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Displacement of the THF solvent molecule from (η^5-C_5H_5)Mn(CO)$_2$THF by simple two electron donor ligands: evidence for a dissociative mechanism and determination of the Mn–THF bond strength

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Abstract

The reaction between CpMn(CO)$_2$THF (Cp = η^5-C_5H_5, THF = tetrahydrofuran) and nitrogen containing ligands is studied in THF solution. In all cases the products of the reaction are the known CpMn(CO)$_2$L complexes (L = piperidine, 4-acetylpyridine). The reaction of the solvated complex with both ligands studied proceeds through a purely dissociative mechanism. In good agreement with previous thermochemical measurements, kinetic analysis yields an average value of 24.0 ± 3.0 kcal mol^{-1} for the CpMn(CO)$_2$–THF bond dissociation energy. The results of the present study clarify the relationship between metal–solvent bond strengths obtained by kinetic methods and those obtained by thermochemical measurements.

Keywords: THF; Dissociative mechanism; Bond strength

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1. Introduction

Coordinatively unsaturated transition metal organometallic complexes have been implicated as intermediates in a variety of chemical reactions including homogenous and heterogeneous catalytic processes [1]. It is generally well established that in condensed phase, the vacant site is often occupied by a solvent molecule [2]. Indeed, even noble gases such as Xe and Kr are capable of binding to the metal center in such complexes [3–5]. Because solvated organometallic molecules are often intermediates in chemical reactions, it is important to elucidate the mechanism of the displacement of the solvent molecule from the coordination sphere of the metal complex. It is equally important, therefore, to establish the strength of the metal–solvent interaction in such molecules. The technique of photoacoustic calorimetry (PAC) has been employed successfully to measure metal–solvent bond strengths [6]. For example, the strength of the interaction between Group 6 metal pentacarbonyls and alkane solvents such as pentane, cyclohexane, and heptane has been determined by PAC to be on the order of 8–17 kcal mol^{-1} [7,8]. Metal–solvent bond strengths have also been determined using kinetic methods. For example, by studying the CO substitution kinetics of W(CO)$_5$Xe, Weiller was able to provide an estimate of 8.4 ± 0.2 kcal mol^{-1} for the strength of the W–Xe interaction [4]. It should be noted, however, that the relationship between bond strengths measured by kinetic methods and those obtained by thermochemical studies is at present unclear and further studies are required.

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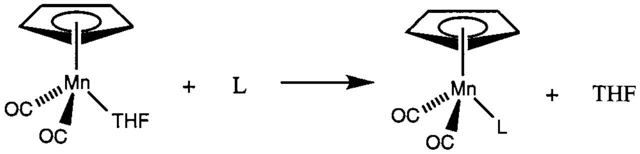
While several mechanistic studies have been performed on the solvated Group 6 metal carbonyls [2] ($M(CO)_5solv$, M = Cr, Mo, W, and solv = solvent) relatively few studies have been aimed at elucidating the mechanism by which $CpMn(CO)_2solv$ complexes react with incoming ligands [9,10]. It is well established that photolysis of $CpMn(CO)_3$ in the gas phase, in inert gas matrices, and in alkane solvent results in the generation of the coordinatively unsaturated $CpMn(CO)_2$ species with a high quantum yield [11–13]. In alkane solvents such as cyclohexane and heptane there is good evidence that the species formed upon photolysis is the solvent stabilized $CpMn(CO)_2solv$ complex [9].

The study of the ligand substitution mechanism is especially interesting for $CpMn(CO)_2solv$ since the possibility exists for the involvement of the elusive ring slipped (η^3-Cp)Mn(CO)$_2$solv intermediate in such reactions. In addition to the general interest in understanding the substitution chemistry of these solvated complexes, studying the displacement of a solvent molecule from the $CpMn(CO)_2solv$ complex is also important since such complexes are often used as precursors in the synthesis of $CpMn(CO)_2L$ (L = ligand) molecules. Since thermal substitution of one CO ligand in $CpMn(CO)_3$ is not possible [14], synthesis of $CpMn(CO)_2L$ complexes is often accomplished by displacement of the weakly bound THF (THF = tetrahydrofuran) solvent molecule by L from the photolytically generated $CpMn(CO)_2THF$ complex [15,16].



