

## ***cis-trans*-Isomerization of $\text{PtCl}_2(\text{PEt}_3)_2$ . The Case for a Consecutive Displacement Mechanism**

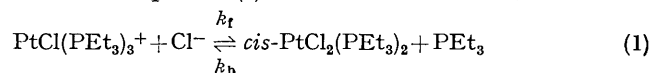
By JOHN POWELL\* and DAVID G. COOPER

(Lash Miller Chemical Laboratories, University of Toronto, Toronto M5S 1A1, Ontario, Canada)

**Summary** Recently reported data thought to be contrary to the consecutive displacement mechanism for  $\text{PR}_3$ -catalysed isomerization of  $\text{PtCl}_2(\text{PEt}_3)_2$  are in fact fully consistent with this mechanism of isomerization.

In a recent communication concerning the mechanism of  $\text{PR}_3$  catalysed *cis-trans*-isomerization of  $\text{PtCl}_2(\text{PEt}_3)_2$  the following observations were reported.<sup>1</sup> (i) In n-hexane- $\text{CH}_2\text{Cl}_2$  solution isomerization of *trans*- $\text{PtCl}_2(\text{PEt}_3)_2$  (ca.  $10^{-4}\text{M}$ ) to *cis*- $\text{PtCl}_2(\text{PEt}_3)_2$  catalysed by excess of  $\text{PEt}_3$  has half lives of the order of seconds at 15 °C. (ii) Addition of an excess of chloride to  $[\text{PtCl}(\text{PEt}_3)_3]\text{ClO}_4$  in MeOH- $\text{CH}_2\text{Cl}_2$ -n-hexane gave no observable reaction (u.v.). (iii)  $\text{PPh}_3$  catalysed the *trans*- to *cis*-isomerization. (iv) Addition of excess of  $\text{PEt}_3$  to *cis*- $\text{PtCl}_2(\text{PPh}_3)_2$  in  $\text{CH}_2\text{Cl}_2$ -MeOH followed 10 min later by isolation of a crystalline product yielded predominantly *cis*- $\text{PtCl}_2(\text{PPh}_3)_2$  (characterized by u.v. and microanalysis). It was concluded that observations (ii) and (iv) are inconsistent with the consecutive displacement mechanism of isomerization.<sup>1</sup> In this communication, we show this conclusion to be erroneous.

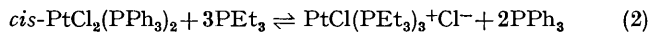
On the basis of (ii), it was concluded that the forward reaction of equation (I) must be slow. In fact, no reaction



is observed in (ii) as in MeOH- $\text{CH}_2\text{Cl}_2$ -n-hexane or in  $\text{CHCl}_3$  solutions [equation (1)] lies well to the l.h.s., *i.e.*  $\text{PtCl}(\text{PEt}_3)_3^+\text{Cl}^-$  is thermodynamically more stable than *cis*- $\text{PtCl}_2(\text{PEt}_3)_2 + \text{PEt}_3$ .† The far-i.r. data in the  $\nu(\text{Pt}-\text{Cl})$  region (see Table) confirm the formation of  $\text{PtCl}(\text{PEt}_3)_3^+\text{Cl}^-$  when 1  $\text{PEt}_3$  per Pt is added to *cis*- $\text{PtCl}_2(\text{PEt}_3)_2$  in  $\text{CHCl}_3$  solution.  $^1\text{H}$  N.m.r. and u.v. studies of *cis*- $\text{PtCl}_2(\text{PEt}_3)_2 + \text{PEt}_3$  (one per Pt) in  $\text{CDCl}_3$  and  $\text{CH}_2\text{Cl}_2$  solutions respectively give spectra identical to those obtained for solutions of  $\text{PtCl}(\text{PEt}_3)_3^+\text{BF}_4^-$ . No resonances assignable to free  $\text{PEt}_3$  are observed in the  $^1\text{H}$  n.m.r. experiment. In contrast, when  $\text{PPh}_3$  is added to  $\text{CHCl}_3$  solutions of *cis*- $\text{PtCl}_2(\text{PEt}_3)_2$  far-i.r. (see Table) and  $^1\text{H}$  n.m.r. spectra show the major solution species to be *cis*- $\text{PtCl}_2(\text{PEt}_3)_2$  and free  $\text{PPh}_3$ , *i.e.* under these conditions,  $\text{PPh}_3$ -containing complexes are thermodynamically less stable than *cis*- $\text{PtCl}_2(\text{PEt}_3)_2$ .

† As found by Haake<sup>4</sup> and commented on by us,<sup>2,3</sup> the use of MeOH as a solvent in (ii) [not present in (i)] stabilizes ionic intermediates and inhibits the *cis-trans*-isomerization probably due in part to the effective solvation of chloride ions by hydroxylic solvents.

