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THE MECHANISM OF FORMATION OF π-ALLYL COMPLEXES: THE REACTION OF $PdCl_4^{2-}$ WITH ISOPRENE IN METHANOL

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Summary

A kinetic study of the reaction between $PdCl_4^{2-}$ and isoprene is described. The results are interpreted in terms of the formation of two π-complexes between palladium(II) and isoprene, one having only one double bond coordinated to the metal, the other being a chelated diene compound. Nucleophilic attack of solvent methanol on these intermediate complexes gives the methoxy π-allyl complex.

Olefin—metal complexes can undergo nucleophilic attack on the coordinated olefin. Such reactions involve either (*i*) attack by the nucleophile directly on the olefin, or (*ii*) attack of the nucleophile on the metal followed by its transfer to the coordinated double bond. Evidence for path (*i*) comes from nucleophilic additions to (diene)MX_2 (M = Pt or Pd) complexes [1,2], and for path (*ii*) from the oxidation of olefins in the presence of $PdCl_4^{2-}$ in water [3].

Conjugated dienes react with $PdCl_4^{2-}$ in alcoholic solvents to give π-allyl complexes [4,5]. This paper describes a mechanistic study of the reaction between $PdCl_4^{2-}$ and isoprene in methanol.

Experimental

Materials

The complex di-μ-chlorobis(4-methoxy-2-methyl-2-butenyl)dipalladium(II) was prepared as previously described [4]. The isoprene was distilled before use and stored under nitrogen in the dark. All other materials were reagent grade.

Kinetic measurements

Reactions were carried out either (*a*) in methanol, at 25° and made up to 1 *M*

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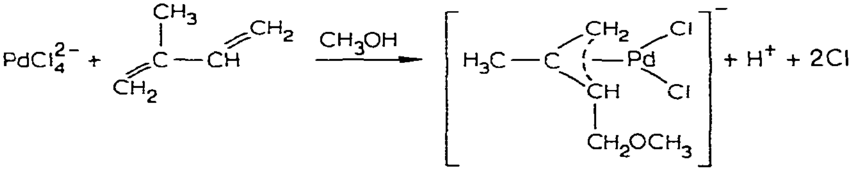
ionic strength with $LiClO_4$, in the presence of varying amounts of LiCl and isoprene, or (*b*) in sec-butyl alcohol at a constant concentration of LiCl but with varying amounts of CH_3OH and diolefin. The progress of the reaction was followed with an OPTICA CF4R recording spectrophotometer equipped with thermostated cell compartment. Spectral changes in the near ultraviolet region were monitored and a single process of spectrophotometric changes was always observed. Optical density readings were taken at various times. The spectrum of the final product was compared with that of an authentic sample [4] in methanol containing an excess of Cl^-. In order to study the effect of the H^+ concentration on the rate, we had to force the reaction to completion, using a higher diolefin concentration and a lower acid concentration. Pseudo-first-order rate constants, $k_{obs.}$ (sec^{-1}), 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:



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 values of the chloride concentration, corresponding to four sets of runs. Within each set of runs, $[Cl^-]$ was kept constant as the analytical concentration of diolefin was changed. In each kinetic run, pseudo-first-order conditions were observed, and the pseudo-first-order rate constants, $k_{obs.}$(sec^{-1}), are listed in Table 1. When the $k_{obs.}$($sec.^{-1}$) values were plotted against the isoprene con-

TABLE 1

VALUES OF k_{obs}(sec^{-1}) FOR THE REACTION OF $PdCl_4^{2-}$ WITH ISOPRENE, IN METHANOL AT 25°

10^2 [isoprene] (*M*)	$[Cl^-]$ (*M*)	$10^3 [H^+]$ (*M*)	$[ClO_4^-]$ (*M*)	$10^4 k_{obs.}$ (sec^{-1})
1.00	0.095		0.906	24.9
1.98	0.095		0.906	45
8.25	0.095		0.906	187
0.94	0.2		0.8	11.6
3.76	0.2		0.8	40
9.4	0.2		0.8	105
10	0.2		0.8	109
1.22	0.51		0.5	4.3
4.88	0.51		0.5	14
7.3	0.51		0.5	23
12.2	0.51		0.5	39
2.2	0.98			3.88
4.4	0.98			6.88
11	0.98			16
0.76	1.0	5.1		1.21
3.81	1.0	5.1		6.33
7.61	1.0	5.1		12.5

