KARPAGAM ACADEMY OF HIGHER EDUCATION

(Deemed to be University Established Under Section 3 of UGC Act 1956)

COIMBATORE-21

Syllabus-I M.Sc Chemistry

ELECTIVE-II **Semester - II**
18CHP205C **ORGANOMETALLIC CHEMISTRY** **4H 4C**

Instruction Hours/week:L: 4 T:0 P:0 Marks: Internal:40 External: 60 Total:100

Scope

Organometallic chemistry frames much of our understanding of the natural world and continues to bring new technologies that are useful to every aspect of human life. Organometallic chemistry is an exciting and challenging course, which helps us to understand the various aspects of metals in biological systems. Organometallic chemistry is a part of our daily life. Organometallic Chemistry interfaces with a myriad of other disciplines and fields. It is fundamental to understand other areas of chemistry, biology and medicine. Due to highly prized nature of organometallic chemistry and its diverse topics, it lays the foundation for extremely productive and exciting career in variety of disciplines as pharmaceutical, agrochemical, mineralogy, molecular biology, biotechnology, nanotechnology, polymer technology, teaching research, scientific publication and so on. The importance of this subject would not diminish over time, so it will remain a promising career path. It deals with different types of metallic complexes with organic ligands.

Programme Outcome

1. To learn about nature of the bonding between organic ligands and metals.
2. To understand about the metal alkyl complexes.
3. To learn about the alkenes and cyclopentadienyl complexes.
4. To understand about the usage of organometallic compounds as catalysts.

Methodology

Blackboard teaching, Powerpoint presentation and group discussion.

UNIT- I

Metal carbonyls: Definition of organometallic compound - 18 electron rule - effective atomic number rule classification of organometallic compounds - the metal carbon bond types - ionic bond - sigma covalent bond - electron deficient bond - delocalised bond - dative bond - metal carbonyl complexes - synthesis - structure and reactions of metal carbonyls - the nature of M-CO bonding - binding mode of CO and IR spectra of metal carbonyls - metal carbonyls- metal carbonyl anions - metal carbonyl hydrides - metal carbonyl halides - metal carbonyl clusters - Wades rule and isolobal relationship - metal nitrosyls - dinitrogen complexes - dioxygen complexes.

UNIT- II

Metal alkyl complexes: Stability and structure - synthesis by alkylation of metal halides - by oxidative addition - by nucleophilic attack on coordinated ligands - metal alkyl and 18 electron rule - reactivity of metal alkyls - M-C bond cleavage reactions - insertion of CO to M-C bonds - double carbonylation - insertions of alkenes and alkynes - insertions of metals with C-H bonds - alkylidene and alkylidyne complexes - synthesis of alkylidene complexes in low oxidation states and in high oxidation states - bonding in alkylidene complexes - synthesis and bonding in alkylidyne complexes - reactivity of alkylidene and alkylidyne complexes.

UNIT- III

Alkene complexes: Synthesis of alkene complexes by ligand substitutuion - by reduction and by metal atom synthesis - bonding of alkenes to transition metals - bonding in diene complexes - reactivity of alkene complexes - ligand substitution - reactions with nucleophiles - olefin hydrogenation - hydrosilation - Wacker process - C-H activation of alkenes - alkyne complexes - bonding in alkyne complexes - reactivity of alkynes - alkyne complexes in synthesis - cobalt catalysed alkyne cycloaddition.

UNIT- IV

Cyclopentadienyl complexes: Metallocenes - synthesis of metallocenes - bonding in metallocenes - reactions of metallocenes - Cp_2Fe/Cp_2Fe+ couples in biosensors - bent sandwich complexes - bonding in bent sandwich complexes - metallocene halides and hydrides - metallocene and stereospecific polymerisation of 1-alkenes - cyclopentadiene as a non-spectator ligand - monocyclopentadienyl (half-sandwich) complexes - synthesis and structures of allyl complexes - arene complexes - synthesis - structure and reactivity of arene complexes - multidecker complexes.

UNIT - V

Organometallic compounds in homogeneous catalytic reactions: Coordinative unsaturation - acid-base behaviour reaction - migration of atoms or groups from metal to ligand - insertion reaction - reactions of coordinated ligands - catalytic reactions of alkenes - isomerisation of alkenes - hydrogenation - hydroformylation and hydrosilation of alkenes - alkene polymerisation and oligomerisation - fluxional molecules.

SUGGESTED RADINGS:

Text Books:

1. Huheey, J. E., (2010). Inorganic Chemistry - Priciples of Structure and Reactivity. Harper International Edition. New York: Harper and Rone.
2. Gopalan R and Ramalingam V (2013), Concise Coordination Chemistry, Vikas Publishing, India
3. Haiduc, J., and Zuckerman, J.J., (1985). Basic Organometallic Chemistry. Brelin: Walter de Gruyter.

Reference Books:

1. Miessler, G. L. & Tarr, Donald A. (2010). *Inorganic Chemistr*. 4th Ed. Pearson.
2. Shriver, D.D., Atkins, P. and Langford, C.H. (2006). *Inorganic Chemistry*. 4th Ed. Oxford University Press.

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LECTURE PLAN

Name of the Staff : **Dr. M. Gopalakrishnan** Department: **Chemistry**

Title of the Paper : **ELECTIVE-II (ORGANOMETALLIC CHEMISTRY)**

Paper Code : **18CHP205C** Class: **I M.Sc-Chemistry**

Year and Semester : 2018–2019 and II-Semester Total hours : 40 Hour

S.No	Lecture hour	Topics	Support material
Total No of Hours Planned For UNIT-I =15			
1.	1	Introduction of organometallic chemistry, Definition and examples	T1: 464-466
2.	1	18 electron rule classification of organometallic compounds	T1: 468
3.	1	Effective atomic number rule for examples of organometallic compounds	T1:467
4.	1	The metal carbon bond types such as ionic bond and sigma covalent bond	T2: 235
5.	1	Electron deficient bond, delocalized bond , dative bond	T1: 470-473
6.	1	Synthesis of metal carbonyl complexes	T1:477-482
7.	1	Structure of metal carbonyls complexes	T1:479
8.	1	Reactivity of metal carbonyls	T1: 470-473
9.	1	The nature of M-CO bonding and IR spectra of metal carbonyls	T1:513-516
10.	1	Metal carbonyls, metal carbonyl anions and hydrides	T1:486
11.	1	Metal carbonyl halides and metal carbonyl clusters	T2: 275-276
12.	1	Wades rule and isolable relationship	T2:418-425,
13.	1	Metal nitrosyls, di-nitrogen complexes	T3:650
14.	1	Synthesis of di-oxygen complexes and reactivity	T3:653
15.	1	Recapitulation and discussion of important questions	

Total No of Hours Planned For UNIT-II =11			
S.No	**Lecture hour**	**Topics**	**Support material**
1.	1	Synthesis of metal alkyl complexes	T1: 506-507
2.	1	Stability and structures of metal alkyl complexes	T1:507
3.	1	Oxidative addition and reductive elimination	T1:534-535
4.	1	Nucleophilic attack on coordinated ligand	T1:535
5.	1	18 electron rule and reactivity of metal alkyls. M-C bond cleavage reactions	T2:241
6.	1	Insertion of CO to M-C bonds and double carbonylation	T2:262
7.	1	Insertions of metals with C-H bonds and alkylidene and alkylidyne complexes	T2:244-245
8.	1	Synthesis of alkylidene complexes in low oxidation states and in high oxidation states	T1: 506-508
9.	1	Bonding in alkylidene complexes	T1: 508
10.	1	Synthesis and bonding in alkylidyne complexes	T1: 510-511, T2: 244
11.	1	Reactivity of alkylidene and alkylidyne complexes	T2: 244
12.	1	Recapitulation and discussion of important questions	
Total No of Hours Planned For UNIT-III =11			
S.No	**Lecture hour**	**Topics**	**Support material**
1.	1	Synthesis of Alkene complexes by ligand substitutuion	T1:492, T2:235
2.	1	Reduction and by metal atom synthesis	T1:493
3.	1	Bonding of alkenes to transition metals	T1:237-238
4.	1	Bonding in diene complexes and reactivity	T1:238

5.	1	Ligand substitution - reactions with nucleophiles and Vaska’s compound	T1:531, T2: 288, 362
6.	1	Olefin hydrogenation and their mechanism	T1: 551,
7.	1	Nucleophilic attack on coordinated ligands	T1:510-512
8.	1	Alkyne complexes and bonding nature	T1:512
9.	1	Alkyl and pentadienyl complexes and reactivity and synthesis	T2:235-237
10.	1	Cobalt catalysed alkyne cycloaddition	T1:291-293
11.	1	Recapitulation and discussion of important questions	

Total No of Hours Planned For UNIT-IV =12

S.No	Lecture hour	Topics	Support material
1.	1	Introduction of cyclopentadienyl complexes (Metallocenes)	T2: 245-247
2.	1	Synthesis of metallocenes by various method	T2: 246
3.	1	Bonding in metallocenes and MO diagramme	T1: 492
4.	1	Reactions of metallocenes - Cp_2Fe/Cp_2Fe+ couples in biosensors	T2: 245-246
5.	1	Synthesis of bent sandwich complexes and their bonding nature	T1: 1122-1123,
6.	1	Cyclooctatetraene and cyclobutadiene complexes	T1: 684-686
7.	1	Synthesis and reactivity of metallocene halides and hydrides	T2: 242-244
8.	1	Metallocene and stereospecific polymerisation of 1-alkenes	T1: 493, T2: 249-252,
9.	1	Half-sandwich complexes-Synthesis and structures	T1:492-493
10.	1	Synthesis, structure and reactivity allyl complexes	T1: 544-550

11.	1	Structure and reactivity of arene complexes-multidecker complexes	T1: 499-501, T2:249
12.	1	Recapitulation and discussion of important questions	

Total No of Hours Planned For UNIT-V =11

S.No	Lecture hour	Topics	Support material
1.	1	Organometallic compounds in homogeneous catalytic reactions: Coordinative unsaturation	T1: 530-533
2.	1	Migration of atoms or groups from metal to ligand	T1: 539 T2:543-547
3.	1	Insertion reaction and Reactions of coordinated ligands	T1: 538-539
4.	1	Hydrogenation and hydroformylation alkenes	T1:551, T2: 291.
5.	1	Hydrosilation of alkenes and Wacker process	T1:293, T2:297
6.	1	Carboxylation of methanol and catalytic reactions of alkenes	T2: 297 T2:293
7.	1	Alkene polymerisation and oligomerisation	T2:301-305
8.	1	Fluxional molecules	T2:252-253
9.	1	Recapitulation and discussion of important questions	
10.	1	Discussion of previous ESE question papers	
11.	1	Discussion of previous ESE question papers	

Text Book:

T1. Miessler, G. L. & Tarr, Donald A. (2010). *Inorganic Chemistr.* 4th Ed. Pearson.

T2. Gopalan R and Ramalingam V (2013), Concise Coordination Chemistry, Vikas Publishing, India

T3.Huheey, J. E., Keiter, E.A. & Keiter, R.L. (2010). *Inorganic Chemistry: Principles of Structure and Reactivity.* 4th Ed. Harper Collins.Pearson.

UNIT- I
SYLLABUS

Definition of organometallic compound - 18 electron rule - effective atomic number rule classification of organometallic compounds - the metal carbon bond types - ionic bond - sigma covalent bond - electron deficient bond - delocalised bond - dative bond - metal carbonyl complexes - synthesis - structure and reactions of metal carbonyls - the nature of M- CO bonding - binding mode of CO and IR spectra of metal carbonyls - metal carbonyls- metal carbonyl anions - metal carbonyl hydrides - metal carbonyl halides - metal carbonyl clusters - Wades rule and isolobal relationship - metal nitrosyls - dinitrogen complexes - dioxygen complexes.

Introduction

Justus von Liebig attempted initial experiments on reaction of carbon monoxide with metals in 1834. However, it was demonstrated later that the compound he claimed to be potassium carbonyl was not a metal carbonyl at all. After the synthesis of [PtCl2(CO)2] and [PtCl2(CO)]2 reported by Schutzenberger (1868) followed by [Ni(CO)4] reported by Mond et al (1890), Hieber prepared numerous compounds containing metal and carbon monoxide.

- Compounds having at least one bond between carbon and metal are known as organometallic compounds.
- Metal carbonyls are the transition metal complexes of carbon monoxide containing metal-carbon bond.
- Lone pair of electrons are available on both carbon and oxygen atoms of carbon monoxide ligand. However, as the carbon atoms donate electrons to the metal, these complexes are named as carbonyls.
- A variety of such complexes such as mono nuclear, poly nuclear, homoleptic and mixed ligand are known.
- These compounds are widely studied due to industrial importance, catalytic properties and structural interest.
- Carbon monoxide is one of the most important π- acceptor ligand. Because of its π-acidity, carbon monoxide can stabilize zero formal oxidation state of metals in carbonyl complexes

SYNTHESIS OF METAL CARBONYLS

Direct Combination

Only Ni(CO)4 and Fe(CO)5 and Co2(CO)8 are normally obtained by the action of carbon monoxide on the finely divided metal at suitable temperature and pressure

$$\mathrm{Ni(s) + 4CO(g) \xrightarrow{30^{o}C,\,1\,atm} Ni(CO)_4(l)}$$

$$\mathrm{Fe(s) + 5CO(g) \xrightarrow{200^{o}C,\,200\,atm} Fe(CO)_5(l)}$$

$$\mathrm{2Co(s) + 8CO(g) \xrightarrow{150^{o}C,\,35\,atm} Co_2(CO)_8(s)}$$

Reductive carbonylation

Many metallic carbonyls are obtained when salts like Ru(acac)3, CrCl3, Re2O7, VCl3, CoS, Co(CO)3, CoI2 etc. are treated with carbon monoxide in presence of suitable reducing agent like Mg, Ag, Cu, Na, H2, AlLiH4 etc.

$$\mathrm{3\,Ru(acac)_3(solution) + H_2(g) + 12\,CO(g) \xrightarrow{150^{o}\,C,\,200\,atm,\,methanol} Ru_3(CO)_{12}}$$

$$\mathrm{CrCl_3(s){+}Al(s){+}6CO(g) \xrightarrow{AlCl_3,\,benzene} Cr(CO)_6(solution)}$$

$$\mathrm{2\,CoI_2 + 8\,CO + 4\,Cu \xrightarrow{200^{\circ}C,\,200\,atm\,press.} Co_2(CO)_8 + 4\,CuI}$$

$$\mathrm{2\,FeI_2 + 5\,CO + 2\,Cu \xrightarrow{200^{\circ}\,C,\,200\,atm\,press.} Fe(CO)_5 + Cu_2I_2}$$

$$\mathrm{2\,CoCO_3 + 8\,CO + 2\,H_2 \xrightarrow{120-200^{\circ}C,\,250-300\,atm\,press} Co_2CO_8 + 2\,CO_2 + 2\,H_2O}$$

$$\mathrm{MoC1_5 + 6\,CO + 5\,Na \xrightarrow{diglyme} Mo(CO)_6 + 5\,NaC1}$$

Preparation of mononuclear carbonyls from iron pentacarbonyl

The labile carbonyl groups in iron pentacarbonyl can be replaced by chloride to give a different metal carbonyl. These reactions are characterized by low yield, which can be improved using high pressure.

$$MoCl_6 + 3Fe(CO)_5 \xrightarrow{110\,^{o}C,\ ether} Mo(CO)_6 + 3FeCl_2 + 9CO$$

$$WCl_6 + 3Fe(CO)_5 \xrightarrow{110\,^{o}C,\ ether} W(CO)_6 + 3FeCl_2 + 9CO$$

PHYSICAL PROPERTIES

State:

Majority of the metallic carbonyls are liquids or volatile solids.

Colour:

Most of the mononuclear carbonyls are colourless to pale yellow. V(CO)6 is a bluish-black solid. Polynuclear carbonyls exhibit are dark in colour.

Solubility:

Metal carbonyls are soluble in organic solvents like glacial acetic acid, acetone, benzene, carbon tetrachloride and ether.

Toxicity:

Due to low melting points and poor thermal stability, they show toxicity related to the corresponding metal and carbon monoxide. Exposure to these compounds can cause damage to lungs, liver, brain and kidneys. Nickel tetracarbonyl exhibits strongest inhalation toxicity. These compounds are carcinogenic over long-term exposure.

Magnetic Property:

All the metal carbonyls other than vanadium hexacarbonyl are diamagnetic. The metals with even atomic number form mononuclear carbonyls. Thus, all the electrons in the metal atoms are paired. In case of dinuclear metal carbonyls formed by metals with odd atomic number, the unpaired electrons are utilized for the formation of metal-metal bonds.

Thermal Stability:

Most of the metal carbonyls melt or decompose at low temperatures. Solid carbonyls sublime in vacuum but they undergo some degree of degradation.

Thermodynamic Stability:

Metal carbonyls are thermodynamically unstable. They undergo aerial oxidation with different rates. Co2(CO)8 and Fe2(CO)9 are oxidized by air at room temperature while chromium and molybdenum hexacarbonyls are oxidized in air when heated.

CHEMICAL PROPERTIES

Ligand substitution reactions:

Substitution of carbon monoxide ligand by various mono dentate and bidentate ligands can be carried out using thermal and photochemical reactions. Monodentate ligands likeisocyanides (CNR), cyanide (CN-), phosphine (PR3) and ethers can partially or completely replace the carbonyl group.

$$\mathrm{Fe(CO)_5 + 2CNR \rightarrow Fe(CO)_3(CNR)_2 + 2CO}$$

$$\mathrm{Ni(CO)_4 + 4CNR \rightarrow Ni(CNR)_4 + 4CO}$$

$$\mathrm{Mn_2(CO)_{10} + PR_3 \rightarrow 2Mn(CO)_4\left(PR_3\right) + 2CO}$$

$$\mathrm{2Fe_2(CO)_{12} + 3py \rightarrow Fe_3(CO)_9(py)_3 + 3Fe(CO)_5}$$

Bidentate ligands like o-phenylene-bis(dimethyl arsine) (diars) and o-phenanthroline(o-phen) can replace carbonyl groups in the multiple of two

$$\mathrm{Mo(CO)_6 + diars \rightarrow Mo(CO)_4(diars) + 2CO}$$

$$\mathrm{Ni(CO)_4 + o\text{-}phen \rightarrow Ni(CO)_2(o\text{-}phen)_2 + 2CO}$$

$$\mathrm{Cr(CO)_6 + 2\,diars \rightarrow Cr(CO)_2(diars)_2 + 4CO}$$

Reaction with halogens

Most of the metal carbonyls react with halogens to give carbonyl halides

$$\mathrm{Fe(CO)_5 + X_2 \rightarrow Fe(CO)_4X_2 + CO}$$

$$\mathrm{Mo(CO)_6 + Cl_2 \rightarrow Mo(CO)_4Cl_2 + 2CO}$$

Halogens can cause cleavage in the metal-metal bonds in case of polynuclear carbonyls

$$\mathrm{Ni(CO)_4 + Br_2 \rightarrow NiBr_2 + 4CO}$$

$$\mathrm{Co_2(CO)_8 + 2X_2 \rightarrow 2CoX_2 + 8CO}$$

Reaction with hydrogen

Some of the carbonyls can be reduced by hydrogen to give carbonyl hydrides

$$\mathrm{Co_2(CO)_8 + H_2 \xrightarrow{165^{O}\,C,\ 200\ atm} 2[Co(CO)_4H]}$$

$$\mathrm{Mn_2(CO)_{10} + H_2 \xrightarrow{200\ atm} 2[Mn(CO)_5H]}$$

Even though, these compounds are named as hydrides, they are known to behave as proton donors. The neutral hydrides like [Co(CO)4H] and [Mn(CO)5H] behave as acids as shown below

$$[\mathrm{Co(CO)_4H}] \rightarrow [\mathrm{Co(CO)_4}]^- + \mathrm{H}^+$$

$$[\mathrm{Mn(CO)_5H}] \rightarrow [\mathrm{Mn(CO)_5}]^- + \mathrm{H}^+$$

Reaction with nitric oxide

A good number of metal carbonyls react with nitric oxide to give carbonyl nitrosyls

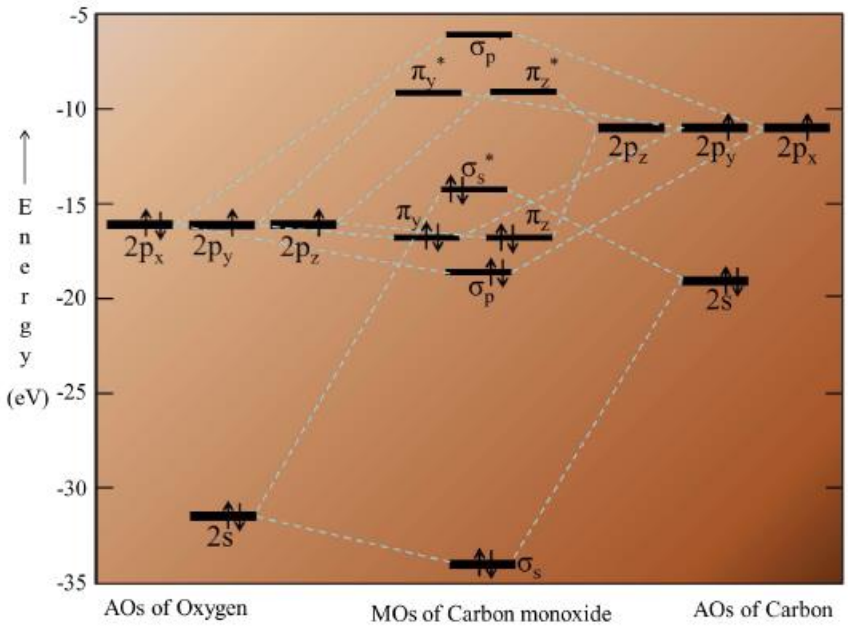
$$\mathrm{Fe(CO)_5} + 2\,\mathrm{NO} \xrightarrow{95^{o}\,\mathrm{C}} \mathrm{Fe(CO)_2(NO)_2} + 3\,\mathrm{CO}$$

$$\mathrm{Co_2(CO)_8} + 2\,\mathrm{NO} \xrightarrow{40^{o}\,\mathrm{C}} 2\,\mathrm{Co(CO)_3(NO)} + 2\,\mathrm{CO}$$

The reaction between iron pentacarbonyl and nitric oxide involves replacement of three carbonyl groups by two nitric oxide molecules. Electronically, this is equivalent as nitric oxide is a three electron donor ligand whereas carbon monoxide is a two electron donor.

BONDING IN METALLIC CARBONYLS

In order to understand the bonding in metal carbonyls, let us first see the MO diagram of carbon monoxide

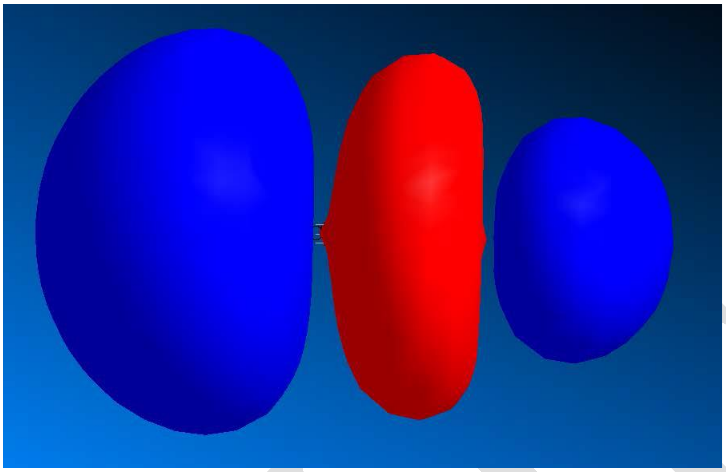


The order of energy of the molecular orbitals and the accommodation of ten electrons of the carbon monoxide can be shown as

$$(\sigma_s^{b})^2\,(\sigma_p^{b})^2\,(\pi_y^{b}{=}\pi_z^{b})^4\,(\sigma_s{*})^2\,(\pi_y{*}{=}\pi_z{*})^0\,(\sigma_p{*})^0$$

(σ_s*) is the highest occupied molecular orbital (HOMO) which can donate the lone pair of electrons for the formation of a OC→M σ bond

$(\pi_y^*=\pi_z^*)$ are the lowest unoccupied molecular orbitals (LUMO) which can accept the electron density from an appropriately oriented filled metal orbital resulting into formation of a M→CO π bond.



Red colour is for positive sign of the wave function while the blue colour indicates negative sign of the wave function

Formation of dative 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←CO σ-bond

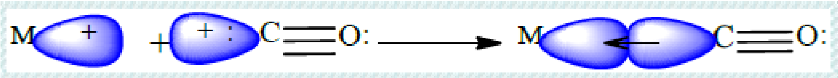
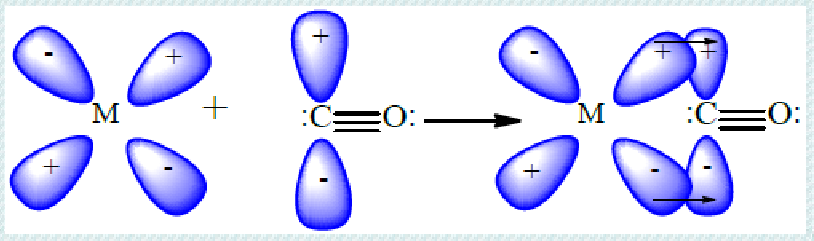


Figure: Formation of a M←CO σ-bond in metal carbonyls

Formation of π-bond by back donation

This bond is formed because of overlapping of filled dπ orbitals or hybrid dpπ orbitals of metal atom with low-lying empty (LUMO) orbitals on CO molecule. i.e. MCO π→



Bridging CO groups

In addition to the linear M-C-O groups, the carbon monoxide ligand is also known to form bridges. This type of bonding is observed in some binuclear and polynuclear carbonyls. It is denoted by μn–CO, where n indicates the number of metals bridged. While n=2 is the most common value, it reaches to be 3 or 4 in certain less common carbonyls.

In a terminal M-C-O group, the carbon monoxide donates two electrons to an empty metal orbital, while in μ2–CO group, the M-C bond is formed by sharing of one metal electron and one carbon electron.

Ni(CO)4,Nickel tetracarbonyl:

Preparation:

It can be prepared by passing carbon monoxide over nickel in the temperature range of 60-100 °C.

$$\mathrm{Ni + 4CO \xrightarrow{60^{0}\,C} Ni(CO)_4}$$

It can be made by heating nickel iodide with carbon monoxide in the presence of copper which acts as a halogen acceptor

$$\mathrm{NiI_2 + 4CO \xrightarrow{Cu} Ni(CO)_4 + CuI_2}$$

Properties:

It is a colourless liquid having melting point -25oC, boiling point 43oC and decomposition temperature in the range of 180–200oC.

It is insoluble in water but dissolves in organic solvents.

It reacts with concentrated sulphuric acid along with detonation

$$\mathrm{Ni(CO)_4 + H_2SO_4 \rightarrow NiSO_4 + H_2 + 4CO}$$

It reacts with moist nitric oxide to give deep blue coloured compound

$$\mathrm{2Ni(CO)_4 + 2NO + 2H_2O \rightarrow 2Ni(NO)(OH) + 8OH^- + H_2}$$

Passing gaseous hydrochloric acid in the solution of nickel tetracarbonyl results in the decomposition

$$\mathrm{Ni(CO)_4 + 2HCl_{(g)} \rightarrow NiCl_2 + H_2 + 4CO}$$

Uses:

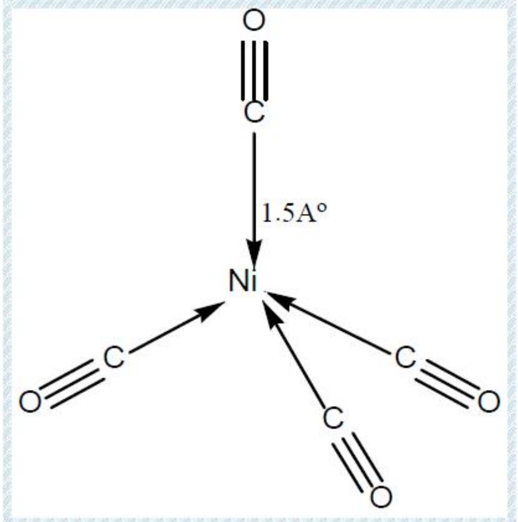
Since Ni(CO)4, on heating, decomposes to metallic nickel, it is used in the production of nickel by Mond’s process.

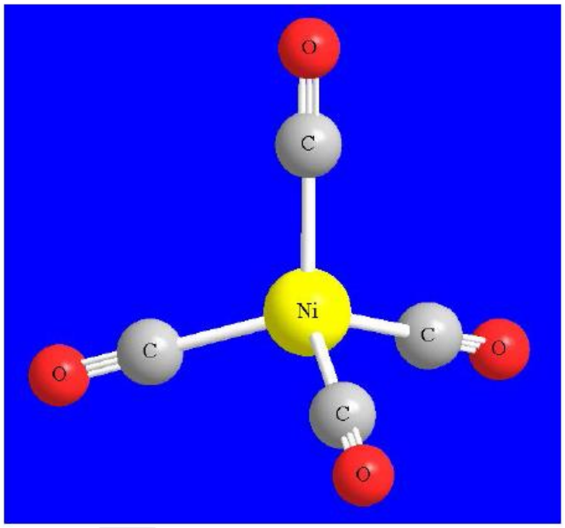
It is used for plating nickel on other metals.

It is used as a catalyst for synthesis of acrylic monomers in plastic industries

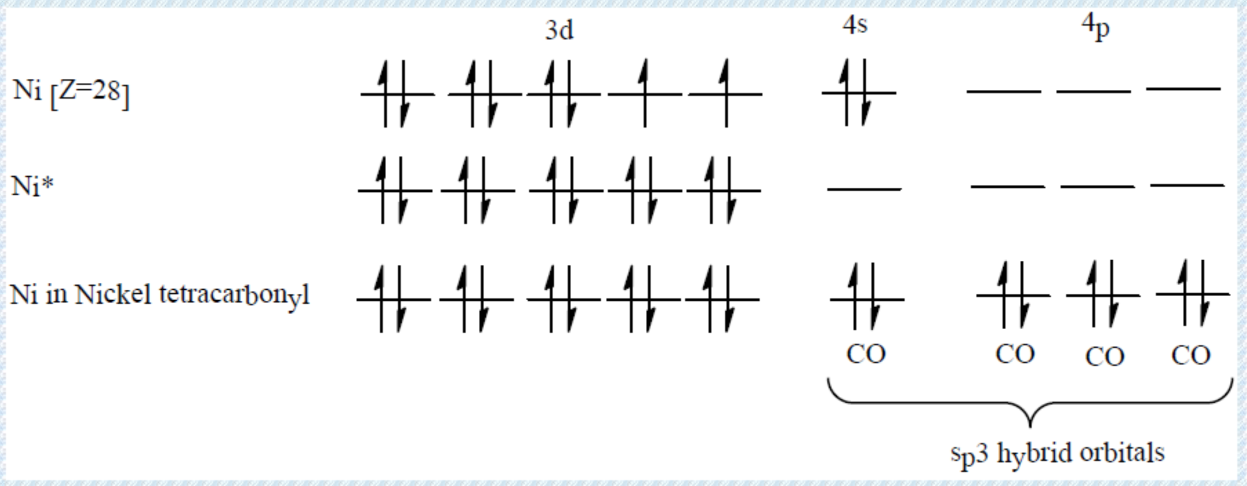
Structure:

Nickel tetracarbonyl has a tetrahedral geometry with Ni-C bond lengths of 1.5 Å. It is also found to be diamagnetic





The structure of Ni(CO) 4 can be explained by considering sp3 hybridization of Ni atom. Since it is diamagnetic, all the ten electrons present in the valence shell of Ni atom (Ni = 3d8 4s2) get paired in 3d orbitals. Thus the valence shell configuration of Ni atom in Ni(CO) 4 molecule becomes 3d10 4s0. OC→Ni bond results by the overlap between the empty sp3 hybrid orbital on Ni atom and the HOMO on C atom in CO molecule as shown below



sp3 hybridization of nickel atom in nickel tetracarbonyl

Acceptance of four electron pairs by nickel in zero oxidation state severely increases the electron density on the nickel atom. According to the electro neutrality principle given by Pauling, the atoms in a molecule share the electron pairs to the extent such that charge on each of the atom remains close to zero. Thus, the nickel atom donates back some electron density from the filled d-orbitals to the low-lying empty (LUMO) orbitals on CO molecule resulting into formation of a double bond. i.e. MCO.

Fe(CO)5, Iron pentacarbonyl

Preparation:

It can be prepared by passing carbon monoxide over iron powder at high temperature and pressure.

$$\mathrm{Fe} + 5\mathrm{CO} \xrightarrow{200^{0}\,\mathrm{C},\,100\ \mathrm{atm.}} \mathrm{Fe(CO)_5}$$

It can also be prepared by carbonylation of ferrous sulphide/iodide in presence of Cu-metal, which acts as a reducing agent

$$2\mathrm{FeS} + 10\mathrm{CO} + 2\mathrm{Cu} \xrightarrow{200^{0}\,\mathrm{C},\,200\ \mathrm{atm.}} \mathrm{Fe(CO)_5} + \mathrm{Cu_2S}$$

Properties:

It is a pale yellow liquid having melting point -20 oC, boiling point 103 oC and decomposition temperature around 250 oC.

It is insoluble in water but soluble in glacial acetic acid, methanol, diethyl ether, acetone and benzene.

Cold solution of iron pentacarbonyl in glacial acetic acid undergoes dimerization under the influence of ultra-violet light

$$2\,Fe(CO)_5 \xrightarrow{h\nu} Fe_2(CO)_9 + CO$$

The reaction of sodium hydroxide with iron pentacarbonyl results in nucleophilic attack by hydroxide ion on the carbonyl group to give a metal carboxylic acid complex. Upon further action with sodium hydroxide, the carboxylic acid gives up carbon dioxide to form a hydrido anion. The protonation of this anion results in the formation of iron tetracarbonyl hydride (Heiber base) as shown below:

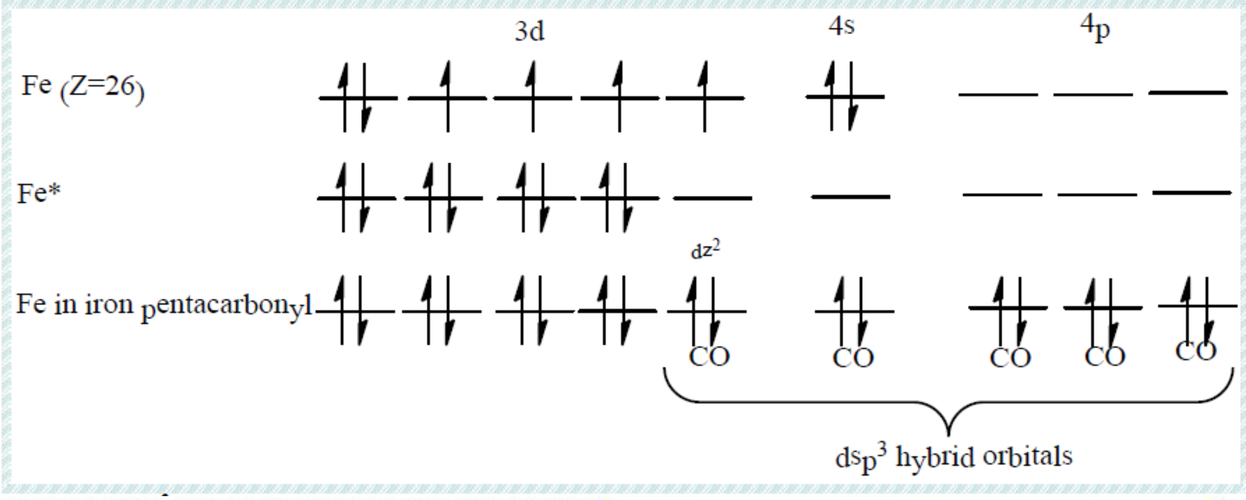
$$Fe(CO)_5 + NaOH \rightarrow Na[Fe(CO)_4COOH]$$

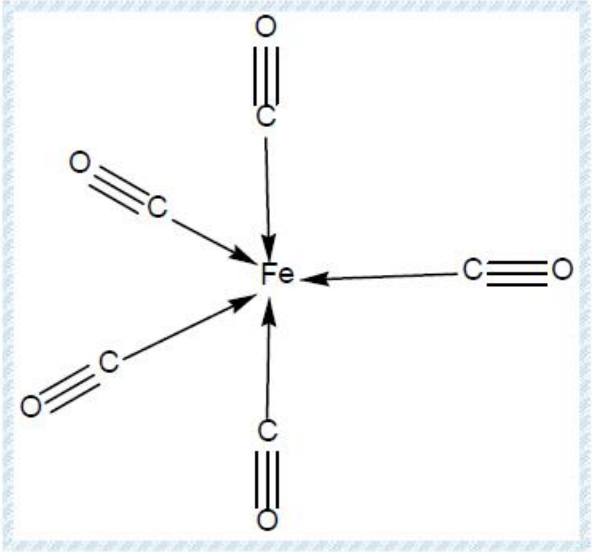
$$Na[Fe(CO)_4COOH] + NaOH \rightarrow Na[HFe(CO)_4] + NaHCO_3$$

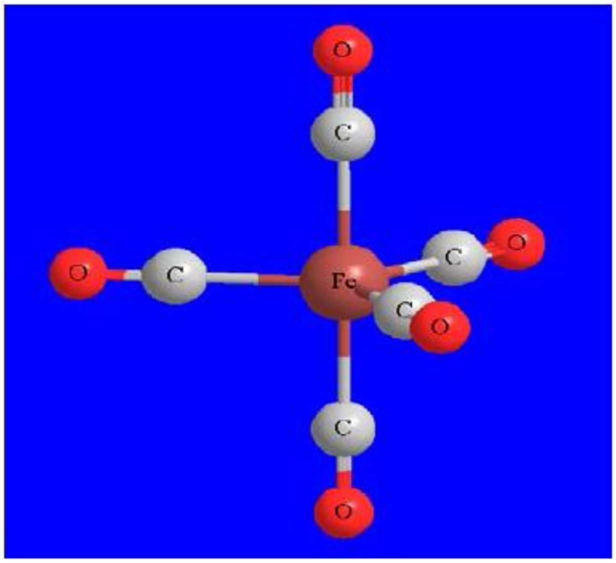
$$Na[HFe(CO)_4] + H^+ \rightarrow [(H)_2Fe(CO)_4] + Na^+$$

Structure:

The structural studies have suggested trigonal bipyramidal geometry for iron pentacarbonyl. The Fe-C distances are found to be 1.80 Å and 1.84 Å for axial and equatorial bonds respectively. The molecule is also found to be diamagnetic







The structure can be explained using dsp^3 hybridization in Fe atom. All eight electrons present in the valence shell of Fe atom (Fe:$3d^64s^2$) get paired in four 3d orbitals. Thus the valence shell configuration of Fe in Fe(CO)$_5$ becomes $3d^84s^0$. The OC→Fe bond results by the overlap between the empty dsp^3 hybrid orbitals on Fe atom and the HOMO on C atom in CO molecule as shown above.

Cr(CO)6, Chromium hexacarbonyl

Preparation:

It can be prepared by carbonylation of chromium chloride with carbon monoxide using a reducing agent like lithium aluminium hydride (LAH).

$$CrCl_3 + 6CO \xrightarrow{LAH,\ 115^{0}\ C,\ 70\ atm} Cr(CO)_6$$

An indirect method of preparation involves an action of carbon monoxide on a mixture of Grignard reagent and anhydrous chromium chloride in ether which is followed by decomposition with an acid to give chromium hexacarbonyl.

$$C_6H_5MgBr + CrCl_3 + CO \xrightarrow{35-70\,atm} Cr(CO)_2(C_6H_5)_4 + MgBrCl + MgBr_2$$

$$Cr(CO)_2(C_6H_5)_4 + 6H^+ \rightarrow Cr(CO)_6 + 2Cr^{+3} + 12(C_6H_5)^- + 3H_2$$

Properties:

It is a white crystalline solid melting above 150 $_{o}$C and boiling at 220 $_{o}$C.

It is insoluble in water but soluble in ether, chloroform, carbon tetrachloride and benzene.

It is not attacked by air, bromine, cold aqueous alkalis, dilute acids and concentrated hydrochloric acid as well as sulphuric acid. It is decomposed by Chlorine gas and concentrated nitric acid. It reacts with fluorine at -75 $_{o}$C to form chromium hexafluoride.

