

Coordination Chemistry II: Isomers and Coordination Geometries

Chapter 9

Monday, November 16, 2015

A Real World Example of Stuff from Class!

UNIVERSITY OF CALIFORNIA,
IRVINE

Synthesis and Structural Analysis of Tris(trimethylsilylcyclopentadienyl) Complexes of Lanthanum and Lutetium

THESIS

Submitted in partial satisfaction of the requirements for the degree of

MASTER OF SCIENCE

In Chemistry

By

[Redacted Name]

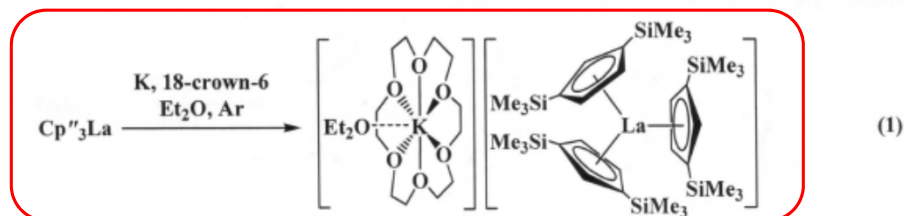
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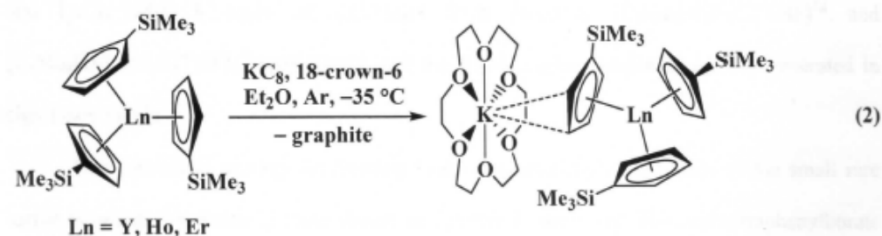
Chapter 1

Introduction and Background

Recent studies of the reductive chemistry of the rare earth metals have shown that trimethylsilylcyclopentadienyl complexes are excellent starting materials for the synthesis of complexes of metals in novel low oxidation states.^{1,2} Lappert and co-workers showed that the bis(trimethylsilyl)cyclopentadienyl complexes, $\text{Cp}''_2\text{Ln}$ [$\text{Cp}'' = 1,3\text{-(Me}_3\text{Si)}_2\text{C}_5\text{H}_3$; $\text{Ln} = \text{La, Ce}$] can be reduced to form crystalline La^{2+} and Ce^{2+} molecular complexes, as in eq 1. More



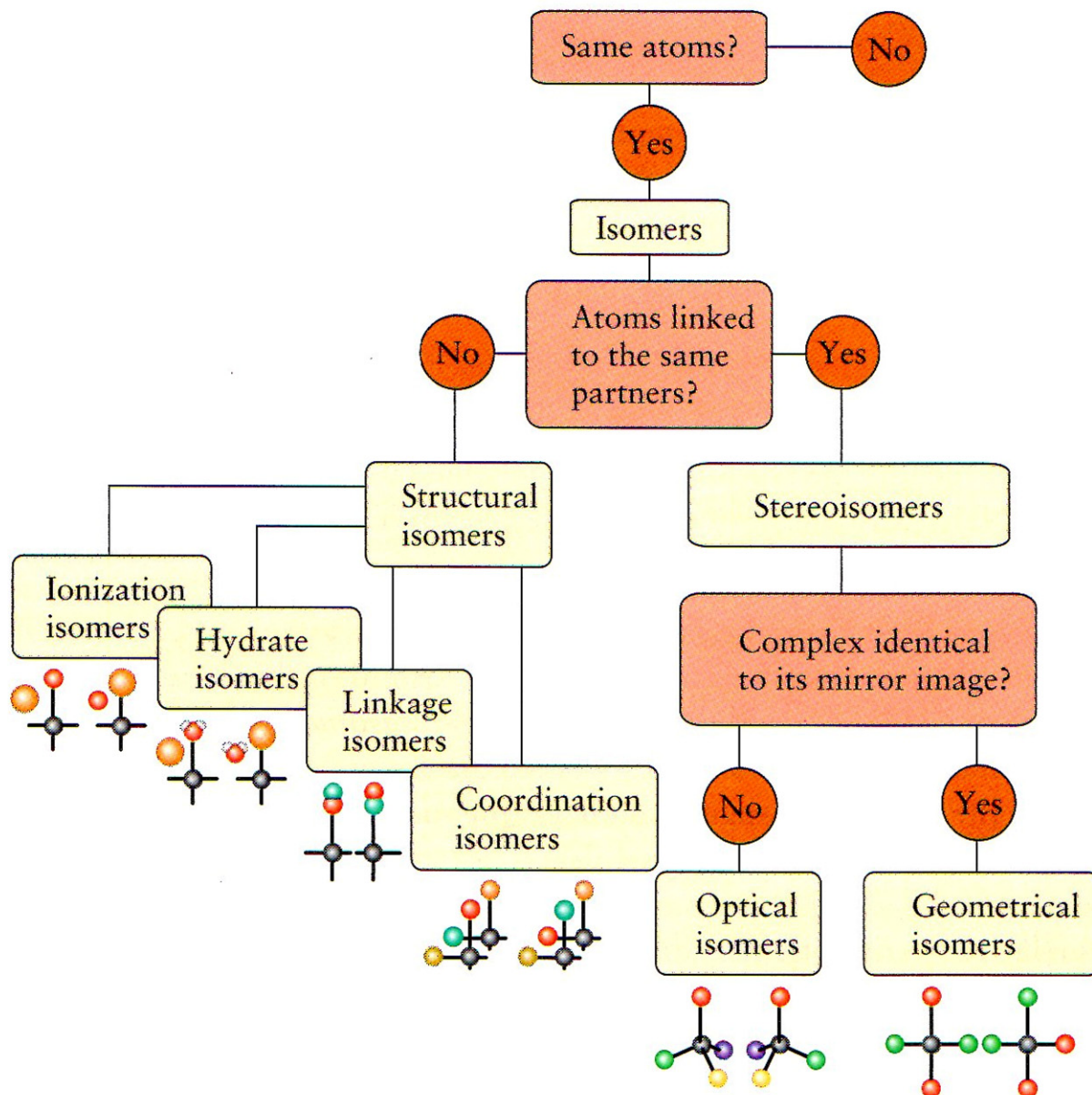
recently, the monosubstituted trimethylsilylcyclopentadienyl ligand, $\text{C}_5\text{H}_4\text{SiMe}_3$ (Cp'), was useful with the smaller rare earths in providing the first crystallographic data on molecular complexes of Y^{2+} , Ho^{2+} , and Er^{2+} , [(18-crown-6)K][$\text{Cp}'_3\text{Ln}$], using $\text{Cp}'_3\text{Ln}$ as precursors, eq 2.^{3,4}