We report in this paper a mechanistic study of the displacement of the THF solvent molecule from $CpMn(CO)_2THF$ by the simple two electron donor ligands piperidine and 4-acetylpyridine.In both cases the reaction proceeds through a purely dissociative pathway involving dissociation of the THF molecule from the manganese complex followed by reaction of the resulting $CpMn(CO)_2$ molecule with the incoming ligand. The kinetic analysis yields an estimate for the $CpMn(CO)_2$–THF bond strength which is in good agreement with the value obtained from thermochemical measurements suggesting that the kinetic method can provide a useful complement to thermochemical studies in determining $CpMn(CO)_2$–solv bond strengths. The results help to clarify the relationship between metal–solvent bond strengths obtained by kinetic methods and those obtained by thermochemical methods such as photoacoustic calorimetry.

2. Experimental

All kinetic studies were conducted using a Hewlett Packard Diode Array Spectrophotometer (HP 8453) equipped with a Peltier temperature controller. A typical kinetic run was performed as follows. A 0.5–1 mM solution of $CpMn(CO)_3$ in THF was degassed by purging with pre-dried Ar for approximately 5 min and then photolyzed for 1 min in a 1 × 1 cm quartz cuvette using the filtered output (300 nm long pass filter) of a 150 Watt Xe arc lamp (Xenon Corp.). The ligand was then added and the reaction followed by monitoring the decay of the $CpMn(CO)_2THF$ complex absorbing at 298 or 530 nm. When 4-acetylpyridine was employed as the ligand, the reaction was followed by monitoring the growth of the product $CpMn(CO)_2$(4-acetylpyridine) complex at 476 nm because the absorption bands of the $CpMn(CO)_2THF$ complex were obscured by those of the ligand. All runs were performed under pseudo first order conditions with the ligand concentration being at least ten times greater than that of the Mn complex. Kinetic runs were conducted over a 10- to 20-fold range of ligand concentrations. Observed rate constants, k_{obs}, were obtained by fitting plots of the absorbance of $CpMn(CO)_2(THF)$ versus time to single exponential functions. In all the kinetic runs residual $CpMn(CO)_3$ was also present. However, there was no evidence to suggest that the parent tricarbonyl participated in the reaction. Studies employing IR spectroscopy clearly showed that the height of the CO stretching absorptions of the residual $CpMn(CO)_3$ complex remained unchanged during the course of the reaction. IR spectroscopy, however, was not used to monitor the reactions because the CO absorptions of both the reactant $CpMn(CO)_2THF$ and product $CpMn(CO)_2L$ (L = piperidine, 4-acetylpyridine) overlapped.

Tetrahydrofuran was freshly distilled from Na/benzophenone under nitrogen. Piperidine (Aldrich) and 4-acetylpyridine (Acros) were used without further purification.

3. Results and discussion

Photolysis of a solution of $CpMn(CO)_3$ in THF results in the generation of a red solution with absorbances at 298, 400, and 530 nm (see Fig. 1). These absorbances are in good agreement with those of the previously observed $CpMn(CO)_2THF$ complex at 400 and 510 nm [10]. At 298 K in the absence of ligand the $CpMn(CO)_2THF$ complex decays over a period of ca. 1 h. As shown in Fig. 2, in the presence of added ligand, $CpMn(CO)_2THF$ exhibits a first order decay and concurrent with the decay of the dicarbonyl a new species grows in at the same rate. In agreement with previous studies [10], for L = piperidine the product is observed

