

# Chelate Ring-Closure Kinetics of $\text{Cr}(\text{CO})_5$ (DPPM) Studied by $^{31}\text{P}$ -NMR Spectroscopy

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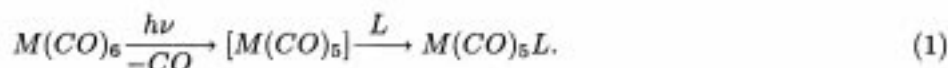
$^{31}\text{P}$ -NMR spectroscopy was used to study the kinetics of the chelate ring-closure reaction in  $\text{Cr}(\text{CO})_5$  (DPPM) where DPPM is bis (diphenylphosphino)methane. DPPM is potentially a bidentate ligand, but in this complex it is coordinated to the transition metal in a monodentate fashion and therefore can undergo chelation. The thermal chelate ring-closure reaction was carried out in an NMR sample tube at a constant temperature and the course of the reaction was quantitatively followed by taking  $^{31}\text{P}$ -NMR spectra in appropriate time intervals. Kinetic results have shown that the chelate ring-closure reaction of  $\text{Cr}(\text{CO})_5$  DPPM is of zero-order. Activation parameters were determined by evaluating the kinetic data. The large negative value of the activation entropy implies that the mechanism of the chelate ring-closure reaction is of associative nature in the transition states. The rate determining step might involve both Cr-CO bond breaking and Cr-P bond making. This will generate a seven coordinate transient complex from which the complete detachment of a CO ligand will lead to the formation of  $\text{Cr}(\text{CO})_4$  (DPPM).

## Introduction

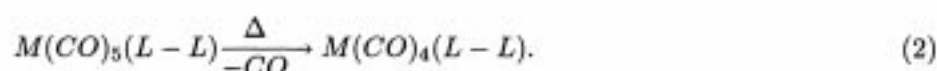
Trivalent phosphorus compounds are commonly used as mono- and bi-dentate ligands in the organometallic and coordination chemistry of the transition metals<sup>1</sup>. Kinetic, catalytic, and structural studies have been performed on organometallic systems incorporating the phosphine ligands. In particular, chelating diphosphine ligands have been shown to influence the product selectivity in the transition metal mediated catalytic reactions<sup>2</sup>. An emblematic example is the different linear to branched product ratio when monodentate versus bidentate phosphine ligands are bound to transition metals used to mediate the oxo process<sup>3</sup>. Entropy plays the key role in the reactivity and the stability of the complexes of chelating diphosphine since the metal-phosphorus bond cleavage at the one end leaves the chelating diphosphine still anchored to the metal by the phosphorus atom at the other end<sup>4</sup>. Thus, the loose end of the chelating diphosphine ligand can easily rebound the transition metal. Another factor playing role in the reactivity and the stability of the metal-diphosphine complexes is the metal-ligand bound enthalpy which can be considered as a sum of the stabilizing metal-phosphorus interaction and of the destabilizing strain energy caused by steric and torsional forces present in the metallacyclic fragment<sup>5</sup>.

From the viewpoint of the mechanistic organometallic chemistry information on chelation of the bidentate phosphine ligands seems to be valuable in designing new homogeneous catalytic processes<sup>6,7</sup>.

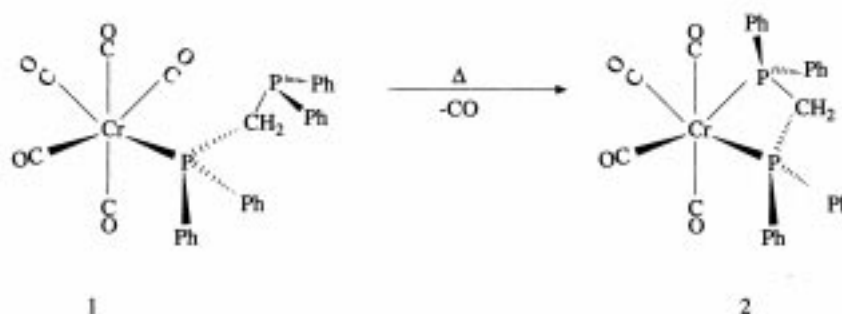
Reactions involving the cleavage and reattachment of a metal-phosphorus bond in a bidentate ligand are of great importance in the catalytic processes. Towards the synthesis of a metal-diphosphine chelate ring the first step is obviously the formation of a complex containing the diphosphine as a monodentate ligand, which then undergoes a ring-closure reaction. Complexes containing diphosphine ligands bonded in monodentate fashion have been generated photochemically or thermally in solution and subjected to thermal chelation<sup>8-10</sup>. The generation and isolation of intermediates containing diphosphine as monodentate ligand has become a popular field of research<sup>11-13</sup>. In this respect it is well-known that the photolysis of  $M(\text{CO})_6$  ( $M = \text{Cr}, \text{Mo}, \text{W}$ ) results in the generation of the transient species,  $[M(\text{CO})_5]$ , which can react with a ligand, L, to form complexes of the type  $M(\text{CO})_5L$  (Equation 1)<sup>14</sup>.



