Observation of the (η^5-C_5H_5)Mn(CO)$_2$(toluene) Complex by Low-Temperature IR Spectroscopy and Determination of the Manganese−Toluene Bond Strength

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Received April 28, 2000

Summary: The (η^5-C_5H_5)Mn(CO)$_2$(toluene) complex formed upon UV photolysis of (η^5-C_5H_5)Mn(CO)$_3$ in heptane solution in the presence of toluene was detected using low-temperature IR spectroscopy. The toluene molecule is most likely bound to the Mn center in an η^2 fashion. The displacement of the toluene ligand by tetrahydrofuran has been studied, and the reaction is found to proceed through a dissociative pathway. Activation analysis yields a value of 14.2 ± 0.8 kcal/mol for the CpMn(CO)$_2$−toluene bond energy.

Introduction

Arene molecules coordinated to a transition metal in an η^2 fashion are often implicated as intermediates in a variety of chemical reactions.[1] While a number of η^2-arene complexes have been synthesized,[2] most such complexes are generally fragile, with the exception of compounds that contain the pentammineosmium(II) $[(NH_3)_5Os]^{2+}$ fragment, which forms thermally stable complexes with arenes and aromatic heterocycles.[3] Recently, Harman and co-workers have shown that the TpRe(CO)$_2$(THF) (Tp = hydridotris(pyrazolyl)borate, THF = tetrahydrofuran) complex reacts with a variety of aromatic molecules (L) to form stable binuclear complexes of the form $\{TpRe(CO)_2\}_2(\mu$-η^2-$\eta^{2'}$-L).[4] Orpen and co-workers detected the presence of the Cp*Re(CO)$_2$(η^2-benzene) [Cp* = η^5-C_5Me_5] complex upon photolysis of Cp*Re(CO)$_3$ in benzene solution to form Cp*(CO)$_2$Re(μ-1,2-η^2-3,4-η^2-C_6H_6)Re(CO)$_2$Cp*.[5] On the basis of this report, we decided to investigate the photochemistry of CpMn(CO)$_3$ [Cp = η^5-C_5H_5] in toluene solution to obtain evidence for the formation of the CpMn(CO)$_2$(toluene) complex. The manganese complex was chosen for several reasons. In contrast to the group 6 metal hexacarbonyls,[6] the photochemistry of the CpMn(CO)$_3$ complex has not been investigated in aromatic solvents. Furthermore, the displacement of a ligand that is weakly bound to the Mn center often proceeds through a dissociative pathway.[7] Thus, in favorable situations it becomes possible to estimate the strength of the CpMn(CO)$_2$−^{w}L (^{w}L = weakly bound ligand) interaction. Since the toluene ligand is not expected to bind strongly to the Mn center, we thought it would be possible to obtain an estimate of the Mn−toluene bond strength by displacement of the arene ligand.

It is well established that UV photolysis of transition metal carbonyls, $L_mM(CO)_n$, in solution phase results in the dissociation of a CO ligand and the generation of the solvent-stabilized $L_mM(CO)_{n-1}$(solvent) complex.[8] For example, the CpMn(CO)$_2$(heptane) complex is efficiently generated upon photolysis of CpMn(CO)$_3$ with UV light in heptane solvent.[9] The well-characterized CpMn(CO)$_2$(THF) complex is also formed when the parent metal tricarbonyl is photolyzed in THF solution.[10] We therefore thought it possible to generate the CpMn(CO)$_2$(toluene) complex by photolysis of CpMn(CO)$_3$ in the presence of toluene. In this paper we provide IR spectroscopic evidence for the formation of the CpMn(CO)$_2$(toluene) complex at low temperatures in which the toluene ligand is most likely bound in an η^2 fashion to the Mn center. The displacement of toluene from the Mn center by THF was studied, and the reaction was found to proceed through a dissociative pathway, providing an estimate for the Mn−toluene bond strength. This paper describes the first direct observation of a CpMn(CO)$_2$−arene complex and also to the best of our knowledge is the first experiment to provide an estimate for the CpMn(CO)$_2$−arene bond strength.

