

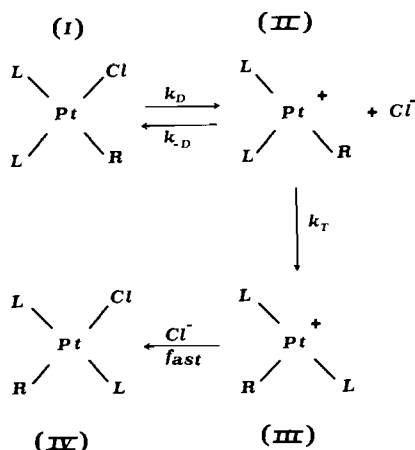
The Role of Three-Coordinate Intermediates in the Uncatalyzed *Cis-Trans* Isomerization of Platinum(II) Complexes and in the Ethylene Insertion into the Platinum-Hydrogen Bond

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The *cis-trans* isomerization of *cis*-[Pt(PEt₃)₂(Me)Cl] readily takes place in apolar solvents, in the presence of traces of free phosphine.¹ We found that this complex spontaneously converts into its *trans* isomer in methanol. The rate of reaction is first-order in the platinum complex and the isomeric equilibrium is well over to the *trans* form. Since isomerization suffers mass law retardation by chloride ion and its rate is very much less than that at which chloride is replaced by solvent the isomerization appears to proceed *via* a dissociative asynchronous mechanism,



in which the rate determining step is the breaking of the Pt-Cl bond of (I) to yield a 3-coordinate "cis-like" intermediate (II). This easily interconverts to its "trans-like" structure (III), which eventually takes up the halide ion to give the *trans*-product. This reaction scheme was originally postulated for the spontaneous isomerization of complexes of the type *cis*-[Pt(PEt₃)₂(aryl)X]² and recent detailed

kinetic studies³ have pointed out that i) the factors affecting the strength of Pt-X bond, *viz.* nature of halide ion, basicity of phosphine or changes in the electron density at the reaction centre produced by substituents on the coordinated aromatic ring, also affect the rate of isomerization, ii) the loss of the leaving halide in the slow step (*k_D*) is not assisted by a rearrangement of the remaining ancillary ligands which maintain much of their original position around the central metal in the cationic 14-electron 3-coordinate intermediate, iii) the energy involved in the interconversion of the "cis-like" into the "trans-like" intermediate (*k_T* step) is very much higher than that for nucleophilic attack on (II).

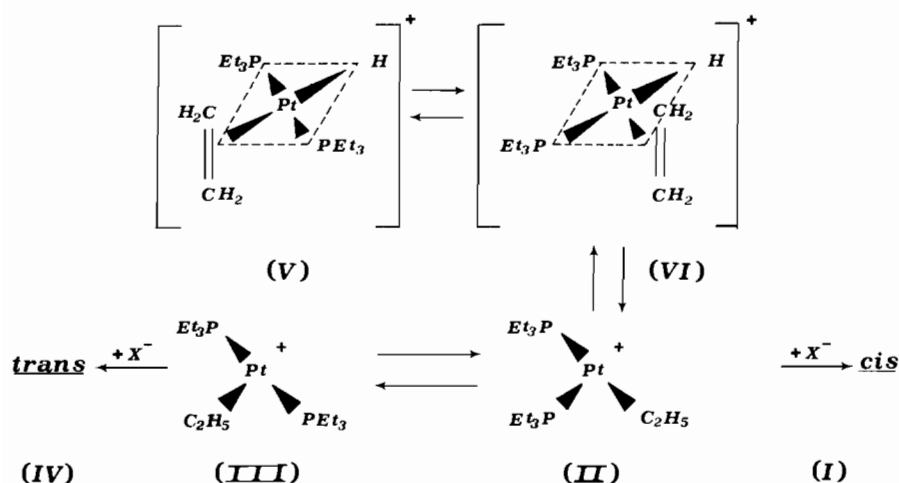
The complex *cis*-[Pt(PEt₃)₂(Et)Cl] isomerizes completely as soon as the solid is dissolved in methanol so that the kinetics were followed either in the presence of a large excess of free Cl⁻ or in isopropanol which is less effective than MeOH in assisting the breaking of the Pt-Cl bond.

Data in Table I show that the presence of an aromatic ring is not a prerequisite for the occurrence of spontaneous isomerizations in these systems.

TABLE I. Rate Constants for Uncatalyzed *Cis-Trans* Isomerization (*k_{is}*) of the Complexes [PtL₂(R)X] at 30 °C (L = triethylphosphine; R = C₆H₅, CH₃, C₂H₅, μ = 0.01 M (LiClO₄)).

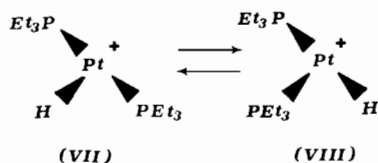
Complex	Methanol 10 ³ <i>k_{is}</i> , s ⁻¹	Isopropanol 10 ³ <i>k_{is}</i> , s ⁻¹
<i>cis</i> -[PtL ₂ (Ph)Cl]	1.50	very slow
<i>cis</i> -[PtL ₂ (Me)Cl]	1.08	very slow
<i>cis</i> -[PtL ₂ (Et)Cl]	very fast	34.0

These observations substantiate and serve to exemplify one of the reaction schemes postulated by Clark^{4,5} for olefin insertion on *trans*-platinum(II) hydrides. For ligands *trans* to hydride which are readily displaced by olefin (*e.g.* acetone⁴ or NO₃⁵) a first step involves the isomerization of a 4-coordinate *trans*-(hydrido)(olefin)platinum(II) cation (V) to the *cis* isomer (VI). Migratory insertion on (VI) leads to the 3-coordinate "cis"-[Pt(PEt₃)₂(alkyl)]⁺, after which the reaction follows a pathway which appears to be identical to that found for the spontaneous isomerization of *cis*-[Pt(PEt₃)₂(Et)Cl]:



The key intermediates in the unassisted isomerization as well as in the insertion process are assumed to be 3-coordinate and not 4-coordinate.

There is no reason to exclude that *trans* → *cis* isomerization in the first step of insertion also proceeds *via* interconversion of an unsymmetric 3-coordinate species,



once we know that the olefin *trans* to hydride is very weakly bonded⁶ and the migratory insertion shifts the isomeric equilibrium towards the *cis*-form (VI). The necessity of requiring the formation of (VI) is questionable, because a possible concerted olefin attack on the “*trans*-like” 3-coordinate (VII), involving a four-centered transition state, can also account for the insertion occurring in those cases in which severe steric restrictions by the ancillary ligands do not allow the olefin and the hydride to take up mutual *cis*-positions in the coordination sphere of a 4-coordinate species.⁷

An easy prediction is that the stereochemistry of the alkyl derivative after insertion will depend not

only on the efficiency with which a nucleophile (either ligand or solvent species)⁸ can block the vacant coordination site on (II) before its conversion to (III), but mainly on all the factors affecting the isomerization rate of (I). The very high rate of isomerization of *cis*-[Pt(PEt₃)₂(Et)Cl] as compared to that of the analogous methyl complex indicates that a longer alkyl chain somehow stabilizes more effectively the “*cis*-like” 3-coordinate intermediate and favours a *trans* configuration for the product of ethylene insertion.

References

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