

Substitution Reactions

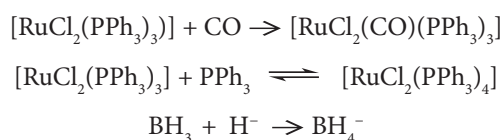
K. Sarath D. Perera

Senior Professor in Chemistry, Department of Chemistry, The Open University of Sri Lanka

A good knowledge in coordination and organometallic chemistry is very useful to a student, who wish to understand chemical transformations taking place around in nature and industry. It also helps to design synthetic routes to target metal complexes. We know that nature very cleverly uses metal complexes to carry out reactions catalytically with a precise selectivity. In enzymes, metal centres such as Zn, Cu, Mo, Fe *etc.* are dressed in organic ligands to perform specific reactions. This article is predominantly focused on the following reaction types; namely, association, dissociation and ligand substitution.

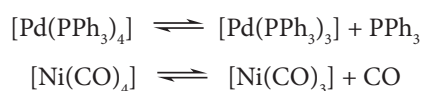
Association reactions

Here, a **coordinationally unsaturated** complex takes up a suitable ligand(s) to form a **coordinationally saturated** (18e) complex, with at least one-unit higher coordination number (C.N.) than the starting complex. Some of these reactions are reversible. For example, (i) $[\text{RuCl}_2(\text{PPh}_3)_3]$ can form an adduct with CO or PPh_3 ; (ii) BH_4^- is formed by associating a hydride ion with BH_3 .



Dissociation reactions

This is the reverse process of an association reaction. Particularly, **coordinationally saturated** compounds undergo this type of reaction to form **reactive, coordinationally unsaturated** compounds. Some of these reactions are reversible. For example, zerovalent Pd(0) complex, $[\text{Pd}(\text{PPh}_3)_4]$ reversibly dissociate one PPh_3 ligand resulting coordinatively unsaturated complex, $[\text{Pd}(\text{PPh}_3)_3]$ which can act as a catalyst.



Ligand substitution reactions

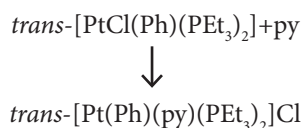
At the end of this type of reactions, the oxidation number (O.N.) and the coordination number of the metal centre remain **unchanged**. Thus, valence electron count (VEC) also remains the same. *e.g.*, formation of $[\text{Ni}(\text{CO})_3(\text{PPh}_3)]$ by reacting one equivalent of PPh_3 with $[\text{Ni}(\text{CO})_4]$



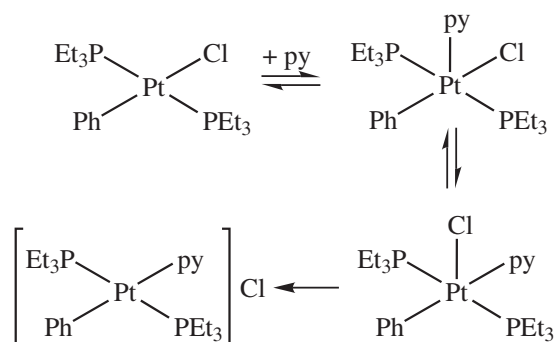
Substitution of a coordinated ligand by an incoming ligand can take place *via* three pathways; (i) **Associative (A)**, (ii) **Dissociative (D)**, and (iii) **Interchange (I)** pathways.

Associative mechanism (A)

Coordinationally unsaturated complexes, particularly 16e square-planar complexes containing metal centers such as Pt(II), Pd(II), Ni(II), Rh(I), Ir(I) and Au(III) undergo substitution reactions *via* a five coordinate, 18e-intermediate which can have either square pyramidal or trigonal bipyramidal geometry. *e.g.*, pyridine (py) substitutes the chloride of *trans*- $[\text{PtCl}(\text{Ph})(\text{PEt}_3)_2]$, to give a salt of the type *trans*- $[\text{Pt}(\text{Ph})(\text{py})(\text{PEt}_3)_2]\text{Cl}$.



This reaction proceeds *via* an **associative** pathway.



