

# Ligand substitution reactions of the CpMn(CO)<sub>2</sub>(cyclohexane) intermediate studied by time-resolved infrared absorption spectroscopy †

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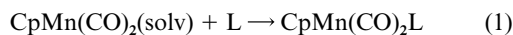
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Time-resolved infrared absorption spectroscopy is used to observe the ligand substitution reactions of the photochemically generated solvated intermediate CpMn(CO)<sub>2</sub>(CyH) (CyH = cyclohexane) with L = cyclopentene, THF, furan, and pyrrolidine to form CpMn(CO)<sub>2</sub>(L). Second-order rate constants and reaction activation parameters are derived. Although the pseudo-first order reaction rate constant is a linear function of ligand concentration over the entire concentration range studied, the observed kinetics for these reactions are most consistent with a dissociative interchange mechanism. A lower limit of  $34 \pm 3$  kJ mol<sup>-1</sup> for the [Cp(CO)<sub>2</sub>Mn]–CyH bond dissociation enthalpy is derived. Reactivity trends among the ligands are discussed, and comparisons are made between the ligand substitution behavior of CpMn(CO)<sub>2</sub>(CyH) and that of other alkane-solvated transition metal intermediates. From these comparisons, it appears that for reaction of a coordinatively unsaturated transition-metal in a given solvent, the relationship between  $\Delta H^\ddagger$  and  $\Delta S^\ddagger$  is determined by the solvent independent of the particular metal complex reacting.

## Introduction

Because of their importance as intermediates in synthetic and catalytic reactions of transition-metal complexes, coordinatively unsaturated organometallic complexes have been of considerable interest for the last two decades. One such species of particular interest is the “CpMn(CO)<sub>2</sub>” fragment produced by photolysis of the stable complex CpMn(CO)<sub>3</sub>.<sup>1</sup> While reactions of the “naked” dicarbonyl intermediate have been studied in the gas phase,<sup>2</sup> almost all of the experimental work on “CpMn(CO)<sub>2</sub>” has concerned its behavior in condensed phases. The spectroscopy and reactions of “CpMn(CO)<sub>2</sub>” have been studied in low-temperature glasses,<sup>3,4</sup> and in solution by photoacoustic calorimetry (PAC),<sup>5,6</sup> low-temperature IR spectroscopy,<sup>7</sup> and fast and ultrafast time-resolved IR absorption spectroscopy (TRIR).<sup>8</sup>

In solution, reactivity of “CpMn(CO)<sub>2</sub>” on the time scale of bimolecular reaction appears to be that of a solvated species, CpMn(CO)<sub>2</sub>(solv) (solv = a molecule of the solvent). While to our knowledge, the rate of solvation of CpMn(CO)<sub>2</sub> has not been measured in alkane solution, its interaction with the solvent in neat silane occurs within tens of picoseconds.<sup>8</sup> The ligand substitution chemistry of solvated CpMn(CO)<sub>2</sub>, reaction (1), has been of some interest as well.



PAC studies<sup>5,6,9</sup> of this reaction were undertaken primarily in order to determine metal–ligand and metal–solvent bond strengths. Studies in which the primary interest was in the kinetics of the reaction itself have generally used time-resolved spectroscopy in order to determine the time-dependent concentrations of CpMn(CO)<sub>2</sub>(solv) and CpMn(CO)<sub>2</sub>L during the course of the reaction. Such studies have been performed in a wide variety of condensed media, including alkanes,<sup>10,11</sup> aromatic solvents,<sup>12</sup> and supercritical fluids.<sup>13,14</sup>

Several studies have been concerned with the mechanism of reaction (1). Bengali and coworkers provided evidence

for a dissociative mechanism<sup>‡</sup> for ligand substitution at CpMn(CO)<sub>2</sub>(toluene)<sup>12</sup> and CpMn(CO)<sub>2</sub>(THF).<sup>15</sup> In the former case, they saw kinetic saturation at high concentrations of L, while in the latter,  $\Delta H^\ddagger$  for the reaction did not depend on the ligand (L = piperidine or acetylpyridine), and was consistent with the CpMn(CO)<sub>2</sub>–THF bond dissociation energy previously determined by PAC.<sup>9</sup> George and coworkers have shown that recombination of CpMn(CO)<sub>2</sub>(solv) with CO in supercritical Kr or Xe also appears to proceed *via* a dissociative pathway.<sup>14</sup> On the other hand, while the kinetics of reaction (1) in room-temperature alkane solution have been interpreted in terms of a dissociative mechanism,<sup>10</sup> a more recent study of the recombination reaction of CpMn(CO)<sub>2</sub>(solv) with CO in alkane solution, also performed in George's laboratory, provided evidence that the reaction in fact follows an associative pathway, although under the conditions of that experiment, a dissociative mechanism could not be ruled out.<sup>11</sup>

Our interest in reaction (1) comes from a slightly different point of view. We have recently performed a series of studies<sup>16–19</sup> on the ligand substitution reactions of the W(CO)<sub>5</sub>(CyH) (CyH = cyclohexane) complex in which we used TRIR to investigate how the electronic and steric properties of the incoming ligand affect the course of the reaction. We undertook the present study for similar reasons. Here, we use TRIR to investigate the reaction of CpMn(CO)<sub>2</sub>(CyH) with four ligands that contain five-membered rings: cyclopentene, furan, THF, and pyrrolidine. We sought to understand how changing the properties of the ligand affects the activation parameters of reaction (1). We also wished to compare the behavior of the CpMn(CO)<sub>2</sub>(CyH) intermediate to that of W(CO)<sub>5</sub>(CyH) and to see what conclusions could be drawn from the similarities or differences we would observe in the kinetics of reaction (1) in the two cases.

‡ Since none of the experiments discussed in this report (including ours) actually detected an intermediate of lower or higher coordination number than the CpMn(CO)<sub>2</sub>(solv) reactant, strictly speaking, all of the experiments point to an interchange mechanism. For the sake of simplicity, we refer to the mechanisms in terms of the dissociative and associative limiting cases most consistent with the particular experimental result at hand.

† Electronic supplementary information (ESI) available: Complete tables of pseudo-first order rate constants  $k_{\text{obs}}$  as a function of [L] and of temperature. See <http://www.rsc.org/suppdata/dt/b3/b302023a/>

## Experimental

The instrument on which these experiments were performed has been described in detail elsewhere,<sup>16</sup> so only a brief description will be given here. A CyH solution containing  $1-3 \times 10^{-3}$  mol L<sup>-1</sup> CpMn(CO)<sub>3</sub> and an at least tenfold excess L is prepared and then degassed with Ar. Reaction takes place in a temperature-controlled ( $\pm 1$  °C) IR cell (0.5–1 mm path length, CaF<sub>2</sub> windows). A pulse of UV light from a XeCl excimer laser (308 nm,  $\sim 20$  ns pulse<sup>-1</sup>, 60–100 mJ pulse<sup>-1</sup>) initiates the reaction by photolyzing the parent complex to the solvated dicarbonyl intermediate. The kinetics of the ensuing reaction are then monitored by observation of the changes in the solution's IR spectrum as a function of time following the photolysis.

