Note

Displacement of the heptane solvent from (η^5-C$_5$H$_5$)Re(CO)$_2$(heptane): A flash photolysis study using infrared detection

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Abstract

The displacement of the heptane solvent molecule from the (η^5-C$_5$H$_5$)Re(CO)$_2$(heptane) complex by a variety of ligands is studied. The substitution reaction proceeds through an I_d mechanism since changes in the electronic and steric properties of the incoming ligand do not influence the reaction rate significantly. Activation parameters suggest a lower limit of 57.3 ± 0.9 kJ/mol for the strength of the Re–heptane interaction.
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1. Introduction

It is well established that coordinatively unsaturated transition metal complexes generated by photolysis of the fully ligated parent, can form weak bonds with alkane solvent molecules [1]. For example, UV photolysis of Cr(CO)$_6$ in cyclohexane solvent forms the Cr(CO)$_5$(cyclohexane) complex within 0.5 ps of CO loss from the chromium center [2]. The bond between the alkane and the metal center can be described as an interaction between the sigma electron density of the alkane C–H bond and an acceptor orbital on the metal center. Because transient metal–alkane complexes have been implicated as intermediates in a variety of reactions [3], many studies have focused on the energetics and mechanism of solvent displacement from the metal center. These investigations have primarily focused on the Group 6 metal carbonyls, M(CO)$_5$(solvent), [M = Cr,

Mo, W], and the CpMn(CO)$_2$(solvent) [Cp = η^5-C$_5$H$_5$] complexes although several other metal–alkane complexes have also been studied [4]. While dependent upon the identity of the metal, kinetic studies in conjunction with thermodynamic measurements using the technique of photoacoustic calorimetry have found that the strength of the metal–alkane bond ranges from 33 to 59 kJ/mol [1].

In contrast to the Group 6 and manganese carbonyls, fewer studies have been performed on the analogous CpRe(CO)$_2$(alkane) species. Previous work has shown that compared to other metal–alkane interactions, the CpRe(CO)$_2$(alkane) bond is among the most stable [4b,5]. Thus, while the Cr(CO)$_5$(heptane) and CpMn(CO)$_2$(heptane) complexes have lifetimes on the microsecond timescale at room temperature, the CpRe(CO)$_2$(heptane) complex has a lifetime of several milliseconds. The anomalous stability of the Re–alkane intermediate allowed for the characterization of the CpRe(CO)$_2$(cyclopentane) and (i-PrCp)Re(CO)$_2$(pentane) (i-PrCp = η^5-(isopropyl)cyclopentadienyl) complexes by NMR spectroscopy [6]. The displacement of

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the heptane solvent from $CpRe(CO)_2(heptane)$ by CO was investigated by George et al. [5] and the reaction was tentatively assigned as proceeding through an interchange mechanism with an activation enthalpy of 46.2 ± 2.0 kcal/mol. The mechanism of the solvent displacement reaction appears to depend upon the strength of the Re–solvent bond. Thus, while dissociative displacement of alkane from $CpRe(CO)_2(alkane)$ can be ruled out, the displacement of the more strongly bound benzene solvent has been shown to proceed via a dissociative mechanism [7]. Furthermore, to our knowledge, there have been no studies that have investigated the effect of altering the electronic and steric properties of the *displacing ligand* (L) on the mechanism and energetics of the following reaction:
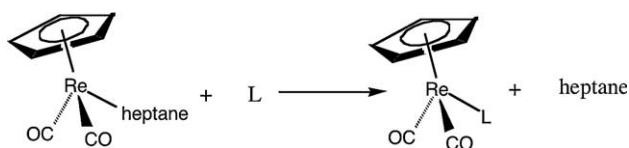
Such experiments can shed further light on the substitution mechanism and energetics. In this paper, we present the results of a flash photolysis study employing infrared detection in which the reaction of the $CpRe(CO)_2(heptane)$ complex with several ligands is investigated yielding an estimate for the strength of the Re–heptane bond.

