### Thermodynamic and Kinetic Aspects of Metal Complexes

(Lecture-3)

#### **B.Sc.** 5<sup>th</sup> Semester (Pass Course)

#### INORGANIC CHEMISTRY

(As per MDU, Rohtak Syllabus)

**Presented by:** 

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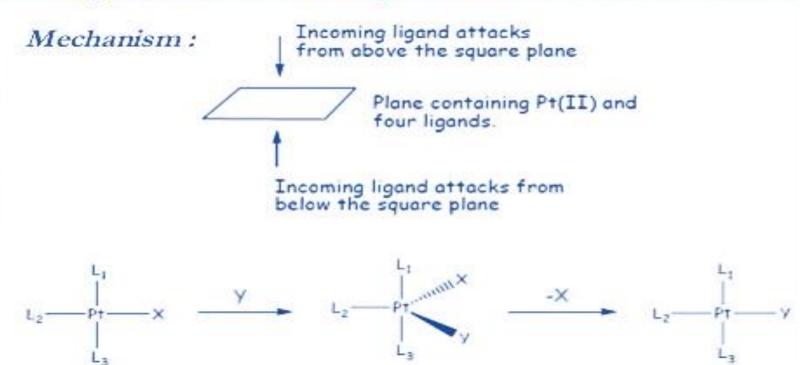
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# CONTINI

- Substitution reaction in square planar complexes
- Types or mechanism of substitution reaction

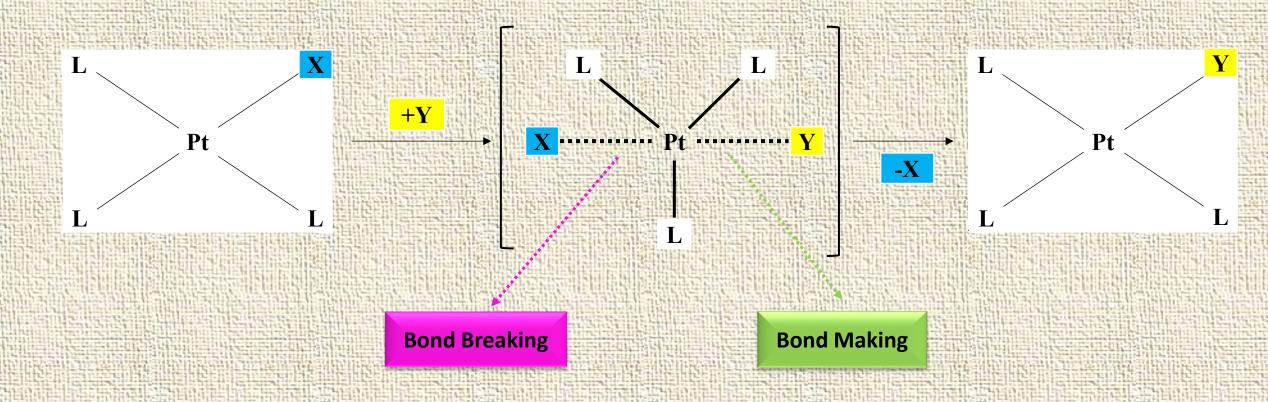


•  $ML_3X + Y \longrightarrow ML_3Y + X$ 



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).

# Mechanism of substitution in Square Planar complexes



# Four classes of Substitution reaction:



1. Associative reaction (A)



2. Dissociative reaction (D)



3. Interchange associative (I<sub>a</sub>)



4. Interchange dissociative (I<sub>d</sub>)

#### 1. Associative reaction (A)

In this type of reaction, the rate determining step is the formation of intermediate with an increased coordination number. This means that Pt-Y bond is first formed before Pt - X begins to break.

#### 2. Dissociative reaction (D)

In this type of reaction, the rate determining step is the formation of the intermediate in which one ligand is lost. This means that Pt–X bond is fully broken before the Pt - Y bond begins to form.

# 3. Interchange Associative (I<sub>a</sub>)

In this type of reaction, the Pt-X bond begins to break before Pt-Y bond is fully formed but bond making is more significant than bond breaking.

# 4. Interchange Dissociative (I<sub>d</sub>)

In this type of reaction, the Pt-Y bond begins to form before the Pt-X bond is fully broken but bond breaking is more significant than bond making.

# SUBSTITUTION REACTIONS IN SQUARE PLANAR COMPLEXES

• Associative - A (2 steps)  $ML_{n}X + Y \rightarrow ML_{n}XY \rightarrow ML_{n}Y + X$ 

• Dissociative - D (2 steps)  $ML_{n}X + Y \rightarrow ML_{n} + X + Y \rightarrow ML_{n}Y + X$ 

Interchange (1 continuous process)
 ML<sub>n</sub>X + Y→ Y--ML<sub>n</sub> --X→ ML<sub>n</sub>Y + X

## For Example:

Mechanism A:
Dissociative
Ligand Exchange

PPh<sub>3</sub>
PPh<sub>3</sub>
PPh<sub>3</sub>
PPh<sub>3</sub>
PPh<sub>3</sub>
PPh<sub>3</sub>
Ph<sub>3</sub>P-Pd
Ph<sub>3</sub>
Ph<sub>3</sub>P-Pd
Ph<sub>3</sub>
Ph<sub>3</sub>P-Pd-SH
Ph<sub>3</sub>P-Pd-SH
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Mechanism B: Associative Ligand Exchange