

Displacement kinetics of 1,5-cyclooctadiene from $M(\text{CO})_4(\eta^{2:2}\text{-1,5-cyclooctadiene})$ ($M = \text{Cr, Mo, W}$) by bis(diphenylphosphino)alkane

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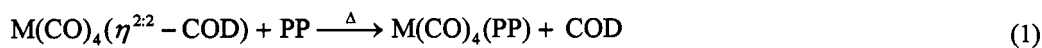
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Abstract: The thermal substitution kinetics of 1,5-cyclooctadiene (COD) from $M(\text{CO})_4(\eta^{2:2}\text{-COD})$ ($M = \text{Cr, Mo, W}$) by bis(diphenylphosphino)alkane, $(\text{C}_6\text{H}_5)_2\text{P}(\text{CH}_2)_n\text{-P}(\text{C}_6\text{H}_5)_2$ ($n = 1, 2, 3$), was studied by quantitative FT-IR spectroscopy. The reaction rate exhibits first-order dependence on the concentration of starting complex, and the observed rate constant depends on the concentrations of both the leaving COD and entering diphosphine ligand. In the proposed mechanism the rate determining step is the cleavage of one of two metal-olefin bonds. A rate-law is derived from the proposed mechanism. The evaluation of the kinetic data gives the activation parameters which tend to suggest an associative mechanism for the molybdenum and tungsten complexes, and a dissociative mechanism for the chromium complexes in transition states. The observed rate constant is found to be dependent on the concentration and the nature of the entering diphosphine ligand.

Introduction

Carbonyl-olefin-metal(0) complexes of the group 6 elements have been used as catalyst in many reactions of olefins, including hydrogenation (1), hydroformylation (2), isomerisation (3), polymerisation (4), and hydrosilation (5), and their catalytic activities have been modified by introducing some donor/acceptor ligands into the complex (6). Kinetic data on the rates and energetics of organometallic reactions have served as a foundation of our understanding of metal-ligand bonds and bond-forming pathways for more than 50 years (7).

Among the well known olefin complexes of the group 6 metals are $M(\text{CO})_4(\eta^{2,2}\text{-COD})$, COD = 1,5-cyclooctadiene, which were synthesized 30 years ago (8). Although displacement of COD from $M(\text{CO})_4(\eta^{2,2}\text{-COD})$ complexes has been used synthetically to prepare a variety of $M(\text{CO})_4\text{L}_2$ complexes (L = phosphorus or nitrogen containing ligands), relatively little work has been carried out on the kinetic study of diene replacement (9). Very recently we reported in full details on displacement kinetics of COD from $\text{Mo}(\text{CO})_4(\eta^{2,2}\text{-COD})$ by a bidentate diphosphine, bis(diphenylphosphino)methane (10). The rate of this thermal substitution reaction exhibits first-order dependence on the concentration of the diene-complex, and the observed rate constant depends on the concentrations of both leaving COD and entering DPPM ligands. In the proposed mechanism the rate determining step is the cleavage of one of two Mo-olefin bonds. Here we would like to report our extended study on the displacement kinetics of COD from $M(\text{CO})_4(\eta^{2,2}\text{-COD})$ (M = Cr, Mo, W) by bis(diphenylphosphino)alkane (PP = $(\text{C}_6\text{H}_5)_2\text{P}(\text{CH}_2)_n\text{P}(\text{C}_6\text{H}_5)_2$, n = 1, 2, 3, denoted as DPPM, DPPE, and DPPP, respectively) with the aim to investigate the dependence of the reaction kinetics on the nature of the metal and on the chain-length of the diphosphine ligand.



The kinetics of these ligand displacement reactions was studied by quantitative FT-IR spectroscopy. Monitoring the intensities of the sharp absorption bands of CO stretching for both the reactant and product gave the changes in their concentrations throughout the reaction.