It reacts with sodium metal in liquid ammonia to give carbonylate anion

$$Cr(CO)_6 + 2\,py \rightarrow \underset{\text{yellowish brown}}{Cr(CO)_4(py)_2} + 2\,CO$$

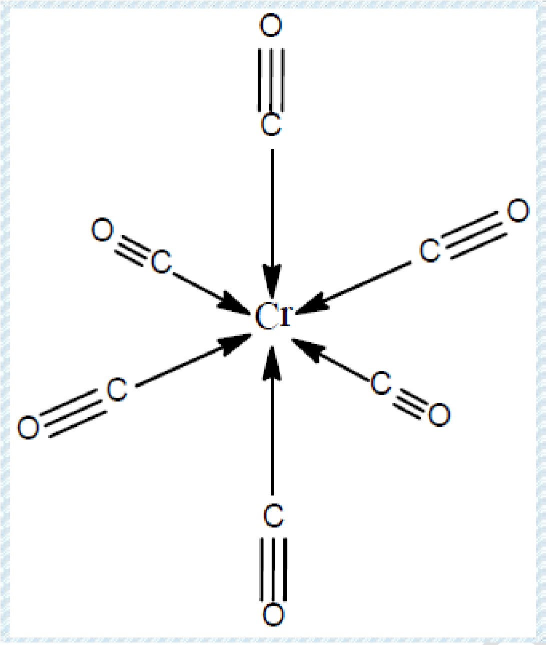
$$2\,Cr(CO)_6 + 5\,py \rightarrow \underset{\text{orange}}{Cr_2(CO)_7(py)_5} + 5\,CO$$

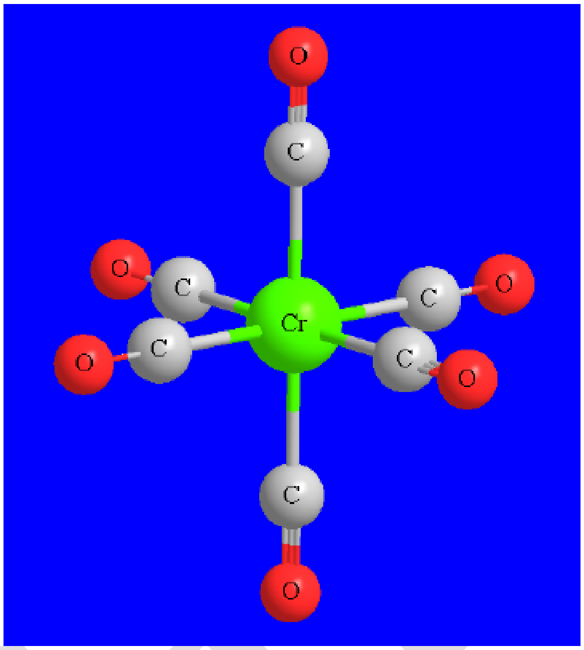
$$Cr(CO)_6 + 3\,py \rightarrow \underset{\text{bright red}}{Cr(CO)_3(py)_3} + 3\,CO$$

It gives substitution reactions with amines like en and py. At higher temperatures (>150^{o}C) several pyridyl derivatives are formed

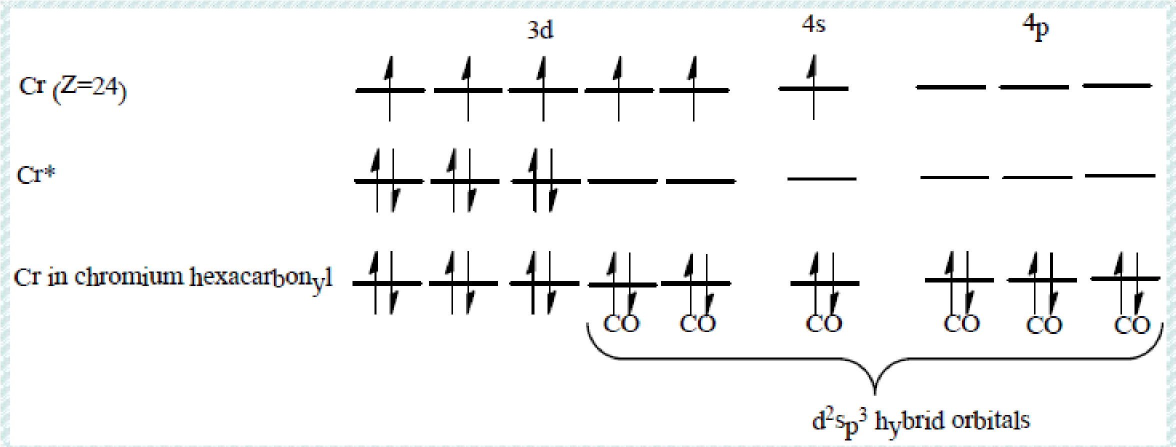
Structure

The structural studies have suggested an octahedral geometry for chromium hexacarbonyl. The Cr-C distance is found to be 1.92 Å while the C-O bond length is 1.16 Å. The molecule is also found to be diamagnetic.





The structure can be explained using d2sp3 hybridization in Cr atom. All six electrons present in the valence shell of Cr atom (Cr: 3d54s1) get paired in three 3d orbitals. Thus the valence shell configuration of Cr in Cr(CO)6 becomes 3d64s0. The OC→Cr bond results by the overlap between the empty d2sp3 hybrid orbitals on Fe atom and the HOMO on C atom in CO molecule as shown below



The MO energy diagram for $Cr(CO)_6$ is shown in the figure below. For the molecular orbitals, 12 electrons are contributed from the lone pairs on the carbon atoms of the six carbon monoxide ligands. The metal contributes six electrons while 24 electrons come from the π system of the six ligands. The

MOs are occupied by these 42 electrons and the t_{2g} level becomes the highest occupied molecular orbital (HOMO) of the metal carbonyl.

POLYNUCLEAR CARBONYLS

$Mn_2(CO)_{10}$, Dimanganese decacarbonyl

Preparation:

It can be prepared by carbonylation of manganese iodide with carbon monoxide using magnesium as a reducing agent.

$$2\,MnI_2 + 10\,CO + \underset{\text{(diethyl ether)}}{2\,Mg} \xrightarrow{25\ ^{o}C,\ 210\ atm.} Mn_2(CO)_{10} + 2\,MgI_2$$

It can also be obtained by carbonylation of anhydrous manganese chloride with carbon monoxide in presence of sodium benzophenone ketyl.

$$2\,MnCl_2 + 10\,CO + 4(C_6H_5)_2\,CONa \xrightarrow{165\ ^{\circ}C,\ 140\ atm.} Mn_2(CO)_{10} + 4(C_6H_5)_2\,CO + 4\,NaCl$$

Properties:

It forms stable golden yellow crystals having melting point of 155 ^{o}C.

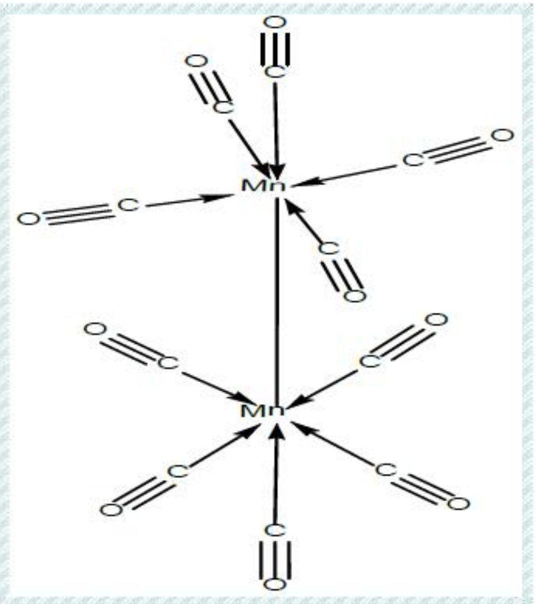
It is oxidized by trace amount of oxygen in solution. Hence, the solution must be stored in inert atmosphere.

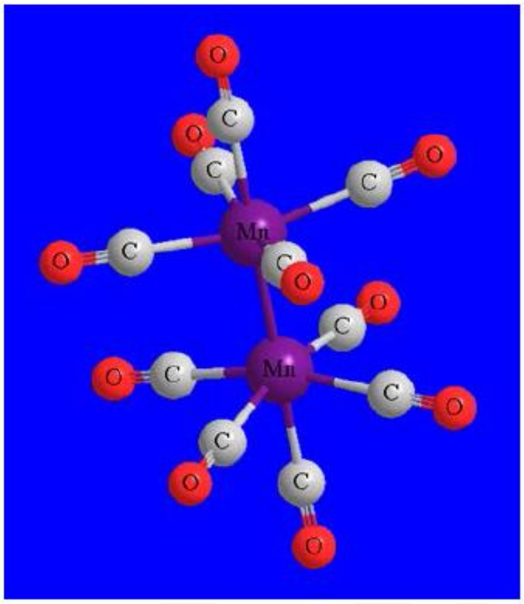
Halogenation of dimanganese decacarbonyl proceeds with breaking of Mn-Mn bond and formation of carbonyl halides

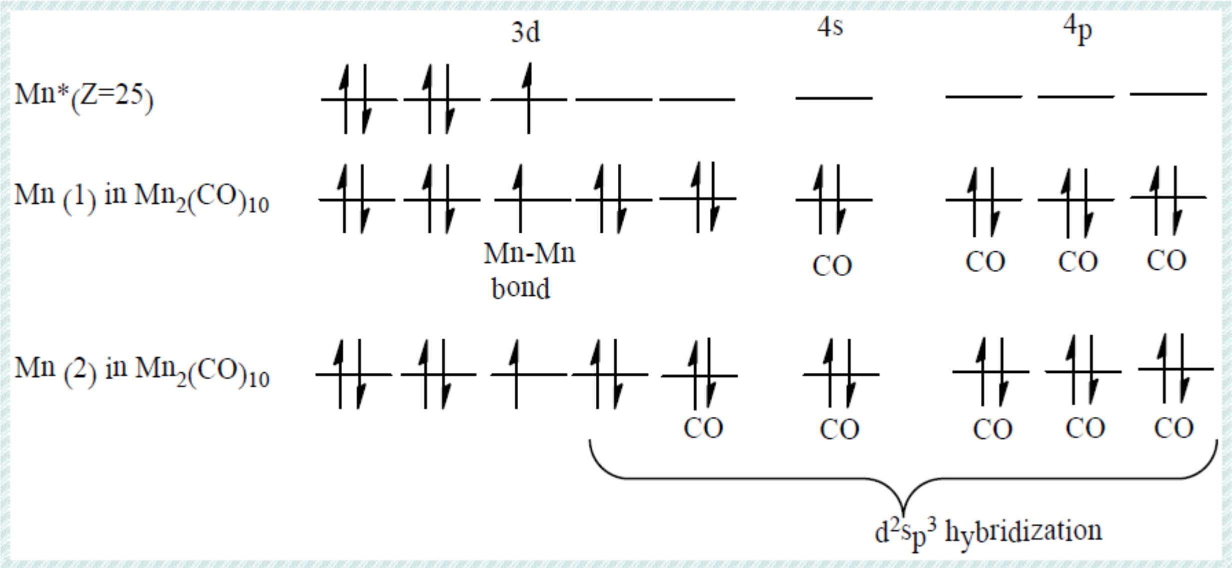
$$Mn_2(CO)_{10} + X_2\,(X = Br, I) \rightarrow 2\,Mn(CO)_5\,X$$

Manganese pentacarbonyl does not exist as Mn (Z=25) has an odd atomic number. However, the structure of dimanganese decacarbonyl consists of two manganese pentacarbonyl groups joined through a Mn-Mn (2.79 Å) bond. The formation of this inter metallic bond effectively adds one electron to each of the manganese atoms. Thus, manganese, an element with odd atomic number forms a binuclear carbonyl. Since the molecule does not have any unpaired electrons, it is diamagnetic. The remaining two members of group VIIB viz. Technetium (Tc) and Rhenium (Re) also form decacarbonyls with similar structures.

Structure







d2sp3 hybridization in dimanganese decacarbonyl.

Co2(CO)8, Dicobalt octacarbonyl

Preparation:
It can be prepared by direct combination of carbon monoxide with cobalt metal.

$$2\,Co + 8\,CO \xrightarrow{200^\circ C,\ 100\ atm} Co_2(CO)_8$$

It can also be prepared by carbonylation of cobalt iodide/cobalt sulphide/cobalt carbonate using reducing agents like copper metal or hydrogen gas.

$$2\,CoS/\,2\,CuI_2 + 8\,CO + 4\,Cu \xrightarrow{200^\circ C,\ 200\ atm} Co_2(CO)_8 + 2\,Cu_2S/\,4\,CuI$$

$$2\,CoCO_3 + 8\,CO + 2\,H_2 \xrightarrow{120\text{-}200^\circ C,\ 250\text{-}300\ atm} Co_2(CO)_8 + 2\,H_2O$$

Properties:

It is an orange crystalline substance having melting point 51oC and turns deep violet upon exposure to air.

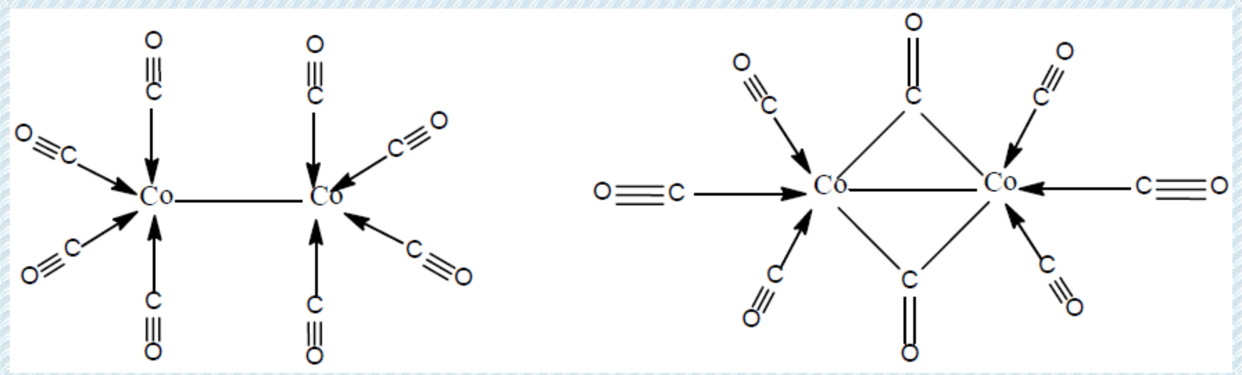
It is soluble in alcohols, ether and carbon tetrachloride.

Upon heating at 50 oC it forms tetracobalt dodecacarbonyl

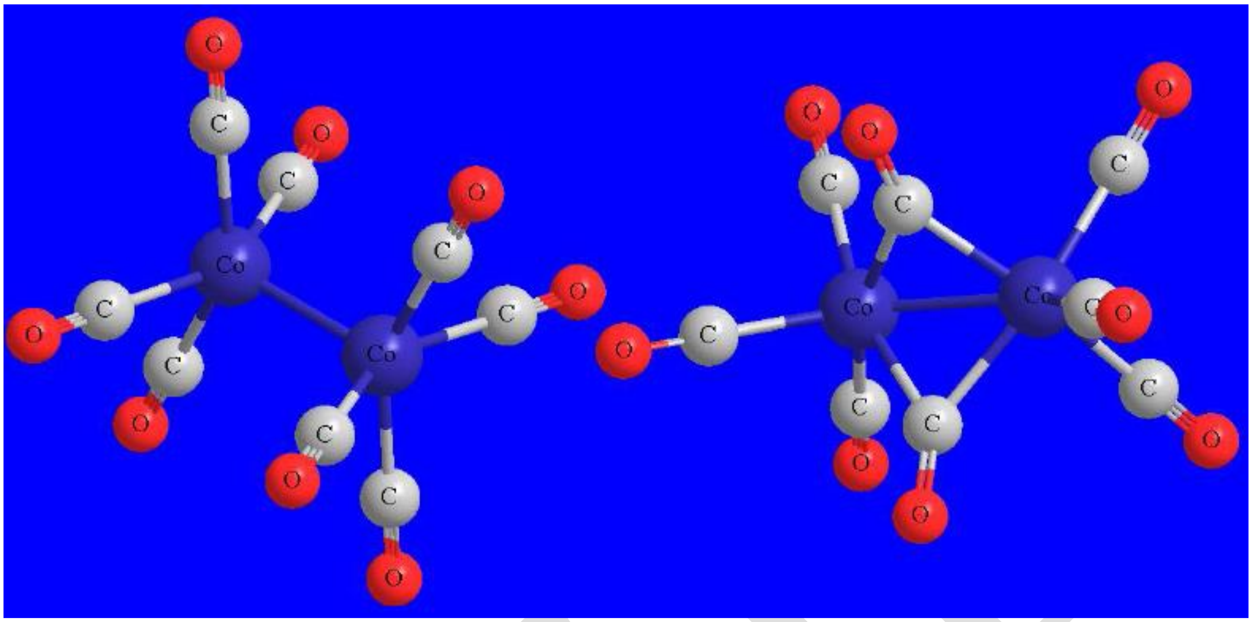
$$2\,Co_2(CO)_8 \xrightarrow{50^\circ C} Co_4(CO)_{12} + 4\,CO$$

It reacts with nitric oxide to form cobalt carbonyl nitrosyl

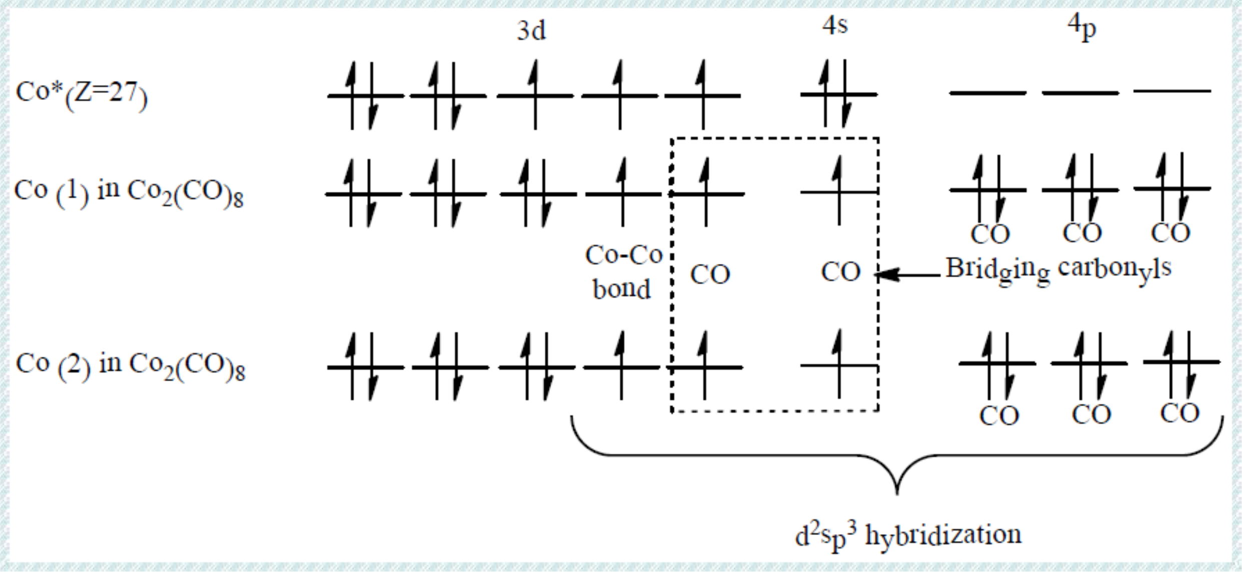
$$Co_2(CO)_8 + 2\,NO \rightarrow [Co^{-}(CO)_8(NO)^{+}]^0 + 2\,CO$$



Dicobalt octacarbonyl is known to exist in two isomeric forms. A bridged structure of this molecule is observed in the solid state as well as solution state at a very low temperature. A non - bridged structure predominates in a solution at temperatures above ambience

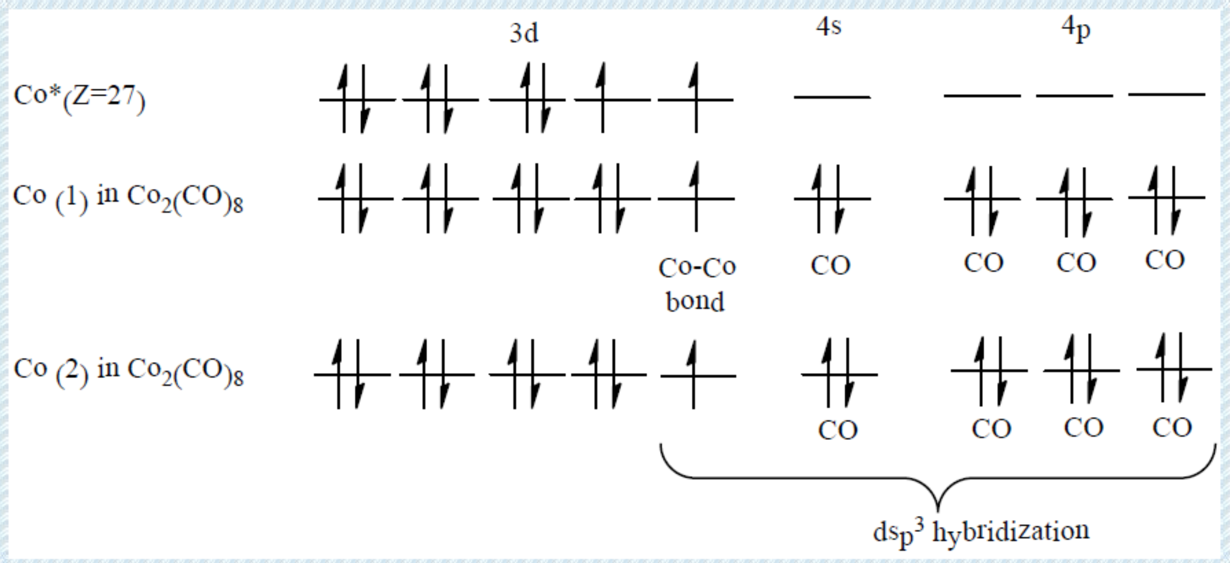


In the bridged structure, the cobalt atoms are in d2sp3 hybrid state. Three such hybrid orbitals on each cobalt atom accept lone pair of electrons from three carbon monoxide molecules to form total six Co←CO coordinate bonds. A Co-Co bond is formed by the overlapping of two half - filled d2sp3 hybrid orbitals on the cobalt atoms. Remaining two half–filled hybrid orbitals on each Co atom overlap with appropriate orbital on carbon atom of the carbonyl to form two bridging CO groups. Thus, all electrons in this molecule are paired and it is diamagnetic.



In the structure without bridge, the cobalt atoms are in dsp3 hybrid state. Out of the five hybrid orbitals on each cobalt atom, four orbitals on each cobalt atom accept a lone pair of electrons from the carbon monoxide molecules to form eight Co←CO coordinate bonds. One half–filled orbitals on each cobalt overlap to form a Co-Co bond

In case of non-bridge structure, Co atoms have dsp3 hybridization as shown below



dsp3 hybridization in dicobalt octacarbonyl

Fe2 (CO) 9, Diiron nonacarbonyl

Preparation:

Cold solution of iron pentacarbonyl in glacial acetic acid undergoes dimerization under the influence of ultra-violet light to give golden yellow crystals

$$2\,Fe(CO)_5 \xrightarrow{h\nu} Fe_2(CO)_9 + CO$$

Properties:

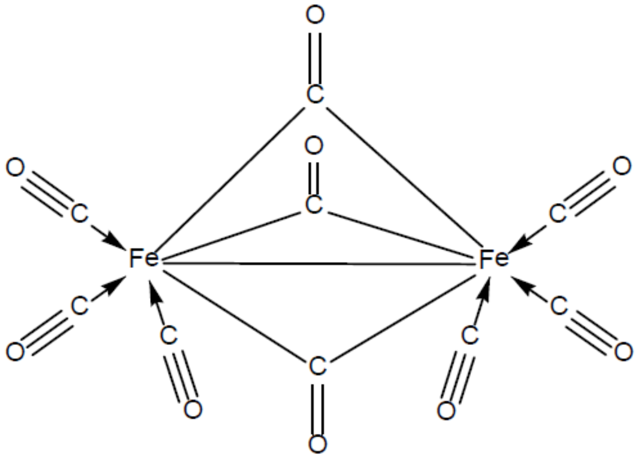
Diiron nonacarbonyl forms golden yellow triclinic crystals melting at 100 oC.

It is insoluble in water but soluble in toluene and pyridine.

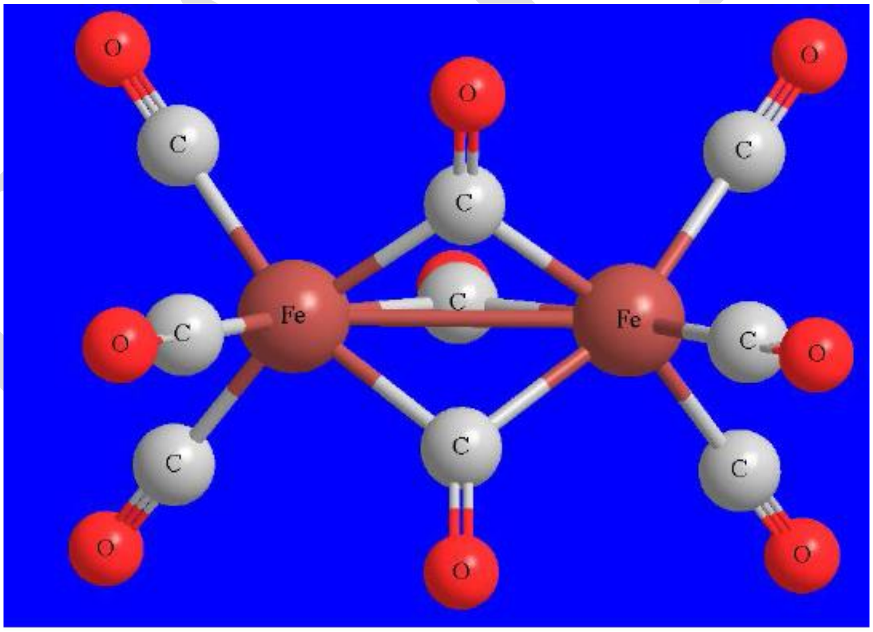
A solution of diiron nonacarbonyl in toluene disproportionates when heated to 70 oC

$$3\,Fe_2(CO)_9 \xrightarrow{70^\circ C,\ Toluene} 3\,Fe(CO)_5 + Fe_3(CO)_{12}$$

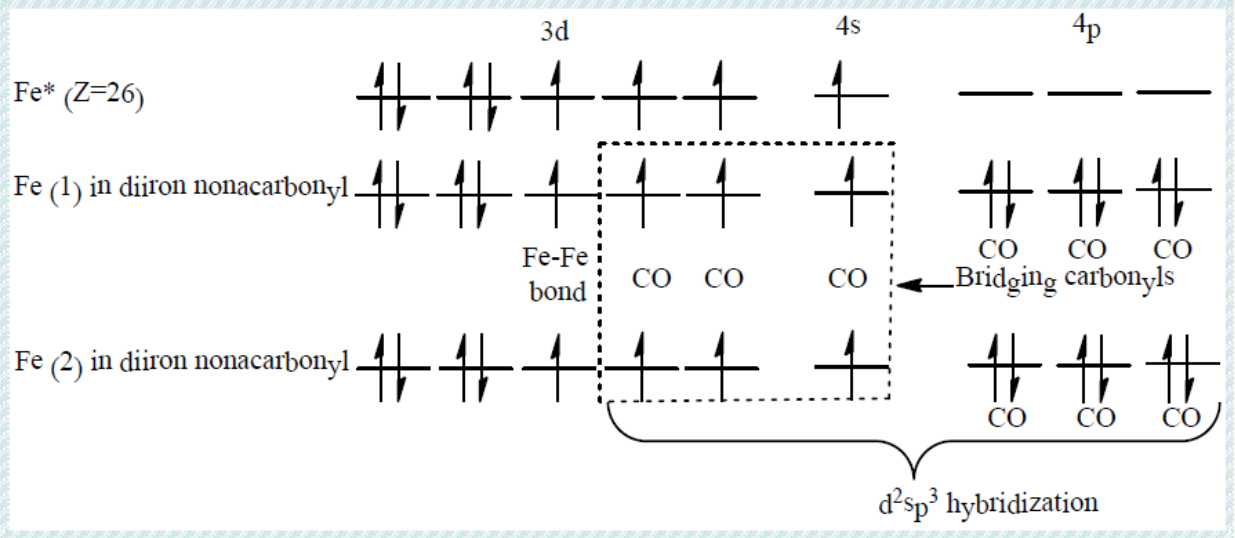
Structure:



Each of the iron atoms in diiron nonacarbonyl has three terminal carbonyl groups. The remaining three carbon monoxide ligands act as μ_2–CO groups. In addition to this, there is a weak Fe-Fe bond (2.46 Å) formed by sharing of two unpaired electrons present in the 3d orbitals of iron atoms. Thus, both the iron atoms in the molecule are identical with coordination number seven. Since the molecule does not have any unpaired electron, it is diamagnetic.



The structure of this molecule can be explained using d^2sp^3 hybridization in Fe atoms as shown in the figure.



d2sp3 hybridization in diiron nonacarbonyl

EFFECTIVE ATOMIC NUMBER (EAN) RULE:

Effective Atomic Number (EAN) is the total number of electrons surrounding the nucleus of a metal in a complex.

Sidgwick's EAN rule / Inert gas rule:

"The EAN of the metal atom in a stable complex is equal to the atomic number of a noble gas found in the same period of the periodic table."

Most of the organometallic compounds including carbonyls and nitrosyls obey the EAN rule.

It is mainly useful in predicting the number of ligands attached to the metal in such compounds.

Calculation of EAN:

An equation for calculating the EAN may be represented as follows:

EAN = Z + a + b + c

Where,

Z = Atomic number of metal atom

a = Number of electrons donated by terminal carbonyl groups

b = Number of electrons donated by bridging carbonyl groups

c = Number of electrons donated by other metal atom for the formation of M-M bonds

The EAN for nickel atom in nickel tetracarbonyl can be calculated as follows:

In nickel tetracarbonyl,

Z = Atomic number of metal atom = Atomic number of nickel atom = 28

a = Number of electrons donated by terminal carbonyl groups = 4 terminal carbonyl groups x 2 electrons donated by each group = 8

b = Number of electrons donated by bridging carbonyl groups = 0 (Because there are no bridge bonds)

c = Number of electrons donated by other metal atom for the formation of M-M bonds = 0 (Because there are no M-M bonds)

Thus,

EAN = Z + a + b + c = 28 + 8 + 0 + 0 = 36

Here, the effective atomic number is found to be 36 which is the atomic number of Krypton (Z=36) which is a noble gas lying in the same period of the periodic table as Ni (Z=28).

Thus, EAN rule is said to be obeyed in nickel tetra carbonyl.

In order to check the validity of the 18- electron rule, we have to put the number of valence electrons of the metal atom in place of atomic number (Z) in the EAN equation.

The valence shell nickel (Ni = 3d8 4s2) atom has 10 valence electrons.

Thus,

The number of valence electrons surrounding the nucleus of the metal atom

= Number of valence electrons of metal atom + a + b + c = 10 + 8 + 0 + 0 = 18

Thus, nickel tetracarbonyl obeys the 18 - electron rule.

The EAN for iron atoms in triiron dodecacarbonyl can be calculated as follows:

In triiron dodecacarbonyl, two iron atoms are bridged and have same environment while the third iron atom has a different bonding environment. Thus, we need to calculate the EAN for both the types of iron atoms separately.

For, bridged iron atoms

Z = Atomic number of metal atom = Atomic number of iron atom = 26

a = Number of electrons donated by terminal carbonyl groups = 3 terminal carbonyl groups x 2 electrons donated by each group = 6

b = Number of electrons donated by bridging carbonyl groups = 2 bridging carbonyl groups x 1electron donated by each group = 2

c = Number of electrons donated by other metal atom for the formation of M-M bonds = 2 Fe-Fe bonds x 1 electron donated by each Fe atom = 2

Thus,

EAN = Z + a + b +c = 26 + 6 + 2 + 2 = 36

Here, the effective atomic number is found to be 36 which is the atomic number of Krypton (Z=36) which is a noble gas lying in the same period of the periodic table as Fe (Z=26).

Thus, EAN rule is said to be obeyed by the bridging Fe atoms in triiron dodecacarbonyl.

In order to check the validity of the 18- electron rule, we have to put the number of valence electrons of the metal atom in place of atomic number (Z) in the EAN equation.

The valence shell nickel (Fe = $3d^6\ 4s^2$) atom has eight valence electrons.

Thus,

The number of valence electrons surrounding the nucleus of the metal atom

= Number of valence electrons of metal atom + a + b + c = 8 + 6 + 2 + 2 = 18

Thus, the bridging Fe atoms in triiron dodecacarbonyl obey the 18 - electron rule.

For, un-bridged iron atom,

Z = Atomic number of iron atom = 26

a = 4 terminal carbonyl groups x 2 electrons donated by each group = 8

b = 0 (Because no bridges are formed)

c = 2 Fe-Fe bonds x 1 electron donated by each Fe atom = 2

Thus,

EAN = Z + a + b + c = 26 + 8 + 0 + 2 = 36

Here, the effective atomic number is found to be 36 which is the atomic number of krypton (Z=36) which is a noble gas lying in the same period of the periodic table as Fe (Z=26).

Thus, EAN rule is said to be obeyed by the non-bridging Fe atom in triiron dodecacarbonyl.

In order to check the validity of the 18- electron rule, we have to put the number of valence electrons of the metal atom in place of atomic number (Z) in the EAN equation.

The valence shell of nickel (Fe = $3d^6\ 4s^2$) atom has 8 valence electrons.

Thus,

The number of valence electrons surrounding the nucleus of the metal atom

= Number of valence electrons of metal atom + a + b + c = 8 + 6 + 2 + 2 = 18

Thus, the non-bridging Fe atom in triiron dodecacarbonyl obeys the 18 - electron rule.

18 Electron Rule

The octahedral complexes obeying the 18-electron rule (18-electron compounds) are especially stable. In order to understand this, consider the energy level diagram of an octahedral complex in presence of a strong field ligand

Electron counting methods:

There are two popular methods giving same results for the electron count. They are Neutral Ligand method (Covalent method)

Donor Pair method (Ionic method)

Neutral Ligand method:

In this method, all the ligands are treated as electrically neutral. It takes into account the number of electrons it can donate in its neutral state. The neutral ligands capable of donating two electrons are designated as L. The ligands like Cl- which can donate one electron in their neutral state are designated as X type ligands. The ligand cyclopentadienyl (η5-C_5H_5) which is a five-electron donor is designated by a combined symbol L_2X. This method is easy to use when the ligands are properly designated. The over emphasis on degree of covalence along with negligence of the charge over the metal ion remain shortcomings of this method. Due to this, it becomes difficult to assign oxidation states to the metal ion resulting in the loss of important information related to the ligands.

The verification of 18-electron rule for a mixed ligand carbonyl complex (η5-C_5H_5)Fe$(CO)_2$Cl can be carried out as follows:

In this complex, the Fe atom has eight valence electrons.

In addition to this, the ligand η5-C_5H_5 when considered as a neutral ligand contributes five electrons.

CO is two-electron donor, thus two CO ligands contribute 4 electrons.

Cl, counted as a neutral species is single electron donor, which contributes one electron in total.

Thus the total electron count can be shown as below

One Fe atom	8 electrons
One (η^5-C_5H_5) ligand (L_2X)	5 electrons
Two CO ligands (L)	4 electrons
One chlorine ligand (X)	1 electron
Total electron count	**18 electrons**

An organometallic compound containing ligands designated by L and X can be shown as $[MX_aL_b]^c$, where a is the number of ligands of type X, b is the number of ligands of type L and c is the charge over the complex.

Electron Count = n + a + 2b – c, where n is the group number of the metal in periodic table.

(η^5-C_5H_5)Fe(CO)$_2$Cl can be represented as [(L_2X)M(2L)(X)] or [MX_2L_4]

Electron Count = n + a + 2b – c = 8 + 2 + 2 x 4 – 0 = 18

Donor Pair method:

According to this method, some ligands are treated as neutral whereas the others are treated as charged. It is assumed that the ligands donate electrons only as pairs. Neutral ligands like CO are considered as two electron donors. Ligands like halides are considered to take an electron from metal and treated as X^-. The ligand (η^5-C_5H_5) is considered as $C_5H_5^-$, which becomes a six-electron donor.

The oxidation state of the metal is calculated as total charge over the complex minus charges over the ligands. The number of electrons contributed by metal is calculated as the group number minus its oxidation number. Finally, the electron count is done as the total of electrons on the metal and the electrons contributed by the ligands.

A sample calculation for (η^5-C_5H_5)Fe(CO)$_2$Cl is provided below:

Here oxidation state of Fe, can be calculated as

-1 + X + 0 -1 = 0

X = +2

The group number of Fe is 8.

Therefore, number of electrons contributed by Fe is 8 - 2 = 6.

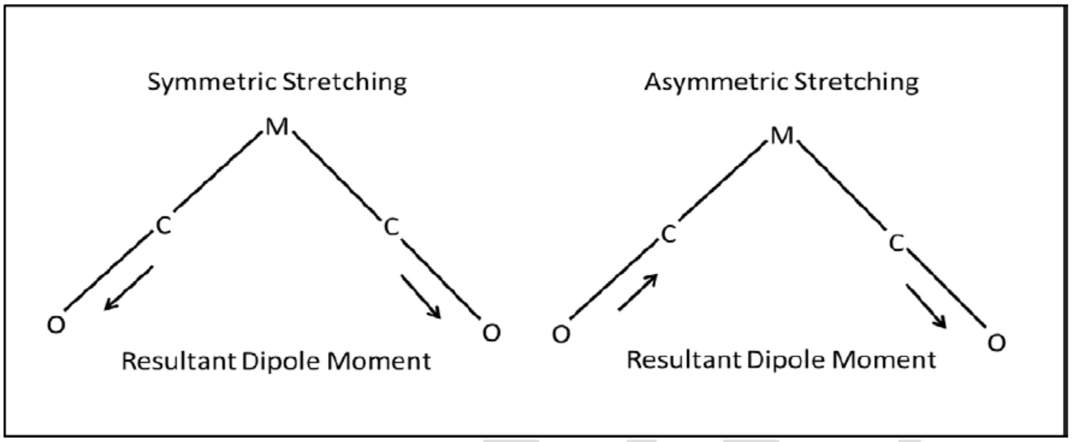
Number of electrons contributed by one $C_5H_5^-$ = 6.

Number of electrons contributed by two CO = 4.

Number of electrons contributed by one Cl- = 2

INFRARED SPECTROSCOPY

The carbonyl groups can have two modes of stretching



Since both of these modes result in change in dipole moment, two bands are expected in the infrared spectra of a terminally ligated carbon monoxide.

The infrared and Raman spectroscopy together can be used to determine the geometry of the metallic carbonyls.

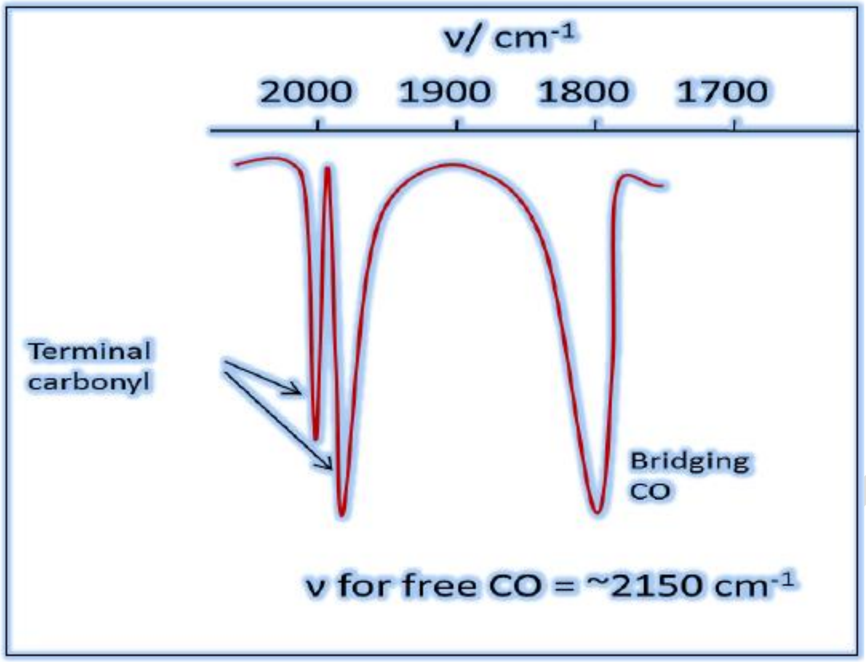
A mono nuclear pentacarbonyl can exist both in square pyramidal and trigonal bipyramidal geometry. Performing infrared spectra after calculating the IR active and Raman active bands in both the possible geometries can provide information about the actual geometry of the molecule Infrared spectroscopy of metallic carbonyls helps in determining the bond order of ligated carbon monoxide.

The C-O bond order and the frequency related to its absorption are directly proportional. Thus, it can be predicted that the frequencies of absorption will be in the order shown below:

Free CO > metal carbonyl cation > neutral metal carbonyl > metal carbonyl anion.

The C-O bonding in terminal carbonyl groups is stronger than the bridged carbonyl groups. Therefore, it is possible to differentiate the terminal carbonyls which absorb in the region of 2050–1900 cm-1 from the bridged carbonyls absorbing below 1900 cm-1.

The change in the intensity of bands related to carbonyl group can provide information for the kinetic studies of the substitution reactions involving replacement of carbonyls



Carbonyl	*Type*	*C-O stretching frequency (cm-1)*
Carbon monoxide	Free	~2150
Mn(CO)6+	Cation	~2090
Cr(CO)6	Neutral	~2000
V(CO)6-	Anion	~1850

Possible Questions

PART-B (6 Mark Questions)

1. Write three different organometallic compounds and draw the structure
2. Explain the general classification of metal carbonyls with examples
3. Account the synthesis method of metal alkyl complexes
4. Explain α and β elimination process
5. States the bonding of alkenes to transition metals
6. Discus the Wacker process with mechanism
7. Explain the Ferrocene structure, bonding and reactivity
8. What are the group 4 metallocene? Why they act as catalyst?
9. Discuss the carboxylation of methanol-mono acetic acid process
10. Organometallic mechanisms discussed in the context of homogeneous catalytic systems.

PART-C (10Mark Questions)

1. Write the following
    - I. Draw the structure of Zesis's salt? Explain the bonind
    - II. Describe synthesis of Ferrocene?
    - III. What are Grubbs' catalysts? Give example
    - IV. What is agostic interaction?

