

CY121

Inorganic & Physical Chemistry

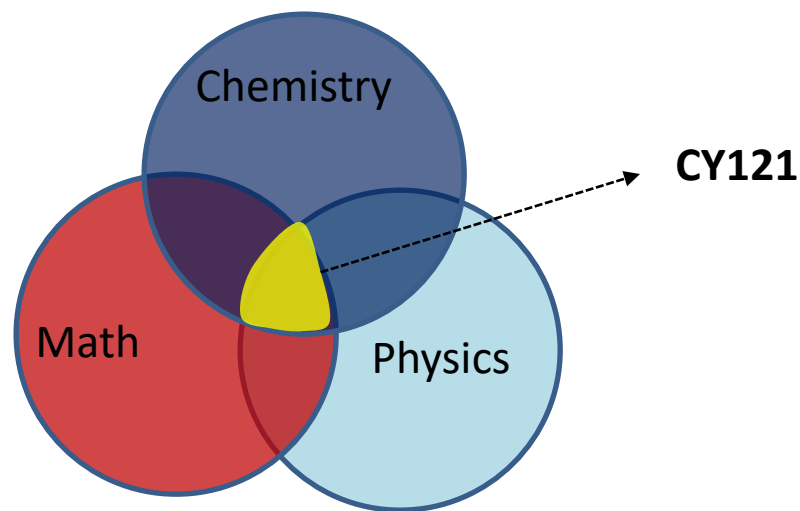
Instructor:

Dr. Debashis Panda

✉ dpanda@rgipt.ac.in

☎ 9455196041

💻 sites.google.com/site/dpanda258



Unit III:

Organometallic Chemistry

- Complexes with Metal-Carbon Sigma Bonds (M-CO)
- Metal Carbonyl Complexes, Zeiss Salt
- Metal-Alkyl Complexes,
- Metal Complexes with Pi Acceptor Ligands,
- Alkene Complexes,
- Fischer Carbene, Schrock Carbene
- Catalysis and Reaction Mechanisms of Metal Complexes.

Why should an engineer learn organometallic chemistry ?

The three major types of applications of organometallic compounds in industry are in the areas of **electronics**, **polymers**, and **organic synthesis**.

LED applications

- Volatile organometallic Me_3E (E = Ga, In, Al, and Sb) compounds are used as precursors to produce thin films of semiconductor materials via metal–organic vapor-phase epitaxy (MOVPE).

Polymer industry

- Polysiloxanes, also known as silicone, are polymers made up of repeating units of siloxane. They have widespread application in a large number of different fields ranging from cookware to construction materials (e.g. GE silicone), medicine, and toys. Pt-based catalysts are commonly applied in the silicone industry for the production of a variety of products.

Organic Synthesis:

- Homogeneous Catalysts for reactions in Pharmaceuticals, Medical, Fertilizers, Chemicals, Electronics industries.

Why should an engineer learn organometallic chemistry ?

Globally 18 Million metric tons/yr of Acetic Acid is produced.

Globally 8.5 Million metric tons/yr of Silicone is produced.

Globally 75.6 Million metric tons/yr of Polypropylene is produced.

Globally 64 Million metric tons/yr of Formaldehyde is produced.

The global pharmaceutical manufacturing market size – \$ 400 bn

- Organosilicon
- Organoboron
- Organogallium
- Organopalladium
- Organolithium
- Organoberyllium

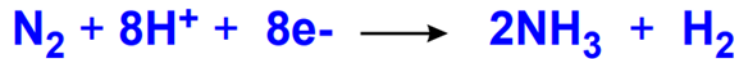
Johnson & Johnson,
Pfizer, Moderna, AstraZeneca
Roche,
AbbVie,
Novartis and
Merck & Co.
Serum Institute of India

Bio-mimicking

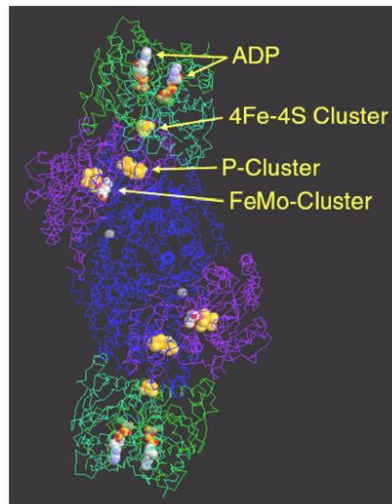
In the Haber catalytic process for converting $\text{N}_2 + 3\text{H}_2$ into NH_3 , over 400°C and 400 atm of H_2/N_2 pressure are required along with a heterogeneous Fe catalyst.

Globally 150 Million metric tons/yr of Ammonia is produced.

The **nitrogenase enzyme** catalyzes the extremely difficult reaction:



The conversion of atmospheric N_2 into NH_3 is a marvel of catalysis and provides the plant with its own fertilizer.



Nitrogenase MoFe-Protein at 1.16 Å Resolution: A Central Ligand in the FeMo-Cofactor

Oliver Einsle,^{1,2} F. Akif Tezcan,² Susana L. A. Andrade,^{1,2}
Benedikt Schmid,² Mika Yoshida,^{1,2} James B. Howard,³
Douglas C. Rees^{1,2*}

A high-resolution crystallographic analysis of the nitrogenase MoFe-protein reveals a previously unrecognized ligand coordinated to six iron atoms in the center of the catalytically essential FeMo-cofactor. The electron density for this ligand is masked in structures with resolutions lower than 1.55 angstroms, owing to Fourier series termination ripples from the surrounding iron and sulfur atoms in the cofactor. The central atom completes an approximate tetrahedral coordination for the six iron atoms, instead of the trigonal coordination proposed on the basis of lower resolution structures. The crystallographic refinement at 1.16 angstrom resolution is consistent with this newly detected component being a light element, most plausibly nitrogen. The presence of a nitrogen atom in the cofactor would have important implications for the mechanism of dinitrogen reduction by nitrogenase.

Biological nitrogen fixation provides the dominant route for the transformation of atmospheric dinitrogen into a bioavailable form, ammonia (I-4). This process is catalyzed by the enzyme nitrogenase, which consists of two component metalloproteins, the Fe-protein and the MoFe-protein. The

homodimeric Fe-protein couples adenosine 5'-triphosphate hydrolysis to interprotein electron transfer and is the only known mechanistically competent source of electrons for the catalytically active component, the MoFe-protein. The latter is organized as an $\alpha_2\beta_2$ tetramer that contains two

Science, 2002, 297, 1696-1700.

Historical Background

In 1760 Cadet of Paris military pharmacy, works on invisible inks based on cobalt salt solutions. For their preparation, he uses cobalt minerals that contain arsenic.

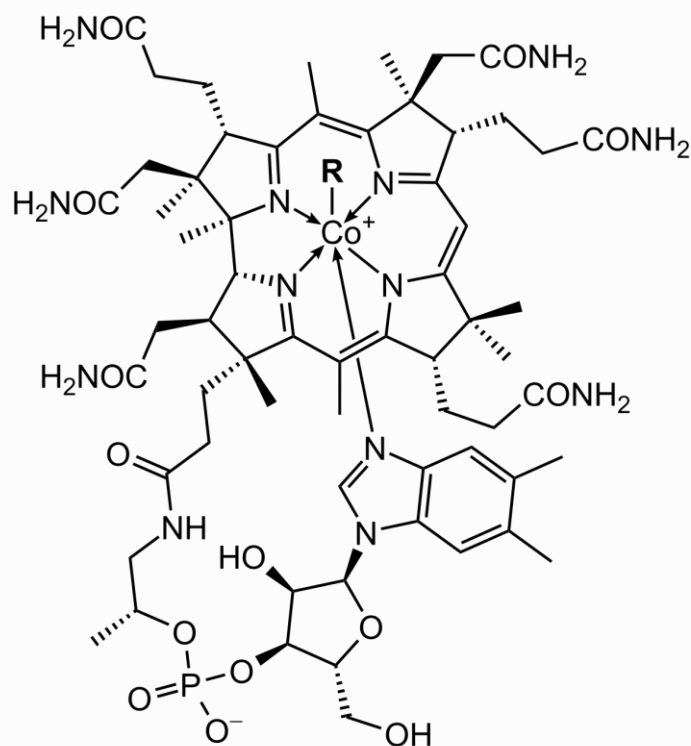


First organometallic compound

- The first olefin complex synthesized in (1827) by Zeise, who obtained yellow needle-like crystals after refluxing a mixture of PtCl_4 and PtCl_2 in ethanol, followed by addition of KCl solution. Zeise's salt ($\text{K}[\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_3] \cdot \text{H}_2\text{O}$ [Potassium trichloro(ethene)platinate(II)]) was the first compound identified as containing an organic molecule attached to a metal using the pi electrons of the organic molecule.
- Reactions between magnesium and alkyl halides, performed by Barbier in (1898) and subsequently by Grignard led to the synthesis of alkyl magnesium complexes now known as Grignard reagents, which used extensively in organic synthesis.

Physiological role

The oldest organometallic compound known, **vitamin B12 coenzyme**. This naturally occurring cobalt complex contains a cobalt–carbon sigma bond



R = 5'-deoxyadenosyl, CH₃, OH, CN



Organometallic Chemistry

- ❖ Organometallic chemistry is the study of compounds containing, and reactions involving, metal-carbon bonds.
- ❖ Main group elements, transition metals as well as lanthanides and actinides form bonds to carbon.
- ❖ They are used widely as reagent or catalysts in organic synthesis.
- ❖ They are getting emphasis due to potential applications in homogeneous catalysts, as reagents in organic synthesis and as markers in molecular biology.

Organometallic Chemistry

- ❖ Organometallic compounds are chemical compounds which contain at least one bond between a metallic element and a carbon atom belonging to an organic molecule.
- ❖ Even metalloid elements such as silicon, tin, and boron are known to form organometallic compounds which are used in some industrial chemical reactions.

