

CHIRALITY IN TRANSITION METAL CHEMISTRY

CHIRALITY: Word **chirality** was used in organometallic and coordination chemistry with the name of Alfred Werner (1866–1919). In 1893, **chirality** was applied by van't Hoff and Le Bel's stereochemical ideas of the tetrahedral nature of the carbon atom to the structure of hexacoordinated (octahedral structure) metal complexes. In 1911, Alfred Werner was predicted the resolution of the two enantiomers of the complexes $[\text{Co}^{\text{III}}(\text{en})_2(\text{NH}_3)\text{X}]\text{X}_2$ where $\text{X} = \text{Cl}, \text{Br}, \text{I}$ (Fig.1). In 1913, Alfred Werner won Nobel Prize for this work.

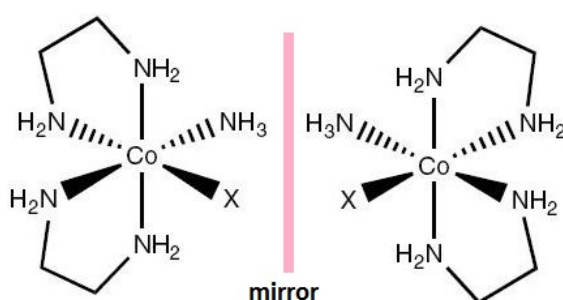


Fig. 1- The cationic part of the two enantiomers of $[\text{Co}^{\text{III}}(\text{en})_2(\text{NH}_3)\text{X}]\text{X}_2$

Chirality is defined by IUPAC as: *The geometric property of a rigid object (or spatial arrangement of points or atoms) of being non-superimposable on its mirror image; such an object has no symmetry elements of the second kind (a mirror plane, $\sigma = S_1$, a centre of inversion, $i = S_2$, a rotation reflection axis, S_{2n}). If the object is superimposable on its mirror image the object is described as being achiral.*

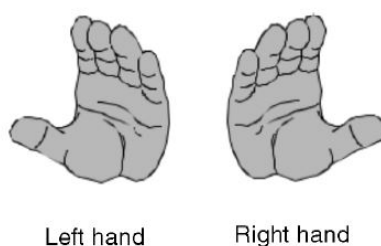


Fig. 2 - The left and right hands are not superimposable objects.

Organometallic compounds- are compounds in which at least one M-C covalent bonds exist. for eg.

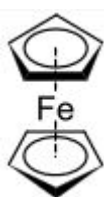


Fig. 3- Ferrocene

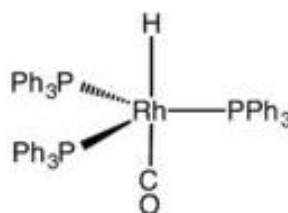


Fig. 4- Tris(triphenylphosphine)rhodium carbonyl hydride / Carbonyl hydrido tris(triphenylphosphine)rhodium(I)

Coordination compounds- are those compounds which retain their identity even when dissolved in water or any other suitable solvent and their properties are completely different from the constituent salts. for eg.

1. $[\text{Cu}(\text{NH}_3)_4]\text{SO}_4$
2. $\text{K}_4[\text{Fe}(\text{CN})_6]$

Enantiomers- are a pair of molecules that exist in two forms which are mirror images of each other but can not be superimposed on one another. Enantiomers exist in two forms and have chiral carbon which forms the center and has 4 atoms or groups attached to it. Two molecules can be called an enantiomer only if the two chiral carbons have different configurations. for eg. Fig. 1

Chiral carbons- a C-atom that is attached to four different atoms / groups / substituents.