DEPARTMENT OF CHEMISTRY

Online questions (Multiple choice questions)

ORGANOMETALLICCHEMISTRY (17CHP205C)

UNIT I

S.No	**Questions**	**Option-A**	**Option-B**	**Option-C**	**Option-D**	**Answer**
1.	Geometry of [Cr((CO)6] is	Octahetral	Tetrahetral	Square pyramidal	Triangular bipyramidal	Octahetral
2.	The total number of electrons present in the atom of the metal forming the complex , including those gained electrons by sharing in the formation of complex is called	Effective atomic number	Effective molecular number	Exclusive atomic number	18 electron	Effective atomic number
3.	The geometry of Fe(CO)5 is	Trigonal pyramidal	Trigonal bipyramidal	Square planar	tetrahedral	Trigonal bipyramidal
4.	The magnetic property of V(CO)6 is	Diamagetic	Paramagnetic	Ferromagnetic	Non-magnetic	Paramagnetic
5.	The physical properties of the metal alkoxides depend on the ----- and ------- of the alkyl group	Size & Shape	Valency & Size	Shape &Valency	Carbonyate ions	Size & Shape
6.	The reaction of Vaskas complex with molecular hydrogen has a characteristic of an -----	Reductive elimination	Oxidative addition	Oxidative elimination	Octahetral	Oxidative addition
7.	An example of oxidative addition is the reaction of ------ molecular hydrogen	Vaskas complex	Octahedral complex	tetrahedral complex	Hydride	Vaskas complex
8.	Vaskas compound absorb oxygen and become ------ colour	Yellow	Orange	Red violet	Green	Orange
9.	carbonyl hydrido complexes are formed by the acidification of -----	Carbonyate ions	Carbenes	carbines	Alkynes	Carbonyate ions
10.	Which of the following act as hydride donars	BH4	CH3	C2H5	NaHSO4	BH4
11.	Complexes with coordinated hydrogen atom are	Hydro compounds	Hydroxide	hydrochloride	Hydride	Hydride
12.	Which does not form the source of hydrogen	NaH	BH4	LiAlH4	H2O	H2O

13.	Metal hydride complexes acts as	Retarding agents	Oxidising agents	reducing agents	Dehydrogenating agents	reducing agents
14.	Double dihydro bridge are found in	B2H6	BH4	NH3	H2Cr(CO)5	B2H6
15.	When dinitrogen functions as a bridging ligand , it usually exhibits ------ coordination	End-on	Side-on	Axial	Urea	End-on
16.	Anionic carbonyl halides are obtained when metal carbonyls are treated with	Carbonyl hydrides	Ionic halides	Radical halides	Nitrosyls	Ionic halides
17.	The general formula for Carbonyl halides is	MX(CO)YX2	HMX(CO)YX2	MX(CO)YN2	MX2	MX(CO)YX2
18.	Mn(CO)5Cl heated in organic solvents at 1200 c it loses	CO2	COCl2	CO	MnCO3	CO
19.	Carbonyl halides react with NH3 to form -----	Amines	Amides	Urea	Thiourea	Urea
20.	Phosgene is also known as -------	Carbonyl bromide	Carbonyl chloride	Carbonyl iodide	Carbonyl fluoride	Carbonyl chloride
21.	Carbonyl chloride is produced in large quantities to make -------	Benzene	Toluene	Xylene	Toluene di isocyanate	Toluene di isocyanate
22.	Isocyanides are better sigma donar and poorer ----- acceptor than carbonyl group complexes.	sigma acceptors	pi donars	pi acceptors	Urea	pi acceptors
23.	Which one of the following is an important building block for the synthesis of many compounds?	Carboxyhemoglobin	Carbon monoxide	Carbonylate	Carbon-di-oxide	Carbon monoxide
24.	Cyanide will preferentially leach sulfide minerals and will react with sulfur to produce ?	Thiocyanate	Potassium cyanide	Sulfocyanate	Hydrogen cyanide	Thiocyanate
25.	Which one of the following salt has a more complex cluster structure?	Sodium salt	Black-T	Potassium salt	Roussin's black	Roussin's black
26.	Metal carbonyls generally have poor solubility with ?	Water	Alcohol	Solvent	Alcohol	Water
27.	The most important technique for characterizing metal carbonyls is ?	UV spectroscopy	Mass Spectroscopy	Infra-red spectroscopy	NMR spectroscopy	Infra-red spectroscopy
28.	All metal carbonyls undergo substitution by ?	Organophosphorus ligands	Phosphine ligands	Ligands	Metal	Organophosphorus ligands

29.	Typical isocyanide ligand is ?	CO	NO	MeNC	CN	MeNC
30.	Metal nitrosyl complexes are complexes that contain ?	Nitric oxide	Nitrosyl	Metal	MeNC	Nitric oxide
31.	Metal nitrosyls are?	Physically important	Mechanically important	Chemically important	Biologically important	Biologically important
32.	Which one of the following is typically adopt one of two bonding modes?	Metal nitrosyl	NO	O2	MeNC	NO
33.	NO ligands can arise by oxidative degradation of other ?	Nitrogen ligands	Cabon ligands	Oxygen ligands	Hydrogen ligands	Nitrogen ligands
34.	Nitrogen is more electronegative than ?	Hydrogen	Oxygen	Carbon	NO	Carbon
35.	The nitroprusside anion,[Fe(CN)5NO]2−, a mixed nitrosyl cyano complex, has pharmaceutical applications as a slow release agent for ?	CN	Fe	NO	C	NO
36.	Which one of the following is an ambidentate ligand?	NO	NO2	Fe	CN	NO2
37.	Which one of the following is highly paramagnetic?	[Ni(CO)4]	[FeF6]3‾	[Ni(CO)4]	[CoF6]3‾	[CoF6]3‾
38.	The Carbonyls which contain more than one metallic atoms are known as ----	Polydentate	Polynuclear	Bidentate	Mononuclear	Polynuclear
39.	[MnRe(CO)9] is an example for	Mononuclear Carbonyl	Homonuclear	Heteronuclear	carbon	Heteronuclear
40.	When Fe is directly reacted with CO at 2000C,100 atm.pressure it gives	Fe(CO)8	Fe(CO)3	Fe(CO)6	Fe(CO)5	Fe(CO)5
41.	When Ni reacted directly with CO at 2000C,100 atm. pressure it gives	Ni(CO)8	Ni(CO)4	Ni(CO)5	Ni(CO)6	Ni(CO)4
42.	When Co reacted directly with Co at 2000C,100 atm. pressure it gives	Co2(CO)8 Co(CO)8		Co3(CO)8	Co2(CO)6	Co2(CO)8 Co(CO)8
43.	The hybridization involved in the complex [Ni(CO)4] is	sp3	sp2	dsp2	dsp3	sp3

44.	Which one is an example for binuclear complex	Mn2(CO)8	Mn2(CO)10	Mn(CO)10	Mn2(CO)6	Mn2(CO)10
45.	Which one is an example for Trinuclear carbonyl	Fe3(CO)12	Co(CO)12	Fe2(CO)12	Fe (CO)12	Fe3(CO)12
46.	The anionic carbonyl complexes are known as -----	Carbonium ion	carbonylate ions	Carbanion	carbenium ion	carbonylate ions
47.	Example for carbonylate ion is	[Co(CO)12] [Co(CO)12]+ [Mn(CO)5]¬- [Mn(CO)5]+		[Mn(CO)5]-	[Mn(CO)5]+	[Mn(CO)5]-
48.	Mn2(CO)10 + H2 →	2Mn(CO)5 Mn(CO)10		2HMn(CO)5	Mn(CO)5	2HMn(CO)5
49.	The allyl group which can function as an one electron donar is known as	Monohapto	Dihapto	Trihapto	Tetra hapto	Monohapto
50.	Metal nitrosyls, compounds have	NO ligands	CO ligands	alkyl ligand	aryl ligand	NO ligands
51.	NO ligand is a stronger pi acceptor than	CO ligands	alkyl ligand	aryl ligand	alkene ligand	CO ligands
52.	Find out one is nitrosyl carbonyls compounds	Ni(CO)4	Rh2(CO)8	Rh4(CO)12	CoNO(CO)3	CoNO(CO)3
53.	Which is not metal dinitrogen compound	CoNO(CO)3	IrCl(N2)(PPh3)2	{[Ru(NH3)5]2(μ-N2)}4+	[FeH(N2)(dmpe)2)]+	IrCl(N2)(PPh3)2
54.	Which is not metal phosphene compound	Fe(PF3)5	Co2(PF3)8	Co2(PH3)8	Fe(CO)5	Fe(CO)5
55.	Which one is not metal dioxygen complexe	Myoglobin	hemoglobin	hemerythrin	vaska compounds	vaska compounds
56.	Myoglobin and hemoglobin are famous examples	Dinitrogen complexes	Dioxygen complexes	Inorganic complexes	Metal carbonyls	Dioxygen complexes
57.	Binding of O2 is usually described as proceeding via ………...from the metal(II) center	Electron transfer	Proton transfer	Oxygen transfer	Nitrogen transfer	Electron transfer
58.	The reaction given below is an example of $[(CO)_5Mn(Me)] + CO \rightarrow [(CO)_5Mn\{C(O)(Me)\}]$	oxidative addition	electrophilic substitution	nucleophilic substitution	migratory	oxidative addition
59.	Metal carbonyls are used in a number of industrially	chlorination	hydration	carbonylation	hydration	carbonylation

	important ………….. reactions					
60.	$CrCl_3 + Al + 6\ CO \rightarrow Cr(CO)_6 + AlCl_3$ This reaction is	oxidation	reduction	formylation	lithiation	reduction

UNIT- II
SYLLABUS

Stability and structure - synthesis by alkylation of metal halides - by oxidative addition - by nucleophilic attack on coordinated ligands - metal alkyl and 18 electron rule - reactivity of metal alkyls - M-C bond cleavage reactions - insertion of CO to M-C bonds - double carbonylation - insertions of alkenes and alkynes - insertions of metals with C-H bonds - alkylidene and alkylidyne complexes - synthesis of alkylidene complexes in low oxidation states and in high oxidation states - bonding in alkylidene complexes - synthesis and bonding in alkylidyne complexes - reactivity of alkylidene and alkylidyne complexes.

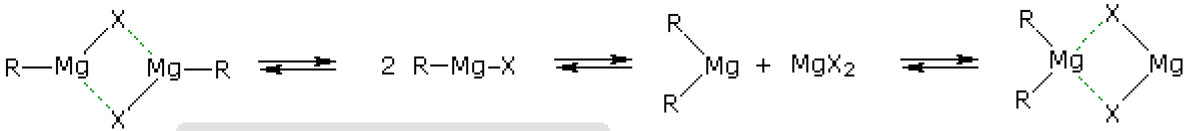
Organic compounds incorporating carbon-metal bonds are called organometallic compounds. Such compounds have been known and studied for nearly 200 years, and their unique properties have been widely used to effect synthetic transformations. Depending on the reduction potential of the metal, the reactivity of organometallic compounds varies markedly, the most reactive requiring low to moderate temperatures and inert conditions (atmosphere and solvents) for preparation and use. In general, the reactivity parallels the ionic character of the carbon-metal bond, which may be estimated from the proton and carbon chemical shifts of methyl derivatives.

% Ionic Character of H_3**C – M**etal $(CH_3)_2Hg < (CH_3)_2Cd < (CH_3)_2Zn < (CH_3)_2Mg < CH_3Li$

The first reported organometallic compounds were prepared by the reductive substitution of alkyl halides, as shown in the following three equations. All these metals have strong or moderate negative reduction potentials, with lithium and magnesium being the most reactive. Halide reactivity increases in the order: Cl < Br < I. Alkylsodium and potassium compounds are not made in this way because Wurtz coupling of the alkyl moiety (giving R–R) tends to predominate. This can also be a problem when allyl or benzyl halides are converted to Grignard or lithium reagents.

Simple alkyl derivatives of all three kinds are pyrophoric (burn spontaneously on exposure to air) and react with water to generate the corresponding alkane (RH); however, the zinc compounds are distinctly less reactive in other respects. Diethylzinc may be prepared and distilled (b.p. 117 ^{o}C) under a protective atmosphere of CO_2. Grignard and alkyl lithium reagents are not distillable liquids, and react rapidly with CO_2 to give carboxylic acid salts.

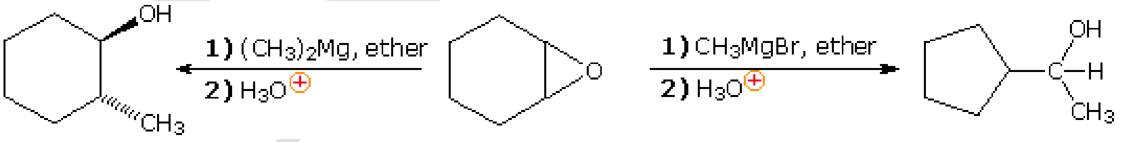
Although the formulas drawn here for the alkyl lithium and Grignard reagents reflect the stoichiometry of the reactions and are widely used in the chemical literature, they do not accurately depict the structural nature of these remarkable substances. Mixtures of polymeric and other associated and complexed species are in equilibrium under the conditions normally used for their preparation. For example, simple alkyl lithiums are largely hexameric clusters in hydrocarbon solvents, but change to tetrameric and dimeric forms in various ether solvents. Grignard reagents require an ether solvent for their formation, and have been crystallized as monomeric and dimeric ether complexes. The following equilibrating species, called the Schlenk equilibrium, have been identified in ether solution.



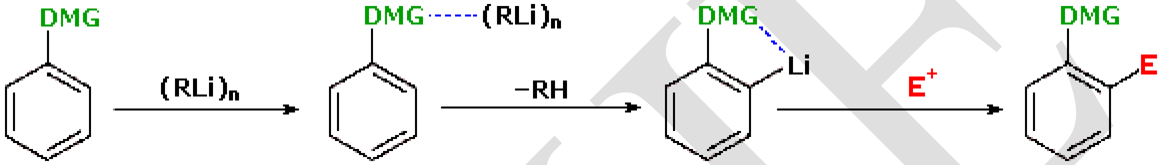
Note, ether solvation is not shown

Since magnesium halides are moderate Lewis acids, their presence in solution may influence the outcome of certain chemical reactions. One example of this perturbation is the reaction of cyclohexene oxide with methylmagnesium bromide, as shown on the right in the following equation. Magnesium bromide rearranges the epoxide to cyclopentanecarbaldehyde, which then adds the Grignard reagent in the expected manner. Dimethylmagnesium, on the other hand, simply adds to the epoxide by opening the strained ring. Methylithium adds in a similar fashion.

Pure dialkylmagnesium reagents may be prepared by alternative routes (vida supra), or by removing the magnesium halide by precipitation (dioxane is added).



Among the most useful reactions for the synthesis of complex molecules are those that achieve direct selective functionalization of a hydrocarbon moiety. Since organometallic reagents function as powerful nucleophiles, selective metal hydrogen exchange, **Metalation**, would represent a powerful first step to that end. The organometal species produced in this way could then react with a variety of common electrophilic reagents (e.g. alkyl halides, carbonyl compounds and halogens). However, with the exception of terminal alkynes such metalations are rare and usually non-specific. Thanks to the seminal work of V. Snieckus (University of Waterloo, Ontario, Canada) the ortho-lithiation of functionally substituted aromatic rings has proven to be a powerful technique for regioselective synthesis. The following equation illustrates this **Directed ortho Metalation (DoM)** reaction, where **DMG** refers to a directing metalation group and **E**$^+$ is an electrophile.



Electrophilic substitution of aromatic rings generally gives a mixture of ortho and para substitution products when an existing substituent activates the ring or meta products when the substituent is deactivating. In the case of anisole the methoxy substituent is a strongly activating group. Electrophilic iodination by the action of molecular iodine in the presence of sodium nitrate and acetic acid (a source of iodinium cation) gives a high yield of para-iodoanisole. By clicking once on the equation, iodination via directed ortho metalation of anisole will be shown. The ortho isomer is the sole product provided excess iodine is avoided. The strongly deactivating sulfonic acid substituent is easily converted to a DMG by amide formation. Clicking the above equation a second time shows the DoM of such an amide. Direct electrophilic substitution would normally occur at the meta position, so the action of the amide DMG is particularly noteworthy. A similar amide derivative of a carboxylic acid substituent may be used for DoM, as shown in the following diagram.

Reactions of Simple Organometallic Compounds

Reactions of organometallic compounds reflect the nucleophilic (and basic) character of the carbon atom bonded to the metal. Consequently, the most common reactions are electrophilic substitutions and additions to unsaturated electrophiles. The electropositive nature of the metal atom or group is an important factor influencing the reactivity of these reagents. Alkyllithium (

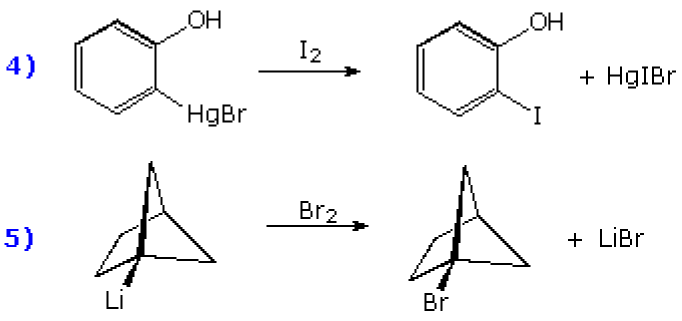
and sodium) compounds are the most reactive of the commonly used compounds in this class, having metal-carbon bonds that are roughly 30% ionic. The carbon-magnesium bond of Grignard reagents is about 20% ionic, and they have proven to be somewhat less reactive. Dialkylzinc reagents have significantly reduced reactivity, and fail to react with carbon dioxide, esters and many aldehydes and ketones. Alkylmercury and lead compounds are the least reactive commonly studied organometallics. The ionic character of the carbon-mercury bond is estimated to be less than 10%. Such compounds react with mineral acids, but not with water or alcohols.

Some examples of the reactions of organometallic compounds with a variety of electrophilic functions are provided in the following three-part chart. The first page of examples show three kinds of electrophilic substitution reactions. The proton is the most common electrophile, and it is well known that reactive organometallic compounds (alkyllithium and Grignard reagents) do not tolerate acidic functional groups such as OH and NH. Ethyl acetoacetate (example 3) has two carbonyl functions which are potential addition sites, but the acidity of the doubly activated methylene group dominates the reactivity. Dialkylmercury compounds are much less reactive, and can be mixed with water or alcohol without change. Examples of halogenation and alkylation are provided in groups II and III. Some alkylation reactions involve free radical intermediates, but most (as shown) may be regarded as modified S_N2 reactions in which metal coordination to the leaving halide (or sulfate) plays an important role.

II. Reaction with Electrophilic Halogen

4)

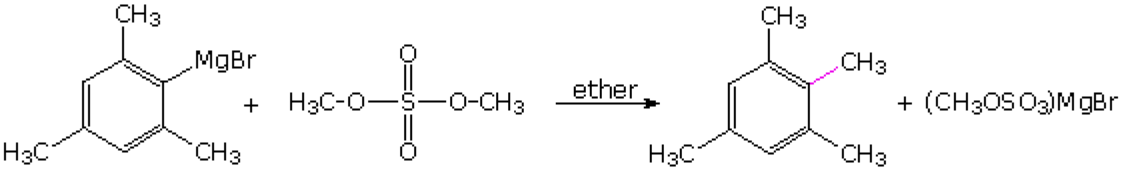
5)



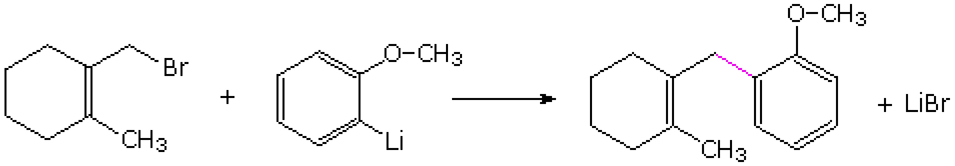
III. Other Electrophilic Substitutions

6) $C_6H_5\text{-}MgBr + CH_2{=}CHCH_2\text{-}Br \xrightarrow{\text{ether}} C_6H_5\text{-}CH_2\text{-}CH{=}CH_2 + MgBr_2$

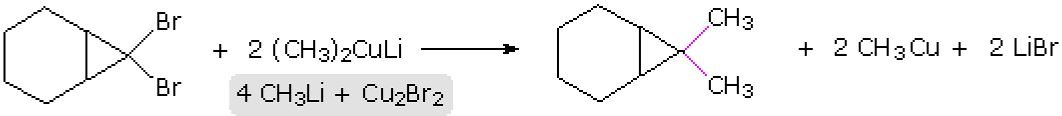
7)



8)



9)



Organometallic compounds having significant carbanion-like behavior are subject to oxidation (electron abstraction) by suitable cations. Two such oxidative couplings are shown in part IV. These serve as a reminder that oxidative conditions should be avoided when using reactive organometallic compounds. The formation of peroxide derivatives on exposure to oxygen presumably takes place by a similar radical coupling ($R\bullet + O_2\bullet^{(-)}$).

The most important and widely used reaction of of organometallic reagents is undoubtedly their addition to carbonyl and nitrile functional groups. Six examples are given in part V, the new C-C bond is colored magenta in each case. Aldehydes, other than formaldehyde, add Grignard and alkyllithium reagents to form 2°-alcohols. Ketones and esters react to give 3°-alcohols (examples 12 & 14). Similar reactions with nitriles (example 16) usually lead to ketones (after hydrolysis), since the intermediate C=N salt is less reactive than a carbonyl group. By working at low temperature, normally incompatible groups may survive in the product. This approach is illustrated in example 15, where 3-bromobenzonitrile is lithiated by a low temperature metal-halogen exchange, and this potentially unstable species immediately reacts with an anhydride to produce a ketone. Similarly selective reactions may be accomplished by using less reactive organometallic reagents, as in examples 13 & 17. Zinc and cadmium compounds are relatively unreactive with esters, as the outcome demonstrates.

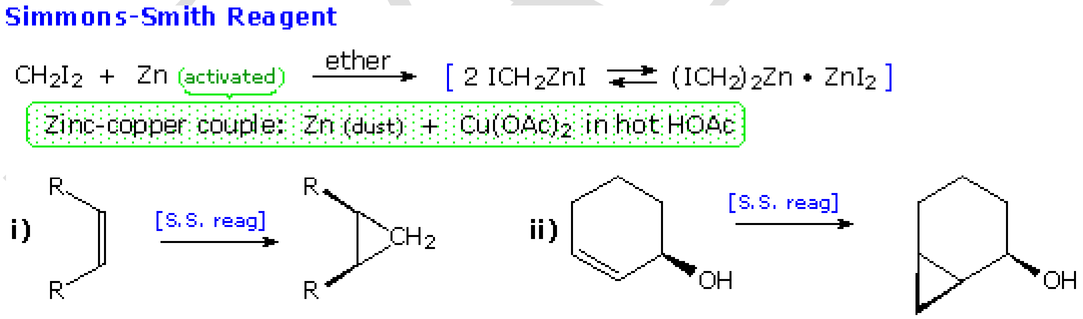
The examples in group VI on the third page illustrate addition reactions to epoxides, carbon dioxide and carbon double bonds activated by conjugation with carbonyl groups. Nucleophilic addition reactions to α,β-unsaturated ketones may take place in two ways: 1,2-addition to the carbonyl function, or 1,4-conjugate addition to the enone. Simple alkyllithium reagents usually add in the 1,2-fashion, but the presence of cuprous salts or the use of Gilman's reagent directs addition in the 1,4-fashion (examples 20 & 21). When the carbonyl function of a ketone is sterically hindered, branched Grignard reagents may react by a hydride transfer mechanism to give a 2º-alcohol corresponding to the ketone (reaction 22). Reductions of this kind are often conducted with aluminum alkoxide salts, and are called Meerwein-Ponndorf-Verley reductions.

Finally, examples 23 & 24 on the third page show facile rearrangements that allyl and homoallyl Grignard reagents are known to undergo. The 2-butenyl-1- magnesium bromide (crotyl Grignard) on the left in equation 23 is in equilibrium with a smaller amount of its 1-butenyl-3-magnesium bromide isomer. Although the crotyl form predominates, it usually reacts by the cyclic transition state shown in brackets to give methallyl addition products. It should also be noted that, regardless of equilibration rates, the carbon-metal bonds in allylic Grignard and zinc reagents are localized in the manner of conventional σ-bonds; whereas the corresponding sodium, potassium and lithium reagents exhibit significant metal bonding to both ends of the allyl moiety in a π-like fashion.

Organometallic Reagents from Geminal Dihalides

The successful preparation of organometallic reagents from dihalides is dependent on the number of carbon atoms separating the halogen groups. For example, 1,4-dibromobutane and para-dibromobenzene react with excess magnesium in ether to generate di-Grignard reagents that may be used in the same manner as any simple Grignard reagent. In the case of para-chlorobromobenzene, the greater reactivity of bromine permits the preparation of para-chlorophenylmagnesium bromide in good yield. When the halogens are separated by only three carbon atoms, three-membered ring formation is common, as in the preparation of cyclopropane from 1,3-dichloropropane by treatment with zinc dust and sodium iodide. It is not surprising then to find that vicinal-dihalides undergo rapid beta-elimination to alkene products when treated with magnesium or zinc. Indeed, this is a useful elimination procedure for vicinal dihalides and related compounds. Reaction of magnesium or zinc with small amounts of 1,2-dibromoethane has been used to activate the metal surface for subsequent reaction with a more sluggish alkyl halide. Ethylene gas is the only organic product formed in this activation stage. In contrast, geminal dihalides, such as methylene iodide and bromide, have proven to form some uniquely useful organometallic reagents, a few of which are described below. When zinc metal is used, it must be activated, often by forming a zinc-copper couple or alloy immediately prior to its use.

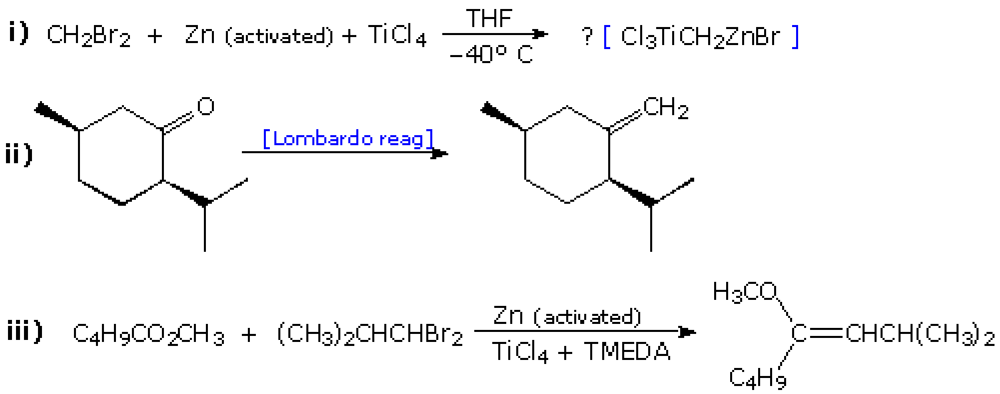
The Simmons-Smith reagent, first prepared by DuPont chemists, is perhaps the best known of these "carbenoid" reagents (so named because metal-halogen loss would result in a carbene species). This ether soluble substance is thought to be an equilibrium mixture of the compounds written in the blue brackets. The chief use of this reagent is the conversion of alkenes to cyclopropanes by CH_2 addition. The addition is stereospecific and suprafacial, so cis alkenes give cis-substituted cyclopropanes, as shown. Neighboring hydroxyl groups appear to coordinate with the reagent, directing the addition to the nearest face of the double bond (example ii) Lombardo's reagent, and several similar organotitanium compounds (e.g. Tebbe's reagent) act to methylenate carbonyl groups



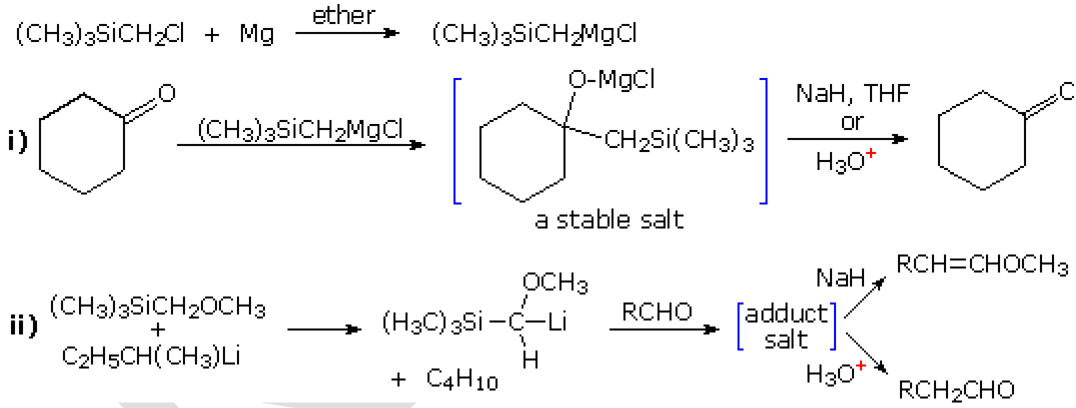
In this sense they mimic Wittig reagents. Because they are less basic than the alkylidenenephosphorane Wittig reagents, Lombardo reagents do not epimerize sensitive ketones, such as used in reaction (ii). Also, enol ether products may be obtained from esters (example (iii). Another Wittig-like reagent, trimethylsilylmethylmagnesium chloride, has been described by Peterson. The initial adduct of this Grignard reagent is a stable salt, which may eliminated by treatment with acid or by exchange of magnesium with an alkali metal cation. The elimination of $(CH_3)_3SiOZ$ (where Z is H or Na) is often stereospecific, being anti with acid and syn with NaH.

Other geminally substituted organometallic reagents have proven useful for the addition of carbinol or methylamino groups.

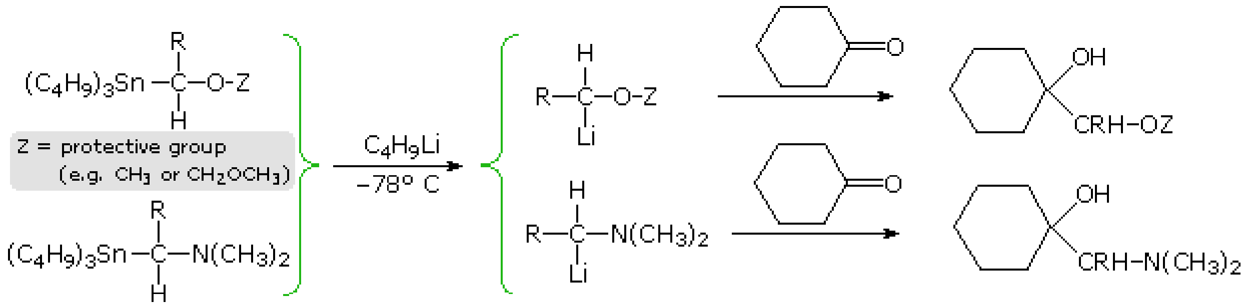
Lombardo's Reagent

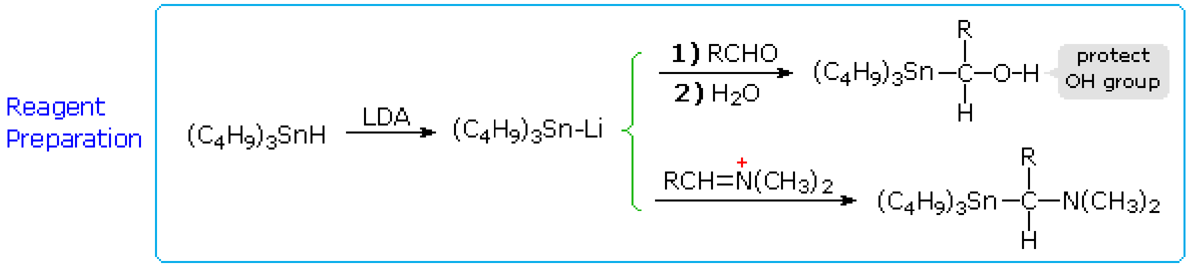


Peterson Reaction



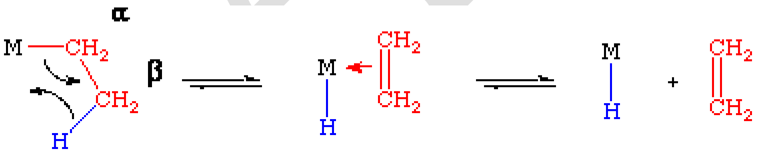
The following equations illustrate two such applications. The necessary functionalized organolithium reagents are prepared by metal-metal exchange with corresponding trialkyltin compounds, which in turn are made by way of lithiated tin reagents (shown in the light blue box). By converting these lithium reagents to Gilman (cuprate) reagents, conjugate addition to enones may be accomplished

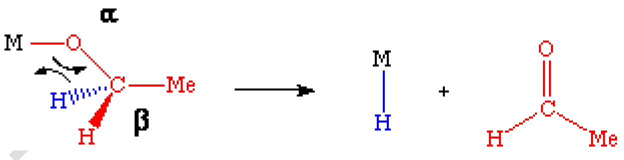




Metal Carbon Cleavage reactions

Beta-hydride elimination is a common reaction in organometallic chemistry. The reaction is simply the transfer of a hydride (hydrogen atom) from the beta-position on a ligand to the metal center. While most common in alkyl complexes, it is also observed with other ligands, one example being alkoxide ligands bound to late transition metal complexes:





The mechanism shown indicates a four-center transition state in which the hydride is transferred to the metal. In some cases, the unsaturated fragment that is formed will remain bound to the metal and in other cases it will either not bind or be displaced by a stronger donor ligand.

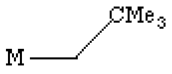
An important prerequisite for beta-hydride elimination is the presence of an open coordination site on the metal complex. If no open site is available, then it will be necessary to displace a ligand before the reaction can occur. In addition, the metal complex will usually have less than 18 electrons, otherwise a 20 electron olefin-hydride would be the immediate product.

The microscopic reverse of a beta-hydride elimination is called an olefin insertion reaction. In many systems there is a rapid, reversible equilibrium between the alkyl complex and the alkene-hydride that results from beta-elimination. Beta-elimination is a very important chain termination step in the polymerization of olefins, in the hydrozirconation reaction and in a variety of catalytic processes.

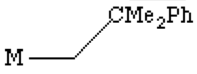
In order to prevent beta-elimination from taking place, one can use alkyls that:

- Do not contain beta-hydrogens.
- Are oriented so that the beta position cannot access the metal center.
- Would give an unstable alkene as the product.

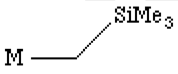
A few of these are shown below:



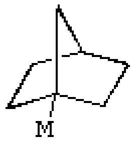
neopentyl



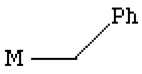
neophyl



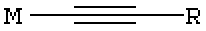
"silyl-neopentyl"



norbornyl

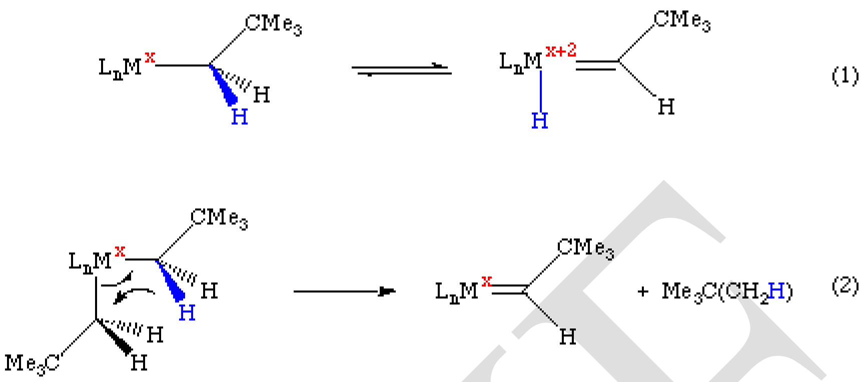


benzyl

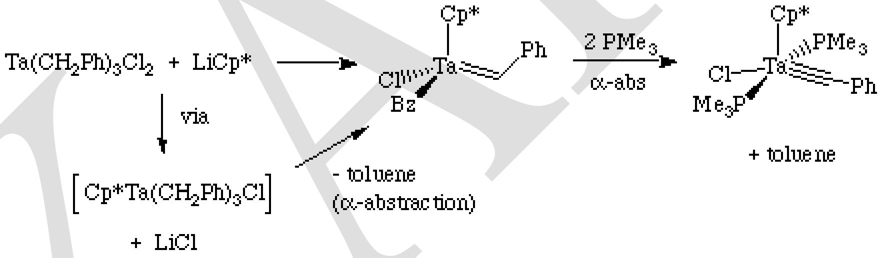


alkynyl

Alpha-hydride elimination is the transfer of a hydride (hydrogen atom) from the alpha-position on a ligand to the metal center. The process can be thought of as a type of oxidative addition reaction as the metal center is oxidized by two electrons (Eq 1). As the reaction involves a formal oxidation of the metal, alpha-elimination can not occur in a d^0 or d^1 metal complex. In these cases, a variant called **alpha-abstraction** can occur. Alpha-abstraction does **not** result in a change of oxidation state and the alpha-hydrogen is transferred directly to an adjacent ligand instead of the metal center (Eq 2):



Alpha-abstraction is a common method for synthesizing high oxidation state alkylidene and alkylidyne complexes. While alpha-elimination requires an open coordination site on the metal complex, alpha-abstraction does not. As shown below, alpha-abstraction may be induced by a steric crowding of the metal; the abstraction can occur spontaneously or be induced by addition of a donor ligand such as a phosphine:

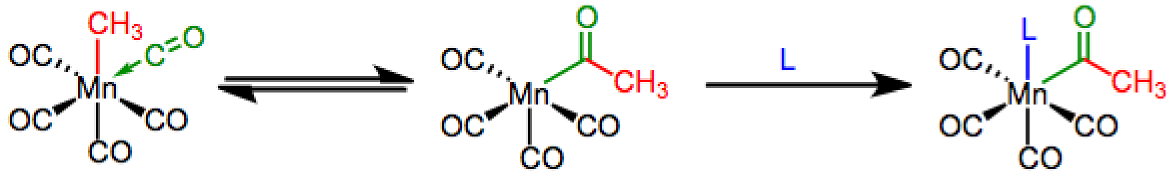


The mechanism of both alpha-elimination and alpha-abstraction proceeds through the same sort of four-center transition state as beta-hydride elimination or sigma bond metathesis. Alpha elimination/abstraction can occur when the metal contains both alpha and beta hydrogens, but is most common when beta-hydride elimination is blocked.

The microscopic reverse of a alpha-hydride abstraction would be a called a **carbon-hydrogen bond activation** in which the C-H bond adds across a metal-ligand bond. In practice, such activations are rare, although highly desirable from the context of functionalization of hydrocarbons.

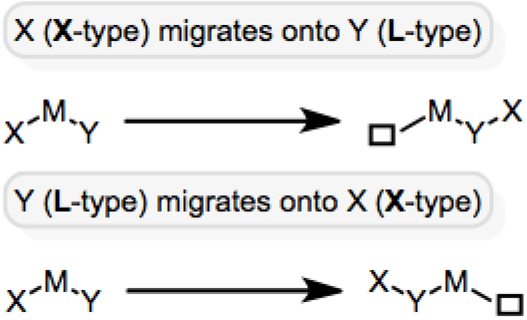
Migratory Insertion: Introduction and CO Insertions

We've seen that the metal-ligand bond is generally polarized toward the ligand, making it nucleophilic. When a nucleophilic, X-type ligand is positioned *cis* to an unsaturated ligand in an organometallic complex, an interesting process that looks a bit like nucleophilic addition can occur.



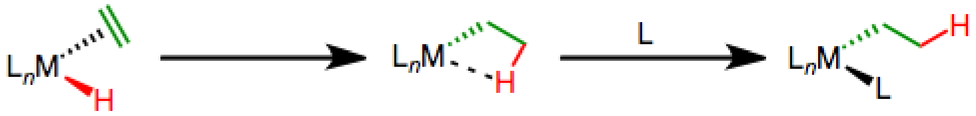
Migratory insertion into a metal-carbon bond.

On the whole, the unsaturated ligand appears to insert itself into the M–X bond; hence, the process is called **migratory insertion**. An open coordination site shows up in the complex, and is typically filled by an added ligand. The open site may appear where the unsaturated ligand was *or* where the X-type ligand was, depending on which group actually moved (see below). There is no change in oxidation state at the metal (unless the ligand is an alkylidene/alkylidyne), but the total electron count of the complex decreases by two during the actual insertion event—notice in the above example that the complex goes from 18 to 16 total electrons after insertion. A dative ligand comes in to fill that empty coordination site, but stay flexible here: L could be a totally different ligand or a Lewis base in the X-type ligand. L can even be the carbonyl oxygen itself!



X can migrate onto unsaturated ligand Y, or Y onto X. The former is more common for CO insertions.

We can distinguish between two types of insertions, which differ in the number of atoms in the unsaturated ligand involved in the step. Insertions of CO, carbenes, and other η^1 unsaturated ligands are called **1,1-insertions** because the X-type ligand moves from its current location on the metal to one spot over, on the atom bound to the metal. η^2 ligands like alkenes and alkynes can also participate in migratory insertion; these reactions are called **1,2-insertions** because the X-type ligand slides two atoms over, from the metal to the distal atom of the unsaturated ligand.



1,2-insertion of an alkene and hydride. In some cases, an agostic interaction has been observed in the unsaturated intermediate.

This is really starting to look like the addition of M and X across a π bond! However, we should take care to distinguish this completely intramolecular process from the attack of a nucleophile or electrophile on a coordinated π system, which is a different beast altogether. Confusingly, chemists often jumble up all of these processes using words like "hydrometalation," "carbometalation," "aminometalation," etc. Another case of big words being used to obscure ignorance! We'll look at nucleophilic and electrophilic attack on coordinated ligands in separate posts.

Reactivity Trends in CO Insertions

Certain conditions *must* be met for migratory insertion to occur: the two ligands undergoing the process must be *cis*, and the complex must be stable with two fewer total electrons. Thermodynamically, the formed Y–X and covalent M–Y bonds must be more stable than the broken M–X and dative M–Y bonds for insertion to be favored. When the opposite is true, the microscopic reverse (**elimination** or **deinsertion**) will occur spontaneously.

