Ligand substitution for square planar complexes

1. Mechanism of ligand substitution for square planar complexes
2. Berry Pseudorotation
3. The trans-effect

Substitution reactions of square planar complexes

Square planar is the common geometry for the following d8 metal ions.

Co^{+}	Ni^{2+}	Cu^{3+}
Rh^{+}	Pd^{2+}	Ag^{3+}
Ir^{+}	Pt^{2+}	Au^{3+}

Kinetics – Ligand Substitution Reactions

Recall: Octahedral $ML_5X + Y \rightarrow ML_5Y + X$ dissociative mechanism

- For Square Planar $ML_3X + Y \rightarrow ML_3Y + X$

X and Y can be any pair of ligands.

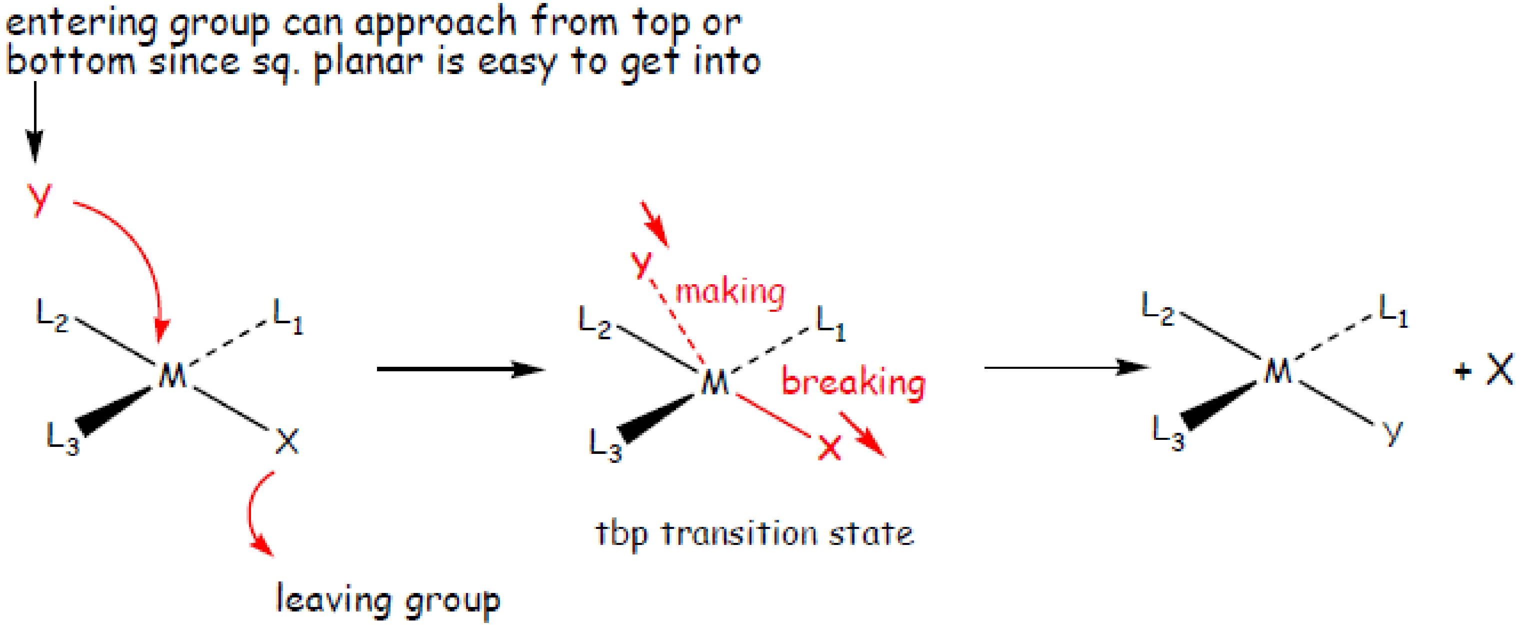
- Rate = k[ML_3X][Y] i.e. second order kinetics so it depends on the nature of

both the leaving group X and the entering group Y.

