Electronic and Steric Influences on the Rate and Energetics of THF and Me$_n$THF (n = 1, 2) Displacement from LRe(CO)$_2$ (L = Tp, Tp*, Cp*) Fragments by Acetonitrile

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The dissociative displacement of the THF solvent molecule from LRe(CO)$_2$−THF (L = Tp, Tp*, Cp*) and of Me$_n$THF (n = 1, 2) from TpRe(CO)$_2$−Me$_n$THF by acetonitrile is studied. While the reactivity of the Re−THF bond depends on the electronic properties of the ancillary ligands (Tp, Tp*, Cp*) attached to the metal center, the lability of the Re−Me$_n$THF bond is primarily influenced by the steric demands of the departing solvent.

Introduction

Since their discovery by Trofimenko in 1966,[1] the "scorpionate" ligands hydridotris(pyrazolyl)borate (Tp) and hydridotris(3,5 dimethylpyrazolyl)borate (Tp*) have been utilized in the synthesis of a wide range of organometallic complexes.[2] These poly(pyrazolyl)borate anions are often viewed as equivalents to the well-known cyclopentadienyl (Cp) and pentamethylcyclopentadienyl (Cp*) ligands, since both sets are facially coordinating six-electron-donor ligands.[2,3] Despite some similarities, there has been contradictory evidence regarding the relative electron-donating capabilities of the two ligand sets.[4,5] A recent comparison of the Tp/Tp* and Cp/Cp* ligands indicates that the relative electron-donating capabilities of these ligands varies with the identity of the metal, with the metal's oxidation state, and with the identity of the other molecules bound to the complex.[6] Substitution of a Cp* ligand with Tp* can have a profound influence upon the reactivity of the resulting complexes. For example, Bergman and co-workers have reported that while the Cp*Ir(PMe$_3$)-(CH$_3$)OTf complex activates C−H bonds in a variety of hydrocarbons under mild conditions, the Tp* analogue is not reactive toward C−H bonds, even under elevated conditions of temperature and pressure.[7,8]

To better understand the influence of these polydentate ligands on the reactivity of the respective complexes, we chose to investigate the displacement of a weakly coordinated ligand, tetrahydrofuran (THF), and its methyl analogues, 2-methyltetrahydrofuran (MeTHF) and 2,5-dimethyltetrahydrofuran (Me$_2$THF), from the Re center in Cp*Re(CO)$_2$, TpRe(CO)$_2$, and Tp*Re(CO)$_2$ fragments. These studies were also motivated by the fact that, in contrast to the Cp/Cp* ligands, relatively little is known about the ligand substitution mechanism of the (Tp/Tp*)M−L complexes.[2,9−14] Also, understanding the mechanism and energetics of the substitution reactions is important, since both Cp*Re(CO)$_2$−THF and TpRe(CO)$_2$−THF have been utilized as precursors for the synthesis of several important substituted rhenium carbonyl complexes.[5,15,16]

The data reported in this paper suggest that the displacement of THF from the Cp*Re(CO)$_2$, TpRe(CO)$_2$, and Tp*Re(CO)$_2$ complexes proceeds through a dissociative mechanism. Surprisingly, reducing the steric bulk of the ancillary ligands by replacing Tp or Tp* with Cp* results in a *more labile* Re−THF bond. Studies with Me$_n$THF solvents indicate that the reactivities of the corresponding TpRe(CO)$_2$−Me$_n$THF bonds are primarily influenced by the steric properties of the departing solvent molecule.

Experimental Section

Kinetic studies were conducted using a Hewlett-Packard diode array spectrophotometer (Model HP 8453) equipped with a Peltier temperature controller. Infrared spectra were ob-