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(1) (a) Parshall, G. W.; Ittel, S. D. In *Homogeneous Catalysis: The Applications and Chemistry of Catalysis by Soluble Transition Metal Complexes*, 2nd ed.; John Wiley and Sons: New York, 1992; Chapter 7. (b) Muetterties, E. L.; Bleeke, J. R. *Acc. Chem. Res.* **1979**, *12*, 325.

(2) (a) Tagge, C. D.; Bergman, R. G. *J. Am. Chem. Soc.* **1996**, *118*, 6908. (b) Sweet, J. R.; Graham, W. A. G. *J. Am. Chem. Soc.* **1983**, *105*, 305. (c) Jones, W. D.; Dong. L. *J. Am. Chem. Soc.* **1989**, *111*, 8722. (d) Higgitt, C. L.; Klahn, A. H.; Moore, M. H.; Oelckers, B.; Partridge, M. G.; Perutz, R. N. *J. Chem. Soc., Dalton Trans.* **1997**, 1269. (d) Boese, R.; Stanger, A.; Stellberg, P.; Shazar, A. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1475. (e) Brauer, D. J.; Krüger, C. *Inorg. Chem.* **1977**, *16*, 884. (f) Stanger, A.; Boese, R. *J. Organomet. Chem.* **1992**, *430*, 235.

(3) Harman, W. D. *Chem. Rev.* **1997**, *97*, 1953.

(4) Gunnoe, T. B.; Sabat, M.; Harman, W. D. *J. Am. Chem. Soc.* **1998**, *120*, 8747.

(5) Heijden, H.; Orpen, A. G.; Pasman, P. *J. Chem. Soc., Chem. Commun.* **1985**, 1576.

(6) (a) Zhang, S.; Dobson, G. R.; Zang, V.; Bajaj, H. C.; van Eldik, R. *Inorg. Chem.* **1990**, *29*, 3477. (b) Zhang, S.; Dobson, G. R. *Organometallics* **1992**, *11*, 2447.

(7) (a) Grills, D. C.; Sun, X. Z.; Childs, G. I.; George, M. W. *J. Phys. Chem.* **2000**, *104*, 4300. (b) Hester, D. M.; Sun, J.; Harper, A. W.; Yang, G. K. *J. Am. Chem. Soc.* **1992**, *114*, 5234. (c) Coleman, J. E.; Dulaney, K. E.; Bengali, A. A *J. Organomet. Chem.* **1999**, *572*, 65. (d) Angelici, Loewen, W. *Inorg. Chem.* **1967**, *6*, 682. (e) Butler, I. S.; Sawai, T. *Inorg. Chem.* **1975**, *14*, 2703. (f) Hart-Davis, A. J.; Graham, W. A. G. *J. Am. Chem. Soc.* **1971**, *93*, 4388.

(8) (a) Lee, M.; Harris, C. B. *J. Am. Chem. Soc.* **1989**, *111*, 8963. (b) Yu, S. C.; Xu, X.; Lingle, R., Jr.; Hopkins, J. B. *J. Am. Chem. Soc.* **1990**, *112*, 3668. (c) Joly, A. G.; Nelson, K. A. *Chem. Phys.* **1991**, *152*, 69.

(9) Creaven, B. S.; Dixon, A. J.; Kelly, J. M.; Long, C.; Poliakoff, M. *Organometallics* **1987**, *6*, 2600.

