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Displacement Kinetics of 1,5-Cyclooctadiene from $Mo(CO)_4(\eta^{2:2}$-1,5-cyclooctadiene) by Bis(diphenylphosphino)methane

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The kinetics of the thermal substitution of 1,5-cyclooctadiene (COD) from $[Mo(CO)_4(\eta^{2:2}$-COD)] (**1**) by bis(diphenylphosphino)methane (DPPM) and the formation of $[Mo(CO)_4(DPPM)]$ (**6**) was studied by quantitative FT-IR spectroscopy. The reaction rate exhibits first-order dependence on the concentration of **1**, and the observed rate constant, k_{obs}, depends on the concentrations of both leaving COD and entering DPPM ligand. From the evaluation of data collected, one can propose a mechanism in which the rate-determining step is the cleavage of one of two Mo–olefin bonds. A rate law is derived from the proposed mechanism. The evaluation of the kinetic data gives the enthalpy of activation $\Delta H^* = 80$ (±1) kJ·mol^{-1} and the entropy of activation $\Delta S^* = -55$ (±2) J·mol^{-1}·K^{-1}. The negative entropy value obtained tends to suggest an associative mechanism in transition states. Material balance and yield of product do not show any significant depletion implying that there is no decomposition in noticeable amounts during the substitution reaction.

Introduction

The tetracarbonyl(η-diene)metal(0) complexes of the group 6 elements have been known for over three decades[1] and used as $M(CO)_4$ transfer reagents to prepare a variety of $M(CO)_4L_2$ compounds (L = donor ligand). Furthermore, $M(CO)_4(\eta$-diene) complexes have been shown to be intermediates in the catalytic transformations of dienes using $M(CO)_6$.[2] Information relevant to the lability of the coordinated dienes is of interest in systematic organometallic synthesis and in the design of homogeneous catalytic processes. However, only little work has been carried out on the displacement of dienes in $M(CO)_4(\eta$-diene) complexes.[3,4] This type of substitution reaction in which a bidentate ligand is replaced by two monodentate ligands has already attracted interests. It has been found that a stepwise replacement of the C=C bonds of diene occurs with the monodentate ligands. However, the monosubstitution product has not been isolated, nor has any compelling evidence like spectral observation been reported for its formation in the solution during the reaction. From the evaluation of the kinetic study, it has been concluded that the cleavage of one of the M–olefin bonds is the rate-determining step in the proposed mechanism.[5,6] The proposed mechanism also involves the formation of the very reactive 14-electron species $M(CO)_4$, which undergoes a fast reaction with the entering ligands since the latter have been used in at least 10-fold excess to ensure the pseudo-first-order condition. From the catalytic standpoint, the concentration of the entering ligand must be low to provide reversible coordination of diene to the transition metal center. In low concentrations of the entering ligand, both the entering and leaving ligands are expected to coordinate the very reactive $M(CO)_4$ fragment. This would reverse the reaction back to $M(CO)_4(\eta$-diene). Therefore, the observed rate constant is expected to depend on the concentration of the leaving ligand in low concentration of entering ligand.

The substitution of diene in the same complex with a bidentate ligand like bis(dialkylphosphino)alkane is thought to be much more interesting, as it is expected to provide more information about the mechanism. As a model reaction, we report here our kinetic study on the substitution of 1,5-cyclooctadiene (COD) in $Mo(CO)_4(\eta^{2:2}$-COD) (**1**) by bis(diphenylphosphino)methane (DPPM). It was found that the labile COD ligand in **1** is replaced by DPPM at an observable rate in the temperature range 35–50 °C to form the known complex $Mo(CO)_4(DPPM)$ (**6**).[7]

$$Mo(CO)_4(\eta^{2:2}\text{-COD}) + DPPM \xrightarrow{\Delta} Mo(CO)_4(DPPM) + COD$$

The kinetics of this substitution reaction was studied by quantitative FT-IR spectroscopy. Since both the reactant and product give sharp absorption bands of the CO stretching, the intensity of which is generally very sensitive to changes in concentration, the use of IR spectroscopy enables one to follow the reaction precisely and to control the material balance and the yield at any conversion up to 80–90%.