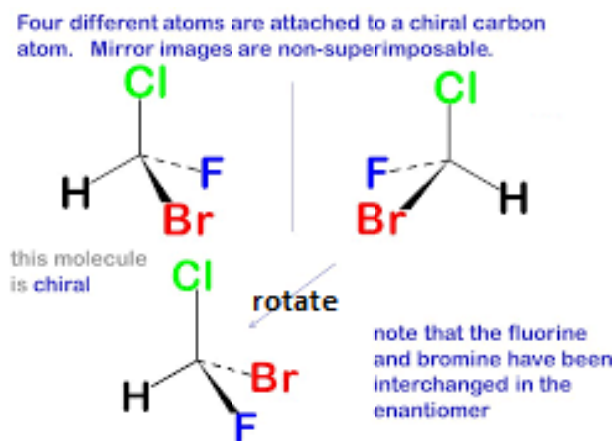


Fig. 5

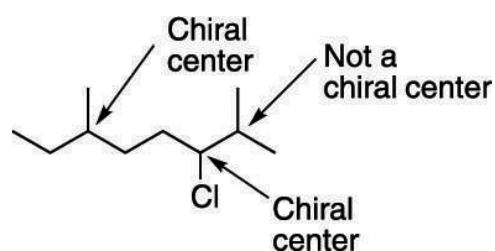


Fig. 6

Point groups of chiral molecules-

- The group C_1 (the identity E)
- The group C_n (an axis C_n and the identity E)
- The group D_n (an axis C_n ; n C_2 axes perpendicular to C_n and the identity E)
- The groups T; O; I. These groups correspond to tetrahedral, octahedral and icosahedral structures.

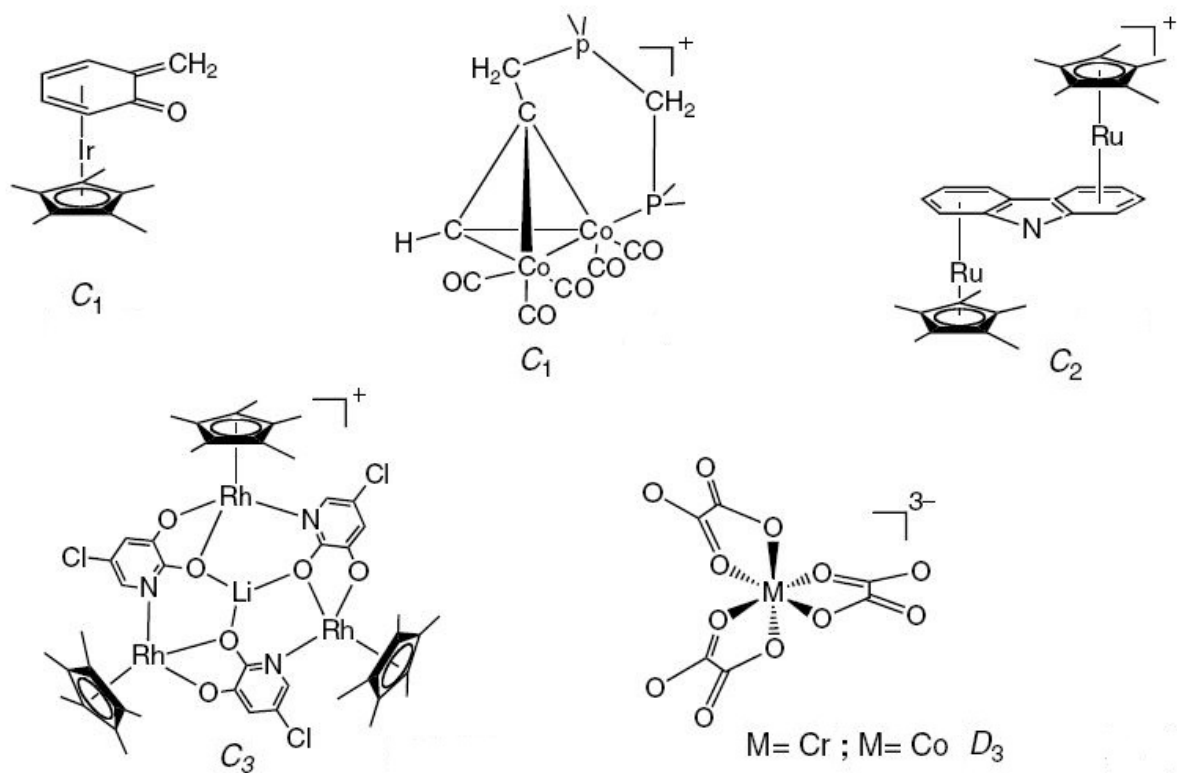


Fig. 7- Some examples of chiral organometallic compounds with different symmetry point groups.