The C–O stretching absorption frequencies of CpMn(CO)<sub>2</sub>L are determined from IR spectra taken of a solution of CpMn(CO)<sub>2</sub> photolyzed in the presence of excess L, using either standard FTIR or time-resolved Step-Scan FTIR (S<sup>2</sup>FTIR) spectroscopy. Once the wavelengths corresponding to absorptions of the intermediate and product have been identified, detailed kinetic measurements are then undertaken. In these experiments, the course of the reaction is monitored by following the time dependence of the absorption of the output of a CW Pb-salt diode laser tuned to a C–O stretching frequency of the intermediate or product. The particular frequency monitored is chosen to maximize S/N and is not always at the actual peak of the absorbance. Since the S<sup>2</sup>FTIR spectra do not show any changes in peak shapes with time, we assume that the temporal changes of a particular C–O stretch will not depend on the specific frequency monitored. The raw signal from the MCT detector (risetime <20 ns) is converted to absorbance, and pseudo-first-order reaction rate constants  $k_{\text{obs}}$  are then determined from the exponential time dependence of  $\Delta A$ . Second-order rate constants and activation parameters are derived from the [L] and temperature dependences of the pseudo-first-order rate constants as described in detail below.

CpMn(CO)<sub>3</sub> is obtained from Aldrich (98%) and used without further purification. CyH is obtained in HPLC or spectrophotometric grade and distilled from Na/benzophenone immediately prior to use to remove remaining traces of water (UV-VIS spectroscopy confirms that, after distillation, the concentration of benzophenone is  $<10^{-6}$  mol L<sup>-1</sup>). Organic reactants are obtained from commercial suppliers in high purity (97–99+%, confirmed by NMR) and distilled from an appropriate drying agent; prior to drying, THF is distilled from CuCl in order to remove any peroxides that may be present.<sup>20</sup>

## Results and discussion

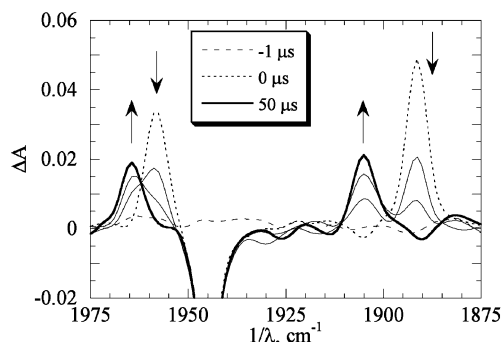
### (a) General observations

The time-resolved spectra from which we determine the kinetics of reaction (1) are in broad terms basically similar for all four ligands studied here. Immediately upon photolysis, to within the instrument response time of  $\sim 20$  ns, the absorbance at 1944 and 2027 cm<sup>-1</sup>, the C–O stretching frequencies of CpMn(CO)<sub>3</sub>, decreases, while two new absorbances appear at 1891 and 1958 cm<sup>-1</sup>. We attribute these changes to photolysis of CpMn(CO)<sub>3</sub> and formation of CpMn(CO)<sub>2</sub>(CyH).<sup>10</sup> The intensities of the absorbances of CpMn(CO)<sub>2</sub>(CyH) then decay exponentially, the rate of decay depending on the particular ligand, ligand concentration, and temperature. As these peaks disappear, two new peaks, corresponding to formation of the CpMn(CO)<sub>2</sub>L product, appear at the same rate to within experimental error. The frequencies of the C–O stretching absorbances for the various CpMn(CO)<sub>2</sub>L complexes are summarized in Table 1. A typical set of room-temperature time-resolved S<sup>2</sup>FTIR spectra are given in Fig. 1 for the reaction of CpMn(CO)<sub>2</sub>(CyH) with cyclopentene (CyPe).

**Table 1** Room-temperature C–O stretching frequencies and force constants<sup>a</sup> ( $10^2$  N m<sup>-1</sup>) for CpMn(CO)<sub>2</sub>L complexes

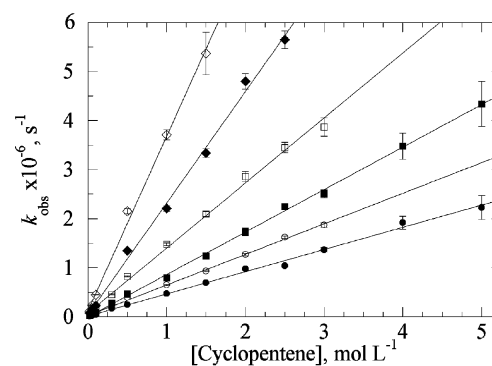
L	$\nu_{\text{CO}}/\text{cm}^{-1}$	$k_{\text{CO}}$	$k_{\text{i}}$
CyH <sup>b</sup>	1891, 1958	14.976	0.521
<i>n</i> -Heptane <sup>c</sup>	1895, 1964	15.054	0.269
Cyclopentane <sup>d</sup>	1893, 1953	14.951	0.466
THF <sup>b</sup>	1864, 1936	14.598	0.552
Furan <sup>b</sup>	1909, 1967	15.185	0.454
Pyrrolidine <sup>b</sup>	1847, 1920	14.345	0.556
CyPe <sup>b</sup>	1905, 1965	15.131	0.461

<sup>a</sup> Force constants calculated by the Cotton–Kraihanzel method (ref. 31). <sup>b</sup> CyH solution (this work). <sup>c</sup> Ref 10. <sup>d</sup> Ref 11.



**Fig. 1** Time-resolved S<sup>2</sup>FTIR spectra for the reaction of CpMn(CO)<sub>2</sub>(CyH) with cyclopentene (CyPe). Shown are spectra taken 0, 5, 10 and 50 μs following photolysis of a  $5 \times 10^{-3}$  mol L<sup>-1</sup> solution of CpMn(CO)<sub>3</sub> in CyH in the presence of 0.2 mol L<sup>-1</sup> CyPe. The arrows indicate the absorptions attributed to CpMn(CO)<sub>2</sub>(CyH) (falling arrows at 1958 and 1891 cm<sup>-1</sup>) and those attributed to CpMn(CO)<sub>2</sub>(CyPe) (rising arrows at 1965 and 1905 cm<sup>-1</sup>).

For reaction with THF, measurements of the kinetics of reaction (1) were made over the temperature range 20–60 °C; for the remaining ligands, the temperature range was 15–55 °C. In all cases, the ligand concentration [L] was varied over a factor of at least 100 (from  $<0.01$  mol L<sup>-1</sup> to  $>1$  mol L<sup>-1</sup>). Typical results are shown in Fig. 2 for the reaction of CpMn(CO)<sub>2</sub>(CyH) with CyPe. Complete tables of pseudo-first order rate constants  $k_{\text{obs}}$  as a function of [L] and of temperature are given in the ESI. †



**Fig. 2** Pseudo-first order rate constant  $k_{\text{obs}}$  for reaction (1): CpMn(CO)<sub>2</sub>(CyH) with L = CyPe as a function of [CyPe] at 15 (●), 20 (○), 25 (■), 35 (□), 45 (◆) and 55 °C (◇). The error bars represent 1σ uncertainties to the fits to the experimental data. The solid lines are least-squares linear fits.

Creaven *et al.*<sup>10</sup> noted that in the absence of added L, CpMn(CO)<sub>2</sub>(solv) reacts with unphotolyzed CpMn(CO)<sub>3</sub> to form Cp<sub>2</sub>Mn<sub>2</sub>(CO)<sub>5</sub> with a single bridging carbonyl ligand. We did not find any evidence in our experiments for significant competition between reaction (1) and dimerization. We do note, however, that the plots of  $k_{\text{obs}}$  as a function of [L] tend to have

small non-zero intercepts, the magnitudes of which are consistent with the expected rate of disappearance of CpMn(CO)<sub>2</sub>(CyH) in the absence of L due to dimerization or reaction with residual H<sub>2</sub>O in the solvent.<sup>10</sup> Since these intercepts are on the order of only 1% of the derived second-order rate constants for reaction (1), no detailed studies were performed of other reactions that might be competing with reaction (1).

