

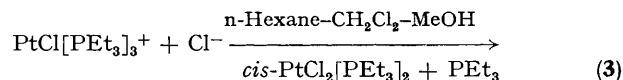
cis-trans Isomerization of $\text{PtCl}_2[\text{PEt}_3]_2$. Evidence against a Consecutive Displacement Mechanism

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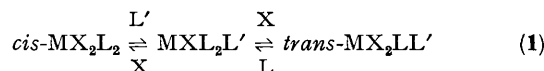
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Summary The complex $\text{PtCl}[\text{PEt}_3]_3^+$ does not react with chloride to form *cis* or *trans* $\text{PtCl}_2[\text{PEt}_3]_2$ and when a different phosphine is used to catalyse the *cis-trans* isomerization of $\text{PtCl}_2[\text{PEt}_3]_2$, the phosphines do not mix during isomerization; these data contradict the consecutive displacement mechanism.

pseudo first-order conditions (approximately 10^{-4}M complex and a thirty fold excess of phosphine) half-lives were of the order of seconds at 15° . This implies that reaction (3)



Two mechanisms have been suggested for the *cis-trans* isomerization of square-planar complexes of the form MX_2L_2 in the presence of a catalyst (L'); (a) a consecutive displacement mechanism¹ [equation (1)], and (b) a mech-

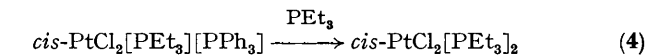
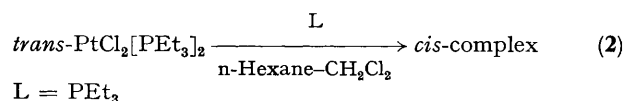


anism should be extremely fast under pseudo first-order conditions if the consecutive displacement mechanism is in operation. However, no reaction was observed when excess of chloride was added to $\text{PtCl}[\text{PEt}_3]_3^+\text{ClO}_4^-$ in MeOH-n-hexane- CH_2Cl_2 solution at room temperature. When LiBr was added to a MeOH solution of $\text{PtCl}[\text{PEt}_3]_3^+\text{ClO}_4^-$, the u.v. spectrum of the product agreed with that of $\text{PtBr}[\text{PEt}_3]_3^+$.

anism involving a distorted five-co-ordinate state in which L' occupies a unique position. This distorted state must be able to undergo fluxional change which interconverts the positions of L and X and, therefore, enables isomerization.² This mechanism, in contrast with the pseudorotation mechanism,³ does not involve a trigonal-bipyramidal state which must generate identity of L and L' at some point.

The consecutive displacement mechanism also implies that the phosphines must mix during isomerization. When excess of PPh_3 was added to a MeOH solution of *trans*- $\text{PtCl}_2[\text{PEt}_3]_2$ the u.v. spectrum of the solution agreed with that of *cis*- $\text{PtCl}_2[\text{PEt}_3]_2$. The product was isolated and micro-analysis also showed it to be *cis*- $\text{PtCl}_2[\text{PEt}_3]_2$. The possibility exists that *cis*- $\text{PtCl}_2[\text{PEt}_3][\text{PPh}_3]$ is formed but PPh_3 might be replaced very rapidly by PEt_3 . However, when excess of PEt_3 was added to a MeOH- CH_2Cl_2 solution of *cis*- $\text{PtCl}_2[\text{PPh}_3]_2$ and allowed to stand for 10 min the u.v. spectrum of the product in MeOH did not correspond to that of *cis*- $\text{PtCl}_2[\text{PEt}_3]_2$ but rather to that of *cis*- $\text{PtCl}_2[\text{PPh}_3]_2$. Micro-analysis of this product showed that at the most, 20% of the phosphines might have exchanged in the time allowed. This exchange is not fast enough to account for phosphine exchange in reaction (4)

No conclusive evidence of phosphine mixing during isomerization has so far been reported.⁴ This, and the rapid reaction of the cation MXL_3^+ with X^- in mechanism (a) was investigated. In an attempt to distinguish between mechanisms (a) and (b) a kinetic study was undertaken [equation (2)]. The reactions were followed spectrophotometrically by monitoring the absorbance change at



268 nm on a Cary 15 spectrophotometer. The study was carried out in a nitrogen atmosphere and using deoxygenated solvents.

These data clearly contradict the consecutive displacement mechanism, and favours fluxional rotation.

Three reactions were observed. The spectral change of the first reaction corresponds to that of *trans*- to *cis*- $\text{PtCl}_2[\text{PEt}_3]_2$. The first reaction was relatively fast and under

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¹ F. Basolo and R. G. Pearson, 'Mechanisms of Inorganic Reactions,' 2nd edn., Wiley, New York, 1967, ch. V; C. H. Langford and H. B. Gray, 'Ligand Substitution Processes,' Benjamin, New York, 1966.

² P. Haake and R. M. Pfeiffer, *J. Amer. Chem. Soc.*, 1970, **92**, 4996.

³ P. Haake and R. M. Pfeiffer, *Chem. Comm.*, 1969, 1330.

⁴ P. Haake *et al.* reported mixing of phosphines (ref. 2) but this was discounted by D. G. Cooper and J. Powell, *J. Amer. Chem. Soc.*, 1973, **95**, 1102.