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

10.1021/om000366k CCC: $19.00
Publication on Web 08/23/2000

Experimental Section

All infrared spectra were obtained using a Graseby-Specac variable-temperature infrared cell employing CaF_2 plates with a 0.5 mm path length. All spectra were obtained at 4−8 cm^{-1} resolution using a Nicolet 510M FTIR.[11] The solutions to be irradiated were prepared in heptane solvent containing 3.1 M toluene and $(3-4) \times 10^{-3}$ M $CpMn(CO)_3$. The solvents were of anhydrous grade and stored under nitrogen (Aldrich). $CpMn(CO)_3$ (Strem) was used as received. Solution transfers were carried out under an Ar atmosphere. The photolysis solution was flowed into the variable-temperature cell and the cell cooled to the desired temperature by employing a dry ice/acetone or a liquid nitrogen/hexane bath. After thermal equilibration, the solution was photolyzed using the unfiltered output of a 150 W Xe arc lamp for 10−15 s. Under these conditions typically 20% of the $CpMn(CO)_3$ was photolyzed. For the kinetic runs, the same procedure was followed, but in addition to the toluene, anhydrous tetrahydrofuran was added to the photolysis solution. Following photolysis, FTIR spectra were obtained at regular intervals and the decay of the $CpMn(CO)_2$(toluene) reactant and the growth of the product $CpMn(CO)_2$(THF) complex was monitored. In some situations, regeneration of $CpMn(CO)_3$ could also be observed due to back-reaction with CO but was typically a minor process (<4%) under the conditions used. All runs were carried out under pseudo-first-order conditions over a 10-fold range of THF concentration. The decay of the reactant complex and the growth of the product complex followed first-order kinetics. The observed rate of reaction, k_{obs}, was obtained by fitting plots of the absorbance of the reactant CO stretching bands versus 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.

Results and Discussion

(a) Product Identity. Photolysis of a 3−4 mM heptane solution of $CpMn(CO)_3$ at 194−211 K results in the depletion of the tricarbonyl complex and formation of a species with CO stretching bands at 1991, 1931, 1954, and 1772 cm^{-1}. These CO stretching bands are attributed to the well-known $Cp_2Mn_2(CO)_5$ dimer that is formed by the reaction between the initially generated $CpMn(CO)_2$(heptane) complex and residual $CpMn(CO)_3$.[9] Since the half-life of the $CpMn(CO)_2$(heptane) complex is expected to be <1 s at 207 K, it is not surprising that this complex is not observed in the present study.[12] As shown in Figure 1, photolysis of a heptane solution of $CpMn(CO)_3$ containing 3.1 M toluene at 211 K shows the generation of a complex with two CO stretching absorbances at 1949 and 1889 cm^{-1}. The number and the intensities of the CO stretching bands are consistent with the formation of a manganese dicarbonyl species. Since this species is formed only in the presence of toluene, it is assigned to the $CpMn(CO)_2$−toluene complex. This result is consistent with the observation that the primary photochemical product upon UV photolysis of $CpMn(CO)_3$ in solvent phase is the $CpMn(CO)_2$(solvent) complex.[9,10] Taking into account solvent shifts, the CO stretching frequencies for the $CpMn(CO)_2$(toluene) complex are similar to those of the $CpMn(CO)_2$(heptane) species observed at 1964 and 1895 cm^{-1}.[9] Since the Mn−heptane interaction almost certainly involves C−H $\sigma \Rightarrow$ metal electron donation,[13] the similar CO stretching frequencies of the $CpMn(CO)_2$(heptane) and $CpMn(CO)_2$(toluene) complexes might imply that the Mn−toluene and the Mn−heptane interactions are identical. There are, however, several arguments against such an assignment. The CO stretching frequencies of the thermally stable and isolable $CpMn(CO)_2$(1-pentene) complex observed at 1966 and 1907 cm^{-1} where the ligand is bound in an η^2 fashion are also similar to those of the $CpMn(CO)_2$(heptane) species.[9,10] Furthermore, it is clear that the $CpMn(CO)_2$(toluene) complex is considerably more stable than the $CpMn(CO)_2$(heptane) species. This difference in stability between the two complexes suggests that the Mn−toluene interaction is significantly different than the Mn−heptane interaction. The other viable mode of coordination of the toluene molecule to the $CpMn(CO)_2$ fragment is through a fixed double bond in the arene ring. There is precedence for this kind of interaction since the analogous $Cp^*Re(CO)_2(\eta^2$-benzene) complex has been observed as an intermediate upon photolysis of $Cp^*Re(CO)_3$ in benzene solvent.[5] In addition, the photochemistry of the group 6 metal hexacarbonyls in aromatic solvents has been investigated, and the results support the conclusion that for molecules such as benzene the aromatic ligand is bound in an η^2 fashion to the metal center.[6a]

