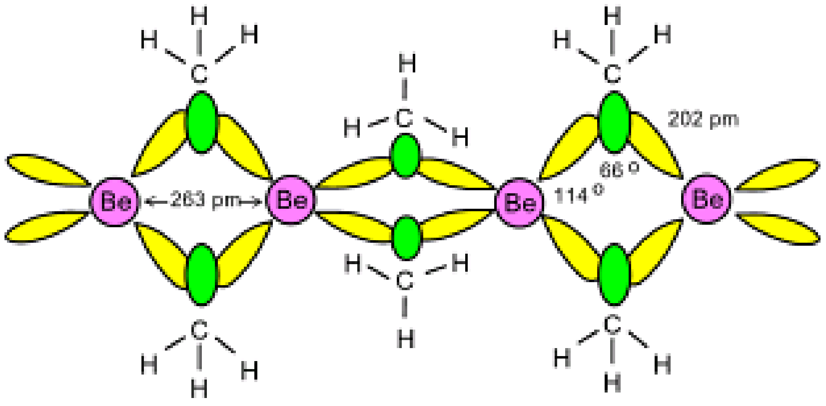
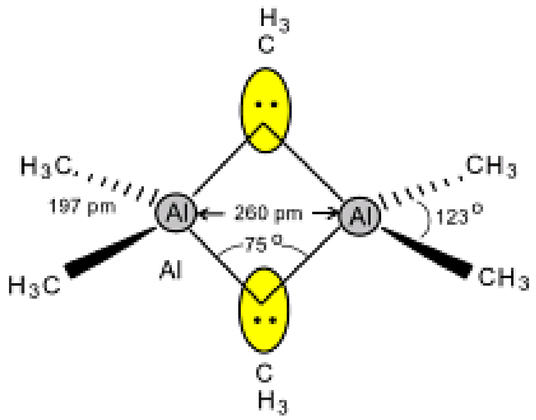
KARNATAKA STATE OPEN UNIVERSITY

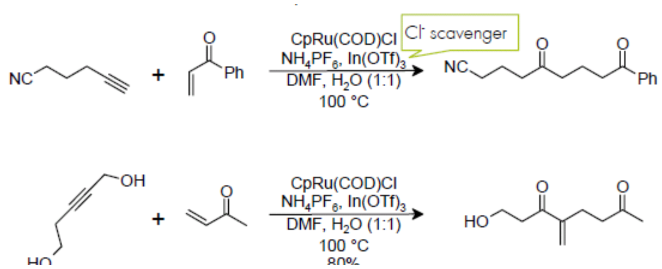
Mukthagangotri, Mysore – 570 006

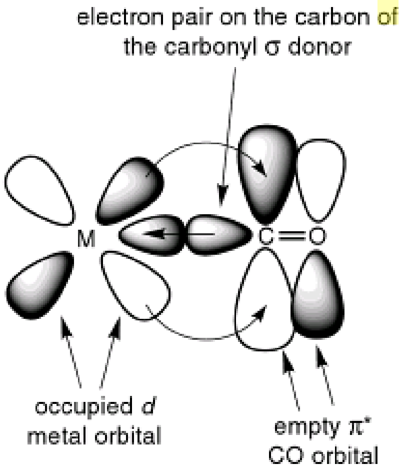
M.Sc. CHEMISTRY

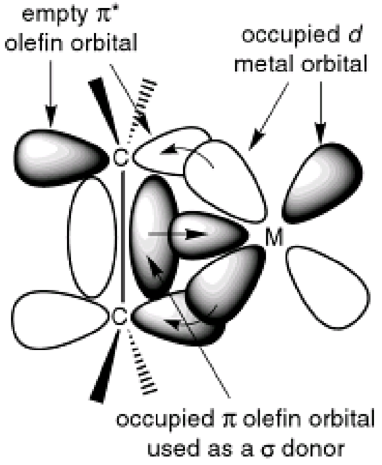
(THIRD SEMESTER)











Course: MCH T 3.1 Block 1, 2,3 and 4

INORGANIC CHEMISTRY- III

M.Sc. CHEMISTRY

THIRD SEMESTER

COURSE: MCHT 3.1

INORGANIC CHEMISTRY-III

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COURSE INTRODUCTION

Chemistry is the experimental and theoretical study of materials properties both at macroscopic and microscopic levels. Inorganic chemistry is concerned with the properties and reactivity of all chemical elements. Advanced interests focus on understanding the role of metals in biology and the environment, the design and properties of materials for energy and information technology, fundamental studies on the reactivity of main group and transition elements, and nanotechnology. Synthetic efforts are directed at hydrogen storage materials and thermoelectric, catalysts for solar hydrogen generation, fullerenes and metal porphyrins, metal clusters and compounds with element-element bonds, as well as nanowires and nanoparticles.

First block in this paper consist reactions of coordination compounds. Coordination compounds exhibits different kind of reactivities. Which are entirely different from the inorganic reactions of main group elements. In order to understand the reactions of coordination chemistry it is very much important to know the structure and geometry of the complexes. This you have studied in II semester. Also it is important to know the CFSE of the lignad. All this previous knowledges will help to understand the reactions of coordination compounds.

In the second block you have introduce to new compounds called organometallic compounds. Which are formed by metal atom and organic lignad. Though they are coordination compounds they are different form them in which the metal atom at least have one M-C bond. Synthesis and nomenclature will be studied in this block

In the third block you are going to study bout organometallic compounds of main group elements and d-blok elements. There is a striking differences are their between these two compounds. Though both have M-C bond, the organomeallic compound of main group elements are almost ionic in nature and carbon attached to metal in these compounds act as a nulceophile. In case of organometallic compounds of d-block elements the M-C bond is neutral and in some compounds it is covalent and in some compounds it is co-ordinate type. In both cases the carbon attached to metal at as electrophile. The synthesis, structure, reactivity and applications of these compounds in organic synthesis will elaborated in this unit.

In the last block you are introduced to a chemistry of main group inorganic compounds. As we know carbon can bon many number of carbon to from chains, rings etc… polymer structures. These properties of carbon made compounds of this element to study in separate branch called organic chemistry. The other compounds belonging to carbon family like silicon and its neighbor family like phosphorous, nitrogen, sulphur do have form polymer structure but their chain length is redistricted to only few numbers. But they forms intersecting structures and exhibit excellent properties. In this unit you are going to study the inorganic polymers of P, N, S and Si elements.

UNIT-1

Structure

1.0 Objectives of the unit

1.1 Introductions

1.2 Reactivity of Transition Metal Complexes

1) Substitution reactions

1.3 Interchange reaction

1.4 Classification of coordination complexes

1.5 Factors affecting the labile/inert nature of complexes

1.6 Mechanisms

1.7 Associative mechanism

1.8 Dissociative mechanism

1.9 Addition (dissociation) reactions

1.10 Redox (e^- transfer) reactions

1.11 Reactions at coordinated ligands (many variants here)

11.12 The evidence for dissociative mechanisms

1.13 Summary of the unit

1.14 Key words

1.15 References for further studies

1.16 questions for self understanding

1.0 Objectives of the unit

After studying this unit you are able to

- Explain the different reactivity of transition metal complexes
- Write the mechanism for substitution reactions transition metal complexes
- Explain the interchange reaction of transition metal complexes
- Identify the factors affecting the labile/inert nature of complexes
- Write the associative mechanism
- Write the dissociative mechanism

1.1 Introductions

The chemistry of coordination compounds has some additional features compare to simple organic / inorganic compounds, due to complexity in geometries and possibilities for rearrangement. The metal atoms posses more variability in their reactions and different factors influence the course of reactions. Reactions of coordination complexes can be conveniently divided into

1. Substitution reactions at the metal center,
2. Oxidation-reduction reactions, and
3. Reactions of the ligands that do not change the attachments to the metal center.

Reactions that include more elaborate rearrangements of ligand structures are more often observed in organometallic compounds.

1.2 Reactivity of Transition Metal Complexes

As mentioned above transition metal complexes exhibit four main types of reactivity. Among them more frequently found reaction is substitution reaction.

1) Substitution reactions

The reaction in which one or more of the lignads present in the coordination compound is replaced by new ligand is called substitution reaction. The general representative equation for substitution recaction is

$$ML_n + L' \rightarrow ML_{n-1}L' + L$$

Example, $[Fe(H_2O)_6]^{3+} + 3\ acac^- \rightarrow Fe(acac)_3 + 6\ H_2O$

[Cu($[Co(OH_2)_6]^{2+} + Cl^- \longrightarrow [Co(OH_2)_5Cl]^+ + H_2O$

Ligand substitution reactions are occurs by either associative or dissociative pathway. Associative reaction intermediate has higher coordination number than reactants or products. Associative substitution reactions are characterized by lower coordination number complexes and the reaction rates depend on the entering group

Example

$$[PtCl(dien)]^+ + I^- \longrightarrow [PtI(dien)]^+ + Cl^-$$

$$[PtCl(dien)]^+ + Br^- \longrightarrow [PtBr(dien)]^+ + Cl^-$$

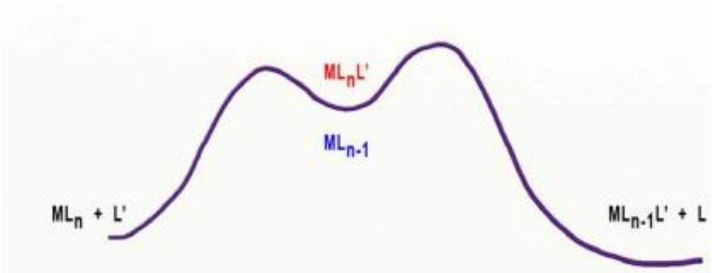
Dissociative reaction intermediate has lower coordination number than reactants or products Dissociative complexes are more observed in octahedral complexes and smaller metal centers. The rates of the reaction depend on leaving group.

$$[Ni(OH_2)_6]^{2+} + NH_3 \longrightarrow [Ni(OH_2)_5(NH_3)]^{2+} + H_2O$$

There are four recognized mechanisms are identified for the ligand substitution in inorganic chemistry they are

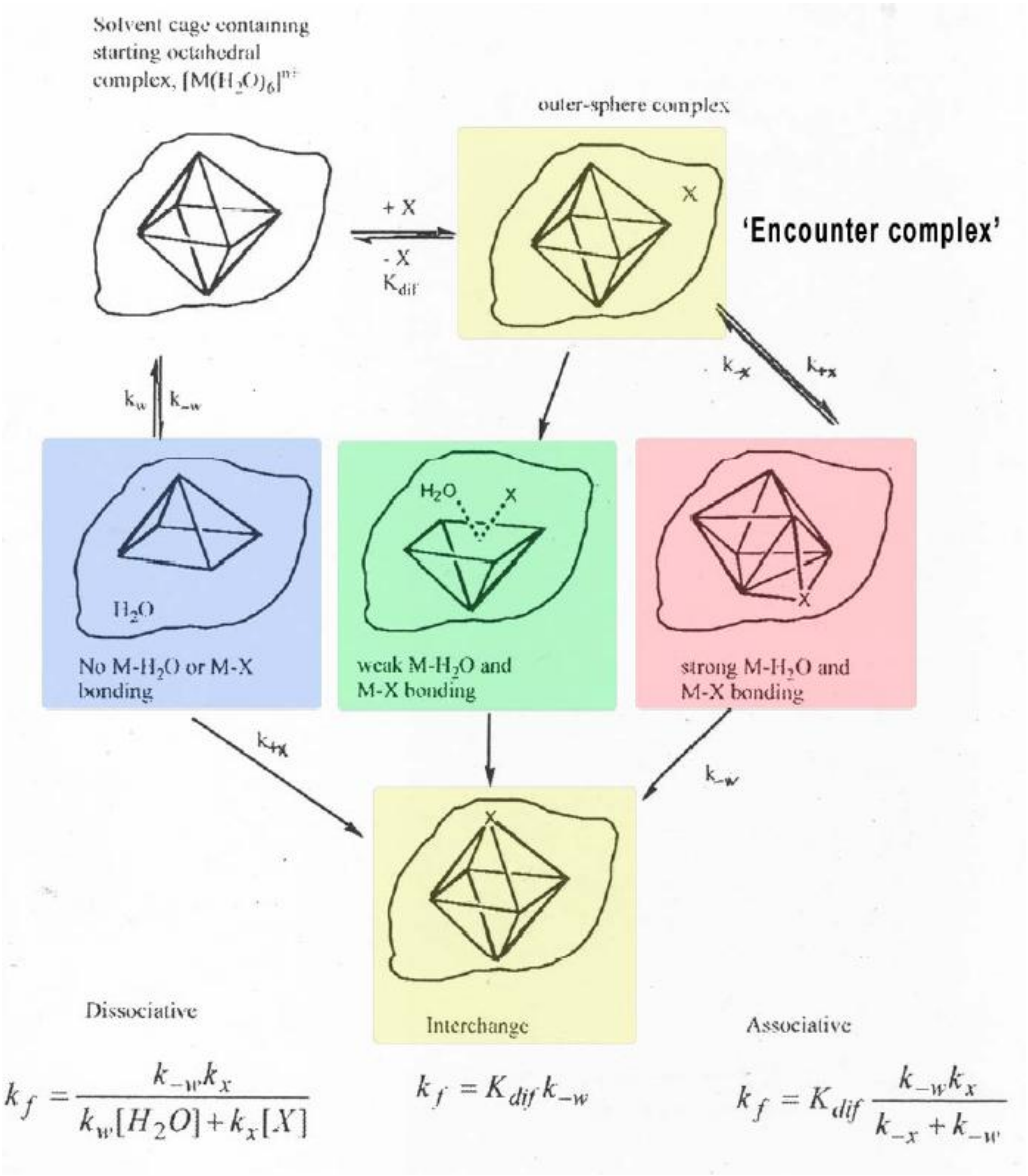
1) Associative (A)
2) Dissociative (D)
3) Associative Interchange (I_A)
4) Dissociative Interchange (I_D)

Associative and Dissociative differ from I_A and I_D respectively in that there is a discrete intermediate of higher or lower coordination number



1.3 Interchange reaction

These are concerted reaction with no discrete intermediate of higher or lower coordination number. More common than true A or D mechanisms based on the Eigen-Wilkins 'encounter complex' model, I_A has both leaving and entering ligands strongly bound in the TS and shows sensitivity to the nature and concentration of L'. I_D has both leaving and entering



ligands weakly bound in the TS and shows little sensitivity to the identity or concentration of L'. In an interchange (I) reaction, a rapid equilibrium between the incoming ligand and the 6-coordinate reactant forms an ion pair or loosely bonded molecular combination taking place. This species (which is not described as having an increased coordination number and is not directly detectable) reacts to form the product and release the initial ligand.

$$ML_5X + Y \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} ML_5X\cdot Y$$

$$ML_5X\cdot Y \xrightarrow{k_2} ML_5Y + X$$

$$\frac{d[ML_5Y]}{dt} = k_2[ML_5X\cdot Y] = \frac{k_2K_1[M]_0[Y]_0}{1 + K_1[Y]_0 + (k_2/k_{-1})} \cong \frac{k_2K_1[M]_0[Y]_0}{1 + K_1[Y]_0}$$

1.4 Classification of coordination complexes

Rate is important for understanding coordination complex chemistry. Depending up on the rate at which the coordination complexes are undergo substitution reaction are classified in to inert, labile, stable and unstable complexes.

a) *Stable and unstable coordination complexes*

The crystal field stabilization energy (CFSE) is an important factor in the stability of transition metal complexes. Complexes with high CFSE tend to be thermodynamically stable (i.e., they have high values of Ka, the equilibrium constant for metal-ligand association). Also they are kinetically stable because ligand substitution requires that they dissociate (lose a ligand), associate (gain a ligand), or interchange (gain and lose ligands at the same time) in the transition state. These distortions in coordination geometry lead to a large activation energy if the CFSE is large, even if the product of the ligand exchange reaction is also a stable complex. For this reason, complexes of Pt^{4+}, Ir^{3+} (both low spin $5d^6$), and Pt^{2+} (square planar $5d^8$) have very slow ligand exchange rates.

There are two other important factors that contribute to complex stability

i) Hard-soft interactions of metals and ligands (which relate to the energy of complex formation)

ii) The chelate effect, which is an entropic contributor to complex stability.

i) *Hard-soft interactions*

Hard acids are typically small, high charge density cations that are weakly polarizable such as H^+, Li^+, Na^+, Be^{2+}, Mg^{2+}, Al^{3+}, Ti^{4+}, and Cr^{6+}. Electropositive metals in high oxidation states are typically hard acids. These elements are predominantly found in oxide minerals, because O^{2-} is a hard base. Some hard bases include H_2O, OH^-, O^{2-}, $F^{-,}$ NO^{3-}, Cl^-, and NH_3. The hard acid-base interaction is primarily electrostatic. Complexes of hard acids with hard bases are stable because of the electrostatic component of the CFSE.

Soft acids are large, polarizable, electronegative metal ions in low oxidation states such as Ni^0, Hg^{2+}, Cd^{2+}, Cu^+, Ag^+, and Au^+. Soft bases are anions/neutral bases such as H^-, C_2H_4, CO, PR_3, R_2S, and CN^-). Soft acids typically occur in nature as sulfide or arsenide minerals.

The bonding between soft acids and soft bases is predominantly covalent. For example, metal carbonyls bind through a covalent interaction between a zero- or low-valent metal and neutral CO to form $Ni(CO)_4$, $Fe(CO)_5$, $Co(CO)_4^-$, $Mn_2(CO)_{10}$, $W(CO)_6$, and related compounds. The preference for hard-hard and soft-soft interactions ("like binds like") is nicely illustrated in the properties of the copper halides:

CuF	CuI	CuF_2	CuI_2
unstable	stable	stable	unstable

The compounds CuF and CuI_2 have never been isolated, and are thermodynamically unstable to disproportionation:

$$2\ CuF(s) \dashrightarrow Cu(s) + CuF_2(s)$$

$$2\ CuI_2(s) \dashrightarrow 2CuI(s) + I_2(s)$$

ii) Chelate and macrocyclic effects

Ligands that contain more than one binding site for a metal ion are called chelating ligands As the name implies, chelating ligands have high affinity for metal ions relative to ligands with only one binding group (which are called monodentate = "single tooth") ligands.

Consider the two complexation equilibria in aqueous solution, between the cobalt (II) ion, $Co^{2+}(aq)$ and ethylenediamine (en) on the one hand and ammonia, NH_3, on the other.

$$[Co(H_2O)_6]^{2+} + 6\ NH_3 \rightleftharpoons [Co(NH_3)_6]^{2+} + 6\ H_2O\ (1)$$

$$[Co(H_2O)_6]2^+ + 3\ en \rightleftharpoons [Co(en)_3]^{2+} + 6\ H_2O\ (2)$$

Electronically, the ammonia and en ligands are very similar, since both bind through N and since the Lewis base strengths of their nitrogen atoms are similar. This means that ΔH° must be very similar for the two reactions, since six Co-N bonds are formed in each case. Interestingly however, we observe that the equilibrium constant is 100,000 times larger for the second reaction than it is for the first.

The big difference between these two reactions is that the second one involves "condensation" of fewer particles to make the complex. This means that the entropy changes for the two reactions are different. The first reaction has a ΔS° value close to zero, because their is the same number of molecules on both sides of the equation. The second one has a positive ΔS° because four molecules come together but seven molecules are produced. The difference between them (ΔΔS°) is about +100 J/mol-K. We can translate this into a ratio of equilibrium constants using $K_f(en)/K_f(NH_3) = e^{-\Delta\Delta G°/RT} \approx e^{+\Delta\Delta S°/R} \approx e^{12} \approx 105$

The chelate effect is entropy-driven. It follows that the more binding groups a ligand contains, the more positive the ΔS° and the higher the K_f will be for complex formation. In this regard, the hexadentate ligand ethylenediamine tetraacetic acid (EDTA) is an optimal ligand for making octahedral complexes because it has six binding groups. In basic solutions where all four of the COOH groups are deprotonated, the chelate effect of the $EDTA^{4-}$ ligand is approximately 1015. This means, for a given metal ion, K_f is 1015 times larger for $EDTA^{4-}$ than it would be for the relevant monodentate ligands at the same concentration. EDTA4- tightly binds essentially any 2^+, 3^+, or 4^+ ion in the periodic table, and is a very useful ligand for both analytical applications and separations. The macrocyclic effect follows the same principle as the chelate effect, but the effect is further enhanced by the cyclic conformation of the ligand. Macrocyclic ligands are not only multi-dentate, but because they are covalently constrained to their cyclic form, they allow less conformational freedom. The ligand is said to be "pre-organized" for binding, and there is little entropy penalty for wrapping it around the metal ion. For example heme b is a tetradentate cyclic ligand which is strongly complexes transition metal ions, including (in biological systems) Fe^{+2}.

b) Labile complex

Labile complexes are those in these complexes, the rate of substitution of ligands is relatively high are called labile complexes ie., the complexes species that react more rapidly

Example; $[Cu(NH_3)_4(H_2O)_2]^{2+}$ is labile. Its aqueous solution is blue in colour. When concentrated hydrochloric acid is added to this solution, the blue solution immediately turns green giving $[CuCl_4]^{2-}$.

c) Inert complex

Inert complexes are those in these complexes, ligands are not exchanged easily. The rate of exchange is very slow. i.e, species that are unstable but survive for minutes or more.

Example:

$[Co(NH_3)_6]^{3+}$ reacts slowly. When this complex is treated with concentrated HCl, no reaction takes place. Only when it is heated with 6M HCl for many hours, one NH_3 is substituted by Cl^{-}.

$$[Co(NH_3)_6]^{3+} \xrightarrow{\text{Conc. HCl}} [Co(NH_3)_5Cl]^{2+} + NH_4^{+}$$

1.5 Factors affecting the labile/inert nature of complexes

1. *Size of the central metal ion*

Smaller the size of the metal ion, greater will be the inertness because the ligands are held tightly by the metal ion therefore the more inert the complex is.

Example:

Lability of $[Mg(H_2O)_6]^{2+} < [Ca(H_2O)_6]^{2+} < [Sr(H_2O)_6]^{2+}$.

2. *Charge on the central metal ion*

Greater the charge on the metal ion, greater will be the inertness of the complex. Example: Lability of $[Na(H_2O)_6]^{+} > [Mg(H_2O)_6]^{2+} > [Al(H_2O)_6]^{3+}$.

3. *d-electron configuration*

If electrons are present in the antibonding eg* orbitals, the complex will be labile because the ligands will be weakly bonded to the metal and hence can be substituted easily. If the complex contains empty t_{2g} orbitals, then it will be labile because ligands can approach easily without much repulsion. In short, if the complex contains less than three d-electrons, it will be labile. Or, if one or more e_g electrons are present, it will be labile. Hence the lability are influenced by d electron configuration of metal ion, d^3, low-spin complexes of d^4, d^5, and d^6 and strong-field d^8 (square planar) coordination compounds exhibit very slow reactions hence they are inert. d^1, d^2, high-spin complexes of d^4, d^5, and d^6 d^7, d^9, d^{10} are exhibit fast reactions hence they are labile. Weak-field d^8 complexes are shows intermediate character.

Following table summarize the lability of complexes with their d electronic configuration of central metal.

No. of d electrons & electron configuration	Nature		Example
d^0	Labile		$[CaEDTA]^{2-}$
d^1; $t_{2g}{}^1\ e_g{}^0$	Labile		$[Ti(H_2O)_6]^{3+}$
d^2; $t_{2g}{}^2\ e_g{}^0$	Labile		$[V(phen)_3]^{3+}$
d^3; $t_{2g}{}^3\ e_g{}^0$		Inert	$[V(H_2O)_6]^{3+}$
d^4 (high-spin); $t_{2g}{}^3\ e_g{}^1$	Labile		$[Cr(H_2O)_6]^{3+}$
d^4 (low-spin); $t_{2g}{}^4 e_g{}^0$		Inert	$[Cr(CN)_6]^{4-}$
d^5 (high-spin); $t_{2g}{}^3\ e_g{}^2$	Labile		$[Mn(H_2O)_6]^{2+}$ +
d^5 (low-spin); $t_{2g}{}^5\ e_g{}^0$		Inert	$[Mn(CN)_6]^{4-}$
d^6 (high-spin); $t_{2g}{}^4\ e_g{}^2$		Inert	$[Mn(H_2O)_6]^{2+}$
d^6 (low-spin); $t_{2g}{}^6\ e_g{}^0$		Inert	$[Fe(CN)6]^{4-}$
d^7, d^8, d^9, d^{10}	Labile		

1.6 Mechanisms

In an aquo complex, the rate of substitution of aquo ligand does not depend on the nature of the incoming ligand. Exchange of aquo ligand by another ligand is always faster than the substitution of one ligand by another.

Explanation; The above observations suggest that the reaction should proceed in two steps

$[M(H_2O)_6]^{n+} + L \rightleftharpoons [M(H_2O)_6L]^{n+}$ (outer-sphere complex)

$[M(H_2O)_6L]^{n+} \longrightarrow [M(H_2O)_5L]^{n+} + H_2O$ (inner sphere aquo ligand exchanges with outer-sphere ligand

Of these two steps, the rate determining step mainly involves the breaking of M-OH$_2$ bond and the influence of the entering ligand is negligible

1.7 Associative mechanism

In this mechnaism the bond formation between the central metal ion and the entering ligand is important. This determines the magnitude of activation energy and hence the rate of reaction. The steps can be represented as follows

$$ML_n + L' \leftrightarrow ML_nL' \rightarrow ML_{n-1}L' + L \text{ or}$$

$$L_5MX + Y \rightleftharpoons L_5MXY$$

$$L_5MXY \longrightarrow L_5MY + X$$

The reaction rate depends on starting complex and incoming ligand concentration. These types of reactions are ensitive to nature of L’ (but solvent effects can sometimes mask this) and occurs in more likely for low coordination number complexes.

1.8 Dissociative mechanism

This mechanism involves the two steps. In the first step, the already attached ligand to the metal breaks and in the second step, the new ligand forms a bond with the central metal ion.

The steps are $ML_n \xrightleftharpoons{slow} ML_{n-1} + L \xrightleftharpoons{\overset{L'}{fast}} ML_{n-1}L'$

In this mechanism, the breaking of the bond between the metal and the already present ligand is important and the magnitude of activation energy depends on this step. These types of reactions are equivalent to a S_N1 reaction in organic chemistry. The reaction rates depend only on concentration of starting complex ML_n. Generally they are insensitive to nature of incoming ligand L’and these reactions are more common for high coordination number complexes and those containing very bulky ligands L.

1.9 Addition (dissociation) reactions

$ML_n + L' \rightarrow ML_nL'$

$[Cu(acac)_2] + py \rightleftharpoons [Cu(acac)_2(py)]$

Tetrahedral (Td) Squarepyramidal (SqPy)

Dissociation (the reverse reaction) usually requires heat or light to occur

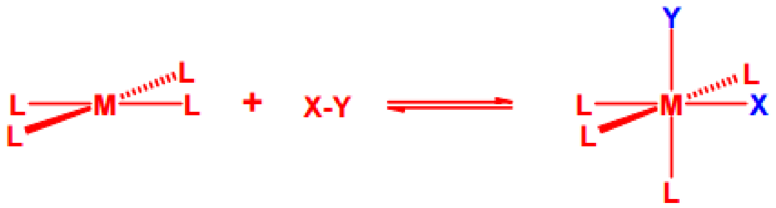
$$[NiCl_2py_4] \xrightarrow[-2py]{180^0C} [NiCl_2py_2] \xrightarrow[-py]{220^0C} [NiCl_2py] \xrightarrow[-py]{350^0C} [NiCl_2]$$

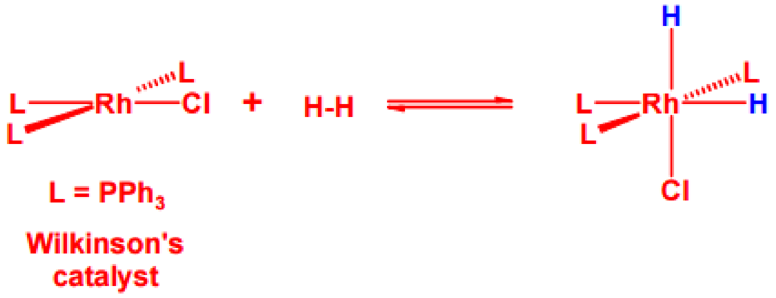
1.10 Redox (e^- transfer) reactions

$$ML_n^{x+} \rightarrow ML_n^{x+1\,+} + e^-$$

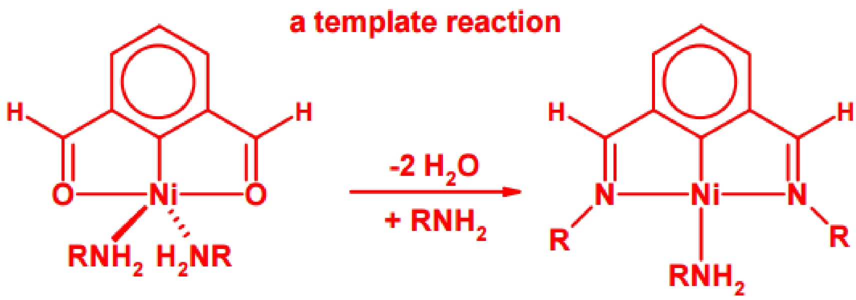
Example $[Ru(NH_3)_6]^{2+} \rightarrow [Ru\ (NH_3)_6]^{3+} + e^-$

Also includes oxidative-addition (and its reverse reductiveelimination),especially of SqP complexes





1.11 Reactions at coordinated ligands (many variants here)



11.12 The evidence for dissociative mechanisms

The evidence for dissociative mechanisms can be grouped as follow

1. The rate of reaction changes only slightly with changes in the incoming ligand. In many cases, aquation (substitution by water) and anation (substitution by an anion) rates are comparable. If dissociation is the rate-determining reaction, the entering group should have no effect at all on the reaction rate. Although there is no specific criterion for this, changes in rate constant of less than a factor of 10 are generally considered to be insignificant for this purpose.
2. The rate of reaction correlates with the metal-ligand bond strength of the leaving group, in a linear free energy relationship (LFER)
3. Activation energies and entropies are consistent with dissociation, although interpretation of these parameters is difficult. Another activation parameter now being measured by experiments at increased pressure is the volume of activation, the change

in volume on forming the activated complex. Dissociative mechanisms generally result in positive values for Av_{act} because one species splits into two, and associative mechanisms result in negative Avact values because two species combine into one, with a presumed volume smaller than the total for the reactants. However, caution is needed in interpreting volume effects because solvation effects, particularly for highly charged ions, may be la

1.13 Summary of the unit

One important indicator of reactivity is the rate of degenerate exchange of ligands. For example, the rate of interchange of the coordinate water in $[M(H_2O)_6]^{n+}$ complexes varies over 20 orders of magnitude. Complexes where the ligands are released and rebound rapidly are classified as labile. Such labile complexes can be quite stable thermodynamically. Typically they either have low-charge (Na^+), electrons in d orbitals that are antibonding with respect to the ligands (Zn^{2+}), or lack covalency (Ln^{3+}, where Ln is any lanthanide).

The lability of a metal complex also depends on the high-spin vs. low-spin configurations when such is possible. Thus, high-spin Fe(II) and Co(III) form labile complexes, whereas low-spin analogues are inert.

Complexes that have unfilled or half-filled orbitals often show the capability to react with substrates. Most substrates have a singlet ground-state; that is, they have lone electron pairs (e.g., water, amines, ethers). These substrates need an empty orbital to be able to react with a metal center. Some substrates (e.g., molecular oxygen) have a triplet ground state. Metals with half-filled orbitals have a tendency to react with such substrates. If the ligands around the metal are carefully chosen, the metal can aid in (stoichiometric or catalytic) transformations of molecules or be used as a sensor.

1.14 Key words

Reactivity of transition metal complexes; Substitution reaction; Interchange reaction; Labile and inert complexes; Associative mechanism; Dissociative mechanism; Redox (e^- transfer) reactions

1.15 References for further studies

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1.16 questions for self understanding

1) What are the different types of reactions observed in transition metal complexes?
2) What is substitution reaction of coordination compound? Give example
3) What is interchange reaction? Give example
4) Discuss the classification of coordination complexes based on reactivity.
5) What are labile and inert complexes? Give examples.
6) Discuss the various factors affecting the labile/inert nature of complexes
7) With example explain the associative mechanism of substitution reaction in transition metal complexes
8) With example explain the dissociative mechanism of substitution reaction in transition metal complexes
9) With example explain the addition (dissociation) reactions of substitution reaction in transition metal complexes
10) Write a note on redox (e^- transfer) reaction in transition metal complexes
11) Write a note on reactions at coordinated ligands
12) Discuss the evidence for dissociative mechanisms

UNIT-2

Structure

2.0 Objectives of the unit

2.1 Introduction

2.2 Transition State or Activated complex

- a) Substrate
- b) Attacking reagents
- i) Electrophilic reagents
- ii) Nuleophilic reagents

2.3 Types of Substitution Reactions

- i) Nucleophilic or Ligand Substitution (S_N) Reactions
- ii) Electrophilic or Metal Substitution (S_E) Reactions

2.4 Mechanism of Nuclephilic (Ligand) Substitution Reaction (S_N Reactions) in Octahedral Complexes

2.5 Relation between intimate and stoichiometric reaction mechanisms

2.6 S_N^1 or Dissociation Mechanism.

2.7 S_N^2 or Association or Displacement Mechanism

2.8 S_N^1 Vs S_N^2 Mechanism

2.9 Factors affecting rates of substitution

2.10 Reactions of Octahedral Complexes – Stereochemical Consequences

2.11 Labile and Inert complexes according to lignad substitution reaction

2.12 Electron transfer reaction

2.13 Summary of the unit

2.14 Key words

2.15 References for further study

2.16 questions for self understanding

2.0 Objectives of the unit

After studying this unit you re bale to

- Identify the types of substitution reactions in transition metal complexes
- Explain the ligand Substitution (S_N) Reactions
- Write the mechanism of nuclephilic substitution reaction in Octahedral Complexes
- Identify the coordination reactions which followsS_N^1 mechanism.
- Recognize the weather the give reaction follows S_N^2 or Association or Displacement Mechanism
- Explain the electron transfer reaction of coordination complexes
- Identify the inner coordination sphere or outer coordination sphere mechanism in electron transfer reaction

2.1 Introduction

The enormous number of coordination compounds undergoes many reactions, but a large number of reactions can be classified into a small number of reaction types. When one ligand replaces another, the reaction is called a substitution reaction. For example, when ammonia is added to an aqueous solution containing Cu^{2+} , water molecules in the coordination sphere of the Cu^{2+} are replaced by molecules of NH3 . Ligands are held to metal ions because they are electron pair donors (Lewis bases). Lewis bases are nucleophiles so the substitution of one nucleophile for another is a nucleophilic substitution reaction. Such a reaction can be illustrated as

$$L_nM–X + L' \rightarrow L_nM–L' + X$$

where X is the leaving group and L' is the entering group. It is also possible to have a metal ion (Lewis acid) replace another in a different type of reaction. Lewis bases are electrophiles, so this type of reaction is an electrophilic substitution, which can be represented as

$$ML_n + M' \rightarrow M'L_n + M$$

Because all of the ligands are leaving one metal ion and attaching to another, this type of reaction is sometimes known as ligand scrambling.

Nucleophilic substitution reactions have rates that vary enormously. For example, the reaction 1 is extremely fast where as reaction 2 is extremely slow

$$[Co(NH_3)_6]^{3+} + Cl^- \rightarrow [Co(NH_3)_5Cl]^{2+} + NH_3 \quad \text{----- (1)}$$

$$[Ni(CN)_4]^{2-} + {}^{14}CN^- \rightarrow [Ni(CN)_3({}^{14}CN)]^{2-} + CN^- \quad \text{----- (2)}$$

Complexes that undergo substitution very slowly are said to be inert; those that undergo rapid substitution are called labile. These qualitative terms have been used as descriptors for substitution reactions for many years. The fact that a complex undergoes substitution very slowly may indicate that there is no low-energy pathway for the reaction even though the product of the substitution reaction may be very stable.

2.2 Transition State or Activated complex

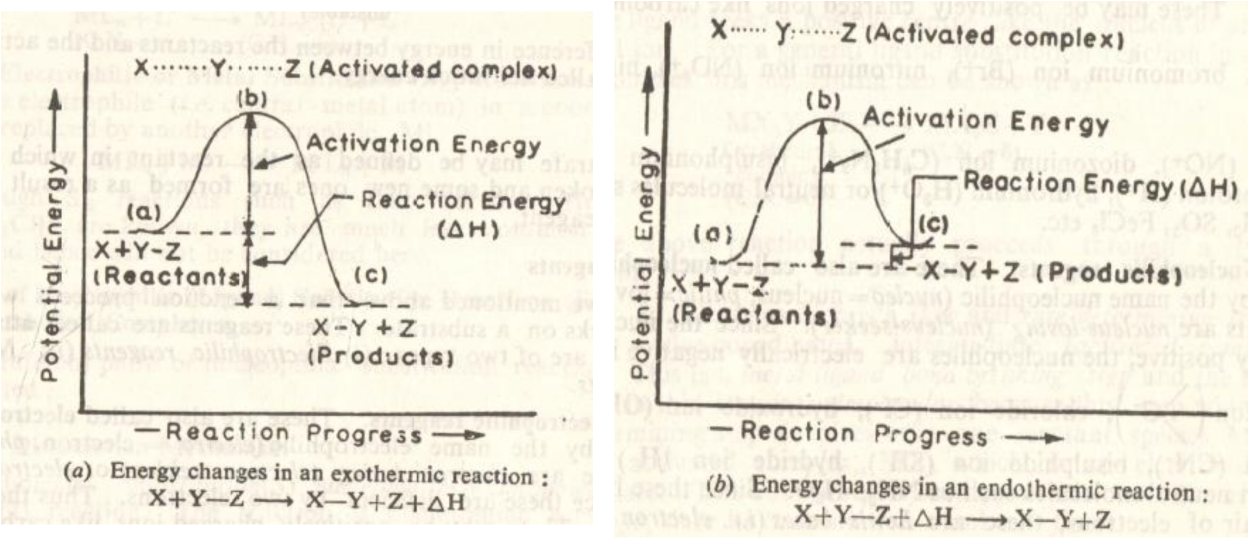
Before starting the study on kinetics and mechanism of ligand substitution reactions in co-ordination compounds the following terms should be defined.

Let us consider the energy changes occurring during the course of the reaction

$$X + Y\text{-}Z \rightarrow X\text{-}Y + Z$$

(Reactant) (Products)

In the starting the X and Y-Z have certain amount of potential energy represented by the point (a) on the curves shown of figure 1. As X approaches to the molecule Y-Z causes an increase their potential energy due to interaction (attraction or repulsion) and reached critical energy state represented by the point (b). At this state Y-Z bond is weakened and partially broken. Same time product X-Y and Z are formed as shown at point (c) in figure 1. In this process the potential energy of the system is again changed in either two ways. Figure 1a illustrate the one way; the reactants originally possess more potential energy than the products and excess energy (= ΔH) is liberated as heat. These kinds of reactions are referred as *exothermic reactions*. Figure 1b shows another way in which the reactants have less potential energy than the products and therefore the reactant absorb heat equal than the products and therefore the reactants absorb heat equal to ΔH from the surrounding during their change into products. These kinds of reactions are called *edothermic reactions*. Obviously ΔH is the energy difference between the reactants and the products in both cases and it is called *reaction energy*.



(*a*) **Energy changes in an exothermic reaction :** $X+Y{-}Z \longrightarrow X{-}Y+Z+\Delta H$

(*b*) **Energy changes in an endothermic reaction :** $X+Y{-}Z+\Delta H \longrightarrow X{-}Y+Z$

Figure 1: Energy changes in an exothermic and endothermic reactions

The above reaction can be visualised as follows. The molecule X approaches Y-Z form a direction remote from Z. While X comes nearest to Y, Z starts being repelled from Y until a stage is reached in which X and Z are loosely attached to Y and approximately equidistant from it. In this stage the species X......Y.....Z is formed and is called *the transition state* or *activated complex* which has following characteristics.

i) In this X to Y and Y to Z distance are slightly greater than the normal bond lengths

ii) It is not true molecules the bonds being partial. Thus it is of a transitory nature and refers to an imaginary molecule and hence cannot be isolated.

iii) It has the maximum energy and hence is the most unstable and has very-very short life time.

Thus the various steps responsible for the reaction are:

$$X + Y\text{-}Z_{(\text{Reactants})} \rightarrow X....Y....Z_{(\text{Activated Complex})} \rightarrow X\text{-}Y + Z_{(\text{Products})}$$

The difference in energy between the reactants in which some bonds are broken and some new ones are formed as a result of the attack of a reagent.

c) Substrate

A substrate may be defined as the reactant in which some bonds are broken and some new ones are formed as a result of the attack of a reagent.

d) Attacking reagents

A reaction proceeds when a reagent attacks on a substrate. These reagents are called attacking reagents and are of two types

i) Electrophilic reagents

ii) Nucleophilic reagents

iii) Electrophilic reagents

These are also called electrophilies (electro = electron, philic = loving) these are electron loving or electron- seeking or electron-pair acceptor. These are Lewis acids (i.e electron pair acceptor) since these are deficient by two electrons. These are either positively charged ions like carbonium ion , bromonium ion (Br^+), nitronium ion (NO_2^+), nitro- sonium ion (NO^+), diozonium ion ($C_6H_5N_2^+$), bisulphonium ion (SO_2OH^+), proton (H^+), hydronium (H_3O^+) or neutral molecules such as BF_3, $AlCl_3$, SO_3, $FeCl_3$ etc.

iv) Nuleophilic reagents

These are also called nucleophilies (nucleo = nucleus, philic = loving) these reagents are nucleus-loving or nucleus-seeker. Since the nucleus is electrically positive the nucleophiles are electrically negative ions like carbonian, chloride ion (Cl^-), hydroxide ion (OH^-) cyanide ion (CN^-), bisulphide ion (SH^-), hydride ion (H^-) or electron- rich neutral molecules such as NH_3, H_2O. Since these have unshared pair of electrons, these are Lewis bases (i.e electron pair donar).

In co ordination chemistry the central metal ion is an electrophile, since it accepts an electron pair while the ligands are nucleophiles because these donate electron pairs. Thus:

$M^{n+}_{\text{(electrophile)(Lewis acid)}} + L_{\text{(Nucleophile) (Lewis base)}} \rightarrow [ML]^{n+}_{\text{(complex)}}$

2.3 Types of Substitution Reactions

Following are the important types of substitution reactions met with in coordination chemistry.

(i) **Nucleophilic or Ligand Substitution (S_N) Reactions**

In these reactions a nucleophile (i.e a ligand, L) in a coordination complex say ML_n is replaced by another nucleophile L^1.

$$ML_n + L^1 \rightarrow ML_{n-1}L^1 + L$$

(ii) **Electrophilic or Metal Substitution (S_E) Reactions**

In these reactions an electrophile (i.e central metal atom) in a coordination complex is replaced by another electrophile M^1.

$$ML_n + M^1 \rightarrow M^1L_n + M$$

Only few S_E reactions for example reaction between Hg^{2+} and $[Co^{II} (NH_3)_5 Cl]^+$ are known and they are much less common than S_N reactions.

2.4 Mechanism of Nuclephilic (Ligand) Substitution Reaction (S_N Reactions) in Octahedral Complexes

Let us consider the following reaction:

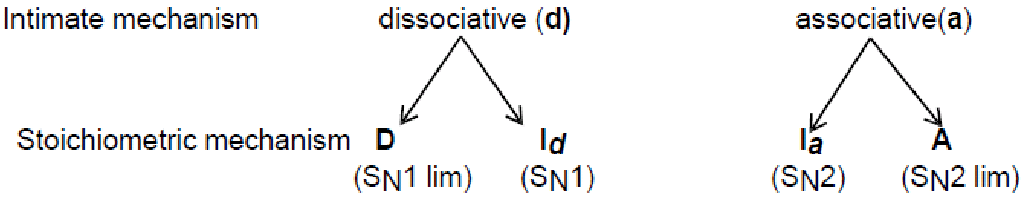
$$L_5MX + Y \rightleftharpoons L_5MY + X,$$

where X is the leaving group and Y is the entering These reactions can be explained in two ways: (1) intimate mechanism and (ii) stoichiometric mechanism

Dissociative and associative activations are known as intimate mechanism. In dissociative activation, breaking of the bond between the metal and the leaving group is important and in associative activation, bond formation between the metal and the entering ligand is important. The sequence of elementary steps from reactants to products is called stoichiometric mechanism.

2.5 Relation between intimate and stoichiometric reaction mechanisms

The following drawing depict the relation between intimate and stoichiometric reaction mechanisms



There are two different paths of nucleophilic substitution reactions are observed for octahedral complexes, they are

2.6 S_N^1 or Dissociation Mechanism.

S_N^1 indicates substitution(S) uncleophilic (N) unimolecular or first order (1) reaction. The reaction is nucleophilic because the incoming ligand seeks a positive centre, i.e, the metal ion. For a general ligand substitution reaction in an octahedral complex this mechanism is represented as follows

$$MX_5Y + Z \rightarrow MX_5Z + Y$$

The above reaction proceeds through in two-step mechanism.

In this step the ligand Y is going to be lost and a five coordinated intermediate (called activated complex) is formed. This step is a slow step therefore it is a rate determination step. This is a metal-ligand bond breaking step and the reaction occurring in this step is unimolecualr. This is because it involves only one reactant species, MX_5Y to form the activated complex MX_5 which is an electron deficient intermediate. This has either square pyramidal or trigonal bipyramidal shape since its co ordination number is five.

$$MX_5Y \xrightarrow[\text{Uni molecular and rate determining step}]{\text{Slow(-Y)}} \underset{\substack{\text{5- coordinated} \\ \text{intermediate} \\ \text{C.N=5}}}{MX_5} + Y$$

In this step MX_5Y is dissociated to give MX_5 hence the name dissociation mechanism.

In the seond step the short-lived penta coordinated intermediate (has very limited stability) is attacked rapidly by the nucleophilic reagent Z to give the complex MX_5Z.

$$MX_5 \xrightarrow[+Z]{\text{Fast}} MX_5Z$$

This is fast and bimolecular reaction. The activation energy for the first step will always high compare to the second step. The rate of overall reaction will depend on the concentration of MX_5Y and not on that of Z. Thus the rate of reaction is first order with respect to MX_5Y and zero order with respect to Z. Hence

$$\text{Rate of reaction} = K\,[MX_5Y]$$

By combining two steps, the formation of MX_5Z can be shown as follows

$$\underset{(C.N = 6)}{MX_5Y} \xrightarrow[\text{Uni molecular and rate determining step}]{\text{Slow(-Y)}} \underset{\substack{\text{5- coordinated} \\ \text{intermediate} \\ \text{C.N=5}}}{MX_5} \xrightarrow{\text{Fast} \quad +Z} \underset{(C.N = 6)}{MX_5Z}$$

The two steps are diagrammatically shown in figure 2.

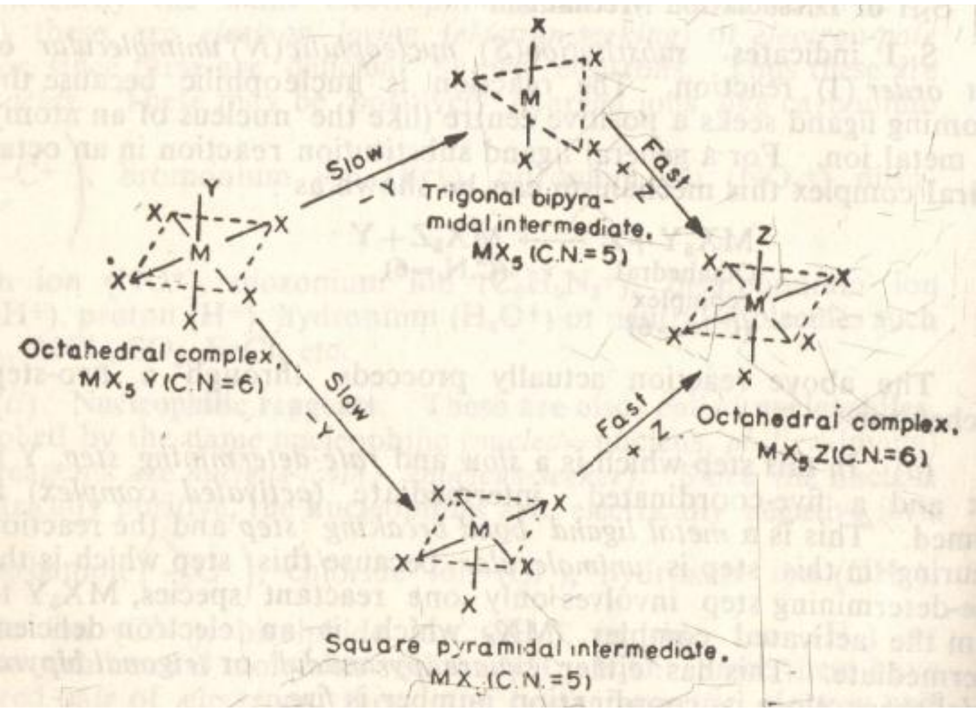


Figure 2: SN1 or dissociation mechanism for the substitution reaction

Because it is the rate of dissociation of the M – X bond that determines the rate of substitution, the rate law involves only the concentration of the starting complex, ML n X

A reaction that has these characteristics is said to follow a dissociative or S_N1 pathway. This mechanism is distinguished by the bond to the leaving group being broken before the bond to the entering ligand starts to form. Some authors define two types of S_N1 substitution.

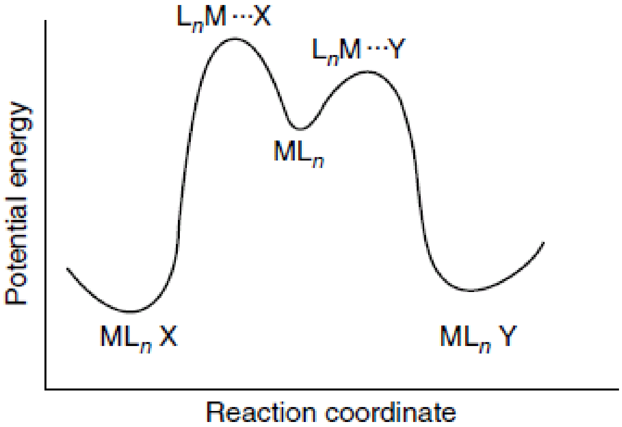


Figure 3: The energy profile for substitution of Y for X in a dissociative mechanism

If the existence of the transition state having lower coordination number is verified, the mechanism is called S_N1(lim), the so-called limiting case. This could also be called the " strict " or " perfect " S_N1 case.

The label S_N1 is used for a reaction in which the transition state of lower coordination number is not demonstrated, but all other factors agree with an S_N1 mechanism. The energy profile for the dissociative pathway is shown in Figure 3.

It is interesting to note that for the reaction $[Co(NH_3)5H_2O]^{3+} + X^- \rightarrow [Co(NH_3)_5 X]^{+2} + H_2O$ the rate constants have been determined at 25°C for a wide range of ligands, X. For several ligands, the rate constants are as follows

$X^- =$	Cl^-	Br^-	NO_3^-	NCS^-	NH_3
$10^6 \times k$, $M^{-1}\,sec^{-1}$	2.1	2.5	2.3	1.3	2

The essential feature of these data is that the rate is independent of the nature of the entering ligand. This behavior is characteristic of an S_N1 substitution mechanism

2.7 S_N^2 or Association or Displacement Mechanism

S_N^2 stands to indicate substitution (S) nucleophilic (N) bimolecular or second order (2) reaction. This also proceeds through the two steps.

(a) This is a slow step and involves the attachment of the incoming nucleophile Z to MX_2Y to form a seven-co ordinatinated unstable intermediate (perhaps transition state) whioch is probably pentagonal bipyramidal in shape. Obviouslyit is a metal ligand bound making step

$$\underset{\text{C.N. = 6}}{MX_5Y} \xrightarrow[\text{Bi molecular and rate determining step}]{\text{Slow(+Z)}} \underset{\text{Unstable seven coordinated intermediate C.N. = 7}}{MX_5YZ}$$

This reaction is rate determining and bi molecular because two reactents viz MX_6Y and Z are involved in this step. Thus the rate of this rate determining reaction is of second order; first order with respect to the complex MX_5Y and first order with respect to the entering ligand Z

i.e Rate of reaction $=K[MX_5Y][Z]$

In this step Z associates with MX_5Y to form MX_5YZ. Hence the name association mechanism

(b) Either at the same time as Z adds to MX_5Y or shortly thereafter Y leaves MX_5YZ rapidly to give MX_5Z this is a fast step.

$$MX_5YZ \xrightarrow[-Y]{\text{Fast}} MX_5Z$$

Seven coordinated unstable intermediate C.N. = 7

C.N. = 6

Both the steps can be represented as

$$MX_5Y \xrightarrow{\text{Slow}(+\,Z)} MX_5YZ \xrightarrow[-Y]{\text{Fast}} MX_5Z$$

C.N. = 6

Bi molecular and rate determining step

Unstable seven coordinated intermediate C.N. = 7

C.N. = 6

Both these steps are shown diagrammatically in figure 4.

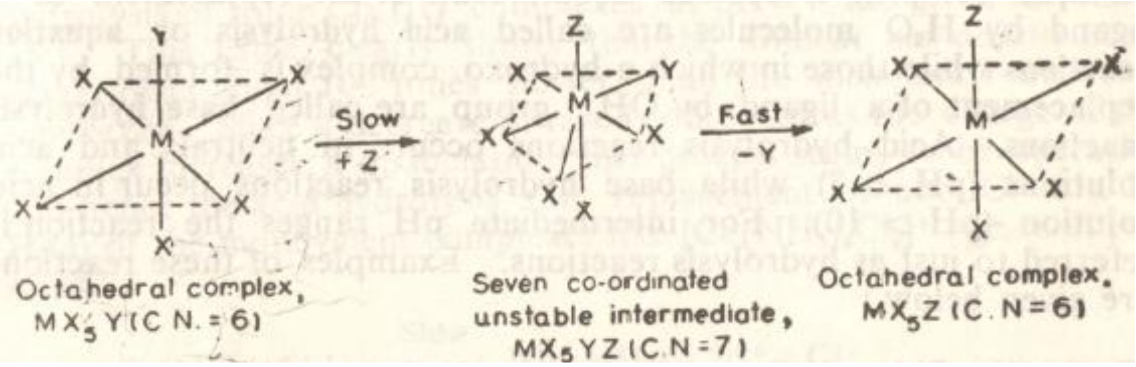


Figure 4: S_N2 or association mechanism for the substitution reaction

The rate law is a function of the concentration of the complex and the entering ligand, the rate law describes an associative or S_N2 process. The associative pathway is characterized by the bond to the entering group being formed while the bond to the leaving group is still intact. In the transition state, the coordination number of the metal is larger than it is in either the reactant or product. In an S_N2 mechanism, the transition state is a complex in which the coordination number increases as the entering group attaches before the leaving group is completely detached. It is sometimes considered that these two processes that can take place to a more or less equal extent (simultaneously in the transition state of the interchange mechanism, as discussed later). In this case, the mechanism is described as S_N2, but this label is also used to describe a second type of associative process. If bond formation to Y is much more important than breaking the bond to X as the transition state forms, the mechanism is described as S_N2(lim) or as a " strictly " S_N2 process. In this case, the transition state is a complex in which both the entering and leaving ligands reside in the coordination sphere of the metal In aqueous solutions, a water molecule can bind to the activated complex to complete the coordination sphere. The complex formed, $[ML_nH_2O]$, has some stability, so it represents a lower energy than the transition state, $[ML_n]$.

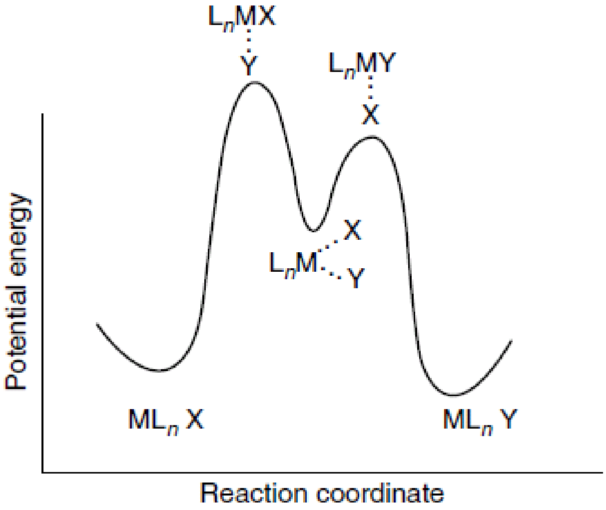


Figure 5: The energy profile for substitution of Y for X in an associative mechanism

Therefore, the complex $[ML_n\ H_2O]$ is known as an intermediate because it is more stable than the transition state either before the H_2O enters or after it leaves. Figure 5 shows the energy profile for a substitution reaction that follows an associative pathway. If the bond to the entering ligand starts to form as the bond to the leaving group is being broken, the pathway is referred to as an interchange mechanism, I. This is an intermediate process in which the bonds to both the entering and leaving groups exist simultaneously. The formation of the new bond may be more important than breaking the bond to the leaving group in some cases. Therefore, the interchange mechanism is a sort of one-step process in which the entering ligand is bonding to the metal as the leaving group moves out of the coordination sphere. If bond formation occurs essentially before the bond to the leaving group is ruptured, the interchange is known as associative interchange, I_a , and this is referred to as S_N2(lim) in older literature. However, if bond breaking to the leaving group is essentially complete before the bond forms to the entering group, the interchange is referred to as dissociative interchange, I_d, which is analogous to S_N2 in older terminology. Both interchange mechanisms can be regarded as S_N2, but with different degrees of overlap in the time scale in which bond making and bond breaking occur. The energy profile for this process is shown in Figure 6.

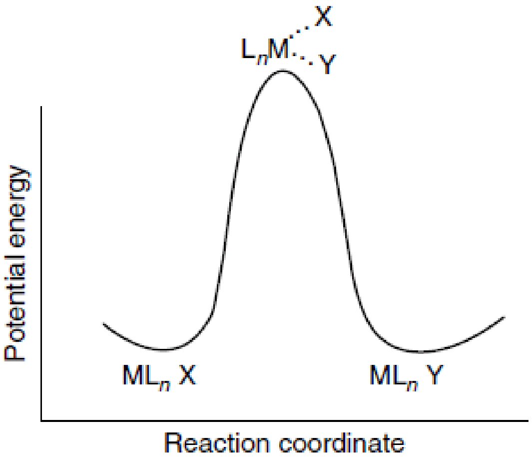


Figure 6: The interchange mechanism for a substitution

2.8 S_N^1 Vs S_N^2 Mechanism

S_N^1 and S_N^2 mechanism can be differential from each other by nothing the following points

(i) Ion S_N^1 process the rate determing slow tep is a metal ligand bond breaking step since the co ordination number of the complex MX_5Y (=6) is decreased to 5 which is þühe co ordination number of the intermediate MX_5. On the other hand in S_N^2 process the rate-determining step involves a metal ligand bond making step since C.N=6 is increased to 7.

(ii) The rate of S_N^1 mechanisum is first order with respect to MX_5Y i.e the rate-determining step in this mechanism is junimolecular. On the other hand the rate determining step for S_N^2 mechanism is bi molecular i.e its rate of reaction is second order : first order with respect to MX_5 Y and first order with respect to Z Thus :

For S_N^1mechanism rate=K[MX_5Y]

And for S_N^2 mechnism rate =K[MX_5Y][Z]

2.9 Factors affecting rates of substitution

Substitution reactions occur as a metal-ligand bond is broken and a different ligand bonds to the metal. Such processes would be related to the properties of the metal and ligand should be expected. Therefore, when substitution occurs, there are some (largely predictable) effects as a result of different sizes and charges of the entering and leaving ligands and the size and charge of the metal ion.

For example, if a substitution reaction proceeds by an S_N1 mechanism, increasing the sizes of the other ligands in the complex helps " pressure " the leaving group, making it more labile. On the other hand, in an S_N2 process, bulky ligands hinder the formation of the bond to the entering ligand, so the effect will be to decrease the rate.

a) *Nature of the entering or leaving group*

Let us consider the complex, $[Co(NH_3)_5X]^{n+}$. The rates of aquation for this complex very much depends on the nature of the leaving group, X As an example, for the complex, $[Co(NH_3)_5(NO_3)]^{2+}$, k is of the order of 10^{-5} s^{-1}. When I^- is present instead of NO_3^-, the rate decreases and is of the order of 10^{-6} s^{-1} for the complex, $[Co(NH_3)_5I]^{2+}$. Both NO_3^- and I^- are leaving groups. The reaction slows down when the leaving group is I^-. In the case of the complex, $[Co(NH_3)_5F]$, the rate is the order of 10^{-8}. That is, the reaction further slows down. Thus it is proved that M-X bond breaking is very much important in aquation reactions than bond formation.

Anation reactions do not depend very much on the nature of the entering group, Y^-. Instead, it is very much dependent on the nature of the bond being broken. Experimental data show that the rate is of the order 10_{-6} for the different entering groups (Y^-), N_3^-, SO_4^{2-} , Cl^- or NCS^- clearly indicating that the rate is independent of the nature of the entering group. Another important experimental support for this observation is that ligand exchange reactions do not take place directly but instead takes place through aquation and then anation.

Example: $[Co(NH_3)_5X]^{2+} + Y^- \rightarrow [Co(NH_3)_5Y]^{2+} + X^-$

In this reaction, X^- is not directly substituted by Y^- . In the first step, aquation takes place, that is, X^- is substituted by H_2O to give $[Co(NH_3)_5(H_2O)]^{3+}$ and then anation reaction takes place in which H_2O is substituted by Y^-. This indicates that the Co-X bond breaking is very much significant and then whatever species is present at a higher concentration will add in anation reaction. Thus, nature of Y^- is not important

b) *Steric effects of inert (non-leaving) ligands*

When the non-leaving ligands are bulky, they will be crowding the central metal ion and hence, the incoming ligand will find it difficult to approach the central metal ion slowing down the rate of reaction taking place by associative mechanism. Instead, if the reaction takes place by dissociative mechanism, (that is, one ligand breaks first and then a new ligand approaches), the rate of the reaction will increase because the crowding around the metal ion is reduced

The size of the ligand that is being replaced influences the rate of substitution, and the effect can be rationalized in the following way. A larger leaving group makes it easier to depart, so the rate of an S_N1 reaction will increase as ligand size increases. A larger ligand generally hinders attachment of the entering group in an S_N2(lim) process, so the rates are generally lower for larger leaving groups. In an S_N2 process, the effects of the size of the leaving group are opposing because both the entering and leaving groups are involved.

The size of the metal ion should also influence the rate of substitution reactions. The larger the metal ion, the less strongly the leaving group is attached, so an S_N1 process should have a higher rate for larger metal ions. In either an S_N2 or S_N2(lim) process, there will be less steric crowding as the bond is formed to the entering group, so the rate should increase for larger metal ions.

c) *Electronic effects of inert ligands*

If the existing ligand is capable of π-donation to the metal and stabilize the transition state, the reaction will be fast. When a reaction takes place by dissociative mechanism, when a ligand leaves, the metal becomes electron deficient. If there is a cis-ligand and if it is capable of donating electrons by forming π-bond with the electron deficient metal, then it stabilizes the transition state by lowering the energy and hence the reaction takes place faster

Example: $[Co(en)_2LX]^{n+}$

If L is cis to the leaving group X, and if it is a good π-donor, the reaction is fast. For example, the rate of the reaction is of the order 10^{-3} s^{-1} in the case of cis- $[Co(en)_2(OH)Cl]^+$ and is of the order of 10^{-4} s^{-1} in the case of trans-$[Co(en)_2(OH)Cl]^+$.

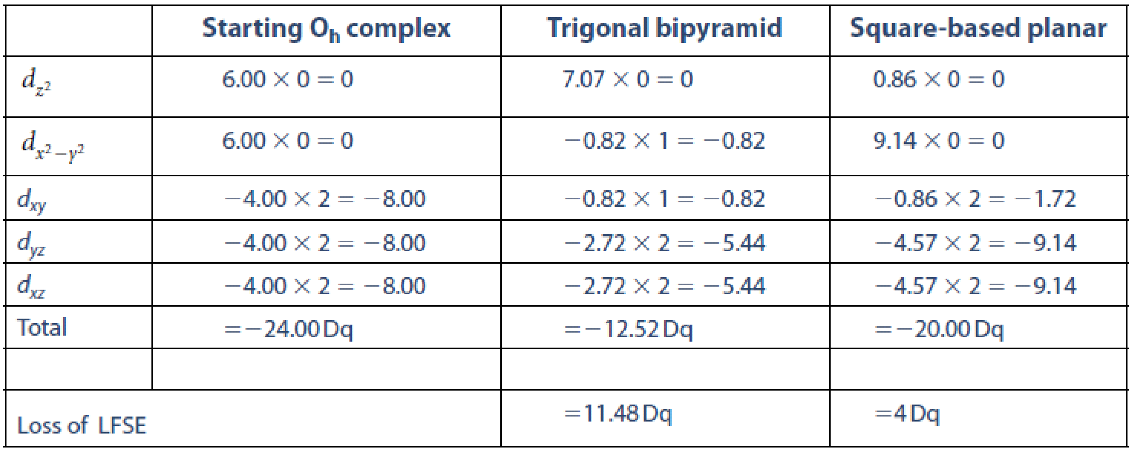
If the ligand is not capable of π-bonding but only a σ-donor such as NH_3, then the reaction will be slow. For example, in the case of cis-$[Co(en)_2Cl_2]^+$, the rate is of the order $10^{-4}s^{-1}$ and in the case of cis-$[Co(en)_2(NH_3)Cl]^{2+}$, the rate is of the order of $10^{-7}s^{-1}$.

d) *Effect of charge*

The increase in positive charge decreases the rate of reaction following a dissociative mechanism because the breaking the metal-ligand bond becomes difficult.

e) Ligand field effects

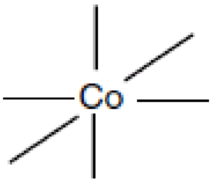
In the course of a substitution reaction in an octahedral complex, the transition state may involve either five bonds to the metal as in an SN1 mechanism or seven bonds as in an SN2 pathway. In either case, the ligand field stabilization energy is different from that of the starting complex. Therefore, part of the activation energy required can be attributed to the amount of ligand field energy lost in forming the transition state. The basis for calculating the ligand field energy in various possible transition states is provided by the orbital energies shown in Table.

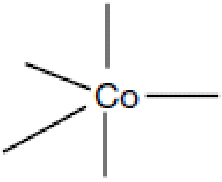


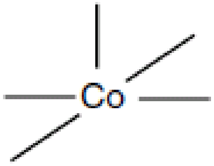
	Starting O_h complex	**Trigonal bipyramid**	**Square-based planar**
d_{z^2}	$6.00 \times 0 = 0$	$7.07 \times 0 = 0$	$0.86 \times 0 = 0$
$d_{x^2-y^2}$	$6.00 \times 0 = 0$	$-0.82 \times 1 = -0.82$	$9.14 \times 0 = 0$
d_{xy}	$-4.00 \times 2 = -8.00$	$-0.82 \times 1 = -0.82$	$-0.86 \times 2 = -1.72$
d_{yz}	$-4.00 \times 2 = -8.00$	$-2.72 \times 2 = -5.44$	$-4.57 \times 2 = -9.14$
d_{xz}	$-4.00 \times 2 = -8.00$	$-2.72 \times 2 = -5.44$	$-4.57 \times 2 = -9.14$
Total	$= -24.00$ Dq	$= -12.52$ Dq	$= -20.00$ Dq
Loss of LFSE		$= 11.48$ Dq	$= 4$ Dq

I

in a strong field. If the process takes place by an SN1 process, the five-bonded transition state may be presumed to have either a trigonal bipyramid or square-based pyramid structure. The orbital energies will be determined as follows







From this example, it can be seen that forming a square-based pyramid transition state results in a loss of only 4Dq, whereas forming the trigonal bipyramid transition state involves the loss of 11.48vDq. In cases where Dq is rather large, this difference is considerable, which means that the square-based pyramid transition state is energetically more favorable than is a trigonal bipyramid. Therefore, the loss of one ligand and its replacement by another resulting in the product having the same configuration as the starting complex is consistent with the transition state being a square-based pyramid. Although the value of Dq may not be great enough to overcome other factors that may favor a trigonal bipyramid transition state for a first-row d^6 ion, it is almost certainly is large enough to do so for a second- or third-row d^6 ion. Thus, the loss of ligand field stabilization is so high that it forces complexes of these ions to undergo SN1 substitution through a square-based pyramid transition state, so the substitution reactions occur with retention of configuration. This is true for complexes of Pt^{4+} , Rh^{3+}, and Ir^{3+} as typified by the reactions

$$\textit{trans}\text{-}[Pt(en)_2Cl_2]^{2+} + 2\,Br^- \rightarrow \textit{trans}\text{-}[Pt(en)_2Br_2]^{2+} + 2\,Cl^-$$

$$\textit{cis}\text{-}[Ru(en)_2Cl_2]^{+} + 2\,I^- \rightarrow \textit{cis}\text{-}[Ru(en)_2I_2]^{+} + 2\,Cl^-$$

Thus, the fact there is no isomerization during substitution is consistent with the transition state being a square based pyramid for second and third row metals. As shown in Figure 7,

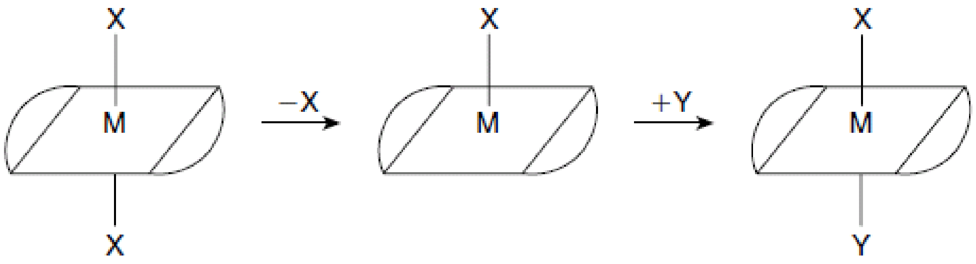


Figure 7: Substitution in which the transition state is a square-based pyramid

substitution would give a product having the same configuration as the starting complex. Having rationalized that the transition state should be a square-based pyramid, it should be mentioned that there are numerous cases in which the transition state appears to be a trigonal bipyramid. with first-row transition metals because if 11.48 Dq must be sacrificed, this would be more likely if Dq is smaller (which it is the case for first-row metals). If a trigonal bipyramid transition state forms, there would be more than one product possible. This can beillustrated by the sequence shown in Figure 8. However, it should be kept in mind that many trigonal bipyramid structures are not rigid, so some rearrangement may occur.

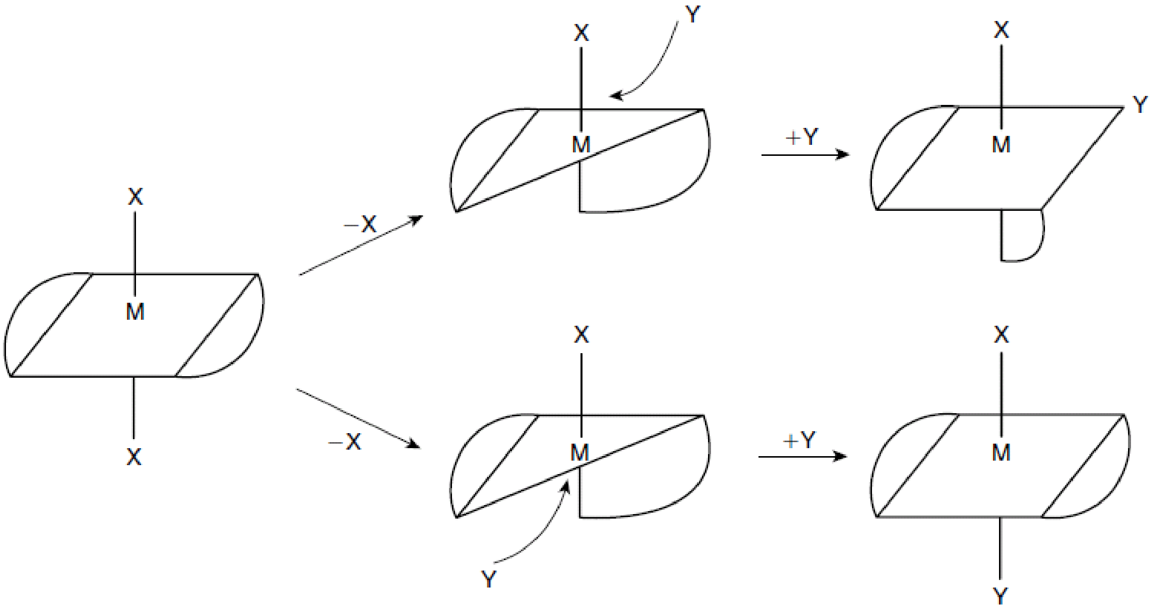
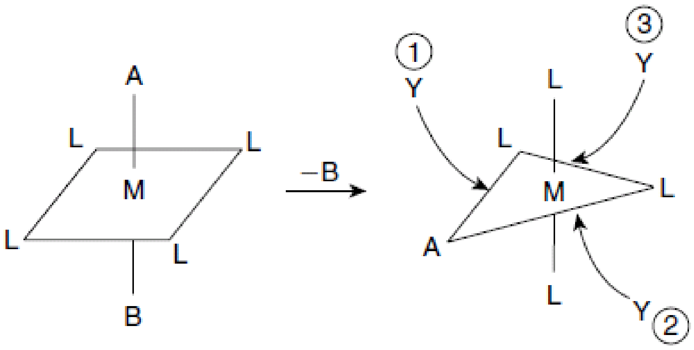


Figure 8: Attack on a trigonal bipyramid transition state during S_N1

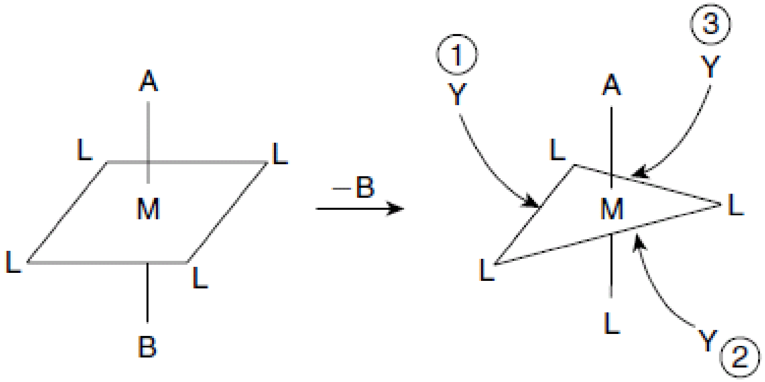
For first-row metals, the number of Dq units lost is the same as for second- and third-row metals, but the magnitude of Dq is smaller. As a result, it is possible to get some rearrangement as substitution occurs. Therefore, the product can be a mixture of both cis and trans isomers.

$$trans\text{-}[ML_4AB] + Y \rightarrow cis,\ trans\text{-}[ML_4AY] + B$$

If this reaction were to take place by formation of a square-based pyramid transition state, the product would have a trans configuration. However, if the transition state is a trigonal bipyramid, the incoming ligand, Y, could enter either cis or trans to A.



In this scheme, it is assumed that there is more room for the entering ligand to attach along an edge of the trigonal plane. From this scheme, it can be seen that attaching by Y on positions 1 and 2 would lead to Y being cis to A, but attaching at position 3 would leave Y trans to A. Thus, if A is in an equatorial position, there are two ways to get a cis product, but only one way to get a trans product. As shown in the following scheme, the situation is different if A is in an axial position in the transition state.

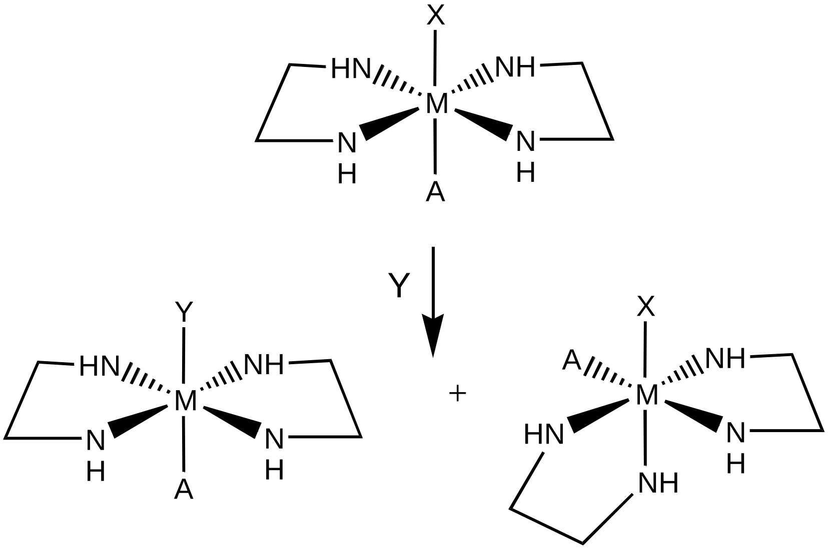


If we again assume that attachment would occur along an edge of the trigonal plane, all three points of attack would complete the square planar arrangement, but all would place Y in positions that are cis to A. Therefore, we would expect that if A is in an axial position in the transition state, the product should be all the cis isomer. In the situation in which A occupies an equatorial position in the transition state, the product would be expected to be two-thirds cis and one-third trans. Next, we must examine the situation that would result if it were equally probable for A to be in an axial or an equatorial position. In that case, the transition state would be an equal mixture of the structures having A axial or equatorial. Once again we assume that attack is equally probably at all positions along the edges of the trigonal bipyramid. If this is true, we should expect the product to consist of five-sixths cis and onesixth trans isomer. It must be emphasized that these are ideal cases and that in real complexes there are two complications. First, it is unlikely for it to be equally probable for A to be in axial and equatorial positions in the transition state. Second, because A and L are different ligands, it is unlikely that attack would be equally probable at any side of the trigonal plane. Steric differences would likely cause Y to have a different probability of entering at the three positions along the edges. The ligand field stabilization energy is only one aspect of the formation of a transition state. Because the reactions are carried out in solutions, solvation of the transition state and the entering ligand may have enough effect to assist in the formation of a particular transition state. Also, the fact that some of the ligands (either those not being replaced or the ligands involved in the substitution) can form π bonds can affect the activation energy. As a result of these factors and the fact that the ligand field model is not really an adequate description of bonding, the foregoing discussion is surely approximate. It is true, however, that the simple approach just described does agree with observations on substitution reactions.

2.10 Reactions of Octahedral Complexes – Stereochemical Consequences

General comments about the stereochemical course of ligand substitution reactions at octahedral complexes

In general, trans-$[M(en)_2ACl]^{n+}$ complexes undergo stereochemical change on hydrolysis, whereas the cis complexes react with retention of the original chirality. This cis isomer generally reacts faster than the trans isomer. Ligands A, that lead to stereochemical change in the trans series are those with pπ orbitals. If the reaction proceeds through a square pyramidal intermediate, retention of configuration observed. Proceeding through a trigonal bipyramidal, there is a high chance of stereochemical change.



2.11 Labile and Inert complexes according to lignad substitution reaction

On the basis of the difference in rates of replacement of one ligand by the other Taube has classified the complexes into two classes:

(i) The complexes in which the ligands are rapidly replaced by others are called labile or non inert complexes.

(ii) The complexes in which substitution takes place slowly are called inert complexes.

In order to make this distinction somewhat quantitative taube suggested that the complexes in which the substitution of ligands takes place in less than one minute are called labile complexes. The reaction conditions are specified as a temperature of 25^0C and 0.1 M solution.

2.12 Electron transfer reaction

Electron transfer reactions are those in which the transfer of an electron from one atom to the other occurs and hence the oxidation state of some atoms changes.

An aqueous solution containing complexes of two different metal ions may make it possible for a redox reaction to occur. In such cases, electrons are transferred from the metal ion being oxidized to the metal ion being reduced. For example

$$Cr^{2+}(aq) + Fe^{3+}(aq) \rightarrow Cr^{3+}(aq) + Fe^{2+}(aq)$$

In this reaction, an electron is transferred from Cr^{2+} to Fe^{3+}, and such reactions are usually called electron transfer or electron exchange reactions. Electron transfer reactions may also occur in cases where only one type of metal ion is involved. For example, the reaction

$$[{}^*Fe(CN)_6]^{4-} + [Fe(CN)_6]^{3-} \rightarrow [{}^*Fe(CN)_6]^{3-} + [Fe(CN)_6]^{4-}$$

represents an electron transfer from $[{}^*Fe(CN)_6\,]^{4-}$ (where *Fe is a different isotope of iron) to Fe^{3+} in $[Fe(CN)_6]^{3+}$. This is an electron transfer in which the product differs from the reactants only in that a different isotope of Fe is contained in the +2 and +3 oxidation states.

Electron transfer between metal ions contained in complexes can occur in two different ways, depending on the nature of the metal complexes that are present.

If the complexes are inert, electron transfer occurring faster than the substitution processes must occur without breaking the bond between the metal and ligand. Such electron transfers are said to take place by an *outer sphere mechanism*. Thus, each metal ion remains attached to its original ligands and the electron is transferred through the coordination spheres of the metal ions.

In the second case, the ligand replacement processes are more rapid than the electron transfer process. If this is the case (as it is with labile complexes), a ligand may leave the coordination sphere of one of the metal ions and be replaced by forming a bridge utilizing a ligand already attached to a second metal ion. Electron transfer then occurs through a bridging ligand, and this is called an *inner sphere mechanism*.

For an outer sphere electron transfer, the coordination sphere of each complex ion remains intact. Thus, the transferred electron must pass through both coordination spheres. Reactions such as the following are of this type (where * represents a different isotope)

$$[{}^*Co(NH_3)_6]^{2+} + [Co(NH_3)_6]^{3+} \rightarrow [{}^*Co(NH_3)_6]^{3+} + [Co(NH_3)_6]^{2+}$$

$$[Cr(dipy)_3]^{2+} + [Co(NH_3)_6]^{3+} \rightarrow [Co(NH_3)_6]^{2+} + [Cr(dipy)_3]^{3+}$$

In the later reaction, the d^4 complex containing Cr^{2+} is inert owing to electron pairing giving the low-spin state. There is an extreme variation in rates from very slow to very fast depending on the nature of the ligands present, and rate constants may vary from 10^{-6} to 10^8 M^{-1} s^{-1}.

The electron exchange between manganate (MnO_4^{2-}) and permanganate (MnO_4^-) takes place in basic solutions, $^*MnO_4^- + MnO^{2-}{}_4 \rightarrow {}^*MnO_4^{2-} + MnO_4^-$

and the reaction obeys the rate law $\text{Rate} = k[{}^*MnO_4^-][MnO_4^{2-}]$

When the solvent contains H^2O^{18}, no 18O is incorporated in the MnO4- produced. Thus, the reaction is presumed not to proceed by forming oxygen bridges. However, the nature of the cations present greatly affects the rate. The rate of the reaction varies with the cation present in the order $Cs^+ > K^+ \approx Na^+ > Li^+$

This supports the belief that the transition state must involve a structure such as

$$^-O_4Mn \cdots M^+ \cdots MnO_4^{2-}$$

Presumably, the function of M^+ is to " cushion " the repulsion of the two negative ions. The larger, softer Cs^+ can do this more effectively than the smaller, harder ions such as Li^+ or Na+. Also, to form these bridged transition states, solvent molecules must be displaced from the solvation sphere of the cations. That process, because of their smaller sizes, would require more energy for the more strongly solvated Li^+ and Na^+ . For the Cs^+ ion, which forms effective bridges, the rate of electron exchange has been found to be linearly related to Cs^+ concentration.

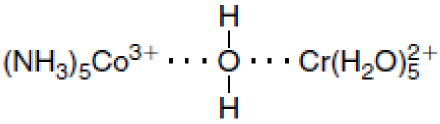
Similar results have been found for the electron exchange between $[Fe(CN)_6]^{3-}$ and $[Fe(CN)_6]^{4-}$. In that case, the acceleratory effects are found to vary with the nature of the cation in the order $Cs^+ > Rb^+ > K^+ \approx NH_4^+ > Na^+ > Li^+$

in accord with the size and solvation effects discussed earlier. For +2 ions, the order of effect on the rate is $Sr^{2+} > Ca^{2+} > Mg^{2+}$, in accord with the decrease in softness of these species. Exchange in these outer sphere cases is believed to involve the formation of bridged species containing cations that are probably less than fully solvated.

