cis-trans-Isomerization of $PtCl_2(PEt_3)_2$. The Case for a Consecutive Displacement Mechanism

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Summary Recently reported data thought to be contrary to the consecutive displacement mechanism for PR_3-catalysed isomerization of $PtCl_2(PEt_3)_2$ are in fact fully consistent with this mechanism of isomerization.

IN a recent communication concerning the mechanism of PR_3 catalysed *cis–trans*-isomerization of $PtCl_2(PEt_3)_2$ the following observations were reported.[1] (i) In n-hexane–CH_2Cl_2 solution isomerization of *trans*-$PtCl_2(PEt_3)_2$ (*ca.* 10^{-4}M) to *cis*-$PtCl_2(PEt_3)_2$ catalysed by excess of PEt_3 has half lives of the order of seconds at 15 °C. (ii) Addition of an excess of chloride to $[PtCl(PEt_3)_3]ClO_4$ in MeOH–CH_2Cl_2–n-hexane gave no observable reaction (u.v.). (iii) PPh_3 catalysed the *trans*- to *cis*-isomerization. (iv) Addition of excess of PEt_3 to *cis*-$PtCl_2(PPh_3)_2$ in CH_2Cl_2–MeOH followed 10 min later by isolation of a crystalline product yielded predominantly *cis*-$PtCl_2(PPh_3)_2$ (characterized by u.v. and microanalysis). It was concluded that observations (ii) and (iv) are inconsistent with the consecutive displacement mechanism of isomerization.[1] 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

$$PtCl(PEt_3)_3^+ + Cl^- \underset{k_b}{\overset{k_f}{\rightleftharpoons}} cis\text{-}PtCl_2(PEt_3)_2 + PEt_3 \qquad (1)$$

is observed in (ii) as in MeOH–CH_2Cl_2–n–hexane or in $CHCl_3$ solutions [equation (1)] lies well to the l.h.s., *i.e.* $PtCl(PEt_3)_3^+Cl^-$ is thermodynamically more stable than *cis*-$PtCl_2(PEt_3)_2$ + PEt_3.† The far-i.r. data in the ν(Pt–Cl) region (see Table) confirm the formation of $PtCl(PEt_3)_3^+Cl^-$ when 1 PEt_3 per Pt is added to *cis*-$PtCl_2(PEt_3)_2$ in $CHCl_3$ solution. ^1H N.m.r. and u.v. studies of *cis*-$PtCl_2(PEt_3)_2$ + PEt_3 (one per Pt) in $CDCl_3$ and CH_2Cl_2 solutions respectively give spectra identical to those obtained for solutions of $PtCl(PEt_3)_3^+BF_4^-$. No resonances assignable to free PEt_3 are observed in the ^1H n.m.r. experiment. In contrast, when PPh_3 is added to $CHCl_3$ solutions of *cis*-$PtCl_2(PEt_3)_2$ far-i.r. (see Table) and ^1H n.m.r. spectra show the major solution species to be *cis*-$PtCl_2(PEt_3)_2$ and free PPh_3, *i.e* under these conditions, PPh_3-containing complexes are thermodynamically less stable than *cis*-$PtCl_2(PEt_3)_2$.

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† As found by Haake[4] and commented on by us, [2,3] 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*-$PtCl_2(PPh_3)_2$ is only very slightly soluble in $CHCl_3$ and CH_2Cl_2. However, addition of 3·5 PEt_3 per Pt to a suspension of *cis*-$PtCl_2(PPh_3)_2$ in $CHCl_3$ results in a homogeneous solution. Far-i.r. (see Table) and ^1H n.m.r. studies show the major platinum complex present in solution to be $PtCl(PEt_3)_3{}^+Cl^-$, *i.e.* the equilibrium in [equation (2)] lies well to the r.h.s.

$$cis\text{-}PtCl_2(PPh_3)_2 + 3PEt_3 \rightleftharpoons PtCl(PEt_3)_3{}^+Cl^- + 2PPh_3 \tag{2}$$

This is further supported by u.v. studies. When excess of PEt_3 is added to either *cis*-$PtCl_2(PEt_3)_2$ or *cis*-$PtCl_2(PPh_3)_2$ in CH_2Cl_2, 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_3 is observed. Addition of MeOH to CH_2Cl_2 solutions of $PtCl(PEt_3)_3{}^+Cl^- + 2PPh_3$ [*i.e.* equation (2)] and cooling results in the isolation of crystals of *cis*-$PtCl_2(PPh_3)_2$. 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.

TABLE

Far-i.r. data in the region 370—250 ± 2 cm^{-1} for *ca.* 10^{-2}M $CHCl_3$ solutions of platinum complexes with and without added phosphines at 32 °C. ν(Pt–Cl) bands are in italics

trans-$PtCl_2(PEt_3)_2$	367s	*338*s	261m		
cis-$PtCl_2(PEt_3)_2$[a]		*314*s[a]	285s[a]		
cis + $3PPh_3$ per Pt	367	338w	*311*s	*286*s	262m
cis + $1PEt_3$ per Pt	366s	328vw	*300*s	263m	
$[PtCl(PEt_3)_3]BF_4$	367s	330vw	*300*s	263m	
cis-$PtCl_2(PPh_3)_2$[b]		*318*s	*293*s		
cis-$PtCl_2(PPh_3)_2$ + 3·5PEt_3 per Pt	367s		*300*s	262m	

[a] *ca.* 10^{-3}M. [b] Nujol mull

The above data are very similar to results obtained for $PtI_2(PMe_2Ph)_2 + PMe_2Ph$,[2] $PdCl_2(PMe_2$ *o*-tolyl$)_2$ + PMe_2-*o*-tolyl,[3] and $PdCl_2(PMe_2$ *o*-tolyl$)_2 + PPh_3$.[3] We conclude that *all* currently available data concerning the tertiary-phosphine-catalysed isomerization of $MX_2(PR_3)_2$ complexes (M = Pd, Pt; X = halide)[1-5] are fully consistent with the consecutive displacement mechanism.

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