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Migration of Anionic Bidentate Ligands between Different Palladium(II) Allyl Complexes

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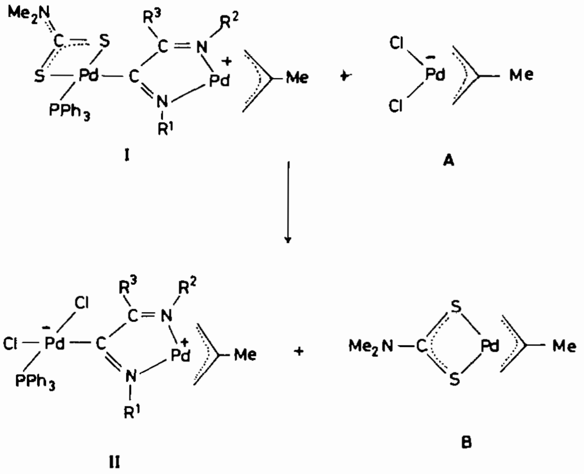
We have studied the mechanism of the following reaction:



Ia : $R^1 = R^2 = p\text{-}C_6H_4OMe$; $R^3 = Me$
Ib : $R^1 = p\text{-}C_6H_4OMe$; $R^2 = R^3 = Me$
Ic : $R^1 = R^2 = p\text{-}C_6H_4OMe$; $R^3 = H$

The reaction was carried out in 1,2-dichloroethane (DCE) with the substrate **I** as perchlorate salt and with an excess of the anion **A** as triethylbenzylammonium salt, under pseudo-first-order conditions. The progress of the reaction was monitored spectrophotometrically (400–500 nm), at constant concentration of ionic species, F = 3 × 10^{-2} *M* (tetrabutylammonium perchlorate). The exchange of ligands takes place via a stepwise mechanism analogous to that observed for the reaction of binuclear cationic complexes of type **I**, containing the *trans*-$PdCl(L)_2$ unit [L = $AsPh_3$, $P(C_6H_4X\text{-}p)_3$] with the anion **A** [1]:

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

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

The rate data are reported in Table I.

For the reactions involving **Ib** and **Ic** a linear dependence of k_{obs} on [A] is observed. This implies that the K[A] term in rate law (1) is ≪1 [1]. For **Ic** the intercept is statistically unsignificant, essentially due to the very high slope.

The intermediate **I···A** is thought to arise from fast reversible interaction through chloride bridges involving the palladium centers of the $Pd(\eta^3\text{-}2\text{-}MeC_3H_4)$ moieties of the starting reactants, as suggested by ^1H nmr and electronic spectral data. This intermediate undergoes a subsequent slow rearrangement (k_2 step) via a trinuclear transition state:

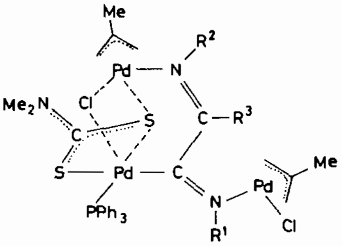


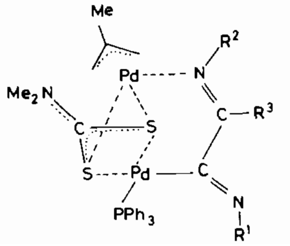
TABLE I. Rate Parameters.

Reaction	T (°C)	k_1 (min^{-1})	k_2 (min^{-1})	K (M^{-1})	k_2 K (M^{-1} min^{-1})
Ia + **A**	15	0.015 ± 0.002	0.61 ± 0.05	12.9 ± 2	7.9
	20	0.027 ± 0.007	1.09 ± 0.2	14.1 ± 4	15.4
	25	0.043 ± 0.009	1.95 ± 0.35	13.8 ± 4	26.9
	30	0.10 ± 0.01	3.3 ± 0.4	14.1 ± 3	46.5
Ib + **A**	30	0.021 ± 0.002	–	–	5.2[a]
Ic + **A**	15	0.04 ± 0.05[b]	–	–	213.0[a]

[a] From the linear plots of k_{obs} *vs.* [A]. [b] Statistically unsignificant at the 95% confidence level of the fit.

The activation process involves opening of the five-membered α-diimino ring and coordination of each imino nitrogen to a palladium allyl unit. The activation parameters for this step (reaction **Ia** + **A**) are: $\Delta H_2^\ddagger = 19.0 \pm 0.1$ kcal mol^{-1}, $\Delta S_2^\ddagger = -1.4 \pm 0.3$ e.u. The small value of the activation entropy agrees with the proposed trinuclear transition state, which involves a concerted intramolecular exchange of ligands.

The parallel step k_1 corresponds to a slow intramolecular rearrangement of **I** to a labile intermediate **I*** which then reacts rapidly with the anion **A** to give the final products. Also for this step the activation parameters ($\Delta H_1^\ddagger = 21.9 \pm 2$ kcal mol^{-1}, $\Delta S_1^\ddagger = 1 \pm 5$ e.u.) point to a transition state involving concerted α-diimino ring opening and migration of the bidentate dimethyldithiocarbamate ligand:



The pre-equilibrium constant appears to be virtually independent of temperature, suggesting a very small standard enthalpy.

On replacing the p-C_6H_4OMe group (R^2) with a methyl group, the k_1 and k_2K terms are markedly reduced as a consequence of the increased stability of the five-membered α-diimino cycle towards ring opening [2, 3]. On the contrary, substitution of the methyl R^3 group by a proton brings about a dramatic increase in the k_2K term, essentially due to an increased k_2 value. This results from a reduced stability of the cycle [2, 3] combined with a much lower steric hindrance of the R^3 substituent.

References

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3 P. L. Sandrini, A. Mantovani, P. Uguagliati and B. Crociani, *Inorg. Chim. Acta, 51,* 71 (1981).