In aqueous solutions, Cr^{2+} is a strong reducing agent, and it reduces Co_{3+} to Co^{2+}. A number of electron transfer reactions involving complexes of these metals have been studied. High-spin c $[Co(NH_3)_5H_2O^*]^{3+} + [Cr(H_2O)_6]^{2+} \rightarrow [Co(NH_3)_5H_2O]^{2+} + [Cr(H_2O)_5H_2O^*]^{3+}$ $^{+}$ (d^7). However, complexes of Cr^{3+} (d^3) and low-spin complexes of Co^{3+}(d^6) are kinetically inert. For the exchange reaction (O* represents ^{18}O)

it was found that the rate law is $\text{Rate} = k[Co(NH_3)_5H_2O^{*3+}][Cr(H_2O)_6{}^{2+}]$

It was also found that the H^2O^* is quantitatively transferred to the coordination sphere of Cr^{3+}. Thus, the indication is that the electron is transferred from Cr^{2+} to Co^{3+}, but the H_2O^* is transferred from Co^{3+} to Cr^{2+} as reduction occurs. It appears that the electron transfer occurs through a bridged transition state that may have the structure



$$(NH_3)_5Co^{3+}\cdots \overset{\displaystyle H}{\underset{\displaystyle H}{O}} \cdots Cr(H_2O)_5^{2+}$$

The H_2O forming the bridge then ends up in the coordination sphere of the kinetically inert Cr^{3+} ion.

A large number of reactions similar to that above have been studied in detail. One such reaction is

$$[Co(NH_3)_5X]^{2+} + [Cr(H_2O)_6]^{2+} + 5\ H^+ + 5\ H_2O \rightarrow [Co(H_2O_6]^{2+} + [Cr(H_2O)_5X]^{2+} + 5\ NH_4^+$$

$[Co(H_2O)_6]^{2+}$ because the high-spin complexes of $Co^{2+}(d^7)$ are labile and undergo rapid exchange with the solvent, which is present in great excess.

In these cases, it is found that X is transferred quantitatively from the Co^{3+} complex to the Cr^{2+} complex as electron transfer is achieved. Therefore, it is likely that electron transfer occurs through abridging ligand that is simultaneously part of the coordination sphere of each metal ion and that the bridging group remains as part of the coordination sphere of the inert complex produced. The electron is thus “ conducted ” through that ligand. Rates of electron transfer are found to depend on the nature of X, and the rate varies in the order

$$I^- > Br^- > Cl^- > F^-$$

However, for other reactions an opposite trend is observed. There are undoubtedly several factors involved, which include F^- forming the strongest bridge but I^- being the best “ conductor ” for the electron being transferred because it is much easier to distort the electron cloud of I^- (it is much more polarizable and has a lower electron affinity). Therefore, in different reactions these effects may take on different weights, leading to variations in the rates of electron transfer that do not follow a particular order with respect the identity of the anion.

2.13 Summary of the unit

Octahedral Substitution Reactions are the most extensively studied reactions of coordination compounds. These reactions can be studied by measuring rates of water exchange in aquo metal ions. The mechanisms of substitution reactions follow either dissociative or associative activation. In most substitution pathways bond formation with incoming lignad (Y) and bond reaking with outgoing ligand (X) is concurrent. In the I (interchange) mechanism, no intermediate phase but various transition states. Difference between A and I mechanism is life time of intermediate state if it is long enough, and can be detected. Dissociative interchange (I_d) bond breaking dominates bond forming associative interchange (I_a) bond formation dominates over bond breaking. In associative (A) and Ia the reaction rate shows a dependence on the entering group (Y); in dissociative (D) and Id very small dependence on entering group. In general it is difficult to distinguish between A and I_a and D and I_d

.2.14 Key words

Ligand Substitution reaction; Metal substitution reaction; S_N^1 or dissociation mechanism; S_N^2 or Association or displacement mechanism; Electron transfer reaction; Inner sphere and outer sphere mechanism

2.15 References for further study

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2.16 questions for self understanding

1) The crucial point about the stereochemical course of a dissociative substitution reaction in an octahedral complex is that the intermediate may be trigonal bipyramidal or square pyramidal and that the two readily interconvert if the intermediate is sufficiently long lived.

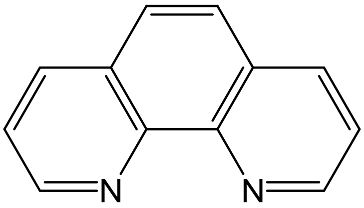
(a) Use a series of simple drawings to illustrate this interconversion.

(b) Explain the following observations concerning the stereochemistry of the products of hydrolysis reactions at octahedral complexes of the type $[Co(en)_2AX]^+$ where A is an inert, π-donor ligand and X is the leaving group.

(i) In complexes where X is cis to A, the product is 100% cis-$[Co(en)_2A(OH_2)]^{2+}$.

(ii) In complexes where X is trans to A, a mixture of cis and trans complexes may result, and the percentage cis increases with the π donor ability of A.

2) When Δ-tris(phen)iron(II) is placed in solution, it slowly racemizes, with a rate constant kr = $6.7 \times 10^{-4}\ s^{-1}$. The rate constant for dissociation of the phenligand is kd = $0.7 \times 10^{-4}\ s^{-1}$. What can be deduced about the mechanism?



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3) When trans-[$Co(en)_2Cl_2]^+$ (en = ethylenediamine) undergoes a ligand substitution reaction, the rate is virtually insensitive to the nature of the entering group. The product is close to 100% trans with very little evidence of the cis product.

(a) Use these observations to make deductions about the mechanism of the reaction. Suggest what experiment(s) you would conduct in order to gather further proof for the proposed mechanism.

(b) Suppose you now decided to study the equivalent reactions of Λ-cis-[$Co(en)_2Cl_2]^+$. Suggest (with reasons) what you would expect the product(s) to be.

4) Discuss the transition state or cctivated complex in substitution reaction of coordination compounds.

5) Write a note on

a) Substrate
b) Attacking reagents
c) Electrophilic reagents
d) Nuleophilic reagents

6) With example explain the nucleophilic or ligand lubstitution (S_N) leactions

7) Discuss the mechanism of nuclephilic (Ligand) Substitution Reaction (S_N Reactions) in Octahedral Complexes

8) Deduce the relation between intimate and stoichiometric reaction mechanisms

9) Explain the S_N^1 or dissociation mechanism in octahedral complexes

10) Discuss the energy profile involved in S_N^1 or dissociation mechanism of octahedral complexes

11) Explain S_N^2 or association or displacement mechanism in octahedral complexes

12) Discuss the energy profile involved in S_N^2 or association displacement mechanism of octahedral complexes

13) Rite the difference between S_N^1 Vs S_N^2 Mechanism in octahedral complexes

14) Explain the factors affecting rates of substitution reaction in octahedral complexes

15) Discuss the stereochemical consequences of substitution reactions octahedral complexes

16) Explain the Labile and Inert complexes according to lignad substitution reaction

17) What is Electron transfer reaction? Give examples

18) With example discuss the inner sphere and outer sphere mechanisms.

UNIT-3

Structure

3.1 Objectives of the unit
3.2 Introduction
3.3 Aquation (Acid Hydrolysis) Reaction of Six- co ordinate Co(III) ammine Complexes
3.4 Hydrolysis Reactions
3.5 Base Hydrolysis Reactions of Six-coordinated Co(II) Ammine Complexes
3.6 S_N^2 Displacement Mechanism.
3.7 S_N^1 Dissociation Mechanism
3.8 Evidence in favour of S_N^1 CB mechanism
3.9 Anation Reaction
3.10 Substitution Reaction without Breaking Metal-Ligand Bond
3.11 Mechanism
3.12 Summary of the unit
3.13 Key words
13.14 references for further studies
3.15 questions for self understanding

3.0 Objectives of the unit

After studying this unit you are able to

- Explain the Hydrolysis Reactions
- Write the mechanism for Base Hydrolysis Reactions of Six-coordinated Co(II) Ammine Complexes
- Draw the mechanism for S_N^2 Displacement Mechanism.
- Write the mechanism for S_N^1 Dissociation Mechanism
- List the Evidence in favour of S_N^1 CB mechanism
- Explain the Anation Reaction
- Recognize the Substitution Reaction without Breaking Metal-Ligand Bond

3.1 Introduction

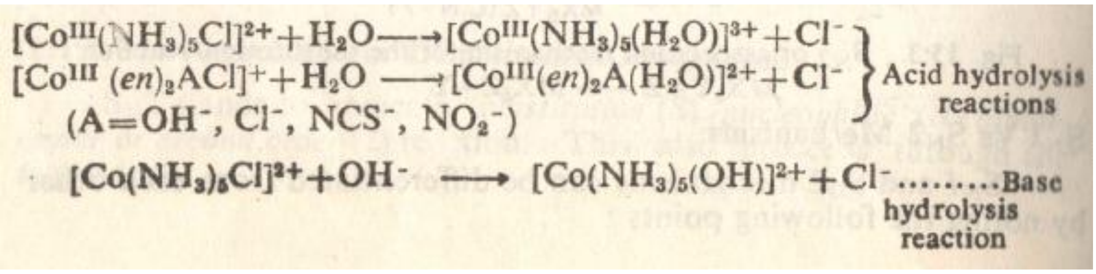
As in many areas of chemistry, there are reactions of coordination compounds that are not what they appear. For example, the reaction $[Co(en)_2F_2]^+ + H^+ \rightleftharpoons [Co(en)_2F(HF)]^{2+}$ appears to be a substitution reaction in which H_2O replaces F^- . However, this reaction has a rate that isntrongly pH dependent, suggesting that the reaction does not follow the usual pattern for complexes of Co^{3+}. Most substitution reactions of complexes of Co^{3+} are independent of the nature of the entering ligand, which indicates that they are formally S_N1 processes. The fact that H^+ is involved suggests that the reaction does not proceed by a dissociative pathway. Instead, the reaction is believed to proceed as follows

$$[Co(en)_2F(HF)]^{2+} + H_2O \rightarrow [Co(en)_2FH_2O]^{2+} + HF$$

The concentration of the conjugate acid is the rate-determining factor because it is the dissociation of that species that leads to the formation of the product. Acid catalysis is observed most often in reactions of complexes containing ligands that are basic (so they can accept protons) or ligands that can form hydrogen bonds. Some complexes of this type include $[Co(NH_3)_5CO_3]^+$, $[Fe(CN)_6]^{4-}$, and $[Co(NH_3)_5ONO]^{2+}$. Other complexes that are susceptible to acid-catalyzed reactions are those that contain coordinated basic ligands that can be dislodged by their bonding to H^+ instead of to the metal ion.

3.2 Hydrolysis Reactions

These are substitution reactions in which a ligand is replaced by a water molecules or by OH^- groups. The reactions in which an aquo complex is formed as a result of the replacement of a ligand by H_2O molecules are called acid hydrolysis or aquation reactions while those in which a hydroxo complex is formed by the replacement of OH^- group called base hydrolysis reactions. Acid hydrolysis reactions occur in neutral and acid solutions (pH <3) while base hydrolysis reactions occur inj acid solution (pH >10). For intermediate pH range the reaction is referred to just ad hydrolysis reactions. Example of these reactions are given below.



$$\left.\begin{array}{l}[Co^{III}(NH_3)_5Cl]^{2+} + H_2O \longrightarrow [Co^{III}(NH_3)_5(H_2O)]^{3+} + Cl^- \\ [Co^{III}(en)_2ACl]^{+} + H_2O \longrightarrow [Co^{III}(en)_2A(H_2O)]^{2+} + Cl^- \\ \quad (A = OH^-, Cl^-, NCS^-, NO_2^-)\end{array}\right\} \text{Acid hydrolysis reactions}$$

$$[Co(NH_3)_5Cl]^{2+} + OH^- \longrightarrow [Co(NH_3)_5(OH)]^{2+} + Cl^- \text{.........Base hydrolysis reaction}$$

3.3 Aquation (Acid Hydrolysis) Reaction of Six- co ordinate Co(III) ammine Complexes

Ammine complexes of Co(III) have been most widely studied. Since work on these complexes has been done exclusively in water the reactions kof the complexes with solvent that NH_3 or ammines like ethylene diamine or its derivatives co ordinated to Co(III) are replaced very slowly by H_2O molecules and hence in acid hydrolysis only the replacement of ligands than amines is usually considered.

The rates of hydrolysis of the reactions of the type

$$[Co(NH_3)_5X]^{2+} + H_2O \rightarrow [Co(NH_3)_6(H_2O)]^{3+} + X^-$$

Have been studied and found to be first order in the complex. Since in aqueous solution the concentration of water is always constant (about equal 55.5 M) the effect of changes in water concentration on the rate of the reaction cannot be determined. Rate laws given below are experimentally indistinguishable in aqueous solution since

$$K = K'[H_2O] = K'[55.5]$$

$$Rate = K'[Co(NH_3)_5X^{2+}]$$

$$K'[Co(NH_3)_5X^{2+}][H_2O]$$

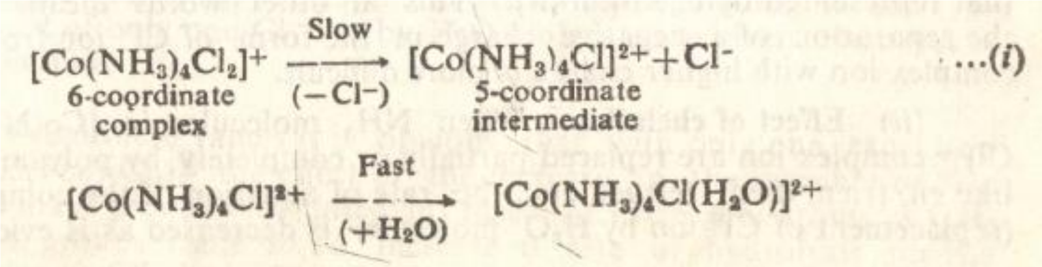
$$K'[Co(NH_3)_5X^{2+}][55.5]$$

Thus the rate law does not tell us wheather H_2O is involved in the rate- determining step.

The rate law given above does not indicate whether these reactions proceed by an S_N^2 displacement of X^- by H_2O lor by an S_N^1 dissociation followed by the addition of H_2O. However a study as to how the following factors affect the rate constant of these reaction can give us an information about the nature of mechanism by which these reactions proceed.

(i) Effect of change on complex

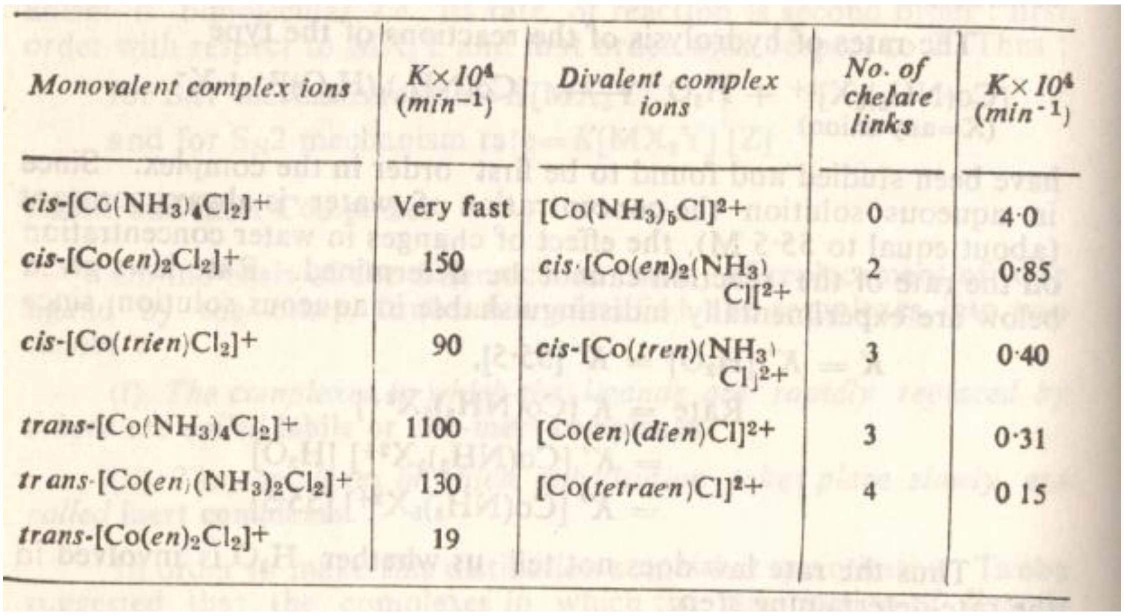
The values of rates of acid hydrolysis of some Co(III) complexes at pH=1 are given in Table . This table clearly shows that the divalent monochloro complexes. Since a decrease in rate is observed as the harge of the complex increases a dissociation S_N^1process seems to be operative and hence the acid hydrolysis (i.e replacement of one Cl ion by H_2O of the monovalent complexes like $[Co(NH_3)_4Cl_2]^+$ occurs in two steps.



$$\underset{\text{6-coordinate complex}}{[Co(NH_3)_4Cl_2]^+} \xrightarrow[(-Cl^-)]{\text{Slow}} \underset{\text{5-coordinate intermediate}}{[Co(NH_3)_4Cl]^{2+}} + Cl^- \quad \ldots(i)$$

$$[Co(NH_3)_4Cl]^{2+} \xrightarrow[(+H_2O)]{\text{Fast}} [Co(NH_3)_4Cl(H_2O)]^{2+}$$

The rates of hydrolysis of some Co(III) complexes at pH = 1 correspond to the replacement of only one Cl in H2O molecule are given in below table



Monovalent complex ions	*K×10⁴ (min⁻¹)*	*Divalent complex ions*	*No. of chelate links*	*K×10⁴ (min⁻¹)*
cis-$[Co(NH_3)_4Cl_2]^+$	Very fast	$[Co(NH_3)_5Cl]^{2+}$	0	4·0
cis-$[Co(en)_2Cl_2]^+$	150	*cis*-$[Co(en)_2(NH_3)Cl]^{2+}$	2	0·85
cis-$[Co(trien)Cl_2]^+$	90	*cis*-$[Co(tren)(NH_3)Cl]^{2+}$	3	0·40
trans-$[Co(NH_3)_4Cl_2]^+$	1100	$[Co(en)(dien)Cl]^{2+}$	3	0·31
trans-$[Co(en)(NH_3)_2Cl_2]^+$	130	$[Co(tetraen)Cl]^{2+}$	4	0·15
trans-$[Co(en)_2Cl_2]^+$	19			

The symbols used represent the following molecules:

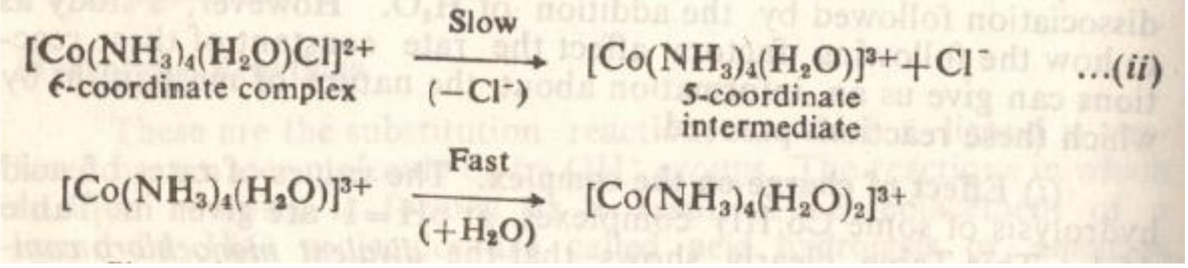
En = ethylene diamine NH_2-CH_2-CH_2-NH_2

Trien = triethylene tetramine .H_2N-$(CH_2)_2$-NH-$(CH_2)_2$-NH-$(CH_2)_2$-NH_3

Dien = diethylene triamine H_2N-$(CH_2)_2$-NH-$(CH_2)_2$-NH_2

Tetraen = tetraethylene pentamine NH_2-$(CH_2)_2$-NH$(CH_2)_2$-NH$(CH_2)_2$-NH_2

The acid hydrolysis of divalent complexes like $[Co(NH_3)_4(H_2O)Cl]^{2+}$ also take place in two steps



Since the energy of charging a sphere varies as $q^2$the change in electrostatic energy on going from 6 to 5 co ordinated complex is $1^2 – 2^2 =3$ [for equation (i)] and 2^2-3^2 =5 [for equation (ii)]. Thus more rapidly than that of $[Co(NH_3)_4(H_2O)Cl]^{2+}$ i.e the acid hydrolysis represented by equation (i) would proceed more rapidly than that represented by equation (ii). This in other words means that the separation of a negative charge in the form of Cl^- ion form a complex ion with higher charge is more difficult.

(ii) Effect of chelation

When NH_3 molecules in $[Co(NH_3)_5Cl]^{2+}$ complex ion are replaced partially or completely by polyamines like en, trien,dien, tetraen etc, the rate of aquation of the complex (replacement of Cl^- ion by H_2O molecules) is decreased as is evident from table . the rates of aquation of the divalent complex ions given in this table show that as the number of –CH_2-CH_2- or –$(CH_2)_2$- chelate links increases the rate values decrease. The effect of chelation should be to shorten the Co-N bond distance and to transfer more charge to the cobalt in chelated complex compared to those containing monodentate ligands. Thus this effect should enchance the rate of aquat*on.* Actually as is evident from table the rates are decreased. Obviously some other factor is responsible for the decrease. A more reliable explanation is that the chelated complex in both the ground state and in the transition state is solvated. Again it is known that the replacement of NH_3 molecules by polymines increases the size of the complex i.e the chelated complex has larger size. The larger size of the ion, less its solvation energy will be and hence less easily it will be formed. Thus the stability of the transition state in which the Cl^- ion id only partially lost and in which the salvation is less efficient will be reduced. The rate of aquation is slow down by chelation because of reduced stability of the transition state due to less efficient salvation. This salvation theory, if true does not distinguish between S_N^1 and S_N^2 mechanisms. All that may be concluded is that ionic bond-breaking in the transition state is important.

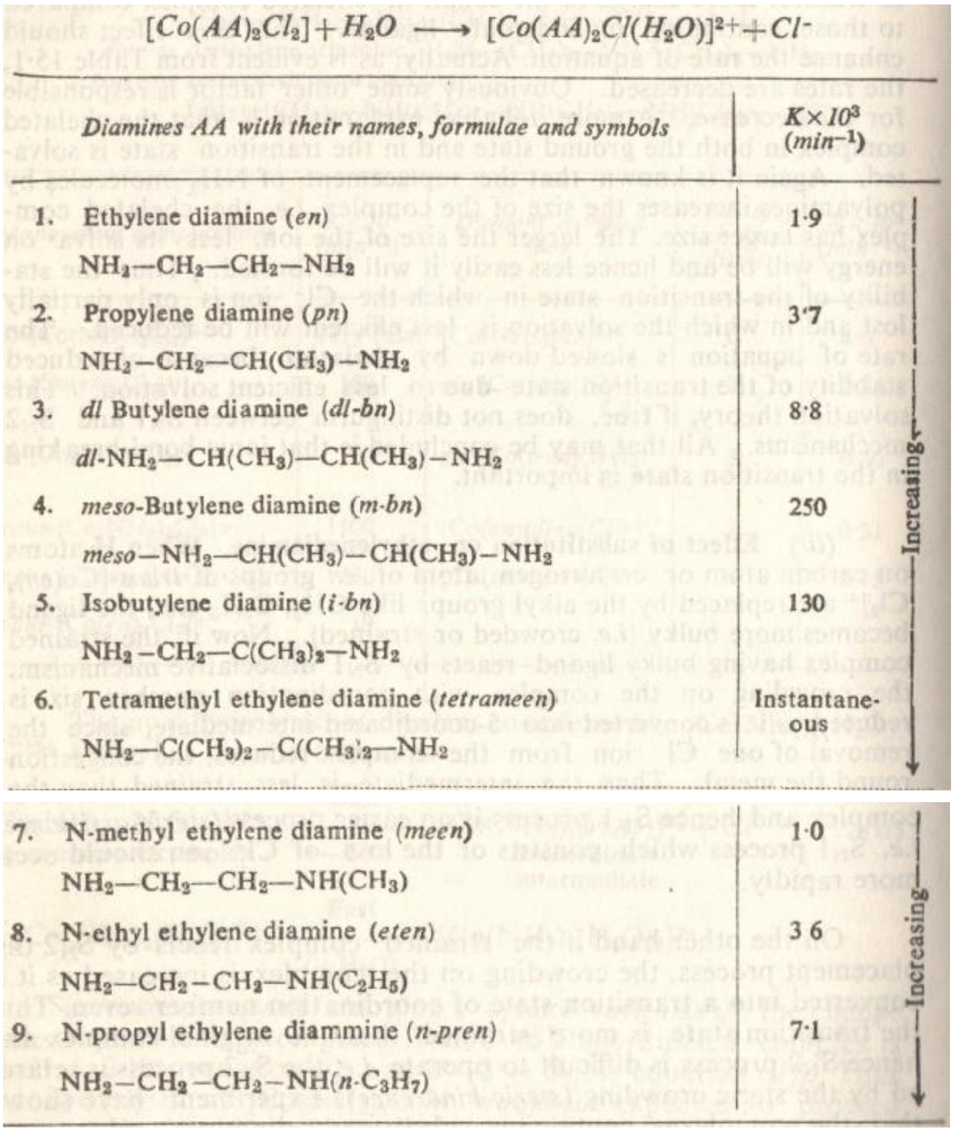
(iii) Effect of substitution on ethylenediamine

When H atoms on carbon atom or on nitrogen atom of en groups of trans-$[Co(en)_2Cl_2]^+$ are replaced by the alkyl groups like CH_3, C_2H_5 etc. The ligand becomes more bulky (i.e crowded or strained). Now if the strained complex having bulky ligand reacts by S_N^1 dissociative mechanism the crowding on the complex with co ordination number six is reduced as it is converted into 5- coordination intermediate since the removal of one Cl^- ion from the complex reduced the congestion round the metal. Thus the intermediate is less strained than the complex and hence S_N^1 process which consists of the loss of Cl^- ion should occur more rapidly.

On the other hand if the strained complex reacts by S_N^2 displacement process the crowding on the complex are increases as it is converted into a transition state of coordination number seven. Thus the tranisition state kis more strained than the original complex and hence S_N^2 process is difficult to operate i.e the S_N^2 process is retarded by the steric crowding experiments have shown that the complexes containing substituted diamines react more rapidly than those having en. In table the rates of hydrolysis of trans- $[Co(AA)_2 Cl_2]^+$ at 25^0 C and pH=1 corresponding to the replacement of only one Cl^- kion by H_2O molecule are given. Here AA is the diamine.

From these values it is obious that with only one exception viz $[Co(i\text{-}bn)_2Cl_2]^+$ the effect of the increase in the number or size of the alkyl groups substituted in place of hydrogen atoms of CH_2 or NH_2 groups leads to an increase in rate of hydrolysis for the loss of one Cl^- ion. The increase in rates observed when more bulky ligands are used is good evidence in favour of S_N^1 mechanism.

Rates of hydrolysis of trans-$[Co(AA)_2Cl_2]^{2+}$ at 250C and pH = 1 in aqueous solution is given in below table



$$[Co(AA)_2Cl_2] + H_2O \longrightarrow [Co(AA)_2Cl(H_2O)]^{2+} + Cl^-$$

Diamines AA with their names, formulae and symbols	$K \times 10^3$ (min^{-1})	
1. Ethylene diamine (*en*) $NH_2—CH_2—CH_2—NH_2$	1·9	Increasing ↓
2. Propylene diamine (*pn*) $NH_2—CH_2—CH(CH_3)—NH_2$	3·7	
3. *dl* Butylene diamine (*dl-bn*) *dl*-$NH_2—CH(CH_3)—CH(CH_3)—NH_2$	8·8	
4. *meso*-Butylene diamine (*m-bn*) *meso*—$NH_2—CH(CH_3)—CH(CH_3)—NH_2$	250	
5. Isobutylene diamine (*i-bn*) $NH_2—CH_2—C(CH_3)_2—NH_2$	130	
6. Tetramethyl ethylene diamine (*tetrameen*) $NH_2—C(CH_3)_2—C(CH_3)_2—NH_2$	Instantaneous	
7. N-methyl ethylene diamine (*meen*) $NH_2—CH_2—CH_2—NH(CH_3)$	1·0	Increasing ↓
8. N-ethyl ethylene diamine (*eten*) $NH_2—CH_2—CH_2—NH(C_2H_5)$	3 6	
9. N-propyl ethylene diammine (*n-pren*) $NH_2—CH_2—CH_2—NH(n\text{-}C_3H_7)$	7·1	

(iv) Effect of leaving group

The rate of aquation of $[Co(NH_3)_5\ X]^{2+}$ corresponding to the replacement of X^- with H_2O molecule depends kon the nature of X^- because the bond- breaking step is important in rate determing step. It has been observed experimentally that the reactivity of X^- groups decrease in the order:

$$HCO_3^- > NO_3^- > I^- > Br^- > Cl^- > SO_4^{2-} > F^- > CH_3COO^- > SCN^- > NO_2^-$$

This order corresponds to the order of the decreasing thermodynamic stability of the complexes formed with these groups. The results of various investigations are in favour of S_N^1 mechanism. Bond-breaking is importent in the activated complex.

3.4 Base Hydrolysis Reactions of Six-coordinated Co(II) Ammine Complexes

Most the kinetic work has been done on six-coordinated Co(III) amine complexes. For ammine complexes of Co(III) containing N-H bonds it has been seen that the rate of base hydrolysis is often as much 10^6 times faster than the corresponding rate of acid hydrolysis. Here we shall discuss the mechanism of the base hydrolysis reaction of $[Co(NH_3)_5Cl]^{2+}$ only. The base hydrolysis reaction represented by

$$[Co(NH_3)_5Cl]^{2+} + OH^- \rightarrow [Co(NH_3)_5(OH)]^{2+} + Cl^-$$

Can proceed by any of the following two mechanism :

3.5 S_N^2 Displacement Mechanism.

According to this mechanism the reaction proceeds as

$$[Co(NH_3)_5Cl]^{2+} \xrightarrow[Rate-\det er \min ing\ step]{Slow\,(+OH^-)} [Co(NH_3)_5(OH)Cl^+] \xrightarrow{Fast\,(-Cl-} [Co(NH_3)_5(OH)]^{2+} + Cl^-$$

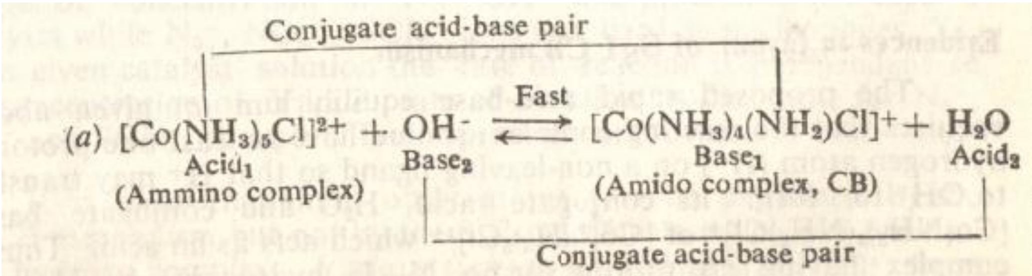
The slow step which is a rate determing step is a second order reaction first order with respect to the complex and first order with respect to the base thus:

Rate of reaction= k [complex][base]

$$=K[Co(NH_3)_5Cl^{2+}][OH^-]$$

3.6 S_N^1 Dissociation Mechanism

This has been suggested by Garrick (1973). Before this mechanism could be applied the complex which acts as a Bronsted acid is converted into its conjugate base (Abbreviated as CB) $[Co(NH_3)_4(NH_2)Cl]^+$ which is obtained by removing a proton (H^+) from the amino group (NH_3) present in the complex. Cb is an amido complex since it contains amido group $:\ddot{N}H_2^-.OH^-$ which is a base is converted into its conjugated acid H_2O



Obviously if K= equilibrium constant for acid-base equilibrium (a) then

$$K = \frac{[CB][H_2O]}{[Co(NH_3)_6Cl^{2+}][OH^-]}$$

$$or \qquad\qquad\qquad \text{--------------- (i)}$$

$$[CB] = \frac{K[Co(NH_3)_5Cl^{2+}][OH^-]}{[H_2O]}$$

CB obtained as above is more labile than the original complex $[Co(NH_3)_5Cl]^{2+}$ and hence undergoes S_N^1 dissociation mechanism by a slow step to lose Cl^- ion gives a 5- co ordinate intermediate.

$$\text{(b)}\ [Co(NH_3)_4(NH_2)Cl]^+ \xrightarrow{Slow(-Cl^-)} [Co(NH_3)_4(NH_2)]^{2+} + Cl^-$$

This is the rate determining and unimolecular step thus

$$\begin{aligned} Rate &= k_1[CB] \\ &= \frac{k_1K[Co(NH_3)_5Cl^{2+}][OH^-]}{[H_2O]} \text{ ---------------- (ii)} \\ &= K_B[complex][Base] \end{aligned}$$

Where K_B= rate constant used for the dissociation of the conjugate base as in (b) step and is equal to $k_1K/[H_2O]$

The intermediate formed as above reacts with the abundant solvent molecules (i.e H_2O molecule) to give the hydroxo complex $[Co(NH_3)_5(OH)]^{2+}$ This is relatively fast step.

$$\text{(c)}\ [Co(NH_3)_4(NH_2)]^{2+} \xrightarrow{Fast\,(+H_2O)} [Co(NH_3)_5(OH)]^{2+}$$

Although base hydrolysis involves an S_N^1 dissociation mechanism yet it is consistant with second-order, first order with respect to the complex and first order with respect to the base (from equation ii)

Since the $S_N{}^1$dissociation step (b) which is the rate determing step uses the conjugate base of the intial complex the symbol $S_N{}^1$ CB (substitution nucleophile, conjugate base) has used by Garrick in place of $S_N{}^1$ symbol.

3.7Evidence in favour of $S_N{}^1$ CB mechanism

The proposed rapid acid-base equilibrium (a) given above requires that the reacting complex should have at least one protonic hydrogen atom (H^+) on a non- leaving ligand so that H^+ may transfer to OH^- to form its conjugate acid, H_2O and conjugate base $[Co(NH_3)_4(NH_2)Cl]^+$ of $[Co(NH_3)_5Cl]^{2+}$ which acts as an acid. Thus a complex having no proton (or no N-H hydrogen) should react with OH^- much more smlowly and the rate of reaction would be independant of the concebtration of OH^- $[OH^-]$. In fact it has been observed that complexes like $[Co(CN)_5Br]$ and trans- $[Co(py)_4Cl_2]^+$ which donot have N-H hydrogen undergo hydrolysis much more slowly in basic solution at a rate which is independant of $[OH^-]$ over a wide range. Thus in the absence of an acidic proton on the ligands an $S_N{}^1$ CB mechanism is not lpossible. The failure of such complexes to undergo rapid base hydrolysis supports the N^1 CB mechanism and the fact that the acid base plroperties of the complexes are more importent to the rate reaction than the nucleophilic properties of OH.

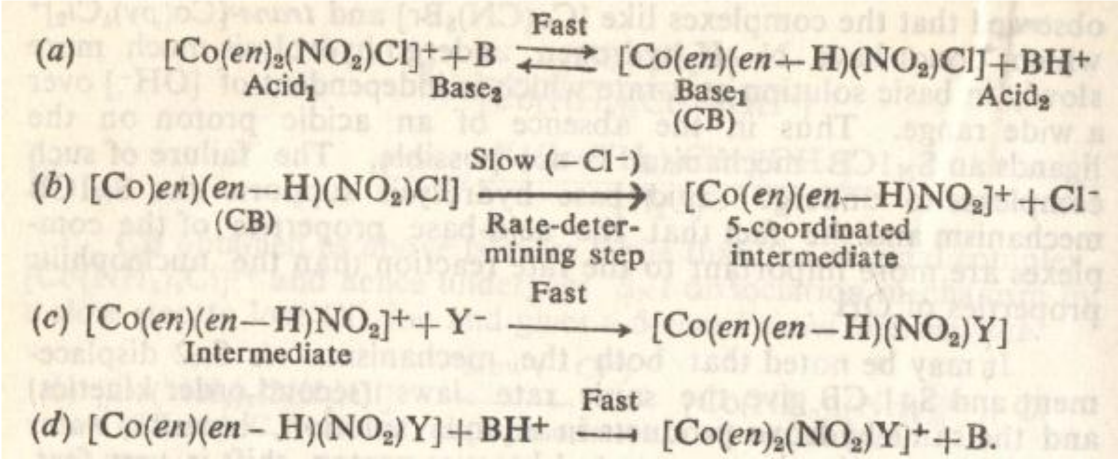
It may be noted that both the mechanism viz $S_N{}^2$ displacement and $S_N{}^1$ CB give the same rate laws (second-order kinetics) and the same hydroxo products in aqueous solution because water is a good co ordinating agent and because proton shifts is very fast. However in a non-hydroxylic solvent (i.e non protonic solvent) different products are predicted to be formed for the mechanisms under the condition that an excess of some nucleophile reagent other than OH^- ion or H_2O (eg NO_2, SCN^-) is present e.g the results obtained for the reaction of the type:

$$[Co(en)_2NO_2Cl]^+ + Y' \xrightarrow{(CH_3)_2SO} [Co(en)_2NO_2Y]^+ + Cl^-$$

$[Y^- = N_3^-, NO_3^- \text{ or } SCN^-]$

Occurring in dimethyl sulphoxide $(CH_3)_2SO$ (which is a non hydroxylic solvent) are readily explained by $S_N{}^1$ CB mechanism but cannot be explained by $S_N{}^2$ mechanism. The fact that these results can be explained by $S_N{}^1$ Cb mechanism is a great evidence in favour of $S_N{}^1$CB mechanism. Above reaction in $(CH_3)_2SO$ is slow (half-life in hours) but when trace amount of OH^- or piperdine (which act as catalysts) are added the reaction is catalysed and thus becomes fast (half-life reduced to minutes) although the same products viz $[Co(en)_2NO_2Y]^+$ is formed in both the cases. Furthermore $[Co(en)_2NO_2Cl]^+$ reacts equally rapidly with equivalent amount of OH^- in the absence of Y^- to form $[Co(en)_2(NO)_2(OH)^-]^+$ it has been shown that $[Co(en)_2NO_2)(OH)]^+$ reacts with Y^- very slowly and hence a rapid S_N^2mechanism with his as an intermediate followed by rapid reaction with Y^- is ruled out. Insted an active 5-coordinated intermediate (S_N^1 mechanism0, $[Co(en)\ (en\text{-}H)NO_2]^+$ is formed in a rate dereminig step by the loss of Cl^- ion form the conjugate base $[CO(en)(en\text{-}H)\ (NO_2)Y]^+$ depends only on the concentration of the base OH^- not on the nature or concentration of Y^-, OH^- and piperidine are used as catalysts while N_3^- SCN^- ions are used as nucleophile Y^- for given catalyst solution the rate of reaction depends of the concentration of Y^- i.e rate of reaction is the same for N_3^- and SCN^- through different procucts are formed in each case.

It is clear that these observation can be explained by the S_N^1CB mechanism but not only the S_N^2 mechanism which can be produce only hydroxo complex. Various steps to get $[Co(en)_2(NO_2)Y]^+$ form $[Co(en)_2(NO_2)Cl^+$ based kon S_N^1CB mechanism are:



$$(a)\quad \underset{\text{Acid}_1}{[Co(en)_2(NO_2)Cl]^+} + \underset{\text{Base}_2}{B} \overset{\text{Fast}}{\rightleftharpoons} \underset{\substack{\text{Base}_1\\ \text{(CB)}}}{[Co(en)(en-H)(NO_2)Cl]} + \underset{\text{Acid}_2}{BH^+}$$

$$(b)\quad \underset{\text{(CB)}}{[Co)en)(en-H)(NO_2)Cl]} \xrightarrow[\substack{\text{Rate-deter-}\\ \text{mining step}}]{\text{Slow }(-Cl^-)} \underset{\substack{\text{5-coordinated}\\ \text{intermediate}}}{[Co(en)(en-H)NO_2]^+} + Cl^-$$

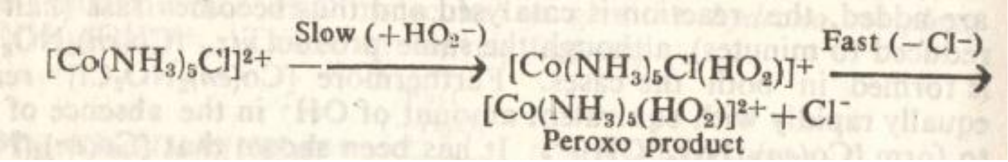
$$(c)\quad \underset{\text{Intermediate}}{[Co(en)(en-H)NO_2]^+ + Y^-} \xrightarrow{\text{Fast}} [Co(en)(en-H)(NO_2)Y]$$

$$(d)\quad [Co(en)(en-H)(NO_2)Y] + BH^+ \xrightarrow{\text{Fast}} [Co(en)_2(NO_2)Y]^+ + B.$$

Further interesting evidence in favour of S_N^1CB mechanism comes from thestudy of the reaction of $[Co(NH_3)_5Cl]^{2+}$ and OH^- in aqueous solution at 25^0C in presence of H_2O when H_2O_2 is added to the reaction mixture of $[Co(NH_3)_5Cl]^{2+}$ and OH^- the following change take place. Since HO_2^-ion in H_2O_2 is a weaker base but a better nucleophile towards metal ions than OH^- the reaction of H_2O_2 with OH^- reduces the concentration of OH^- and increases that of H_2O thus the reaction between OH^- and H_2O thus the reaction between OH^- and H_2O_2 occurs.

$$OH^- + H_2O_2 \rightarrow H_2O + HO_2^-$$

The tendency of O_2H^-ion to act better nucleophile than OH^- should therefoe increase the rate of base hydrolysis reaction buy it comnpared to OH_if it attacks the metal by S_N^2 mechanism to form the peroxo product as shown below



On the other hand if thereaction occurs by an S_N^1CB mechanism (i.e if the function of $OH^-$is to form the conjugate base by removing a proton) the addition of H_2O_2 to the reaction mixture should reduce the rate of base hydrolysis reaction compared to OH^- because of the reduction in the concentration of OH^- ions as is evident from the equilibrium represented by equation(i) to the concentration of $OH^-[OH^-]$. Experimentally it has been seen that when 0.018M H_2O_2 is added to a reaction mixture consisting of 0.0029 M $[Co(NH_3)_5Cl]^{2+}$ and 0.0029 M OH^- in aqueous solution at 25^0C there is decrease in the value of rate constant by a factor of 3.6 i.e if K_A= rate constant in the absence of H_2O_2 and K_p=rate constant in the presence of H_2O_2 then K_A/K_p=3.6 this experimental data supports S_N^1 CB mechanism.

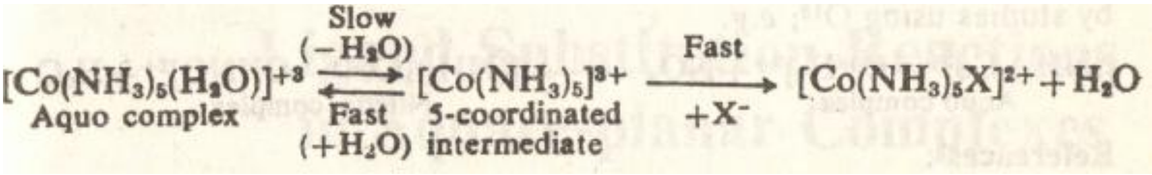
3.8 Anation Reaction

These are the reaction in which an aquo ligand (i.e H_2O molecule) from an aqquo complex is replaced from the co ordination shell by some anion

$[Co(NH_3)_5(H_2O)]^{3+} + X^- \rightarrow [Co(NH_3)_5X]^{2+} + H_2O$

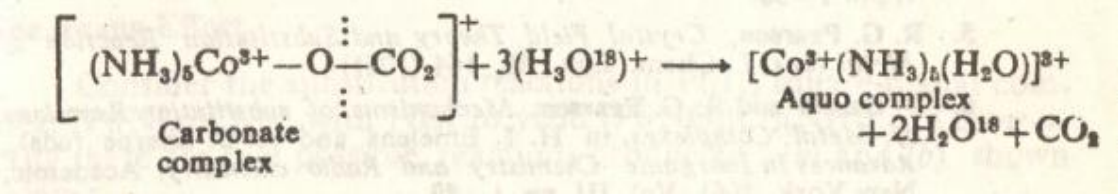
Thus we find that an anion reaction is the reverse of acid hydrolysis reaction

Kinetic studies of these reactions in aqueous solution show that these are bimolecular reactions with a rate which depends on the concentration of the complex and X however this information alone is not sufficient to prove that these reactions are bimolecular. The some second order kinetics would be observed for a unimolecular process such as:



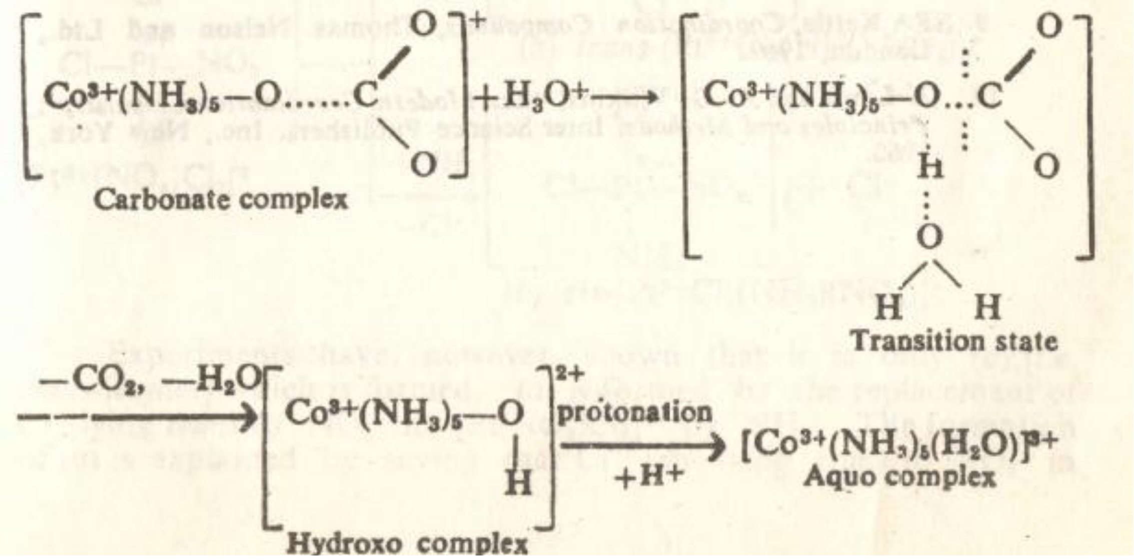
3.9 Substitution Reaction without Breaking Metal-Ligand Bond

There are reactions in which ligand exchange takes place with out breaking the metal ligand bond. One well known reaction is the preparation of an aquo complex $[Co^{3+}(NH_3)_5(H_2O)]^{3+}$ from its correspondiong carbonato complex $[Co^{3+} (NH_3)_5 CO_3]^+$ with the production kof CO_2. When this reaction is carried out in presence of $(H_3O^{18})^+$ none of O^{18} is found in the resulting aquo complex and CO_2. Hence CO_2 is produced by the cleavage of C-O bond which keeps Co-O bond intact during the aquation reaction



3.10 Mechanism

The most likely path for this reaction is believed to involve proton attack on the oxygen atom bonded to Co followed by the expulsion of Co_2 and H_2O and then protonation of the hydroxo complex.



Thus this is a decarboxylation reaction rather than an acid hydrolysis reaction.

Another interesting reaction which takes place without the cleavage kof metal ligand bond is the formation of a nitrio complex $[Co^{3+} (NH_3)_5ONO]^{2+}$ from its corresponding aquo complex $[Co^{3+} (NH_3)_5(H_2O)]^{3+}$

$$\underset{Aquo\,Complex}{[Co^{3+}(NH_3)_5(H_2O)]^{3+}} + NO_2^- \rightarrow \underset{Nitrito\,complex}{[Co^{3+}(NH_3)_5ONO]^{2+}} + H_2O$$

The reaction is quit rapid which in itself suggests that Co-O bond is not broken. Confirmatery evidence for this view is provided by studies O^{18} e.g

$$\underset{Aquo\,Complex}{[NH_3)_5\,Co^{3+} - O^{18}H_2]^{3+}} + NO_2^- \rightarrow \underset{Nitrito\,complex}{[(NH_3)_5Co^{3+} - O^{18}NO]^{2+}} + H_2O$$

3.11 Summary of the unit

Ligand substitution reactions of coordination compounds have been studied as intensively as any class of inorganic reactions. These are the reactions for which the generalized equation may be written. $MX_n + Y \rightarrow MX_{n-1}Y + X$

M is a metal atom and X and Y are any two ligands. (One of the ligands involved is often also the solvent species.) The general form encompasses both some very fast and some quite slow reactions as well as coordination compounds of both transition and nontransition metals. The bulk of the experimental work, however, is concerned with those complexes of transition metals which are nonlabile. That is, the majority of the effort to date has been devoted to the study of reactions slow enough to be accessible to classical kinetic techniques.

3.12 Key words

Hydrolysis Reactions; Base Hydrolysis Reactions of Six-coordinated Co(II) Ammine Complexes; S_N^2 Displacement Mechanism; S_N^1 Dissociation Mechanism; Evidence in favour of S_N^1 CB mechanism; Anation Reaction; Substitution Reaction without Breaking Metal-Ligand Bond

13.13 references for further studies

1) Reaction Mechanisms of Metal Complexes; R W Hay; *Elsevier*, **2000**.

2) Concepts and models of inorganic chemistry, 3rd ed; Douglas; *John Wiley & Sons*, **2006**.

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6) Inorganic Chemistry; James E. House; *Academic Press*; **2008**.

3.14 questions for self understanding

a) Write a note on Aquation (Acid Hydrolysis) Reaction of Six- co ordinate Co(III) ammine Complexes

2) What are Hydrolysis Reactions? Explain with example

3) Write a note on Base Hydrolysis Reactions of Six-coordinated Co(II) Ammine Complexes

4) Discuss S_N^2 Displacement Mechanism.

5) Discuss S_N^1 Dissociation Mechanism

6) Account for the evidence in favour of S_N^1 CB mechanism

7) What is Anation Reaction? Explain with example

8) Write a note on substitution reaction without breaking metal-ligand bond

9) Write the mechanism for

3.12 Summary of the unit substitution reaction without breaking metal-ligand Bond

UNIT-4

Structure

4.0 Objectives of the unit
4.2 Ligand Substitution Reaction in Square planar Complex
4.3 The Trans-Effect
4.4 Uses of Trans-Effect
4.5 Distinguish between cis- and trans isomers of $[PtA_2X_2]^0$ type complexs.
4.6 Theories of Trans-Effect
4.7 Experimental evidence in favour of polarisation theory
4.8 π- Bonding Theory
4.9 Mechanism of Substitution Reactions
4.10 Factors affecting the rates of substitution reactions in square planar complexes
4.11 Cis-trans isomerisation in planar complexes.
4.12 Summary of the unit
4.13 Key words
14.15 References for further study
4.16 Questions for self understanding

4.0 Objectives of the unit

After studying this unit you are able to

- Explain the ligand substitution reaction in square planar Complex
- Distinguish between cis- and trans isomers of $[PtA_2X_2]^0$ type complexs
- Expalin the the Trans-Effect
- Identify the uses of Trans-Effect
- Predict the structure of product using trans effect
- Point out the experimental evidence in favour of polarisation theory
- Explain the π- Bonding Theory
- List the factors affecting the rates of substitution reactions in square planar complexes

4.1 Introduction

Square planar is the common geometry for the following d^8 metal ions. For square planar both bond-breaking and bond making are important in the reaction mechanism (i.e. an associative mechanism). Entering group can approach from top or bottom since sq. planar is easy to get into. Initial attack by the entering group at a square planar Pt(II) centre is from above or below the plane. Nucleophile Y then coordinates to give a trigonal bipyramidal intermediate species which loses X with retention of stereochemistry

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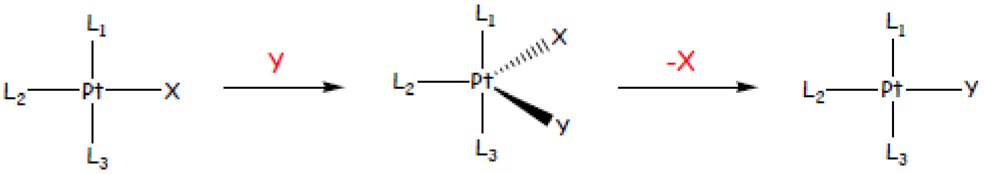


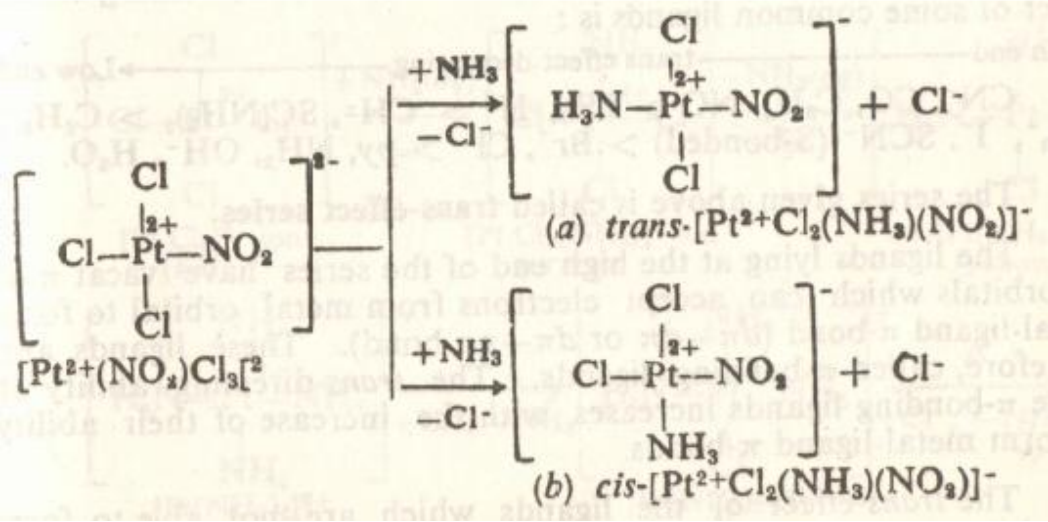
The incoming ligand approaches a vacant axial site of the square planar complex to form a square pyramidal intermediate (or transition state). Intramolecular rearrangement via a trigonal bipyramid generates a different square pyramidal structure with the incoming ligand now in the basal plane. (This motion is closely related to the Berry Pseudorotation mechanism). The reaction is completed by the leaving group departing from an axial site. Note that the stereochemistry of the complex is retained during the substitution process.

4.2 Ligand Substitution Reaction in Square planar Complex

Much of the discussion in this chapter deals with the kinetics and mechanism of substitution reactions of Pt(II) square-planar complexes. It will be seen that these complexes generally proceed by bimolecular displacement (S_N^2) mechanism while octahedral compexes run by dissociative process as we have already seen.

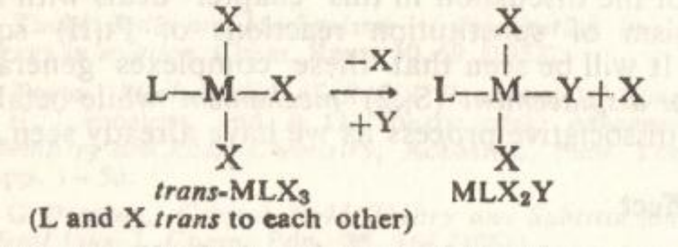
4.3 The Trans-Effect

Consider the substitution reaction in Pt(II) square planar complex $[Pt(NO_2)Cl_3]^{2-}$ with NH_3 to yield $[Pt(NO_2)Cl_2(NH_3)]^-$. Theoretically there are two possible reaction products: (a) and (b) sho



Experiments have however shown that it is only (A) (i.e trans-isomer) which is formed (a) is formed by the replacement of Cl^- lying trans to NO_2^- in $[Pt(NO_2)Cl_3]^{2-}$ by NH_3. The formation of (a) is explained by saying that Cl ion lying trans to NO_2^- in $[Pt(NO_2)Cl_2]^{2-}$ is far more easily replaced by NH_3 than either of the two Cl^- ions lying to NO_2^- ion. The phenomena of such type of replacement is called trans effect. Groups like NO_2^- which direct the entering ligand to occupy the position trans to them are called trans directing groups and the property of these groups due to which the groups lying trans to them are replaced far more readily by the entering ligand is called trans- directing character (or trans directing influence or simply trans-effect).

Chatt et al have proposed that the trans-effect of a group co ordinate to a metal ion is the tendency of that group to direct an incoming group to occupy the position trans to that group. Trans effect is also defined as the effect of a co ordinated group on the rate of the replacement of a group lying trans to it in a metal, complex e.g in the trans form of square-planar complex MLX_3 (L and X are trans to each other), if the ligand X which is trans to L is rapidly replaced by another group say Y to give MLX_2Y, L is said to have large trans effect or trans directing character. Thus L has greater trans effect than X (L>X).



By measuring rates a series of ligand can be put into an order of decreasing trans-effect. Such an order would not necessarily be invaient but might depend on the metal complex and also on the incoming group Y the approximate order of decreasing trans effect of some common ligans is

High end-------------------trans effect decresing------------------Low end

$$CN^-, CO, C_2H_4, NO > PR_3, H^- > CH^-, SC(NH_2)_2 > C_6H_5^-$$
$$NO_2^-, I^-, SCN^- (S-bonded) > Br^-, Cl^- > py, NH_3\, OH^-, H_2O$$

The series given above is called trans-effect series.

The ligand lying at the high end of series have vacat π or π^* orbitals which can accept electrons from metal orbital to form metal-ligand π-bond (dπ-dπ or dπ-pπ bond). These ligand ae therefore called π-bonding ligand. The trans-directing ability to form metal ligand π-bonds.

The trans-effect of the ligands which are not able to form metal-ligand π-bonds increases with the increase of their polarizability e.g

------------polarisabiliy increases→

$Cl^- < Br^- < I^-$

---------------trans-effect increases→

Most of the work on trans-effect has been done square planar Pt(II) complexes.

4.4 Uses of Trans-Effect

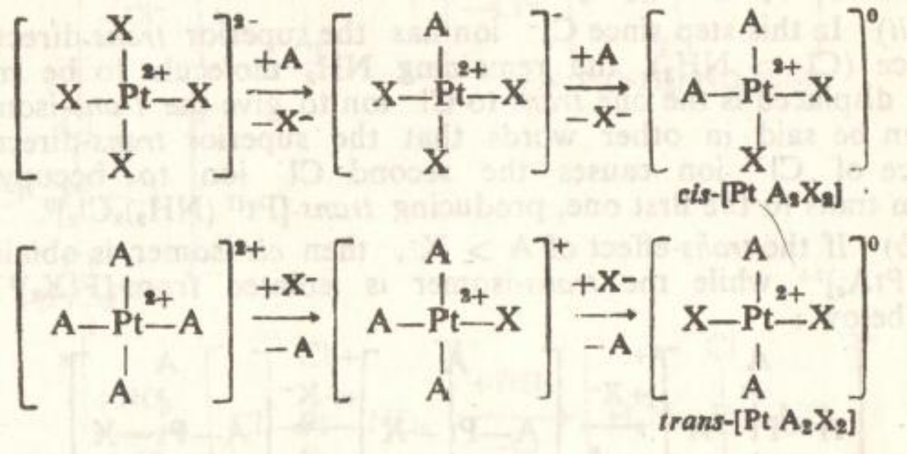
The following are important uses.

(1) Synthesis of Pt(II) Complexes

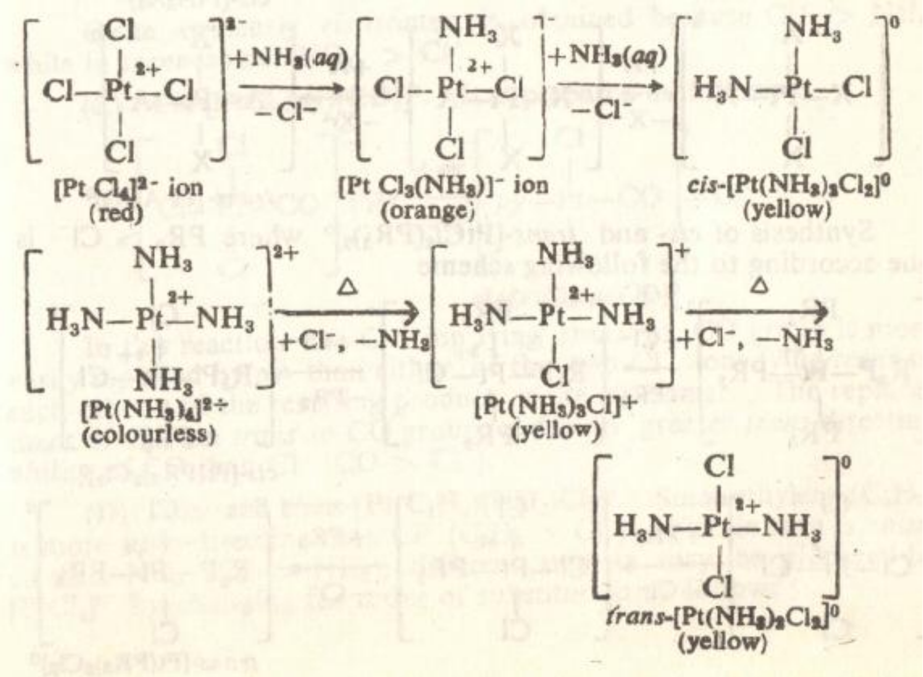
The presentation of the following Pt(II) complexes illustrate the synthesis uses of trans effect.

(A) Synthesis of cis-and trans $[PtA_2X_2]^0$. here A=amine NH_3 PR_3 and X=halide ion, NO_2, SCN^- the synthesis of these isomers is based on the following facts.

(a)If tyhe trans effect of X^- is greater than that of A ($X^->A$), the cis isomer is obtained from $[PtX_4]^2$ while the trans-isomer is isolated from $[PtA_4]^{2+}$ as shown below.



For the synthesis of cis and trans $[Pt(NH_3)_2Cl_2]$ where $Cl^- > NH_3$ the following scheme is applied.



Cis-isomer is obtained by treating $[Pt^{11} Cl_4]^{2+}$ ion with NH_3. The reaction giving the cis-isomer proceeds through the following two steps.

(i) In this step any of the four Cl^- ions is replaced by NH_3 molecule to give $[Pt^{11} (NH_3)Cl_3]^-$ ion

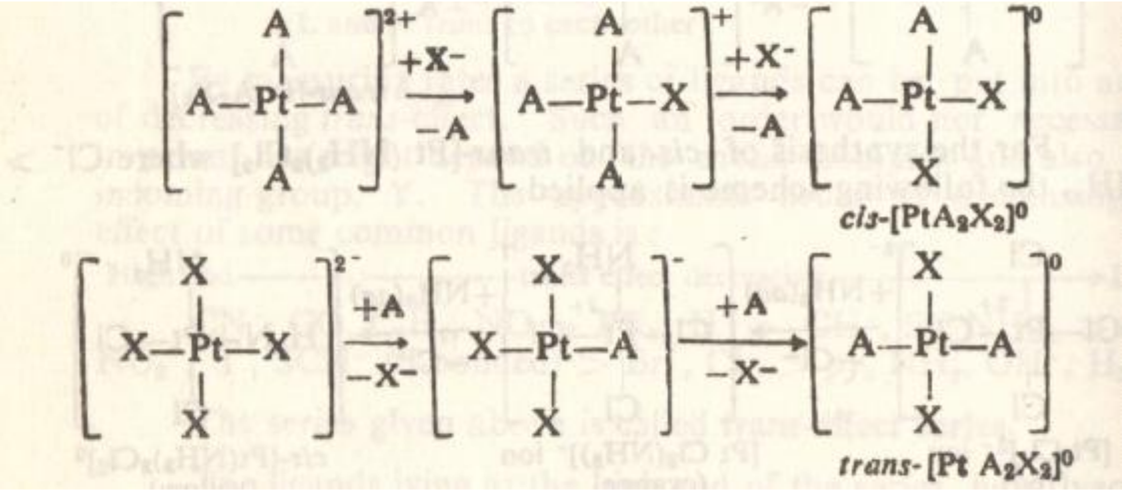
(ii) In this step since Cl ion has a greater trans-directing influence than NH_3 ($Cl^- > NH_3$). Cl^- ion lying trans to another Cl^- in $[Pt\ Cl_3(NH_3)]^-$ is readily replaced by NH_3 than is the Cl^- ion lying trans to NH_3

The trans isomer is obtained by heating $[Pt^{11} (NH_3)_4]^{2+}$ ion with Cl^- ion i.e with HCl). Here also the reaction proceeds through two steps.

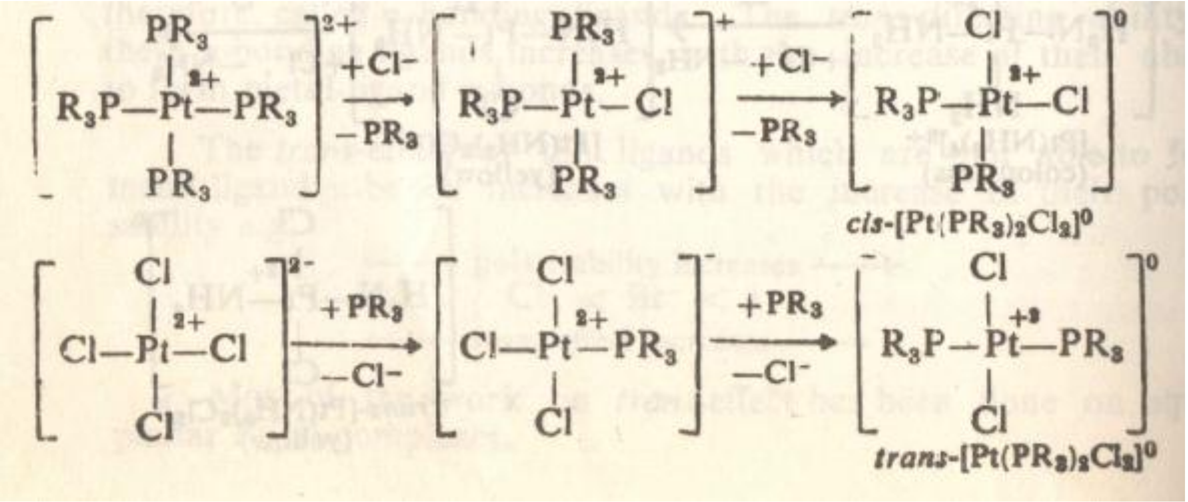
(i) In this steps any of the four NH_3 molecules is replaced by Cl^- ion to give $[Pt(NH_3)_3\ Cl]^+$ ion

(ii) in this step since Cl^- ion has the superior trans-directing influence ($Cl > NH_3$) the remaining NH_3 molecules to be most readily displaced is the one trans to Cl^-ion to give the trans-isomer. This can be said in other words that the superior trans-directing influence of Cl^- ion causes the second Cl^- ion to occupy a position trans to the first kone producing trans $[Pt^{II} (NH_3)_2Cl_2]^0$.

(b) If the trans-effect of $A > X^-$ then cis-isomer is obtained from $[PtA_4]^{2+}$ while trans-siomer is isolated from $[PtX_4]^{2-}$ as shown below.



Synthesis of cis-and trans-$[PtCl_2(PR_3)_2]^0$ where $PR_3 > Cl^-$is done according to the following scheme

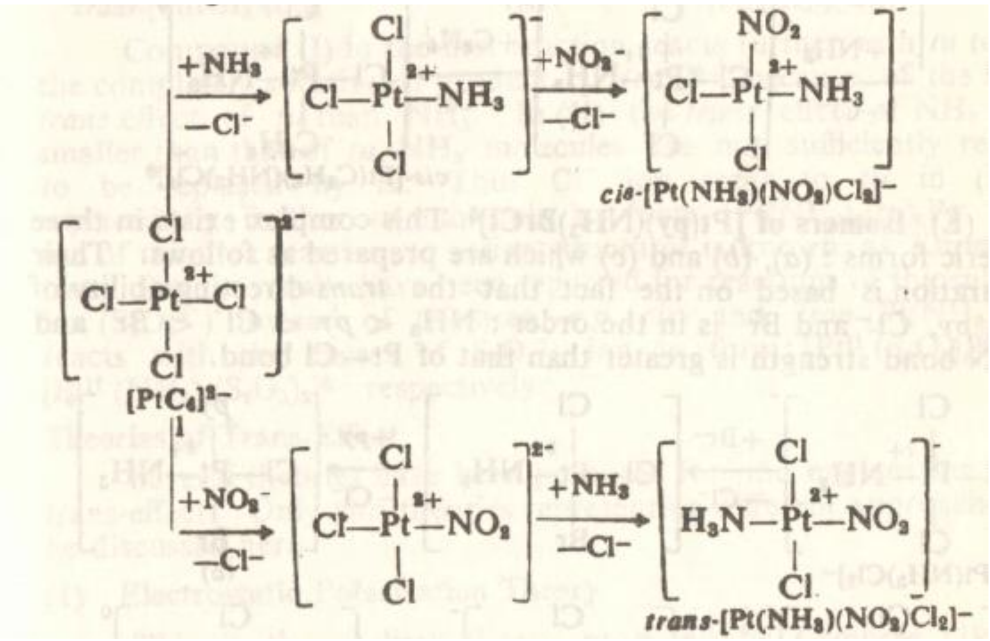


In the first reaction PR_3 molecules lying trans to another molecule is more easily replaced by Cl^- ion than is PR_3 molecules lying trans to Cl^- ion and thus cis-isomer is obtained. The formation of cis-isomer shows that PR_3 has greater trans effect than Cl^- ion. On the basis of similar reasoning the formation of trans-siomer can also be explained.

(B) Cis-and trans $[PtCl_2(NO_2)(NH_3)]^0$

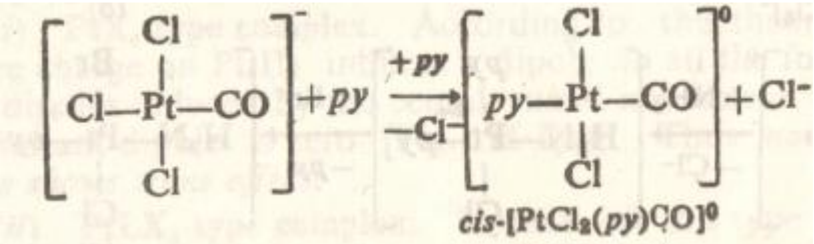
The preparation of the two isomers is based on the fact that the trans directing ability of Cl^- NH_3 and NO_2^- groups is in the order $NH_3<Cl^-<NO_2^-$.

The cis-isomer is made by the action of NH_3 on $PtCl_4^{2-}$ and of NO_2^- on the product. The trans-isomer is obtained by reversing the order of reagent addition.



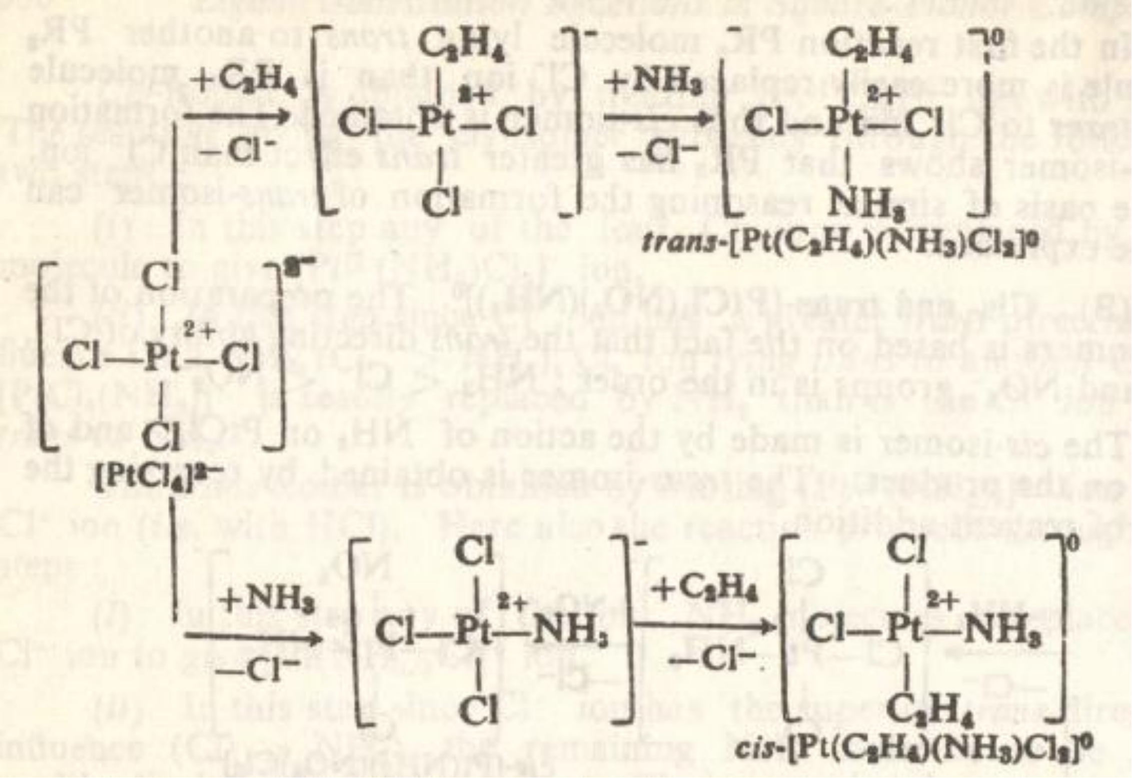
Quit evidently cis-isomer is obtained because $Cl^- > NH_3$ while in trans-isomer $NO_2^- > Cl^-$

(C) Cis-$[PtCl_2(py)(CO)]^0$ it is prepared as follows.



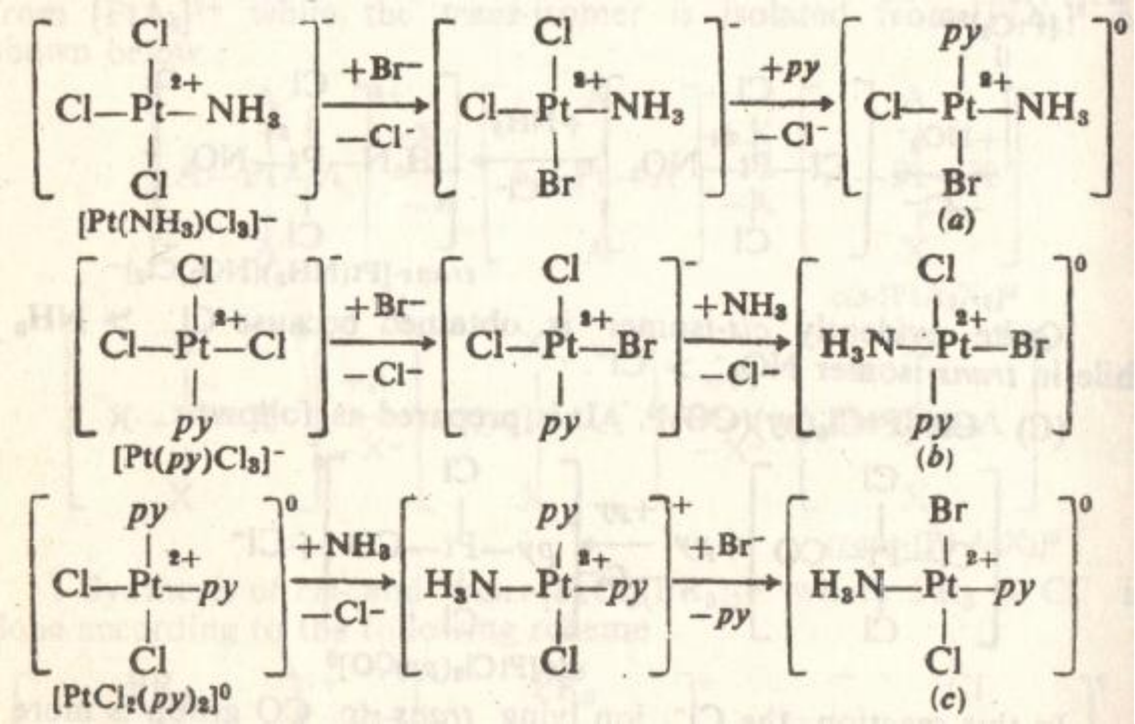
In this reaction the Cl^- ion lying trans to CO group is more easily replaced by py than either of the two Cl^- ions lying trans to each other and the resulting product is the cis-isomer. The replacement of Cl^- ion trans to CO group is due to greater trans directing ability of CO than Cl ($CO > Cl^-$).

(D) Cis- and trans –$[Pt(C_2H_4)(NH_3)Cl_2]^0$. Since ethylene (C_2H_4) is more trans- directing Cl^- ($C_2H_4 > Cl^-$) which in turn is more so than NH_3 ($Cl^- > NH_3$), different isomers may be prepared by $[PtCl_4]^{2-}$ by changing the order of substitution as follows.



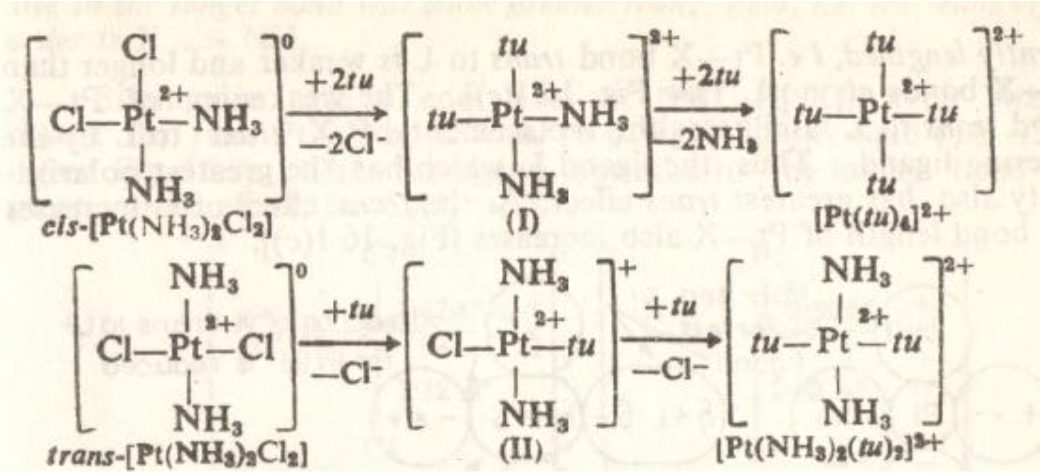
(E) Isomers of [Pt(py)NH$_3$)BrCl]^0

This complex exits in three isomers forms: (a) (b) nand (c) which are prepared as follows. Their preparation is based on the fact that the trans-directing ability of NH$_3$, py, Cl$^-$ and Br$^-$ is in the order: NH$_3$ < py < Cl$^-$ <Br$^-$ and Pt-N bond strength is greater than of Pt-Cl bond.



4.5 Distinguish between cis- and trans isomers of [PtA$_2$X$_2$]^0 type complexs.

In addition to this utility in the synthesis of the desired Pt(II) complexes the trans effect has also been used by Russion chemists to distinguish the cis and trans isomers of [PtA$_2$X$_2$]^0 type complexes (A=NH$_3$ or amine X=a megative group),



e.g cis- $[Pt(NH_3)_2Cl_2]$ reacts with thoure NH_2 $CS.NH_2$ (abbreviated as tu) to give $[Pt(tu)_4]^2$ where as under the same conditions the trans- $[Pt(NH_3)_2Cl_2]^0$ sives $[Pt(tu)_2(NH_3)_2]^{2+}$ Compound (I) in the first reaction reacts further with tu to give the completely substituted product, $[Pt(tu)_4]^{2+}$ because of the larger trans effect of tu than NH_3 molecules are not sufficiently reactive to be replaced by tu. Thus Cl^- ion trans to tu in (II) is replece dby further tu molecule to form $[Pt(NH_3)_2(tu)_2]^{2+}$. The use of thiourea reaction to assign structures is known as Kurnakov's test. Similar result have been reported for reactions of thiosulphate ion ($S_2O_3^{2-}$ insted of thioure e.g cis- and tran $[Pt(NH_3)_2Cl_2]^0$ reacts with the excess of S_2 O_3^{2-} ion form $[Pt^{II}$ $(S_2O_5)_4]^{5-}$ and $[Pt^{II}$ $(NH_3)_5$ $(S_2O_3)_2]^{2-}$ respectively.

4.6 Theories of Trans-Effect

Several theories have been proposed for the explanation of the trans- effect. Only two theories representing different approaches will be discussed here:

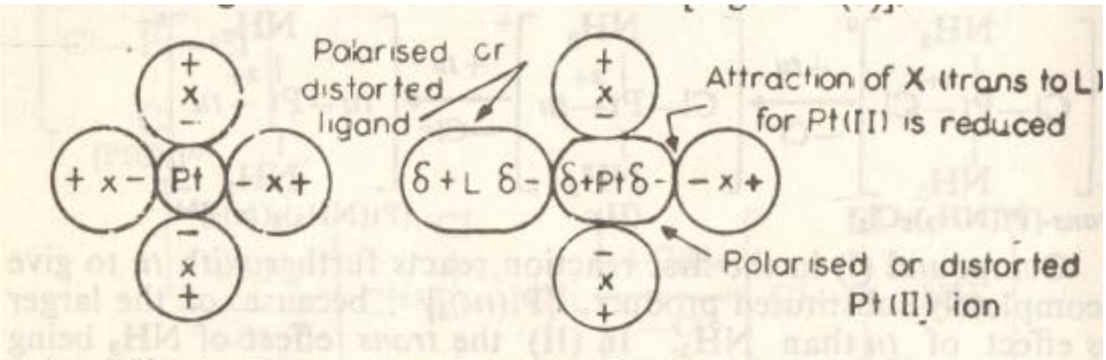
(1) Electrostatic Polarisation Theory

This is the earlist theory proposed by Grinberg (1927) to account for the trans-effect and is a thermodynamic approach.

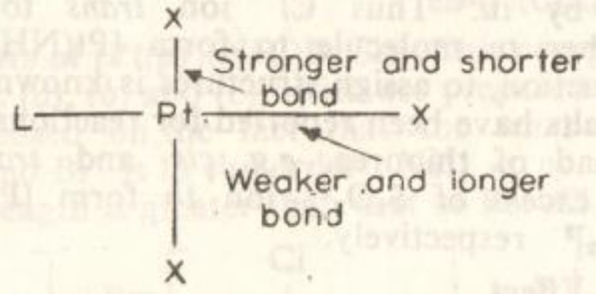
In order to understand this theory we shall consider the following two types of square planar complexes of Pt(II).

(i) PtX_4 type complex. According to this theory the primary positive charge on Pt(II) induces a dipole in all the four X''s ligands. These dipoles induced by the central metal ion cancel each other and the resultant dipole is zero . thus none of the four ligands shows trans effect.

(ii) $PtLX_3$ type complex. In case of this type of complex as well the primary positive charge on Pt(II) induces a dipole in all the four ligands. The two X's ligands which are similar and trans to each other balance other while the other two ligand viz L and X (Also trans to each other) donot, since L is larger and has greater polarizability than X. The net result is that the dipole induced by the positive charge of Pt(II) on the ligand L both become polarised or distorated . this polarization takes place in such a way that the positive charge at the point of pt(II) directly opposite (i.e trans) to L is reduced. Hence the attraction of X for Pt(II) is also reduced and the bond trans to L is weakened and consequently lengthed i.e Pt-X bond trans to L is weaker and longer than Pt-X bonds cis to L. The weakening of Pt-X bond trans to L facilitates the replacement of X trans to L by the entering ligand. Thus the ligand L which has the greatest polarizability also has greatest trans effect. As the trans effect of L increases the bond length of Pt-X also increases. (figure 1)



(*a*) **PtX_4 complex** (*b*) **PtX_3L complex**



(*c*) **PtX_3L complex with bonds of unequal length**
(L shows greater *trans* effect than X)

Figure 1: Electronic polarization theory to explain the trans-effect in square-planar complexes. This diagram represent the polarization of metal ion induced by highly polarisable ligand, L, in MX3L as compared to MX4 (signs show only polarisation effect; the central atom normally carries a positive charge and the ligands are electrondonating)

This theory predicts that the trans-effect will be importent only if the central metal is itself polarisable

4.7 Experimental evidence in favour of polarisation theory

We have seen that if L is highly polarisable in PtX_3L complex, Pt-X bond trans to L is longer than the Pt-X bond cis to L i.e as the trans of L increases the length of Pt-X bond also increases . this fact become evident when we find that Pt-X bond trans to X^- in the complexes of $[Pt(NH_3)X_3]^-$ type (were X=Cl, Br^-) is longer than the pt-X bond cis to it . thus the ligand opposite to the longer bond will show greater trans effect i.e the trans effect order id X^- $>NH_3$.