When L is a bidentate ligand (denoted as L-L), the primary photolysis product  $M(\text{CO})_5(L-L)$  will undergo a subsequent thermal ring-closure reaction as shown in Equation 2<sup>15</sup>.



This step has attracted much attention from various investigators<sup>16,19</sup> since it occurs over a wide time scale, ranging from milliseconds to several hours depending on the nature of the metal center and the bidentate ligand. In general the rate constant for such ring-closure reactions has been found to be independent of the concentration of L-L, and activation parameters (especially the activation entropy) have been used for assigning the nature of the mechanism. This type of chelation has been studied for a variety of bidentate ligands by using UV-visible<sup>20,22</sup> or IR spectroscopy<sup>23-25</sup>. Here we would like to report for the first time on the use of NMR spectroscopy to study the kinetics of a thermal ring-closure reaction in  $\text{Cr}(\text{CO})_5(\text{DPPM})$  where DPPM is bis(diphenylphosphino)methane.



Eq-3

## Experimental

All the reactions and manipulations were carried out either *in vacuo* or under a dry and deoxygenated nitrogen atmosphere. Solvents were distilled after refluxing over metallic sodium or phosphorus pentoxide under nitrogen for 3-4 days and stored until used. Hexacarbonylchromium(0) and bis(diphenylphosphino)methane were purchased from Aldrich Chemical Co. Ltd., Dorset, England and used without further purification. Purification and crystallization of the complexes were followed by taking IR spectra from solution on a Perkin-Elmer 1430 electronic Ratio Recording spectrophotometer at appropriate intervals. <sup>1</sup>H-, <sup>13</sup>C- and <sup>31</sup>P-NMR spectra were recorded on a Bruker AC-80 spectrometer (80.131 Hz for <sup>1</sup>H, 20.149 Hz for <sup>13</sup>C and

32.442 Hz for  $^{31}\text{P}$ ). TMS was used as internal reference for  $^1\text{H}$ -, and  $^{13}\text{C}$ -NMR, and phosphoric acid (85%) in capillary tube as external reference for  $^{31}\text{P}$ -NMR. Elemental analyses were carried out on a Hewlett-Packard 185 CHN analyzer.

**Pentacarbonylbis(diphenylphosphino)methanechromium(0),  $\text{Cr}(\text{CO})_5(\text{DPPM})$ , 1:** A solution of  $\text{Cr}(\text{CO})_6$  (0.95 g, 4.3 mmol) in THF (200 mL) was irradiated for 60 minutes at room temperature under nitrogen atmosphere. 1.65 g (4.3 mmol) of DPPM was added to this solution and stirred for 2 hours at room temperature. After evaporation of THF in vacuum from the solution, the residue was dissolved in toluene (10 mL). Cooling down this solution to  $-35^\circ\text{C}$  yielded pale yellow crystals which were separated from the mother liquor and washed with n-hexane (1.9 g, 77% yield). Elemental analysis: Calc.: H 3.85%, C 62.5%; Found: H 3.94%, C 63.2%  $^{13}\text{C}$ -NMR ( $\delta$  in ppm, rel. TMS, in toluene- $d_8$ ;  $J(^{13}\text{C}-^{31}\text{P})$  coupling constants are given in parantheses): for the CO groups 22.52 (6.6 Hz), 216.76 (13 Hz); for the phenyl carbons (on the coordinated phosphorus atom) 137.68 (i, 15, 7.6 Hz), 132.67 (o, 21 Hz), 130.05 (m), 128.43 (p); for the phenyl carbons (on the uncoordinated phosphorus atom) 135.92 (i, 36, 4.1 Hz), 131.91 (o, 10.8 Hz), 128.67 (m), 128.35 (p); for  $\text{CH}_2$  32.92 (32, Hz);  $^{31}\text{P}$ -NMR (in ppm rel.  $\text{H}_3\text{PO}_4$ , in toluene- $d_8$ )  $\delta = 46.5$  ppm (coordinated) and  $-27.2$  ppm (uncoordinated),  $J(^{31}\text{P}-^{31}\text{P})=84$  Hz; IR (in n-hexane):  $\nu(\text{CO})=2062, 1939, 1904\text{ cm}^{-1}$ .

