Kinetic and Mechanistic Study of the Displacement of η^2-Coordinated Arenes from Cp*Re(CO)$_2$(η^2-C$_6$H$_5$R) (R = H, CH$_3$, C(CH$_3$)$_3$): Evidence for a Dissociative Mechanism and Estimation of the Re−(η^2-Arene) Bond Strength

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The displacement of the arene molecule from Cp*Re(CO)$_2$(η^2-arene) (arene = benzene, toluene, *tert*-butylbenzene) by pyridine in heptane solution is studied. The rate constants for arene dissociation from the Re center are found to vary in the order Cp*(CO)$_2$Re−(η^2-toluene) < Cp*(CO)$_2$Re−(η^2-benzene) ≈ Cp*(CO)$_2$Re−(η^2-*tert*-butylbenzene) and are a function of the steric and electronic properties of the arene substituents. Activation parameters yield a lower limit of 19−21 kcal/mol for the Cp*(CO)$_2$Re−(η^2-arene) bond strength.

Introduction

Arene molecules coordinated to transition-metal centers in an η^2 fashion are often invoked as intermediates in a variety of catalytic processes.[1] Several such complexes have now been isolated and characterized.[2] Our interest in these systems stems from a report by Orpen and co-workers in which they detected the presence of the Cp*Re(CO)$_2$(η^2-benzene) (Cp* = η^5-C$_5$Me$_5$) complex upon photolysis of Cp*Re(CO)$_3$ in benzene solution.[3] This complex was stable for several hours, ultimately dimerizing with the loss of a benzene molecule to form Cp*(CO)$_2$Re(μ-(1,2-η^2):(3,4-η^2)-C$_6$H$_6$)Re(CO)$_2$Cp*. On the basis of this report, we were interested in estimating the strength of the Re−η^2-benzene interaction by studying the rate of displacement of the benzene molecule from the Re center by a two-electron-donor ligand. A similar method was used successfully to estimate the strength of the Mn−toluene interaction in CpMn(CO)$_2$-(η^2-toluene).[4] In addition, because metal−η^2-arene complexes are intermediates in a variety of chemical reactions, we were also interested in determining the mechanism by which the arene molecule is displaced from the Re center. In this paper we report the results of a study in which the strength of the Re−η^2-arene interaction is estimated for arene = benzene, toluene, *tert*-butylbenzene. The results show that for the three arenes studied, the displacement of the arene molecule

from the Re center by pyridine proceeds via a dissociative pathway, The unimolecular rate constant for the reaction

[R = H, CH$_3$, C(CH$_3$)$_3$]
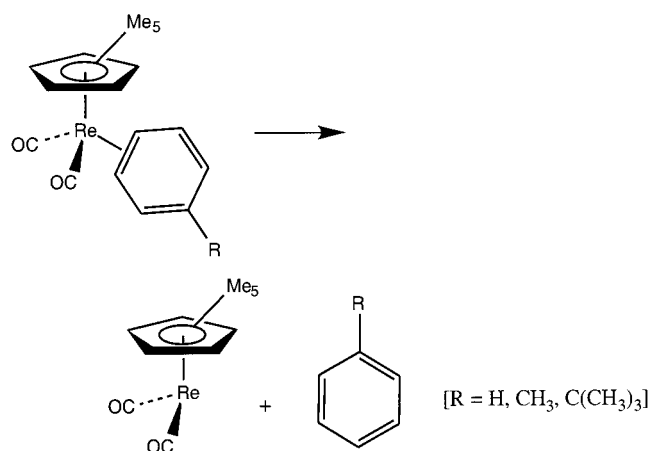
was extracted from the data and correlated with the electronic and steric properties of the arenes studied. The results show that the rate constant for the above reaction is a function of the steric bulk of the arene ligand, and a lower limit of 19−21 kcal/mol is obtained for the strength of the Cp*(CO)$_2$Re−(η^2-arene) interaction.