Some points for symmetry

- ✚ Crystals are defined based on symmetry. The symmetry being referred to in this context is geometrical symmetry. (Danish physician Nicholas Steno in 1669, gave **law of the constancy of interfacial angles**. This law is also known as *first law of crystallography*.)

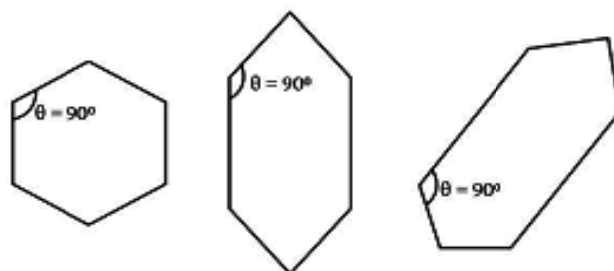


Fig. 8 - Constancy of interfacial angles

- ✚ **Law of the constancy of interfacial angles:** *The angle between two adjacent faces called the interfacial angle of the crystal of a particular substance. **Goniometer** instrument is used for the measurement of interfacial angles.*
- ✚ Symmetry helps to reduce the '*infinite*' amount of information (like thermal conductivity and optical activity) required to describe a crystal into a finite (*preferably small*) amount of information.
- ✚ Any property of a crystal will have at least the symmetry.
- ✚ Symmetry exists everywhere. All you have to do is open your eyes to see it. As symmetry is pleasing to the eye, designing and art places a lot of importance in symmetry.

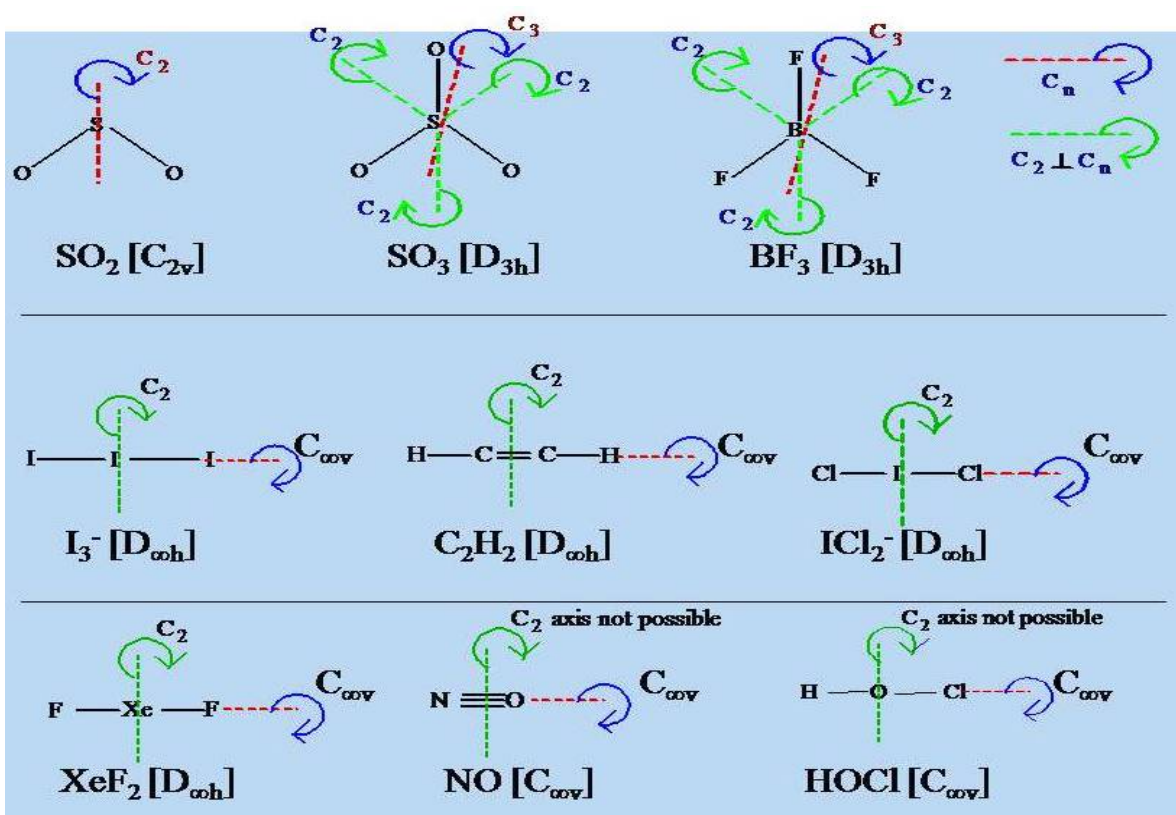
Symmetry of What?