### (b) Spin state of the intermediate

In their picosecond studies of photolysis of CpMn(CO)<sub>3</sub> in neat SiEt<sub>3</sub>H, Harris and coworkers reported spectroscopic evidence for production of CpMn(CO)<sub>2</sub> in both triplet and singlet spin states, and the results of calculations that indicate that the triplet is the ground electronic state of CpMn(CO)<sub>2</sub>.<sup>8</sup> Therefore, it is worth considering the electronic state or states responsible for the reactivity we observe in our experiment. Both the spectroscopic and the kinetic results of our study imply that the reactivity observed on the μs time scale is due solely to a singlet species.

First of all, we observe that the C–O stretches of the dicarbonyl intermediate observed in the present work are similar to those that Harris and coworkers attributed to the singlet state in their report, and we see no evidence in our experiment for the existence of a second dicarbonyl species produced at the photolysis flash. Furthermore, the contrast in the kinetic behavior exhibited by CpMn(CO)<sub>2</sub> with that of the isoelectronic complex CpCo(CO) provides additional evidence that the Mn complex reacts *via* a singlet state. “CpCo(CO)” has been observed to react at an essentially diffusion-limited rate (bimolecular rate constants of 10<sup>9</sup>–10<sup>10</sup> L mol<sup>-1</sup> s<sup>-1</sup>), independent of the reaction partner, in liquefied rare gases<sup>21</sup> and in room-temperature alkane solution.<sup>21,22</sup> These results imply that CpCo(CO) remains essentially unsolvated. Such behavior has been predicted theoretically for triplet transition metal (TM) intermediates.<sup>23</sup> In contrast,<sup>10,11,14</sup> “CpMn(CO)<sub>2</sub>” reacts some 2–3 orders of magnitude more slowly, typical for a singlet species with significant metal–solvent interaction.

As has been pointed out previously,<sup>8</sup> in solution, the conversion of a coordinatively unsaturated intermediate from a triplet to a singlet is not simply electronic excitation: it is a simultaneous spin change and solvation, a process for which the activation barrier can be quite small. For example, Poliakov and Turner<sup>24</sup> found that in a CH<sub>4</sub> matrix, the activation energy for conversion of triplet Fe(CO)<sub>4</sub> to singlet Fe(CO)<sub>4</sub>(CH<sub>4</sub>) is <30 kJ mol<sup>-1</sup>. The measured limits for production of singlet Fe(CO)<sub>4</sub>(alkane) at room temperature (>700 ps<sup>25</sup> and <1 μs<sup>26</sup>) indicate that in solution, the barrier is of similar size. It seems reasonable to assume that production of singlet CpMn(CO)<sub>2</sub>(CyH) from triplet CpMn(CO)<sub>2</sub> also has an activation energy of that magnitude, and therefore that the bimolecular reactions that we observe are those of singlet CpMn(CO)<sub>2</sub>(CyH).

### (c) Mechanism: the associative limit

One important concern in kinetic studies is the use of kinetic data to help establish a mechanism. It has been pointed out that in cases where [L] ≪ [solv], the kinetic results for reaction (1) can be mechanistically ambiguous;<sup>27</sup> recently, George and coworkers<sup>11</sup> have discussed the ambiguities in the context of an investigation of the recombination of CpMn(CO)<sub>2</sub>(solv) with CO. In an experiment such as the one performed here, however, there can be additional sources of ambiguity that arise for entirely different reasons.<sup>28</sup> In order to illustrate how these mechanistic ambiguities affect the present experiment, and to show what information we can obtain in spite of them, we consider in turn the two limiting mechanisms for the reaction and how we can understand our results in light of the predictions made by them.

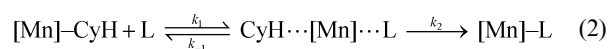
In all four of the systems studied here, *k*<sub>obs</sub> is a linear function of [L] over the entire concentration range studied. In the case of

**Table 2** Second-order rate constants (*k*<sub>a</sub>) for reaction (1)<sup>a</sup>

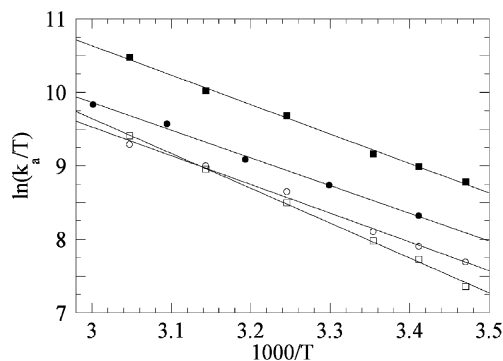
<i>T</i> /°C	<i>k</i> <sub>a</sub> /10 <sup>6</sup> L mol <sup>-1</sup> s <sup>-1</sup>			
	THF	Furan	Pyrrolidine	CyPe
15		0.629 (0.024)	1.88 (0.15)	0.453 (0.010)
20	1.20 (0.04)	0.793 (0.011)	2.35 (0.11)	0.667 (0.023)
25		0.986 (0.020)	2.84 (0.10)	0.872 (0.021)
30	1.89 (0.03)			
35		1.76 (0.02)	4.94 (0.05)	1.51 (0.04)
40	2.76 (0.10)			
45		2.59 (0.10)	7.16 (0.02)	2.46 (0.09)
50	4.63 (0.18)			
55		3.56 (0.05)	11.6 (0.3)	4.00 (0.11)
60	6.22 (0.47)			

<sup>a</sup> Derived as the slopes to linear fits to *k*<sub>obs</sub> as a function of [L], weighted by the uncertainties in *k*<sub>obs</sub>; see the text. 1σ uncertainties in *k*<sub>a</sub> are given in parentheses.

L = CyPe, Fig. 2, at *T* ≤ 35 °C, we were able to measure *k*<sub>obs</sub> to [L] = 6 mol L<sup>-1</sup>, corresponding to [L]/[CyH] ≈ 1. The simplest mechanism that can account for such behavior is an associative (A) mechanism, reaction (2):



This scheme predicts that, assuming steady-state kinetics in CyH ⋯ [Mn] ⋯ L, *k*<sub>obs</sub> = *k*<sub>a</sub>[L] for all values of L, where *k*<sub>a</sub> = *k*<sub>1</sub>*k*<sub>2</sub>/(*k*<sub>-1</sub> + *k*<sub>2</sub>).<sup>29</sup> Values of *k*<sub>a</sub> derived from the slopes of linear fits to *k*<sub>obs</sub> (shown in Fig. 2 for L = CyPe) are summarized in Table 2. Eyring analyses of *k*<sub>a</sub> are shown graphically in Fig. 3, and the activation parameters derived from these analyses are summarized in Table 3. Several aspects of these results run counter to what might be expected from associative behavior, however. For example, for L = pyrrolidine, THF, and furan the activation enthalpy derived from the temperature dependence of “*k*<sub>a</sub>” is the same to within experimental error. For an associative reaction, we would expect that the enthalpic barrier would be lower for a more electron-donating ligand which could better stabilize the electron-poor transition state. § This kind of behavior is observed, for example, in the ligand substitution reactions of W(CO)<sub>5</sub>(CyH),<sup>16–19,30</sup> for which the activation enthalpy for reaction with furan is some 20 kJ mol<sup>-1</sup> higher than that for reaction with pyrrolidine.<sup>17,19</sup> The contrasting behavior of the Mn and W systems is shown graphically in



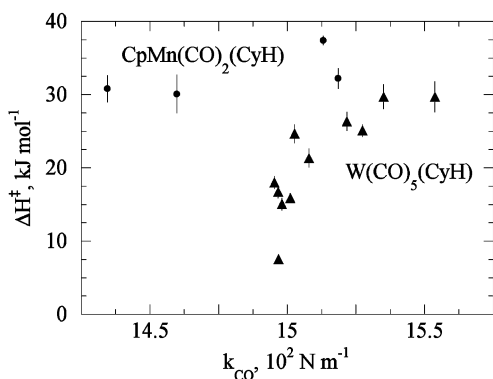
**Fig. 3** Eyring analyses of the second-order rate constants *k*<sub>a</sub> for reaction (1) for L = THF (●), furan (○), pyrrolidine (■) and CyPe (□). The solid lines are least-squares linear fits to the data.

