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Ligand substitution kinetics in $M(CO)_4(\eta^{2:2}$-norbornadiene) complexes (M = Cr, Mo, W): displacement of norbornadiene by bis(diphenylphosphino)alkanes

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Abstract

The thermal substitution kinetics of norbornadiene (NBD) by bis(diphenylphosphino)alkanes (PP), $(C_6H_5)_2P(CH_2)_nP(C_6H_5)_2$ ($n = 1, 2, 3$) in $M(CO)_4(\eta^{2:2}$-NBD) complexes (M = Cr, Mo, W), were studied by quantitative FT-IR spectroscopy. The reaction rate exhibits first-order dependence on the concentration of the starting complex, and the observed rate constant depends on the concentration of the leaving NBD ligand and on the concentration and the nature of the entering PP ligand. In the proposed mechanism there are two competing initial steps: an associative reaction involving the attachment of the entering PP ligand to the transition metal center and a dissociative reaction involving the stepwise detachment of the diolefin ligand from the transition metal center. A rate law is derived from the proposed mechanism. The activation parameters are obtained from the evaluation of the kinetic data. It is found that at higher concentrations of the entering ligand, the associative path is dominant, while at lower concentrations the contribution of the dissociative path becomes significant. Both the observed rate constant and the activation parameters show noticeable variation with the chain length of the diphosphine ligand. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Substitution; Diphosphinoalkanes; Norbornadiene; Chromium; Molybdenum; Tungsten

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1. Introduction

The thermal substitution kinetics of 1,5-cyclooctadiene (COD) by bis(diphenylphosphino)alkanes (PP), $(C_6H_5)_2P(CH_2)_nP(C_6H_5)_2$ ($n = 1, 2, 3$) in $M(CO)_4(\eta^{2:2}$-COD) complexes (M = Cr, Mo, W), were recently reported [1]. It was found that the weakly bound COD ligand is replaced by PP at an observable rate in the temperature range 35–90°C to form the known complexes $[M(CO)_4(PP)]$ as the final product [2]. The kinetics of this thermal substitution reaction were studied by quantitative FT-IR spectroscopy. A rate law was derived from the proposed mechanism in which the rate determining step is the cleavage of one of two metal–olefin bonds. The reaction rate exhibits first-order dependence on the concentration of $[M(CO)_4(\eta^{2:2}$-COD)], and the observed rate constant depends on the concentrations of both leaving COD and entering PP ligands. Both the observed rate constant and the activation parameters show little variation with the chain length of the diphosphine ligand, but significant changes are observed as the central metal atom is varied. Here, we report our extended study on the displacement kinetics of norbornadiene, NBD, from $M(CO)_4(\eta^{2:2}$-NBD) (M = Cr (**1A**), Mo (**2A**), W (**3A**)) by bis(diphenylphosphino)alkanes (PP), $(C_6H_5)_2P(CH_2)_nP(C_6H_5)_2$ ($n = 1$ (**B**), 2 (**C**), 3 (**D**)) with the aim to investigate the dependence of the reaction kinetics and the mechanism on the nature of the leaving diene ligand.

$$\underset{\mathbf{1A–3A}}{M(CO)_4(\eta^{2:2}\text{-NBD})} + \underset{\mathbf{B–D}}{PP} + NBD \xrightarrow{\Delta} \underset{\mathbf{1B–3D}}{M(CO)_4(PP)}$$

M = Cr, Mo, W; PP = $(C_6H_5)_2P(CH_2)_nP(C_6H_5)_2$;
$n = 1, 2, 3$

Quantitative FT-IR spectroscopy was used to study the kinetics of these ligand displacement reactions.

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Monitoring the intensities of the absorption bands of the CO stretching vibrations for both the reactant and product enables one to determine the changes in their concentrations, thus to follow the reaction precisely, and to check the material balance and the yield throughout the reaction.

2. Experimental

All of reactions and manipulations of the complexes were carried out either in vacuum or under a dry and oxygen free nitrogen atmosphere. Solvents were distilled after refluxing over metallic sodium or phosphorous pentoxide for 3–4 days and stored under nitrogen until used. Hexacarbonylchromium(0), hexacarbonylmolybdenum(0), hexacarbonyltungsten(0), norbornadiene (**A**), bis(diphenylphosphino)methane (**B**), 1,2-bis-(diphenylphosphino)ethane (**C**), and 1,3-bis(diphenylphosphino)propane (**D**) were purchased from Aldrich, Dorset, UK. The thermal reactions and other treatments of organometallic compounds such as purification and crystallization were followed by taking IR spectra at appropriate time intervals. NMR spectra were recorded on a Bruker DPX 400 spectrometer (400.132 MHz for ^{1}H, 161.996 MHz for ^{31}P, and 100.613 MHz for ^{13}C). TMS was used as internal reference for ^{1}H- and ^{13}C-NMR chemical shifts. Phosphoric acid (85%) in a capillary tube was used as external reference for ^{31}P-NMR chemical shifts. Infrared spectra were recorded from solutions on a Perkin–Elmer 16 PC FT-IR spectrometer. Photochemical reactions were carried out in an immersion-well apparatus [3] (solidex glass, $\lambda > 280$ nm) by using a Hanau TQ 150 high-pressure mercury lamp, which was cooled by circulating water or cold methanol. 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.