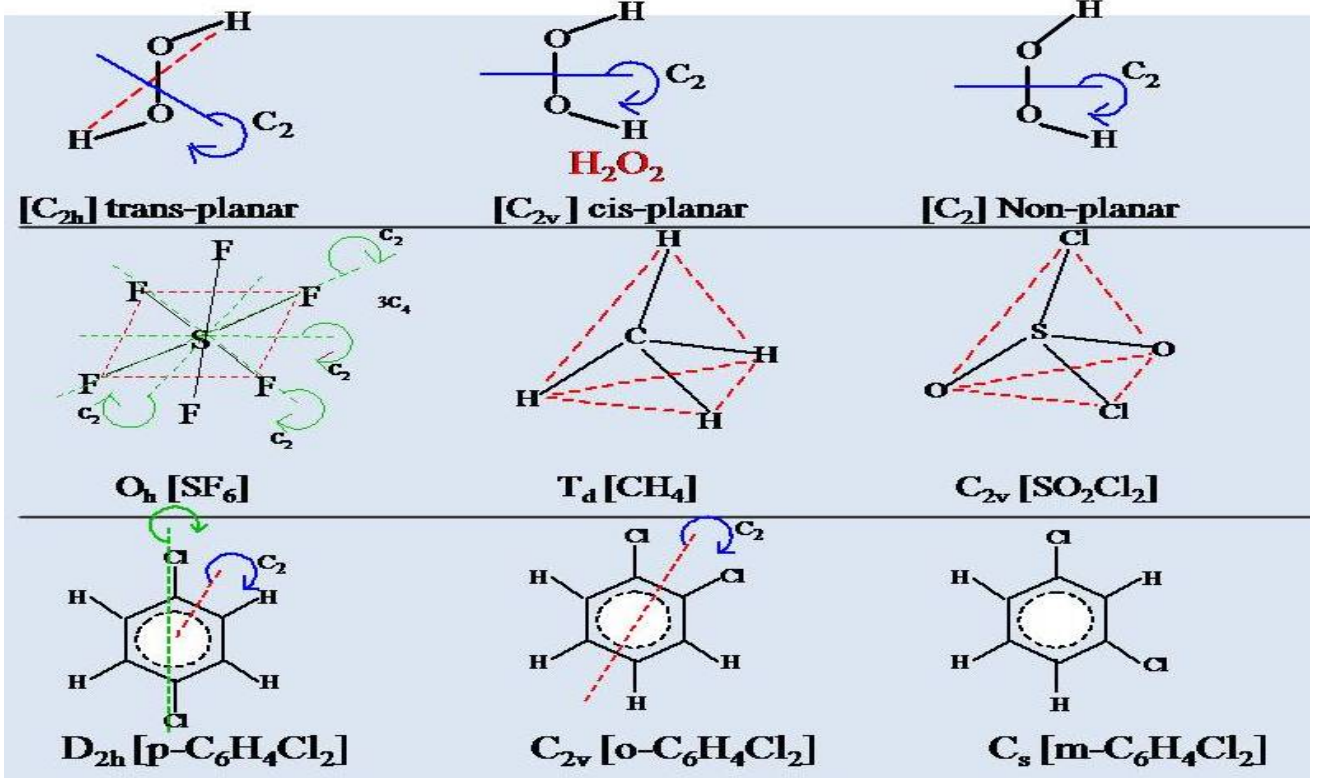
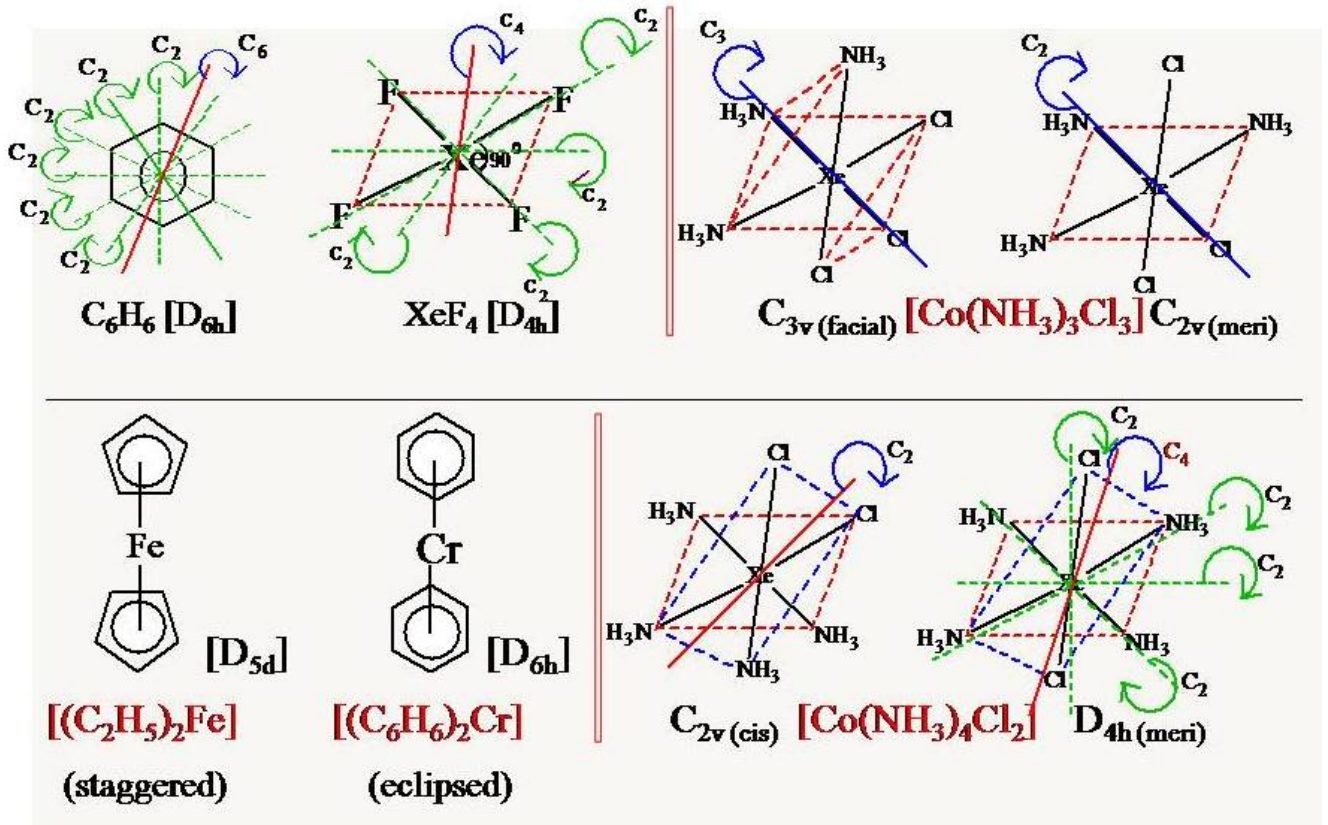
- ❑ The symmetry under consideration could be of one the following entities:
 - Lattice ➤ Crystal ➤ Molecule ➤ Unit cell