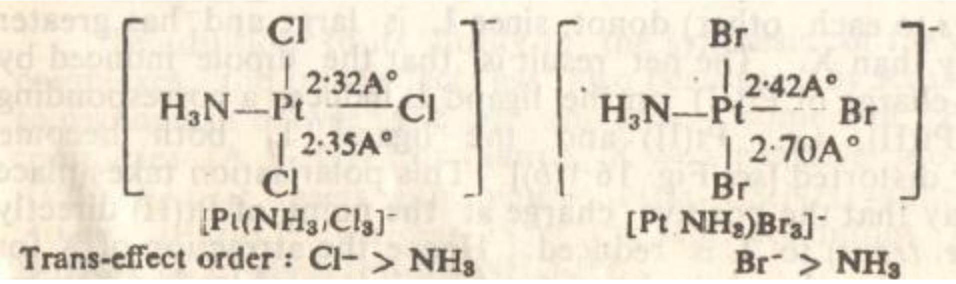


Figure 2: Trans order of $X^-$and NH_3 in $[Pt(NH_3)X_3]^-$ type complex

Similarly in case of complexes of $[Pt(C_2H_4)X_3]^-$ type (where X=Cl^- Br^- the Pt-X bond trans to C_2H_4 is longer than that cis to it. Thus the ligand opposite to longer bond has greater trans effect. i.e $C_2H_4>X^-$

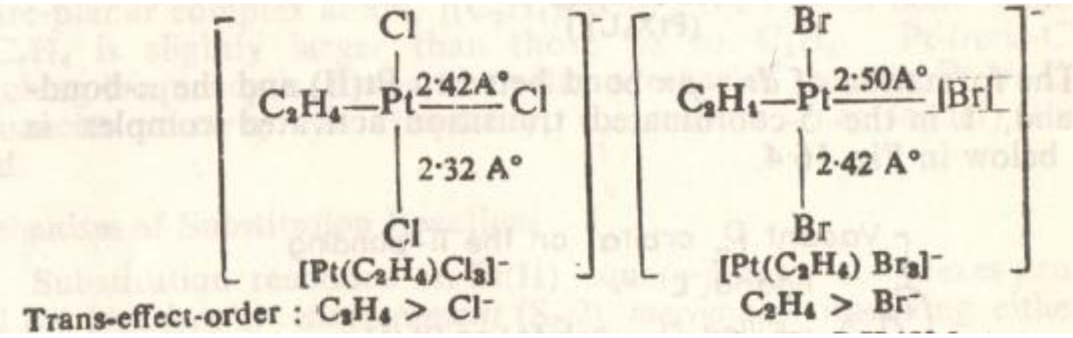


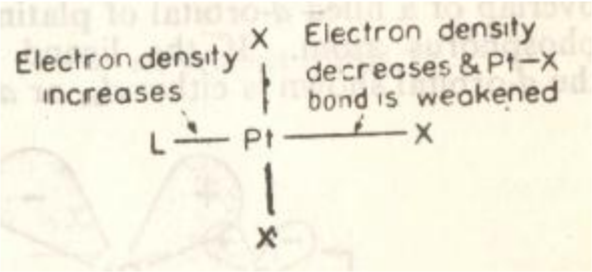
Figure 3: trans order of $X^-$and C_2H_4 in $[Pt(NH_3)X_3]^-$ type complex

4.8 π- Bonding Theory

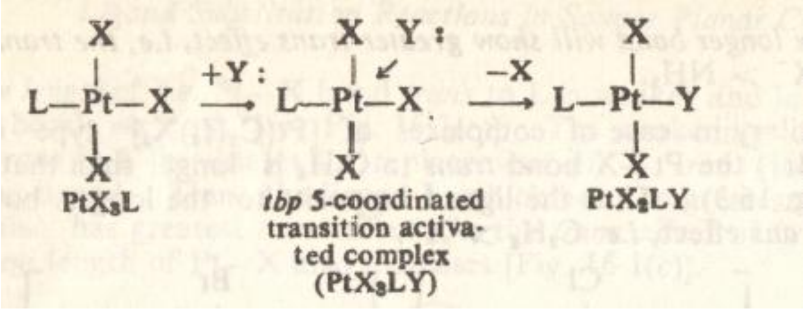
Electrostatic polarisation theory can well explain the trans effect of the ligands lying at the low end of the series like H_2O, OH^- NH_3 etc. However this theory cannot explain the high trans effect of the π- bonding ligands like PR_3 NO, CO, C_2H_4 CN^- which lie at the high end of the series π-bonding theory which is due to chatt (1955) and Orgel (1956) accounts well for the high trans effect of such ligands.

According to this theory the vacant π and π^* orbitals of the π- bonding ligand accept a pair of electron from the filled d-orbitals of the metal d_{xz} or d_{yz} orbital) to form metal-ligand π-bond (dπ-dπ or dπ-pπ bond)

In case of Pt(II) square planar complex, PtX_3L (L is the π-bonding ligand) the d_{yz} orbital of Pt(II) with a pair of electrons overlaps with the empty p_z orbital of the π-bounding ligand L to form the dπ-pπ bond between Pt(II) and L. The formation of the π-bond in the complex increases the electron density in the direction of L and diminishes it in the direction of the ligand X trans to L thus Pt-X bond trans to L is weakened.



The weakening of Pt-X bond trans to L fascilitates the approach of the entering ligand say Y: with its lone pair in the direction of diminished electron density to form the five coordinated transition state complex $PtLX_3Y$ which on losing X yields $PtLX_3Y$. In the formation of PTX_2Y the ligand X trans to L is replaced by the incoming group Y. the transition state complex has distorated triangonal bipyramidal (tbp) structure in which two X's group which are cis to L both in the intial and final states from the apexes.



The formation of dπ-pπ bond between Pt(II) and the π-bonding ligand L in the 5- coordinated transition activated complex is shown below in figure 4.

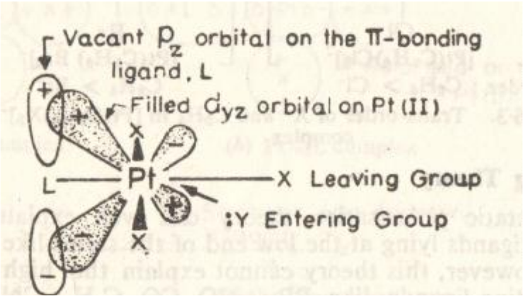


Figure 4: formation of dπ-dπ bond in tbp 5-coordinated activated complex formed during the substitution reaction in Pt(II) square-planar complexe $PtLX_3$

Smaller d-orbital lobes adjacent to the group X which is to be replaced by Y may be noted in the figure 4.

A schematic representation of double bond ib Pt=PR_3 is shown in figure 5 σ-bond is formed by the donation of a pair of electronics from phosphorus to platinum and the π-bondby the overlap of a filled d-orbital of platinum and a vacant d-orbital of phosphorus atom. If the ligand PR_3 and X are in the xy plane. The d-orbital shown is either d_{xz} or d_{yz}

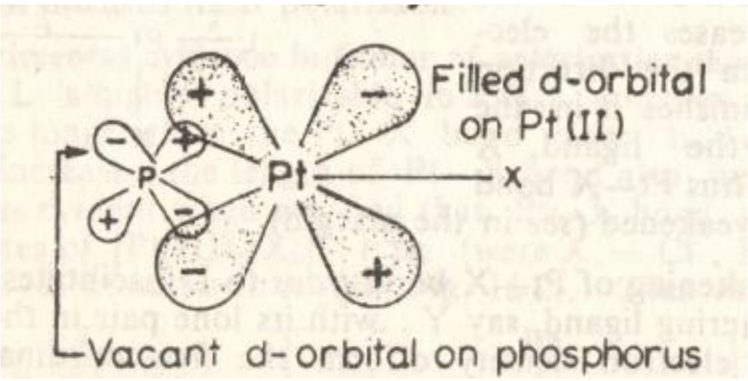


Figure 6: Schematic representation of R_3P-Pt double bond

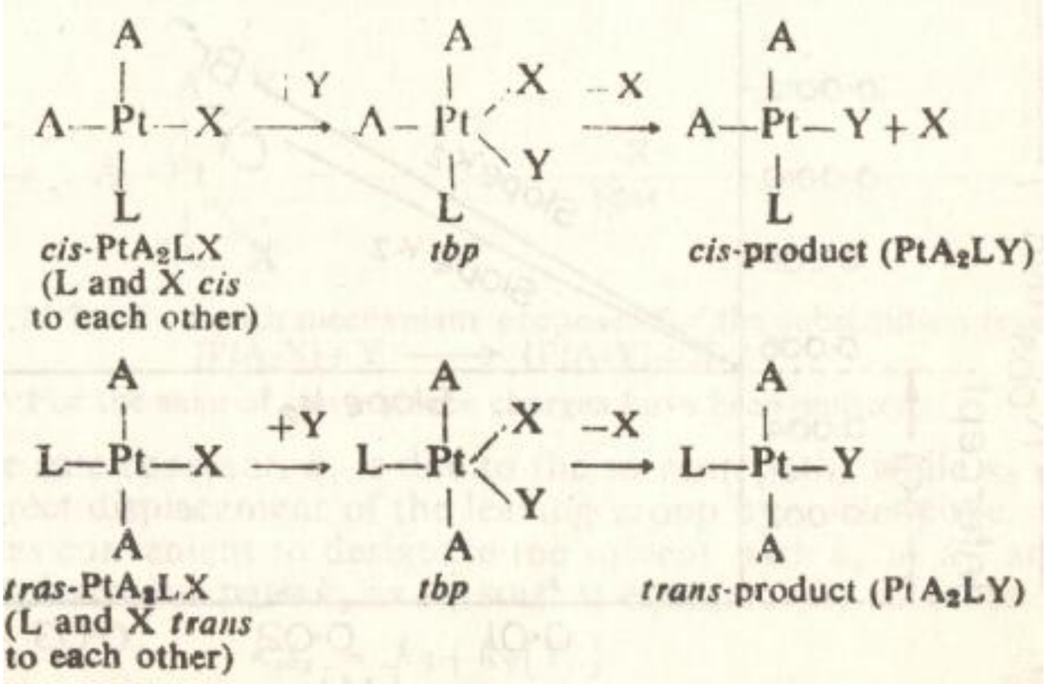
Chatt et al emphasises that the removal of charge from Pt(II) by π-bonding of L enhances the addition of the entering group Y and favours a more rapid reaction. According to Orgel the formation of π-bond between Pt(II) and π-bonding ligand L enhances the stability of the 5-coordinated transition state complex thus lowering the activation energy for its formation and seepding up the reaction.

That the formation of π-bond weakens the metal-ligand bond trans to a π-bonding ligand is evident from the fact that in the square planar complex anion $[(C_2H_4)PtCl_3]$ the Pt-Cl bond trans to C_2H_4 is slightly larger than those cis to C_2H_4. Pt-trans-Cl stretching frequency is lower than the average of the two Pt- cis-Cl frequencies. Lower the frequency the weaker the bond.

4.9 Mechanism of Substitution Reactions

Substitution reaction in Pt(II) square-planar complexes proceed by bimolecular displacement S_N^2 mechanism involving either the solvent or the entering ligand as the nucleophilic agent. Experimental evidence in favour of S_N^2 mechanism has been presented. Because of steric and electronic reasons the co ordination number of the metal is increased to include the entering ligand. The metal is exposed for attack above and below the plane. Furthermore Pt(II) which is a d^3 system has a vacant p_z orbital of relatively low energy which accepts the pair of electrons donated by the entering ligand.

Substitution reactions of cis- and trans PtA_2LX with Y to yield PtA_2LY have been explained on the basis of nucleophilic attack of Y through trigonal bipyramidal (tbp) structure. The process is entirely stereospecific : cis-PtA_2LX yields cis product and trans gives trans.



Martin and his student have shown that the rates of hydrolysis reaction of the four complexes viz $[PtCl_4]^2$, $[Pt(NH_3)Cl_3]$, a small effect), and $[Pt(NH_3)_3Cl]^+$ vary only by a factor of two (quite a small effect), although the charge on the reactant Pt(II) complex charges from -2 to +1. This variation in rate is remarkably small. The breaking of a Pt-Cl bond should become much more difficult in this series of four complexes as the charge on the complex becomes more positive. However the formation of a new bond (i.e the attraction of Pt for a nucleophile) should increase in the same order. Since there is small effect of charge of charge on the complex on the rate of reaction both Pt-Cl bond breaking and Pt.....OH_2 bond making are of comparable importance. This ios a strong evidence in favour of $S_N{}^2$mechanism.

For the substitution reaction of square planar complex $[PtA_3X]^{n+}$ with Y^- to yield $[PtA_3Y]^{n+}$ in water involves a complication since the solvent water also behaves as a potential ligand.

$$[PtA_3X]^{n+}+Y^- \rightarrow [PtA_3Y]^{n+}+X^-$$

For this reaction a two-term rate law is given by the expression

$Rate=k_1[PtA_3X^{n+1}]+k_2[PtA_3X^{n+}][Y^-]$

Here k_1 = first order rate constant for solvent controlled reaction.

K_2 = second order rate constant for reaction with Y^-

A convenient analysis of rate constant can be made by running the reactions with a large excess of nucleophile Y^-. Under this condition the observed rate constant k_{obs} is pseudo first order and is related to k_1 and k_2 as

$$K_{obs}=k_1+k_2[Y]$$

This equation shows that for the same complex with different reagents linear plots of k_{obs} aganist nucleophile concentration [Y].

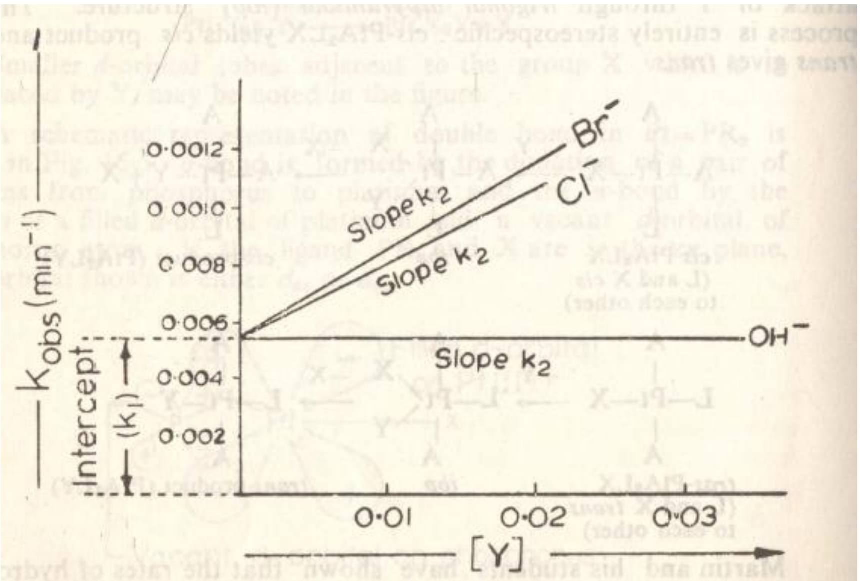


Figure 6: Plot of observed rate-constant K_{obs} for the reaction$[Pt^{2+}(dien)Cl]^{+}+Y^{-} \rightarrow [Pt^{2+}(dien)Y]^{+}+Cl^{-}$ against concentration of the nucleophile [Y]

Dien ≡ $NH_2(CH_2)_2NH(CH_2)_2NH_2$.

Should be obtained having the same intercepts k_1 and different slopes k_2

The rate-law represented by equation (ii) indicates that the reaction of $[PtA_3X]^{n+}$ with Y^- to yield $[PtA_3Y]^{n+}$ is occurring by two path mechanism only one of which involves Y^- in the rate-determine step. These two paths are shown in fig. The upper path is the solvent path (also called Y^- independent path) and lower path is the direct path (reagent path). In the solvent path the solvent H_2O replaces X^- in a slow and is subsequently replaced by Y^-in a rapid step. Experience shows that Y^- independent path is not an S_N^1 process, but is a direct (S_N^2) displacement of leaving group- by nucleophile in brobably the second order path while the solventy path gives pseudo first order kinetics.

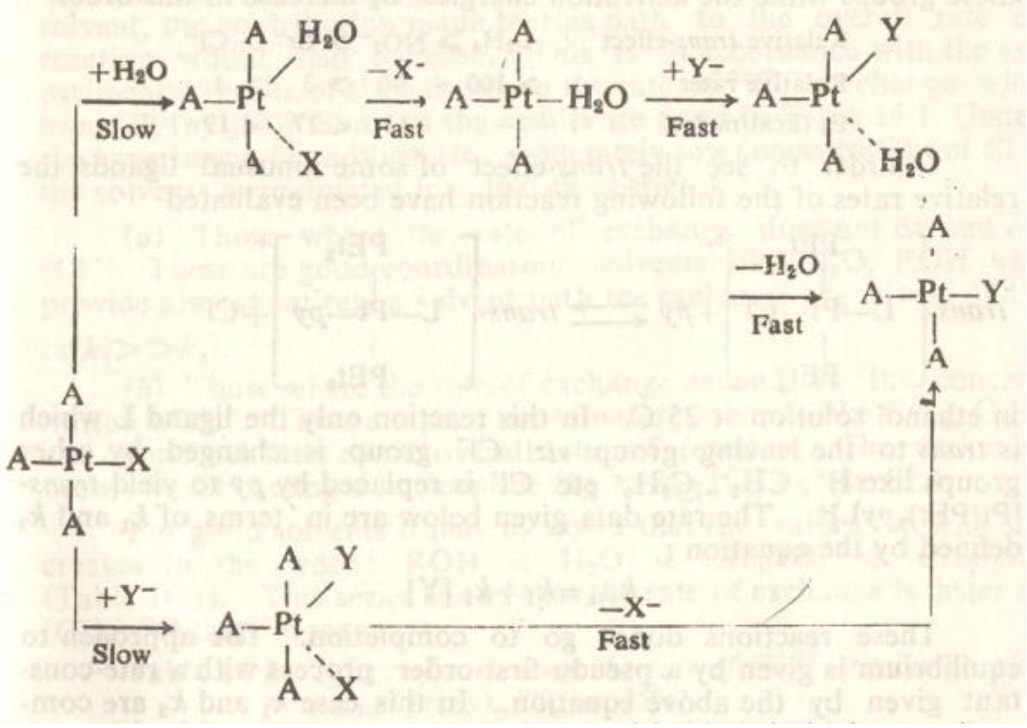


Figure 7: Two-path mechanism proposed for the substitution reaction $[PtA_3X + Y \rightarrow [PtA_3Y] + X$ for the sake of convenience charge have been omitted

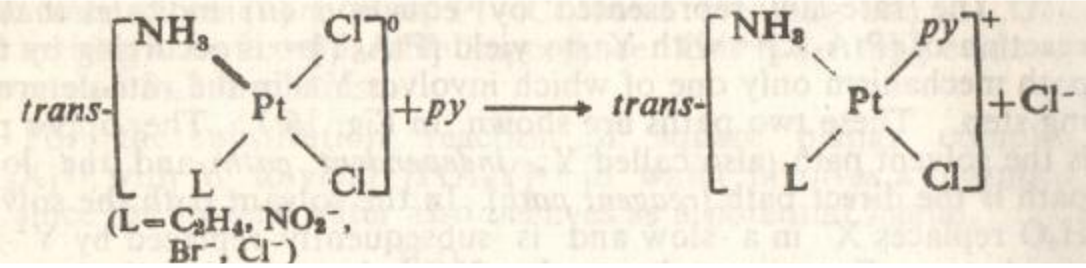
The rate constant k_1 is due to the solvent path while k_2 is due to the direct displacement of the leaving group by nucleophile. Thus it becomes convenient to designate the solvent path k_1 as k_2 and the direct displacement path k_2 as k_y so that equation (ii) becomes

$$K_{obs}=k_s+k_y[Y^-]$$

4.10 Factors affecting the rates of substitution reactions in square planar complexes

Most of the kinetic data available deal with effect of various factors on the rates of substitution reactions in Pt(II) square planar complexes. Some factors are:

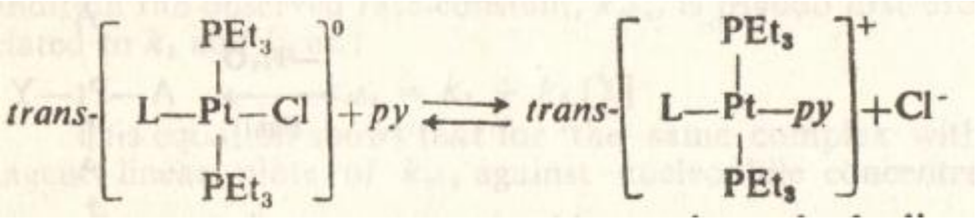
(i) *Trans-effect.* In order to see the effect of ligands L trans to the leaving group Cl^- in some analogous Pt(II) square-planar complexes relative rates of the following reaction have been studied.



In this reaction it has been found that when L is replaced by C_2H_4 NO_2^-, Br^- or Cl^- in the complex $[Pt(NH_3)Cl_2L]^0$ the relative rates of reaction decrease with the decrease of relative trans-effect of these groups while the activation energies E_a increase in this order.

$$\text{Re}\,lative\,trans - effect\, C_2H_4 \geq NO_2^- > Br^- > Cl^-$$
$$\text{Re}\,lative\,rates{:}{>}100 > 90 > 3 > 1$$
$$E_a\,(kcal/mole){:}{-}11 < 17 < 19$$

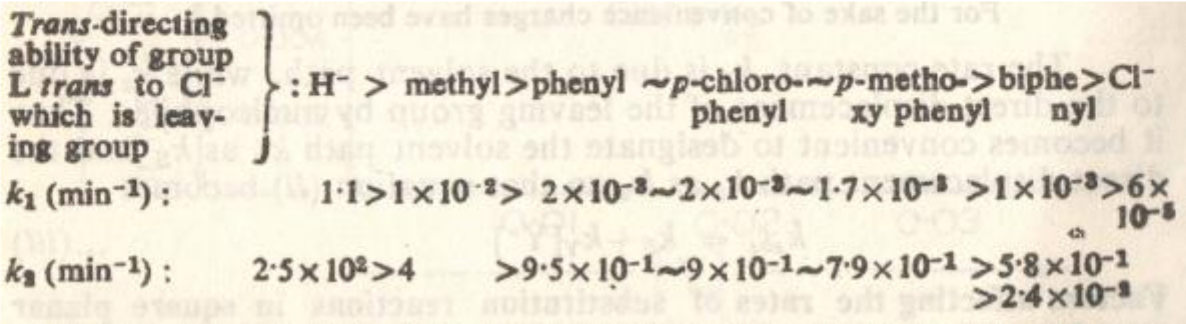
In order to see the trans effect of some unusual ligands the relative rates of the following reactions have been evaluated



In ethanol solution at 25^0C. in this reaction only the ligand L which is trans to the leaving group viz Cl^- group is changed by other group like H^- CH_3^- , $C_6H_5^-$ etc. Cl^- is replaced by py to yield trans- $[Pt(Pet)_2pyL]^+$. The rate data given below are in terms of k_1 and k_2

$$K_{obs}=k_1+k_2[Y]$$

These reactions donot go to completion. The approach to equilibrium is given by a pseudo-first-order process with a rate-constant given by the above equation. In this case k_1 and k_2 are composite quantities for forward and reverse reactions and both contribute to the overall observed rates



Trans-directing ability of group L *trans* to Cl^- which is leaving group : H^- > methyl > phenyl ~ *p*-chlorophenyl ~ *p*-methoxy phenyl > biphenyl > Cl^-

k_1 (min^{-1}) : $1{\cdot}1 > 1\times10^{-2} > 2\times10^{-3} \sim 2\times10^{-3} \sim 1{\cdot}7\times10^{-3} > 1\times10^{-3} > 6\times10^{-5}$

k_2 (min^{-1}) : $2{\cdot}5\times10^{2} > 4 > 9{\cdot}5\times10^{-1} \sim 9\times10^{-1} \sim 7{\cdot}9\times10^{-1} > 5{\cdot}8\times10^{-1} > 2{\cdot}4\times10^{-3}$

These result show that the effect on the rates reaction of different L groups trans to Cl^- which is being replaced by py decreases in the following order.

$H^{-} > methyl > phenyl \sim p-chlorophenyl$ ....this order of trans effect of these groups.

(ii) *Effect of leaving group.* The reaction :

$$[Pt^{2+}(dien)X]^{+} + py \rightarrow [Pt(dien)(py)]^{2+} + X^{-}$$
$$[X = NO_3^{-}, H_2O, Cl^{-}.etc$$

has been studied and the rates of reaction have been obtained. The rates of reaction show that if the leaving group X^- is replaced by NO_3^-, H_2O, Cl^-, Br^-,I^-, N_3^- SCN^-, NO_2^- and CN^- the rates decrease in order:

$NO_3^- > H_2O > Cl^- > Br^- > I^- > N_3^- > SCN^- > NO_2^- > CN^-$

note that in the square planar complex $[Pt(dien)X]^+$ three co ordination positions are always occupied by the inert dien ligand while the fourth one is occupied by X^- which may be NO_3^-, H_2O Cl^- etc.

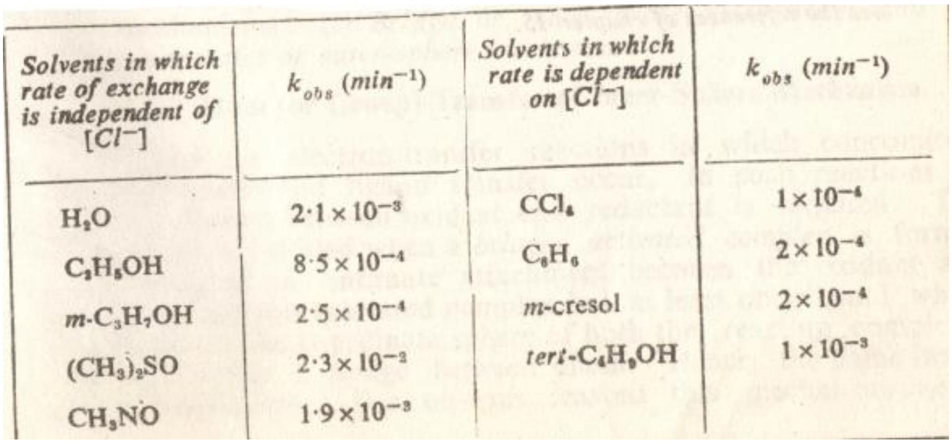
(iii) *Solvent effect.*

Since there is considerable evidence of the fact that in the solvent path the solvent replaces X^- directly it is to be expected that with the increase in the coordinating ability of the solvent the contribution made by this path to the overall rate of reaction would also increase. This is in accordance with the experimental result of the solvent on the rate of $^{36}Cl^-$ exchange with trans $[Pt(py)_2Cl_2]$ some of the results are given in table. Under the experimental condition viz moderately low concentration of Cl^- the solvents were divided into two categories:

(a) Those where the rate of exchange does not depend kon [Cl^-]. These are good coordinating solvents like H_2O, ROH and provide almost entirely a solvent path for exchange (k_s>>k_{cl}[Cl^-] or k_1>>k_2).

(b) Those where the rate of exchange depends on the concentration of Cl^-. These are poor coordinating solvents like CCl_4, C_6H_6 and contribute little to the overall rate of reaction. The exchange occurs by Cl^- acting a nucleophile (k_s<k_{cl} [Cl^-] or k_1<k_2).

For good solvents it may by noted that values of K_{obs} increases in the order: ROH<H_2O<CH_3NO_2<$(CN_3)_2SO$ $(CH_3)_2SO$ than in water



Solvents in which rate of exchange is independent of [Cl^-]	k_{obs} (min^{-1})	*Solvents in which rate is dependent on* [Cl^-]	k_{obs} (min^{-1})
H_2O	$2{\cdot}1 \times 10^{-3}$	CCl_4	1×10^{-4}
C_2H_5OH	$8{\cdot}5 \times 10^{-4}$	C_6H_6	2×10^{-4}
m-C_3H_7OH	$2{\cdot}5 \times 10^{-4}$	*m*-cresol	2×10^{-4}
$(CH_3)_2SO$	$2{\cdot}3 \times 10^{-2}$	*tert*-C_4H_9OH	1×10^{-3}
CH_3NO	$1{\cdot}9 \times 10^{-3}$		

(iv) *Effect of charge on the complex.* This has already been discussed under Mechanism of substitution reaction

4.11 Cis-trans isomerisation in planar complexes.

Cis- trans isomerisations in Pt(II) complexes arenot common yet they do occur. Unfortunately neithrt kinetic nor exchange studies have been made to obtain information in the mechanism of isomerisations. However some observations suggest that the isomerisation proceeds by an inter moleculer process. The strongest evidence in support of this process is thet a trace of some catalyst is required for these isomerisations.

Since substitution reaction of Pt(II) complexes are generally sterospecific (i.e they proceed with retention of configuration), cis-trans isomerisation is explained in terms of two-steps mechanism which is shown below in fig for the isomerisation of cis-$[Pt(PR_3)_2Cl_2]^0$ in solution containing excess of PR_3 to the corresponding tras-isomer. In the first step the Cl^- group is replaced by the catalyst PR_3 to form $[Pt(PR_3)_3Cl]^+$. In thesecond step the reverse happens and trans-$[Pt(PR_3)_2Cl_2]^0$ is formed along with the catalyst steps have been shown as (i) and (ii)

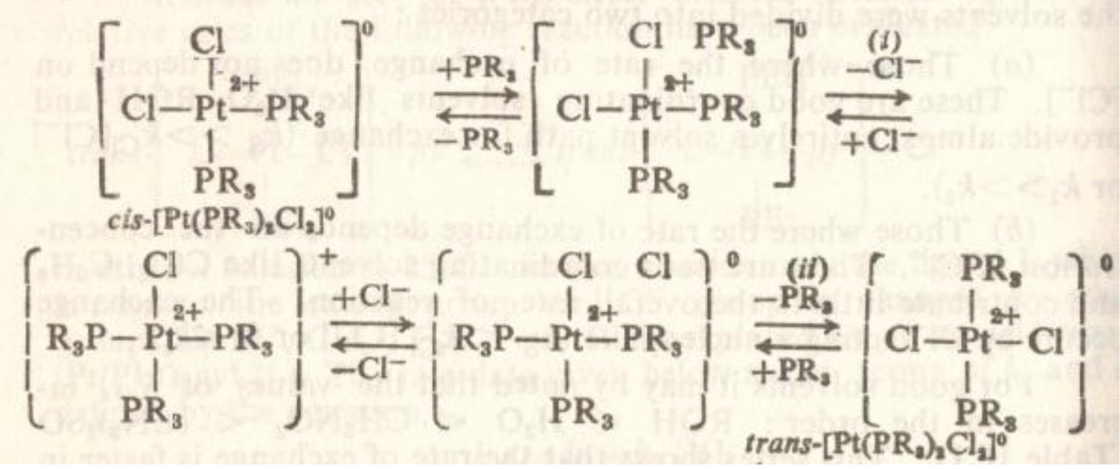


Figure 8: Two-step mechanism for isomerisation of cis-$[Pt(PR_3)_2Cl_2]^0$ to the corresponding trans-form.

4.12 Summary of the unit

It is observed that during the substitution reactions of square planar metal complexes, some ligands preferentially direct the substitution trans to themselves. i.e., the choice of leaving group is determined by the nature of ligand trans to it. The Trans effect can be defined as the effect of a ligand over rate of substitution of another ligand positioned trans to it in the square planar complexes.

In general there are two factors contributing to trans direction of substitution as described below:

1) Trans influence: This is a thermodynamic factor. Some ligands weaken the M-L bond trans to them in the ground state and thus by facilitating the substitution.

E.g. Strong σ- donors like H^-, I^-, Me^-, PR_3 etc., destabilize the M-L bond trans to themselves and thus by bringing the easy substitution of that ligand.

2) Trans effect: This is a kinetic factor and considered as true trans effect. It occurs by the stabilization of the transition state.

E.g. The strong π-acceptors like NO^+, C_2H_4, CO, CN^- etc., stabilize the transition state by accepting electron density that the incoming nucleophilic ligand donates to the metal through π-interaction.

Note: This is debatable since the π-interaction may increase the strength of M-L bond especially in the trans position.

In the 5-coordinate Trigonal bipyramidal transition state, the electrostatic repulsion is decreased due to removal of electron density in the equatorial plane. The removal of electron density if facilitated by the π-interaction of the trans directing ligand.

The Trans effect can dictate the product formed in the substitution reactions. The classic example of Trans effect is the synthesis of cisplatin, cis-diamminedichloridoplatinum(II). It is prepared by substituting the two chloro groups of $[PtCl4]^{2-}$ by ammonia molecules.

4.13 Key words

Ligand substitution reaction in square planar complex; Trans-Effect; Theories of Trans-Effect; π- Bonding Theory ; Mechanism of Substitution Reactions; Cis-trans isomerisation in planar complexes.

14.15 References for further study

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4.16 Questions for self understanding

1) Write a note on ligand substitution reaction in square planar complex

2) What is Trans-Effect? Explain with example

3) Discuss the uses of trans-effect

4) How do you distinguish between cis- and trans isomers of $[PtA_2X_2]^0$ type complexs.

5) Explain the different theories of trans-effect

6) Give an account for experimental evidence in favour of polarisation theory

7) What is π- Bonding Theory? Explain briefly

8) Write a note on mechanism of substitution reactions in square planar complexes

9) Discuss factors affecting the rates of substitution reactions in square planar complexes

10) Write a note on Cis-trans isomerisation in square planar complexes.

UNIT-5

Structure of the unit

5.0 Objectives of the unit
5.1 Introduction
5.2 Classification of organometallic compounds
5.2.1 Classification based on the types of ligands
  a) *Simple organometallic compounds*
  b) *Mixed organometallic compounds*
  i) *Derivatives of main group elements*
  ii) *Derivatives of transition elements*
5.2.2 Classification based on the nature of bond
  i) *Ionic Organometallic compounds*
  ii) *Sigma bonded Organomatallic compounds*
  iii) *Multicentered bonded organometallic compounds*
  iv) *Pi bonded Organometallic compounds*
5.3 Hepticity of organometallic compounds
5.4 Hapticity vs. denticity
5.5 Nomenclature of organometallic compounds
5.6 Organometallic compounds of elements in Groups 3 through 12
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5.9 Organometallic compound with unsaturated molecules and substituent groups
5. 10 Ocenes
5.11 16 and 18 electron rules
5.12 The 18 electron rule
  a) Method 1: The ionic (charged) model
  b) Method 2: The covalent (neutral) model.
5.13 Electron donation of common ligands
5.14 Comparison of two methods
5.15 Counting of electrons and finding metal-metal bonds
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5.0 Objectives of the unit

After studying this unit you are able to

- Explain the difference between organometallic compounds and coordination compounds
- Naming the organometallic compounds according to IUPAC nomenclature
- Classify the given organometallic compounds based on hapticity
- Classify the given organometallic compounds based on hapticity
- Classify the given organometallic compounds based on polarity of M-C bond types
- Count the electrons surrounding to central metal in organometaalic compounds

5.1 Introduction

Organometallic chemistry deals with the molecules containing a metal-carbon bond. Many chemist say that for a compound to be classified as an organometallic compound, the type of metal-carbon bonding in a molecule should be covalent or partially covelent in nature. But the scientific community defines an organometallic compound as one in which there is a bonding interaction it may either ionic or covalent, localized or delocalized between one or more carbon atoms of an organic group or molecule and a main group transition, lanthanide or actinide metal atoms. Organic derivatives of the metalloids such as boron, silicon, germanium, arsenic and tellurium are also included in this definition. It is very well understood that the element to which carbon is bound is more electropositive than carbon in organometallic compound.

Traditional chemists didn’t agree to classify metal-cyanide complex as an organometallic while many scientist refer to molecule such as the well known Wilkinson’s catalyst as organometallic though it lack the required metal carbon bond.

5.2 Classification of organometallic compounds

Based on the periodic table, organometallic compounds can broadly classify in to transition metal, maingroup metal and lanthanide/actinide based organometallics. Among these transition metal organometallic chemistry is most well developed, mechanistically understood and widely utilized.

5.2.1 Classification based on the types of ligands

The organometallic compounds are classified in a number of ways. The first type of classification is based on the types of groups (ligands) bonded to metallic atom

According to this classification organometallic compounds are of types they are

c) *Simple organometallic compounds*

The simple organimetallic compounds are those which have only hydrocarbon radical or hydrogen atom attached to the metal atom. e.g, $(C_2H_5)_4Pb$, $(CH_3)_3SnH$,

These compounds may be symmetrical eg $(C_2H_5)_2Hg$, $(C_2H_5)_4Pb$ or unsymmetical eg.$C_2H_5HgC_4H_9$

d) *Mixed organometallic compounds*

Mixed organometallic compounds are those which have groups other than hydrocarbon radicals or hydrogen atom also attached directly to the metal atom. eg, C2H5MgBr, (C4H9)2SnCl2, C6H5SbO(OH)2

Second type of organometallic compounds classification as follows

iii) *Derivatives of main group elements*

Organometallic compounds of main group generally form σ-covalent bonds except for alkali metals and alkaline erths which form largely ionic compounds electron-deficient structures are formed by elements like ithium, beryllium and aluminium.

iv) *Derivatives of transition elements*

The transition elements form organometallic compounds with π bonding ligands. Organometallic compounds of transition elements are not stable at room temperature, thus organometallic compounds of transition elements must have the π-bonding ligands as a binary ligands. Because the presence of π-bonding ligand in organometalic compounds of transition lements increases the stability of the σ-bond and thus makes the compound stable.

The Third type of organometallic compounds is based on the type of bond between the metal and ligand. The reactivity and the structure of organometallic compounds are correlated with the character of the metal-carbon bond. There are three types of bonds and hence these compounds are mainly classified into the following three types

5.2.1 Classification based on the nature of bond

Another method of classification of organic compounds is based on the nature of metal-carbon bond present in the organometallic compounds. According to this classification the organometallic compounds are classified in to

v) *Ionic Organometallic compounds*

Ionic organometallic compounds are predominantly with highly electropositive elements of group 1 and group 2. Such compounds are very reactive and are quit unstable, highly polar, and conducting in nature. These organometallic compounds are soluble in highly polar organic solvents like tetrahydrofuran (THF) and dimethylformamide (DMF) but insoluble in non-polar solvents like Benzene, toluene et…. Organometalic compounds show a gradual transition from ionic to σ-bonded covalent froms. Thus alyls of sodium are more ionic and less covalent than those of lithium. These compounds are unstable in air and readily hydrolyzed in water to liberate the hydrocarbon with the formation of hydroxide. Their stabilities depends on the stability of the organic radical R-, thus $C_6H_5^-Na^+$ and $C_5H_5^-Na^+$ are stable due to the stabilization of the negative charge through the π-electron density.

vi) Sigma bonded Organomatallic compounds

Sigma bonded organometallic compounds are formed by predominantly low reactive metals. Metal-Carbon σ-bonds are characterized by a normal two electron two centre bond. Metalloid-carbon bonds are also considered as a σ-bond. The example for σ-bonded organometallics are dialkyl zinc, cadmium and mercury. These are low viscosity, high density and intensely reactive liquids. The mercury compounds are highly poisonous.

Generally non-transition elements form the σ-bonded covalent organometallic compounds. The polarity of the bond depends mainly on the difference in electronegativity between metal atom and carbon and also bepends on the metal orbital which are available, the steric requirements and the polarisability of the electron cloud. Ex. $B(CH_3)_3$; $Al(CH_3)_3$; $Si(CH_3)_4$; $Pb(C_6H_5)_3$

Transition metals can also form metal-carbon σ-bonds with organic groups provided some additional π bonding ligands are also present in the molecule attached directly to the metallic atom. ex $CH_3Mn(CO)_3$, π-$C_6H_5Fe(CO)_3R$ etc….

These compounds have predominantly 2-electron-2-centred σ-bond formed between the organic group and the metal atom M, though the bonds have much ionic character due to the electronegativity differences. Normal valence rules apply to the bonding and the structure of these compounds. The strength of M-C bond depends on the nature of the R group and also on the nature of other ligands present on M, those having π-acceptor ligands like CO, cp, PR_3 etc… provide more stability to M-C bonds.

In the covalent organometallic compounds the σ-bonded groups have been arranged about the metal atom in a way which is determined by the hybridization of the metal atomic orbitals. Thus depending upon the hybridization of the metal atomic orbitals different types of structures are observed.

Thus in the structure of $(CH_3)_4Si$ the four methyl groups are occupying the four corner of a tetrahedron while silicon is attached at the centre. The dimetic cyclo-octadiene rhodium chloride is having a square planar structure

Hybrid	Number of bonding groups	Geometrical shape
sp	2	Linear
sp^2	3	Equilateral triangle
sp^3	4	tetrahedral
dsp^2	4	Square planar
dsp^3	5	Trigonal bipyramid
dsp^3	6	Octahedral

vii) Multicentered bonded organometallic compounds

Multicentered bonded organometallic compounds are predominantly formed by electron deficient atoms like boron, aluminium, beryllium etc.. Beryllium forms a number of polymeric dialkyls and aluminium forms a few dimeric trialkyls. This type of organometallics involves electron-deficient bridging structure and multicentre bonds. The aluminium organometallics retain their dimeric structures both in the solution state and in the vapor phase.

viii) Pi bonded Organometallic compounds

Pi bonded Organometallic compounds are predominantly formed by transition elements. There are plenty of organometallic derivatives with a π-bond between the metal and the carbon atom of the ligand are known. The thransition metal Pi bonded Organometallic compounds are subdivided in to two types.

The first type of Pi bonded Organometallic compounds are those in which a normal σ-bond is formed initially by donation of ligand electrons to the metal. This is followed by back donation of metal electrons on to the vacant π-orbitals of the ligand. This results the formation of π-bond and this phenomenon is called back bonding or dative bonding.

Back bonding will occur if the valence shell of the metal is nearly complete. In such cases only metal will donate its electrons to the ligand. Also ligand should have vacant π-orbitals, then only it will accept the electrons from the metal.

The ability of a ligand to enter into back bonding by accepting electron density from the metal into its vacant π-orbitals is called π-acidity.

Carbonyl (CO), cyanide (CN^-) ligands have high π-acidities and these stabilize low oxidation states of the metal in the complex. For example, the oxidation states of metals in $[Ni(CO)_4]$ and $[Mn(CO)_6]^-$ are zero and -1respectively.

The second type of organometallics are those in which donation of lectrons from the ligand to the metal as well as back donation of the electrons from the metal to the ligand are both accomplished by π-orbitals of the ligand. Such complexes are designated as π-complexes. Ethylene ($H_2C{=}CH_2$) and cyclopentadienide anion ($C_5H_5^-$) from π-complexes with metal. For example tris(π-ethylene)nickel(0) and ferrocene

The first prepared dicyclopentadienyl-metal compound is ferrocene. In this compound both dontation and bacj acceptance of electrons takes place through π-orbitals of the cyclopentadienyl ligand. The composition of ferrocene is expressed as $(\pi\text{-}C_5H_5)_2Fe$. The two cyclopentadienyl ring in the ferrocene are staggered conformation with respect to each other. Where as in the corresponding ruthenium compound ruthenocene $(\pi\text{-}C_5H_5)_2Ru$ the cyclopentadienyl rings are in eclipsed conformation. The compounds like ferrocene and ruthenocene are called sandwich compounds since the metal atom lies in between the two cyclopentadienyl rings.

5.3 Hepticity of organometallic compounds

The term hepticity refers to the number of carbon atoms of a ligand that are attached to the metal atom in an organometallic compound. Hepticity may vary from one to eight and it is designated as η^1, η^2, η^3……. η^8 (η = eta).

For example: in ferrocene the πelectron cloud of each cyclopentadienyl group is delocalized over all the five carbon atoms of the ring this implies that all the five carbon atoms of the cyclopentadienyl ligand are bound to iron. Hence cyclopentadienyl is a pentahapto ligand. Therefore the ferrocene is expressed as $(\eta^5\text{-}C_5H_5)_2Fe$ rather than $(\pi\text{-}C_5H_5)_2Fe$

Similarly in Zeise's slat the π-electron cloud of the ethylene group is delocalied over both the carbons and is involved in bonding. Hence ethylene is a dihapto ligand and the composition of Zeise's salt is expressed as $[Pt(\eta^2\text{-}C_2H_4)Cl_3]^-$

5.4 Hapticity vs. denticity

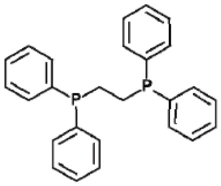
Polydentate ligands can coordinate via multiple coordination sites within the ligand. Denticity refers to the number of donor groups in a single ligand that bind to a central atom in a coordination complex. In many cases, only one atom in the ligand binds to the metal, so the denticity equals one, and the ligand is said to be monodentate

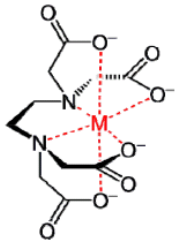
Examples: 1,2-bis(diphenylphosphino)ethane, ($Ph_2PCH_2CH_2PPh_2$)

Dichloro[ethane-1,2-diylbis(diphenylphosphane)- κ^2 P]nickel(II)

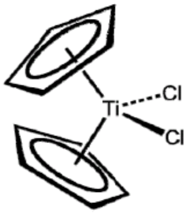
Titanocene dichloride: (Cp_2TiCl_2)

Dicholorobis(η^5-2,4-cyclopentadien-1-yl)titanium





Metal-EDTA **chelate**



Denticity is distinguished from hapticity, in which electrons of a bond or conjugated series of bonds are linked to the central metal without the metal-ligand bond being localized to a single ligand atom

5.5 Nomenclature of organometallic compounds

The international union of pure and applied chemists (IUPAC) has adopted a set of norms for naming organometallic compounds. These norms are commonly referred as IUPAC rules of organometallic nomenclature. Those are summarized as follows.

1. The positive ion is named first followed by the negative ion, irrespective of whether the coordination sphere is cationic or anionic.
2. Ligands in the coordination sphere are named as follows

a) Negative ligands are named by adding the suffix 'o' to their respective stem name,

For example Cl^- is named as chloro,

H^- is named as Hydrido

O^{2-} is named as oxo

S^{2-} is named as sulfide

However organic carbanions and radicals are not named by adding suffix ‘o’ to their stems. They retain their original names. For example,

CH_3^- and $CH_3^\bullet$ are named as methyl

$C_2H_5^-$ and $C_2H_5^\bullet$ are named as ethyl

$C_3H_5^-$ and $C_3H_5^\bullet$ are named as allyl

$C_6H_5^-$ and $C_6H_5^\bullet$ are named as phenyl

b) Neutral ligands have no special ending. For example

C_2H_5 is named as acetylene
NH_3 is named as amine
H_2O is named as aqua
C_6H_6 is named as benzene
CH_2 is named as carbene
CO is named as carbonyl
C_2H_4 is named as ethylene
NO is named as nitrosyl
C_6H_5N (py) is named as pyridine

c) Positive ligands are named by adding suffix ‘ium’ to their respective stem name. For example,

$[NH_2\text{-}NH_3^+]$ is maned as hydrazonium
NO^+ is named as nitrosonium

3. If there are more than one ligands of same type, The following prefixes are used to indicate their multiplicity.

Number of ligand	prefix
2	di
3	tri
4	tetra
5	penta
6	hepta and so on…

4. If there are more than one ligands of different types these are arranged in alphabetical order. Prefixes di, tri, tera, etc… are not considered in the alphabetical arrangement.
5. After naming the ligands in alphabetical order and indicating their respective numbers, then added the name of the metal mentioning its oxidation sate along with roman number placed in a simple parenthesis. If the oxidation sate of metal is zero, then it is to be depicted in Arabic script.

   For example,

   $[Hg(CH_3)Cl]$ is named as Chloromethylmercury(II)

   $Mn_2(CO)_{10}$ is named as Decacarbonyldimanganease(0)

   $[(C_2H_5)_3Sn]^+$ is named as triethyltin(IV)ion
6. If the coordination sphere is anionic, suffix-ate is added to the name of the metal. For example, $Na[Sn(C_2H_5)_3$ is named as Sodium triethylstannate(II)
7. Some organometalics involves polysyllabic ligands, i.e, the ligands having their name with a numerical indication. The names of common polysyllabic ligands are given below,

NH_2-CH_2-CH_2-NH_2 (en)	is named as ethylene diamine
PF_3	trifluorophosphine
$P(C_6H_5)_3$	triphenylphosphine
C_5H_5	Cyclopentadienyl (cp)
$C(C_6H_5)_2$	diphenylcarbene

If more than one polysyllabic ligands of the same ypes are present in the coordination shere of the organometallic compound, their multiplicity is indicated by the prefixes bis, tris, etc… instead of bi, tri, etc…..

Number of polysyllabic ligands	prefix
2	bis
3	tris
4	tetrakis
5	pentakis
6	hexakis and so on…..

The name of the polysyllabic ligand is written in simple bracket. For example,

$Fe(C_5H_5)_2$	Bis(cyclopentadienyl)iron(II)
$[Ir(CO)Cl(C_2H_4)\{(C_6H_5)_3P\}_2]$	Carbonylchloro(ethylene)bis(triphenylphosphine)iridium(I)

In some cases, the prefix bis, tris etc may be used even when the ligand is not a polysyllabic one. For example,

The complex $[Ni(C_3H_5)_2]$ has two allyl ligands in the coordination sphere. Here allyl is not polysyllabic ligand but if the name of the above complex is written a diallylnickel(II), it gives the impression that two allyl units have combined to form a ligand. To avoid this confusion, the name of the complex is better written as bis(allyl)nickel(II).

8. If the composition of the complex invoIes a solvent of crystallization, the name of the complex is to be successively followed by (i) number of molecules of solvent of crystallization and (ii) name of the solvent. The latter two entities are to be spaced by a hyphen. For example,

   $[Pt(C_2H_4)Cl_3]^-.H_2O$ is named Trichloro(ethylene)-platinate(II)ion.1-water
9. In case of bridging, dimeric organometallic compounds, the bridging ligands are indicated by adding notation 'μ' to the name of bridging ligands. For example,

   $(C_2H_4)_2Rh$ is named as Bis(ethylene)rhodium(I)-μ-dichloro-bis(ethylene)rhodium(I)
10. In case a bridging, dimeric organometallic compound contains a metal-metal bond, its name ends with a reference to the metal-metal bond. For example,

    Is named dicarbonyl(cyclopentadienyl)manganese(I)-μ-carbene-dicarbonyl(cyclopentadineyl)manganese(I)(Mn-Mn)
11. In case, where more than one carbon atoms of the ligand are direcly bound to the metal, the hapticity of the coordinating group is indicated along with the ligand. For example, in cyclopentadienyl complexes, the ligand is bound to the metal by all its five carbon atoms therefore it is considred as pentahapto ligand and is prefixed with notation η^5. Thus the correct IUPAC name and composition of ferrocene is written as follows,

    $Fe(\eta^5-C_5H_5)_2$ Bis(η^5-cyclopentadienyl)iron(II)

    Ethylene is bound to the metal through both its carbons therefore it is called as dihapto ligand and indicated by the notation η^2. Thus the correct composition and IUPAC name of Zeise's salt is written as follows,

    $K[Pt(\eta^2-C_2H_4)Cl_3].H_2O$ Potassium trichloro-(η^2-ethylene)palatinate(II)-1-water

5.6 Organometallic compounds of elements in Groups 3 through 12

Coordination nomenclature is the main nomenclature method used to name organometallic compounds containing elements of Groups 3-12. The metal is always the central atom. Linear formulae are composed of the symbol of the central atom, followed by the ligands, in alphabetical order if more than one ligand is present. In a line formula, a coordination entity is always placed in square brackets. No brackets are indicated when the structure is based on developed organic formulas.

Compounds consisting solely of individual metal atoms joined to a carbon atom of one or more organyl substituent groups and/or to one or more hydrogen atoms are named by citing the names of such organic groups or hydrogen in alphanumerical order, followed by the name of the metal. The presence of hydrogen attached to a metal atom must always be indicated by the prefix 'hydrido'.

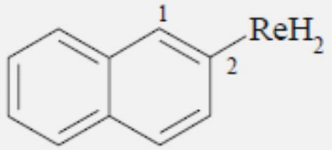
Examples:

$[Hg-CH_3]^+$

methylmercury(1+)

$[Zn(CH_3)_2]$

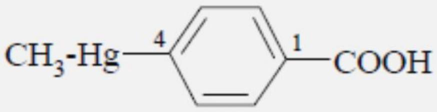
dimethylzinc



dihydrido(naphthalen-2-yl)rhenium

$[Cu-C\equiv C-CH_3]$

(prop-1-yn-1yl)copper

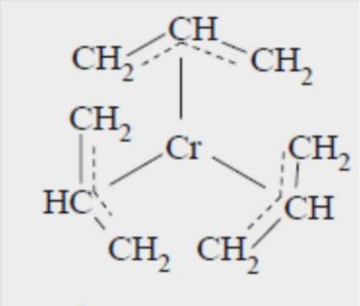


(4-carboxyphenyl)methylmercury

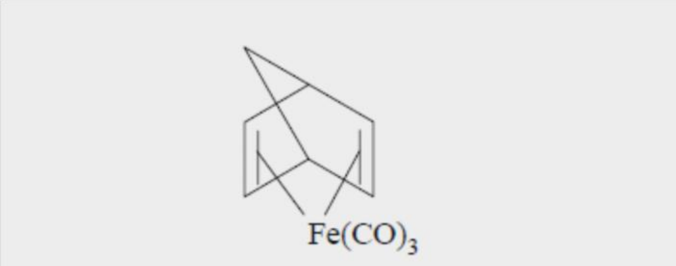
5.7 Organometallic groups with multicenter bonding to carbon atoms

In order to indicate multicenter bonding to carbon atoms, for example in an unsaturated system, the name of the ligand is preceded by the prefix 'η' (eta) A right superscript is added to the symbol η to indicate the number of atoms that bind to the metal. When it is necessary to indicate that all unsaturation sites are not bonded to the metal, numerical locants are added in front of the symbol η. It may also be necessary to denote a single atom in the ligand that is directly attached to the metal; in this case, the symbol κ (kappa) is cited before the element symbol that indicates the specific position that is bonded to the metal.

Examples:



tris(η^3-allyl)chromium

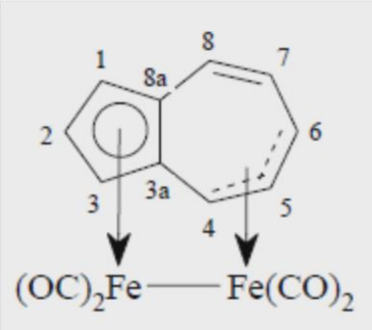


(η^4-bicyclo[2.2.1]hepta-2,5-diene)tricarbonyliron

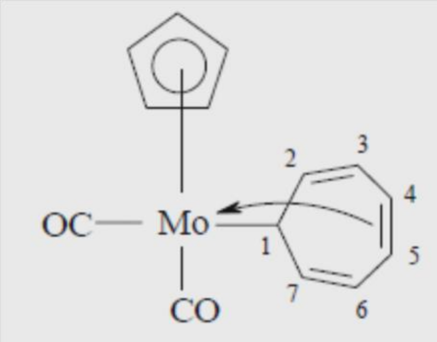
5.8 Bridging organometallic groups with multicenter bonding to carbon atoms.

The prefix ‘μ’ is added to the name of organometallic groups to indicate bridging between two metal atoms. Locants for the ‘η’ positions are separated by the colon and direct bonding between metal atoms is indicated as mentioned in below example.

Example:



[μ-(1,2,3,3a,8a-η:4,5,6-η)-azulene]-pentacarbonyldiiron (*Fe–Fe*)

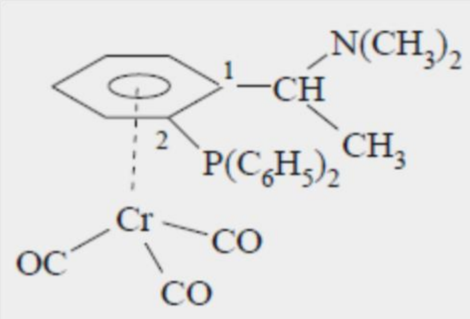


dicarbonyl[(4,5-η,κ*C*1)-cyclohepta-2,4,6-dien-1-yl](η5-cyclopentadienyl)molybdenum

5.9 Organometallic compound with unsaturated molecules and substituent groups

Organic molecules used as ligands are named substitutively in accordance with principles, rules and conventions of substitutive nomenclature and cited in the name of the organometallic compound with the appropriate hapto symbols. This method is preferred to that consisting of using prefixes only to denote characteristic groups in the organic part of the organometallic compound.

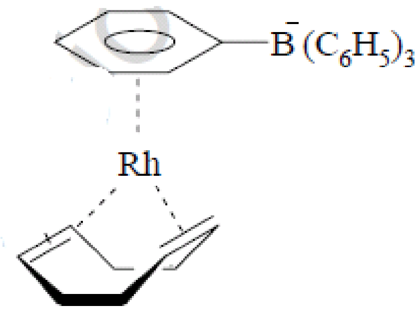
Example:



tricarbonyl{1-[2-(diphenylphosphanyl)-η6-phenyl]-*N*,*N*-dimethylethanamine}chromium
or tricarbonyl{[1-[1-(dimethylamino)ethyl)]-2-(diphenylphosphanyl)-η6-benzene}chromium
(in the second name, the benzene ring is treated as the principal group because it is the part of the ligand attached to the metal; this method as yet has not official sanction)

In zwitterionic complexes, in which a noncoordinated atom of the ligand carries a charge which is offset by the opposite charge at the metal atom, the charge of the ligand is indicated by the appropriate ligand name ending, while the charge of the central atom is not indicated.

Example:



(η^4-cycloocta-1,5-diene)[(η^6-phenyl)triphenylboranuide]rhodium
(η^4-cycloocta-1,5-diene)[(triphenylboranuidyl)-η^6-phenyl]rhodium

5. 10 Ocenes

"Ocenes" are bis(η^5-cyclopentadienyl) complexes of certain metals. The names ferrocene, ruthenocene, osmocene, nickelocene, chromocene, cobaltocene and vanadocene are names for compounds corresponding to 'bis(η^5-cyclopentadienyl)metal', where the metal atom is Fe, Ru, Os, Ni, Cr, Co, and V. These names are substituted in accordance with the principles, rules and conventions of substitutive nomenclature, using suffixes or prefixes to denote characteristic groups.

Examples:

A number of unsaturated organic anions and molecules such as allyl, cyclopentadienyl, ethylene and benzene can bind to a metal in more than one way. The different modes are distinguished by the number of carbon atoms participating in linkage with the metal. The hepto symbol 'η' called eta with a numerical superscript provides a topological description by indicating the connectivity between the ligand and the central atom.

5.11 16 and 18 electron rules

The tendency of transition metals to form complexes in which the metal has an effective atomic number (EAN) corresponding to the next higher inert gas has long been recognized. The number of valence electrons (NVE) consists of the valence electrons of the metal and those electrons donated by or shared with the ligands, and would be 18 for an inert-gas configuration. However, the diamagnetic organometallic complexes of Groups IVB-VIII, essentially all of the well-characterized compounds have 16 or 18 metal valence electrons.

Two postulates or rules for organometallic complexes and their reactions are proposed.

1. Diamagnetic organometallic complexes of transition metals may exist in a significant concentration at moderate temperatures only if the metal's valence shell contains 16 or 18

electrons. A significant concentration is one that may be detected spectroscopically or kinetically and may be in the gaseous, liquid, or solid state.

2. Organometallic reactions, including catalytic ones, proceed by elementary steps involving only intermediates with 16 or 18 metal valence electrons.

It is apparent that application of these rules requires that care be exercised in reaching conclusions on the NVE of a metal complex. Association or dissociation of the compound may occur. For example, $Ni[PPh_3]_4$ is substantially dissociated in solution into $Ni[PPh_3]_3$ and PPh_3. π-Ally1 palladium chloride is a 16 electron complex, with chloride ions bridging in a dimeric structure.

The 16 and 18 Electron Rule severely restricts the types of reaction which a particular complex may undergo. Dissociation or association of Lewis acid ligands may occur with either 16- or 18-electron complexes. Lewis base ligand dissociation, reductive elimination, insertion, and oxidative coupling are restricted to 18-electron complexes. Lewis base ligand association, oxidative addition, deinsertion, and reductive decoupling reactions can occur only with 16-electron complexes.

5.12 The 18 electron rule

Just as organic chemists have their octet rule for organic compounds, organometallic chemists have the 18 electron rule. And just as the octet rule is often violated, the 18 electron rule also. However, both serve a useful purpose in predicting reactivity. Each derives from a simple count of the number of electrons that may be accommodated by the available valence orbitals

This rule was first formulated by Irwing in 1921 with a view to extend the octet theory of G. N. Levis based on the static atom model beyond argon in the periodic table.

$$V_s = S - e$$

Where V_s = the number of shared electrons of a given atom in a compound

S = number of electrons required for the completion of its valence shell and

e = the number of valence electrons in the isolated atoms.

For example $NH_3 \rightarrow 3 = 8-5$

$Ni(CO)_4 \rightarrow 8 = 18-10$

$Cr(CO)_6 \rightarrow 12 = 18-6$

This rule was applied based on the assumption that the ligands are Lewis bases and the metal atoms/ions were Lewis acids. This rules state that, *thermodynamically stable transition metals* *organometallic compounds are formed when the sum of the metal d-electrons and the electrons supplied by the surrounding ligands equal to 18*. An alternate and general statement is that, *when the metal achieves an outer shell configuration of* ns^2, $(n-1)d^{10}$, np^6 *there will be 18 electrons in the valence orbitals and a stable configuration is attained and resulting organometalic complex becomes more stable.* By counting the numbers of outer shell electrons surrounding to each metal atom in a complex, it is possible to predict whether the complex will be stable and whether there will be metal-metal (M-M) bond present or not.

There are two methods of electron counting are employed they are

1) The oxidation state counting methods and
2) The neutral atom counting methods

The neutral atom counting methods is more foolproof because it does not require the correct assignment of oxidation states metal. Because some time it is difficult to assign the oxidation state of metal in organometallic compounds. The oxidation state method is followed when it follows the changes in the oxidation state of metal centre in a reaction.

Knowing how many valence electrons "belong to" a transition metal complex, it is possible to make predictions about the mechanisms of reactions and the possible modes of reactivity. There are two distinct methods that are used to count electrons, *the neutral or covalent method* and *the effective atomic number or ionic method*. These are simply two different accounting systems that gives the same final answer.

c) Method 1: The ionic (charged) model

The basic premise of this method is that, remove all of the ligands from the metal and, if necessary, add the proper number of electrons to each ligand to bring it to a closed valence shell state.

For example, removing ammonia from metal complex, NH_3 has a completed octet and acts as a neutral molecule. When it bonds to the metal center it does so through its lone pair (in a classic Lewis acid-base sense) and there is no need to change the oxidation state of the metal to balance charge. Thus ammonia is considered as a neutral two-electron donor.

In contrast, removing a methyl group from the metal and complete its octet, then formally it will be CH_3^-. If this methyl anion bonded to the metal, the lone pair forms metal-carbon bond and the methyl group acts as a two-electron donor ligand. Notice that to keep charge neutrality it must oxidize the metal by one electron (i.e. assign a positive charge to the metal). This, in turn, reduces the d-electron count of the metal center by one.

d) Method 2: The covalent (neutral) model

The major premise of this method is that, remove all of the ligands from the metal, but rather than take them to a closed shell state, do whatever is necessary to make them neutral.

Let's consider ammonia once again. When it remove from the metal, it is a neutral molecule with one lone pair of electrons. Therefore, as with the ionic model, ammonia is a neutral two electron donor.

Diverging from the ionic model when considering a ligand such as methyl, when it removing from the metal and make the methyl fragment neutral, then it is a neutral methyl radical. Both the metal and the methyl radical must donate one electron each to form our metal-ligand bond. Therefore, the methyl group is a one electron donor, not a two electron donor as it is under the ionic formalism.

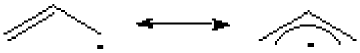
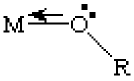
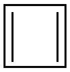
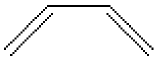
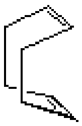
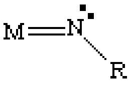
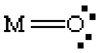
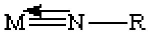
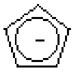
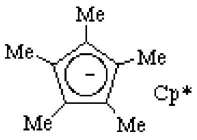
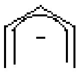
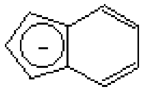
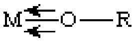
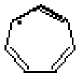
Then it is obvious that where did the other electron "go"? It remains on the metal and is counted there. In the covalent method, metals retain their full complement of d electrons because we never change the oxidation state from zero; i.e. Fe will always count for 8 electrons regardless of the oxidation state and Ti will always count for four.

Notice that this method does not give any immediate information about the formal oxidation state of the metal, so it is necessary to go back and assign that in a separate step. For this reason, many chemists (particularly those that work with high oxidation state complexes) prefer the ionic method.

5.13 Electron donation of common ligands

Below table provides some common transition metal ligands and the number of electrons that each donates to a metal center. Some ligands can donate a variable number of electrons.

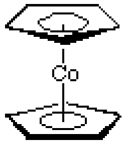
For example, an alkoxide, M-OR, can donate two to six electrons depending on the hybridization of the oxygen atom.

	Neutral/Covalent	**Oxid State/Ionic**
R (H, Me, Et, Pr, H) -CN, OH, Cl, OR (sp^3), acyl, NO (bent)	1	2
PR_3, amines, ethers, NH_3, R_2S, CO, RCN, RNC, olefins, acetylenes (sometimes), ketones	2	2
 (allyl)  (sp^2 alkoxide)	3	4
NO (linear)	3	2 (NO^+)
   (1,5-COD) Acetylenes (sometimes)	4	4
  (bent imido) (oxo)	2	4
  (linear imido) (oxo)	4	6
 Cp    (Indenyl)  (linear alkoxide)	5	6
Arenes (benzene etc.)	6	6
C_7H_7	7 	6 (as a cation) 8 (as an anion)
cyclooctatetraene (COT)	8 (max)	10 (as 2-)

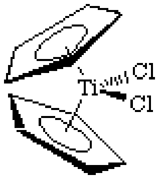
5.14 Comparison of two methods

The most critical point should remember is that like oxidation state assignments, electron counting is formalism and does not necessarily reflect the distribution of electrons in the molecule. However, these formalisms are very useful and both will give the same answer.

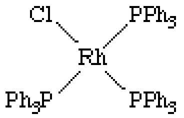
Consider the following simple examples. It is important to notice how some ligands donate the same number of electrons no matter which formalism one can choose, while the number of d-electrons and donation of the other ligands can differ.



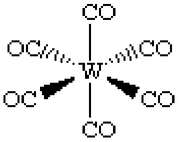
	ionic		**covalent**
Co^{II}	7 e^-	Co	9 e^-
2 Cp^-	12 e^-	2 Cp•	10 e^-
Total	19 e^-	**Total**	19 e^-



	ionic		**covalent**
Ti^{IV}	0 e^-	Ti	4 e^-
2 Cl^-	4 e^-	2 Cl•	2 e^-
2 Cp^-	12 e^-	2 Cp•	10 e^-
Total	16 e^-	**Total**	16 e^-



	ionic		**covalent**
Rh^{I}	8 e^-	Rh	9 e^-
Cl^-	2 e^-	Cl•	1 e^-
3 PPh_3	6 e^-	3 PPh_3	6 e^-
Total	16 e^-	**Total**	16 e^-



	ionic		**covalent**
W^{0}	6 e^-	W	6 e^-
6 CO	12 e^-	6 CO	12 e^-
Total	18 e^-	**Total**	18 e^-

5.15 Counting of electrons and finding metal-metal bonds

Since metal carbonyl compounds contain the metal in low oxidation state, there are many compounds that possess M-M bonds and fall into the category of metal carbonyl cluster.

To determine the total number of M-M bond and to find out the number of bonds each metal makes with the other metal atoms in a cluster, the following procedure is followed. This procedure applies only to those complexes having a nuclearity ≤ 4. The electronic structure is easily understandable in terms of an electron pair bond between each adjacent pair of metal atoms with each metal atom attaining the 18 electron configuration.

Calculating the M-M bond

i) Determine the total valance electrons (TVE) in the entire molecule.(i.e., the number of valence electrons of the metal plus the number of electrons from each ligand and the charge) and say it is A

ii) Subtract this number from n X18 where n is the number of metals in the complex i.e., (n X 18) – A and say it is B

iii) a) B divide by 2 (i.e, B/2) gives the total number of M-M bonds in the complex.

b) A divided by n (i.e. A/n) gives the number of electrons per metal. It the number of electron per metal is 18 it indicates that there is no M-M bond. If it is 17 electrons, it is indicates that there is one M-M bond and if it is 16 electrons it indicates that there are 2 M-M bonds and so on…

This rule works best for low-valent metal with small ligands of σ-donors and π-acceptors. Such ligands are small enough to allow the metal to be co-ordinatively saturated and give a large value of splitting

It is important to note that for a main group organometallics and organomatallic compounds of f-block elements, the 18 electron rule will not be applicable. There are many exceptions to 18 electron rule among transition metal organometallics. Some of the common exception for 18 electron rule is listed below.

a) Metal with d18 electron:

The d^{18} metals have a tendency to form square planar 16-electron complexes. This tendency is weak for group 8 (Fe, Ru and Os) in zero oxidation state and strong for group 9, 10 and 11 [(Rh(I), Pd(II), Pt(II), Au(III)]. It is well known that square planar 16 electron complexes of d^8 metals result in completely filled orbitals except the high energy orbital $d_{x^2-y^2}$.

b) Metal with d^0 electrons:

Many high valent d^0 complexes have a lower electron count than 18. Also sterically demanding bulky ligands force complexes to have less than 18 electrons.

c) The 18 electrons rule fails when bonding of organometallic cluster of moderate to big sizes is considered. The bonding of cluster and their stabilities are therefore considered under other electron counting rules.

d) The rule is not applicable to organometallic compounds of main group metals as well as those of lanthanide and actinide metals.

5.16 Summary of the unit

Compounds that contain a metal-carbon bond, R-M, are known as "organometallic" compounds. Organometallic compounds of Li, Mg (Grignard reagents) are amongst some of the most important organic reagents. Many other metals have been utilised, for example Na, Cu and Zn. Organometallic compounds provide a source of nucleophilic carbon atoms which can react with electrophilic carbon to form a new carbon-carbon bond. This is very important for the synthesis of complex molecules from simple starting materials.

To rationalise the general reactivity of organometallics it is convenient to view them as ionic, so R-M = R^-M^+. The most important reactions is this chapter are the reactions of organolithiums, RLi, and Grignard reagents, RMgX, with the carbonyl groups in aldehydes, ketones and esters to give alcohols. However, we will also look at some useful reactions involving Cu, Zn and Hg (mercury).

The reaction of a metal with an organic halide is a convenient method for preparation of organometallic compounds of reasonably active metals such as lithium, magnesium, and zinc. Ethers, particularly diethyl ether and oxacyclo-pentane (tetrahydrofuran), provide inert, slightly polar media in which organometallic compounds usually are soluble.

5.17 Key words

Classification of organometallics; Hepticity; Denticity; Nomenclature of organometallic; Bridging organometallic; 18 electron rule; Ocenes; The ionic (charged) model; : The covalent (neutral) model.

5.18 References for further study

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2) Organomettalic Chemistry; Sodhi G.S.; *Ane Books Pvt Ltd*, **2009**.

3) The Organometallic Chemistry of the Transition Metals; Robert H. Crabtree; *John Wiley & Sons*, **2011**.

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5) Organometallic Chemistry, Volume 33; M. L. H. Green, Green M*; Royal Society of Chemistry*, **2007**.

5.19 Questions for self understanding

1) Suggest and draw possible 18 electron structures formed from the following combinations of metals and ligands.
   a) Ru, CO, CH_3, PMe_3
   b) Mo, Allyl, Cp, NO
   c) Rh dppe(Chelating), μ-CO, HC≡CH
   d) Ir, Cp, H, PMe_3
2) Using the 18 electron rule determine the value of n in the following complexes.
   i) $Na_2Fe(CO)_n$
   ii) $W(\eta^6\text{-}C_6H_6)(CO)_n$
   iii) $Cr(\eta^3\text{-}C_5H_5)(CO)_n(CH_3)$
   iv) $MnBr(CO)_n$
   v) $Rh(\eta^5\text{-}C_5H_5)(CO)_n$
   vi) $IrBr_2(CO)_n(PPh_3)_2(CH_3)$
3) Predict the formal oxidation state of the metal, d-electron count, total valence electrons (TVE) and number of M-M nonds for following molecules.
   a) $[CpCo(CO)_2(\mu\text{-}CO)]$
   b) (Cyclo-C_4H_4) $PdCl_2$
   c) $(\eta^3\text{-allyl})_2Ni$
   d) $CpMo(CO)_3$
   e) $Ru(PPh_3)_2Cl(NO)$
   f) Linear NO
   g) $Cp(\eta^6\text{-}C_6H_6)Mn$
   h) $Cp_2ZrH(CH_2\text{-}CH_2\text{-}CH_3)$
   i) $CpMn(CO)_3$
   j) Cp_2ZrCl_2
4) In the following complex $[M\ (\eta^3\text{-}(C_5H_5)(CO)_5]$ if M is a first row transition element, Prodict the stability of compound.
5) The complex [M (η6-C6H6)(CO)2] obeys the 18 electron rule and has one metal-metal (M-M) double bond. Predict the M and sketch the probable structure of complex.

6) Determine the number of M-M bonds in the following complexes with obeys the 18 electron rules.
7) The given complexes are thermodynamically stable. Comment on the nature of NO in these complexes. Which among them is expected to have a shorter Metal-Nitrogen bond? Give the reasons.

8) What are organometallic compounds? Give examples

9) Discuss the classification of organometallic compounds

10) How organometallic compounds are classified based on the types of ligands? Give examples

11) How organometallic compounds are classified based on the nature of bond? Give examples

12) What is hepticity of organometallic compounds?

13) Explain the differences between hapticity and denticity? Illustrate with example.

14) Disuses the nomenclature of organometallic compounds

15) Disuses the nomenclature of organometallic groups with multicenter bonding to carbon atoms

16) Disuses the nomenclature of bridging organometallic groups with multicenter bonding to carbon atoms.

17) Disuses the nomenclature of organometallic compound with unsaturated molecules and substituent groups

18) What are ocenes? Give examples

19) Explain the significance of 16 and 18 electron rules

20) Write a note on 18 electron rule

21) With example discuss the counting of electrons surrounding to central metal using
a) The ionic (charged) model
b) The covalent (neutral) model.

22) Write a note on electron donation of common ligands

23) Compare the ionic (charged) model and covalent (neutral) model and write the merits and demerits

24) Discuss briefly about counting of electrons and finding metal-metal bonds in organometallic compounds.

UNIT-6

Structure

6.1 Introduction

6.1 Organometallic compounds of main group elements

6.1.1 Properties of main group organometallics

6.2 Preparation of main group organometallic compounds

6.3 Organometallic compounds of group 1A metals

6.3.1 Structure of organolithium compounds

6.4 Organometallic compounds of group IIA metals

6.4.1 Organomegnesium compounds

6.4.2 Structure of oranomegnesium compound

6.4.3 Reactions of Grignard reagent

6.5 Organoberyllium compounds

6.5.1 Structure of organoberyllium compounds

6.6 Organometallic compounds of group IIIa metals

6.6.1 Synthesis of organoaluminium compounds

6.6.2 Structure of organoalumnium compounds

6.6.3 Reactions of organoaluminum compounds

6.8 key words

6.9 references for further study

6.10 Questions for self understanding

6.0 Objectives of the unit

After studying this unit you are able to

- Identity the organometallic compounds of main group elements
- Explain the different properties of main group organometallics
- Write the preparation of main group organometallic compounds
- Explain the structure of oranomegnesium compound
- Explain structure of organolithium compounds
- Explain structure of organoalumnium compounds

6.1 Introduction

The increase in emphasis on the chemistry of organometallic compounds has been one of the dominant changes in chemistry. Organometallic compounds have been known since the discovery of Zeise's salt in 1827 and the preparation of metal alkyls by sir Edward Frankland in 1849. But the discovery of ferrocene and Ziegler-Natta polymerization took the organometallic chemistry on a different level of interest

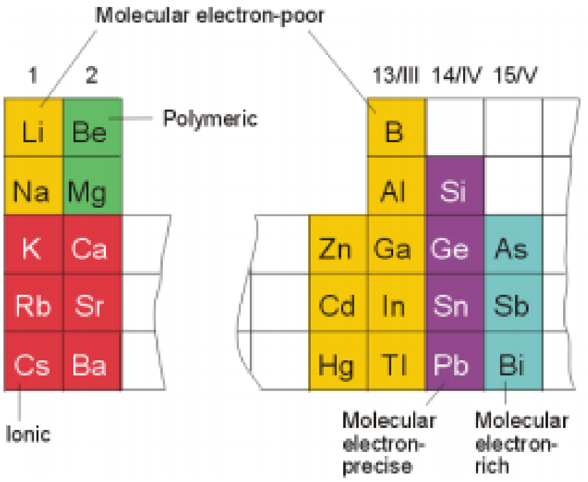
Although there are numerous organomettlaic compounds of all the elements in any specific group, those of one are generally more important. For example in group 1A the organometallic compounds of lithium are more numerous than those of sodium or postassium. Accordingly most of the discussion will focus on the one or two elements that have the most extensive organometallic chemistry.

6.1 Organometallic compounds of main group elements

The main group elements of the periodic table are those elements that belong to the "s" and "p" blocks. There is a strong conceptual link between the element hydrides and organometallic derivatives. In the language introduced by Roald Hoffman, a singly-bonded hydrocarbon anion group is “isolobal” with a hydride anion. Two fragments are isolobal when the number, symmetry properties, energies, shape, and electron occupancy of their outer orbitals are comparable.

An isolobal relationship between groups can be symbolized by a double-headed arrow with a ‘lobe’ below the arrow. Isolobal groups can be formally exchanged in a molecule without changing the overall bonding situation.

The table at right places the methyl derivatives of the main group elements into the periodic system. They are classified into ionic, electron poor, electron precise and electron rich. Some elements of main group do not form stable organometallic derivatives of primary longer chain alkyl groups because of instability towards β-elimination. For most elements methyl derivatives, the phenyl derivatives are known these are often quite stable and considerably less reactive.



6.1.1 Properties of main group organometallics

They tend to be oxidized easily. Many are flammable in air consequently they are reducing agents. They have nucleophilic character. The more electropositive the metal, the more carbanionic the organic group is. Thus alkyl lithium reagents and Grignard reagents are usually reacting as nucleophiles.

Electron-deficient organometallics are powerful Lewis acids and they form complexes with Lewis bases and for this reason, basic solvents such as ethers are extensively used to stabilize reactive organometallic reagents. An exception is n-butyl lithium, which is prepared and reacted in hexane solution. Amines, pyridine, and Me_2S are all used as stabilizing agents for reactive organometallics.

6.2 Preparation of main group organometallic compounds

Main group organometallic compounds vary widely in their properties and reactivities just as do the elements from which they are produced. These compounds may be lithium alkyls, Grignard reagents or organotin compounds. Accordingly there is no universal method for preparing the compounds. Some of the types of reactions that have widely employed are mentioned here.

Reaction of metals and alkyl halides

This technique is most appropriate when the metal is highly reactive. It should be keep in mind that even though a formula may be written as if the species is a monomer, several types of organometallic compounds are associated. Examples of this type of reactions are

$$2\ Li + C_4H_9Cl \rightarrow LiC_4H_9 + LiCl$$

$$4\ Al + 6\ C_2H_5Cl \rightarrow [Al(C_2H_5)_3]_2 + 2\ AlCl_3$$

$$2\ Na + C_6H_5Cl \rightarrow NaC_6H_5 + NaCl$$

The most important reaction of this type is that in which Grignard reagents are produced

$$RX + Mg \xrightarrow{\text{dry ether}} RMgX$$

The reactivity of the metal can be enhanced by its amalgamation with sodium

$$4\ Pb/Na\ amalgam + 4\ C_2H_5Cl \rightarrow 4\ NaCl + Pb(C_2H_5)_4$$

$$2\ Hg/Na\ amalgam + 2\ C_6H_5Br \rightarrow Hg(C_6H_5)_2 + 2\ NaBr$$

It is freq with a different metal. This principle is used for preparation for following reagent.

$$2\ Zn/Cu + 2\ C_2H_5I \rightarrow Zn(C_2H_5)_2 + ZnI_2 + 2\ Cu$$

Alkyl group transfer reactions

The reaction between a metal alkyl and a covalent halide of another element is sometimes made possible by the fact that transfer of the alkyl group leads to a crystalline product. An example of this type is the reaction between a sodium alkyl and a covalent halide such as $SiCl_4$

$$4\ NaC_6H_5 + SiCl_4 \rightarrow Si(C_6H_5)_4 + 4\ NaCl$$

The formation of sodium chloride is a strong driving force in this reaction. The hard-soft interaction principle is conveniently worked in this case because of the favorable interaction of Na^+ with Cl^-. Other examples of this type of reaction are as follows

$$2Al(C_2H_5)_3 + 3\ ZnCl_2 \rightarrow 3\ Zn(C_2H_5)_2 + 2\ AlCl_3$$

$$2\ Al(C_2H_5)_3 + 3\ Cd(C_2H_3O_2)_2 \rightarrow 3\ Cd(C_2H_5)_2 + 2\ Al(C_2H_3O_2)_3$$

Because mercury is easily reduced dialkylmercury compounds are useful reagents for preparing a large number of alkyls of other metals by group transfer reaction. This is illustrated by the following example.

$$3\ Hg(C_2H_5)_2 + 2\ Ga \rightarrow 2\ Ga(C_2H_5)_3 + 3\ Hg$$

$$Hg(CH_3)_2 + Be \rightarrow Be(CH_3)_2 + Hg$$

$$3\ HgR_2 + 2\ Al \rightarrow 2\ AlR_3 + 3\ Hg$$

$$Na(excess) + HgR_2 \rightarrow 2\ NaR + Hg$$

Reaction of a Grignard reagent with metal halides

Although Grignard reagents generally react by transferring alkyl groups, this is one of the most widely applicable way in which metal metals are obtained. The following are typical reactions of this type.

$$3\ C_6H_5MgBr + SbCl_3 \rightarrow Sb(C_6H_5)_3 + 3\ MgBrCl$$

$$2\ CH_3MgCl + HgCl_2 \rightarrow Hg(CH_3)_2 + 2\ MgCl_2$$

$$2\ C_2H_5MgBr + CdCl_2 \rightarrow Cd(C_2H_5)_2 + 2\ MgBrCl$$

Reactions of an olefin with hydrogen and a metal

In some cases it is possible to synthesize a metal alkyl directly from the metal. An important case of this type is

$$2\ Al + 3\ H_2 + 6\ C_2H_4 \rightarrow 2\ Al(C_2H_5)_3$$

$$2\ CH_3Cl + Si \xrightarrow[300\,°C]{Cu} (CH_3)_2SiCl_2$$

6.3 Organometallic compounds of group 1A metals

The metals in Group IA (Li, Na, K, Rb, Cs, and Fr) are called the alkali metals because they all form hydroxides (such as NaOH) that were once known as alkalies.

The electron configurations of the alkali metals are characterized by a single valence electron. As a result, the chemistry of these elements is dominated by their tendency to lose an electron to form positively charged ions (Li^+, Na^+, K^+).

There is an enormous organometallic chemistry associated with the group IA metals particularly lithium and sodium. Lithium alkyls can be prepared by the reaction of the metal and alkyl halides For this process suitable solvents include hydrocarbons, benzene and ether, lithium alkyls are also be prepared by the reactions of metal with mercury alkyl.

$$2\ Li + RX \rightarrow LiR + LiX$$

Compounds of lithium with aryl groups can be prepared by the reaction of butyllithium with an aryl halide

$$2LiC_4H_9 + ArX \rightarrow LiAr + BuX$$

Lithium reacts with acetylene in liquid ammonia solution to give the mono and dilithium acetylides, LiC≡CH and LiC≡CLi, with the evolution of hydrogen, which illustrates the slight acidity of acetylene. One commercial use of LiC ≡CH is in one step of the synthesis of vitamin A.