2.1. *Tetracarbonyl($\eta^{2:2}$-norbornadiene)metal(0)*

Tetracarbonyl($\eta^{2:2}$-norbornadiene)chromium(0), Cr-$(CO)_4(\eta^{2:2}$-NBD) (**1A**), and tetracarbonyl($\eta^{2:2}$-norbornadiene)molybdenum(0), $Mo(CO)_4(\eta^{2:2}$-NBD) (**2A**), were prepared by refluxing a solution of hexacarbonylmetal(0) and NBD in isooctane as described in the literature [4]. The reaction solution is evaporated to dryness. Crystallization from *n*-hexane solution yields yellow crystals of the complexes. Tetracarbonyl($\eta^{2:2}$-norbornadiene)tungsten(0), $W(CO)_4(\eta^{2:2}$-NBD) (**3A**), was prepared by refluxing $W(pip)_2(CO)_4$ and NBD in *n*-hexane as described in the literature [5]. The reaction mixture is cooled down to 0°C and the polymeric material precipitated is removed by filtration. The remaining orange solution is allowed to stand at -35°C for 1 day for crystallization. The orange crystals are dried in vacuum.

2.2. *Tetracarbonyl-bis(diphenylphosphino)alkane-metal(0)*

Equimolar amounts (ca. 1 mmol) of $M(CO)_4(\eta^{2:2}$-NBD) (**1A**–**3A**) and PP=$Ph_2P(CH_2)_nPPh_2$ ($n = 1$, 2, 3) (**B**–**D**) were dissolved in toluene (50 ml) and refluxed for several minutes. Cooling the solution to -35°C yields pale yellow crystals of $M(CO)_4(PP)$ (**1B**–**3D**) which are separated from the supernatant liquid by decantation and dried under vacuum and identified by ^{13}C- and ^{31}P-NMR spectroscopy [6].

2.3. *Kinetic measurements*

All kinetic measurements were conducted on toluene solutions in a Specac Variable Temperature IR-Liquid Cell with a 0.129 mm path length and calcium fluoride windows. Extinction coefficients of $M(CO)_4(\eta^{2:2}$-NBD) (**1A**–**3A**) and $M(CO)_4(PP)$ (**1B**–**3D**) were determined from toluene solutions of the pure complexes by plotting the absorbance of the νCO IR band with the highest frequency versus the concentration of the respective complex in the range 5×10^{-4} to 2×10^{-3} mol l^{-1} (Table 1). Using these values, the concentrations of the complexes during the reactions of **1A**–**3A** with PP could be determined from the measured IR absorbances at any stage of the reactions. Thus the material balance could also be checked at any point of conversion.

The $M(CO)_4(\eta^{2:2}$-NBD) complexes were added to the solutions of the diphosphine in toluene at low temperature to avoid any reaction. The initial concentration $[C_0]$ of the complexes was around 0.01 mol l^{-1}. A sample of this solution was transferred into the Specac Variable Temperature IR-Liquid Cell P/N 21500, which is controlled by an Automatic Temperature Controller P/N 20120, preheated to the reaction temperature. The IR spectra were recorded periodically as the reaction proceeded at constant temperature. The rates of the reaction were determined by following the disappearance of the highest-frequency νCO band of the educt, since it was the only distinct band that does not overlap with the bands of the products. In this way, quantitative data on the rates of reactions were collected easily and accurately. The graphical evaluation of the data provides the observed rate constants. In order to study the dependence of the rate on the leaving NBD and entering PP, the kinetic experiments were performed by varying the concentrations of PP (0.01–1.4 mol l^{-1}) or NBD (0.0–0.1 mol l^{-1}) in the solutions of **1A**–**3A** ($C_0 = 0.009$ mol l^{-1}) at 40°C (M = Cr), 45°C (M =

Table 1
The CO stretching frequencies (cm^{-1}) for the complexes and molar extinction coefficient ($l\ mol^{-1}\ cm^{-1}$) for the highest-frequency band in toluene

Complex	$\varepsilon \times 10^{-3}$ ($l\ mol^{-1}\ cm^{-1}$) for $A_{1(2)}$	$A_{1(2)}$	$A_{1(1)}$	B_1	B_2
$Cr(CO)_4(\eta^{2:2}$-NBD) (**1A**)	3.4	2026	1935	1948	1899
$Mo(CO)_4(\eta^{2:2}$-NBD) (**2A**)	2.4	2039		1948	1896
$W(CO)_4(\eta^{2:2}$-NBD) (**3A**)	1.9	2038		1945	1893
$Cr(CO)_4$(DPPM) (**1B**)	3.3	2012	1922	1903	1891
$Mo(CO)_4$(DPPM) (**2B**)	3.5	2012	1930	1901	1890
$W(CO)_4$(DPPM) (**3B**)	4.5	2012	1923	1902	1889
$Cr(CO)_4$(DPPE) (**1C**)	3.0	2020	1929	1917	1897
$Mo(CO)_4$(DPPE) (**2C**)	3.1	2017	1928	1908	1897
$W(CO)_4$(DPPE) (**3C**)	1.3	2023	1936	1908	
$Cr(CO)_4$(DPPP) (**1D**)	4.5	2015	1935	1907	1890
$Mo(CO)_4$(DPPP) (**2D**)	4.2	2015	1930		1883
$W(CO)_4$(DPPP) (**3D**)	1.9	2016	1933	1901	1888

Mo), and 90°C (M = W). The activation parameters were determined from the temperature dependence of the observed rate constant in the range 5–90°C.