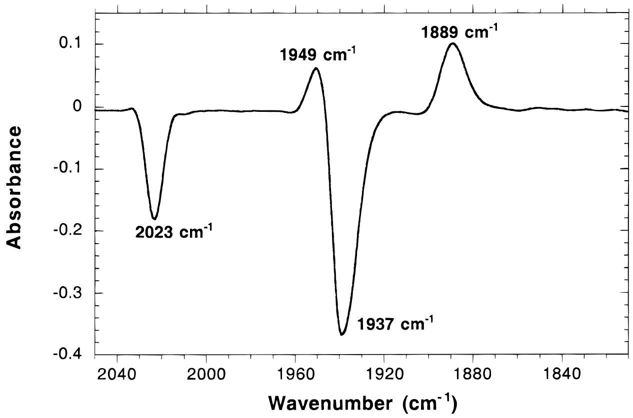

Figure 1. Difference FTIR spectrum obtained upon UV photolysis of a 3 mM solution of $CpMn(CO)_3$ in heptane with 3.1 M toluene at 211 K. The negative peaks at 2023 and 1937 cm^{-1} are due to the depletion of the parent metal tricarbonyl, and the positive peaks at 1949 and 1889 cm^{-1} are due to the formation of the $CpMn(CO)_2$(toluene) complex.

Recently, Casey and co-workers photolyzed $(\eta^5$-$MeC_5H_4)Mn(CO)_3$ in toluene solution at −78 °C to obtain evidence for the formation of the corresponding toluene complex.[14] However, after photolyzing the solution for 60 min only the CO-bridged $(\eta^5$-$MeC_5H_4)Mn_2(CO)_5$ dimer complex was observed. The origin of the discrepancy between the results of the present study and the results reported by Casey is not clear at the present time.[15]

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[11] The fwhm of the CO stretching absorbances were 13 cm^{-1} at the temperatures employed in the study.

[12] Half-life of the $CpMn(CO)_2$(heptane) complex was calculated from the activation parameters reported in ref 9.

[13] Hall, C.; Perutz, R. N. *Chem. Rev.* **1996**, *96*, 3125.

[14] Casey, C. P.; Czerwinski, C. J.; Fraley, M. E. *Inorg. Chim. Acta* **1998**, *280*, 316.

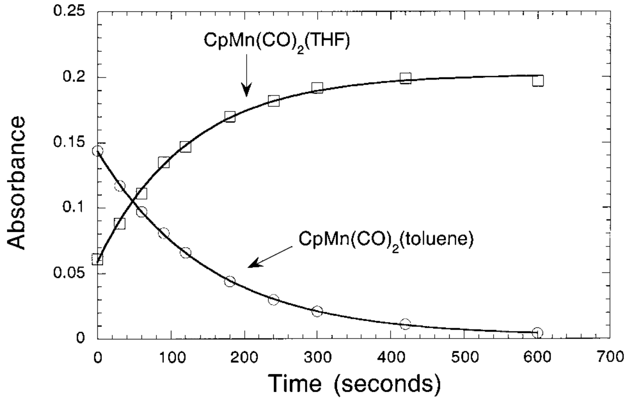

Figure 2. Decay of the CpMn(CO)$_2$(toluene) complex and concurrent growth of the CpMn(CO)$_2$(THF) complex at 207 K in heptane solution in the presence of 3.1 M toluene and 0.16 M THF. The solid lines represent first-order exponential fits to the data.

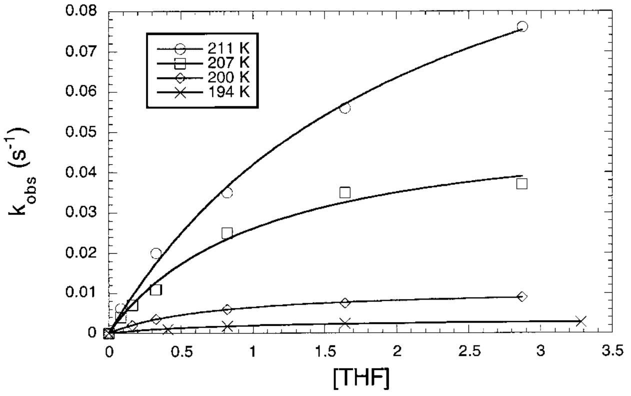

Figure 3. Plot of k_{obs} vs THF for the reaction of CpMn(CO)$_2$(toluene) with tetrahydrofuran to form CpMn(CO)$_2$(THF).