Organometallic compounds can be defined as compounds that contain at least one chemical bond between a carbon atom of an organic moiety and a metal. The metal can be alkaline, alkaline earth, transition metal, lanthanide, or a metalloid such as boron, silicon, and phosphorus. Therefore, metal–phosphine complexes are also often included in this category, although they do not contain a typical metal–carbon bond – they are more commonly referred to as “metal–organic compounds.”

Classification of Organometallic Compounds

On this basis of nature of metal- carbon bond organometallic compounds are classified in to

❑ Ionic bonded organometallic compounds:

The organometallic compounds of alkali, alkaline earth metals, Lanthanides and Actinides are predominantly form ionic compounds. These are generally colourless compounds extremely reactive, non-volatile solids and insoluble in organic solvents.

Examples: $\text{Ph}_3\text{C}^-\text{Na}^+$, Cp_2Ca , Cs^+Me^- , Na^+Cp^-

❑ Covalent bonded organometallic compounds:

1) σ - bonded organometallic compounds:

These are the compounds in which carbon atom of the organic ligand is bonded to the metal by a 2 electron, 2 centred ($2e-2c$) covalent bond.

Generally formed by most of the elements with values of electronegativity are higher than 1.

Examples: $\text{Ni}(\text{CO})_4$, $\text{Fe}(\text{CO})_5$

Classification of ligands based on hapticity

❑ Covalent bonded organometallic compounds:

2) π - bonded organometallic compounds:

These are alkene, alkyne or some other carbon group has a system of electron in π - orbitals overlap of these π - orbitals with vacant orbitals of the metal atom gives rise to arrangement in which the metal atom is bonded to several carbon atom instead of to one.

Examples: $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Fe}]$, $\text{K}[\text{PtCl}_3(\eta^2\text{-C}_2\text{H}_2)]$ (Zeise's salt)

❑ Multicentre bonded organometallic compounds:

The compounds in which a loosely bonded electron deficient species exist with the coordination of metal like Li, Be, Al...etc

Examples: MeLi or $(\text{CH}_3)_4\text{Li}_4$, Al_2Me_6

Classification of ligands based on hapticity

In hapto classification organic ligands are classified according to “number of carbon atoms within a bonding distance of metal atom or the no. of carbon atoms through which an organic ligand is attached to central metal atom” is known as “hapticity” of the ligand.

This is represented by the symbol “ η^n ” appearing before the symbol of the ligand. Where, n- hapticity of the ligand.

Monohepto ligands (η^1): Organic ligands attached to the metal through one carbon.Ex: $-\text{CH}_3$, $-\text{C}_2\text{H}_5$

Dihepto ligands (η^2) : Example: $\text{CH}_2=\text{CH}_2$, $\text{K}[\text{PtCl}_3(\eta^2\text{-C}_2\text{H}_2)]$ (Zeise's salt)

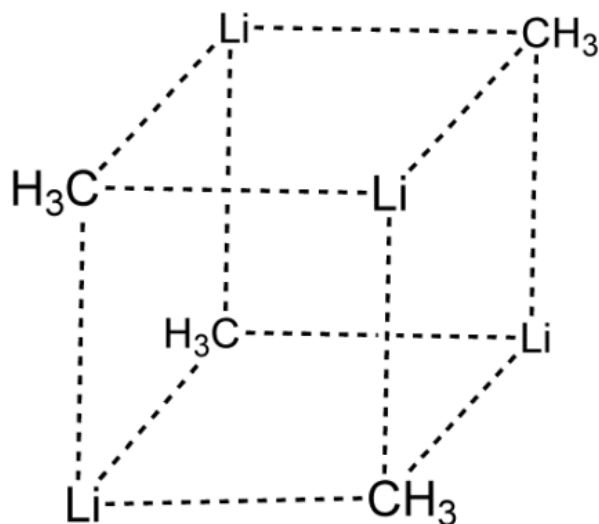
Trihepto ligands (η^3): Example:Allylic radical $\text{CH}_2=\text{CH}-\text{CH}_2\cdot$

Tetrahepto ligands (η^4): Example: Butadiene $\text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2$

Pentahepto ligands (η^5): Example: Metallocene $\text{M}(\eta^5\text{-C}_5\text{H}_5)_2$

Hexahepto ligands (η^6): Example: Dibenzene Chromium $\text{Cr}(\eta^6\text{-C}_6\text{H}_6)_2$

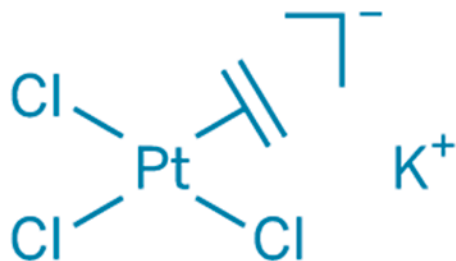
Structure of Methyl Lithium



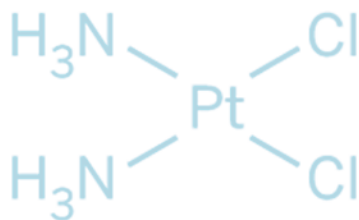
- A characteristic feature of methyl lithium is ability to form oligomeric units in solution as well as in the solid state. The structure of solid methyl lithium is described as cubic body-centered packing of $(\text{LiCH}_3)_4$ units, it consisting of Li_4 -tetrahedra with methyl groups capping the triangular faces.
- The symmetric combination of three Li 2s orbitals on each face of the Li_4 tetrahedron and one sp^3 hybrid orbital from CH_3 gives an orbital that can accommodate a pair of electron to form a 4c-2e bond.
- *The building blocks of the lattice are distorted cubes, with alternate occupation of the corners by carbon and lithium atoms. This is **hetero-cubane** type of arrangement for the $(\text{AB})_4$ types of species. A very closer study of the Li-C distances reveals that the methyl groups of one $(\text{LiCH}_3)_4$ units interact with the Li atoms of a neighboring Li_4 -tetrahedron. These intermolecular forces are responsible for the low volatility and the insolubility of LiCH_3 in non-solvating media.*

Structure of Zeise's salt

$\text{K}[\text{PtCl}_3(\eta^2\text{-CH}_2=\text{CH}_2)]:$ Potassiumtrichloro(ethene)platinate(II)



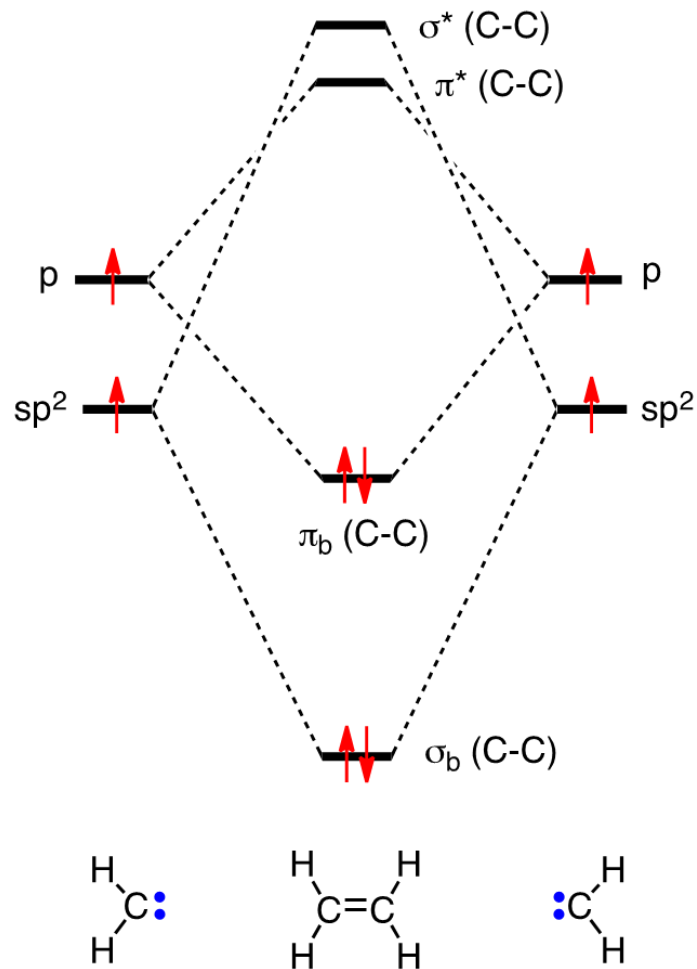
Zeise's salt



**Peyrone's salt
(cisplatin)**

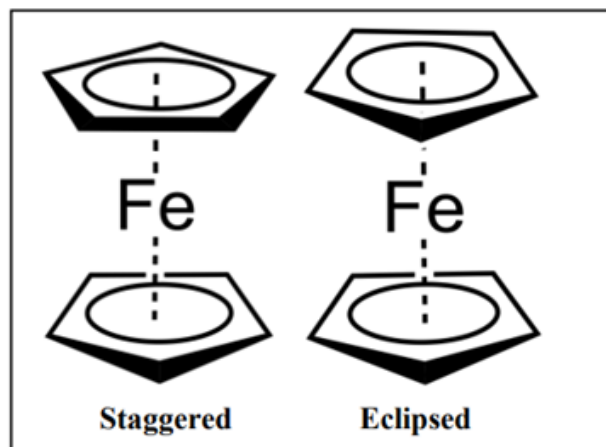
- Zeise's salt was the first organometallic compound to be isolated in pure form (1825 by William Zeise). It is a square planar complex **with 16 electrons**.
- The π -acid ligand donates electron density into a metal d-orbital. The metal donates electrons back from a filled d-orbital into the empty π^* antibonding orbital of the ligand (hence the description π -acid ligand). Both of these effects tend to reduce the C-C bond order, leading to an elongated C-C distance.
- The C-C distance, 1.375 Å, is slightly longer than the value found in free ethylene (1.337 Å), indicating some $d\pi\text{-}p\pi^*$ back-bonding from the platinum atom to C_2H_4 .
- Back-bonding is also indicated by a bending of the four hydrogen atoms away from the Pt atom.
- The Pt-Cl bond trans to the ethylene group is significantly longer than the cis- Pt-Cl bonds.