In order to attempt the synthesis of other Ln^{2+} ions along similar lines, the synthesis of previously unknown tris(trimethylsilylcyclopentadienyl) complexes was necessary. Although $\text{Cp}'_3\text{Ln}$ ($\text{Ln} = \text{Ce},^5 \text{Nd},^6 \text{Y},^4 \text{Ho},^3 \text{Er}^3$) complexes readily can be prepared from LnCl_3 and three equiv of KCp' , it was unknown whether these complexes could be obtained with all the rare earth

Isomerism

Coordination complexes often have a variety of isomeric forms



Structural Isomers

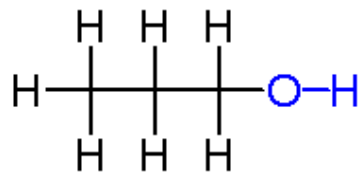
Molecules with the same numbers of the same atoms,
but in different arrangements.

Isomers generally have distinct physical and chemical properties.

One isomer may be a medicine while another is a poison.

Type 1: **Structural isomers** differ in how the atoms are connected.
As a result, they have different chemical formulas.

e.g., C_3H_8O

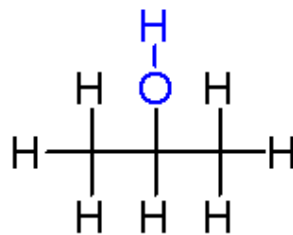


I

1-propanol

m.p. -127°C

b.p. 97°C

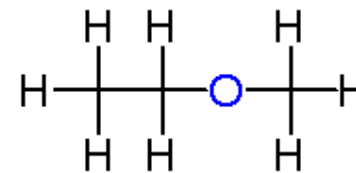


II

2-propanol

m.p. -89°C

b.p. 83°C



III

methoxyethane

m.p. -139°C

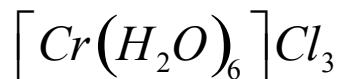
b.p. 8°C

Structural Isomers

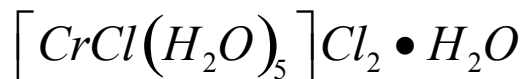
Structural (or constitutional) isomers are molecules with the same kind and number of atoms but with different bond arrangements

In coordination complexes there are four types of structural isomers:

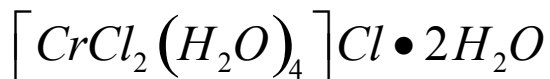
- ***hydrate (solvent) isomerism* occurs when water (or another solvent) can appear within the primary or secondary coordination sphere of a metal ion**



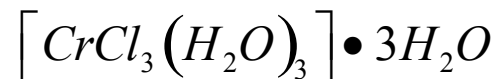
violet crystals



blue-green crystals

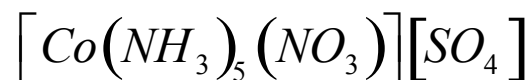
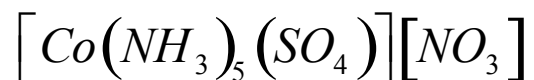


dark green crystals



yellow-green crystals

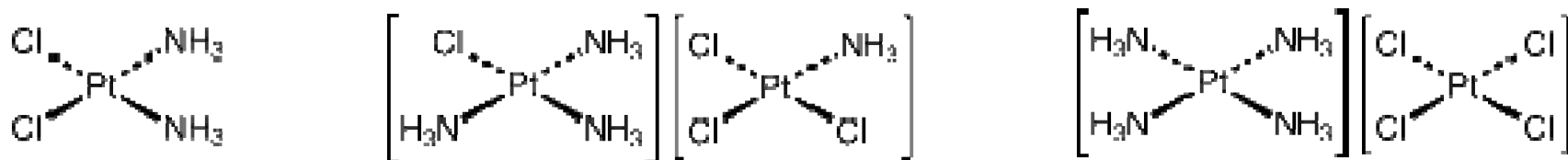
- ***ionization isomers* afford different anions and cations in solution**



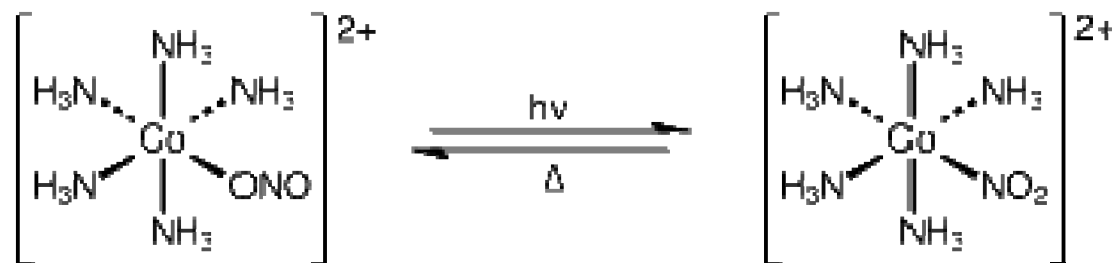
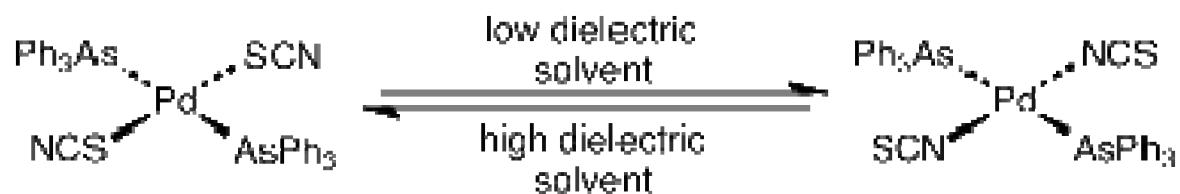
Structural Isomers

In coordination complexes there are four types of structural isomers

- coordination isomerism* occurs when ligands can be distributed differently between two or more metals