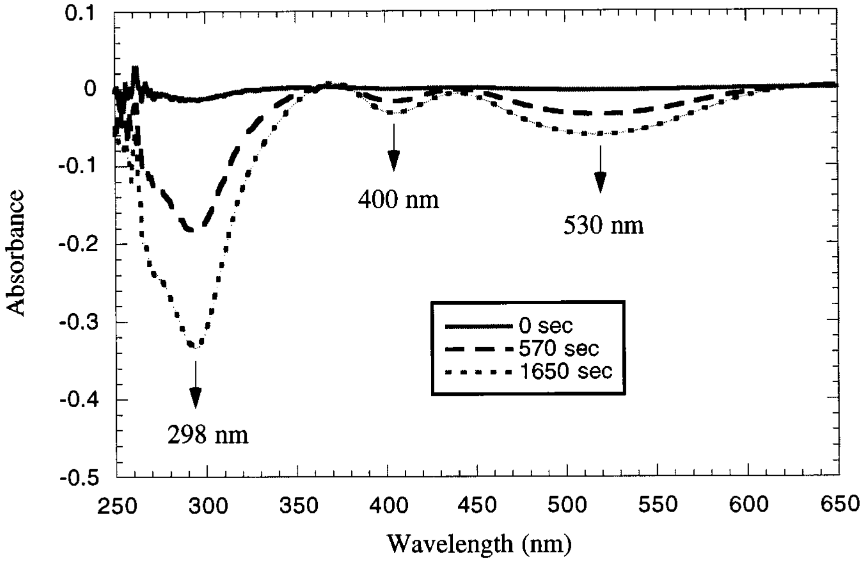
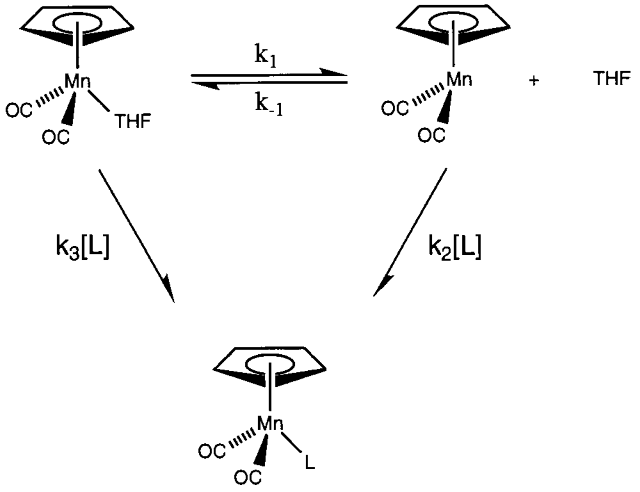


Fig. 1. Difference spectra showing the decay of the $CpMn(CO)_2THF$ complex at 298 K in the absence of added ligand. Peaks marked with a ↓ arrow decrease with time and are associated with the $CpMn(CO)_2THF$ complex.

at 442 nm and for L = 4-acetylpyridine at 476 and 630 nm (see Fig. 3).

As shown in Fig. 4a and b, the observed rate constant, k_{obs}, varies linearly with ligand concentration at all the temperatures studied. A linear dependence of k_{obs} on [L] is consistent with both a dissociative and associative mechanism of THF displacement from the Mn center (Scheme 1). If the reaction occurs through an associative mechanism (i.e. $k_1 = 0$) then $k_{obs} = k_3[L]$ and the slope of a plot of k_{obs} versus [L] should yield k_3, the bimolecular rate constant for the reaction. Since the reaction is studied at different temperatures, an Eyring plot should yield the activation enthalpy and entropy for this reaction. The activation parameters obtained from the Eyring plots are inconsistent, however, with an associative mechanism of THF displacement by L. For example, if an associative mechanism is assumed (i.e. $k_{obs} = k_3[L]$) then the activation entropy associated with k_3 is quite positive ($\Delta S^\ddagger = 16 \pm 5$ e.u.) and the activation enthalpy of 24 ± 2 kcal mol^{-1} has a value equal to the $CpMn(CO)_2$–THF bond dissociation energy [17]. For an associative mechanism it is expected that $\Delta S^\ddagger$ will be negative to slightly positive reflecting the increased order in the transition state [4,18]. Furthermore, since the $CpMn(CO)_2$–THF bond energy has been determined by photoacoustic calorimetry to be 24 ± 2 kcal mol^{-1} [17], it is expected that if the reaction proceeded through an associative mechanism $\Delta H^\ddagger$ would be considerably less than this value. Therefore, the possibility that the reaction has an associative component is ruled out (i.e. $k_3 = 0$).