MO of Ethylene



Structure of ferrocene

$[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)_2]$: bis(η^5 -cyclopentadienyl) iron(II)



- Ferrocene is known as a “sandwich” compound.
- It occurs as highly stable orange crystals with a melting point of 174° C.
- Terms of bonding, the iron center in ferrocene is usually assigned to the +2 oxidation state.
- Each **cyclopentadienyl** (Cp) ring is then allocated a single negative charge, bringing the number of π -electrons on each ring to six, and thus making them aromatic.
- In solid state at low temperature, the rings are staggered. The rotational barrier is very small, with free rotation of the rings.
- **Extremely low temperature that is Below 110 K, the Cp rings are ordered and eclipsed.**

General Trends for the Transition Metals

Group 8 Metals								
d^3	d^4	d^5	d^6	d^7	d^8	d^9	d^{10}	$d^{10}s^1$
21 Sc Scandium	22 Ti Titanium	23 V Vanadium	24 Cr Chromium	25 Mn Manganese	26 Fe Iron	27 Co Cobalt	28 Ni Nickel	29 Cu Copper
39 Y Yttrium	40 Zr Zirconium	41 Nb Niobium	42 Mo Molybdenum	43 Tc Technetium	44 Ru Ruthenium	45 Rh Rhodium	46 Pd Palladium	47 Ag Silver
57 La Lanthanum	72 Hf Hafnium	73 Ta Tantalum	74 W Tungsten	75 Re Rhenium	76 Os Osmium	77 Ir Iridium	78 Pt Platinum	79 Au Gold

Early Transition Metals

low electronegativities

higher oxidation states

“harder” metal centers

OXOPHILIC!!

Late Transition Metals

higher electronegativities

lower oxidation states

“softer” metal centers

Effective Atomic Number (EAN) : 18 Electron "Rule"

Organic compounds, of course, follow the **8 electron rule**: there can only be a maximum of **8 valence electrons** around a **carbon center**.

“When the central metal ion or atom of a complex compound acquires noble gas electronic configuration $(n-1)d^{10} ns^2 np^6$ there will be 18 electrons in the valence orbitals (or valence shell) and the electronic configuration will be closed and stable.” It is known as the **18-electron rule**.

Complexes with $18e^-$ counts are referred to as **saturated**, because there are no empty low-lying orbitals to which another incoming ligand can coordinate.

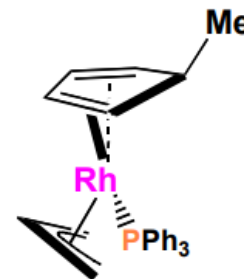
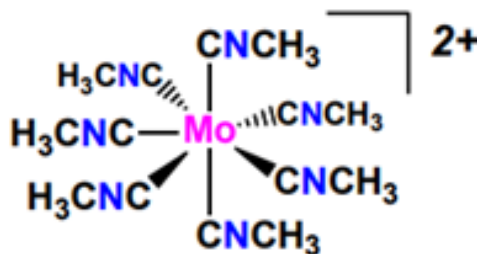
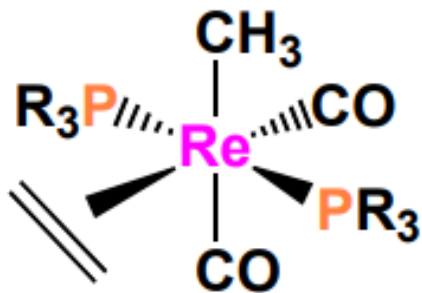
Complexes with counts lower than $18e^-$ are called **unsaturated** and can electronically bind additional ligands.

Examples of 18 Electron "Rule"

To determine the electron count for a metal complex:

1) Determine the oxidation state of the transition metal center(s) and the metal centers resulting d-electron count. To do this one must:

- a) note any overall charge on the metal complex
 - b) know the charges of the ligands bound to the metal center (ionic ligand method)
 - c) know the number of electrons being donated to the metal center from each ligand (ionic ligand method)
- 2) Add up the electron counts for the metal center and ligands



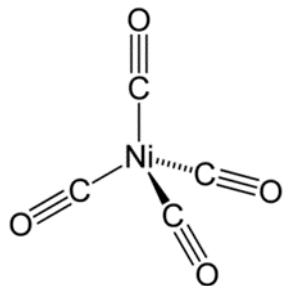
Exceptions to 18 Electron "Rule"

Group 8 Metals								
d^3	d^4	d^5	d^6	d^7	d^8	d^9	d^{10}	$d^{10}s^1$
21 Sc Scandium	22 Ti Titanium	23 V Vanadium	24 Cr Chromium	25 Mn Manganese	26 Fe Iron	27 Co Cobalt	28 Ni Nickel	29 Cu Copper
39 Y Yttrium	40 Zr Zirconium	41 Nb Niobium	42 Mo Molybdenum	43 Tc Technetium	44 Ru Ruthenium	45 Rh Rhodium	46 Pd Palladium	47 Ag Silver
57 La Lanthanum	72 Hf Hafnium	73 Ta Tantalum	74 W Tungsten	75 Re Rhenium	76 Os Osmium	77 Ir Iridium	78 Pt Platinum	79 Au Gold

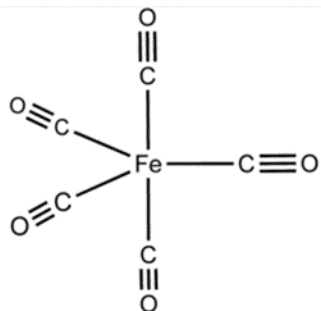
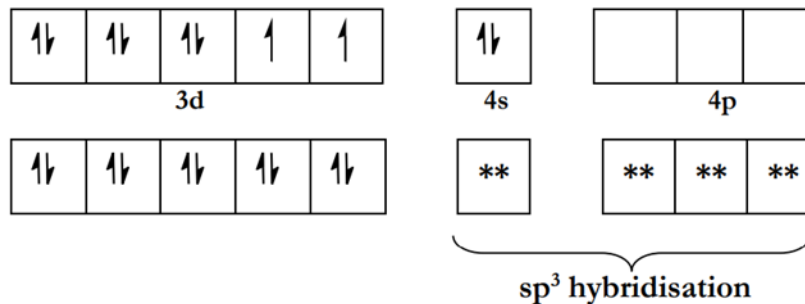
Early Transition Metals	Middle Transition Metals	Late Transition Metals
<i>16e and sub-16e configurations are common</i>	<i>18e configurations are common</i>	<i>16e and sub-16e configurations are common</i>
<i>Coordination geometries higher than 6</i>	<i>Coordination geometries of 6 are common</i>	<i>Coordination geometries of 5 or lower</i>

Compound	EAN		18 e ⁻		Stability
	count	No. Of e ⁻	Count	No. Of e ⁻	
Ti(CO)₆	Total no. of e ⁻	22	Total no. Of Valence e ⁻	04	Unstable
	6CO×2e ⁻	12	6CO×2e ⁻	12	
	Total	34	Total	16	
V(CO)₆	Total no. of e ⁻	23	Total no. Of Valence e ⁻	05	Stable (exception)
	6CO×2e ⁻	12	6CO×2e ⁻	12	
	Total	35	Total	17	
[V(CO)₆]⁻	Total no. of e ⁻	23	Total no. Of Valence e ⁻	05	Stable anion
	6CO×2e ⁻	12	6CO×2e ⁻	12	
	Charge	01	Charge	01	
	Total	36	Total	18	

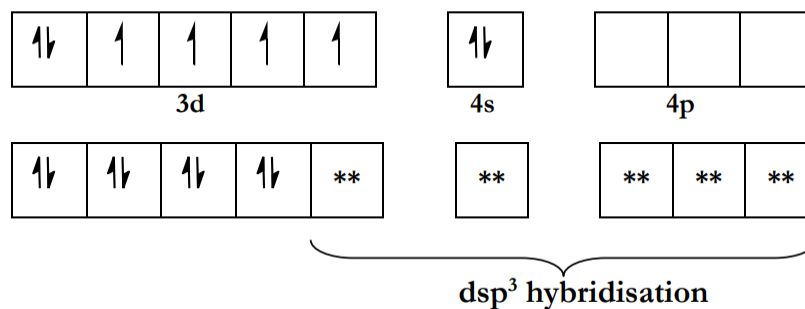
Structure and bonding of Metal Carbonyl Complexes:



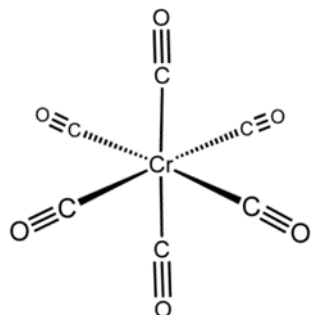
(Ni = [Ar] 3d⁸ 4s²)



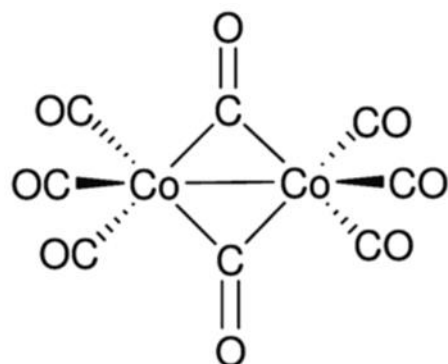
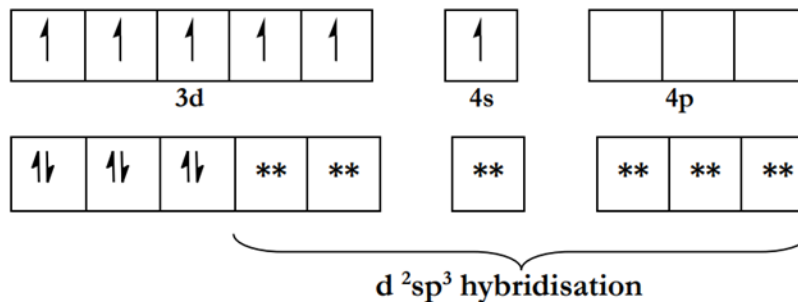
(Fe = [Ar] 3d⁶ 4s²)