- linkage isomerism* occurs when a ligand can bind in different ways to a metal

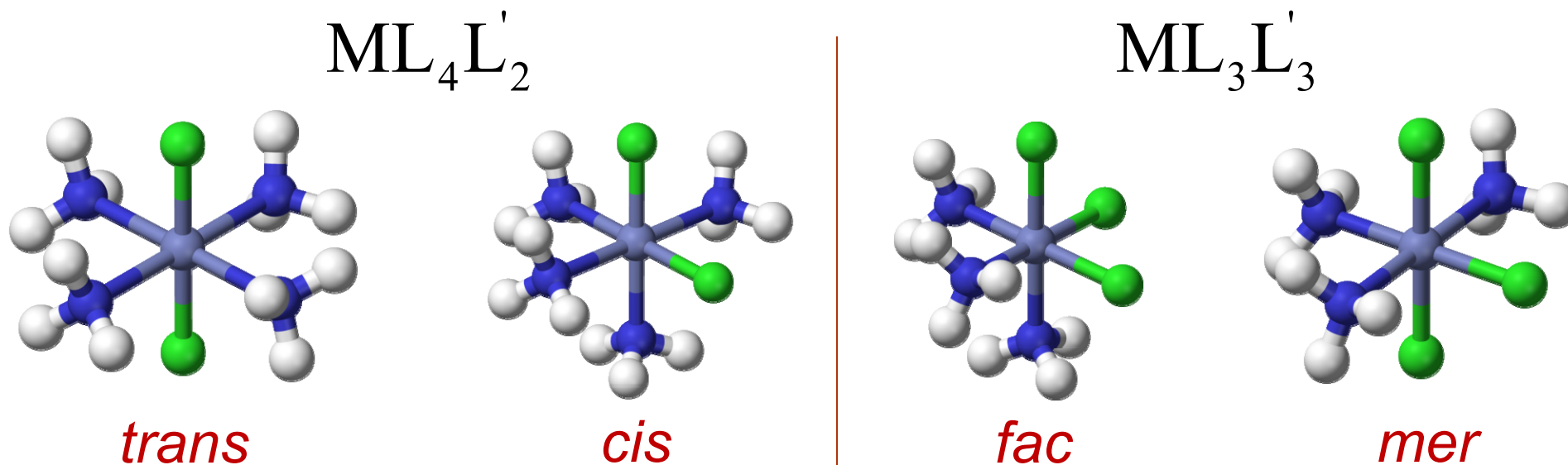


Stereoisomers

The second major class of isomer. Here, the atoms have the same bonding partners but are arranged differently in 3D space.

Two types: **geometrical** and **optical** isomers.

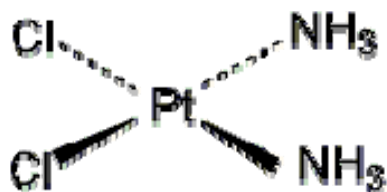
geometrical isomers have ligands at different locations relative to one another.



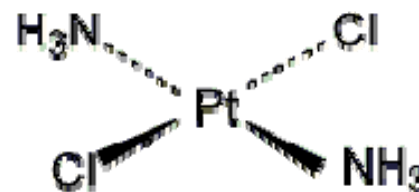
geometrical isomers can occur for octahedral and square planar but not tetrahedral complexes

Stereoisomers

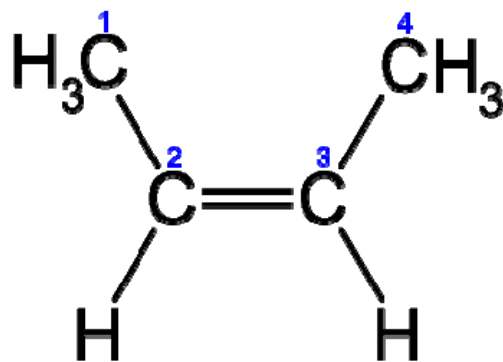
other examples:



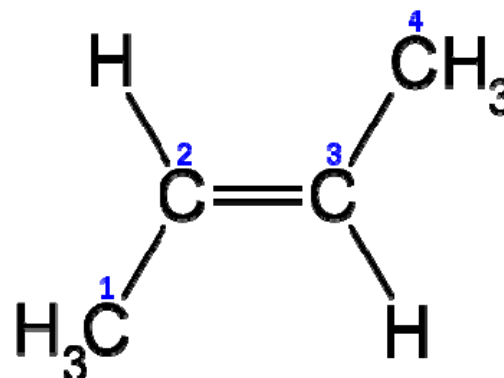
Cisplatin
Anti-cancer drug



Transplatin
Toxic



cis-2-butene

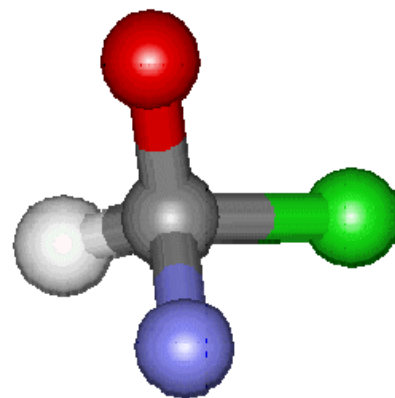
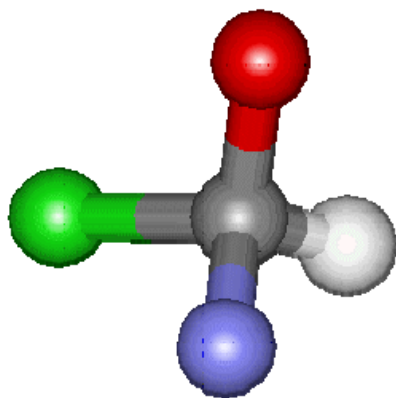


trans-2-butene

Stereoisomers

optical isomers are nonsuperimposable mirror images of each other.

a tetrahedral molecule with four different groups



no rotation allows the two molecules to be superimposed



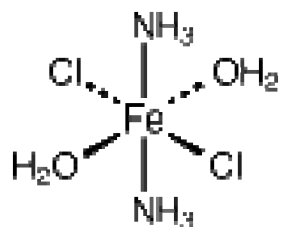
mirror

Optical isomers are said to be **chiral** (not superimposable). A chiral molecule and its mirror image form a pair of **enantiomers**. Each of the enantiomers has **handedness** (left “**L-**” or right “**D-**”).

