

## MECHANISM OF FORMATION OF $\pi$ -ALLYL COMPLEXES: THE REACTION OF $\text{PdCl}_4^{2-}$ WITH 1,3-CYCLOHEXADIENE IN METHANOL

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### SUMMARY

The results of a kinetic study of the reaction between  $\text{PdCl}_4^{2-}$  and 1,3-cyclohexadiene are interpreted in terms of intermediate formation of a  $\pi$ -complex of palladium(II) with 1,3-cyclohexadiene, having only one double bond coordinated to the metal. Nucleophilic attack of methanol, from outside the coordination sphere of the metal, on the coordinated olefinic double bond, then gives the methoxy- $\pi$ -allyl complex.

### INTRODUCTION

Most  $\text{Pd}^{\text{II}}$  reactions with organic substrates give oxidized organic products and palladium(0)<sup>1</sup>, however in some cases the oxidation state of the metal remains unchanged. An example is the formation of  $\pi$ -allyl complexes usually prepared from  $\text{PdCl}_2$  and monoolefins, including allyl alcohol<sup>2</sup> and allyl halides<sup>3</sup>, or conjugated dienes<sup>4</sup>. Recently we carried out a mechanistic study of the reaction between  $\text{PdCl}_4^{2-}$  and allyl alcohol<sup>5</sup> or allyl ether<sup>6</sup> in protic solvents, the rate expression for the formation of the  $\pi$ -allyl complex,  $[(\pi\text{-C}_3\text{H}_5)\text{PdCl}_2]^-$ , being the same as that reported by Henry<sup>7,8</sup> for the oxidation of the olefins by  $\text{PdCl}_4^{2-}$  in water:

$$\text{rate} = \frac{k \cdot [\text{olefin}] \cdot [\text{PdCl}_4^{2-}]}{[\text{H}^+] \cdot [\text{Cl}^-]^2}$$

A mechanism involving solvent coordination to the metal prior to attack the olefinic double bond was proposed in order to account for the kinetic law. This paper reports on the mechanism of the reaction between 1,3-cyclohexadiene and  $\text{PdCl}_4^{2-}$  in methanol.

### EXPERIMENTAL

#### Materials

Di- $\mu$ -chlorobis(4-methoxy-2-cyclohexenyl)dipalladium(II) was prepared by literature methods<sup>4</sup>. 1,3-Cyclohexadiene was distilled before use and stored under nitrogen in the dark. All other materials were reagent grade chemicals.

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*Kinetic measurements*

Reactions were carried out in methanol at 25° and 1 M ionic strength with LiClO<sub>4</sub>, in the presence of variable amounts of LiCl and 1,3-cyclohexadiene, or in *sec*-butyl alcohol in the presence of a constant concentration of LiCl and variable amounts of CH<sub>3</sub>OH and diolefin. Progress of the reaction was followed with an OPTICA CF4R recording spectrophotometer equipped with thermostated cell compartment. Optical density readings in the near UV region were recorded at various time intervals. The methanol solution spectrum of the final product was identical to that of an authentic sample<sup>4</sup>, independently prepared and containing an excess of Cl<sup>-</sup>. With acid solutions, it was necessary to use a higher olefin concentration in order to force the reaction to completion. In acid media, in fact, the methoxy group in the  $\pi$ -allylic ligand is easily cleaved.

Pseudo first-order rate constants,  $k_{\text{obs}}$  (sec<sup>-1</sup>), were calculated from the slopes of linear plots of  $\log (A_{\infty} - A_t)$  vs. time ( $A$  is the optical density).