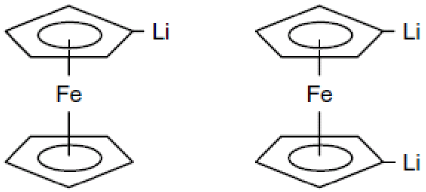
Lithium alkyls are used in processes such as polymerization and in transfer of alkyl groups in many types of reactions. Some examples are the following

$$BCl_3 + 3\ LiR \rightarrow 3\ LiCl + BR_3$$

$$SnCl_4 + LiR \rightarrow LiCl + SnCl_3R \text{ (and other products)}$$

$$3\ CO + 2\ LiR \rightarrow 2\ LiCO + R_2CO$$

One of the most interesting organometallic compounds of a transition metal is ferrocene). Butyllithium reacts with ferrocene to produce the mono and dilithiated compounds that have the following structures



These reactive compounds are useful for preparing numerous other derivatives of ferrocene. As would be expected, lithium alkyls react with any trace of moisture. These extremely reactive compounds are also spontaneously flammable in air.

$$LiR + H_2O \rightarrow LiOH + RH$$

6.3.1 Structure of organolithium compounds

A great deal of effort has been directed to determining the structures of lithium alkyls. It has been determined that in hydrocarbon solutions the dominant species is a hexamer when the alkyl groups are small. In the solid phase, the structure is body-centered cubic with the $(LiCH_3)_4$ units at each lattice site. Each unit is a tetramer in which the four lithium atoms reside at the corners of a tetrahedron and the methyl groups are located above the centers of the triangular faces. The carbon atoms of the alkyl groups are bound to the three lithium atoms at the corners of the triangle. This structure is shown in Figure 1.

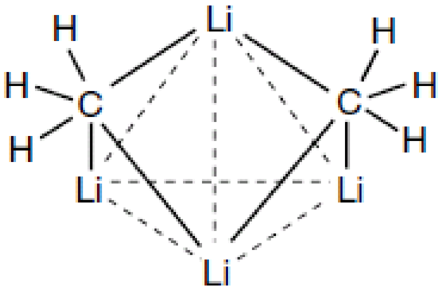


Figure 1: The structure of the tetramer of methyllithium. Only two of the four methyl groups are shown

Bonding of the methyl group to three lithium atoms involves an sp^3 orbital on the methyl group simultaneously overlapping three orbitals (they may be 2s or hybrids of 2s and 2p orbitals) on the Li atoms. This can be shown as illustrated in Figure 2.

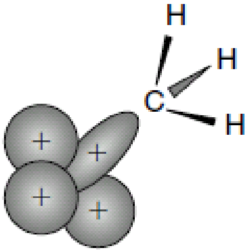


Figure 2: Orbital overlap leading to the formation of a two electron three center bond in $[Li(CH_3)_4]$.

Although this picture of the bonding in methyllithium is generally adequate, it is probably an oversimplification of the true situation. Three-center two-electron bonds exist in numerous types of compounds (such as diborane), but it may be in this case that there is also some weak interaction between the lithium atoms

6.4 Organometallic compounds of group IIA metals

Alkaline earth metals are the six elements forming Group IIa in the Periodic Table: beryllium (Be), magnesium (Mg), Calcium (Ca), Barium (Ba), Strontium (Sr), and Radium (Ra). Their oxides are basic (alkaline), especially when combined with water

Although some organometallic compounds of calcium, barium, and strontium are known, they are far less important than those of beryllium and magnesium.

6.4.1 Organomegnesium compounds

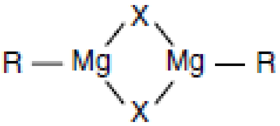
One of the most important discoveries in organometallic chemistry is made in 1900 by Victor Grignard. His work has enormous importance because it led to the chemistry of a class of compounds that are now referred to as Grignard reagents, and they are prepared by the reaction of magnesium with an alkyl halide in a solution of dry ether. The process can be represented by the equation

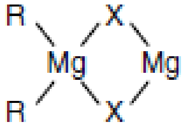
6.4.2 Structure of oranomegnesium compound

Evaporation of the excess ether results in the formation of an “ etherate ” containing the solvent bonded to the magnesium. The formula for this product is represented as $RMgX_2.2R_2$ O, and the structure is a distorted tetrahedron. However, even in solution “ RMgX ” exists as aggregates with the dimer being the dominant species. The equilibriumcan involve other species, and the composition depends on the nature of the alkyl group, which can function as an electron pair donor; the association is hindered by complex formation between the solvent and RMgX.

$$2\ RMgX \rightleftharpoons (RMgX)_2$$

$$2\ RMgX \rightleftharpoons MgR_2 + MgX_2$$





$$2\ RMgX \rightleftharpoons RMg^+ + RMgX_2^-$$

6.4.3 Reactions of Grignard reagent

The reactivity of the Grignard reagents varies with the nature of the halogen as followa I > Br > Cl, it is also found that the alkyl compounds are more reactive than the aryl compounds. One of their important types of Grignard reagent is that lengthening a carbon chain in the reaction with a primary alcohol

$$ROH + CH_3MgBr \rightarrow RCH_3 + Mg(OH)Br$$

When a secondary alcohol is used the reaction can be shown as

$$RR'HCOH + CH_3MgBr \rightarrow RR'HC\text{–}CH_3 + Mg(OH)Br$$

Grignard reagents react with formaldehyde to give primary alcohol

The reaction of ($HCHO + RMgCl \rightarrow RCH_2OH + MgCl_2$ are a carboxylic acid

$$CO_2 + RMgX \xrightarrow{H_2O} RCOOH + MgXOH$$

Reactions of RMgX with RCHO leads to a secondary alcohol while the reaction with an ester, RCOOR' gives a tertiary alcohol after acidifying the products of the initial reactions. The reaction of a Grignard reagent with sulfur is complex, but it can be represented by the equation

$$48\ RMgX + 7\ S_8 \xrightarrow{H^+} 16\ RSH + 16\ R_2S + 24\ MgS + 24\ MgX_2$$

6.5 Organoberyllium compounds

In addition to magnesium, there is an extensive chemistry of organoberyllium compounds. The alkyl compounds are obtained most conveniently by the reaction of beryllium chloride with a Grignard reagent.

$$BeCl_2 + 2\ CH_3MgCl \rightarrow Be(CH_3)_2 + 2\ MgCl_2$$

Because beryllium is a Lewis acid, it remains attached to the solvent in the reaction (ether). Beryllium alkyls can also be produced by the reaction of the chloride with a lithium alkyl or by reaction with a dialkylmercury

$$BeCl_2 + 2\ LiCH_3 \rightarrow Be(CH_3)_2 + 2\ LiCl$$

$$Be + Hg(CH_3)_2 \rightarrow Be(CH_3)_2 + Hg$$

Beryllium alkyls are spontaneously flammable in air and produced aberyllium oxide. Dimethylberyllium reacts explosively with water, and some of its other properties resemble those of trimethylaluminum because the metals have a strong diagonal relationship that relates to their similar charge-to-size ratios.

6.5.1 Structure of organoberyllium compounds

The structure of dimethylberyllium is similar to that of trimethylaluminum except for the fact that the beryllium compound forms chains, whereas the aluminum compound forms dimers. Dimethylberyllium has the structure shown in Figure 3. The bridges involve an orbital on the methyl groups overlapping an orbital (best regarded as sp^3) on the beryllium atoms to give two-electron three-center bonds. Note that the bond angle Be –C– Be is unusually small. Because beryllium is a Lewis acid, the polymeric $[Be(CH_3)_2]_n$ is separated when a Lewis base is added and adducts form. For example, with phosphine the reaction is

$$[Be(CH_3)_2]_n + 2n\ PH_3 \rightarrow [(H_3P)_2Be(CH_3)_2]$$

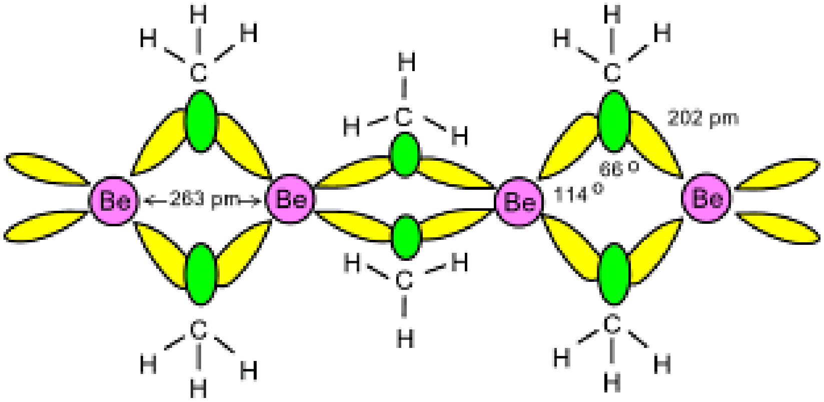
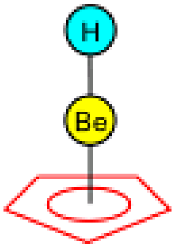


Figure 3: The structure of dimethylberyllium

An unusual type of organometallic compound of beryllium is that in which it is coordinated to a cyclopentadienyl ring



In addition to the hydrogen compound, others have been prepared that contain a halogen or a methyl group

6.6 Organometallic compounds of group IIIa metals

The organometallic chemistry of members of group IIIA is relatively much less important than that of aluminum. There is an extensive organic chemistry of aluminum, for example, triethylaluminum is used in the Ziegler-Natta process for polymerization of alkenes.

As a result of extensive dimerization, aluminum alkyls have the general formula $[AlR_3]_2$. It is interesting that $B(CH_3)_3$ does not undergo molecular association and it has a boiling point of -26°C. Although it does not react with water, $B(CH_3)_3$ is spontaneously flammable in air. Trimethylgallium (b.p. 55.7°C) and triethylgallium (b.p. 143°C) show almost no tendency to form dimers under most conditions. In contrast to the behavior of trimethylboron and

$$[Al(CH_3)_3]_2 + 12\ O_2 \rightarrow 6\ CO_2 + 9\ H_2O + Al_2O_3$$

trimethylgallium, the boiling point of trimethylaluminum, which exists as $[Al(CH_3)_3]_2$, is 126°C and that of $[Al(C_2H_5)_3]$ is 186.6°C, even though the aluminum compounds have lower molecular weights. Aluminum alkyls react with many substances and are spontaneously flammable in air

6.6.1 Synthesis of organoaluminium compounds

Aluminum alkyls can be prepared in several ways. In one process, aluminum reacts with alkyl halides to produce $R_3Al_2Cl_3$ (known as the sesquichloride),

$$2\ Al + 3\ RCl \rightarrow R_3Al_2Cl_3$$

The product undergoes a redistribution to produce R_4AlCl_2 and R_2AlCl_4. The reaction of aluminum with HgR_2 results in transfer of alkyl groups

$$3\ HgR_2 + 2\ Al \rightarrow [AlR_3]_2 + 3\ Hg$$

Mixed alkyl hydrides can be prepared by the reaction

$$2\ Al + 3\ H_2 + 4\ AlR_3 \rightarrow 6\ AlR_2H$$

The Al– H bond is sufficiently reactive that alkenes give an insertion reaction

$$R_2AlH + C_2H_4 \rightarrow R_2AlC_2H_5$$

6.6.2 Structure of organoalumnium compounds

The aluminum alkyls dimerize extensively. The structure of $[Al(CH_3)_3]_2$ is shown in Figure 4 . In this case, an orbital on the methyl group overlaps with orbitals on two aluminum atoms to give three-center two-electron bonds. Although there are four bonds to each aluminum atom, the orientation of the bonds deviates considerably from typical tetrahedral cases. Because the distance between the aluminum atoms is relatively short, there may be some partial bonding between them.

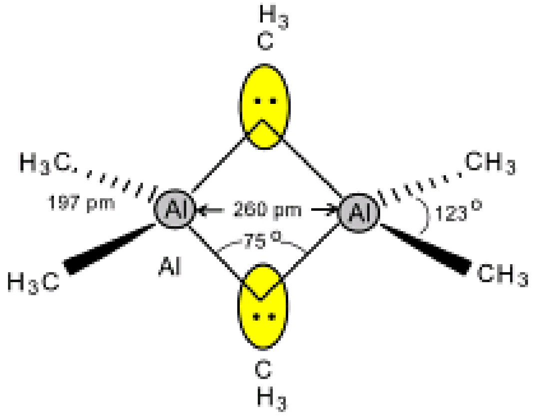


Figure 4: The structure of trimethylaluminum

Note that the angle between the bonds to the two terminal CH_3 groups is quite close to that corresponding to sp^2 hybrid orbitals on the aluminum atoms. This would leave p orbitals available to form a σ bond between the aluminum atoms. It should also be noted that the $Al–C_t$ bonds are considerably shorter than the $Al–C_b$ bonds (b and t signify bridged and terminal, respectively).

6.6.3 Reactions of organoaluminum compounds

Aluminum alkyls undergo many reactions that are typical of covalent metal compounds. Compounds containing methyl, ethyl, and propyl groups ignite spontaneously in air. The reactions with water take place with explosive violence when the alkyl groups contain four or fewer carbon atoms.

$$Al(C_2H_5)_3 + 3\ H_2O \rightarrow Al(OH)_3 + 3\ C_2H_6$$

The reaction of an aluminum alkyl with an alcohol is also violent, but it can be mediated by carrying out the reaction in a dilute solution of an inert solvent.

$$AlR_3 + 3\ R'OH \rightarrow Al(OR')_3 + 3\ RH$$

Aluminum alkyls also undergo reactions in which they function by transferring alkyl groups

$$2\ Al(C_2H_5)_3 + 3\ ZnCl_2 \rightarrow Zn(C_2H_5)_2 + 2\ AlCl_3$$

Reactions of this type can be carried out with other metal halides

6.7 Summary of the units

Main group metals (Groups 1, 2, 3, 4) make large variety of M-C bonds. The main group M-C bonds are extremely reactive e.g. organolithium, Grignard reagents, etc… LiMe spontaneously inflammable in air, $(BeMe_2)_n$ catches fire in dry CO also. The strength of M-C bonds decreases down a group hence the formation of $M\text{-}R_n$ compounds becomes more endothermic. One reason is the increasing disparity in energies of the C and M frontier orbitals. Main feature to consider is the polarity of the M-C bond i.e. the electronegativity difference. All organometallic compounds are thermodynamically unstable with respect to reaction with O_2 and H_2O but some are kinetically stable (inert) usually due to high activation energy. Organolithium species tend to oligomerise in solution and in the solid state. Methyllithium is actually cubic body-centered $(LiCH_3)_4$ units.

6.8 key words

Main group elements; organolithium compounds; organomegnisium compounds; Grignard reagent; organoberilium compounds; organoaluminium compounds.

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6.10 Questions for self understanding

1) From what you know about the nature of $B(CH_3)_3$ and $Al(CH_3)_3$, what would be a reasonable value for the solubility parameter for $B(CH_3)_3$? Explain your answer.

2) Speculate on the degree of aggregation of C_2H_5MgCl in the solvents dioxane and benzene, assuming that the concentration is the same in both solvents. If there would be a difference, explain why.

3) Write complete equations to show the following reactions

   (a) The reaction of butyllithium with cadmium chloride

   (b) The reaction of ethyl magnesium bromide with acetaldehyde

   (c) The reaction of methyllithium with bromine

   (d) The reaction of triethylaluminum with methanol

   (e) The reaction of triethylaluminum with ethane

4) Write complete equations for the following processes:

   (a) The preparation of butyl lithium

   (b) The reaction of butyl lithium with water

   (c) Dissolving of beryllium in sodium hydroxide

   (d) Preparation of phenyl sodium

   (e) Reaction between ethanol and lithium hydride

5) Complete and balance the following

   a) $LiC_2H_5 + PBr_3 \rightarrow$

   (b) $CH_3MgBr + SiCl_4 \rightarrow$

(c) $NaC_6H_5 + GeCl_4 \rightarrow$

(d) $LiC_4H_9 + CH_3COCl \rightarrow$

(e) $Mg(C_5H_5)_2 + MnCl_2 \rightarrow$

6) Discuss the synthesis and properties of organometallic compounds of main group elements

7) Write a note on organometallic compounds of group 1A metals

8) Discuss the structure of organolithium compounds

9) Discuss the use of organolithium compounds in organic synthesis

10) Write a note on organometallic compounds of group IIA metals

11) What are organomegnesium compounds? Discuss the different methods of their synthesis

12) Discuss the structure of oranomegnesium compound

13) Explain the reactions of Grignard reagent with different organic compounds

14) Write a note on organoberyllium compounds

15) Discuss the structure of organoberyllium compounds

16) Write a note on organometallic compounds of group IIIa metals

17) Explain the different methods of synthesis of organoaluminium compounds

18) Discuss the structure of organoalumnium compounds

19) Explain the reactions of organoaluminum compounds

UNIT-7

Structure

7.0 Objectives of the unit

7.1 Introduction

7.2 Compounds with metal-carbon multiple bonds

7.3 Alkylidene Complexes

7.4 Differences between Fischer and Schrock alkylidene complex

7.5 Structure

7.6 Bonding

7.7 Spectroscopic Features

7.8 Synthesis

7.9Reactions

7.10 Alkylidynes

7.11 Structure

7.12 Bonding

7.13 Classification of the Alkylidyne Ligands

7.14 Synthesis

7.15 Reactions of Carbynes

7.16 Trans Influence of Carbyne Ligands

7.17 Alkyne Metathesis

7.18 Role of carbene and carbine complexes in organic synthesis

7.19 Summary of the unit

7.20 Key words

7.21 References for further studies

7.22 Questions for self understanding

7.0 Objectives of the unit

After studying this unit you are able to

- Identify the organometallic compounds with metal-carbon multiple bonds
- Explain the synthesis and structure of Alkylidene Complexes
- Explain the synthesis and structure of Alkylidynes
- Recognize the differences between Fischer and Schrock alkylidene complex
- Explain the Classification of the Alkylidyne Ligands
- Explain the role of carbene and carbine complexes in organic synthesis

7.1 Introduction

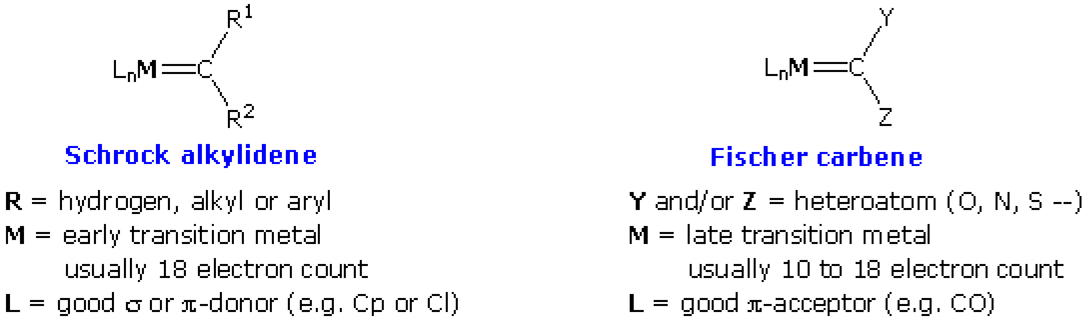
So far we have looked at the donor atoms that provide one pair of electrons to a metal. In chelation, two donor atoms on the same ligand can provide a total of four electrons to the metal. In addition, some ligands can form double (or triple) bonds to a metal, providing four or even six electrons from one donor atom. Oxides may be the most common multiply-bonded ligand. In biology, attention has turned to the role of iron and copper oxides as active intermediates in a variety of enzymes that use molecular oxygen to oxidize substrates. A second important class of metal-ligand multiple bonds is the carbenes. Carbenes contain metal-carbon double bonds. They are often divided into two classes: Fischer carbenes and Schrock carbenes or alkylidenes. After a discovery of compounds with metal-carbon double bond, metal-carbon triple bonded systems provide a logical synthetic challenge. As with carbine complexes there are M≡C-R stabilized by carbonyls and related ligands and complexes of metals in high oxidation states (d^0)

7.2 Compounds with metal-carbon multiple bonds

The metal alkyl complexes are characterized by presence of one σ-bond between metal and carbon atom of the ligand. The compounds with metal-carbon double bonds are first discovered in 1964 by E.O. Fisher. They are two types $(CO)_5M=C(R)(OR')$ where M = Cr, Mo, W) and they are formally derived from the coordination of a carbine :CR2 to a metal centre. They have also called as carbine complexes. The metal is in a low oxidation state and the bonding of the arbene ligand is reminiccent to that of CO. A second group of M=C compounds are with a highly oxidized metal centre and are discovered by R.R. Schrock and described as alkylidine complexes. The formation of M-C multiple bonds is propounced for metals which are also known to foem M-M multiple bonds readily. For example Ta, Cr, Mo, W, and Re. Mononuclear alkylidene complexes of elements ot Fe, Co, and Ni triads are much less common.state

7.3 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



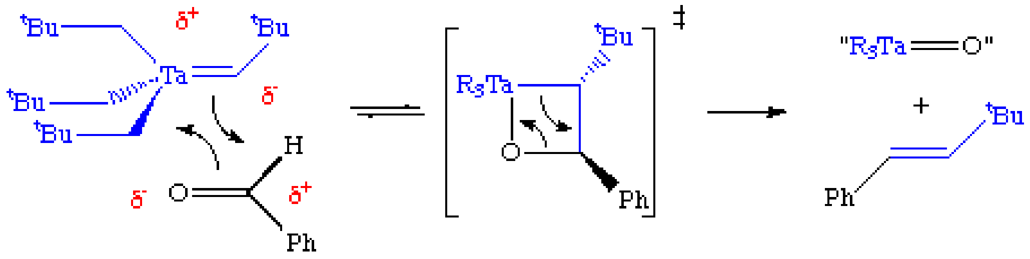
R = hydrogen, alkyl or aryl
M = early transition metal
usually 18 electron count
L = good σ or π-donor (e.g. Cp or Cl)

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)

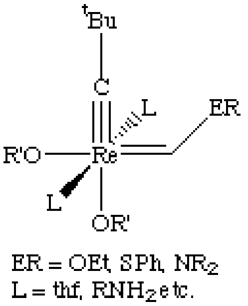
Figure 1: Structure of Fischer and Schrock carbenes

Alkylidene ligands possess a metal-carbon double bond and are closely related to Fischer carbenes. Alkylidene ligands (A) usually have one or two alkyl substituents on the alpha carbon atom unlike Fischer carbenes (B) which usually have a heteroatom substituent on the alpha carbon atom. These are sometimes called Schrock carbenes or Schrock alkylidenes in honor of R. R. Schrock who discovered the first example, Ta(CH-t-Bu)(CH_2-t-Bu)$_3$, in the 1970's.

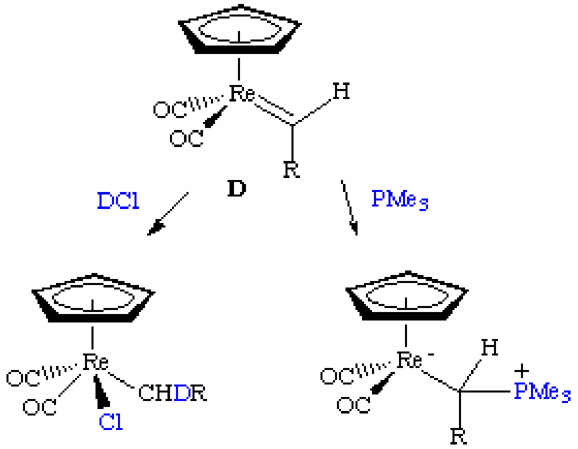
Schrock carbenes are typically found on high oxidation state metal complexes (early to mid transition metals). This polarizes the metal-carbon double bond so that a partial negative charge can be assigned to the alpha carbon atom. Hence, Schrock alkylidenes tend to be nucleophilic at the alpha carbon, an example of which is their Wittig-like reaction with ketones and aldehydes. As one moves to the right in the periodic table, the oxophilicity (propensity for binding to oxygen) of the transition metal decreases, making this reaction less favored.



Schrock alkylidene complexes are usually electron deficient or contain strong pi-donating ligands. Contrast this to Fischer carbenes which are typically low valent, low oxidation state complexes containing strong pi-acid (acceptor) ligands such as CO. However, the distinction is sometimes blurred. There are now examples of high oxidation state heteroatom-substituted alkylidenes that do not react like carbenes (C) as well as carbenes that are both electrophilic and nucleophilic (D).



C



7.4 Differences between Fischer and Schrock alkylidene complex

Fischer Carbenes	**Schrock Alkylidenes**
Nucleophillic attacks at carbon atom of carbene (carbon is electron deficient)	Electrophillic attacks at carbon atom of alkylidene (carbon is electron-rich)
Electrophillic attacks on metal center (metal is more electron-rich, often d^6 18 e-system)	Nucleophillic attacks on metal center (metal is electron-deficient, usually d^2 or d^0 16 or 14 e^- count)
Carbene is *stabilized* by heteroatom groups that can p-bond to it. Likes NR_2, SR, OR, or Ph groups.	Alkylidene is *destabilized* by heteroatom groups that can p-bond to it. Strongly prefers H or simple alkyl groups.
Later transition metals favored, especially with d6 counts (carbene as neutral 2e-donor ligand)	Early transition metals favored, especially with d^0 centers (alkylidene as dianionic $4e^-$ donor)

7.5 Structure

The carbene moiety is a neutral, two electron donor ligand. Most carbenes in free state are unstable but get stabilized on coordination to metals. The coordinated carbene has plane triangular geometry the carbon being sp^2 hybridized. The Fisher carbene organometallics may be described by the resonating structure shown figure 2.

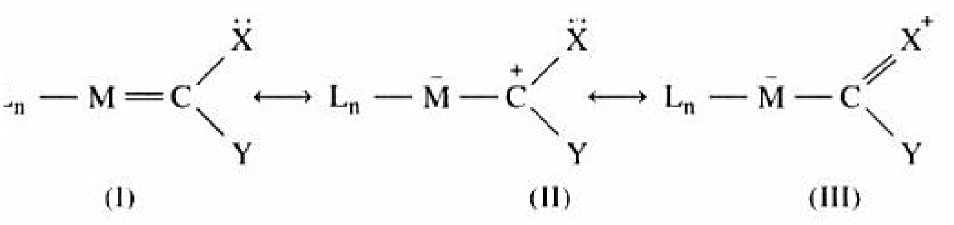


Figure 2: Resonance structure of a Fischer carbine complex

The directive force for the creation of structure (I-III) arises due to several factors. The auxiliary ligands, L are π acceptors and tend to draw the metal electron cloud towards themselves (structure I) the metal in turn draws the π electrons of the double bond towards itself by way of electromeric effect.

As a result the metal acquires a negative charge while the carbon acquires a positive charge (structure II). The heteroatom X donates its p electron density to the vacant p orbital of carbon, forming double bond, C=X (structure III).

Each of the structure (I-III) shown in Fig explain one or the other structural aspect of the carbene complexes and hence is important in its own right. The metal-carbon bond length in such complexes is shorter than the metal-carbon single bond distance, reflecting the importance of structure (I). molecular orbital calculations suggest that the carbene carbon carries a positive charge, indicating the importance of structure (II). Due to the presence of positive charge on the carbon atom of the ligand, the Fischer caebenes are electrophilic in nature. The bond between carbon and heteroatom (X) is shorter than the C-X bond distance. Thus the carbon-heteroatom bond has double bond character as shown in structure(III). Moreover there is a barrier to C-X bond rotation and this too brings home the importance of structure (III).

The Schrock carbene organometallics may be described by the resonating structures shown in figure 3.

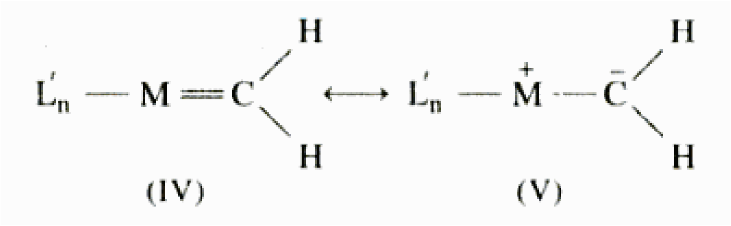
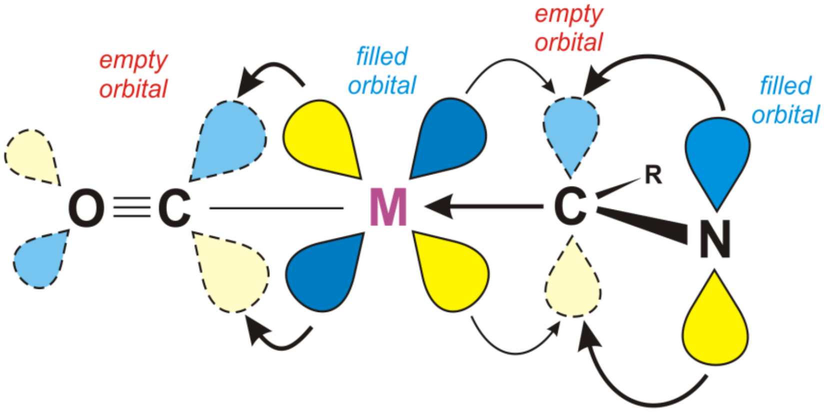


Figure 3: Resonance structure of a Fischer carbine complex

The auxiliary ligands L_n are non- π accepting in nature. Therefore these do not draw the electron density of the metal towards themselves to a very large extent. The π electron cloud of the metal carbon double bond, therefore shifts towards the carbon atom of the carbene ligand. The carbon acquires a negative charge (structure V) and for this reason, the Schrock caebenes are nucleophilic in nature. Moreover the substituentrs opn the carbon atom of carbene are non-π donating types. Therefore unlike Fisher carbenes there is a single bond between the carbene carbon and the substitutent group.

7.6 Bonding

The carbene carbon is sp^2 hybridised. One of the sp^2 hybrid orbitals overlap with the orbital of the substituent X. while the second sp^2 hybrid orbital overlap with the orbital of substituent Y. the third sp^2 hybrid orbital having a lone pair of electrons in case of Fischer carbenes. In addition there is a vacant $2p_z$ orbital on the carbon atom of the carbene lignad. The electronic arrangement in a Fischer carbene is shown figure 4.

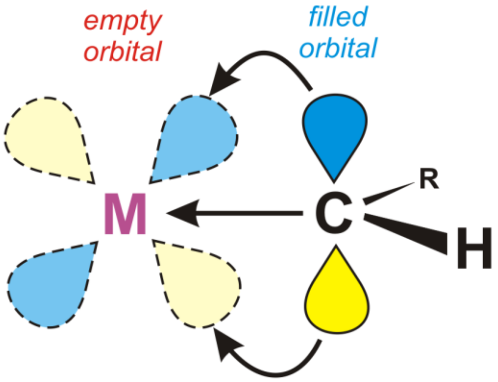


competition for π-backbonding from the metal and the lone pair orbital(s) on the functional group(s) to the carbene empty orbital (N and S the best, then O, Ph, and other π-donating or lone pair containing groups)

Figure 4: Bonding in Fischer carbenes

The non-bonded sp^2 hybrid orbital of carbene overlap with a suitable hybrid orbital of the metal. In this combination the lone pair in the sp^2 hybrid orbital of the ligand is donated to the metal resulting in the formation of σ bond. A filled d orbital of the metal then overlap with the empty P_Z orbital of carbon. In this combination the metal back donates its electron to the caebene ligand, resulting in the formation of a π bond. Thus the metal- carbon linkage acquires a double character.

In case of Schrock carbenes, the non bonding sp^2 hybrid oprbital and the vacant $2p_z$ orbital on carbon contain one electron each. This arrangement is shown in figure 5.



both the sp^2 and p orbitals on the alkylidene are filled (thus the -2 charge) and both can strongly donate to the empty orbitals on the early transition metal (only one empty d orbital is shown)

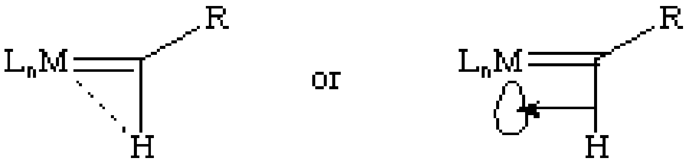
Figure 4: Bonding in Schrock carbenes

These two partially filled carbene orbital overlap with two suitable metal orbitals each of which has one electron.

7.7 Spectroscopic Features

In the ^1H NMR, the alkylidene proton is typically found in the range of 5 to 15 ppm although shifts as low as -2 ppm have been reported. In the ^{13}C NMR, the alpha carbon is typically found in the range of 220 to 260 ppm although values ranging from 200 to 325 ppm have been observed. The JCH for the alpha carbon varies widely for reasons discussed below.

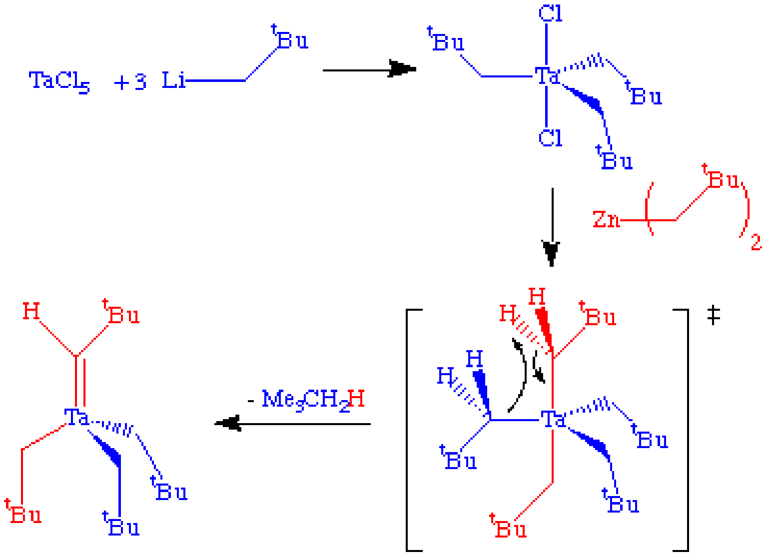
An unusual aspect of alkylidene complexes is a distortion wherein the M-C-C angle is typically much greater than the 120 degrees predicted by simple sp^2 hybridization. Typical M-C-C angles are in the range of 160 to 170 degrees! This distortion has been attributed to an agostic interaction of the alpha proton with the metal as shown below. It can be thought of as the M-H electron pair donating into a vacant d-orbital on the metal center and is most common for electron-deficient complexes (especially for tantalum alkylidenes)



Spectroscopic evidence for this distortion can be found in JCH. A typical sp^2 carbon atom has a JCH of 160 Hz. In these distorted alkylidenes, JCHis typically around 120 Hz and can be as low as 90 Hz when the distortion is severe. At this point, the alkylidene looks more like an alkylidyne-hydride complex than an alkylidene. Infrared spectroscopy will often show a C-H stretch of reduced frequency for the alpha proton (2600 cm-1 is typical). In cases where the site for the agostic interaction is blocked, JCH values of 150-160 Hz are typically found and the alkylidene is relatively undistorted.

7.8 Synthesis

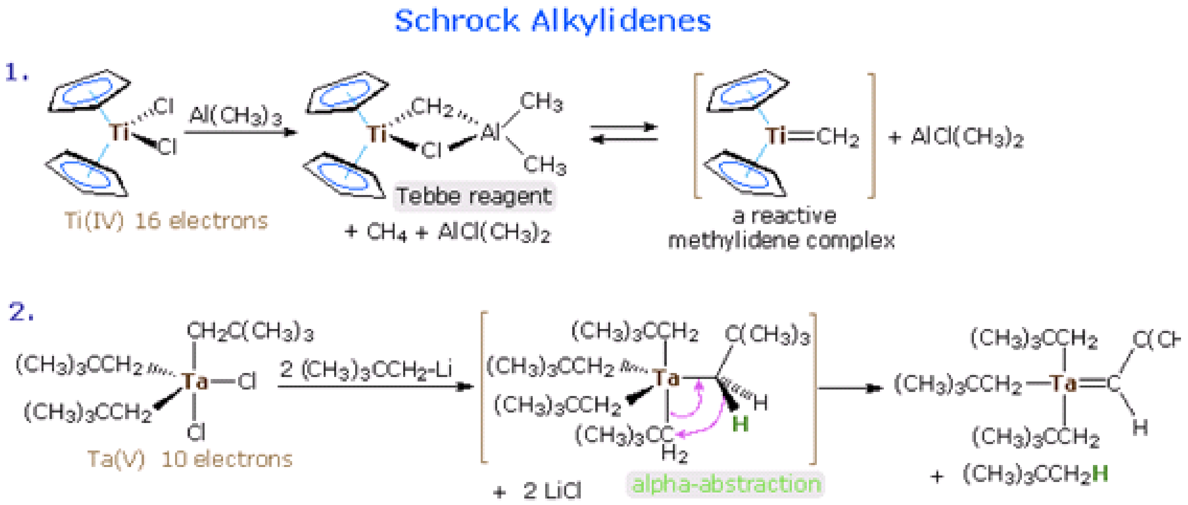
Alkylidenes can be made through many different ways. One of the most common is an alpha-abstraction reaction. This methodology was used to prepare the first example of an alkylidene.

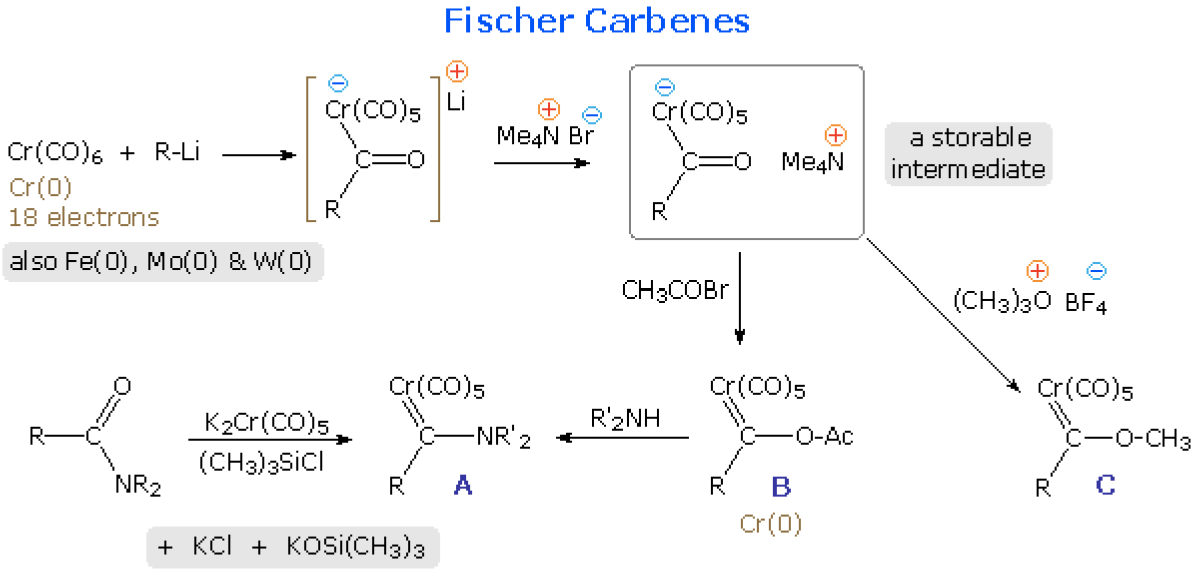


The putative intermediate in this reaction is pentakis(neopentyl)tantalum(V), but this has not been observed spectroscopically. Other methods have also been used such as reduction of alkyl halide complexes and transfer of an alkylidene from a phosphorane or another metal complex (For example, Grubbs has used these methods to synthesize his olefin metathesis catalysts).

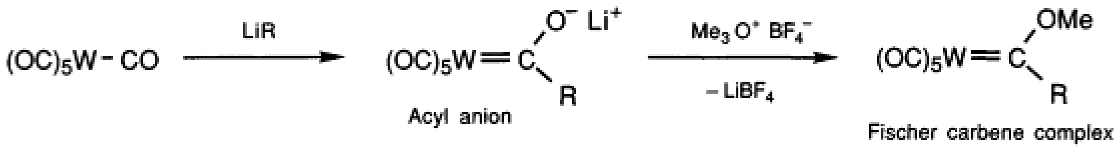
Reaction of a Wittig reagent ($R_3P{=}CR'_2$) with a metal oxo complex is not a common reaction; apparently the metal-oxo bond strength is too favorable.

The preparation of typical alkylidene complexes of both types are shown in the following diagram, beginning with Schrock alkylidenes. The second diagrams display the Fischer carbene

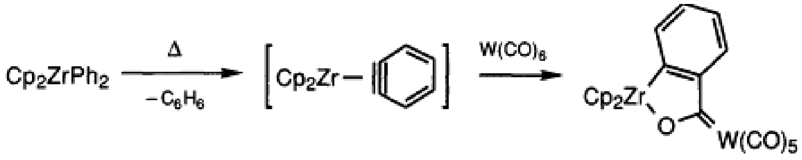




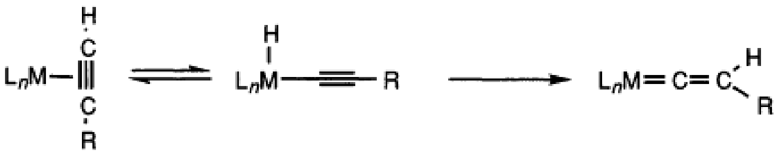
From Metal carbonyls



This is the most widely applied preparative method. Isocyanide complexes react similarly even with weaker nucleophiles such as secondary amines or alcohols.



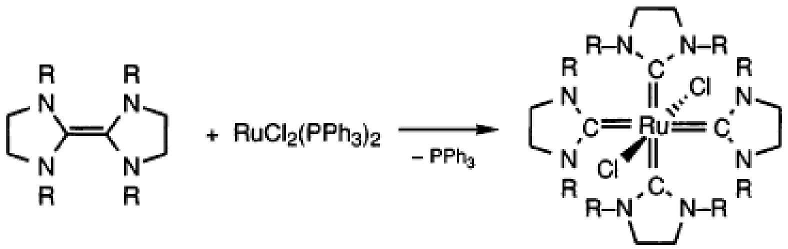
By rearrangements of coordinated ligands



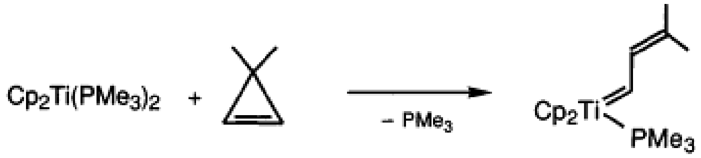
L_nM = $CpMn(CO)_2$, $CpRe(CO)_2$, $CpML_2^+$ (M = Fe, Ru, Os), CpRhL

From activated olefins

Very electraon rich olefins such as tetrakis(dialkylamino) substituted ethylene are able to react with noble metals under C=C bond cleavage. Ru and Pt complexes of this type are known



Stained cyclic olefins can be ring opened to give alkylidine compounds.

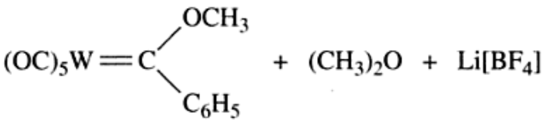


The following are some of the important methods for synthesis of Fisher and Schrock carbene complexes.

1. Substitution reactions

$W(CO)_6 + C_6H_5^- Li^+ \rightarrow Li^+[W(CO)_5(COC_6H_5)]^-$

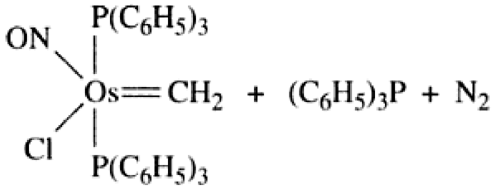
$Li^+[W(CO)_5 (COC_6H_5)]^- + [(CH_3)_3O]BF_4 \longrightarrow$



$$(OC)_5W{=}C\begin{matrix}OCH_3\\ C_6H_5\end{matrix} + (CH_3)_2O + Li[BF_4]$$

2. Interception of free carbene.

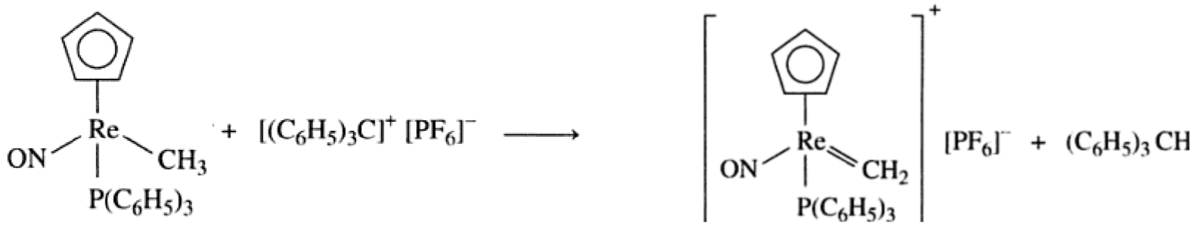
$$[Os\{(C_6H_5)_3P\}_3Cl(NO)] + CH_2N_2 \longrightarrow$$



3. α-Deprotonation of metal-alkyl groups.

$$[Ta(\eta^5\text{–}C_5H_5)_2(CH_3)_2]^+ + NaOCH_3 \longrightarrow$$
$$[Ta(\eta^5\text{–}C_5H_5)_2(CH_3)(CH_2)] + CH_3OH + Na^+$$

4. Hybride ion abstraction from metal-alkyl groups.

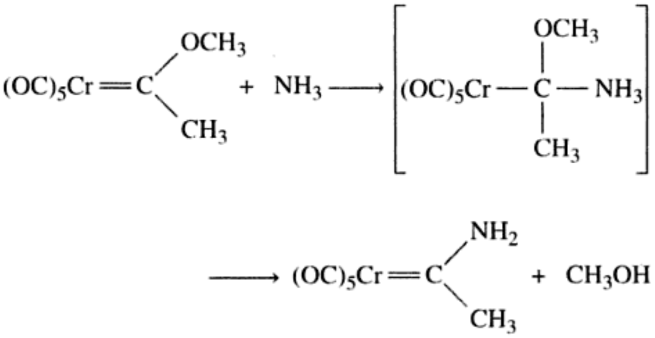


7.9Reactions

The important reactions of carbene complexes are described below

1. Nucleophilic reactions

   The electrophilic nature of Fisher carbenes prompts their reaction with nucleophiles.

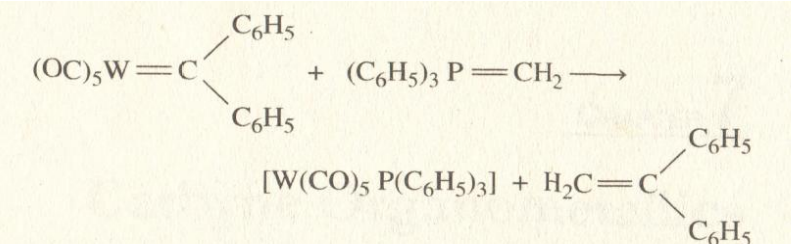


2. Electrophilic reaction

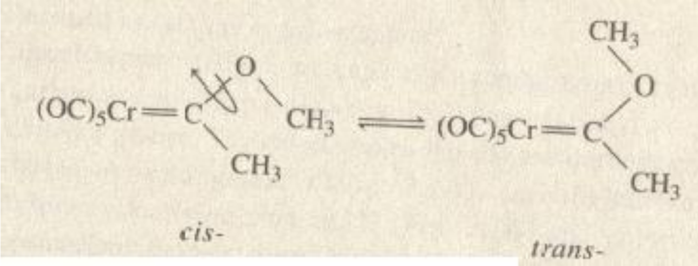
   The nucleophilic nature of Schrock carbenes prompts their reaction with electrophiles.

$$[Ta(\eta^5\text{-}C_5H_5)_2(CH_3)(CH_2)] + (CH_3)_3Al \longrightarrow$$
$$[Ta(\eta^5\text{-}C_5H_5)_2(CH_3)(CH_2\text{–}Al(CH_3)_3]$$

3. Wittig-type reaction



The complex pentacarbonyl[methoxy(methyl)carbene] chromium(0) exists as a mixture of cis and trans conformations at 233K. as the temperature rises the rotation about carbon-oxygen bond becomes more feasible.

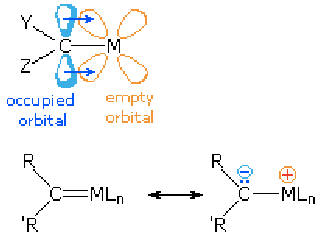


At room temperature the complex exits exclusively ion trans- form.

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.

Schrock Alkylidene Complexes

Bonding Descriptions

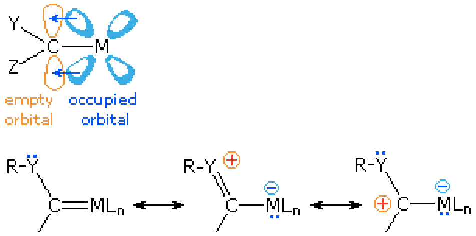


Properties

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

Bonding Descriptions



Properties

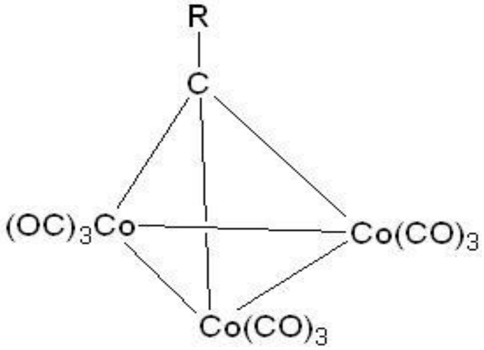
Metal:	electron rich attacked by electrophiles stabilized by electron accepting ligands
Carbon:	carbocation-like attacked by nucleophiles stabilized by heteroatom substituents
C=M:	relatively weak low rotational barrier

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).

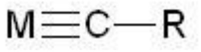
7.10 Alkylidynes

Alkylidynes are also called as carbynes. Alkylidynes are characterized by a metal to carbon triple bond, making them part of organometallic chemistry. The metal to carbon triple bond makes them similar to the more studied alkylidene, which is merely a metal to carbon double bond. As with alkylidenes, alkylidynes are also classified as Fischer and Schrock. These ligands are useful synthetically and can be made in a variety of ways. They are considered to be soft ligands especially the Fischer type.

Carbynes can bond to a metal terminally through the carbon, or can bond with up to 3 metals forming a capped-like structure



Capped Bonding Mode



Terminal Bonding Mode

Alkylidyne ligands are linear with the carbon having sp hybridization. The length of the metal to carbon bond varies between 1.65 and 1.90 Ǻ depending on the metal.

The ligand are generally a combination of halogens and carbonyls, phosphine derivatives, cyclopenradienyl or other coordinating groups. Typical examples include tetracarbonylchloro (methylcarbyne) tungsten(I) , carbonylchloro[2-methylphenyl)carbyne] osmium(I) and chloro(η^5- cyclopentadienyl)(ethylcarbyne)bis(trimethylphoisphine)tantalum(II)

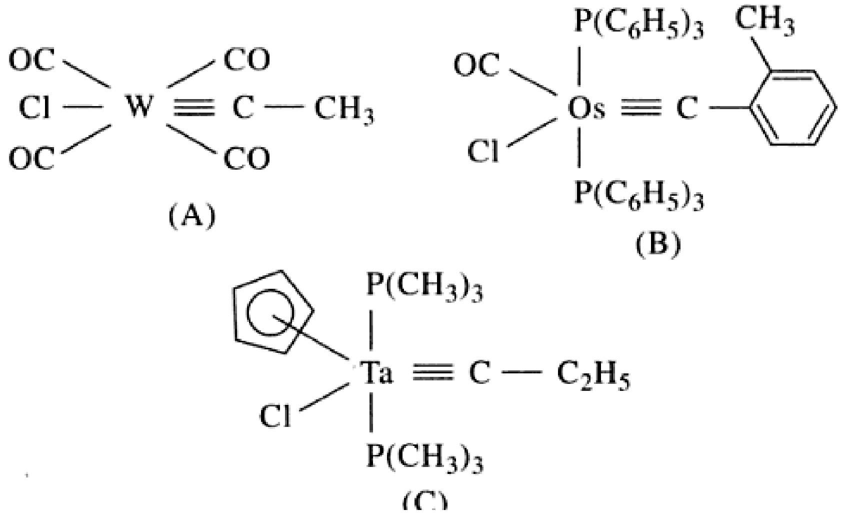
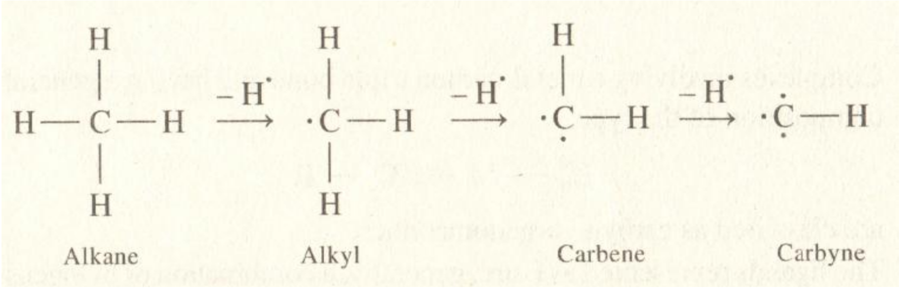


Figure 5 : Structure of some carbyne complexes

7.11 Structure

Alkylidyne can act as a terminal bonding structure, a capped bonding structure, and something right in between, a bridging structure. The carbyne ligand may be visualized as being formed by successively removing three hydrogen radicals (H) from methane

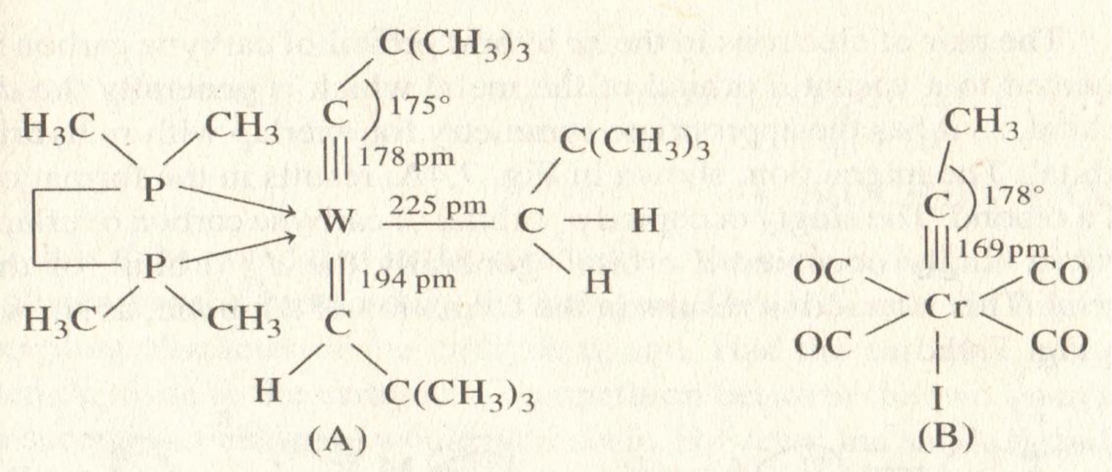


Accordingly the carbyne group may be considered as

1. A neutral (HC) three electron donor or
2. A positively charged (HC^+) two electron donor

As has already been stated we shall follow the first criterion while describing structure and bonding in carbyne complexes.

The metal- carbon bond distance in carbyne(M≡C-R) is shorter than that in carbenes (M = CHR) or in alkyls ($M\text{-}CH_2R$). this is best demonstrated in [1,2-bis[(dimethylphosphno)ethane]} (t-butylcarbene) (t-butylcarbyne)(neopentyl)tungsten(I) complex the structure of which is depicted in fig . this organometrallic compound involves a tungsten- carbon single bond (W-C). a tungsten- carbon souble bond (W=C) and a tungsten-carbon triple bond (W≡C). their bond lengths are 255 pm, 2194 pm and 178 pm respectively. Thus the metal carbyne bond length is the shortest, consistent with a bond order of three. In case of tetracarbonyliodo (methylcarbyne) chromium (I) complex the corresponding bond length is even smaller (169 pm).



The M≡C-R bond axis is expected to be linear. However small deviation form perfectly linear geometry do occur frequently. Fro example in {1,2-bis[(dimethylphosphano)ethane]} (t-butylcarbene)-(t-butylcarbyne)(neopentyl)(tungsten(I) complex the W≡C-C$(CH_3)_3$ bond angle is 175^0 while in tetracarbonyliodo(methylcarbyne)chromium (I) complex the Cr≡C-C-CH_3 bond angle is 178^0 . these deviation are attributed to intermolecular interactions and packing effects in the crystal lattice.

7.12 Bonding

The model based on the complementarily of σ and π bonds, which we had used to explain the bonding in olefin organimetallics may be rationalized for metal-carbyne bonding as well. The carbon of the M≡C-R unit is sp hybridized. Of the two sp hybrid orbitals one in used for forming a bond with R functional group (alkyl or aryl) while the other houses two paired up electrons. In addition there are two degenerate p orbitals on carbon-the p_x and p_y orbitals. One of these contains a single unpaired electrons while the second is vacant. The orientation of orbitals around carbyne carbon is shown in figure 6.

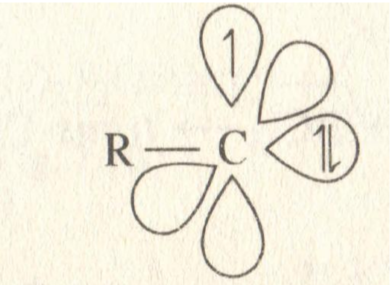


Figure 6: orientation of orbitals on carbine carbon

The pair of electrons in the sp hybrid orbital of carbyne carbon is donated to a vacant d orbital of the metal which is generally the d_z^2 orbital, as it has the appropriate symmetry for overlap with sp hybrid orbital. The interaction shown in fig resulting in the formation of a σ bond. The singly occupied p_y orbital of carbyne carbon overlaps with a singly occupied d orbital of the metal. This interaction results in the formation of a π bond, as shown in figure 7.

Finally the vacant p_x orbital of the carbon overlaps with the filled d_{xz} orbital of the metal. The electron pair in the d_{xy} orbital is donated to the vacant p_x orbital resulting in the formation opf the second π bond

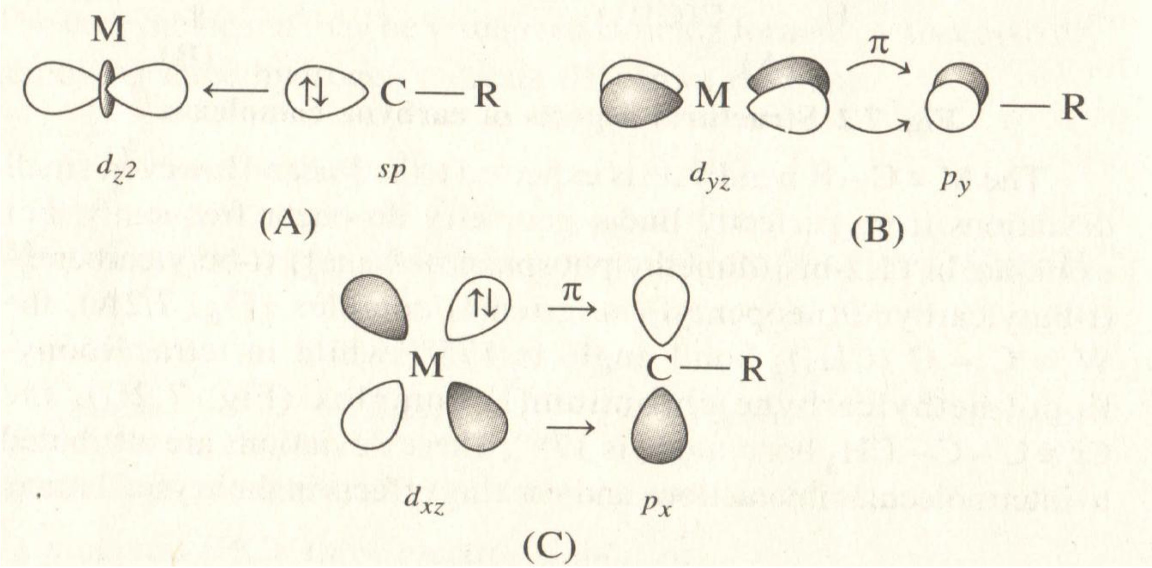


Figure 8: Bonding in metal-carbyne complexes

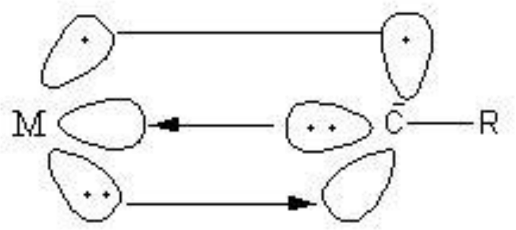
7.13 Classification of the Alkylidyne Ligands

There are two main classifications of the alkylidynes; like alkylidenes, there are Fischer- and Schrock-type alkylidynes

Fischer Carbynes

Fischer carbynes were first made in 1973 by Fischer himself. He produced them via electrophilic abstraction of methoxide from a methoxide methyl carbene. Fischer carbynes are classified by being able to be stabilized by heteroatoms and found typically bonded with low oxidation state transition metals (usually later transition metals). Fischer carbynes usually other have π–acceptor ligands on the metal making the carbyne essentially electrophilic.

A Fischer carbyne can be looked at as a doublet carbyne in the way it bonds. The lone pair of electrons on the carbon atom covalently bond to the metal; it also forms a covalent π bond with the metal, and has an empty orbital ready to accept electrons from a filled metal orbital. Therefore the ligand is an LX type ligand using the covalent method:

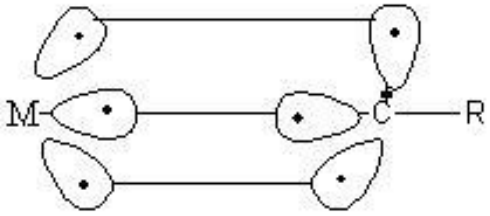


Fischer, or doublet type carbyne

The carbyne complexes that are formed are usually 18 electrons because the CR bond is mostly covalent. Tungsten is a very common metal used to make Fischer carbynes.

Schrock Carbynes

Schrock carbynes have no heteroatoms, and are found with high oxidation state metals (early transition metals). The other ligands on the metal are usually strong σ-donors, which makes the carbon essentially nucleophilic. The Schrock carbyne is an example of a quartet carbyne. It forms 3 covalent bonds to the metal because it has 3 unpaired electrons. The ligand is of the X_3 type. They usually form complexes with less than 18 electrons and the metals tend to be d^0.

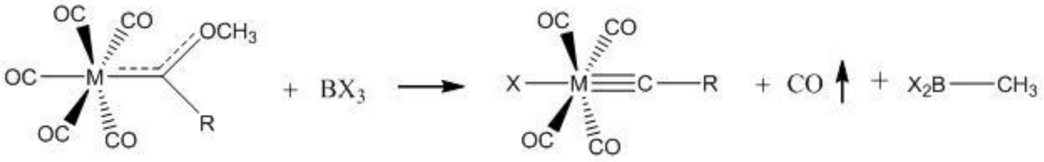


Schrock, or quartet type carbyne

A very common metal for Schrock carbynes is Molybdenum. Schrock Carbynes can be made from reducing a Fischer carbyne or by α-elimination.

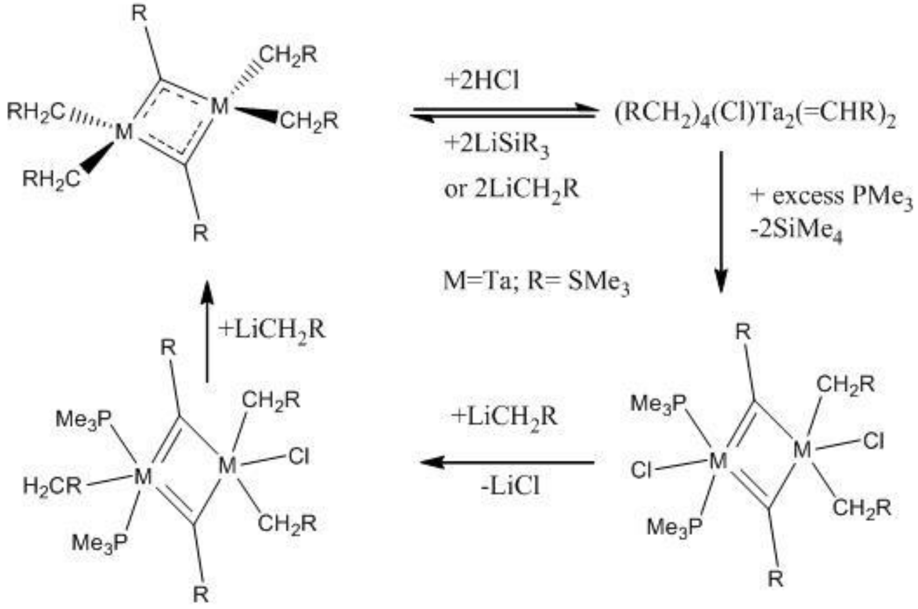
7.14 Synthesis

Ernst Otto Fischer et al. were the first to discover the possibility of the terminal alkylidyne



M = Cr, Mo, W; R= CH_3, C_6H_5; X = CL, Br, I

A plausible reaction cycle is illustrated below, it was experimentally determined and analyzed by X. Liu et al



7.15 Reactions of Carbynes

Various Reactions of carbynes have been extensively studied such as nucleophilic attack at the carbon centre, electrophilic attack at the carbyne carbon, substitution of the spectator ligands by nucleophilic attack at the metal centre, oxidation and reduction at the metal centre, modification or substitution of the ligand on the carbyne or transfer of the carbyne ligands.

Nucleophilic Addition

NucleophilicAddition is common for Fischer carbyne complexes that carry a δ^+ charge on either the central metal atom or at the carbyne carbon atom.

Nucleophilic Addition at Carbyne C

In cationic carbynes, the addition of the nucleophile will proceed exclusively at the carbyne carbon. This is because the LUMO is located on the carbyne C and it has a sufficiently large gap between this molecular orbital and the next highest LUMO located on the metal centre. There are many examples of nucleophiles that show this type of reactivity (mostly anionic) such as: phosphines, Grignards, halogens, CN^-, OR^-, and SR^- .

General Reaction Scheme

$$L_nM{\equiv}CR^+ + Nu^- \rightarrow L_nM{=}C(R)(Nu)$$

Example

$$Cp(CO)_2M({\equiv}C\text{-}Ph)^+ + Nu^- \rightarrow Cp(CO)_2M[{=}C(Nu)(Ph)]$$

$$M = Mn, Re$$

$$Nu = F, Cl, Br, I, C_{10}H_7Se, Bu$$

Electrophilic Addition

Electrophilic Addition is possible in Schrock-type carbynes which carry a δ^- charge on the central metal atom.

Reactions with Protonic Acids

H^+ can add to electron-rich carbyne ligands to yield a hydridocarbene compound. The final product will differ depending on the strength of the acid. For a strong acid, the H^+ will add to the carbyne carbon to produce a carbene; and the counter ion will add to the metal centre producing a neutral product. However, if the acid is has a weakly coordinating anion, then a cationic hydriodcarbene will be produced.

Example 1, using a strong acid

$$Cp(CO)_2W({\equiv}CR) + HCl \rightarrow Cp(CO)_2(I)W[{=}C(H)(R)]$$

Example 2, using an acid with a weakly coordinating anion

$$(Cl)(L_4)W{\equiv}C\text{-}R + CF_3SO_3H \rightarrow [(Cl)(L_4)W{=}(CHR)]^+[CF_3SO_3]^-$$

Reactions with Lewis Acids

Similar to addition of H^+, other Lewis acids (such as $AlMe_3$) can add to a metal-carbyne complex.

Coupling of Carbyne Ligands

Coupling reactions in carbyne complexes leads to either an alkyne or alkyne complex1. Coupling can be induced in carbyne complexes by three methods:

1. Reductive coupling – occurs when a dimeric carbene is formed with reduction at both metal centres.
2. Oxidative coupling – occurs when a dimeric carbene is formed with oxidation at both metal centres.
3. Coupling at Terminal Carbynes – terminal carbynes will combine to form a bridging ligand between the two metal centres.

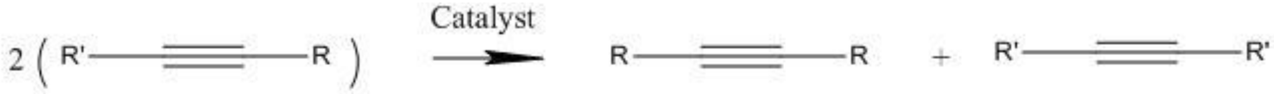
7.16 Trans Influence of Carbyne Ligands

Carbynes are σ-donor π-donor type ligands like nitrides, imido, oxide and sulphide type ligands. It is difficult to fully generalize the strength of the structural trans effect and kinetic trans effect because it can be effected by other ligands present and relies heavily on the oxidation state and d-count of the central metal atom. However, it can be shown that in most cases that carbynes have very strong structural trans effect due to the σ-donation and π-donation from the ligand which destabilizes the bond trans to the carbyne. This effect can be utilized in the conversion of Fischer carbenes to carbynes. Fischer-type carbenes are characterized by the prescense of π-donor ligands (CO is a good example) and low oxidation state mid-to-late transition metals. At the transition state (the cation-anion species), the substitution of the new X ligand does not happen at the position trans to the CO ligand, but instead at the position trans to the carbyne ligand. This indicates the high trans effect of the carbyne ligand.

7.17 Alkyne Metathesis

There are two different types of catalysis. The first is homogeneous catalysis, in which the catalyst is the same phase as the reactants being catalyzed. The second is heterogeneous catalysis, in which the catalyst is not in the same phase as the reactants being catalyzed.

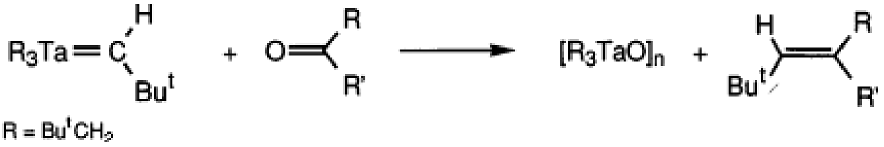
A metathesis reaction has the general scheme



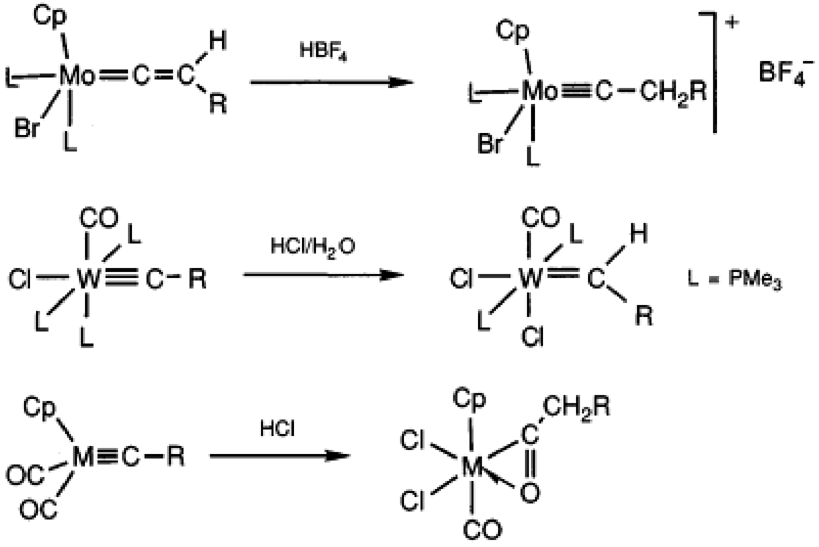
When using either heterogeneous or homogenous catalysts, a carbyne is an involved intermediate. These intermediates are proven by using EPR studies.

7.18 Role of carbene and carbine complexes in organic synthesis

Alkylidene complexes LnM=CR_2 have a formal similarity with ketones O=CR_2 and with phosphorus ylids $R_3P=CR_2$ (Wittig reagents) and indeed similar chemical behavior has been observed. Alkyliden complexes free of heteroatoms and ligands such as CO are the most reactive due to the oxophilic character of early transition metals they readily react with carbonyl compounds under carbine transfer to give olefins

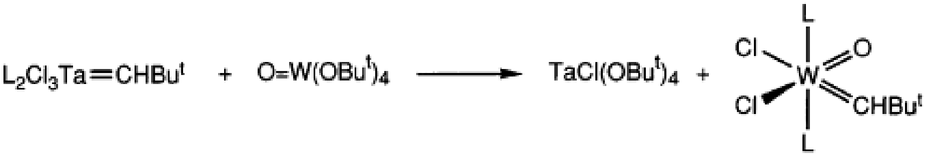


Alkylidenes and alkylidynes rect readily with Bornsted acids. This is a vcomon method for the interconvrsion of Alkylidenes and alkylidynes, for the transformation in to alkyls and of vinylidine complexes into alkyldynes



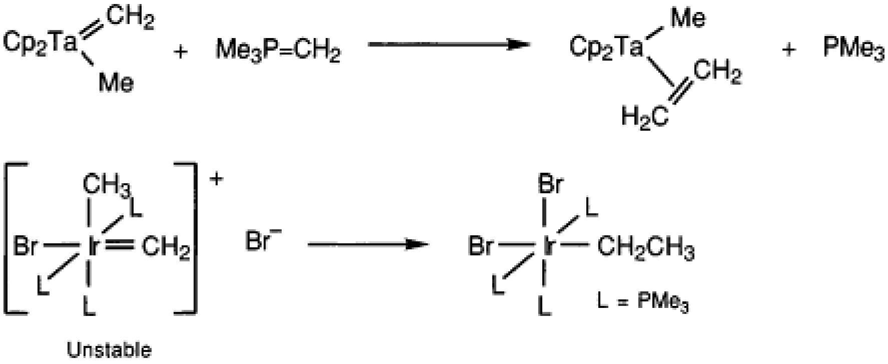
Alkylidene transfer

Alkylidene ligands have been shown to undergo intermolecular exchange reactions



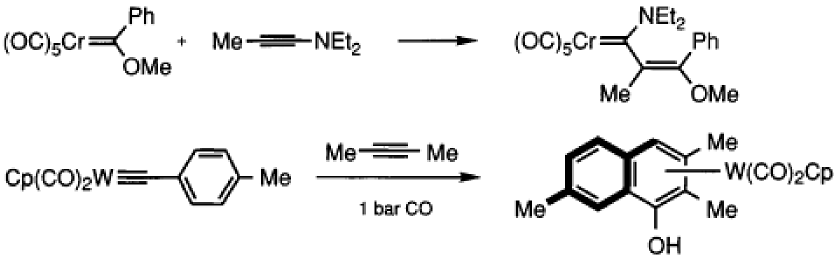
Akylidene-alkyl coupling reactions

Alkylidnes ligands ay react with nucleophiles either intra or intrmolecularly with formation of new C-C bonds. Reactions of this kind have been used as models for the formation of hydrocarbons from unstable surface species during the reaction of CO

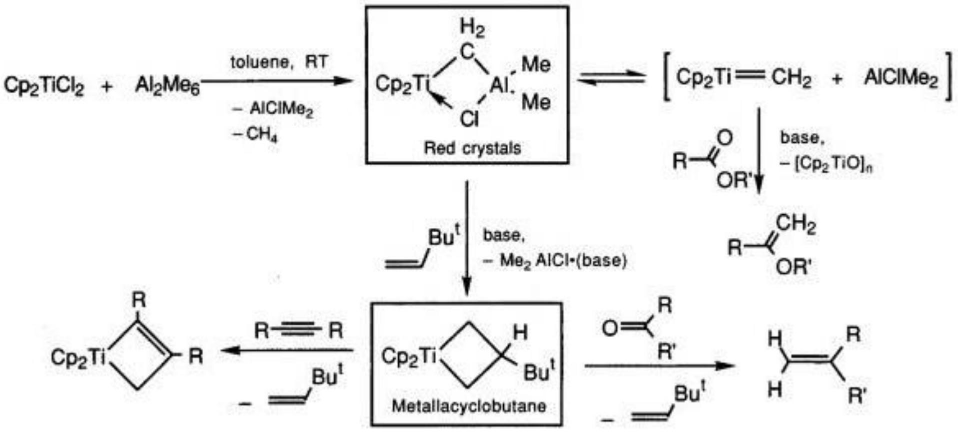


Reactions with alkenes and alkyes

The reactivity of alkylidenes with unsaturated organic molecules is widely exploried in the synthesis. The insertion and cyclization reactions with alkynes are typical examples.



A compound with particular widespread synthetic application is the *Tebbe reagent* which can be regarded as the protected form of the unstable ($Cp_2Ti{=}CH_2$). Many of its reations are complementary to Wittig reagents.

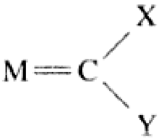


Alkylidene and alkylidynes characteristics reactions are the ability to form metallacycles. This tendency is exploited in organic synthesis, in olefin metathesis and for the formation of alkylidene-bridged theteronuclear metal clusters.

The development of meta; alkylidene chemistry was the fundmantal importance for the olefin metathesis

7.19 Summary of the unit

Compounds containing a formal metal-carbon double bond are classified as carbene organometallics. Their general composition may be represented as



When X or Y are the substituents having heteroatoms such as oxygen, nitrogen or halogens the compounds are called Fisher carbene complexs. When X and Y are hydrogen or hydrocarbon groups, the compounds are called Schrock carbene complexes or alkylidene complexes. Pentacarbonyl(methoxyphenylcarbene)tungsten(0) is an example of a Fisher complex. (η^5-cyclopentadienyl)methyltantalum(III) is example of a schrock carbene complex. In addition complexes with carbene ligands having cumulated double bonds are also known. Dicarbonyl (η^5-cyclopentadienyl) (dimethylvinylidene) manganese(II) and dicarbonyl(η^5-cyclopentadienyl)(dimethylallenylidene) manganese(II) are example of such complexes. Cyclocarbene ligands too form oprganometallic derivatives. Pentacarbonyl(diphenyl[propylidene) chromium(0) being a representative example. Complexes involving a metal-carbon triple bond having a general composition of the type L_n-M≡C-R are classified as carbyne organomerallics. The metal- carbon bond distance in carbyne(M≡C-R) is shorter than that in carbenes (M = CHR) or in alkyls (M-CH_2R). The M≡C-R bond axis is expected to be linear. However small deviation form perfectly linear geometry do occur frequently. The carbon of the M≡C-R unit is sp hybridized. Of the two sp hybrid orbitals one in used for forming a bond with R functional group (alkyl or aryl) while the other houses two paired up electrons. In addition there are two degenerate p orbitals on carbon-the p_x and p_y orbitals. One of these contains a single unpaired electron while the second is vacant.

7.20 Key words

Metal-carbon multiple bonds; Alkylidene complexes; Alkylidynes complexes; Fischer and Schrock alkylidene; Alkyne Metathesis

7.21 References for further studies

1) Organometallics: Complexes with transition metal-carbon [sigma]-bonds, Volume 1; Manfred Bochmann; *Oxford University Press*, **1994**.

2) Organomettalic Chemistry; Sodhi G.S.; *Ane Books Pvt Ltd*, **2009**.

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7.22 Questions for self understanding

1) Is the existence of geometrical isomerism possibilities in carbene complexes?

2) Why are Fisher carbenes generally less reactive than Schrock carbenes?

3) Write a note on compounds with metal-carbon multiple bonds

4) What are Alkylidene complexes? Give examples

5) What are Fischer and Schrock alkylidene complex?

6) Write the differences between Fischer and Schrock alkylidene complex

7) Explain the structure alkylidene complex

8) Discuss the bonding modes of lignads in alkylidene complex

9) Discuss the spectroscopic features alkylidene complex

10) Discuss the synthesis alkylidene complex

11) Discuss the reactions of alkylidene complex

12) What are alkylidynes complexes? Give examples?

13) Explain the structure of alkylidynes complexes

14) Discuss the bonding in alkylidynes complexes

15) Write a note on classification of the alkylidyne ligands

16) Explain the different methods of Synthesis of alkylidynes complexes

17) Discuss the reactions of carbynes

18) Explain the trans influence of carbyne cigands

19) Discuss the alkyne Metathesis

20) Write a note on role of carbene and carbine complexes in organic synthesis

UNIT-8

Structure

8.0 Objectives of the unit
8.2 Transition metal-π complexes
8.3 Olefin Organometallics
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8.3.2 Bonding
8.3.4 Synthesis
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8.4 Alkyne Organometallics
8.4.1 Structures
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8.5.1 Structure
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8.6 Cyclopentadienyl Organometallics
8.6.1 Ferrocene
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8.7 Arene Organometallics
8.7.1 Di(η^6-benzene)chromium(0)
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8.8 Allyl Organometallics
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8.12 Questions for self understanding

8.0 Objectives of the unit

After studying this unit you are able to

- Identify the different transition metal-π complexes
- Explain the synthesis, structure and reactivity of olefin organometallics
- Explain the synthesis, structure and reactivity of alkyne organometallics
- Explain the synthesis, structure and reactivity of cyclopentadienyl organometallics
- Explain the synthesis, structure and reactivity of cyclobutadienyl organometallics
- Explain the synthesis, structure and reactivity allyl organometallics
- Explain the synthesis, structure and reactivity arene organometallics

8.1 Introduction

The interaction of transition metals with unsaturated molecules has led to fundamental insights in the nature of the chemical bond which, in turn, has provided the basis of important present-day applications such as transition metal mediated synthesis or homogeneous and heterogeneous catalysis. This slim volume outlines the chemistry and discusses the bonding in of some of the most important classes of organometallic compounds: the complexes of transition metals with π-ligands such as alkenes, alkynes, arenes, and cyclopentadienyl and allyl ligands. The material covered follows on from Organometallics I which covers the chemistry of complexes with metal-carbon delta-bonds. Synthetic and reactivity aspects of each class of compounds are illustrated with pertinent examples from the recent chemical literature. Highlighted excursions relate the fundamental chemistry to current synthetic or catalytic applications.

8.2 Transition metal-π complexes

There are many complexes formed between transition metals in relatively low oxidation sates with unsaturated organic molecules. One such class of compounds is the metal -π organic complexes. These complexes are characterized by their chemical and thermal stability relative to complexes containing metal-carbon σ bonds, their ability to undergo facile intramolecular rearrangements and with a few exceptions by their diamagnetism. The diamagnetic character of metal-π-complexes can be readily understood by postulating an inert gas electronic configuration for the metal atom. The assumption there is that the number of electrona in the metal (n)d, (n+1) s, and (n+1)p orbitals including contribution from the ligands will total 18.

The metal π-organic complexes have characteristic geometries which distinguish them as a class from other organometallic compounds. Specifically in metal π-organic complexes the meta; atom is out of the molecular plane of planar ligands or is displaced from axis of linear lignads. These geometic features have their origin in a type of metal-lignad bonding that is unique to metal π-organic complexes. For simplicity organometallic π-complexes may be classified with respect to four categories depending on both their geomrtric and bonding properties. They are sandwich complexes, oleifin complexes, acetylene complexes and π-allyl complexes.

A description of the bonding of π-conjugated ligands to a transition metal which involves a synergic process with donation of electrons from the filled π-orbital or lone electron pair orbital of the ligand into an empty orbital of the metal (donor–acceptor bond), together with release (back donation) of electrons from an nd orbital of the metal (which is of π-symmetry with respect to the metal–ligand axis) into the empty π*- antibonding orbital of the ligand. The electrons are taken from a d-orbital of the metal, and usually placed into an antibounding molecular orbital of the ligand, which causes the bond order of that ligand to decrease.

8.3 Olefin Organometallics

The first transition metal olefin complex to be synthesized was Zeise's salt, potassium trichloro (η^2-ethylene) palatinate (II) 1-water $K[Pt(\eta^2\text{-}C_2H_4)]\ H_2O$.

