligand: while a more substituted molecule can donate more electron density to the transition state, steric hindrance from the substituents tends to make reaction by more substituted ligands less facile.

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Supporting Information Available: Tables of pseudo-first-order reaction rate constants for reaction 1, and Figures S1 and S2. This material is available free of charge via the Internet at http://pubs.acs.org.

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