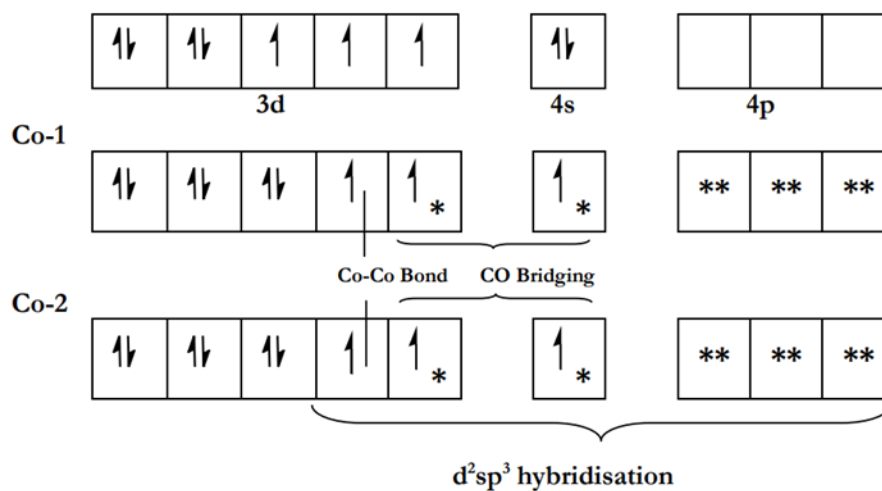
Structure and bonding of Metal Carbonyl Complexes:



(Cr = [Ar] 3d⁵ 4s¹)



(Co = [Ar] 3d⁷ 4s²)



MO of M-L bonding

Spectroscopic Symbols- ground state

Depends on the specific group

by symmetry:	Principal rotation axis (C_n)	Center of inversion (i)	plane to princ. axis (σ_v)	plane \perp to princ. axis (σ_h)
symmetric	A	g	1	'
antisymmetric	B	u	2	"

C_2 :
 $p_x \rightarrow -p_x$
 $p_y \rightarrow -p_y$
 $\Rightarrow B$

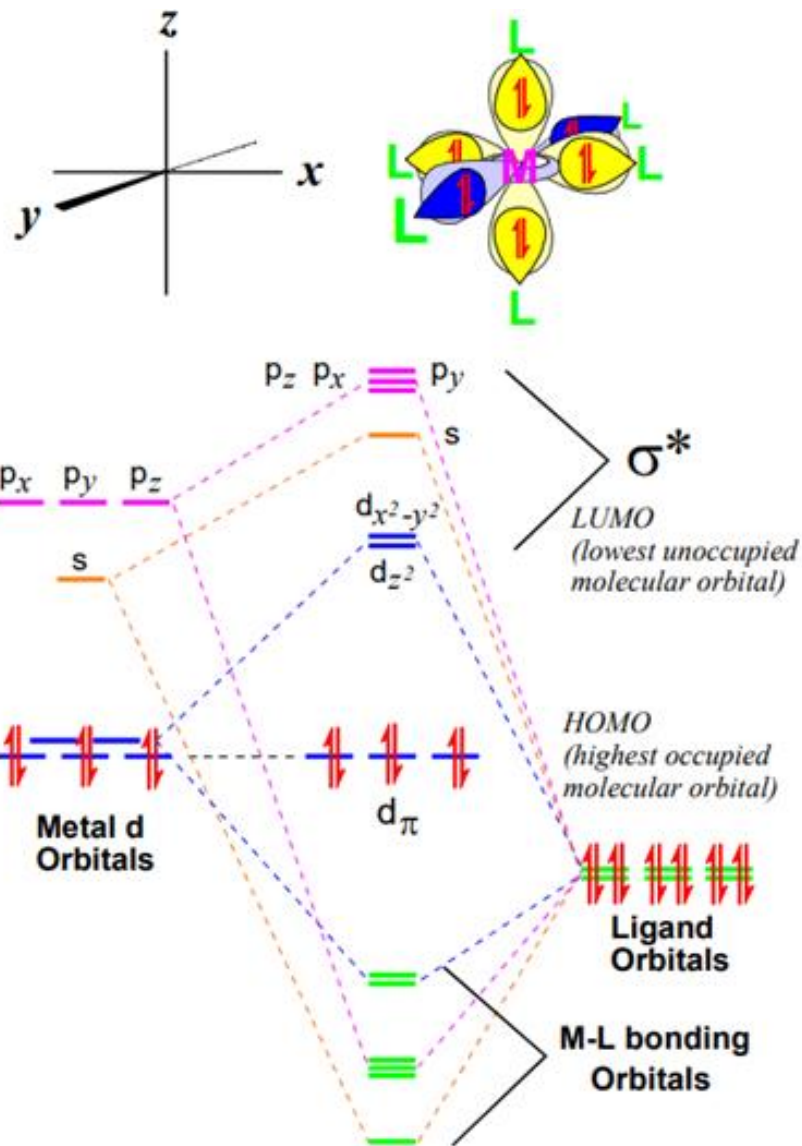
i :
 $d_{xy} \rightarrow d_{xy}$
 (similarly all d)
 $\Rightarrow g$

C_4 :
 $p_x \rightarrow p_y$
 $p_y \rightarrow -p_x$
 $\Rightarrow E$

by degeneracy:
 1: A, B
 2: E
 3: T

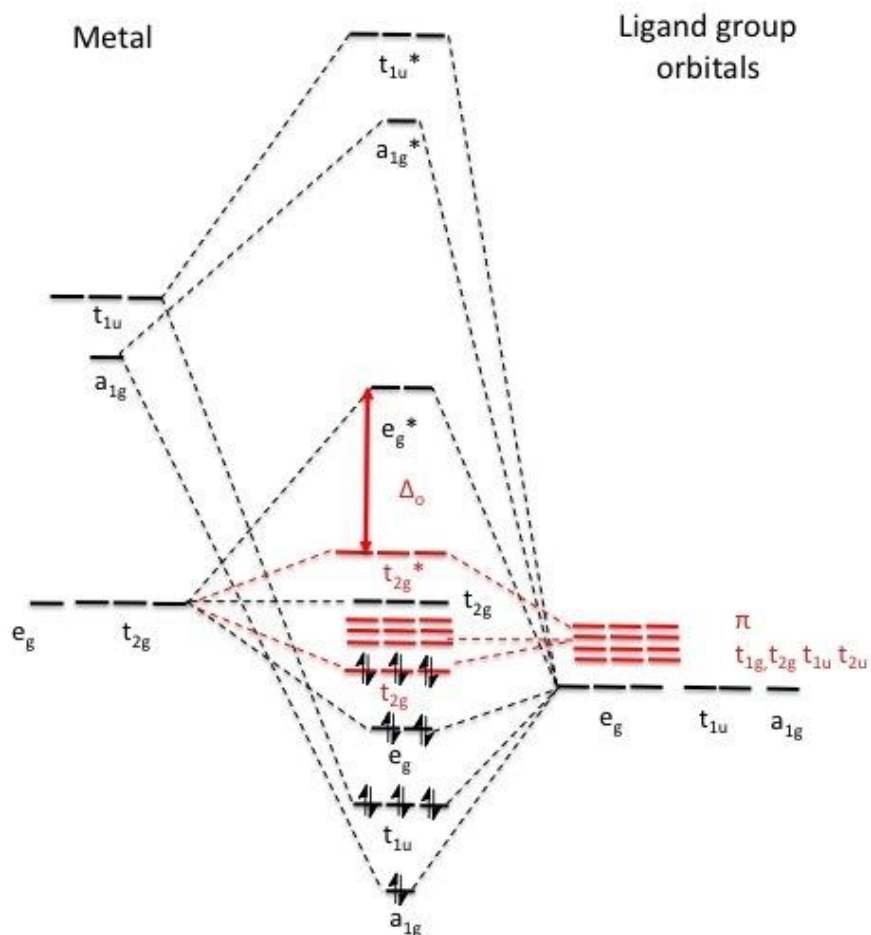


ψ_i	G	R_3	O_h	T_d	D_{4h}	C_{4v}	C_{2v}	D_{3v}
s		s_g	A_{1g}	A_1	A_{1g}	A_1	A_1	A_{1g}
p_x		p_u	T_{1u}	T_1	E_u	E	B_1	E_u
p_y							B_2	
p_z					A_{2u}	A_1	A_1	A_{2u}
d_{z^2}		d_g	E_g	E	A_{1g}	A_1	A_1	E_g
$d_{x^2-y^2}$					B_{1g}	B_1	A_1	
d_{xy}			T_{2g}	T_2	B_{2g}	B_2	A_2	A_{1g}
d_{xz}					E_g	E	B_1	
d_{yz}							B_2	

