

Reactivity of complex combinations

- Complex combinations, like simple ones, participate in a wide variety of chemical reactions involving different mechanisms and rates.
- Despite the difficulties in interpreting kinetic data and formulating reaction mechanisms, the reactivity of complex combinations is discussed on the basis of the following reaction types:
 - **substitution reactions;**
 - **addition reactions;**
 - **insertion reactions;**
 - **redox reactions;**
 - **metal-templated reactions.**

Substitution reactions

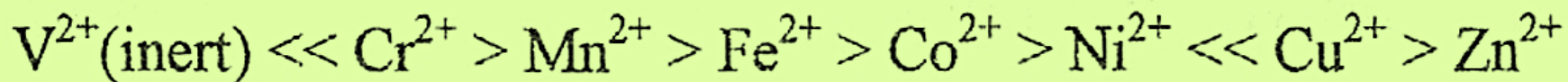
- Substitution reactions of $[ML_n]^{m+}$ complex ions refer to the replacement of a ligand L in the coordination sphere by another ligand L' (anion or neutral molecule), or the replacement of the complex generator M by another central ion M', while preserving the chemical conformation of the original complex.



- Depending on the nature of the processes taking place, the following types of substitution reactions are distinguished:
 1. Protonation - deprotonation reactions;
 2. Anation reactions;
 3. Acid/alkali hydrolysis reactions;
 4. Central ion substitution reactions;
 5. Isomerization reactions;
 6. Substitution reactions of other ions, atoms or groups of atoms in the compound with the role of ligand.

Substitution reactions

- In order to participate in substitution reactions, complex combinations must exhibit a certain *lability*.
- **Degree of lability** of complex combinations of *d-block* metals can be correlated with the electronic configuration of the central metal ion.
- It is found that all combinations with d^{3-8} configurations are kinetically labile, and their lability varies in order:

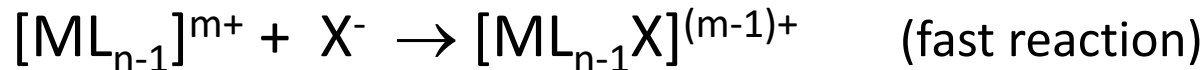


- Combinations of metal ions with d^4 , d^5 and d^6 configurations are relatively inert to substitution reactions.
- **Substitution reactions** depend on *the nature of the metal ion (by electronic configuration and oxidation state), the ligands existing in the coordination sphere, the nature of the reactant, the reaction medium* etc.

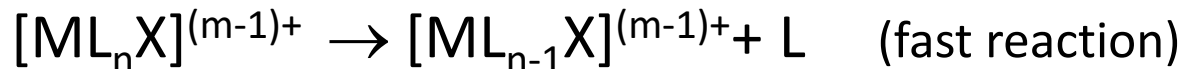
Substitution reactions

Mechanism of substitution reactions

- Most of the substitution reactions of complex combinations take place following a **nucleophilic substitution (SN) mechanism**, which can be either SN1 or SN2.
- The **SN1** (asynchronous nucleophilic substitution) **mechanism** involves a dissociation process in the first step, followed by nucleophilic attack by an X⁻ reactant:



- The **SN2 mechanism** involves the formation of an intermediate with a higher coordination number than the original complex:



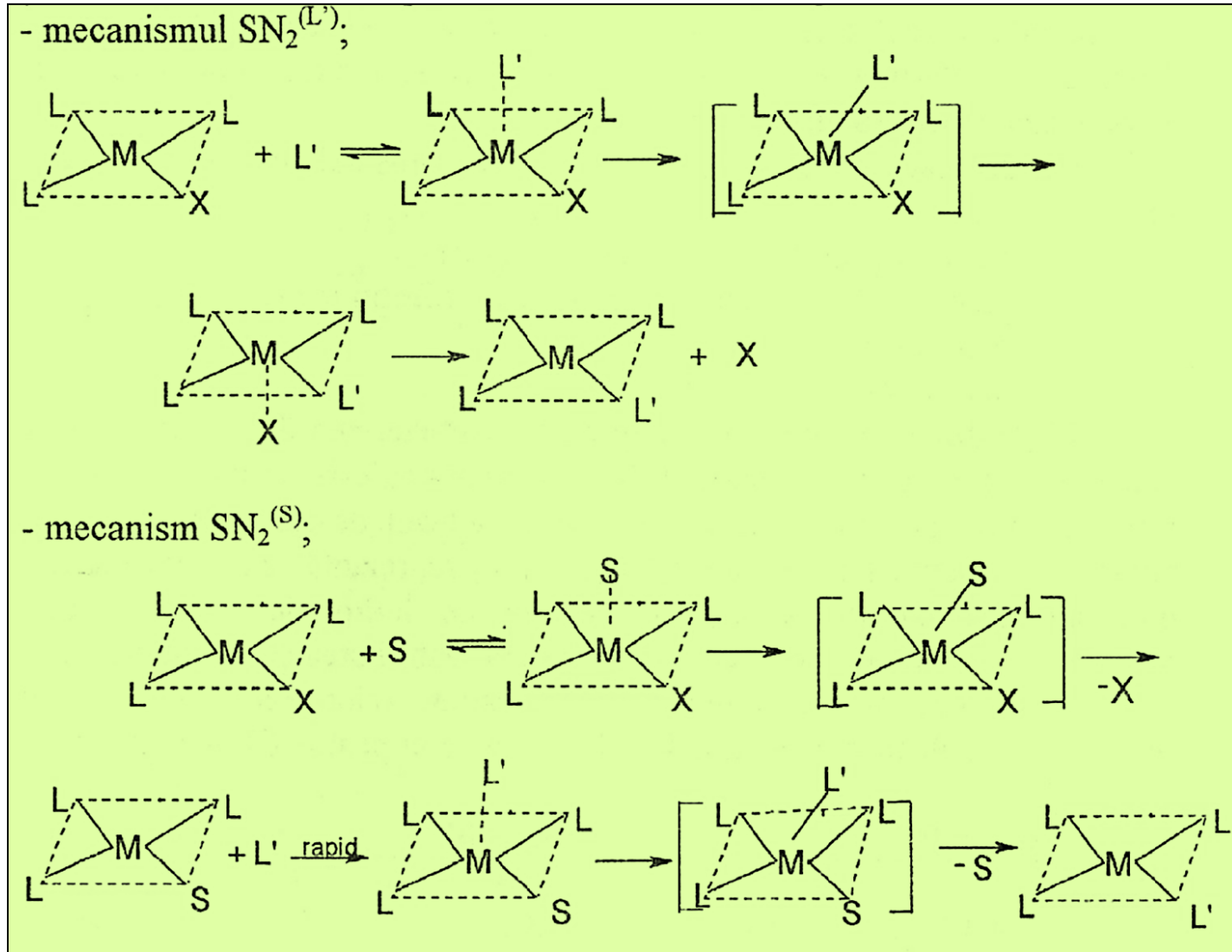
Substitution reactions

Mechanism of substitution reactions

The SN2 mechanism, also called **synchronous**, can proceed in two ways:

- by attracting a ligand, $\text{SN}_2^{(\text{L}')}$, into the coordination sphere;

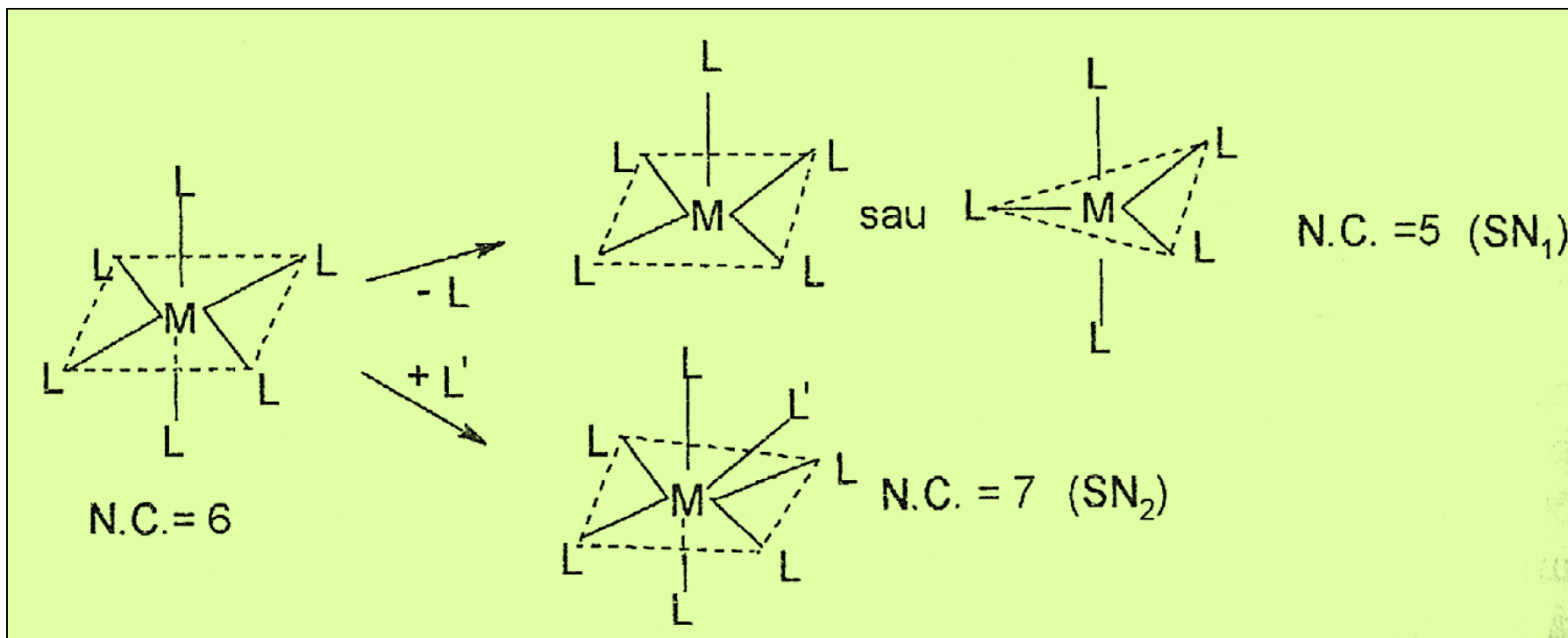
- by attraction into the coordination sphere of an $\text{SN}_2^{(\text{S})}$ solvent molecule.