Chirality

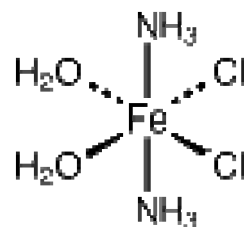
As we discussed in Chapter 4, the easiest way to determine if a molecule is chiral is to determine its point group:

- if a molecule has only proper rotations it must be chiral



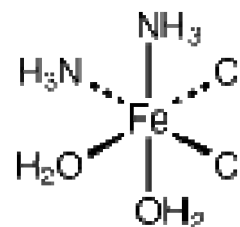
trans,trans-[Fe(NH₃)₂(H₂O)₂Cl₂]

*D*_{2h}
not chiral



trans,cis-[Fe(NH₃)₂(H₂O)₂Cl₂]

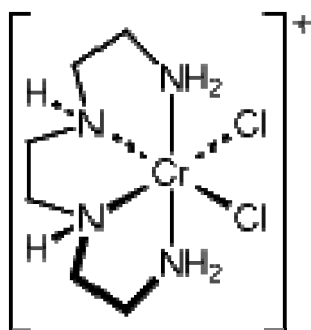
*C*_{2v}
not chiral



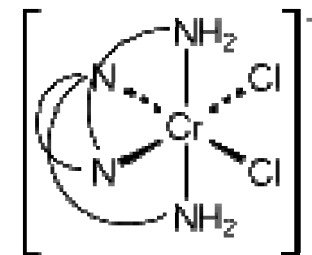
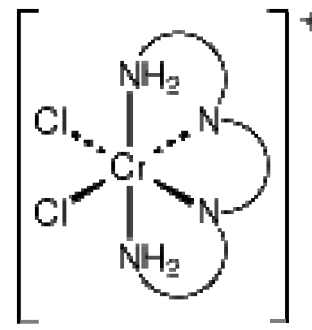
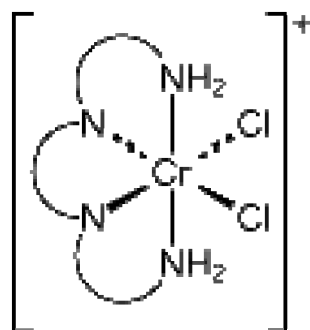
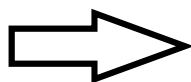
cis,cis-[Fe(NH₃)₂(H₂O)₂Cl₂]

*C*₁
chiral

- application of this rule to compounds with chelating ligands reveals the importance of rings in the chirality of coordination complexes

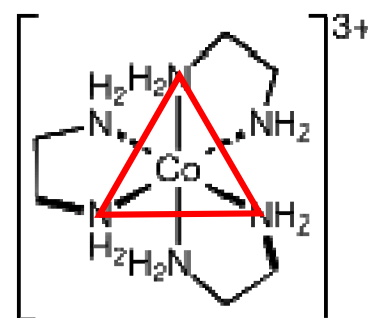
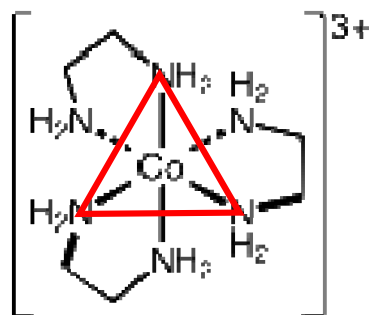


*C*₂
chiral

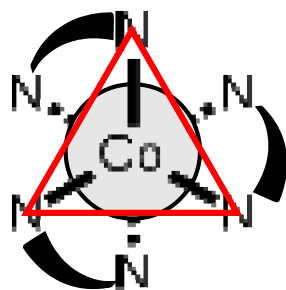


Chelate Ring Conformations

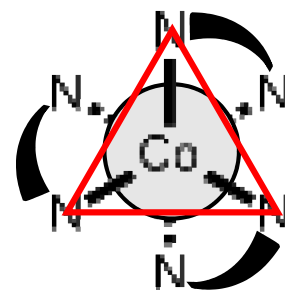
Chelating ligands also impart chirality because of the direction of the chelate ring.



left-handed screw
(twists counterclockwise
moving away)



Λ isomer



Δ isomer

right-handed screw
(twists clockwise
moving away)

Ligand Ring Conformations

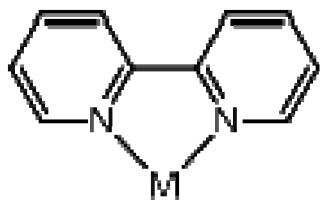
For non-planar chelating ligands it is also possible to have different conformations of the chelate ring.



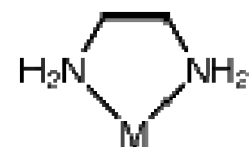
planar



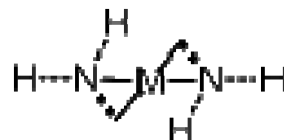
non-planar



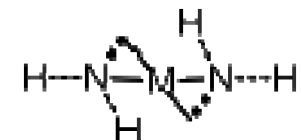
rotate to put the
C-C bond behind the
metal