(b) Kinetic Study. Photolysis of a 3−4 mM heptane solution of CpMn(CO)$_3$ in the presence of 3.1 M toluene and added THF results in the formation of both the CpMn(CO)$_2$(toluene) complex and the previously characterized CpMn(CO)$_2$(THF) molecule.[10] The toluene complex undergoes a smooth and complete conversion to the more stable THF complex over time, and the rate of this conversion depends on the THF concentration. The CpMn(CO)$_2$(toluene) complex undergoes a first-order decay, and the CpMn(CO)$_2$(THF) complex grows in at the same rate (see Figure 2).

Scheme 1

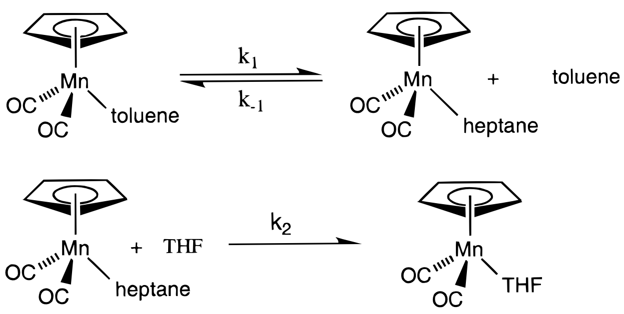

Table 1. Rate Constants and Rate Constant Ratios Derived from the Double Inverse Plot Shown in Figure 4[a]

temperature	10^3k_1 (s^{-1})	k_2/k_{-1}	r^2
194	4.3 ± 0.4	2.4 ± 0.3	0.998
200	11.9 ± 0.6	3.6 ± 0.3	0.999
207	44.0 ± 3.8	3.5 ± 0.4	0.998
211	84.3 ± 6.0	2.6 ± 0.3	0.995

[a] Uncertainties are reported at the 1σ level from linear least-squares fit to the data shown in Figure 4. The r^2 values refer to the quality of the linear fit to the data in Figure 4.

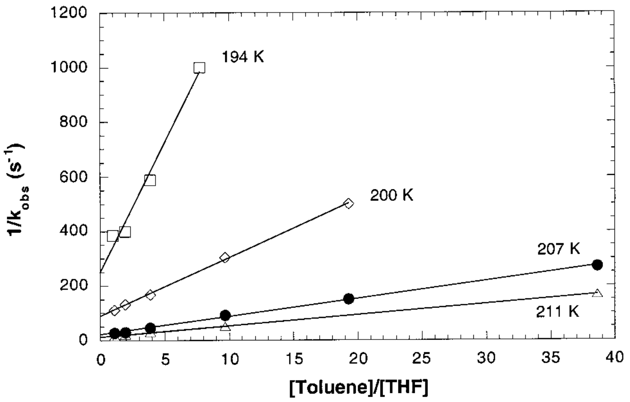

Figure 4. Double inverse plot of $1/k_{obs}$ vs toluene/THF. The intercept yields $1/k_1$, and the slope is equal to k_{-1}/k_1k_2.

As shown in Figure 3, a plot of the observed rate constant, k_{obs}, versus [THF] shows that k_{obs} approaches a limiting value at high THF concentration. Such a variation of k_{obs} with [THF] indicates that the displacement of the toluene ligand from the Mn center by THF follows a dissociative pathway (see Scheme 1).[16] The mechanism of toluene displacement is very similar to the displacement of other ^{w}L from CpMn(CO)$_2$(^{w}L) complexes.[7]

Assuming a steady-state concentration of the CpMn(CO)$_2$(heptane) intermediate, the dependence of k_{obs} on THF concentration is given by

$$k_{obs} = \frac{k_1k_2[\mathrm{THF}]}{k_{-1}[\mathrm{toluene}] + k_2[\mathrm{THF}]} \qquad (1)$$

Thus, under conditions where k_{-1}[toluene] ≫ k_2[THF], k_{obs} will be a linear function of [THF], but at high [THF] when k_{-1}[toluene] ≪ k_2[THF], k_{obs} will approach the limiting value of k_1, the unimolecular rate constant for the dissociation of the CpMn(CO)$_2$−toluene bond. Values for k_1 and k_2/k_{-1} shown in Table 1 can be extracted from the data by recasting eq 1 in the form

$$\frac{1}{k_{obs}} = \frac{1}{k_1} + \frac{k_{-1}[\mathrm{toluene}]}{k_1k_2[\mathrm{THF}]} \qquad (2)$$

and plotting $1/k_{obs}$ vs [toluene]/[THF] (see Figure 4). Such a plot is expect to be linear, yielding a slope of k_{-1}/k_1k_2 and an intercept of $1/k_1$.