Experimental Section

All kinetic studies were conducted using a Hewlett-Packard diode array spectrophotometer (HP 8453) equipped with a Peltier temperature controller. Infrared spectra were obtained at 2 cm^{-1} resolution using a Nicolet 750 Magna IR spectrometer employing a 0.5 mm IR cell with CaF$_2$ windows. A typical kinetic run was performed as follows. A 0.3−0.6 mM heptane solution of Cp*Re(CO)$_3$ approximately 2.5 M in arene was photolyzed for 2 min in a 1 × 1 cm quartz cuvette using the unfiltered output of a 150 W Xe arc lamp (Xenon Corp.) to generate the Cp*Re(CO)$_2$(η^2-arene) complex. After photolysis, the pyridine ligand was added and the reaction followed by monitoring the growth of the Cp*Re(CO)$_2$(pyridine) complex

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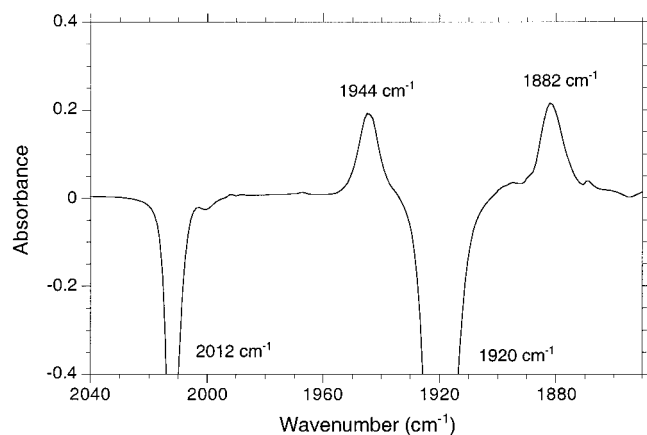(4) Bengali, A. A. *Organometallics* **2000**, *19*, 4000.

Figure 1. Difference IR spectrum obtained upon photolysis of a 4 mM heptane solution of $Cp^*Re(CO)_3$ containing 2.3 M benzene at 298 K. Negative absorptions are due to the depletion of $Cp^*Re(CO)_3$, and positive absorptions are due to the formation of the $Cp^*Re(CO)_2(\eta^2\text{-benzene})$ complex.

absorbing at 400 and 467 nm. The effective wavelength range in these experiments was from 290 to 700 nm. All runs were performed under pseudo-first-order conditions with the ligand concentration being at least 10 times greater than that of the Re–arene complex. Kinetic runs were conducted over a 10–20-fold range of ligand concentrations. Observed rate constants, k_{obs}, were obtained by fitting plots of the absorbance of $Cp^*Re(CO)_2(pyridine)$ vs time to single-exponential functions. Rate constants were determined by linear least-squares fits to the concentration dependence of k_{obs} and are reported with 1σ uncertainties. The error in the activation parameters obtained from Eyring plots are at the 95% confidence level and were obtained from a linear least-squares fit weighted by the variance in the rate constants.

All arenes were of 99%+ purity and were obtained from either Aldrich or Acros. $Cp^*Re(CO)_3$ was obtained from Strem and used as received. Pyridine (99%+ purity, anhydrous) and 1-hexene (99%+ purity) were also used without further purification.

Results and Discussion

IR Studies. An infrared spectrum obtained upon photolysis of a 3–4 mM heptane solution of $Cp^*Re(CO)_3$ at 298 K with UV light results in the generation of several peaks in the CO stretching region.[5] The positions of all the peaks are consistent with the formation of the $Cp^*_2Re_2(CO)_5$ complex, which has been observed before.[6] Thus, under the present experimental conditions there is no evidence for the formation of the $Cp^*Re(CO)_2(heptane)$ complex that has been observed previously on the millisecond time scale.[7] As shown in Figure 1, photolysis of a heptane solution of $Cp^*Re(CO)_3$ containing 2.3 M benzene generates a product with CO stretching absorbances at 1944 and 1882 cm^{-1}. If the photolysis of the $Cp^*Re(CO)_3$ complex is carried out in neat benzene, two peaks at 1938 and 1872 cm^{-1} are observed. The positions of these CO bands are identical with those observed by Orpen and co-workers at 1938

(5) At 298 K peaks due to the dimer are observed at 1987, 1970, 1930, 1901, and 1714 cm^{-1}.