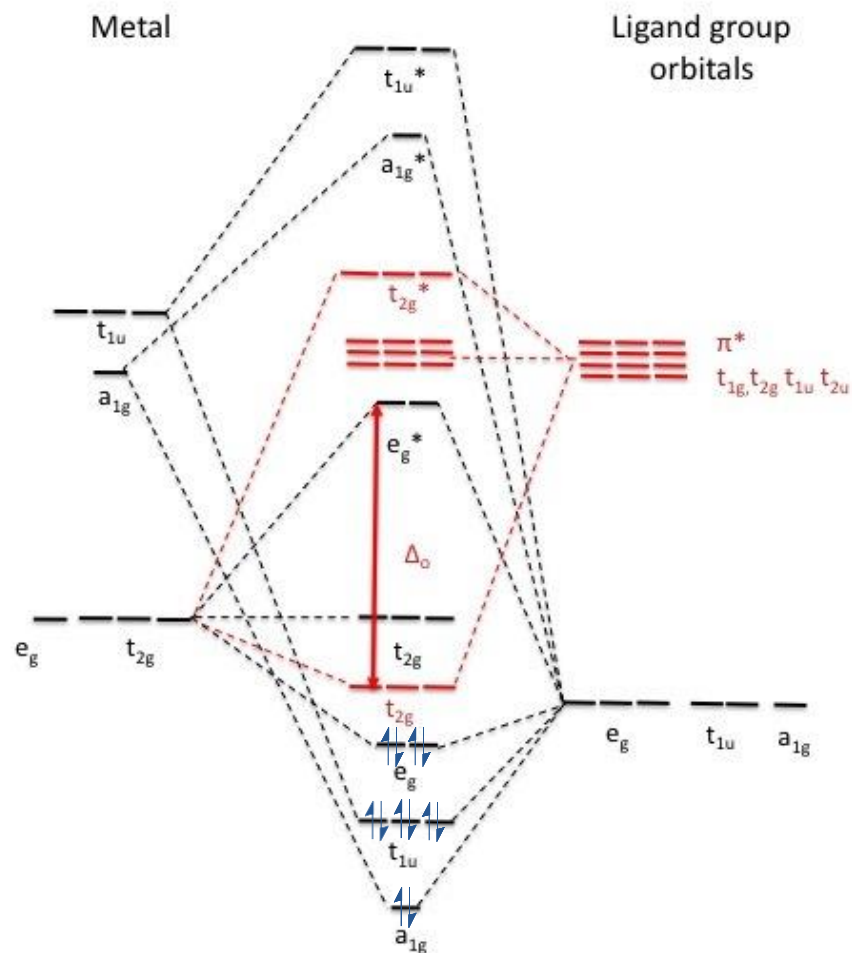


MO of M-L bonding

σ donor, π donor



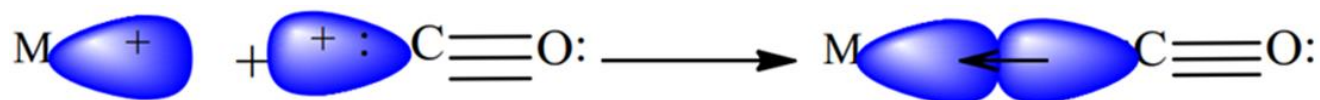
σ donor, π acceptor



Bonding in metal carbonyls

Formation of M-C σ -bond:

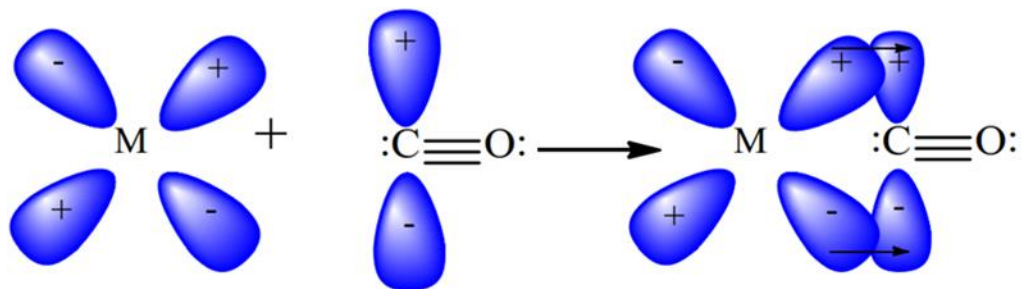
The overlapping of empty hybrid orbital (a blend of d, s and p orbitals) on metal atom with the filled hybrid orbital (HOMO) on carbon atom of carbon monoxide molecule results into the formation of a $M \leftarrow CO$ σ -bond.



Formation of π -bond by back donation:

This bond is formed because of overlapping of filled $d\pi$ orbitals or hybrid $d\pi$ orbitals of metal atom with low-lying empty (LUMO) orbitals on CO molecule.

i.e. $M \xrightarrow{\pi} CO$

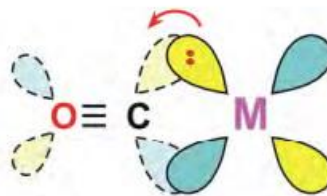


Bonding in metal carbonyls

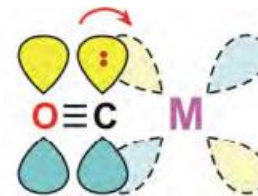
Three types (two of which are important) of CO-Metal bonding interactions:



CO-M sigma bond



M to CO pi backbonding



CO to M pi bonding
(rare)

M-C bond: increases
C-O bond: increases
 ν_{CO} freq: increases

increases
decreases
decreases

increases
decreases
decreases



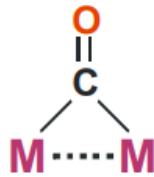
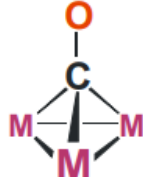
Carbonyl IR Stretching Frequencies

- The **position** of the carbonyl bands in the IR depends mainly on the **bonding mode** of the CO (terminal, bridging) and the **amount of electron density on the metal being π -backbonded to the CO**.
- The **number** (and intensity) of the carbonyl bands one observes depends on the **number of CO ligands present** and the **symmetry** of the metal complex. There are also secondary effects such as Fermi resonance and overtone interactions that can complicate carbonyl IR spectra.

Bonding in metal carbonyls

Bonding Modes:

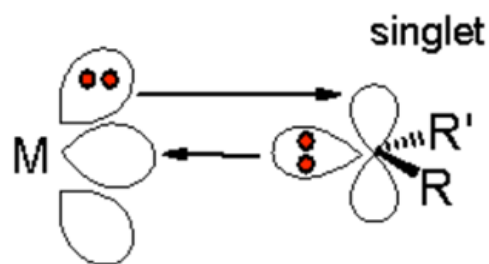
As one goes from a terminal CO-bonding mode to μ_2 -bridging and finally μ_3 -bridging, there is a relatively dramatic drop in the CO stretching frequency seen in the IR.

				
	free CO	terminal mode	μ_2 -bridging	μ_3 -bridging
ν_{CO} IR (cm^{-1})	2143	2120 - 1850	1850 - 1720	1730 - 1500

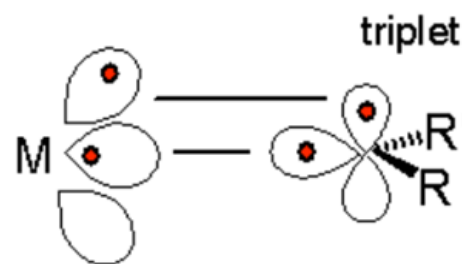
Metal-Carbene Complex

The organometallic compounds containing metal–ligand multiple bonds of the types, $M=X$ and $M\equiv X$ ($X = C, N, O$) are of current interest as they are valuable intermediates in many important catalytic cycles.

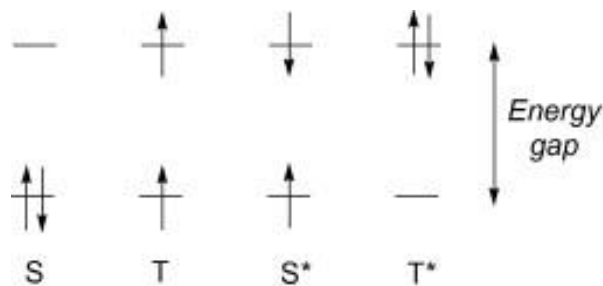
Comparison of Fischer Carbene and Schrock carbene:



Fischer



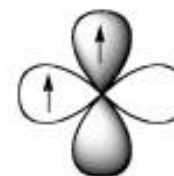
Schrock



* Excited state for the carbene



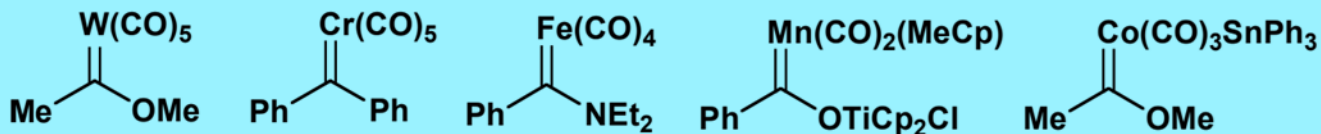
Singlet state



Triplet state

Fischer Carbene & Schrock Carbene

Representative Fischer Carbenes:



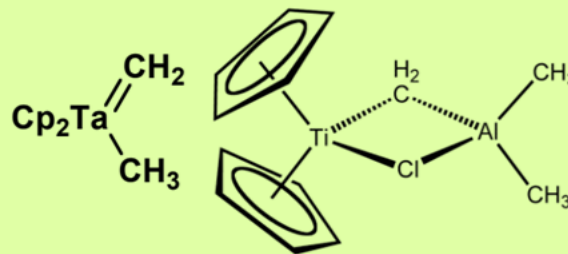
Fischer carbenes are found with :

low oxidation state metals;
middle and late transition metals Fe(0), Mo(0), Cr(0), W(0);
pi-electron acceptor metal ligands;
pi-donor substituents on methylene group such as alkoxy and amino groups.