Although (iv) above initially may seem incompatible with this statement, this is not so. *cis*-PtCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> is only very slightly soluble in CHCl<sub>3</sub> and CH<sub>2</sub>Cl<sub>2</sub>. However, addition of 3.5 PEt<sub>3</sub> per Pt to a suspension of *cis*-PtCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> in CHCl<sub>3</sub> results in a homogeneous solution. Far-i.r. (see Table) and <sup>1</sup>H n.m.r. studies show the major platinum complex present in solution to be PtCl(PEt<sub>3</sub>)<sub>3</sub><sup>+</sup>Cl<sup>-</sup>, *i.e.* the equilibrium in [equation (2)] lies well to the r.h.s.



This is further supported by u.v. studies. When excess of PEt<sub>3</sub> is added to either *cis*-PtCl<sub>2</sub>(PEt<sub>3</sub>)<sub>2</sub> or *cis*-PtCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> in CH<sub>2</sub>Cl<sub>2</sub>, the absorption bands at 323 and 330 nm respectively disappear and in the latter case a strong absorption at *ca.* 260 nm characteristic of free PPh<sub>3</sub> is observed. Addition of MeOH to CH<sub>2</sub>Cl<sub>2</sub> solutions of PtCl(PEt<sub>3</sub>)<sub>3</sub><sup>+</sup>Cl<sup>-</sup> + 2PPh<sub>3</sub> [*i.e.* equation (2)] and cooling results in the isolation of crystals of *cis*-PtCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>. Isolation of this product can be ascribed to its low solubility and the fact that the equilibrium in equation (2) is a dynamic one, thus resulting in precipitation of the least soluble complex rather than the thermodynamically preferred complex in solution.

<sup>1</sup> W. J. Louw, *J.C.S. Chem. Comm.*, 1974, 353.

<sup>2</sup> D. G. Cooper and J. Powell, *J. Amer. Chem. Soc.*, 1973, **95**, 1102.

<sup>3</sup> D. G. Cooper and J. Powell, *Canad. J. Chem.*, 1973, **51**, 1634.

<sup>4</sup> P. Haake and R. M. Pfeiffer, *J. Amer. Chem. Soc.*, 1970, **92**, 4996, and 5243.

<sup>5</sup> P. Haake and R. M. Pfeiffer, *Chem. Comm.*, 1969, 1330.

TABLE

Far-i.r. data in the region 370–250 ± 2 cm<sup>-1</sup> for *ca.* 10<sup>-2</sup>M CHCl<sub>3</sub> solutions of platinum complexes with and without added phosphines at 32 °C. ν(Pt–Cl) bands are in italics

<i>trans</i> -PtCl <sub>2</sub> (PEt <sub>3</sub> ) <sub>2</sub>	.. ..	367s	338s	261m
<i>cis</i> -PtCl <sub>2</sub> (PEt <sub>3</sub> ) <sub>2</sub> <sup>a</sup>	.. ..	314s <sup>a</sup>	285s <sup>a</sup>	
<i>cis</i> + 3PPh <sub>3</sub> per Pt	.. ..	367	338w	311s 286s 262m
<i>cis</i> + 1PEt <sub>3</sub> per Pt	.. ..	366s	328vw	300s 263m
[PtCl(PEt <sub>3</sub> ) <sub>3</sub> ]BF <sub>4</sub>	.. ..	367s	330vw	300s 263m
<i>cis</i> -PtCl <sub>2</sub> (PPh <sub>3</sub> ) <sub>2</sub> <sup>b</sup>	.. ..	318s	293s	
<i>cis</i> -PtCl <sub>2</sub> (PPh <sub>3</sub> ) <sub>2</sub> + 3.5PEt <sub>3</sub> per Pt	.. ..	367s	300s	262m
<sup>a</sup> <i>ca.</i> 10 <sup>-2</sup> M. <sup>b</sup> Nujol mull				

The above data are very similar to results obtained for PtI<sub>2</sub>(PMe<sub>2</sub>Ph)<sub>2</sub> + PMe<sub>2</sub>Ph,<sup>2</sup> PdCl<sub>2</sub>(PMe<sub>2</sub> *o*-tolyl)<sub>2</sub> + PMe<sub>2</sub>-*o*-tolyl,<sup>3</sup> and PdCl<sub>2</sub>(PMe<sub>2</sub> *o*-tolyl)<sub>2</sub> + PPh<sub>3</sub>.<sup>3</sup> We conclude that *all* currently available data concerning the tertiary-phosphine-catalysed isomerization of MX<sub>2</sub>(PR<sub>3</sub>)<sub>2</sub> complexes (M = Pd, Pt; X = halide)<sup>1–5</sup> are fully consistent with the consecutive displacement mechanism.

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