## RESULTS AND DISCUSSION

The reaction:

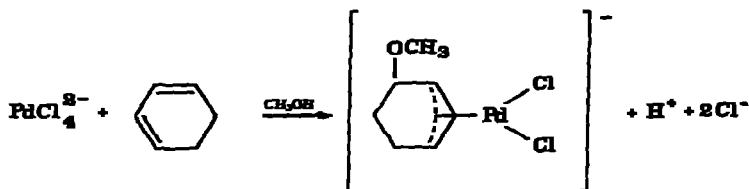


TABLE 1

VALUES OF  $k_{\text{obs}}$  (sec<sup>-1</sup>) FOR THE REACTION OF  $\text{PdCl}_4^{2-}$  WITH 1,3-CYCLOHEXADIENE AT 25° IN METHANOL;  $[\text{PdCl}_4^{2-}]10^{-3}$  M

$10^2 \times [1,3\text{-cyclohexadiene}]$ M	$[\text{Cl}^-]$ M	$10^3 \times [\text{H}^+]$ M	$[\text{ClO}_4^-]$ M	$10^3 \times k_{\text{obs}}$ (sec <sup>-1</sup> )
1.36	0.14		0.85	8.05
3.15	0.14		0.85	19.00
6.80	0.14		0.85	39.00
10.45	0.14		0.85	60.00
1.3	0.24		0.75	4.60
5.00	0.24		0.75	18.00
8.3	0.24		0.75	30.00
1.00	0.498		0.5	2.20
5.35	0.498		0.5	10.80
8.60	0.498		0.5	16.80
1.00	1.00			1.16
4.80	1.00			5.30
8.35	1.00			9.08
9.60	1.00			10.60
5.20	1.00	9.2		6.00
6.60	1.00	9.2		8.04
10.40	1.00	9.2		13.30
14.95	1.00	9.2		19.30

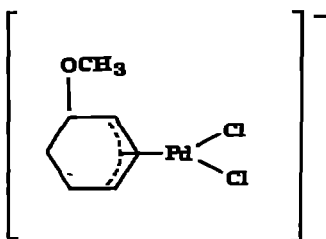
proceeds to completion at 25° in methanol in a single observable step in the presence of lithium chloride. Kinetic runs were carried out at four different chloride ion concentrations. Within each set of runs,  $[\text{Cl}^-]$  was kept constant as the concentration of diolefin was changed. In each kinetic run, pseudo first-order conditions were maintained and the pseudo first-order rate constants for reaction in methanol,  $k_{\text{obs}}(\text{sec}^{-1})$ , are listed in Table 1.

Plots of  $k_{\text{obs}}(\text{sec}^{-1})$  vs. 1,3-cyclohexadiene concentration at constant  $[\text{Cl}^-]$ , are straight lines with zero intercept (Fig. 1). The slopes of plots of  $k_{\text{obs}}(\text{sec}^{-1})$  vs. [1,3-cyclohexadiene],  $k_m(\text{sec}^{-1} \cdot M^{-1})$ , on the other hand, depend linearly on  $1/[\text{Cl}^-]$  (Fig. 2). Furthermore, no dependence of the rate on the acid concentration was observed.

Based on these findings, the kinetics take the form:

$$k_{\text{obs}} = \frac{k \cdot [1,3\text{-cyclohexadiene}]}{[\text{Cl}^-]}$$

Under our experimental conditions (high  $\text{Cl}^-$  concentration), the reaction product is:



formed by a splitting of the corresponding chloride bridge by the excess of  $\text{Cl}^-$ . A possible mechanism, which can account for the observed rate law is shown in Fig. 3. This mechanism involves the formation of a  $\pi$ -complex of palladium(II) with 1,3-cyclohexadiene, having only one double bond coordinated to the metal, in a fast pre-