Substitution reactions

Mechanism of substitution reactions

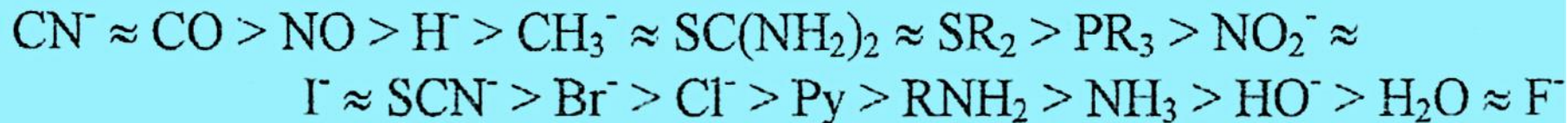
- Both mechanisms result in the formation of pentacoordinated complexes. Experimental data indicate the formation in the first step of the intermediate with a solvent molecule, SN_2^S .
- For an octahedral complex, the two mechanisms can be schematized as follows:



Substitution reactions

Trans effect

- A general phenomenon found in square-planar complexes is that a ligand has a greater stabilizing/stabilizing effect on another ligand located in the *trans* position relative to it than on ligands located in the *cis* position. **This effect is known as the *trans effect*.**
- The strength of the bond between the ligand in the *trans* position and the central metal ion, hence the strength of the *transeffect*, varies in order:

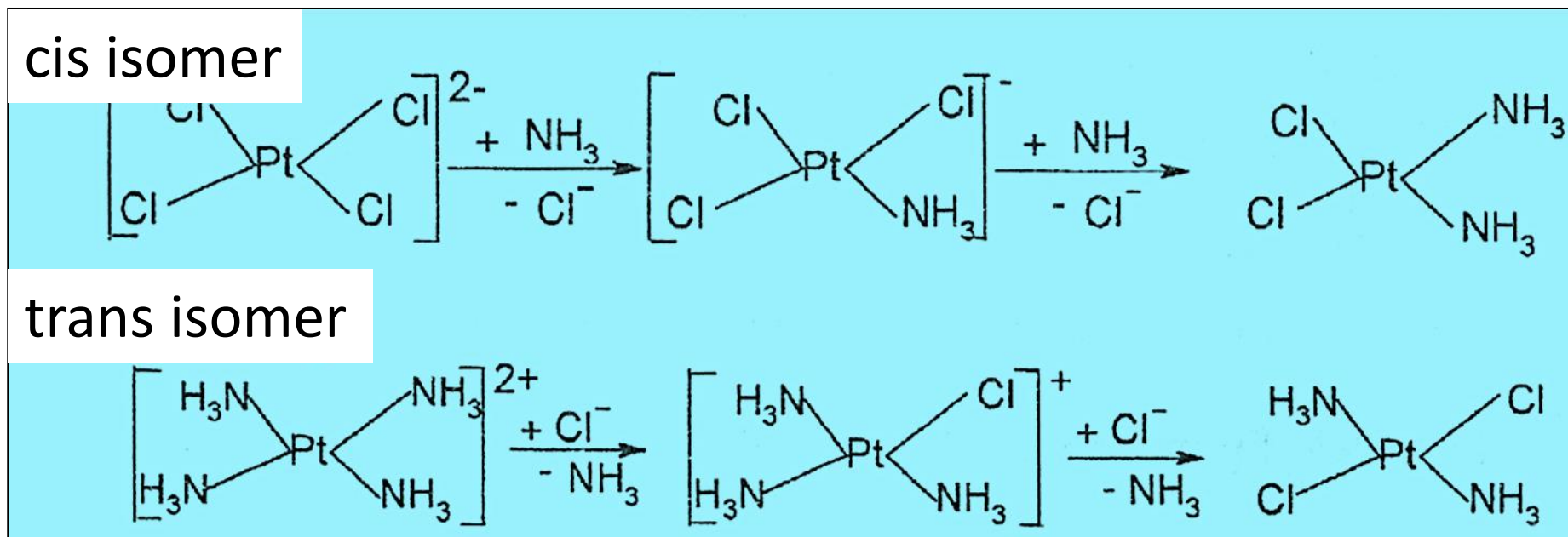


- Knowing the order of the *trans* effect of a ligand, one can predict the sequence of reactions that must be followed in order to obtain a particular geometric isomer.