Experimental Section

All of the reactions and manipulations were carried out either in vacuum or under a dry and deoxygenated nitrogen atmosphere. Solvents were distilled after refluxing over metallic sodium or phosphorus pentoxide

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under nitrogen for 3–4 days and stored until used. Hexacarbonylmolybdenum(0), 1,5-cyclooctadiene, bis(diphenylphosphino)methane, and trimethyl phosphite were purchased from Aldrich Chemical Co., Ltd., Dorset, England, and used without further purification. The thermal reactions and other treatments of organometallic compounds such as purification and crystallization were followed by taking IR spectra at appropriate intervals. NMR spectra were recorded on a Bruker AC-200 spectrometer (200.131 MHz for ^{1}H, 81.011 MHz for ^{31}P, and 50.28 MHz for ^{13}C). Phosphoric acid (85%) in a capillary tube was used as external reference for ^{31}P-NMR chemical shifts, while TMS was used as internal reference for ^{1}H-, and ^{13}C-NMR chemical shifts. Infrared spectra were recorded from solution on a Perkin-Elmer 16 PC FT-IR spectrometer. Elemental analyses were carried out on an HP 185 CHN analyzer. A circulating thermostat bath (Heto CB 11e) was used to provide a constant temperature during the kinetic measurements. Ethylene glycol was circulated from the thermostat through the heating jacket of the reaction vessel.

Tetracarbonyl($\eta^{2:2}$-1,5-cyclooctadiene)molybdenum(0), $Mo(CO)_4(\eta^{2:2}-C_8H_{12})$ (1). 1 was prepared according to the procedure described in the literature[1a] with minor modifications. A 1.0-g amount (3.7 mmol) of $Mo(CO)_6$ and 2.0 mL (13 mmol) of COD in *n*-heptane (30 mL) are refluxed for 24 h at the boiling point of *n*-heptane. Solvent and excess COD are removed in vacuum, and the residue is dissolved in *n*-hexane and filtered. Cooling the solution to −35 °C yields yellow crystals of $Mo(CO)_4(\eta^{2:2}$-COD), which are dried in vacuum and identified by means of IR and NMR spectroscopy. Anal. Calcd for $C_{12}H_{12}O_4Mo$: C, 45.50; H, 3.79. Found: C, 44.89; H, 3.59. ^{1}H-NMR (chloroform-*d*) (ppm): =CH, 4.13; CH_2, 2.04, 1.68. ^{13}C-NMR (benzene-d_6) (ppm): CO, 216.48, 216.43; CH_2, 29.44; =CH, 94.39. IR (CO; toluene): 2034.5, 1939.5, 1889.5 cm^{-1}.

(Bis(diphenylphosphino)methane)tetracarbonylmolybdenum(0), $Mo(CO)_4(C_{25}H_{22}P_2)$ (6). A 0.3-g amount (1 mmol) of 1 and 0.36 g (1 mmol) of DPPM are dissolved in 20 mL of toluene. The reaction mixture is refluxed for 1 day at 45 °C. Cooling the solution up to −78 °C yields pale yellow crystals of 6, which are dried and identified by means of IR and NMR spectroscopy. Calcd for $C_{29}H_{22}O_4P_2Mo$: C, 58.80; H, 3.74. Found: C, 57.00; H, 3.66. ^{13}C-NMR (chloroform-*d*) (ppm) [$J(^{31}P-^{13}C)$ (Hz) in parentheses]: CO, 218.85 (20.2), 210.47 (17.3); CH_2, 49.7 (36.8); C_6H_5, 136.2 (36.6), 131.6 (13.8), 128.7 (9.8), 130.17. IR (CO; toluene): 2021.5, 1925.5, 1913, 1889 cm^{-1}.

Kinetic Measurements. All spectral measurements were recorded in toluene. IR cells with a 0.1946-mm path length and calcium fluoride windows were used. Extinction coefficients of $Mo(CO)_4(\eta^{2:2}$-COD) (1) and $Mo(CO)_4$(DPPM) (6) were determined from the toluene solutions of the pure complexes in the concentration range 5×10^{-4}–2×10^{-3} mol·L^{-1}. The molar extinction coefficients of 2514 L·cm^{-1}·mol^{-1} at 2034.5 cm^{-1} for 1 and 3520 L·cm^{-1}·mol^{-1} at 2021.5 cm^{-1} for 6 were determined by plotting the absorbance at the highest frequency peak of both complexes versus their concentrations. By using these values, the concentrations of 1 and 6 during the reaction of $Mo(CO)_4(\eta^{2:2}$-COD) with DPPM could be determined from the measured IR absorbances at any stage of the reaction, with a standard deviation of 5×10^{-5} mol·L^{-1}. Thus the material balance could also be checked at any point of conversion.