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tained at 1 cm^{-1} resolution employing a 0.5 mm IR cell with CaF$_2$ windows. A typical kinetic run employing UV–vis detection was performed as follows. Approximately 2–3 mg of Cp*Re(CO)$_3$, TpRe(CO)$_3$, or Tp*Re(CO)$_3$ was added to an anaerobic 1 × 1 cm quartz cuvette, followed by addition of 1.0–2.4 mL of THF, MeTHF, or Me$_2$THF solvent using a gastight syringe. The resulting solution was photolyzed for 1–2 min using the unfiltered output of a 150 W Xe arc lamp (Xenon Corp.) to generate the corresponding Re–THF or Re–Me$_n$THF complex. After photolysis, the solution was thermally equilibrated and an appropriate volume of acetonitrile (0.1–1.5 mL) was added such that the total solution volume was 2.5 mL. The reaction was followed by monitoring the decay of the reactant complex absorbing at 376 nm. To minimize temperature fluctuations, in runs employing a large volume of CH$_3$-CN (≥0.5 mL), the acetonitrile was preheated to the reaction temperature before addition to the photolyzed solution. It was noted that TpRe(CO)$_3$ had limited solubility in Me$_2$THF. However, addition of CH$_3$CN yielded complete dissolution of the Re complex. It was also found that, to achieve acceptable reproducibility, the THF solvent had to be thoroughly deoxygenated prior to runs employing the Cp*Re(CO)$_3$ complex.

All runs were performed under pseudo-first-order conditions, with the acetonitrile concentration being at least 10 times greater than that of the Re–THF or Re–Me$_n$THF complex. Kinetic runs were conducted over at least a 10-fold range of ligand concentrations. Observed rate constants, k_{obs}, were obtained by fitting plots of the absorbance of the Re–THF or Re–Me$_n$THF complex vs time to a single-exponential function. Rate constants were determined by weighted nonlinear least-squares fits to the concentration dependence of k_{obs} and are reported with 1σ uncertainties. The errors in the activation parameters obtained from Eyring plots are at the 95% confidence level. The run-to-run reproducibility was found to be ~5–10%.

All solvents used in the experiment, tetrahydrofuran (THF), 2-methyltetrahydrofuran (MeTHF), 2,5-dimethyltetrahydrofuran (Me$_2$THF), and acetonitrile (CH$_3$CN), either were anhydrous grade or were dried over CaH$_2$ and were of ≥97%+ purity (Aldrich or Acros). The Me$_2$THF solvent was a mixture of cis and trans isomers. The TpRe(CO)$_3$ complex was synthesized according to literature procedures.[5] A similar procedure, although not published previously, was also used to prepare the Tp* analogue. The purities of both products were checked by infrared spectroscopy. The Cp*Re(CO)$_3$ complex was purchased from Strem Chemicals and used as received. All manipulations were carried out under an Ar atmosphere.

Results and Discussion

(a) Reactivity of TpRe(CO)$_2$(THF). Photolysis of a ~2 mM THF solution of TpRe(CO)$_3$ yields a complex with IR absorptions at 1905 and 1823 cm^{-1}, similar to those of the well-characterized TpRe(CO)$_2$(THF) complex.[5,16] Addition of acetonitrile to the solution resulted in the displacement of the THF ligand from the Re center and the formation of the TpRe(CO)$_2$(CH$_3$CN) complex (Figure 1). Acetonitrile was chosen as the incoming ligand for the displacement of THF because the resulting product has previously been isolated and the reaction proceeds to completion without side reactions.[16] Furthermore, the relatively high molar concentration of CH$_3$CN (19.1 M) allows for the displacement kinetics to be studied over a wide range of incoming ligand concentrations.

The TpRe(CO)$_2$(THF) complex undergoes a first-order decay in the presence of acetonitrile, and the TpRe(CO)$_2$-(CH$_3$CN) complex grows in at a similar rate. An isos-
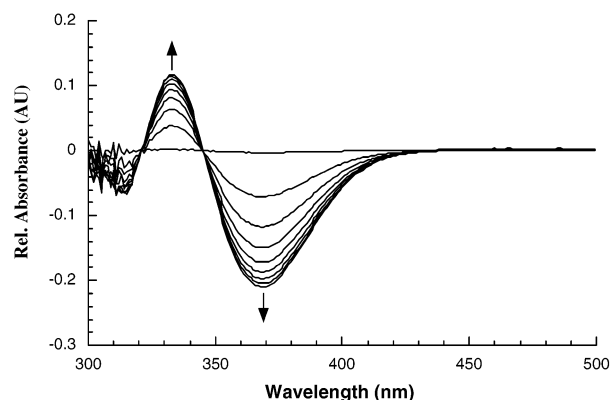

Figure 1. Difference UV–vis spectra obtained at 300 s intervals following the addition of 1.9 M acetonitrile to a THF solution containing TpRe(CO)$_2$(THF) at 323 K.

bestic point is observed at 344 nm, providing strong evidence for the conversion of the reactant to a single product. The observed rate constant, k_{obs}, does not vary linearly with [CH$_3$CN] but instead approaches a limiting value at high [CH$_3$CN] (Figure 2).