Substitution reactions

Trans effect

- Based on the principle of *trans*-influence it was possible to direct the synthesis to obtain *cis* and *trans* isomers of $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$:

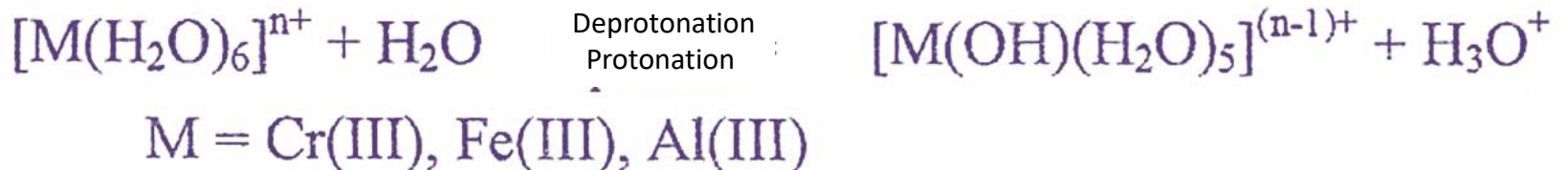


- Analysis of these two processes leads to the conclusion that in the first step any of the four platinum ligands can be substituted, they are equivalent; in the second step, the second ligand becomes *trans* to the ligand with the stronger *trans* effect.

Substitution reactions

Protonation - deprotonation reactions

- In aqueous solutions, some aquacomplexes yield protons to water molecules (deprotonate), forming hydroxo-complexes:



- In the case of divalent metals, deprotonation takes place in the basic medium:



- The deprotonation reaction is a first step in the hydroxide precipitation process, and protonation leads to the dissolution of hydroxides with the replenishment of aquacomplexes.
- In general, coordination increases the acidic character of ligands, especially in the aqua- and amino-complex class. The increase in acidity of the coordinated H₂O and NH₃ molecules is attributed to the change in their charge density, which will lead to proton ionization.

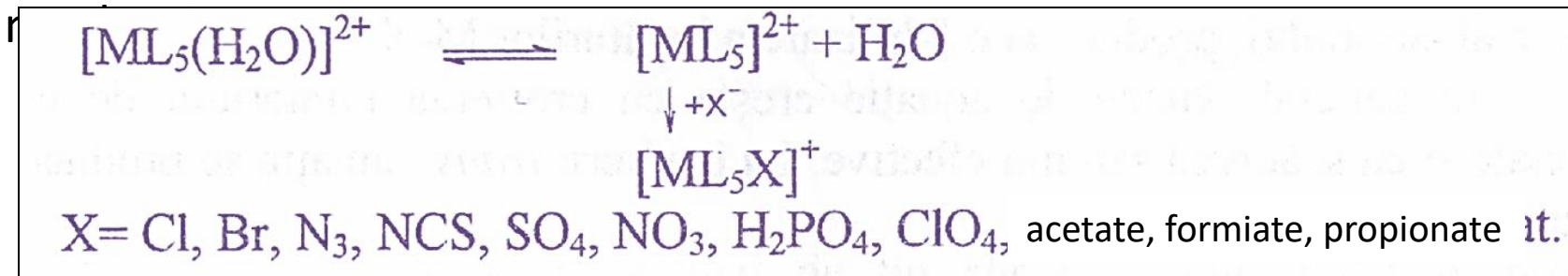
Substitution reactions

Anatation reactions

- The anatation reaction consists of the substitution of a water molecule in the coordination sphere with any anion:



- In divalent complexes, anatation proceeds by a dissociative



- For the other complexes (especially trivalent ones), anatation proceeds with the formation of an outer sphere complex (SN2-type mechanism).



Substitution reactions

Acid hydrolysis reactions (aquation)

- Aquation reactions are the reverse of anation reactions, involving the replacement of a ligand with a water molecule and the production of an aquacomplex:



- The process of acid hydrolysis is explained by the partial solvation of anionic ligands which favours their gradual removal from the complex:



- The aquation content depends on many factors: the nature of the central ion, the nature of the substituted ligand and inert ligands, the effective charge of the complex ion, the chelating phenomenon, the formation of π bonds, the acidity of the solution, the nature of the solvent, the concentration, etc.
- Aquation velocities decrease, depending on the nature of the metal ion, in the order: Cr(III) > Co(III) > Ru(III) > Rh(III) > Ir(III). Aquation speed increases with increasing number of cycles chelated and decreasing effective load. In *trans* isomers, aquation occurs faster than in *cis* isomers.