$Mo(CO)_4(\eta^{2:2}$-COD) was added into the preheated solution of DPPM in toluene. The initial concentration of 1 was $C_0(\mathbf{1}) = 0.01$ mol·L^{-1}. Samples of the solution for IR measurements were withdrawn periodically (every 5 min) from the reaction vessel using a syringe. The rates of the reaction were determined by following the disappearance of the highest frequency peak of the educt 1 since it was the only distinct peak which did not overlap with the peaks of the product 6. By this way, quantitative data on the rates of reactions were obtained easily and accurately. The graphical evaluation of the data provided the observed rate constants. In order to study the dependence of the rate on leaving COD and entering DPPM ligands, the kinetic experiments were performed at 45 °C by varying the concentrations of DPPM or COD in the solution of 1 ($C_0(\mathbf{1}) = 0.01$, $C(\text{DPPM}) = 0.005$–1.0, $C(\text{COD}) = 0$–0.1 mol·L^{-1}). The activation parameters were obtained from the temperature dependence of the observed rate constant in the range 35–50 °C. In addition, the kinetic study was repeated in the presence of another potential ligand such as $P(OCH_3)_3$ together with DPPM in order to obtain more information about the intermediates. This reaction yielded [$Mo(CO)_4$(DPPM)], *cis*-[$Mo(CO)_4(P(OCH_3)_3)_2$], and *cis*-[$Mo(CO)_4$(DPPM)($P(OCH_3)_3$)].

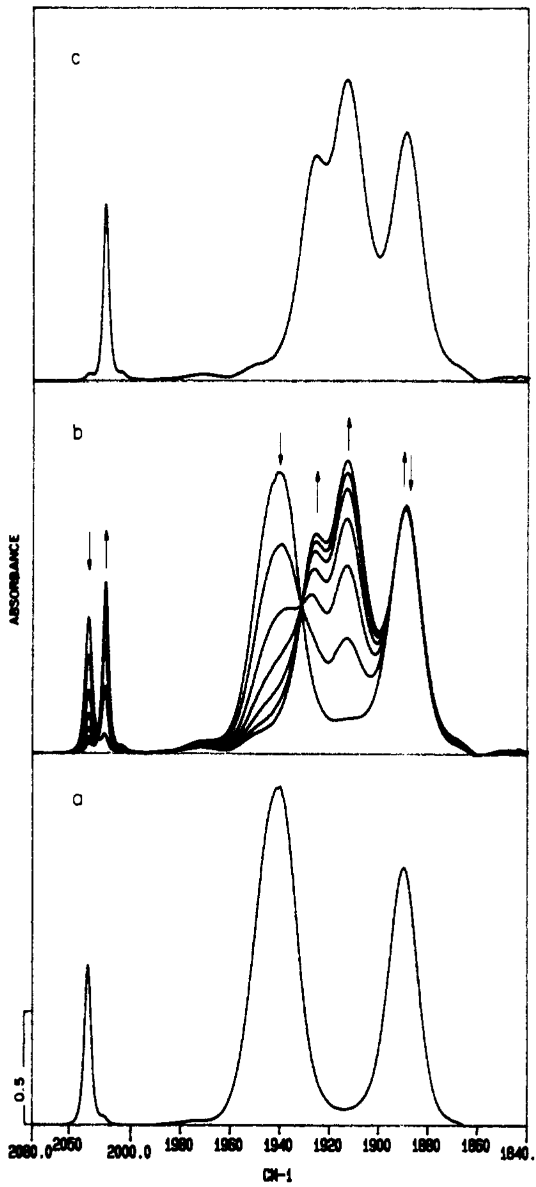

Figure 1. IR spectra of (a) $Mo(CO)_4(\eta^{2:2}$-COD), (b) $Mo(CO)_4(\eta^{2:2}$-COD) and $Mo(CO)_4$(DPPM) during the substitution reaction, and (c) $Mo(CO)_4$(DPPM) in toluene.

Results and Discussion

The IR absorption spectrum of $Mo(CO)_4(\eta^{2:2}$-COD) (1) taken in toluene (Figure 1a) gives three absorption bands in the CO-stretching region indicating that the complex has a local C_{2v} symmetry for its $Mo(CO)_4$ moiety and thus a CO stretching vibrational pattern ($2A_1 + B_1 + B_2$).[8] Two of the four bands expected are obviously overlapping. The ^{1}H-NMR spectrum of 1 gives three signals at 4.13 (=CH), 2.04, and 1.68 ppm (–CH_2–). The signal of the olefinic proton shows a remarkable coordination shift. The $^{13}C\{^1H\}$-NMR spectrum of 1 shows two signals with relative intensities of 1:1 for carbonyl groups and two signals for the COD ligand. The carbonyl signal at lower magnetic field is assigned to the CO groups trans to the COD.[9] The signal of the olefinic carbon atoms at 94.39 ppm is highly shifted toward the higher magnetic field compared to the free COD molecule as expected.[10]