While the saturation behavior of k_{obs} in these plots may be the result of solvent effects caused by the large [CH$_3$CN], the internal consistency of the data presented in this paper suggests that this is not the case. The saturation behavior of k_{obs} is inconsistent with an associative or interchange mechanism of THF displacement by CH$_3$CN. Instead, the curvature of the k_{obs} vs [CH$_3$CN] plot implies that the overall substitution mechanism includes the presence of consecutive steps where at least one of the steps is reversible.

Thus, the data are consistent with a dissociative mechanism of THF substitution which requires the reversible disruption of the Re–THF bond before the CH$_3$CN ligand binds to the metal center:
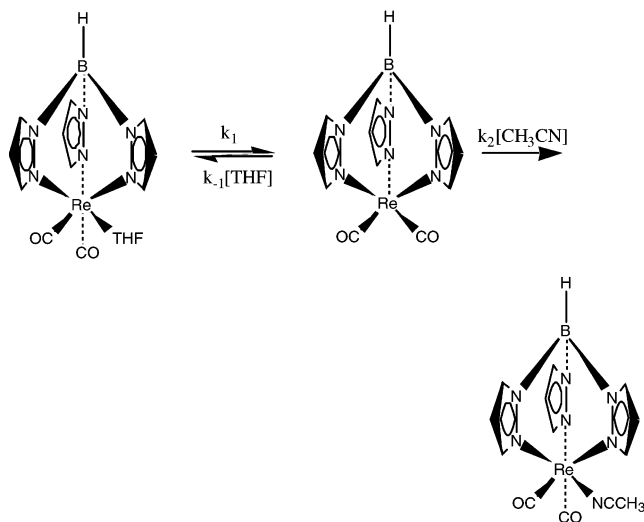
When the TpRe(CO)$_2$ fragment is treated as a steady-state intermediate, the dependence of k_{obs} on [CH$_3$CN] can be derived as

$$k_{obs} = \frac{k_1 k_2 [\text{CH}_3\text{CN}]}{k_{-1}[\text{THF}] + k_2 [\text{CH}_3\text{CN}]} \quad (1)$$

According to eq 1, at low [CH$_3$CN] k_{obs} will exhibit a

Table 1. Values of k_1 ($\times 10^3$ s^{-1}) (k') Obtained from a Nonlinear Least-Squares Fit to the k_{obs} Data According to Eq 3 Modified by Using Appropriate Values for a in the Case of MeTHF and Me$_2$THF[a]

T (K)	Cp*[Re] THF	Tp*[Re] THF[b]	Tp[Re]		
			THF[c]	MeTHF[d]	Me$_2$THF[e]
333			11.4 ± 0.6 (3.1 ± 0.2)		
323		36.7 ± 1.7 (2.6 ± 0.3)	3.87 ± 0.20 (2.8 ± 0.3)	11.7 ± 0.6 (3.3 ± 0.3)	
313		10.2 ± 0.5 (3.3± 0.3)	1.16 ± 0.10 (2.8 ± 0.3)	3.40 ± 0.17 (3.5 ± 0.3)	21.6 ± 0.9 (9.1 ± 0.9)
308					13.8 ± 0.7 (7.1 ± 0.9)
303	9.24 ± 0.49 (3.5 ± 0.4)	2.85 ± 0.13 (2.9 ± 0.3)	0.292 ± 0.014 (3.0 ± 0.3)	0.880 ± 0.035 (3.7 ± 0.3)	7.31 ± 0.26 (7.6 ± 0.7)
293		0.706 ± 0.033 (3.0 ± 0.3)		0.205 ± 0.010 (4.0 ± 0.4)	1.99 ± 0.10 (6.3 ± 0.8)