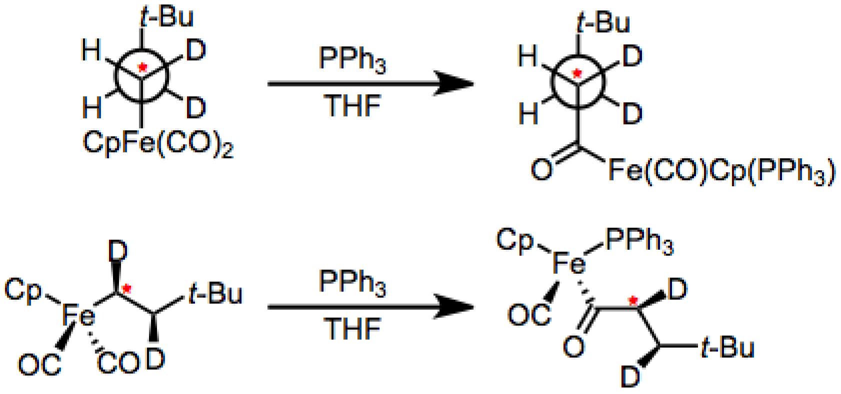
Migratory aptitudes for insertion into CO have been studied extensively, and the general conclusion here is "it's complicated." A few ligands characterized by remarkably stable metal-ligand bonds don't undergo insertion for thermodynamic reasons—the M–X bond is just too darn strong. Perfluoroalkyl complexes and metal hydrides are two notable examples. Electron-withdrawing groups on the X-type ligand, which strengthen the M–X bond, slow down insertion (likely for thermodynamic reasons though…Hammond's postulate in action).

What factors affect the relative speed (kinetics) of favorable insertions? Sterics is one important variable. Both 1,1- and 1,2-insertions can relieve steric strain at the metal center by spreading out the ligands involved in the step. In 1,2-insertions, the X-type ligand removes itself completely from the metal! Unsurprisingly, then, bulky ligands undergo insertions more rapidly than smaller ligands. Complexes of the first-row metals tend to react more rapidly than analogous second-row metal complexes, and second-row metal complexes react faster than third-row metal complexes. This trend fits in nicely with the typical trend in M–C bond strengths: first row < second row < third row. Lewis acids help accelerate insertions into CO by coordinating to CO and making the carbonyl carbon more electrophilic. For a similar reason, CO ligands bound to electron-poor metal centers undergo insertion more rapidly than CO's bound to electron-rich metals. Finally, for reasons that are still unclear, one-electron oxidation often increases the rate of CO insertion substantially.

Although the thermodynamics of alkene 1,2-insertion are more favorable for metal-carbon than metal-hydrogen bonds, M–H bonds react *much* more rapidly than M–C bonds in 1,2-insertions. This fact has been exploited for olefin hydrogenation, which would be much less useful if it had to complete with olefin polymerization (the result of repeated insertion of C=C into M–C) in the same reaction flask! More on that in the next post.

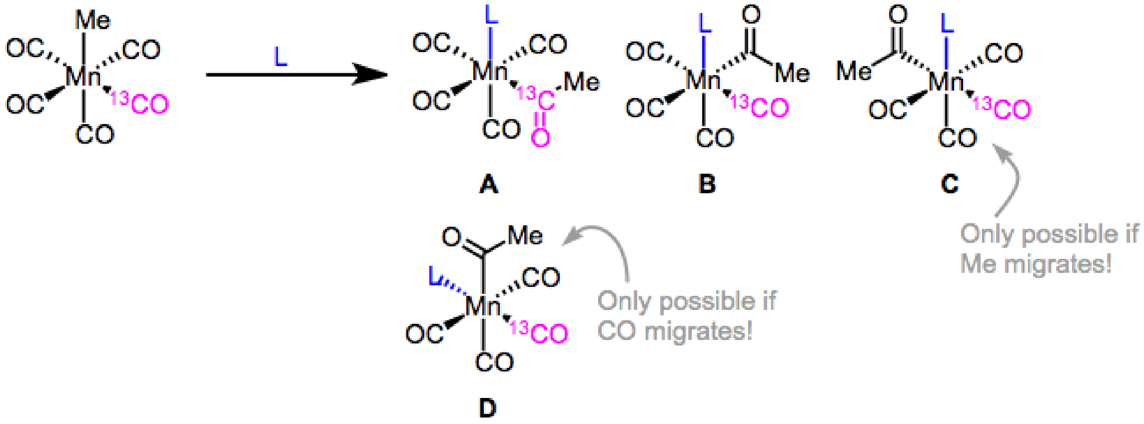
Stereochemistry in CO Insertions

Migratory insertion steps are full of stereochemistry! Configuration at the migrating alkyl group is retainedduring insertion—a nice piece of evidence supporting a concerted, intramolecular mechanism of migration.



Migratory insertion occurs with retention of configuration at the migrating alkyl group. Two different views of the same reaction are shown here.

What about stereochemistry at the metal center? Migratory insertion may create a stereogenic center at the metal—see the iron example above. Whether the X-type ligand moves onto the unsaturated ligand or *vice versa* will impact the configuration of the product complex. Calderazzo's study of this issue is one of my favorite experiments in all of organometallic chemistry! He took the simple labeled substrate in the figure below and treated it with dative ligand, encouraging insertion. Four products of insertion are possible, corresponding to reaction of the four CO ligands *cis* to the methyl ligand. Try drawing a few curved arrows to wrap your mind around the four possibilities, and consider both CO migration and Me migration as possible at this point.



Only possible if Me migrates!

Only possible if CO migrates!

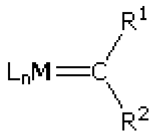
Insertion of the labeled complex shown could produce four products. Calderazzo did not observe product **D**, supporting a mechanism involving Me migration to CO.

Note that product **D** is impossible if we only allow the Me group to migrate—the spot *trans* to the labeled CO is another CO ligand, so that spot can only pick up L if CO migrates (not if Me migrates). On the other hand, product **C** must have come from the migration of Me, since the Me group has moved from a *cis* to a *trans* position relative to the labeled CO in product **C**. Calderazzo observed products **A**, **B**, and **C**, but not **D**, supporting a mechanism involving Me migration. Other experiments since support the idea that most of the time, the alkyl group migrates onto CO. Slick, huh?

I won't address insertions into alkylidenes, alkylidynes, and other one-atom unsaturated ligands in this post, as insertions into CO are by far the most popular 1,1 insertions in organometallic chemistry. In the next post, we'll dig more deeply into 1,2-insertions of alkenes and alkynes.

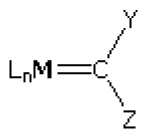
Alkylidene Complexes

Transition metal complexes incorporating a formal metal-carbon double bond are termed alkylidene or carbene complexes. Two general classes are recognized, **Schrock alkylidenes** and **Fischer carbenes**. General structures for these reactive compounds are shown below, together with some of their characteristics.



Schrock alkylidene

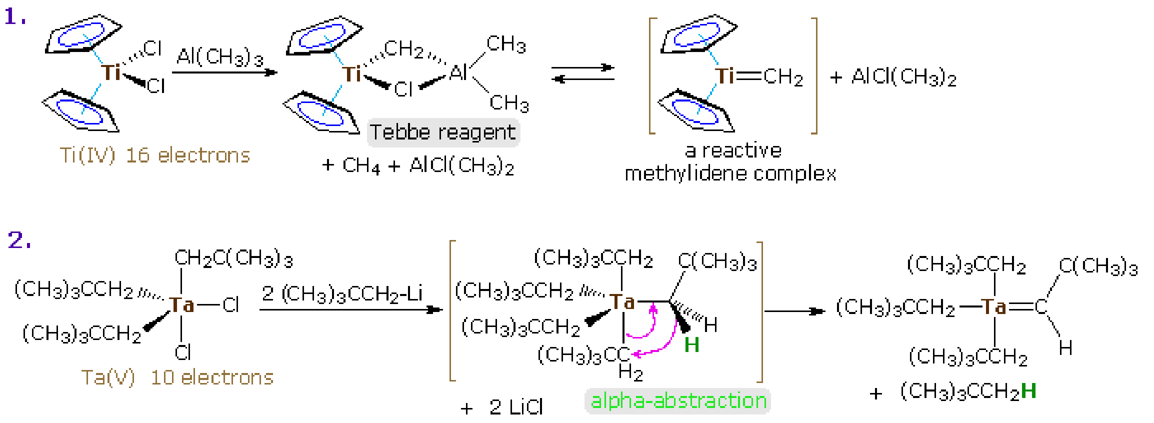
R = hydrogen, alkyl or aryl
M = early transition metal
usually 18 electron count
L = good σ or π-donor (e.g. Cp or Cl)



Fischer carbene

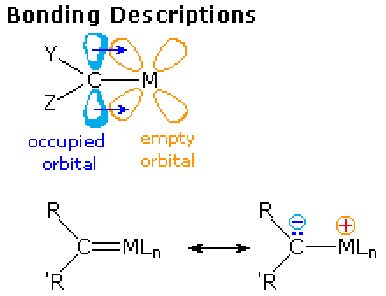
Y and/or **Z** = heteroatom (O, N, S --)
M = late transition metal
usually 10 to 18 electron count
L = good π-acceptor (e.g. CO)

The preparation of typical alkylidene complexes of both types are provided in the following diagram, beginning with Schrock alkylidenes. Clicking on the diagram will display the Fischer carbene examples (A, B & C), and these illustrations may be cycled by repeated clicking.



The properties and chemical behavior of Schrock and Fischer alkylidenes are substantially different, reflecting the metal-carbene bonding. As noted in the following diagram, the metal of a Schrock alkylidene is electrophilic, and is stabilized by electron donating ligands as well as backbonding from an occupied p-orbital of the carbon atom. This results in a strong metal-to-carbon double bond. The overall bonding in the complex leaves the carbon atom nucleophilic. Fischer carbenes have nearly opposite properties. The metal is electron rich, in part because of coordinate donation of an electron pair from the carbene carbon atom and CO ligands. Competition for the d-electrons of the metal takes place between electron withdrawing ligands, such as CO, and the empty p-orbital on carbon. This in turn, is stabilized by overlap with electron pairs on the heteroatom substituents (note the resonance structures). The resulting C=M multiple bond is weakened, and has a low barrier to rotation. Many of the chemical properties of Fischer carbenes are ester-like. Nucleophilic substitution takes place by way of a tetrahedral intermediate. Also, alpha-hydrogen atoms, e.g. $(CO)_5Cr=C(OCH_3)CH_3$, have enhanced acidity (pKa = 12.3).

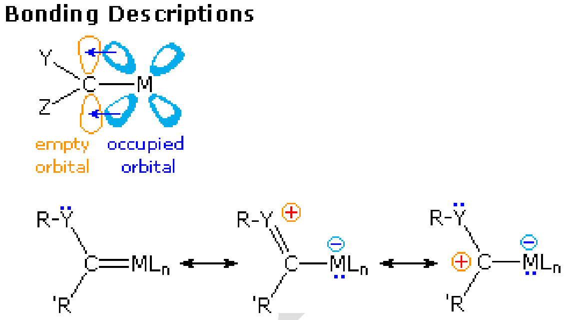
Schrock Alkylidene Complexes



Properties

Metal:	electron deficient attacked by nucleophiles stabilized by electron donating ligands
Carbon:	carbanion-like attacked by electrophiles destabilized by heteroatom substituents
C=M:	relatively strong large rotational barrier

Fischer Carbene Complexes



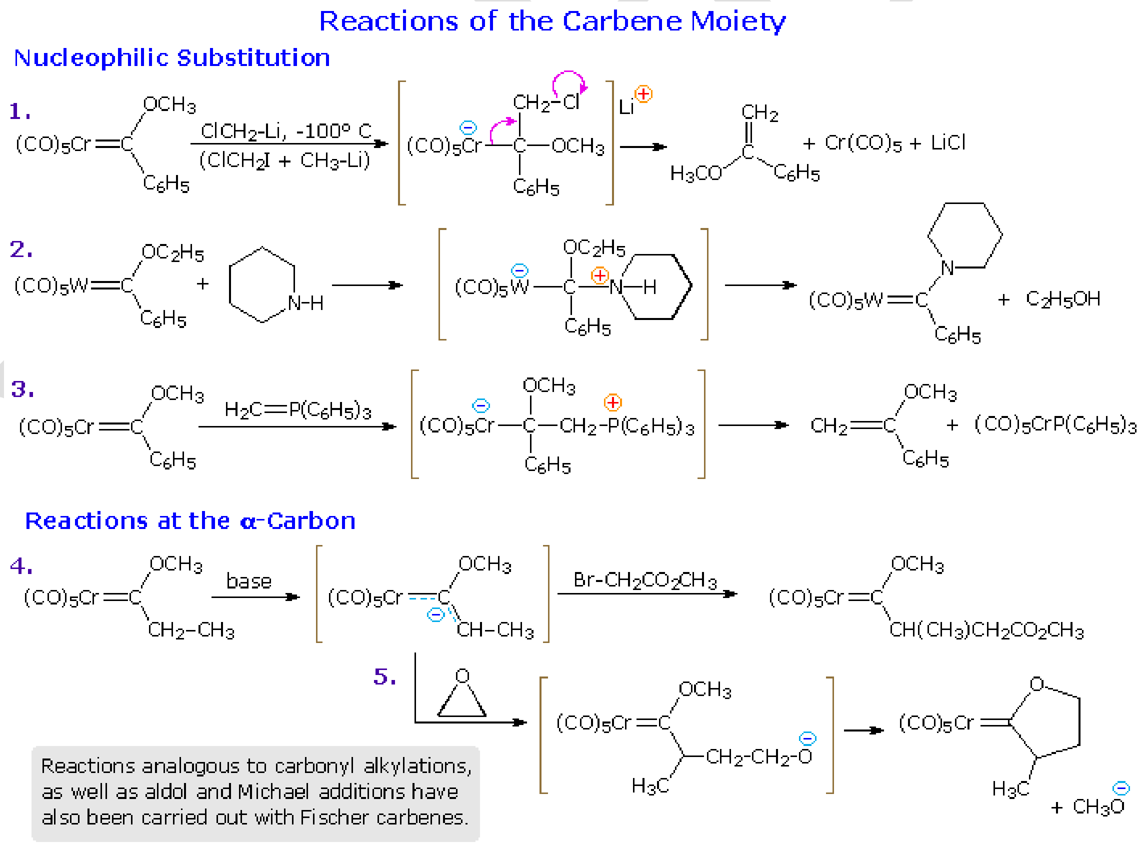
Properties

Metal:	electron rich attacked by electrophiles stabilized by electron accepting ligands
Carbon:	carbocation-like attacked by nucleophiles stabilized by heteroatom substituents
C=M:	relatively weak low rotational barrier

Reactions of Alkylidene Complexes

The alkylidene complexes described above undergo many interesting and synthetically useful reactions. Since the carbene moiety of a Fischer carbene has many of the characteristics of a carbonyl group, it is instructive to begin our survey with some ester-like transformations. The following diagram incorporates four pages of reactions that may be viewed by repetitive clicking on the diagram itself. The first page displays a few carbonyl-like reactions, which mimic organolithium addition to ketones (eq. # 1), ester amination (eq. # 2), the Wittig reaction (eq. # 3) and alpha-carbon alkylation (eq. # 4). Equation # 5 shows a sequence involving epoxide alkylation, followed by an intramolecular trans-esterification analog. The second page of reactions begins with an equation illustrating the reductive and oxidative removal of the metal component of the carbene. Note that DMSO also served as the oxidant in the Swern oxidation. The next two equations (# 7 & 8) demonstrate the dienophilic activation provided by a Fischer carbene. In most cases the carbene is a stronger activating group than the corresponding ester. The last equation shows an unusual case of thermal [2+2]-cycloaddition, which does not take place with the ester equivalent.

Fischer Carbene Reactions



Reactions analogous to carbonyl alkylations, as well as aldol and Michael additions have also been carried out with Fischer carbenes.

The third and fourth pages of reactions are unique to transition metal complexes of the Fischer and Schrock type. Metallocyclobutanes are believed to be key intermediates in these transformations, as shown. Reversible loss of CO ligands frees coordination sites and facilitates the oxidative addition of alkenes or alkynes. Since the cyclopropanation reaction on page three requires an electron withdrawing group on the alkene reactant, a bonding interaction of the electrophilic beta-carbon with the nucleophilic metal is expected. If the resulting metallocyclobutane is saturated, a reductive elimination gives a cyclopropane product. However, metallocyclobutenes derived from alkyne reactants undergo electrocyclic ring opening to a new alkylidene species. This in turn may react with other suitably located double bonds. Finally, a useful phenol synthesis known as the Dötz reaction is described on the fourth page. The unsaturated carbene supplies three carbon atoms and a carbon monoxide unit to the product phenol, and the alkyne reactant provides the remaining carbons. Oxidative addition produces a metallocyclobutene in the initial step, which is then followed by ring-opening, insertion and ring closure steps. The aromatic product is released from the stable cobalt tricarbonyl complex by treatment with mild oxidizing agents.

Most of the Fischer carbenes used in the reactions listed above are zero valent metal complexes. Although this is not a necessary condition {$Cp(CO)_2Fe=CH_2$ has been used for cycloproanation}, it is a common feature of many such reactions. Schrock alkylidenes generally incorporate metals having higher oxidation states, and because of the electrophilic nature of the metal their reactivity is significantly different. The following diagram shows two typical transformations of these alkylidene complexes. Olefination of carbonyl functions may be effected by Tebbe's reagent, which is the source of a Ti(IV) methylene complex. Unlike the Simmons-Smith reagent, it olefinates ester and amide carbonyl functions, as well as aldehydes and ketones.

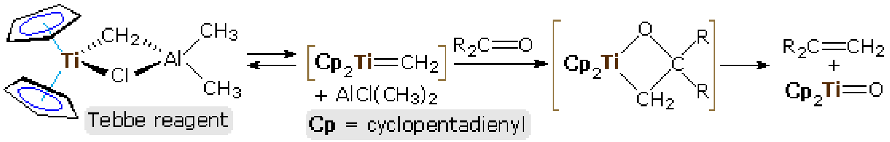
The most important reaction of these alkylidene complexes is undoubtedly **olefin metathesis**, a redistribution of the carbon groups joined by double (or triple) bonds. Applications of this reaction range from novel polymerizations to selective carbo and heterocyclic ring formation. Industrially important olefin metathesis operations are conventionally carried out with heterogeneous catalysts such as MoO_3 on alumina. Following a suggestion by French chemist Y. Chauvin, T. Katz, R. Grubbs and R. Schrock have demonstrated convincingly that alkylidene or carbene complexes are necessary intermediates in this remarkable transformation, which proceeds by way of metallocyclobutane species. By clicking on the diagram a general mechanism for olefin metathesis will be displayed

Alkylidene Reactions

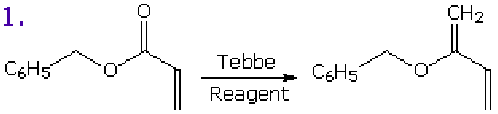
The mechanism shown at the top of the second illustration demonstrates the general form of olefin metathesis, but does not treat subtle factors such as regioselectivity and catalytic turnover. Many structural features of a metathesis catalyst may be changed and adjusted to suit the type of reaction desired. A ROMP catalyst, for example, should complex preferentially with the ring double bond, inducing ring cleavage and formation of a new catalytic site. For a RCM reaction, the catalyst should complex with a pendant acyclic double bond and release the endocyclic product once the intramolecular metathesis has been completed. Although heterogeneous metathesis catalysts generally incorporate high oxidation state transition metals, studies of discrete homogeneous complexes have shown this is not a necessary condition. Indeed, an early experiment by Katz used a Fischer carbene to effect metathesis.

Much effort has been devoted to creating metathesis catalysts with improved binding and turnover characteristics to fit specific transformations. A few of the resulting catalytic complexes are shown in the bottom half of the second illustration. Schrock's molybdenum catalysts generally show high reactivity, but tend to be air sensitive and intolerant of some functional groups. The research group of R. Grubbs (Cal. Tech.) has produced a family of easily handled ruthenium catalysts that have proven effective and valuable tools in the field of synthetic organic chemistry.

Carbonyl Olefination



1.



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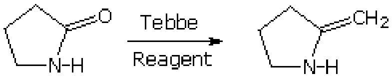

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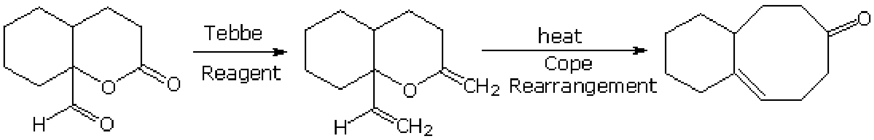
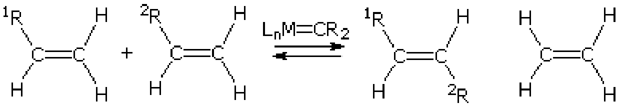
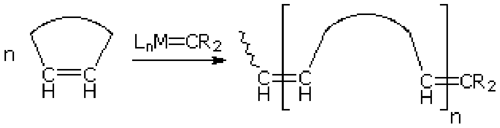


Olefin Metathesis

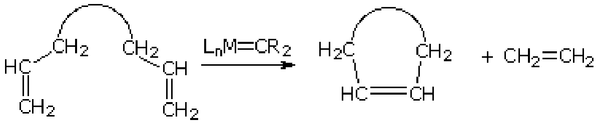
Cross-Metathesis



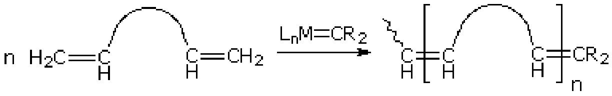
ROMP
Ring Opening
Metathesis Polymerization



RCM
Ring Closing Metathesis



ADMP
Acyclic Diene
Metathesis Polymerization



Possible Questions

PART-B (6 Mark Questions)

1. Definition of organometallic compound and give three examples
2. The general preparation methods of metal carbonyls with examples
3. WriteStability and structures of metal alkyl complexes
4. Explain Oxidative addition and nucleophilic attack on organometallic compound
5. Synthesis of alkene complexes by various methods
6. Discus the hydrosilation process with examples
7. Explain the half sandwich compound, bonding and reactivity
8. Explain the polymerization reactions with examples?
9. Discuss the Redox reactions in Vaska's complexes
10. Hydrogenation of olefin with mechanism

PART-C (10 Mark Questions)

1.Write the following

   a. Calculate the 18-electron rule? $Co_2(CO)_8$ and $V(CO)_6$
   b. Account the synthesis method of metal alkyl complexes

DEPARTMENT OF CHEMISTRY

Online questions (Multiple choice questions)

ORGANOMETALLICCHEMISTRY (17CHP205C)

UNIT II

S.No	Questions	Option-A	Option-B	Option-C	Option-D	Answer
1.	Metal alkyls complexes containing metal and carbon…	sigma bond	pi-bond	ionic bond	covalent bond	sigma bond
2.	Which one of the following is metal alkyl complexes	CH3MgCl	Zesis salt	Mo=Cph2	ClMo=Cph2	CH3MgCl
3.	The reactivity of the alkyl ligand is inversely related to the electronegativity of the	ligand centre	metal centere	negative carbon	pasitive carabon	metal centere
4.	organometallic chemists in the 1920s got the idea that metal-carbon bonds were ….. in general	Strong	moderate	week	van der waals forces	week
5.	What is the major decomposition pathways of metal alkyl complexes?	a-hydride elimination	E2-elimination	E1-elimination	β-hydride elimination	β-hydride elimination
6.	Wich one the bond is more stronger	M-C	M=C	M-H	M-H-C	M-H
7.	Find out the β-hydrogen in following compounds	M-CH3	M-H	M-CH2CH3	M-CH2	M-CH2CH3
8.	β-hydride elimination is the most common.	inorganic compound	organometallic compound	Materials	organic compounds	organometallic compound
9.	Cobalt os mainly ------ in its salt	positive	Negative	Dipositive	tripositive	Dipositive

10.	Vitamin B12 consist of a highly substituted porphyrin like corrin ring in which a Co3+ ion is bound to the --- nitrogen atom	3	4	1	2	4
11.	the structure of vitamin B12 is similar to many haem iron compounds . it is called ---	Haemoglobin	Myoglobin	Albumin	Cobalamin	Cobalamin
12.	Vitamin B12 contains a --- group in the sixth coordination position	Amino	Cyanide	Keto	carbon	Cyanide
13.	Vitamin B12 contains a cyanide group in the sixth position is also called	Cyanocobalamine	Cytochrome	Hemoglobin	Myoglobin	Cyanocobalamine
14.	The erivative of vitamin B12 concentrated in the liver is equivalent to --- ppm vitamin	1	2	3	4	1
15.	The average human beings contain total of ---- of vitamin B12	2-5 mg	3-5 mg	2-3 mg	1-2 mg	2-5 mg
16.	the principle role of vitamin B12 cyanocobalamin is the maturation of -----	Hemoglobin	Myoglobin	Erythrocytes	carbon	Erythrocytes
17.	the normal human diet contains between --- of vitamin B12 daily	5µg-15 µg	10µg-15 µg	2µg-5 µg	6µg-15 µg	5µg-15 µg
18.	Alkaline solution of cyanocobalamine can be reduceds to give bith Co(II) and ---- species	Co(IV)	Co(III)	Co(I)	carbon	Co(I)

19.	The alkaline solution of cyanocobalamine can be reduced to give both Co(II) and Co(I) species called vitamin B12r and	Vitamin B12S	Vitamin B12H	Vitamin B12t	VitaminB12K	Vitamin B12S
20.	Vitamin B12S readily loses the --- from the sixth coordination position .	Cyanide	Amino	Keto	carbon	Cyanide
21.	Vitamin B12S is a powerful ---	Oxidising agent	Reducing agent	Protecting	Initiating agent	Reducing agent
22.	The structure of vitamin B12 is similar to many haem iron compounds . it is called ----	Cobalamin	Haemoglobin	Albumin	Myoglobin	Cobalamin
23.	The number of heam group present in heamoglobin -----	1	2	3	4	4
24.	The binding power of heamoglobin with oxygen is PH dependent this effect is known as ----	Cooperativity effect	Bohr effect	Symmetry effect	Assymmetry effect	Bohr effect
25.	The heam group in heamoglobin consist of ---- atom	Fe	Mn	Mg	Co	Fe
26.	which one of the following is commonly used as the starting material for the synthesis of group 4 metal cyclopentadienyl complexes?	CpSiMe3	NO	MeNC	Metal nitrosyl	CpSiMe3
27.	Which complexes are	Cyclopentadienyl	Tricyclopentadienyl	Monocyclopentadie	Biscyclopentadienyl	Biscyclopentadien

	called metallocenes?			nyl		yl
28.	Which statement is incorrect about CO ligands?	A CO ligand can accept electrons into its π* MO; this weakens the C–O bond	In the IR spectrum of Fe(CO)5, absorptions assigned to the CO stretching modes are at higher wavenumber than that of free CO	CO ligands can adopt terminal, μ and μ3 bonding modes; the amount of back donation depends on the bonding mode	Fluxional behaviour is common in metal carbonyl compounds, and can be investigated by 13C NMR spectroscopy	In the IR spectrum of Fe(CO)5, absorptions assigned to the CO stretching modes are at higher wavenumber than that of free CO
29.	Which of the following orders is correct for Tolman cone angles for PR3 ligands?	PMe3 > PEt3	PnBu3 > PtBu3	PMePh2 > PMe2Ph		PMePh2 > PMe2Ph
30.	Which metal centre does not obey the 18-electron rule?	Fe in Fe(η5-C5H4COMe)2	Co in Co2(CO)8	Ru in [Ru(η6-C6Me6)2]2+	V in V(CO)6	V in V(CO)6
31.	From which reaction are you unlikely to isolate the stated product?	2Na + Mn2(CO)10 → 2Na[Mn(CO)5]	Na3[IrCl6] Ir2(CO)8	OsO4 Os3(CO)12	Fe(CO)5 + I2 → Fe(CO)4I2 + CO	Na3[IrCl6] Ir2(CO)8
32.	Match up the total valence electron (ve) count with the metal core shape. Which one is incorrect?	48 ve; triangle	74 ve; trigonal bipyramid	86 ve; octahedron	90 ve; trigonal prism	74 ve; trigonal bipyramid
33.	The reaction: Mn(CO)5Me + CO → Mn(CO)5(COMe) is an example of:	a ligand addition	a β-elimination	an oxidative addition	an alkyl migration	an alkyl migration
34.	The conversion of Mn2(CO)9(PPh2H) to Mn2(CO)8(μ-PPh2)(μ-H) is best described in terms of loss of CO in	an oxidative addition	a substitution reaction	α-hydrogen abstraction	β-hydrogen elimination.	an oxidative addition

	association with:					
35.	Consider the compound (C8H8)Ru(CO)3. Which is likely to be the best description of the C8H8 ligand?	It is bonded in an η8-manner to the Ru atom and one 1H NMR signal	It is bonded in an η4-manner to the Ru atom, but one 1H NMR signal	It is bonded in an η3-manner to the Ru atom and the 1H NMR spectrum	It is bonded in an η2-manner to the Ru atom and the 1H NMR spectrum	It is bonded in an η4-manner to the Ru atom, but one 1H NMR signal is observed in the limiting high temperature spectrum
36.	Which statement about (η5-Cp)2Fe2(CO)4 is incorrect?	Trans and cis isomers exist and are both present in solution at 298 K	The Fe2 unit is supported by two bridging CO ligands	Reaction with Na produces [(η5-Cp)Fe(CO)2]–	Reaction with Br2 gives (η5-Cp)FeBr2(CO)2	Reaction with Br2 gives (η5-Cp)FeBr2(CO)2
37.	Match the ligand to the number of electrons available for bonding to a low oxidation state metal. Which pair is incorrect?	NO; 2	PPh3; 2	CH2=CHCH=CH2 ; 2 or 4	Ph2PCH2CH2PPh2; 2 or 4	NO; 2
38.	Which compound is most likely to undergo oxidative addition of H2?	RhCl(PPh3)3	Fe(CO)5	[RhI4(CO)2]–	[HFe(CO)4]–	RhCl(PPh3)3
39.	In a metal alkyl compound, which σ-bonded R group could undergo β-hydrogen elimination?	Et	CH2Ph	CH2CMe3	Me	Et
40.	Which statement about ferrocene is incorrect?	I2 oxidizes ferrocene to give a diamagnetic cation	The ligands in ferrocene undergo electrophilic substitution with RCOCl	The Fe centre in ferrocene can be protonated by treatment with concentrated H2SO4	In the gas phase, the C5H5 rings in ferrocene are eclipsed	I2 oxidizes ferrocene to give a diamagnetic cation
41.	Which statement about nickelocene	Nickelocene is isoelectronic and	Nickelocene is paramagnetic	Nickelocene can be oxidized to give a	Reaction of nickelocene with Na/Hg in EtOH	Nickelocene is isoelectronic and

	is incorrect?	isostructural with ferrocene		paramagnetic monocation	gives (η5-C5H5)(η3-C5H7)Ni	isostructural with ferrocene
42.	For which cluster is the stated structure for the metal core inconsistent with the cluster electron count?	Os3(CO)12Br2; triangle	Rh4(CO)12; tetrahedron	[Os6(CO)18]2–; octahedron	Rh6(CO)16; octahedron	Os3(CO)12Br2; triangle
43.	Which of the following compounds contains a square planar metal centre?	Ni(CO)4	Ir(CO)Cl(PPh3)2	Ni(η3-C3H5)2	Cr(NO)4	Ir(CO)Cl(PPh3)2
44.	A Fischer-type carbene contains all but one of the following. Which is the odd one out?	An M=C bond	A nucleophilic carbene centre	A low oxidation state metal centre	A heteroatom (e.g. O) attached to the metal-bound C atom	A nucleophilic carbene centre
45.	Which of the following σ-bonded alkyl groups can undergo β-hydrogen elimination?	CH2CH3	CH2Ph	CH3	CH2SiMe3	CH2CH3
46.	Which of the following statements is correct about the metal-bound arene ring in (η6-C6H6)Cr(CO)3?	The metal-bound ring is more susceptible to attack by electrophiles than free C6H6	The metal-bound ring is more susceptible to attack by nucleophiles than free C6H6	The metal-bound ring readily undergoes addition reactions, whereas free C6H6 does not	The metal-bound ring is less susceptible to attack by nucleophiles than free C6H6	The metal-bound ring is more susceptible to attack by nucleophiles than free C6H6
47.	The reaction of (η6-C7H8)Mo(CO)3 with [Ph3C][BF4] results in:	proton abstraction and formation of [(η7-C7H7)Mo(CO)3]-	proton abstraction and formation of [(η5-C7H7)Mo(CO)3]-	hydride abstraction and formation of [(η7-C7H7)Mo(CO)3]+	hydride abstraction and formation of [(η5-C7H7)Mo(CO)3]+	hydride abstraction and formation of [(η7-C7H7)Mo(CO)3] +
48.	Which statement is incorrect about the reaction of NaH with C5H6?	H2 is liberated	Covalent NaCp is formed	NaH can be replaced by Na in the reaction	The C5 ring changes from being puckered to planar	Covalent NaCp is formed

49.	The solid state structure of Me2Be:	consists of monomers with linear Be	consists of dimers with trigonal planar Be	is trimeric with trigonal planar Be	is polymeric with tetrahedral Be	is polymeric with tetrahedral Be
50.	In the solid state structure of EtMgBr etherate, the Mg centre is:	linear	bent	trigonal planar	tetrahedral	tetrahedral
51.	Which statement about NaBPh4 is incorrect?	It is sparingly soluble in water	It is an ionic salt	It can be made by reacting BF3 with PhMgBr and then adding NaCl	It can be made from the reaction between BPh3 and NaPh	It is sparingly soluble in water
52.	Which statement about organoaluminium compounds is incorrect?	Dimers of AlMe3 possess delocalized Al–C–Al bonding interactions	The bonding in Al2Me4Cl2 can be described in terms of a localized scheme	In Al2Ph4(μ-C≡CPh)2, the bridge bonds can be described in a similar way to those in Al2Me4(μ-Ph)2	Al2{CH(SiMe3)2}4 contains an Al–Al bond	In Al2Ph4(μ-C≡CPh)2, the bridge bonds can be described in a similar way to those in Al2Me4(μ-Ph)2
53.	In (η5-C5R5)2Sn, the tilt angle, α, between the two η5-C5R5 rings varies with R; when α = 180˚, the rings are parallel. Which is the correct ordering of α as a function of R?	H > Ph	Ph > Me	H > Me	Me > Ph	Ph > Me
54.	The solid state structure of Me3PbCl is:	monomeric with tetrahedral Pb	dimeric with trigonal bipyramidal Pb	polymeric with trigonal bipyramidal Pb	polymeric with octahedral Pb	polymeric with trigonal bipyramidal Pb
55.	Arsenic forms R3As and R5As compounds. Which synthetic routes would it be most reasonable to use?	R3As from AsCl3 and a suitable Grignard reagent; R5As from AsCl5 and a Grignard reagent	R3As from AsCl3 and a suitable Grignard reagent; R5As from oxidative addition of Cl2 to R3As and treatment with RLi	R3As from AsCl3 and R2Zn; R5As from AsCl5 and a Grignard reagent	R3As from As and RCl; R5As from oxidative addition of Cl2 to R3As and treatment with RLi	R3As from AsCl3 and a suitable Grignard reagent; R5As from oxidative addition of Cl2 to R3As and

						treatment with RLi
56.	Match the shape of the molecule in the solid state to the formula. Which pair is correct?	Me3Sb; trigonal planar at Sb	(2,4,6-tBu3C6H2)2As2; the As2C2 unit is linear	{(Me3Si)2CH}4Sn2; the Sn2C4 unit is non-planar	Ph5Sb; trigonal pyramidal at Sb	{(Me3Si)2CH}4Sn2; the Sn2C4 unit is non-planar
57.	In which reaction is the group 13 or 14 element reduced?	Me2GeCl2 + 2Li → Me2Ge + 2LiCl	GaCl3 + 3LiCp → Cp3Ga + 3LiCl	GeCl4 + RLi → RGeCl3 + LiCl2	MeLi + MeI + TlI → Me3Tl + 2LiI	Me2GeCl2 + 2Li → Me2Ge + 2LiCl
58.	Which statement is correct?	In the solid state, Cp2Pb has a polymeric structure	R2Ge species are stable at 298 K for R = Me and R = Et	The solid-state structure of Al2Me6 shows that the Al–C(terminal) and Al–C(bridge) bond lengths are the same	TeCl4 reacts with MeLi in Et2O below room temperature to give Me6Te	In the solid state, Cp2Pb has a polymeric structure
59.	Which statement is incorrect about [(C5Me5)2Ga]+?	[(C5Me5)2Ga]+ is isostructural with [(C5Me5)2Al]+	The solution 1H NMR spectrum (298 K) of [(C5Me5)2Ga]+[BF4]– is inconsistent with the solid-state structure of this compound	[(C5Me5)2Ga]+ can be prepared by treating (C5Me5)3Ga with tetrafluoroboric acid	The oxidation state of Ga in [(C5Me5)2Ga]+ is +3	[(C5Me5)2Ga]+ is isostructural with [(C5Me5)2Al]+
60.	Which statement is incorrect about the reaction of NaH with Ph3CH?	The product contains the [Ph3C]+ ion	H2 is liberated	An ionic salt is formed	The product is red in colour	The product contains the [Ph3C]+ ion

UNIT- III

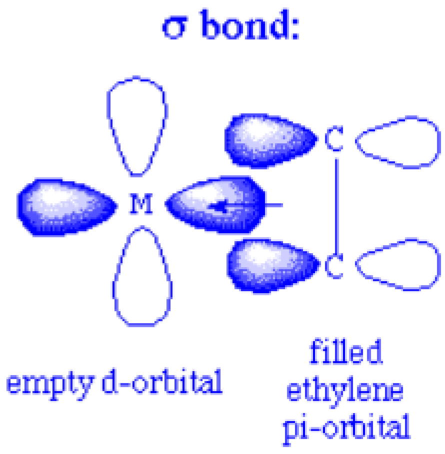
SYLLABUS

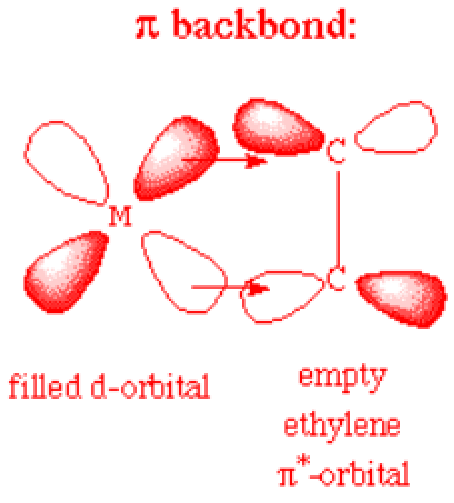
Synthesis of alkene complexes by ligand substitutuion - by reduction and by metal atom synthesis - bonding of alkenes to transition metals - bonding in diene complexes - reactivity of alkene complexes - ligand substitution - reactions with nucleophiles - olefin hydrogenation - hydrosilation - Wacker process - C-H activation of alkenes - alkyne complexes - bonding in alkyne complexes - reactivity of alkynes - alkyne complexes in synthesis - cobalt catalysed alkyne cycloaddition.

Alkene or olefin ligands are common in organotransition metal chemistry. In fact, the first organotransition metal complex, Zeise's salt ($K[PtCl_3(C_2H_4]\cdot H_2O$) was an alkene complex although its true nature was not unambiguously determined until about 100 years after its discovery.

Bonding and Structure in Alkene Complexes

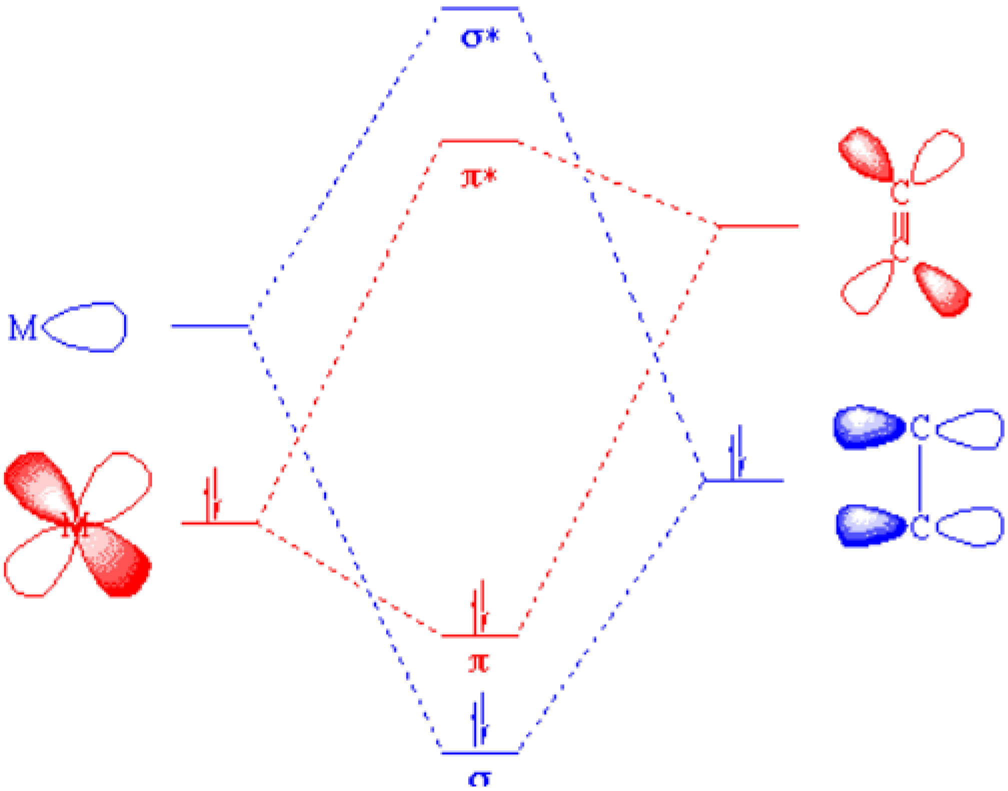
The bonding in alkene complexes is described by the **Dewar-Chatt-Duncanson model**, which provides us with a bonding picture not unlike that seen in carbonyl or phosphine complexes. A sigma-type donation from the C=C pi orbital with concomitant pi-backbonding into an empty pi* orbital on the ethylene presents us with a synergistic bonding situation: the greater the sigma donation to the metal, the greater the pi-backbonding:



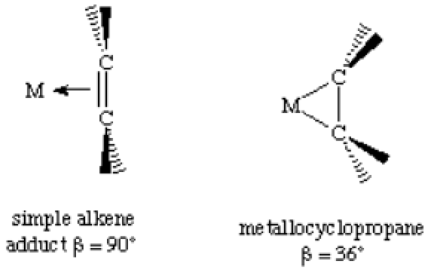


The greater the electron density back-donated into the pi* orbital on the alkene, the greater the reduction in the C=C bond order. An alternative way of stating this would be to say that the hybridization of the alkene carbon changes from sp^2 to sp^3 as back-donation increases. Either formalism describes two limiting structures: a planar olefin adduct and a metallocyclopropane.