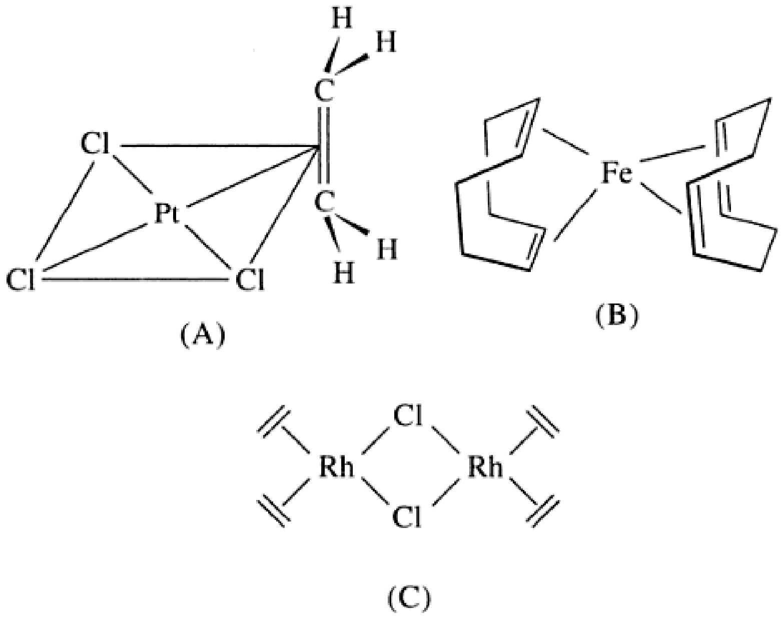
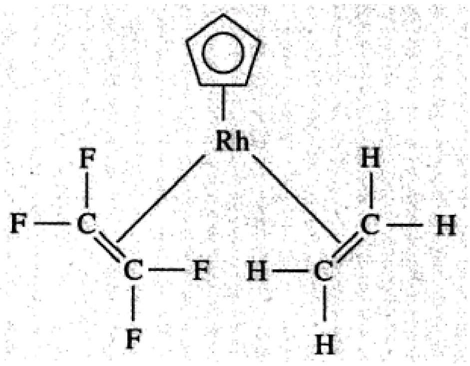


Figure 1 structure of some olefin complexes

Thereafter a wide array of olefin complexes were isolated and charactersized. Some of these, especially those belonging to group 3-5 of periodic table, were not very stable. However the complexes of later transition metals, including those of copper (I), silver(I) and Gold(I) were and presented interesting structural features. The dihapto olefin moiety is coordinated to the metal through the double bondComplexes in which the olefin ligand is chelating are also known Bis (η^4- cycloocta-1, 5-diene) iron (0) is an example of sunch a complex it structure is depicted in fig . dimeric bridging complexes of olefins too exits. In these the alkene ligands occupy terminal positions, for example, bis(η^2- ethylene) rhodium (I)-μ-dichloro- bis (η^2-ethylene)rhodium(I). it is a chloro- bridged complex involving terminal ethylene ligands and its structure is shown in figure 1.

The complex (η^5-cyclopentadienyl) (ethylene) (tetrafluoro-ethylene) rhodiuom(I), involves free as well as substituted olefin ligands in its coordination sphere.

The carbon atoms of the tetrafluorothylene moiety are closer to the metal as compared to the carbon of ethylene. The HCH bond angle is larger (138^*) than the FCF bond angle (106^o)



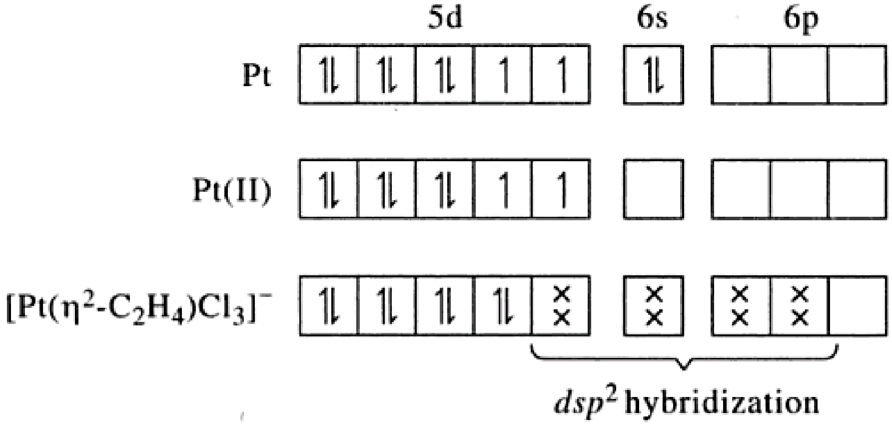
The rotational barrier along the Rh-C_2F_4 bond axis is larger than that for the Rh-C_2H_4 bond axis. The reason being that the electronegative fluoro substituents cause the extent of back bonding from the metal to the lignd to enhance as compared to the back bonding in the corresponding ethylene ligand . the double bond character in tetrafluoroethylene lignad is higher than that in the unsubstituted ethylene lignad. Therefore the rotational barrier in the former is larger.

Olefin complexes are largely diamagnetic in nature and the effective atomic number rule is followed in most of the complexes.

8.3.1 Structure

By considering Zeise's salt as the representative example it is easy to discuss the structure of olefin complexes. Aspects arising out of the attachment of ethylene ligand to the metal ion in this compound may be extrapolated to other olefin complexes as well.

In Zeise's salt the central platinum(II) ion undergoes dsp^2 hybridization using 5d, 6s and two of its 6p orbitals. Accordingly there is square planar coordination around platinum(II) ion. In this three co-ordination sites are occupied by chlorine atoms the fourth by ethylene group. The carbon-carbon double (C=C) of the latter is perpendicular to the plane of $[PtCl_3]$ residue. As a result the repulsion between hydrogen atom of ethylene and chlorine atom at the remaining three coordination sites is minimized.



Both carbon atoms of ethylene are equidistant form the central platinum(II) ion. The carbon – carbon bond distance is increased form 133.7 pm in free ethylene to 137.5 pm ion the complex. Moreover the originally planar ethylene molecules becomes slightly distorted on complexation its hydrogen atom are titled backwards with respect to the square planar arrangement,

8.3.2 Bonding

Two components define the bonding of ethylene to platinum(II) ion in Zeise's salt: these are sigma and pi. The σ component arises because of donation of electrons from filled π orbitals of ethylene top a vacant dsp^2 hybrid orbital of the metal (figure 2A). The π component arises because of the back donation of electron form a filled d orbital of the metal to the vacant, anti-bonding π^* orbital of ethylene (figure 2B).

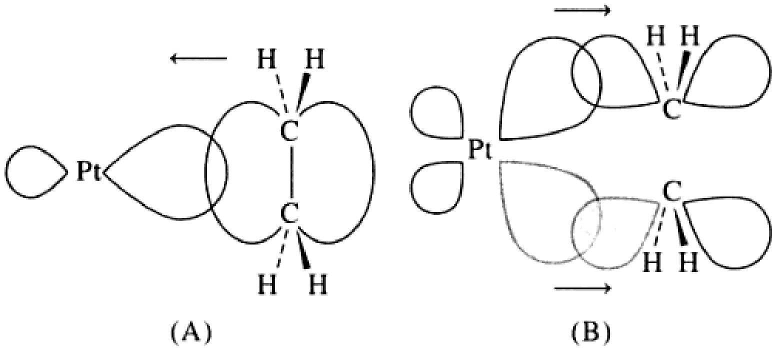


Figure 2: Bonding in Zeise's salt. (A) σ-bonding and (B) π-bonding

The two components involved in metal –olefin bonding reinforce each other synergistically i.e σ-bonding strengthens π bonding and vice versa. The perpendicular orientation of the ethylene group, with respect to the square planar skeleton, enables it to adjust its filled π and empty π^{-*} orbitals for effective overlap with the metal orbitals. Since the anti-bonding π^{-*} orbitals of ethylene are used in π bonding the carbon-carbon bond in the complex weakens and as stated earlier lengthens.

The degree of back bonding depends to quite some extent on the nature of substituents on ethylene ligands. Electron withdrawing substitutents increase the ability of the olefin to accept electrons form the metal thereby strengthening the metal-ligand bond. Therefore tetrafluororthylene forms more stable complexes as compared to ethylene itself. The alkyl substituted olefins on the other hand form less stable complexes as compared to unsubstituted analoges. Two reasons may be ascribed to this observation. Firstly the alkyl groups being electron releasing, decrease the ability of olefin to enter into π bonding: secondly replacement of hydrogen by relatively large alkyl groups results in steric over-crowdedness.

8.3.4 Synthesis

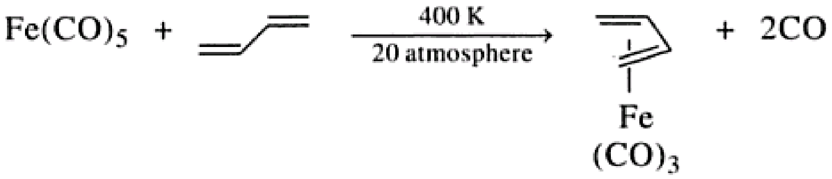
The following are some of the common and general methods for the preparation of olefin complexes.

1. Substitution reactions

$$K_2[PtCl_4] + C_2H_4 + H_2O \rightarrow K[Pt(\eta^2\text{–}C_2H_4)Cl_3]\cdot H_2O + KCl$$

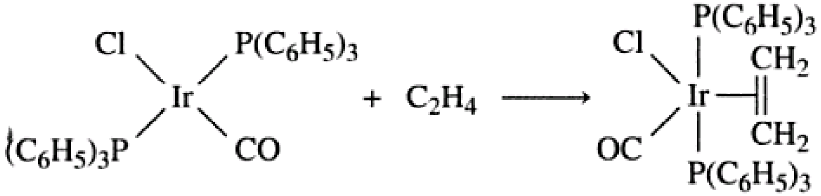
(Fig. 3.1A)

$$[Re(CO)_5Cl] + C_2H_4 + AlCl_3 \rightarrow [Re(\eta^2\text{–}C_2H_4)(CO)_5]^+ [AlCl_4]^-$$

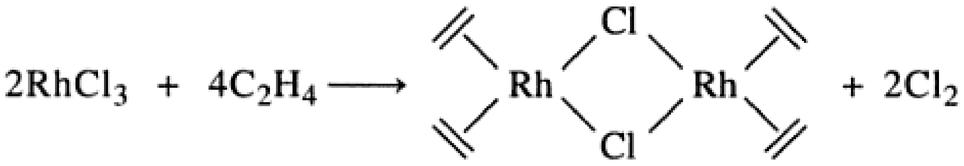


2. Additional reactions

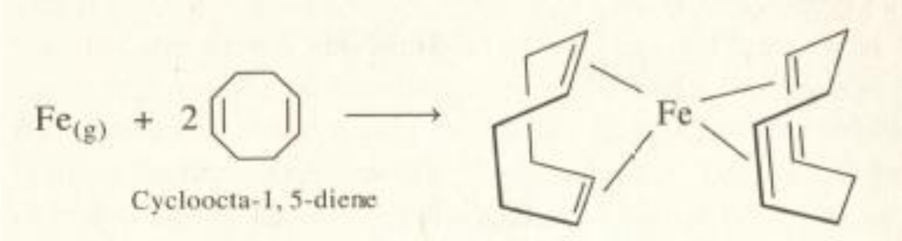
$$AgNO_3 + 2C_2H_4 \rightarrow [Ag(\eta^2\text{–}C_2H_4)_2]NO_3$$



3. Reduction reactions.



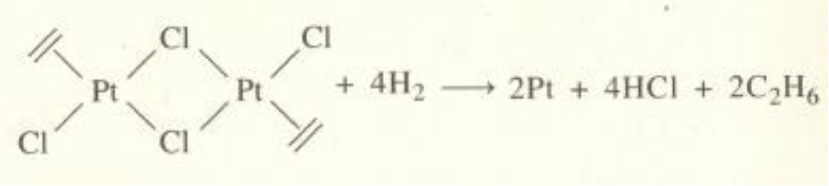
4. Vapor phase condensation reaction



8.3.5 Reactions

Important reactions of olefin complexes are described below

1. *Redox reaction*



2. *Substitution reaction*

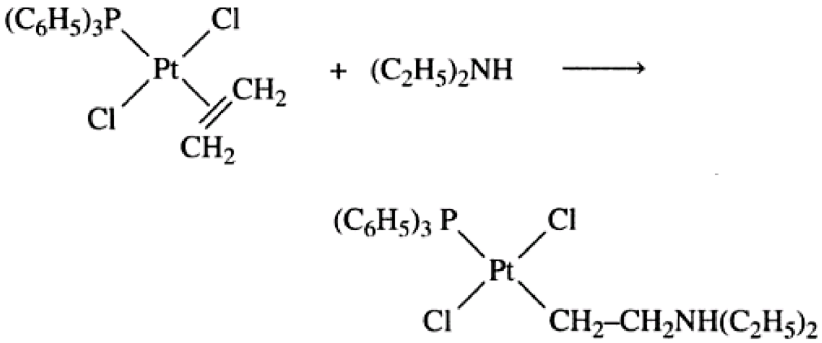
$$[Pt\{(C_6H_5)_3P\}_2(C_2H_4)] + C_{60} \longrightarrow [Pt\{(C_6H_5)_3P\}_2(\eta^2\text{-}C_{60})] + C_2H_4$$

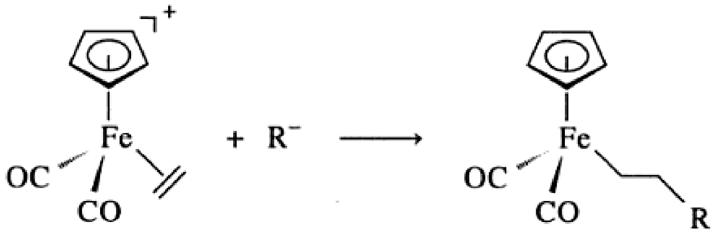
C_{60} is an allotropic form of carbon, called *buckminsterfullerene*. Like olefins it becomes coordinated to the metal through a double bond.

$$[Ni\{(C_6H_{11})_3P\}_2(\eta^2\text{–}C_2H_4)] + O_2 \longrightarrow [Ni\{C_6H_{11})_3P\}_2(O_2)] + C_2H_4$$

3. *Nucleophilic attack*

When olefins become coordinated to the metal, their characteristics do change. Free olefin undergo eletrophilic attack rther than nucleophilic attack. However on complexing with the metal these become susceptible to nucleophilic attack rather than electrophilic attack. The reason being that the carbons of olefins acquire positive charge as a result of donation of π electrons to the metal.





8.4 Alkyne Organometallics

The alkynes like alkenes, coordinate to the metals largely through π- electrons. However unlike the olefin which have one π bond, the alkynes have two π bonds mutually perpendicular to each other. As a result there are a greater number of bonding possibilities of acetylene and its derivatives than of ethylene and its derivatives. This makes the chemistry of metal- alkynes more complicated than that of metal- alkenes. .

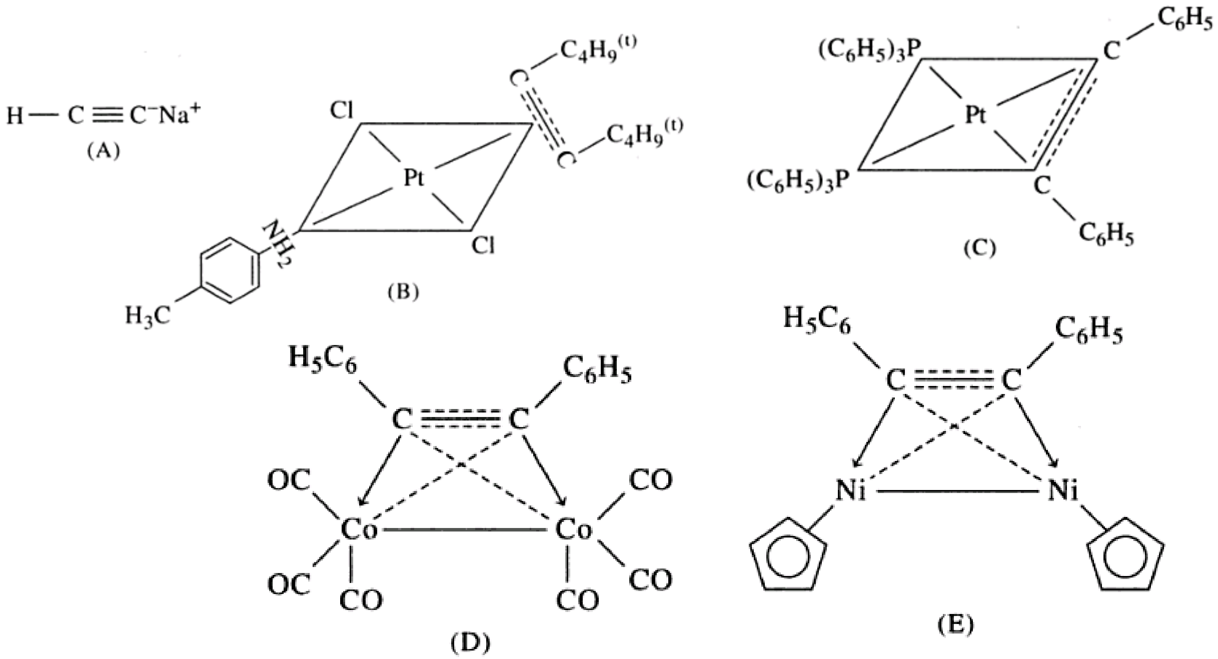


Figure 3: Structure of some alkyne complexes

Alkali metals and alkaline earth metals from alkyne complexes in which π-electron cloud plays no role rather the alkyne group is deprotonated and there is ionic interaction between the metal and the ligand. Such organometallics are referred to as acetylides. The structure of sodium acetylide is show in figure 3A

Several molecular skeletons are possible in cases where the coordination of alkyne moiety is through π electrons. The alkyne group may occupy one coordination site as in case of dichloro (η^2- di-t-butylacetylene) (4-methylaniline) platinum (II) or two coordination sites as in case of (η^2- diphenylacetylene)bis(triphenylphosphine)platinum(0). Tricarbonylcobalt(0)-μ-(diphenylacetylene)- tricarbonylcobalt(0) (Co-Co) and (η^5- cyclopenradienyl)nickel(I)- μ-(diphenylacetylene)-(η^5-cyclopenradienyl) nickel(I) (Ni-Ni) offer example in which the alkyne ligand is bridging.

8.4.1 Structures

The metal-alkyne organometallics largerly have the following three types of structure as shown in figure 4.

1. *Monodentate Monometallic Derivatives*

   In these complexes one of the alkyl π bond is coordinated to the metal atom while the second π bond is not involved in bonding. This type of bonding behavior is depicted in fig . Dichloro(η^2- di-t-butylacetylene) (4-methylaniline)platinum(II), whose structure is presented in fig is an example of an alkyne complex of monodentate monometallic type.

2. *Bidentate Monometallic derivatives*

   In such case one of the π electron pair of the alkyne moiety becomes coordinated to the metal atom the second perpendicular π electron cloud interacts with the vacant p or d orbitals of the same metal and forms another bond. This type of coordination is represented in fig. the (η^2-diphenylacetylene) bis (triphenylphosphine) platinum(0) complex comes under this category.

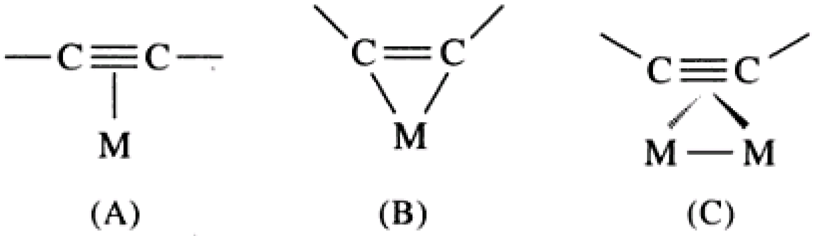


Figure 4: Different bonding modes of alkyne ligand

3. Bidentate Bimetallic Derivatives.

   In these compounds one carbon- carbon π electron pair of the alkyne affects coordination to one metal atom while the other carbon-carbon π electron pair affects coordination to the second metal atom. This type of bonding behavior is depicted in fig the alkyne ligand acts as a briding group between the two metals. Most bidentate bimetallic alkyne complexes possess a metal-metal bond as well. The tricarbonylcobalt(0)-μ-(diphenylacetylene)-tricarbonylcobalt(0) (Co-C0) omplex belongs to the bidentate bimetallic classification of alllkyne organometallics.

8.4.2 Bonding

The alkyne ligand binds to the metal in much the same way as the alkene ligand. The difference however is that whereas an olefin group has one π and one π^* orbital for coordinating to the metal, an alkyne group has two π and two π^* orbitals for this purpose. One set of π and π^* orbitals is mutually perpendicular to the other set of these orbitals.

In monodentate monometallic cases only one π and one π^* orbital of the ligand are involved in bonding. The sigma component of the bonding arises because of donation of electrons from the filled π orbital of alkyne to a vacant orbital of the metal. The retrodative π component arises due to back donation of electrons from a filled orbital of the metal to the vacant, anti-bonding π^* orbital of the alkyne.

The two components sigma and pi involved in metal-alkyne coordination acr synergistically. The σ bonding strengthens π bonding and vice versa. Since anti-bonding π^* orbitals of alkyne moiety are involved in bonding, the carbon-carbon triple bond is weakened and therefore, lengthened. For example the carbon- carbon bond length in dichloro(η^2-di-t-buylacetylene) (4-methylaniline)platinum(II) is 124 pm, compared to 120 pm in the uncomplexed ligand.

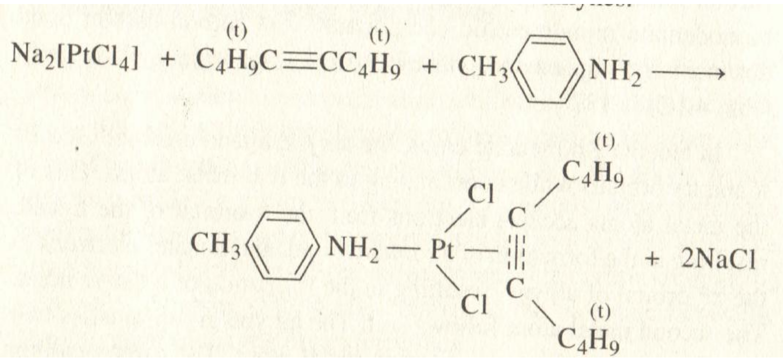
In bidentate monometallic cases, one set of π and π^* orbitals participates in bonding in the same manner as for monodentate monometallic complexes. Form the other set the π oprbital donates electron to the vacant p or d orbitals of the metal atom. The carbon – carbon bond in such cases gets more weakened as compared to monodentate monometallic compounds. The carbon-carbon bond distance in (η^2-di[phenylacetylene) bis(triphenylphosphine)platinum(0) is 132 pm.

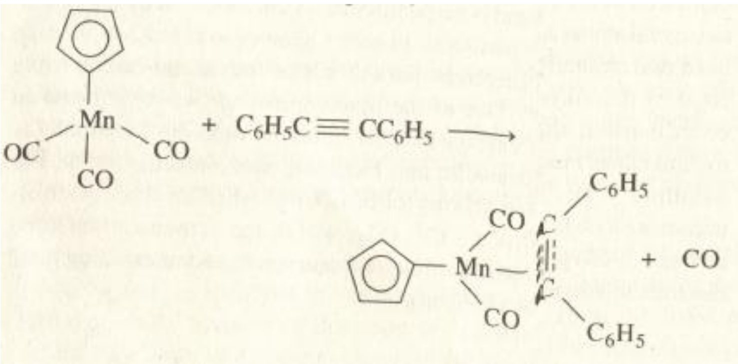
In bidentate bimetallic cases the alkyne ligand uses both sets of π and π^* orbitals while coordinating to the two metal atoms. One of the metal atoms accepts electrons from the π orbital of the ligand, resulting in the formation of a forward bond, and donates electrons to the π^* orbital of alkyne, resulting in the formation of a dative bond. The second metal atom follows suit. The alkyne group satisfies two coordination position around each metal atom. The carbon-carbon bond axis of the ligand is perpendicular to the metal-metal bond. The two meatl atoms are positioned in such a manner so as to allow overlap from two mutually perpendicular orbitals on the carbon-carbon triple bond of the alkyne. Due to the involvement of two π^* orbitals in coordination the carbon-carbon bond is weaker than that for monodentate monometallic and bidentate monometallic cases. For example in tricarbonylcobalt(0)-μ-(diphenylacetylene)-tricarbonylcobalt(0) (Co-Co) the carbon-carbon bond distance is 146 pm, which is longer than even the corresponding bond distance in ethylene.

8.4.3 Synthesis

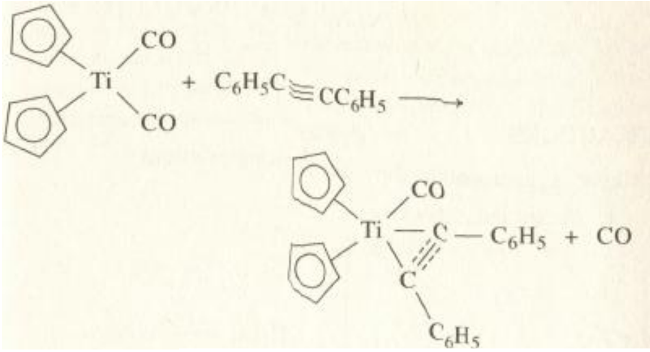
The following are some of the important methods for preparing metal-alkyne complexes

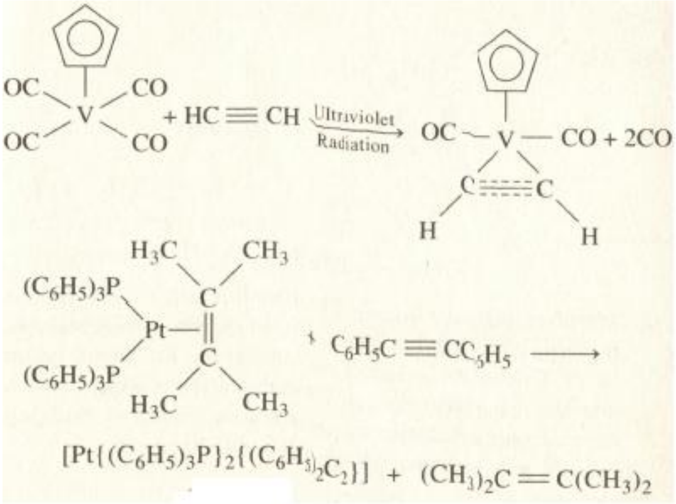
1. *Monodentate monometallic derivatives of alkynes*





2. *Bidentate monometallic derivatives of alkynes*





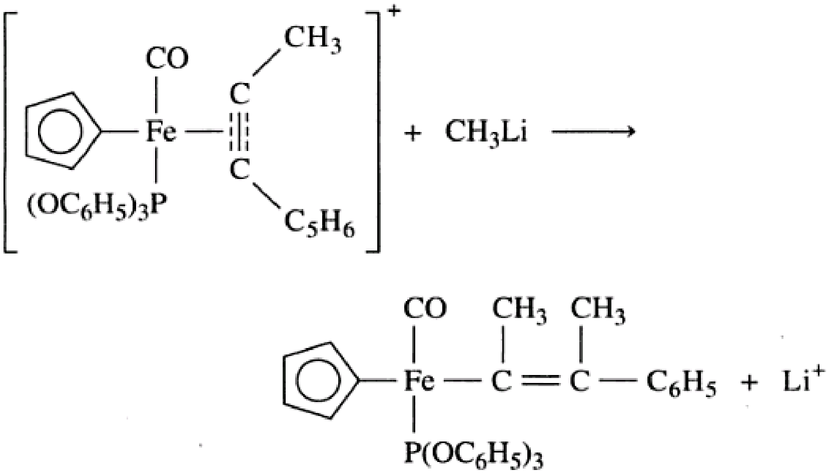
3. *Bidentate bimetallic derivatives of alkynes*

$$[Ni(\eta^5\text{–}C_5H_5)(CO)]_2 + C_6H_5C\equiv CC_6H_5 \longrightarrow [Ni_2(\eta^5\text{–}C_5H_5)_2\{(C_6H_5)_2C_2\}] + 2CO$$

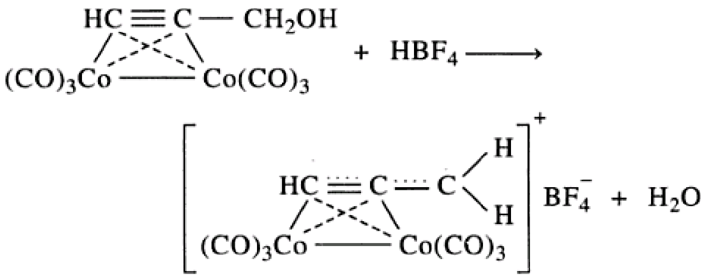
8.4.4 Reactions

Alkyne organometallic show the following reactions

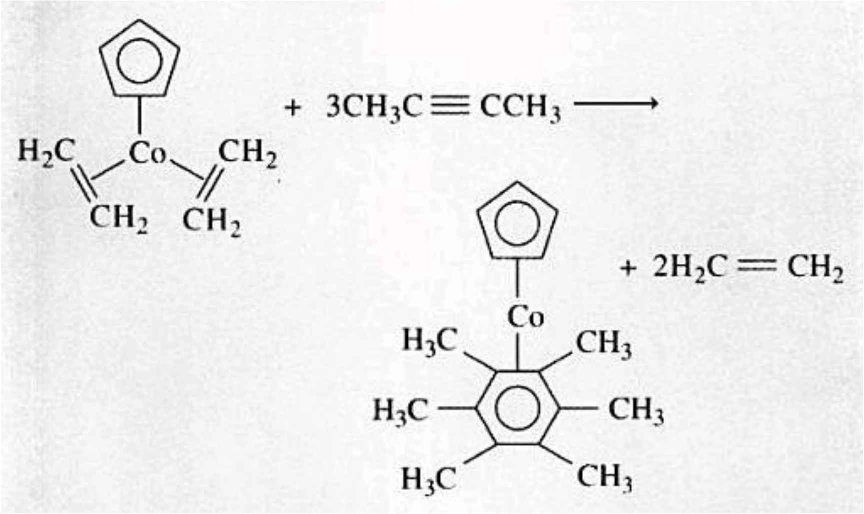
1. *Nucleophilic attack*



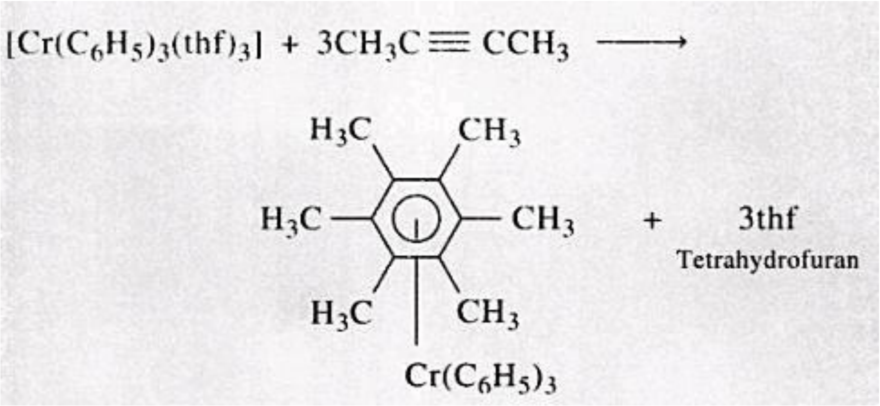
2. Metal-stabilized cations: the coordination of alkynes as bridging group reduces the reactivity of carbon-carbon multiple bond. This allows selective reactions at the functional group attached to the alkyne moiety. For example those alkynes which have alcoholic substituents and are coordinated as bridging ligands may be converted into metal-stabilized cations.



Reactions of alkynes with metal complexes can lead to di-, tri- or tetra-merization of organic groups. For example (η^5- cyclopentadienyl) bis (η^2- ethylene)cobalt(0) can cause cyclotrimerization of dimethylacetylene



Cyclotrimerization can also be caused by reaction with triphenyltris(tetrahyrofuran) chromium(III)



Oligomerization of alkynes provides a route to synthesis of metal-arene complexes.

8.5 Cyclobutadienyl Organometallics

Cyclobutadiene C_4H_4 the structure of which is shown in Figure 5. A is not a very stable molecules. There are two reasons for its instability. Firstly it process a bent skeleton with a bond angle of 90^0 as a result of which it is a several strained molecules. Secondly it is a non-aromatic compound. It has four π electrons and does not follow the (4n+2) 2π electron rule called *Huckel's rule of aromaticity*.

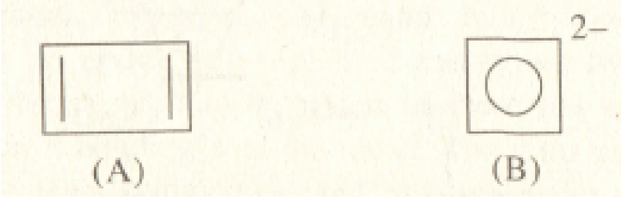


Figure 5: Structure of (A) cyclobutadiene and (B) cyclobutadienyl dianion

A metal or a metal ion may donate two electrons to cyclobutadiene and convert into cyclobutadienyl anion. The latter has six π electrons, follows (4n+2)π rule and becomes coordinated to the metal. It need be emphasized here that free coordinated to a metal.

The cyclobutadienyl ligand is thus a six electron donor. Its hapticity is four: that is it becomes attached to the metal through all the four carbons. It is therefore designated an η^4 – cyclobutadienyl.

Onely few cyclobutadienyl organometallic compounds are known (figure 6). Tricarbonyl (η^4-cyclobutadienyl) iron(II) is one of the few stable complexes of this ligand. Its structure is show is fig (η^4-Cyclobutadienyl)(η^4-cyclopentadienyl)cobalt(III) is an example of a complex involving two cyclic and aromatic system.

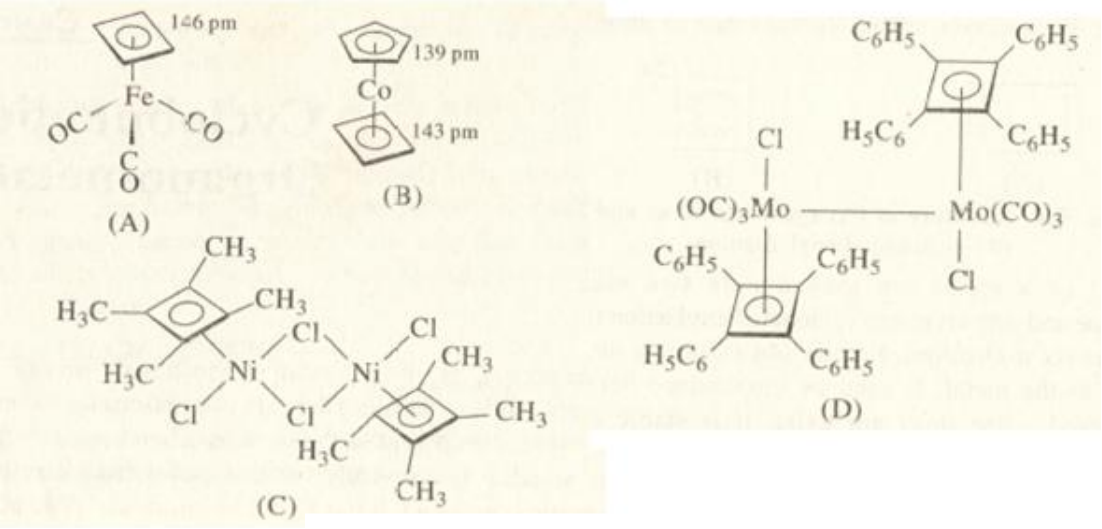


Figure 6: structure of some cyclobutadienyl complexes

Bridging complexes involving terminal (η^4- cyclobutadienyl) groups are also known Chloro(η^4-tetramethylcyclobutadienyl)nickel(IV)-μ-dichloro-chloro(η^4-tetramethylcyclobutadienyl) nickel(IV), the structure of which is depicted in Fig is a representative case. Dimeric complexes involving metal-metal bonds are also known for this ligand, bis[(tricarbonyl)chloro(η^4-tetraphenylcyclobutadienyl)molybdenum(III)]

8.5.1 Structure

Cyclobutadiene is a reactangular molecule with alternate single and double bonds. However on coordinating to a metal, it acquires a square geometry. This is borne out by the fact that in tricarbonyl(η^4-cyclobutadienyl)iron(II) complex all four carbon-carbon bond lengths are equal measuring 146 pm each. In (η^4- cyclobutadienyl)(η^5-cyclopentadienyl)cobalt(III) all four carbon-carbon bond distance in η^4- cyclobutadienyl ligand are 143 pm while all five bond distance in η^5-cyclopentadienyl ligand are 139 pm.

8.5.2 Bonding

The four p_z orbitals (one on each carbon) of the cyclobutadiene ring combine to yield four molecular orbitals. These may be grouped into three types on the basis of their symmetries. The lowest energy molecular orbital, designated as ψ_1 enters into σ bonding with the metal. It has no node. Next higher in energy are two degenerate molecular orbital ψ_2 and ψ_3. Each of these has one node and participates in π bonding with the metal. The remaining molecular energy molecular orbital is designated as ψ_4 and enters into δ bonding with the metal. The enegy pattern of cyclobutadiene molecular orbials is depicted in figure 7.

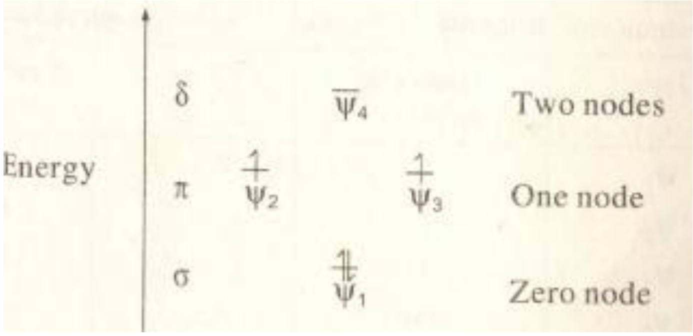


Figure 7: energy pattern of molecular orbitals of cyclobutadiene

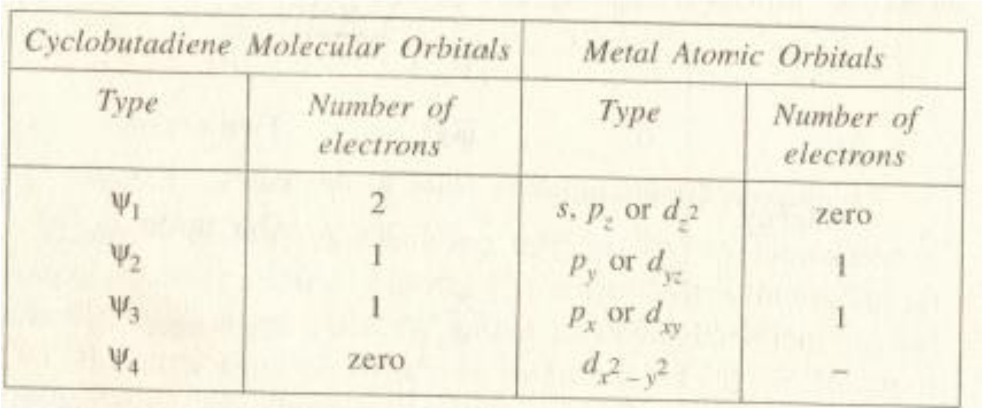
Of the four π electrons of cyclobutadiene two are paired-up in ψ_1 molecular orbital, while each of the ψ_2 and ψ_3 molecular orbital has one unpaired electrons. The electronic configuration may be shown as.

$\psi_1^2\psi_1^2\psi_1^2$

This indicates the paramagnetic nature of cyclobutadiene.

During the formation of organometallic compounds the molecular orbitals of the metal. The criteria of combine with suitable atomic orbitals of the metal. The criteria of combination is dictated by symmetry considerations. A ligand orbital will combine with that atomic orbital of the metal with which its symmetry matches.

The ψ_1 orbital of the ligand may merge with s, p_z or $d_z{}^2$ orbital of the metal. The metal atomic orbital need be vacant so as to accommodate two electrons of the ψ_1 molecular orbital of the ligand. The ψ_2 molecular orbital of cyclobutadiene may combine with either p_y or d_{yz} atomic orbital of the metal. Since the ψ_2 orbital has a single electron, the metal p_y ir d_{yz} orbital too should have one unpaired electron. Likewise the singly occupied ψ_3 molecular orbital of cyclobutadiene merges with the singly occupied p_x and d_{xy} atomic orbital of the metal. The ψ_4 orbital of the lignad is essentially non-bonding through it has the symmetry to combine with the $d_{x^2-y^2}$ atomic orbital of the metal. The possible combinations of ligand molecular orbitals and the metal atomic orbitals are summarized in table



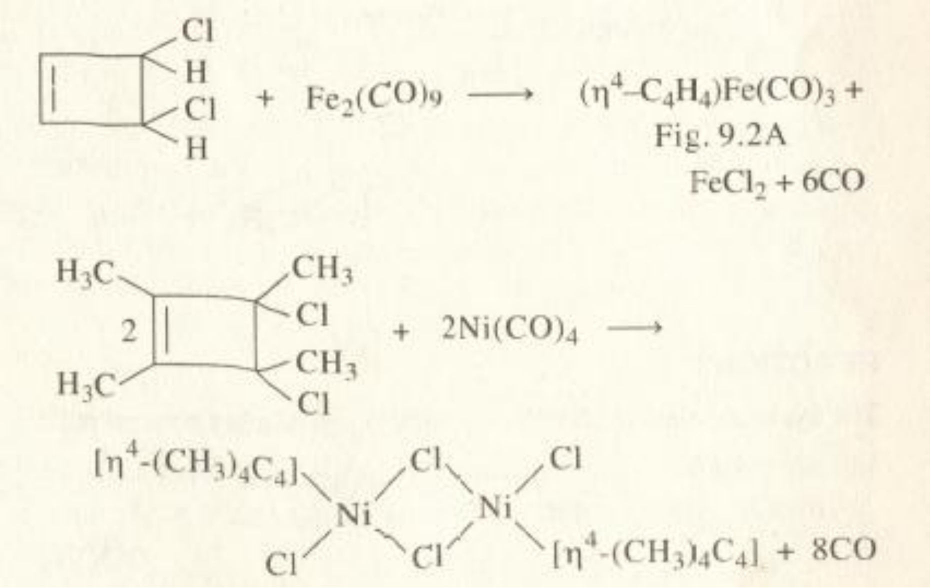
Cyclobutadiene Molecular Orbitals		Metal Atomic Orbitals	
Type	Number of electrons	Type	Number of electrons
ψ_1	2	s, p_z or d_{z^2}	zero
ψ_2	1	p_y or d_{yz}	1
ψ_3	1	p_x or d_{xy}	1
ψ_4	zero	$d_{x^2-y^2}$	–

In all six electrons are involved in metal-ligand bonding. Of these four are contributed by the ligand two by the metal. In fact the two electrons contributed by the metal are responsible for transforming cyclobutadiene to cyclobutadienyl anion. The anion is stabilized by coordination since the sextet of electrons imparts aromatic character to it. Moreover as a result of the combination of singly occupied ψ_2 and ψ_3 molecular orbitals of cyclobutadiene with singly occupied metal atomic orbitals, electron pairing takes place. This phenomenon converts the paramagnetic cyclobutadiene to diamagnetic cyclobutadienyl anion and contribution to the stability of the complexes.

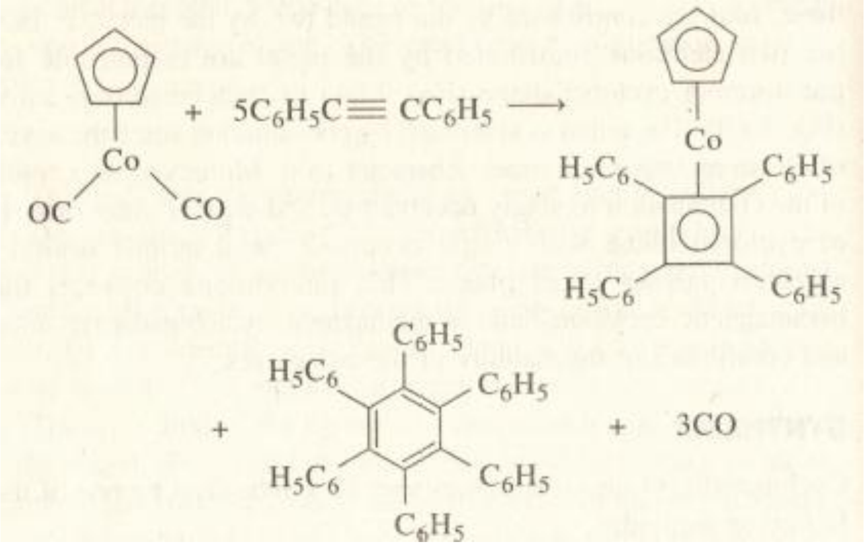
8.5.3 Synthesis

Cyclobutadienyl organometallics may be synthesized by one of the following methods.

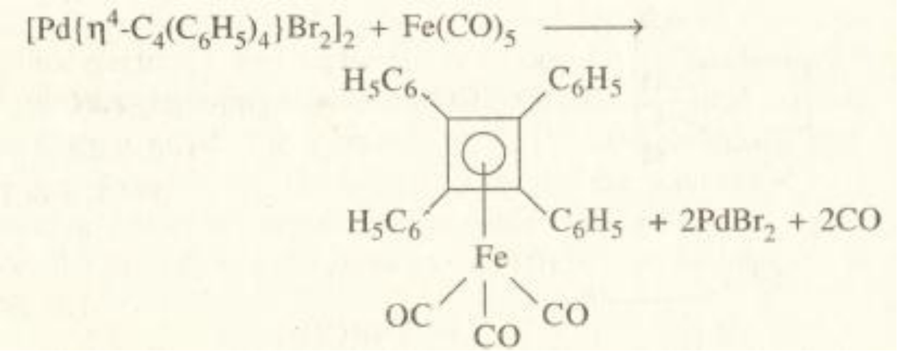
1. Dehalogenation of cis-3,4-dichlorocyclobutadiene.



2. Dimerization of alkynes.



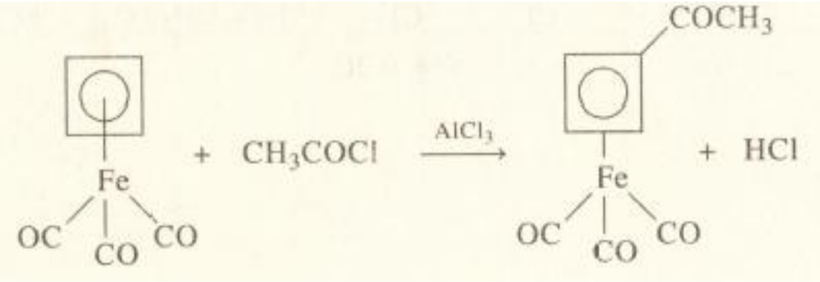
3. Ligand transfer



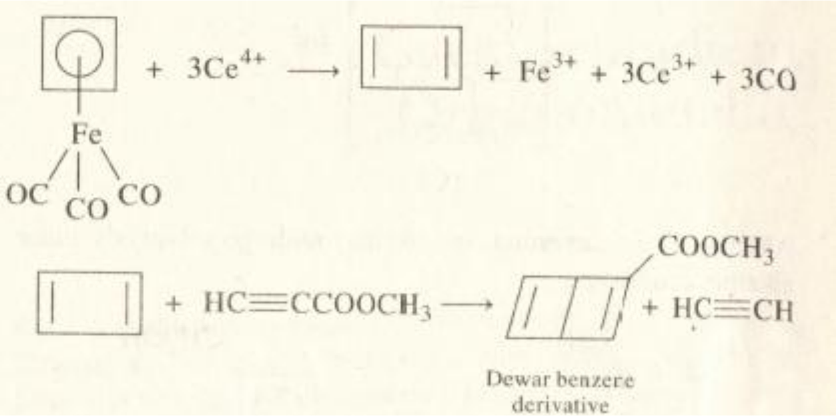
8.5.4Reaction

the cyclobutadienyl complexes show the following general reactions.

1. Electrophilic substitution: tricarbonyl (η^4-cyclobutadienyl) iron(II) for example undergoes Fridel- Crafts acylation.

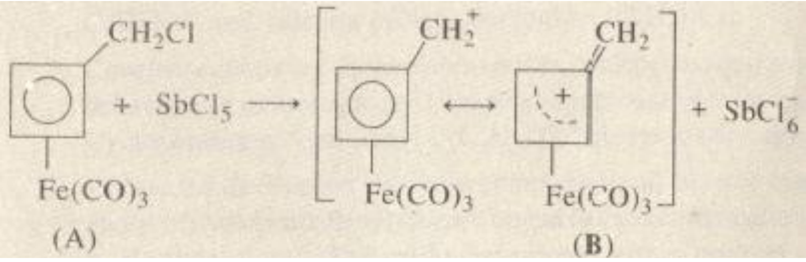


2. Oxidation: during low temperature oxidation with cerium(IV) ions. Free cyclobutadiene is liberated from its complexes. It then interacts with alkynes to yield analogs of Dewar form of benzene

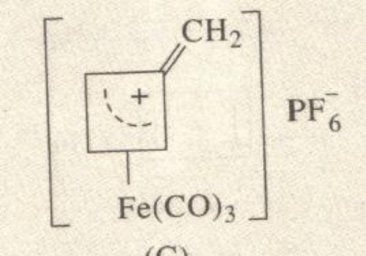


It is possible to stabilize carbenium ions through coordination with metals?

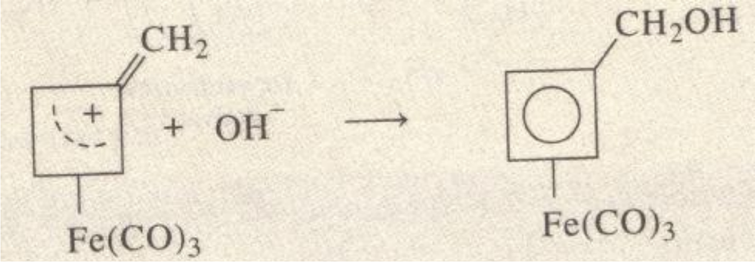
Carbenium ions are normally not very stable. However on coordinating to a metal, these become relatively more stable. A case in point is the tricarbonyl [η^4-(chloromethyl)cyclobutadienyl] iron(II) complex (A). on reacting with antimony (V) chloride, it loses the chloride ion.



The resulting carbenium ion (B) is quite stable. It may be isolated as hexafluorophosphate(V) salt (C). Alternatively the carbenium ion (B) may undergoes solvolysis under alkaline condition.



(C)



8.6 Cyclopentadienyl Organometallics

Cyclopentadine is a weak acid. On reaction with a base it deprotones forming a symmetrical cyclopentadienyl anion $C_5H_5^-$. The latter possesses a sextet of π electrons and hence is aromatic in nature. All the five carbon-carbon bond lengths in the cyclopentadienyl anion are equivalent which shows that the π electron cloud is delocalized throughout the pentagonal ring.

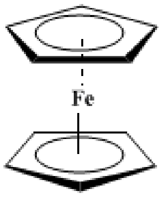
Cyclopentadienyl is a versatile ligand. It forms complexes with a wide spectrum of metals both transition and non-transition ones. Metal cyclopentadienyls may be classified into three broad types.

1. Ionic derivatives. These are formed from $C_5H_5^-$ and M^{n+} units. The two chemical entities are held together by electrostatic forces of attraction. Examples include sodium cyclopentadienide. $C_5H_5^-Na^+$ and calcium cyclopentadienide $(C_5H_5)_2Ca$.
2. Covalent derivatives. In these derivatives cyclopentadienyl moiety behaves as a monohapto(η^1) ligand and is σ bonded to the metal. Cyclopentadienylthallium (I), $(C_5H_5)_2TI$. Belongs to this category

3. Pi bonded derivatives. In these compounds all the five carbon atoms of cyclopenradienyl ring are bonded to the metal atom through π electron cloud. The cyclopentadienyl group behaves as a pentahapto (η^5) ligand. Ferrocene or bis (η^5-cyclopentadienyl)iron (II) belongs to this category. It is unquestionably the most important metallocene.

8.6.1 Ferrocene

Ferrocene is an organic crystalline solid that exits in monoclinic from at room temperature. Between 110-164K it is triclinic while below 110K it exits in orthorhombic modification. It melts at 446K, sublimes at 673K and decomposes beyond 743K. it is diamagnetic in nature dissolves in most organic solvents but is insoluble in water. It remains stable in air.



8.6.2 Structure

As shown in fig the iron in ferrocene is sandwiched between the two cylopentadienyl rings. The π electrons cloud of each ring is delocalized over all five carbon atoms. We have already stated that the two cyclopentadienyl rings have staggered configuration relative to each other. However in gaseous state the two cyclopentadienyl groups acquire eclipsed configuration with respect to each other. The energy barrier to ring rotation is very small. The hydrogen atoms of the ring are bent towards the iron atom.

8.6.3 Bonding

The bonding in ferrocene is best explained by molecular orbital theory. The construction of molecular orbital for this compound proceeds in the following three steps.

Step 1. Combining of atomic orbitals of a cyclopentadienyl ring to form molecular orbitals.

The five p_z orbitals (one on each carbon) of the cyclopentadienyl ring combine with each other to give five molecular orbitals. These five molecular orbitals may be classified into three types on the basis of their symmetry. The lowest energy molecular orbital has a perfect cyclindrical symmetry and enters into σ bonding with metal orbitals. It has no nodes and is designated by symbol a. next higher in energy are two degenerate molecular orbitals each having one node. These enter into π bonding with metal and are designated as e_1 orbitals. The remaining two molecular orbitals are the least symmetrical, each having two nodes. These are the highest energy molecular orbitals, which enter into δ bonding with metal and are designated as e_2 orbitals. The energy pattern of the cyclopentadienyl molecular orbitals along with their shapes are depicted in figure 8.

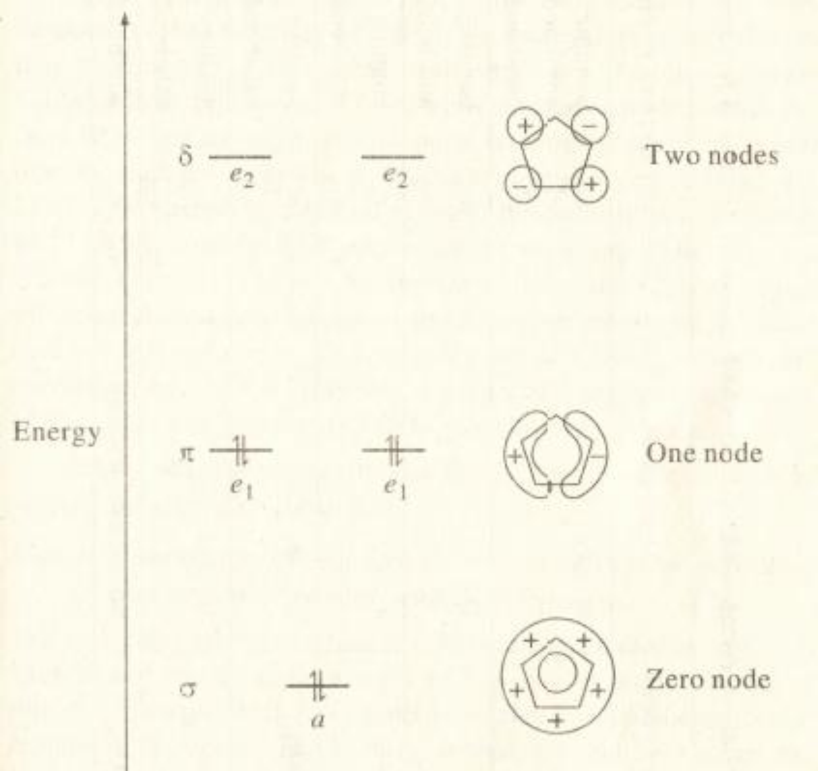
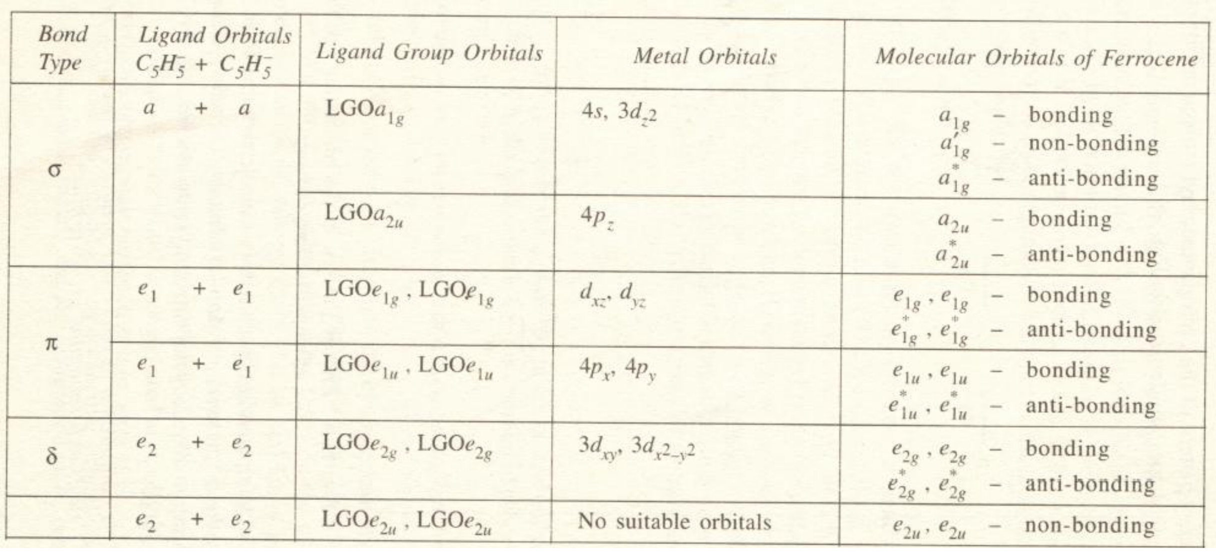


Figure 8: energy [attren of the molecular orbitals of a cyclopentadienyl group

The cyclopentadienyl anion is a six electron donor. These electrons occupy the a and two e_1 molecular orbitals. Therefore the electronic configuration of each cyclopentadienyl ring in ferrocene may be written as $a^2\ e_1^4\ e_2^0$

Step 2. Combination of molecular orbitals of two cyclopentadienyl rings to form ligand groups orbitals



Bond Type	Ligand Orbitals $C_5H_5^- + C_5H_5^-$	Ligand Group Orbitals	Metal Orbitals	Molecular Orbitals of Ferrocene
σ	$a + a$	LGOa_{1g}	$4s$, $3d_{z^2}$	a_{1g} – bonding a'_{1g} – non-bonding a^*_{1g} – anti-bonding
		LGOa_{2u}	$4p_z$	a_{2u} – bonding a^*_{2u} – anti-bonding
π	$e_1 + e_1$	LGOe_{1g} , LGOe_{1g}	d_{xz}, d_{yz}	e_{1g} , e_{1g} – bonding e^*_{1g} , e^*_{1g} – anti-bonding
	$e_1 + e_1$	LGOe_{1u} , LGOe_{1u}	$4p_x$, $4p_y$	e_{1u} , e_{1u} – bonding e^*_{1u} , e^*_{1u} – anti-bonding
δ	$e_2 + e_2$	LGOe_{2g} , LGOe_{2g}	$3d_{xy}$, $3d_{x^2-y^2}$	e_{2g} , e_{2g} – bonding e^*_{2g} , e^*_{2g} – anti-bonding
	$e_2 + e_2$	LGOe_{2u} , LGOe_{2u}	No suitable orbitals	e_{2u}, e_{2u} – non-bonding

The five molecular orbitals on one cyclopentadienyl ring combine in pairs with a similar set from the second cyclopentadienyl ring to give ten ligand group (LGO_s). in this combination the wave functions of the molecular orbitals of the two cyclopentadienyl rings may be added to or subtracted form each other. Addition of wave functions leads to gerade(g) LGO_s while subtraction leads to ungerade (u) LOG_s. for example combination of lowest energy molecular orbitals, each designated as a yields two ligand group orbitals viz $LGOa_{1g}$ – formed by addition of wave functions of two a orbitals and $LGOa_{2a}$-formed by subtraction of wave functions of two a orbitals. Likewise the two degenerate e_1 molecular orbitals on one cyclopentadienyl ring combine with their counterparts on the other cyclopentadienyl ring to yield two degenerate $LGOe_{1g}$ orbitals and two degenerate $LGOe_{1u}$ orbitals. On similar lines, two degenerate $LGOe_{2g}$ and two degenerate $LGOe_{2u}$ orbitals are also formed.

Step 3. Combination of ligand group orbitals with atomic orbitals of iron to form molecular orbitals of ferrocene

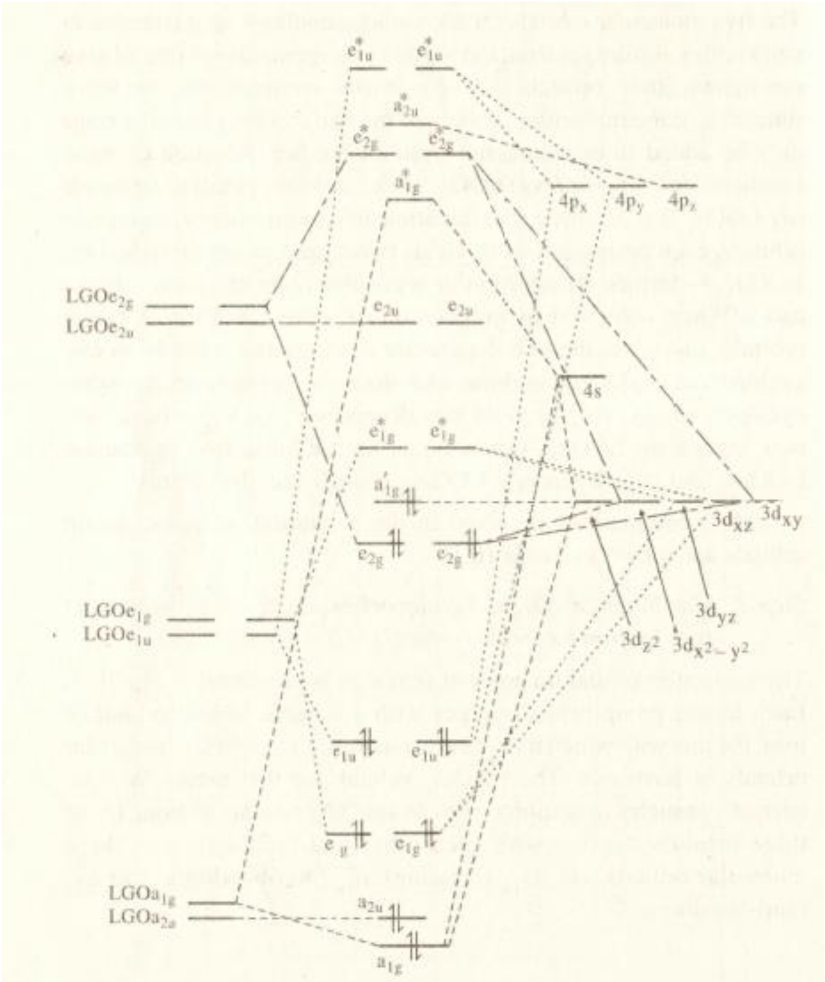


Figure 9: Molecular orbital diagram of ferrocene

The molecular orbital diagram of ferrocere is presented in fig . each lignd group orbital merges with a suitable atomic orbitals of iron, the one with which its symmetry matches , to yield the molecular orbitals of ferrocene. The LGOa$_{1g}$ orbital, for that matter has the correct symmetry to combine with 4s and 3d$_z$2 orbitals of iron. These three orbitals overlap with each other and then split into three molecular orbitals viz a$_{1g}$ (bonding) $a_{1g}^{'}$ (non-bonding) and a_{1g}^{*} (anti-bonding)

The LGOa$_{2a}$ orbital can formally combine with 4p$_z$ orbital of iron. However there is a wide difference between the energies of these two orbitals. Nevertheless the combination does take place and results in the formation of two molecular orbitals viz, a$_{2a}$ (bonding) and a_{2a}^{*} (anti-bonding). However the a$_{2a}$ orbital has a very little component of 4p$_z$ orbital and for this reason we have not drawn a line joining these two orbitals. Likewise the a_{2a}^{*} molecular orbital has a very little contribution from the LGOa$_{2a}$ orbital and therefore we have refrained from joining these orbitals in figure 9.

The two degenerate ligand group orbitals LGOe$_{1g}$ have appropriate symmetry to enter into combination with 3d$_{xz}$ and 3d$_{yz}$ orbitals of iron. Two degenerate bonding molecular orbitals, designated as e$_{1g}$ and two degenerate anti-bonding molecular orbitals, designated as e_{1g}^{*} are formed as a result of this combination. Similarly the two degenerate ligand group orbitals LGOe$_{1u}$ combine with 4p$_x$ and 4p$_y$ orbitals of iron, giving two degenerate bonding molecular orbitals e$_{1u}$and two degenerate anti-bonding molecular orbitals $e_{1u\cdot}^{*}$.

The two degenerate ligand group orbitals LGOe$_{2g}$ have the same symmetry as the 3d$_{xy}$ and $3d_{xy}\, and\, 3d_{x^2-y^2}$ orbitals of iron. Their combination gives four molecular orbitals- two bonding, represented as e$_{2g}$ and two anti-bonding represented as e_{2g}^{*} . The symmetry of ligand group orbitals, LGOe$_{2a}$ does not amtch with any of the metal orbitals. Accordingly these reamin in non-bonding mode and are designated as e$_{2a}$ molecular orbitals.

The combinations involved in the formation of molecular orbitals of ferrocene from ligand group orbitals of cyclopentadienyl groups and atomic orbitals of iron are shown in table

Ferrocene is an 18 electron system as illustrated below

Fe(II) = $6e^-$

$2C_5H_5$: 2x $6e^-$ =$12e^-$

Total =$18e^-$

As per fig the electronic configuration of ferrocene may be written as

$$a_{1g}^2\, a_{2u}^2\, e_{1u}^4\, e_{1u}^4\, e_{2g}^4\, a'^2_{1g}$$

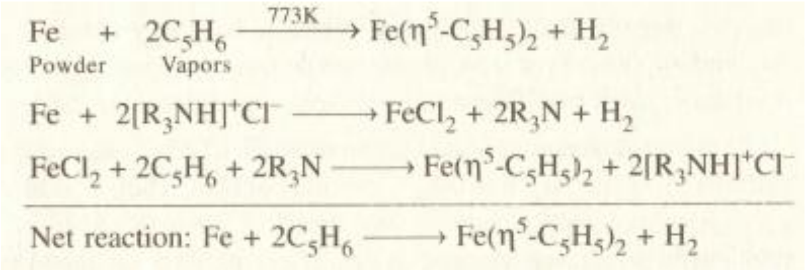
This indicates diamagnetic nature for organometallic.

The molecular orbital diagram of ferrocene (which may be visualized as being composed of Fe(II) ion and two $C_5H_5^-$ units) cannot be generalized for other metallocenes. The energy sequence of different molecular orbitals or the energy difference between any two molecular orbitals change with the chemical environment. A difference pattern resuls if the metal is changed or if the hydrogen atoms of the cyclopentadienyl rings are replaced by difference substituents.

8.6.4 Synthesis

The important methods for the synthesis of ferrocene are as follows

1. From iron



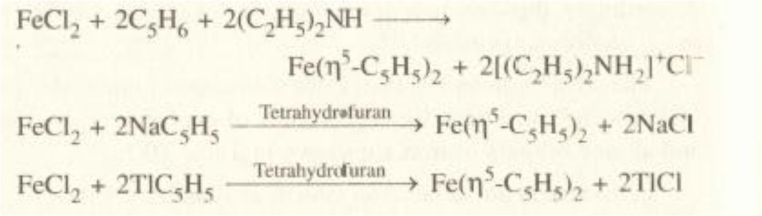
$$\underset{\text{Powder}}{Fe} + \underset{\text{Vapors}}{2C_5H_6} \xrightarrow{773K} Fe(\eta^5\text{-}C_5H_5)_2 + H_2$$

$$Fe + 2[R_3NH]^+Cl^- \longrightarrow FeCl_2 + 2R_3N + H_2$$

$$FeCl_2 + 2C_5H_6 + 2R_3N \longrightarrow Fe(\eta^5\text{-}C_5H_5)_2 + 2[R_3NH]^+Cl^-$$

$$\text{Net reaction: } Fe + 2C_5H_6 \longrightarrow Fe(\eta^5\text{-}C_5H_5)_2 + H_2$$

2. From iron(II) chloride

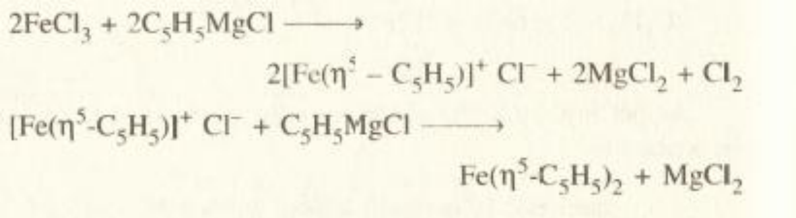


$$FeCl_2 + 2C_5H_6 + 2(C_2H_5)_2NH \longrightarrow Fe(\eta^5\text{-}C_5H_5)_2 + 2[(C_2H_5)_2NH_2]^+Cl^-$$

$$FeCl_2 + 2NaC_5H_5 \xrightarrow{\text{Tetrahydrofuran}} Fe(\eta^5\text{-}C_5H_5)_2 + 2NaCl$$

$$FeCl_2 + 2TlC_5H_5 \xrightarrow{\text{Tetrahydrofuran}} Fe(\eta^5\text{-}C_5H_5)_2 + 2TlCl$$

3. From iron(II) chloride



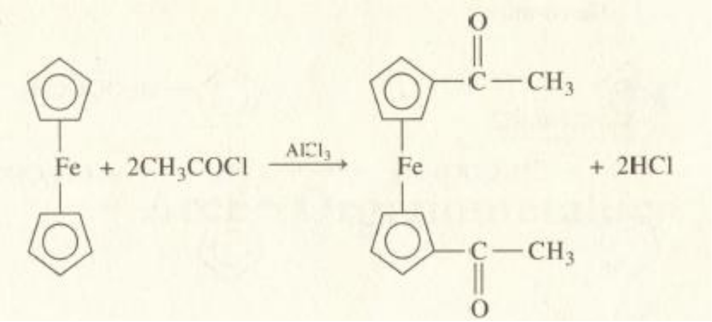
$$2FeCl_3 + 2C_5H_5MgCl \longrightarrow 2[Fe(\eta^5 - C_5H_5)]^+\,Cl^- + 2MgCl_2 + Cl_2$$

$$[Fe(\eta^5\text{-}C_5H_5)]^+\,Cl^- + C_5H_5MgCl \longrightarrow Fe(\eta^5\text{-}C_5H_5)_2 + MgCl_2$$

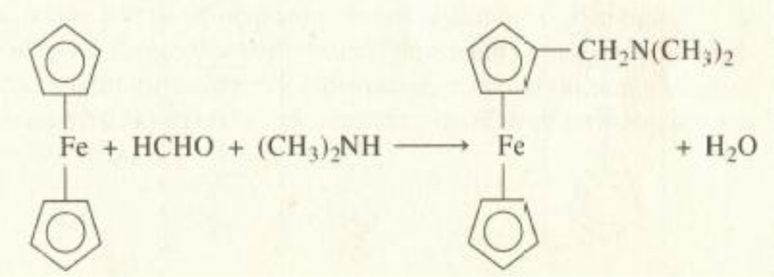
8.6.5 Reaction

The following are the important reactions of ferrocene.

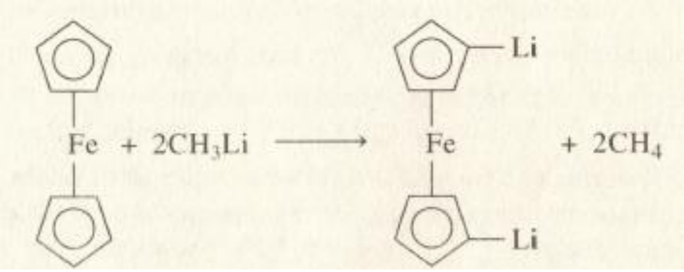
1. Fridel-Crafts acylation.



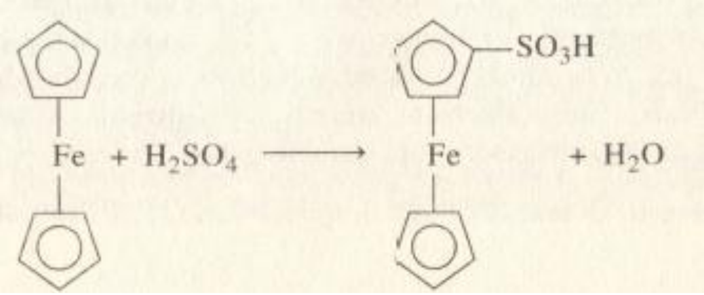
2. Mannich reaction



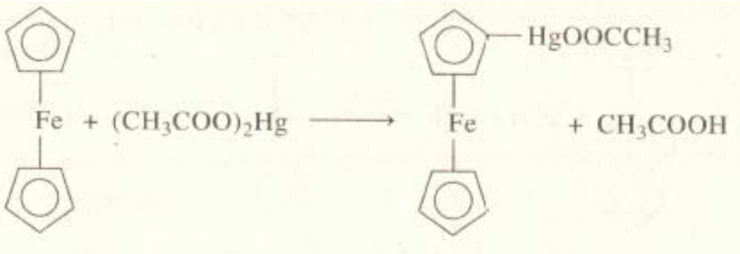
3. Metallation



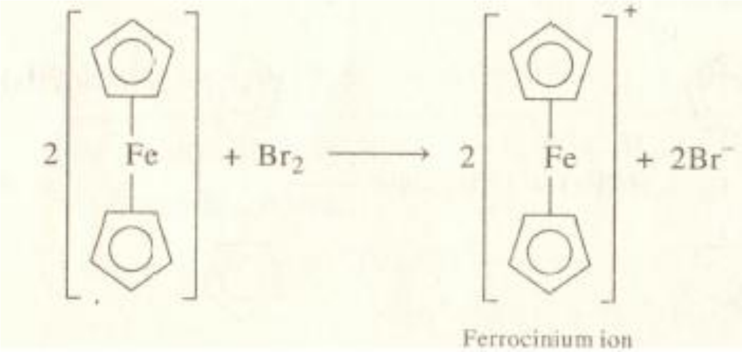
4. Sulfonation



5. Mercuration

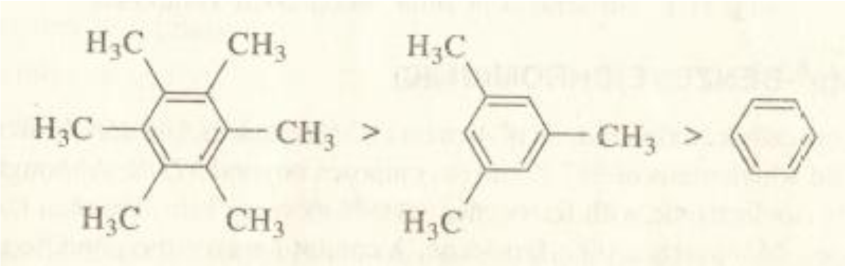


6. Oxidation



8.7 Arene Organometallics

Most of the metals of 3d transition series and a few 4d and 5d series from arene complexes. The stability of these compounds increase with the number of electron releasing substituents attached to the aromatic system. For example the stability of arene complexes various in the order



Benzene and its substituted analogs act as hexahapto ligands or six electron donors.

A metal-arene complex exits in range of composition. In some cases the coordination sphere contains only arene ligands, for example di(η^6- benzene) ruthenium(II) ion. In others arene ligand may be present in concert with other groups for example (η^6-benzene) tricarbonychromium(0) and (η^6-benzene) (η^5-cyclopentadienyl)manganese(I). Bridging complexes involving terminal arene groups are also known (η^5- benzene)chlororuthenium(II)-μ-dichloro-(η^6-benzene)chlororuthenium(II) is an example of such a complex.

The most important arene complex however is di(η^6-benzene)chromium(0), $[Cr(\eta^6-C_6H_6)_2]$. Its structure is presented in figure 10. The chemistry of metal-arene organometallic compound is discussed by consider it as a representative compound.

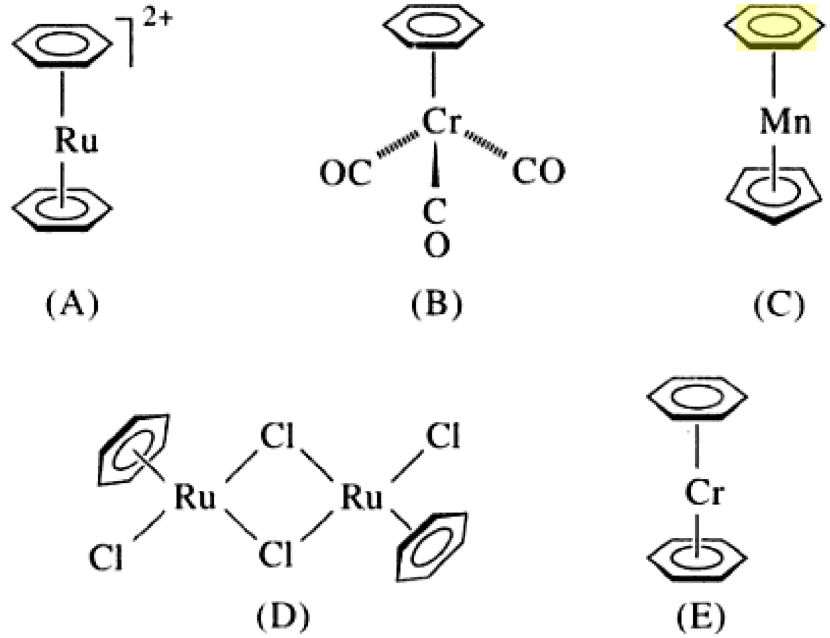


Figure 10 : Structure of some metal-arene complexes

8.7.1 Di(η^6-benzene)chromium(0)

A sandwich compound di(η^6-benzene)chromium(0) is a dark brown solid which metals of 557K and decomposes beyond 573K. Although it is isoelectronic with ferrocene yet it is more air sensitive than the latter. Moreover unlike ferrocene it cannot survive the conditions required for aromatic substitution reactions. It is diamagnetic in nature and is soluble in non-polar solvents.

8.7.2Structure

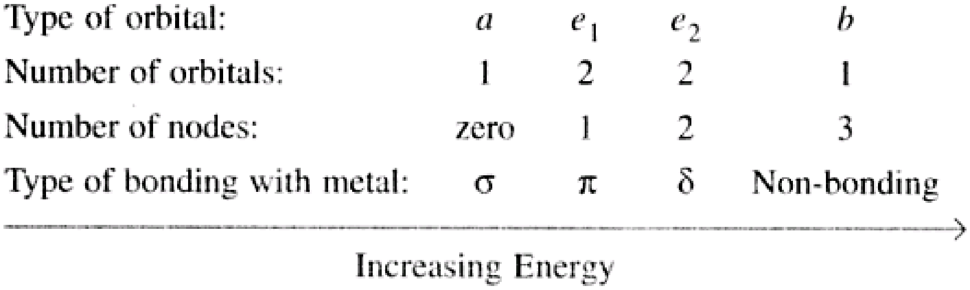
The molecular structure of di(η^6-benzene)chromium(0) comprises of plane parallel rings in eclipsed configuration lying above and below the chromium atom (figure). The rotational barrier about the ring axis is very low and is about 4 KJ mol^{-1}. The rings are quite labile and may be displaced by other ligands. The distance between the benzene rings is approximately the same as the van der Waals separation between two π- system (322 pm). The carbon-hydrogen bonds are tilted slightly towards the metal. All the carbon-carbon bond lengths are equivalent. However these are slightly larger than those in free benzene. This may be attributed to the involvement of anti-bonding orbitals of benzene moieties in metal lignad coordination.

8.7.3 Bonding

The bonding in di(η^6-benzene)chromium(0) may be explained on the basis of molecular orbital theory. As in the case the ferrocene the construction of molecular orbitals of this compound proceeds in the following three steps.

Step1. Combination of atomic orbitals of a benzene ring to form molecular orbitals

The six p_x orbitals (one on each carbon) of the benzene ring combine with each other to give six molecular orbitals. These may be classified into four group viz a, e_1, e_2 and b on the basis of their symmetries. In the order of increasing energy these orbitals are represented as



Type of orbital:	*a*	e_1	e_2	*b*
Number of orbitals:	1	2	2	1
Number of nodes:	zero	1	2	3
Type of bonding with metal:	σ	π	δ	Non-bonding

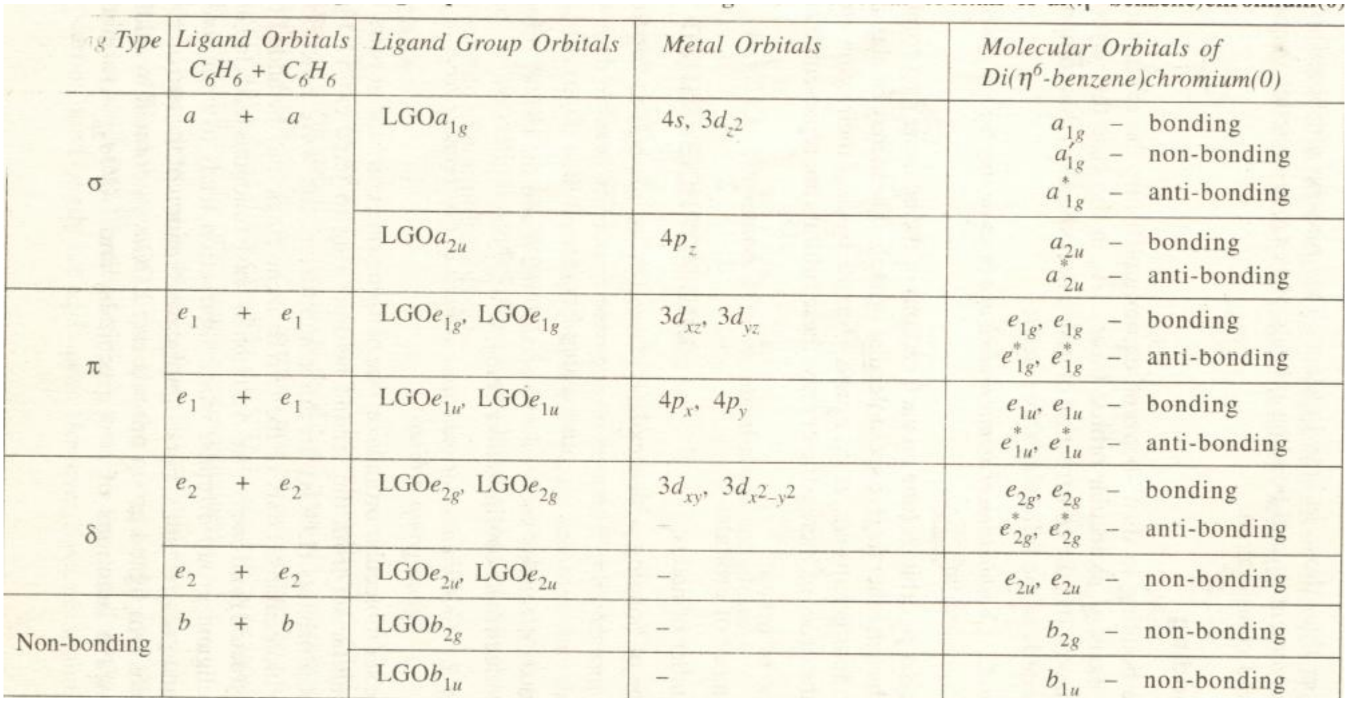
$$\xrightarrow{\hspace{20em}}$$

Increasing Energy

The six electrons successively occupy the a and the two e_1 orbitals, the electronic configuration being $a^2\, e_1^2\, e_1^2$

Step2. Combination of molecular orbitals of two benzene rings to form ligand group orbitals

The six molecular orbitals on one benzene ring combine in pairs with a similar set from the second benzene ring to yield twelve ligand group orbitals (LGOs).



g Type	Ligand Orbitals $C_6H_6 + C_6H_6$	Ligand Group Orbitals	Metal Orbitals	Molecular Orbitals of Di(η^6-benzene)chromium(0)
σ	$a + a$	LGOa_{1g}	$4s$, $3d_{z^2}$	a_{1g} – bonding a'_{1g} – non-bonding a^*_{1g} – anti-bonding
		LGOa_{2u}	$4p_z$	a_{2u} – bonding a^*_{2u} – anti-bonding
π	$e_1 + e_1$	LGOe_{1g}, LGOe_{1g}	$3d_{xz}$, $3d_{yz}$	e_{1g}, e_{1g} – bonding e^*_{1g}, e^*_{1g} – anti-bonding
	$e_1 + e_1$	LGOe_{1u}, LGOe_{1u}	$4p_x$, $4p_y$	e_{1u}, e_{1u} – bonding e^*_{1u}, e^*_{1u} – anti-bonding
δ	$e_2 + e_2$	LGOe_{2g}, LGOe_{2g}	$3d_{xy}$, $3d_{x^2-y^2}$	e_{2g}, e_{2g} – bonding e^*_{2g}, e^*_{2g} – anti-bonding
	$e_2 + e_2$	LGOe_{2u}, LGOe_{2u}	–	e_{2u}, e_{2u} – non-bonding
Non-bonding	$b + b$	LGOb_{2g}	–	b_{2g} – non-bonding
		LGOb_{1u}	–	b_{1u} – non-bonding

In this combination the wave function of the molecular orbitals of the two benzene rings may be added to or subtracted from ech other. Addition of wave functions leads to gerade (g) ligand group orbitals, while subtraction leads to ungerade(u) ligand group orbitals. For example combination of the two a orbitals yields two ligand group orbitals viz LGOa$_{1g}$ formed by addition of wave function of two a orbitals and LGOa$_{2u}$- formed by subtraction of wave function of two a orbitals. Likewise the two degenerate e$_1$ molecular orbitals on one benzene ring combine with the two degenerate e$_1$ molecular orbitals on the other benzene ring to give four ligand group orbitals viz two degenerate LGOe$_{1g}$ orbitals and two degenerate LGOe$_{2u}$ orbitals. The two b orbitals combine by addition to yield LGOb$_{2g}$ orbitals, and by subtraction to yield LGOb$_{1u}$ orbital.

