

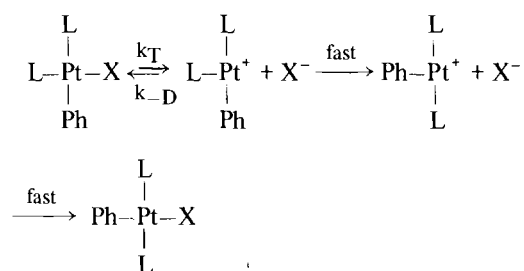
## Factors Affecting Dissociative and Associative Mechanisms on Platinum(II) Complexes

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The *cis-trans* isomerization of square planar platinum(II) complexes is a topological conversion which presents at least two important reasons for a detailed mechanistic investigation: (i) it does occur, although substitutions on these systems generally take place with complete retention of configuration, (ii) *cis-trans* isomerizations have been postulated in many catalysis mechanisms. As far as catalyzed isomerizations are concerned nowadays the mechanistic discussion is widely open on two alternative hypotheses: (i) intramolecular isomerization of a 5-coordinated intermediate<sup>1</sup>, (ii) a multi-stage reaction, each step of which involves retention of configuration<sup>2</sup>. Some time ago<sup>3</sup> we proposed that the spontaneous isomerization of *cis*-Pt(PEt<sub>3</sub>)<sub>2</sub>(*o*-MeC<sub>6</sub>H<sub>5</sub>)Cl in protic solvents proceeds with a dissociative mechanism, according to the reaction scheme:



which accounts for a chloride mass law retardation and a great difference in rate between solvolysis and isomerization. The rate determining step is the breaking of the metal-chloride bond to yield a 3-coordinated cationic intermediate which can recombine with chloride in two alternate ways, one leading to a *cis* and the other to a *trans* product. This conclusion was a surprising one in that there is substantial evidence for a 5-coordinated species of platinum (II) either as discrete compounds or reaction inter-

mediates, while the existence of 3-coordinated species had not been postulated before. The necessity of finding more examples and studying the factors affecting the dissociation arises from the growing number of important processes in which a vacant coordination site on platinum seems to be a condition for the occurrence of the reaction. The presence of 3-coordinated species of Pt(II) as intermediates has been invoked in the mechanism of olefin insertion into the platinum-hydrogen bond<sup>4</sup> and in the thermal decomposition of Pt(PPh<sub>3</sub>)<sub>2</sub>(Bu<sup>n</sup>)<sub>2</sub>,<sup>5</sup> in the kinetics of the conversion of methyl carbonyl into acetyl derivatives,<sup>6</sup> and in the reverse reaction, *viz.* the alkyl migration from carbon monoxide to platinum.<sup>7</sup>

Analysis of the kinetic data in table I shows that (i) *ortho*-substitutions on the aromatic ring cause a large decrease in the rate of the bimolecular path ( $k_1$ ) as a result of the increased congestion and destabilization of the five coordinated transition state. In the complex Pt(PEt<sub>3</sub>)<sub>2</sub>(2,4,6-Me<sub>3</sub>C<sub>6</sub>H<sub>2</sub>)Br, with the methyl groups of the ligand extending just in the plane of the trigonal bipyramidal transition state, this congestion is at its peak<sup>8</sup> so that the dissociative path, which represents a negligible contribution to the reactivity in unhindered systems, becomes the rate determining step of both isomerization and substitution ( $k_1/k_{is} = 1$ ); (ii) the hypothesis that after the breaking of the Pt-X bond the remaining groups in the cationic intermediate maintain much of their original position around the central metal finds support in the slight changes produced in the  $k_{is}$  values by steric hindrance. Furthermore, *cis*-Pt(PEt<sub>3</sub>)<sub>2</sub>(2,4,6-Me<sub>3</sub>C<sub>6</sub>H<sub>2</sub>)Br is completely converted into the corresponding *cis*-iododerivative in the presence of I<sup>-</sup> which has a scavenger effect in capturing the intermediate before the distortion of ligands leading to isomerization ( $k_T$  step) takes place; (iii) in the *cis-trans* isomerization, electron releasing *p*-substituents on the aromatic ring tend to stabilize the transition state relative to the initial state and electron attracting groups will have the reverse effect. It can be concluded, therefore, that the overall electron release by the substituents follows the same sequence as the rate, *viz.* CH<sub>3</sub> > H > F. At this early stage of the research these results, while suggesting extensive electronic interaction between the metal ion and the coordinated aryl group, do

TABLE I. Rate Constants for *Cis-Trans* Isomerization ( $k_{is}$ ) and Halide Substitution by MeOH ( $k_1$ ) for the Complexes Pt(PEt<sub>3</sub>)<sub>2</sub>(R)X in Methanol at 30 °C.

Complex	$10^3 k_{is}$ s <sup>-1</sup>	$10^3 k_1$ s <sup>-1</sup>
<i>cis</i> -PtL <sub>2</sub> (Ph)Br	1.07	6,000
<i>cis</i> -PtL <sub>2</sub> ( <i>o</i> -MeC <sub>6</sub> H <sub>4</sub> )Br	0.72	53
<i>cis</i> -PtL <sub>2</sub> ( <i>o</i> -EtC <sub>6</sub> H <sub>4</sub> )Br	0.55	16
<i>cis</i> -PtL <sub>2</sub> (2,4,6-Me <sub>3</sub> C <sub>6</sub> H <sub>2</sub> )Br	0.19	0.19
<i>cis</i> -PtL <sub>2</sub> ( <i>p</i> -MeC <sub>6</sub> H <sub>4</sub> )Br	2.50	4,240
<i>cis</i> -PtL <sub>2</sub> ( <i>p</i> -FC <sub>6</sub> H <sub>4</sub> )Br	0.24	4,240
<i>cis</i> -PtL <sub>2</sub> (C <sub>6</sub> H <sub>5</sub> )Cl	2.2	3,330
<i>cis</i> -PtL <sub>2</sub> (C <sub>6</sub> H <sub>5</sub> )I	0.39	2,900

not allow a quantitative interpretation of the role of the *p*-substituents in terms of resonance and inductive effects. On the other hand, the fact that *p*-substituents hardly affect the rate of halide displacement by solvent is indicative that the bimolecular process is less sensitive and therefore less diagnostic than the dissociative one in revealing electronic interactions between metal and aryl ligands. Likewise the dissociative process, being

immediately related to the breaking of the Pt–X bond, is more effective than the bimolecular path in discriminating the sequence of the leaving group lability in the order Cl > Br > I, which parallels the “softness” of halides.

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