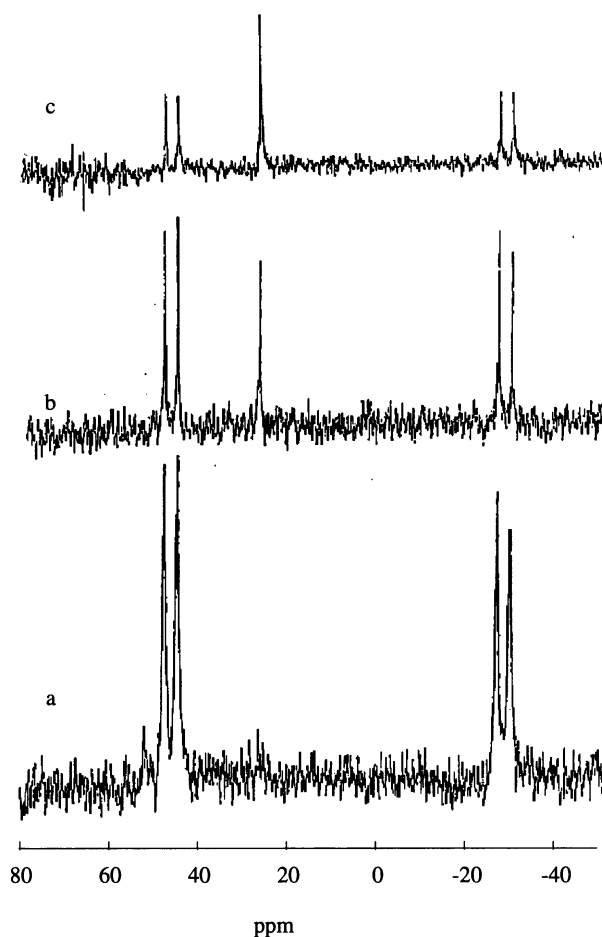
**Tetracarbonylbis(diphenylphosphino)methanechromium(0),  $\text{Cr}(\text{CO})_4(\text{DPPM})$ , 2:** To a solution of  $\text{Cr}(\text{CO})_4(\eta^{2:2}-1,5\text{-cyclooctadiene})^{26}$  (0.85 g, 3.1 mmol) in toluene (20 mL) was added 1.2 g (3.1 mmol) DPPM and the solution was stirred for 3 hours at  $60^\circ\text{C}$ . After filtration and reduction of the volume to 5 mL the solution was cooled down to  $-35^\circ\text{C}$  and left at that temperature for one day. The pale yellow crystals of 2 were separated from the mother liquor and washed with n-hexane (1.5 g, 88% yield). Elemental analysis: Calc. H 4.04%, C 63.5%; Found H 4.09%, C 64.1%  $^{13}\text{C}$ -NMR ( $\delta$  in ppm, rel. TMS, in toluene- $d_8$ ;  $J(^{13}\text{C}-^{31}\text{P})$  coupling constants are given in parantheses): for the CO groups 228.87 (20 Hz), 221.7 (9.5 Hz); for the phenyl carbons (on the coordinated phosphorus atom) 136.52 (i, 36 Hz) 131.21 (o, 12 Hz), 128.72 (m, 9 Hz), 130.09 (p); for  $\text{CH}_2$  47.69 (36 Hz);  $^{31}\text{P}$ -NMR (in ppm rel.  $\text{H}_3\text{PO}_4$ , in toluene- $d_8$ )  $\delta = 26.6$  ppm; IR (in n-hexane):  $\nu(\text{CO})=2012, 1922, 1903, 1891\text{ cm}^{-1}$ .