2. Experimental

The laser flash photolysis apparatus consists of a Continuum Nd:YAG laser (Surelite I-10) operating at 266 nm (50 mJ/pulse) with a 1 Hz repetition rate. After two harmonic separators, a Pelin-Broca prism (CVI optics) was used to separate the residual 532 nm second harmonic from the 266 nm pump beam. The monitoring system included a Laser Components liquid nitrogen cooled Pb-salt diode laser (tunable range from 1930 to 1850 cm^{-1}) and a Kolmar Technologies MCT detector fitted with a Ge window (70 ns risetime). The signal was captured by a LeCroy 5310 A digital storage oscilloscope and sent to a computer for data analysis. The IR probe beam was focused through a 1/8 m Oriel 77250 monochromator with a 200 line/mm grating which is blazed at 5 µm to afford an operating resolution of 4 cm^{-1}. The pump beam was de-focused by a 200 mm CaF_2 plano concave lens to ensure a beam diameter of 25 mm at the cell. The UV pump and 5–6 mm IR probe beams were combined prior to passing through the temperature controlled IR cell (Harrick Scientific) using a UV/IR dichroic mirror. The photolysis solution was circulated through the IR cell (0.75 mm pathlength, CaF_2 windows) to ensure that a fresh sample was photolyzed

by each laser shot. The solution temperature ($\pm 1 \, ^\circ C$) was monitored by inserting a thermocouple tip into the circulating solution located at the exit of the IR cell. Signal was averaged over ten laser shots.

The photolysis solution was made by canulating under an Ar atmosphere the required volume of heptane (Acros, anhydrous grade) into a 100 mL round bottom flask containing a weighed amount of $CpRe(CO)_3$ resulting in a ≈ 0.6 mM solution. The required volume of ligand was syringed in and the solution was circulated through the IR cell under an Ar atmosphere. All runs were conducted under psuedo first-order conditions. The observed rate constants, k_{obs}, were obtained by fitting the decrease in the signal of the $CpRe(CO)_2(heptane)$ complex to a first-order exponential function. Rate constants are reported with 1σ uncertainties and the errors in the activation parameters are at the 95% confidence level.

All reagents were anhydrous grade with 99% purity and were purchased from either Aldrich or Acros. The metal complex $CpRe(CO)_3$ was >97% purity and used as received.

3. Results and discussion

Photolysis of a 0.6 mM heptane solution of $CpRe(CO)_3$ with 266 nm light at 294 K results in the generation of a long lived transient (≈ 5 ms) absorbing at 1892 cm^{-1}. This transient is formed within the laser flash and by reference to previous studies is assigned to the $CpRe(CO)_2(heptane)$ complex which has been observed at 1945 and 1890 cm^{-1} [5]. In the presence of 1-hexene, the $CpRe(CO)_2(heptane)$ transient decays at a rate equal to the formation of the resulting $CpRe(CO)_2(1\text{-hexene})$ product observed at 1907 cm^{-1} (see Fig. 1). As shown in Fig. 2, k_{obs}, is a linear function of the 1-hexene concentration which was varied over a ten-fold range
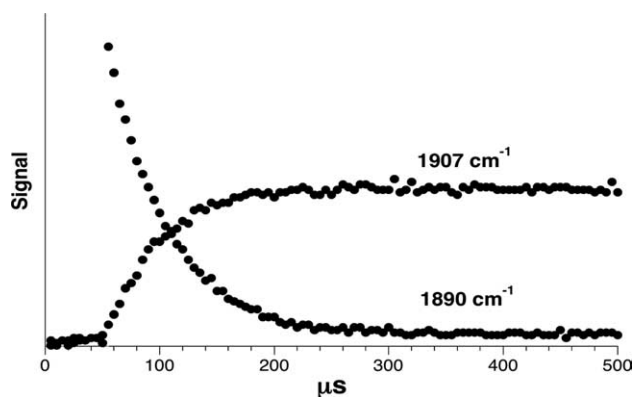