not chiral



λ isomer



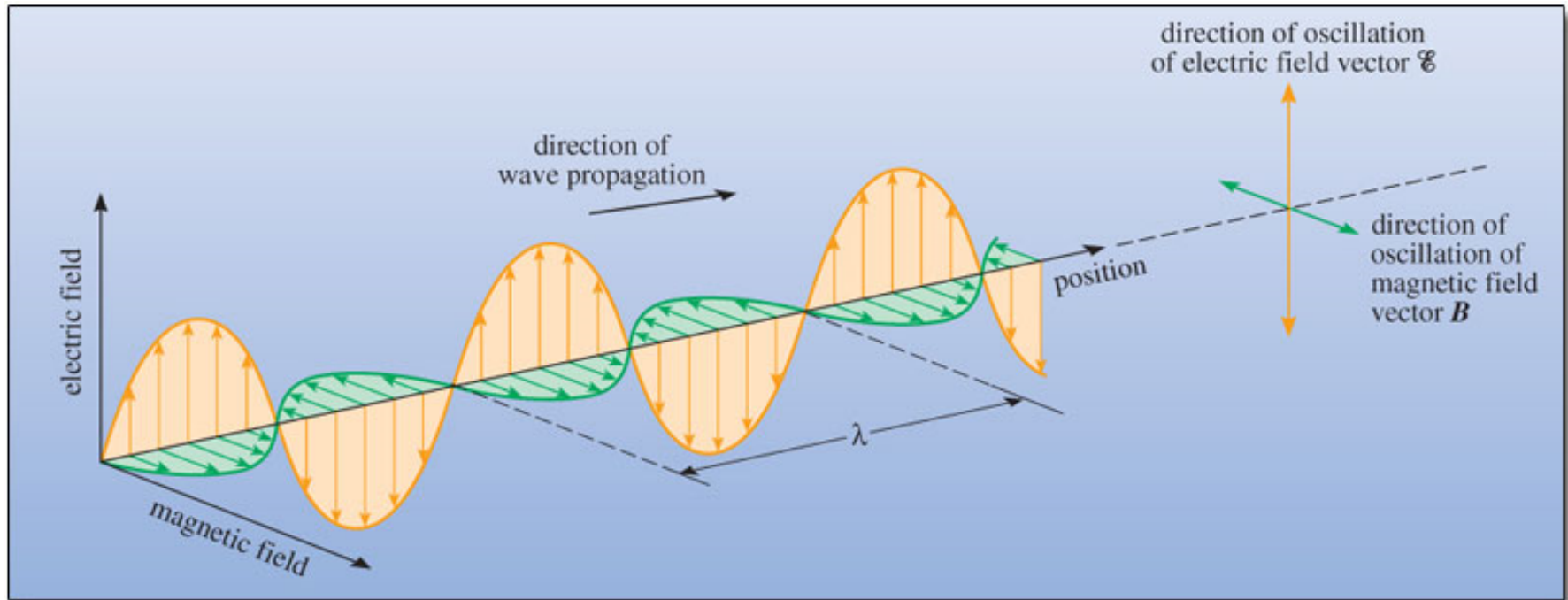
δ isomer

keep in mind the barrier to a ring flip is usually $1-2 \text{ kcal mol}^{-1}$, so the two isomers will interconvert in solution

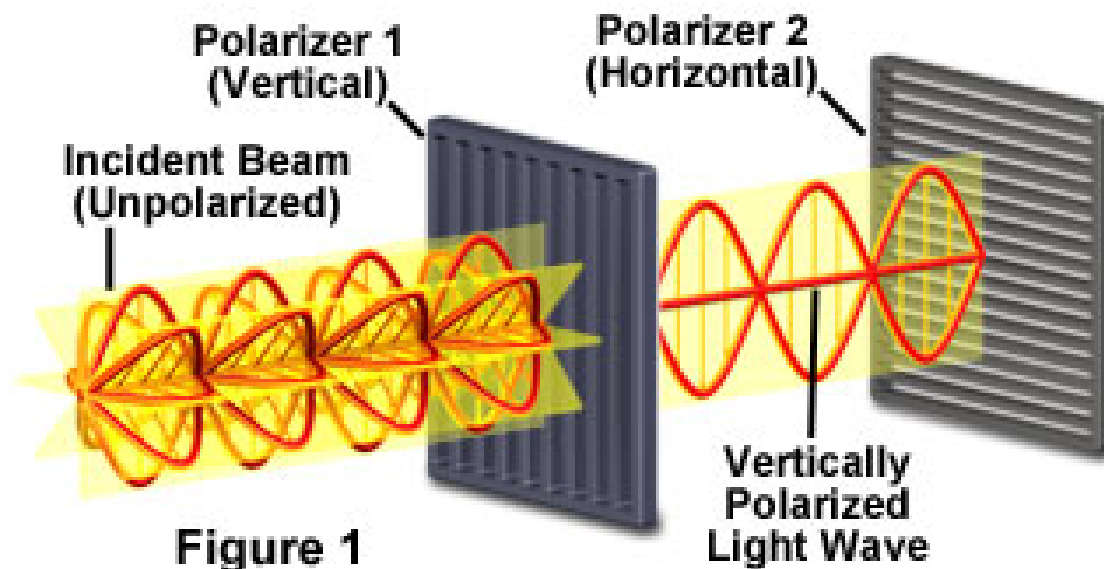
Chirality

- Optical isomerism cannot occur in square planar complexes.
- Enantiomeric pairs have identical physical and chemical properties in nearly every respect.
- Enantiomers *will* interact differently with other chiral objects, such as chiral molecules (e.g., proteins) and circularly-polarized light.
- Enantiomers rotate plane-polarized light in opposite directions.

Plane-Polarized Light



Polarization of Light Waves

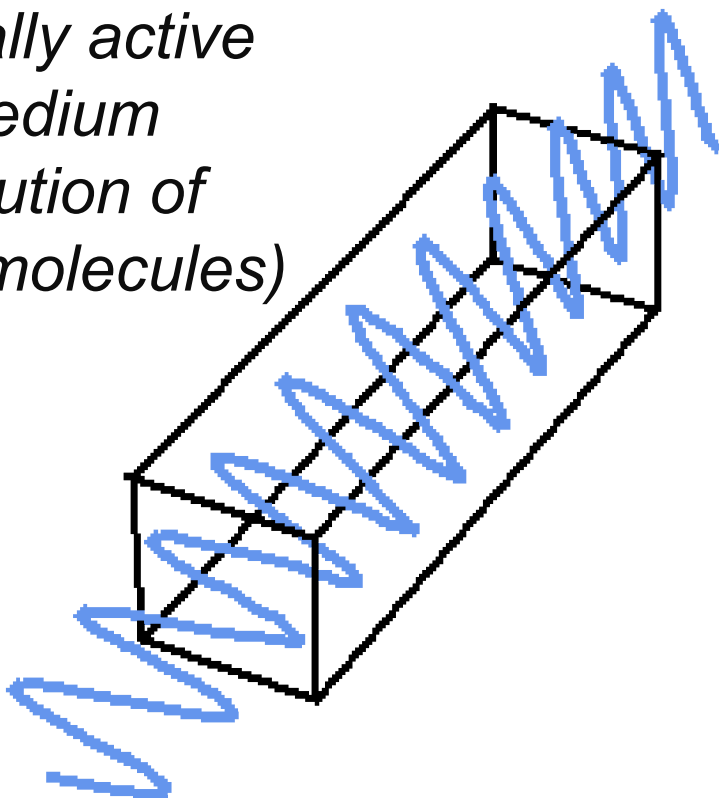


Optical Activity

The ability to rotate the plane of polarization of light, a characteristic property of chiral molecules.