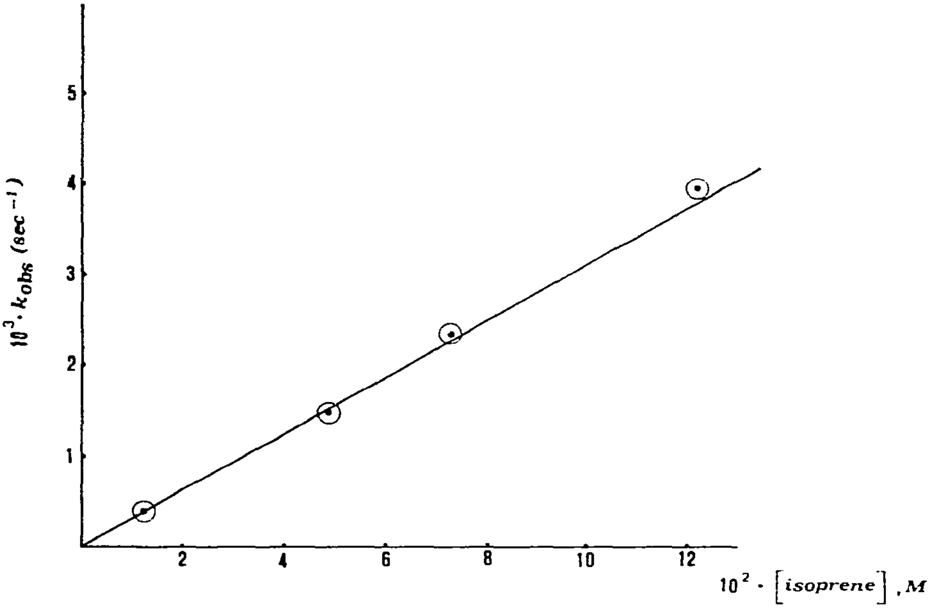


Fig. 1. Plot of the $k_{obs.}$(sec^{-1}) vs. isoprene concentration for the reaction of $PdCl_4^{2-}$ with isoprene in methanol. [Cl^-] = 0.51; [ClO_4^-] = 0.5.

centrations at constant [Cl^-], straight lines with zero intercepts were obtained (Fig. 1). Fig. 2 shows the linear relationship between the $k \cdot [Cl^-]^2$ values and the Cl^- concentrations. [k(sec$^{-1}\cdot$M^{-1}) is the slope of the plots of $k_{obs.}$(sec^{-1}) vs. [isoprene] at constant [Cl^-].]

On the basis of these findings, and in view of the fact that no influence of the H^+ concentration on the rate was observed, the following kinetic law can be formulated:

$$k \cdot [Cl^-]^2 = k_1 + k_2 \cdot [Cl^-] \tag{1}$$

and thus:

$$k = \frac{k_1}{[Cl^-]^2} + \frac{k_2}{[Cl^-]} \tag{2}$$

k is the slope of the plots of $k_{obs.}$(sec^{-1}) vs. [isoprene] at constant [Cl^-] and consequently it can be substituted with the ratio $k_{obs.}$/[isoprene]. The kinetic law then becomes:

$$\frac{k_{obs}}{[\text{isoprene}]} = \frac{k_1}{[Cl^-]^2} + \frac{k_2}{[Cl^-]} \tag{3}$$

Therefore:

$$k_{obs.} = \left\{ \frac{k_1}{[Cl^-]^2} + \frac{k_2}{[Cl^-]} \right\} \cdot [\text{isoprene}] \tag{4}$$

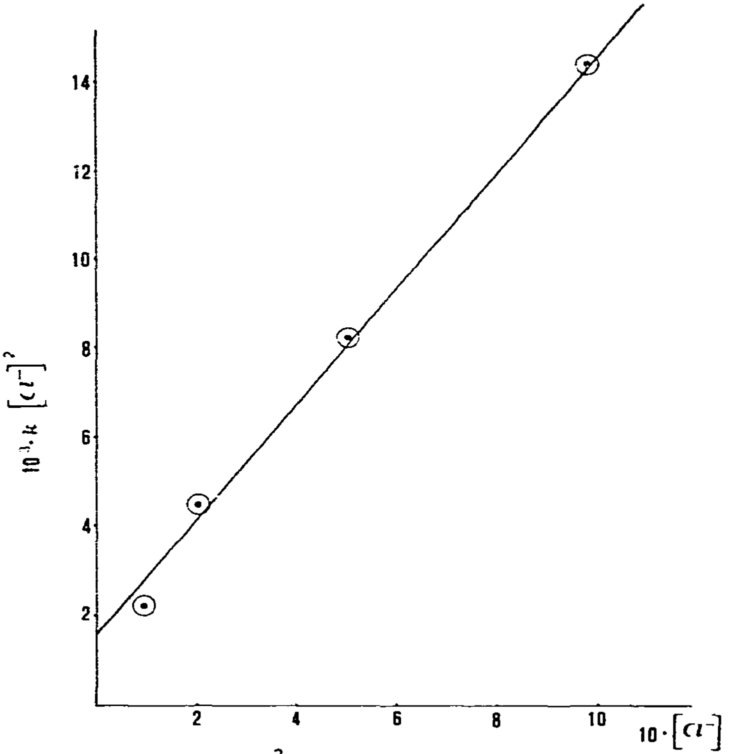
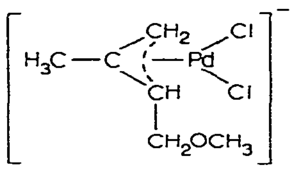