The substitution reaction of **2A** with DPPM in tenfold excess at 20°C was repeated ten times under identical conditions to check the reproducibility and to calculate the indeterminate errors for the kinetic data. The error in the observed rate constant values was found to be less than ±2%.

3. Results and discussion

The IR absorption spectra of both the $M(CO)_4(\eta^{2:2}$-NBD) and $M(CO)_4$(PP) complexes taken in toluene show four absorption bands in the CO stretching region indicating a *cis* arrangement of four CO groups in the pseudo-octahedral coordination sphere of the metal (Table 1). Thus, the $M(CO)_4$ moiety in the complexes has a local C_{2v} symmetry with $2A_1 + B_1 + B_2$ CO stretching modes [7]. The complexes **2A**, **3A**, **3C**, and **2D** give only three IR CO stretching bands indicating that the two of the four expected bands are accidentally degenerate.

The kinetics of the thermal substitution of NBD from **1A**–**3A** by bis(diphenyl-phosphino)alkanes were followed by using the quantitative FT-IR spectroscopy. In the νCO region of the IR spectrum, the absorption bands of **1A**–**3A** are gradually replaced by the new bands of the corresponding product $M(CO)_4$(PP) in the course of the displacement reaction. The gradual change in the IR spectrum during the reaction of $Mo(CO)_4(\eta^{2:2}$-NBD) (**2A**) with DPPM at 20°C is depicted in Fig. 1 as an illustrative example. The observation of narrow isosbestic points indicates a straightforward conversion of the reactant into the product without side or subsequent reactions [8]. In other words, there are only two absorbing species throughout the reaction. Another point emerging from the inspection of the IR spectra at a first glance is that the highest-frequency bands of the reactant and product remain well resolved during the whole reaction. These two IR bands are selected to follow the consumption of the reactant and the growth of the product, respectively.

The concentration versus time graph for the course of the thermal substitution reaction shows an exponential decay for the starting complex and an exponential growth for the product (Fig. 2(a)). The logarithmic plot of the concentration of the reactant against time gives a straight line for the aforementioned reaction even at low concentrations of bis(diphenylphosphino)-alkane (Fig. 2(b)). This indicates that the displacement of NBD from **1A**–**3A**) by PP obeys pseudo-first-order kinetics over at least four half-lives. The slope of the straight line gives the observed rate constant, k_{obs} [s^{-1}], for the pseudo-first-order thermal substitution reaction.

The kinetic data for the NBD substitution in $M(CO)_4(\eta^{2:2}$-NBD) by the diphosphinoalkanes can be interpreted by considering a multi-step mechanism sim-

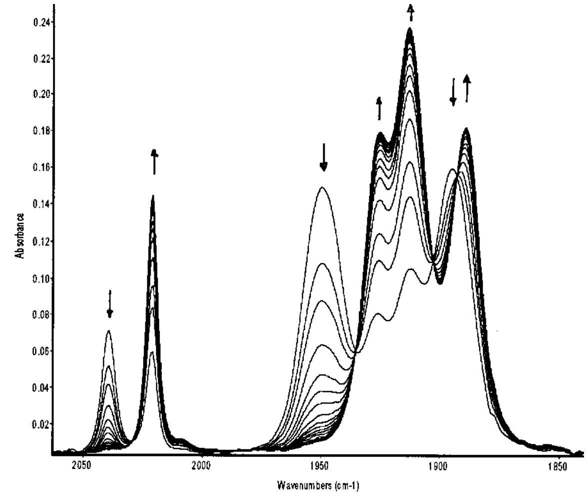


Fig. 1. The FT-IR spectra taken in the course of the thermal substitution reaction of **2A** with DPPM at 20°C with a time interval of ca. 20 min. $[DPPM]_0/[\mathbf{2A}]_0 = 10$.

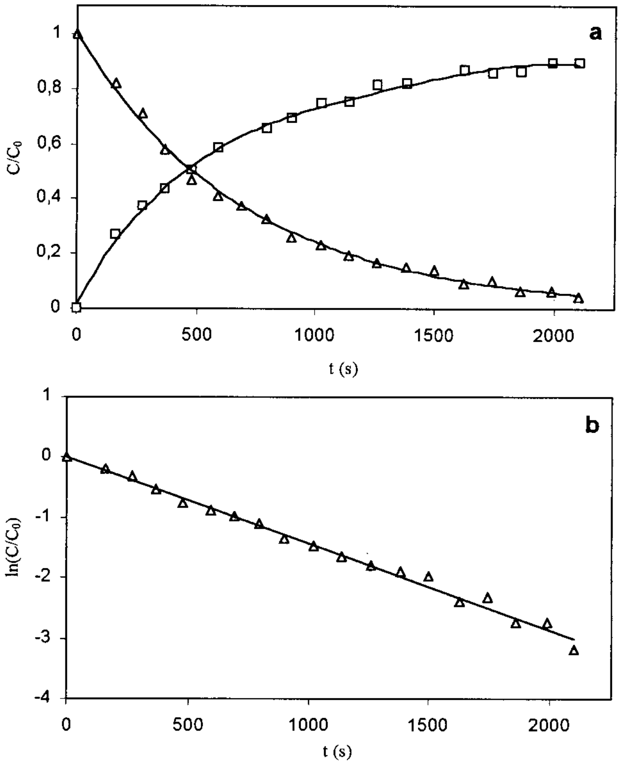


Fig. 2. (a) The normalized concentration vs. time plot for the substitution reaction of **2A** (△) with DPPM at 15°C forming **2B** (□), $[PP]_0/[\mathbf{2B}]_0 = 10$; (b) plot of the first-order kinetics for the same reaction.

ilar to the one proposed for the COD substitution in the $M(CO)_4(\eta^{2:2}\text{-COD})$ complexes by PP [1]. The reaction mechanism is complicated, because the thermal reaction is a ligand exchange reaction, where one has to consider the effect of both the bidentate leaving and bidentate entering ligands on the reaction mechanism. Furthermore, additional experiments are required to collect evidence for the intermediates in the proposed mechanism. Therefore, in what follows, all the kinetic data and the other experimental evidence will be discussed before giving the proposed mechanism, which will then be shown to be in agreement with the experimental observations.