Scheme 1.

For a dissociative mechanism, the dependence of k_{obs} on [L] can be derived by assuming a steady state concentration of $CpMn(CO)_2$.

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

Because in the present work [THF] ≫ [L] and a plot of k_{obs} versus [L] does not show any deviation from linearity, it is assumed that $k_{-1}[THF] \gg k_2[L]$. The k_{obs} expression then reduces to,

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

and a plot of k_{obs} versus [L]/[THF] yields a slope of $(k_1 k_2)/k_{-1}$. Since this reaction was studied at several temperatures, activation parameters were obtained and are presented in Table 1 along with values for the rate constants. The overall enthalpy of activation for this reaction is composed of the enthalpies of activation for each step in the reaction mechanism. Thus, from the

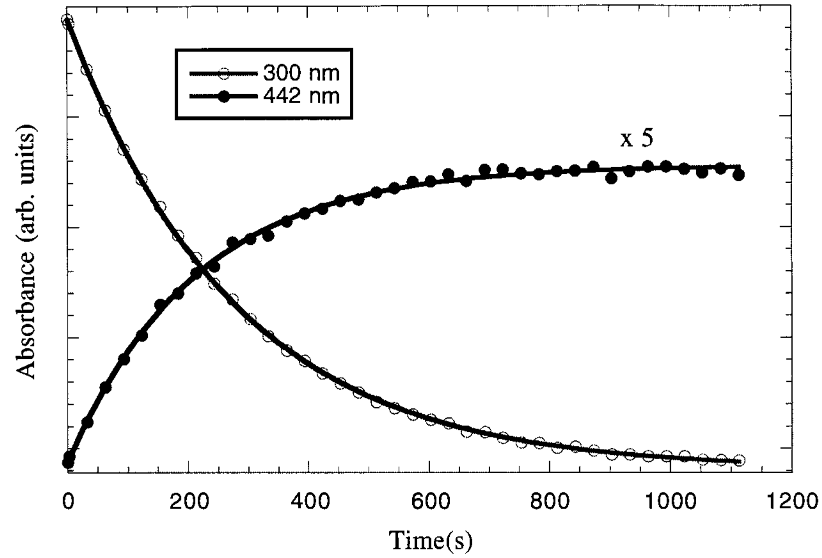


Fig. 2. Kinetic traces obtained when $CpMn(CO)_2(THF)$ reacts with 0.14 M piperidine at 293 K. Growth of the product was monitored at 442 nm and decay of the $CpMn(CO)_2(THF)$ complex was observed at 298 nm. Note that in the case of the product the absorbance values are multiplied by a factor of five. Solid lines represent single exponential fits to the data.

slope of the Eyring plot the quantity $\Delta H_1^{\ddagger} + (\Delta H_2^{\ddagger} - \Delta H_{-1}^{\ddagger})$ can be determined. Since gas phase studies have shown that reactions between the unsolvated $CpMn(CO)_2$ fragment and various ligands proceed with a negligible activation barrier [13], the activation enthalpies associated with k_{-1} and k_2 are expected to be insignificant (i.e. $\Delta H_2^{\ddagger}$ $\Delta H_{-1}^{\ddagger}$ ca. 0). Consequently, a value for $\Delta H_1^{\ddagger}$ can be determined from the Eyring plot shown in Fig. 5 and this number is a measure of the $CpMn(CO)_2$–THF bond dissociation energy. Values of 23.3 ± 2.0 kcal mol^{-1} for L = piperidine and 24.7 ± 2 kcal mol^{-1} for L = 4-acetylpyridine (see Table 1) are consistent with a previously determined value of 24 ± 2 kcal mol^{-1} for the $CpMn(CO)_2$–THF bond energy obtained by thermochemical measurements [17].