Fig. 2. Plot of the $k.[Cl^-]^2$ values vs. Cl^- concentration for the reaction of $PdCl_4^{2-}$ with isoprene in methanol [k(sec^{-1}·M^{-1}) is the slope of linear plots of $k_{obs.}$(sec^{-1}) vs. isoprene at constant [Cl^-].]

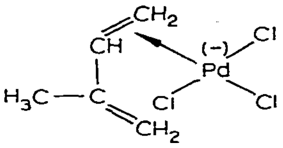
It is noteworthy that expression (4) is different from the kinetic law observed for the reaction between $PdCl_4^{2-}$ and 1,3-cyclohexadiene, for which the term $k_1/[Cl^-]^2$ is absent [6]. However, for the reaction of isoprene with $PdCl_4^{2-}$, k_2 is about nine times higher than k_1 [$k_1 = 1.5 \cdot 10^{-3}$ (sec^{-1} · M); $k_2 = 1.3 \cdot 10^{-2}$(sec^{-1})]. Under the experimental conditions used, involving the presence of a large excess of Cl^- the product is:



which is formed by splitting of the corresponding chloride bridge by the excess of Cl^-.

A possible mechanism which can account for the observed rate law (4) is shown in Fig. 3. This mechanism involves the formation, in a fast pre-equilibrium, of a π-complex of palladium(II) with isoprene, having only one double bond coordinated to the metal. Complex (I) is in equilibrium with the complex

(II), in which both double bonds are coordinated to the metal. This sequence also involves the species:



in which the olefin has a cisoid configuration. The nucleophilic attack by methanol, from outside the coordination sphere of the metal, on the intermediates (I) and (II) is the rate determining process in the reaction. Evidence for the formation of the complex (I), as a reaction intermediate, comes also from the isolation at low temperature of a similar compound involving butadiene as ligand [7]. Furthermore the absence of any dependence of the rate on [H$^+$] indicates that methanol does not coordinate to the metal in any step of the overall reaction. However, an alternative mechanism involving, in fast preequilibria between $PdCl_4^{2-}$ and isoprene, the formation of the π-complexes (I) and (II) (Fig. 3), followed by a slow nucleophilic attack by the coordinated Cl$^-$, and then a fast solvolysis of the halide bonded to the organic moiety, cannot be excluded a priori on the basis of the kinetic results. In order to distinguish between these different paths we carried out additional experiments using sec-butyl alcohol as solvent and varying the concentration of methanol dissolved in it. The final product, as revealed by the UV spectrum, is a π-allyl compound, and the reaction proceeds through a single observable stage.

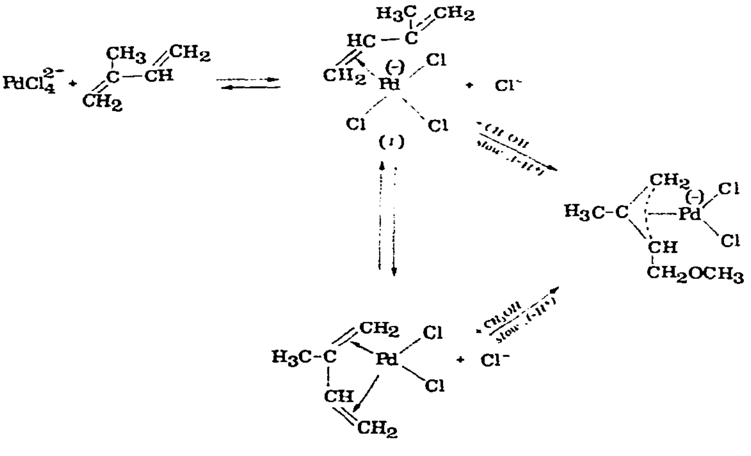


Fig. 3. Proposed mechanism.