A series of experiments was performed to check whether a CO detachment would occur as an initial step and to obtain evidence for the formation of possible intermediates. First of all, none of the three starting complexes **1A**–**3A** gives any reaction in the absence of entering ligand upon heating to the temperature at which the ligand substitution takes place at an appreciable rate. Consequently, one can assume that the observed rate constant (k_{obs}) is zero at zero concentration of entering ligand (DPPM, DPPE or DPPP). In a similar reaction under 1 atm CO at the same temperature, the starting complex is completely converted into the corresponding hexacarbonylmetal(0) within 2–4 h. Heating solutions of the starting complexes **1A**–**3A** in the presence of equimolar amounts of PP under a CO atmosphere at the same temperature gives rise to the predominant formation of $M(CO)_4(PP)$, together with $M(CO)_5(PP)$ and $M(CO)_6$ in low concentrations (less than 15 and 5%, respectively). The observation of pentacarbonyl-diphosphinechromium(0) [9] in the latter experiment is a compelling evidence for the formation of intermediates in which the diphosphine is bound to the metal in monodentate fashion. It indicates further that the CO detachment does not occur as an initial step. Working in the presence of ten-fold excess of PP, $M(CO)_4(PP)$ is the sole product.

Thermal substitution reaction of **1A** with DPPE (one-fold) was also performed in the presence of one- or two-fold $P(OCH_3)_3$ at 85°C. The following five complexes could be detected in the reaction mixture: *cis*-$[Cr(CO)_4(P(OCH_3)_3)_2]$, *trans*-$[Cr(CO)_4(P(OCH_3)_3)_2]$, $[Cr(CO)_4(DPPE)]$ (**1C**), *cis*-$[Cr(CO)_4(P(OCH_3)_3)(DPPE)]$, and *trans*-$[Cr(CO)_4(P(OCH_3)_3)(DPPE)]$. The most distinguishable CO-stretching frequencies for these complexes were 2023 cm^{-1} for *cis*-$[Cr(CO)_4(P(OCH_3)_3)_2]$, 1912 cm^{-1} for *trans*-$[Cr(CO)_4(P(OCH_3)_3)_2]$, 2016 cm^{-1} for *cis*-$[Cr(CO)_4(P(OCH_3)_3)(DPPE)]$, 1905 cm^{-1} for *trans*-$[Cr(CO)_4(P(OCH_3)_3)(DPPE)]$, and 2020 cm^{-1} for **1C** [10,11]. The same reaction was performed by using **3A** instead of **1A** in order to reduce the number of the products as tungsten prefers only *cis*-isomers. Substitution reaction of **3A** with DPPE (one-fold) was performed in the presence of one- or two-fold $P(OCH_3)_3$ at 65°C. The IR spectrum at the end of the reaction shows the presence of only three different products. These are *cis*-$[W(CO)_4(P(OCH_3)_3)_2]$, *cis*-$[W(CO)_4(P(OCH_3)_3)(DPPE)]$, and $[W(CO)_4(DPPE)]$ (**3C**). The most distinguishable CO-stretching frequencies for these complexes were 2032 cm^{-1} for *cis*-$[W(CO)_4(P(OCH_3)_3)_2]$, 2026 cm^{-1} for *cis*-$[W(CO)_4(P(OCH_3)_3)(DPPE)]$, and 2023 cm^{-1} for **3C** [10,11]. Although the ligand exchange reactions of *cis*-$[W(CO)_4L_2]$ complexes with L′ (both L and L′ are monodentate phosphine ligands) are known at high temperatures [12], no detectable change was observed upon heating the solution of $[W(CO)_4(DPPE)]$ and $P(OCH_3)_3$ to 65°C. Thus, the formation of *cis*-$[Cr(CO)_4(P(OCH_3)_3)(DPPE)]$, *trans*-$[Cr(CO)_4(P(OCH_3)_3)(DPPE)]$, and *cis*-$[W(CO)_4(P(OCH_3)_3)(DPPE)]$ in the aforementioned experiments indicates a stepwise displacement of NBD in the thermal substitution reaction of $M(CO)_4(\eta^{2:2}\text{-NBD})$ instead of a CO detachment.