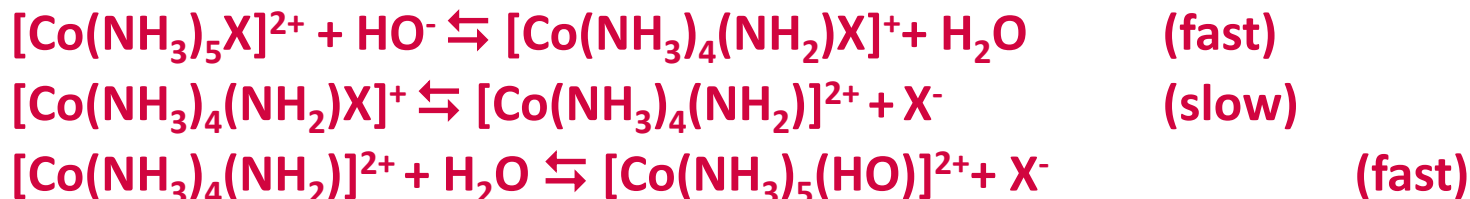
Substitution reactions

Basic hydrolysis reactions (olation)

- Olation reactions consist of the replacement of a ligand in the coordination sphere by the hydroxyl ion HO⁻, with the formation of hydroxocomplexes:



- Ingold et al. consider that in alkaline medium the very rapid hydrolysis of these complexes proceeds by an S_N2 mechanism, by direct attack of the hydroxyl ion on the complex.
- Govrik et al. propose a mechanism in which a rapid equilibrium first occurs between the complex ion and the conjugate base (S_N1-BC). This is subsequently removed by dissociation of the halogen ion into an intermediate, coordinatively unsaturated species, which rapidly aquatizes, generating a hydroxocomplex:



Substitution reactions

Central ion substitution reactions

- Central metal ion substitution reactions are less frequent and take place on an equilibrium basis:



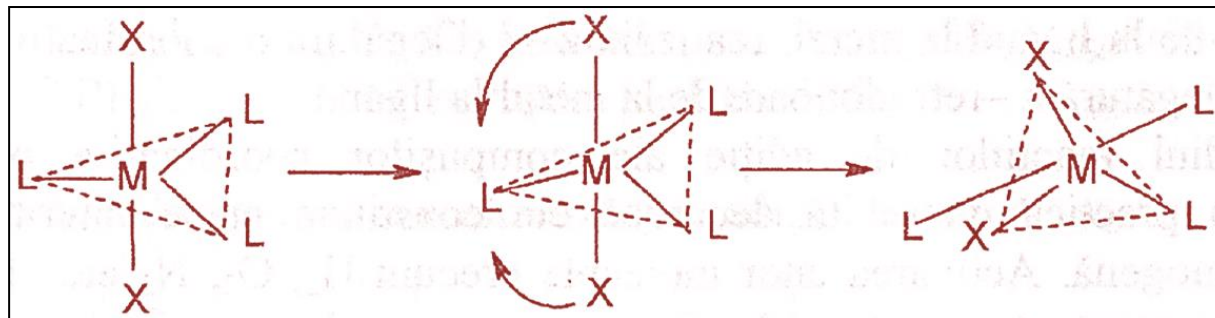
- This type of reaction belongs to the electrophilic substitution (ES) category.



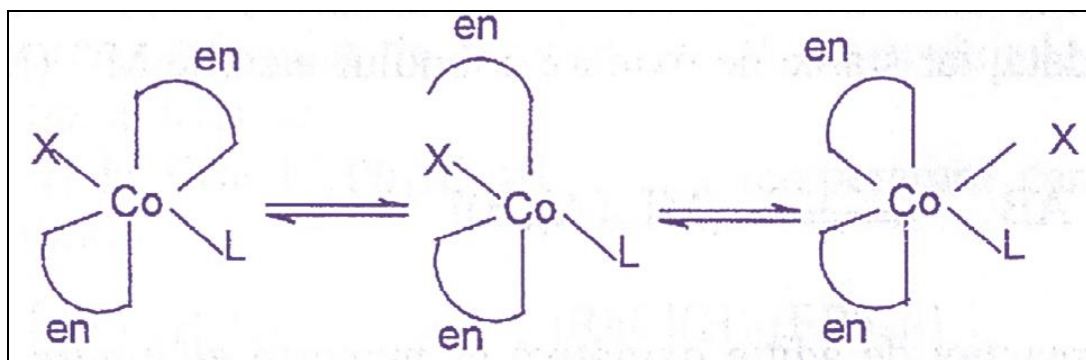
Substitution reactions

Isomerisation reactions

- Quadratic-planar Pt(II) and octahedral Co(III) complexes often form pentacoordinated activated complexes with bipyramidal-trigonal geometry. The interchange of axial and equatorial ligands, in a complex with bipyramidal-trigonal geometry, can be described as a pseudo-rotation through a quadratic pyramid.



- In the case of chelating ligand complexes, isomerisation can occur by breaking the metal-ligand bond without substitution. Substitution of $[[\text{CoLX}(\text{en})_2]^+$ type Co(III) complexes leads to *trans-cis* isomerisation only when the reaction takes place in basic medium.



Addition reactions

- Addition reactions are characteristic of unsaturated coordinative complexes. *Coordinative unsaturation* means the presence of vacant positions in the coordination sphere of the respective complements.