Table 2 lists kinetic data, k'_{obs}(sec^{-1}), related to the reactions carried out in sec-butyl alcohol. The linear dependence of the rate on the isoprene concentration (Fig. 4) and the lack of dependence of the rate on [H$^+$] were again observed. Fig. 5 shows the plot of the slopes of k'_{obs}(sec^{-1}) vs. [isoprene], k_s (sec^{-1}·M^{-1}), against the methanol concentration at constant [Cl$^-$]. The de-

TABLE 2

VALUES OF k'_{obs}(sec^{-1}) FOR THE REACTION OF $PdCl_4^{2-}$ WITH ISOPRENE IN sec-BUTYL ALCOHOL IN THE PRESENCE OF VARYING AMOUNTS OF METHANOL AT 25°

10^3 [isoprene] (M)	10^2 [Cl^-] (M)	10^3 [H^+] (M)	[CH_3OH] (M)	$10^4 k'_{obs}$ (sec^{-1})
6.48	2.94			7
32.4	2.94			26.8
64.8	2.94			55.6
6.48	2.94		1.25	11.1
32.4	2.94		1.25	47.1
64.8	2.94		1.25	97
6.48	2.94		2.5	16.6
32.4	2.94		2.5	76.6
64.8	2.94		2.5	153
9.43	2.94	5.8	2.5	22
47.1	2.94	5.8	2.5	110
94.3	2.94	5.8	2.5	222

pendence of the rate on the methanol concentration lends support to the mechanism shown in Fig. 3, which involves an "*exo*" attack by methanol on the coordinated olefin. Further evidence for this mechanism is given by some results obtained for the reaction of $PdCl_4^{2-}$ with isoprene in the presence of

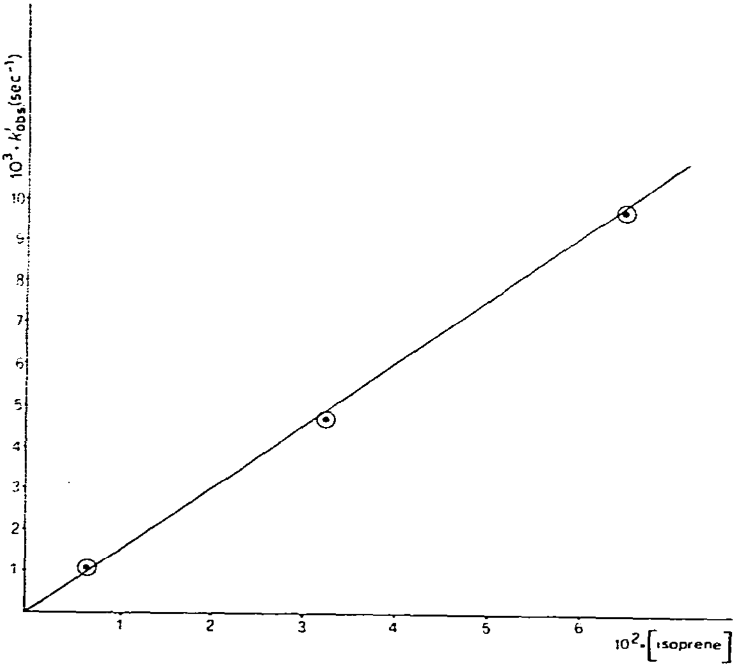


Fig. 4. Linear dependence of the k'_{obs}(sec^{-1}) values vs. the isoprene concentration for the reaction of $PdCl_4^{2-}$ with isoprene in sec-butyl alcohol. [Cl^-] = $2.94 \cdot 10^{-4}$ M; [CH_3OH] = 1.25 M.