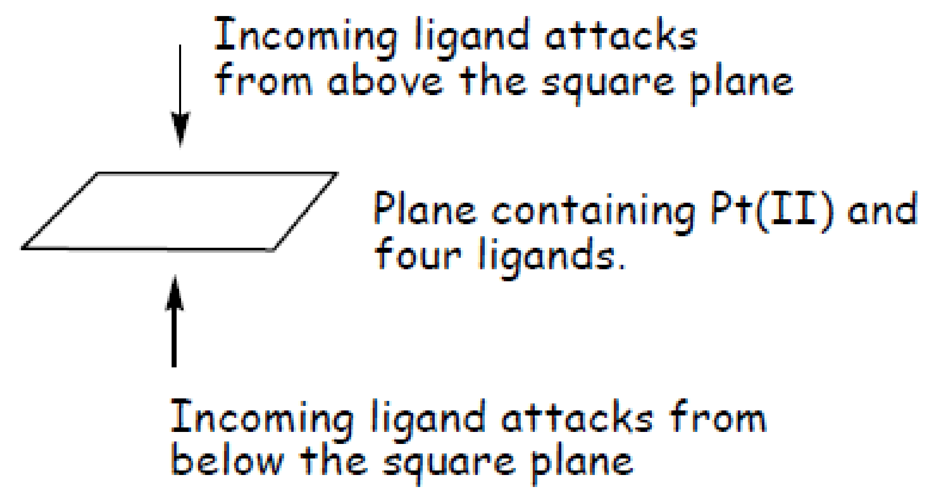
- Steric crowding slows down the reaction.
- Evidence for an **associative mechanism.**

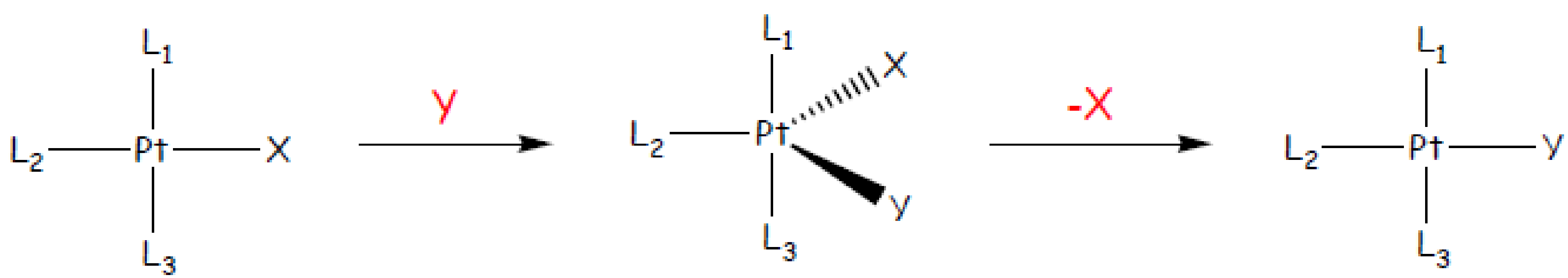
1. Mechanism for Square Planar Ligand Substitution

- For square planar **BOTH bond-breaking and bond making are important in the** reaction mechanism (i.e. an associative mechanism).



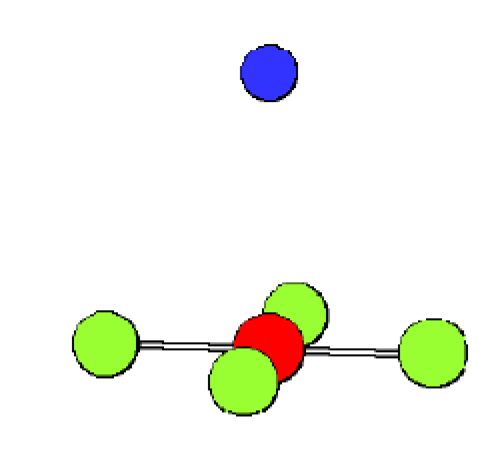
- **Stereospecific** - X (leaving group) is trans to L_2 and so is Y (entering group)





Initial attack by the entering group at a square planar Pt(II) centre is **from above or below the plane**. Nucleophile Y then coordinates to give a **trigonal bipyramidal intermediate species** which loses X with **retention of stereochemistry**.

- **The incoming ligand (coloured blue) approaches a vacant axial site of the square planar complex to form a square pyramidal intermediate (or transition state).**

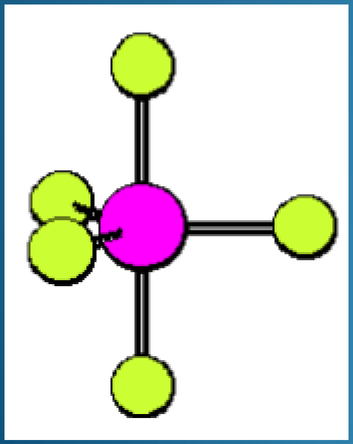


Intramolecular rearrangement via a **trigonal bipyramid generates a different square** pyramidal structure with the incoming ligand now in the basal plane. (This motion is closely related to the **Berry Pseudorotation** mechanism).

