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Mechanism of Exchange of Ancillary Ligands between Different Pd(II) Allyl Complexes

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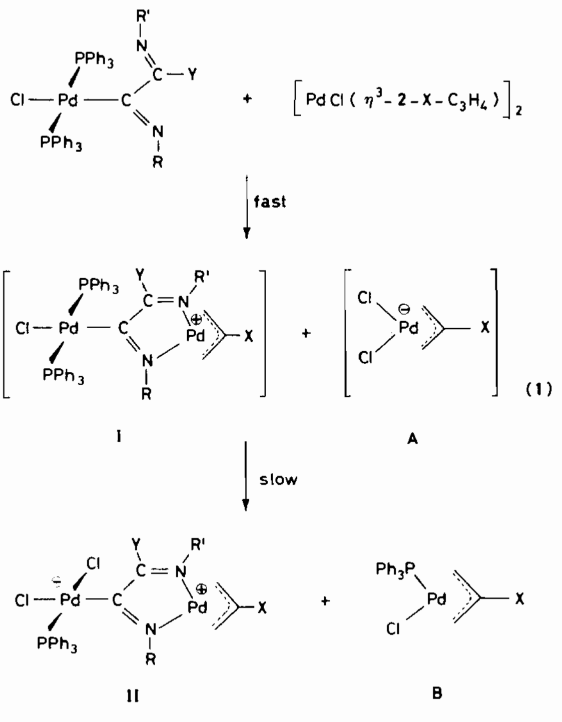
In the course of our studies on the coordinating properties of 1,4-diaza-2,3-butadien-2-yl-palladium(II) derivatives [1] we have found that their reaction with $[PdCl(\eta^3\text{-}2\text{-}X\text{-}C_3H_4)]_2$ proceeds as follows [2]:



Y = Me; R = R' = p-C_6H_4OMe : Ia; IIa
Y = H; R = R' = p-C_6H_4OMe : Ib; IIb
Y = Me; R = p-C_6H_4OMe, R' = Me : Ic; IIc
X = H, Me

The slow step of reaction 1 involves exchange of PPh_3 of I with a chloride ligand of the anion A, yielding the binuclear zwitterionic compounds II along with the neutral product B.

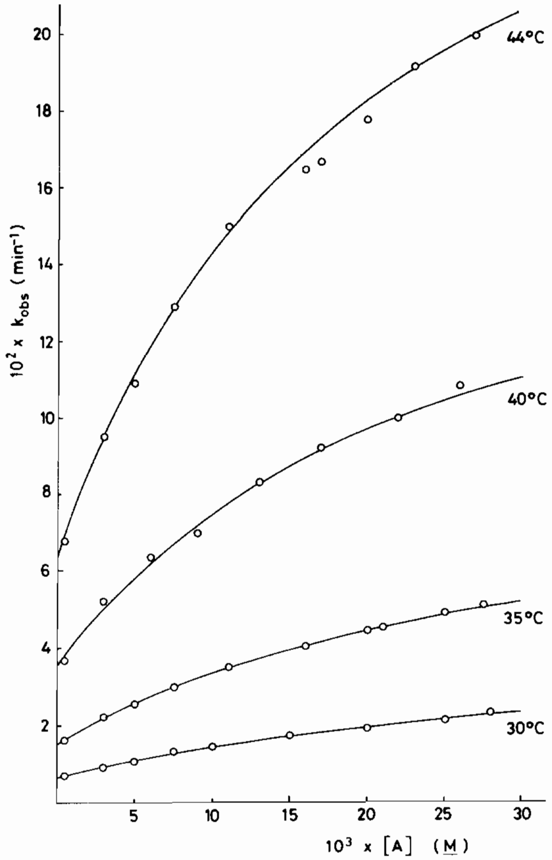


Fig. 1. Dependence of k_{obs} on the concentration of A for the reaction *Ia* + A at various temperatures (F = 3 × 10^{-2} *M*).

We have now carried out a kinetic study of the slow step in 1,2-dichloroethane (DCE) starting from the binuclear cationic substrate I (as perchlorate salt) [2] and an excess of the anion A (as triethylbenzylammonium salt) in order to provide pseudo-first-order conditions. The total concentration of ionic species (F) was kept constant by appropriate additions of tetrabutylammonium perchlorate. The kinetics were followed by standard spectrophotometric techniques in the 500–460 and 310–300 nm ranges.