The combinations involved in the formation of ligand group orbitals are shown in above table

Step3. Combination of ligand group orbitals with atomic orbitals of chromium to form molecular orbitals of di(η^6-benzene)chromium(0).

Each ligand group orbital merges with a suitable atomic orbital of chromium the one with which its symmetry matches to yield the molecular orbitals of di(η^6-benzene)chromium(0) this combination is set out in figure 11.

The LGOa$_{1g}$ orbital has the correct symmetry to combine with 4s and 3d$_z{}^2$ orbitals of chromium despite the fact that there is a large difference in the energies of these two orbitals. Two molecular orbitals are formed out of this combination viz a$_{2u}$ – bonding and a^*_{2u} -anti-bonding. However the a$_{2u}$ orbital has a very small component of 4p$_z$ orbital and therefore we have refrained from drawing a line joining these two orbitals. Similarly the a^*_{2u} molecular orbital has a very little component of LGOa$_{2u}$ orbital and we have not drawn a line joining these two orbitals.

The two degenerate ligand group orbitals, LGOe$_{1g}$ have the correct symmetry to combine with 3d$_{xz}$ and 3d$_{yz}$ orbitals of chromium. Two degenerate bonding molecular orbitals, designated as e$_{1g}$ and two degenerate bonding molecular orbitals, designated as e$_{1g}$ and two degenerate anti-bonding molecular orbitals designated as $e^*_{1g'}$ are formed as aresult of this combination. Likewise the two degenerate LGOe$_{1u}$ orbitals combine with 4p$_x$ and 4p$_y$ orbitals of chromium giving two degenerate bonding molecular orbitals e$_{1u}{}^{'}$.

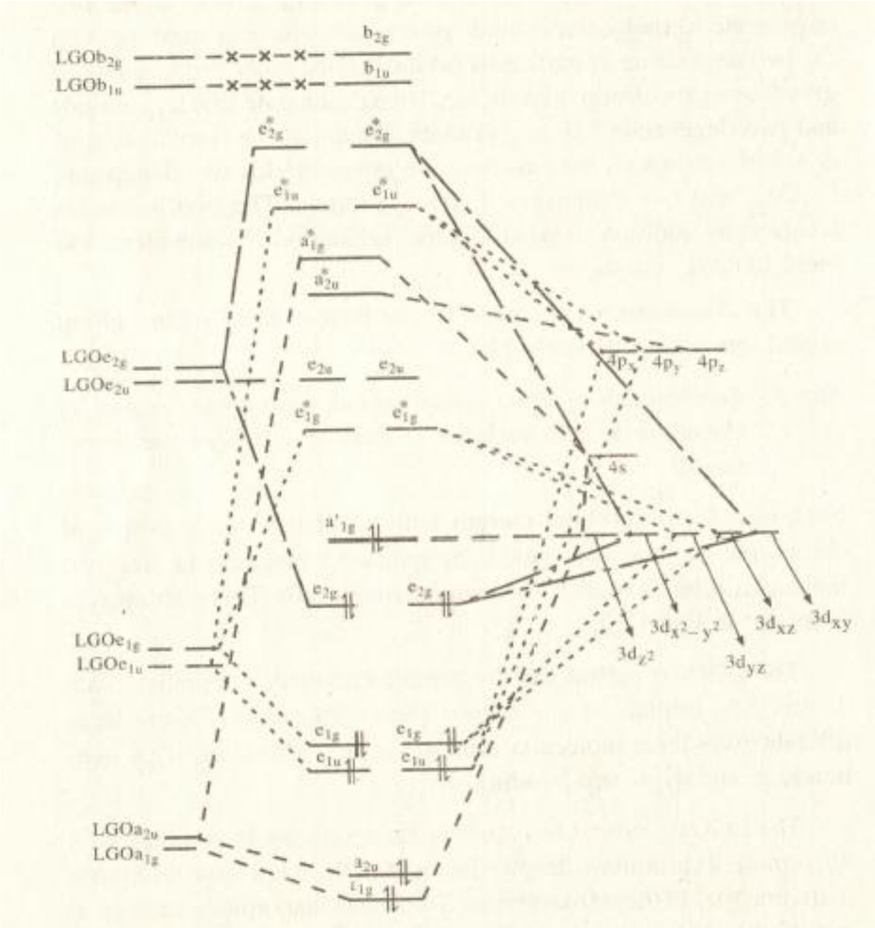


Figure 11: molecular orbital diagram of di (η^6-benzene)chromium(0)

The two degenerate ligand group orbitals LGOe$_{2g}$ have the same symmetry as the d$_{xy}$ and $d_{x^2-y^2}$ orbitals of chromium. Their combination gives rise to four molecular orbitals- two bonding designated as e$_{2g}$ and two anti-bonding, designated as $e^*_{2g'}$. The symmetry of LGOe$_{2u}$ orbitals does not match with any of the metal orbital, therefore these remain non-bonding and are designated as e$_{2u}$ molecular orbitals. The symmetries of LGOb$_{2g}$ and LGOb$_{lu}$ orbitals too do not match with that of any chromium orbital. Accordingly these also remain non-bonding and are represented as b$_{2g}$ and b$_{1u}$ non-bonding molecular orbitals.

The combinations involved in the formation of molecular orbitals of di(η^6-benzene)chromium(0). From ligand group orbitals of benzene and the atomic orbitals of chromium are shown

di(η^6-benzene)chromium(0). Is an 18 electron system as illustrated below.

Cr: = 6e$^-$

$2C_6H_6$: 2x $6e^-$ $=12e^-$

Total $=18e^-$

As per the electronic configuration of di(η^6-benzene)chromium(0). May be written as:

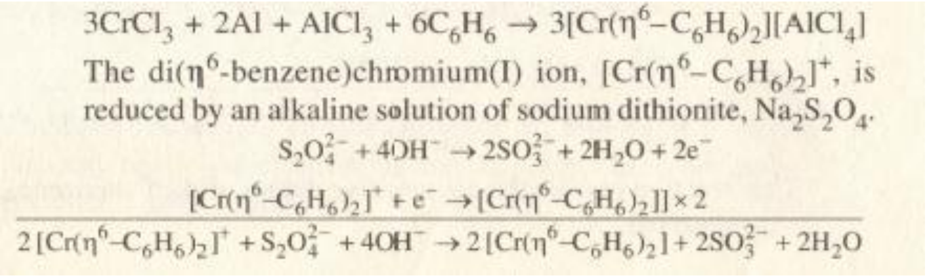
$$a_{1g}^{2}\, a_{2u}^{2}\, e_{1u}^{4}\, e_{1g}^{4}\, e_{2g}^{4}\, a'^{2}_{1g}$$

This indicates the diamagnetic nature of the organometallic system.

8.7.4 Synthesis

Di(η^6-benzene)chromium(0). May be synthesized by the following methods.

1. Fischner-Hafner method.



$$3CrCl_3 + 2Al + AlCl_3 + 6C_6H_6 \rightarrow 3[Cr(\eta^6\text{–}C_6H_6)_2][AlCl_4]$$

The di(η^6-benzene)chromium(I) ion, $[Cr(\eta^6\text{–}C_6H_6)_2]^+$, is reduced by an alkaline solution of sodium dithionite, $Na_2S_2O_4$.

$$S_2O_4^{2-} + 4OH^- \rightarrow 2SO_3^{2-} + 2H_2O + 2e^-$$

$$[Cr(\eta^6\text{–}C_6H_6)_2]^+ + e^- \rightarrow [Cr(\eta^6\text{–}C_6H_6)_2]] \times 2$$

$$2[Cr(\eta^6\text{–}C_6H_6)_2]^+ + S_2O_4^{2-} + 4OH^- \rightarrow 2[Cr(\eta^6\text{–}C_6H_6)_2] + 2SO_3^{2-} + 2H_2O$$

2. *Grignard reagent method*

$$CrCl_3 + 3C_6H_5MgCl + 3(C_2H_5)_2O \rightarrow [Cr(C_6H_5)_3\{(C_2H_5)_2O\}_3] + 3MgCl_2$$

The tris(diethylether)triphenylchromium(III) complex undergoes a free radical rearrangement and reduction to yield di(η^6-benzene)chromium(I) ion $[Cr(\eta^6\text{-}C_6H_6)_2]^+$.

$$[Cr(C_6H_5)_3\{(C_2H_5)_2O\}_3] \rightarrow [Cr(\eta^6\text{–}C_6H_6)_2]^+C_6H_5^- \quad 2CH_3CHO + C_4H_{10} + (C_2H_5)_2O$$

The driving force of this reaction is the reduction of chromium(III) to chromium(I) the latter being a stable half-filled $3d^5$ system.

The di(η^6-benzene)chromium(I) ion is reduced to di(η^6-benzene)chromium(0) by alkaline dithionite ions, as been shown above

8.7.5 Reaction

The following are some of the important reaction of di(η^6-benzene)chromium(0).

1. Aerial oxidation.

$$[\mathrm{Cr}\,(\eta^6\text{–}C_6H_6)_2] \rightarrow [\mathrm{Cr}\,(\eta^6\text{–}C_6H_6)_2]^+ + e^-] \times 4$$

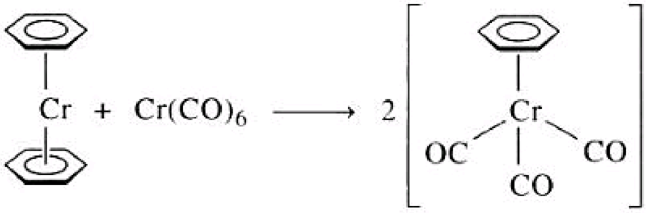
$$2H_2O + O_2 + 4e^- \rightarrow 4OH^-$$

$$\overline{4[\mathrm{Cr}\,(\eta^6\text{–}C_6H_6)_2] + 2H_2O + \underset{\text{Air}}{O_2} \rightarrow 4[\mathrm{Cr}\text{–}(\eta^6\text{–}C_6H_6)_2]^+ + 4OH^-}$$

This reaction reveals the air sensitive nature of di(η^6-benzene)chromium(0).

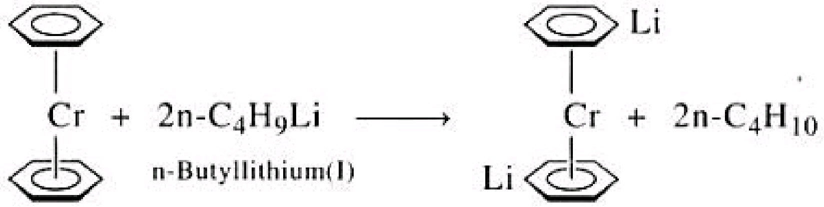
2. *Ligand replacement*

As has been stated the benzene rings in di(η^6-benzene)chromium(0) are quite labile. Thus one or both the rings may be displaced for example.



$$[\mathrm{Cr}(\eta^6\text{–}C_6H_6)_2] + 6PF_3 \rightarrow [\mathrm{Cr}(PF_3)_6] + 2C_6H_6$$

3. *Metallation*



This reaction occurs ion the presence of N,N,N”,N’ –tetramethylethylenediamine. The π coordinated benzene is metallated more easily than the free benzene. This shows that the kinetic acidity of benzene increases as a result of π bonding to the metal.

8.8 Allyl Organometallics

The allyl groups (C_3H_5-) is a versatile ligand. It can coordinate to the metal; through one carbon atom, that is acts as a monohapto (η^1) ligand, or through all the three carbon atoms, that is as a trihapto (η^3) ligand. The latter bonding mode is more common. As a triapto group the allyl moiety behavaves as a three carbon delocalized system and forms half-sandwich type of compounds.

The allylic ligand is (allyl) pentacarbonylmanganese (I) complex acts as a monodentate group. The composition of this organometallic derivative may, therefore, be represented as [Mn(η^1-

$C_3H_5)(CO)_5]$ while its structure may be depicted as in fig. the (allyl) tricarbonyliodoiron(II) complex on the other hand has a trihapto allyl group. Its composition is written as $[Fe(\eta^3\text{-}C_3H_5)(CO)_3I]$ and its structure is shown in figure 12

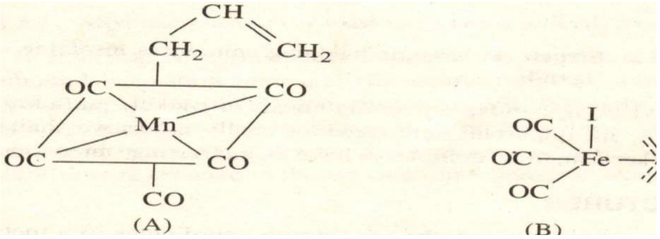


Figure 12: Structure of some allyl complex

In bridging complexes the allyl ligand may occupy terminal position. Such is the case with (η^3-2-phenylallyl)palladium(II)-μ-dichloro-(η^3-2-phenyallyl)palladium(II), the structure of which is shown in fig . it may also act as a briding ligand by η^1-bonding to one metal atom and η^2-bonding to the second metal atom. Such I sthe case with (Acetylacetonato)platinum(II)-μ-di-(η^1,η^2-allyl)-(acetyacetonato)platiunum(II) the structure of which is depicted in figure 13

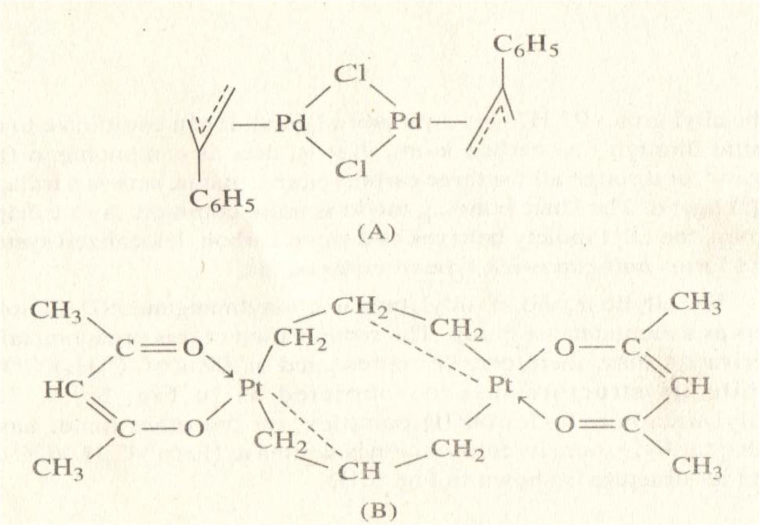


Figure 13: Structure of some bridging complexes involving allyl complexes.

Allyl compounds especially those of nickel, palladium and platinum are important homogeneous catalysts as we shall see in the nest section these complexes have an interesting stereochemistry.

8.8.1 Structure

As a monohapto ligand the allyl group coordinates to a metal in a manner shown in structure (I) of the figure 14 as a trihapto lignad, its coordination to metal may be represented by structures

(II-IV). In the latter structure, the delocalized anion $CH_2{=}CH{-}CH_2^-$ acts as a four electron donor. In this all there carbon-carbon bond lengths are equal.

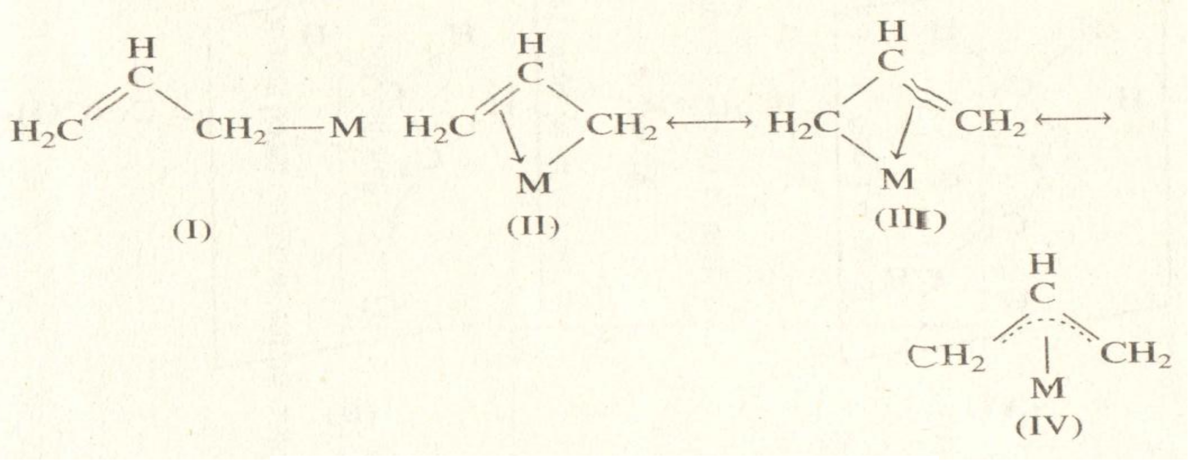


Figure 14: Bonding Models of some allyl ligand

The bis(allyl)nickel(II) complex involves trihapto allyl groups. Its composition $[Ni(\eta^3\text{-}C_3H_5)_2]$, indicates the possibility of cis- and trans- isomerism. The structure of these geometrical isomers are illustrated in figure 15A and 15.B respectively.

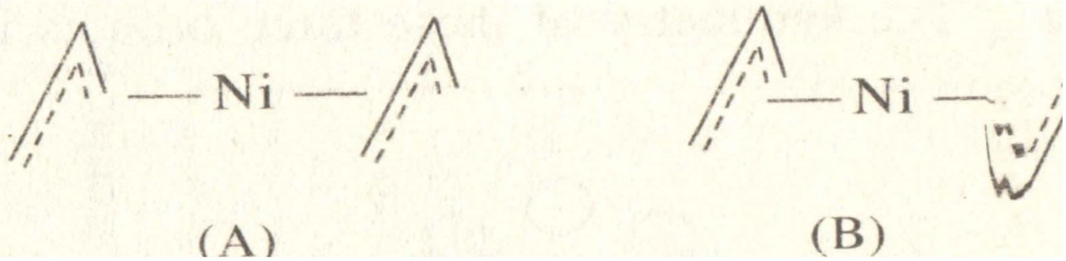


Figure 15: Allyl complex may exist (A)-Cis and (B)-trans isomer

In addition to geometrical isomers the organometallic allyl compounds also show anti-and syn-conformational isomers (figure 16).

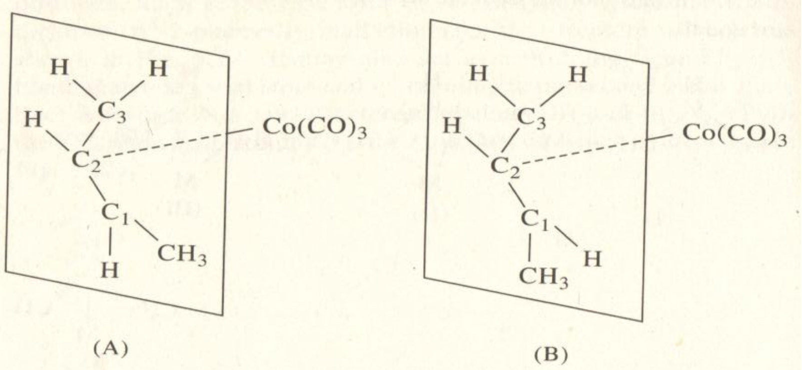


Figure 16: Allyl complexes may exist as (A) anti-; and (B) syn-isomers

These are possible with terminal substituted ligands. When the terminally substituted group and the hydrogen atom on the central carbon atom are oriented in the same direction, the isomer is syn- when these two entities are oriented in the opposite directions the isomers is anti Tricarbonyl(η^3-1-methylallyl(I) complex for example exists in its anti and syn isomeric forms.

8.8.2 Bonding

The bonding in η^3- allyl complex may be qualitatively described in terms of molecular orbital theory. The $2p_z$ orbitals on the three allylic carbon atoms combine to give three molecular orbitals, designated as ψ_1, ψ_2 and ψ_3. The symmetry of these orbitals is shown in figure 17.

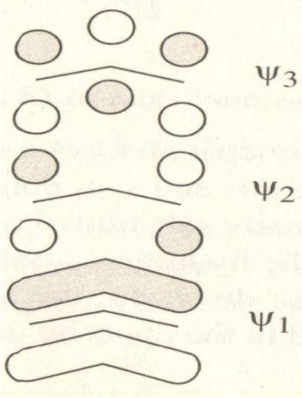


Figure 17: Molecular orbitals of allyl anion

Characteristics of allyl molecular orbitals and their possible combinations with metal atomic

Allyl Molecular orbitals			Metal Orbitals	Bonding Mode
Type	Number of	Number of electrons		
ψ_1	Zero	2	S,p_z,d_{z^2}	Ligand to metal sigma bonding
ψ_2	1	2	P_y,d_{yz}	Ligand to metal pi bonding
ψ_3	2	Zero	P_x,d_{xz}	Metal to ligand pi bonding $\psi_3 \xleftarrow{\pi} M$

The ψ_1, ψ_2 and ψ_3 molecular orbitals of allyl anion have zero one and two nodes respectively. The four electrons of allyl anion occupy ψ_1, ψ_2 orbitals while the ψ_3 orbitals is vacant. Thus the electronic configuration of the ligand is

$$\psi_1^2,\psi_2^2,\psi_3^0$$

The characteristics of the three molecular orbitals of the allyl ligand are presented in Table. During complexation, these orbitals overlap with the atomic orbitals of the metal. The criteria of overlap are dictated by the symmetry factor. An allyl molecular orbital will overlap with that atromic orbital of metal which has the closest symmetry to it.

The ψ_1 orbital would combine with the s,p_z or $d_z{}^2$ orbital of the metal. In this combination ψ_1 orbital will donate two electrons to the metal, resulting in the formation of a σ bond that is

$\psi_1 \xrightarrow{\sigma} M$.

The ψ_2 orbital has appropriate symmetry to overlap with p_y or d_{yz} atomic orbital of the metal. It too donates both its electrons to either of these metla orbitals, resulting in the formation of a π bond that is

$\psi_2 \xrightarrow{\pi} M$

The vacant ψ_3 orbital of the allyl ligand accepts electron from P_x or d_{xz} orbital of the metal, resulting in dative π bonding, that is $\psi_3 \xleftarrow{\pi} M$. The possible combination of the allyl molecular orbitals with the metal, atomic and the type bonding resulting thereform are highlighted in table

8.8.3 Synthesis

Allyl organometallics may be synthesized by the following methods

1. Metahesis

$$NiBr_2 + 2C_3H_5MgBr \xrightarrow{263\ K} [Ni(\eta^3\text{-}C_3H_5)_2] + 2MgBr_2$$

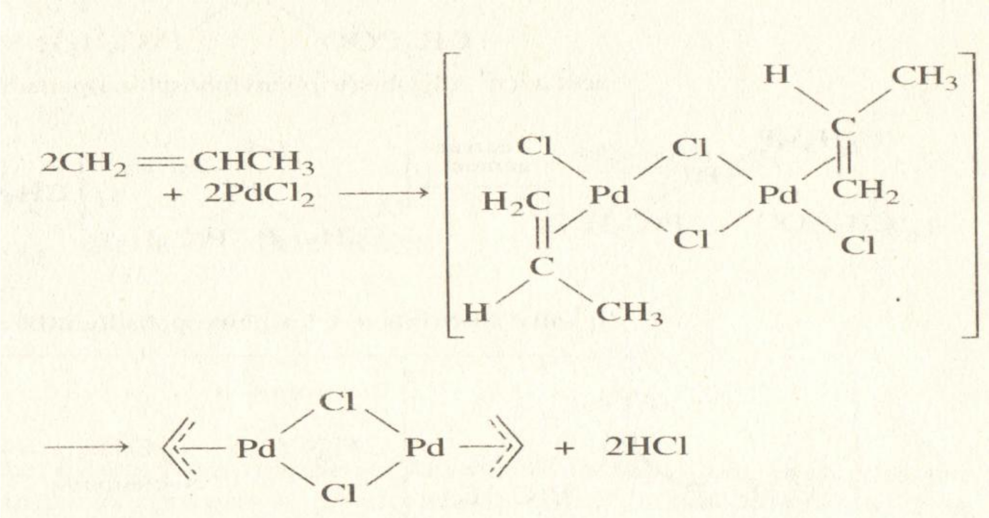
2. Rearrangement

$$Na[Mn(CO)_5] + C_3H_5Cl \rightarrow [Mn(\eta^1\text{-}C_3H_5)(CO)_5] + NaCl$$
$$[Mn(\eta^1\text{-}C_3H_5)(CO)_5] \xrightarrow{350\ K} [Mn(\eta^3\text{-}C_3H_5)(CO)_4] + CO$$

3. Oxidative addition

$$[Fe(CO)_5] + C_3H_5I \rightarrow [Fe(\eta^3\text{-}C_3H_5)(CO)_3I] + 2CO$$

4. Addition followed by elimination

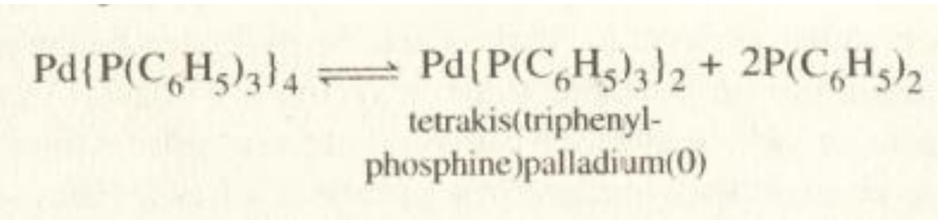


8.8.4 Reactions

The important reaction of metal-allyls are given below.

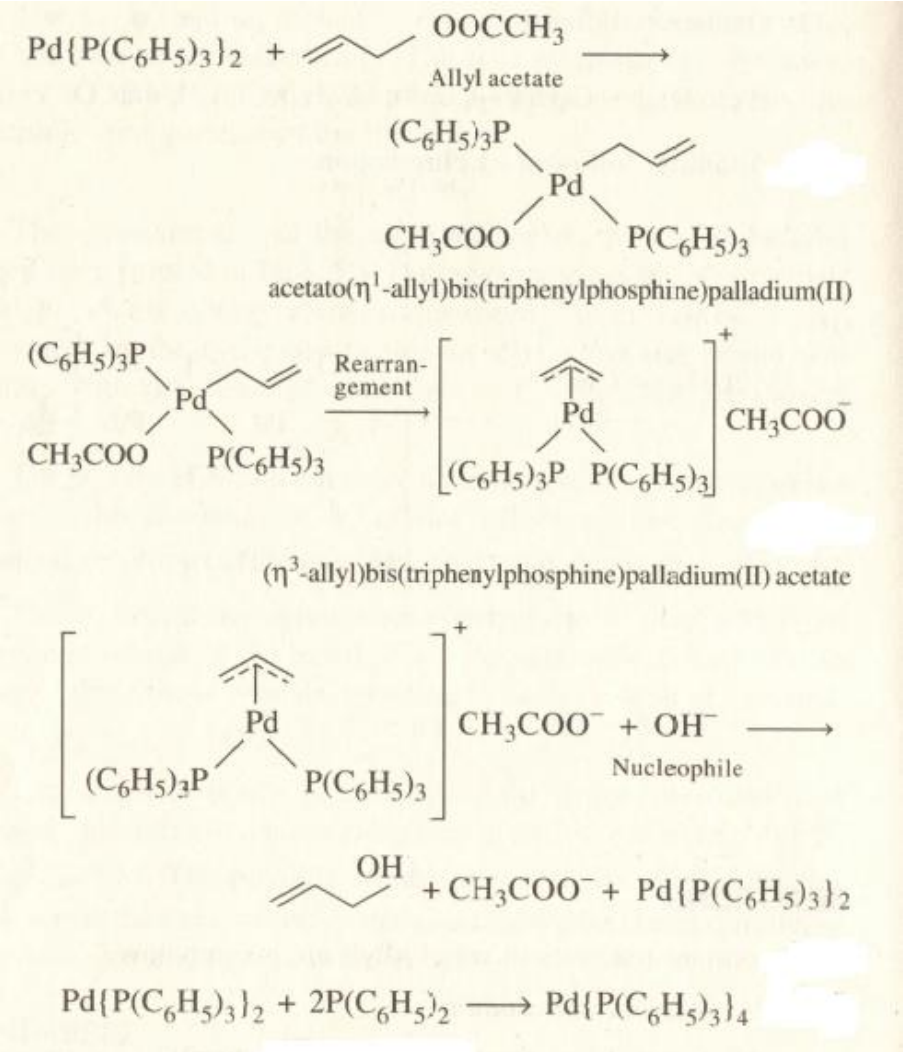
1. Nucleophilic substitution

   Allyl complexes serves as selective electrohilic substrates in organic synthesis. These are attacked at the terminal carbon of allyl moiety by nucleophiles as demonstrated by the following examples.



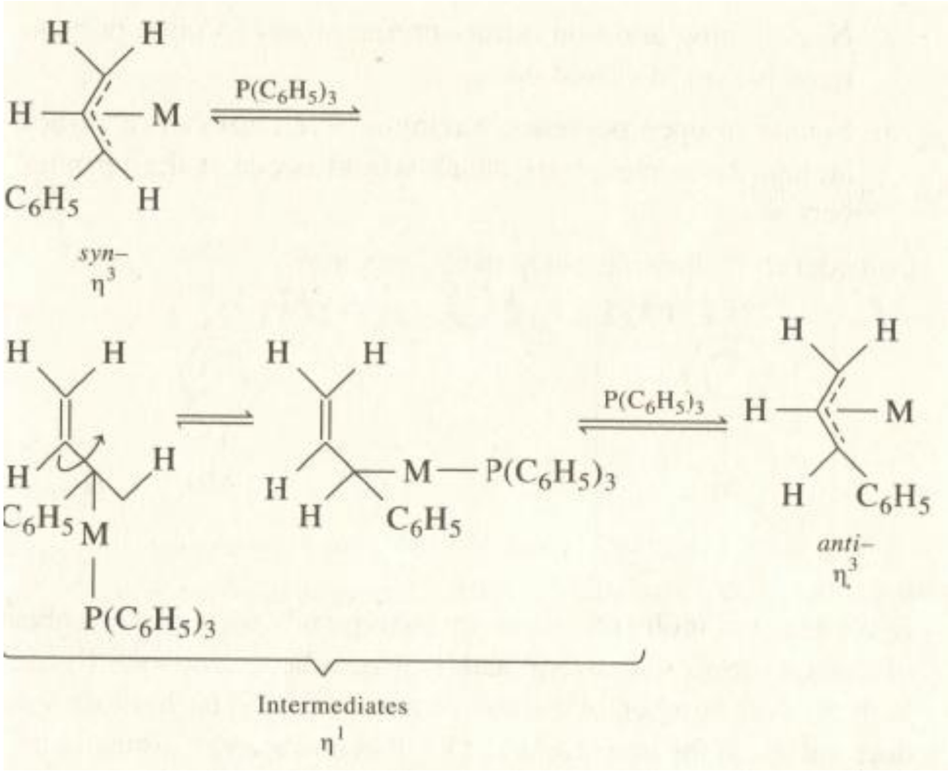
$$Pd\{P(C_6H_5)_3\}_4 \rightleftharpoons Pd\{P(C_6H_5)_3\}_2 + 2P(C_6H_5)_2$$

tetrakis(triphenyl-
phosphine)palladium(0)



2. Anti-syn Interchange

Complexes of terminally substituted allys may exits in anti- or syn conformational forms. The anti- form in which the substituent on terminal carbon an the hydrogen on the middle carbon are on opposite sides, may rapidly convert into syn- from in which the two substituents are on the same side. However in solution and in presence of a Lewis base, such as triphenylphosphine the interconcersion is slowed down and it becomes possible to isolate anti- and syn- conformational isomers.



The Lewis base, triphenylphosphine in this case displaces the olefinic bond converting η^3-allyl to η^1-allyl. In the latter state free rotation is possible around carbon-carbon and metal-carbon bonds. As a result of these rotations the syn-anti conversion is accomplished.

In the absence of the Lewise base the free rotation about the carbon-carbon and metal-carbon bonds is very rapid. It is so rapid interconversion is called fluxional behaviour. However when the Lewis base is coordinated to the metal, the energy barrier to rotation increases. As a result the rotations about carbon-carbon and metal carbon bonds slow down and thus it beomes possible to separate the two fonformational isomers.

8.9 summary of the unit

Among the most distinctive aspects of organometallic chemistry is the ability of a wide variety of ligands containing π-electron systems to form π-bonds to metals. η^2-Alkene (olefin) complexes now exist of every transition metal and constitute one of the most important classes of coordination compounds. Ethylene donates electron density to the metal in a σ fashion, using its π bonding electron pair. At the same time, electron density can be donated back to the ligand in a π fashion from a metal d orbital to the empty π* orbital of the ligand. Structural consequences of back-donation are, 1. lengthening of the C=C bond 2. Reduction of the angles around C from ca. 120^o (sp^2 hybridized) toward angles typical of tetrahedral sp^3-C. In the extreme, the C=C bond length reaches values more typical of C-C single bonds, with formation of two distinct metal-carbon σ bonds. The resulting complex is more appropriately described as a metallacyclopropane. As relatively weak σ-donors and π-acceptors, alkenes are easily displaced. Alkene complexes can be convenient starting materials for synthesis of new compounds

8.10 Key words

Transition metal-π complexes; Olefin organometallics; Alkyne organometallics; cyclopentadienyl organometallics; cyclobutadienyl organometallics; Allyl organometallics; Arene organometallics

8.11 References for further studies

1) Organometallics: Complexes with transition metal-carbon [sigma]-bonds, Volume 1; Manfred Bochmann; *Oxford University Press*, **1994**.
2) Organomettalic Chemistry; Sodhi G.S.; *Ane Books Pvt Ltd*, **2009**.
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8.12 Questions for self understanding

1) What are transition metal-π complexes? Give examples
2) Write a note on different types of transition metal-π complexes
3) What are olefinorganometallics? Give examples
4) Discuss the structure and bonding in olefinorganometallics
5) Explain the different methods of synthesis of olefinorganometallics
6) Discuss the different types of reactions exhibited by olefinorganometallics
7) What are alkyne organometallics? Give examples
8) Write a note on structures and bonding in alkyne organometallics
9) Discuss briefly on synthesis and reactions of alkyne organometallics
10) What are cyclobutadienyl organometallics? Give examples
11) Explain the structure and bonding in cyclobutadienyl organometallics
12) Discuss briefly the various methods of Synthesis of cyclobutadienyl organometallics
13) Explain the various reactions of cyclobutadienyl organometallics

14) What are cyclopentadienyl organometallics? Give examples

15) Write a note on structure of ferrocene

16) Explain the methods of synthesis ferrocene

17) Discuss the reaction ferrocene

18) What are arene arganometallics? Give examples

19) Discuss the structure and bonding in arene arganometallics

20) Write a note on synthesis of arene arganometallics

21) What are allyl organometallics? Give examples

22) Explain the structure and bonding in allyl organometallics

23) Discuss the synthesis and reactions of allyl organometallics

UNIT-9

Structure

9.0 Objectives of the unit
9.1 Introduction
9.2 Organolithium reagents
9.3 Properties of organolithium compounds
9.4 Structure and bonding in organolithium compounds
9.5 Reactions of organolithium compounds
9.6 Organomagnesium compound
9.9 Lithium diorganocopper reagents, Gilman reagents
9.10 Structure and bonding in Gilman reagents
9.11 Reactions of Gilman reagents
9.12 Organometallic Compounds of Aluminium
9.13 Preparation of organoaluminium compounds
9.14 Properties organoaluminium compounds
9.15 Structure and Bonding in organoaluminium compounds
9.16 Reactions of organoaluminium compounds
9.17 Organometallic Compounds of Mercury
19.18 Preparation
9.19 Properties of organomercury compounds
9.20 Structure and Bonding in organomercury compounds
9.21 Reactions of organomercury compounds
9.22 Summary of the unit
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9.0 Objectives of the unit

After studying this unit you are able to

- Explain the properties of organolithium compounds
- Identify the structure and bonding in organolithium compounds
- Explain the synthesis and reactions of organomagnesium compound
- Identify the use of Lithium diorganocopper reagents, Gilman reagents
- Write the structure and bonding in Gilman reagents
- Explain the properties of rganometallic compounds of aluminium
- Explain the properties organometallic compounds of mercury

9.1 Introduction

Organometallic compounds are molecules with a metal-carbon bond. All metals in the periodic table form organometallic compounds. Two of the most useful are magnesium and lithium. All organic halides, including alkyl halides, react with magnesium metal to give compounds with the formula RMgX, known as organomagnesium halides. Organomagnesium compounds are more commonly referred to as Grignard reagents. Lithium: Lithium will also react with alkyl halides to make an organolithium compound. Because lithium only has one valence electron, it takes two equivalents of Li to react with an alkyl halide. One lithium ends up on the carbon to give the alkyl lithium compound. The other ends up as LiBr. When Li reacts with an alkyl halide, a salt (lithium halide) is formed, whose stability is the primary thermodynamic driving force of the reaction. Due to the larger difference between the electonegativities of C and Li, the C-Li bond in organolithium compounds has more ionic character and C is more negatively polarized. The higher polarization makes R in RLi a harder nucleophile compared to RMgX, which explains why lithium organyls and Grignard reagents react differently when adding to certain carbonyl compounds.

9.2 Organolithium reagents

a) Direct Method

Reaction of lithium metal with an organic halide in a suitable organic solvent leads to the preparation of an organolithium reagent.

$$2Li + RX \rightarrow RLi + LiX$$

Here R may be alkyl or aryl group. The organolithium compounds rapidly react with oxygen and moisture and thus for their preparation dry solvents and apparatus should be used and also air should be excluded by using an inert atmosphere. For inert atmosphere, dinitrogen (N_2) or argon gas is normally used.

Methyl halides (MeX) (X = Cl, Br, I) react with lithium metal in diethyl ether; however, alkyl iodides are not used since they undergo side reaction, and are not suitable reagents. Benzyl chloride ($C_6H_5CH_2Cl$) also undergoes similar side reaction to generate 1, 2- diphenylethane. The n-butyllithium, obtained from reaction of n-butyl chloride or bromide with lithium metal in hexane or ether, is most frequently used reagent. Its solution in hexane is commercially available. Phenyllithium can be readily prepared in good yield from the reaction with bromobenzene or iodobenzene; chlorobenzene reaction is very slow and often not used. Bromobenzene is more commonly used as compared to iodobenzene.

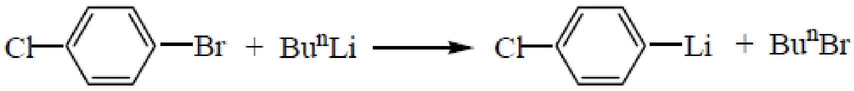
$$RI + RLi \longrightarrow R{-}R + LiI$$

$$C_6H_5CH_2Cl + C_6H_5CH_2Li \longrightarrow C_6H_5CH_2CH_2C_6H_5 + LiCl$$

b) Metal-Halogen Exchange

In this method, an organolithium compound reacts with an organic halide. The formation of R'Li occurs if R' is more electronegative than R and it varies with the unsaturation in the organic group ($Csp > Csp^2 > Csp^3$). The unsaturation leads to the formation of more stable carbanion. Reactions of butyllithium with $Ph_2C{=}CHBr$ and PhBr form $Ph_2C{=}CHLi$ and PhLi respectively. Among aryl halides, the reactivity order is I > Br >Cl > F. Interestingly, reaction of BuLi with ClC_6H_4Br gives 90% ClC_6H_4Li. It may be pointed out that the metal-halogen exchange reactions are regiospecific.

$$RLi + R'X \longrightarrow R'Li + RX$$



c) Metal-Hydrogen Exchange – Metallation

The exchange of metal with hydrogen is known as metal-hydrogen exchange and this process is known as metallation. The process of metallation involves nucleophilic attack of an organolithium reagent on the acidic hydrogen. For example, reaction of organolithium RLi with hydrocarbon R'H gives R'Li and RH, also reaction of R_2NLi with R'H gives R'Li.

$$R'H + RLi \longrightarrow R'Li + RH$$

$$R'H + R_2NLi \longrightarrow R'Li + R_2NH$$

The reactions will proceed to right only if hydrocarbon R'H is more acidic than RH or R_2NH. For example, reaction of phenylethyne (PhC_2H) with PhLi gives PhC_2Li and PhH, because PhC_2H is more acidic than PhH.

$$PhC{\equiv}CH \ + \ PhLi \longrightarrow PhC{\equiv}CLi \ + \ PhH$$

It may be interesting to note that the coordination of the lithium to a base increases nucleophilic character of carbon bonded to lithium. Thus the reactivity of organolithium compounds is more in ethers than in hydrocarbons because ethers with oxygen donor atoms bind to lithium.

d) Metal-Metal Exchange

In this method, an organolithium reagent is used to prepare other organolithium compounds of organic compounds. For example, phenyl lithium reacts with tetravinyltin in ether to generate vinyllithium reagents. Here tin bonded to vinyl moiety is exchanged by Li bonded to phenyl. Similarly, allyllithium can be prepared.

$$(H_2C{=}CH)_4Sn \ + \ 4PhLi \longrightarrow 4(H_2C{=}CHLi) \ + \ Ph_4Sn$$

9.3 Properties of organolithium compounds

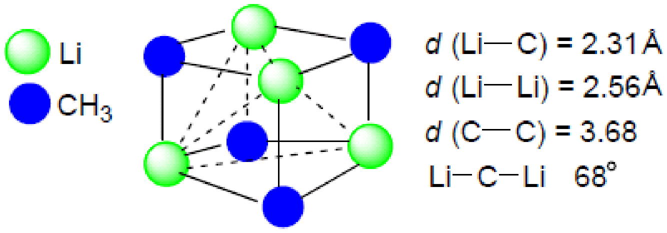
Organolithium compounds are soluble in hydrocarbons such as n-hexane, ethers etc. They are highly volatile and can be sublimed in vacuum. They readily react with water and air, and are often flammable. The high polarity of R^-Li^+ bonds leads to strong association of organolithium moieties in their solid, liquid and gas states. Mostly, lithium alkyl and aryl compounds exist as aggregates in the solid, solution, and even in gas states. In the solid state, methyllithium and ethyllithium (RLi) exist as tetramers, $(RLi)_4$ (R = Me, Et). Methyl lithium is tetramer in diethyl ether and THF, but insoluble in cyclohexane, toluene and benzene. Ethyllithium exists as an hexamer in cyclohexane, toluene and benzene, but is tetramer in diethyl ether and THF. BunLi is tetamer in diethyl ether and THF, hexamer in toluene, benzene and cyclohexane. ButLi is tetramer in each of the above mentioned solvents. Phenyl lithium is a dimer in Et_2O and THF, and also $Li_2\{C(SiMe_3)_3\}_2$ is a dimer.

Organolithium reagents are easily aggregated, with lithium coordinating to more than one carbon atom and carbon coordinating to more than one lithium atom.

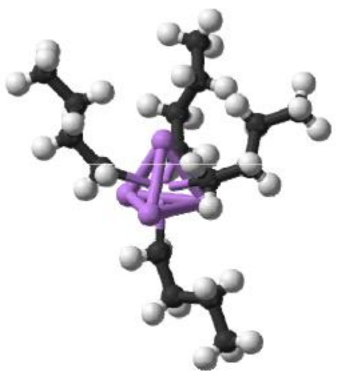
9.4 Structure and bonding in organolithium compounds

Organolithium compounds form oligomers (low molecular weight polymers). This oligomerization can be explained in terms of multicenter two electron bonds. The structure of $(MeLi)_4$ tetramer can be described in two ways , According to one description, Li atoms lie at the corners of a tetrahedron, and four methyl groups are centered over the facial planes in μ3-modes.

And according to second description, Li and C atoms occupy alternate corners of a cube and each Me group is similarly bonded in μ$_3$-mode. The structures of $(EtLi)_4$ and THF /diethyl ether adducts, namely, $(MeLi{\cdot}THF)_4$, and $(PhLi{\cdot}Et_2O)_4$ are similar, except each Li is bonded in addition to O atoms from THF (C_4H_8O), or Et_2O. Solid methyllithium has cubic body-centered packing of $(LiCH_3)_4$ units, the latter consisting of Li_4^- tetrahedron with methyl groups capping the triangular faces. In the aggregates $(LiR)_n$, the "electron deficiency" is compensated for by the formation of n-Butyllithium deficiency multicenter bonds.



Schematic drawing of the unit $(LiCH_3)_4$



n-Butyllithium

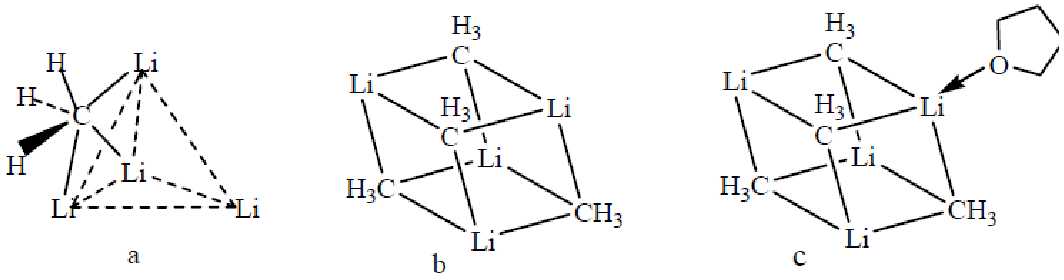


Figure 1: Structure of tetramethyllithium $(MeLi)_4$ (a, b) and $(MeLi.THF)_4$ (c)

Below figure shows overlap of orbitals

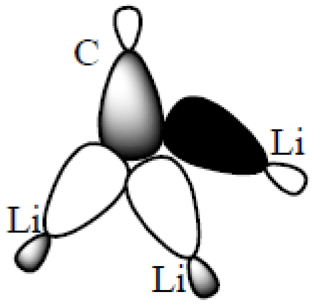


Figure 2: Orbital overlap along one face formed by three Li

The formation of bonds may be understood as follows. Consider the bonding of CH_3 over the plane formed by three Li atoms as shown in Figure 1a. If CH_3 is treated as a radical with C atom considered sp^3 hybridized, and again each Li atom is treated as sp^3 hybridized, then one sp^3 orbital with one electron from C atom, one sp3 from one Li with one unpaired electron, and two empty sp^3 orbitals from two lithium atoms combine as shown Figure 2. forming four center two electron (4c-2e) bonds. Same process repeats with other three methyl groups over remaining three faces of the tetrahedron.

In $\{PhLi{\cdot}(tmen)\}_2$, sp^2 orbital of C of Ph group with one electron, one Li atom with one electron, and one empty orbital of second Li atom form 3c-2e bond (Li-C-Li bond). Alkali metals (Li^+, Na^+, K+) are also known to form π - complexes with rings such as cyclopentadienyl (Cp, $C_5H_5^-$). A simplified view of bonding in $\{PhLi{\cdot}(tmen)\}_2$ is a dimer with Li bonded to N, N-chelating, tmen (Me_2N-CH_2-CH_2-NMe_2) ligands. The THF(C_4H_8O), Et_2O and tmen are Lewis bases which are forming coordinate bonds to Li center.

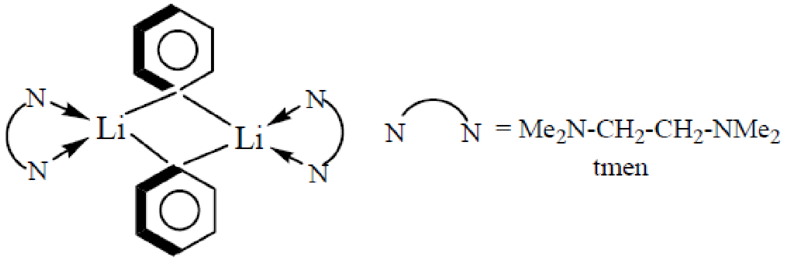
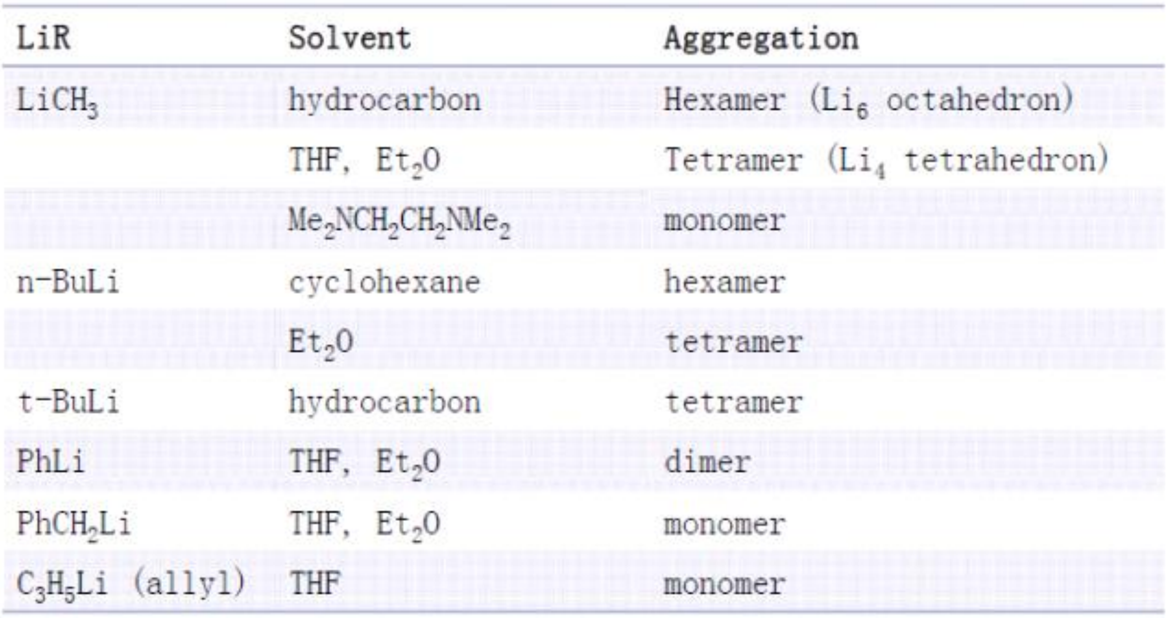


Figure3: Structure of phenyllithium dimer $(PhLi.tmen)_2$



LiR	Solvent	Aggregation
$LiCH_3$	hydrocarbon	Hexamer (Li_6 octahedron)
	THF, Et_2O	Tetramer (Li_4 tetrahedron)
	$Me_2NCH_2CH_2NMe_2$	monomer
n-BuLi	cyclohexane	hexamer
	Et_2O	tetramer
t-BuLi	hydrocarbon	tetramer
PhLi	THF, Et_2O	dimer
$PhCH_2Li$	THF, Et_2O	monomer
C_3H_5Li (allyl)	THF	monomer

Three general factors affect aggregation: the electrostatic interaction between opposite charges, the coordination sphere of lithium (solvent molecules or Lewis base) and the steric hindrance of the hydrocarbon part.

Lithium alkyls are often considered to be carbanionic (R^-) in reactions. The reactivity of organolithium compounds depends on differences in aggregation and nature of solvent. The reactivity of methyllithium $(MeLi)_4$ towards a substrate in THF is 10^4 times less than that of benzyllithium ($LiCH_2Ph$).

9.5 Reactions of organolithium compounds

Organolithium undergo thermal decomposition to form different products. For example, BunLi in boiling octane involves α-elimination reaction forming butene-1. Methyllithium decomposes at 250^oC to give CH_4 and CH_2Li_2, while at higher temperature, LiC ≡CLi, LiH and Li are formed. The ease of decomposition of organoalkali metal compounds has been found to be potassium > sodium > lithium.

$$BuLi \longrightarrow CH_3CH_2CH{=}CH_2 \quad + \quad LiH$$

$$2MeLi \longrightarrow CH_4 \; + \; CH_2Li_2$$

Organolithium compounds undergo a variety of reactions which illustrate their versatility in organic synthesis. Some general reactions are described below. They are highly reactive towards oxygen.

For example, methyl, ethyl and phenyl derivatives ignite in air. In general, sodium and potassium compounds are more easily oxidized than the lithium compounds, and the oxidation route occurs in two step reaction path. Hydrolysis of RO_2Li and ROLi will yield RO_2H and ROH respectively. For example, $(BuLi)_4$ in diethyl ether at -78^oC gave BuOH after hydrolysis. Likewise, $(BuLi)_6$ in benzene gave BuOH. Other oxidants such as iodine and sulfur also react with organolithium compounds (RLi) to form R-I and R-S_x-R compounds

$$RLi \; + \; O_2 \longrightarrow RO_2Li$$

$$RO_2Li \; + \; RLi \longrightarrow 2ROLi$$

$$RLi \xrightarrow{I_2} RI \; + LiI$$

$$RLi \xrightarrow{S} RSxR \; + \; Li_2S$$

Organolithium compounds readily react with a variety of proton sources to give hydrocarbon, RH. Reaction of methyllithium with ethanol in diethyl ether forms CH_4 and EtOLi and with HBr(g), it forms CH_4 and LiBr. Similarly, reactions of RLi with H_2O, R'SH, R_2'NH and Ph_2CH_2 forming hydrocarbons RH, and lithium salts. Organic halides such as bromobenzene undergo exchange reaction with RLi forming PhLi and RBr (equation 22). Organolithium compounds react with some solvents and deprotonate them. For example, Et_2O reacts with RLi to give RH, CH_2=CH_2 and $LiOCH_2CH_3$. Similarly, BuLi rapidly cleaves tetrahydrofuran after metallating it at 2-position. Organometal halides R'_3ECl (E = Si, Sn, Pb) react with organolithium compounds to generate R'_3ER and also undergo Wurtz coupling.

$$\mathrm{MeLi} + \mathrm{EtOH} \longrightarrow \mathrm{CH_4} + \mathrm{EtOLi}$$

$$\mathrm{MeLi} + \mathrm{HBr} \longrightarrow \mathrm{CH_4} + \mathrm{LiBr}$$

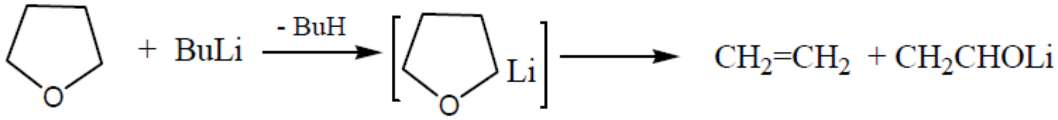
$$\mathrm{RLi} \xrightarrow{\mathrm{H_2O}} \mathrm{RH} + \mathrm{LiOH}$$

$$\mathrm{RLi} \xrightarrow{\mathrm{R'SH}} \mathrm{RH} + \mathrm{LiSR'}$$

$$\mathrm{RLi} \xrightarrow{\mathrm{R_2'NH}} \mathrm{RH} + \mathrm{LiNR_2'}$$

$$\mathrm{RLi} \xrightarrow{\mathrm{Ph_2CH_2}} \mathrm{RH} + \mathrm{LiCHPh_2}$$

$$\mathrm{RLi} \xrightarrow{\mathrm{PhBr}} \mathrm{PhLi} + \mathrm{RBr}$$

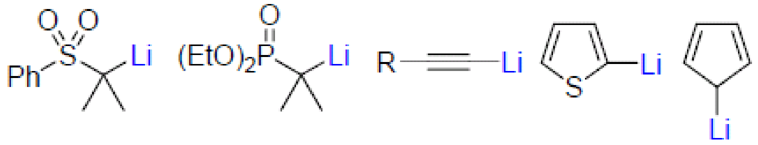


$$\mathrm{RLi} + \mathrm{R'ECl} \longrightarrow \mathrm{R'ER} + \mathrm{LiCl}$$

$$\mathrm{RLi} + \mathrm{R'X} \longrightarrow \mathrm{R\text{-}R'} + \mathrm{LiCl}$$

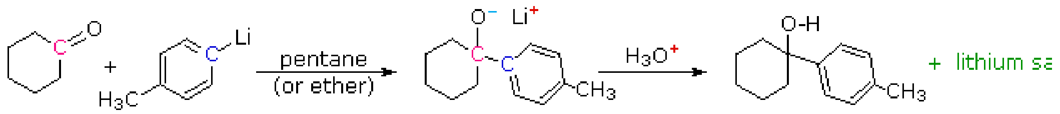
Metalation or Li/H exchange reaction

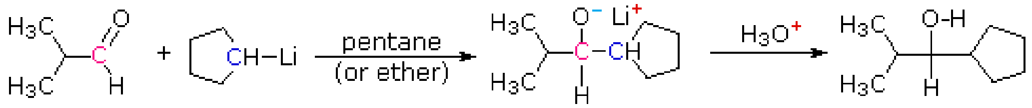
The metalation reaction is an important synthetic method for the preparation of many organolithium compounds.

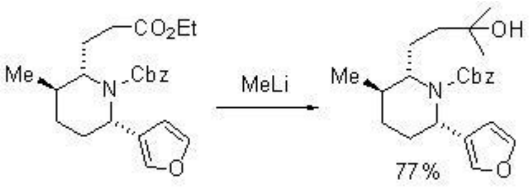


The reaction of Organolithium compounds with different functional groups of organic compounds and corresponding products formed are summarized below

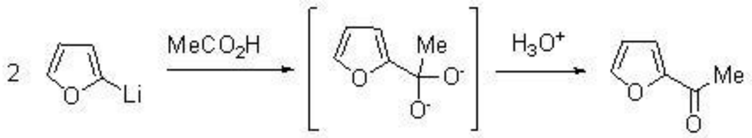
- Organolithium compounds react with ketones and aldehydes produces alcohols.

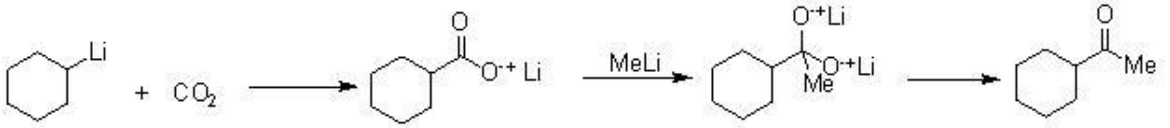




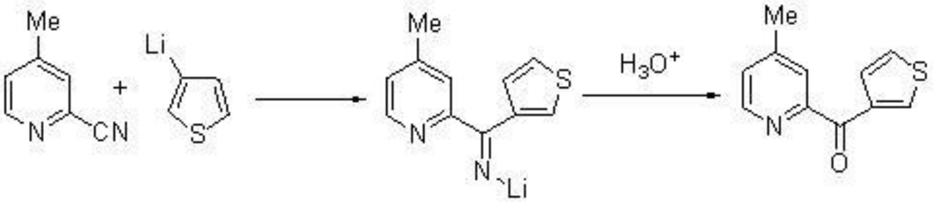


- Organolithium compounds react with carboxylic acid salts and acid chlorides yields the corresponding ketone.

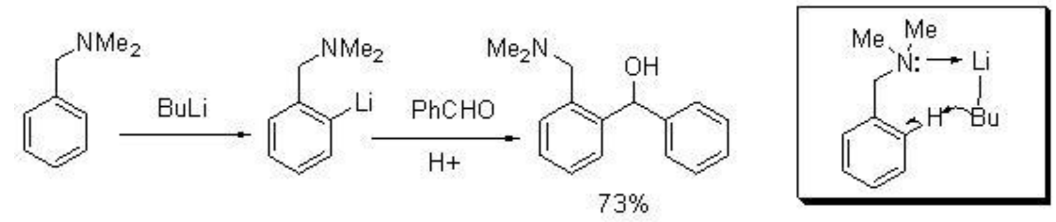


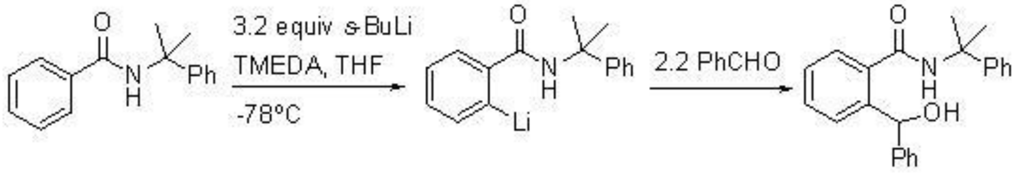


- Organolithium compounds react with isonitriles gives the corresponding lithium aldimine. Subsequent hydrolysis effectively converts the organolithium compound to its aldehyde.

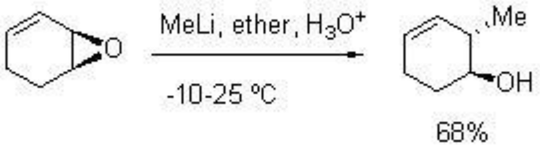


- The ortholithiation is useful reaction because the starting material does not need to have a halogen atom. For examples, in the case of benzyldimethylamine, the nitrogen atom directs attack of the butyllithium Likewise, N-cumylbenzamide with excess secondary butyllithium in the presence of TMEDA gives orotholithiated intermediate that could readily reacted with benzaldehyde with 80% yield.

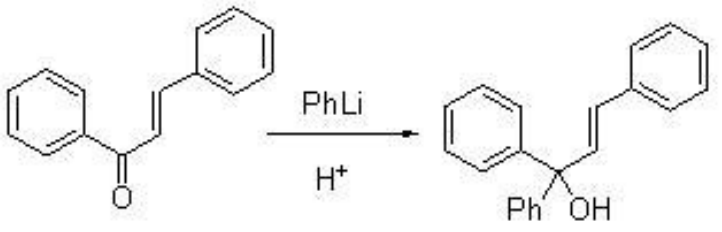




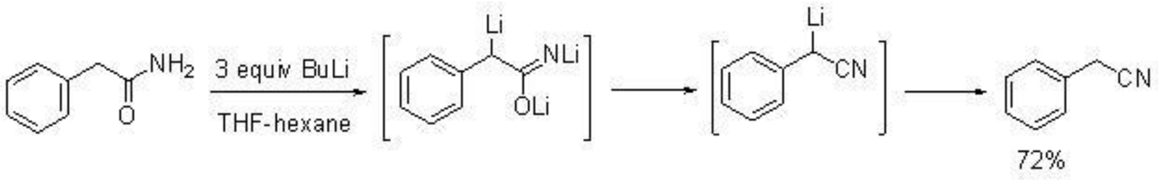
- Organolithium compounds react with certain epoxides to the corresponding alkanes.

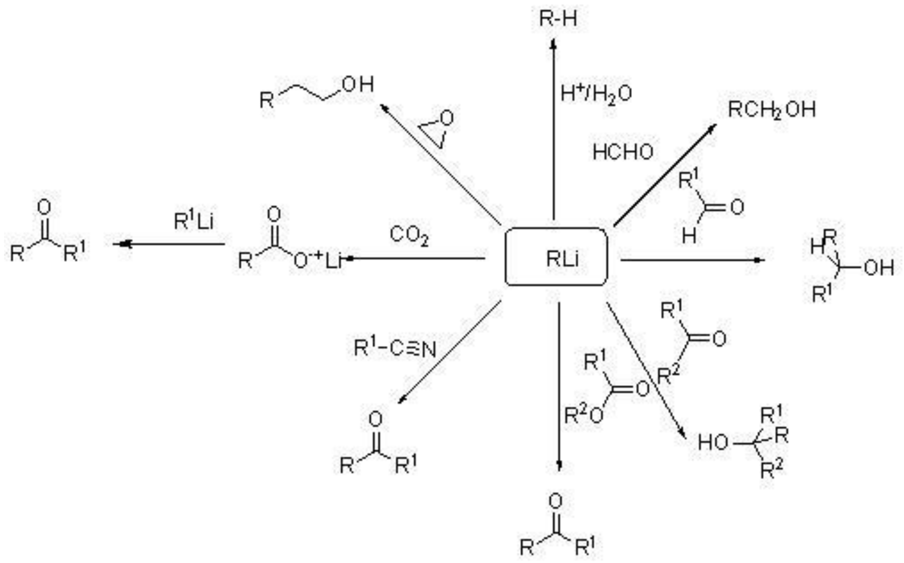


- In the case of Grignard reagents, α,β-unsaturated carbonyl compounds undergo reaction either at 1,2- or 1,4-addition depending on the structure of the carbonyl compound. The main reason is steric hinderance. While the organolithium reagents undergo reaction exclusively to give 1,2-addition products



- Primary amides undergo reaction with excess organolithium to give a nitrile.





9.6 Organomagnesium compound

All organic halides, including alkyl halides, react with magnesium metal to give compounds with the formula RMgX, known as organomagnesium halides This reaction occurs with 1°, 2°, 3°, alkenyl, aryl, and alkynyl halides. The halide can be Cl, Br, or I, but not F. In the reaction, the Mg metal is oxidized to Mg^{2+}. The alkyl halide is reduced. Organomagnesium compounds are more commonly referred to as Grignard reagents after Victor Grignard, who discovered them in the early 1900s. Grignard reagents are formed via the action of an alkyl or aryl halide on magnesium metal. Typical solvents are Et_2O and THF. The reaction proceeds through single electron transfer. The addition of I_2 activates the Mg surface, MgI_2 thus formed, binds the last traces of water in the reaction mixture.

$$Mg + RX \xrightarrow{Et_2O} RMgX(Et_2O)_n \qquad X = Br, I$$

9.7 Structure and bonding in organomagnesium compounds

In the synthesis of Grignard compounds (organomagnesium halides, RMgX), the solvent, which is usually diehtyl ether or tetrahydrofuran (THF), plays a most crucial role. The magnesium atom of a Grignard compound lacks four electrons to achieve an electron octet. If the synthesis is carried out in diethyl ether or THF, the magnesium atom is additionally complexed by two solvent molecules. This is possible due to the lone electron pairs of the solvent's oxygen atom. As a result, the magnesium atom achieves an electron octet and the Grignard compound is thus stabilized. In etherial solution Grignard compounds mainly form dimers in which two magnesium atoms are connected through two halogen atom bridges. In addition, each magnesium is complexed by one alkyl and one solvent substituent. These Grignard compound dimers are in equilibrium with the corresponding magnesium dihalide and the dialkylmagnesium compound. Such equilibrium is also known as Schenk equilibrium. Thus Grignard reagents form varying amounts of diorganomagnesium compounds (R = organic group, X = halide) as shown figure 5.

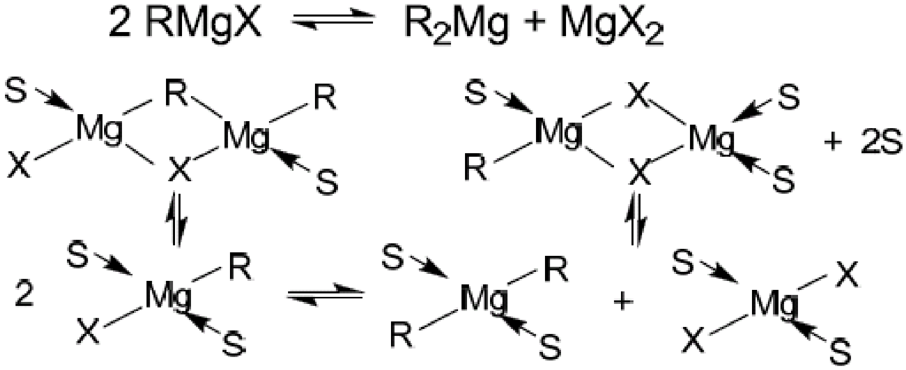


Figure 5: Equilibrium of various organomagnesium compounds in solution

Grignard reagents and organolithiums are interesting because they have opposite reactivity to the starting alkyl halide. The C-X bond is polarized such that the carbon is electrophilic. Since carbon is more electronegati ve than magnesium or lithium, the C-metal bond is polarized so that the carbon is negatively charged or nucleophilic. This sort of reversal of reactivity is referred to as umpolung reactivity. Umpolung means pole reversal in German. In chemistry it means a reversal of polarity, such as going from electrophilic to nucleophilic.

i) Organolithium and magnesium reagents are strong bases

They are protonated by water. An H from water replaces the metal to give an alkane. Thus, the overall reaction is replacement of a halide first with the metal then with H. Since the C-H bond is very weakly acidic (pKa = 51 for alkanes), organolithium and magnesium compounds are extremely strong bases. They can be used to deprotonate weak acids in organic chemistry. Butyl lithium is commonly used for this purpose. Note that because of their strong basicity, RLi and RMgX reagents cannot be used in the presence of OH, NH, or SH bonds. These would need to be protected first.

ii) Organolithium and magnesium reagents are also strong nucleophiles

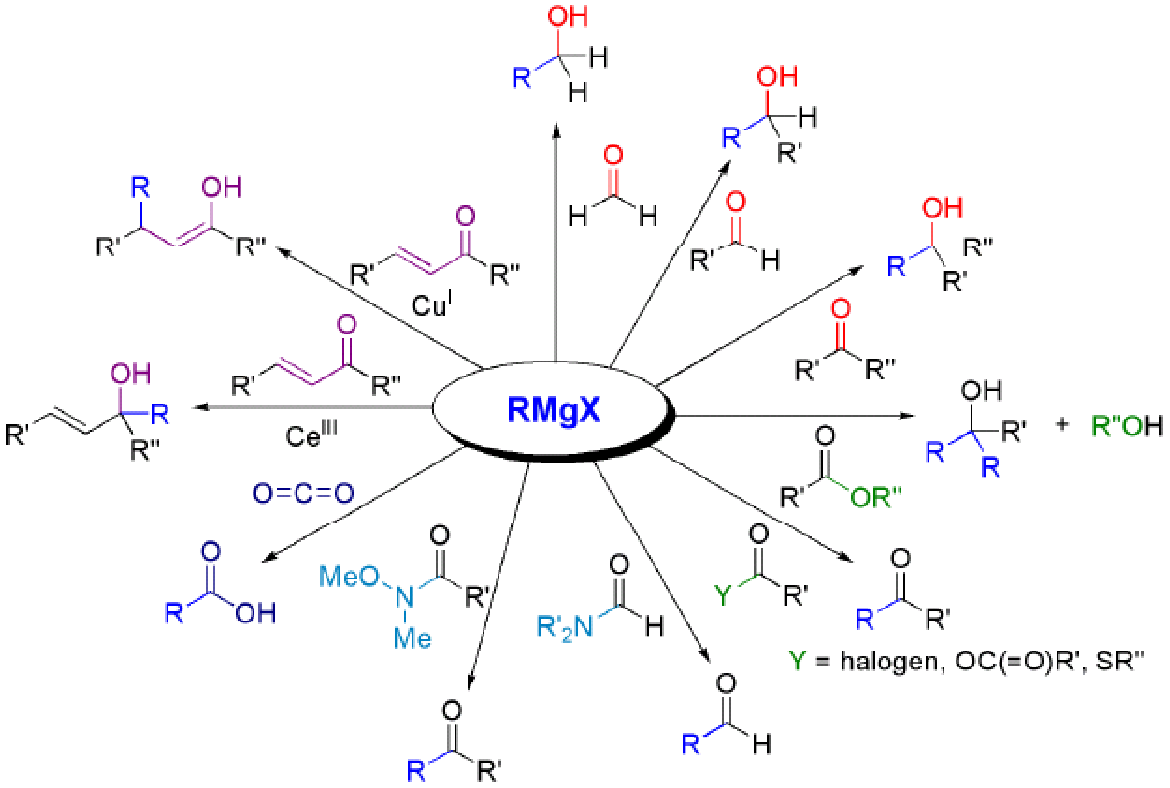
Grignard and organolithium compounds will add to epoxide electrophiles. Since they are strong nucleophiles, they add to the less substituted carbon in an S_N2-like reaction

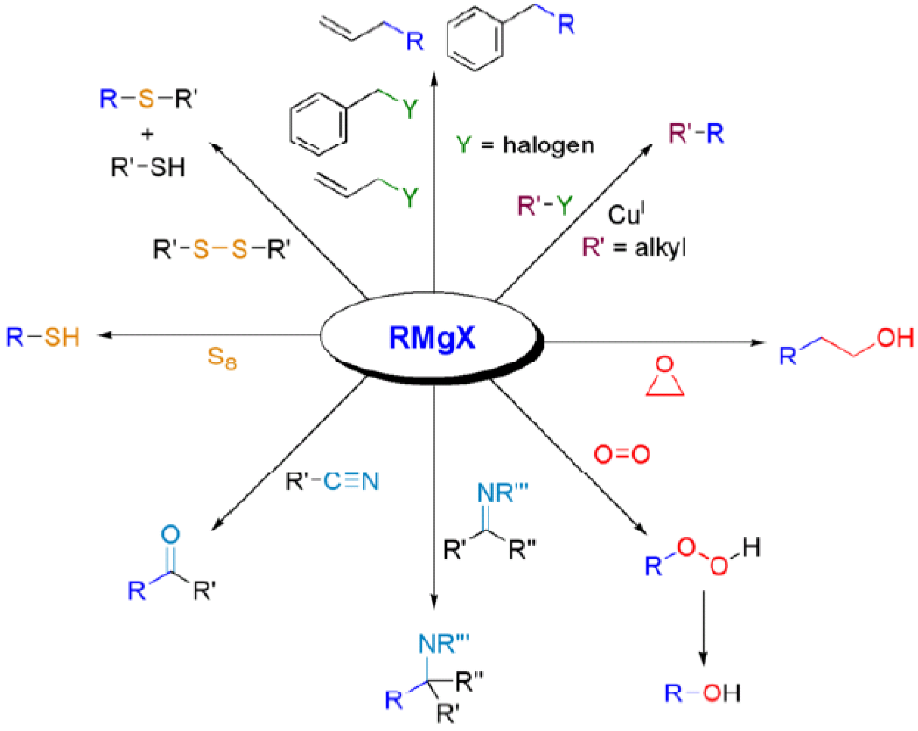
9.8 Reactions of organomagnisium reagents

The Grignard reaction is a general term for various chemical reactions involving Grignard reagents. Organomagnisium compound reacting with ketone and aldehydes produce alcohols. In addition reactions with esters, amides, acid chlorides, carbon dioxide, nitrile, alkyl halides, metallic halides and other substances are also widely used.

- Group of aldehydes, ketones, esters, anhydrides, acid chlorides and amides. In these reactions, the alkyl, aryl or vinyl group having carbanionic character become attached to the carbonyl carbon and the magnesium halide to the oxygen of the carbonyl group to give a complex (addition product). These addition products on decomposition with proton source give the corresponding alcohols.

The reactions of organomagnisum compounds with various functional groups and corresponding product formation is summarized in below chart.



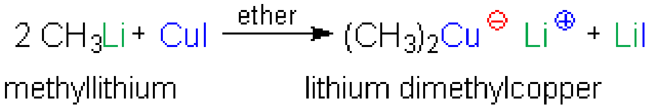


9.9 Lithium diorganocopper reagents, Gilman reagents

Copper metal usually cannot react directly with alkyl halides to give an organocopper compound. Reaction of 2 equivalents of an organolithium compound with CuI produces a dialkylcuprate (R2Cu^{-}Li^{+}), which are also known as Gilman reagents.

The Gilman reagent will react with other organic halides to replace the halide with the organic group on the copper center. This represents another way to make C-C bonds. The organic group on the copper can be sp^{3} or sp^{2} hybridized carbon. The organic halide can also be an sp^{3} or sp^{2} hybridized carbon. Note that RLi and RMgX cannot generally do substitution on organohalides. Gilman reagents can also react with epoxides in the same way as RLi and RMgX reagents.

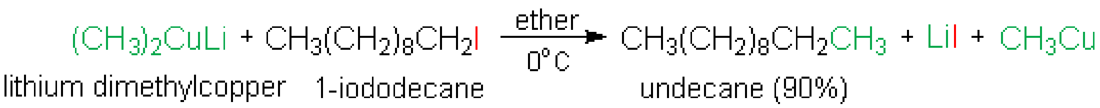
When lithium dialkylcopper compounds, also known as Gilman reagents (after Henry Gilman), are converted by alkyl bromides, chlorides, or iodides, the cross-coupling products are obtained in good yields. Alkyl fluorides do not react with Gilman reagents. Gilman reagents can be synthesized through the treatment of the corresponding alkyllithium compound with copper(I) iodide in diethyl ether.



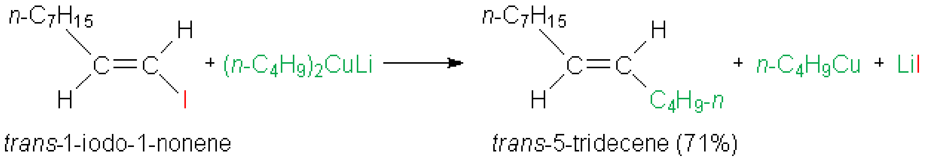
$$2\,CH_3Li + CuI \xrightarrow{\text{ether}} (CH_3)_2Cu^{\ominus}\ Li^{\oplus} + LiI$$

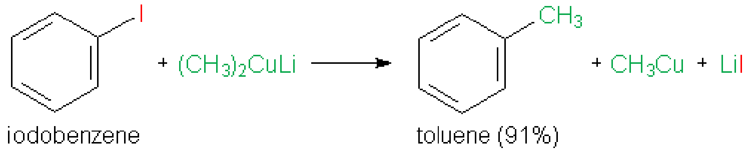
methyllithium lithium dimethylcopper

In the reaction between a Gilman reagent and an alkyl halide, the alkyl halide's halide is exchanged for an alkyl group of the Gilman reagent. Thus, a new carbon-carbon bond is formed. The reaction through which "asymmetric" alkanes may be produced yields a product that is composed of the Gilman reagent's and alkyl halide's alkyl groups (cross-coupling). The reaction between $(CH_3)_2CuLi$ and 1-iododecane in diethyl ether at 0 °C, for instance, results in a 90% yield of undecane



The alkyl cross-coupling reaction with Gilman reagents may also be carried out with aryl, vinyl, allyl, and benzyl halides. However, in these cases, one equivalent of the Gilman reagent's alkyl groups disappears





9.10 Structure and bonding in Gilman reagents

The standard formulas written for Gilman reagents R_2CuLi are simply stoichiometric conclusions drawn from the chemical amounts used to prepare them. It is thought the actual identity of such reagents is more complex. The reagent is thought as dimeric clusters. The following two possible structures shown in figure 6 are proposed one with and one without bridging alkyl ligands.

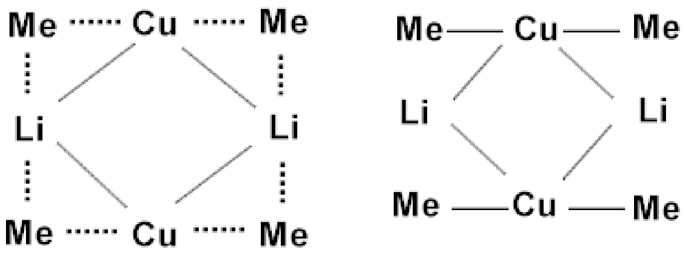


Figure 6: structure of Gilman reagent in solution

It has also been shown, using 1H and ^{7}Li NMR, that the Gilman reagents do not exist as simply one entity (whether shown as a monomer or a dimer), but rather exist as a complicated equilibrium mixture of three distinct entities: R_2CuLi, R_3CuLi_2, and $R_5Cu_3Li_2$. It appears that the solvent used, whether diethyl ether, THF, or a combination of the two, has an important bearing on the actual identity of the organocopper reagent.

9.11 Reactions of Gilman reagents

1) Formation of alkanes

Lithium dialkylcuprate reacts with an alkylhalide (1^{o} best; 2^{o} and 3^{o} face elimination) in Et_2O or THF. Primary dialkylcuprates work best; steric hindrance makes 2^{o} and 3^{o} dialkylcuprates less reactive. The general halide reactivity pattern as follows I > Br > Cl (with tosylate a better leaving group than any of the halogens).

ex. $(CH_3CH_2CH_2)_2CuLi + CH_3CH_2CH_2CH_2Br \longrightarrow$

$$\underset{\text{heptane}}{CH_3CH_2CH_2CH_2CH_2CH_2CH_3} + \underset{\text{(unreactive)}}{CH_3CH_2CH_2Cu} + LiBr$$

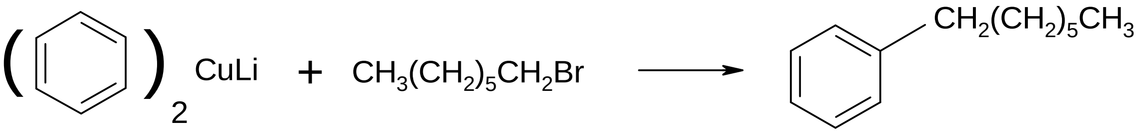
With highly reactive organometallics, like organolithiums and Grignard reagents, one often finds unwanted competition from side reactions, such as metal-halogen exchange

$R\text{-}M + R'X \longrightarrow R\text{-}X + R'M$ instead of the desired

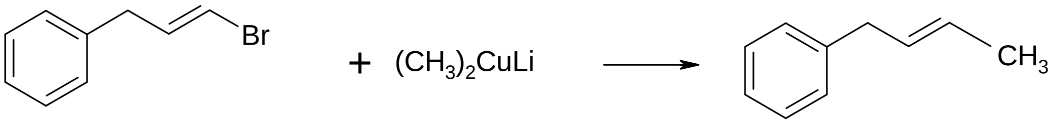
$R\text{-}M + R'X \longrightarrow R\text{-}R' + MX$

2) Other hydrocarbon coupling

Lithium diarylcuprates as well as lithium dialkylcuprates can be involved

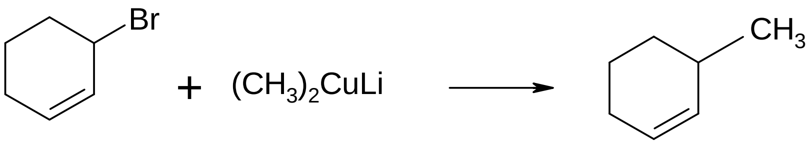


The halide may even be vinyl or aryl (usually very unreactive toward nucleophilic attack; organolithium and Grignard reagents are ineffective)



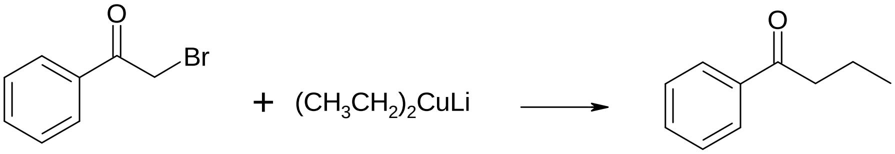
Note: complete retention of stereochemistry (trans stays trans)

Benzylic and allylic halides are smoothly converted into alkylbenzenes and substituted alkenes respectively by Gilman reagents.



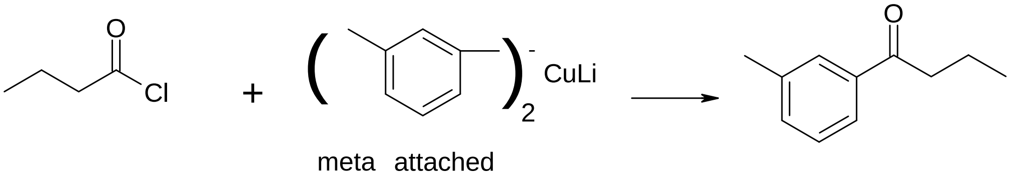
3) α-Haloketones

These react with dialkylcuprates to give α-alkylated ketones.