Results and Discussion

The absorption bands of $M(\text{CO})_4(\eta^{2,2}\text{-COD})$ in the CO stretching region of the IR spectrum are gradually replaced by new bands of the corresponding product $M(\text{CO})_4(\text{PP})$ in the course of the displacement reaction. The gradual change in the IR spectrum during the reaction of $\text{W}(\text{CO})_4(\eta^{2,2}\text{-COD})$ with DPPM at 90°C, as an example, is depicted in Fig. 1. The observation of nice isosbestic points indicates a straightforward conversion of

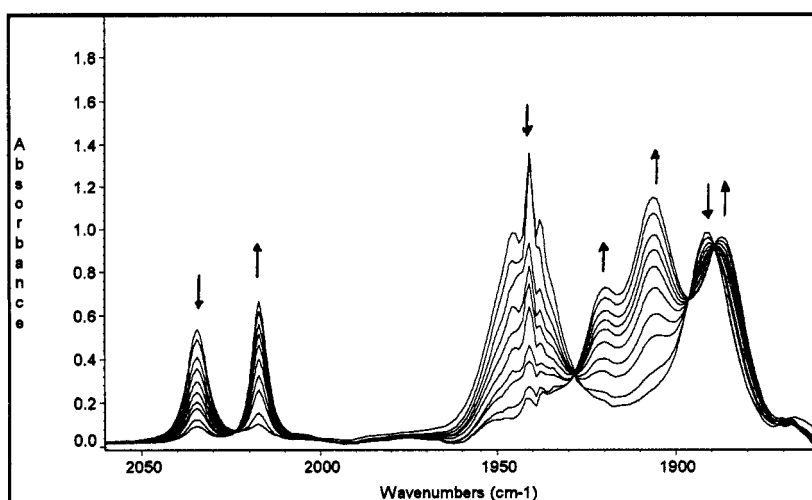


Fig.1 The gradual change in the IR spectrum during the reaction of $\text{W}(\text{CO})_4(\eta^{2,2}\text{-COD})$ with DPPM to yield $\text{W}(\text{CO})_4(\text{DPPM})$ at 90°C.

the reactant into the product without side or subsequent reactions (11). In other words there are only two absorbing species throughout the reaction. The highest frequency bands of the reactant and product 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 and the growth of the product, respectively.

The mechanism (Scheme 1) proposed for the COD substitution from $\text{M}(\text{CO})_4(\eta^{2,2}\text{-COD})$ by DPPM (10) is shown to be valid also for the same reactions of chromium and tungsten analogues with all of the diphosphines studied. The rate of the reaction exhibits first-order dependence on the concentration of $\text{M}(\text{CO})_4(\eta^{2,2}\text{-COD})$ and the observed rate constant, k_{obs} , depends on the concentration of both leaving COD and entering PP ligand.

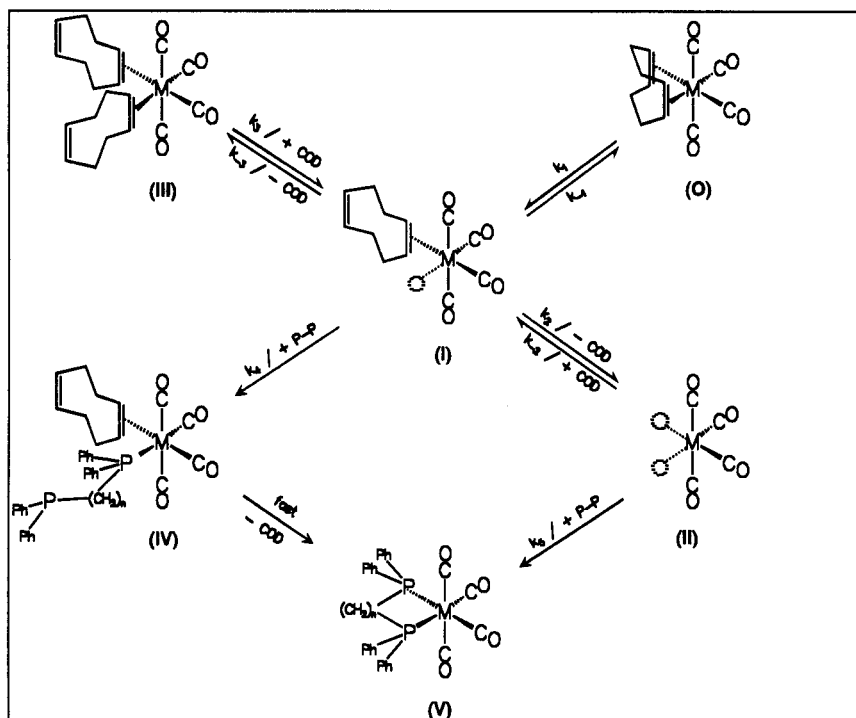
$$\text{rate} = k_{\text{obs}} [\text{M}(\text{CO})_4(\eta^{2,2}\text{-COD})] \quad (2)$$