Confirmation of the dissociative nature of THF displacement from the Mn center is obtained by comparing the various rate constants and activation enthalpies for the two ligands studied. It is expected that if the mechanism is truly dissociative then the activation enthalpies will be independent of the nature of the incoming nucleophile. As shown in Fig. 5 and Table 1, the activation enthalpies are essentially identical for the two ligands even though there is a significant difference in the electronic and steric properties of the ligands. The difference in the rate constants between the ligands

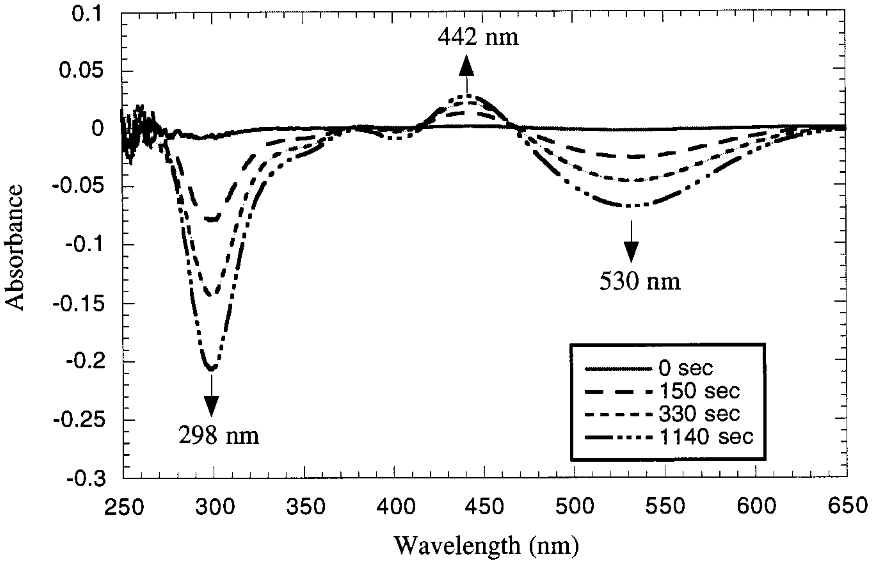


Fig. 3. Difference spectra showing growth of the $CpMn(CO)_2(pip)$ complex at 442 nm and decay of the $CpMn(CO)_2THF$ complex at 298 and 530 nm.