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(15) We had originally thought that the difference between our results and those reported by Casey et al. may have been due to a difference in photolysis time since in this study we photolyze for only 10−15 s. Therefore, it seemed possible that if the Mn−toluene complex itself is photolabile, then prolonged photolysis would destroy the complex and generate the metal dimer species. However, the CO stretching absorbances due to the CpMn(CO)$_2$(toluene) complex steadily increased with prolonged photolysis when CpMn(CO)$_3$ was photolyzed in heptane solution with 3.1 M toluene for 15 min at 207 K.

(16) We have included the CpMn(CO)$_2$(heptane) complex as a viable intermediate in the reaction since the Mn−heptane bond energy has been determined to be 8−9 kcal/mol (see ref 18).

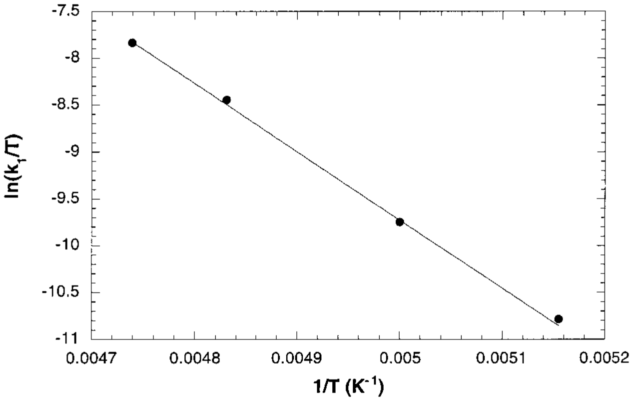

Figure 5. Eyring plot of $\ln(k_1/T)$ vs $1/T$: $\Delta H^{\ddagger}_1 = 14.2 \pm 0.8$ kcal/mol and $\Delta S^{\ddagger}_1 = 6.0 \pm 3.0$ eu.

As shown in Figure 5, activation parameters associated with k_1 can be determined by constructing an Eyring plot. The resulting activation enthalpy of $\Delta H^{\ddagger}_1 = 14.2 \pm 0.8$ kcal/mol for this reaction step is expected to be related to the Mn−toluene bond dissociation energy. A moderately positive activation entropy of $\Delta S^{\ddagger}_1 = +6.0 \pm 3.0$ eu is consistent with dissociation of the toluene ligand from the Mn center and reflects the increased disorder in the transition state. Previous studies have shown that for other $CpMn(CO)_2(^{W}L)$ systems, the activation enthalpy for the $Mn-^{W}L$ bond-breaking step is in good agreement with $CpMn(CO)_2-^{W}L$ bond energies obtained from thermochemical methods such as photoacoustic calorimetry (PAC).[7b,c] Thus, the value of 14.2 kcal/mol is expected to be a measure of the $CpMn(CO)_2(\eta^2$-toluene) bond energy if there is no residual solvation of the $CpMn(CO)_2$ fragment in the transition state by either toluene or heptane; otherwise the activation enthalpy provides a lower limit to the Mn−toluene bond energy. The only other systems for which metal−arene bond energies have been determined using thermochemical measurements are the $Cr(CO)_5$(arene) [arene = benzene, fluorobenzene] complexes.[6b] Using the technique of photoacoustic calorimetry, the $Cr(CO)_5$−benzene bond dissociation energy has been measured to be 15 kcal/mol, similar to the 13.8 ± 0.8 kcal/mol estimate obtained by Weitz and co-workers by studying the displacement of benzene from the $(CO)_5Cr$−benzene complex in the gas phase.[17] Both experimental values for the strength of the $(CO)_5Cr$−benzene interaction are similar to the 14.2 kcal/mol estimate for the $CpMn(CO)_2$−toluene bond strength obtained in this study. The values of k_2/k_{-1} do not vary significantly with temperature, suggesting that the activation barriers for the reaction of $CpMn(CO)_2$(heptane) with toluene and THF are similar (i.e., $\Delta H_2^{\ddagger} - \Delta H_{-1}^{\ddagger} \approx 0$). Our results do suggest that THF reacts approximately 3 times faster with $CpMn(CO)_2$(heptane) than does toluene. Thus, it is likely that the faster reaction of the $CpMn(CO)_2$(heptane) complex with THF is due to entropic factors. However, the uncertainty in the k_2/k_{-1} ratios does not permit us to reach a firm conclusion at this time.