X-ray crystallographic studies confirm that the as the C-C bond length increases, the CH_2 plane is distorted from the ideal planar geometry of an alkene:



The structural distortion of a bound alkene can also be detected by NMR: the J_{CH} of alkene-like sp^2 carbons is typically around 160 Hz whereas sp^3-like carbons have a J_{CH} around 120 Hz. Unlike carbonyl stretching frequencies, the C=C IR band (around 1500 cm^{-1}) is usually weak and not well-correlated to C-C bond length.



Electronic factors play a large role in the binding of alkenes to transition metals. For example, tetrafluoroethylene will bind more tightly than ethylene to a low valent metal complex because the presence of electron-withdrawing groups on the olefin results in poorer sigma donation and lowers the energy of the pi* orbital (providing better overlap for backbonding). Likewise, ethylene (like carbon monoxide) is a poor ligand for d^0 metal complexes because there are no d-electrons to engage in back-bonding.

The stability of alkene complexes also depends on steric factors as well. An empirical ordering of relative stability would be:

tetrasubstituted < trisubstituted < trans-disubstituted < cis-disubstituted < monosubstituted < ethylene.

Synthesis of Alkene Complexes

1. Ligand substitution reactions.
2. Reduction of a higher valent metal in the presence of an alkene.
3. From alkyls and related species:
    - reductive elimination (of an allyl and hydride, for example).
    - hydride abstraction from alkyls
    - protonation of sigma-allyls
    - from epoxides (indirectly)

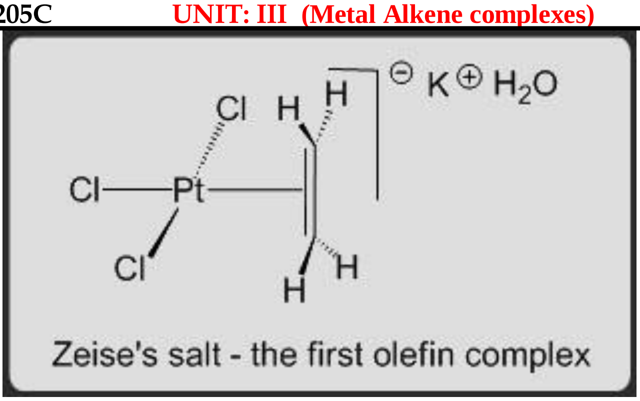
Substitution Reaction Mechanisms

When we discuss a substitution reaction in inorganic chemistry we ask ourselves questions about these aspects of the reaction:

- **Stoichiometric mechanism** -- What are the steps involved? Does a ligand dissociate during the reaction, etc.?
- **Intimate mechanism** -- What factors specifically affect the rate constant of a particular step? Why is the rate faster for R=Me than for R=Ph etc.?

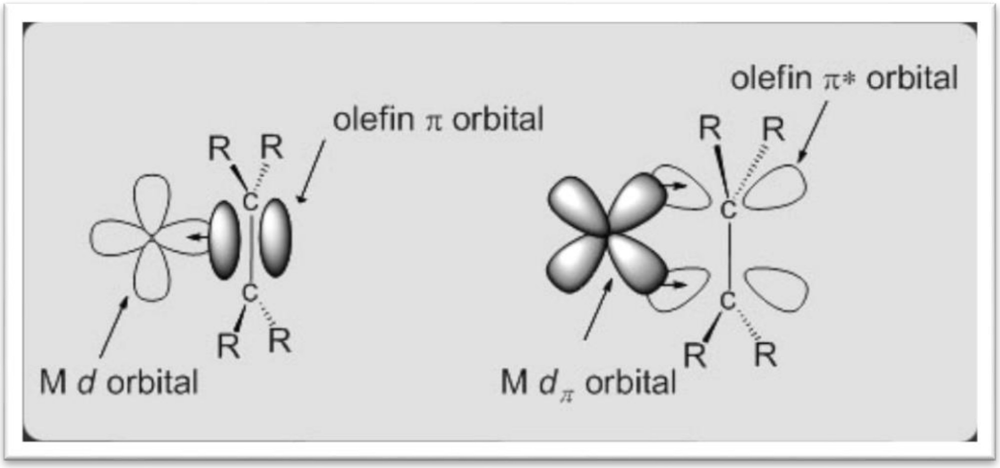
In particular, we need to ask if a reaction proceeds through an **intermediate**. This immediately raises the question, "what is an intermediate?" On the potential energy diagram shown below, an intermediate is drawn and connected to the reactants and products by the blue line. But what if the energy barrier to get out of this potential well is so small that we can't detect it? To us, the reaction coordinate might appear not to include an intermediate at all as indicated by the red line.

Though the first metal olefin complex dates back a long time to the beginning of 19th century, its formulation was established only a century later in the 1950s. While reacting K_2PtCl_4 with EtOH in 1827, the Danish chemist Zeise synthesized the famous Zeise's salt $K[PtCl_3(C_2H_4)]\cdot H_2O$ containing a Pt bound ethylene moiety and which incidentally represented the first metal–olefin complex.



Zeise's salt - the first olefin complex

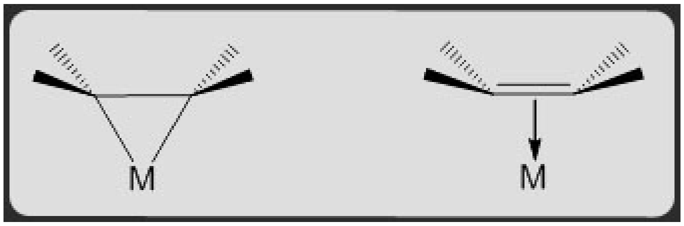
The metal−olefin bonding interaction is best explained by the *Dewar−Chatt* model, that takes into account two mutually opposing electron donation involving σ−donation of the olefinic C=C π−electrons to an empty d_π metal orbital followed by π−back donation from a filled metal d_π orbital into the unoccupied C=C π* orbital. Quite understandably so, for the d^0 systems, the formations of metal−olefin complexes are not observed. The extent of the C=C forward π-donation to the metal and the subsequent π−back donation from the filled d_π orbital to the olefinic C=C π* orbital have a direct bearing on the C=C bond of the metal bound olefinic moiety in form of bringing about a change in hybridization as well as in the C−C bond distance.



If the metal to ligand π−back donation component is smaller than the ligand to metal σ−donation, then the lengthening of the C−C bond in the metal bound olefin moiety is observed. This happens primarily because of the fact that the alkene to metal σ−donation removes the C=C π−electrons away from the C−C bond of the olefin moiety and towards the metal center, thus, decreasing its bond order and increasing the C−C bond length. Additionally, as the metal to ligand π−back donation increases, the electron donation of the filled metal d_π orbital on to the π* orbital of the metal bound olefin moiety is enhanced. This results in an increase in the C−C bond length. The lengthening of the C−C bond in metal bound olefin complex can be correlated to the π−basicity of the metal. For example, for a weak π−basic metal, the C−C bond lengthening is anticipated to be small while for a strong π−basic metal, the C−C lengthening would be significant.

Another implication of ligand−metal π−back donation is in the observed change of hybridization at the olefinic C atoms from pure sp^2, in complexes with no metal to ligand π−back donation, to sp^3, in complexes with significant metal to ligand π−back donation, is observed. The change in hybridization from sp^2 to sp^3 centers of the olefinic carbon is accompanied by the substituents being slightly bent away from the metal center in the final metalacyclopropane form (Figure 3). This change in hybridization can be conveniently detected by ^{1}H and ^{13}C NMR spectroscopy. For example, in case of the metalacyclopropane systems, which have strong metal to ligand π−back donation, the vinyl protons appear 5 ppm (in the ^{1}H NMR) and 100 ppm (in the ^{13}C NMR) high field with respect to the respective position of the free ligands.

An interesting fallout of the metal to ligand π−back bonding is the tighter binding of the strained olefins to the metal center as observed in the case of cyclopropene and norbornene. The strong binding of these cyclopropene and norbornene moieties to the metal center arise out of the relief of ring strain upon binding to the metal. Lastly, in the metal−olefin complexes having very little π−back bonding component, the chemical reactivities of the metal bound olefin appear opposite to that of a free olefin. For example, a free olefin is considered electron rich by virtue of the presence of π−electrons in its outermost valence orbital and hence it undergoes an electrophilic attack. However, the metal bound olefin complexes having predominantly σ−donation of the olefinic π−electrons and negligible metal to ligand π−back donation, the olefinic C becomes positively charged and hence undergoes a nuclophilic attack. This nature of reversal of olefin reactivity is called *umpolung* character.



Metal alkene complexes are synthesized by the following methods.

i. Substitution in low valent metals

$$AgOSO_2CF_3 + C_2H_4 \longrightarrow (C_2H_4)AgOSO_2CF_3$$

ii. Reduction of high valent metal in presence of an alkene

$$(cod)PtCl_2 + C_2H_4 \longrightarrow [PtCl_3(C_2H_4)]^- + Cl^-$$

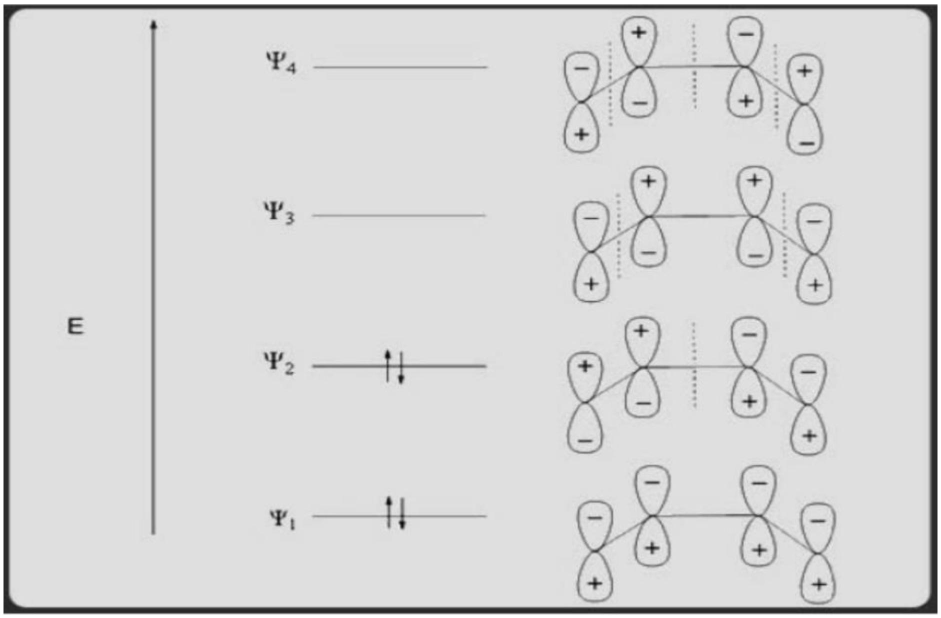
iii. From alkyls and related species

$$Cp_2TaCl_3 + n\text{-}BuMgX \longrightarrow \{Cp_2TaBu_3\}$$

$$\{Cp_2TaBu_3\} \xrightarrow[\text{reductive elimination}]{\beta\text{-elimination}} Cp_2TaH(1\text{-Butene}) + Butene + Butane$$

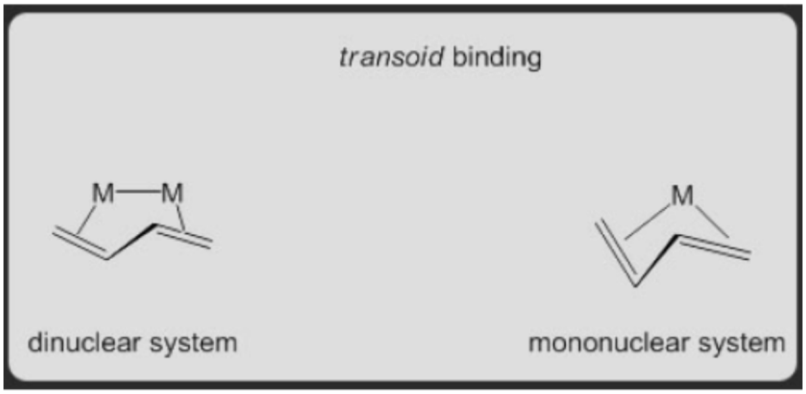
Diene complexes

1,3−Butadiene is a 4e−donor ligand that binds to a metal in a cisoid conformation. The Dewar−Chatt model, when applied to 1,3−butadiene, predicts that the ligand may bind to metal either as a L2 (π2) donor type, similar to that of an alkene, or as an LX2 (σ2π) donor type, similar to that of a metalacyclopropane form. The L2 binding of 1,3−butadiene is rare, e.g. asin (butadiene)Fe(CO)3, while the LX2 type binding is more common, e.g. as in Hf(PMe3)2Cl2. An implication of the LX2 type binding is in the observed shortening of the C2−C3 (1.40 Å) distance alongside the lengthening of the C1−C2 (1.46 Å) and C3−C4 (1.46 Å) distances



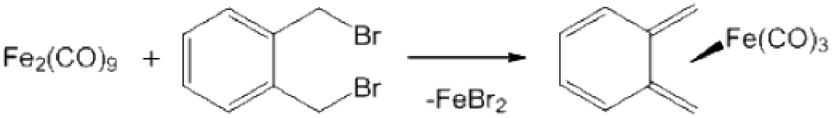
The molecular orbitals of the 1,3−butadiene ligand comprises of two filled Ψ1 (HOMO−1) and Ψ2 (HOMO) orbitals and two empty Ψ3 (LUMO) and Ψ4 (LUMO+1) orbitals. In a metal−butadiene interaction the ligand to metal σ−donation occurs from the filled Ψ2 orbital of the 1,3−butadiene ligand while the metal to ligand π−back donation occurs on to the empty Ψ3 orbital of the 1,3−butadiene ligand.

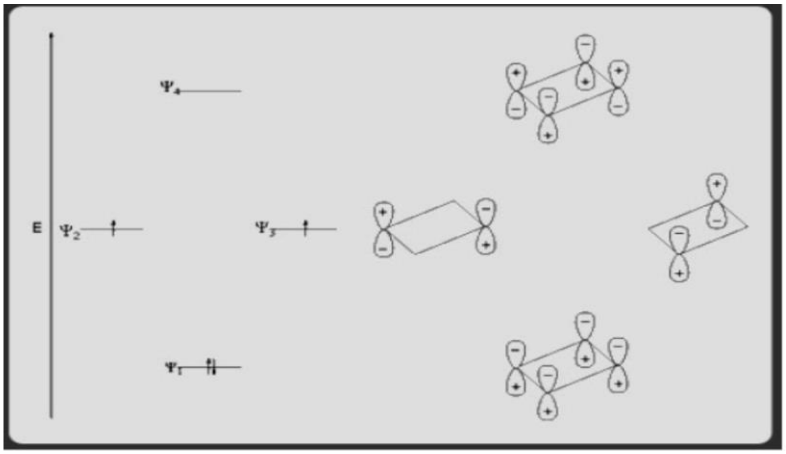
Though *cisoid* binding is often observed in metal butadiene complexes, a few instances of *transoid* binding is seen in dinuclear, *e.g.* as in $Os_3(CO)_{10}(C_4H_6)$, and in mononuclear complexes *e.g.* as in $Cp_2Zr(C_4H_6)$.



Metal cyclobutadiene complexes

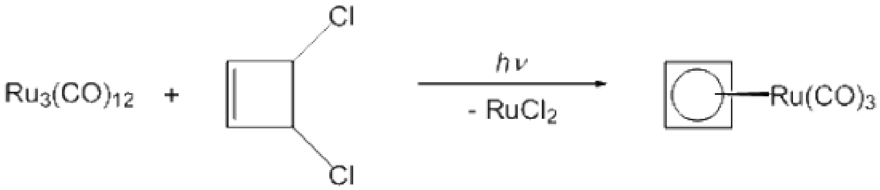
Metal butadiene complexes are usually prepared by the same methods used for synthesizing metal alkene complexes. Two noteworthy synthetic routes are shown below.





Cyclobutadiene is an interesting ligand because of the fact that its neutral form, being anti–aromatic (4π–electrons), is unstable as a free molecule but its dianionic form is stable because of being aromatic (6π–electrons). Consequently, the cyclobutadiene ligand is stabilized by significant metal to ligand π–back donation to the vacant ligand orbitals.

A synthetic route to metal cyclobutadiene complex



Reaction of alkenes

The metal alkene complexes show the following reactivities.

i. Insertion reaction,

These reactions are commonly displayed by alkenes as they insert into metal–X bonds yielding metal alkyls. The reaction occurs readily at room temperature for X = H, whereas for other elements (X = other atoms), such insertions become rare. Also, the strained alkenes and alkynes undergo such insertion readily.

$$PtHCl(PEt_3)_2 + C_2H_4 \rightleftharpoons PtEtCl(PEt_3)_2$$

ii. *Umpolung* reactions

Umpolung reactions are observed only for those metal–alkene complexes for which the metal center is a poor π–base and as a result of which the olefin undergoes a nuclophilic attack

iii. Oxidative addition

Alkenes containing allylic hydrogens undergo oxidative addition to give a allyl hydride complex.

Transition metal alkyl complexes play a critical role in a variety of important organometallic reactions such as olefin polymerization and hydroformylation. Early attempts to synthesize these complexes were unsuccessful, so it was originally thought that such species were inherently unstable due to weak metal-carbon bonds. In fact, the issue is not their thermodynamic stability (M-C bond dissociation energies are typically 40-60 kcal/mol with 20-70 kcal/mol being a practical range), but their **kinetic** stability. More on this below.

Allyl ligands are ambidentate ligands that can bind in both a monohapto and trihapto form. The trihapto form can be expressed as a number of difference resonance forms as shown here for an unsubstituted allyl ligand:

η^1-form

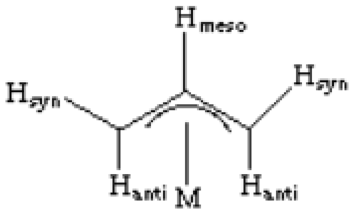
η^3-form

Counting electrons in allyl complexes is easy. For the monohapto form, simply consider it to be an alkyl ligand (1 or 2 electron donor depending which formalism you use). In the trihapto form, it is easiest to think of it as an alkyl (1 or two electrons) + a neutral alkene (2 electrons) for a total of 3 or 4 electrons donated.

Structure and Bonding

In the trihapto form, the C-C distances and bond angles are about what we'd expect, 1.35 to 1.40 Angstroms (comparable to that in ferrocene, for example) with a C-C-C angle of 120 degrees. The two C-C bonds are usually the same length, but there are some exceptions, particularly when strongly pi-bonding ligands are trans to the allyl ligand.

The plane of the allyl ligand is typically tilted away from perpendicular to maximize orbital overlap. Krüger et. alreport on the neutron diffraction structure of an allyl complex. They found that H_{meso} and H_{syn} are bent towards the metal (7 and 13 degrees from planar) while H_{anti} is bent 31 degrees away. In this particular example, the Ni-C1 and Ni-C3 distances are approximately 2.03 Angstroms and Ni-C2 is 1.98 Angstroms



Spectroscopic Features of Allyl Ligands

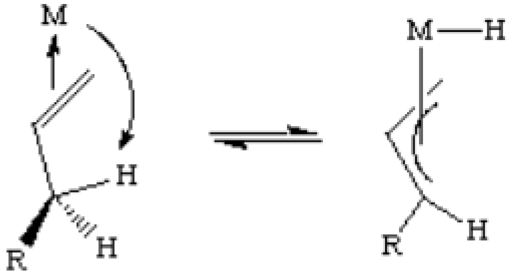
The static ^{1} NMR structure of a typical trihapto allyl has H_{anti} at 1 - 3 ppm, H_{syn} at 2 - 5 ppm and H_{meso}around 4 - 6.5 ppm. There is no syn-anti proton-proton coupling. In the ^{13}C NMR, the terminal carbons appear between 80 - 90 ppm and the central carbon from 110-130 ppm.

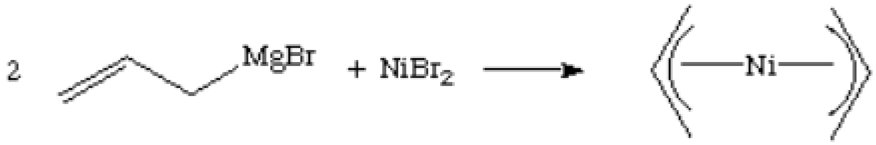
Allyl ligands can be fluxional on the NMR time scale, but we won't discuss an example here.

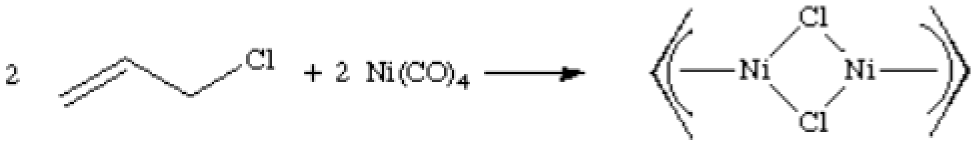
Synthesis of Allyl Complexes

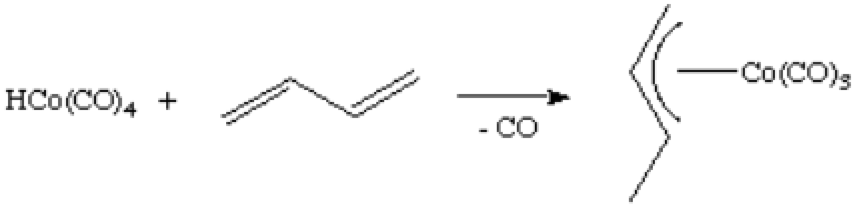
Most syntheses of trihapto allyl complexes involve the synthesis of a monohapto complex which then displaces a ligand to give the trihapto form. Common methods for the synthesis of allyl complexes include:

1. From an alkene via hydrogen attack on the metal. In the example below, note that if we then put the hydrogen on the other terminal carbon, we have accomplished an overall 1,3-hydrogen shift.
2. Nucleophilic or electrophilic substitution at the metal using an allylic substrate.
3. Oxidative addition of an allylic substrate to a low valent metal center.
4. Protonation or insertion of a 1,3-diene complex.
5. **5.** There are several other method



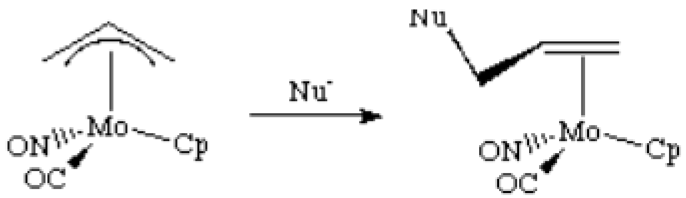


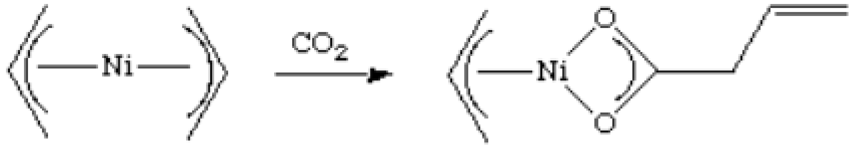


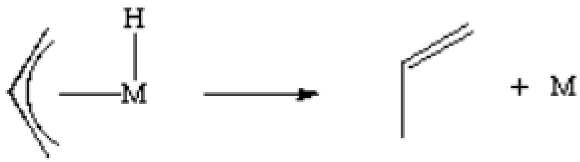


Reactions of Allyl Complexe

1. With nucleophiles. This is **stereoselective** if the metal is not attacked first. Attack occurs on the face opposite the metal and usually at the terminal carbon.
2. With electrophiles.
3. Insertion reactions.
4. Reductive elimination.





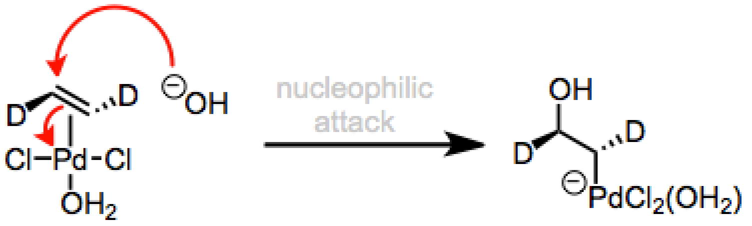


Metal alkene complexes reactivity

The reactivity patterns of alkene and alkyne ligands are remarkably similar to those of carbon monoxide: nucleophilic attack and migratory insertion dominate their chemistry. The important issues of **site selectivity** and **stereoselectivity** come into play when considering alkenes and alkynes, however—the fundamental questions are…

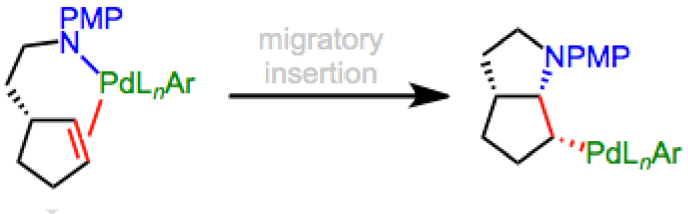
- Which atom gets the nucleophile/migrating group?
- Which atom gets the metal?
- What is the relative orientation of the nucleophile/migrating group and the metal (*cis* or *trans*)?

The wide variety of what we might generally call "**atom-metallation**" processes (carbopalladation, carboauration, aminopalladation, oxypalladation, etc.) may involve external nucleophilic addition to the π system, with attachment of the metal to the carbon that was not attacked. The net result is the addition of atom and metal across the π bond, in a *trans* or *anti* orientation. The *anti* orientation results because the nucleophile attacks the face opposite the metal center. A *cis* orientation of nucleophile and metal is indicative of a migratory insertion pathway (see below). In the example in the following figure, the metal alkyl was converted into a chlorohydrin using copper(II) chloride and LiCl (with stereospecific inversion). Subsequent epoxide formation with NaOH afforded only the *cis* diastereomer, supporting the *trans* configuration of the metal alkyl.



Nucleophilic attack on a coordinated alkene or alkyne is always trans, or anti.

Migratory insertion of alkenes and alkynes, like insertions of CO, can be thought of as an internal attack by a nucleophile already coordinated to the metal center. Migratory insertion is the C–C bond-forming step of **olefin polymerization**, and some fascinating studies of this reaction have shown that the alkyl group (the growing polymer chain) migrates to the location of the olefin (not the other way around). Migratory insertion is also important for the **Heck reaction**—in this case, the olefin inserts into a Pd–C_{sp}^{2} bond. Finally, a large number of metal-catalyzed addition reactions rely on migratory insertion as the key C–X bond-forming step. *cis*-Aminopalladation is one example.



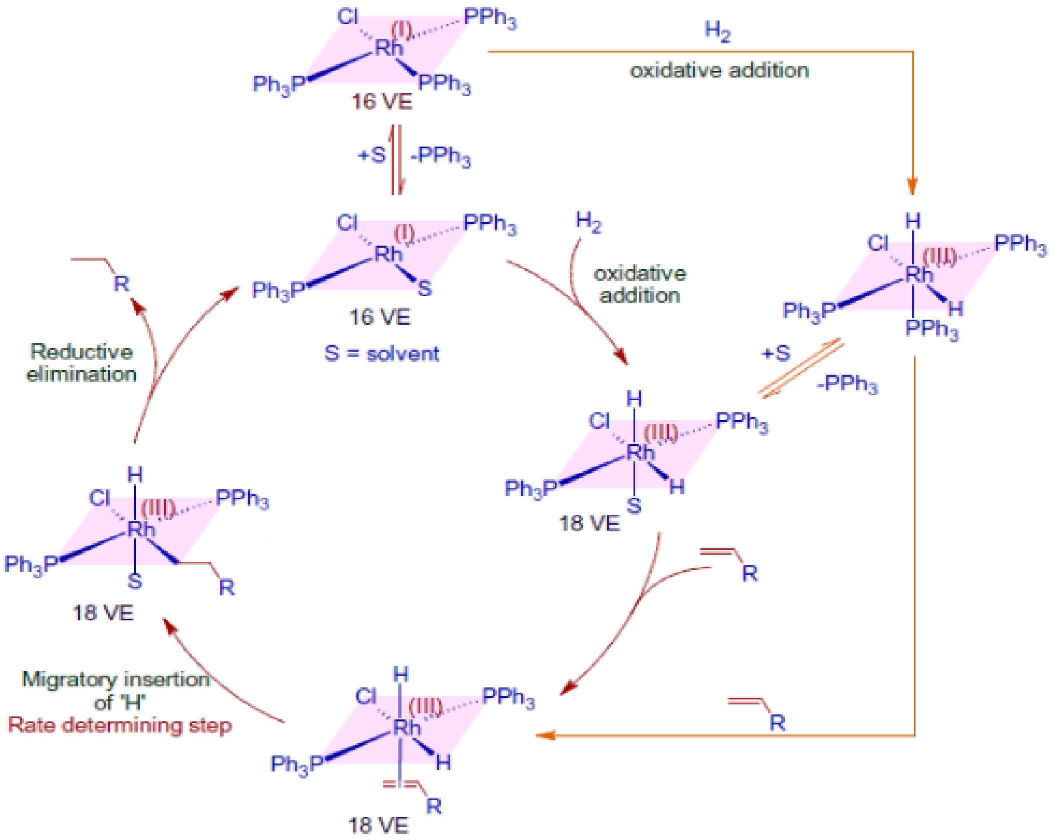
cis-Aminopalladation via migratory insertion. Two new bonds are established with stereospecificity!

Importantly, migratory insertion of alkenes and alkynes into M–X bonds takes place in a *syn* or *cis* fashion—the metal and the migrating group (X) end up on the same face of the π system. The site selectivity of migratory insertion may be controlled by either steric factors or the π system's electronics, although the former is more common, I'd say. Electronics are at play in Wacker oxidations of 1-alkenes, for example, which exclusively yield methyl ketones.

Finally, **electrophilic attack** on π systems coordinated to electron-rich metals can also happen, although it's much rarer than nucleophilic attack. Usually these reactions involve coordination of the electrophile to the metal, followed by migratory insertion. We'll hear more about this in a future post on electrophilic attack on coordinated ligands. Coming up next: cyclic π systems!

Olefin hydrogenation

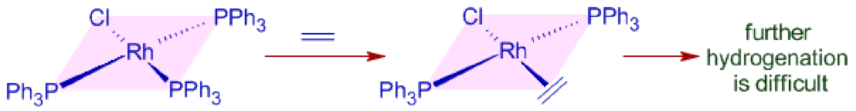
Wilkinson's catalyst is best known for catalyzing the hydrogenation of olefins with molecular hydrogen. The mechanism of this reaction involves the initial dissociation of one or two triphenylphosphine ligands to give 14- or 12-electron complexes, respectively, followed by oxidative addition of H_2 to the metal. Subsequent π-complexation of alkene, migratory insertion (intramolecular hydride transfer or olefin insertion), and reductive elimination complete the formation of the alkane product



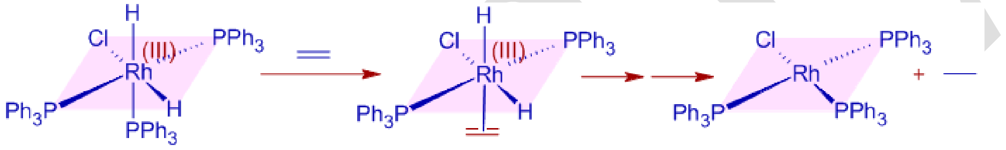
Above mechanism is supported by following observations.

The rate of reaction decreases when excess of PPh_3 is added; indicating the initial dissociation of one of the PPh_3 ligand before dihydrogen activation.

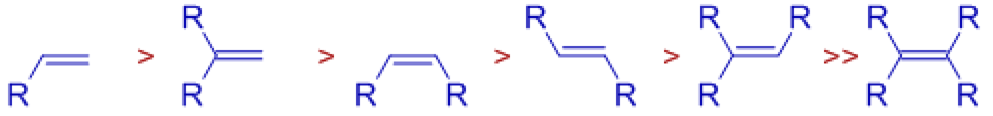
It is observed that strong π-acids like ethylene act as poisons by binding strongly with the electron rich Rh metal center and inhibit hydrogenation.



Though ethylene cannot be hydrogenated in presence of Wilkinson's catalyst under normal conditions, hydrogen transfer can be achieved with preformed dihydrido complex.

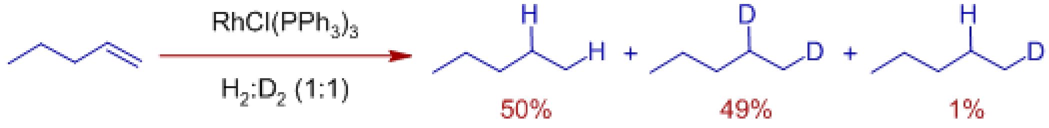


The rates of hydrogenations decrease with increase in the alkyl group substitution on double bond mirroring their relative binding affinities to the metal center. It is also partly due to steric factors.



Therefore, for a successful hydrogenation, oxidative addition of dihydrogen prior to the binding of olefin is crucial.

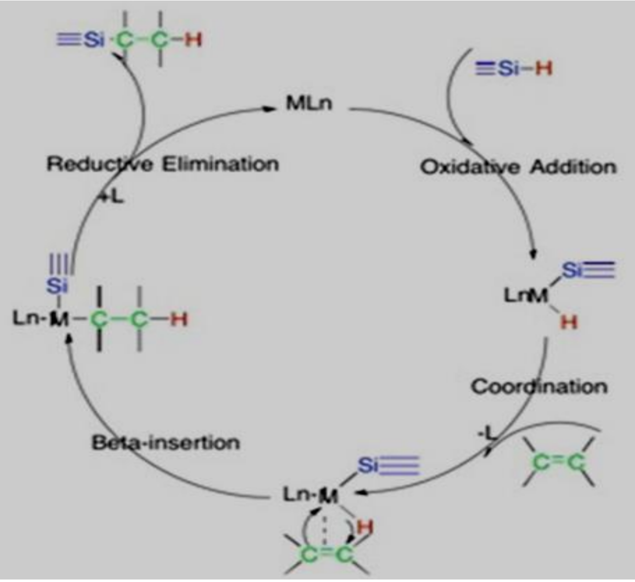
* There is minimal scrambling of H/D in the product, when an equimolar mixture of H_2 and D_2 are used.



This indicates the formation of dihydrido complex that transfers both of its hydrido ligands to the olefin and that the final reductive elimination step is very fast and irreversible.

Hydrosilation

Hydrosilylation, also known as hydrosilation, is one of the most useful catalytic reactions leading to the formation of organsilanes and organosilicones, which have a variety of applications in industry and as intermediates in organic chemistry. Hydrosilylation occurs via the addition of H-Si to an unsaturated bond such as carbon-carbon bond, carbon-oxygen bond, carbon-nitrogen bond, nitrogen-nitrogen bond and nitrogen-oxygen bond using a metal catalyst, Lewis Acid, or radical initiator. The basic reaction can be described using the following scheme:



In the first step a Si-H bond undergoes oxidative addition to a metal center. The alkene coordinates and then undergoes insertion. The hydrogen is then added to the alkene through H beta-insertion. In the final step the alkylsilyl Pd(II) complex undergoes reductive elimination to deliver the adduct and return the metal to the original oxidation state

The reactivity of hydrosilylation is influenced by many factors: substrate, silane, transition metal catalyst, ligand etc. which makes the reaction diverse as well as complicated. Studies have been performed to determine the reactivity influenced by each of these factors. Because there are a large variety of substrates that can be used, we will focus on alkenes. Here are some general rules:

Reaction rate: 1-alkene > 2-alkene > 3-alkene

Generally, the more substituted the alkene group, the slower the reaction would be. This is due to the more substituted alkene group being bulkier, therefore it will be harder for the alkene coordination to happen to the metal. More substituted alkene groups also make it more difficult for the H atom to undergo compete beta-insertion.

Reaction rate: $SiHCl_3 > (C_6H_5)_3SiH > (C_2H_5)_3SiH$

$V_0(10^5)$: 110 12 1.2

From this set of data, we can derive that the rate of reactivity would increase depending on the substituted groups on the silanes. The order of reactivity is: chlorine > aromatic rings > alkanes. However, this rule is not always true. If we substituted the aromatic groups in $(C_6H_5)_3SiH$ with Cl, the reaction rate would be:

Reaction rate: $(C_6H_5)_3SiH > (C_6H_5)_2SiH_2 > (C_6H_5)SiH_3$

$V_0(10^5)$: 12 1.7 0.69

This shows that the substituted groups do not affect the reactivity individually. The overall regularity for change of silanes is complicated and varies with each group

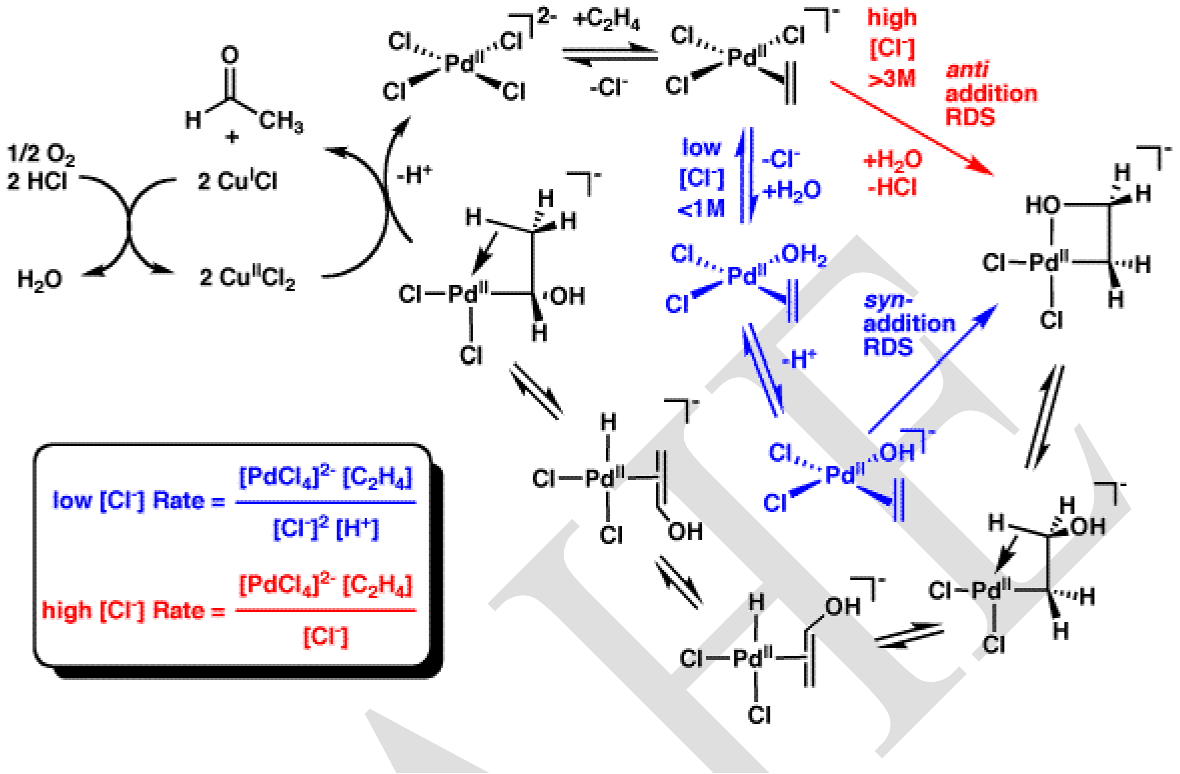
Wacker process

Acetaldehyde (CH_3CHO), also called **ethanal**, an aldehyde used as a starting material in the synthesis of 1-butanol (*n*-butyl alcohol), ethyl acetate, perfumes, flavourings, aniline dyes, plastics, synthetic rubber, and other chemical compounds. It has been manufactured by the hydration of acetylene and by the oxidation of ethanol (ethyl alcohol). Today the dominant process for the manufacture of acetaldehyde is the Wacker process, developed between 1957 and 1959, which catalyzes the oxidation of ethylene to acetaldehyde. The catalyst is a two-component system consisting of palladium chloride, $PdCl_2$, and copper chloride, $CuCl_2$.

$$\underset{\text{ethylene}}{2\,CH_2{=}CH_2} + O_2 \xrightarrow{PdCl_2,\ CuCl_2} \underset{\text{acetaldehyde}}{2\,CH_3CHO}$$

Pure acetaldehyde is a colourless, flammable liquid with a pungent, fruity odour; it boils at 20.8 °C (69.4 °F).

The reaction mechanism for the industrial Wacker process (olefin oxidation via palladium(II) chloride) has received significant attention for several decades. Aspects of the mechanism are still debated. A modern formulation is described below



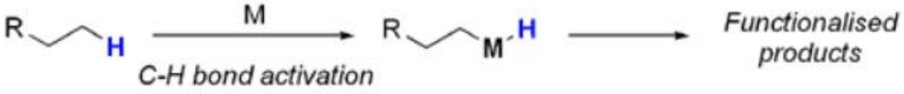
Ethylene and oxygen are passed co-currently in a reaction tower at about 130 °C and 400 kPa. The catalyst is an aqueous solution of $PdCl_2$ and $CuCl_2$. The acetaldehyde is purified by extractive distillation followed by fractional distillation. Extractive distillation with water removes the lights ends having lower boiling points than acetaldehyde (chloromethane, chloroethane, and carbon dioxide) at the top, while water and higher-boiling byproducts, such as acetic acid, crotonaldehyde or chlorinated acetaldehydes, are withdrawn together with acetaldehyde at the bottom. Due to the corrosive nature of catalyst, the reactor is lined with acid-proof ceramic material and the tubing is made of titanium.