§ A reviewer has suggested the possibility that the similarity of Δ*H*<sup>‡</sup> for L = THF, furan, and pyrrolidine may be due to an associative reaction in which increasing steric hindrance happens to compensate for decreasing electron-donating ability. While we cannot absolutely eliminate this possibility, we do not think that it can provide a full explanation for our results, since they would be inconsistent with a D mechanism even under those circumstances.<sup>28</sup>

**Table 3** Activation parameters for “ $k_a$ ” of reaction (1)<sup>a</sup>

Ligand	$\Delta H^\ddagger/\text{kJ mol}^{-1}$	$\Delta S^\ddagger/\text{J mol}^{-1} \text{K}^{-1}$	$\Delta G^\ddagger (293 \text{ K}),^b/\text{kJ mol}^{-1}$	$\Delta G^\ddagger (293 \text{ K}),^c/\text{kJ mol}^{-1}$
THF	30.1 (2.6)	-26.0 (14.7)	37.7 (2.6)	37.6
Furan	32.2 (1.4)	-22.0 (12.4)	38.6 (1.4)	38.6
Pyrrolidine	30.8 (1.8)	-17.5 (11.5)	35.9 (1.8)	36.0
CyPe	37.4 (0.6)	-6.3 (5.1)	39.2 (0.6)	39.1

<sup>a</sup> 1 $\sigma$  uncertainties in parentheses. <sup>b</sup> Determined from the activation parameters given in this table. <sup>c</sup> Extrapolated from values of  $k_a$  given in Table 2.

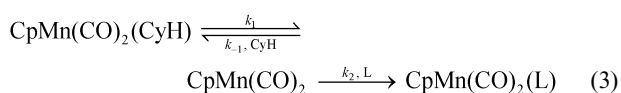


**Fig. 4**  $\Delta H^\ddagger$  for ligand substitution at  $\text{CpMn}(\text{CO})_2(\text{CyH})$  (●) and  $\text{W}(\text{CO})_5(\text{CyH})$  (▲) as a function of the C–O stretching force constant<sup>31</sup> in the product complex (in the case of  $\text{W}(\text{CO})_5(\text{CyH})$ , this is the force constant for the carbonyl *trans* to L). Error bars represent 1 $\sigma$  uncertainties.

Fig. 4, in which  $\Delta H^\ddagger$  is plotted as a function of  $k_{\text{CO}}$ , the C–O stretching force constant<sup>31</sup> in the product complex (for  $\text{W}(\text{CO})_5\text{L}$ , we use  $k_{\text{CO}}$  for the carbonyl *trans* to L). For reaction of  $\text{W}(\text{CO})_5(\text{CyH})$ , there is quite clearly an inverse correlation between  $\Delta H^\ddagger$  and the electron-donating ability of the incoming ligand, while for  $\text{CpMn}(\text{CO})_2(\text{CyH})$ , no such correlation is observed. Furthermore, for the ligands studied here,  $\Delta S^\ddagger$  of reaction (1) is near zero, rather than significantly negative as would be expected for an associative reaction. Also, as discussed in detail below, analysis of the reaction in terms of a dissociative mechanism yields additional results that are difficult to reconcile with a purely A reaction.

#### (d) Mechanism: the dissociative limit

Since some aspects of the kinetic behavior of  $\text{CpMn}(\text{CO})_2(\text{CyH})$  are unexpected for a reaction proceeding *via* an associative pathway, we consider the results in terms of a dissociative mechanism as well. Perhaps counterintuitively, even though the functional form of  $k_{\text{obs}}$  as a function of [L] agrees with the behavior predicted by an associative pathway, the experimental results are not necessarily inconsistent with dissociative (D) substitution, reaction (3):



While in principle this mechanism predicts saturation kinetics ( $k_{\text{obs}}$  reaches a limiting value of  $k_1$  at high [L]),<sup>29</sup> in practice, under typical TRIR experimental conditions, it is unlikely that kinetic saturation will be observed in a “non-coordinating” solvent. This result is *not* because we only sample  $k_{\text{obs}}$  in the rising portion of the saturation curve: as we have noted, for  $\text{L} = \text{CyPe}$ ,  $k_{\text{obs}}$  remains a linear function of [L] even at  $[\text{CyH}]/[\text{L}] = 1$ . Rather, as we show in detail elsewhere,<sup>28</sup> since [L] and [CyH] are not independent, it is possible in our experiment for  $k_{\text{obs}}$  to remain (at least to within the scatter of the data) a linear function of [L] at all values of [L] even if the reaction is purely D.

Other researchers have eliminated the mutual dependence of [solv] and [L] by adding a diluent (“dil”) that binds much less strongly to the metal center than does solv.<sup>12,32</sup> Since [M]–dil is much more weakly bound than [M]–solv, there should not be a significant amount of [M]–dil present at any time during the reaction, which would thus enable alteration of [solv] (and therefore the ability to test the [solv]/[L] dependence of  $k_{\text{obs}}$ ) independent of [L]. Unfortunately, in the present case, such an experiment is not feasible. The only solvents that bind significantly less strongly to TM intermediates than alkanes are fluoroalkanes,<sup>33</sup> which are not miscible with CyH over the temperature range of the experiments performed here.¶

Another method that has been used to analyze dissociative ligand substitution reactions<sup>34</sup> makes use of eqn. (4), derived from eqn. (3) by assuming steady-state kinetics in the “naked” unsolvated intermediate  $\text{CpMn}(\text{CO})_2$ :

$$\frac{1}{k_{\text{obs}}} = \frac{1}{k_1} + \frac{k_{-1}}{k_1 k_2} \frac{[\text{solv}]}{[\text{L}]} \quad (4)$$

For a dissociative reaction, a “double inverse plot” of  $1/k_{\text{obs}}$  as a function of [solv]/[L] should be linear with an intercept that is independent of L. For a given ligand and temperature, the ratio of the intercept to the slope will give  $k_2/k_{-1}$ ; this ratio is normally expected to be near unity, since the unsolvated intermediate should not discriminate strongly among possible reaction partners.

Several complications can arise in the practical application of eqn. (4), however. As noted above,  $\text{CpMn}(\text{CO})_2(\text{CyH})$  can react with unphotolyzed  $\text{CpMn}(\text{CO})_3$  or impurities in the solution, which means that  $k_{\text{obs}}$  will always have a component that is independent of [L]. In an analysis according to the A mechanism, this component can be ignored, since a plot such as that shown in Fig. 2 automatically separates the [L]-dependent and [L]-independent components of  $k_{\text{obs}}$  into the slope and intercept of the linear fit. In the case of an attempted analysis of D behavior, however, the presence of a concentration-independent component of  $k_{\text{obs}}$  will lead to curvature in the double inverse plot, especially at low [L] where the competition with reaction (1) from other processes that remove  $\text{CpMn}(\text{CO})_2(\text{CyH})$  from the solution is greatest.