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The IR absorption spectrum of $Mo(CO)_4$(DPPM) (**6**) shows four absorption bands in the CO-stretching region (Figure 1c) which clearly suggests a C_{2v} symmetry for the $Mo(CO)_4$ moiety having a CO stretching pattern of $2A_1 + B_1 + B_2$.[7,11] In the $^{13}C\{^1H\}$-NMR spectrum of **6** two signals are observed for the carbonyl groups in addition to the signals of the DPPM ligand. The more deshielded carbonyl signal is assigned to the CO groups trans to the DPPM ligand, which is a weaker π-acceptor compared to carbon monoxide. In addition, carbonyl groups trans to phosphorus ligands are expected to show a larger $^2J(^{31}P-^{13}C)$ coupling.[12] The $^{31}P\{^1H\}$-NMR spectrum of **6** shows a singlet at 0.0 ppm relative to H_3PO_4.[13]

The kinetics of the substitution of COD in $Mo(CO)_4(\eta^{2:2}$-COD) by DPPM was followed with quantitative FT-IR spectroscopy. In the CO-stretching region of the IR spectrum, three absorption bands of $Mo(CO)_4(\eta^{2:2}$-COD) (two of four are overlapping) are replaced by the four new bands for $Mo(CO)_4$(DPPM) after the complete reaction (Figure 1a,c). When the reaction is conducted for example at 45 °C, a gradual decrease is observed in the intensities of the absorption bands for **1** while new four bands for the product **6** are concomitantly growing (Figure 1b). The observation of nice isosbestic points indicates a straightforward conversion of the reactant into the product without side or subsequent reactions.[14] In other words, there are only two absorbing species throughout this reaction.

A brief inspection of the spectra in Figure 1 shows that the highest frequency bands of the reactant and product at 2034.5 and 2021.5 cm^{-1}, respectively, do not overlap and remain well resolved during the whole reaction. Therefore, these two IR bands are selected to follow the consumption of the educt **1** and the growth of the product **6**, respectively.

Figure 2a shows a plot of concentration versus time for the thermal substitution reaction of **1** with DPPM at 45 °C, for which the time-resolved spectra are given in Figure 1. This graph shows an exponential decay for the starting material **1** and an exponential growth for the product **6**. The logarithmic plot of the concentration of **1** against time gives a straight line (Figure 2b) for the aforementioned reaction even at low concentration of DPPM. This indicates that the displacement of COD from $Mo(CO)_4(\eta^{2:2}$-COD) by DPPM obeys the pseudo-first-order kinetics with a correlation coefficient around 0.99. The slope of the straight line gives the observed rate constant, k_{obs} (s^{-1}).

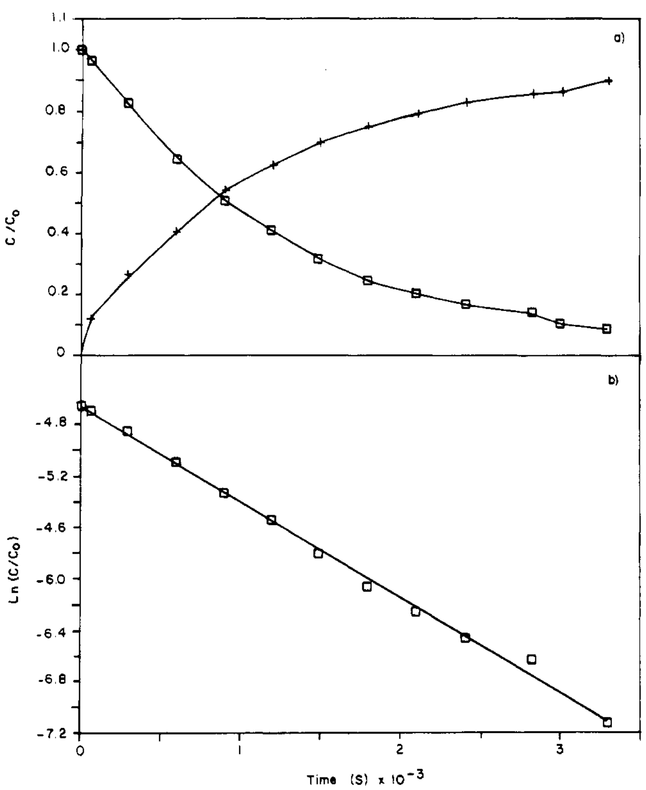

Figure 2. Time-dependent behavior of concentrations of $Mo(CO)_4(\eta^{2:2}$-COD) and $Mo(CO)_4$(DPPM): (a) Concentration versus time plot for the substitution reaction (□, $Mo(CO)_4(\eta^{2:2}$-COD); +, $Mo(CO)_4$(DPPM)); (b) plot of the first-order reaction kinetics for the substitution reaction.