$$k_{\text{obs}} = k_1 - \frac{k_1 k_{-1}}{k_{-1} + k_2 + k_4 [\text{PP}] - \frac{k_2}{1 + \frac{k_5 [\text{PP}]}{k_{-2} [\text{COD}]}}} \quad (3)$$

From supplementary experiments performed to get the details of this mechanism a number of key points emerge that can be summarized in point form as follows:

- No noticeable change is observed in concentration of $\text{M}(\text{CO})_4(\eta^{2,2}\text{-COD})$ in the absence of diphosphine at temperature at which ligand substitution takes place normally by an appreciable rate. This clearly indicates that the observed rate constant is zero at zero concentration of diphosphine ($\lim_{[\text{PP}] \rightarrow 0} k_{\text{obs}} = 0$).

SCHEME 1 Mechanism proposed for the substitution of COD from $\text{M}(\text{CO})_4(\eta^{2,2}\text{-COD})$ by bis(diphenylphosphino)ethane (PP).



- As the concentration of the entering ligand increases gradually, the observed rate constant increases and reaches a saturation limit at high concentrations of PP ($\lim_{[PP] \rightarrow \infty} k_{\text{obs}} = k_1$).
- Increasing concentration of COD causes a decrease in the observed rate constant. The plot of the observed rate constant versus the concentration of COD is curved downward starting with a positive intercept ($\lim_{[COD] \rightarrow 0} k_{\text{obs}} = k_1 - k_1 k_{-1} / (k_{-1} + k_2 + k_4 [PP])$) and reaching another saturation limit at high concentrations ($\lim_{[COD] \rightarrow \infty} k_{\text{obs}} = k_1 - k_1 k_{-1} / (k_{-1} + k_4 [PP])$).
- In experiments with varying concentration of trimethylphosphite relative to [PP], the observation of *cis*-[M(CO)₄(P(OMe)₃)(PP)] as a product provides compelling evidence for the formation of IV as an intermediate.

The observed rate constant shows dependence on the chain length of $\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2$ ($n = 1-3$). For a better appreciation of this dependence, the values of $1/(k_1 - k_{\text{obs}})$ instead of k_{obs} (Eq. 3) are plotted against the concentration of diphosphine (Fig. 2). Up to 0.1 M concentration which corresponds to four-fold of diphosphine relative to the starting complex, all of the three diphosphines show the same effect; the value of $1/(k_1 - k_{\text{obs}})$, thus k_{obs} , increases slightly with the increasing concentration of diphosphine. At higher concentrations of diphosphine, however, the observed rate constant shows strong dependence on the concentration and the nature of the entering ligand. This observation indicates that the last term in the expression for $1/(k_1 - k_{\text{obs}})$ is negligible at high concentrations of diphosphine. The order observed for the $1/(k_1 - k_{\text{obs}})$ value (DPPM < DPPE < DPPP) is consistent with the basicity of the chelating diphosphines (12). The activation parameters are found to have very similar values for all of the three diphosphine.