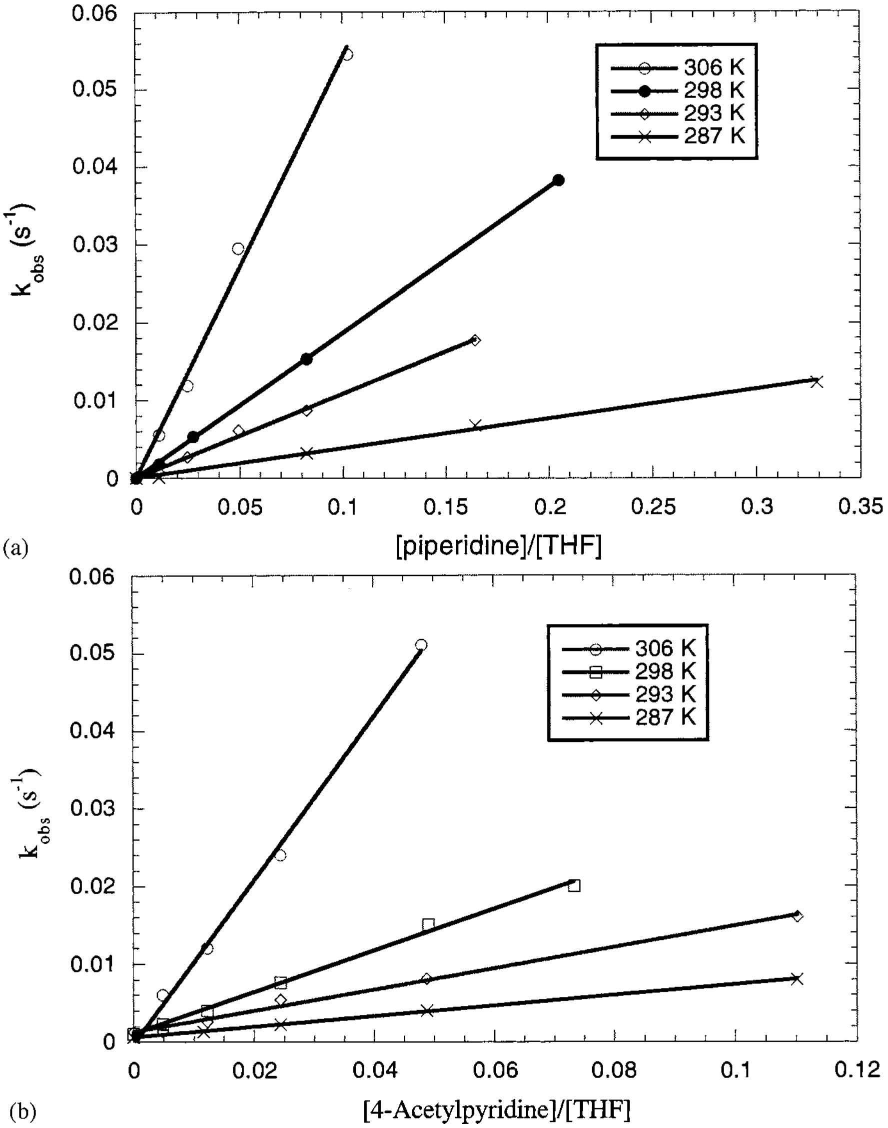


Fig. 4. (a) A plot of k_{obs} versus [piperidine]/[THF] at four temperatures for the reaction of $CpMn(CO)_2(THF)$ with piperidine in THF solvent. (b) Plot of k_{obs} versus [4-acetylpyridine]/[THF] for the reaction of the Mn complex with 4-acetylpyridine in THF solvent.

is attributed to differences in k_2, the step involving the reaction of the unsolvated dicarbonyl with ligand. Clearly, k_2 will be different for 4-acetylpyridine and piperidine and our results suggest that 4-acetylpyridine reacts approximately twice as fast with the unsolvated $CpMn(CO)_2$ fragment than does piperidine.

Further confirmation of the dissociative nature of the substitution mechanism was obtained by conducting mixed solvent experiments where the concentration of the solvent (THF) was varied by addition of cyclohexane, a relatively non-coordinating solvent. According to Eq. (2), a change in the concentration of THF should affect the observed rate constant (k_{obs}) *only* if the mechanism is dissociative. Indeed, at 293 K in the presence of 0.13 M piperidine, when the concentration of THF was decreased by a factor of two, the value of the observed rate constant roughly doubled increasing from $1.9 \pm 0.2 \times 10^{-3}$ to $4.4 \pm 0.4 \times 10^{-3}$ s^{-1}. While these results should be interpreted with some caution since the nature of the solvent environment is undoubtedly changed by the replacement of 50% of the THF by the non-polar cyclohexane, the results clearly indicate that the rate of the reaction is a sensitive function of the solvent characteristics. It is expected that if the reaction had a significant associative component the observed rate would not exhibit such a strong dependence on the solvent environment.