- **The coordinative unsaturation** can be cancelled by the presence of ligands that have the ability to function as "bridging ligands" (X-, HO-) and lead to the formation of polynuclear compounds.
- The occurrence of an addition reaction implies the existence of class "b" ligands (phosphines, arsines, CO) in the coordination sphere, which cause a localized electron density on the non-binding or weakly binding orbitals of the metal ion.
- **The coordinative unsaturation can be correlated with the d configuration of transition metal ions.** Thus, for d⁶-configuration ions, hexacoordination exhibits a saturated structure, while for d¹⁰-configuration ions, pentacoordination and tetracoordination respectively represent such structures.

Addition reactions

- The study of addition reactions of complex combinations is of particular **practical importance**, as they are *intermediate steps in homogeneous catalysis*.
- The addition reaction involves the attack of a molecule AB on a complex species [ML_n] with the formation of an addition compound [ML_n(AB)]. The reaction can go one of two ways:

1. by oxidative addition (coordinative dissociation), when the AB molecule is weakened or cleaved and the oxidation state of the metal ion M^{p+} (M = Ni; Pd; Pt) changes:



The reverse of the oxidative addition reaction is called **reductive elimination** and has implications for obtaining some organic compounds.

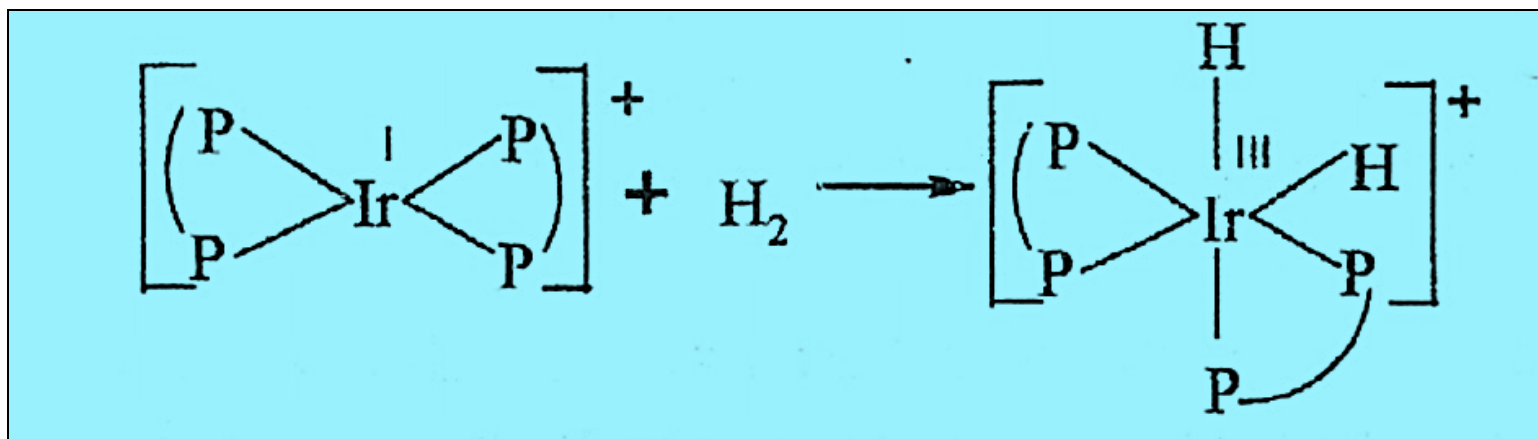
2. by coordinative addition, when the coordinating molecule does not dissociate and the oxidation state of the metal ion remains unchanged:



Addition reactions

Hydrogen addition

- Hydrogen activation by addition to transition metal coordination compounds is an important step in the homogeneous catalytic hydrogenation process.
- Hydrogen addition only occurs in coordination compounds where the central metal ion has the d8 configuration.
- Hydrogen addition is achieved by *oxidative addition*:



Addition reactions

Addition of carbon monoxide

- The first coordinative compound for which the property of reversibly fixing carbon monoxide has been established is Vaska's complex, $[\text{IrCl}(\text{CO})(\text{PPh}_3)_2]$, according to equilibrium:



- In the presence of air the reverse reaction takes place followed by the addition of molecular oxygen.
- A similar behaviour is also shown by the $[\text{Ir}(\text{P-P})_2]\text{X}$ complex which leads to the formation of a pentacoordinated adduct. They can also reversibly bind CO and other complexes such as:



Addition reactions

Addition of molecular nitrogen

- Although the nitrogen molecule is fairly inert, it can still participate in a number of addition reactions to complex *d-metal* combinations.