Fig. 1. Decay of the $CpRe(CO)_2(heptane)$ complex at 324 K ([1-hexene] = 0.47 M) observed at 1892 cm^{-1} and concurrent growth of the $CpRe(CO)_2(1\text{-hexene})$ product at 1907 cm^{-1}.
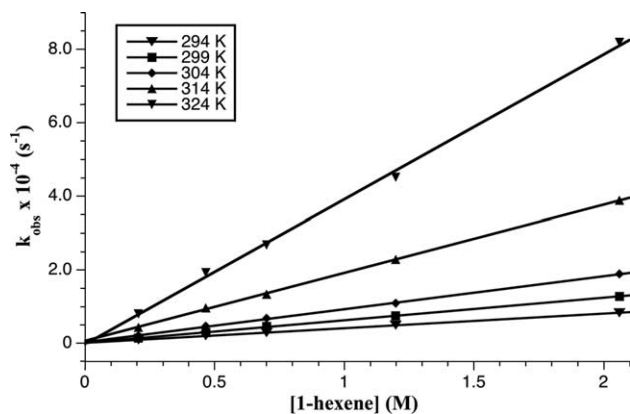
Fig. 2. A plot of k_{obs} vs. [1-hexene] from 294 to 324 K.

Fig. 3. An Eyring plot obtained from the second order rates constants for the reaction of CpRe(CO)$_2$(heptane) with various ligands.

(0.21–2.1 M). Unfortunately, as noted in previous studies, a linear dependence of k_{obs} on [L] does not assist in distinguishing between associative, dissociative, or interchange mechanisms of solvent displacement from the metal center [8]. We therefore investigated the reactivity of the CpRe(CO)$_2$(heptane) complex with other nucleophiles to assist in the determination of the substitution mechanism.

The results shown in Table 1 suggest that the reactivity of the ligands with CpRe(CO)$_2$(heptane) increases in the order, 1-hexene < 1-methylpiperidine (CH$_3$Pip) < tetrahydrofuran (THF) < piperidine.

Thus, at 294 K piperidine reacts almost three times faster with CpRe(CO)$_2$(heptane) than does 1-hexene. The higher reactivity of piperidine relative to 1-hexene in analogous reactions has been observed previously. For example, piperidine displaces heptane from Cr(CO)$_5$(heptane) ≈ 4 times faster than does 1-hexene [9].

Given the large difference in the electron donating and bonding properties of the 1-hexene and piperidine ligands, the relatively small difference in the respective reaction rates seems to rule out both an associative and I_a pathway but favors an I_d mechanistic assignment for the substitution reaction. An I_d mechanism would imply that the reaction proceeds through a single transition state in which the Re–heptane bond is mostly

broken with the incoming ligand either present in the first solvation shell or loosely bound to the metal center. Importantly, the reaction rate would not exhibit a strong dependence on the electronic and steric properties of the incoming ligand, as observed. The displacement of the cyclohexane solvent from the analogous CpMn(CO)$_2$(cyclohexane) complex was also shown to be consistent with an I_d mechanism [4e].

Characterization of the transition state as one in which the Re–heptane bond is mostly broken without significant Re–L bond formation, is consistent with the trend in the activation parameters obtained from the Eyring plots shown in Fig. 3 and presented in Table 2

The activation enthalpies increase from 46.1 kJ/mol (piperdine) to 57.3 kcal/mol (1-hexene) as the nucleophilicity of the incoming ligand decreases suggesting that the transition state becomes more dissociative with respect to the Re–heptane interaction. The activation entropies are also consistent with this trend since they become more positive when the incoming ligand is varied from piperdine to 1-hexene. The increase in the activation enthalpy as the ligand is changed from piperidine to CH$_3$Pip is most likely due to increased steric hindrance at the nitrogen donor ligand. Thus, relative to piperidine, the Re–heptane bond has to be disrupted to a greater degree before the CH$_3$Pip ligand can bond to the metal center. The activation parameters suggest that the