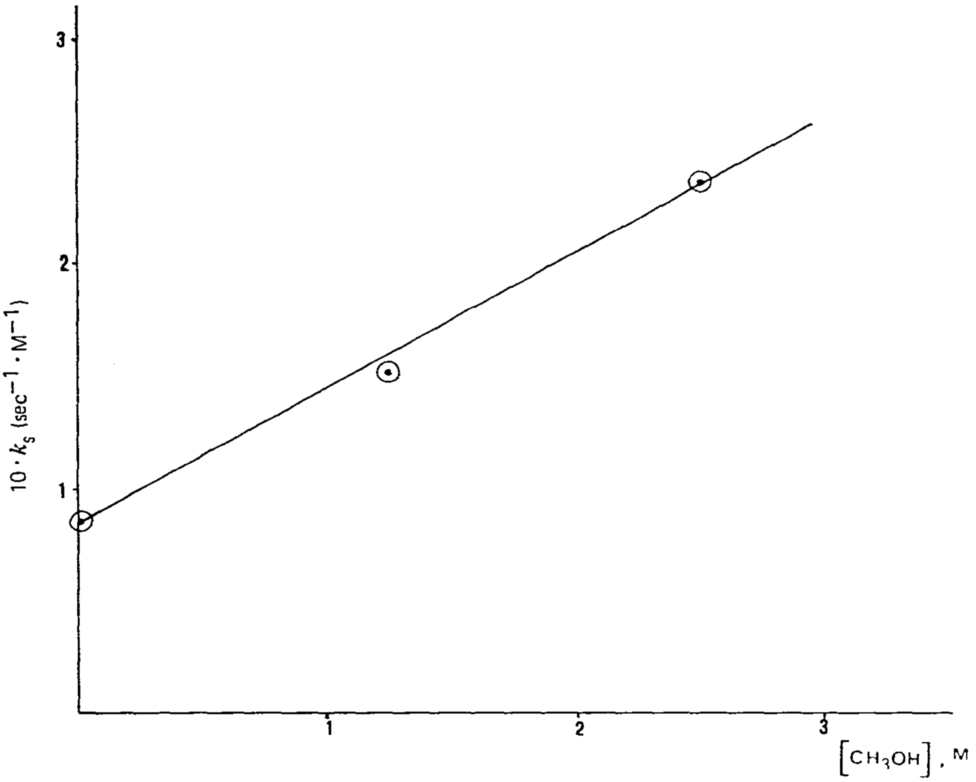
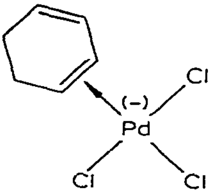


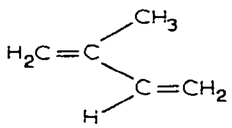
Fig. 5. Plot of the k_s(sec^{-1}·M^{-1}) values vs. the methanol concentration for the reaction of $PdCl_4^{2-}$ with isoprene in sec-butyl alcohol in the presence of varying amount of CH_3OH. [Cl^-] = const. = $2.94 \cdot 10^{-2}$. [k_s(sec^{-1}·M^{-1}) is the slope of linear plots of $k'_{obs.}$(sec^{-1}) vs. isoprene.]

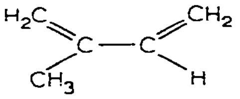
acetate ion in methanol. The kinetic law [8], in this last case, is only consistent with an external attack of the CH_3COO^- on both the intermediates (I) and (II) (Fig. 3).

It is interesting to note that in the reaction between $PdCl_4^{2-}$ and 1,3-cyclohexadiene, in methanol, the term $1/[Cl^-]^2$ in the rate equation is absent [6]. This means that the only reaction intermediate which is present in this case is:



In the case of the isoprene, which is a linear conjugated olefin, both the cisoid and transoid forms can exist, although the transoid form is the more stable [9]:





When the linear conjugated olefin coordinates to the metal it can assume both a transoid configuration or a cisoid disposition. This explains the sequence of equilibria in the mechanism shown in Fig. 3 and the rate equation (4).

Acknowledgement

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References

1 W.A. Whitla, H.M. Powell and L.M. Venanzi, Chem. Commun., (1966) 310.
2 C. Panattoni, G. Bombieri, E. Forsellini, B. Crociani and U. Belluco, J. Chem. Soc. D, (1969) 187.
3 P.M. Henry, J. Amer. Chem. Soc., 86 (1964) 3246.
4 S.D. Robinson and B.L. Shaw, J. Chem. Soc., (1963) 4806.
5 S.D. Robinson and B.L. Shaw, J. Chem. Soc., (1964) 5002.
6 R. Pietropaolo, E. Rotondo, F. Faraone and D. Pietropaolo, J. Organometal. Chem., 60(1973) 197.
7 M. Donati and F. Conti, Tetrahedron Lett., (1966) 1219.
8 R. Pietropaolo and F. Faraone, unpublished data.
9 L. Pauling, La natura del legame chimico, Italiane, Rome, 1960 p. 311.