The substitution kinetics of COD in $\text{M}(\text{CO})_4(\eta^2\text{-COD})$ by DPPM was studied for all of the three metal at different temperatures (Fig. 3). The activation parameters obtained from the Eyring plots can be used to understand the nature of the mechanism. The large negative value of the activation entropy for the molybdenum

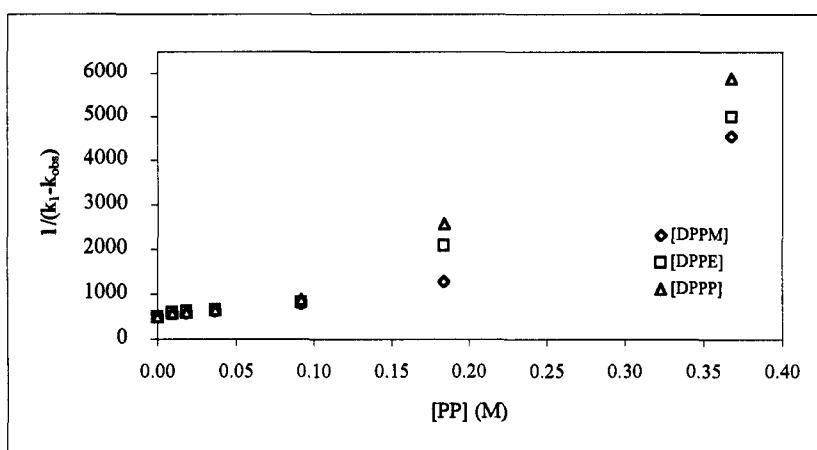


Fig. 2 The dependence of k_{obs} on the nature and concentration of diphosphine at 318 K. $1/(k_1 - k_{\text{obs}}) = k_{-1} + k_2 + k_4 [PP] - k_2 / (1 + k_5 [PP] / k_{-2} [COD])$.

and tungsten complexes ($\Delta S^* = -59 \pm 2$ and $-73 \pm 2 \text{ JK}^{-1} \text{ mol}^{-1}$, respectively) is indicative for an associative mechanism in transition states. Support for this assignment comes from the comparison of the activation enthalpies with the metal-olefin bond energies. The activation enthalpy is expected to approach the metal-COD bond energy for a predominantly dissociative mechanism, whereas for an associative process ΔH^* is expected to be rather smaller than the metal-COD bond energy (13). The activation enthalpies for molybdenum and tungsten complexes ($\Delta H^* = 78 \pm 1$ and $89 \pm 1 \text{ kJmol}^{-1}$, respectively) are smaller than the corresponding metal-olefin bond