[a] [Re] = Re(CO)$_2$. [b] $\Delta H^{\ddagger}_1 = 24.0 \pm 0.9$ kcal/mol, $\Delta S^{\ddagger}_1 = +9.2 \pm 2.7$ eu. [c] $\Delta H^{\ddagger}_1 = 23.9 \pm 0.9$ kcal/mol, $\Delta S^{\ddagger}_1 = +4.1 \pm 3.0$ eu. [d] $\Delta H^{\ddagger}_1 = 24.7 \pm 0.8$ kcal/mol, $\Delta S^{\ddagger}_1 = +9.1 \pm 2.5$ eu. [e] $\Delta H^{\ddagger}_1 = 21.3 \pm 1.2$ kcal/mol, $\Delta S^{\ddagger}_1 = +2.3 \pm 4.0$ eu.
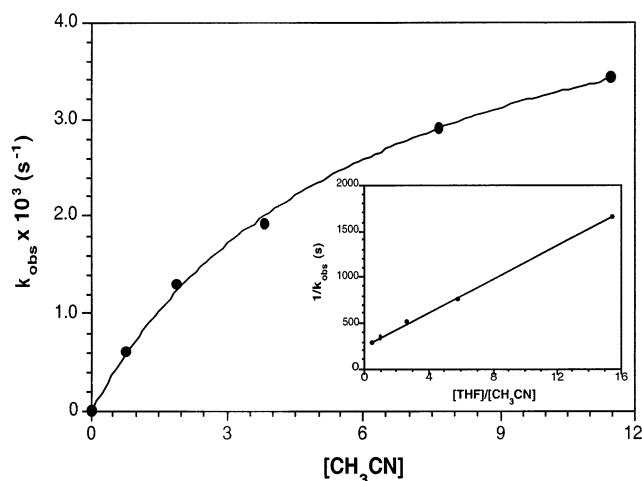
Figure 2. Plot of k_{obs} vs [CH$_3$CN] at 323 K. The solid line represents a nonlinear least-squares fit to the data according to eq 3. The inset shows a plot of $1/k_{obs}$ vs [THF]/[CH$_3$CN]. The linearity of this plot is consistent with eq 1.

linear dependence on the incoming ligand concentration but at high [CH$_3$CN] it will approach a limiting value as the dissociation of the TpRe(CO)$_2$–THF bond becomes the rate-determining step.

An alternative mechanism which is also consistent with the observed nonlinear k_{obs} behavior involves the reversible dechelation of one arm of the Tp ligand to yield the 16-electron intermediate [η^2-TpRe(CO)$_2$(THF)], which then traps CH$_3$CN and goes on to form the product. There is evidence for such a $\eta^3 \rightarrow \eta^2$ hapticity shift in the chemistry of Tp*Rh and TpIr complexes.[11,13] However, if this mechanism were operative, k_{obs} would be independent of the concentration of THF. The results of a mixed-solvent experiment in which heptane was added as a diluent showed that when the concentration of THF was reduced by a factor of 2 from 11.8 to 5.9 M, at 60 °C with 0.76 M CH$_3$CN, k_{obs} increased by roughly the same factor, from $(2.1 \pm 0.1) \times 10^{-3}$ to $(5.2 \pm 0.3) \times 10^{-3}$ s^{-1}. While use of heptane as the diluent will affect the polarity of the solvent, the large change in k_{obs} is consistent only with a pathway that includes reversible displacement of the THF solvent. Furthermore, it is also chemically unreasonable to suggest that a presumably strong Re–pyrazolyl bond would dissociate in preference to the more labile Re–THF bond.

The mechanism presented here is also consistent with previous studies which suggest that most complexes containing the Tp ligand undergo dissociative ligand substitutions.[9,10,13] Evidently, the dissociative mecha-

nism is preferred over an associative pathway, due to the presence of the facially coordinating Tp ligand, which enforces a strict octahedral geometry around the metal center and thus prevents the formation of an intermediate with increased coordination number. An unusual instance, however, has been reported by Mayer et al., who demonstrated that substitution of the triflate ligand by acetonitrile from the Tp(Ph)Re(NTol)OTf complex occurred via an associative pathway.[12] Consistent with this mechanistic assignment, but in contrast to the results of the present study (see below), they found that substitution of Tp with the more sterically encumbered Tp* slowed the reaction rate.