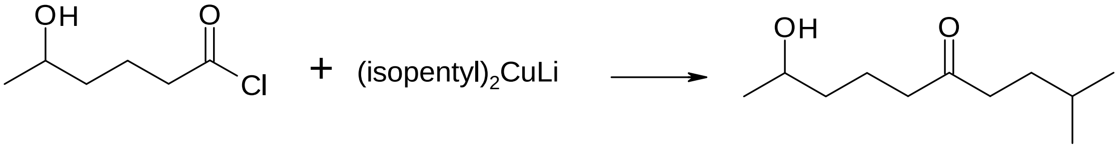


4) Acid

These react with dialkylcurprates to give ketones



Organolithium and Grignard reagents also react with acid chlorides but the product is a tertiary alcohol similar to their attacks on ketones. Organocopper compounds are less reactive toward ketones and the reaction stops at that stage. This lower reactivity widens the application of the method. Unlike organolithium and organomagnesium (Grignard) reagents, the organocopper reagents do not react with functional groups that cannot be present around the organolithium or organomagnesium reagents; i.e. -OH, -NH_2, C=O, or COOH. (The more reactive organo compounds protonate to form alkanes) Interestingly, organocopper reagents are more reactive toward alkyl halides than organolithium or Grignard reagents.

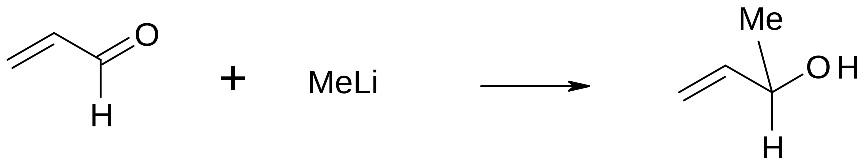


5) α,β-Unsaturated Carbonyls

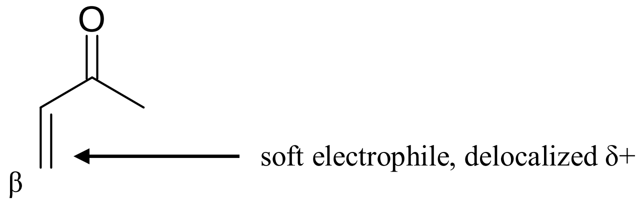
These react with dialkylcuprates in a 1,4 - conjugate addition process. Organolithium and organomagnesium attack by a 1,2 - direct addition process.

1,4 addition (Michael addition):

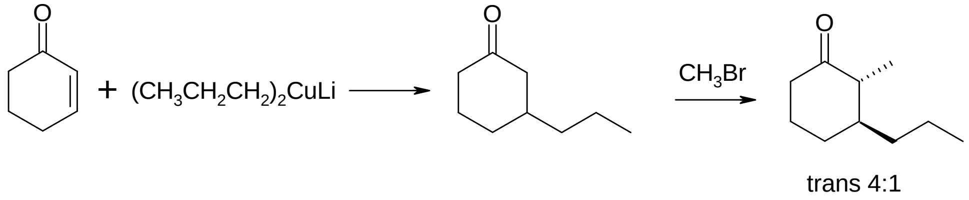
1,2 addition



Methyllithium is considered a “hard nucleophile” because the negative charge is localized on the carbon atom. Lithium dimethylcuprate is a “soft nucleophile” because the large transition metal atom is more polarizable (available d orbitals) and the negative charge is somewhat delocalized over the carbon and copper atoms. Hard nucleophiles attack at the carbonyl carbon and soft nucleophiles attack at the β-carbon

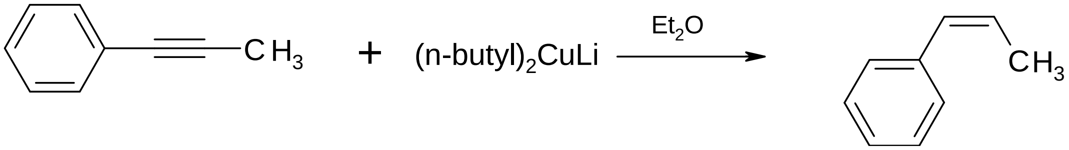


Since the first isolable intermediate in the 1,4- addition process is an enolate ion, it could be trapped by another alkylating species (like R-X) instead of simply protonating and an α,β-dialkylation of the unsaturated carbonyl compound can be accomplished.

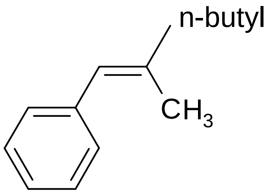


6) Disubstituted acetylenes

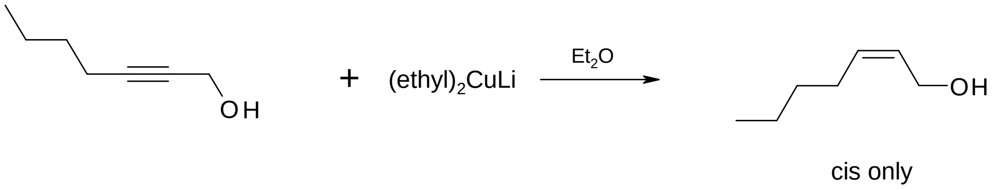
These react with the organocopper reagent to form reduced stereoselective cis-alkenes



Interestingly, if THF is used as solvent instead of diethyl ether, an addition product is formed as well as the reduction product. For the example above, the addition product would be

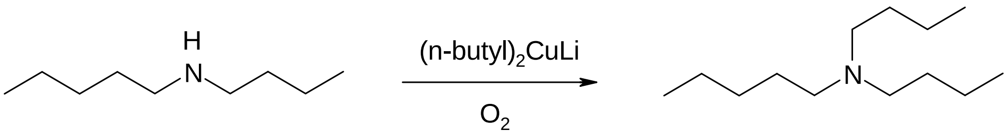


The method will also work on functionalized acetylenes. The yield is not particularly high (58%) but efficient for many purposes

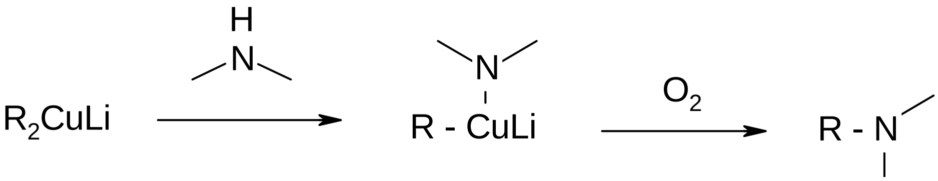


7) Prima

These react with organocuprates to form N-alkylated amines

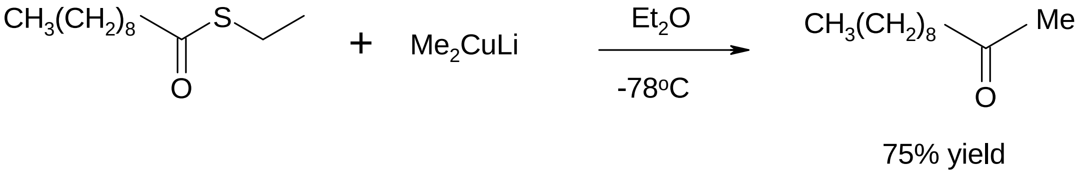


The method above is called an oxidative coupling. The presence of oxygen (bubbled into the mixture) is crucial for meaningful yields. The reaction apparently proceeds in the following fashion



8) S-alkyl thioesters

These react with Gilman reagents to form ketones. Unlike the reaction of acid chlorides with organocopper reagents, these reactions need only one equivalent of organocuprate instead of three equivalents for optimal yields. Reaction time is between 30 min. and 2 hours



9.12 Organometallic Compounds of Aluminium

The application of organoaluminium compounds as a organo-metallic compounds is connected with a knowledge of their reactions with electron donors. For example, the reactions with nitriles, ketones, esters, ethers, alkyl chlorides, vinyl chloride, and acid chlorides as the electron donors.

The aluminium atom has free 3p and 3d-orbitals characterized by fairly low energies. They permit ready formation of complexes with electron donors. The first stage of the reaction of an organoaluminium compound with an electron donor involves formation of the corresponding donor-acceptor complex which is often stable enough to be separated. Knowledge of the structure of the complexes formed is very important for an elucidation of the reaction course and mechanism. Schematically the formation of a complex may be represented as follows

$$D + AlX_3 \leftrightarrow D \rightarrow AlX_3$$

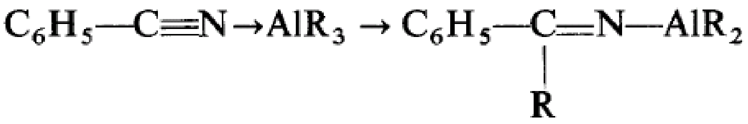
where D = electron donor and X = alkyl, aryl, halogen, etc.

At suitable temperatures the complex will enter into further reactions. These may include addition, reduction, elimination, insertion, and cycliza-tion. It should be emphasized that with electron donors such as nitriles. ketones. esters, ethers. etc., organoaluminium compounds react in similar fashions and according to like mechanisms. This fact enables some general conclusions to be drawn, the recognition of which may facilitate studies of new reactions.

Reactions of organoaluminium compounds with nitriles as electron donors afford 1: 1 complexes which are stable at room temperature, linear in structure, and which may be represented as follows

$$C_6H_5{-}\overset{\delta+}{C}{\equiv}\overset{\delta-}{N}\rightarrow AlR_3$$

At elevated temperature this complex undergoes an addition reaction to yield an aluminium ketimine derivative



$$C_6H_5{-}C{\equiv}N\rightarrow AlR_3 \rightarrow C_6H_5{-}\underset{\displaystyle R}{\underset{|}{C}}{=}N{-}AlR_2$$

9.13 Preparation of organoaluminium compounds

The alkylaluminium halides and aluminium alkyls can be synthesized by direct reaction of an alkyl halide with aluminium. The sesquihalide mixture (R_2AlX and $RAlX_2$) can be separated into its components, or can be further reacted with Na metal to get trialkylaluminium. This method is very useful for the synthesis of trimethylaluminium. Reactions of aluminium halides with organomagnesuim halides (RMgX) or organolithium (RLi) in Et_2O lead to the formation of an etherate complex of R_3Al, and thermal heating removes Et_2O forming R_3Al. But if R_3Al is thermally unstable, then it may be difficult to remove Et_2O by heating.

$$RX + Al \longrightarrow R_2AlX + RAlX_2 \xrightarrow[-NaX]{Na} R_3Al$$

$$3RMgX + AlX_3 \xrightarrow[-3MgX_2]{} R_3Al(OEt_2) \xrightarrow[-Et_2O]{\Delta} R_3Al$$

Organoaluminium compounds can be prepared in the laboratory by gently heating aluminium metal with diorganomercury(II) (R_2Hg), and this transfer of R groups from Hg to Al is known as transmetallation. Here R may be alkyl, or aryl group. This method requires that both organomercury and resulting organoaluminium compounds are thermolabile. The unsymmetrical aluminium compounds R_2AlR' can be prepared by the reaction of organoaluminium halides by reacting alkalimetal hydrides, and which can be readily added to unsaturated hydrocarbons such as alkenes, or alkynes. The reaction of R_2AlCl with organolithium also gives unsymmetrical organoaluminium R_2AlR' compounds. In these methods higher temperature can lead to disproportionation and should be avoided.

$$3R_2Hg + 2Al \longrightarrow 2R_3Al + 3Hg$$

$$R_2AlCl \xrightarrow[-LiCl]{LiH} R_2AlH \xrightarrow{CH_2=CHR'} R_2AlCH_2CH_2R'$$

$$R_2AlCl + R'Li \xrightarrow[-LiCl]{} R_2AlR'$$

Direct reaction of aluminium metal with hydrogen in the presence of trialkyl aluminium (R_3Al) gives R_2AlH, which reacts with alkene to yield R_3Al. This method is very useful for an alkene with high reactivity such as ethylene ($CH_2=CH_2$). The use of alkene $CH_2=CR_2$ directly in place of R_3Al also gives $(R_2CHCH_2)_3Al$. Both these methods used for large scale synthesis of organoaluminium compounds. It may pointed out that Al does not react with H_2 to form AlH_3, but in presence of aluminium alkyl, it picks up hydrogen to form, R_2AlH. For R = Et and R′ = H, triethyl aluminium will be formed

$$2Al + 3H_2 + 4R_3Al \longrightarrow 6R_2AlH \xrightarrow{CH_2=CHR'} 6R_2AlCH_2CH_2R')$$

$$2Al + 3H_2 + 6CH_2=CR_2 \longrightarrow 2(R_2CHCH_2)_3Al$$

The mixed organoaluminium compounds of the type $RnAlX_{3-n}$ can be prepared by reacting R_3Al with AlX_3 (X = halide or other anions, such as OR or OR′).

9.14 Properties organoaluminium compounds

Organoaluminium compounds are sensitive to air, water, alcohols and many other compounds. Despite the fact that these compounds are extremely susceptibile to oxidation and hydrolysis and handling being hazardous, still they are industrially prepared on very large scale. Organoaluminium compounds are generally liquid or low-melting solids and are often miscible with hydrocarbons solvents. They are volatile at moderate temperatures. Lower alkyls are extremely reactive liquids and are spontaneously flammable. The Al-C and Al-H bonds have considerable covalent character, although electronegativity suggests that bonds are polar. Organoaluminium compounds have tendency to oligomerize into dimers, trimers or tetramers.

9.15 Structure and Bonding in organoaluminium compounds

Trimethylaluminium is a dimer, Me_6Al_2, in solid as well as vapour states, unlike Me_3B which is a monomer. Dimerization is attributed to bigger size of Al versus B atoms which poses less steric problem for the former than for the latter element. The association nature of other organoaluminium compounds is as follows: Et_3Al, n-Pr_3Al, n-Bu_3Al, Ph_3Al, Me_2AlX (X = H, Cl, Br, I), are dimers, t-Bu_3Al and i-Bu_3Al are monomers, and Me_2AlF is a tetramer. Triorganoaluminium compounds, R_3Al dimerize via alkyl or aryl groups, and R_2AlX dimerize via X groups.

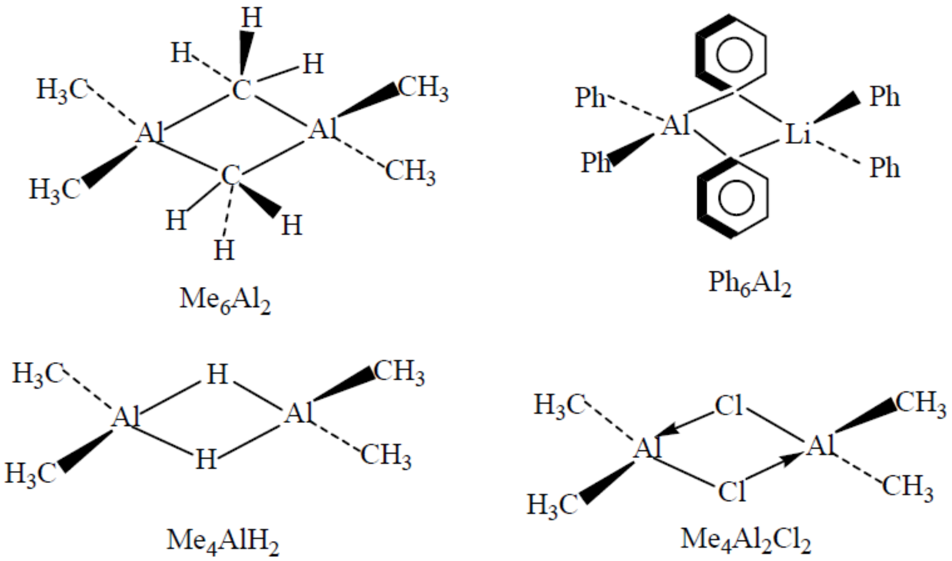


Figure 7: Structure of organoaluminium compounds

The structures of some dimeric organoaluminium compounds are shown in figure 7. The bonding in Me_6Al_2 and analogous compounds can be readily understood as follows. Dimeric Me_6Al_2 is made from dimerization of two Me_3Al units. Each of four terminal methyl groups forms 2c-2e (two center two electron) Al-C bonds and two bridging methyl groups form 3c-2e Al-C-Al bonds (three center two electron). If each CH_3 group bridging two Al centers is treated as a radical with C atom considered sp^3 hybridized, and again each Al atom is treated as sp^3 hybridized, then one sp^3 orbital with one electron from C atom, one sp^3 orbital of one Al with one electron, and one empty sp^3 orbital of second Al atom combine as shown in figure. 8 forming three center two electron (3c-2e) bonds. The second Al-C-Al bridge is similarly formed except first Al sp^3 orbital will be empty and second Al sp^3 orbital will have one electron. The hydride bridging in $Me_4Al_2H_2$ can be similarly explained in terms of 3c-2e bonds. Here one H atom shares its s-orbital (containing one electron) with one sp3 orbital from one Al atom (containing one electron) and one empty sp^3 orbital of second Al atom. The bridging groups like Cl^- form one covalent bond with one Al atom and a coordinate bond using lone of electron to second Al atom. The bridging pattern of Ph groups in Ph_6Al_2 is similar to that shown in figure 7.

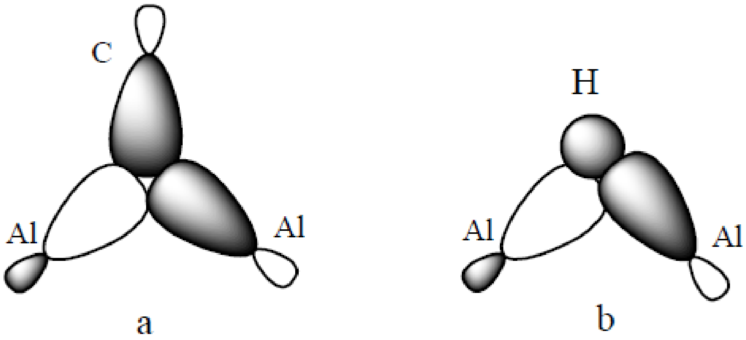
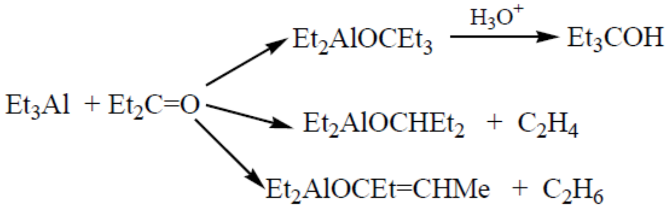
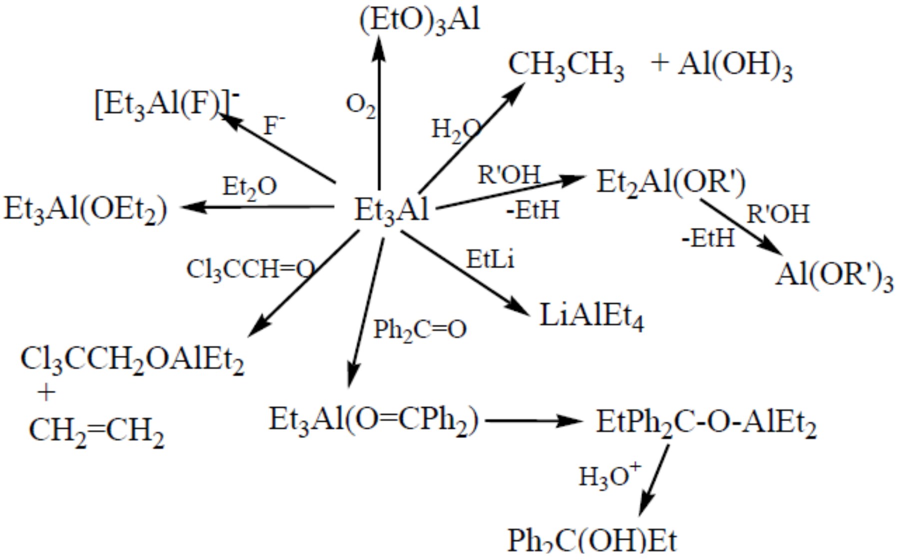


Figure 8: Orbital overlap along one Al-C-Al bridge (a) and one Al-H-Al bridge (b)

9.16 Reactions of organoaluminium compounds

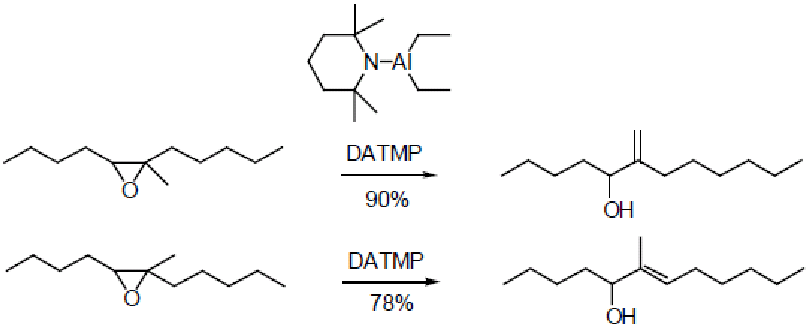
Organoaluminium compounds undergo a wide variety of reactions, some of which are given in below chart using Et_3Al as an example. It can be seen that reaction with oxygen gave triethoxyaluminium, and that with water, it formed aluminum hydroxide. It is possible water may initially form an adduct, $Et_3Al(OH_2)$ in Lewis-acid base terminology, followed by hydrolysis to form, $Et_2Al(OH)$ and ethane, and finally, $Al(OH)_3$. Similar arguments appear to hold true for the reaction with R′OH. Reaction with EtLi transfers Et^- group to Al to generate $LiAlEt_4$, and likewise, fluoride ion and diethyl ether form adducts. The reaction with diphenyl ketone involves transfer of Et^- group from Al metal center to electrophilic carbon center of ketone; corresponding reaction with an aldehyde led to evolution of ethylene. However, reaction of Et_3Al with $Et_2C{=}O$, a ketone having β-hydrogen, such as ethyl group undergoes different reactions.





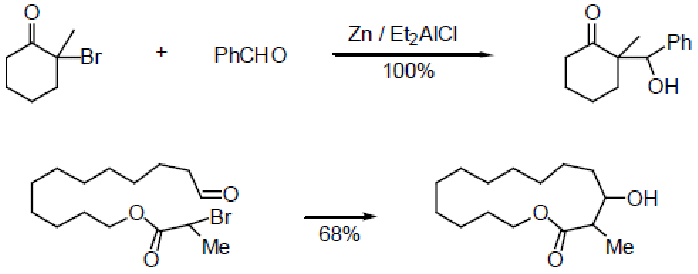
Epoxide – Allylic Alcohol Rearrangement

The reaction of epoxides with a strong base constitutes a well-known synthetic method for the preparation of allylic alcohols. The reaction proceeded stereo- and regioselectively with organoaluminuamides



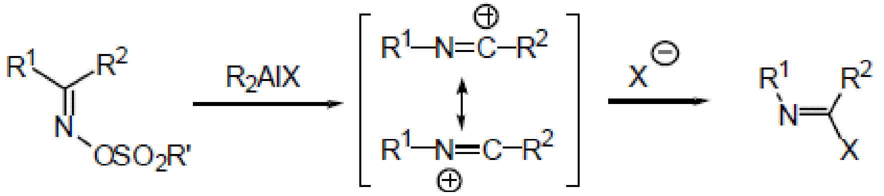
Aldol Synthesis

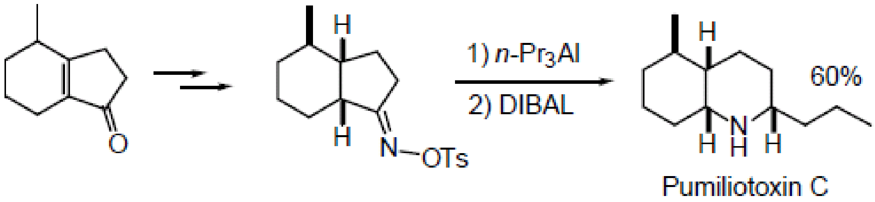
Complexes of organoaluminum compounds and ketones led to a variety of reactions. An example is the reaction of haloketone and aldehyde. The critical part of the process is the coupled attack of the α-haloketone by diakylakuminum chloride and zinc dust which generates an aluminum enolate regioselectively. The method was used for short synthesis of medium and large ring compounds.



Beckmann Rearrangement Using Organoaluminum Reagent

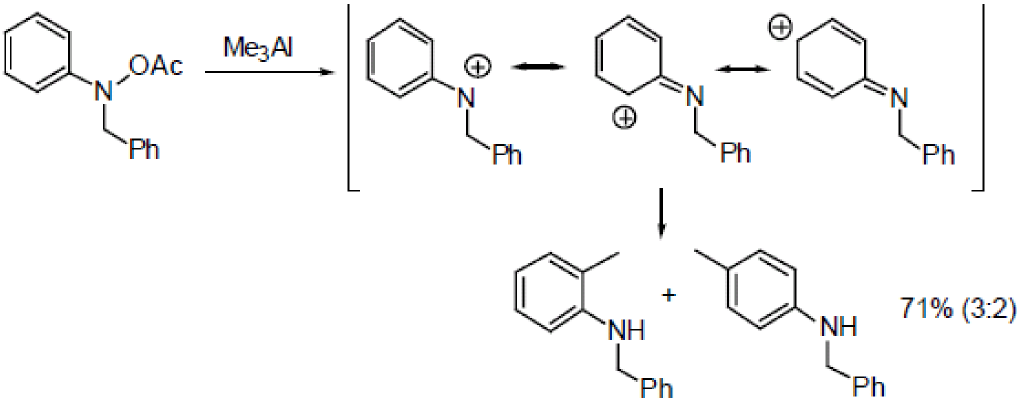
The Beckmann rearrangement is the skeletal rearrangement of ketoximes in the presence of certain acids under aqueous conditions to give amides or lactams. Reexamination of this reaction using organoaluminum reagents under aprotic conditions led to the abstraction of the sulfonyl group, followed by capture of the intermediary iminocarbocation or alkylidyneammonium ion with the nucleophilic group (X; R_2AlX (X = R, SR’, SeR’)) on the aluminum. Thus, aluminum reagents act not only as a Lewis acid but also as a base. This method opens a new synthetic entry to a variety of alkaloides such as Pumiliotoxin C.

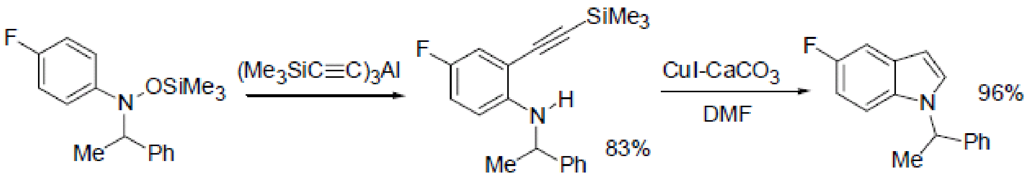




Nucleophilic Aromatic Substitution

Arylhydroxyamines behave in a different manner from alkylhydroxyamines on treatment with organoaluminum compounds. The highly oxygenophilic organoaluminum reagent can cleave the N–O bond heterolytically to yield a phenylaminyl cation, which undergoes nucleophilic attack by an alkylaluminum at the ortho or para position of the aromatic ring. The synthetic potential of this novel reaction has been demonstrated by the synthesis of indol derivatives





9.17 Organometallic Compounds of Mercury

Organic mercury compounds are characterised by covalent bonds between carbon and mercury. In the past they were used for instance as herbicides and fungicides in plant protection (e.g. seed treatment), and as wood preservatives. Nowadays they are still used as disinfectants. Dialkylmercury compounds are very versatile starting materials for the synthesis of many organometallic compounds of more elctropositive metals by transmetallation

19.18 Preparation

There are several methods for the preparation of organomercury(II) compounds and some of these are delineated below.

(a) Transmetallation

Organolithium and organomagnesium reagents have been extensively used for the preparation of organomercury(II) compounds by reacting them with mercury(II) halides or other mercury(II) salts. Here organic groups from RLi or RMgX substrates are transferred to Hg metal center and the process is known as transmetallation. The range of organomercury(II) compounds will depend upon the available organolithium or organo- magnesium reagents.

For example, reaction of phenyllithium with $HgCl_2$ forms phenyl-mercury(II) chloride. Similarly, reaction of PhMgBr (from PhBr and Mg in diethyl ether) with $HgCl_2$ yields PhHgCl. Organometallic compounds of other metals (B, Sn etc.) have also transferred organic groups to mercury for the preparation of organomercury compounds.

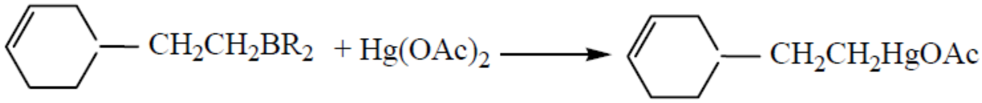
$$RLi + HgX_2 \longrightarrow RHgX + LiX$$

$$X = Cl, Br, I$$

$$RMgX + HgX_2 \longrightarrow RHgX + MgX_2$$

$$X = Cl, Br, I$$

$$Ph_3Sn(CH_2)SR + HgCl_2 \longrightarrow PhHgCl + Ph_2ClSn(CH_2)SR$$



(b) Mercury-Hydrogen Exchange – Mercuration

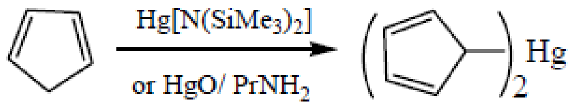
The replacement of hydrogen of an organic compound (e. g. R-H) by mercury is known as mercuration, and this process is electrophilic substitution reaction. For aliphatic hydrocarbons, it is limited to hydrocarbons with acidic hydrogen atoms, and this process occurs readily with aromatic hydrocarbons. Below reacion shows that both RHgX and R_2Hg can be obtained, the latter compound requires more forcing conditions.

$$RH + HgX_2 \xrightarrow{-HX} RHgX \xrightarrow[-HX]{RH} R_2Hg$$

The choice of X depends on the organic substrate and it should be more easily replaced by R group. Thus usually X = Cl, OAc, NO_3, NR_2 (R = $SiMe_3$) are used. A few examples given below demonstrate the use of this method. Reactions of $Hg[(N(SiMe_3)_2]_2$ with phenyl acetylene (PhC≡CH), acetone (MeCOMe) and cyclopentadiene form $(PhC{\equiv}C)_2Hg$, $(MeCOCH_2)_2Hg$ and $(C_5H_5)_2Hg$ respectively. The use of excess $HgCl_2$ in presence of NaOAc yields permercurated $C_5(HgCl)_6$ (here all hydrogen atoms are replaced by six HgCl moieties).

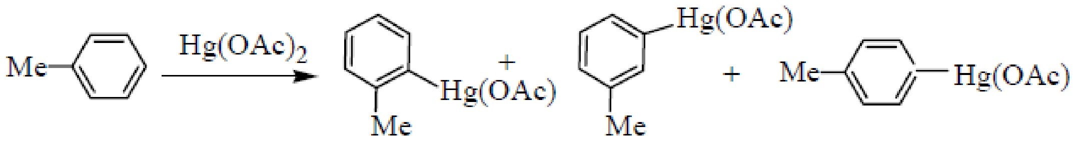
$$Hg[N(SiMe_3)_2] + PhC{\equiv}CH \longrightarrow [PhC{\equiv}C]_2Hg$$

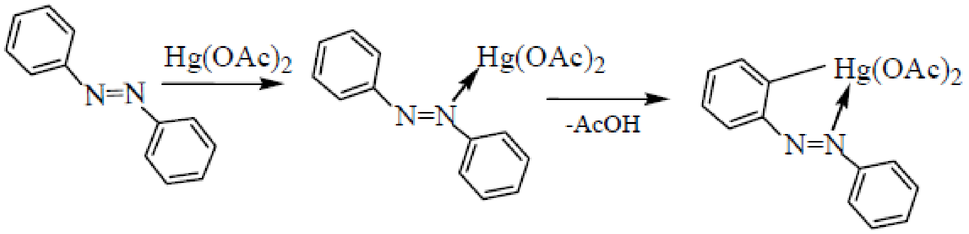
$$Hg[N(SiMe_3)_2] + MeCOMe \longrightarrow (MeCOCH_2)_2Hg$$



The mercuration of arenes, an electrophilic substitution, lacks selectivity and results in all possible ring substituted products.

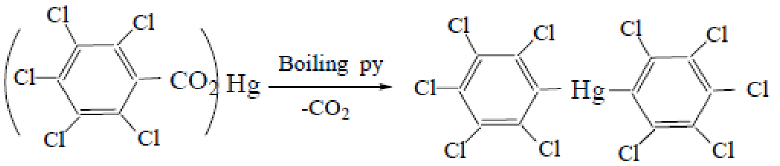
For example, mercuration of toluene with $Hg(OAc)_2$ under refluxing conditions yields a mixture of o-, m- and p-$CH_3C_6H_4Hg(OAc)$ isomers and addition of HBr to resulting isomers can convert them into o-, m-, & p-$CH_3C_6H_4HgBr$ compounds. The reaction conditions change the amounts of each isomer. Mercuration of benzene occurs at $110^{o}C$ in presence of glacial acetic acid. The mercuration of azobenzene occurs at ortho position due to coordination of Hg by N donor atom followed by formation of Hg-C bond as shown below.

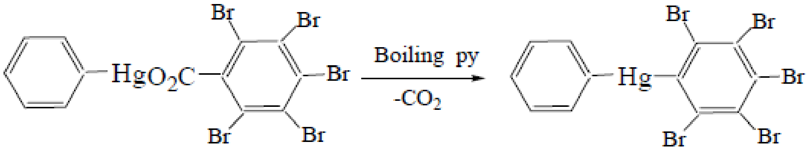




(c) Decarboxylation

Organomercury compounds can also be prepared by the decarboxylation of alkyl, aryl, or heteroaryl carboxylates of mercury by thermal or UV irradiation methods. The presence of electronegative atoms present in aryl or aryl moieties bonded to Hg salts via O atoms, as well as addition of donor solvents such as H_2O, py etc. facilitate the decarboxylation. Reactions of pentahalophenyl carboxylates and trifluoroacetate compounds of Hg(II), undergoing decarboxylation. It may be noted that photodecomposition of $(CF_3CO_2)_2Hg$ to $(CF_3)_2Hg$ occurs at much lower temperature ($-160^{o}C$), unlike more forcing conditions. Other mercury carboxylates such as $Hg(O_2CC_6F_5)_2$, $Hg(O_2CCCl_3)_2$, and $Hg(O_2CC_6H_2\text{-}2,4,6\text{-}NO_2)_2$ also undergo similar reactions to form, $Hg(C_6F_5)_2$, $Hg(CCl_3)_2$, and $Hg(C_6H_2\text{-}2,4,6\text{-}NO_2)_2$ respectively. Bis(trichloromethyl)mercury, $Hg(CCl_3)_2$, can be made also by the reaction of mercury halides with sodium trichloroacetate in 1, 2-dimethoxyethane.





$$(CF_3CO_2)_2Hg \xrightarrow{300^{o}C} F_3C\text{-}Hg\text{-}OOCCF_3$$

$$(CF_3CO_2)_2Hg \xrightarrow[K_2CO_3]{200^{o}C} F_3C\text{-}Hg\text{-}CF_3$$

$$(Cl_3CCO_2)Na + HgCl_2 \xrightarrow[-CO_2]{-NaCl} Cl_3C\text{-}Hg\text{-}CCl_3$$

(d) Insertion Method

Organomercury compounds are also prepared by using azo compounds. Reaction of diazomethane with $HgCl_2$ under mild conditions in diethyl ether solvent involve insertion of CH_2 group between Hg and Cl.

$$HgCl_2 + CH_2N_2 \xrightarrow[-N_2]{ether} ClCH_2\text{-}Hg\text{-}Cl \xrightarrow[-N_2]{CH_2N_2} ClCH_2\text{-}Hg\text{-}CH_2Cl$$

9.19 Properties of organomercury compounds

Organomercury compounds such as RHgX with X = halide (Cl, Br, I), or pseudo halide (CN, SCN), or other anions such as OH, etc. are solid compounds and are soluble in various organic solvents such as methanol, ethanol etc. When anion X = NO_3^-, RCO_2^-, or SO_4^{2-}, the compounds are salt-like with weak Hg-anion covalent interaction. Dialkyl- and diaryl-mercury compounds are colorless solids. While dialkyl compounds are liquids, or low-melting solids, diarylmercury compounds are usually solids. Their solubility in water is limited, and in general they are unaffected by water and react very slowly with air. They are thermally and photochemically not very stable and should be stored in dark. They are toxic, particularly lower dialkyls such as Me_2Hg, Et_2Hg etc. and develop appreciable vapour pressure. Diarylmercury compounds such as Ph2Hg are less toxic.

9.20 Structure and Bonding in organomercury compounds

The geometry around Hg center in its R_2Hg compounds is linear or bent. For example, C-Hg-C angles in CF_3-Hg-CF_3, Ph-Hg-Ph, p-MeC_6H_4-Hg-C_6H_4Me-p, and o-MeC_6H_4-Hg-C_6H_4Me-o are 180, 176.9, 180, and 178.0^o respectively. In Ph-Hg-Ph, mercury atom is out of plane of Ph rings; the p-tolyl rings are planar in p-MeC_6H_4-Hg-C_6H_4Me-p and in o-MeC_6H_4-Hg-C_6H_4Me-o the angle between planes is 58.9^o. The structure of Me_2Hg is expected to be linear similar to CF_3-Hg-CF_3. Similarly, RHgX compounds, where X is a halide or pseudo halide, are linear or bent. In compounds in which X is like acetate, then C-Hg-X angle varies according to how strongly X is binding to Hg. In Ph-Hg-OAc, the angle C-Hg-O is 170^o. The geometry is not trigonal planar for RHgX with chelating X, such as 8-hydroxyquinoline (oxine), rather it is usually labelled as distorted T-shaped. In PhHg(oxine), structure (angles C-Hg-O, 142^o, C-Hg-N, 144^o) resulted when compounds was crystallized from methanol and structure with angles C-Hg-O, 175^o, C-Hg-N, 113^o resulted when it was crystallized from CCl_4. Figure 9 depicts structures of some organomercury compounds. The two coordinate linear or bent structures can be easily understood that Hg is sp hybridized involving 6s-6p orbitals. Each sp-hybridized orbital of Hg with one electron forms covalent bond with sp^3, sp^2 or sp hybrid orbitals of C of alkyl or aryl group or unsaturated organic group as the case may be group, (R), having Hg-C bonds. In RHgX compounds an halogen will use its sp3 hybrid orbital in forming covalent bond with Hg sp-hybrid orbital. Figure 10 depicts overlap of orbitals in Hg-C bonds.

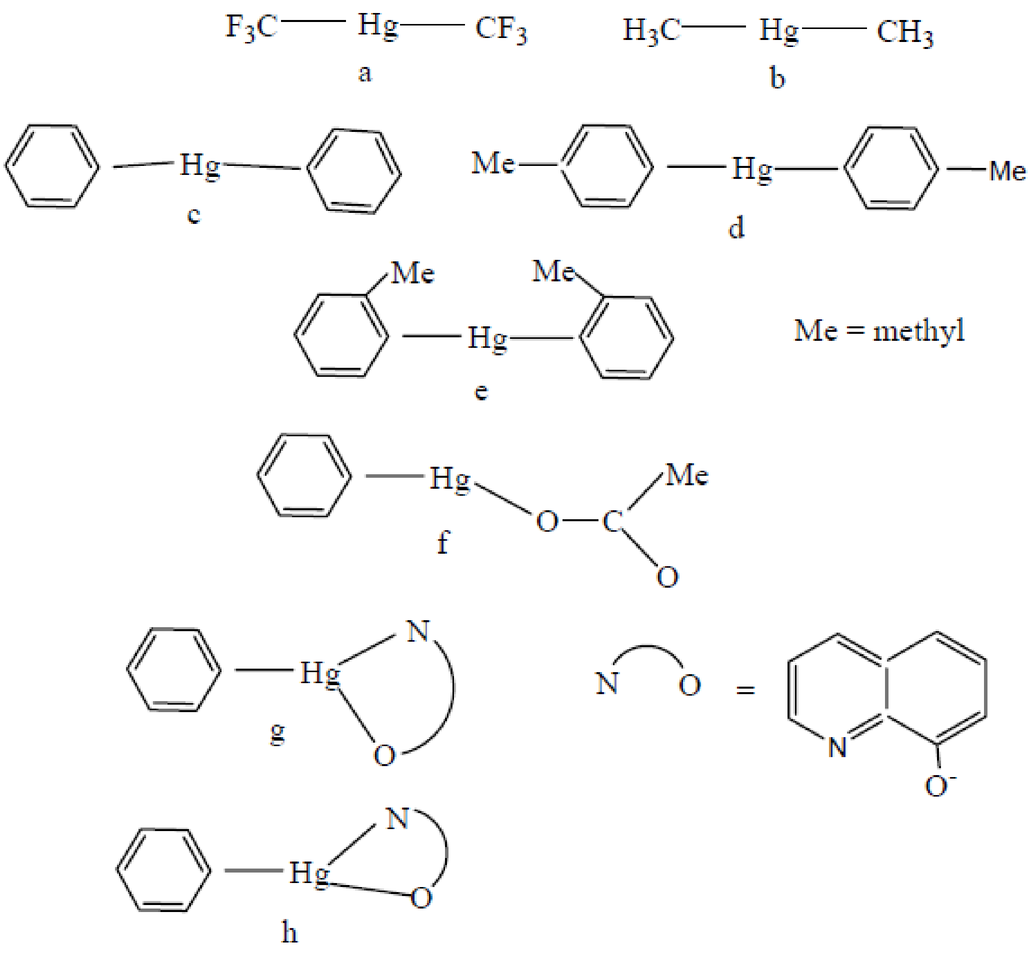


Figure 9: Structures of some organomercury compounds

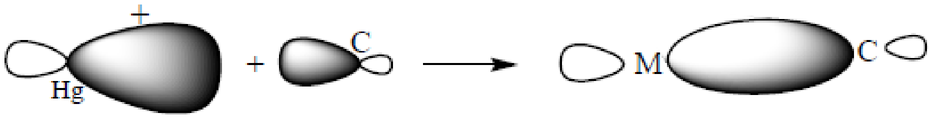
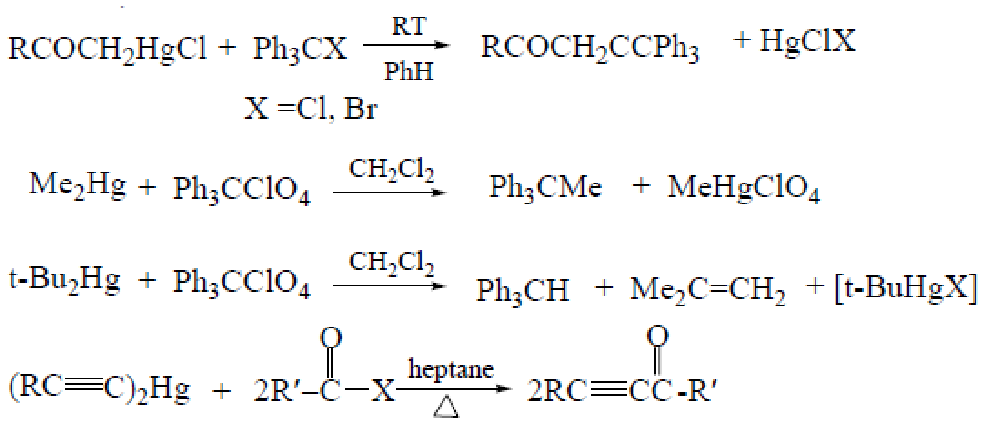


Figure 10: Bonding in linear molecules

9.21 Reactions of organomercury compounds

The Hg-C bond or Hg-X bonds in organomercury compounds undergo a variety of reactions. Organomercury compounds are not very reactive towards oxygen, water, alcohols, carbonyl compounds, and simple alkyl halides. It may be noted that some organomercurials do react with air and precautions need to be taken. Representative reactions of organomercurials are discussed below.

Organomercury compounds undergo alkylation, arylation and acylation reactions. It may be pointed out that organomercurials with simple organic groups have low nucleophilic character towards organic halides. The electrophilic alkylating reagents such as triarylmethyl halides react with nucleophilic organomercurials (having electron withdrawing groups such as α-carbonyl groups). The triarylmethyl halides and perchlorates can alkylate organomercurials to give coupled products; however, β–elimination occurs with t-Bu_2Hg. Alkylating reagents such as Ph_3CX for X = BF_4 or $HgBr_3$ can also be used. The acyl halides are more reactive than alkyl halides and acylation of orgaomercurials occurs more readily.



$$RCOCH_2HgCl + Ph_3CX \xrightarrow[PhH]{RT} RCOCH_2CPh_3 + HgClX$$

$$X = Cl, Br$$

$$Me_2Hg + Ph_3CClO_4 \xrightarrow{CH_2Cl_2} Ph_3CMe + MeHgClO_4$$

$$t\text{-}Bu_2Hg + Ph_3CClO_4 \xrightarrow{CH_2Cl_2} Ph_3CH + Me_2C{=}CH_2 + [t\text{-}BuHgX]$$

$$(RC{\equiv}C)_2Hg + 2R'{-}\overset{O}{\overset{\|}{C}}{-}X \xrightarrow[\Delta]{heptane} 2RC{\equiv}C\overset{O}{\overset{\|}{C}}{-}R'$$

The mercury-carbon bond is stable to water and to alcohols, but mineral acids such as HCl cleave Hg-C bonds in R_2Hg compounds. The carboxylic acids, such as acetic acid, cleave only one Hg-C bond. It may be significant to note that the mercury-aryl bond undergoes protonlysis more readily than does the mercury-alkyl bond. The order of cleavage of Hg-R bond has been observed to be Me < p-chlorophenyl < phenyl < p-tolyl < p-anisyl. The organomercurials R2Hg and RHgX both react with halogens (Cl_2, Br_2 and I_2) to form RX and HgX_2 as the final products.

$$\text{R-Hg-R} + \text{HCl} \longrightarrow \text{R-Hg-Cl} + \text{RH}$$

$$\text{R-Hg-Cl} + \text{HCl} \longrightarrow \text{Cl-Hg-Cl} + \text{RH}$$

$$\text{R-Hg-R} + \text{AcOH} \longrightarrow \text{R-Hg-OAc} + \text{RH}$$

$$\text{R-Hg-R} + \text{Cl-Cl} \longrightarrow \text{R-Hg-Cl} + \text{RCl}$$

$$\text{R-Hg-Cl} + \text{Cl-Cl} \longrightarrow \text{Cl-Hg-Cl} + \text{RCl}$$

The organic groups bonded to mercury are labile and can be transferred to other metals and this process is known as transmetallation. This method is a classical synthetic route and has been used conveniently for the synthesis of organometallic compounds of other metals. The organometallic compounds of transition, main group metals including sulfur, selenium and tellurium have been prepared.

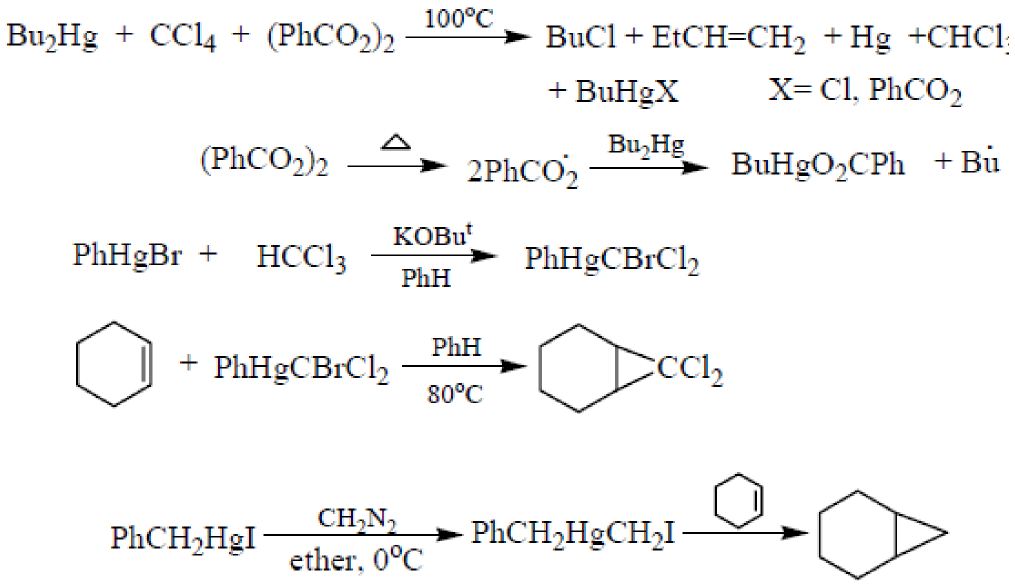
$$R_2Hg + R'\text{–}M \longrightarrow RHgR' + \text{R-M}$$

$$R_2Hg + 2M \longrightarrow Hg + 2\text{R-M}$$

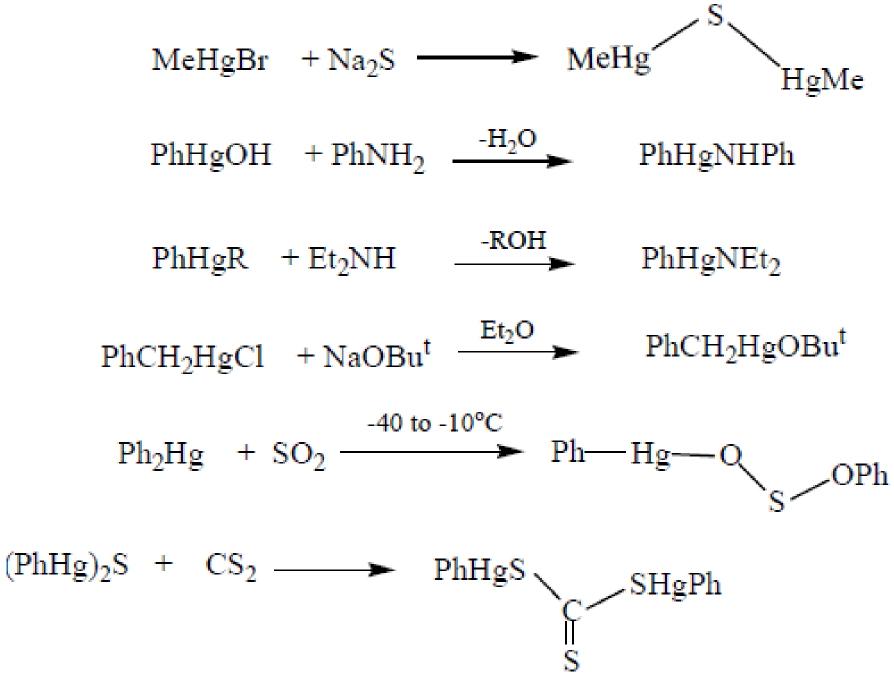
$$R_2Hg + MX \longrightarrow \text{R-M} + RHgX$$

$$\longrightarrow \text{R-M} + Hg + RX$$

Photolysis of Ph_2Hg with CCl_4 at 100°C yielded, PhHgCl, PhCl and C_2Cl_6 (hexachloroethane). The nature of products may depend on the organomercurial used. Reaction of Bu_2Hg with CCl_4 at 100°C in presence of benzoyl peroxide as initiator, can lead to the formation of alkylmercury chloride and other products including β-elimination product, an alkene. Trihalomethylmercury derivatives ($PhHgCBrCl_2$) can be readily made from reaction of PhHgBr with $CHCl_3$ in presence of KOBut in benzene solvent. Further reaction with an alkene formed a cyclopropane. The insertion of CH_2 in Hg-I bond formed $PhCH_2HgCH_2I$, which reacted with an alkene to form cyclopropane.



Some other reactions of organomercury compounds are shown below such as reactions of RHgBr with Na_2S, PhHgOH with $PhNH_2$, PhHgOR with Et_2NH, $PhCH_2HgCl$ with NaOBut , R_2Hg with SO_2, $(PhHg)_2S$ with CS_2.



9.22 Summary of the unit

Lithium-Organolithium compounds are used in the synthesis of organic and inorganic compounds. In organic reactions, they are used for generating carbanions (R^-) necessary for organic reactions as described in lithium section. In some reactions, organolithium compounds are considered as radicals, R·.

Aluminium- Organoaluminium compounds such as Et_3Al are very important commercially as activators for olefin polymerization catalysts. They are also widely used as reducing and alkylating agents for transition metal complexes. Trialkylaluminium compounds are better alkylating agents than dialkylaluminium halides. Dialkylaluminium hydrides, R2AlH, are used for C−H bond formation by cleaving C−O, C−X, C−N and C−S bonds.

Mercury- Organomercury compounds are very useful for the preparation of other organometallic compounds of other metals by transmetallation process. Perhalogeno alkyl derivatives, $Hg(CF_3)2$, $Hg(CCl_3)_2$ are useful reagents for transferring CX_3, CX_2 and CX groups to other elements. Organomercury compounds are also used in organic synthesis, in seed dressings, and as fungicides.

9.23 Key words

Organolithium reagents; Organomagnesium compound; Lithium diorganocopper reagents, Gilman reagents; Organoaluminium compounds; Organomercury compounds

9.24 References for further studies

1) Organometallic Chemistry; R. C. Mehrotra; *New Age International*, **2007**.

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9.25 Questions for self understanding

1) What are rrganolithium reagents? Give examples

2) Discuss the properties of organolithium compounds

3) Explain the structure and bonding in organolithium compounds

4) Write the different reactions of organolithium compounds

5) What are organomagnesium compound? Give examples

6) What are Gilman reagents? Give examples

7) Discuss the structure and bonding in Gilman reagents

8) Briefly explain the reactions of Gilman reagents

9) What are Organoaluminium compounds? Give examples

10) Explain the preparation of organoaluminium compounds

11) What are the properties organoaluminium compounds shows?

12) Discuss the structure and bonding in organoaluminium compounds

13) With examples explain the reactions of organoaluminium compounds

14) What are organomercury compounds? Give examples

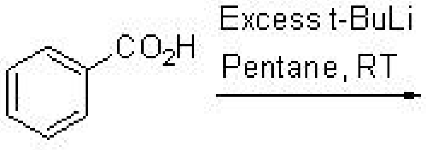
15) How organomercury compounds are prepared?

16) Discus the properties of organomercury compounds

17) Discus the structure and bonding in organomercury compounds

18) With example explain the reactions of organomercury compounds

19) Predict the products in following reactions

1.


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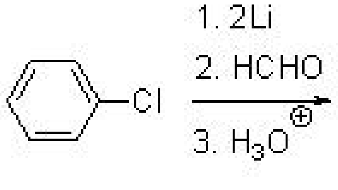

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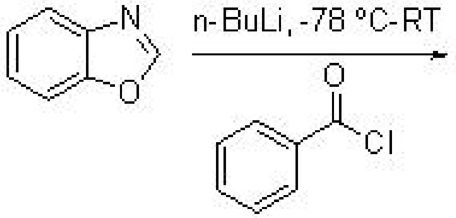

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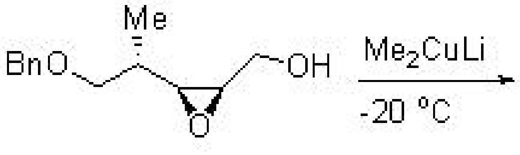


UNIT-10

Structure

10.0 Objectives of the unit

10.1 Introduction

10.2 Organorhodium compounds

10.3 π-bonding of metals with olefins

10.4 Synthesis of metals-olefin complexes

10.5 Structure of metals-olefin complexes

10.6 Reactions of metals-olefin complexes

10.7 Wacker process.

10.8 Heck reaction

10.9 Alkene isomerization in Heck reaction

10.10 Mechanism

10.11 Carbonylation

a) Hydroformylation

b) Advantages of using [Rh] over [Co]

c) Mechanism

10.12 Reppe chemistry

10.13 Olefin isomerization

10.14 Summary of the unit

10.15 key words

10.16 References for further study

10.17 questions for self understanding

10.0 Objectives of the unit

After studying this unit you are able to

- Explain the use of organorhodium compounds
- Write the formation π-bonding of metals with olefins
- List the synthesis of metals-olefin complexes
- Structure of metals-olefin complexes
- Explain the reactions of metals-olefin complexes
- Write the mechanism of Wacker process.
- Write the mechanism of Heck reaction
- Write the mechanism of Alkene isomerization in Heck reaction
- Write the mechanism of Hydroformylation

10.1 Introduction

The organoruthenium compounds find extensive applications in organic synthesis. Ruthenium complexes have been the most common catalysts used for alkene metathesis. The synthetic utilities of the reaction have increased with the development of the Grubb's catalysts, which are stable to Lewis acids, tolerant to an array of functional groups and allow the reactions to perform in aqueous and alcohol solution. Among them, intramolecular processes dominate the synthetic applications and the alkenes having a=CH_2 unit are generally used so that one of the product is ethylene that can escape from the reaction medium and drives the equilibrium toward the desired cyclized product. One of the more attractive features of this method is the ability to form macrocyclic compounds, which is otherwise difficult to accomplish.

The organopalladium compounds are generated in situ for the synthesis. The importance organopalladium compounds lies in their ability to facilitate reactions that would not takes under normal conditions. This section covers the palladium-catalyzed C-C bond formations. The palladium-catalyzed C-C cross-coupling of organoboranes, organoboronic acids, and organoboronic esters with organic halides is called ‘Suzuki coupling'. This reaction has become extremely popular and covers about a quarter of all palladium-catalyzed coupling reactions. The initial process consists of hydroboration of an alkyne with borane, followed by palladium(0)-catalyzed C-C cross-coupling of the organoborane with aryl halides. The hydroboration is usually regioselective for the less hindered position and addition of boron and hydrogen occurs cis stereospecifically.

10.2 Organorhodium compounds

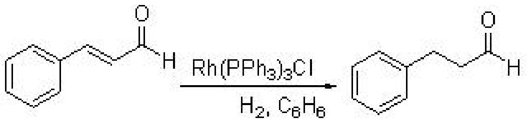
Organorhodium compounds are used as soluble catalysts for effecting many useful organic transformations. This section covers some of the important processes.

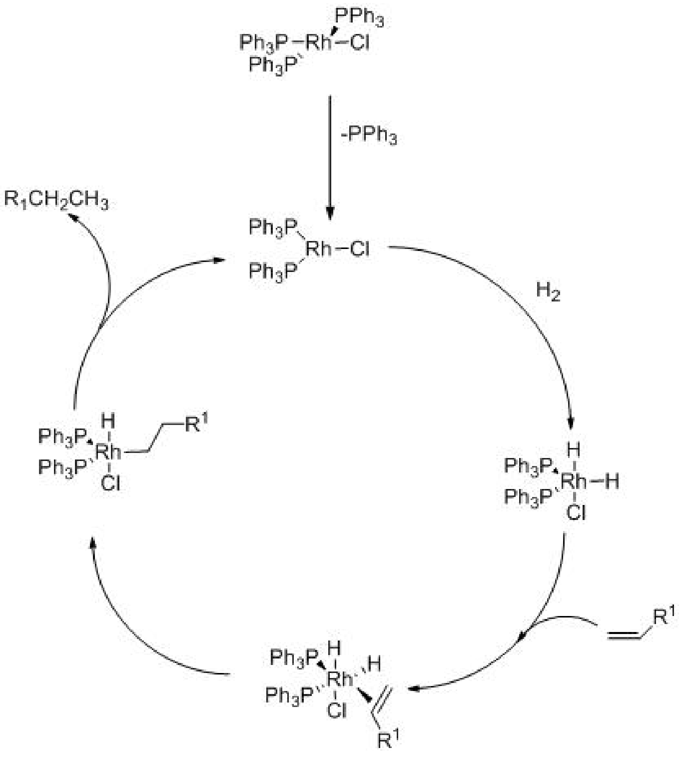
Reactions of Alkenes

The addition of hydrogen to alkenes using transition metal catalysis occupies an important position in organic synthesis. Homogeneous hydrogenation processes offer distinct advantage over their heterogeneous counterparts, for example, superior chemo-, regio- and stereoselectivity. One of the most versatile metal catalysts for double bond saturation in the homogeneous phase is Wilkinson's catalyst, [$RhCl(PPh_3)_3$]. It is prepared by the reaction of $RhCl_3$ with excess of PPh_3 in boiling EtOH.

$$RhCl_3\,3H_2O + PPh_3 \xrightarrow[\text{Boiling}]{\text{EtOH}} (PPh_3)_3RhCl$$

Wilkinson's catalyst and its modified forms have been extensively used for the hydrogenation of alkenes. Functional groups like oxo, cyano, nitro, choro and azo are compatible under ordinary temperature and pressure. If the functional groups are properly situated chelate on the active Rh and can thus direct hydrogenations providing high degree of selectivity.

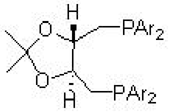




The mechanism of the reaction is shown abow

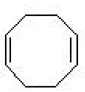
The coordination complex is a square planar 16 electron complex whose stability is due to filled bonding molecular orbitals. The complex loses a PPh_3 to form a 14 electron complex which coordinates with alkene and then undergoes oxidative addition with hydrogen. This is followed by transfer of hydrogen to carbon from Rh to form alkyl Rh intermediate. Then, second hydrogen migrates to carbon leading to reductive elimination of saturated product. In this step, rhodium is electrophilic and hydride transfer is nucleophilic. In some cases, however, an alternative reaction pathway seems to have been operating. This pathway first involves the addition of hydrogen to rhodium prior to the complexation of alkene. The evidence for this path comes from the fact that addition of hydrogen to the $[RhCl(PPh_3)_2 (\eta\text{-}C_2H_4)]$ is not feasible

Subsequently, chiral rhodium(I)-phosphine complexes have been developed for asymmetric hydrogenation of alkenes. Among the vast number of chiral catalysts, Rh(I) diphosphine complexes revealed to be the most efficient for asymmetric reduction of functionalized alkenes. For examples, α-piperonylidine succcinic acid half-ester with hydrogen in the presence of precatalyst prepared in situ by mixing of (*S*,*S*)-MOD-DIOP with $[Rh(COD)Cl]_2$ affords the product in 93% ee.

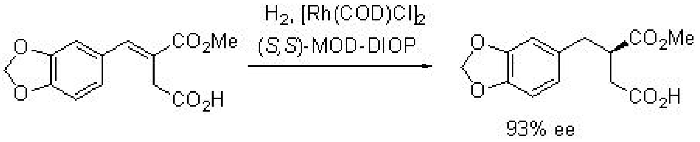


Ar = 4-OMe-3,5-Me_2-C_6H_2

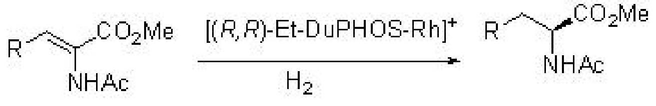
(*S*,*S*)-MOD-DIOP

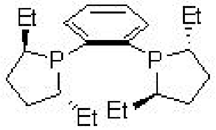


COD

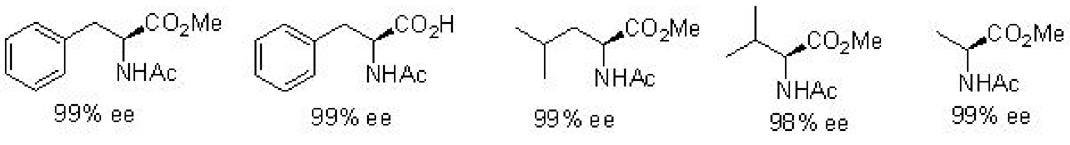


A series of chiral rhodium(I)-diphosphine complexes have been explored for the hydrogenation of a enamides to afford α-amino esters. For examples, N-acetyl- α -enamides with β -substituents can be reduced using the (*R*,*R*)-Et-DuPHOS-Rh complexes with excellent enantioselectivity.



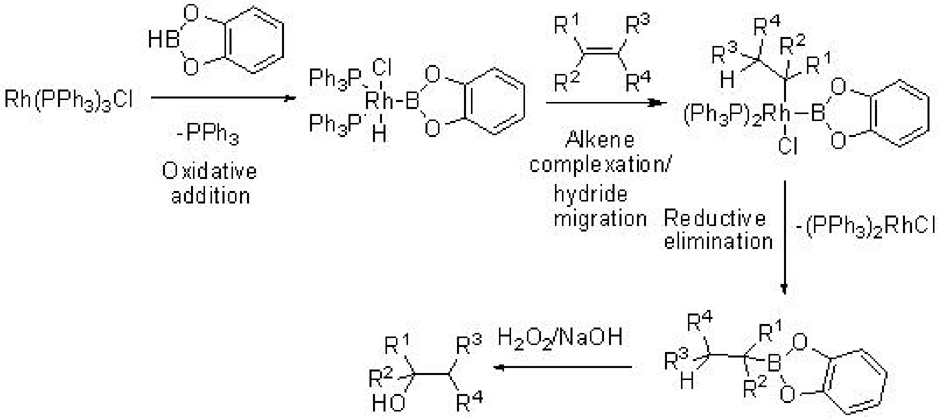


(*R*,*R*)-DuPHOS

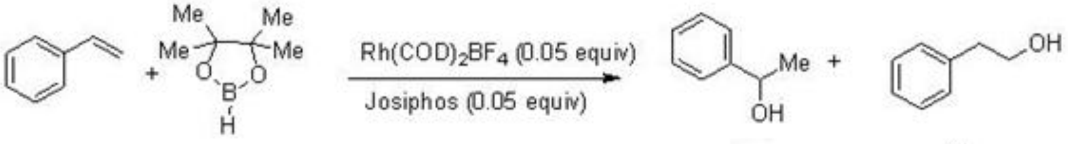


Hydroboration

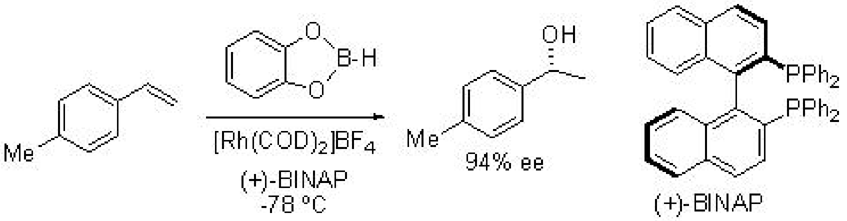
Another interesting application of Wilkinson's catalyst is its use in the hydroboration of alkenes and alkynes. The reactions sensitive to steric effects, and afford diastereoselectivity that is complementary to the uncatalyzed hydroborations. Thus, it has been extensively used in natural product synthesis for the hydroboration of carbon-carbon multiple bonds. The proposed mechanism is analogy with that of the hydrogenation of alkenes.



Besides Wilkinson's catalyst, various other hydroboration catalysts based on rhodium have been used. The variation in ligand leads to changes in regio- and stereoselectivities. For an example, the hydroboration of styrene can be directed to the internal secondary borane by the use of $Rh(COD)_2\ BF_4$ as a catalyst.

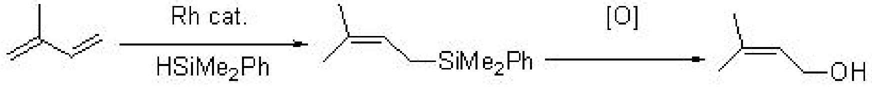


Several studies have subsequently focused on the development of boron hydrides and their application for asymmetric hydroboration with chiral rhodium complexes. For example, 4-methylstyrene reacts with catecholborane in the presence of cationic rhodium-BINAP complex with excellent enantioselectivity

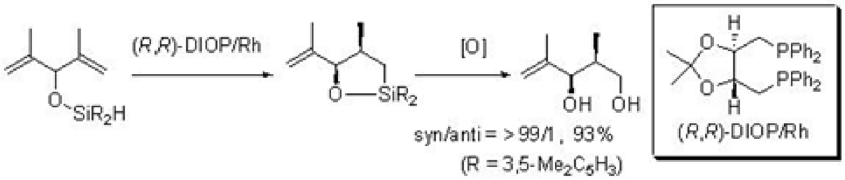


Hydrosilylation

Hyrosilylation of alkenes is not only of industrial importance, but also one of the most practical means that afford functionalized organosilicon compounds of synthetic applications. The rhodium(I)-catalyzed hydrosilylation of alkenes with anti-Markovnikov selectivity provides an effective route for the synthesis of 1-silylalkanes. The adducts can be subjected to an efficient oxidative cleavage of the silicon-carbon bond transforming into 1-alkanols

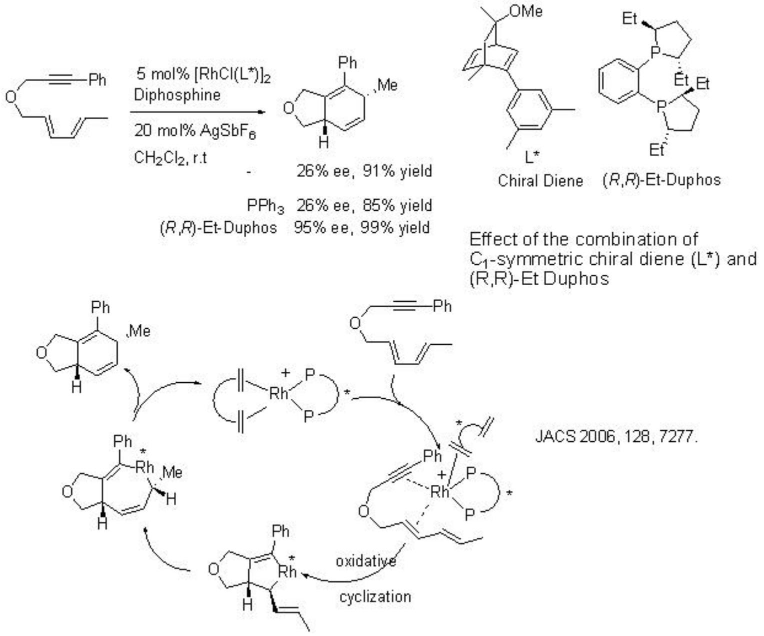


Asymmetric version of the reaction can be accomplished with high enantioselectivity. For an example, Rh-BINAP complexes catalyze asymmetric intramolecular hydrosilylation of alkenes with high enantioselectivity.



Cycloaddition

Chiral rhodium-phosphine complexes can be employed as effective catalysts for cycloaddition reactions. For examples, rhodium(I)-complexes having diene and chiral bisphosphines catalyze intramolecular (4+2)-cycloadditions with excellent enantioselectivity.

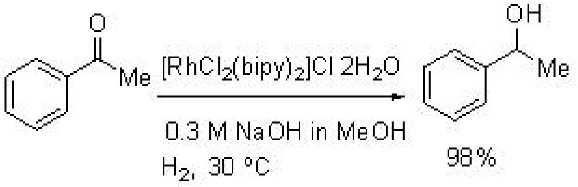


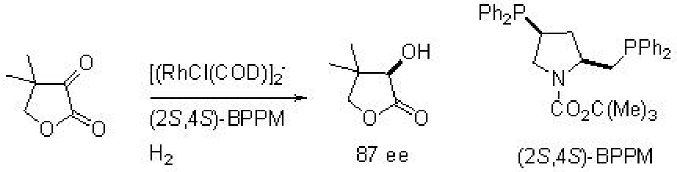
Effect of the combination of C_1-symmetric chiral diene (L*) and (R,R)-Et Duphos

JACS 2006, 128, 7277.

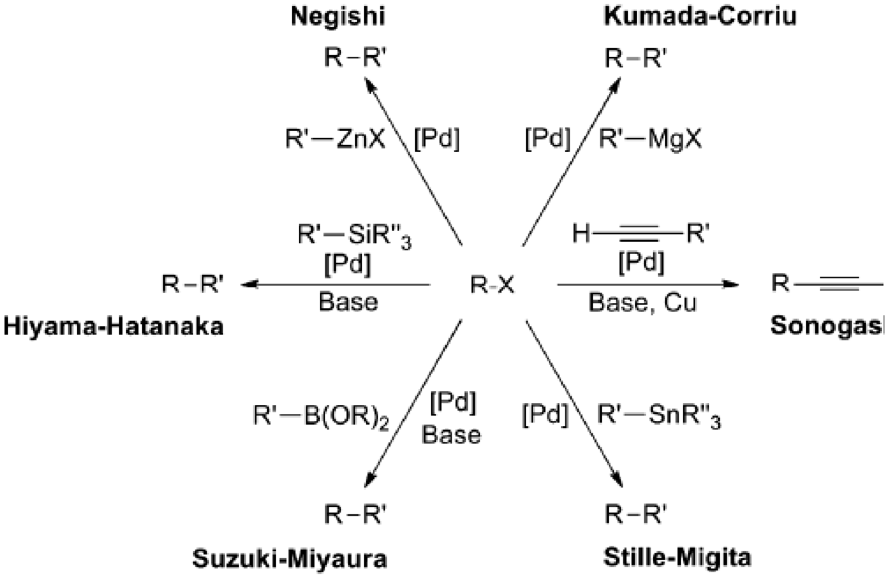
Hydrogenation of Carbonyl Groups

Limited rhodium complexes have shown good catalytic activity towards to the reduction of ketonic substrates possessing no functionality adjacent to the carbonyl group. The asymmetric version of the reaction can be accomplished using chiral rhodium complex. For an example, chiral rhodium-phosphine complex is used for the hydrogenation of ketopantolactone with good enantioselectivity

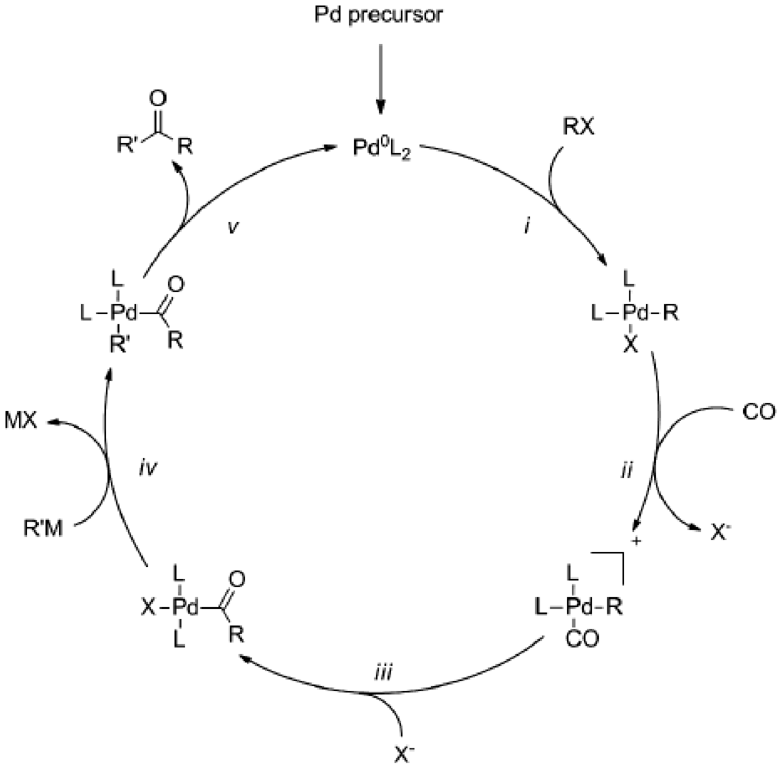




Palladium(0)-catalyzed reactions have found widespread use in many areas of organic chemistry. Due to their impressive range of functional group tolerance and high chemo- and regioselectivity, many different reactions are included in this type of reaction. All of which are initiated by the oxidative addition of an electrophile, typically an aryl/vinyl halide or a sulfonate such as a triflate or a tosylate (hereafter denoted X).



Instead of discussing all the possible routes for the formation of organopalladium species, the below scheme will briefly describe five fundamental processes involved in the catalytic cycles of the Pd(0)-catalyzed reactions.



Oxidative Addition

The palladium source should be a 16- or 18-electron species. This complex must quickly become an activated 14-electron species through the loss of two ligands in solution. This catalytically active Pd(0)L2 species then coordinates to the □-system in the electrophile, followed by the migration of Pd to a possible transition state, where the metal binds in a η2 fashion over the C-X bond in the electrophile. The cleavage of one covalent bond (C-X) and form two new bonds (R-Pd-X) occurs. For this reason, a non-bonded electron pair on palladium becomes involved in a new bond which results in an increase in the oxidation state of Pd from 0 to +2. The oxidation of Pd will change the tetrahedral geometry into a square planar complex. Generally, this step is favored by electron-donating monodentate phosphine or carbene ligands.

Coordination and Insertion

The next step is the coordination of R-X to palladium. This is considered to be an associative substitution supported by the relatively stable 18-electron intermediate, but could possibly be a dissociative exchange with a weakly bound anion such as triflate or tosylate. With the X and the electrophile in a cis relationship on palladium the organyl group migrates to the R carbon and an organopalladium complex is formed, or expressed another way undergoes a 1,1- insertion into the Pd-organyl bond.

Transmetallation

The step following insertion in cross-coupling usually involves the reaction of an organometallic or organometalloid nucleophile with the Pd complex. This process is defined as transmetallation and delivers the organonucleophile to the Pd center. The process is driven by the difference in electronegativity of the two metals. Thus, palladium must be the more electronegative metal for transmetallation to occur.

Reductive Elimination

The product-forming step in most Pd(0)-catalyzed reactions is reductive elimination. This step proceeds through a three-centered transition state in order to form a new C-C bond between the electrophilic acyl/alkyl/aryl group and the nucleophile. The non-bonded electron pair in palladium that was involved in a new bond in the previous oxidative addition step is now returned and the catalytically active $Pd(0)L_2$ species is regenerated.

10.3 π-bonding of metals with olefins

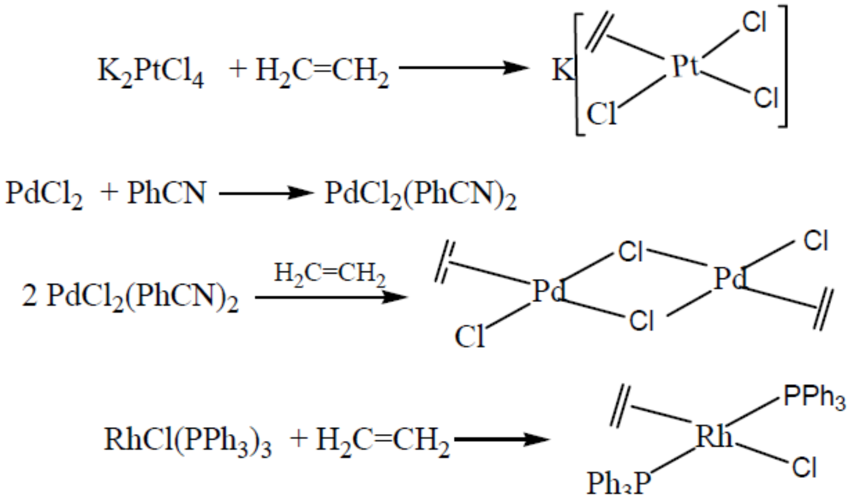
As we know a double bond is made up of one σ- and one π-bonds. It is known to act as a donor ligand via π-electrons (Lewis base), similar to other Lewis bases such as NH_3, H_2O, THF, Et_2O, etc. which form bonds via σ-electrons. Metal –alkene complexes are known for nearly all the d-block elements, however, the most stable complexes are formed by the elements late in the transition series.

Alkenes, alkynes and other π-systems can be excellent ligands for transition metals. As a consequence of this binding the nature of the π-system changes from weakly nucleophilic to electrophilic. For metal-alkene bonds to be strong, and hence for the formation of a stable complex, a metal should form a π-bond with the empty π*- orbitals over a double bond.

10.4 Synthesis of metals-olefin complexes

When ethene ($H_2C=CH_2$) is passed through an acidic solution of K_2PtCl_4, $K[Pt(\eta^2\text{-}C_2H_4)Cl_3]\cdot H_2O$ is formed and it is called Zeise’s salt,. This reaction is very slow and needs high pressure, and long time however, an addition of stannous chloride ($SnCl_2$) catalyzes the reaction and is complete in 4 h at ambient temperature and pressure.

Palladium(II) chloride can be dissolved in benzonitrile (PhCN) on heating $PdCl_2(NCPh)_2$ is formed which is the staring material. Reaction of $PdCl_2(NCPh)_2$ with ethylene ($H_2C{=}CH_2$) displaces PhCN forming chloride-bridged dimer, $[Cl(\eta^2\text{-}C_2H_4)Pd(\mu\text{-}Cl)_2Pd(\eta^2\text{-}C_2H_4)Cl]$. Reaction of Wilkinsons's catalyst $RhCl(PPh_3)_3$ with ethene displaces one PPh_3 forming ethene complex, $RhCl(PPh_3)_2(\eta^2\text{-}C_2H_4)$.



10.5 Structure of metals-olefin complexes

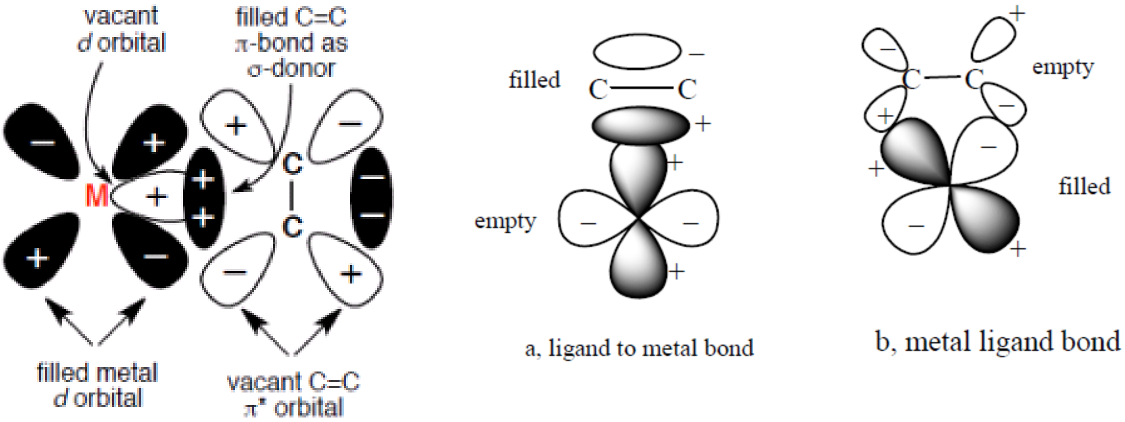
The Dewar-Chatt-Duncanson model explains the type of chemical bonding between an unsaturated ligand and a metal forming a π complex. The π-acid ligand donates electron density into a metal d-orbital from a π-symmetry bonding orbital between the carbon atoms. The metal donates electrons back from a filled t_{2g} d-orbital into the empty π* antibonding orbital of the ligand (similar to dihydrogen σ-complexes). Both of these effects tend to reduce the C-C bond order, leading to an elongated C-C distance and a lowering its vibrational frequency.

For example, In the nickel compound $Ni(CH_2CH_2)(PPh_3)_2$ the C-C bond distance is 143 pm (vs. 134pm for free ethylene).

The interaction can cause carbon atoms to "rehybridize“,

For example, in metal alkene complexes from sp^2 towards sp^3, which is indicated by the bending of the hydrogen atoms on the ethylene back away from the metal.

Figure 1 shows bonding in metal-alkene complexes represented in simplistic manner. The π-electrons from double bond donate electrons to empty metal d-orbital forming σ-bond (Fig. 1a), and metal filled d-orbital forms π-bond with empty π*-orbitals of double bond(Fig. 1b). This mode of σ-π bond formation is synergic, according to which a σ-bond is strengthened by π-bond formation due to greater flow of electron density form metal to ligand and π-bond formation is strengthened by σ-bond formation due to greater flow of electron density form ligand to metal.



a, ligand to metal bond

b, metal ligand bond

Figure 1: Metal-olefin bonding

In extreme cases of strong backbonding from a π- basic metal to the alkene ligand leads to form a metalacyclopropane structure. In this structure the metal-alkene system can be considered as an η^2 structure. In this η^2 structure, the C atoms of the alkene rehybridize close to sp^3. There are two σ- bonds are formed to the metal centre hence the Dewar-Chatt-Duncanson model no longer applies. These two extremes are often referred to as X type and L type ligands and their bonding mode is shown in figure 2.