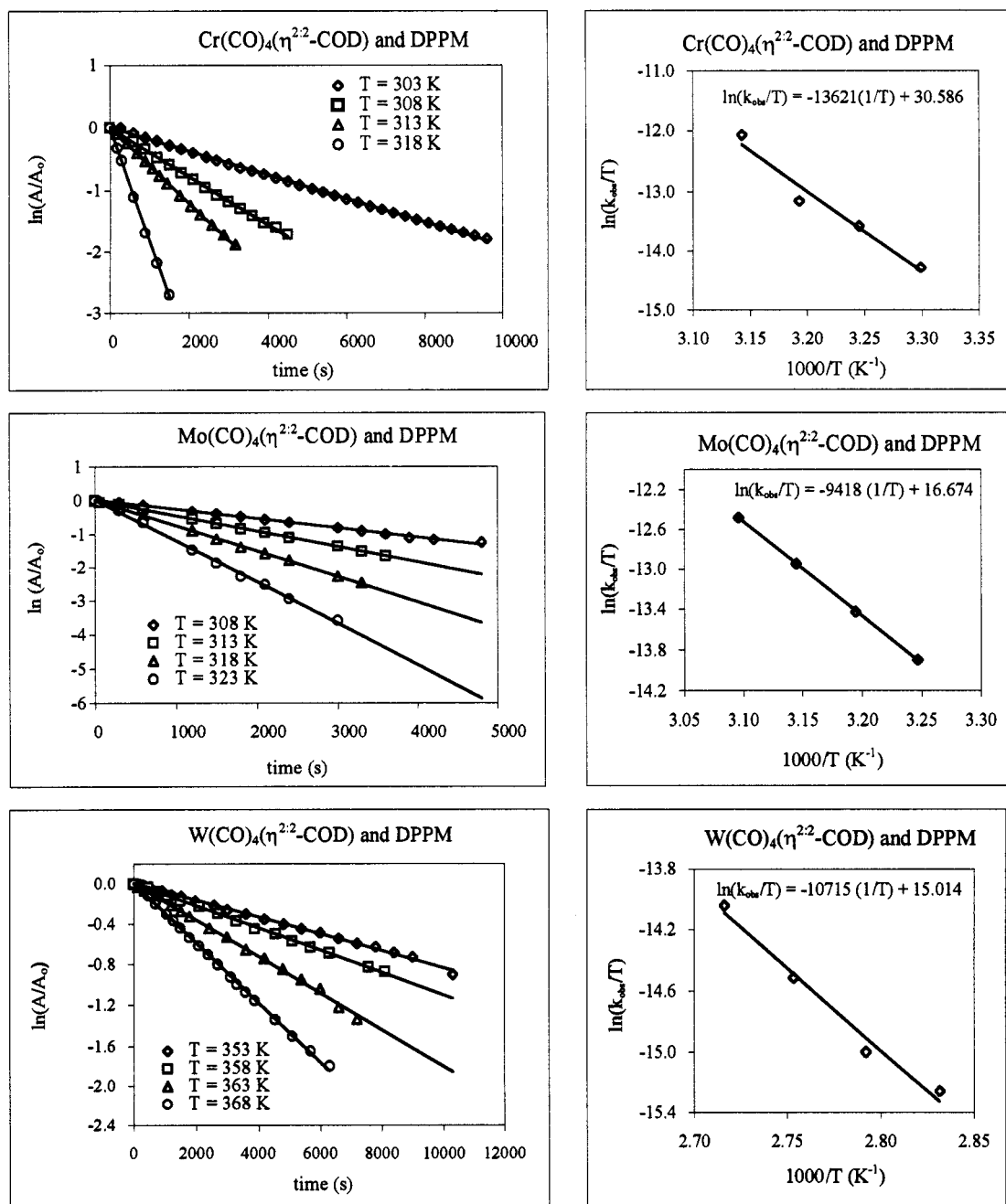


Fig. 3 Absorbance versus time (left) and Eyring (right) plots for the substitution of COD ligand in $M(\text{CO})_4(\eta^{2,2}\text{-COD})$ ($M = \text{Cr, Mo, W}$) by DPPM.

energy (14). By contrast, for the chromium complex ΔS^* has large positive value ($57 \pm 2 \text{ JK}^{-1} \text{ mol}^{-1}$) and ΔH^* has a value of $113 \pm 1 \text{ kJmol}^{-1}$, as large as the metal-olefin bond energy (13). This indicates that the substitution of COD in $\text{Cr}(\text{CO})_4(\eta^2\text{-COD})$ by diphosphine proceeds through a mechanism which is of predominantly dissociative nature in transition states. The assignment of a dissociative mechanism for the chromium complexes and an associative mechanism for the molybdenum and tungsten complexes is consistent with the known general trend that the octahedral chromium(0) complexes undergo substitution reactions of dissociative nature because of the small size while substitutions on the larger molybdenum and tungsten usually follow an associative mechanism (14).

Acknowledgement

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