The reaction is completed by the leaving group departing from an axial site. Note that the **stereochemistry of the complex is retained during the substitution process.**

2. Berry Pseudorotation

The animation below shows a trigonal bipyramidal molecule ML5 undergoing Berry
pseudorotation.
This occurs in, for example, $Fe(CO)_5$, for which ^{13}C NMR spectroscopy cannot distinguish axial and equatorial CO environments, due to the rapid interchange.
The same process can occur in main group compounds like PF_5.



Ligands 2 and 3 move from axial to equatorial positions in the trigonal bipyramid whilst ligands 4 and 5 move from equatorial to axial positions.
Ligand 1 does not move and acts as a pivot.
At the midway point (transition state) ligands 2,3,4,5 are equivalent, forming the base of a square pyramid.
The motion is equivalent to a 90^o rotation about the $M-L_1$ axis

Square Planar Substitution Reactions

Examples:

$$ML_2X_2 + L' \xrightarrow{\text{solvent}} MLL'X + L$$

Factors Which Affect The Rate Of Substitution

i). Role of the Entering Group

ii). The Role of The Leaving Group

iii). The Nature of the Other Ligands in the Complex

iv). Effect of the Metal Centre

i). Role of the Entering Group

- The rate of substitution is proportional to the nucleophilicity of entering group
- i.e. for most reactions of Pt(II), the rate constant increases in the order: H_2O < NH_3 = py < Br^- < I^- < CN^-
- The ordering is consistent with **Pt(II)** being a **soft metal centre.**

ii). The Role Of The Leaving Group

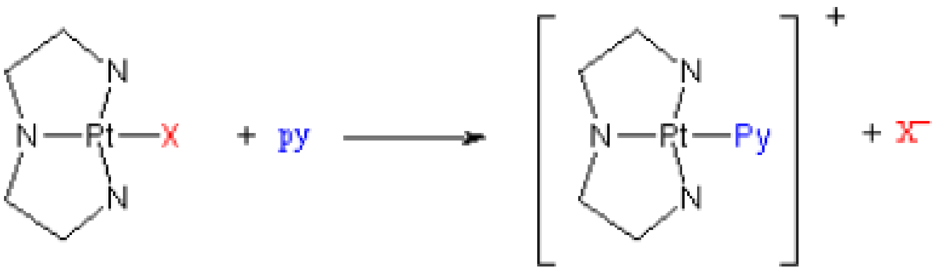
For the reaction

$[Pt(dien)X]^+ + py \longrightarrow [Pt(dien)(py)]^+ + X^-$

in H_2O at 25^{0}C the sequence of lability is;

H_2O > Cl^- >Br^- > I^- > N_3^- > SCN^- > NO_2^- > CN^-

with a spread of over 10^6 in rate across series.



- the leaving group does not affect the nucleophilic discrimination factors only the intrinsic reactivity.
- the series tend to parallel the strength of the Metal-L bond.

iii). The Nature of other Ligands in the Complex

3. The trans effect

Definition;

- The *trans effect* is best defined as the effect of a coordinated ligand upon the rate of substitution of ligands opposite to it.

  Or The ability of a ligand in a square planar complex to direct the replacement if the ligand trans to it.

- The trans effect is given as the following series:

$$CN^- > NO_2^- > I^- = SCN^- > Br^- > Cl^- > py > NH_3 > H_2O$$

The Trans Effect in Practice

1. $[Pt(NH_3)_4]^{2+} \xrightarrow{2Cl^-} [Pt(NH_3)_2Cl_2]$

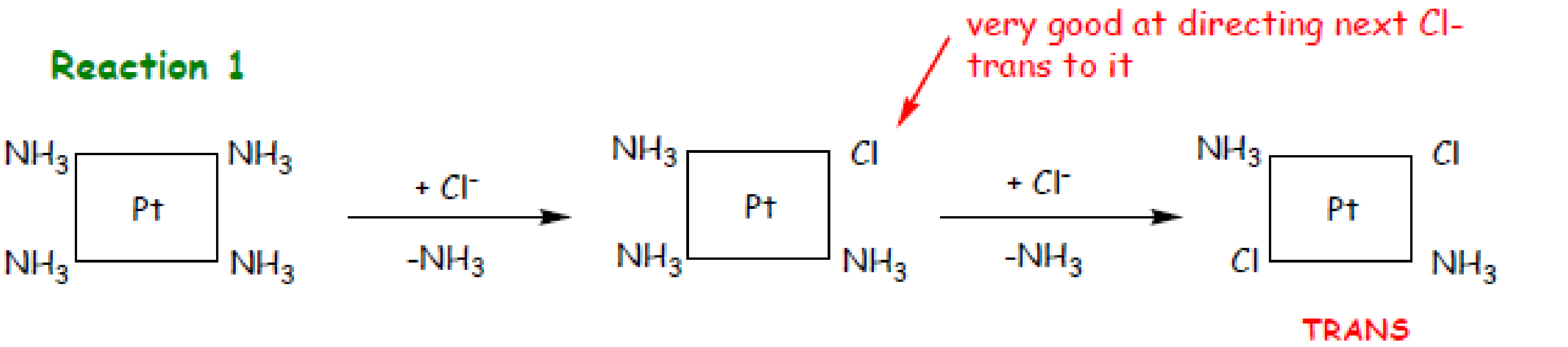
   TRANS

2. $[Pt(Cl)_4]^{2-} \xrightarrow{2NH_3} [Pt(NH_3)_2Cl_2]$

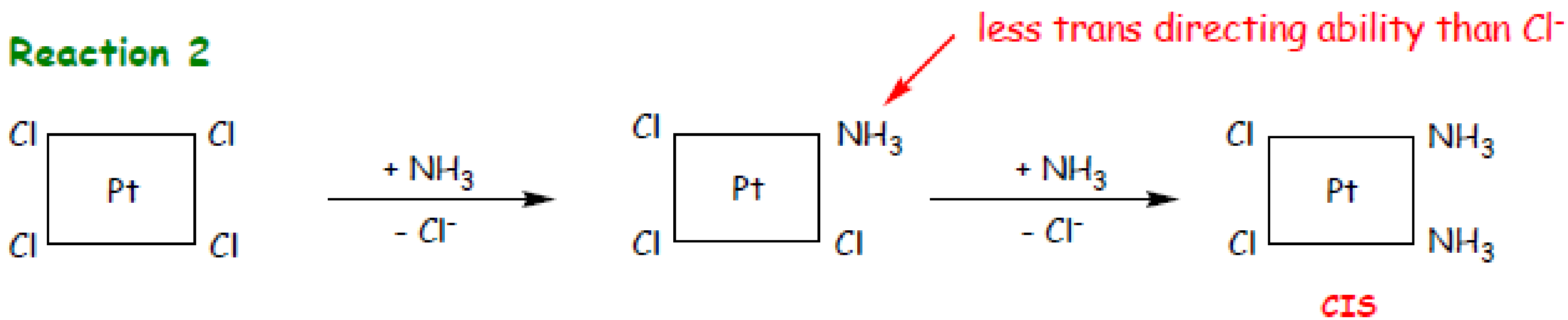
   CIS

why the different isomers ?