Since in these reactions THF is not only a solvent but also a reactant, eq 1 must be modified to take into account the fact that addition of increasing amounts of CH$_3$CN necessarily decreases the concentration of THF. The concentration of THF may be expressed as

$$[\text{THF}] = [\text{THF}]_0 - a[\text{CH}_3\text{CN}] \qquad (2)$$

Here [THF]$_0$ is the concentration of pure THF (12.3 M) and a is the ratio of the concentrations of pure THF and acetonitrile (0.64). Substitution of eq 2 into 1 yields

$$k_{obs} = \frac{k_1 k'[\text{CH}_3\text{CN}]}{12.3 + (k' - a)[\text{CH}_3\text{CN}]} \qquad (3)$$

$$k' = \frac{k_2}{k_{-1}}$$

A two-parameter nonlinear least-squares fit of the data in the k_{obs} vs [CH$_3$CN] plots according to eq 3 yielded values of k_1 and k' at several temperatures and are presented in Table 1.

Estimate of the TpRe(CO)$_2$–THF Bond Enthalpy. The activation enthalpy of 23.9 ± 0.9 kcal/mol associated with the k_1 step is related to the strength of the Tp(CO)$_2$Re–THF interaction. The moderately positive activation entropy of $+4.1 \pm 3.0$ eu is also consistent with the dissociation of the Re–THF bond in the transition state. Interestingly, the k' values suggest that CH$_3$CN reacts approximately 3 times faster with the TpRe(CO)$_2$ fragment than does THF. Importantly, within experimental error, this ratio remains invariant with temperature, suggesting that either the activation enthalpies for the k_{-1} and k_2 steps are significant yet similar or that they are both near zero. It is more likely that the TpRe(CO)$_2$ fragment reacts with both THF and CH$_3$CN without an activation barrier, since it has been demonstrated that a number of 16-electron organome-

tallic fragments react with a variety of ligands without an enthalpic barrier (<2 kcal/mol).[17-21] It is therefore reasonable to suggest that the activation enthalpy of 23.9 kcal/mol for the k_1 step does not overestimate the strength of the Re–THF bond. However, as in the case of the M(CO)$_5$–alkane/arene (M = Cr, W) complexes, metal–solvent bond strengths obtained by kinetic methods frequently underestimate the actual values by several percent.[22-24] Therefore, the activation enthalpy may in fact provide a lower estimate for the Tp(CO)$_2$Re– THF bond dissociation enthalpy.

The activation enthalpy may underestimate the true bond enthalpy if the Re–THF bond is not fully dissociated in the transition state.[25] Residual bonding between Re and THF in the transition state implies, paradoxically, that the transition state has a lower enthalpy than the postulated TpRe(CO)$_2$ intermediate. However, the kinetic requirement is that the free energy of the transition state must be equal to or higher than that of the intermediate. Thus, if the increase in enthalpy as the Re–THF bond continued to dissociate past the transition state were to be offset by an increase in entropy, the free energy of the TpRe(CO)$_2$ intermediate would be equal to or lower than that of the transition state, as required. In the present case, the moderately positive activation entropy suggests that the true Re– THF bond enthalpy is not significantly higher than 24 kcal/mol.

(b) Reactivity of Cp*Re(CO)₂(THF) and Tp*Re-(CO)₂(THF). To investigate the effect of altering the electronic and steric properties of the ancillary ligands attached to the metal center upon the reactivity of the Re–THF bond, experiments were also conducted with the Tp*Re(CO)$_2$(THF) and Cp*Re(CO)$_2$(THF) complexes. As shown in Figure 3, the k_{obs} vs [CH$_3$CN] plots for both Tp* and Cp* show the same features as in the case of the TpRe(CO)$_2$(THF) complex, suggesting a similar mechanism of THF displacement. However, the values of the limiting rate constant, k_1, are very different and vary in the order Tp < Tp* < Cp*. Unexpectedly, Cp*Re(CO)$_2$(THF) reacts 32 times *faster* than TpRe-(CO)$_2$(THF) and more than 3 times faster than Tp*Re-(CO)$_2$(THF) (see Table 1). Since the substitution follows a dissociative pathway, and the Tp and Tp* ligands are significantly bulkier than Cp*,[6] we expected the Re– THF bond to be more labile in the TpRe(CO)$_2$(THF) and Tp*Re(CO)$_2$(THF) complexes. However, the opposite reactivity is observed. Clearly, the relative lability of the Re–THF bond in these complexes is governed by electronic rather than steric factors.