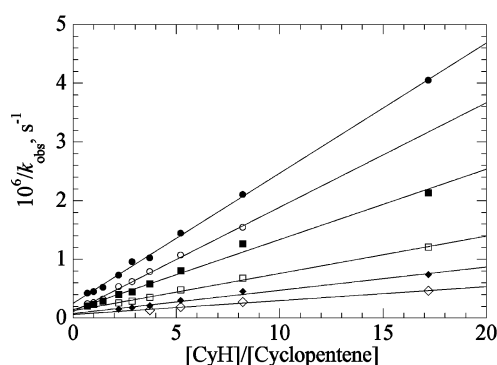
Fig. 5 shows a set of double inverse plots for reaction with CyPe at  $[\text{CyPe}] \geq 0.2 \text{ mol L}^{-1}$ , *i.e.* for ligand concentrations where the [CyPe]-independent contribution to  $k_{\text{obs}}$  is not significant. These plots are indeed linear. They do, however, reveal a second problem with the use of a double-inverse plot: as the temperature increases, the maximum concentration at which it is possible to obtain an accurate measurement of  $k_{\text{obs}}$  decreases. In particular, in our apparatus, the maximum  $k_{\text{obs}}$  that we can measure accurately is  $\sim 6 \times 10^6 \text{ s}^{-1}$ . For relatively rapidly reacting ligands such as pyrrolidine, it may not be possible for us to measure  $k_{\text{obs}}$  at high [L] at any temperature above the freezing point of CyH. The absence of data points near the origin of a double-inverse plot will necessarily increase the uncertainty in the intercept, due to its extrapolation from points relatively far from the origin.

¶ We are currently undertaking a series of experiments to measure rate constants for these reactions in heptane/perfluoroalkane mixtures; perfluoroalkanes are miscible with heptane above  $\sim 35^\circ \text{C}$ .<sup>32</sup>

**Table 4** Values of the rate constant  $k_1$  and  $k_2/k_{-1}$  for reaction (1)<sup>a</sup>

$T/^\circ\text{C}$	Ligand	$k_1/10^6 \text{ s}^{-1}$	$k_2/k_{-1}$	$T/^\circ\text{C}$	Ligand	$k_1/10^6 \text{ s}^{-1}$	$k_2/k_{-1}$	
15	CyPe	2.77 (0.59)	1.88 (0.22)	35	CyPe	10.9 (2.9)	1.31 (0.27)	
	Furan	2.38 (1.05)	2.96 (1.17)		Pyrrolidine	12.7 (2.4)	4.02 (0.65)	
	Pyrrolidine	2.61 (0.56)	8.22 (1.25)	40	THF	9.13 (1.78)	3.69 (0.24)	
20	CyPe	5.24 (1.23)	1.31 (0.24)		45	CyPe	13.1 (3.5)	1.92 (0.88)
	THF	5.48 (2.53)	2.60 (0.91)			Pyrrolidine	23.4 (17.3)	3.37 (1.10)
	Furan	4.75 (2.86)	1.81 (1.24)	50	THF	18.6 (7.6)	2.67 (0.53)	
	Pyrrolidine	7.38 (2.64)	5.38 (1.17)		55	CyPe	17.3 (4.2)	2.41 (0.25)
25	CyPe	6.72 (1.17)	1.28 (0.18)	Furan		15.7 (4.2)	2.58 (0.55)	
	Furan	8.94 (6.65)	1.18 (0.70)	60	THF	23.6 (19.7)	2.85 (0.85)	
	Pyrrolidine	4.29 (1.18)	3.85 (0.67)					
30	THF	7.60 (2.54)	2.84 (0.61)					

<sup>a</sup> Determined by using eqn. (4) as described in the text. In most cases, the parameters reported were determined as the average of linear fits to several different subsets of the data.  $1\sigma$  uncertainties, given in parentheses, include both the standard deviation of the average, and the uncertainties of the individual fits.

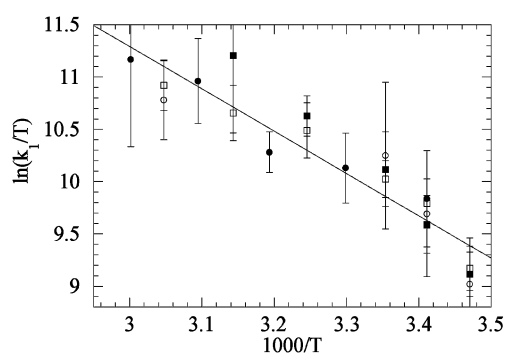


**Fig. 5** “Double inverse” plots of  $10^6/k_{\text{obs}}$  as a function of  $[\text{CyH}]/[\text{L}]$  for  $\text{L} = \text{CyPe}$  (for measurements made with  $[\text{CyPe}] \geq 0.2 \text{ mol L}^{-1}$ ) at 15 (●), 20 (○), 25 (■), 35 (□), 45 (◆) and 55 °C (◇). The solid lines are least-squares linear fits to the data.

The results of analyses of double inverse plots are given in Table 4. In the ideal case, of course, a linear fit to a set of data points should not depend on what subset of the points is chosen for the fit. In the present study, due to the scatter in the data, and the possibility of interference from competing reactions, this ideal case unfortunately does not apply. Therefore, in order to estimate the true uncertainty in the intercepts of the plots, we fit different subsets of the data points, and report  $k_1$  and  $k_2/k_{-1}$  as derived from several independent data fits. In some cases (particularly for reactions of furan, which we have previously observed to be a difficult ligand to work with<sup>17</sup>), the scatter in the data was sufficiently severe, or the number of measurements at high  $[\text{L}]$  sufficiently small, that it was impossible to obtain a consistent or meaningful fit to the data (*e.g.* some subsets of the data would yield negative intercepts). These cases are not included in the data shown in Table 4. We do note, however, that it is possible to obtain reasonable fits for these data sets in which the intercept is restricted to its value in the reaction with CyPe.

Within the rather large error bars resulting from the difficulties in the analysis described above, the values of  $k_1$  determined in this fashion do seem to be independent of the ligand. An Eyring analysis of the temperature dependence of this “ $k_1$ ” is shown in Fig. 6. This analysis leads to  $\Delta H^\ddagger = 34 \pm 3 \text{ kJ mol}^{-1}$ ,  $\Delta S^\ddagger = -3 \pm 10 \text{ J mol}^{-1} \text{ K}^{-1}$  for the  $k_1$  step. In the dissociative limit, this reaction step is the breaking of the  $[\text{Mn}]$ -CyH bond, and hence  $\Delta H^\ddagger$  for this step would correspond to the  $\text{Cp}(\text{CO})_2\text{Mn}$ -CyH bond dissociation energy (BDE).

In fact, the analysis performed in the current study actually only provides a *lower limit* to the  $[\text{Mn}]$ -CyH BDE. One reason that we only obtain a lower limit to the BDE rather than the



**Fig. 6** Eyring plot for “ $k_1$ ” (derived from eqn. (4) as described in the text) for reaction of  $\text{CpMn}(\text{CO})_2(\text{CyH})$  with THF (●), furan (□), pyrrolidine (■) and CyPe (◇). The solid line is a least-squares linear fit to the data points, weighted by the  $1\sigma$  uncertainties shown.

BDE itself is that our results do not exclude the possibility that the A and D pathways operate simultaneously. Dobson and coworkers<sup>34</sup> have shown that if a reaction proceeds *via* competing A and D mechanisms, if  $k_1$  can be measured independently, then it is possible to “correct” a double inverse plot by explicit inclusion of an  $[\text{L}]$  dependent term, leading to replacement of the left hand side of eqn. (4) with  $1/(k_{\text{obs}} - k_a[\text{L}])$ . This analysis thus enables division of the observed reactivity into associative and dissociative components.  $\Delta H^\ddagger$  for an associative reaction should always be lower than the  $[\text{Mn}]$ -CyH BDE (or else the intermediate would have enough enthalpy to react dissociatively). Thus, if both pathways are operating, “ $\Delta H^\ddagger$ ” determined for the  $k_1$  step under the assumption that there is no associative reaction will always underestimate the true BDE. While the values of  $k_1$  measured here for the different ligands are within experimental error of being equal, their uncertainties are sufficiently large that the possibility of competing A and D reaction cannot be excluded. Since we have no positive evidence for the existence of such competition, we did not attempt to analyze the double inverse plots in the manner discussed by Dobson and coworkers.