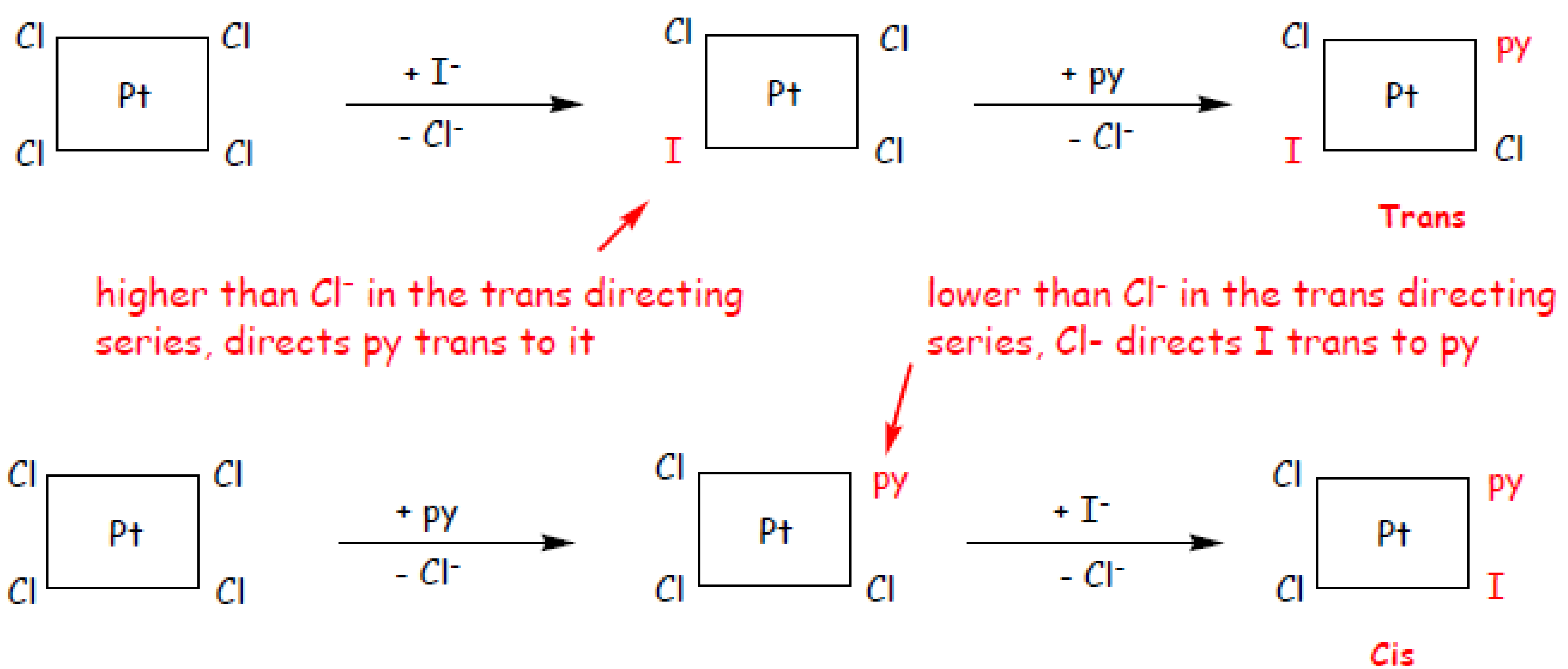
Reaction 1



Reaction 2

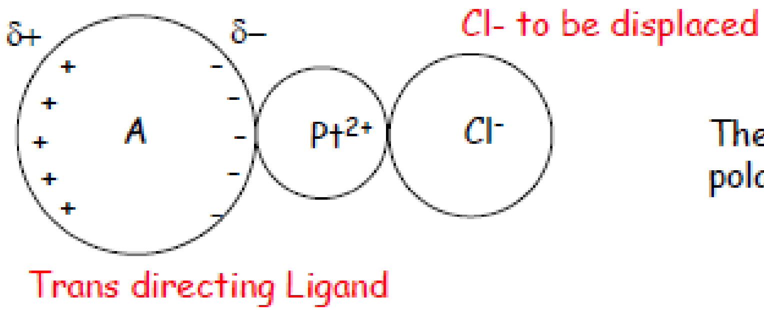


- Conclusion: Cl^- has a **greater trans directing** effect than NH_3.
- Trans directing series $Cl^- > NH_3$
- Depends on order in which the reagents are added as to which geometric isomer is formed so has uses for devising synthesis of Pt(II) complexes.
- e.g. consider the preparation of cis and trans $PtCl_2I(py)$ from $PtCl_4^{2-}$, I^- and py.

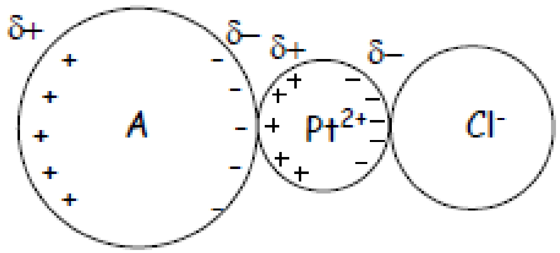


Polarization Theory

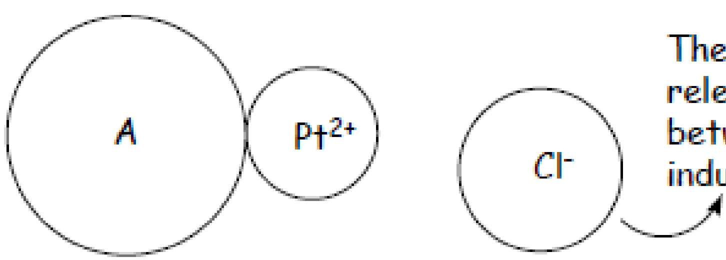
For explaining the kinetic trans effect in square planar Pt(II) complexes



The Pt(II) cation induces a dipole in the polarizable trans-directing ligand *A*.