A very fast spectral change takes place at the outset, which is followed by a much slower variation of optical density. Figure 1 shows the dependence of pseudo-first-order rate constants (k_{obs}) on the concentration of A for the reaction Ia + A at various temperatures and at a value of F of 3 × 10^{-2} *M*. As can be seen, all these plots are curvilinear with non-zero intercepts. These experimental findings and electronic and ^{1}H NMR spectral evidence suggest the following step-wise mechanism:

TABLE I. Substituent Effects on Rate and Equilibrium Parameters.

Reaction	T (°C)	10^2 k_1 (min^{-1})	10^2 k_2 (min^{-1})	K (M^{-1})
Ia + A	30	0.65 ± 0.04	4.82 ±0.6	23.2 ± 5
Ib + A	30	1.27 ± 0.06	18.57 ± 1	21.4 ± 2
Ia + A	40	3.52 ± 0.2	17.6 ± 1	39.4 ± 7
Ic + A	40	0.94 ± 0.05		

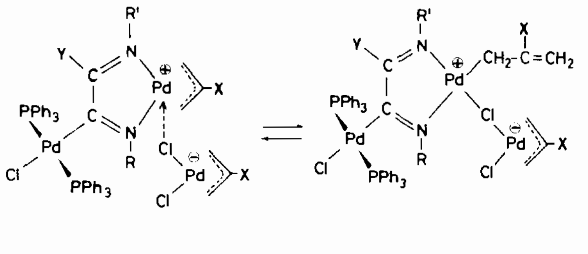
Ia : Y = Me; R = R' = p-C_6H_4OMe
Ib: Y = H; R = R' = p-C_6H_4OMe
Ic: Y = Me; R = p-C_6H_4OMe, R' = Me
X = Me

$$\begin{tikzcd}
I + A \arrow[r, shift left, "K"] \arrow[dr, "k_1"'] & I\text{------}A \arrow[l, shift left] \arrow[r, "k_2"] & II + B \arrow[dl, "+A"', "\text{fast}"] \\
 & I^* &
\end{tikzcd}$$

$$k_{obs} = \frac{k_1 + k_2K[A]}{1 + K[A]}$$

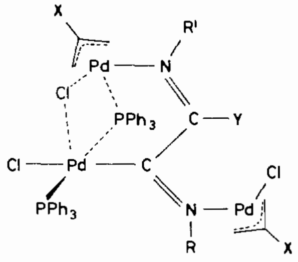
The formation of the final products occurs *via* two parallel stages (k_1 and k_2). The first stage implies a fast association pre-equilibrium between the cationic substrate I and the anionic reactant A. The pre-equilibrium constant K increases with increasing temperature and decreases with increasing total concentration of ionic species (see further).

The intermediate I------A is formed by interaction of the starting reactants probably through a bridging chloride:



I------A

Proton NMR spectra at 35 °C of equimolar mixtures of I and A indicate that an interaction occurs between the cation and the anion causing a fast *syn–anti* exchange of the allylic protons of I, whereas the η^3-allyl moiety of A is scarcely affected [2]. The intermediate I-------A undergoes a subsequent slow reaction leading to the final products, for which we suggest a trinuclear transition state:



The activation process involves opening of the 5-membered α-diimino ring and coordination of each imino nitrogen to a palladium allyl moiety. Further evidence is now emerging in the literature for α-diimino ligands bridging two metallic centers [1b, 3].

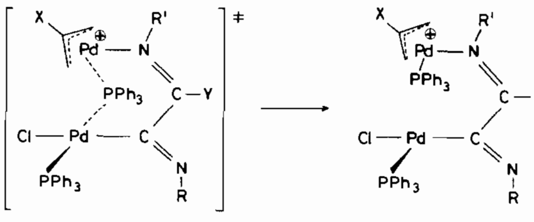
The parallel step k_1 involves a slow intramolecular rearrangement of substrate I to a labile intermediate I*, which then reacts rapidly with the anion to give the final products.

The following activation parameters were obtained for the reaction in Fig. 1:

$$k_1: \Delta H^{\ddagger} = 30.5 \pm 0.5 \text{ Kcal/mol}; \Delta S^{\ddagger} = 24.0 \pm 1.5 \text{ e.u.}$$

$$k_2: \Delta H^{\ddagger} = 24.0 \pm 0.3 \text{ Kcal/mol}; \Delta S^{\ddagger} = 6.8 \pm 0.9 \text{ e.u.}$$

The small positive value of the activation entropy for the k_2 step is in agreement with the proposed trinuclear transition state, in which a concerted intramolecular exchange of ligands occurs with a small change of degrees of freedom. The highly positive value of the activation entropy for the k_1 step suggests that an unassisted dissociation takes place. In this case, we can envisage an activation process involving either opening of the 5-membered α-diimino ring or dissociation of one phosphine ligand, or a combination of both such alternatives:



I*

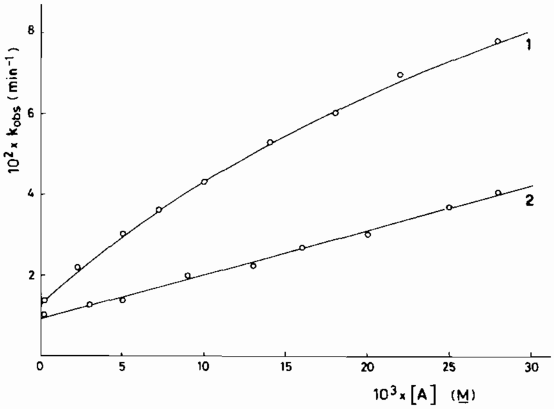


Fig. 2. Dependence of k_{obs} on [A] for the reactions: *Ib* + A at 30 °C (curve 1) and *Ic* + A at 40 °C (curve 2) (F = 3 × 10^{-2} *M*).

The above discussed mechanism is also supported by rate effects caused by changes in the substituents on the 5-membered α-diimino ring of the cationic substrate (Table I).

When the methyl Y substituent of *Ia* is replaced by a proton (*Ib*) an overall increase in reaction rate occurs. At 30 °C the k_1 term is almost doubled, while k_2 undergoes a fourfold increase. The equilibrium constant K is very little affected. On the contrary, when one of the N-substituents is a methyl group (*Ic*), a marked decrease in rate is observed and the k_1 term at 40 °C is reduced to about one-fourth. These changes in k_1 values agree with an activation process which implies opening of the 5-membered α-diimino ring. The observed variation in reactivity, in fact, parallels the order of stability of such a ring with different substituents, as it emerges from dissociation equilibrium studies that we have carried out with simple organic α-diimines [4]. The almost fourfold increase in the k_2 term further supports the hypothesis that the activation process for this stage involves opening of the 5-membered ring and formation of a trinuclear activated complex, which are expected to be favoured by the combined lower stability of the ring and lower steric hindrance of the proton Y substituent in *Ib*. The markedly lower k_1 value for the reaction of *Ic* with A is clearly due to the higher stability of the 5-membered ring caused by the more electron-donating imino nitrogen. These substituent effects on k_1 strongly suggest that opening of the 5-membered ring of the cationic substrate plays a major role in the stage k_1. However, most recent studies that we are pursuing indicate that this term is also affected by the nature of the exchanging phosphine ligand.

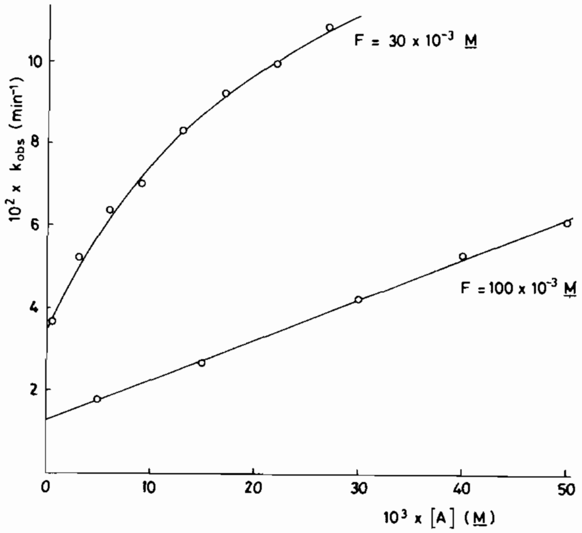


Fig. 3. Dependence of plots of k_{obs} *vs.* [A] on F for the reaction *Ia* + A at 40 °C.

The presence of a methyl group on the imino nitrogen also causes such a dramatic decrease in the pre-equilibrium constant value as to make the plot of k_{obs} *versus* the anion concentration linear throughout the concentration range examined (Fig. 2).

As expected, the equilibrium constant K involving association of oppositely charged ions decreases with increasing total concentration of ionic species (F) in the reaction medium, to the extent that the rate law may change from curvilinear to linear, other things being equal (Fig. 3).

The dependence of K on temperature leads to the following standard thermodynamic parameters: $\Delta H^\circ = 10.7 \pm 0.5$ Kcal/mol; $\Delta S^\circ = 41.6 \pm 1.5$ e.u.

The formation of the intermediate I-------A is an endothermic process with a highly positive entropy. In this case, the negative entropy of association is more than offset by a highly positive desolvation entropy (defreezing of solvent molecules).

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