**Kinetic Measurements:** 40 mg of  $\text{Cr}(\text{CO})_5(\text{DPPM})$  (0.072 mmol) was dissolved in 2.5 mL toluene- $d_8$  under nitrogen atmosphere in a NMR sample tube of 10 mm diameter which was evacuated and filled with nitrogen gas. The solution was frozen by immersing the sample tube in liquid nitrogen and evacuated in vacuum, and then the NMR sample tube was sealed. Reaction was started by heating the sample to the temperature of the measurement.  $^{31}\text{P}$ -NMR spectra (200 scans) were recorded periodically every hour at preset constant temperatures between 100 and  $110^\circ\text{C}$ . The changes in concentrations of reactant 1 and product 2 during the reaction were determined from the changes in the normalized peak intensities. The rate constants were obtained from the graphical evaluation of the concentration versus time data.

## Results and Discussion

In the  $^{31}\text{P}$ -NMR spectrum the complex  $\text{Cr}(\text{CO})_5(\text{DPPM})$ , 1, gives two doublets at 46.5 and  $-27.2$  ppm while the chelate complex 2 shows only one singlet at 26.6 ppm. The spectrum of 1 constitutes a typical AB spin pattern with a coupling constant of  $^2J(^{31}\text{P}-^{31}\text{P})=84$  Hz. Since these two complexes are distinguishable in the  $^{31}\text{P}$ -NMR spectrum, this technique can be used to follow the conversion of 1 to 2. Figure 1 shows the changes in the  $^{31}\text{P}$ -NMR spectrum during the ring-closure chelation reaction of 1 at  $105^\circ\text{C}$ . One observes a gradual decrease in the peak intensities of 1 and a concomitant grow-up of a new peak for product 2. By monitoring the changes in the peak intensities one can quantitatively determine the changes in the

concentrations of both the reactant and the product. Figure 2 shows the time-dependent behaviour of the concentration of the product **2** at three different temperatures (100, 105, and 110 °C). The concentration of product **2** increases linearly with time indicating that the chelate ring-closure reaction of **1** obeys zero-order kinetics. The slope of the straight line gives the rate constant,  $k$ , in  $\text{mol. L}^{-1}.\text{s}^{-1}$  of the reaction (Table 1). Included in Table 1 are also the half-life values of this zero order chelate ring-closure reaction which were calculated from the rate constant,  $k$ , and the initial concentration of reactant,  $[\mathbf{1}]_0 = 2.88 \times 10^{-2} \text{ M}$ , ( $t_{1/2} = [\mathbf{1}]_0 / 2k$ )<sup>27</sup>.



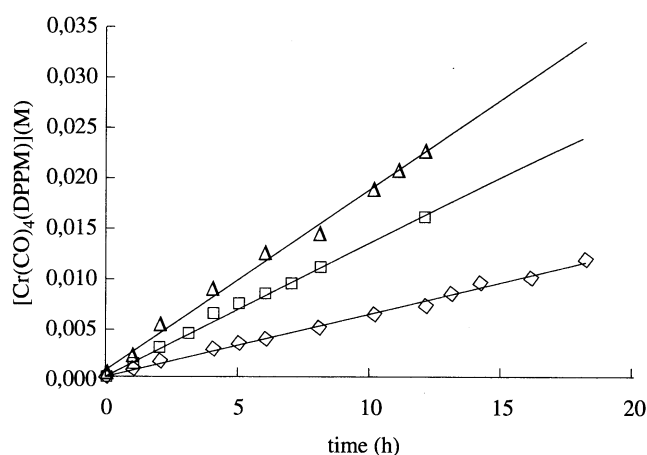
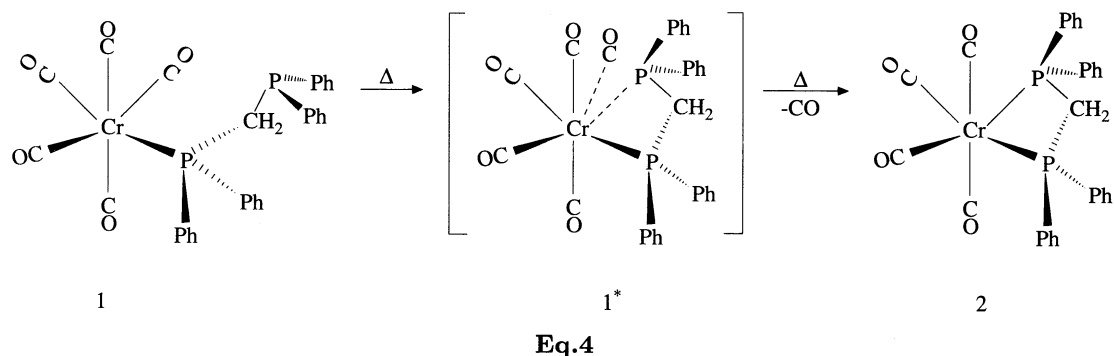
**Figure 1.**  $^{31}\text{P}$ -NMR spectra taken during chelate ring-closure reaction of  $\text{Cr}(\text{CO})_5(\text{DPPM})$ , **1** at 105 °C after a) 0, b) 3, c) 10h