Schrock carbenes are found with:

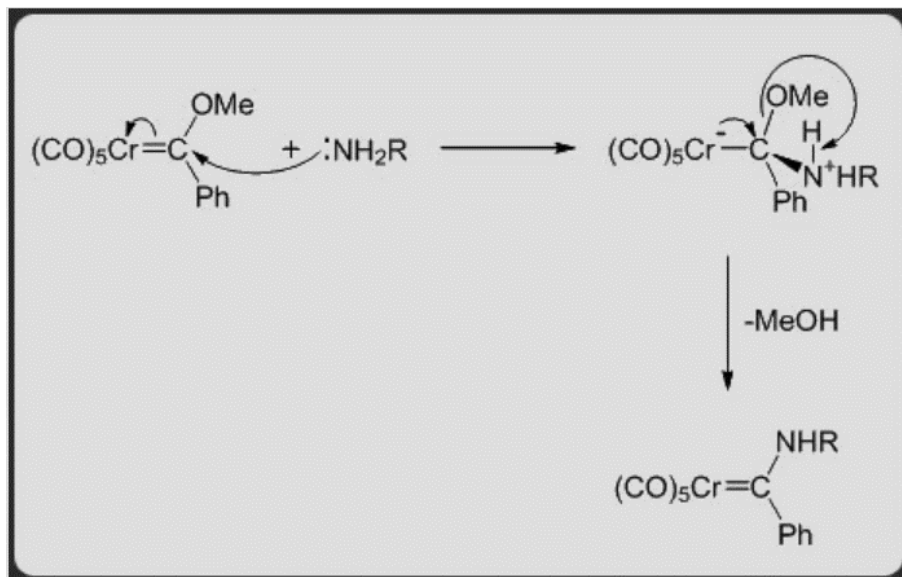
high oxidation states
early transition metals Ti(IV), Ta(V)
non pi-acceptor ligands
non pi-donor substituents

Representatives:

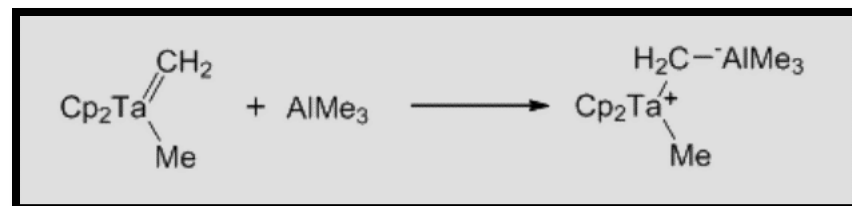


The reactivity of Fischer and Schrock carbene complexes

The Fischer type carbene complexes **undergo attack by nucleophiles** at its carbene-C center.



The Schrock type carbene complexes **undergo attack by electrophiles** at its carbene-C center.



Organometallic reactions

- Loss or gain of ligands
- Molecular rearrangement
- Formation or breaking of metal-metal bonds
- Reactions at the ligands themselves

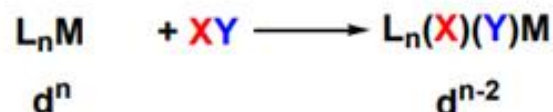
- I. Reactions involving gain or loss of ligands
 - A. Ligand dissociation and substitution
 - B. Oxidative addition
 - C. Reductive elimination
 - D. Nucleophilic displacement
- II. Reactions involving modification of ligands
 - A. Insertion
 - B. Carbonyl insertion (alkyl migration)
 - C. Hydride elimination
 - D. Abstraction

Addition or dissociation vs oxidative addition or reductive elimination

<i>Type of Reaction</i>	<i>Change in Coordination Number</i>	<i>Change in Formal Oxidation State of Metal</i>
Addition	Increase	None
Dissociation	Decrease	None
Oxidative addition	Increase	Increase
Reductive elimination	Decrease	Decrease

Oxidative Addition

When addition of ligands is accompanied by oxidation of the metal, it is called an oxidative addition reaction



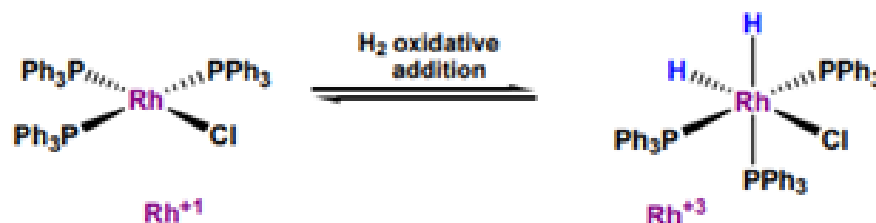
Requirements for oxidative addition

- availability of nonbonded electron density on the metal,
- two vacant coordination sites on the reacting complex (L_nM), that is, the complex must be coordinatively unsaturated,
- a metal with stable oxidation states separated by two units; the higher oxidation state must be energetically accessible and stable.

OX state of metal increases by 2 units

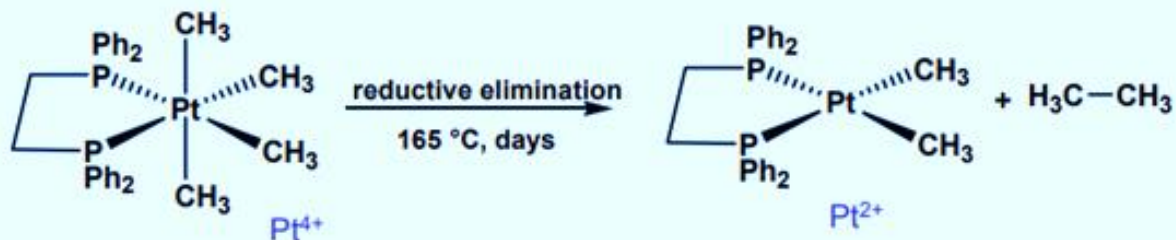
Coordination number increases by 2 units

2 new anionic ligands are added to the metal



Reductive Elimination

Almost the exact reverse of Oxidative Addition



Oxidation state of metal decreases by 2 units

Coordination number decreases by 2 units

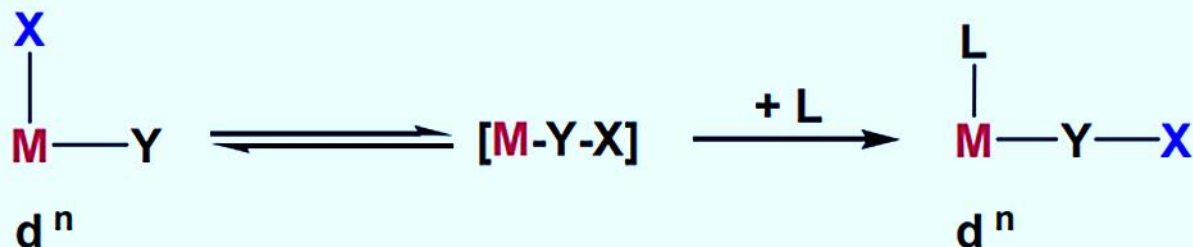
2 cis oriented anionic ligands form a stable σ bond and leave the metal

Factors which facilitate reductive elimination

- a high formal positive charge on the metal,
- the presence of bulky groups on the metal, and
- an electronically stable organic product.

Cis orientation of the groups taking part in reductive elimination is a MUST

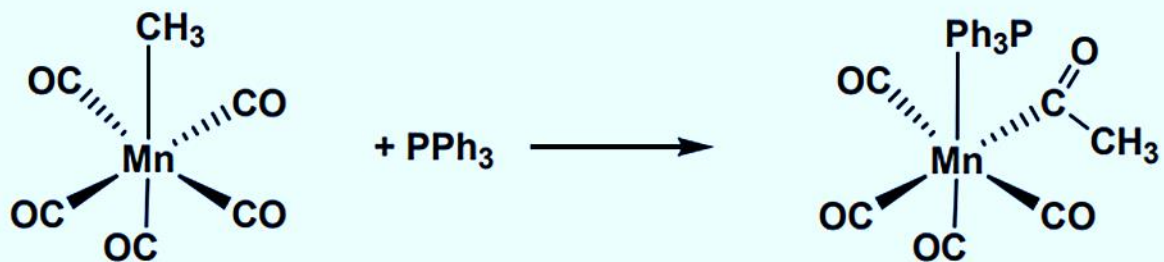
Migratory Insertion



No change in the formal oxidation state of the metal

A vacant coordination site is generated during a migratory insertion (*which gets occupied by the incoming ligand*)

The groups undergoing migratory insertion **must be cis** to one another



These reactions are enthalpy driven and although the reaction is entropy prohibited the large enthalpy term dominates

Comparing Catalyst efficiency

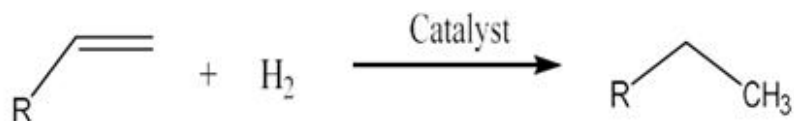
Turnover Number (TON)

TON is defined as the amount of reactant (in moles) divided by the amount of catalyst (in moles) times the percentage yield of product. A large TON indicates a stable catalyst with a long life.

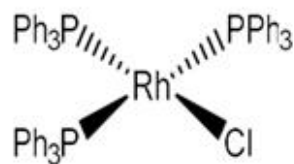
Turnover Frequency (TOF)

It is the number of passes through the catalytic cycle per unit time (often per hour). Effectively this is dividing the TON by the time taken for the reaction. The units are just time^{-1} . A higher TOF indicates better efficiency for the catalyst

Alkene Hydrogenation (Wilkinson's Catalyst)