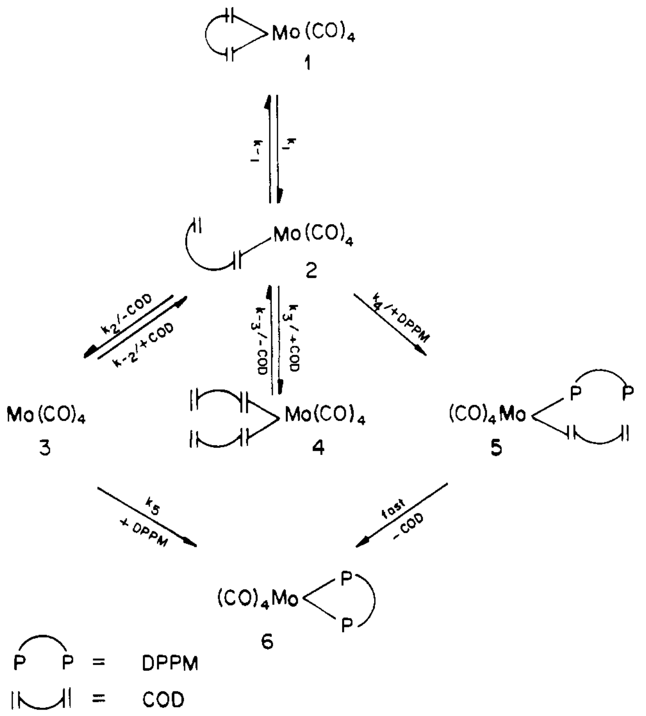

Figure 3. Proposed mechanism for the substitution reaction of COD in $Mo(CO)_4(\eta^{2:2}$-COD) with DPPM.

The thermal reaction of $Mo(CO)_4(\eta^{2:2}$-COD) with DPPM is a ligand exchange reaction. Therefore one has to consider the effect of entering and leaving ligand in order to study the reaction kinetics of the ligand substitution reaction. At this point it is important to consider all the possible steps in the substitution reaction to propose a reaction mechanism which will be in agreement with the experimental results (Figure 3). The reaction involves a stepwise displacement of COD from **1**. The initial, rate-determining step is the partial cleavage of the metal–diene bond.[5,6] A series of experiments were performed to check whether a CO detachment would occur as an initial step. As mentioned before, heating a pure solution of **1** in toluene at 45 °C did not give any reaction at all. In a similar reaction under CO pressure (1 atm) at the same temperature, the complex **1** was completely converted into hexacarbonylmolybdenum(0) within a period of 4 h. Heating a solution of **1** in the presence of 1 equimolar DPPM under CO pressure at the same temperature gave rise to the formation of 80% $Mo(CO)_4$(DPPM), 15% $Mo(CO)_5$(DPPM), and 5% $Mo(CO)_6$. Working in the presence of 10-fold excess of DPPM, one obtained solely the final product **6**. All these results, in particular the formation of $Mo(CO)_5$(DPPM), indicate that the initial step is the partial cleavage of the metal–diene bond, not the CO detachment. Displacement of bidentate chelate rings can be best attributed to a ring-opening mechanism where the intermediate, **2**, can either return to the starting material **1** by the ring-closure step or go on to the next steps. Competition between associative and dissociative processes involving entering and leaving ligands will determine the subsequent steps. The

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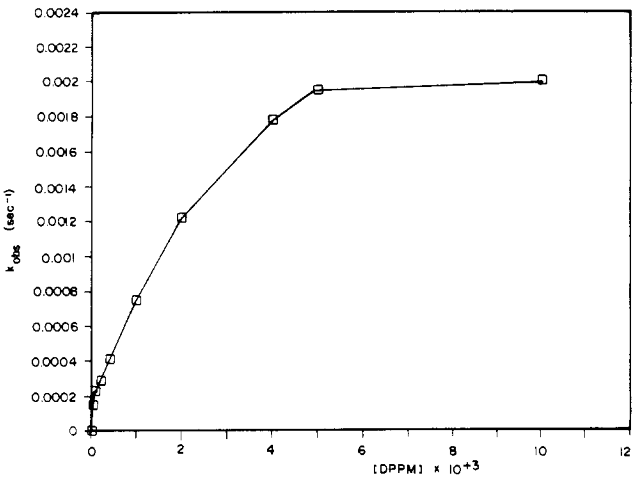

Figure 4. Variation of the observed rate constant with the concentration of DPPM at 45 °C.