The concentration of the entering ligand (DPPM, DPPE, and DPPP) plays an important role in the rate of the reaction via the observed rate constant (Table 2, Fig. 3). k_{obs} gradually increases with the increasing concentration of the entering ligand. At high concentrations of the entering ligand, the increase in the observed

Table 2
The observed rate constants (k_{obs}) at various concentrations of entering ligand (DPPM, DPPE and DPPP) for the substitution of norbornadiene in **1A** at 85°C [a]

[PP]/[**1A**]	$k_{obs} \times 10^4$ (s^{-1})		
	DPPM	DPPE	DPPP
10	3.60	6.38	11.8
20	8.12	13.8	25.5
40	13.8	25.7	39.2
60	16.6	41.0	45.2
100	22.0	54.5	63.9
150	–	65.8	69.8

[a] $[\mathbf{1A}]_0 = 9.00$ mM.

rate constant is retarded as if it were approaching a saturation limit. However, it has been realized that this is due to the limited solubility of the bis(diphenylphosphino)alkane in toluene even at high temperature of the measurement. Inspection of Fig. 3 shows further that the observed rate constant, k_{obs}, depends not only on the concentration, but also on the nature of the entering ligand. This observation implies that the substitution reaction is associative in nature [13]. This is one of the experimental results implying that an associative first step should be incorporated into the mechanism, proposed for the COD substitution in the same kind of complexes by diphosphines [1]. The increasing order of the observed rate constant, DPPM < DPPE < DPPP, nicely correlates with the basicity of the chelating diphosphines [14] and the metal–diphosphine bond strength [15].

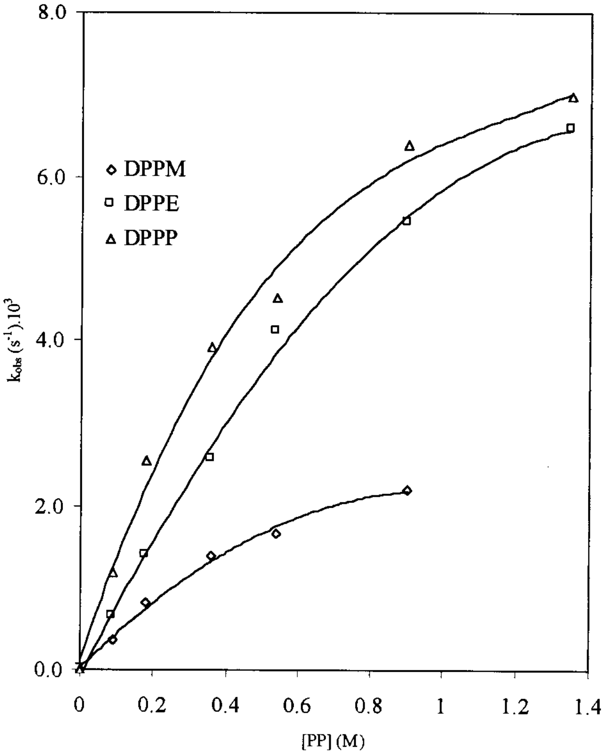


Fig. 3. Variations in the observed rate constants (k_{obs}) with the concentration of entering ligand for the substitution of norbornadiene in **1A** at 85°C. $[\mathbf{1A}]_0 = 9$ mM.

Table 3
The observed rate constants (k_{obs}) at various concentrations of leaving ligand (NBD) for the substitution of norbornadiene in **1A** at 85°C [a]

[NBD]/[**1A**]	$k_{obs} \times 10^4$ (s^{-1})
0	2.97
1	2.18
2	1.97
4	1.70
6	1.70
10	1.68

[a] $[\mathrm{DPPE}]_0 = [\mathbf{1A}]_0 = 9.00$ mM.

The effect of the leaving group on the rate of the thermal substitution reaction was also studied by varying the concentration of NBD but keeping the [DPPE]/[**1A**] ratio constant at one (Table 3). The plot of k_{obs} versus the concentration of NBD (Fig. 4) is curved downward with a positive intercept, indicating the presence of a complex mechanism in which increasing concentration of NBD causes a decrease in k_{obs} [16]. This clearly suggests that the substitution rate of NBD is retarded by the presence of NBD in the solution. In other words, the starting material, **1A**, is stabilized by the presence of excess NBD. This observation is important in proposing a mechanism for the thermal ligand substitution reaction. As the concentration of NBD goes to infinity, k_{obs} approaches a limiting value, which can be obtained from Fig. 4.

At this point one can give the proposed mechanism that will be in agreement with the experimental results for the thermal NBD substitution in $M(CO)_4(\eta^{2:2}$-NBD) by PP (Scheme 1). The mechanism essentially resembles the one proposed for the stepwise displacement of COD from $M(CO)_4(\eta^{2:2}$-COD) by PP [1], where the initial, rate-determining step is the cleavage of one of the metal–olefin bonds [17] and all the possible steps are considered in the substitution reaction. The only difference between the two mechanisms is the incorporation of an associative initial step into the mechanism proposed for the thermal NBD substitution in $M(CO)_4(\eta^{2:2}$-NBD) by PP (Scheme 1). Thus, there are two initial steps, which are competing with each other. One is an associative reaction involving the attachment of entering PP ligand to the transition metal center. The other is a dissociative reaction involving the stepwise detachment of the diolefin ligand. In the dissociative path, the intermediate **I** may produce the starting complex by reattachment of the free C=C bond of NBD, or bind irreversibly a PP ligand, yielding the