light rotated counterclockwise

*optically active
medium
(solution of
chiral molecules)*

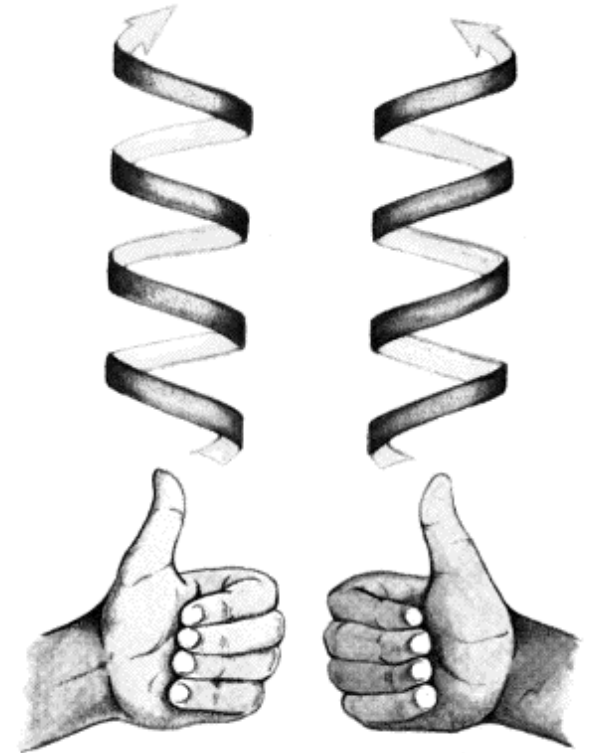
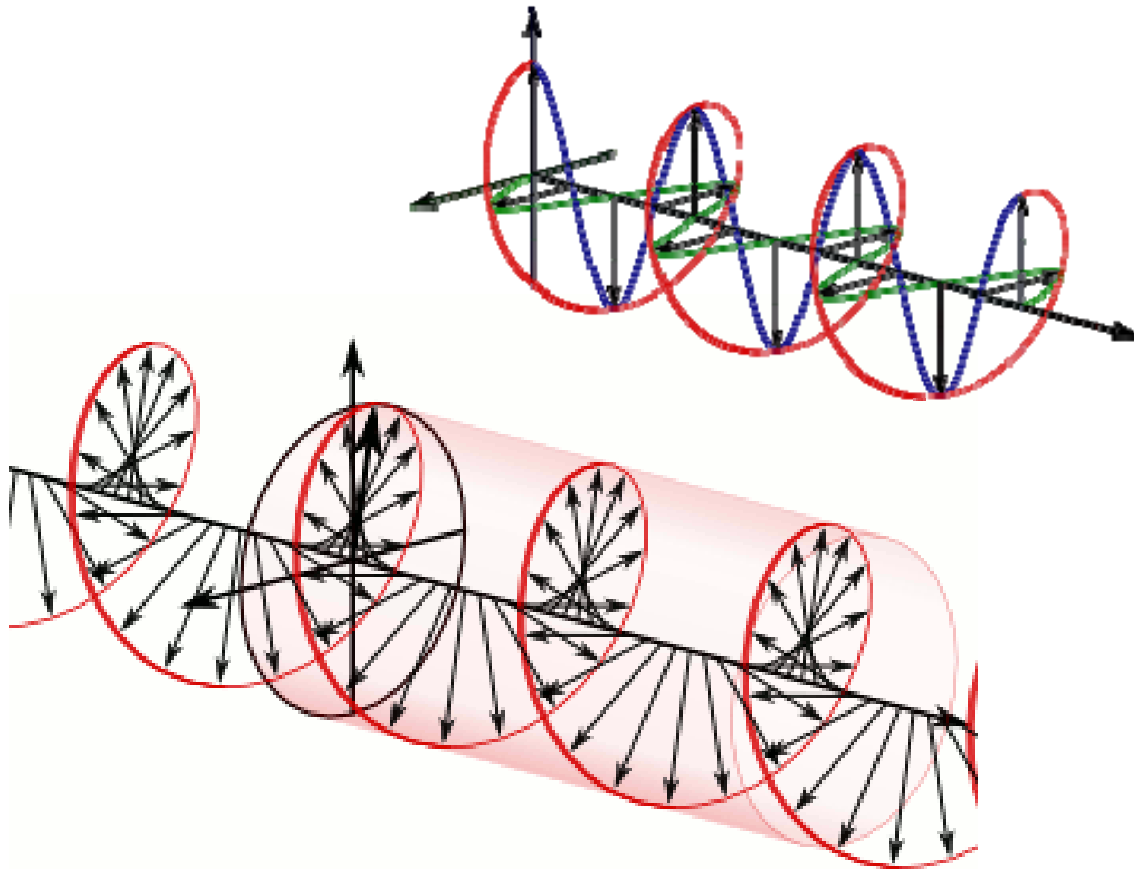


*plane polarized light
(light passed through a polarizer)*

- Identically prepared solutions of the two enantiomers of a chiral molecule rotate the polarization plane through equal angles in opposite directions.
- A mixture of equal amounts of the two enantiomers (a **racemic mixture**) or an achiral substance do not exhibit this effect.
- Used to study reactions, in optics, and to measure the concentration of chiral molecules, such as dextrose.

Circularly-Polarized Light

**circularly polarized light:
E-field forms a helix, which is a chiral object**



clockwise corkscrew motion = right-handed helix

Enantiomers absorb different amounts of left- and right-circularly polarized light. This is used in ***circular dichroism*** spectroscopy.

Coordination Geometries

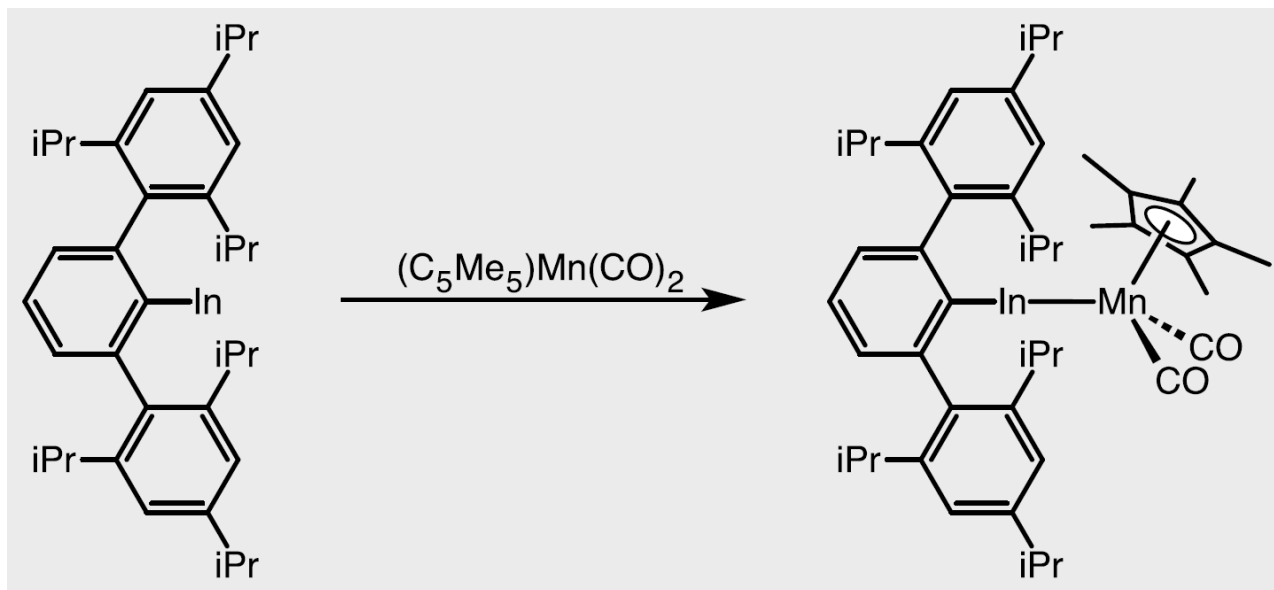
Factors affecting coordination geometries