The lower limit for the  $\text{Cp}(\text{CO})_2\text{Mn}$ -CyH BDE determined here is similar to that determined by PAC measurements for the  $\text{Cp}(\text{CO})_2\text{Mn}$ -(*n*-heptane) BDE, 33–37  $\text{kJ mol}^{-1}$ .<sup>5a,9</sup> Similarly, in their TRIR study of its recombination reaction with CO, George and coworkers<sup>14</sup> determined a lower limit of 36  $\pm 2 \text{ kJ mol}^{-1}$  for the  $\text{Cp}(\text{CO})_2\text{Mn}$ -(*n*-heptane) BDE, but pointed out that these values seem to be inconsistent with the BDEs of  $(\text{CO})_5\text{M}$ -(*n*-heptane) ( $\text{M} = \text{Cr}, \text{W}$ ), which appear to be closer to 50–60  $\text{kJ mol}^{-1}$ .<sup>35,36</sup> On the other hand, DFT calculations (Gaussian 98,<sup>37</sup> B3LYP/CEP-31G\* level) that we recently performed yield values of 31.6 and 39.0  $\text{kJ mol}^{-1}$ , respectively, for

the  $\text{Cp}(\text{CO})_2\text{Mn}-(\text{CyH})$  and  $(\text{CO})_5\text{W}-(\text{CyH})$  BDEs. These values are for gas-phase species, and thus may underestimate the condensed-phase BDEs, since they do not take residual solvation of the “naked” fragment into account. They do seem to confirm, however, that the  $\text{Cp}(\text{CO})_2\text{Mn}-(\text{CyH})$  BDE is significantly weaker than that of  $(\text{CO})_5\text{W}-(\text{CyH})$ . If the solvation energies of  $\text{CpMn}(\text{CO})_2$  and  $\text{W}(\text{CO})_5$  are similar, the calculated value of the  $\text{Cp}(\text{CO})_2\text{Mn}-(\text{CyH})$  BDE is consistent with the experimentally determined lower limit.

Another reason that our determination of  $\Delta H^\ddagger$  can only be considered a lower limit to the BDE is that even if the reaction proceeds by a single pathway, that pathway need not be D. To prove the D mechanism, one must observe unsolvated  $\text{CpMn}(\text{CO})_2$  as an intermediate, which is not possible in an instrument with ns time resolution. But beyond this technical limitation, some of the results that we do obtain are difficult to reconcile with purely D reaction. While accurate values of  $\Delta S^\ddagger$  are notoriously difficult to obtain from Eyring plots, analysis of “ $k_1$ ” yields a near-zero activation entropy, which is surprising for a bond-breaking reaction step. This difficulty is also seen in an Eyring analysis of  $k_{\text{obs}}$ : if the reaction is purely D,  $k_{\text{obs}}$  at low [L] will be proportional to  $k_1 k_2 / k_{-1}$ ,<sup>11,27,28</sup> and the value of  $\Delta S^\ddagger$  determined from  $k_a$  should thus be positive. Our observation that  $\Delta S^\ddagger$  (determined from  $k_a$ ) is near zero implies that the reaction is not proceeding by a D mechanism.

An additional difficulty with the assumption that reaction (1) proceeds in the D limit is the behavior of the ratio  $k_2/k_{-1}$ , particularly for L = pyrrolidine. While in our experiment we cannot determine  $k_{-1}$  and  $k_2$  independently, we can determine the differences ( $\Delta H^\ddagger_2 - \Delta H^\ddagger_1$ ) and ( $\Delta S^\ddagger_2 - \Delta S^\ddagger_1$ ) from the temperature dependence of  $k_2/k_{-1}$ . Such an analysis yields for L = pyrrolidine  $\Delta H^\ddagger_2 - \Delta H^\ddagger_1 = -23.3 \pm 8.1 \text{ kJ mol}^{-1}$ , which would mean that reaction of  $\text{CpMn}(\text{CO})_2$  with CyH must have an activation enthalpy at least that high. Such a large enthalpic barrier to solvation would be surprising, to say the least. ||

We began our analysis by pointing out that a D reaction can show apparently A behavior. To conclude it, we note that an A mechanism can show apparently D behavior as well, *i.e.* by yielding a linear double inverse plot.<sup>28</sup> If the mechanism is purely A, then the intercept of the double inverse plot will be proportional to  $1/k_a$ , and an Eyring analysis of “ $k_1$ ” will give the same  $\Delta H^\ddagger$  (although a different  $\Delta S^\ddagger$ ) as an analysis of  $k_{\text{obs}}$ .<sup>11</sup> While on the one hand,  $\Delta H^\ddagger$  determined from analysis of “ $k_1$ ” is very nearly the average of the determinations of  $\Delta H^\ddagger$  made by analysis of  $k_a$ , on the other, the intercepts of the double inverse plots, particularly for THF and pyrrolidine, are not consistent with those expected from an A mechanism (which should be  $R/k_a S_0$ ,<sup>28</sup> where  $R$  is the molar volume ratio of L and solv, and  $S_0$  the concentration of pure solvent).

The above analysis provides ways of explaining the reactions in terms of the limiting mechanisms, and indicates that apparently neither explanation is completely satisfactory; that is, the reaction does not appear to be going by either of the extreme mechanistic possibilities. In our view, the best way to understand this system is to conclude that the reaction proceeds *via* a dissociative interchange ( $I_d$ ) mechanism. This mechanism is consistent both with the aspects of the results that imply an early transition state (*e.g.* the near independence of  $\Delta H^\ddagger$  on the incoming ligand) as well as with those that imply that the

incoming ligand is involved in the reaction before desolvation of the intermediate is complete.

### (e) Reactivity trends and comparisons to other systems

$\Delta H^\ddagger$  of reaction (1) is significantly higher for L = CyPe than it is for the other ligands studied here. This difference appears to be primarily a steric effect. Previous workers have shown that the angle  $\theta$  between the two carbonyl groups in  $\text{CpMn}(\text{CO})_2\text{L}$  can be estimated from the relative intensities of the two C–O stretches.<sup>3,10</sup> Such an analysis indicates that while for the other three ligands,  $\theta \approx 100^\circ$  (slightly lower for pyrrolidine), for CyPe,  $\theta \approx 94^\circ$ , indicating additional steric crowding by the  $\eta^2$  ligand. We have previously found that  $\Delta H^\ddagger$  for ligand substitution at  $\text{W}(\text{CO})_5(\text{CyH})$  by 2- and 2,5-substituted THF is significantly higher than what would be predicted based on electronic effects alone.<sup>18</sup> A further indication that the high  $\Delta H^\ddagger$  for reaction with CyPe is a steric rather than electronic effect can be gleaned from the IR spectra of the product complexes (Table 1). While one might think *a priori* that of the four ligands used in the present study, the alkene would be the most strongly electron-withdrawing, surprisingly,  $k_{\text{CO}}$  is actually highest for furan. This observation implies that the backbonding to CyPe is not particularly strong, consistent with steric interference that restricts the geometry to one with limited orbital overlap between the HOMO of  $\text{CpMn}(\text{CO})_2$  and the  $\pi^*$  orbitals of CyPe. In contrast to  $\text{CpMn}(\text{CO})_2\text{L}$ , for  $\text{W}(\text{CO})_5\text{L}$ ,  $k_{\text{CO}}^{\text{trans}}$  is indeed higher for L = 1-hexene than it is for L = furan, and  $\Delta H^\ddagger$  for reaction of 1-hexene with  $\text{W}(\text{CO})_5(\text{CyH})$ <sup>30</sup> is not higher than what would be expected from a purely electronic effect.