In summary, experimental evidence seems to support that syn-addition occurs under low-chloride reaction concentrations (< 1 mol/L, industrial process conditions), while anti-addition occurs under high-chloride (> 3mol/L) reaction concentrations, probably due to chloride ions saturating the catalyst and inhibiting the inner-sphere mechanism. However, the exact pathway and the reason for this switching of pathways is still unknown.

C-H activation of alkenes

Transition metal catalysis lies at the heart of modern innovative science. As the field has matured, new areas have emerged that challenge the frontiers of synthetic organic chemistry. The capacity to activate a specific 'inert' C-H bond and transform it to a more versatile functional group is an emerging area in chemistry. To expand this area in organic synthesis, the challenge is to identify novel strategies for the formation of organo-metal intermediates under mild conditions and to discover new methods for their subsequent functionalisation. This process is perhaps the ultimate synthetic transformation and presents an exciting and fundamental challenge for chemists.

We are interested in developing new inter- and intramolecular C-C bond forming reactions catalysed by transition metals. In particular, our research focuses on the activation of C-H bonds and we are investigating methods by which *sp, sp^2 and sp^3 hybridised C-H bonds can be activated by transition metal catalysts under ambient conditions* to form a diverse range of useful molecular architectures.



C-H Activation and Functionalisation

Target Structures for C-H Activation

The first reported organometallic compounds were prepared by the reductive substitution of alkyl halides, as shown in the following three equations. All these metals have strong or moderate negative reduction potentials, with lithium and magnesium being the most reactive. Halide reactivity increases in the order: Cl < Br < I. Alkylsodium and potassium compounds are not made in this way because Wurtz coupling of the alkyl moiety (giving R–R) tends to predominate. This can also be a problem when allyl or benzyl halides are converted to Grignard or lithium reagents.

R-X + Zn ——> R-Zn-X An Alkyl Zinc Reagent 1850 E. Frankland

R-X + Mg ——> R-Mg-X A Grignard Reagent 1900 V. Grignard

R-X + 2Li ——> R-Li + LiX An Alkyl Lithium Reagent 1917 W. Schlenk (1930 K. Ziegler)

PART-B (6 Mark Questions)

1. Writeeffective atomic number rule with examples
2. The general preparation methods of metal carbonyls hydride with examples
3. Explain the steps ofoxidative addition and reductive elimination reaction
4. Insertions reaction of alkenes and alkynes complexes
5. Synthesis of metal alkene complexes by various methods.
6. Discus the C-H activation of alkenes process
7. Preparation of the half sandwich compound, reactivity
8. Brief reaction mechanism of Ziegler-Natta catalyst
9. Write the reaction and mechanism of Cobalt catalysed alkyne cycloaddition?
10. Brief reaction mechanism of Wilkinson's catalyst

PART-C (10 Mark Questions)

1. (i) Explain Oxidative addition and nucleophilic attack on organometallic compound
   (ii) Discuss the Redox reactions in Vaska’s complexes

DEPARTMENT OF CHEMISTRY

Online questions (Multiple choice questions)

ORGANOMETALLICCHEMISTRY (17CHP205C)

UNIT III

S. No	Questions	Option-A	Option-B	Option-C	Option-D	Answer
1	Ethyl malonate is prepared from	Potassium cyano acetate	Sodium cyano acetae	Magnesiun cyano acetate	Barium cyano acetate	Potassium cyano acetate
2	Which statement is correct?	Cp2Mg is monomeric	Cp2Ca is monomeric	Cp2Be is polymeric	Cp2Sr is monomeric	Cp2Mg is monomeric
3	Which statement is incorrect about the reaction of Na with naphthalene in THF?	A diamagnetic salt is formed	A coloured solution is formed	Naphthalene is reduced	The product is a reducing agent	A diamagnetic salt is formed
4	The main tin-containing product of the reaction of R3SnCl (R = alkyl or aryl) with Mg is:	R2SnCl2	R3SnMgCl	Sn2R6	R4Sn	Sn2R6
5	1,2-(Me2As)2C6H4 is important as:	a chelating ligand for heavy d-block metals	a chelating ligand for early, first row d-block metals	a chelating ligand for alkali metal ions	a chelating ligand for lanthanoid metal ions	a chelating ligand for heavy d-block metals
6	The room temperature 13C NMR spectrum of 6Li labelled [tBuLi]n exhibits a 9-line multiplet for the quaternary	n = 8	n = 4	n = 6	n = 9	n = 4

	carbon atoms. Assuming that the molecule is sterochemically non-rigid at this temperature, what value of n is consistent with these data? (6Li, I = 1).					
7	Which statement is correct about R3E compounds where E is a group 15 element?	As group 15 is descended, the Lewis acidity of R3E increases	As group 15 is descended, the Lewis basicity of R3E decreases	Whereas R3NO is stable at 298 K with respect to reduction to R3N, R3Bi is difficult to oxidize to R3BiO	The oxidative addition of RX to R3E occurs most easily for E = Bi	As group 15 is descended, the Lewis basicity of R3E decreases
8	Match the molecule to the shape at the central atom centre. Which pairing is correct?	In(CH2Ph)3; trigonal pyramidal	Me3Al(py) (py = pyridine); tetrahedral	R2Ge (R = CH(SiMe3)2); linear	Me2TeCl2; tetrahedral	Me3Al(py) (py = pyridine); tetrahedral
9	Which statement about a catalyst is incorrect?	The presence of a catalyst speeds up a reaction	The presence of a catalyst changes the rate of a reaction	In some reactions, one of the products acts as a catalyst for the forward reaction	During use, a catalyst may be poisoned	The presence of a catalyst speeds up a reaction
10	Which of the following criteria is least importan t for a homogeneous, organometallic catalyst?	The metal centre must normally be able to accommodate both a 16 or 18 valence electron count	The metal centre must be able to tolerate more than one ligand geometry	The metal centre must be able to undergo oxidation and reduction reactions	The catalyst must be contain a third row d-block metal	The catalyst must be contain a third row d-block metal
11	Match the	cis-[Rh(CO)2I2]–;	RhCl(PPh3)3; alkene	HRh(PPh3)3;	HCo(CO)4;	HRh(PPh3)3;

	compound formula to its application as a catalyst or catalyst precursor in the stated process. Which pair is incorrect?	Monsanto acetic acid synthesis	hydrogenation	asymmetric hydrogenation	hydroformylation of alkenes	asymmetric hydrogenation
12	Hydroformylation of alkenes may lead to alcohol and aldehyde products. Which statement is correct?	The stereoselectivity of the reaction gives the aldehyde:alcohol ratio	The chemoselectivity of the reaction gives the n:i aldehyde ratio	The regioselectivity of the reaction gives the aldehyde:alcohol ratio	The regioselectivity of the reaction gives the n:i aldehyde ratio	The regioselectivity of the reaction gives the n:i aldehyde ratio
13	In the Tennessee–Eastman acetic anhydride process, the catalyst is cis-[Rh(CO)2I2]–. Which sequence of steps best describes the primary catalytic cycle?	Oxidative addition of MeI and loss of CO; Me migration; addition of 2 CO; elimination of MeC(O)I	Oxidative addition of MeI; Me migration; CO addition; elimination of MeC(O)I		Loss of CO; oxidative addition of MeI; Me migration; addition of 2 CO; elimination of MeC(O)I	Oxidative addition of MeI; Me migration; CO addition; elimination of MeC(O)I
14	Which statement is incorrect about chemisorption of CO on a metal (M) surface?	CO molecules are activated	IR spectroscopy can be used to study the system	M–C bonds are formed	The CO molecules must be terminally bound	The CO molecules must be terminally bound
15	Which statement is incorrect abou	The catalyst used commercially is α-Fe;	Chemisorption of N2 and H2 activates	A high temperature is needed because	Both a high temperature and	A high temperature is needed because the

	t the industrial Haber process for NH3 production ?	catalyst promoters are added	the molecules, weakening and cleaving their bonds	the forward reaction is endothermic	pressure are required	forward reaction is endothermic
16	The following statements are about catalytic converters. Which one is incorrect?	Permissible emission gases are CO2, N2 and H2O	The precious metals Rh, Pt and Pd are used in 3-way converters	Ce2O3/CeO2 is an "O2 storage" additive	Rh catalyses the oxidation of NO	Rh catalyses the oxidation of NO
17	In the hydrogenation of alkenes using Wilkinson's catalyst, the active catalyst is RhCl(PPh3)2 (or RhCl(PPh3)2(solvent)). The first step in the catalytic cycle is:	alkene coordination	oxidative addition of H2	loss of PPh3	loss of Cl–	oxidative addition of H2
18	A key feature of the Fischer-Tropsch process is:	hydrocarbon formation	alkene hydrogenation	alkene polymerization	hydroformylation	hydrocarbon formation
19	Which step, taken from a catalytic cycle, is an example of reductive elimination?	Loss of RCH2CH3 from Rh(H)2(CO)(PPh3)2(CH2CH2R)	Conversion of Rh(CO)2(PPh3)2(CH2CH2R) to Rh(CO)(PPh3)2(COCH2CH2R)	Reaction of Rh(CO)(PPh3)2(CH2CH2R) with H2	Loss of RCH=CHR from PdX(PPh3)2(CHRCH2R) and formation of Pd(H)X(PPh3)2	Loss of RCH2CH3 from Rh(H)2(CO)(PPh3)2(CH2CH2R)
20	Which of the following compounds is a	HCo(CO)3	HRh(CO)(PPh3)3	[Rh(CO)2I4]–	Pd(PPh3)4	HCo(CO)3

	16-electron species and is an active catalyst?					
21	Typical Grubbs' catalysts contain:	Ru; a carbene ligand	Rh; a carbene ligand	Ru; an alkene ligand	Mo; a carbene ligand	Ru; a carbene ligand
22	Adsorption of a species X onto a surface with concomitant surface–X bond formation is called:	chemisorption	catalysis	desorption	physisorption	chemisorption
23	Which statement is incorrect about zeolites?	No zeolites occur naturally	Zeolites are aluminosilicates	Each zeolite contains channels of a specific size	A zeolite functions as an acid catalyst, e.g. in the alkylation of aromatic compounds	No zeolites occur naturally
24	A Schrock-type catalyst for alkyne metathesis may contain:	high oxidation state tungsten and a W=CR2 unit	low oxidation state tungsten and a W=CR2 unit	low oxidation state tungsten and a W≡CR unit	high oxidation state tungsten and a W≡CR unit	high oxidation state tungsten and a W≡CR unit
25	One of the following ligands is chiral. Which is it?	Me2PCH2CH2PPh2	Me2PCH2CH2PMe2	Me2PCHMeCH2PMe2	Me2PCH2CH2AsMe2	Me2PCHMeCH2PMe2
26	Ziegler-Natta catalysis is associated with:	alkene hydrogenation	alkene polymerization	hydroformylation of alkenes	alkyne metathesis	alkene polymerization
27	The oxidation of SO2 to SO3:	is thermodynamically favourable, but is slow under ambient conditions	is thermodynamically unfavourable under ambient conditions	has a low activiation energy under ambient conditions	is explosive under ambient conditions, and the reaction must be controlled on	is thermodynamically favourable, but is slow under ambient conditions

					an industrial scale	
28	What would be the main reason for replacing the PPh3 ligands in a catalyst by P(C6H4SO3-)3ligands?	To increase the leaving group ability of the ligand	To increase the steric demands of the ligand, making it harder to replace	To increase the water solubility of the catalyst	To increase the solubility of the catalyst in organic solvents	To increase the water solubility of the catalyst
29	Alkynes are more electro negative than alkenes and are therefore better	π acceptors	π donar	σ acceptor	σ donar	π acceptors
30	In allyl complexes it can function as a three electron donar is called	monohapto	Dihapto	Trihapto	tetra hapto	Trihapto
31	In allyl complexes geometrical isomers are known which arise because of the position of ---- relative to other ligands	Central allyl carbon atom	terminal allyl carbon atom	Central metal atom	Carbon- carbon bond	Central allyl carbon atom
32	[Rh(Cl)(PPh3)] is called --------	Vaskas compound	Wilkinsons catalyst	Zigler natta catalyst	carbon	Wilkinsons catalyst
33	Electron transfer reaction in which oxidant gains the same number of electrons as the reductant loses -	Complementary electron transfer reaction	Elementary electron transfer reaction	Primary electron transfer reaction	Secondary electron transfer reaction	Complementary electron transfer reaction

	----					
34	The main success of homogeneous catalysis is the conversion of methanol to	Acetic acid	Oxalic acid	Sulphuric acid	hydrochloric acid	Acetic acid
35	The catalyst used for the conversion of methanol to acetic acid	Sr salt	Pt salt	Rh salt	Ag salt	Rh salt
36	The process of conversion of methanol to acetic acid using Rh salt as catalyst is called	Canizzaro reaction	Aldol condensation	Reformatsky reaction	Monsanto acetic acid process	Monsanto acetic acid process
37	In Monsanto acetic acid process inversion of takes place	CO	CO2	SO2	NO2	CO
38	Who proposed the conversion of acetic anhydride from methyl acetate in Monsanto manner	Bethe	Prevost	Mannich	tennesee eastman	tennesee eastman
39	The process in which the catalytic addition of molecular oxygen to alkene	Wacker process	Contact process	Heat process	Haber process	Wacker process

	is called					
40	The product of wacker process is given as	Aldehydes	Ketones	Ozonide	Alkane	Aldehydes
41	The product formed , when the acidification of carbonylate ion	Carbonyl hydrido complex	Carbonyl complex	Carboxylate anion	carbon	Carbonyl hydrido complex
42	Which is the relatively expensive catalyst used in hydroformylation	Cobalt	Rhodium	Copper	Nickel	Rhodium
43	The uses of which catalyst will continue to increase in hydroformylation chemistry	Cobalt	Copper	Rhodium	Zinc	Rhodium
44	who proposed the most widely accepted mechanism for hydrofomylation	Watson and Crick	Cannzaro	Wittig	Heck and Breslow	Heck and Breslow
45	Hydroformylation is carried out in such a way that aldehydes are reducesd to give	Alcohols	Acids	ketones	carbon	Alcohols
46	The reaction of an alkene with carbnmonoxide and hydrogen,	Hydroformylation	Hydroxylation	Hydrogenation	carbon	Hydroformylation

	catalysed by cobalt or rhodium salt, to form an aldehyde is called					
47	In hydroformylation cobalt and ----- are used as catalysis	Rhodium	Bismath	copper	Nickel	Rhodium
48	Many of the properties of metal complexes are dictated by which structure?	Chemical	Physical	Electron	Electronic	Electronic
49	Which isomerism occurs when the bonds are themselves different?	Stereo	Optical	Cis-trans	Structural	Structural
50	which is highest melting halide	NaCl	NaBr	NaF	NaOH	NaF
51	When the triphenyl phosphine ligands are replaced by chiral phosphines the catalyst becomes chiral and converts prochiral alkenes into enantiomerically	Symmetric hydrogenation	Asymmetric hydrogenation	Hydrogenation	Desociation	Asymmetric hydrogenation

	enriched alkanes via the process called ?					
52	The original catalyst was HCo(CO)4, discovered by ?	Chernyaev	Wilkinson's	Otto Roelen	Flemming	Otto Roelen
53	Which one of the following is a carbonyl complex?	RhCl(PPh3)3	RhCl(CO)(PPh3)2	PPh3	HCo(CO)3	HCo(CO)3
54	Hydroformylation, also known as ?	oxo synthesis	Oxo production	Oxo reduction	Oxo decomposition	Oxo synthesis
55	Monsanto process operates at a pressure of ?	30-60 atm	40-70atm	20-60atm	30-50 atm	30-60 atm
56	Which speed up inner sphere reactions?	Increasable ligands	Ligand	Reducible ligands	Metal	Reducible ligands
57	Ligands that are able to bridge are required for ?	Inner sphere mechanism	Rates of reaction	Sphere mechanism	Outer sphere mechanism	Inner sphere mechanism
58	Which one of the following depend on the ability of the electron to “tunnel” through the ligands from one metal to the other?	Speed of reaction	Ability of reaction	Rates of reaction	Catalyst	Rates of reaction
59	In reduction the metal ion	Less positively charged	More positively charged	Negatively charged	Less negatively charged	Less positively charged

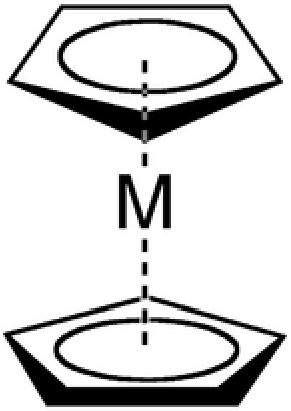
	becomes ?					
60	Chloride is said to have a stronger trans effect than ?	Iodine	Ammonia	CN	NO2	Ammonia

UNIT-4

SYLLABUS

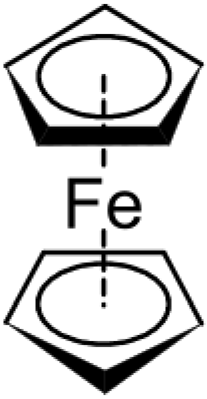
Metallocenes - synthesis of metallocenes - bonding in metallocenes - reactions of metallocenes - Cp_2Fe/Cp_2Fe+ couples in biosensors -bent sandwich, complexes - bonding in bent sandwich complexes - metallocene halides and hydrides - metallocene and stereospecific polymerisation of 1-alkenes - cyclopentadiene as a non-spectator, ligand - monocyclopentadienyl (half-sandwich) complexes - synthesis and structures of allyl complexes - arene complexes - synthesis - structure and reactivity of arene complexes - multidecker complexes.

History



A **metallocene** is a compound typically consisting of two cyclopentadienyl anions (Cp, which is $C_5H_5^-$) bound to a metal center (M) in the oxidation state II, with the resulting general formula $(C_5H_5)_2M$. Closely related to the metallocenes are the metallocene derivatives, e.g. titanocene dichloride, vanadocene dichloride. Certain metallocenes and their derivatives exhibit catalytic properties, although metallocenes are rarely used industrially. Cationic group 4 metallocene derivatives related to $[Cp_2ZrCH_3]^+$ catalyze olefin polymerization. Metallocenes are a subset of a broader class of organometallic compounds called sandwich compounds.

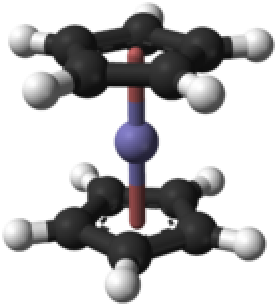
In the structure shown at right, the two pentagons are the cyclopentadienyl anions with circles inside them indicating they are aromatically stabilized. Here they are shown in a staggered conformation.



Ferrocene

The first metallocene to be classified was ferrocene, and was discovered simultaneously in 1951 by Kealy and Pauson, and Miller et al. Keally and Pauson were attempting to synthesize fulvalene through the oxidation of a cyclopentadienyl salt with anhydrous $FeCl_3$ but obtained instead the substance $C_{10}H_{10}Fe$ At the same time, Miller *et al* reported the same iron product from a reaction of cyclopentadiene with iron in the presence of aluminum, potassium, or molybdenum oxides. The structure of "$C_{10}H_{10}Fe$" was determined by Wilkinson et al. and by Fischer et al. These two were awarded the Nobel Prize in Chemistry in 1973 for their work on sandwich compounds, including the structural determination of ferrocene. They determined that the carbon atoms of the cyclopentadienyl (Cp) ligand contributed equally to the bonding and that bonding occurred due to the metal d-orbitals and the π-electrons in the p-orbitals of the Cp ligands. This complex is now known as ferrocene and the group of transition metal dicyclopentadienyl compounds is known as metallocenes and have the general formula $[(\eta^5\text{-}C_5H_5)_2M]$. Fischer et al. first prepared the ferrocene derivatives involving Co and Ni. Often derived from substituted derivatives of cyclopentadienide, metallocenes of many elements have been prepared.

Definition



Ball-and-stick model of a metallocene moleculewhere the cyclopentadienyl anions are in a staggered conformation. The purple ball in the middle represents the metal cation.

The general name metallocene is derived from ferrocene, $(C_5H_5)_2Fe$ or Cp_2Fe, systematically named bis(η^5-cyclopentadienyl)iron(II). According to the IUPAC definition, a metallocene contains a transition metaland two cyclopentadienyl ligands coordinated in a sandwich structure, i.e., the two cyclopentadienyl anions are on parallel planes with equal bond lengths and strengths. Using the nomenclature of "hapticity", the equivalent bonding of all 5 carbon atoms of a cyclopentadienyl ring is denoted as η^5, pronounced "pentahapto". There are exceptions, such as uranocene, which has two cyclooctatetraene rings sandwiching a uranium atom.

In metallocene names, the prefix before the *-ocene* ending indicates what metallic element is between the Cp groups. For example in ferrocene, iron(II), ferrous iron is present.

In contrast to the more strict definition proposed by IUPAC, which requires a d-block metal and a sandwich structure, the term metallocene and thus the denotation *-ocene*, is applied in the chemical literature also to non-transition metal compounds, such as barocene (Cp_2Ba), or structures where the aromatic rings are not parallel, such as found in manganocene or titanocene dichloride (Cp_2TiCl_2).

Some metallocene complexes of actinides have been reported where there are three cyclopendadienyl ligands for a monometallic complex, all three of them bound η^5.

Classification

There are many (η^5-C_5H_5)–metal complexes and they can be classified by the following formulas:

Formula	**Description**
$[(\eta^5\text{-}C_5H_5)_2M]$	Symmetrical, classical 'sandwich' structure
$[(\eta^5\text{-}C_5H_5)_2ML_x]$	Bent or tilted Cp rings with additional ligands, L
$[(\eta^5\text{-}C_5H_5)ML_x]$	Only one Cp ligand with additional ligands, L ('piano-stool' structure)

Metallocene complexes can also be classified by type:

1. Parallel
2. Multi-decker
3. Half-sandwich

4. Bent or tilted
5. More than two Cp ligands

Synthesis of metallocenes

There are three main routes that are normally employed in the formation of these types of compounds:

Using a metal salt and cyclopentadienyl reagents

Sodium cyclopentadienide (NaCp) is the preferred reagent for these types of reactions. It is most easily obtained by the reaction of molten sodium and dicyclopentadiene. Traditionally, the starting point is the cracking of dicyclopentadienyl, the dimer of cyclopentadiene. Cyclopentadiene is deprotonated by strong bases or alkali metals.

$MCl_2 + 2\ NaC_5H_5 \rightarrow (C_5H_5)_2M + 2\ NaCl$ (M = V, Cr, Mn, Fe, Co; solvent = THF, DME, NH_3)

$CrCl_3 + 3\ NaC_5H_5 \rightarrow [(C_5H_5)_2Cr] + \frac{1}{2}\ \text{"}C_{10}H_{10}\text{"} + 3\ NaCl$

NaCp acts as a reducing agent and a ligand in this reaction.

Using a metal and cyclopentadiene

This technique provides using metal atoms in the gas phase rather than the solid metal. The highly reactive atoms or molecules are generated at a high temperature under vacuum and brought together with chosen reactants on a cold surface.

$M + C_5H_6 \rightarrow MC_5H_5 + \frac{1}{2}\ H_2$ (M = Li, Na, K)

$M + 2\ C_5H_6 \rightarrow [(C_5H_5)_2M] + H_2$ (M = Mg, Fe)

Using cyclopentadienyl reagents

A variety of reagents have been developed that transfer Cp to metals. Once popular was thallium cyclopentadienide. It reacts with metal halides to give thallium chloride, which is poorly soluble, and the cyclopentadienyl complex. Trialkyltin derivatives of Cp^- have also been used.

Many other methods have been developed. Chromocene can be prepared from chromium hexacarbonyl by direct reaction with cyclopentadiene in the presence of diethylamine; in this case, the formal deprotonation of the cyclopentadiene is followed by reduction of the resulting protons to hydrogen gas, facilitating the oxidation of the metal centre.[9]

$Cr(CO)_6 + 2\ C_5H_6 \rightarrow Cr(C_5H_5)_2 + 6\ CO + H_2$

Metallocenes generally have high thermal stability. Ferrocene can be sublimed in air at over 100 °C with no decomposition; metallocenes are generally purified by vacuum sublimation. Charge-neutral metallocenes are soluble in common organic solvents. Alkyl substituted derivative are particularly soluble, even in alkane solvents.

Structure

A structural trend for the series MCp_2 involves the variation of the M-C bonds, which elongate as the valence electron count deviates from 18.

$M(C_5H_5)_2$	r_{M-C} (pm)	Valence electron count
Fe	203.3	18
Co	209.6	19
Cr	215.1	16
Ni	218.5	20
V	226	15

In metallocenes of the type $(C_5R_5)_2M$, the cyclopentadienyl rings rotate with very low barriers. Single crystal X-ray diffraction studies reveal both eclipsed or staggered rotamers. For non-substituted metallocenes the energy difference between the staggered and eclipsed conformations is only a few kJ/mol. Crystals of ferrocene and osmocene exhibit eclipsed conformations at low temperatures, whereas in the related bis(pentamethylcyclopentadienyl) complexes the rings usually crystallize in a staggered conformation, apparently to minimize steric hindrance between the methyl groups.Spectroscopic properties

Vibrational (infrared and Raman) spectroscopy of metallocenes

Infrared and Raman spectroscopies have proved to be important in the analysis of cyclic polyenyl metal sandwich species, with particular use in elucidating covalent or ionic M–ring bonds and distinguishing between central and coordinated rings. Some typical spectral bands and assignments of iron group metallocenes are shown in the following table:

Spectral frequencies of group 8 metallocenes			
	Ferrocene (cm^{-1})	**Ruthenocene (cm^{-1})**	**Osmocene (cm^{-1})**
C–H stretch	3085	3100	3095
C–C stretch	1411	1413	1405
Ring deformation	1108	1103	1096
C–H deformation	1002	1002	995
C–H out-of-plane bend	811	806	819
Ring tilt	492	528	428
M–ring stretch	478	446	353
M–ring bend	170	185	–

NMR (^{1}H and ^{13}C) spectroscopy of metallocenes

Nuclear magnetic resonance (NMR) is the most applied tool in the study of metal sandwich compounds and organometallic species, giving information on nuclear structures in solution, as liquids, gases, and in the solid state. ^{1}H NMR chemical shifts for diamagnetic organotransition-metal compounds is usually observed between 25 and 40 ppm, but this range is much more narrow for diamagnetic metallocene complexes, with chemical shifts usually observed between 3 and 7 ppm.

Mass spectrometry of metallocenes

Mass spectrometry of metallocene complexes has been very well studied and the effect of the metal on the fragmentation of the organic moiety has received considerable attention and the identification of metal-containing fragments is often facilitated by the isotopedistribution of the metal. The three major fragments observed in mass spectrometry are the molecular ion peak, $[C_{10}H_{10}M]^+$, and fragment ions, $[C_5H_5M]^+$ and M^+.

Derivatives

Main article: Sandwich compound

After the discovery of ferrocene, the synthesis and characterization of derivatives of metallocene and other sandwich compounds attracted researchers' interests.

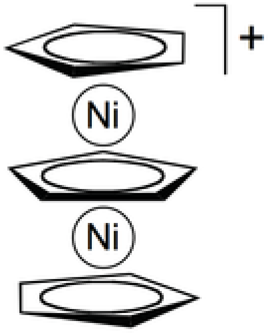
Metallocenophanes

Metallocenophanes feature linking of the cyclopentadienyl or polyarenyl rings by the introduction of one or more heteroannular bridges. Some of these compounds undergo thermal ring-opening polymerizations (ROP) to give soluble high molecular weight polymers with transition metals in the polymer backbone. Ansa-metallocenes are derivatives of metallocenes with an intramolecular bridge between the two cyclopentadienyl rings.

Polynuclear and heterobimetallic metallocenes

- Ferrocene derivatives: biferrocenophanes have been studied for their mixed valence properties. Upon one-electron oxidation of a compound with two or more equivalent ferrocene moieties, the electron vacancy could be localized on one ferrocene unit or completely delocalized.
- Ruthenocene derivatives: in the solid state biruthenocene is disordered and adopts the transoid conformation with the mutual orientation of Cp rings depending on the intermolecular interactions.
- Vanadocene and rhodocene derivatives: vanadocene complexes have been used as starting materials for the synthesis of heterobimetallic complexes. The 18 valence electron ions $[Cp_2Rh]^+$ are very stable, unlike the neutral monomers Cp_2Rh which dimerize immediately at room temperature and they have been observed in matrix isolation.

Multi-decker sandwich compounds



Nickel triple-decker sandwich complex

Triple-decker complexes are composed of three Cp anions and two metal cations in alternating order. The first triple-decker sandwich complex,$[Ni_2Cp_3]^+$, was reported in 1972. Many examples have been reported subsequently, often with boron-containing rings.

Metallocenium cations

The most famous example is ferrocenium, $[Fe(C_5H_5)_2]^+$, the blue iron(III) complex derived from oxidation of orange iron(II) ferrocene (few metallocene anions are known).

Applications

Many derivatives of early metal metallocenes are active catalysts for olefin polymerization. Unlike traditional and still dominant heterogeneous Ziegler-Natta catalysts, metallocene catalysts are homogeneous. Early metal metallocene derivatives, e.g. Tebbe's reagent, Petasis reagent, and Schwartz's reagent are useful in specialized organic synthetic operations.

Bond type

Cp-ligands are generally bound via all 5 carbon atoms to a metal centre (η^5-coordination π-complexes). In rare cases, the Cp unit can bond via a three-carbon π-complex, like in $[(\eta^3\text{-Cp})WCp(CO)_2]$; or it can bond by one carbon in a simple σ bond, as in $[(\eta^1\text{-Cp})FeCp(CO)_2]$.

π-complexes

Metals and cyclopentadienyl anions connected by π bonds are called π-complexes. Unlike a normal σ bond in which two atoms share one electron pair, some or all of the π electrons of the Cp are coordinated to the metal center. π-complexes, especially in the η^5-type coordination mode, are the most typical of the three types of complexes. Almost all of the transition metals, that is, group 4 to 10 metals, employ this coordination mode. η^3-type π-complexes are also seen, depending on the electronic configuration of the metal centre. In this mode, three atoms are bonded to the metal as an allyl anion ligand, and the remaining two of the Cp are more like a simple alkene.

σ-complexes

σ-complexes have a direct σ-bond between the metal and one of the carbons of the cyclopentadienyl group. Typical examples of this type of complex are group 14 metal complexes such as $CpSiMe_3$, Cp_2Sn, and CpPb. $CpSiMe_3$ is commonly used as the starting material for the synthesis of group 4 metal cyclopentadienyl complexes.

Ionic complexes

Ionic complexes primarily involve alkali metal cations and alkali earth metals cations connected to cyclopentadienyl anions. These complexes are not ionic, but the bonding is probably highly polar and often η^1 bonding is indicated. Ionic type complexes are generally synthesized directly by reaction of cyclopentadiene and the metal in a non-aromatic solvent. These complexes can be good starting materials for several π-type cyclopentadienyl complexes.

Synthesis of Cp complexes

Most cyclopentadienyl complexes are prepared by treating a metal halide with sodium cyclopentadienide (NaCp). For the preparation of some particularly robust complexes, cyclopentadiene is employed in the presence of a conventional base such as NaOH. Specialized alternatives to NaCp include trimethylsilyl cyclopentadiene, ($CpSiMe_3$), and thallium cyclopentadienide (CpTl) in an ethereal solvent. Most Cp complexes have various other ligands besides a cyclopentadienyl ligand, such as carbonyl, halogen, alkyl, and so on. Biscyclopentadienyl complexes are called metallocenes. It is often the case that these complexes are thermally stable, and they are used for various catalysts. For example, some of the early transition metal complexes, such as Cp_2TiCl_2 and Cp_2ZrCl_2 with aluminoxane as a co-catalyst, can catalyze olefin polymerization. Such species are called Kaminsky-type catalysts

The pentamethylcyclopentadienyl ligand(Cp*) is an important ligand in organometallic compounds arising from the binding of the five ring-carbon atoms in C 5Me− 5, or Cp*$^{-}$, to metals. Relative to the more common cyclopentadiene (Cp) ligand, Cp* offers certain features that are often advantageous. Being more electron-rich, Cp* is a stronger donor and is less easily removed from the metal. Consequently, its complexes exhibit increased thermal stability. Its steric bulk allows the isolation of complexes with fragile ligands. Its bulk also attenuates intermolecular interactions, decreasing the tendency to form polymeric structures. Its complexes also tend to be highly soluble in non-polar solvents.

Metallocene halides and hydrides

Metallocene dihalides have been prepared from main group and cyclopentadienides and the appropriate tetrahalide, cyclopentadienides and a lower oxidation state halide,7 or by halogen exchange with an alkali-metal Reaction (1) has previously been employed, but less satisfactorily than in the present study.

Like regular metallocenes, bent metallocenes are synthesized by a variety of methods but most typically by reaction of sodium cyclopentadienide with the metal halide. This method applies to the synthesis of the bent metallocene dihalides of titanium, zirconium, hafnium, and vanadium:

$2\ NaC_5H_5 + TiCl_4 \rightarrow (C_5H_5)_2TiCl_2 + 2\ NaCls$

In the earliest work in this area, Grignard reagents were used to deprotonate the cyclopentadiene.[3]

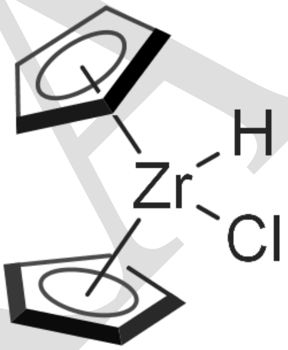
Niobocene dichloride, featuring Nb(IV), is prepared via a multistep reaction that begins with a Nb(V) precursor r:[4]

$NbCl_5 + 6\ NaC_5H_5 \rightarrow 5\ NaCl + (C_5H_5)_4Nb$ + organic products

$(C_5H_5)_4Nb + 2\ HCl + 0.5\ O_2) \rightarrow [\{C_5H_5)_2NbCl\}_2O]Cl_2 + 2\ C_5H_6$

$2\ HCl + [\{(C_5H_5)_2NbCl\}_2O]Cl_2 + SnCl_2 \rightarrow 2\ (C_5H_5)2NbCl_2 + SnCl_4 + H_2O$

Bent metallocene dichlorides of molybdenum and tungsten are also prepared via indirect routes that involve redox at the metal centers.

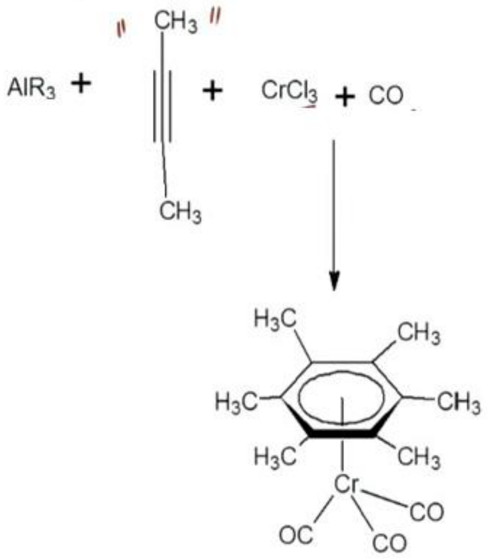


Now, obviously you do not have a cycle, when you have only two atoms, which are coordinated to the metal, but I just wanted to point out here that, the eighteen electron rule turns out to be reasonably important. You can have sixteen electron complexes, but nevertheless, going beyond eighteen is more difficult than having complexes which have less valance electrons than eighteen. So here I have shown you a platinum complex, which looks like a piano stool complex, but only one of the double bonds in the benzene ring is coordinated to the platinum atom. So, platinum is in the zero oxidation state and you have two try fennel phosphine is coordinated to it so you have sixteen valance electrons system, sixteen valance electron system and you do not go to the twenty valance electrons system which would be formed, if you were to have a symmetrically eta six coordinative benzene ring. You will also notice that, this now has got bond alternation, that is a very clear indication of the double and single bond, there are isolated and are now, not really conjugated with another, with one another.

So this, the bond which is right next to the double bond which is coordinated, is in fact, a long bond and then, two short bonds are there, one is, 1.33 Angstroms and the other is, 1.36 Angstrom units. And the bond that is coordinated to the metal, is in fact, lengthened significantly which is indicative of the fact that the double bond has been weakened quite a bit by interaction with the platinum. Electron density from the pie molecule orbital has been donated to the metal and the pie star orbital has been populated. As a result, this

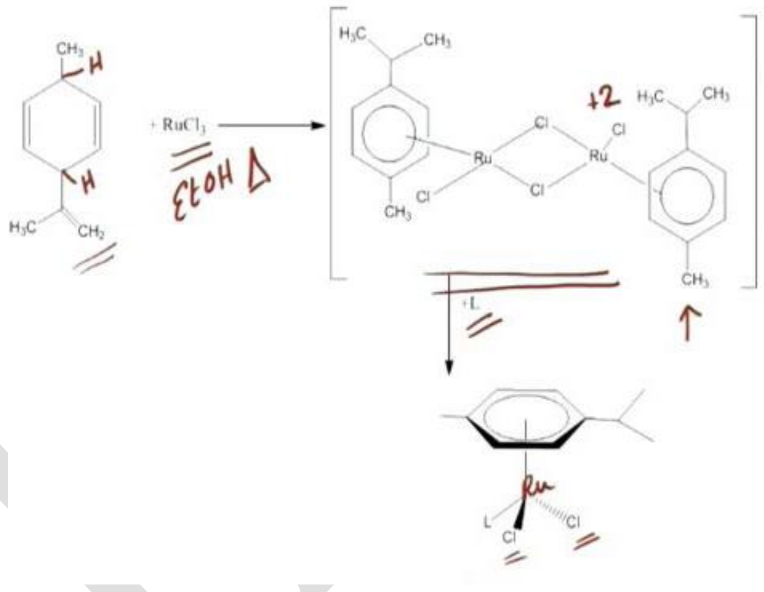
Now, the aromatic ring system, that is coordinated to the metal, can in fact be synthesized in the coordination sphere of the metal atom, through a reduction reaction, which is accomplished by the organic ligand. In the previous instance, we used an inorganic reducing agent to reduce the chromium to chromium zero. Here, in this example, what we are doing is, reducing the ruthenium three. We are going to reduce the ruthenium 3 to ruthenium two species, but we will do this, using the aromatic ligand system, that is present here.

Templated synthesis of Piano stool complexes



So two hydrogens are here, which in fact, can be used for the reduction reaction and as that is happening, you lose those two hydrogens as Hcl. And you end up with an aromatic ring system, coordinated to the ruthenium. Notice that, here ruthenium is in the plus two oxidation state and you will also notice that, this is completely an inorganic compound, except for the organic aromatic ligand, that is present here. It is possible to reduce it in the, or rather convert it from the dimeric state to the monomeric state by using a good ligand.

So, if you add, good l plus by which I mean, a strong ligand, which will coordinate very effectively to the metal. It could be anything from a phosphine or a periedienein or triethylamine or any ligand, you, which is suitable for stabilizing ruthenium, when you end up with piano stool complex, where the aromatic ring system is now coordinated to



ruthenium. So here is ruthenium, coordinated to the aromatic ring system and supported by three legs, two of which are chlorides.

So, two of them are chlorides and one of them is a ligand that you added. This provides a very convenient way of generating the half sandwich complexes, because this reaction is conveniently performed in a refluxing ethanol. You can just heat ethanol and the philanderine, which is this molecule, to generate this cyclic aromatic ring system coordinated to the metal. Now, not only is it possible to generate ethyl six molecules. In the previous aromatic ring system we have six carbons, attached to the metal atom. In this case, you have seven carbon atoms attached to the metal. You will notice that, C seven H eight is a cyclic molecule, which is not conjugated to start with. And you have three aromatic or three non aromatic double bonds which are capable of coordination to the molybdenum. Molybdenum of course, requires only, molybdenum requires only, 3 into 2, 6 pi electrons from the cyclohexatriene and it has got a saturated carbon centre, which is indicated by two coloured hydrogens. Now one of them can be removed as H minus, along with this pair of electrons. So, this is accomplished very effectively with a trityle cation. The trityle cation is a stable cation, which is capable of removing hydrogen hydride ion. So if this hydrogen is removed as H minus, you will end up with a cyclohecta trinyl cation.

This cation would be pseudo, would be aromatic, because it now has six pi electrons and one p orbital which is vacant. So, you have six pi electrons in a cyclic system and all the criteria required for making an aromatic pie system is satisfied. Only difference is that, you are now attached, you are now attached to the pie system, to molybdenum atom. And, this gives you a cyclohector trinyle molybdenum tricarbonyl. Now, because you have removed this molecule, you have removed the trityle cation, which has now become trifennel methane, you have removed trifennel methane by removing this hydrogen, as H minus and Ph 3 C plus, you are left with BF 4 minus, which is contrion present here.

You will notice that, in this molecule all the seven carbon atoms are almost equally bound to the metal atom. So that is why we call it a, eta seven complex. And all of these are again half sandwich complexes, meaning the system has got one pie system, pie ring system, which is coordinated to the metal. And, not only is it possible to expand the ring size from six to seven, it is also possible to go down from four to three. Remember we talked about four, five and six being the most popular ring systems, but it is also possible to have 3 and 7. 7 is what we discussed earlier and here we have cyclopropanyle bromide, which now means to lose Br, as Br minus. It needs to lose Br as Br minus, to form cyclopropanyle cation, which would be aromatic in the coordination sphere, nickel tetra carbonal, you end up with a dimeric complex, where two nickel atoms are interacting with the cyclo propynyle group, and bromide is in fact a bridge.

Notice that, in this molecule, nickel bromide, Ni 2 Br 2, exist in an unusual oxidation state of nickel one. If you only take this fact, but normally by convention you consider the cyclo propynyle cation, which is coordinated to the nickel, as an anionic group. So this confusion is there for most organic molecules because, by convention we take them as the negatively charged species, which would be anti aromatic.

But we know that, from the way in which it was made and in fact, it has been made by generating the cation. Nevertheless, the molecule can be treated with ligand, like pyridine and you can generate, once again generate now, a piano stool which is only three pointed. It has got a three pointed leg and it has also got a three pointed stool, to support the person sitting on it.