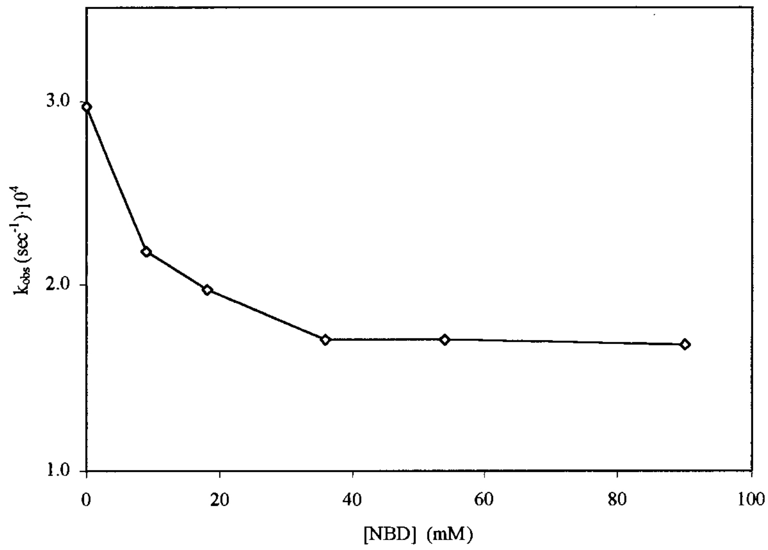


Fig. 4. Variations in the observed rate constants (k_{obs}) with the concentration of NBD for the substitution of NBD in **1A** with DPPE at 85°C. $[\mathbf{1A}]_0 = [DPPE]_0 = 9.00$ Mm.

intermediate **III** in which both of the potentially bidentate ligands (NBD and PP) are bonded to the transition metal center in monodentate fashion. Furthermore, complete detachment of NBD from **I** can take place to yield a 14 electron species (**II**), which is very unstable and reacts very fast with PP to form the complexes **1B**–**3D**. The intermediate **III** will also produce the complexes **1B**–**3D** upon detachment of NBD, followed by the fast ring-closure of the PP ligand.

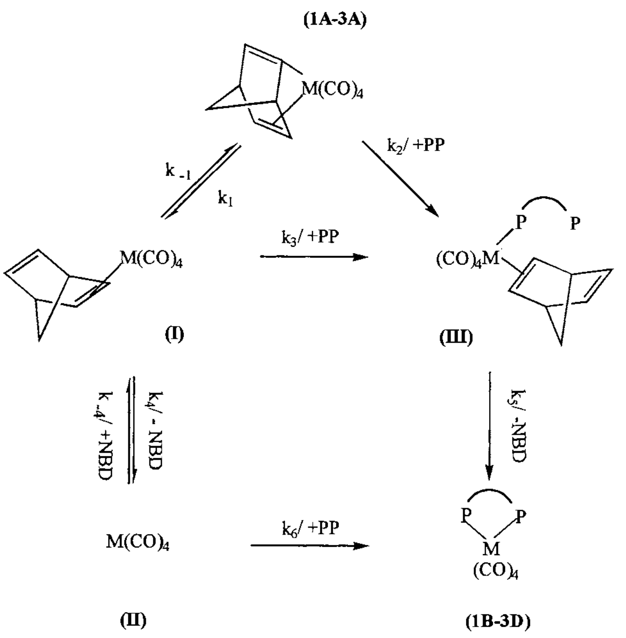
The proposed mechanism (Scheme 1) comprises a series of steps and therefore involves several intermediates. The observation of $Cr(CO)_5(DPPE)$, *cis*- and *trans*-$[Cr(CO)_4(P(OCH_3)_3)(DPPE)]$, and *cis*-$[W(CO)_4(P(OCH_3)_3)(DPPE)]$ as products of the thermal substitution of NBD from $M(CO)_4(\eta^{2:2}\text{-NBD})$ by PP in the presence of $P(OCH_3)_3$ provides a compelling evidence for the formation of **III** as intermediate in the reaction mechanism given in Scheme 1. Please recall that the results of our experiments under CO atmosphere and in the presence of $P(OCH_3)_3$ indicate a stepwise displacement of NBD in the thermal substitution reaction of $M(CO)_4(\eta^{2:2}\text{-NBD})$ instead of CO detachment. The intermediate **I** is known from the flash photolysis and the low-temperature matrix isolation studies in the literature [18]. There is no evidence for the formation of *cis*-$M(CO)_4(\eta^2\text{-NBD})_2$ from the intermediate **I** upon reversible coordination of a second NBD molecule, even though similar complexes have already been isolated [19]. However, such an intermediate would not affect the rate expression and is not shown in the Scheme 1.

By applying the well-known steady-state approximation for intermediates **I**, and **II**, the following rate law can be derived for the thermal NBD substitution in $M(CO)_4(\eta^{2:2}\text{-NBD})$ by PP:

$$\text{RATE} = k_{obs}[M] \quad (1)$$

$$k_{obs} = k_1 + k_2[PP] - \frac{k_1 k_{-1}}{k_{-1} + k_4 + k_3[PP] - \dfrac{k_4}{1 + \dfrac{k_6[PP]}{k_{-4}[NBD]}}} \quad (2)$$

where $[M]$ denotes the concentration of the starting $M(CO)_4(\eta^{2:2}\text{-NBD})$ complex. It is obvious that at very high concentrations of the entering ligand, the observed rate constant will be converted to a two-term rate



Scheme 1.

Table 4
The observed rate constants obtained for the substitution reaction of starting complexes **1A**–**3A** at different temperatures [a]

Starting complex	T (K)	$k_{obs} \times 10^4$ (s^{-1})		
		DPPM	DPPE	DPPP
1A	348	2.00	3.67	6.60
	353	3.09	5.73	8.10
	358	3.81	6.38	11.8
	363	5.33	9.29	13.2
2A	278	4.94	11.6	14.8
	283	7.76	17.8	23.8
	289	14.2	28.9	32.2
	293	18.3	37.4	45.9
3A	323	1.91	3.77	5.68
	328	2.16	5.58	8.17
	333	2.88	7.10	9.45
	338	4.24	10.4	11.5

[a] $[PP]_0/[M]_0 = 10$.