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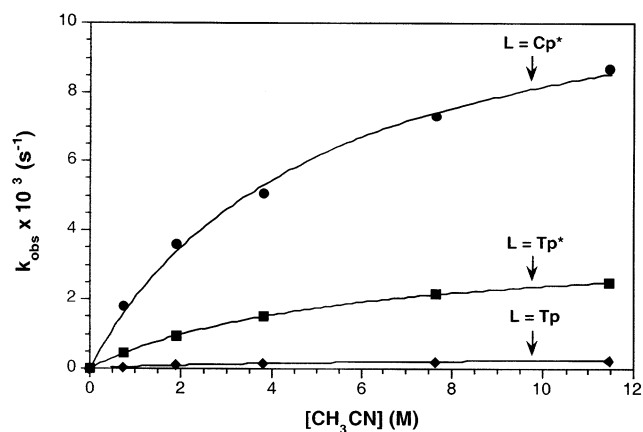
Figure 3. Plots of k_{obs} vs [CH$_3$CN] for LRe(CO)$_2$(THF) at 303 K. The solid lines represent fits to the data according to eq 3.

Previous studies have shown that the relative electron-donating capabilities of the Cp*, Tp*, and Tp ligands toward a Re center increase in the order Tp < Tp* < Cp*.[6] It is therefore reasonable to assume that the degree of THF→Re σ donation will be reduced in the electron-rich Cp*Re(CO)$_2$(THF) complex relative to the Tp and Tp* analogues, resulting in a more labile Re– THF bond. The influence of electronic factors upon the reactivity of weak metal–solvent bonds has literature precedence in a related system. Bergman and co-workers found that displacement of weakly coordinated triflate was significantly slower from Tp*Ir(PMe$_3$)(CH$_3$)-OTf than from the Cp* analogue.[7,8] This difference in reactivity was substantial enough to make Tp*Ir(PMe$_3$)-(CH$_3$)OTf unreactive toward the activation of C–H bonds, while the Cp* analogue was able to accomplish the reaction under mild conditions.

The activation enthalpies associated with k_1 for Tp*Re(CO)$_2$(THF) and its Tp analogue are within experimental error, suggesting that there is a very small difference in the Re–THF bond strengths in these complexes. While the Tp* complex reacts faster than the Tp analogue, the data suggest that this difference in reactivity may not simply be a result of the greater steric bulk of the Tp* ligand but that the better electron donor abilities of the Tp* ligand must also be considered.

As shown in Table 1, the differences in the overall rate of displacement of the THF ligand from the three complexes are due to variations in k_1, not k''. Thus, the coordinatively unsaturated fragments TpRe(CO)$_2$, Tp*Re-(CO)$_2$, and Cp*Re(CO)$_2$ all react approximately 3 times faster with CH$_3$CN than with THF. Furthermore, the value of k'' is insensitive to temperature, which, as discussed earlier, implies that the reaction of the 16-electron intermediates with both THF and CH$_3$CN proceeds without a significant activation barrier.

(c) Reactivity of TpRe(CO)₂(Me$_n$THF) (n = 1, 2). To study the effect of varying the electronic and steric properties of the departing solvent molecule upon the rates of the substitution reaction, experiments similar to those described above were conducted with MeTHF and Me$_2$THF as the solvent. The k_{obs} vs [CH$_3$CN] plots exhibit saturation behavior, and it may be concluded that, like THF, both MeTHF and Me$_2$THF undergo dissociative displacement from the Tp(CO)$_2$Re complex by CH$_3$CN. There are, however, some important differ-

ences in the rate constants for the displacement reactions, since the magnitude of k_1 increases with the degree of methyl substitution (see Table 1).