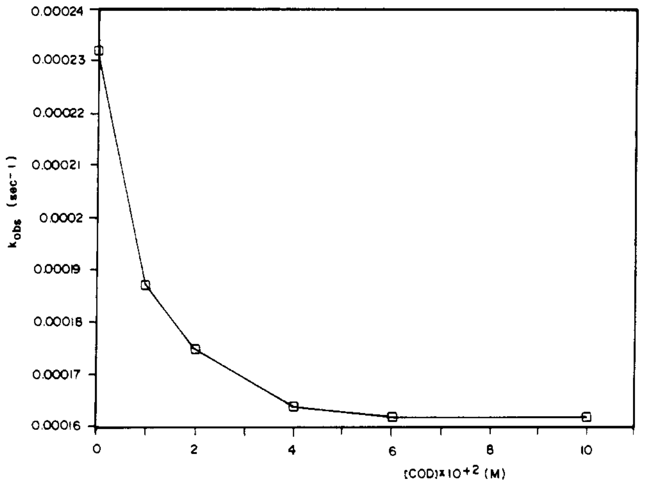

Figure 5. Variation of the observed rate constant with the concentration of COD at 45 °C.

intermediate **2** may undergo an associative reaction with DPPM or COD leading to the formation of intermediates **5** or **4**, respectively, whereby DPPM and COD are bonded to the transition metal in a monodentate fashion. A complete dissociation of COD from the intermediate **2** may also take place leaving unstable transient intermediate $Mo(CO)_4$, **3**, which will react immediately with DPPM to form the final product **6**. On the other hand, when COD is dissociated from the intermediate **5** the rapid ring-closure reaction of DPPM also leads to the formation of the final product **6**. By application of the well-known steady-state approximation for intermediates **2**–**4**, the rate is found to be as follows:

$$\text{rate} = k_{\text{obs}}[\mathbf{1}]$$

$$k_{\text{obs}} = k_1 - \frac{k_1 k_{-1}}{k_{-1} + k_2 + k_4[\text{DPPM}] - \dfrac{k_2}{1 + \dfrac{k_5[\text{DPPM}]}{k_{-2}[\text{COD}]}}}$$

In what follows we are going to show that the proposed mechanism is in agreement with the experimental results.

First of all, when the complex $Mo(CO)_4(\eta^{2:2}\text{-COD})$ is dissolved in toluene and left at 45 °C in the absence of DPPM for about 2 h, one observes no noticeable change in the concentration. This clearly suggests that the observed rate constant k_{obs} is zero at zero concentration of DPPM, as the proposed mechanism predicted. The limit of k_{obs} approaches zero, when concentration of DPPM goes to zero.

$$\lim_{[\text{DPPM}]\to 0} k_{\text{obs}} = 0$$

As the amount of the entering ligand increases gradually, k_{obs} increases and reaches a saturation limit at high concentrations; thus, it becomes independent of concentration of DPPM (Figure 4). This observation can also be predicted from the proposed mechanism. An inspection of the formula for k_{obs} derived from the proposed mechanism shows that increasing the concentration of DPPM causes the k_{obs} value to increase logarithmically. The limit of k_{obs} approaches k_1 as the concentration of DPPM goes to infinity.

$$\lim_{[\text{DPPM}]\to\infty} k_{\text{obs}} = k_1 = 2.0 \times 10^{-3}\ \text{s}^{-1}$$

The effect of the leaving group, COD, on the rate of substitution reaction was also studied by varying the concentration of COD but keeping the concentration of DPPM constant at 0.01 mol·L^{-1} (1-fold). The plot of k_{obs} versus [COD] (Figure 5) is curved downward, with positive intercept, indicating the presence of a complex mechanism[15] in which increasing concentration of COD causes a decrease in k_{obs}. This clearly suggests that the substitution rate of COD in **1** is retarded by the presence of COD in the solution. In other words, the starting material **1** is stabilized by the presence of excess COD. Again, this experimental observation is consistent with the predictions of the proposed mechanism. As the concentration of COD goes to infinity, k_{obs} approaches a limit value which can be obtained from Figure 5:

$$\lim_{[\text{COD}]\to\infty} k_{\text{obs}} = k_1 - \frac{k_1 k_{-1}}{k_{-1} + k_4[\text{DPPM}]} = 1.62 \times 10^{-4}\ \text{s}^{-1}$$

On the other hand, as the concentration of COD goes to zero, k_{obs} approaches another limit value which can also be ascertained from Figure 5 (the intercept):

$$\lim_{[\text{COD}]\to 0} k_{\text{obs}} = k_1 - \frac{k_1 k_{-1}}{k_{-1} + k_2 + k_4[\text{DPPM}]} = 2.32 \times 10^{-4}\ \text{s}^{-1}$$