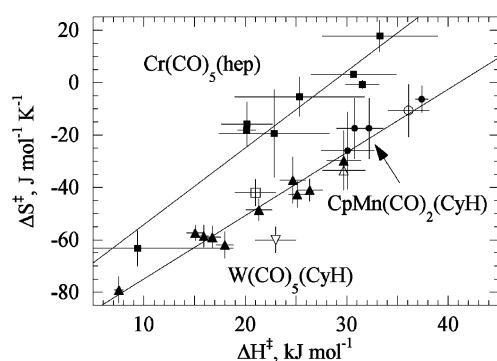
Although  $\Delta H^\ddagger$  of reaction (1) is similar for THF, furan and pyrrolidine, there are nonetheless significant differences in their reactivities, as can be seen from the results given in Table 2, Fig. 3, and the ESI. † Over the temperature range studied here, at a given temperature,  $k_a$  decreases in the order pyrrolidine > THF > furan, identical to that found in their reactions with  $\text{W}(\text{CO})_5(\text{CyH})$ . While for reactions of  $\text{CpMn}(\text{CO})_2(\text{CyH})$ , it is tempting, based on the near-independence of  $\Delta H^\ddagger$  on the ligand, to make arguments about the effect of the ligand on the activation entropy, our data are not unambiguous in this regard. For example, in the present case, unlike that of  $\text{W}(\text{CO})_5(\text{CyH})$ ,<sup>18</sup> there is not any obvious correlation between  $k_{\text{CO}}$  and  $\Delta S^\ddagger$ . Furthermore, the nature of the Eyring analysis makes division of  $\Delta G^\ddagger$  into enthalpic and entropic components necessarily rather imprecise, so that it is impossible for us to state definitively whether the differences in the behavior of the ligands are due to entropic or enthalpic factors. Clearly, the more basic ligand reacts more quickly; the differences are, however, much less dramatic than they were in the reactions of  $\text{W}(\text{CO})_5(\text{CyH})$ , consistent with our conclusion that  $\text{CpMn}(\text{CO})_2(\text{CyH})$  reacts *via* dissociative interchange with a relatively early transition state.

Finally, we turn to a consideration of the reactions of  $\text{CpMn}(\text{CO})_2(\text{CyH})$  in the broader context of the chemistry of alkane-solvated transition-metal intermediates. We have already mentioned the contrast in the ligand dependence of  $\Delta H^\ddagger$  between  $\text{CpMn}(\text{CO})_2(\text{CyH})$  and  $\text{W}(\text{CO})_5(\text{CyH})$ . To our knowledge, besides the studies of these two systems performed in our laboratory, the only other extensive kinetic study of the reactions of a particular alkane-solvated intermediate to have appeared in the literature is a report by Dobson and Zhang of ligand substitution at  $\text{Cr}(\text{CO})_5(\text{hep})$  (hep = *n*-heptane) with a variety of organic ligands.<sup>38</sup> For L = THF (the only organic ligand to have been measured for both intermediates), activation parameters of  $\Delta H^\ddagger = 17.2 \pm 0.8 \text{ kJ mol}^{-1}$  and  $\Delta S^\ddagger = -32.6 \pm 2.5 \text{ J mol}^{-1} \text{ K}^{-1}$  were reported for reaction of  $\text{Cr}(\text{CO})_5(\text{hep})$ . Although this result is consistent with the observation that  $\text{Cr}(\text{CO})_5(\text{alkane})$  complexes tend to react more dissociatively than analogous  $\text{W}(\text{CO})_5(\text{alkane})$  complexes<sup>39</sup> (*e.g.* for reaction of  $\text{W}(\text{CO})_5(\text{CyH})$  with THF,<sup>16</sup>  $\Delta H^\ddagger = 15.2 \pm 0.9 \text{ kJ}$

|| We note that it is in fact possible to reconcile this observation with a D mechanism. Since ground-state  $\text{CpMn}(\text{CO})_2$  is a triplet while  $\text{CpMn}(\text{CO})_2(\text{CyH})$  is apparently a singlet, it is possible that the difference in  $\Delta H^\ddagger$  is in fact due to differences in the location on the potential energy surface of the singlet–triplet surface crossing relative to unsolvated  $\text{CpMn}(\text{CO})_2$ . Our calculation of a difference in activation enthalpies of  $\sim 20 \text{ kJ mol}^{-1}$  is in fact remarkably similar to the observation of an energetic barrier of  $\leq 30 \text{ kJ mol}^{-1}$  for “solvation” of triplet  $\text{Fe}(\text{CO})_4$  in a  $\text{CH}_4$  matrix.<sup>24</sup> While we have no direct evidence in favor of this conjecture, neither can we exclude it based on our experimental results.

mol<sup>-1</sup> and  $\Delta S^\ddagger = -57.3 \pm 10.5 \text{ J mol}^{-1} \text{ K}^{-1}$ ), both  $\Delta H^\ddagger$  and  $\Delta S^\ddagger$  are considerably lower for the reaction of Cr(CO)<sub>5</sub>(hep) with THF than they are for the analogous reaction of CpMn(CO)<sub>2</sub>(CyH), even though they are both first-row complexes that appear to react more or less dissociatively.

Fig. 7 shows  $\Delta S^\ddagger$  plotted as a function of  $\Delta H^\ddagger$  for ligand substitution reactions of these three intermediates. In all three cases, a general trend can be seen: as  $\Delta H^\ddagger$  increases, so does  $\Delta S^\ddagger$ . Such “compensation effects” have long been known,<sup>40</sup> and in the case of solvated TM intermediates, this effect has been explained in terms of the reaction becoming more dissociative as  $\Delta H^\ddagger$  increases.<sup>18,38</sup> Fig. 7 reveals, however, a much more surprising correlation: When  $\Delta S^\ddagger$  is plotted as a function of  $\Delta H^\ddagger$  for ligand substitution reactions of [M]-alkane, results for W(CO)<sub>5</sub>(CyH) and CpMn(CO)<sub>2</sub>(CyH) lie on a *single* line, while those for Cr(CO)<sub>5</sub>(hep) lie on a *different* one. This difference in the kinetics of Cr(CO)<sub>5</sub>(hep) on the one hand from those of W(CO)<sub>5</sub>(CyH) and CpMn(CO)<sub>2</sub>(CyH) on the other is unlikely to be due to systematic differences in the way the data were collected: activation parameters reported by Dobson and coworkers for the reaction of W(CO)<sub>5</sub>(CyH) with 1-hexene<sup>30</sup> are consistent with our results for other ligands, Fig. 7, and pseudo-first order reaction rate constants for reaction of W(CO)<sub>5</sub>(CyH) with 1-hexene measured in our laboratory<sup>41</sup> are the same, to within experimental error, as those reported by Dobson *et al.*<sup>30</sup>



**Fig. 7**  $\Delta S^\ddagger$  as a function of  $\Delta H^\ddagger$  for ligand substitution reactions of various alkane-solvated transition metal intermediates. Shown are results for reactions of CpMn(CO)<sub>2</sub>(CyH) (●, this work), W(CO)<sub>5</sub>(CyH) (▲, △),<sup>16–19,30</sup> and Cr(CO)<sub>5</sub>(*n*-heptane) (■)<sup>38</sup> with organic ligands, and for recombination of [M] with CO for [M] = CpMn(CO)<sub>2</sub>(*n*-heptane) (○),<sup>11</sup> W(CO)<sub>5</sub>(CyH) (▽),<sup>35</sup> and Cr(CO)<sub>5</sub>(*n*-heptane) (□).<sup>35</sup> The solid lines are least-squares linear fits to the data for Cr(CO)<sub>5</sub>(heptane) and to the combined data for W(CO)<sub>5</sub>(CyH) and CpMn(CO)<sub>2</sub>(CyH). Error bars are 1σ uncertainties as reported in the original sources.