So here is the nickel atom. Now, attached to two pyridine ligands and it has got a bromide and a cyclo propynyle group. So if you were to use the anionic method or the, let us use the neutral method this time, you have three electrons from the C 3 Ph 3 unit, and you have two into two, from the pyridine units, so that will give you four electrons. And you also have the bromine, which is in the neutral method, giving one electron, so nickel has got ten electrons and so you would form this nice, eighteen electron system. So the total works out to be, eighteen valance electrons. platinum is in the zero oxidation state and you have two try fennel phosphine is coordinated to it so you have sixteen valance electrons system, sixteen valance electron system and you do not go to the twenty valance electrons system which would be formed, if you were to have a symmetrically eta six coordinative benzene ring. You will also notice that, this now has got bond alternation, that is a very clear indication of the double and single bond, there are isolated and are now, not really conjugated with another, with one another.

So, a multitude of metal sandwich complexes can be made, which are all half sandwich in nature. Now I want to move on to bent metallocenes. What are bent metallocenes? The metallocenes of the sandwich complexes are systems, where the metal was in fact, symmetrically held in between two flat pi systems. So, there are two flat pi systems, and the metal was sandwiched between the two units. And just now, we have looked at a series of systems, where the metal is just attached to, attached from one side, with a pi system and the other side is supported by a variety of father ligands.

So, instead of combination, instead of supporting it, in this fashion with three ligands, one can also think of supporting the metal or bending the sandwich in this fashion, so that if you have vacant, if you have vacant orbitals on the metal atom, these can also coordinate. This happens very readily, in the early transition metals. So, early transition metals have in fact, three orbitals on the metal. The dx square minus, y squared, the dxy and dz squared.

So, there are three different orbitals on a metal, which are available for bonding. If you have a titanium four plus, just interacting with two cyclo pentadienyl units. So all of them will be empty. All three orbitals will be empty. So these orbitals are now available for coordination with the metal atom. So here I have shown you, a set of molecules,

which are capable of interacting with more ligands, just because they have got these empty deorbitals, which are available for interaction. First let us take the tetra cyclopentadynyle titanium.

So, you have Cp 4 Ti. So you take TiCl 4 and treat it with four molecules of cyclo pentadynyle anion, and you end up with this molecule, which if you want to write an eighteen electron structure, it would be difficult to do so. But if you bend the cyclo pentadynyle units sufficiently, you can attach the cyclo pentadiene unit in a sigma fashion. You can attach the cyclo pentadynyle units in a sigma fashion or eta one fashion, in this molecule.

Notice that, there is nothing which distinguishes the ring A, ring B, the ring C and the ring D, other than the hapticity that is associated with them. So there is a very rapid exchange of, A with C or B with C, and that leads to some fluxional behavior, which we will talk about in a future lecture. But these molecules, right now this is a sixteen valance electron system. These molecules are quite stable and turn out to be an interesting class of molecules, where the cyclopentadynyle ring systems are just bent, a little bit backward from the usual orientation. So, this bending back, allows for exposure of these orbitals, which are there in the x y plane and, so allows for interaction with the metal atom, with other ligand atoms.

So, I have shown you a variety of molecules here, but let us take some specific examples now. Let us take Cp 2 TiCl 2 and, Cp 2 TiCl 2 is titanium four plus. This is titanium four plus, you can reduce it with zinc and use carbon monoxide, in the reaction medium and that gives you TiCO twice. So here is a molecule, which is titanium in the plus two oxidation state. Remember, there are three orbitals that were available on the titanium.

So, we can in fact, add six electrons, if it was titanium four plus. Now you have a plus two system, so you end up adding only two other ligands. So, that gives you, two other ligands in the coordination sphere of the titanium and you have a bent sandwich structure. So, this is a game, the bent sandwich structure, which we just talked about, where the cyclo pentadiene units are coordinated in a eta one fashion. This is the way you would end up making it. Now having talked about bent sandwiches, species which will encounter later, during catalysis. Let us take a look at, what would happen if you have a open sandwich. These are molecules which are not appreciated a lot, because you do not have a very stable cyclo pentadienyl unit, which is aromatic. So, this cyclo pentadienyl unit is aromatic. Whereas, if you have a acyclic version.

This is the repulsion that is going to happen, the place where the repulsion happen between the two hydrogens. To avoid this interaction, you would either have to twist the CH 2 group or you would have to widen the two ends of the pentadienyl unit and both of these movements, of these cyclic pi systems, would destroy the metal interacting with the pie bonds. So what will happen is that, you will end up, weakening the metal pentadienyl bond, and it would make the pentadienyl unit more reactive. And that is probably one reason, why ruthenium complex has been isolated and characterised crystallographically and has been found to be more stable than the iron system itself.

Possible Questions

PART-B (6 Mark Questions)

1. Write the general classification of metal carbonyls with examples
2. The general preparation methods of metal carbonyls halide with examples
3. Explain the steps of oxidative addition and reductive elimination reaction
4. Insertions reaction of alkenes and alkynes complexes
5. Synthesis of alkene complexes by various methods
6. Discus the Ferrocene structure, bonding and reactivity
7. Preparation of the bend sandwich compound, explain the bonding
8. Write the mechanism of Wacker process with mechanism?
9. Brief reaction mechanism of heterogeneous catalytic systems
10. Write the reaction mechanism of homogeneous catalytic systems

PART-C Marks Questions)

1 . Give the brief discussion on Ferrocene preparation, properties and chemical reactivity

DEPARTMENT OF CHEMISTRY

Online questions (Multiple choice questions)

ORGANOMETALLICCHEMISTRY (17CHP205C)

UNIT IV

S.No	Questions	Option-A	Option-B	Option-C	Option-D	Answer
1	Who introduced the concept of the trans effect in platinum chemistry?	Chernyaev	Wilkinson's	Otto Roelen	Jahn-Teller	Chernyaev
2	Metallocene compounds must contain a metal that is sandwiched between	two Ethylene	two cyclopentadienyl	one cyclopentadienyl	Three Ethylene	two cyclopentadienyl
3	Metallocene compounds also called as…… compounds	sandwich	halfsandwich	vaska	wilkinson	sandwich
4	Which one following ligand to prepare the metallocene compounds	Ethelene	cyclopentadiene	cyclopropene	cylobutane	cyclopentadiene
5	Find out metallocene compound	titanocene dichloride	titanium dichloride	titanium dioxide	titanium trichloride	titanium dichloride
6	The first metallocene is……	titanocene	zirconocene	ferrocene	cyclopentadiene	Ferrocene
7	The two cyclopentadienyl anions are on ……. planes	plannar	twised	antiparallel	parallel	parallel
8	The general nomenclature of bonding in metallocene	sigma	Pi	covalent	hapticity	hapticity

9	MCl2 + 2 NaC5H5 →…… …...+ 2 NaCl	(C5H5)2M	(C5H5)2M	(C6H6)2M	(C4H8)2M	(C5H5)2M
10	Catalyze olefin polymerization	[Cp2FeCH3]+	[Cp2ZrCH3]+	[Cp2MgCH3]+	[Cp2RuCH3]+	[Cp2ZrCH3]+
11	Which one following compound as not early metal metallocene derivatives	Tebbe's reagent	Petasis reagent	Schwartz's reagent	Ferrocene	Ferrocene
12	Ferrocenium salts are sometimes used as ….. oxidizing agents	one-electron	two-electron	four-electron	three-electron	one-electron
13	This salt is composed of the cation [Fe(C5H5)2]+ and the….	BF2	BF1	BF4	BF3	BF4
14	Ferrocenium tetrafluoroborate salt used as	catalyst	biosensor	light emiter		biosensor
15	Calculate the 18 e- rule of [(η5-C5H5)2Fe].	17	16	22	18	18
16	Cr(CO)6 + 2 C5H6 → …….. + 6 CO + H2	Cr(C5H5)2	Cr(C5H6)2	Cr(C4H4)2	Cr(C4H6)2	Cr(C5H5)2
17	Find out which one is not metallocene compound	titanocene dichloride	vanadocene dichloride	Ferrocene	HRh(CO)(PPh3)3	HRh(CO)(PPh3)3
18	The well known example of half-sanwhich compound	(C5H5)2M	R2SnCl2	(C4H4)Fe(CO)3	Cr(C4H6)2	(C4H4)Fe(CO)3
19	The most stable metallocene ------	Sodium cyclopenta dienide	Ferrocene	Thallium cyclopentadiene	nickel	Ferrocene

20	Give example for the compound wich contain more than two cyclopentadienyl rings	Tetrakiscyclopetadienyl uranium	Ferrocene	Sodium cyclopentadienide	thallium	Tetrakiscyclopetadienyl uranium
21	Give an example for the compound which containing only one cyclopentadienyl ring	Tetrakiscyclopetadienyl uranium	Ferrocene	Sodium cyclopentadienide	thallium	Sodium cyclopentadienide
22	the compounds having only one cyclopentadienyl ring are commonly known as ----	Sandwich compound	Openfaced sandwich compound	Closed faced sandwich compound	triple decckers	Openfaced sandwich compound
23	Ferrocene undergoes Vilsmeir reaction to yield------	Amino ferrocene	Ferrocene carboxyladeyde	Notro ferrocene	chloro ferrocene	Ferrocene carboxyladeyde
24	Ring substituted ferrpocene reacts with acetic acid through the formation of ---- ion	α Carbonium ion	β carbonium ion	α Carbanion	β Carbanion	α Carbonium ion
25	Arene complexes are mostly synthesized by ------- reaction	Aldol condensation	Beckmann rearrangement	Reduction reaction	Friedel crafts reaction	Friedel crafts reaction
26	During the preparatio of Arene complexes ---- is used to reduced the metal salt to a lower oxidation state.	Aluminium	Paladium	Chromium	NIckel	Aluminium
27	Benzene is coordinated to	$AlCl3$	$LiCl3$	$TiCl4$	H-Pd	$AlCl3$

	chromiu in arene complexes with the assistance of ----					
28	The melting point of Dibenzene chromium is ----- 0c	270	170	280	260	280
29	The success of the fischer Hafner method depends upon the particular ------	Amine	Arene	Aliphatic compound	aromatic compound	Arene
30	In an interchange (I) reaction, a rapid equilibrium between the incoming ligand and the 6-coordinate reactant forms an ?	Ion	Too loosely bonded molecular combination	Ion pairs	Tightly bonded molecular combination	Ion pairs
31	Larger electrostatic attraction between the positive metal ion and the negative ligand should?	Speeds the dissociation	slow the dissociation	Does not affect the dissociation	Not react with dissociation	Slow the dissociation
32	Dissociative mechanisms generally result in which values for Avact?	Positive	Alkaline	Neutral	Negative	Positive
33	Grignard reagents add to the carbonyl group of ketones to form	primary alcohol	secondary alcohol	tertiary alcohol	isobutyl alcohol	tertiary alcohol
34	Perkin reaction is a reaction related to	aldol condensation	cannizzaroreaction	witting reaction	mannich reaction	aldol condensation
35	Perkin reaction involves the addition	aliphatic	aromatic	alicyclic	cyclic	aromatic

	of acid anhydrides to which type of aldehydes in the presence of the sodium salts of the acids from which the anhydride is derived.					
36	Knoevenagal reaction involves the interaction of an aromatic aldehyde and an active methylene compound in the presence of an amine like	piperidine	methylamine	aniline	triethylamine	piperidine
37	Reformatsky reaction consists in reacting aldehydes and ketones with α-bromo esters in the presence of	magnesium	zinc	cadmium	zinc amalgam	zinc
38	Aldol condensation provides a useful route for the preparation of	α,β-unsaturated carbonyl compounds	β,γ- unsaturated carbonyl compounds	β-hydroxy carbonyl compounds	γ-hydroxy carbonyl compounds	α,β-unsaturated carbonyl compounds
39	Reformatsky reaction provides a suitable route for the preparation of	α-hydroxy esters	β- hydroxy esters	γ- hydroxy esters	α,β- hydroxy esters	β- hydroxy esters
40	Wolff-kishner reduction of carbonyl compounds to hydrocarbons involves the treatment of the	semicarbazide	hydroxylamine	hydrazine	2,4-dinitrophenylhydrazine	hydrazine

	carbonyl compound in the presence of strong base, with					
41	Which one of the following compound will give cannizzaro's reaction?	CH3CHO	C6H5CH2CHO	(CH3)2C-CHO	CH3CH2CHO	(CH3)2C-CHO
42	Acetophecarbon undergoes self condensation in the presence of aluminium tert-butoxide to give	syn-triphenyl benzene	benzalacetophecarbon	dipcarbon	acetophecarbon	dipcarbon
43	Acrolein is formed by the reaction of	formaldehyde and acetaldehyde	acetaldehyde and benzaldehyde	benzaldehyde and formaldehyde	acetaldehyde and acetone	formaldehyde and acetaldehyde
44	Effect of dehydration of diacetone alcohol to give mesityl oxide in presence of	NaoH	pyridine	iodine	primary amine	iodine
45	Aldol obtained by the condensation of benzaldehyde and acetaldehyde is unstable and looses a molecule of water to give	benzyledeneacetone	chinnamic acid	diacetone alcohol	cinnamaldehyde	cinnamaldehyde
46	claisen condensation is carried out by using ester having α-hydrogen atom to give	β-keto ester	γ- keto ester	α- keto ester	σ- keto ester	β-keto ester
47	Dickmann condensation also known as	knoevenagal condensation	cannizaro reaction	claisen condensation	aldol condensation	claisen condensation

	intramolecular					
48	Cyclic ketones are prepared by the	cannizaro reaction	dickmann condensation	claisen condensation	aldol condensation	dickmann condensation
49	Ethyl esters of adipic acid undergoes a Dickmann condensation to give	cyclo butacarbon	cyclo hexacarbon	cycloheptacarbon	cyclopentacarbon	cyclopentacarbon
50	In cannizzaro reaction, alkoxide is used as base the product is	ketones	esters	alcohol	salts of acids	esters
51	PETN is	pentaerythritol tetranitrate	pentaerythritol trinitrate	phenylethylene trinitrate	polyethylene tetranitrate	pentaerythritol tetranitrate
52	Reaction used to prepare acetoacetic ester from ethyl acetate is known as	Michael reaction	cannizzaro reaction	claisen condensation	claisen-schmodt reaction	claisen condensation
53	Which of the following methods can be used to estimate keto-enol content in acetoactic ester?	Gass chromatography	Mass Spectroscopy	NMR Spectroscopy	UV Spectroscopy	NMR Spectroscopy
54	Who has established experimentally that acetoacetic ester exists in both keto- and enol- forms	Frankland	Duppa	Knorr	Perkin	Knorr
55	Acetoacetic ester reacts with phenol to give substituted coumarin. This reaction is known as	pechmann condensation	knoevenagal condensation	perkin reaction	claisen condensation	pechmann condensation
56	Two mols of acetoactic ester interact in the	antipyrine	4-methyluracil	dihydroacetic acid	methyl iso-oxazolone	dihydroacetic acid

	presence of NaHCO3 to give					
57	which one of the following is non-enolisable keto-ester	CH3COCH2COOC2H5	CH3COCH(R)COOC2H5	CH3COC(R2)COOC2H5	CH3COOC2H5	CH3COC(R2)COOC2H5
58	Which one of the following is not an active methylene compound?	ClCH2COOC2H5	CH3COCH2COCH3	CH3COCH2COOC2H5	NC-CH2COOC2H5	ClCH2COOC2H5
59	Malonic ester reacts with urea in presence of POCl3 to	vernol	barbituric acid	luminal	parabonic acid	barbituric acid
60	synthetic applications of cyanoacetic acid closely resembles to	malonic ester	acetoaceticester	nitroacetic ester	chloroacetic ester	malonic ester

UNIT- V
SYLLABUS

Coordinative unsaturation - acid-base behaviour reaction - migration of atoms or groups from metal to ligand - insertion reaction - reactions of coordinated ligands - catalytic reactions of alkenes - isomerisation of alkenes - hydrogenation - hydroformylation and hydrosilation of alkenes - alkene polymerization and oligomerisation - fluxional molecules.

Homogeneous catalysis

Contribution of homogeneous catalytic process in chemical industry is significantly smaller compared to heterogeneous catalytic process, it is only about 17-20 %. But importance of homogeneous catalysis is increasing significantly. The significance of homogeneous catalysis is growing rapidly particularly in the area of pharmaceutical and polymer industry. Some of the important industrial processes include:

1. Oxidations of alkenes such as production of acetaldehyde, propylene oxide etc.
2. Polymerization such as production of polyethylene, polypropylene or polyesters.

A new major development in homogeneous catalysis is the application of organometallic complexes as catalysts. The use of organometallic catalysts has revolutionized the homogeneous processes increasing economic viability. Another new area is bio-catalysis involving enzymes catalysts. Enzyme catalysts are highly selective and active for production of fine chemicals, pharmaceuticals etc. Enzyme catalysts are discussed in a separate section.

In homogeneous catalysis, all the reactants and catalysts are present in a single fluid phase and usually in the liquid phase. Homogeneous catalysts are the simple molecules or ions such as HF, H2SO4, Mn+2 as well as complex molecules such as organometallic complexes, macrocyclic compounds and large enzyme molecules.

Advantages

Advantages of homogeneous processes can be summarized as follows:

- In many reactions, homogeneous catalysts are more active and/or selective compared to heterogeneous catalysts.
- In homogeneous catalysis, the catalysts are molecularly dispersed within the fluid. Hence, pore diffusion limitations are absent. However, bulk phase mass transfer limitation may occurs.

- Catalytic chemistry and mechanism for homogeneous catalysis are better studied and understood. Therefore, it is easier to control and manipulate the process parameters.

Types of reactions

Several homogeneous catalytic systems are :

1. Acid base catalysis
2. Catalysis by metal ions
3. Catalysis by organometallic complexes
4. Catalysis by Lewis acids

1. Catalysis by acids or bases

Acid –base catalysts are used in the following types of reactions:

i. Condensation

ii. Dehydration

iii. Hydrolysis

iv. Halogenations

a) Acid catalyzed condensation

Acid catalyzed condensation of phenol and acetone to bisphenol which is an important intermediate in the manufacture of epoxy resin and polycarbonates.

$$CH_3COCH_3 + 2\phi - OH + 2H^+ \longrightarrow OH - \phi - C(CH_3)_2 - \phi - OH + H_2O$$

$$\phi = \text{benzyl group}$$

ii. Acid catalyzed synthesis of ethyl acetate ester from ethanol and acetic acid

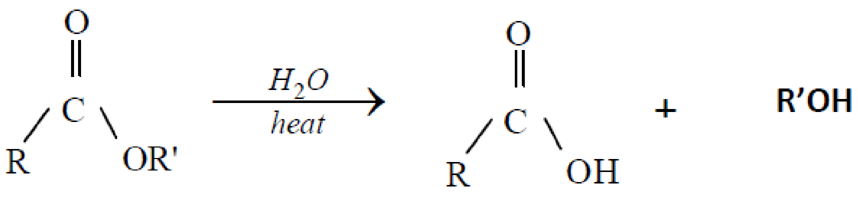
$$\mathrm{CH_3CH_2OH + CH_3COOH \rightleftharpoons CH_3COOCH_2CH_3 + H_2O}$$

b) Acid catalyzed dehydration of ethyl alcohol to ethylene

$$CH_3CH_2OH \xrightarrow{H^+} CH_2 = CH_2 + H_2O$$

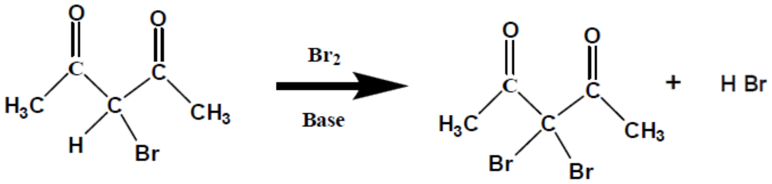
Hydrolysis of esters

Hydrolyses of carboxylic esters to form the parent carboxylic acid and an alcohol.



d) Acid or base catalyzed halogenations

Ketones can be halogenated in the presence of acid or base and X2(X= Cl, Br).



2. Catalysis by metal ion

Metal ions can act as catalysts. Metal ions function in different ways

1. Metal ion can act as a “super acid”. It introduces positive charge into the substrate, making it more susceptible toward nucleophilic attack.

2. Metal ions can also act as templates. Metal ions are able to coordinate to more than 2 ligands and thereby bring the molecules together.

3. Metal ions can act as redox catalysts. Many metal ions can accept or donate electrons by changing their oxidation state and thereby participate in redox reactions.

a) Catalysis by Cu2+ ions

Cu2+ ions are very effective catalysts for the hydrolysis of α-amino acid esters.

$$CHRNH_2 - COOCH_3 \xrightarrow[H_2O]{Cu^{2+}} CHRNH_2 - COOH + CH_3OH$$

b) Catalysis by Mg2+ ions

Hydrolysis of phosphate esters is catalyzed by metal ions, usually Mg^{2+}.

$$CH_3 - COOPO_3 \xrightarrow[H_2O]{Mg^{2+}} CH_3COOH + H_3PO_4$$

3. Catalysis by organometallic complexes

Presently, organometallic catalysts play major role in homogeneous catalysis. Organometallic complex consist of a central transition metal ion bonded to organic ligands such as R2C=CR2, RCO, R3P, R3N, CO etc. Catalysis occurs through dissociation of ligands followed by co-ordination of reactant molecule to the metal ion. The transition metal ions react through exchange of d electrons. Organometallic complexes usually have octahedral or tetrahedral geometry. Reactions catalyzed by organometallic complexes include hydrogenation, hydroformylation, carbonylation and decarbonylation, hydrocarbon rearrangement, partial oxidations etc.

Effect of ligands

The nature of surrounding ligands is very important in organometallic catalysis and known as ligand effect. The product distribution depends on the ligand environment around the metal center. Using the same metal center, different products can be obtained with the same substrate when associated ligands are changed around the metal center.

Ligand types

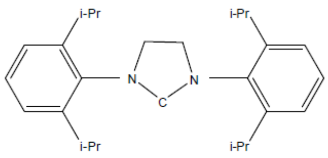
Phosphine based ligands (PR3 ; where R= t-Bu, n-Bu, Ph, CH3O, CF3CH2O, Cl, CF3) are most widely used. The alkyl phosphines are strong bases and are σ donor ligands while the organophosphites, P(OR)3 , are strong π acceptors and form stable complexes with electron rich transition metal by accepting π electrons.

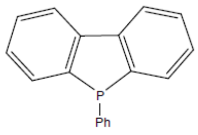
Other ligands that are used are discussed below

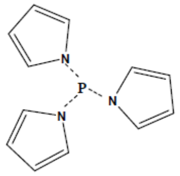
1. Hydrocarbyl group : Cyclopentadieneyl ligands (Cp) are associated with metals such as Ti, Zr, Hf . The Cp2TiCl2 catalyst is used in ethylene polymerization. Ruthenium complexes containing aromatic ligands are used for hydrogen transfer reactions such as transfer of hydrogen from alcohol to ketone producing another alcohol.

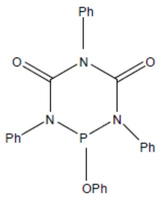
2. Alkoxide, imides and imido are used as anionic ligands in zirconium and titanium catalysts for the polymerization of alkene. These are mostly used in combination with cyclopentadienyl ligands.

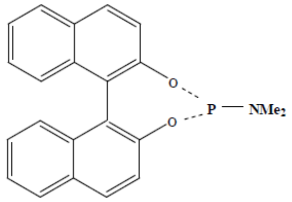
3. Nitrogen ligands include pyridine and imidazole ligands. They are more stable than phosphine based ligands. Enzyme catalysts contains mostly nitrogen ligands in the form of imidazoles or porphyrins binding to metals such as copper or iron.Some other ligands such as phosphine with nitrogen substituents, carbon based ligands are also shown in Fig. 2.

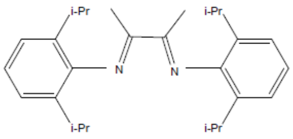








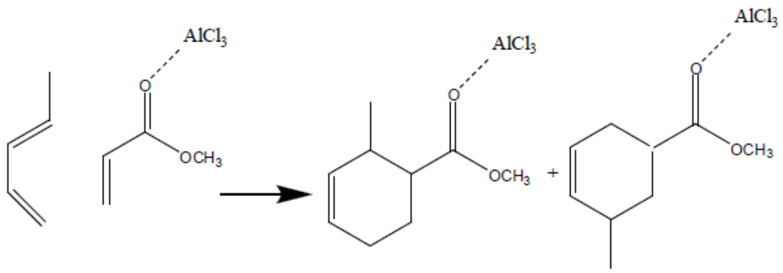




4. Catalysis by Lewis acids

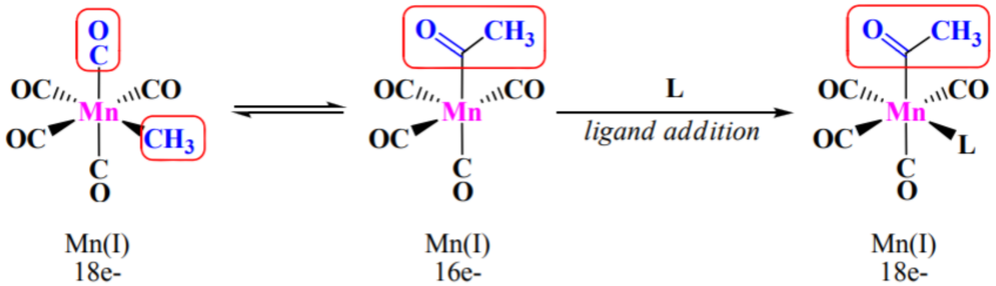
a. Diels alder reactions

Reaction of diene with a mono-ene form cyclohexene derivativeis shown below.



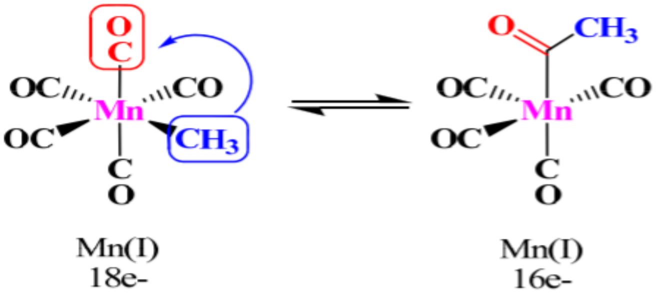
Migratory

Insertion

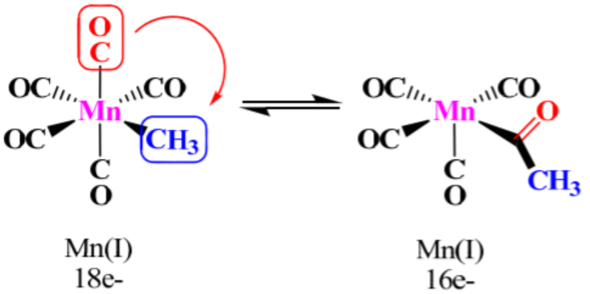


The opposite of a migratory insertion is sometimes referred to as elimination. Common anionic and neutral ligands that undergo migratory insertions with one another: Anionic: H-, R- (alkyl), Ar- (aryl), acyl-, O2- (oxo) Neutral: CO, alkenes, alkynes, carbenes

The anionic ligand does a nucleophillic-like attack on the neutral ligand. This involves the anionic ligand moving to the site where the neutral ligand is coordinated. An empty coordination site is left behind.

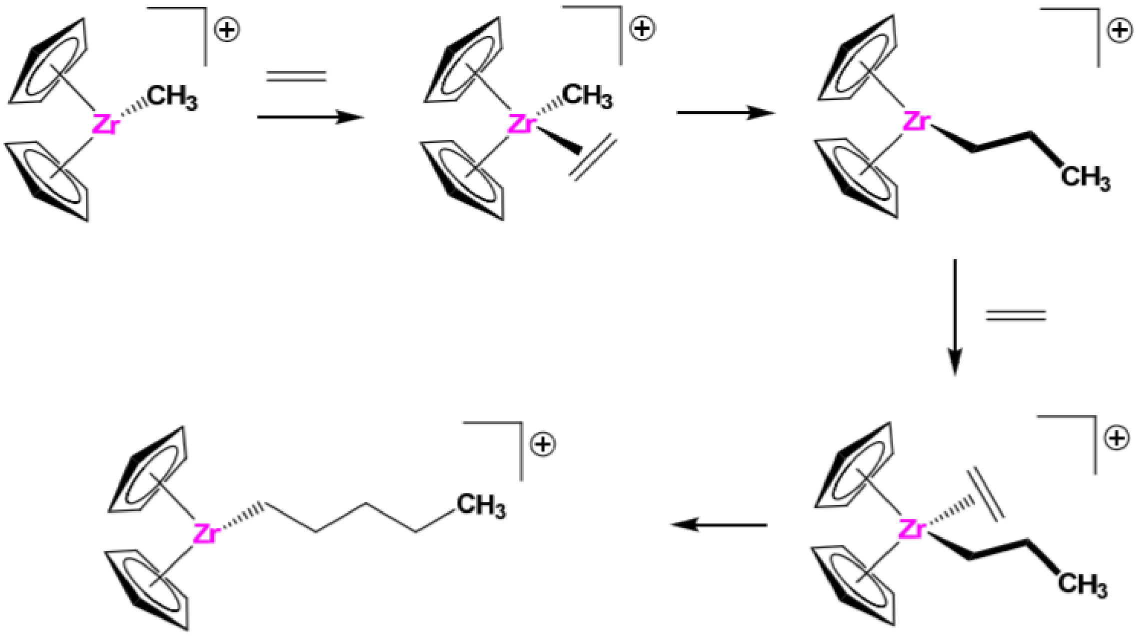


The neutral ligand moves over to where the anionic ligand is coordinated and "inserts" into the anionic ligand-metal bond to generate the new anionic ligand. An empty coordination site is left behind where the neutral ligand originally was located

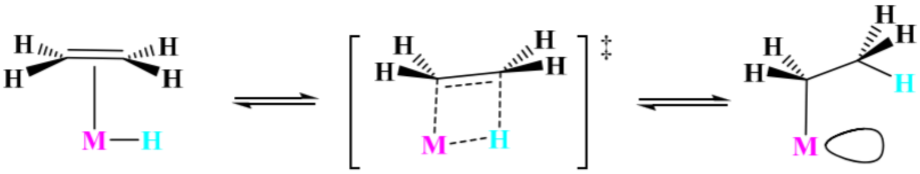


Alkene Migratory Insertions

Alkene and hydride/alkyl migratory insertions are extremely important in industry

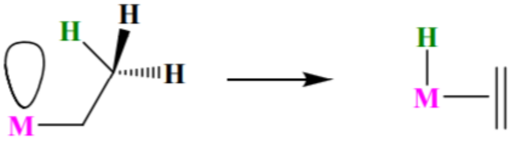


An alkene and a hydride usually react via migration of the hydride to the coordinated alkene ligand. The reverse reverse reaction reaction is called a β -elimination elimination and is favored favored in the presence of an empty metal orbital cis to the alkyl ligand.



Eliminations

β-hydride elimination



α-hydride elimination

Carbonyl elimination or decarbonylation

Catalysis

$$A+B \longrightarrow C+D$$

Catalyst Heterogeneous Catalysis: Heterogeneous Catalysis: Catalyst and reactants are in different phases Catalyst and reactants are in different phases 95% of all chemical and petrochemical processes use heterogeneous catalysis.

Homogeneous Catalysis: Catalyst is in the same phase as that of the reactants Generally employed, when selectivity is important and isolation of products from the reaction mixture can easily be achieved.

H l omogeneous catalysts are More selective towards the formation of a single product More active More easily p studied to understand the chemical and mechanistic aspects More easily modifiable for optimizing selectivity However, they Are more sensitive to permanent deactivation Are more sensitive to permanent deactivation Lead to more difficulty in separation of products from catalyst

Terminologies in Catalysis

Turn Over (TO): Corresponds to one loop through the catalyst cycle. One equivalent of reactants is converted to one equivalent of products.

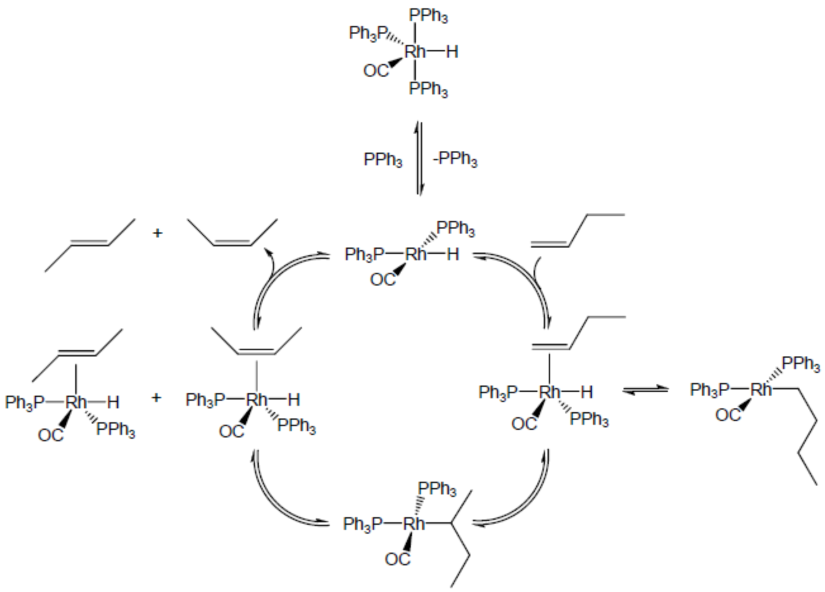
Turn Over Number (TON): The absolute number of passes through the catalytic cycle before the catalyst becomes deactivated. It is defined as the amount of reactant (moles) divided by the amount of catalyst (moles) times the percentage yield of the product. Often mol% o f catl t a ys t is use d to express TON. 10 mol% = 10 TON, 1 mol% = 100 TON, 0.01 mol% = 10,000 TON **Turn Over Frequency TOF)**: The number of passes through the catalytic cycle per unit time (sec, min or h). This number is usually determined by taking the number of moles of product produced, dividing that by the number of moles of catalyst used in the reaction, and then by the time taken to produce the given amount of product. The units, therefore are usually just time-1 therefore, are usually just time 1. For a good catalyst, TON, TOF and selectivity (chemo-, region- and enantioselectivity) should be high.

Alkene Isomerization

- Many transition metal complexes are capable of catalyzing the 1,3-migration of hydrogen substituents in alkenes, a reaction that has the net effect of moving the C=C group along the chain of the molecule.
- This is often a side reaction in other types of catalytic alkene reactions, desired or not according to circumstances.
- Two mechanisms are most commonly found:

1. via alkyl intermediates.
2. via 3-allyl intermediates.

- Note that in each cycle, all the steps are reversible, so that the substrates and products are in equilibrium, and therefore although a non-thermodynamic ratio of alkenes can be formed at early reaction times, the thermodynamic ratio is eventually formed if the catalyst remains active long enough.



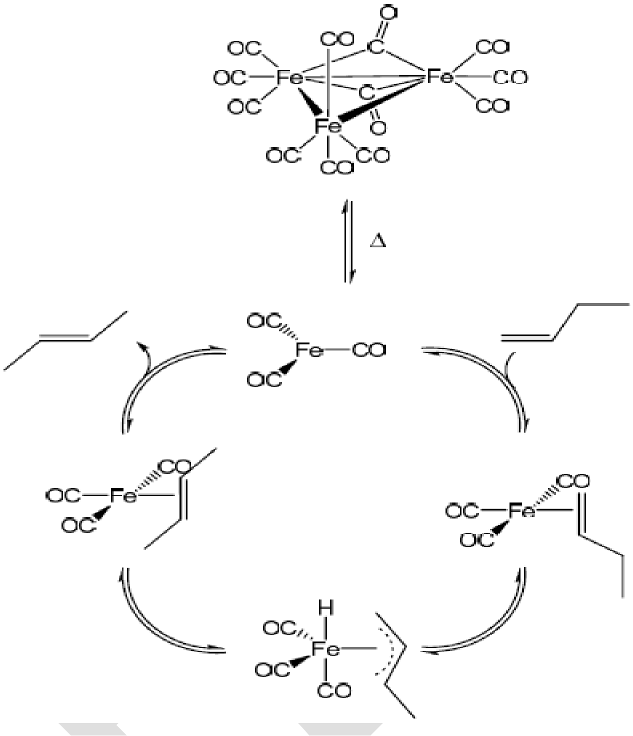
Allyl mechanism

- The second common mechanism involves allyl intermediates and is adopted by catalysts having ***two 2e vacant sites but no hydrides***.
- It has been established for the case of Fe3(CO)12 as catalyst, a system in which “Fe(CO)3,” formed by fragmentation of the cluster on heating, is believed to be the active species.
- Thus the cluster itself is an example of a catalyst precursor.
- As a 14e species, Fe(CO)3 may not have an independent existence in solution, but may always be tied up with substrate or product (***or even solvent***).
- In this mechanism the C−H bond at the activated allylic position of the alkene undergoes an ***oxidative addition*** to the metal.
- The product is an □**3-allyl hydride**. Now, we only need a reductive elimination to give back the alkene.
- Again, we can have nonproductive cycling if the H returns to the same site it left, rather than to the opposite end of the allyl group.

An experimental distinction can be made between both the alkyl and allyl routes by means of

a crossover experiment using the mixture of C5 and C7 alkenes.

- For the allyl mechanism, we expect the D to end up only in the corresponding product having undergone an intramolecular 1,3 shift.
- For the hydride mechanism, the D will be transferred to the catalyst that can in turn transfer it by crossover to the C5 product.



Alkene Hydrogenation

Hydrogenation catalysts add molecular hydrogen to the C=C group of an alkene to give an alkane.

- Three general types have been distinguished, according to the way each type activates H2.

1. oxidative addition

2. heterolytic activation

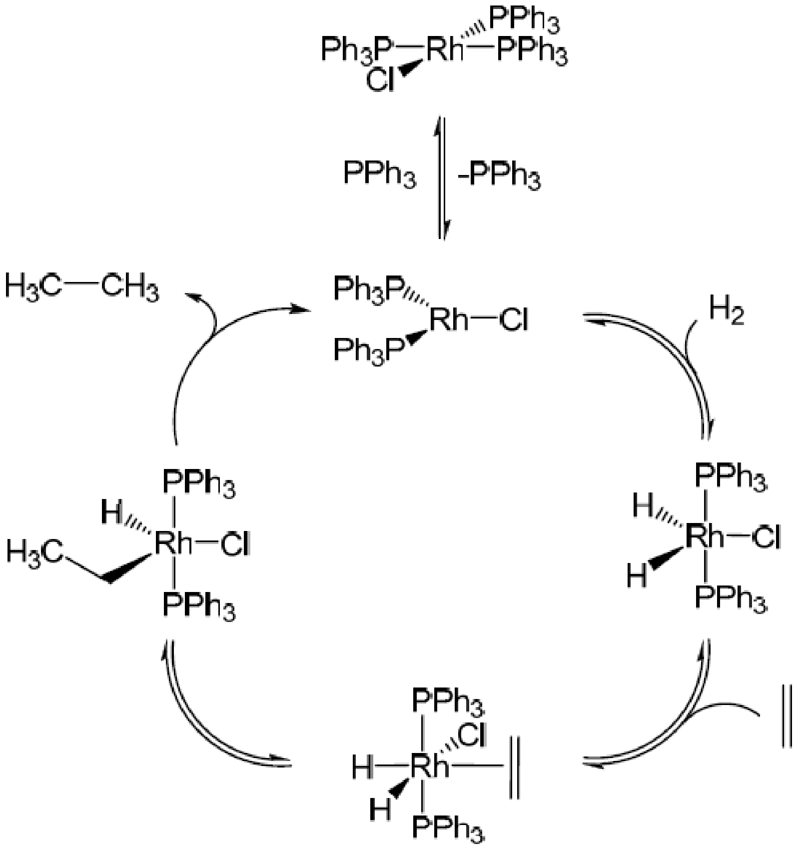
3. homolytic activation

Perhaps the most important group employs oxidative addition, of which RhCl(PPh3)3 ***(Wilkinson’s catalyst)*** is the best known.

- Hydrogen addition to give a dihydride leads to labilization of one of the PPh3 ligands (high trans effect of H) to give a site at which the alkene binds.
- The alkene inserts, as in isomerization, but the intermediate alkyl is irreversibly trapped by reductive elimination with the second hydride to give an alkane.
- This is an idealized mechanism. In fact, RhCl(PPh3)3 can also lose PPh3 to give RhCl(PPh3)2,

and dimerize via halide bridges and each of these species have their own separate catalytic cycles that can be important under different conditions.

- Indeed, RhCl(PPh3)2 reacts so much faster with H2 than does RhCl(PPh3)3 that the vast majority of the catalytic reaction goes through RhCl(PPh3)2 under most conditions.
- By reversibility arguments, the more rapid oxidative addition of H2 to the 3-coordinate d8 RhCl(PPh3)2 to give 5-coordinate d6 RhH2Cl(PPh3)2 relative to the corresponding 4-coordinate→6-coordinate conversion is consistent with the tendency for faster reductive elimination from 5-coordinate d6 species discussed in previous lectures ***(TBP Y-type intermediate)***.
- The following mechanism in illustrates a case where H2 adds before the olefin. Sometimes the olefin adds first (the olefin mechanism) as is found for [Rh(dpe)(MeOH)2]BF4.