The close agreement of the kinetic parameters despite the significant electronic and steric differences between the ligands studied, and the dependence of the observed rate on the THF concentration, provides strong evidence for a dissociative mechanism of THF

Table 1
Rate constants obtained for the thermal reaction of CpMn(CO)$_2$(THF) with piperidine and 4-acetylpyridine[a]

Ligand	Solvent	T (K)	$((k_1k_2)/k_{-1}) \times 10^2$ (s^{-1})[b]
4-Acetylpyridine	THF[c]	287	6.8 ± 0.1
		293	13.6 ± 0.8
		298	28.0 ± 0.7
		306	105.6 ± 5.0
Piperidine	THF	287	3.8 ± 0.2
		293	10.8 ± 0.5
		298	18.7 ± 1.0
		306	53.8 ± 3.0

[a] The rate constants were obtained from the slopes of the plots shown in Fig. 4a,b.

[b] For ligand = piperidine, $\Delta H_1^{\ddagger}+(\Delta H_2^{\ddagger}-\Delta H_{-1}^{\ddagger}) = 23.3 \pm 2.0$ kcal mol^{-1}, $\Delta S_1^{\ddagger}+(\Delta S_2^{\ddagger}-\Delta S_{-1}^{\ddagger}) = +17.7 \pm 5.0$ e.u. For ligand = 4-acetylpyridine, $\Delta H_1^{\ddagger}+(\Delta H_2^{\ddagger}-\Delta H_{-1}^{\ddagger}) = 24.7 \pm 2.0$ kcal mol^{-1}, $\Delta S_1^{\ddagger}+(\Delta S_2^{\ddagger}-\Delta S_{-1}^{\ddagger}) = +23.7 \pm 6.0$ e.u.

[c] [THF] = 12.3 M.

displacement from the Mn center. A dissociative mechanism of solvent displacement from the Mn center is consistent with previous studies where the substitution of *cis*-cyclooctene from CpMn(CO)$_2$(*cis*-C$_8$H$_{14}$) by PPh$_3$ and the displacement of SBu$_2$ from CpMn(CO)$_2$(SBu$_2$) by P(OMe)$_3$ proceeded by purely dissociative pathways [19,20].

While the relationship between metal–solvent bond strengths obtained by kinetic methods and those determined by thermochemical measurements is not yet well established, our results do help in clarifying the connection. The close agreement between the CpMn(CO)$_2$–THF bond strength obtained from the kinetic and thermodynamic studies implies that the unsolvated CpMn(CO)$_2$ complex undergoes very little electronic and steric reorganization as it reacts with THF. Because the activation enthalpy for the dissociation of the Mn–THF bond is not significantly lower than the Mn–THF bond strength measured by PAC, our results also imply that in the transition state the CpMn(CO)$_2$ fragment is not stabilized to a significant extent by the THF solvent molecule. By contrast, the (CO)$_5$W–heptane and (CO)$_5$W–cyclohexane bond strengths determined by studying the substitution kinetics of the solvated complexes were approximately 6 kcal mol^{-1} lower than those obtained by photoacoustic calorimetry [21]. The difference between the two numbers may be attributed to partial solvation of the transition state by the alkane solvent in the kinetic study. In the present case, however, the excellent agreement between the CpMn(CO)$_2$–THF bond strength obtained by thermochemical measurements and by the present kinetic method suggests that the kinetic method can be very useful in the determination of CpMn(CO)$_2$–solv bond strengths.