1. more bonds = greater stability because a bonding pair of electrons is lower in energy than an unbonded electron pair
2. *d*-orbital occupancy – the coordination geometry will adjust to accommodate non-bonding electron pairs in the *d*-orbital manifold
3. sterics – larger ligands favor lower coordination numbers; smaller ligands favor higher coordination numbers
4. crystal packing effects and solvation effects

VSEPR provides an excellent estimate of coordination geometry for p-block metals but its accuracy is not as good for transition metals, lanthanides, and actinides

Coordination Number 1

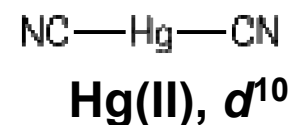
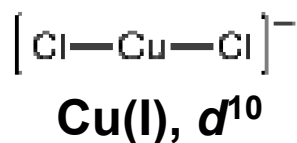
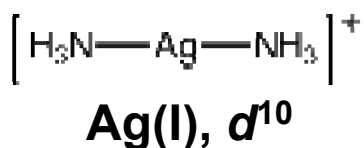
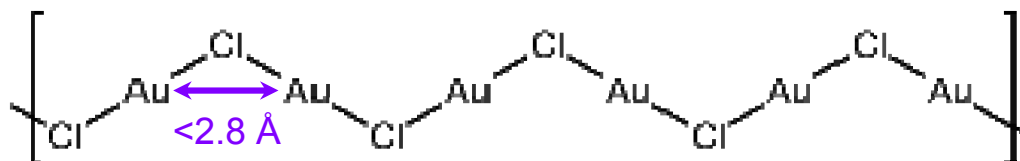
A very rare coordination number that is known in the gas phase and for a couple of *p*-block elements



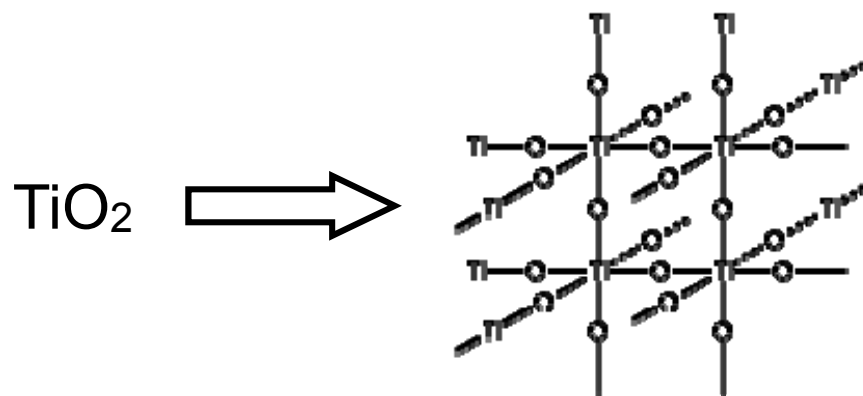
- also isolable for thallium, but both require this sterically demanding ligand
- must be prepared in the absence of coordinating solvents (NH_3 , H_2O , py, THF, Et_2O , etc)
- once prepared it will readily coordinate other ligands or even bond with other metal complexes

Coordination Number 2

Known for both sterically contrived environments and for metals with high d -electron counts (d^{10})



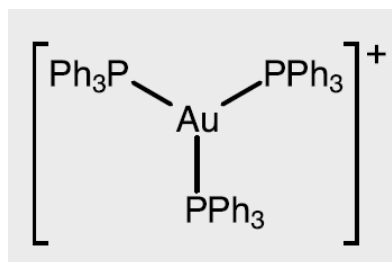
The formula does not always indicate the coordination geometry



Coordination Number 3

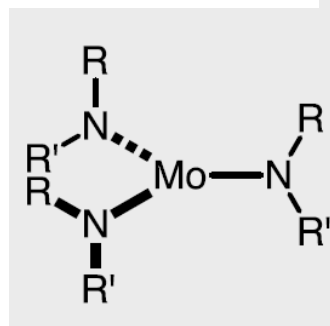
A somewhat common coordination number for d^{10} metals or complexes with bulky ligands

- main group metals (with a lone pair) often adopt trigonal pyramidal geometries for CN 3
- three-coordinate transition metal complexes are often trigonal planar

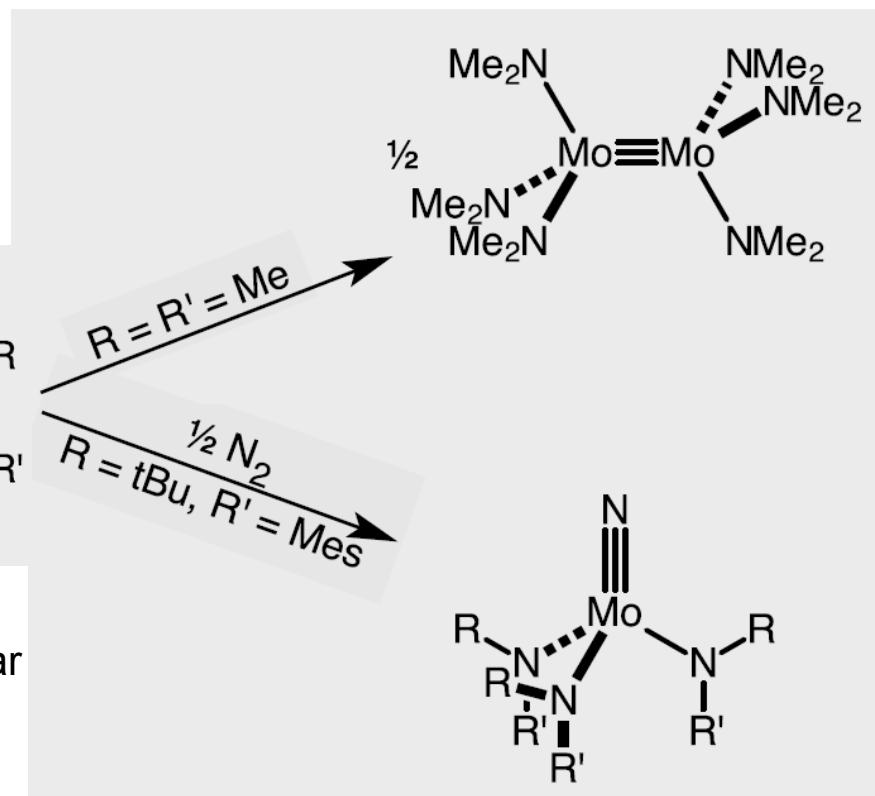


$[\text{Au}(\text{PPh}_3)_3]^+$
trigonal planar
 D_{3h}

Reactivity is a common theme for three coordinate complexes. Reactive intermediates are often three coordinate species.