Hydroformylation

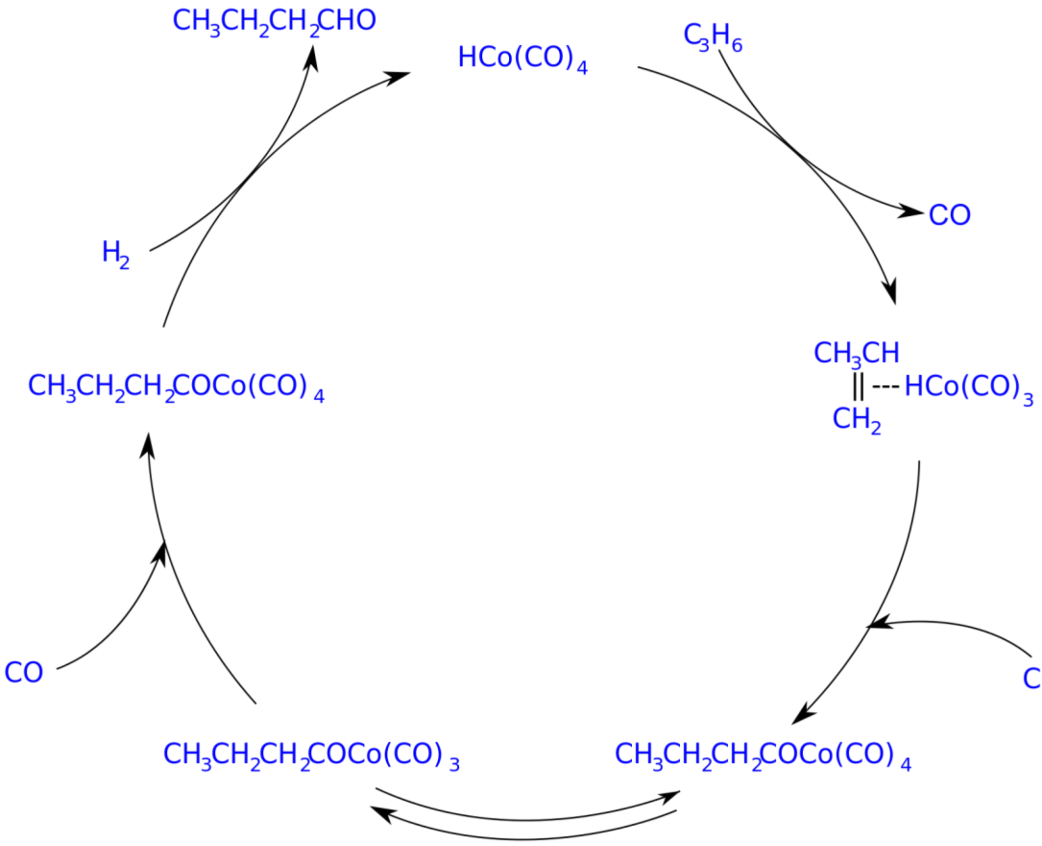
The hydroformylation reaction involves conversion of alkene to aldehyde in the presence of CO and hydrogen. The reaction is given as

$$H_2 + CO + CH_3CH{=}CH_2 \rightarrow CH_3CH_2CH_2CHO \text{ ("normal")}$$

$$H_2 + CO + CH_3CH{=}CH_2 \rightarrow (CH_3)_2CHCHO \text{ ("iso")}$$

The process is carried out over cobalt or rhodium complex based catalysts. Both linear and branched chain products can be produced. Linear aldehydes are more valuable feed stock for plasticizers and linear alcohols. Hence, the main objective of process is to have high selectivity for more useful linear product.

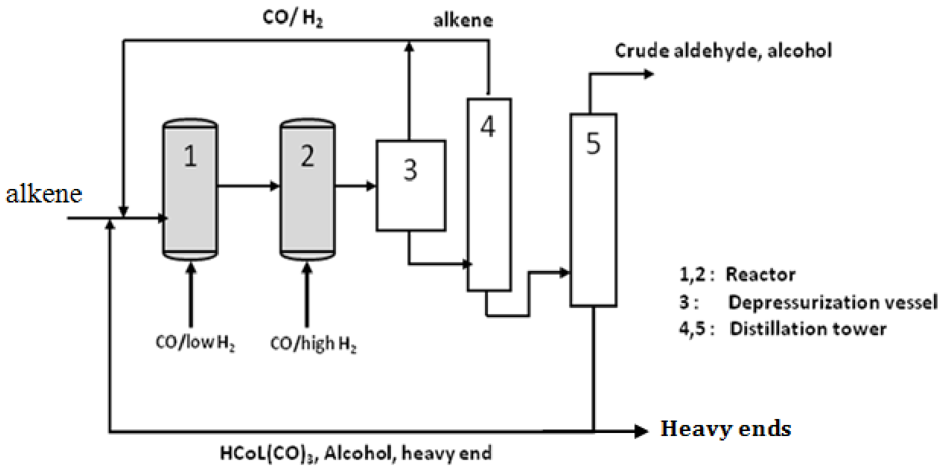
In cobalt complex catalyzed hydroformylation reaction the catalytically active form is $HCo(CO)_4$complex. The sequence of hydroformylation process for linear aldehyde formation is shown below.



The first step is the replacement of CO ligand by an alkene. In the next step hydride migration to alkene occurs producing alkyl cobalt complex in which alkyl may be either linear or branched. In the subsequent step one incoming CO occupies the vacant site. It is followed by migration of the alkyl to a co-ordinated CO to give an acyl-complex. In the final step dihydrogen reacts with acyl complex to form aldehyde product and regenerate the starting hydrido-cobalt-carbonyl complex. In cobalt catalyzed hydroformylation the hydrogenation step is rate determining.

Process

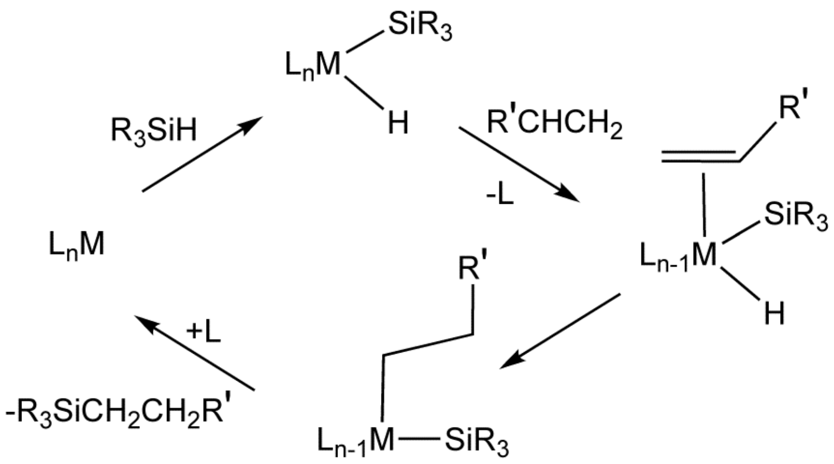
Hydroformylation of both higher and lower alkenes can be carried out using $HCo(CO)_3L$ complex. Reaction is done in two stages as shown in Fig. 2, to limit the hydrogenation of alkene. In the first reactor, low hydrogen partial pressure is used, and in the second reactor high hydrogen partial pressure is used to ensure hydrogenation of aldehyde to alcohol. The unreacted alkenes and gases are recycled back to the first reactor. Multiple distillation columns are used to separate the unreacted reactants and catalysts. Catalysts remain in the bottom phase of the distillation column and recycled back. The aldehydes and alcohols are collected as overhead products from the distillation tower.



Process flow diagram hydroformylation process

Hydrosilation

Hydrosilylation, also known as hydrosilation, is one of the most useful catalytic reactions leading to the formation of organsilanes and organosilicones, which have a variety of applications in industry and as intermediates in organic chemistry. Hydrosilylation occurs via the addition of H-Si to an unsaturated bond such as carbon-carbon bond, carbon-oxygen bond, carbon-nitrogen bond, nitrogen-nitrogen bond and nitrogen-oxygen bond using a metal catalyst, Lewis Acid, or radical initiator. The basic reaction can be described using the following scheme:



In the first step a Si-H bond undergoes oxidative addition to a metal center. The alkene coordinates and then undergoes insertion. The hydrogen is then added to the alkene through H beta-insertion. In the final step the alkylsilyl Pd(II) complex undergoes reductive elimination to deliver the adduct and return the metal to the original oxidation state

The reactivity of hydrosilylation is influenced by many factors: substrate, silane, transition metal catalyst, ligand etc. which makes the reaction diverse as well as complicated. Studies have been performed to determine the reactivity influenced by each of these factors. Because there are a large variety of substrates that can be used, we will focus on alkenes. Here are some general rules:

Reaction rate: 1-alkene > 2-alkene > 3-alkene

Generally, the more substituted the alkene group, the slower the reaction would be. This is due to the more substituted alkene group being bulkier, therefore it will be harder for the alkene coordination to happen to the metal. More substituted alkene groups also make it more difficult for the H atom to undergo compete beta-insertion.

Reaction rate: $SiHCl_3 > (C_6H_5)_3SiH > (C_2H_5)_3SiH$

$V_0(10^5)$: 110 12 1.2

From this set of data, we can derive that the rate of reactivity would increase depending on the substituted groups on the silanes. The order of reactivity is: chlorine > aromatic rings > alkanes.

However, this rule is not always true. If we substituted the aromatic groups in $(C_6H_5)_3SiH$ with Cl, the reaction rate would be:

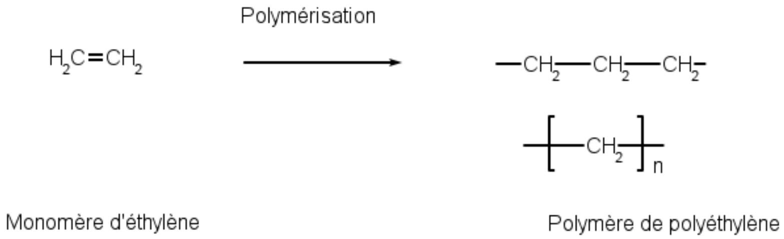
Reaction rate: $(C_6H_5)_3SiH > (C_6H_5)_2SiH_2 > (C_6H_5)SiH_3$

$V_0(10^5)$: 12 1.7 0.69

This shows that the substituted groups do not affect the reactivity individually. The overall regularity for change of silanes is complicated and varies with each group

Polymerization of Alkenes

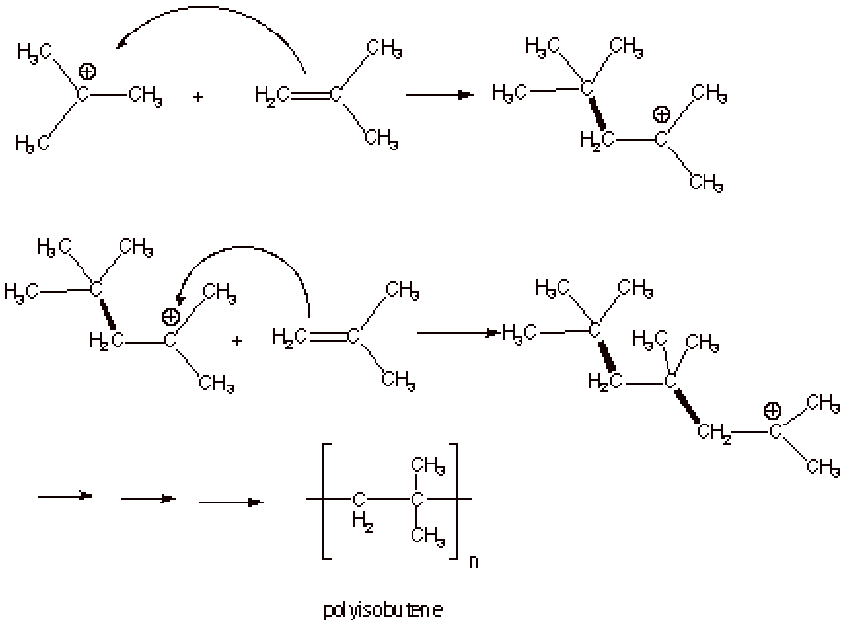
One of the most important technical reactions of alkenes is their conversion to higher-molecular-weight compounds or **polymers**. A polymer is defined as a *long-chain molecule with recurring structural units*. Thus polymerization of propene gives a long-chain hydrocarbon with recurring



Cationic Polymerization

We have seen that the addition of a proton to an alkene linkage gives a carbocationic species, which is a strong electrophile. Such carbocations are highly reactive and quickly react with available nucleophiles. In the case of hydrogen chloride addition, the carbocations react with chloride ion as the nucleophile, to yield the addition product, an alkyl halide. When there is no strong nucleophile present and when the solvent is even weakly nucleophilic (water, alcohols, etc.), the carbocation reacts with the solvent nucleophiles to give an alcohol or an ether.

Consider the case where the solvent is not nucleophilic and there are no other strong nucleophiles present in abundance. *If the alkene is present at high concentration, the alkene can act as a nucleophile toward the carbocation*, forming a dimeric species containing a new carbon-carbon bond and also a new carbocation center. This process is illustrated below for the case of isobutene. When this second (dimer) carbocation reacts with another molecule of isobutene, still another C-C bond is formed, giving a trimeric species. This can continue until a large number (n) of isobutene molecules is incorporated into the final product, which is called a polymer, specifically polyisobutene.

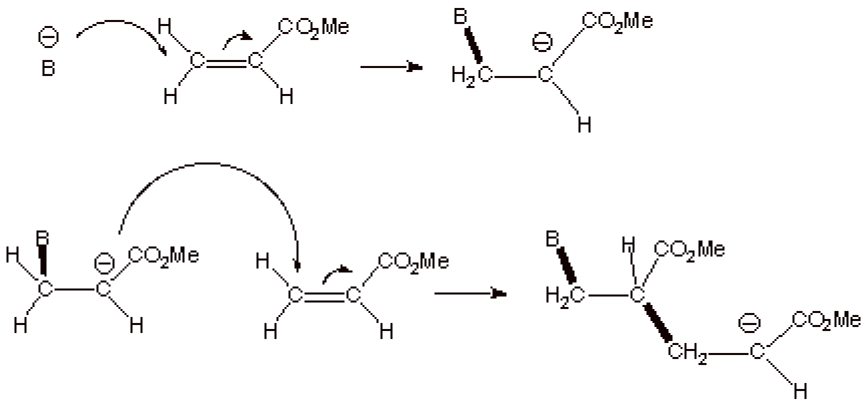


polyisobutene

(butyl rubber)

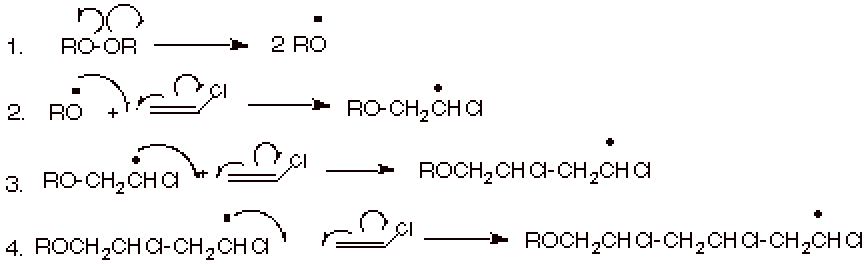
- This kind of polymerization is called *cationic polymerization,* because it involves a chain process which is propagated by carbocation intermediates.
- Cationic polymerization of simple alkenes is especially efficient for alkenes which form relatively stable carbocations (note the tertiary carbocation intermediate) and which have one double bond terminus of the alkene unsubstituted, so as to minimize steric effects in the TS for the addition reaction.
- Thus, isobutene is especially amenable to cationic polymerization, but other alkenes with electron donating groups (oxygen and nitrogen-based functionalities) are also efficiently polymerized.
- Polymer Nomenclature: There are several methods of naming polymers. The simplest method is simply to place the name of the starting alkene (called the monomer) in parenthesis and add the prefix poly, as shown above for polyisobutene.In contrast to cationic polymerization, anionic polymerization is relatively efficient when the intermediate anionic species is relatively stabilized. Since alkyl groups are donor groups, simple alkenes are not polymerized efficiently by the anionic method. An example of an alkene which is readily polymerized anionically is methyl acrylate, an alkene which has a

strongly electron withdrawing ester function (carbomethoxy). The intermediate anions will (hopefully) be recognized as ester *enolate* anions.



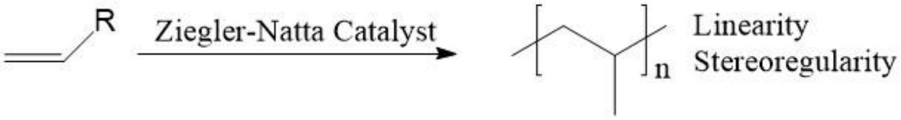
Radical Polymerization.

You may recall that radical centers are stabilized by either electron donating or withdrawing groups, and especially by conjugating groups. Consequently, radical polymerization is one of the more general methods of polymerization. In fact, even ethylene is readily polymerized to give the familiar polymer poly(ethylene). The mechanism of radical polymerization is illustrated below for the polymerization of chloroethene (vinyl chloride).

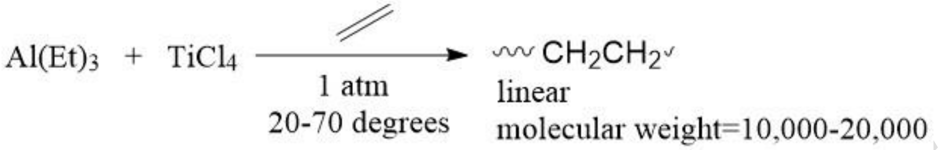


Olefin Polymerization with Ziegler-Natta Catalyst

The Ziegler-Natta (ZN) catalyst, named after two chemists: Karl Ziegler and Giulio Natta, is a powerful tool to polymerize α-olefins with high linearity and stereoselectivity (Figure 1). A typical ZN catalyst system usually contains two parts: a transition metal (Group IV metals, like Ti, Zr, Hf) compound and an organoaluminum compound (co-catalyst). The common examples of ZN catalyst systems include $TiCl_4$ + Et_3Al and $TiCl_3$ + $AlEt_2Cl$.



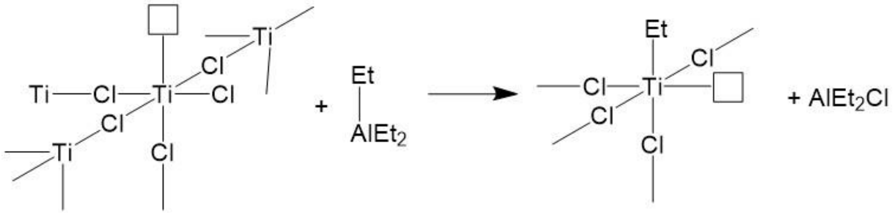
In 1953, German chemist Karl Ziegler discovered a catalytic system able to polymerize ethylene into linear, high molecular weight polyethylene which conventional polymerization techniques could not make. The system contained a transition metal halide with a main group element alkyl compound



Following the catalytic design, Italian chemist Giulio Natta found that polymerization of α-olefins resulted in stereoregular structures, either syndiotactic or isotactic, depending on the catalyst used. Because of these important discoveries, Karl Ziegler and Giulio Natta shared the Nobel Prize in Chemistry in 1963.

Activation of Ziegler-Natta catalyst

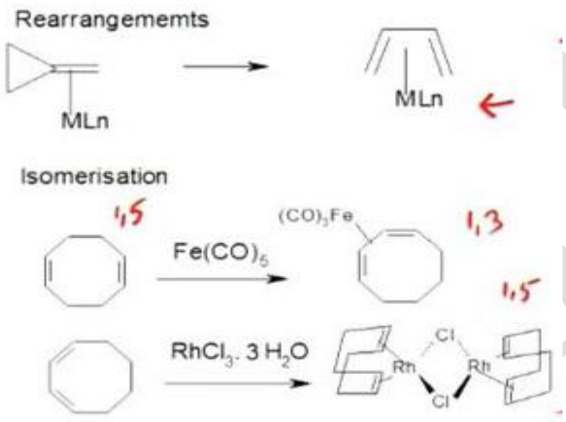
It is necessary to understand the catalyst's structure before understanding how this catalyst system works. Herein, $TiCl_4$+$AlEt_3$ catalyst system is taken as an example. The titanium chloride compound has a crystal structure in which each Ti atom is coordinated to 6 chlorine atoms. On the crystal surface, a Ti atom is surrounded by 5 chlorine atoms with one empty orbital to be filled. When Et_3Al comes in, it donates an ethyl group to Ti atom and the Al atom is coordinated to one of the chlorine atoms. Meanwhile, one chlorine atom from titanium is kicked out during this process. Thus, the catalyst system still has an empty orbital. The catalyst is activated by the coordination of $AlEt_3$ to Ti atom.



Fluxional Properties of Organometallics

Molecules are dynamic and organometallic compounds are quite dynamic and flux, that is the meaning of the term fluxionality.

We are very often accustomed to looking at static crystal structures, but molecules are not static and they keep walking, they can sometimes talk and many times they are dancing all the time. So, if you want to think of a molecule as a static picture, you are missing out on what it can really do and what it is really doing.



Both rearrangements and fluxionality come into this group and by rearrangement, I wish to talk about systems where there are rearrangements of the size of the ring. For example here there is a methylene cyclopropane that is rearranged to a butadiene complex or you have a 1, 5 cyclooctodiene, which is rearranged to a 1, 3 cyclooctodiene. Similarly 1, 3 cyclooctodiene which is rearranged to 1, 5 system.

So, these are rearrangements whereas fluxional behavior is distinguished from rearrangements by the fact that the ring system or the carbon framework that is attached to the metal is not changed. It is only the arrangement of the ring with respect to the metal or with respect to another part of the organometallic molecule which is changing. So, here for example, I have shown for you ferrocene, which is eclipsed and one ring is substituted with a methyl group. This position of the methyl group if the ferrocene is in an eclipse form would be looking like this where the hydrogens of one ring are on top of the other.

one methyl group will be on top of another hydrogen atom here and this would be energetically unfavorable situation, and it would like to move over to a system where you have the metals staggered with respect to the other hydrogens. However, the energy difference between these two forms is very small, so you have rapid exchange between these two structural reforms and that is what we are talking about as fluxional behavior.

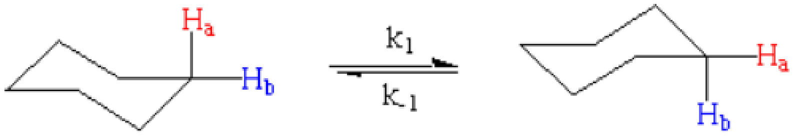
Dynamic Exchange Processes

Classical kinetics can often be used to determine the rate constant and activation energy of a chemical reaction. In a typical study, changes in concentration of products and/or reactants versus time are monitored using any number of experimental techniques (IR, NMR and UV-VIS are the most common). This method works well for reactions that take place on the laboratory time scale (minutes to hours) where the rate constants for the reactions are typically 10^{-6} to 10^{-3} s^{-1}.

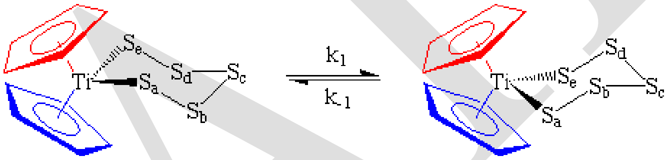
This analysis becomes more complicated when we have to consider reversible reactions or systems that are at equilibrium. For example:

1. If we are interested in the energy barrier to interconversion between two isomers but the two isomers can not be resolved or separated, then we can't use this approach (since their concentrations would be constant with time).
2. If the rate of the reaction is very fast, we'd have an equilibrium mixture before we could even obtain the first measurement.

The prototypical example of such a system is the axial-equatorial interconversion of the chair form of cyclohexane. At room temperature the axial and equatorial protons are interchanged by a dynamic (**fluxional**) process in which the ring undergoes a "chair-chair" conformation change. As shown here, H_a and H_b are interchanged between axial and equatorial positions.



An organometallic system that undergoes a similar interconversion, but at higher temperature is the bent metallocene complex, Cp_2TiS_5. In the structures below, notice that S_a and S_e of the pentasulfide unit are closer to one cyclopentadienyl ring than the other. This creates two chemically and magnetically in equivalent Cp rings which appear as separate signals in the ^1H or ^{13}C NMR spectrum. Above room temperature, Cp_2TiS_5 undergoes a chair-chair rearrangement which effectively switches the polysulfide ligand from one side of the molecule to the other. As far as our NMR spectrometer is concerned, the two Cp rings (conveniently marked in blue and red) appear to have exchanged positions even though they did not actually move. The sulfurs have been marked to show you that this process is **not** merely rotation of the entire molecule by 180 degrees, but an inversion of the ring



Possible Questions

PART-B (6 Mark Questions)

1. What is organometallic chemistry? bond type, examples and why its important?
2. Write a note on effective atomic number rule with example of four metal complexes
3. Draw the structure and Calculate the 18 electron rule for the following metal carbonyl compounds
    a. i) $Fe(CO)_5$ ii) $Mn(CO)_{10}$ iii) $Fe_2(CO)_9$ iv) $Co_2(CO)_8$
4. Explain the general preparation and properties of metal carbonyls with suitable examples,
5. Write the short notes of M-C bond cleavage reactions with examples
    a. i). α–hydride elimination ii) β– hydride elimination iii) Reductive elimination
6. Explain the following reaction:
    i) 1,1 and 1,2 insertion reaction ii) Synthesis of alkylidene complexes
    ii) iii) Synthesis of metal alkene complexes
7. Preparation of the half sandwich compound, reactivity
8. Brief reaction mechanism of Ziegler-Natta catalyst

PART-C (10 Mark Questions)

1. (i) Synthesis of alkene complexes by various methods
   (ii) Explain the steps ofoxidative addition and reductive elimination reaction

2. (i) Discuss the Redox reactions in Vaska's complexes
   (ii)Hydrogenation of olefin with mechanism

DEPARTMENT OF CHEMISTRY

Online questions (Multiple choice questions)

ORGANOMETALLICCHEMISTRY (17CHP205C)

UNIT V

S.No	Questions	Option-A	Option-B	Option-C	Option-D	Answer
1	The reaction of σ-bromo esters with carbonyl compounds in presence of zinc to produce β-hydroxy esters, this reaction is known as	perkin reaction	aldol condensation	reformatsky reaction	claisen reaction	reformatsky reaction
2	lithium aluminium hydride converts acetophecarbon to	primary alcohol	secondary alcohol	tertiary alcohol	hydrocarbons	secondary alcohol
3	In wolff-kishner reduction, treatment of carbonyl compounds with hydrazine followed by a strong base in solvents like	benzene	piperidine	diethylene glycol	polyethylene glycol	diethylene glycol
4	In meerwein pondorf verley reduction, carbonyl compounds treated with aluminium isopropoxide in isopropyl alcohol to give	alcohol + amine	alcohol + acetone	ester + acetone	acid + acetone	alcohol + acetone
5	In knoevenagal condensation, acetaldehyde treated with malonic acid in presence of very weak base to give	acrolein	mesityl oxide	crotonic acid	cinnamic acid	crotonic acid

6	Cinnamic acid is obtained from reaction of	acetaldehyde + malonic ester	benzaldehyde + malonic ester	formaldehyde + malonic acid	acetaldehyde + cyanoacetic ester	benzaldehyde + malonic ester
7	The correct combination of metal, number of carbonyl ligands & the charge for a metal carbonyl complex [M(CO)x] that satisfy the 18 electron rule is	) M = Ti, x = 6, z = 1	M = V, x = 6, z = 1	M = Co, x = 4, z = 2	M = Mo, x = 5, z = 1	M = V, x = 6, z = 1
8	The stable cyclopentadienyl complex of beryllium is	[Be(η5 - C5H5)2]	[Be(η5 - C5H5) (η3 - C5H5)]	[Be(η1 - C5H5) (η3 - C5H5)]	[Be(η1 - C5H5) (η5 - C5H5)]	[Be(η1 - C5H5) (η5 - C5H5)]
9	For a reaction, trans $[IrCl(CO)(PPh_3)_2]$ + Cl_2 → trans $[IrCl_3(CO)(PPh_3)_2]$ the correct observation	νCO (product) > νCO (reactant)	νCO (product) < νCO (reactant)	νCO (product) = νCO (reactant)	νCO (product) = νCO (free CO)	νCO (product) > νCO (reactant)
10	The substitution of η^5 – Cp group with nitric oxide is the easiest for	η^5 - Cp_2 Fe	η^5 - Cp_2 CoCl	η^5 - Cp_2 Co	η^5 - Cp_2 Ni	η^5 - Cp_2 Ni
11	The molecule shown below obeys 18 e^- rule. The two ‘M’ satisfying the condition are (CO)5M=C(OMe)(Ph)	Cr, Re^+	Mo, V	V, Re^+	Cr, V	Cr, Re^+
12	The ligand in uranocene is	C8H82-	C5H52-	C6H6	C4H42-	C8H82-
13	In metal-olefin interaction, the extent of increase in	leads to a decrease in C = C bond length	change the formal oxidation state of the metal	change the hybridization of the olefin carbon from	increases with the presence of electron electron	change the hybridization of the olefin carbon from sp^2

	metal → olefin π-back donation would			sp^2 to sp^3	donating substituent on the olefin	to sp^3
14	The oxidation state of molybdenum in $[(\eta^7$ – tropylium) $Mo(CO_3)]^+$ is	+2	+1	0	-1	+1
15	The nature of metal-metal bonds in $[W_2(OPh)_6]$ is	1	2	3	4	3
16	The reaction given below is an example of $[(CO)_5Mn(Me)] + CO \rightarrow [(CO)_5Mn\{C(O)(Me)\}]$	oxidative addition	electrophilic substitution	nucleophilic substitution	migratory insertion	migratory insertion
17	Which of the following is not suitable as catalyst for hydroformylation ?	C8H82-	HCo(CO)3PBu3	HRh(CO)(PPh3)3	H2Rh(CO)(PPh3)2 Cl	H2Rh(CO)(PPh3)2Cl
18	The ligand(s) that is (are) fluxional in $[(\eta^5 - C_5H_5)(\eta^1 - C_5H_5)Fe(CO)_2]$ in the temperature range 221-298K, is (are)	$\eta^5 - C_5H_5$	$\eta^1 - C_5H_5$	$\eta^5 - C_5H_5$ & CO	$\eta^1 - C_5H_5$ & CO	$\eta^1 - C_5H_5$
19	The oxidation state of the Ni & the number of metal – metal bonds in $[Ni_2(CO)_6]^{2-}$ that are consistent with the 18 electron rule are	Ni(-2) & 1 bond	Ni (IV), 2 bond	Ni (-1), 1 bond	Ni (IV), 3 bond	Ni (-1), 1 bond
20	The product of the reaction of the propene, CO & H_2 in the presence of	Butanoic Acid	Butanal	2-butacarbon	Methylpropanoate	Butanal

	$Co_2(CO)_8$ as a catalyst is					
21	The hapticities ‘K’ & ‘L’ of the arene moieties in the diamagnetic complex $[(\eta^K - C_6H_6)Ru(\eta^L - C_6H_6)]$ respectively are	6 & 6	4 & 4	4 & 6	6 & 2	4 & 6
22	Reductive elimination step in the hydrogenation of alkenes by Wilkinson catalyst results in (neglecting solvent in coordination sphere of Rh)	T-shaped $[Rh(PPh_3)_2Cl]$	Trigonal - planar $[Rh(PPh_3)_2Cl]^{2+}$	T-shaped $[Rh(H)(PPh_3)_2Cl]^+$	Trigonal-planar $[Rh(H)(PPh_3)_2]$	T-shaped $[Rh(PPh_3)_2Cl]$
23	The oxidative addition & reductive elimination steps are favoured by	Electron rich metal centers	Electron deficient	Electron deficient & electron rich metal centers respectively	Electron rich & electron deficient metal centers respectively	Electron rich & electron deficient metal centers respectively
24	Identify the order according to increasing stability of the following organometallic compounds, $TiMe_4$, $Ti(CH_2Ph)_4$, $Ti(i\text{-}Pr)_4$ & $TiEt_4$.	$Ti(CH_2Ph)_4 < Ti(i\text{-}Pr)_4 < TiEt_4 < TiMe_4$	$TiEt_4 < TiMe_4 < Ti(i\text{-}Pr)_4 < Ti(CH_2Ph)_4$	$Ti(i\text{-}Pr)_4 < TiEt_4 < TiMe_4 < Ti(CH_2Ph)_4$	$TiMe_4 < TiEt_4 < Ti(i\text{-}Pr)_4 < Ti(CH_2Ph)_4$	$TiMe_4 < TiEt_4 < Ti(i\text{-}Pr)_4 < Ti(CH_2Ph)_4$
25	Among the metals, Mn, Fe, Co, & Ni, the ones those would react in its native form directly with CO giving metal carbonyl compounds are	Co & Mn	Mn & Fe	Fe & Ni	Ni & Co	Fe & Ni

26	In the hydroformylation reaction, the intermediate $CH_3CH_2CH_2Co(CO)_4$	Forms an acyl intermediate $CH_3CH_2CH_2COCo(CO)_3$	Forms an adduct with an olefin reactant	Reacts with H_2	Eliminates propane	Forms an acyl intermediate $CH_3CH_2CH_2COCo(CO)_3$
27	Reaction of $Fe(CO)_5$ with OH^- leads to complex A which on oxidation with MnO_2 gives B. Compounds A & B respectively are	$[HFe(CO)_4]^-$ & $Fe_3(CO)_{12}$	$[Fe(CO)_5(OH)]^-$ & $Fe_2(CO)_9$	$[Fe(CO)_4]^{2-}$ & $Mn_2(CO)_{10}$	$[HF(CO)_4]^-$ & Fe_2O_3	$[HFe(CO)_4]^-$ & $Fe_3(CO)_{12}$
28	The number of metal-metal bonds in the dimers $[CpFe(CO)(NO)]_2$ & $[CpMo(CO)_3]_2$ respectively are	two & two	two & three	one & three	zero & one	zero & one
29	In the trans-$PtCl_2L(CO)$ complex, the CO streching frequency for L=NH_3, pyridine, NMe decreases in order	pyridine > NH_3 > NMe_3	NH_3 > pyridine > NMe_3	NMe_3 > NH_3 > pyridine	pyridine > NMe_3 > NH_3	pyridine > NMe_3 > NH_3
30	The greater stability of $((CH_3)_3C\text{-}CH_2\text{-})_4Ti$ (A) compared to that of $((CH_3)_2CH\text{-}CH_2\text{-})_4Ti$ (B) due to	Hyperconjugation present in complex (A)	β-hydride elimination is not possible in complex (A)	Steric protection of titanium from reactive species in complex (A)	The stronger nature of Ti-C bond in complex (A)	β-hydride elimination is not possible in complex (A)
31	The carbonyl resonance in ^{13}C NMR spectrum of $[(\eta^5 - C_5H_5)Rh(CO)]_3$ (^{103}Rh, nuclear spin I = ½, 100 %) shows a	Terminal CO	μ2 - CO	μ3 - CO	η^5 - C_5H_5	μ2 - CO

	triple at -65° owing to the presence of					
32	The complex that DOES NOT obey 18 – electron rule is :	$[(\eta\text{-}C_5H_5)]$ $RuCl(COPPh_3)]$	$[W(CO)_3(SIMe_3)(Cl)(NCMe)_2]$	$[IrCl_3(PPh_3)_2(AsPh_2)]^-$	$[Os(N)Br_2(PMe_3)(NMe_2)]^-$	$[Os(N)Br_2(PMe_3)(NMe_2)]^-$
33	The final product of the reaction $[Mn(CO)_6]^+$ + MeLi → is	$[Mn(CO)_6]^+ Me^-$	$[Mn(CO)_5Me]$	$[Mn(CO)_6]$	$[(MeCO)Mn(CO)_5]$	$[(MeCO)Mn(CO)_5]$
34	In the cluster $[Co_3(CH)(CO)_9]$ obeying 18 electron rule, the number of metal-metal bonds & bridging ligands respectively are	3 & 1 CH	0 & 3 CO	3 & 1 CO	6 & 1 CH	3 & 1 CH
35	Which statement about a catalyst is incorrect?	The presence of a catalyst speeds up a reaction	The presence of a catalyst changes the rate of a reaction	In some reactions, one of the products acts as a catalyst for the forward reaction	During use, a catalyst may be poisoned	The presence of a catalyst speeds up a reaction
36	Which of the following criteria is least important for a homogeneous, organometallic catalyst?	The metal centre must normally be able to accommodate both a 16 or 18 valence electron count	The metal centre must be able to tolerate more than one ligand geometry	The metal centre must be able to undergo oxidation and reduction reactions	The catalyst must be contain a third row d-block metal	The catalyst must be contain a third row d-block metal
37	Match the compound formula to its application as a catalyst or catalyst precursor in the stated process. Which pair is incorrect?	cis-[Rh(CO)2I2]–; Monsanto acetic acid synthesis	RhCl(PPh3)3; alkene hydrogenation	HRh(PPh3)3; asymmetric hydrogenation	HCo(CO)4; hydroformylation of alkenes	HRh(PPh3)3; asymmetric hydrogenation
38	Hydroformylation of alkenes may lead to alcohol and aldehyde	The stereoselectivity of the reaction gives the aldehyde:alcohol ratio	The chemoselectivity of the reaction gives the n:i aldehyde ratio	The regioselectivity of the reaction gives the	The regioselectivity of the reaction gives	The regioselectivity of the reaction gives the n:i aldehyde ratio

	products. Which statement is correct?			aldehyde:alcohol ratio	the n:i aldehyde ratio	
39	In the Tennessee–Eastman acetic anhydride process, the catalyst is cis-[Rh(CO)2I2]–. Which sequence of steps best describes the primary catalytic cycle?	Oxidative addition of MeI and loss of CO; Me migration; addition of 2 CO; elimination of MeC(O)I	Oxidative addition of MeI; Me migration; CO addition; elimination of MeC(O)I		Loss of CO; oxidative addition of MeI; Me migration; addition of 2 CO; elimination of MeC(O)I	Oxidative addition of MeI; Me migration; CO addition; elimination of MeC(O)I
40	Which statement is incorrect about chemisorption of CO on a metal (M) surface?	CO molecules are activated	IR spectroscopy can be used to study the system	M–C bonds are formed	The CO molecules must be terminally bound	The CO molecules must be terminally bound
41	Which statement is incorrect about the industrial Haber process for NH3 production?	The catalyst used commercially is α-Fe; catalyst promoters are added	Chemisorption of N2 and H2 activates the molecules, weakening and cleaving their bonds	A high temperature is needed because the forward reaction is endothermic	Both a high temperature and pressure are required	A high temperature is needed because the forward reaction is endothermic
42	The following statements are about catalytic converters. Which one is incorrect?	Permissible emission gases are CO2, N2 and H2O	The precious metals Rh, Pt and Pd are used in 3-way converters	Ce2O3/CeO2 is an "O2 storage" additive	Rh catalyses the oxidation of NO	Rh catalyses the oxidation of NO
43	In the hydrogenation of alkenes using Wilkinson's catalyst, the active catalyst is RhCl(PPh3)2 (or RhCl(PPh3)2(solvent)). The first step in the catalytic cycle is:	alkene coordination	oxidative addition of H2	loss of PPh3	loss of Cl–	oxidative addition of H2
44	A key feature of the Fischer-Tropsch process is:	hydrocarbon formation	alkene hydrogenation	alkene polymerization	hydroformylation	hydrocarbon formation

45	Which step, taken from a catalytic cycle, is an example of reductive elimination?	Loss of RCH2CH3 from Rh(H)2(CO)(PPh3)2(CH2CH2R)	Conversion of Rh(CO)2(PPh3)2(CH2CH2R) to Rh(CO)(PPh3)2(COCH2CH2R)	Reaction of Rh(CO)(PPh3)2(CH2CH2R) with H2	Loss of RCH=CHR from PdX(PPh3)2(CHRCH2R) and formation of Pd(H)X(PPh3)2	Loss of RCH2CH3 from Rh(H)2(CO)(PPh3)2(CH2CH2R)
46	Which of the following compounds is a 16-electron species and is an active catalyst?	HCo(CO)3	HRh(CO)(PPh3)3	[Rh(CO)2I4]–	Pd(PPh3)4	HCo(CO)3
47	Typical Grubbs' catalysts contain:	Ru; a carbene ligand	Rh; a carbene ligand	Ru; an alkene ligand	Mo; a carbene ligand	Ru; a carbene ligand
48	Adsorption of a species X onto a surface with concomitant surface–X bond formation is called:	chemisorption	catalysis	desorption	physisorption	chemisorption
49	Which statement is incorrect about zeolites?	No zeolites occur naturally	Zeolites are aluminosilicates	Each zeolite contains channels of a specific size	A zeolite functions as an acid catalyst, e.g. in the alkylation of aromatic compounds	No zeolites occur naturally
50	A Schrock-type catalyst for alkyne metathesis may contain:	high oxidation state tungsten and a W=CR2 unit	low oxidation state tungsten and a W=CR2 unit	low oxidation state tungsten and a W≡CR unit	high oxidation state tungsten and a W≡CR unit	high oxidation state tungsten and a W≡CR unit
51	One of the following ligands is chiral. Which is it?	Me2PCH2CH2PPh2	Me2PCH2CH2PMe2	Me2PCHMeCH2PMe2	Me2PCH2CH2AsMe2	Me2PCHMeCH2PMe2
52	Ziegler-Natta catalysis is associated with:	alkene hydrogenation	alkene polymerization	hydroformylation of alkenes	alkyne metathesis	alkene polymerization
53	The oxidation of	is thermodynamically	is thermodynamically	has a low	is explosive under	is thermodynamically

	SO2 to SO3:	favourable, but is slow under ambient conditions	unfavourable under ambient conditions	activiation energy under ambient conditions	ambient conditions, and the reaction must be controlled on an industrial scale	favourable, but is slow under ambient conditions
54	What would be the main reason for replacing the PPh3 ligands in a catalyst by P(C6H4SO3-)3ligands?	To increase the leaving group ability of the ligand	To increase the steric demands of the ligand, making it harder to replace	To increase the water solubility of the catalyst	To increase the solubility of the catalyst in organic solvents	To increase the water solubility of the catalyst
55	Metal nitrosyl complexes are complexes that contain ?	Nitric oxide	Nitrosyl	Metal	MeNC	Nitric oxide
56	Metal nitrosyls are?	Physically important	Mechanically important	Chemically important	Biologically important	Biologically important
57	Which one of the following is typically adopt one of two bonding modes?	Metal nitrosyl	NO	O2	MeNC	NO
58	NO ligands can arise by oxidative degradation of other ?	Nitrogen ligands	Cabon ligands	Oxygen ligands	Hydrogen ligands	Nitrogen ligands
59	Nitrogen is more electronegative than ?	Hydrogen	Oxygen	Carbon	NO	Carbon
60	The nitroprusside anion,[Fe(CN)5NO]2−, a mixed nitrosyl cyano complex, has pharmaceutical applications as a slow release agent for ?	CN	Fe	NO	C	NO