Unlike other solvated organometallic complexes like (η^6-Arene)Cr(CO)$_2$solv and M(CO)$_5$THF (M = Cr, Mo, W) which react primarily through an interchange or associative process with donor ligands [22,23], CpMn(CO)$_2$THF reacts through a purely dissociative mechanism. This difference in the pathway of solvent displacement is even more surprising given that in the case of the manganese complex a ‘ring slip’ of the Cp ligand from η^5 to η^3 coordination would allow accommodation of the incoming nucleophile without displacement of the solvent molecule. A dissociative pathway of ligand substitution for the CpMn(CO)$_2$THF complex is

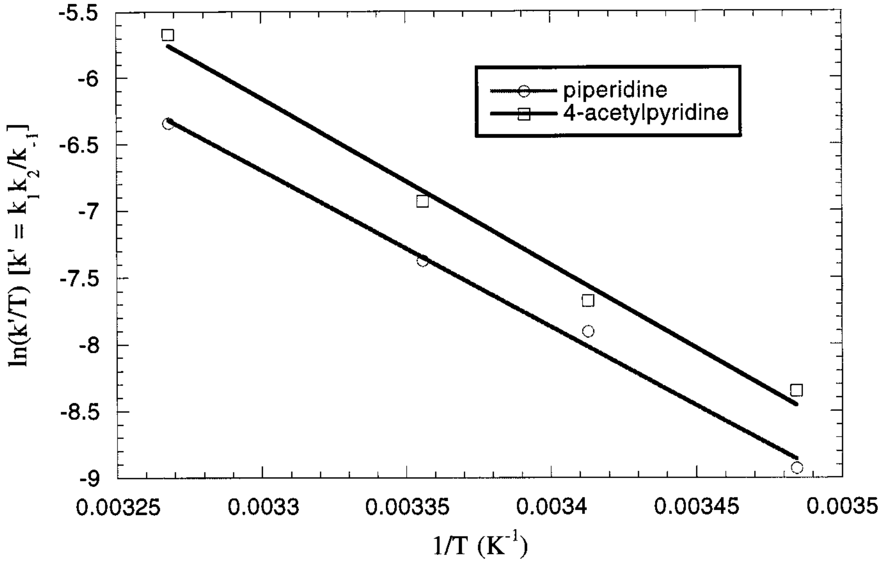


Fig. 5. An Eyring plot of ln (k'/T) where $k' = (k_1k_2)/k_{-1}$ for L = piperidine and 4-acetylpyridine. From the slope of this plot $\Delta H_1^{\ddagger}$ which is associated with the CpMn(CO)$_2$–THF bond dissociation energy is determined to be 23.3 ± 2.0 kcal mol^{-1} for L = piperidine and 24.7 ± 2.0 kcal mol^{-1} for L = 4-acetylpyridine (see Table 1).

consistent with the relative stabilities of the coordinatively unsaturated and unsolvated (η^6-Arene)Cr(CO)$_2$, M(CO)$_5$, and CpMn(CO)$_2$ complexes. Gas phase flash photolysis studies indicate that the CpMn(CO)$_2$ fragment reacts with CO at rates that are roughly an order of magnitude slower than the corresponding reactions of the (η^6-Arene)Cr(CO)$_2$ and M(CO)$_5$ fragments [13,24]. Consequently, it is reasonable to expect that the unsolvated CpMn(CO)$_2$ fragment will have a relatively longer lifetime in the solution phase compared to the (η^6-Arene)Cr(CO)$_2$ and M(CO)$_5$ fragments. Therefore, relative to the (η^6-Arene)Cr(CO)$_2$ and M(CO)$_5$ fragments displacement of a solvent molecule from the CpMn(CO)$_2$solv complex is more likely to proceed through a dissociative pathway than an associative one.

4. Conclusion

The reaction between CpMn(CO)$_2$(THF) and simple two electron donor ligands L (L = piperidine, 4-acetylpyridine) proceeds through a dissociative mechanism resulting in the formation of the corresponding CpMn(CO)$_2$L complex. The kinetic analysis yields an average value of 24.0 ± 3.0 kcal mol^{-1} for the CpMn(CO)$_2$–THF bond energy in good agreement with a value of 24 ± 2 kcal mol^{-1} obtained from previous thermochemical studies. The results of the present study provide an important comparison between the activation enthalpies of solvent displacement from a metal center and metal–solvent bond strengths obtained by thermochemical methods.

Acknowledgements

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