Dissociative mechanism (D)

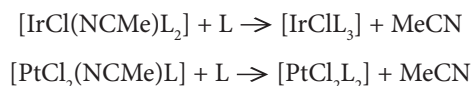
Coordinatively saturated complexes undergo this type of substitution reactions; first dissociating a ligand to create a vacant site, and then vacant site is occupied by the incoming ligand. In some cases, solvent molecules with donor atoms can temporarily occupy the vacant site.

Interchange mechanism (I)

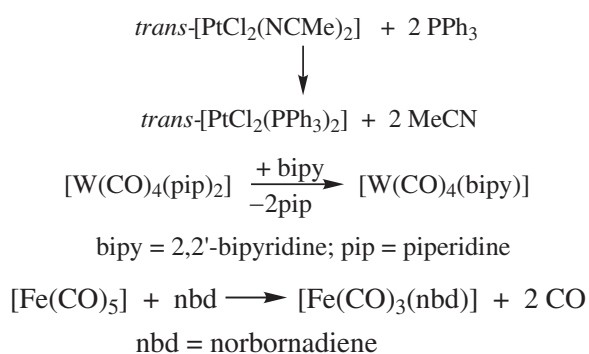
An interchange mechanism takes place in a **single step**, where the leaving and entering groups exchange *via* an **activated complex**. This activated complex is not a true intermediate. The rate of the interchange process is expected to depend on the nature of the entering group and its concentration.

Mono-, di- and tri-substitution reactions

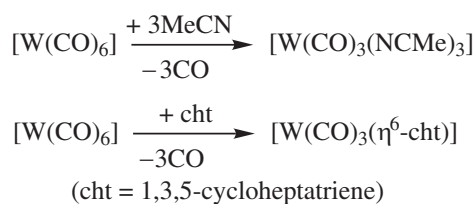
In a mono substitution reaction, one labile ligand (*e.g.* MeCN) is replaced by another ligand (*e.g.* L = PPh₃).



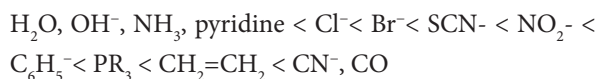
In a di-substitution reaction, two ligands are replaced by another ligand/s. This can be viewed as two mono substitution reactions, taking place one after the other.



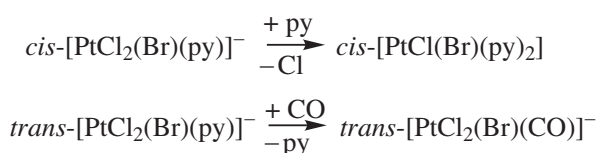
In a tri-substitution reaction, three ligands are replaced by another ligand/s.

**Trans effect**

The *trans*-effect can be observed in ligand substitution reactions of square-planar complexes, which consider the influence of a ligand on the ligand *trans* to it. A strong ligand may replace a labile *trans*-ligand by an incoming ligand. The order of the *trans*-effect of some common ligands is given below.



For example, reaction of one equivalent of pyridine with *cis*-[PtCl₂(Br)(py)]⁻ gives *cis*-[PtClBr(py)₂]⁻; and reaction of one equiv. of CO with *trans*-[PtCl₂(Br)(py)]⁻ gives *trans*-[PtCl₂(Br)(CO)]⁻.

**Problems**

- Identify the product(s) of the following reactions.
 - BF₃ + Et₂O
 - PtCl₂ + 2 NaCl
 - PtCl₂ + 2 MeCN
 - [IrCl(CO)(PPh₃)₂] + NaCN
 - cis*-[PtCl₂(PPh₃)₂] + 2 MeMgI
 - [Mo(CO)₆] + 2 piperidine
 - [PdCl₂(nbnd)] + 2 PPh₃
 - [PdCl₂(NCPh)₂] + bipy
- How would you prepare *trans*-[PtBr₂(py)(CO)] from [PtBr₄]²⁻ if the *trans* effect order is CO > Br⁻ > py?
- How would you prepare *cis*-[NiCl₂(CO)(NH₃)] from [NiCl₄]²⁻ if the *trans* effect order is CO > Cl⁻ > NH₃.
- [Pt(NH₃)₄]²⁺ undergoes an associative substitution reaction with Cl⁻ to give an intermediate (**X**) which rapidly loses a ligand (**Y**) to form a square planar complex cation (**Z**). Identify (**X**), (**Y**) and (**Z**).