The induced dipole in ligand *A* induces a dipole in the polarizable Pt(II) cation.

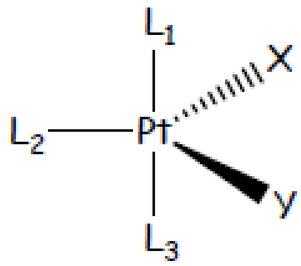


The chloride anion trans to *A* is more easily released due to the extra repulsive forces between its negative charge and the induced dipole of the Pt(II) cation.

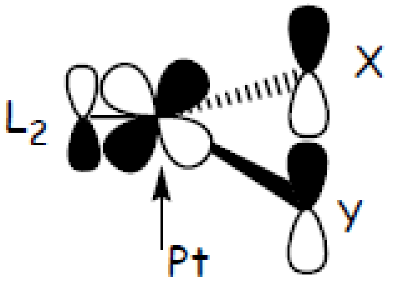
- Support for this theory is demonstrated by looking at the trans-directing series.
- The more polarizable ligands such as SCN^-, and I^- and the ligands containing π-clouds e.g. CN^- are high in the series, whereas less polarizable ligands such as ammonia or water are lower in the series.
- Additional support comes from the observation that Pt(II) complexes demonstrate a more pronounced trans effect than those of the less polarizable Pd(II) and Ni(II) cations.

Other contributing factors to the trans-effect

- In the trigonal plane of the 5-coordinate transition state or intermediate, a π-bonding interaction can occur between a metal d-orbital (e.g. d_{xy}) and suitable orbitals (p atomic orbitals, or molecular orbitals of p-symmetry) of ligand L_2 (the ligand trans to the leaving group) and Y (the entering group).
- These 3 ligands and the metal centre can communicate electronically through π-bonding only if they all lie in the same plane in the transition state or intermediate.
- **This implies the 5-coordinate species must be trigonal pyramidal.**



trigonal bipyramidal
transition state or intermediate



π-bonding in the trigonal plane

Rules:

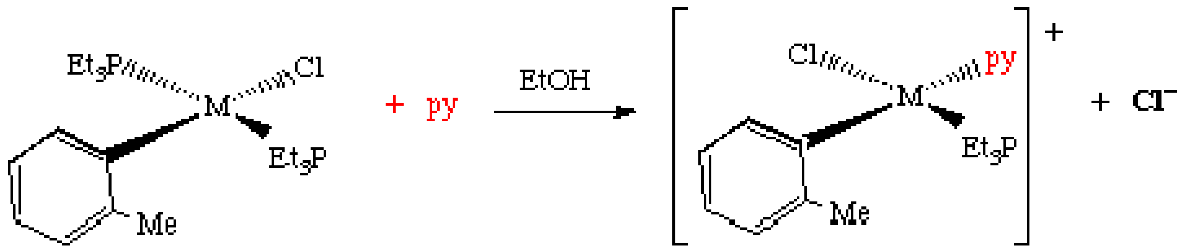
- It is easier to replace Cl^- than most other ligands.
- If you want to displace some other ligands with Cl^- you must use a huge excess of Cl^-
- If there is more than one possibility for replacing the Cl^-, the one that is replaced is the one **trans to the ligand higher in the series.**
- Part of the general order for the trans effect (the ability of ligands to direct trans-substitution) is shown below:

$CN^- > NO_2^- > I^- > SCN^- > Br^- > Cl^- > py > NH_3 > H_2O$

- A strong π-acceptor e.g. CN^- will stabilize the transition state by accepting electron density that the incoming nucleophile donates to the metal centre, and will **thereby facilitate substitution at the site trans to it.**

iv). Effect of the Metal Centre

- The order of reactivity of a series of isovalent ions is;
  Ni(II) > Pd(II) >> Pt(II)
- This order of reactivity is the same order as the tendency to form 5-coordinate complexes.
- More ready the formation of a 5-coordinate intermediate complex, the greater the stabilization of the transition state and so the greater the bimolecular rate enhancement.



- M (II) Ni k = 33 M^{-1} sec^{-1}
  Pd k = 0.58 M^{-1} sec^{-1}
  Pt k = 6.7×10^{-6} M^{-1} sec^{-1}