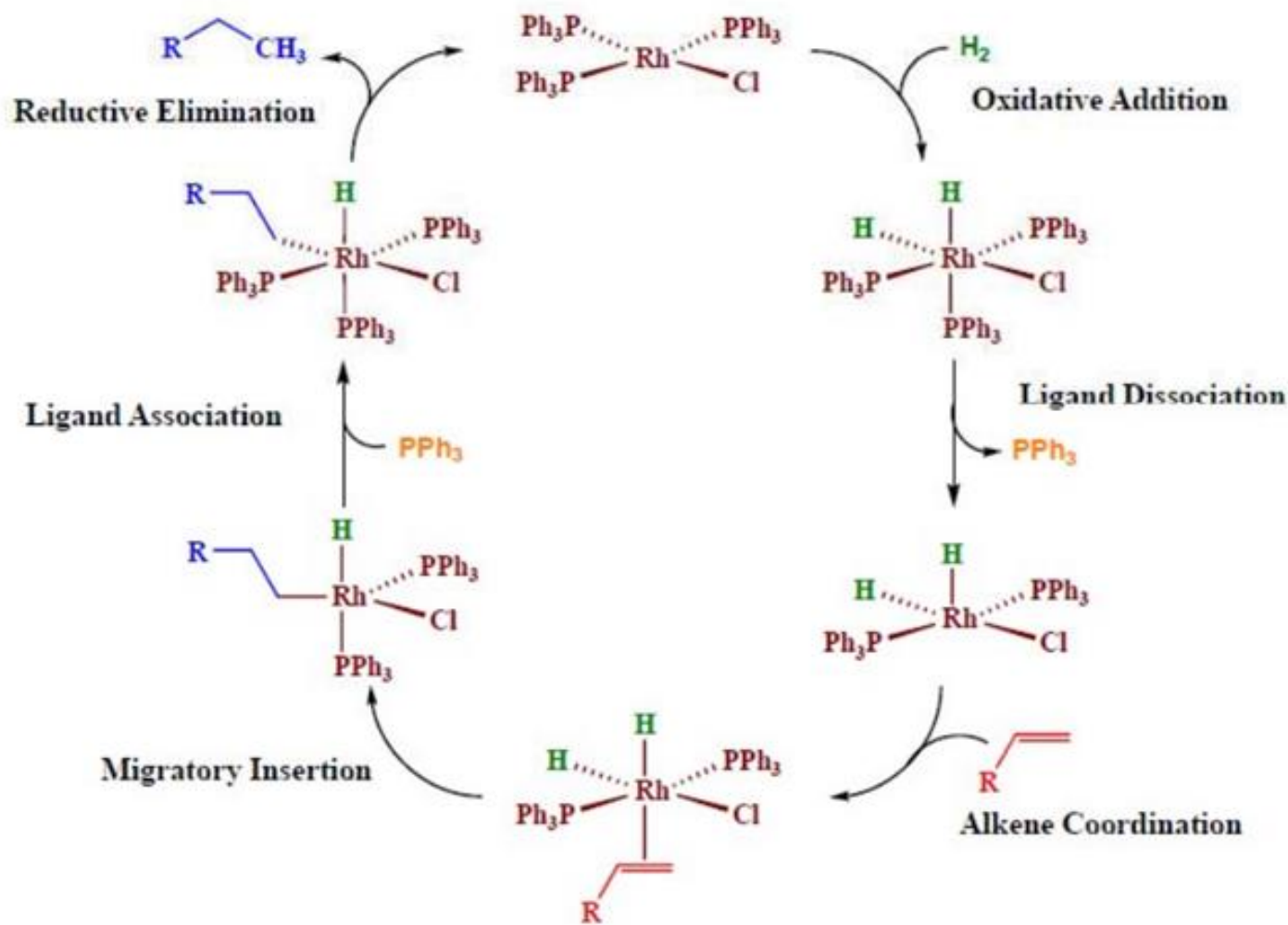


The most commonly used catalyst is the Wilkinson's Catalyst

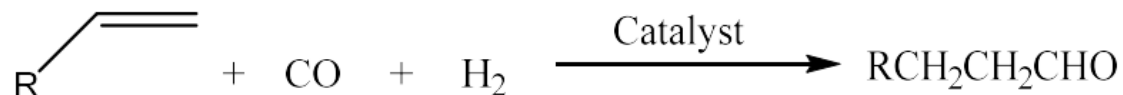


- Many alkenes are hydrogenated with hydrogen at 1 atm pressure or less.
- Wilkinson's catalyst is highly sensitive to the nature of the phosphine ligand and the alkene substrate.
- Analogous catalysts with alkyl phosphine ligands are inactive.
- Highly hindered alkenes and ethylene are not hydrogenated by the catalyst.

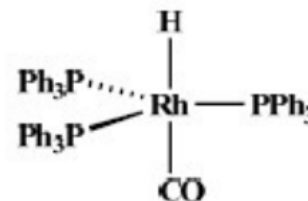
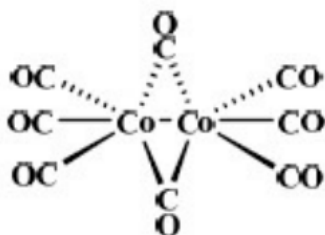
Alkene Hydrogenation (Wilkinson's Catalyst)



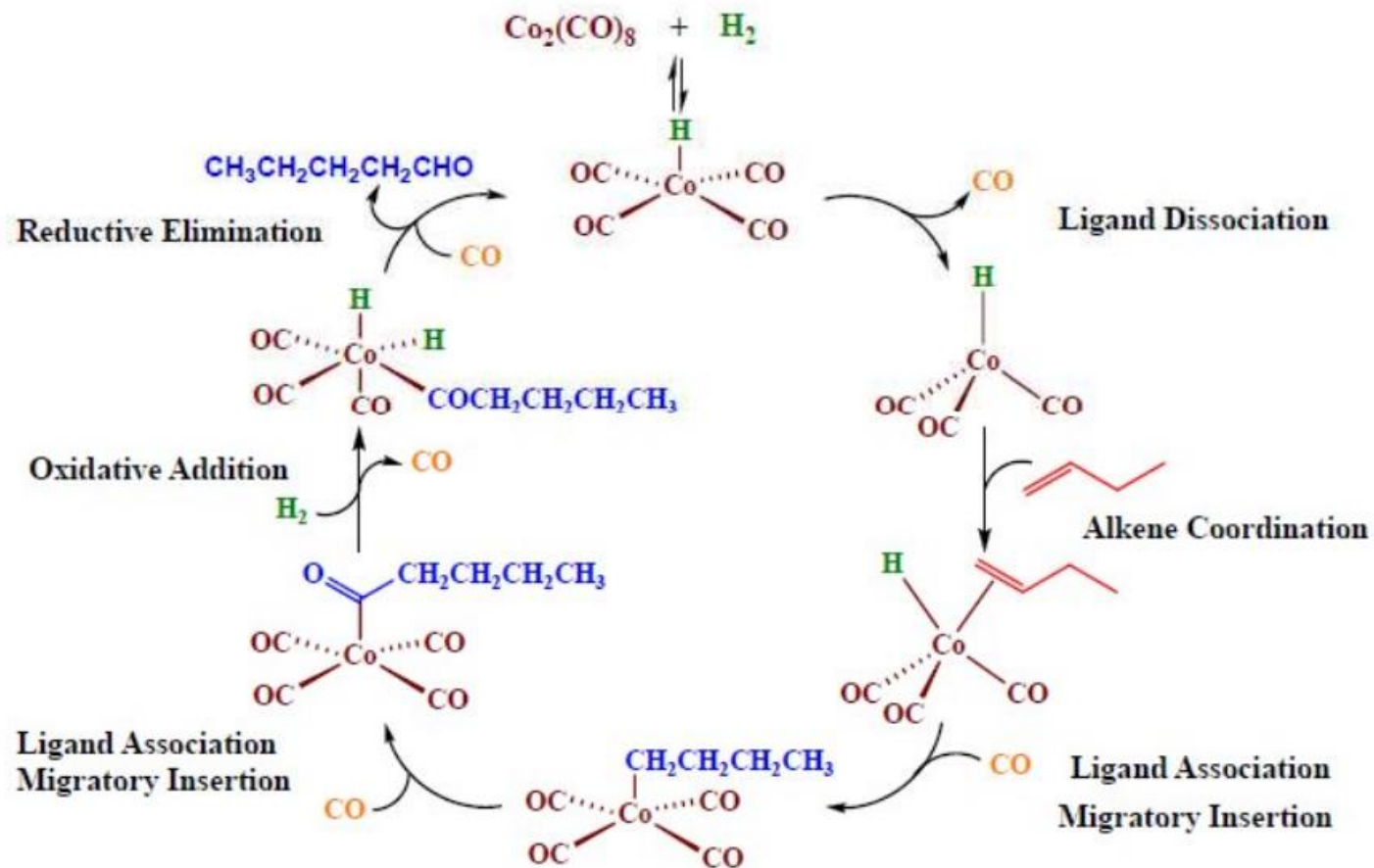
Hydroformylation



- Both cobalt and rhodium complexes are used as catalysts.
- Alkene isomerization, alkene hydrogenation and formation of branched aldehydes are the possible side reactions.
- Cobalt catalysts operate at 150 °C and 250 atm, whereas Rhodium catalysts operate at moderate temperatures and 1 atm.
- Rhodium catalysts promotes the formation of linear aldehydes. Cobalt catalysts do so if modified with alkylphosphine ligands.