(6) (a) Hoyano, J. K.; Graham, W. A. G. *J. Am. Chem. Soc.* **1982**, *104*, 3722. (b) Foust, A. S.; Hoyano, J. K.; Graham, W. A. G. *J. Chem. Soc., Chem. Commun.* **1982**, 27.

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Table 1. CO Stretching Frequencies (ν_{CO}) of the $Cp^*(CO)_2Re-(\eta^2\text{-}C_6H_5R)$ Complexes in Heptane Solution with ~3 M Arene at 298 K

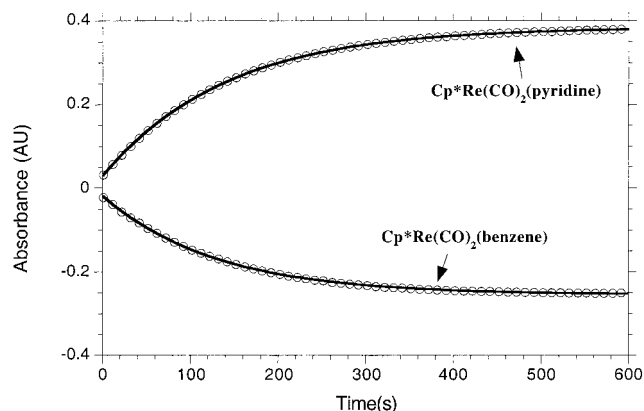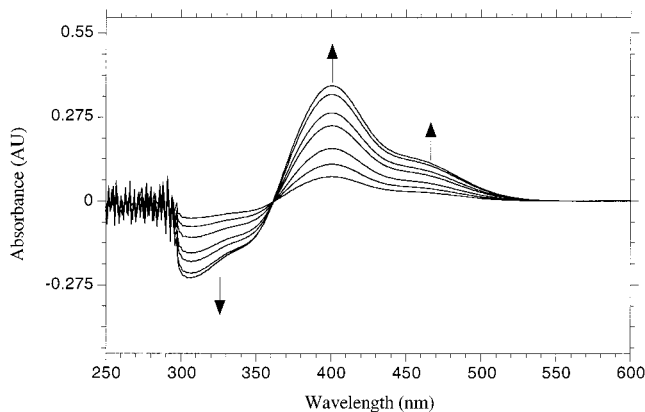| R	ν_{CO} (cm^{-1})	R	ν_{CO} (cm^{-1})
H[a]	1944, 1882	$C(CH_3)_3$[a]	1942, 1879
CH_3[a]	1945, 1882	C_6H_{11}	1943, 1880
CH_2CH_3	1945, 1883		

[a] Arenes used in the kinetic study.

Figure 2. Kinetic traces obtained when a heptane solution of $Cp^*Re(CO)_2(\eta^2\text{-benzene})$ reacts with 1.24 M pyridine in the presence of 4.48 M benzene at 298 K. Solid lines represent first-order exponential fits to the data.

and 1870 cm^{-1} for the $Cp^*Re(CO)_2(\eta^2\text{-benzene})$ complex in neat benzene.[3] Therefore, taking into account slight solvent-induced shifts, we conclude that the species observed upon photolysis of $Cp^*Re(CO)_3$ in heptane solution in the presence of benzene is the $Cp^*Re(CO)_2(\eta^2\text{-benzene})$ complex. As shown in Table 1, the CO stretching bands of other $Cp^*Re(CO)_2(arene)$ complexes generated in this study are very similar to those of the $Cp^*Re(CO)_2(\eta^2\text{-benzene})$ complex. Consequently, we believe that all three arene molecules used in the kinetic study are coordinated to the Re center in an η^2 fashion. The IR spectra do not show evidence for the formation of C–H activation products, since the resulting species would have CO bands at higher frequency relative to the parent $Cp^*Re(CO)_3$ due to the formal oxidation of the Re(I) center to Re(III). It is interesting to note that the frequencies of the CO stretching bands of the $Cp^*Re(CO)_2(\eta^2\text{-arene})$ complexes are almost identical with those of the $Cp^*Re(CO)_2Kr$ complex which have been observed previously at 1944 and 1882 cm^{-1},[7] suggesting that the electron densities at the Re center are similar in the two complexes. Since the Re–Kr interaction involves only Kr→Re σ donation and the arene is most likely a better σ donor than Kr, the similar CO stretching frequencies for the two complexes suggests that there is significant Re–arene π back-bonding in the $Cp^*Re(CO)_2(\eta^2\text{-arene})$ complexes.