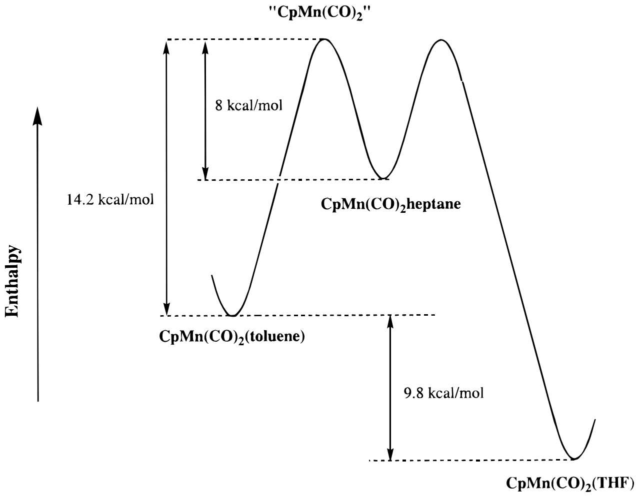

Figure 6. Relative enthalpy profile for the reaction $CpMn(CO)_2(\eta^2$-toluene) + THF ⇒ $CpMn(CO)_2(THF)$ + toluene.

Since the activation enthalpy for the dissociation of the THF ligand from $CpMn(CO)_2$−THF has been determined previously to be 24.0 ± 2.0 kcal/mol,[7c] and from PAC measurements the $CpMn(CO)_2$−heptane bond energy[18] has been estimated at 8 ± 1 kcal/mol, the results of this study may be used to construct an energetic profile for the displacement of toluene by THF from $CpMn(CO)_2$(toluene) (see Figure 6). Thus, the Mn−toluene complex is approximately 10 kcal/mol less stable than $CpMn(CO)_2(THF)$. Since the $CpMn(CO)_2(THF)$ complex has not been isolated to date, it is unlikely that the corresponding $CpMn(CO)_2$(toluene) complex can be isolated and characterized at room temperature.

Conclusion

Photolysis of $CpMn(CO)_3$ in heptane solution with 3.1 M toluene at 194−211 K results in the generation of the $CpMn(CO)_2$(toluene) complex. The toluene ligand is most likely bound in an η^2 fashion to the metal center. The mechanism of the displacement of the toluene ligand from the metal center by tetrahydrofuran has been investigated, and the results show that the reaction proceeds through a dissociative pathway. From an analysis of the activation parameters, the $CpMn(CO)_2$−toluene bond strength is estimated to be 14.2 ± 0.8 kcal/mol. Combining these results with the previously measured $CpMn(CO)_2$−THF bond energy suggests that the toluene complex is approximately 10 kcal/mol less stable than the THF complex and would therefore be difficult to isolate at room temperature. Further experiments utilizing the technique of laser flash photolysis are underway to study the interaction of the $CpMn(CO)_2$ and the analogous $CpRe(CO)_2$ fragment with a variety of substituted benzenes to map out the dependence of metal−arene bond strength on the nature of the arene.

Acknowledgment. This research was supported by grants from the Camille and Henry Dreyfus Foundation (Award No. SU-95-047) and Research Corporation (Grant No. CC4352).

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[17] Wells, J. R.; House, P. G.; Weitz, E. *J. Phys. Chem.* **1994**, *98*, 8343.

[18] Yang, P.-F.; Yang, G. K. *J. Am. Chem. Soc.* **1992**, *114*, 6937.