From these four limit values of k_{obs} at [DPPM] = 0, ∞ and [COD] = 0, ∞, one can obtain the following relationships for the substitution reaction at 45 °C:

$$k_{-1} = 11.34 k_4[\text{DPPM}]$$

$$k_{-1} = 23.14 k_2$$

$$k_4[\text{DPPM}] = 2.04 k_2$$

There are two important points to notice: The first point is that k_{-1} is much larger than both k_2 and k_4[DPPM]. This might be attributed to the chelate effect.[16] The second point is that k_4[DPPM] is about twice k_2. This is not unexpected, because the formation of the unstable $Mo(CO)_4$ species from $Mo(CO)_4(\eta^2\text{-COD})$ (**2**) is not likely in the presence of strong ligands such as DPPM or COD. In addition to the reaction with DPPM, **2** can also bind another COD molecule to form $Mo(CO)_4(\eta^2\text{-COD})_2$ (**4**). This seems to be likely, as the *cis*-$M(CO)_4(\eta^2\text{-olefin})_2$ complexes have already been isolated.[17] Although **4** can be formed

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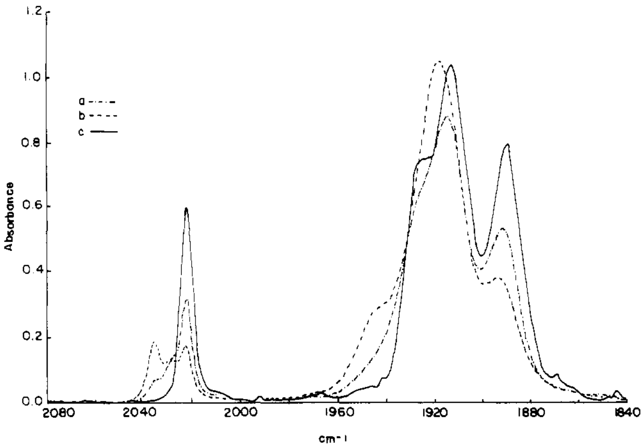

Figure 6. IR spectra at the end of the reaction of $Mo(CO)_4(\eta^{2:2}$-COD) with DPPM (a) in the presence of 1-fold $P(OCH_3)_3$, (b) in the presence of 2-fold $P(OCH_3)_3$, and (c) without $P(OCH_3)_3$ at 45 °C in toluene.

as an intermediate in equilibrium, this equilibrium step does not appear in the formula of k_{obs}.

In order to elucidate structural information about the possible intermediates, for example **5**, more experiments are required. One experiment designed to get evidence for the formation of **5** as an intermediate is the substitution reaction conducted in the presence of trimethyl phosphite at 45 °C. First, the thermal substitution reaction of **1** with DPPM (1-fold) was performed in the presence of 1-fold $P(OCH_3)_3$. Although, at least six complexes are possibly generated in the solution, the IR spectrum at the end of the reaction shows the existence of only three different products (Figure 6a). These are *cis*-[$Mo(CO)_4(P(OCH_3)_3)_2$], [$Mo(CO)_4$(DPPM)], and *cis*-[$Mo(CO)_4(P(OCH_3)_3)$(DPPM)]. The most distinguishable CO-stretching frequencies for these complexes are 2035 cm^{-1} for *cis*-[$Mo(CO)_4(P(OCH_3)_3)_2$],[18] 2028.4 cm^{-1} for *cis*-[$Mo(CO)_4(P(OCH_3)_3)$(DPPM)],[19] and 2021.5 cm^{-1} for [$Mo(CO)_4$(DPPM)]. The same reaction was performed using a 2-fold excess of $P(OCH_3)_3$, which causes a decrease in the amount of $Mo(CO)_4$(DPPM) and a concomitant increase in the amount of *cis*-[$Mo(CO)_4(P(OCH_3)_3)_2$] (Figure 6b). In each set of experiments, *cis*-[$Mo(CO)_4(P(OCH_3)_3)$(DPPM)] is clearly seen from the IR-absorption band that comes around 2028.4 cm^{-1}. The observation of *cis*-[$Mo(CO)_4(P(OCH_3)_3)$(DPPM)] as a product provides compelling evidence for the formation of **5** as an intermediate. In separate experiments it was shown that neither $Mo(CO)_4$(DPPM) nor [$Mo(CO)_4(P(OCH_3)_3)_2$] gives any reaction with trimethyl phosphite or DPPM at the same temperature. This indicates that the intermediate *cis*-[$Mo(CO)_4(P(OCH_3)_3)$(DPPM)] is a kinetic product.