Kinetic Studies. The UV–vis spectrum of the $Cp^*Re(CO)_2(\eta^2\text{-arene})$ complexes obtained upon photolysis of a heptane solution of $Cp^*Re(CO)_3$ containing 2.3–2.8 M arene shows the presence of two peaks at 305–340 nm of roughly equal intensity. As shown in Figure 2, upon addition of pyridine the absorbance of the $Cp^*Re(CO)_2(\eta^2\text{-arene})$ complex undergoes a first-order decay and new peaks attributed to the formation of the $Cp^*Re(CO)_2(pyridine)$ complex grow in at 400 and 463 nm at the same rate. The positions of these product bands are very similar to those observed for the previously char-

Figure 3. Difference spectra obtained at 298 K showing growth of the $Cp^*Re(CO)_2(pyridine)$ complex and the decay of the $Cp^*Re(CO)_2(\eta^2\text{-benzene})$ complex. The reaction mixture contains [benzene] = 4.48 M and [pyridine] = 1.24 M.

Figure 4. Plots of k_{obs} vs [pyridine] for the reaction of $Cp^*Re(CO)_2(\eta^2\text{-benzene})$ with pyridine to form $Cp^*Re(CO)_2$-(pyridine). In all the runs the concentration of benzene was held constant at 2.3 M.

acterized $CpRe(CO)_2(pyridine)$ complex.[8] As shown in Figure 3, the reaction of the $Cp^*Re(CO)_2(\eta^2\text{-benzene})$ complex with pyridine to form the $Cp^*Re(CO)_2(pyridine)$ complex proceeds smoothly, with an isosbestic point indicating the conversion of the reactant to a single product.

The observed rate of growth of the product complex is a function of [pyridine], and as shown in Figure 4, the observed rate constant, k_{obs}, obtained from a first-order fit to the growth of the Re−pyridine product complex increases with pyridine concentration and ultimately approaches a limiting value at all temperatures studied. A similar dependence of k_{obs} on pyridine concentration is observed for all of the $Cp^*Re(CO)_2(\eta^2\text{-arene})$ complexes studied, suggesting a common mechanism of arene displacement from the Re center. The observation that k_{obs} reaches a limiting value at high pyridine concentration is evidence for the presence of a reversible step in the displacement of the arene molecule from the Re center by pyridine. The most plausible mechanism is one that involves dissociative loss of the arene ligand from the Re center (Scheme 1). Note that, in this mechanism, the $Cp^*Re(CO)_2(heptane)$ complex is invoked as an intermediatee, since it has been observed previously on the millisecond time scale.[7] Assuming a steady-state concentration of the $Cp^*Re(CO)_2(heptane)$ intermediate, the dependence of k_{obs} on ligand (L) concentration may be derived as

$$k_{obs} = \frac{k_1 k_2 [L]}{k_{-1}[arene] + k_2[L]} \tag{1}$$

Values for k_1 and k_2/k_{-1} may be extracted from the data by recasting eq 1 in the form

$$\frac{1}{k_{obs}} = \frac{1}{k_1} + \frac{k_{-1}[arene]}{k_1 k_2[L]} \tag{2}$$

Thus, k_1 and k_2/k_{-1} may be determined from the intercept and slope of a plot of $1/k_{obs}$ vs [arene]/[L], respectively.