**Table 1.** Rate constant ( $k$ ), half life ( $t_{1/2}$ ), and Gibbs free energy of activation ( $\Delta G^*$ ) for the chelate ring-closure reaction of  $\text{Cr}(\text{CO})_5(\text{DPPM})$ , **1**, at three different temperatures

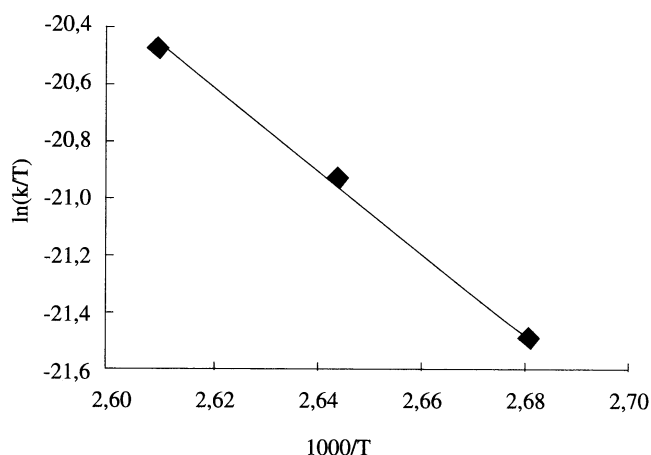
T(K)	$k \times 10^{-7} (\text{mol.L}^{-1}.\text{S}^{-1})$	$t_{1/2}(\text{hour})$	$\Delta G^*(\text{kJ.mol}^{-1})$
373	1.71	23.4	140.3
378	3.09	12.7	140.5
383	4.94	8.1	140.7

Using the Eyring plot (Figure 3), the enthalpy and the entropy of activation for the chelate ring-closure reaction of **1** were found to be  $\Delta H^* = 122.8 \text{ kJ.mol}^{-1}$  and  $\Delta S^* = -46.8 \text{ J. mol}^{-1}.\text{K}^{-1}$ , respectively. The Gibbs free energies of activation were calculated from the enthalpy and the entropy of activation at three different temperatures and were listed in Table 1.

Activation parameters may be evaluated for obtaining a clue about the nature of the mechanism.<sup>28,29</sup> The large negative value of the activation entropy implies that the mechanism of the chelate ring-closure reaction is of associative nature in the transition states. The rate determining step might involve both Cr-CO bond breaking and Cr-P bond making. This will generate a seven coordinate transient complex,  $1^*$  (Eq.4).



**Figure 2.** Time dependent behaviour of the concentration of  $\text{Cr}(\text{CO})_5(\text{DPPM})$ , **2**, at 100 (◇) 105(□), and 110°C (△).



**Figure 3.** Eyring plot of data obtained from the chelate ring-closure reaction of **1** at three different temperatures

On of the four CO groups cis to the DPPM ligand is expected to detach from complex  $1^*$  because of the cis-labelization effect of the loose phosphorous atom in DPPM in the transition state<sup>30</sup>. In general, the octahedral chromium(0) complexes have been found to undergo substitution reactions of dissociative nature because of the small size while substitutions on the larger molybdenum and tungsten usually follow an associative mechanism<sup>31</sup>. In contrast to the general trend, the chelate ring-closure reaction of **1** is unambiguously found to be of associative nature. This difference can be attributed to the fact that the chelate ring-closure reaction of **1** was carried out in a sealed NMR tube in which a CO pressure could build up during the experiment. Increasing CO pressure may facilitate an associative transition state. The effect of CO pressure on the rate of the chelation is obviously insignificant since CO can not compete with the chelating bidentate DPPM ligand for coordinating the chromium under the experimental conditions.

## Acknowledgment

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