- The equilibria for obtaining complexes with N₂ as ligand can be:



- The most important complexes containing N₂ as a ligand are:



Addition reactions

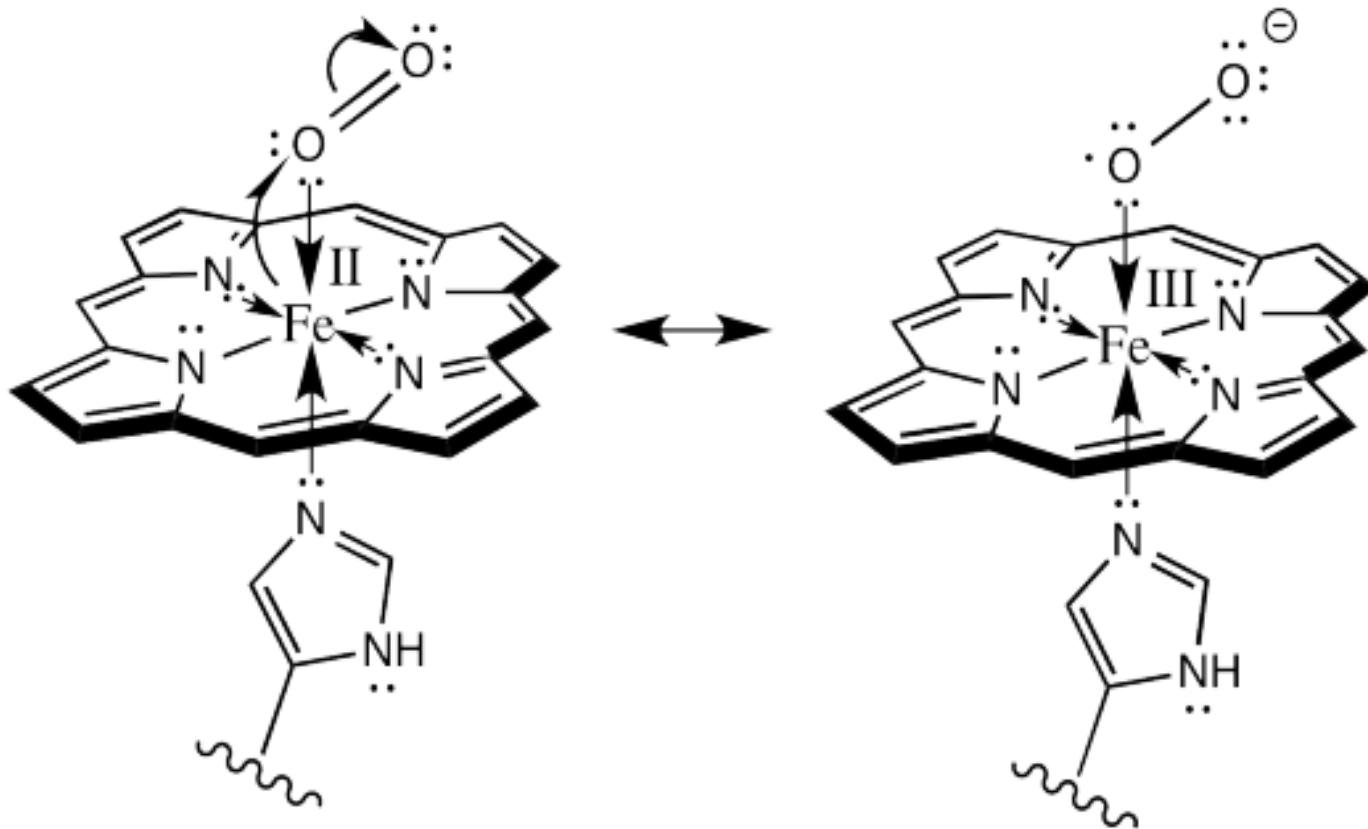
Addition of molecular oxygen

- **The reversible addition of molecular oxygen (O_2)** by synthetic or natural co-ordinating compounds is of particular importance for many chemical, biochemical and industrial processes.
- **Compounds that reversibly fix (bind) O_2 , with the formation of metal-dioxide adducts, are called *oxygen transporters*.**
- **Some metal complexes have the ability to achieve complex equilibrium by forming adducts with O_2 without the metal (M) or ligands (L) irreversibly oxidising.**
- Such systems, known as *oxygen transporters*, have biological implications in the transport and storage of molecular oxygen.

Addition reactions

Addition of molecular oxygen

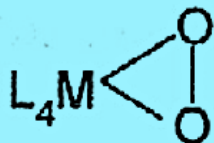
- For the reaction to be characteristic of an oxygen carrier, it must be reversible, and upon dissociation of the oxygenated form of the complex, $[M(L)]$ and O_2 are formed.



Addition reactions

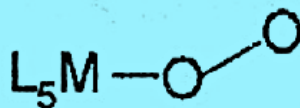
Addition of molecular oxygen

- The spectral and magnetic properties of O_2 adducts, such as the reversibility of oxygen fixation, have raised some questions about their interpretation and the nature of the metal- O_2 bond.
- Depending on the stereochemistry of the O_2 adducts, they can be:
 - **symmetric monomers (J.S. Griffith type);**
 - **asymmetric monomers (L. Pauling);**
 - **symmetric dimers with O-O bridge.**



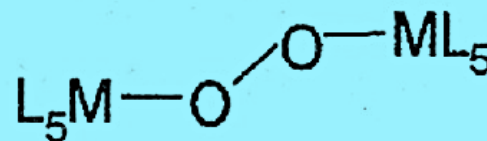
a)

symmetric



b)

asymmetric



c)

symmetric dimers in bridge

Insertion reactions

- **Insertion reactions** comprise those reactions in which a Y group interposes (inserts) itself between the metal and a ligand originally coordinated to the central atom:



- Formally, such a reaction can be seen as an addition of a covalent metal compound M-L to an unsaturated molecule Y:



- Metal-ligand (M-X) bonds that can participate in insertion reactions are: M-H, M-C, M-N, M-O and M-M.
- According to the mechanism on the basis of which insertion reactions take place, they can be classified into:
 - *stoichiometric reactions*, when a well-defined compound results;
 - *catalytic reactions*, in which the metal is present in small amounts and catalyses the reaction between two or more substrates.