Table 1
Second order rate constants for the reaction of the CpRe(CO)$_2$(heptane) complex with various ligands

T (K)	Second order rate constants, $k \times 10^{-3}$ (M^{-1} s^{-1})			
	1-Hexene	CH$_3$Pip	THF	Piperidine
294	3.99 ± 0.05	6.54 ± 0.12	9.19 ± 0.47	11.7 ± 0.6
299	6.09 ± 0.07	9.78 ± 0.12	14.0 ± 0.5	15.6 ± 0.4
304	8.95 ± 0.12	15.4 ± 0.4	19.2 ± 0.8	22.0 ± 0.4
314	18.5 ± 0.2	27.3 ± 0.4	35.7 ± 1.3	41.1 ± 2.7
324	39.3 ± 0.9	54.4 ± 1.2	64.9 ± 4.0	72.3 ± 4.1

The rate constants were obtained from the slopes of the k_{obs} vs. [L] plots shown in Fig. 1 in the case of L = 1-hexene.
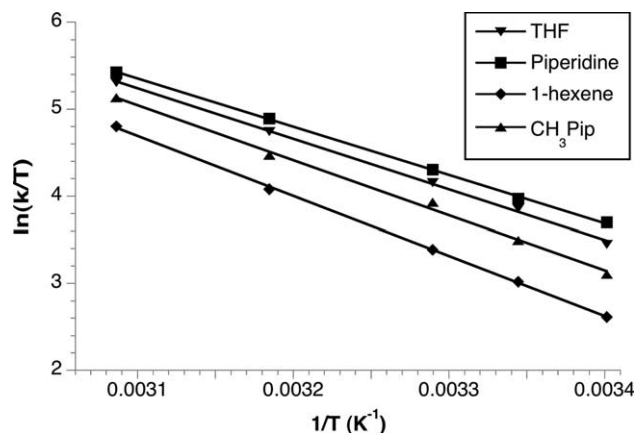
Table 2
Activation parameters obtained from the Eyring plots shown in Fig. 3 for the reaction of CpRe(CO)$_2$(heptane) with ligand, L

Ligand	$\Delta H^{\ddagger}$ (kJ/mol)	$\Delta S^{\ddagger}$ (J/mol K)
1-Hexene	57.3 ± 0.9	$+19.0 \pm 3.0$
CH$_3$Pip	52.5 ± 2.3	$+1.0 \pm 7.0$
THF	48.2 ± 1.4	-4.5 ± 4.4
Piperidine	46.1 ± 0.8	-10.2 ± 2.5

CpRe (CO)$_2$–heptane bond strength has a lower limit of 57.3 kJ/mol, greater than the 46.2 kJ/mol estimate obtained from previous kinetic studies [5]. This estimate is consistent with the observation that among other metal–alkane complexes, the Re–heptane bond is the strongest metal–alkane interaction [4b,5]. It is worth noting that the lower limit of the metal–alkane bond strength in the analogous CpMn(CO)$_2$(alkane) (alkane = heptane, cyclohexane) complex has been estimated at $\approx$33 kJ/mol [4e,10]. Thus, as is often the case with third row versus first row metals, the Re–heptane bond is considerably stronger than its first row congener.

4. Conclusions

The substitution of the weakly coordinated heptane solvent molecule from the CpRe(CO)$_2$(heptane) complex by a variety of ligands has been investigated. The rate of the displacement reaction does not vary significantly despite differences in the electronic and steric properties of the incoming ligands. This observation suggests that the heptane solvent is displaced from the Re center by an I_d mechanism. The activation parameters suggest that the transition state for this reaction becomes more ''dissociative'' as the ligand is varied from piperidine to 1-hexene. Thus, the activation enthalpy of 57.3 kJ/mol obtained from the reaction of CpRe(CO)$_2$(heptane) with 1-hexene provides a lower limit to the Re–heptane bond strength.

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