Table 6
The observed rate constants obtained at different temperatures for **1A** [a]

T (K)	$k_{obs} \times 10^4$ (s^{-1})
348	1.13
353	1.87
358	2.97
363	4.58

[a] $[DPPE]_0/[\mathbf{1A}]_0 = 1$, $[\mathbf{1A}]_0 = 9.00$ mM.

constant, i.e. $\lim_{[PP] \to \infty} k_{obs} = k_1 + k_2[PP]$. Although such an approximation would simplify the system enormously, the limited solubility of diphosphine in toluene does not allow very high PP concentrations. The rate expression given above can be used to explain all the experimental results at the available concentrations of diphosphine.

In a multistage reaction the rate-limiting step is that for which the rate of conversion of molecules is the lowest; on this definition it is not necessarily the step with the smallest rate constant. Rate-determining step is often used synonymously, but it is a little misleading, because in general, the rate of a multistage reaction is a composite of the rates of all the individual steps and is not determined by any single one of them [20]. In other words, more than one step may limit the reaction rate. Activation parameters are the basis for the determination of the nature of a mechanism [13]. However, the complexity of the mechanism proposed for the displacement reactions of **1A**–**3A** with the entering ligands, unfortunately, does not allow us to determine the rate constants for the individual steps. Although interpretation of activation parameters for such rate regimes is always open to debate, we determined the activation enthalpy and entropy from the temperature dependence of k_{obs} to get at least some clue about the nature of mechanism. For this purpose, thermal substitution reactions were performed at 75, 80, 85, and 90°C for **1A**, 5, 10, 15, and 20°C for **2A**, and 50, 55, 60, and 65°C for **3A** in the presence of ten-fold excess of diphosphine ligand to provide pseudo-first-order conditions. The observed rate constants obtained for the substitution of NBD in **1A**–**3A** with three different entering ligands at the given temperatures are listed in Table 4. The enthalpy of activation, $\Delta H^{\ddagger}$, and the entropy of activation, $\Delta S^{\ddagger}$, are calculated from these data by using the Eyring equation and given in Table 5. The large negative values of the entropy of activation for all the substitution reactions imply an associative mechanism in the transition state [21]. 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 [22]. In other words, the dependence of the rate on the ligand type and concentration can be easily explained by a displacement mechanism, which proceeds via the formation of a seven coordinated complex in the transition state [23].

The NBD substitution in **1A** was carried out at four different temperatures in the presence of one-fold DPPE for a better appreciation of the effect of entering ligand concentration on the activation parameters. From the observed rate constants at these temperatures (Table 6) the activation enthalpy and activation entropy values were found to be $\Delta H^{\ddagger} = 95$ kJ mol^{-1} and $\Delta S^{\ddagger} = -49$ J mol^{-1} K^{-1}, respectively. Comparing to the values in Table 5 ($\Delta H^{\ddagger} = 63$ kJ mol^{-1} and $\Delta S^{\ddagger} = -135$ J mol^{-1} K^{-1}), one observes a decrease in both the activation enthalpy and entropy when the entering

Table 5
The activation enthalpy and the activation entropy values for the substitution of NBD in **1A**–**3A** [a]

	$\Delta H^{\ddagger}$ (kJ mol^{-1})			$\Delta S^{\ddagger}$ (J mol^{-1} K^{-1})		
	1A	**2A**	**3A**	**1A**	**2A**	**3A**
DPPM	63 ± 2	58 ± 2	46 ± 2	-135 ± 5	-98 ± 4	-176 ± 6
DPPE	58 ± 2	51 ± 2	57 ± 2	-146 ± 6	-117 ± 4	-135 ± 5
DPPP	49 ± 2	47 ± 2	38 ± 2	-167 ± 6	-131 ± 5	-188 ± 6

[a] $[PP]_0/[M]_0 = 10$, $[M]_0 = 9.00$ mM.

ligand concentration was increased ten times. This result indicates that the contribution of the dissociative path becomes noticeable at lower concentrations of entering ligand. This is also indicative of the competition between the associative and dissociative paths in the proposed mechanism (Scheme 1). At higher concentration of entering ligand, the associative path is dominant, while at lower concentrations the contribution of the dissociative path becomes significant.

In addition, in a dissociative mechanism, the rate-limiting step involves only bond breaking as in M–NBD bond, whereas in an associative mechanism, the rate-determining step involves both bond breaking in M–NBD and bond making in M-(entering ligand) [24]. It is expected that the enthalpy of activation, $\Delta H^{\ddagger}$, would approach the M–NBD bond energy for a predominantly dissociative process and be rather independent of the nature of the entering ligand, whereas for an associative process $\Delta H^{\ddagger}$ is expected to be smaller than M–NBD bond energy [25]. The metal–ligand bond strength is known only for **2A**, **2B**, **2C**, and **2D**. The Mo–NBD bond energy is known to be 111.6 kJ mol^{-1} in literature [15] and the activation enthalpies for NBD substitution in **2A** are found to be $\Delta H^{\ddagger} = 58$, 51 and 47 kJ mol^{-1} for DPPM, DPPE, and DPPP, respectively. Thus, this also clearly indicates that substitution reaction of **2A** with DPPM, DPPE or DPPP has an associative mechanism in the transition state. The bond-energy measurement of **1A** and **3A** was not found in the literature. However, according to the activation data, the same result could be arrived at for the substitution reaction of **1A** and with **3A** DPPM, DPPE and DPPP.