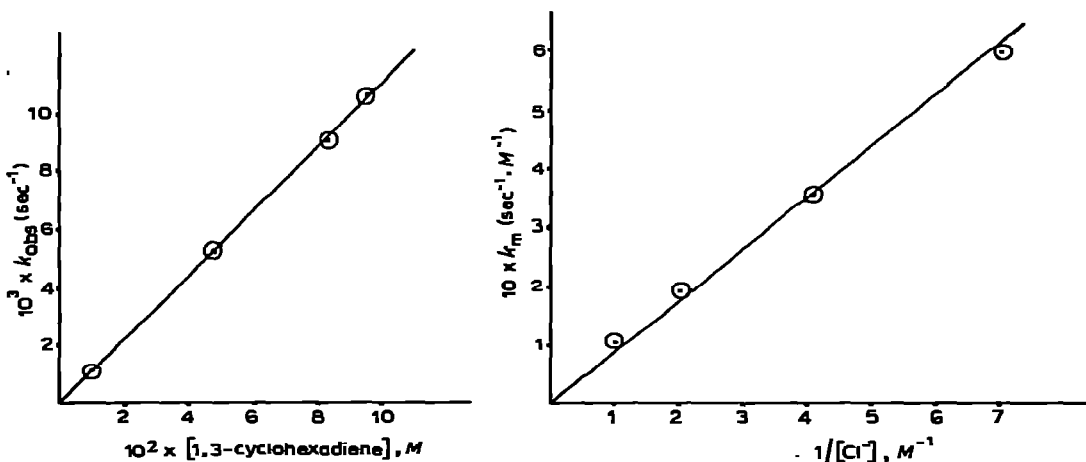


Fig. 1. Plot of  $k_{\text{obs}}(\text{sec}^{-1})$  values vs. the cyclohexadiene concentration in methanol at constant  $[\text{Cl}^-]$  (1 M).

Fig. 2. Dependence of the slopes,  $k_m(\text{sec}^{-1} \cdot M^{-1})$ , of plots of  $k_{\text{obs}}(\text{sec}^{-1})$  vs. [1,3-cyclohexadiene] on  $1/[\text{Cl}^-]$  in methanol.

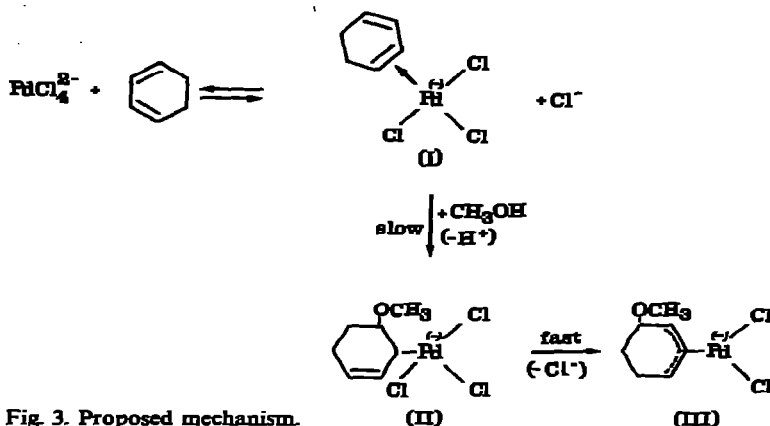


Fig. 3. Proposed mechanism.

equilibrium step. Nucleophilic attack of the methanol, from outside the coordination sphere of the Pd<sup>II</sup>, on the coordinated double bond to give the intermediate (II), which rapidly rearranges giving the final  $\pi$ -allyl complex (III), is the rate determining step. Evidence for the formation of the intermediate  $\pi$ -olefin compound (I) comes from the work of Donati and Conti<sup>9</sup>, who isolated, at low temperatures, an analogous complex, containing coordinated 1,3-cyclooctadiene. This fact also excludes a possible mechanism involving, in fast pre-equilibria, formation of a diene  $\pi$ -complex followed by nucleophilic attack on a terminal olefinic carbon by uncoordinated Cl<sup>-</sup>, which finally undergoes fast substitution by CH<sub>3</sub>O<sup>-</sup>. Furthermore, the rate dependence on 1/[Cl<sup>-</sup>] and the absence of any dependence of  $k_{obs}$  (sec<sup>-1</sup>) values of [H<sup>+</sup>] indicate that methanol does not coordinate to the metal in any step of the overall reaction.