Redox reactions

- **Redox reactions**, which are most common in inorganic chemistry, are also found in complex combination chemistry.
- Redox reactions of complex combinations can occur with or without change in the oxidation state of the ligands and with electron transfer only between the central metal ions, resulting in a change in their oxidation states.



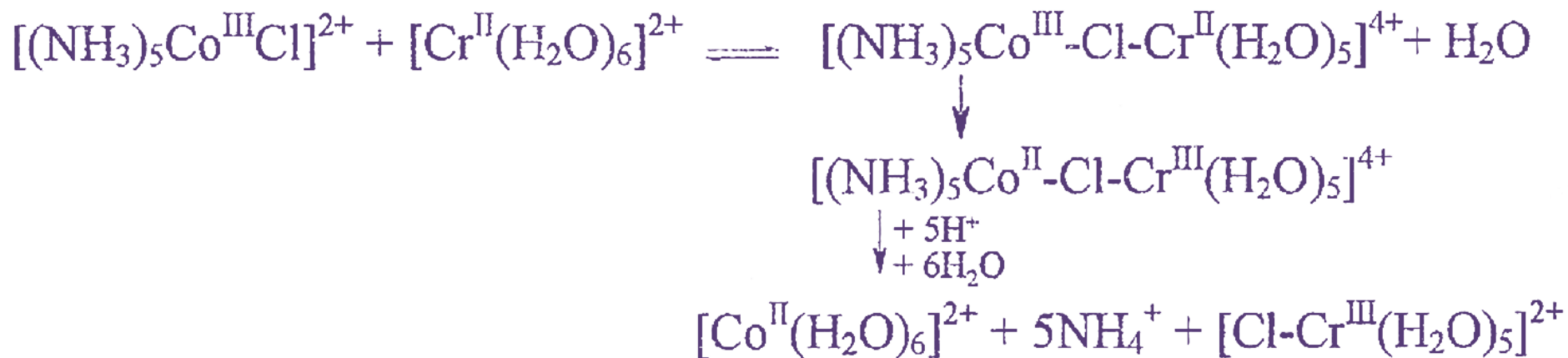
- Redox reactions of complex combinations can generally proceed through two types of mechanisms:
 - a) inner sphere,**
 - b) the outer sphere.**

Redox reactions

- **Outer sphere mechanism** implies that the reductant remains outside the coordinating sphere of the oxidant and vice versa. One such reaction is that between Fe(II) and Ir(IV):



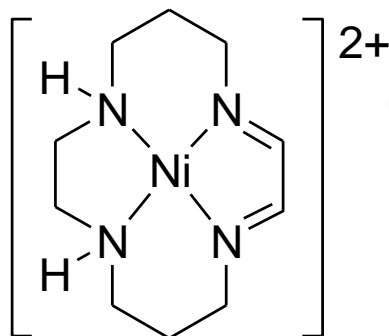
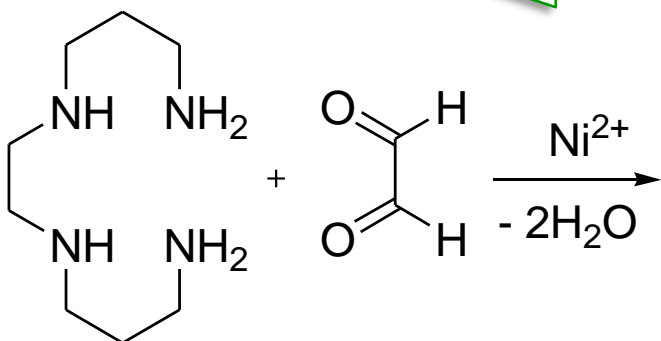
- **Inner sphere mechanism** results from the transfer of an electron via a ligand acting as a bridge between the metal ions involved:



Metal-templated reactions

A metal ion like Ni(II) can be used in the assembly of a ligand group.

The ligands then react with each other to form a **macrocyclic ligand**.



This process, called **metal-templated synthesis**, can be applied to produce a variety of macrocyclic ligands.

It is a **condensation reaction**, in which bonds are formed between two ligands and small molecules (here H₂O) are removed.

Once formed, the macrocycle is stable and the metal ion can be removed.

In the absence of the metal ion, the respective macrocyclic ligand cannot form.