The starting complexes **1A**–**3A** are assumed to have the same structure [26]. The diphosphines essentially act as bidentate ligands. Because of these similarities in the structure of starting complexes and in the ligating behavior of the diphoshines, a common mechanism is expected to be valid in each of the $M(CO)_4(\eta^{2:2}\text{-NBD})$ complex series. Variation in the rate within a reaction series may be caused by changes in the enthalpy or entropy of activation. If these quantities vary in a parallel fashion, compensating each other to produce minor changes in the free energy of activation of the process under investigation, thus a plot of $\Delta H^{\ddagger}$ versus $\Delta S^{\ddagger}$ will be linear. This is a consequence of the extrathermodynamic relationship [27], $\Delta H^{\ddagger} = T_c \Delta S^{\ddagger}$. This linear relationship between entropy and enthalpy of activation is also referred to as the isokinetic relationship or the compensation effect, and considered as a test for reaction series with a common mechanism. The slope of the linear plot of $\Delta H^{\ddagger}$ versus $\Delta S^{\ddagger}$ is T_c, the compensation or isokinetic temperature, at which all the reaction represented on the line occur at the same rate. The existence of an isokinetic plot for a reaction series implies that the relative order of rates for all the reactions in the series is simply inverted on passing the compensation temperature. By using the data in Table 5, $\Delta H^{\ddagger}$ versus $\Delta S^{\ddagger}$ plots are drawn for the substitution reaction of **1A**–**3A** with DPPM, DPPE or DPPP (Fig. 5). The slopes of the lines give T_c values of 447, 359, and 328 K for the respective reaction series with a correlation coefficient 0.998, 0.997, and 0.974, respectively.

Taking together all the experimental data on the substitution of NBD in $M(CO)_4(\eta^{2:2}\text{-NBD})$ given above and the previously reported results on the substitution of COD in $M(CO)_4(\eta^{2:2}\text{-COD})$ with diphosphinoalkanes [1], one can understand the effect of the leaving bidentate ligand on the reaction kinetics and mechanism. From the mechanistic standpoint, substitution of the ligands NBD in $M(CO)_4(\eta^{2:2}\text{-NBD})$ (M = Cr, Mo, W) and COD in $M(CO)_4(\eta^{2:2}\text{-COD})$ (M = Mo and W) (**1**–**2**) has associative nature in the transition states, whereas substitution of COD in $Cr(CO)_4(\eta^{2:2}\text{-COD})$ has a dissociative character. Reason for this behavior can be sterical crowding around the small chromium atom. As a bidentate ligand, 1,5-cyclooctadiene requires larger coordination volume than norbornadiene, a point, which can be figured out from the structural data of the complexes of both ligand [26,28]. The term coordination volume comprises the bite angle as well as the space required by the ligand in the coordination sphere of the metal. When diphosphine is substituted in place of COD in $Cr(CO)_4(\eta^{2:2}\text{-COD})$ it will be of dissociative nature in transition states. From the kinetic point of view, one can compare the substitution rates of diene in the tetracarbonyl($\eta^{2:2}$-diene)metal(0) complexes with diphosphinoalkanes. In terms of the diene replacement rate, $Mo(CO)_4(\eta^{2:2}\text{-NBD})$ is found to be the most labile complex, while $W(CO)_4(\eta^{2:2}\text{-COD})$ is the least labile one in the presence of bidentate diphosphines. The lability of NBD in the $M(CO)_4(\eta^{2:2}\text{-NBD})$ complexes with respect to substitution with diphosphine increases in the order Cr < W < Mo. This order changes as W < Mo < Cr for COD substitution in $M(CO)_4(\eta^{2:2}\text{-COD})$. $Cr(CO)_4(\eta^{2:2}\text{-NBD})$ is found to be

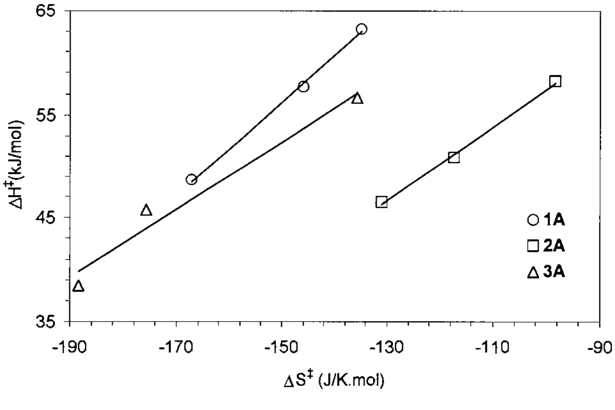


Fig. 5. Plot of $\Delta H^{\ddagger}$ vs. $\Delta S^{\ddagger}$ for the NBD substitution in **1A**–**3A** by DPPM, DPPE, and DPPP.

the most inert complex with respect to the NBD substitution. This can be ascribed to the comfortable coordination of the NBD, which requires less space than the COD around the central chromium atom. With respect to the COD substitution, $W(CO)_4(\eta^{2:2}\text{-COD})$ is found to be the most inert complex which might be attributed to the size compatibility of the diene ligand and the central atom.

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