To support the mechanism of the reaction presented in Scheme 1, further experiments were conducted. If the mechanism is dissociative, then the value of k_1 should
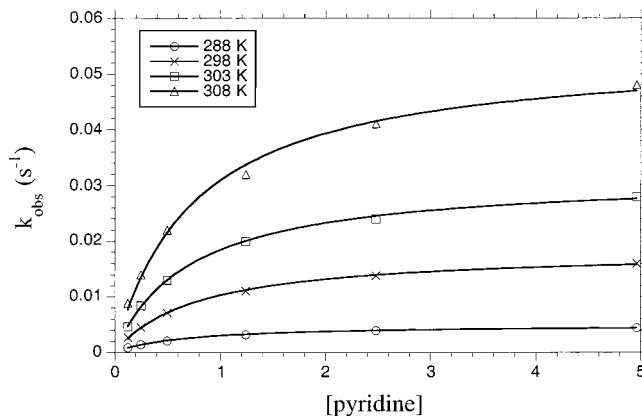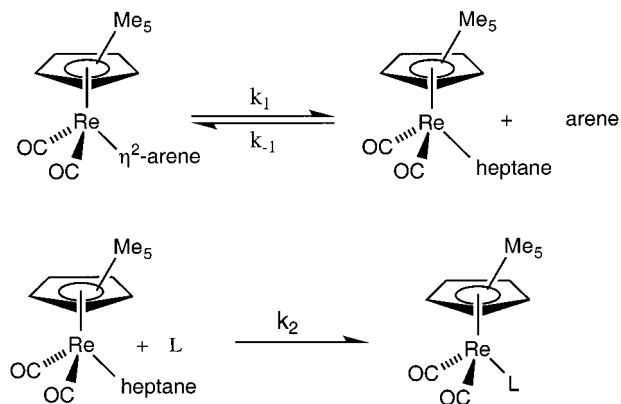
Scheme 1

be independent of the nature of the ligand used to displace the arene. Thus, experiments were conducted at 298 K in which a heptane solution of $Cp^*Re(CO)_2$-($\eta^2\text{-benzene}$) containing 2.3 M benzene was reacted with L = 1-hexene instead of pyridine to yield the Cp^*Re-$(CO)_2(1\text{-hexene})$ product.[9] As with the pyridine ligand, k_{obs} shows saturation behavior and a plot of the data according to eq 2 yields $k_1 = (18.2 \pm 1.8) \times 10^{-3}$ s^{-1} in agreement with a value of $(17.2 \pm 0.7) \times 10^{-3}$ s^{-1} obtained when pyridine is used as the ligand (see Figure 5). Interestingly, when L = 1-hexene, $k_2/k_{-1} = 1.2 \pm 0.1$, suggesting that the $Cp^*Re(CO)_2(heptane)$ intermediate is not very selective in its reaction with 1-hexene and benzene. By comparison, $k_2/k_{-1} = 3.3 \pm 0.2$ when L = pyridine, indicating that the reaction of $Cp^*Re(CO)_2$-(heptane) with pyridine is approximately 3 times faster than its reaction with 1-hexene. This observation is not surprising, since pyridine is expected to be a better nucleophile than 1-hexene.

To provide further support for the mechanism presented in Scheme 1, two additional sets of experiments were conducted. In the first set, the concentration of pyridine was held constant while [benzene] was varied, and in the second set, [benzene] was held constant and

(8) Giordano, P. J.; Wrighton, M. S. *Inorg. Chem.* **1977**, *16*, 160.

(9) Formation of the $Cp^*Re(CO)_2(1\text{-hexene})$ complex was confirmed by photolyzing a heptane solution of $Cp^*Re(CO)_3$ in the presence of benzene and 1-hexene. CO stretching bands of the $Cp^*Re(CO)_2(1\text{-hexene})$ complex were observed at 1958 and 1885 cm^{-1}, similar to those observed at 1955 and 1884 cm^{-1} for the well-characterized $Cp^*Re(CO)_2$-(2-pentene) adduct (see: Zhuang, J.-M.; Sutton, D. *Organometallics* **1991**, *10*, 1516).

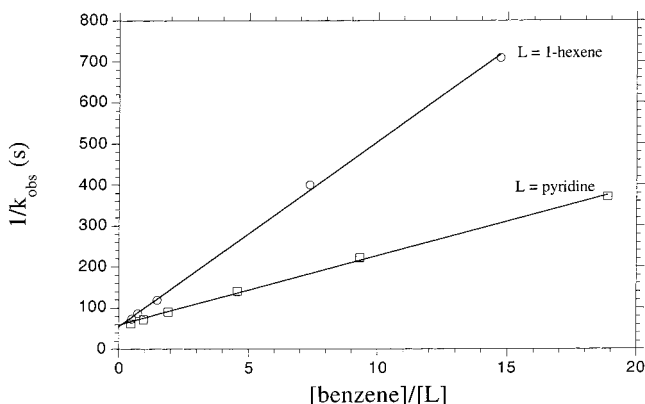**Figure 5.** Double inverse plots obtained at 298 K for the reaction of Cp*Re(CO)$_2$(η^2-benzene) with L = 1-hexene, pyridine. Note that both plots have similar intercepts, consistent with a dissociative mechanism of arene displacement from the Re center (see text).