There are five ways for describe the above summary:-

S. No.	Symmetry element	Symmetry operator	Symbol
1	Proper axis of symmetry	Rotation about the axis	C
2	Point of symmetry	Inversion through the point	i
3	Plane of symmetry	Reflection in the plane	σ
4	Improper axis of symmetry	Rotation about the axis followed by reflection into the plane	$S, C \perp \sigma$
5	Identity	No operations	I, E

Some examples of compounds with points group:-

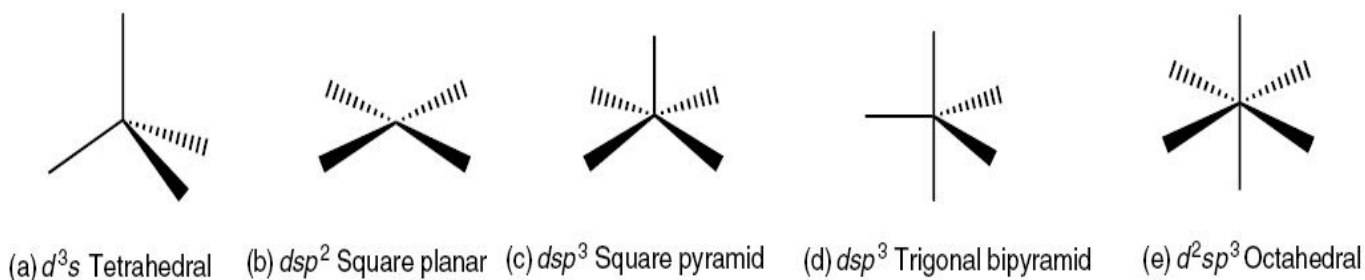




Main Features of Chirality in Organometallic and Coordination Chemistry:

- (i) Metal coordinated to different types of ligands
- (ii) Tetrahedral complexes
- (iii) Planar chirality
- (iv) Metal with achiral chelating ligands leading to helical geometries
- (v) Metal surrounded by four ligands or two bis(chelate) ligands leading to a complex with an axis of chirality or axial chirality

(i) Metal coordinated to different types of ligands:



Coordinated metal centres: when d orbitals as well as s and p orbitals are available

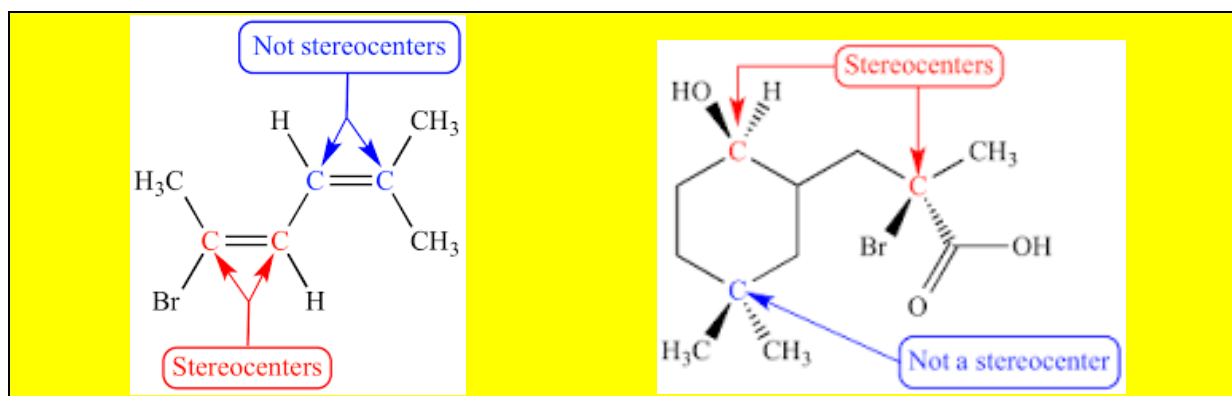
Fig. 9

In these different cases, the metal and its ligands form a stereogenic element with the metal at the centre.

Note: In Figure 9(e) $M(a,b,c,d,e,f)$ (OC-6), if all the ligands (a,b,c,d,e,f) are different then there are **15 possible isomers**.

Stereogenic element: is an atom (center), axis, or plane that is the focus of stereoisomerism. *Stereogenic element gives different isomers when atoms or groups attached to it are interchanged.* These isomers are called **stereoisomers**. Because the structures of the molecules are the same but their spatial arrangements are different from each other. Fig. 9

Note: Enantiomers are equal in all their physical properties except for their optical rotation. That is, they rotate the plane polarized light (PPL) by equal amounts in opposite directions.