The material balance does not show a significant depletion up to 80–90% conversion. This may be attributed to the fact that the strong DPPM ligand forms the stable $Mo(CO)_4$(DPPM) complex. Therefore, the presence of excess DPPM or COD in the reaction solution does not affect the material balance and the yield of $Mo(CO)_4$(DPPM) formed in each set of experiments.

The thermal substitution reaction of $Mo(CO)_4(\eta^{2:2}$-COD) with DPPM was performed at four different temperatures (35, 40, 45, 50 °C) in the presence of a 10-fold excess of DPPM to ensure the pseudo-first-order condition. The observed rate constant values obtained at four different temperatures in the range 35–50 °C (Figure 7) as well as the free energy of activation calculated are given in Table 1. From the Eyring plot the enthalpy of activation and the entropy of activation are found to be $\Delta H^* = 80\ (\pm 1)\ kJ{\cdot}mol^{-1}$ and $\Delta S^* = -55\ (\pm 2)\ J{\cdot}mol^{-1}{\cdot}K^{-1}$, respectively. The negative value of ΔS^* is consistent with an S_N2 or associated mechanism in the transition states.[20] If some associated species were a reactive form of the complex, an equilibrium between the free complex and this species would result in a ligand dependence of the rate constants at low ligand concentrations.[21] In other words, the dependence of the reaction rate on ligand concentration can be easily explained by a displacement mechanism which proceeds via the formation of a seven-coordinate complex in the transition states.[22] Although this is uncommon for octahedral complexes, they may undergo substitution reaction by way of an associative mechanism.[20–23]

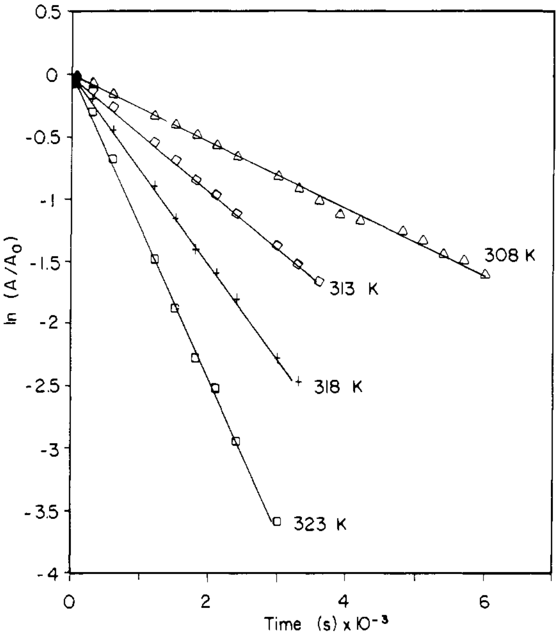

Figure 7. First-order kinetics for the displacement reaction of COD from $Mo(CO)_4(\eta^{2:2}$-COD) by DPPM in the temperature range 35–50 °C.

Table 1. Observed Rate Constant Values Obtained at Different Temperatures in the Presence of 10-Fold Excess DPPM with Standard Deviations in Parentheses

T (K)	$10^4 k_{obs}$ (s^{-1})	ΔG^* ($kJ{\cdot}mol^{-1}$)	T (K)	$10^4 k_{obs}$ (s^{-1})	ΔG^* ($kJ{\cdot}mol^{-1}$)
308	2.67(0.10)	96.5(0.1)	318	7.45(0.17)	97.0(0.1)
313	4.61(0.06)	96.6(0.1)	323	11.9(0.7)	97.3(0.1)

In addition, the rate-determining step involves only bond breaking (Mo–COD bond) in the dissociative S_N1 mechanism and both bond breaking (Mo–COD) and bond making (Mo–DPPM) in the associative S_N2 mechanism.[23] The enthalpy of activation is expected to approach the Mo–COD bond energy for a predominantly dissociative process and to be rather independent of the nature of the entering ligand, whereas for an associative process ΔH^* is expected to be rather smaller than the Mo–COD bond energy.[24] Mo–COD bond energy is 108 $kJ{\cdot}mol^{-1}$.[25] ΔH^* for the displacement of COD from $Mo(CO)_4(\eta^{2:2}$-COD) depends on the entering ligand,[3] and is 80 $kJ{\cdot}mol^{-1}$ when DPPM is used as the entering ligand. Thus this also clearly indicates that substitution of COD in $Mo(CO)_4(\eta^{2:2}$-COD) with DPPM proceeds through an associative S_N2 mechanism in the transition states.

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