Table 2. Rate Constants for the Reaction of Cp*Re(CO)$_2$(η^2-arene) with Pyridine Obtained from a Linear Least-Squares Fit to the Data According to Eq 2

arene	temp (K)	$10^3 k_1$ (s^{-1})	k_2/k_{-1}
benzene[a]	288	4.70 ± 0.20	3.9 ± 0.2
	298	17.2 ± 0.7	3.3 ± 0.2
	303	32.7 ± 1.4	2.9 ± 0.1
	308	48.6 ± 3.2	3.9 ± 0.3
toluene[b]	298	5.34 ± 0.70	3.7 ± 0.5
	308	17.4 ± 0.9	3.9 ± 0.2
	313	33.0 ± 1.7	3.5 ± 0.2
	318	51.3 ± 3.0	4.1 ± 0.3
tert-butylbenzene[c]	288	4.83 ± 0.56	3.4 ± 0.4
	293	9.25 ± 1.3	2.9 ± 0.4
	298	18.0 ± 2.0	3.0 ± 0.3
	308	47.6 ± 5.0	3.7 ± 0.4

[a] $\Delta H_1^\ddagger = 20.8 \pm 0.8$ kcal/mol, $\Delta S_1^\ddagger = +3.4 \pm 2.0$ eu. [b] $\Delta H_1^\ddagger = 20.9 \pm 1.5$ kcal/mol, $\Delta S_1^\ddagger = +1.6 \pm 3.6$ eu. [c] $\Delta H_1^\ddagger = 19.4 \pm 1.8$ kcal/mol, $\Delta S_1^\ddagger = -1.5 \pm 4.5$ eu.

[pyridine] varied. Data from both sets of experiments was analyzed according to eq 2. At 298 K, both experiments yield similar values (within 2σ) of (17.2 ± 0.7) × 10^{-3} and (19.4 ± 1.0) × 10^{-3} s^{-1} for k_1. The close agreement between the k_1 values obtained under different experimental conditions is consistent with the conclusion that the displacement of arene from the Re center by pyridine (and 1-hexene) follows a dissociative pathway. Because the metal center in these complexes is sterically encumbered, it is not surprising that the Re−arene bond has to be broken before the ligand can approach the Re center.

Values of k_1 and k_2/k_{-1} for the three arenes employed in this study are presented in Table 2. The data suggest that the rate constants for arene dissociation (k_1) from the Re center increase in the order Cp*(CO)$_2$Re−(η^2-toluene) < Cp*(CO)$_2$Re−(η^2-benzene) ≈ Cp*(CO)$_2$Re−(η^2-*tert*-butylbenzene). The variation in these rate constants can be explained by taking into account both steric and electronic differences in the monosubstituted aromatic molecules. Although toluene is sterically larger than benzene, it dissociates at a slower rate from the Re center than does benzene. Since −CH$_3$ is an electron-releasing substituent, the slower rate of toluene dissociation compared to that of benzene is primarily due to electronic factors. Even though the −CH$_3$ and −C(CH$_3$)$_3$ groups have similar electron-donating abili-