However an alternative mechanism involving a fast pre-equilibrium between PdCl<sub>4</sub><sup>2-</sup> and 1,3-cyclohexadiene leading to the  $\pi$ -complex (I) (Fig. 3), which undergoes a slow nucleophilic attack by the coordinated Cl<sup>-</sup> on the coordinated double bond

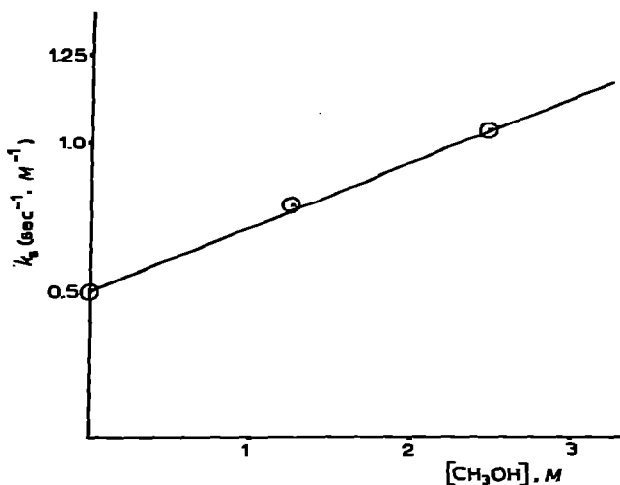


Fig. 4. Dependence of the slopes,  $k_s$  (sec<sup>-1</sup> · M<sup>-1</sup>) of plots of  $k_{obs}$  (sec<sup>-1</sup>) vs. [1,3-cyclohexadiene] on the CH<sub>3</sub>-OH concentration at constant [Cl<sup>-</sup>] ( $2.86 \cdot 10^{-2}$  M) in *sec*-butyl alcohol.

TABLE 2

VALUES OF  $k'_{\text{obs}}$  ( $\text{sec}^{-1}$ ) FOR THE REACTION OF  $\text{PdCl}_2^{2-}$  WITH 1,3-CYCLOHEXADIENE IN SEC-BUTYL ALCOHOL IN THE PRESENCE OF VARIABLE AMOUNTS OF METHANOL AT  $25^\circ$ ;  $[\text{PdCl}_2^{2-}] = 3 \times 10^{-4} \text{ M}$

$10^3 \times [1,3\text{-cyclohexadiene}]$ <i>M</i>	$10^2 \times [\text{Cl}^-]$ <i>M</i>	$10^3 \times [\text{H}^+]$ <i>M</i>	$[\text{CH}_3\text{OH}]$ <i>M</i>	$10^3 \times k'_{\text{obs}}$ ( $\text{sec}^{-1}$ )
3.41	2.86			1.95
17.00	2.86			8.45
34.1	2.86			16.60
3.41	2.86		1.25	2.68
17.00	2.86		1.25	12.90
34.10	2.86		1.25	26.50
3.41	2.86		2.50	3.80
17.00	2.86		2.50	19.20
34.10	2.86		2.50	38.40
7.07	2.86	5.08	2.50	7.50
35.40	2.86	5.08	2.50	36.50
70.70	2.86	5.08	2.50	80.50

followed by a fast solvolysis of the halide, cannot be excluded, *a priori*, on the basis of the kinetic data.

In order to distinguish between such possible reaction paths we carried out additional experiments, using *sec*-butyl alcohol,  $\text{CH}_3\text{CH}(\text{OH})\text{CH}_2\text{CH}_3$ , as solvent and varying the concentration of dissolved methanol. The final product detected from the characteristic UV spectrum, is a  $\pi$ -allyl compound.

Table 2 lists kinetic data  $k'_{\text{obs}}$  ( $\text{sec}^{-1}$ ) for reactions carried out in *sec*-butyl alcohol. The linear dependence of the rate on the 1,3-cyclohexadiene concentration and the lack of dependence of the rate on  $[\text{H}^+]$  were still observed. Fig. 4 shows the plot of slopes of  $k'_{\text{obs}}$  ( $\text{sec}^{-1}$ ) vs.  $[1,3\text{-cyclohexadiene}]$ ,  $k_s$  ( $\text{sec}^{-1} \cdot \text{M}^{-1}$ ), against the methanol concentration at constant  $[\text{Cl}^-]$ . The dependence of the rate on the methanol concentration supports the proposed mechanism, shown in Fig. 3, which considers "eso" attack of  $\text{CH}_3\text{OH}$  on the coordinated olefinic double bond. The intercept, in Fig. 4, is attributed to solvent reactivity. However, we do not exclude the possibility that under other conditions, involving other solvents, a different mechanism may be operative for such a reaction.

#### ACKNOWLEDGEMENT

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