The CO stretching frequencies of the corresponding TpRe(CO)$_2$(Me$_n$THF) complexes increase as the degree of methyl substitution increases.[26] Thus, Me$_2$THF projects *less* electron density onto the metal center than does THF. This trend, while opposite of that expected from a consideration of electronic effects, is consistent with an increase in F-strain that occurs between the increasingly bulky Me$_n$THF ligand and the sterically encumbered TpRe(CO)$_2$ fragment. The trend in CO stretching frequencies suggests that, relative to THF, increased steric hindrance prevents the MeTHF and Me$_2$THF solvents from achieving an optimum bonding interaction with the sterically hindered Re center. Thus, as observed, the lability of the Re−Me$_n$THF bond increases in the order Re−THF < Re−MeTHF < Re−Me$_2$THF. It is interesting to note that when the electronic and steric properties of the departing ligand are kept constant, the reactivity of the Re−THF bond depends primarily upon the electronic properties of the ancillary ligands (Cp*, Tp, Tp*) attached to the metal center. However, when the electronic and steric properties of the metal fragment are kept constant, the lability of the metal−solvent bond is primarily influenced by the steric demands of the departing solvent molecule but not its electronic properties.

As shown in Table 1, the activation enthalpies corresponding to the dissociation of the Re−THF and Re−MeTHF bonds are similar and ∼3 kcal/mol greater than that of the Re−Me$_2$THF bond. The activation entropies also do not show a clear trend. Given the uncertainties in the activation parameters, it is difficult to assess whether the differences in k_1 are due to enthalpic or

entropic factors, although it does appear that the greater reactivity of the Re−Me$_2$THF bond is in part due to a lower activation enthalpy and hence a weaker bond. The k'' values suggest that the reactivity of the TpRe(CO)$_2$ intermediate toward the Me$_n$THF solvents decreases as the degree of methyl substitution increases. Thus, consistent with the greater steric bulk of the Me$_2$THF solvent, THF reacts with TpRe(CO)$_2$ almost twice as fast as does Me$_2$THF. The lack of a significant dependence of k'' values on temperature implies that this difference in reactivity may have an entropic rather than enthalpic origin; however, the uncertainty in the k'' values prevents us from reaching a firm conclusion.

Conclusion

The displacement of the THF solvent from the Cp*Re(CO)$_2$(THF), TpRe(CO)$_2$(THF), and Tp*Re(CO)$_2$(THF) complexes by acetonitrile proceeds through a dissociative mechanism. The ancillary ligands Cp*, Tp, and Tp* influence the reactivity of the Re−THF bond primarily through an electronic effect. Thus, the rate of dissociation of the Re−THF bond is greater in the relatively electron rich Cp*Re(CO)$_2$(THF) complex than in the more sterically encumbered TpRe(CO)$_2$(THF) and Tp*Re(CO)$_2$(THF) complexes. Lower limits of 23.9 ± 0.9 and 24.0 ± 0.9 kcal/mol are obtained for the strength of the Re−THF interaction in TpRe(CO)$_2$(THF) and Tp*Re(CO)$_2$(THF), respectively.

The influence of the electronic and steric properties of the departing solvent on the reactivity of the metal−solvent bond was investigated by studying the displacement of MeTHF and Me$_2$THF from the TpRe(CO)$_2$ fragment by acetonitrile. These reactions were also found to proceed through a dissociative mechanism. Importantly, the lability of the Re−Me$_n$THF bond was found to be primarily influenced by the steric rather than the electronic properties of the departing solvent molecule. Thus, the rate of dissociation of the TpRe(CO)$_2$−Me$_2$THF bond was 25 times faster than that of the corresponding TpRe(CO)$_2$−THF bond.

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(26) Of the two CO stretching bands for the TpRe(CO)$_2$(Me$_n$THF) complexes, only the lower frequency stretch is observed. The higher energy band is obscured by the parent tricarbonyl peak. The lower frequency bands are observed at 1822.7 cm^{-1} (THF), 1824.9 cm^{-1} (MeTHF), and 1826.8 cm^{-1} (Me$_2$THF). This trend is not merely due to solvent shifts, since the CO bands of the parent tricarbonyl change by less than 0.5 cm^{-1} in the different solvents (THF, MeTHF, and Me$_2$THF).