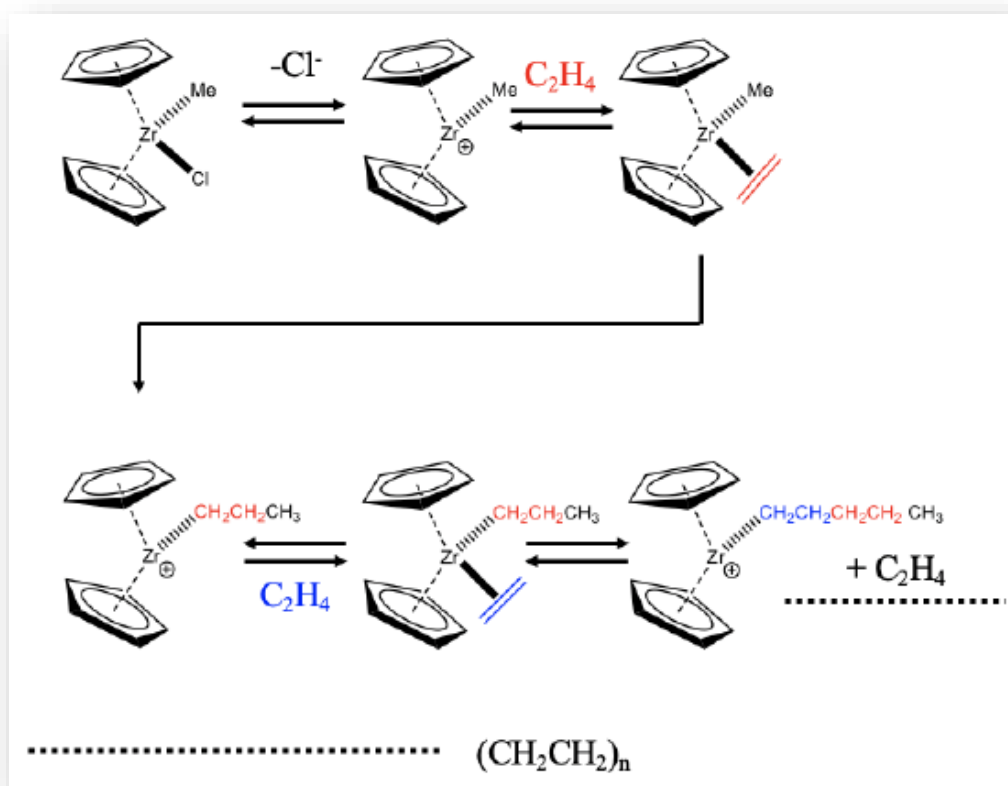
Hydroformylation



Ziegler-Natta polymerizations

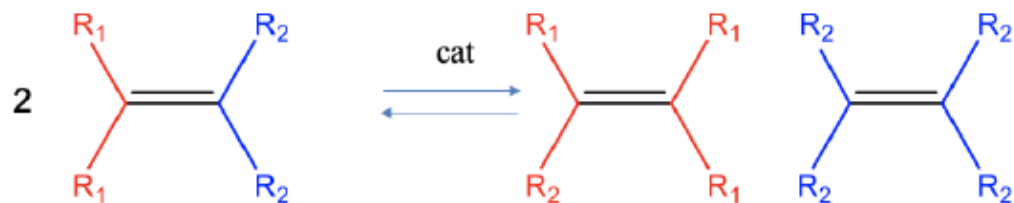
Another example of an organometallic catalytic reaction is the Ziegler-Natta olefin polymerization. This reaction is of high industrial importance for the production of olefins like polyethylene. The mechanism for the homogeneous catalysts is generally well understood. Homogeneous catalysts are typically metallocene catalysts.

An example of a Zirconium-based Ziegler-Natta catalyst

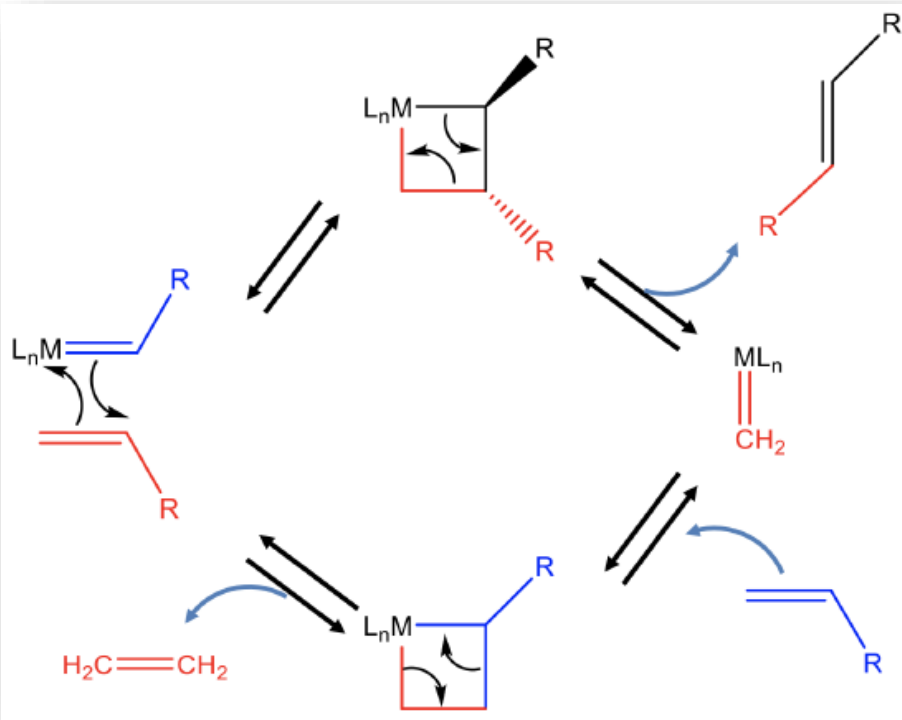


The catalyst is a coordinatively unsaturated complex cation with two cyclopentadienyl rings and a methyl group. The catalyst is formed from its precatalyst, a neutral molecule with an additional chloro ligand. The catalyst oxidatively adds an olefin like an ethylene molecule to the coordinatively unsaturated site. This step is followed an olefin insertion step that produces a propyl group. The migratory insertion leads to the formation of a vacant site, that can be re-occupied by another ethylene molecule. This molecule can insert into the propyl chain thereby prolonging the propyl chain to a pentyl chain. The olefin insertion step generates another vacant site that can be reoccupied by a new ethylene molecule. Repeating the catalytic cycle many times eventually leads to polyethylene.

Olefin Metathesis



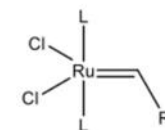
Mechanism of Olefin Metathesis



Catalysts



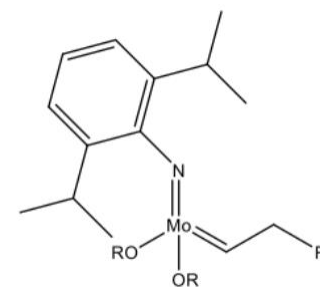
Robert Grubbs



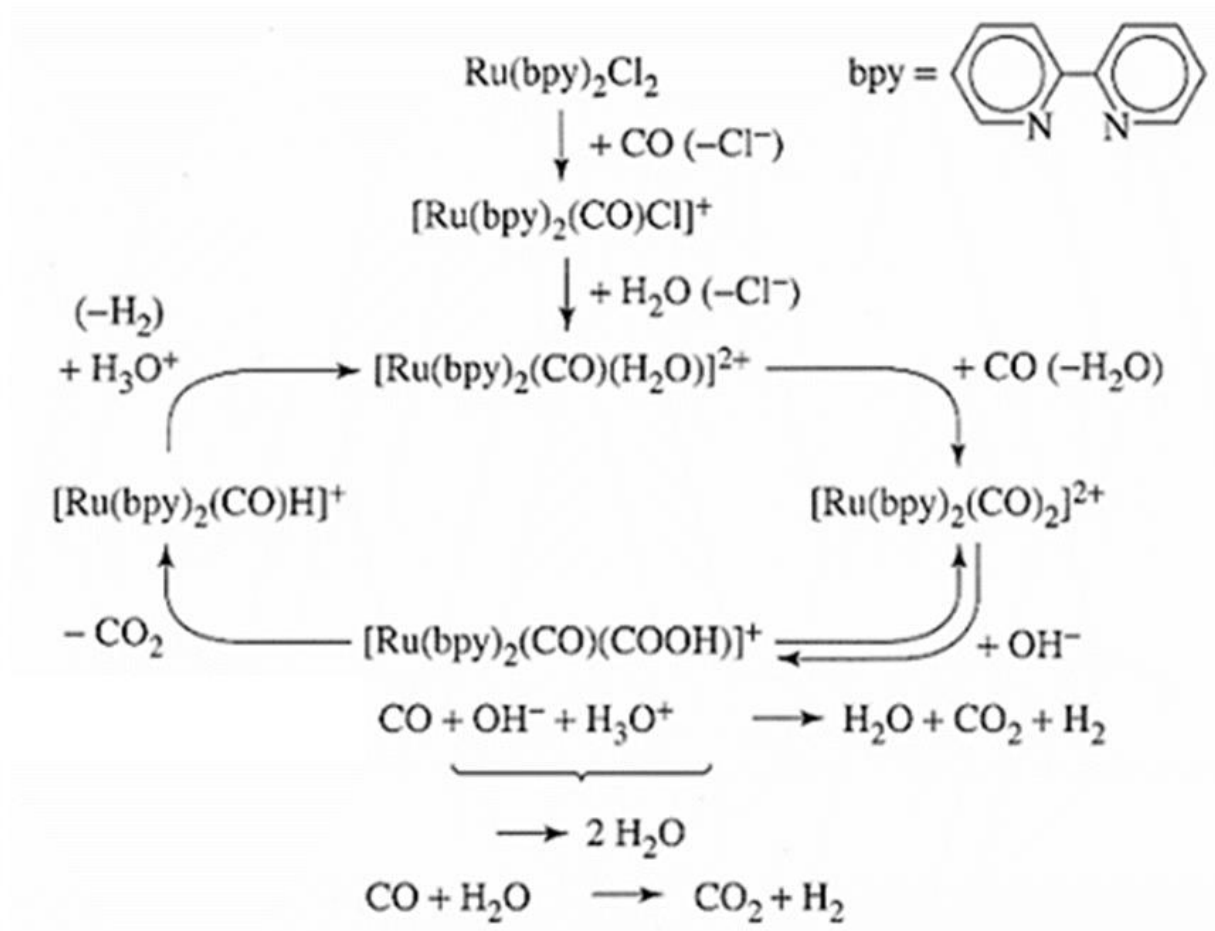
L=bulky phosphine



Richard Shrock

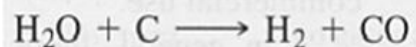


Homogenous Catalysis of water gas shift reaction



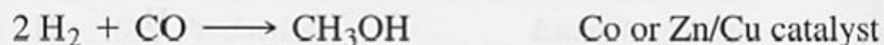
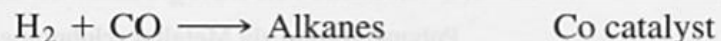
Heterogenous water gas shift reaction

This reaction occurs at elevated T and P
between water and natural sources of carbon

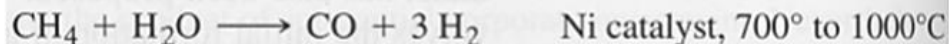


Synthesis gas or syn gas

Fischer-Tropsch process produce hydrocarbons,
alcohols, alkenes, and other products from syn gas



Steam reforming natural gas + steam to CO + hydrogen



Water gas shift reaction recycling the CO to react further with steam