The structure of type Fig. 9(a) is well known in organometallic chemistry, in particular among the complexes of manganese and rhenium, for example the resolved enantiomeric complexes of $[\text{Mn}(\text{C}_5\text{H}_5)(\text{NO})\text{COP}(\text{C}_6\text{H}_5)_3]\text{X}$ and $[\text{Re}(\text{C}_5\text{H}_5)(\text{NO})\text{CH}_3\text{P}(\text{C}_6\text{H}_5)_3]\text{X}$.

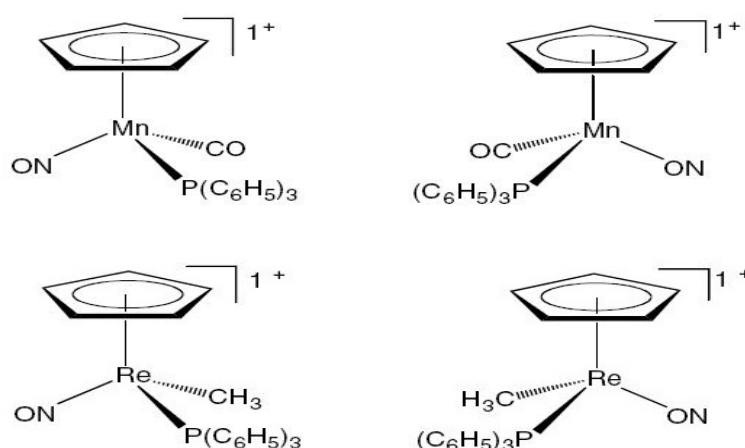


Fig. 10- The cationic parts of $[\text{Mn}(\text{C}_5\text{H}_5)(\text{NO})\text{COP}(\text{C}_6\text{H}_5)_3]\text{X}$ and $[\text{Re}(\text{C}_5\text{H}_5)(\text{NO})\text{CH}_3\text{P}(\text{C}_6\text{H}_5)_3]\text{X}$.

(ii) Tetrahedral complexes

Many clusters with low nuclearity (from two to four), which do not have an atom at the centre of the pyramid, exist in a tetrahedral structure and are chiral if the four vertices, metallic or not, are different. This is the case, for example, of the tetranuclear cluster $[\text{FeCoCr}(\text{Cp})(\text{CO})_8][\mu_3\text{S}]$.

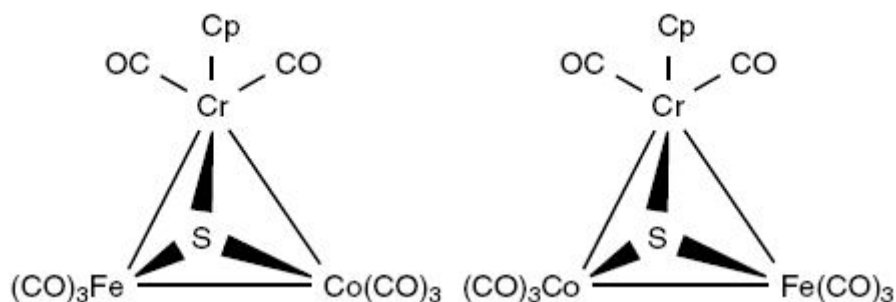


Fig. 11- Two enantiomers of a chiral trinuclear cluster.

(iii) Planar chirality:

This group includes an important part of organometallic chemistry, that of arene, ferrocene and cymanthrene complexes and certain complexes of rhodium and iridium. In this case the chiral element is composed of the metal and the prochiral ligand. Fig. 12 represents the two enantiomers of the 1,2-disubstituted ferrocene complex.