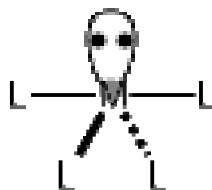
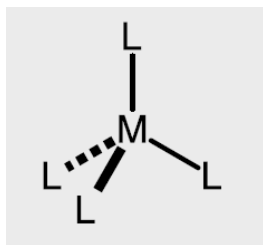
$\text{Mo}(\text{NRR}')_3$
trigonal planar
 D_{3h} or D_{3d}



Coordination Number 4

Four-coordinate complexes are common throughout the Periodic Table. There are three important four-coordinate geometries:

- **tetrahedral**
 - favored geometry based on sterics only
 - minimizes L–L interactions
 - ‘normal’ unless there is an electronic reason for another geometry
- **see-saw**
 - primarily observed in *p*-block metals (e.g., TeCl_4 and SF_4)
 - occurs when central atom has four ligands and one non-bonding electron pair
- **square planar**
 - known for *p*-block metals with four ligands and two non-bonding electron pairs
 - common for transition metals with a d^8 electron count and a low spin configuration: central metal has four non-bonding electron pairs but one pair resides in d_{z^2}

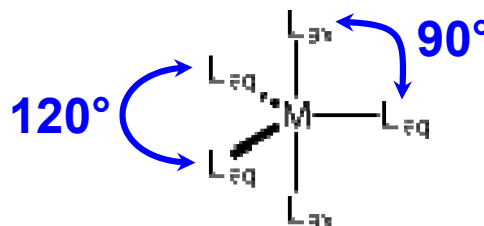


Coordination Number 5

Another common coordination number with two common geometries

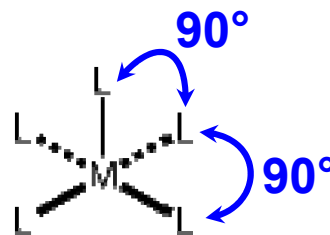
- trigonal bipyramidal

- three equivalent equatorial sites
- two equivalent axial sites

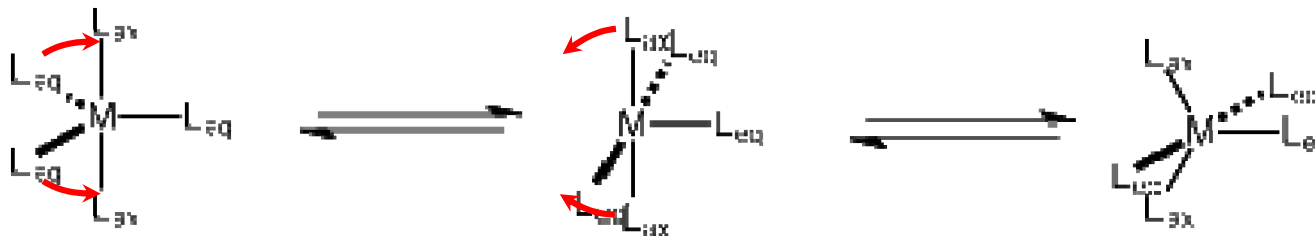


- square pyramidal

- one unique apical ligand
- four equivalent basal ligands



The energy difference between tbp and sq-pyr is usually small and the rate of interconversion is often fast in solution:



$$\Delta G^\ddagger \text{ 8-12 kcal mol}^{-1}$$

Coordination Number 6

Very common for transition metal ions.

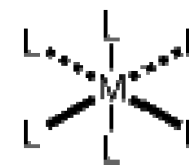
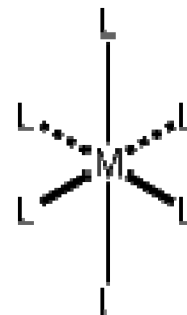
- **octahedral is the basic structure**

- all M–L distances equivalent
- all L–M–L angles are 90°



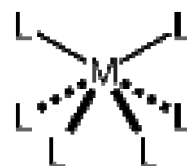
- **tetragonal distortion**

- axial positions are different than equatorial
- all L–M–L angles still 90°



- **trigonal distortion**

- change to L–M–L bond angles
- M–L bond distances may or may not be the same



Coordination Number 7

Less common than 4, 5, and 6 coordinate. Occurs with electron-poor metals and small ligands

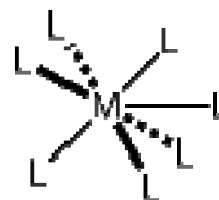
- pentagonal bipyramid
 - five equatorial ligands and two axial ligands



- capped prismatic structures



e.g., $[\text{NbF}_7]^{2-}$

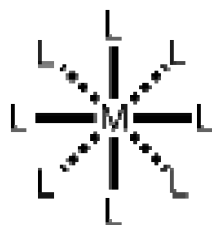


e.g., $\text{WBr}_3(\text{CO})_4$

Coordination Number 8 and Higher

Coordination numbers 8 and higher are uncommon for transition metals but often observed for lanthanides and actinides

- For CN 8 the most common geometry is the square anti-prism

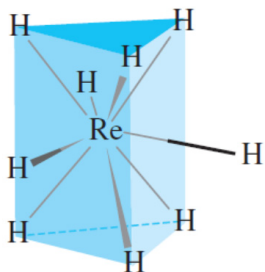


square anti-prism

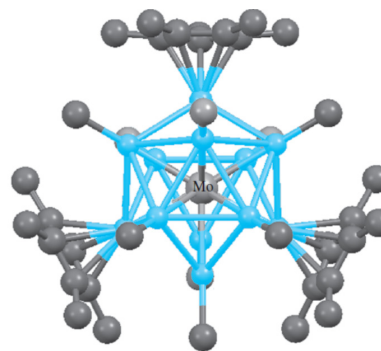


bicapped
trigonal prism

- higher CNs do not have regular geometric shapes
 - typically observed for small chelate ligands such as NO_3^- and OAc^-



e.g., $[\text{ReH}_9]^{2-}$



e.g., $[\text{Mo}(\text{ZnCH}_3)_9(\text{ZnC}_5\text{Me}_5)_3]$