ties,[10] the rate constant for the dissociation of *tert*-butylbenzene is greater than that for toluene. Clearly, this difference in the rate of dissociation is due to steric factors. The rate constant for the dissociation of *tert*-butylbenzene is slightly greater than that for benzene because the increased steric interactions between the Cp*Re(CO)$_2$ fragment and *tert*-butylbenzene offset the electronic influence of the −C(CH$_3$)$_3$ group. Thus, the data suggest that the rate constants for the displacement of monosubstituted arenes from Cp*Re(CO)$_2$(η^2-arene) are affected by both electronic and steric factors. Electron-donating substituents lower the rate of dissociation, while arenes with bulky substituents cause the rate to increase. It is interesting to note that, in the case of the Cr(CO)$_5$ fragment, the rate of arene displacement from Cr(CO)$_5$ varies in the order Cr(CO)$_5$(η^2-toluene) < Cr(CO)$_5$(η^2-*tert*-butylbenzene) < Cr(CO)$_5$(η^2-benzene).[11] Since Cr(CO)$_5$ is less sterically encumbered than Cp*Re(CO)$_2$, the Cr−arene bond is affected to a lesser degree by the steric bulk of the arene ligand. Thus, *tert*-butylbenzene is displaced at a slower rate than benzene from the chromium center.

To ascertain the origin of the differences in k_1 between the various Cp*Re(CO)$_2$(η^2-arene) complexes, the arene displacement reactions were conducted at different temperatures to determine the enthalpy and entropy changes accompanying the dissociative process. The results, obtained from Eyring plots and presented in Table 2, suggest that the dissociation of the arene molecule from Cp*(CO)$_2$Re-arene proceeds with $\Delta H^\ddagger = 19-21$ kcal/mol and $\Delta S^\ddagger = -1.5$ to $+3.4$ eu. Unfortunately, the errors in the $\Delta H^\ddagger$ and $\Delta S^\ddagger$ values do not allow us to determine whether the differences in k_1 are due to changes in the activation enthalpy or variations in the entropy of activation. The activation enthalpy is expected to be related to the Cp*(CO)$_2$Re−(η^2-arene) bond strength if there is no residual solvation of the Cp*Re(CO)$_2$ fragment by either the arene or heptane in the transition state. However, the near-zero value of $\Delta S^\ddagger$ suggests that there is still some solvation of the Cp*Re(CO)$_2$ fragment in the transition state. Thus, it is reasonable to assume that the value of 19−21 kcal/mol for the activation enthalpy is a lower limit to the Cp*Re(CO)$_2$−arene bond strength. As expected, the Cp*(CO)$_2$Re−(η^2-arene) bond is significantly stronger than the Cp(CO)$_2$ Mn−(η^2-toluene) interaction, which was estimated to be 14.2 ± 0.8 kcal/mol by a similar kinetic method.[4] From the ratios of k_2/k_{-1} it is clear that pyridine reacts approximately 3−4 times faster with the Cp*Re(CO)$_2$(heptane) intermediate than does the arene. The k_2/k_{-1} ratios do not show a definite temperature dependence, which may suggest that the displacement of heptane from Cp*Re(CO)$_2$(heptane) by either pyridine or arene proceeds with similar activation enthalpies. Thus, the faster rate of reaction of the Cp*Re(CO)$_2$−heptane intermediate with pyridine may be due to entropic factors. However, the uncertainties in the k_2/k_{-1} ratios do not permit us to reach a firm conclusion.

Conclusion

In this paper we report the formation of Cp*Re(CO)$_2$-(η^2-arene) complexes (arene = benzene, toluene, *tert*-

(10) Hansch, C.; Leop, A.; Unger, S. H.; Kim, K. H.; Nikaitani, O.; Lien, E. J. *J. Med. Chem.* **1973**, *16*, 1207.
(11) Zhang, S.; Dobson, G. R. *Polyhedron* **1990**, *9*, 2511.

butylbenzene) upon photolysis of a heptane solution of $Cp*Re(CO)_3$ in the presence of arene. The mechanism for the displacement of the arene molecule from the Re center by pyridine has been studied, and the reaction is found to proceed through a dissociative pathway. The unimolecular rate constant for the dissociation of the $Re-(\eta^2\text{-arene})$ bond is extracted from the data and is found to increase in the order $Cp*(CO)_2Re-(\eta^2\text{-toluene})$ < $Cp*(CO)_2Re-(\eta^2\text{-benzene})$ ≈ $Cp*(CO)_2Re-(\eta^2\text{-}tert\text{-}$ butylbenzene). Activation parameters yield a lower limit of 19−21 kcal/mol for the strength of the $Re-\eta^2\text{-arene}$ interaction.