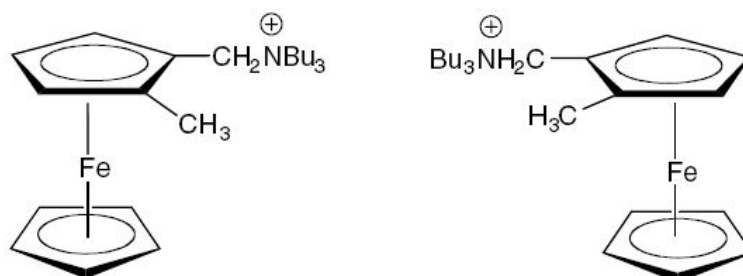


Fig. 12- two enantiomers of the 1,2-disubstituted ferrocene complex.

(iv) Metal with achiral chelating ligands leading to helical geometries:

This type of chiral element is often found in coordination chemistry, in particular for all the hexacoordinated octahedral complexes of type $M(L^2)_2A_2$, in which at least two ligands in a *cis*-position are bis(chelate).

In the case of $M(L^2)_2A_2$ the complex has C_2 symmetry, whereas for $M(L^2)_3$ the symmetry is D_3 . This is shown in Fig. 13 for the cationic part of the complexes $[Ru(bpy)_2py_2]X_2$ (py = pyridine) and $[Ru(bpy)_3]X_2$.

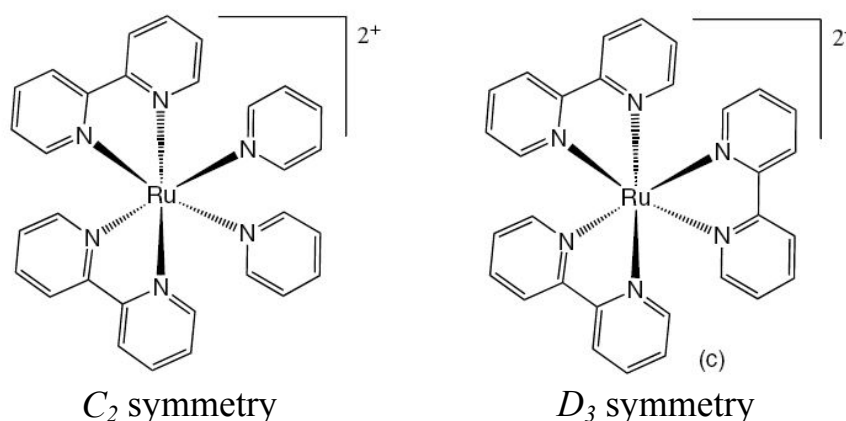


Fig. 13- Cationic part of the complexes $[Ru(bpy)_2py_2]X_2$ and $[Ru(bpy)_3]X_2$.

(v) Metal surrounded by four ligands or two bis(chelate) ligands leading to a complex with an axis of chirality or axial chirality:

A square planar complex of the type ML_4 can be chiral even if the ligands surrounding the metal are achiral. Axial chirality may also originate from two *trans* coordinated monodentate ligands formed of planar rings having substituents large enough to prevent free rotation about the axis that joins them.

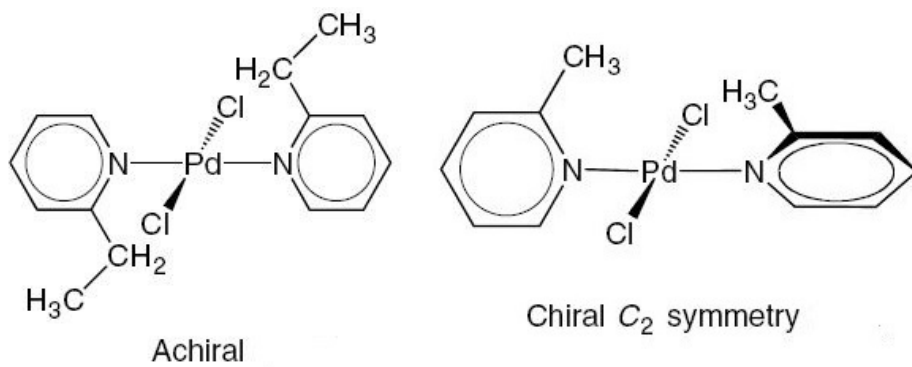


Fig. 14- Achiral and chiral tetracoordinated Pd (II) complexes.