Several discussions of effects of the entropy of activation on the kinetics of ligand substitution at alkane-solvated TM intermediates have appeared in the literature.<sup>11,16,35</sup> These discussions all concerned the case of solvent effects on the reaction of a particular coordinatively unsaturated TM complex with a specific ligand. Thus, Breheny *et al.*<sup>35</sup> observed that for recombination of M(CO)<sub>5</sub>(alkane) with CO,  $\Delta H^\ddagger$  was essentially solvent-independent, but  $\Delta S^\ddagger$  was not; work in our laboratory<sup>16</sup> showed that for substitution at W(CO)<sub>5</sub>(CyH) by THF, over the temperature range studied, deuterating the solvent lowers  $k_a$  even though  $\Delta H^\ddagger$  is also lowered; and George and coworkers<sup>11</sup> found that the relative stabilities of CpM(CO)<sub>2</sub>(solv) (M = Mn, Re; solv = heptane, cyclopentane) as a function of solvent are strongly related to entropic factors. To our knowledge, however, no one has considered the possibility that in ligand substitution at alkane-solvated TM complexes, there may be solvent entropic effects operating that are *independent* of the particular coordinatively unsaturated complex reacting. The data shown in Fig. 7 hint at the existence of such effects. Not only do the

results for the two CyH complexes lie on one line while those for Cr(CO)<sub>5</sub>(hep) lie on another, but the slopes of the two lines –  $(2.41 \pm 0.14) \times 10^{-3} \text{ K}^{-1}$  for the CyH complexes,  $(2.93 \pm 0.34) \times 10^{-3} \text{ K}^{-1}$  for Cr(CO)<sub>5</sub>(hep) – are nearly identical. It is as if, for a given  $\Delta H^\ddagger$ ,  $\Delta S^\ddagger$  is simply offset by a constant amount ( $16 \pm 9 \text{ J mol}^{-1} \text{ K}^{-1}$ ) when the solvent is changed; in other words, there appears to be a compensation effect across solvents as well as across ligands.

It has been shown<sup>40d</sup> that for a reaction whose kinetics are measured in two different solvents, differences in solvent reorganization energy can lead to a compensation effect if this energy is large compared to the energy change in the process under study. While the DFT calculations discussed above imply that solvation energetics (on the order of 10 kJ mol<sup>-1</sup>) do not dominate the overall activation energy of reaction (1), we cannot exclude differences in reorganization energy as an explanation for the differences in reactions in hep and CyH. Another possible explanation for the solvent dependence of the relation between  $\Delta H^\ddagger$  and  $\Delta S^\ddagger$  for reaction (1) is that it is a result of differences in solvent viscosity. Over the temperature range in which the experiments were performed, CyH is more than twice as viscous as hep.<sup>42</sup> Therefore, the “solv” molecule being released from the intermediate has more freedom to move about in the solvent when solv = hep than when solv = CyH, reducing hindrance to the motions of low-frequency vibrations such as metal–solv bending and internal rotation. This process will in turn will give the transition state additional entropy in hep relative to CyH.

Fig. 7 also shows the relation between  $\Delta H^\ddagger$  and  $\Delta S^\ddagger$  for recombination of Cr(CO)<sub>5</sub>(hep),<sup>35</sup> CpMn(CO)<sub>2</sub>(hep),<sup>11</sup> and W(CO)<sub>5</sub>(CyH)<sup>35</sup> with CO. In all three cases,  $\Delta S^\ddagger$  lies below the data points for the other reactions in the same solvent. That is, in comparison to the reactions of the organic ligands,  $\Delta H^\ddagger$  for recombination is higher than expected based on the observed  $\Delta S^\ddagger$  (alternatively, one could say that  $\Delta S^\ddagger$  is lower than expected based on the observed  $\Delta H^\ddagger$ ). The deviation of CO from the behavior of the other ligands presumably is due to a combination of electronic and steric factors. Unlike the ligands studied here, CO is both a poor electron donor and a strong electron acceptor. As was mentioned above, at least for an associative process,  $\Delta H^\ddagger$  for reaction (1) rises as a ligand’s ability to donate electrons decreases, apparently because such ligands are less able to stabilize the electron-poor ligand exchange transition state. Furthermore, unlike all of the other ligands studied, CO bonds to the metal *via* orbitals that are cylindrically symmetric with respect to the M–L bond. This symmetry, combined with the small size of CO, means that CO will be sterically much less demanding than organic ligands that have more directed orbitals. Thus, we would expect  $\Delta V^\ddagger$ , and hence  $\Delta S^\ddagger$ ,<sup>43</sup> to be lower for recombination with CO than for exchange by the other ligands.

The net effect of this simultaneous raising of  $\Delta H^\ddagger$  and lowering of  $\Delta S^\ddagger$  will be to make reaction with CO more associative (or at least apparently more associative) than reaction with other ligands. In addition to explaining the apparently anomalous behavior of CO relative to organic ligands, these considerations can reconcile the conclusion of George and coworkers<sup>11</sup> that reaction (1) appears to proceed *via* an I<sub>a</sub> mechanism for solv = hep and L = CO with the conclusion reached in the present work that for solv = CyH and L = an organic ligand, the reaction mechanism appears to be best described as I<sub>d</sub>.

## Conclusions

In the present study, we have used TRIR to measure ligand substitution at cyclohexane (CyH)-solvated CpMn(CO)<sub>2</sub>. Our results enable us to reach several conclusions:

1. The reaction of CpMn(CO)<sub>2</sub>(CyH) is mechanistically ambiguous, the form of the pseudo-first order rate constant being consistent with the predictions of both limiting mechan-

isms (dissociative and associative). This ambiguity is apparently fundamental and due to the solvent's participation as a reagent.

2. Despite this mechanistic ambiguity, we have determined that the results (in particular, the lack of a strong dependence of  $\Delta H^\ddagger$  on the ligand) are most consistent with a dissociative interchange ( $I_d$ ) mechanism. Analysis of the results allows us to place a lower limit of  $34 \pm 3 \text{ kJ mol}^{-1}$  on the  $\text{Cp}(\text{CO})_2\text{Mn}-\text{CyH}$  bond dissociation energy.

3. The reaction activation parameters  $\Delta H^\ddagger$  and  $\Delta S^\ddagger$  are positively correlated (*i.e.* show a "compensation effect"). From our observation that the explicit relation between  $\Delta H^\ddagger$  and  $\Delta S^\ddagger$  is identical to that observed for reactions of  $\text{W}(\text{CO})_5$ - $(\text{CyH})$ , but significantly different from that observed for reactions of  $\text{Cr}(\text{CO})_5(\text{hep})$ , we conclude that this relation is determined primarily by the solvent in which reaction takes place rather than by any particular innate properties of the solvated coordinatively unsaturated complex.

Further studies are currently underway in our laboratory to resolve the mechanistic ambiguities and to further clarify the relationship between the solvent and the activation parameters of ligand substitution at a solvated intermediate.

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