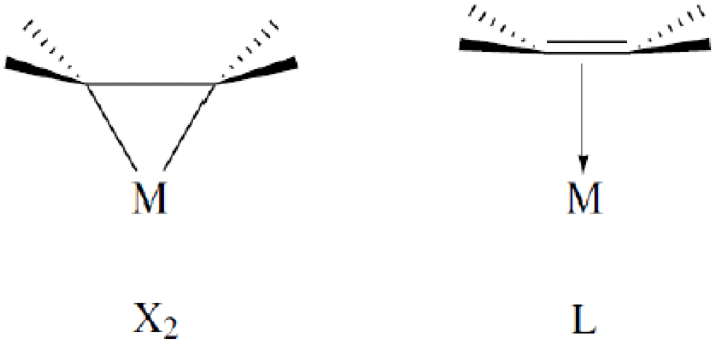


Figure 2: two types of metal-olefin complex structure

In both cases the ligand is considered as a 2e donor in the covalent model. In the ionic model, the X_2 configuration has a 2- charge and is considered a 4e donor and the L configuration does not change the oxidation state of the metal and is still considered a 2e donor. Thus one can consider L as an intermediate structure in the oxidative addition of the alkene ligand to form X_2. The C atoms of the alkene rehybridize close to sp^3. Apart from crystallographic studies ^1H and ^{13}C NMR spectroscopy are useful tools in determining the nature of a metal alkene bond. The difference between the L and X_2 structural configurations are also borne out in their electronic and hence chemical properties. In the L configuration the C atoms tend to carry a δ^+ charge due to σ- donation to the metal which is not reciprocated by back donation from the metal. Metal-alkene complexes having the L type configuration are therefore susceptible to nucleophilic attack at the alkene C atoms. This is in contrast to electrophilic attack often observed for free alkenes. This change in reactivity upon complexation is also known as “umpolung” which can be translated as a reversal in polarity. In the X_2 configuration the C atoms are negatively charged and are susceptible to electrophilic attack.

Factors favoring X_2-type binding

The following factor favors the formation of X_2 type bonding in metal-olefin complexes.

- i) strong donor ligands
- ii) a net negative charge on the complex and
- iii) low-oxidation state metals

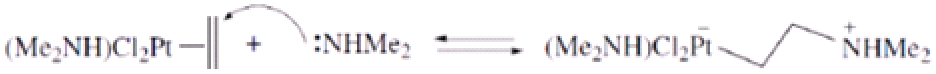
10.6 Reactions of metals-olefin complexes

A lot of chemistry is observed in metal-olefin complexes.

Insertion intoM-L s bonds to form higher alkanes

$$\mathrm{AuMe(PPh_3) + CF_2{=}CF_2 \longrightarrow \{(CF_2{=}CF_2)AuMe(PPh_3)\} \longrightarrow Au(CF_2{-}CF_2Me)(PPh_3)}$$

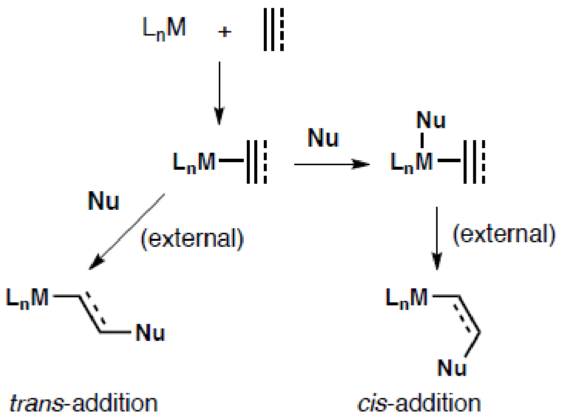
Nucleophilic attack



The addition of the nucleophile can be external or internal and attack of nucleophile on ligand is favored by

i) saturated metal center, ii) π-accepting ligands, iii) electron-poor metal centers, iv) cationic complexes and iv) soft nucleophiles

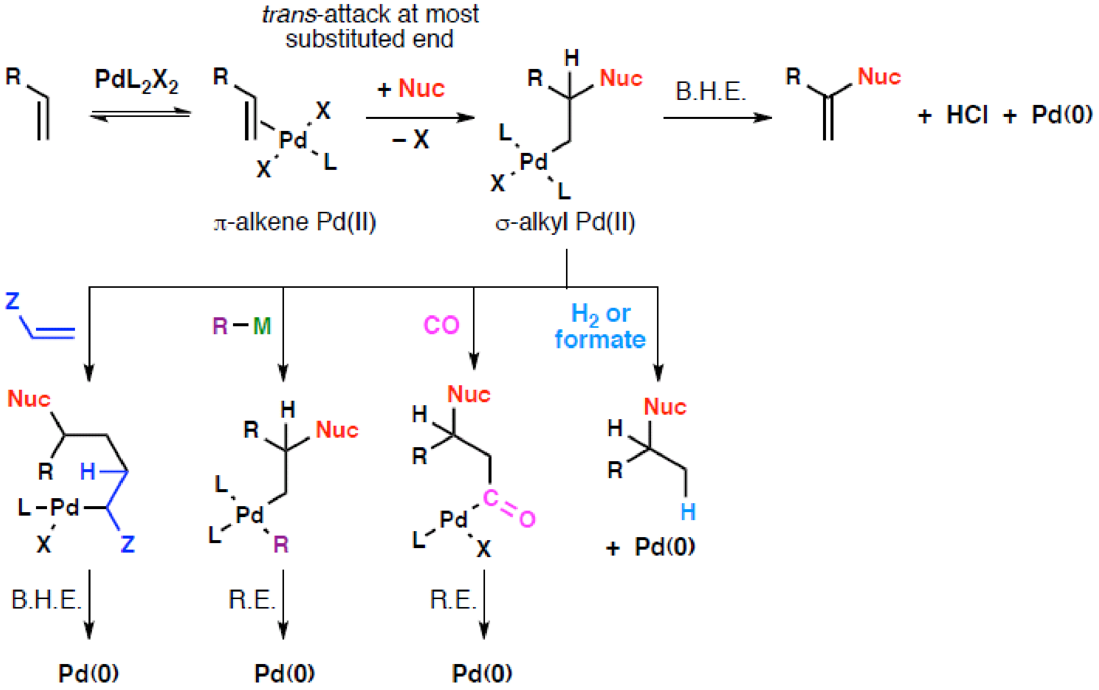
The reaction can be represented as follows



The resulting σ-alkyl or σ-alkenyl complexes can proceed to do other reactions.

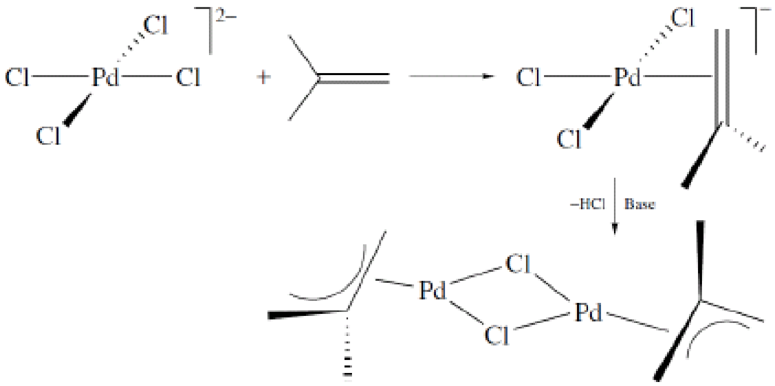
Palladium (II)-Catalyzed Additions

$PdCl_2$ and $Pd(OAC)_2$ are commonly used metal compounds for this reaction. The strong donor ligands like phosphines tend to shut down reactivity therefore weaker donor ligands like pyridines are used. Acceptor ligands like nitriles also work well.



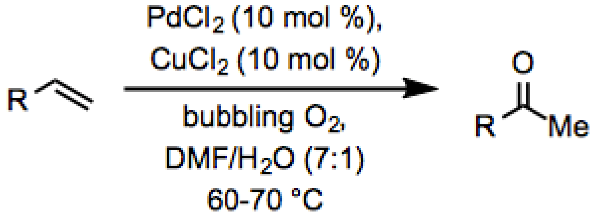
All transformations involving the σ-alkyl palladium intermediate will eventually generate Pd(0). Either stoichiometric amounts of metal are needed or a reoxidant must be present

Oxidative addition



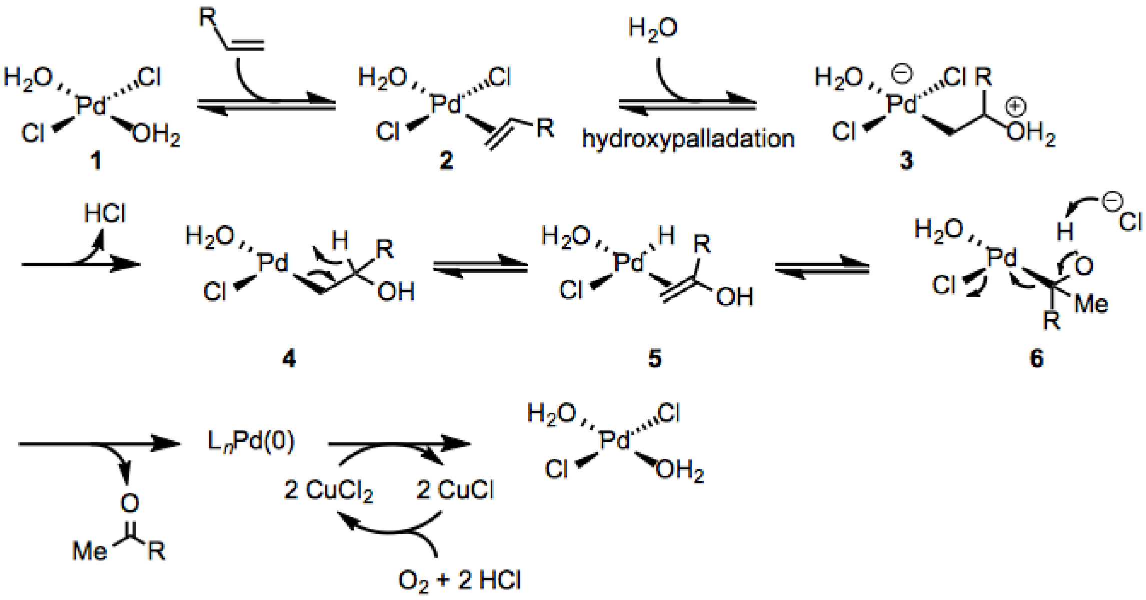
10.7 Wacker process

The stoichiometric conversion of ethylene to acetaldehyde by an acidic, aqueous solution of PdCl$_2$ is called Wacker process. Wacker process is generally used in industry for the manufacture of ethanol by oxidizing ethene. Bubbling ethylene and oxygen when treated by an acidified water solution of palladium and cupric chlorides yield acetaldehyde. The reaction is catalyzed by PdCl$_2$-CuCl$_2$. During the reaction initially palladium forms a complex with ethylene, and is reduced to Pd(0), then reoxidized by Cu(II). The process is run in a vessel at 50–130°C and at pressures of 3–10 atm. Regeneration of cupric chloride occurs in a separate oxidizer.

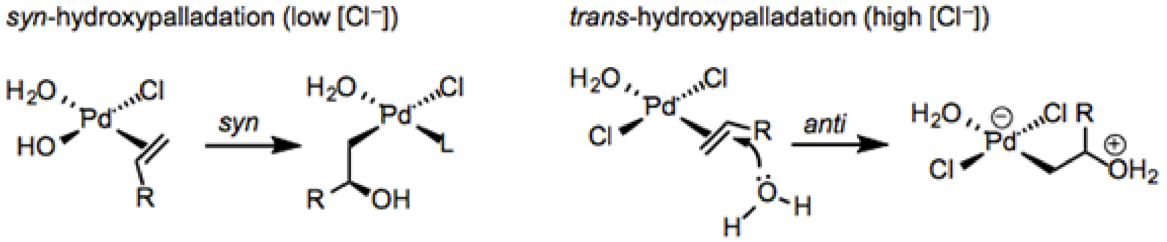


Mechanism

The first step of the Wacker oxidation involves coordination of the alkene to the palladium to form π-complex. In the next step Hydroxypalladation occurs to yield either zwitterionic complexor neutral complex depending on the mode of hydroxypalladation. In the final step β-hydride elimination occurs to afford enol complex which re-inserts into the Pd-H bond followed by chloride-assisted deprotonation affords carbonyl compound and palladium(0). Oxidation of palladium(0) by copper(II) then occurs to regenerating palladium(II) specie



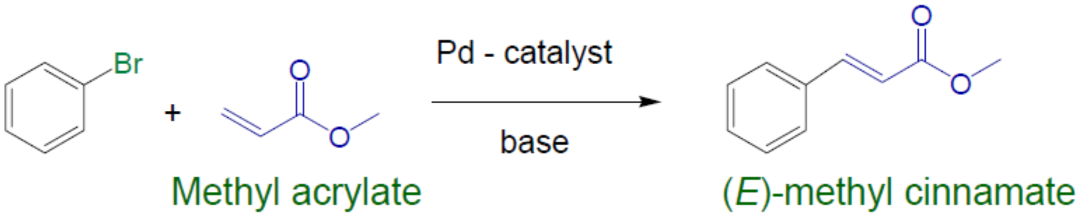
The mode of hydroxypalladation is an important issue for the Wacker oxidation. Hydroxypalladation may occur either in a syn fashion through an inner-sphere mechanism or in an anti fashion via nucleophilic attack on the coordinated alkene.



The mode of hydroxypalladation can influence the site selectivity of the reaction. Markovnikov-type addition of water to the more substituted carbon of the alkene forms a methyl ketone, while attack of water at the less substituted position ultimately yields an aldehyde.

10.8 Heck reaction

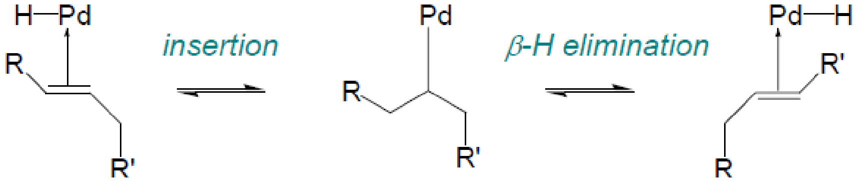
Palladium catalyzed Vinylation of aryl halides in the presence of a base is referred to as the "Heck reaction". The conventional Heck coupling is based on an aryl iodide or bromide and a terminal alkene. The reaction is most efficient when the alkene possesses an electron-withdrawing group such as CO_2R or CN.



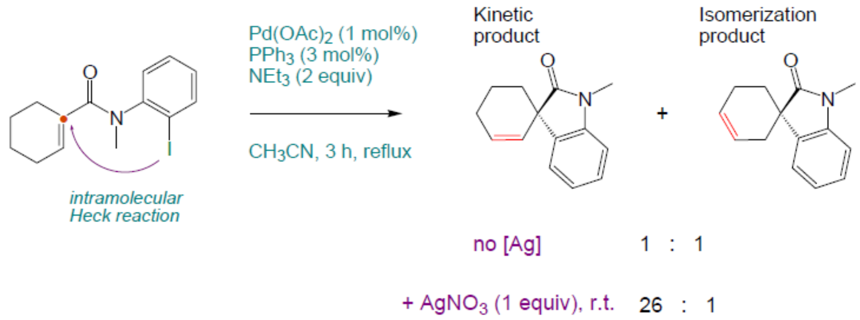
$Pd(OAc)_2$ is the most common catalyst used in heck reaction, the base is usually an amine, K_2CO_3 or Ag_2CO_3. Phosphines are used to prevent deposition of Pd(0) mirror. The catalytic cycle for the Heck reaction involves a series of transformations around the palladium catalyst. The palladium(0) compound required in this cycle is generally prepared in situ from a palladium(II) precursor. The reaction begins by oxidative addition of the aryl halide to the palladium, which is followed by coordination and migratory insertion of the olefin to the palladium. Bond rotation then places the two groups trans to each other to relieve the steric strain and subsequent β-hydride elimination results in a trans final product. Base mediated reductive elimination regenerates the palladium(0) catalyst

10.9 Alkene isomerization in Heck reaction

For some R and R' groups, reversible β-H elimination can lead to alkene isomerization



This isomerization is minimized in the presence of silver salts.



10.10 Mechanism

The mechanism of Heck reaction involves the oxidative addition of the halide, migratory insertion (or carbopalladation) of the olefin, and β-hydride elimination to form the product. The palladium(0) catalyst is then regenerated using a base in the reductive elimination step. There are two possible mechinsms are proposed for Heck reaction. They are

i) Neutral mechanism and

ii) Cationic mechanism

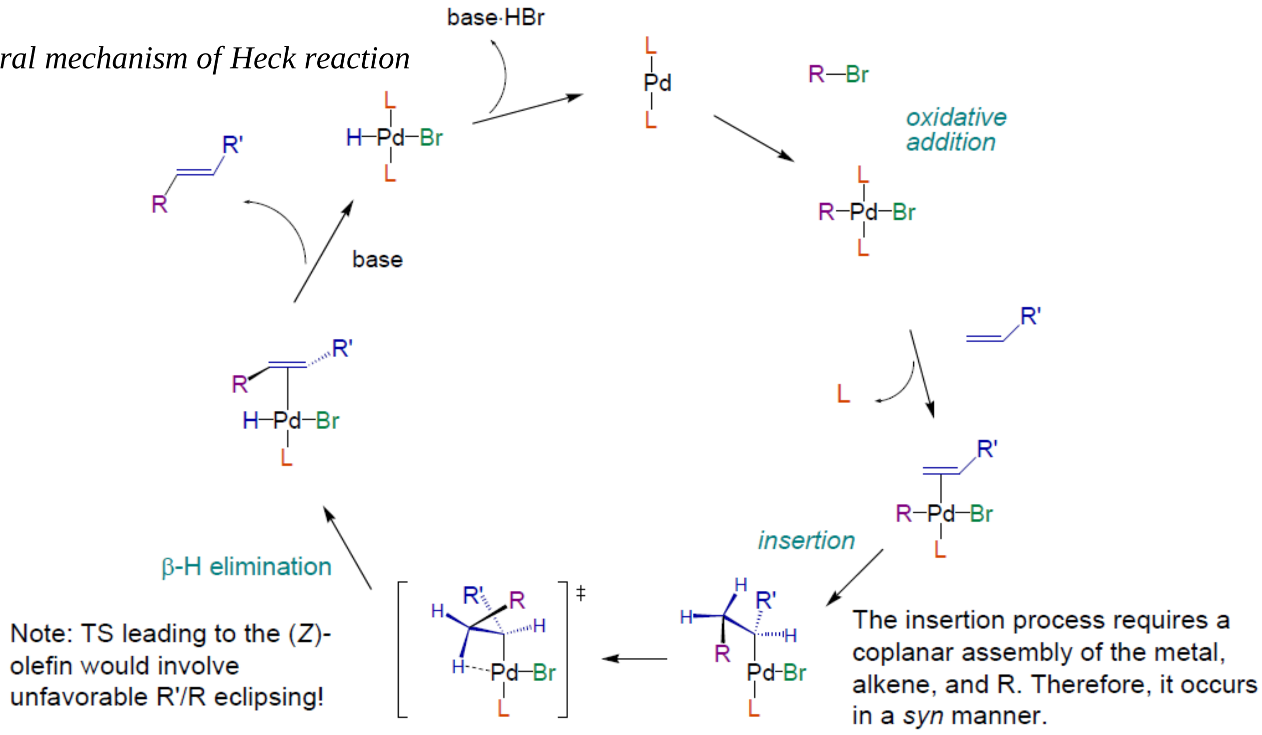
a) Neutral mechanism of Heck reaction

This mechanism operates when X = Cl^-, Br^- or I^- and involves dissociation of a neutral ligand. The neutral Heck reaction is faster with electron poor olefins (in the presence of a good π-acceptor/poor σ-donor group). The reaction is inhibited by bidentate phosphines

b) Cationic mechanism of Heck reaction

This operates with labile X (OTf^-) or with Ag^+ or Tl^+ salts capable of halide abstraction. Faster dissociation of the olefin from the cationic Pd helps to minimize alkene isomerization. The reaction is faster with "electron rich" olefins (bearing π-donor groups).

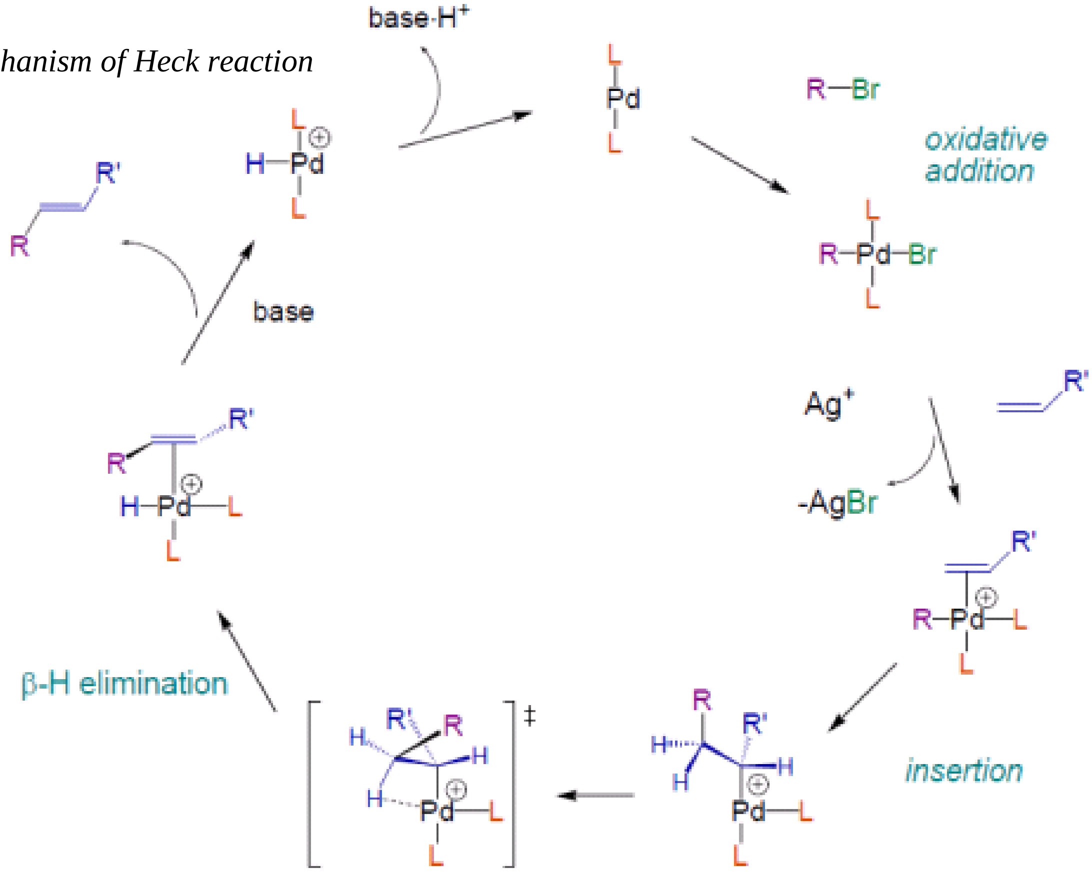
Neutral mechanism of Heck reaction



Note: TS leading to the (*Z*)-olefin would involve unfavorable R'/R eclipsing!

The insertion process requires a coplanar assembly of the metal, alkene, and R. Therefore, it occurs in a *syn* manner.

Cationic mechanism of Heck reaction

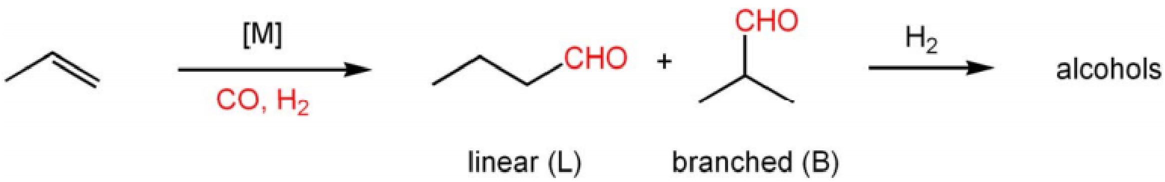


10.11 Carbonylation

Carbonylation reactions involves the introduce carbon monoxide into organic and inorganic substrates. Useful organic chemicals are prepared by carbonylations reactions. Carbonylations produce organic carbonyls, i.e., compounds that contain the C=O functional group such as aldehydes, carboxylic acids, and esters. Carbonylations are the basis of two main types of reactions, hydroformylation and Reppe Chemistry.

d) Hydroformylation

Hydroformylation, also known as the oxo process, refers to the catalyzed conversion of olefin, carbon monoxide and hydrogen to an aldehyde. The reaction is known as hydroformylation because it appears that the product is derived from addition of the C-H bond of formaldehyde across the carbon-carbon double bond of the olefin.



d tributylphosphine, and HRh(CO)(PPh$_3$)$_3$. The cobalt-based catalysts require high pressures of CO + H_2 (100-300 atm) and temperatures of greater than 150^0 C whereas the rhodium catalyst is active at one atmosphere of CO/H_2 and at modest temperatures although reaction rates are significantly higher at higher temperatures and pressures. The rhodium catalyst shows a much greater regioselectivity than the cobalt catalysts for the formation of the linear product, which is typically much more desirable commercially.

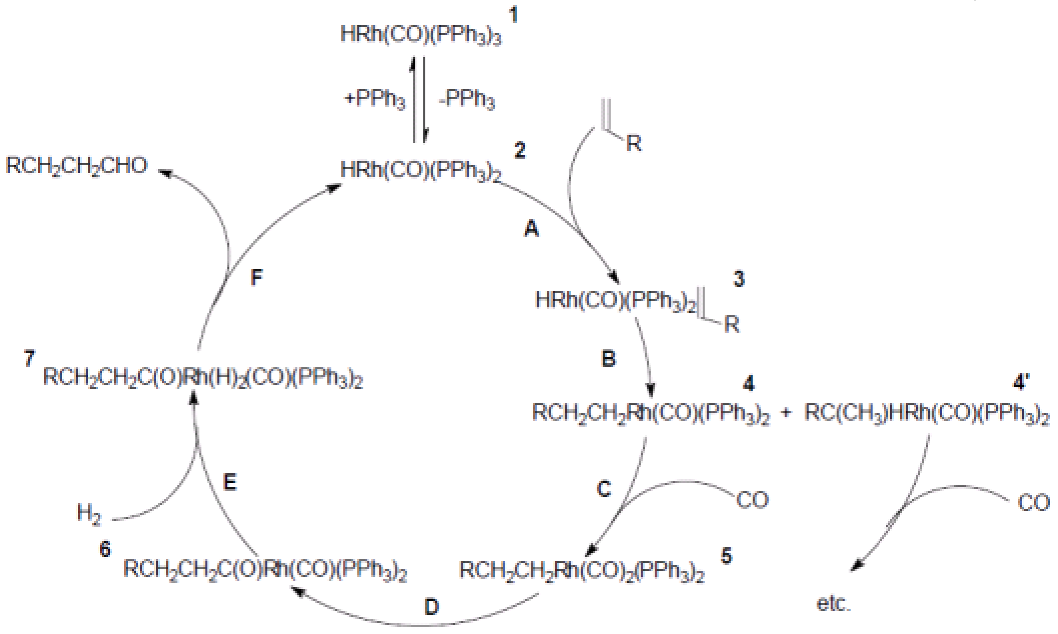
	Catalysts		
	Co	Co/phosphine	Rh/phosphine
Reaction Pressure (bar)	200-300	50-100	7-25
Reaction Temperature (°C)	140-180	180-200	90-125
L:B of aldehyde	4:1	9:1	19:1
Catalyst	[$HCo(CO)_4$]	[$HCo(CO)_3(PBu_3)$]	[$HRh(CO)(PPh_3)_3$] / PPh_3 up to 1:500
Main Products	aldehydes	alcohols	aldehydes
Hydrogenation to alkanes (%)	1	15	0.9

e) Advantages of using [Rh] over [Co]

[Rh] is 1000 times more active and uses of excess PPh_3 allows high linear aldehyde selectivity. Also use of PPh_3 increases catalyst stability and prolongs its life. [Rh] has low volatility so purification of product is simpler.

f) Mechanism

The generally accepted mechanism for the rhodium catalyzed hydroformylation reaction is shown below.



Reactions A-F are reversible. Coordination numbers of the rhodium complexes range from 4-6 and the number of valence electrons cycles between 16 and 18 through a combination of ligation, oxidative addition, or reductive elimination. Note that dissociation of PPh_3 from $HRh(CO)(PPh_3)_2$, an $18e^-$ species, is a necessary step in order to generate a vacant coordination site to bind the olefin. Added triphenylphosphine reduces the concentration of the active $16e^-$ species, but it also suppresses the the formation of $HRh(CO)_2(PPh_3)_2$, precursor to $HRh(CO)_2(PPh_3)$, which is also active in hydroformylation but has a much lower regioselectivity. The greater steric bulk of the two phosphorus ligands in compound 3 most likely results in greater selectivity for formation of the primary alkyl complex 4 versus secondary alkyl complex 4' in step B. Formation of the secondary alkyl complex in step B will result in branched product.

10.12 Reppe chemistry

Reppe Chemistry involves addition of carbon monoxide and an acidic hydrogen donor to the organic substrate. Large-scale applications of this type of carbonylation are the conversion of methanol to acetic acid. Acetic anhydride is also prepared by a carbonylation of methyl acetate. In these reactions (hydrocarboxylation and hydroesterification) alkenes and alkynes are the substrates. This method is used to produce propionic acid from ethylene:

$RCH{=}CH_2 + H_2O + CO \rightarrow RCH_2CH_2CO_2H$

These reactions require metal catalysts, which bind and activate the CO

Hydroesterification reaction is similar to hydrocarboxylation reaction but alcohols are used instead of water.

10.13 Olefin isomerization

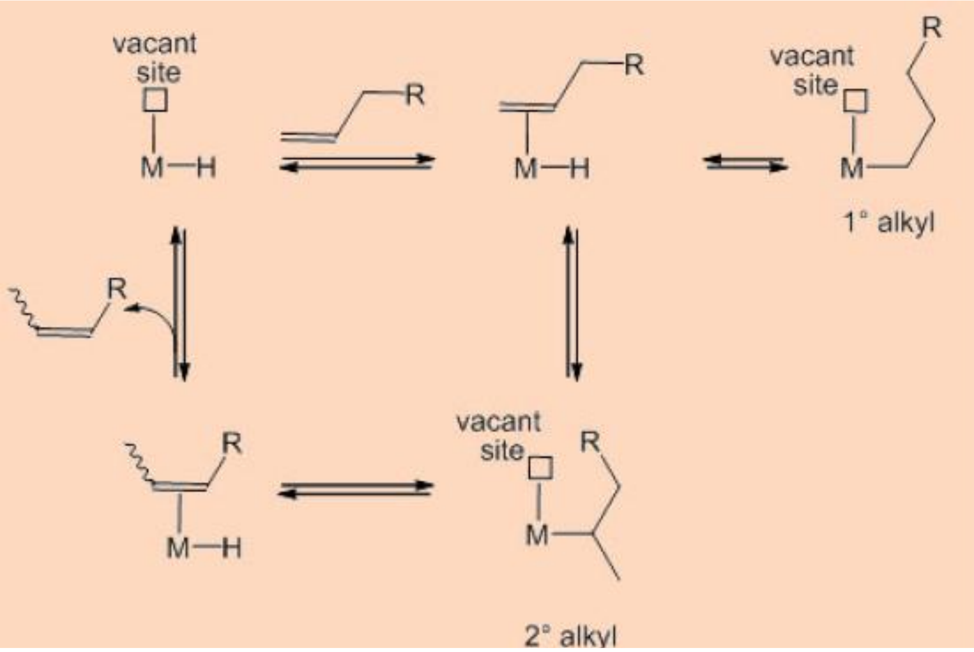
One of the most important exploits of the organometallic chemistry is its application in the area of homogeneous catalysis. Double-bond migration in olefins is one of the simplest and most thoroughly studied catalytic reactions. Alkene isomerization is a transformation that involve a shift of a double bond to an adjacent position followed by 1,3−migration of a H atom. The isomerization reaction is transition metal catalyzed

The alkene isomerization reaction may proceed by two pathways, (i) one through a η^1−alkyl intermediate and (ii) the other through η^3−allyl intermediate.

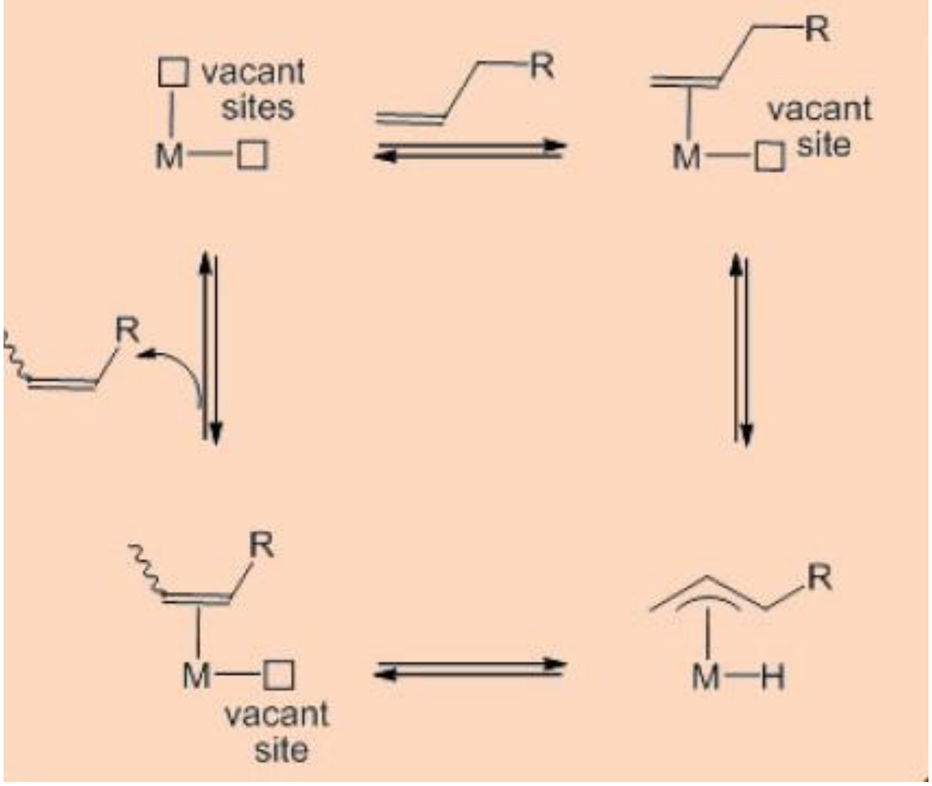
In the η^1−alkyl pathway, an alkene first binds to a metal at a vacant site next to M−H bond and then subsequently undergoing an insertion into the M−H bond thus creating back the vacant site. The resultant species then undergoes a H atom transfer from the alkyl moiety to give the isomerized olefin along with the regeneration of the M−H species.

The η^3−allyl mechanism requires the presence of two vacant sites. This mechanism goes through a η^3−allyl intermediate formed by a C−H activation at the allylic position of the olefin formed after binding to the metal and alongside leads to the formation of a M−H bond. Subsequent H transfer from the metal back to the η^3−allyl moiety leads to the alkene isomerized product.

η^1–alkyl pathway



η^3–allyl pathway



10.14 Summary of the unit

The palladium-catalyzed C-C cross-coupling of alkenes with alkenyl triflates (bromides, iodides) and aryl triflates (bromides, iodides) to give substituted alkenes in the presence of stoichimoetric amount of triethylamine is called Heck. The amine serves to reduce Pd(II) to the catalytically active Pd(0) complex. The amine also plays an important role in that it neutralizes the acid formed in the reaction (TfOH, HBr or HI). Asymmetric intramolecular Heck reaction has been accomplished in the presence of (R)-BINAP. The C-C cross-coupling reaction of organocopper reagents with electrophiles is a well known method and does not require the presence of transition metals as catalyst. Nevertheless, it is found that palladium can accelerate the reaction. The palladium-catalyzed C-C cross-coupling of in situ generated alkynylcopper reagents with aryl as well as alkenyl halides is known as the Sonogashira Coupling (Scheme 8-9). The reaction takes place smoothly under mild conditions in the presence of catalytic amount of copper(I) iodide and tolerates a variety of functional groups in both coupling partners including hydroxo, carbonyl, amino, acyloxy, acetal, esters, amides etc. Thus, this reaction has been extensively used to the synthesis of many natural products and pharmaceuticals and macromolecules. The palladium-catalyzed C-C cross-coupling reaction of organotin reagents with electrophiles to give dienes is called ‘Stille Coupling' although Stille and Migita independently investigated this reaction. The main advantage of this method is that a lot of functional groups like aldehydes, ketones, esters, nitriles, amines as well as alcohols are tolerated. In comparison to Suzuki coupling no base is needed. Therefore, organometallic compounds having tin as well as boron can be coupled selectively via tin. However, toxicity concerns are the major disadvantage of the cross-coupling of organostannanes. Both inter- and intramolecular reactions have been explored and widely applied in the synthesis of complex molecules.

10.15 key words

Organorhodium compounds; π-bonding of metals with olefins; Metals-olefin complexes; Wacker process; Heck reaction; Alkene isomerization in Heck reaction; Carbonylation; Hydroformylation; Reppe chemistry.

10.16 References for further study

1) Organometallic Chemistry; R. C. Mehrotra; *New Age International*, **2007**.

2) Organometallic Chemistry of the Transition Elements; Florian P. Pruchnik; *Springer Science & Business Media*, **1990**.

3) Inorganic chemistry; 3rd ed. Gary L. Miessler, Donald A. Tarr *Rex Bookstore, Inc.***2004**.

4) Advanced Inorganic Chemistry: Vollume II. Gurdeep Raj; *Krishna Prakashan Media*, **2010**.

10.17 questions for self understanding

1) What are organorhodium compounds? Give examples

2) Discuss the π-bonding of metals with olefins

3) Explain the synthesis of metals-olefin complexes

4) Discuss the structure of metals-olefin complexes

6) Write a note on reactions of metals-olefin complexes

7) Write a brief note on Wacker process.

8) What is Heck reaction? With example explain the mechanism

9) Discuss the Alkene isomerization in Heck reaction

10) What is Carbonylation? What are the catalysts used for this reaction.

11) Write a note on folowings

   a) Hydroformylation
   b) Advantages of using [Rh] over [Co]
   c) Mechanism

12) Discus Reppe chemistry

13) Give a brief account on olefin isomerization and its application

UNIT-11

Structure

11.0 Objectives of the unit
I1.1 Introduction
11.2 Olefin metathesis
11.3 Types of olefin metathesis
11.4 Ring-Opening Metathesis Polymerization (ROMP)
11.5 Ring-Closing Metathesis (RCM)
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11.7 Mechanism of olefin metathesis
11.8 Catalysis for olefin metathesis
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11.9 Factors affecting the olefin metathesis
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11.12 Size of the ring to be formed
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11.0 Objectives of the unit

After studying this unit you are able to

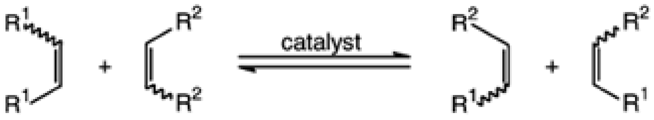
- Explain the different types of olefin metathesis
- Write the mechanism of olefin metathesis
- Identify the suitable catalysis for olefin metathesis
- List out the factors affecting the olefin metathesis
- Explain the Sonogashira Coupling and write the mechanism
- Explain the Stille coupling and write the mechanism
- Explain the Buchwald reaction and write the mechanism
- Explain the Pauson-Khand reaction and write the mechanism

I1.1 Introduction

The olefin metathesis reaction was reported as early as 1955 in a Ti(II)-catalyzed polymerization of norbornene. 15 years later, Chauvin first proposed that olefin metathesis proceeds via metallacyclobutanes. It is now generally accepted that both cyclic and acyclic olefin metathesis reactions proceed via metallacyclobutane and metal-carbene intermediates.

11.2 Olefin metathesis

In recent years, olefin metathesis has emerged as a powerful tool for carbon–carbon bond formation and has enabled the synthesis of rings of different sizes. Olefin metathesis is a metal-catalyzed transformation, which acts on carbon-carbon double bonds and rearranges them via cleavage and reassembly. *Mutual exchange of alkylidine groups between two substituted alkenes in the presence of a transition metal catalyst* (scheme 1) *is termed as olefin metathesis*.



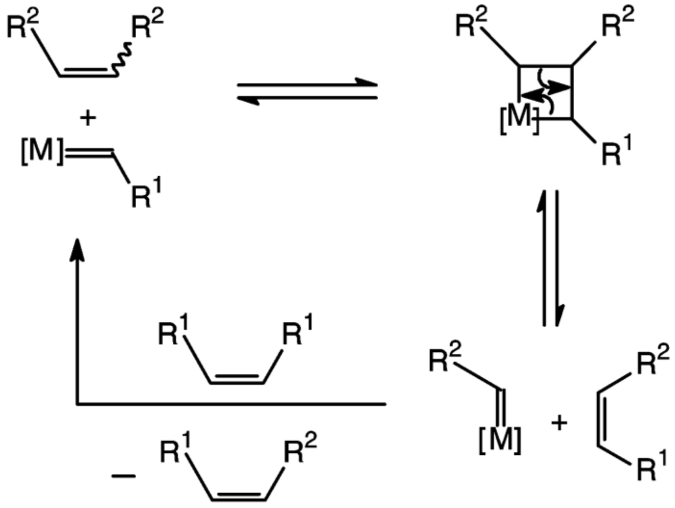
Scheme 1.

This reaction was discovered in the mid-1950s. The mechanism of this reaction was first introduced by Chauvin, according to his mechanism the coordination of an olefin to a metal carbene catalytic species leads to the reversible formation of a metallacyclobutane. This intermediate then proceeds by cycloreversion via either of the two possible paths

1) Non-productive: resulting in the re-formation of the starting materials or

2) product-forming: yielding an olefin that has exchanged a carbon with the catalyst's alkylidene. Since all of these processes are fully reversible only statistical mixtures of starting materials as well as all of possible rearrangement products are produced in the absence of thermodynamic driving forces.

It is now well established that metathesis proceeds through a [2 + 2] cycloaddition between an alkene and a metal carbene complex followed by cycloreversion as proposed by Herisson and Chauvin (scheme 2).



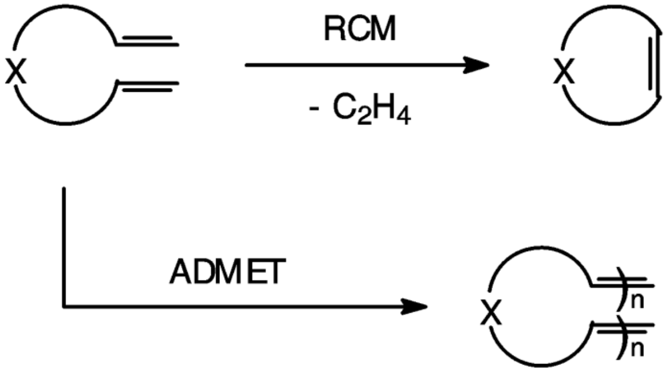
Scheme 2.

There are two major approaches that are commonly employed to drive the reaction towards the desired products. One tactic is to rely on Le Chatelier's principle by continuously removing one of the products from the reaction system in order to shift the equilibrium in favor of the other product. This method is especially effective in the case of cross-metathesis (CM) reactions involving terminal olefins, ring-closing metathesis (RCM) and acyclic diene metathesis polymerization (ADMET), because the volatile ethylene gas by-product formed in these processes can be easily removed.

The other approach capitalizes on the ring strain of cyclic olefins such as cyclooctenes and norbornenes. The energy released during the ring-opening of these compounds is sufficient to drive forward reactions such as ring-opening cross metathesis (ROCM), and ring-opening metathesis polymerization (ROMP). In addition, in some instances, substrate concentration (which often distinguishes ADMET from RCM) or the catalysts' sensitivity to olefin substitution can also be taken advantage of to influence product selectivity. All of these methods are currently successfully employed in the synthesis of a large variety of small, medium, and polymeric molecules, as well as novel materials.

Common rings such as 5–7 membered ones are easily synthesized by these methods. However, formation of medium or large rings by these methods either proceeds with low yields or does not proceed at all due to unfavourable enthalpic and entropic factors.

The intramolecular olefin metathesis of an α,ω-diolefin leading to cycloalkenes is known as ring-closing metathesis (RCM) (scheme 3). The driving force for this reaction is the release of highly volatile ethylene.



Scheme 3

11.3 Types of olefin metathesis

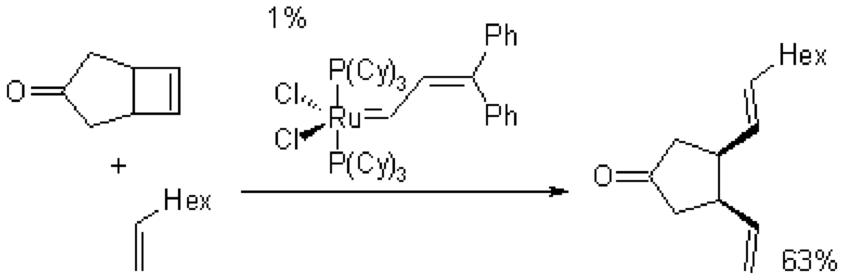
The use of metathesis in chemical synthesis has been directly correlated to improvement in metal-carbene catalysts. The chemists mostly responsible for developing such catalysts are Robert H. Grubbs, Yves Chauvin and Richard R. Schrock who shared a Nobel Prize in chemistry 2005 for the development of the metathesis reaction in organic synthesis. Olefin metathesis can be utilized in the following types of reactions shown below

11.4 Ring-Opening Metathesis Polymerization (ROMP)

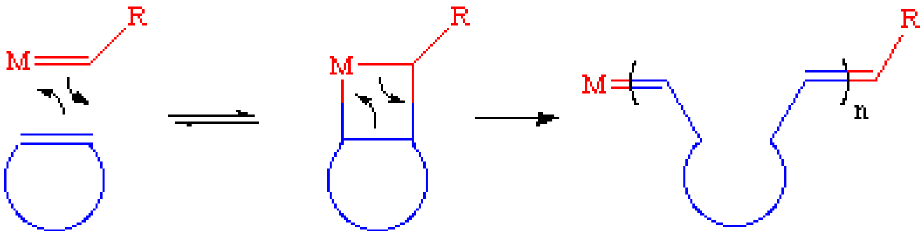
Ring Opening Metathesis Polymerization (ROMP), a term first introduced by chemist Robert Grubbs, is a variant of the olefin metathesis reaction. *The ruthenium carbene-catalyzed ring opening reaction of strained cyclic olefins to produce stereoregular and monodisperse polymers and co-polymers is called Ring Opening Metathesis Polymerization.*

ROMP is thermodynamically favored for strained ring systems, such as 3-, 4-, 8- and larger-membered compounds.When bridging groups are present (bicyclic olefins) the ΔG of polymerization is typically more negative as a result of increased strain energy in the monomer.

Block copolymers can be made by sequential addition of different monomers (a consequence of the "living" nature of the polymerization).

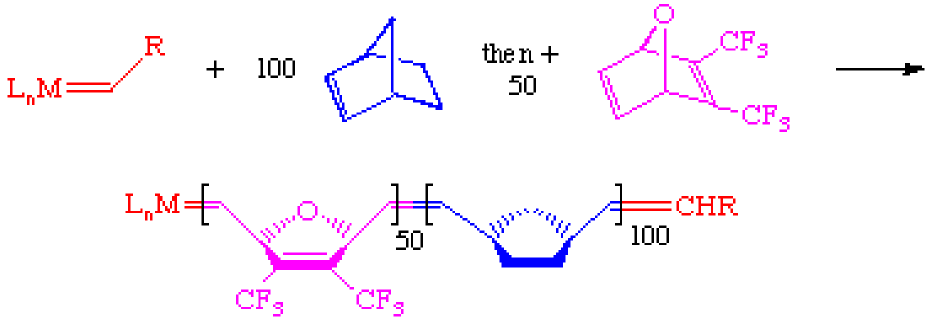


The mechanism of the ROMP reaction involves an alkylidene catalyst and is identical to the mechanism of olefin metathesis with two important modifications. First, as the reaction involves a cyclic olefin, the "new" olefin that is generated remains attached to the catalyst as part of a growing polymer chain as is shown below with a generic strained cyclic olefin



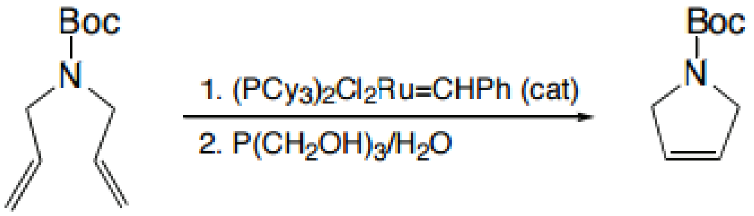
The second difference is that the driving force for the ROMP reaction is the relief of ring strain. Therefore, the second step shown above is essentially irreversible. Olefins such as cyclohexenes or benzene have little or no ring strain and cannot be polymerized because there is no thermodynamic preference for polymer versus monomer. The polymers produced in the ROMP reaction typically have a very narrow range of molecular weights, something that is very difficult to achieve by standard polymerization methods such as free radical polymerization.

An important feature of this mechanism is that ROMP systems are typically living polymerization catalysts. For example, one can polymerize 100 equivalents of norbornene and then add a second monomer after the first one is consumed. ROMP is a superior method for making diblock and triblock co-polymers and permits one to tailor the properties of the resulting material.



11.5 Ring-Closing Metathesis (RCM)

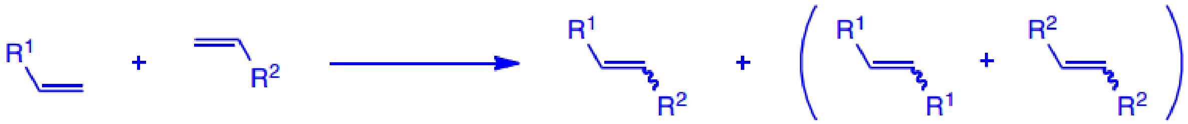
As the name implies, this is the reverse of the ROMP reaction. In order to make it work, the ring being formed cannot have appreciable ring strain. *Intermolecular olefin metathesis of two terminal alkenes, yields the E- or Z cycloalkene by liberating volatile ethylene is called Ring-closing metathesis (RCM).*



As the RCM and ROMP processes involve equilibria, the RCM reaction sometimes involves running the experiment at low dilution so that most of the reactions are intra- rather than intermolecular. The reaction can be driven to the right by the loss of ethylene. The development of well-defined metathesis catalysts that are tolerant of many functional groups yet reactive toward a diverse array of olefinic substrates has led to the rapid acceptance of the RCM reaction as a powerful method for forming carbon-carbon double bonds and for macrocyclizations. Where the thermodynamics of the closure reaction are unfavorable, polymerization of the substrate can occur. This partitioning is sensitive to substrate, catalyst, and reaction conditions.

11.6 Cross Metathesis (CM)

The transalkylidenation of two terminal alkenes under release of ethene, catalyzed by ruthenium carbenoids is called cross metathesis. Statistically, the reaction can lead to three possible pairs of geometric isomers, i.e. E/Z pairs for two homocouplings and the cross-coupling (R-CH=CH-R, R'-CH=CH-R', and R-CH=CH-R') - a total of 6 products.

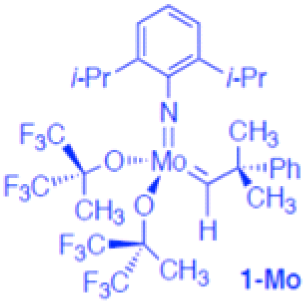


Cross-Metathesis (CM)

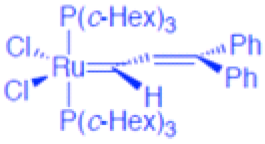
The selectivity of this reaction is currently undergoing further study, but various examples exist in which two alkenes with different reactivity give the cross-coupled product with excellent yields and excellent selectivity.

Self-dimerization reactions of the more valuable alkene may be minimized by the use of an excess of the more readily available alkene.

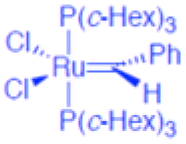
The well-defined catalysts shown below have been used widely for the olefin metathesis reaction. Titanium- and tungsten-based catalysts have also been developed but are less used. Schrock's alkoxy imidomolybdenum complex 1-Mo is highly reactive toward a broad range of substrates; however, this Mo-based catalyst has moderate to poor functional group tolerance, high sensitivity to air, moisture or even to trace impurities present in solvents, and exhibits thermal instability.



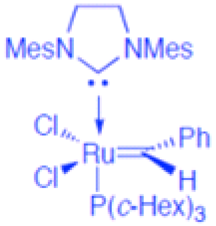
1-Mo



2-Ru



3-Ru
(Grubbs' 1st Generation Catalyst)



4-Ru
(Grubbs' 2nd Generation Catalyst)

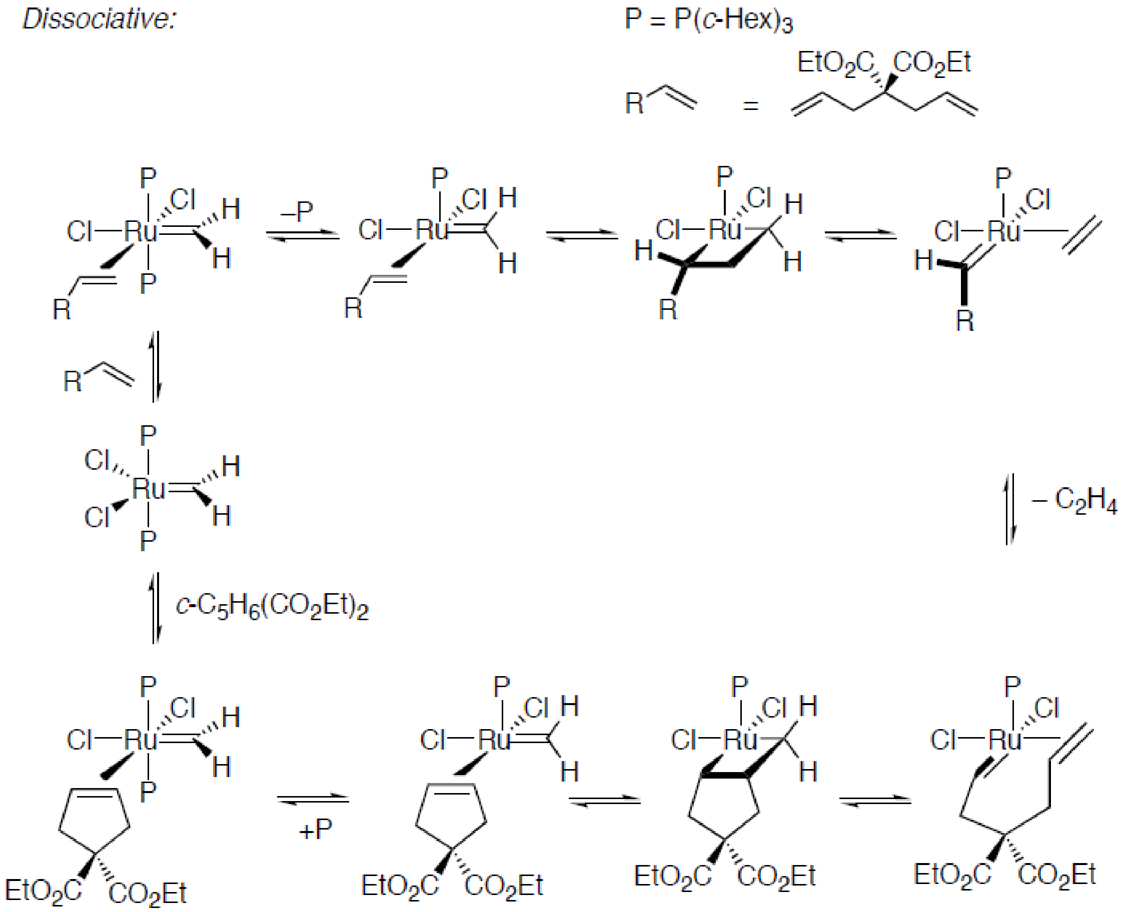
Grubbs' Ru-based catalysts exhibit high reactivity in a variety of ROMP, RCM, and CM processes and show remarkable tolerance toward many different organic functional groups. The electron-rich tricyclohexyl phosphine ligands of the d6 Ru(II) metal center in alkylidenes 2-Ru and 3-Ru leads to increased metathesis activity. The NHC ligand in 4-Ru is a strong -donor and a poor -acceptor and stabilizes a 14 e– Ru intermediate in the catalytic cycle, making this catalyst more effective than 2-Ru or 3-Ru.

The Ru-based catalysts show little sensitivity to air, moisture or minor impurities in solvents. These catalysts can be conveniently stored in the air for several weeks without decomposition. All of the catalysts above are commerically available, but 1-Mo is significantly more expensive.

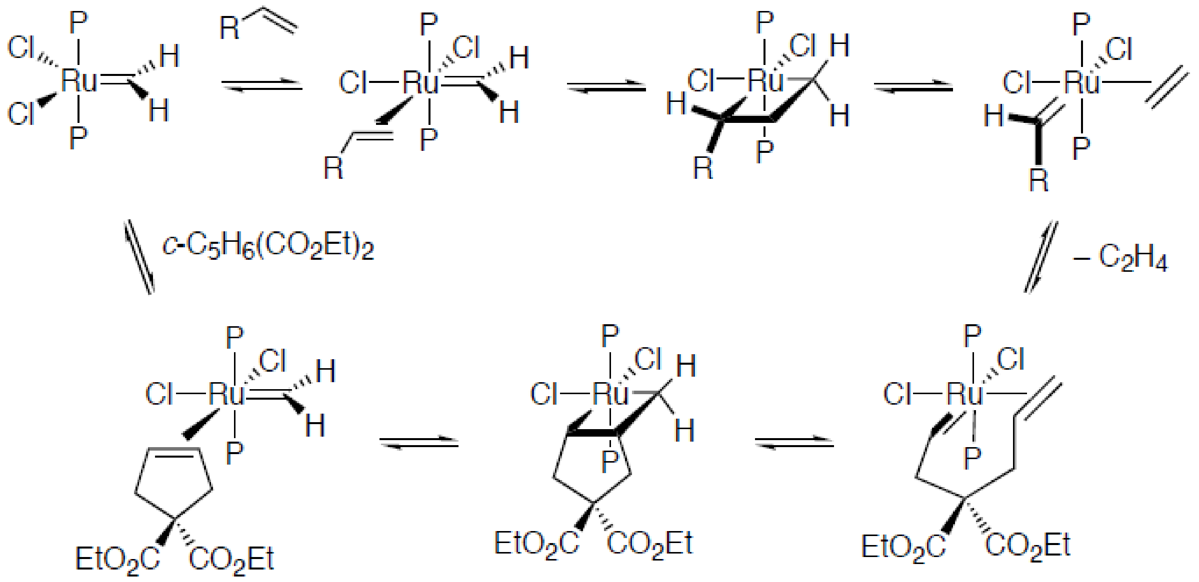
11.7 Mechanism of olefin metathesis

A kinetic study of the RCM of diethyl diallylmalonate using a Ru-methylidene describes two possible mechanisms for olefin metathesis. The "dissociative" mechanism assumes that upon binding of the olefin a phosphine is diplaced from the metal center to form a 16-electron olefin complex, which undergoes metathesis to form the cyclized product, regenerating the catalyst upon recoordination of the phosphine.

The "associative" mechanism assumes that an 18-electron olefin complex is formed which undergoes metathesis to form the cyclized product. Addition of 1 equivalent of phosphine (with respect to catalyst) decreases the rate of the reaction by as much 20 times, supporting the dissociative mechanism. It was concluded in this study that the "dissociative" pathway is the dominant reaction manifold (>95%).



Associative:



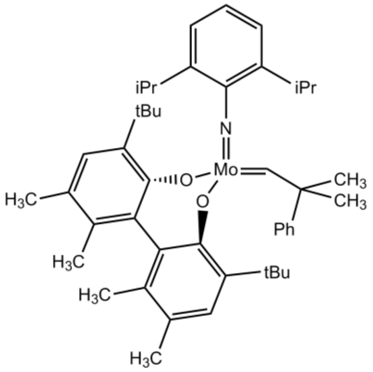
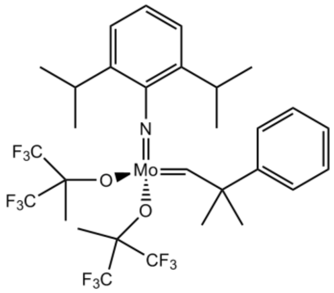
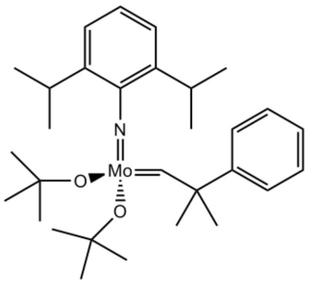
11.8 Catalysis for olefin metathesis

Olefin metathesis reactions are generally catalyzed by metal complexes. Traditional catalysts are prepared by a reaction of the metal halides with alkylation agents. For example WCl_6–EtOH–$EtAlCl_2$. Modern catalysts are well-defined organometallic compounds and are of two main categories. They commonly called as Schrock catalysts and Grubbs' catalysts.

Schrock's Metathesis Catalyst

Schrock catalysts are molybdenum(IV)- and tungsten(IV)-based organometallic compounds.

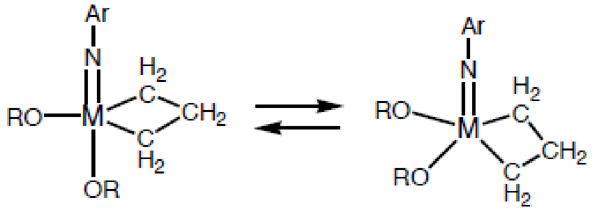
Commercially available, as is synthetic precursor $Mo(CHt\text{-}Bu)(NAr)(OTf)_2(dme)$.

Schrock's catalyst are highly sensitive to moisture therefore they must be handled under Ar or N_2 using dry solvents and substrates. These catalysts are relatively intolerant to protons on heteroatoms like RCOOH, RSH, ROH, etc and some functionalities like RCHO, But they are tolerant to S, P and nitrile functional groups

Structural Features

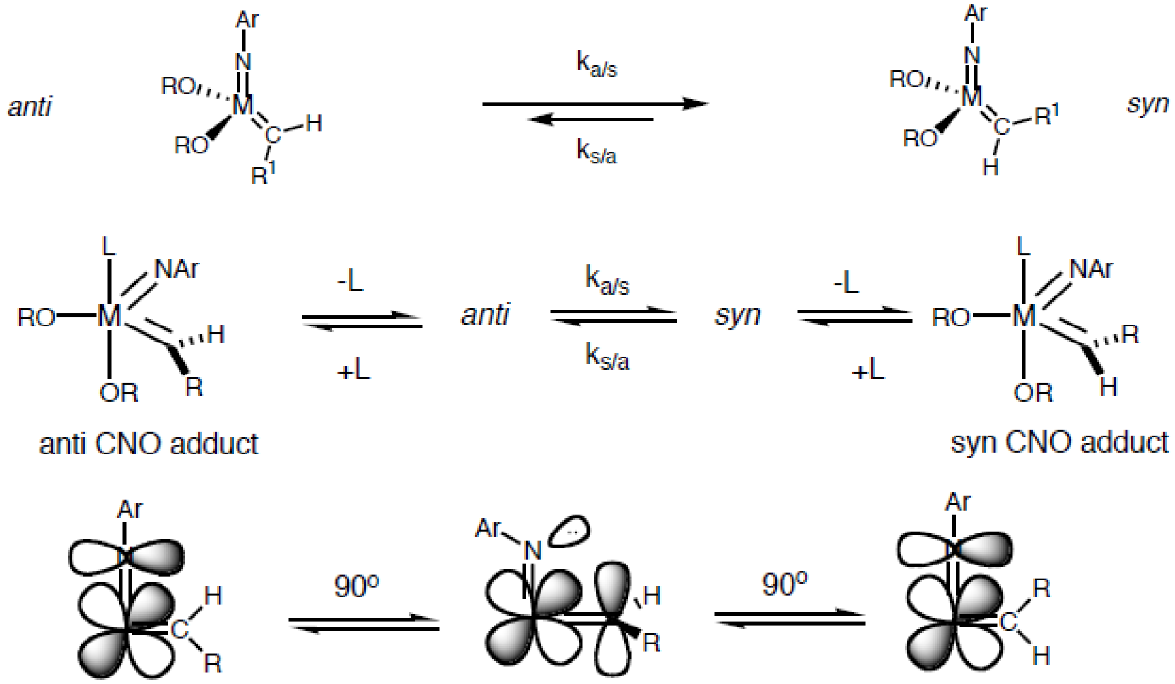
Schrock's catalyst are Electon deficient compound since the central metal Mo(VI) is a 14 electron species. They adopt pseudo-tetrahedral coordination sphere structure.



Trigonal bipyramidal Square planar

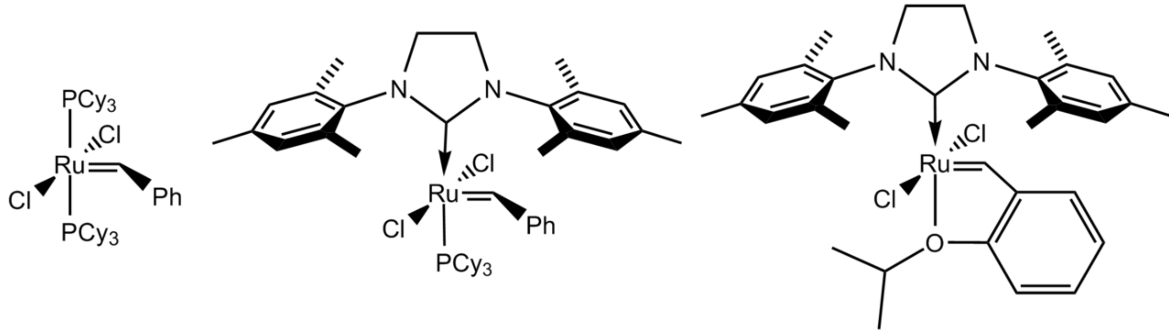
Usually NAr ligand, OR ligands, and initial alkylidene need to be bulky to allow for isolation of the catalyst The Electron withdrawing alkoxides increase electrophilicity of metal center, hence increases the reactivity.

There are two isomeric structures are possible they are syn and anti isomers Rate of interconversion between two rotamers is dependent on metal ligands and substrate. Generally, syn isomer is more stable and anti isomer is more reactive. Electron withdrawing alkoxide substituents and bulky aryl groups decrease $k_{s.a}$



Grubbs' Metathesis Catalyst

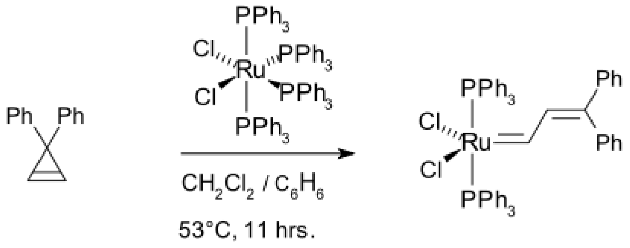
Grubbs' catalysts are ruthenium(II) carbenoid complexes. Grubbs' catalysts are often modified with a chelating isopropoxystyrene ligand to form the related Hoveyda–Grubbs catalyst. They are reasonably stable toward H_2O, O_2, and minor impurities present in the reaction medium therefore they can be easily handled.



Grubb’s catalysts are generally low reactive compare to Molybdenum imido alkylidene catalyst (Schrock catalysts) but they exhibit high functional group tolerance. The catalytic activity increases in the presence of halides and the order of reactivity is I < Br < Cl. This is because the olefin is bound tightest for Cl complex since Cl is smallest. The large halogens disfavor olefin binding due to steric crowding. The catalyst activity also increases in the presence of Phosphine ligands as cone angle and eletron donating ablilty increase. This is because as cone angle increases, dissociation of phosphine more facile for steric reasons and more electon donating ligand labilizes trans ligand and stabilizes vacant orbital in 14 e- intermediate.

First generation Grubbs catalysts

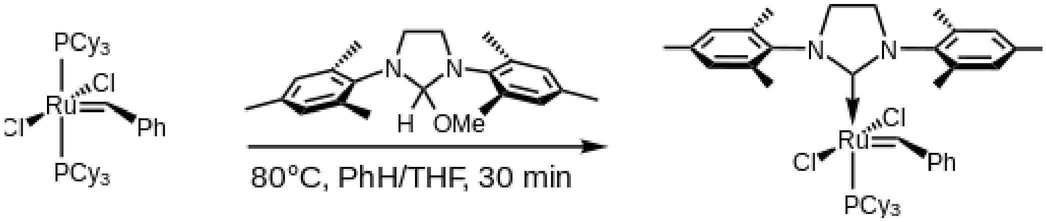
In 1992 the first ruthenium catalyst for olefin metathesis was discovered and tt was prepared from reaction between $RuCl_2(PPh_3)_4$ and diphenylcyclopropene. This ruthenium catalyst is now known as the first generation Grubbs catalyst. It is easily synthesized from $RuCl_2(PPh_3)_3$, phenyldiazomethane, and tricyclohexylphosphine in a one-pot synthesis



These Ruthenium-based complexes have good functional group compatibility but they are high moister sensitivity complexes therefore they need to be handled in anhydrous solvents under inert atmospheric condition.

Second generation Grubbs catalysts

Ruthenium catalysts with N-heterocyclic carbene (NHC) ligands are more reactive than the first generation catalyst, but maintain the high functional group tolerance and air and moisture stability. These are called second generation Grubbs catalyst. The second generation catalyst has the same uses in organic synthesis as the first generation catalyst, but generally with higher activity. This catalyst is stable toward moisture and air, thus is easier to handle in the lab.



In recent development phosphine ligand is replaced with an N-heterocyclic carbene (NHC), which is characteristic of all 2nd generation type catalysts.

11.9 Factors affecting the olefin metathesis

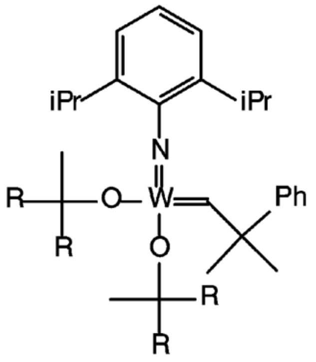
The efficiency of RCM depends on to what extent the competing acyclic diene metathesis polymerization (ADMET) (scheme 3) can be overcome. Concentration of the substrate helps to reduce ADMET to some extent. However, the success of a ring-closure reaction through olefin metathesis is influenced to a great extent by a number of factors. These include

1) Efficiency of the catalyst,
2) Nature of the resulting rings
3) Size of the rings to be formed and
4) functional groups/substituents present in the substrate.

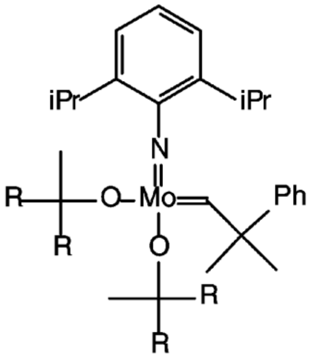
11.10 Influence of catalyst on RCM

The classical olefin metathesis catalysts composed of transition metal salts and their complexes with main group alkylating agents such as WCl_6/Bu_4Sn, MoO_3/SiO_2, $Re_2O_7/N_2O_3Cl_2$) were inefficient for RCM. An efficient RCM catalyst should be a good initiator of metathesis, should react exclusively or at least preferentially with olefins over the other polar groups present in the olefinic substrate and should be stable to air and moisture. The mechanism of olefin metathesis proposed by Herisson and Chauvin (scheme 2) guided the design and development of active catalysts. According to this mechanism, stabilized alkylidine-transition metal complexes should be efficient initiators. In fact, Fu and Grubbs first demonstrated that tungsten and molybdenum alkylidines 1a,b and 2a,b, developed by Schrock for polymerization initiator, can induce RCM for the formation of 5–7 membered rings. However, W and Mo have a strong tendency to react with polar groups such as hydroxyls, aldehydes, carboxylic acids etc in addition to olefins. Thus, W and Mo catalysts are highly oxophilic and have poor functional group tolerance.

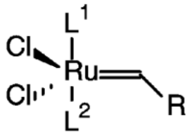
Compared to W and Mo, Ru reacts preferentially with olefins over the polar groups. A systemic investigation by Grubbs and coworkers led to the discovery of ruthenium carbene complexes of the general formula as in structure 3 as active catalysts for RCM.



1, **a**, R = Me
b, R = CF_3



2, **a**, R = Me
b, R = CF_3



3, **a**, $L^1 = L^2 = PPh_3$
$R = CH{:}CPh_2$
b, $L^1 = L^2 = PCy_3$
$R = CH{:}CPh_2$
c, $L^1 = L^2 = PCy_3$
R = Ph

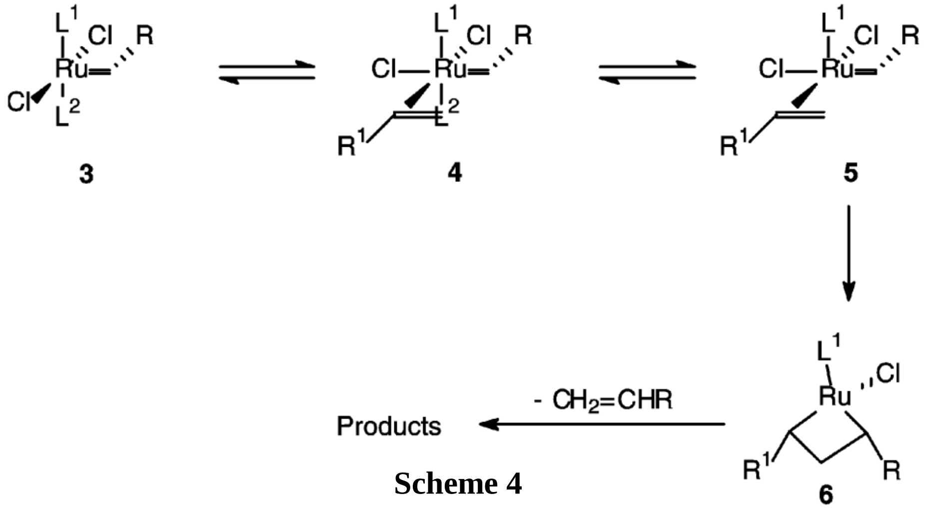
The initiating ability of the catalyst 3 depends on the substituent ‘R’, while the activity of the catalyst 3 is dependent on the type of ligands L^1 and L^2. An understanding of the detail steps involved during metathesis enables to understand how the ligands $L^1$and L^2 influence the reactivity of the catalyst.

Based on the reactivity trend of a number of catalysts, Grubbs proposed a three-step sequence for metathe metathesis (scheme 4):

(i) Olefin coordination to the metal centre to form the species 4,

(ii) Dissociation of one of the ligands (L^2) to form 5, and

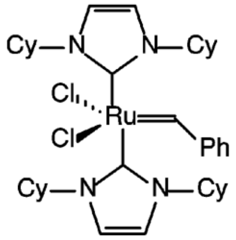
(iii) Formation of the metallocyclobutane 6 followed by cycloreversion to the product.



Scheme 4

For productive metathesis, the dominant pathway is the dissociation of one of the ligands, thus, any variation of the ligands or substituent R that assist ligand dissociation make 3 an active catalyst. A bulkier and more strongly electron-donating ligand helps in dissociation of the other ligand as well as stabilize the reactive intermediate 5. For example, a ligand more basic and bulkier than PPh_3 increases the stability and reactivity of a catalyst. Thus, 3b is a more active RCM catalyst than the catalyst 3a. The catalyst 3c has significantly improved activity over the catalyst 3b due to its high rate of initiation. The bulk of the Ph group probably assists ligand (phosphine) dissociation.

The catalyst 7 having more basic and bulkier N-heterocyclic carbene (NHC) than PCy_3, would be expected to be more active than the catalyst 3c, but however does not show any improved activity. However, catalysts 8 and 9 having NHC and PCy_3 as the ligands (L^1 and L^2 in 3) show enhanced metathesis activity. The more strongly electron-donating NHC ligand enhances the dissociation of the more labile phosphine and more efficiently stabilizes the electron-deficient intermediate 5 (scheme 4). This accounts for the increased reactivity of the catalysts 8 and 9. The reactivities of 8 and 9 are superior to that of the catalyst 3c and are comparable to the reactivity of the Schrock catalyst 2b but with greater functional group tolerance. However, easy accessibility and low cost of the catalyst 3c make it the most popular catalyst and it has been widely used for various synthetic purposes.The following examples illustrate how RCM of diolefins is influenced by these catalysts.



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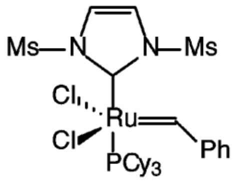

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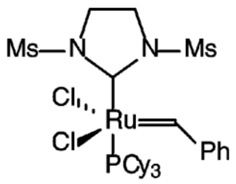

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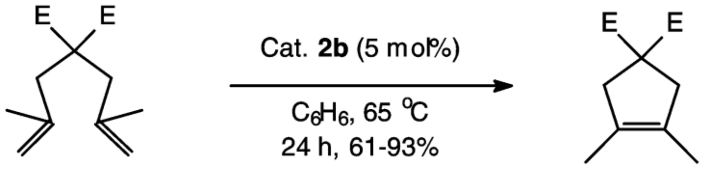
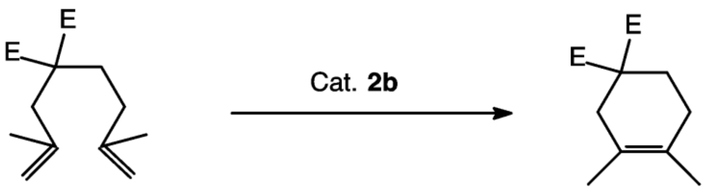
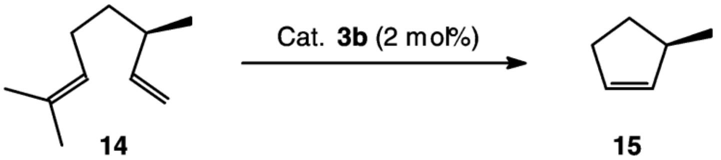


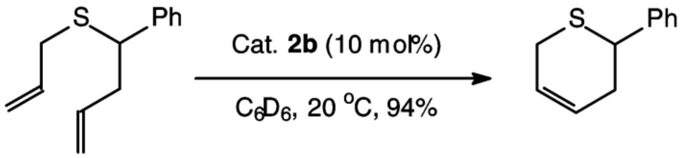
10 **11**



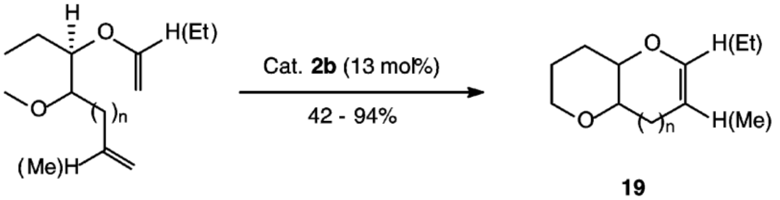
12 **13**



14 **15**



16 **17**



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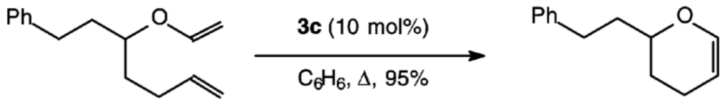
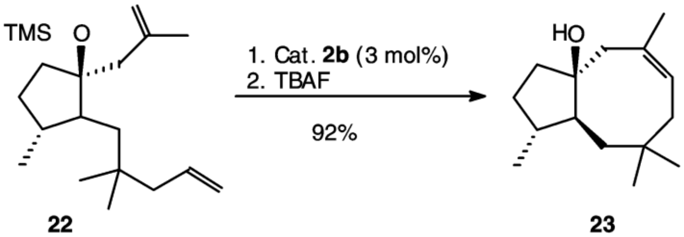
n = 1, 2

18



20 **21**



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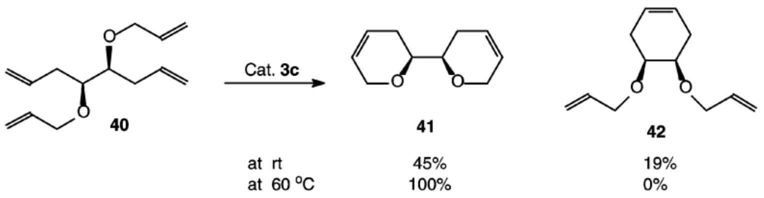
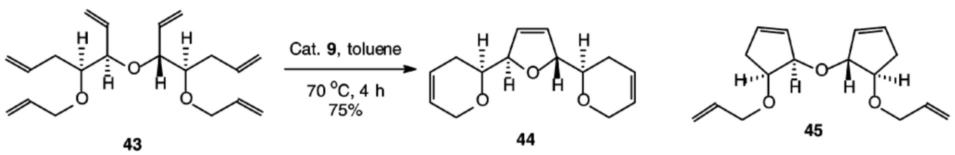
The dienes 10 and 12 undergo ring closure very efficiently using the Mo catalyst 2b to give the tetrasubstituted cyclopentene 11 and cyclohexene derivative 13 in 93% and 61% yields respectively. However, RCM of the dienes 10 and 12 does not proceed at all with Grubbs' catalyst 3c. Similarly, the diene 14 undergoes ring closure7 with 2 mol% of the Mo catalyst 2b to give the cyclopentene 15 quantitatively, while the same cyclization with Ru catalyst 3c proceeds with lower yield 2b. These examples illustrate the efficiency of the Mo catalyst to induce metathesis of substituted olefins.

RCM of the sulphur containing diene 16 proceeds smoothly in the presence of the catalyst 2b but fails in the presence of the Ru carbene 3c. The difference in reactivities of the Mo and Ru carbenes for effecting the cyclisation of 16 has been explained by 'mismatch' of the 'hard' Mo^{vi} centre with 'soft' sulphur or phosphine functionalities. For RCM of dienes with vinyl ether as one of the alkene units, Mo catalyst 2b is required. Thus, dienes 18 undergo smooth ring closure with the Mo carbine 2b to produce the cyclic vinyl ethers 19 in good to excellent yields. On the contrary, the Ru catalyst 3c proved to be totally ineffective for the cyclization of enol ethers. This failure of the Rucatalyst has been attributed to the formation of the inert carbenes from rapid reaction of the vinyl ethers with Ru catalysts. However, Sturino and Wong have demonstrated that vinyl ethers can also be cyclised with Grubbs' catalyst 3c as illustrated by conversion of 20 to 21.

11.11 Nature of the resulting rings (carbocycle or heterocycle)

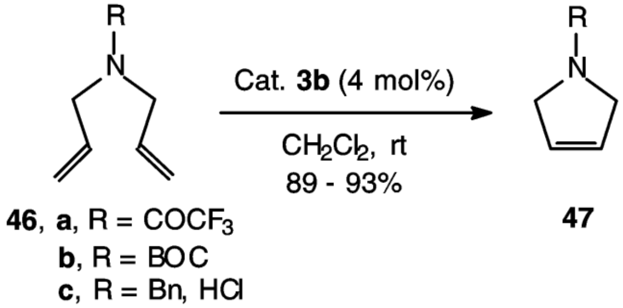
Olefin metathesis has been efficiently employed for the construction of both carbocycles as well as oxygen heterocycles. However, when there is a possibility of the formation of carbocycles as well as oxygen heterocycles of the same size, it is the latter one which is favoured. For example, the tetraene 40 in the presence of Grubbs' catalyst 3c at RT for 1 h produces the bicyclic ether 41 in 45% yield with 19% yield of the carbocycle 42. The same reaction, when carried out at 60°C, forms the bicyclic ether 41 as the only product. Similarly, cyclization of the tetraene 43 with Grubbs' catalyst 9 leads to the exclusive formation of the tricyclic ether 44 without any trace of the carbocycle 45. The formation of nitrogen heterocycles by RCM of dienes containing nitrogen atoms between two alkene units does not proceed due to the basicity and nucleophilicity of the N atoms which deactivate the catalyst through coordination with the metal centre of the catalyst.

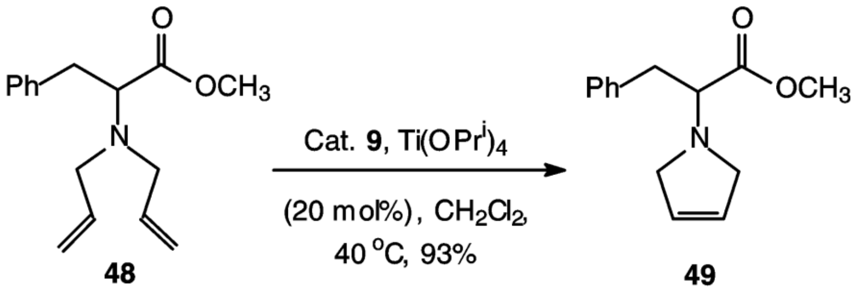




In such cases, the substrates have to be deactivated either by conversion to the amides, carbamates, or sulphonamides or by protonation. Grubbs and coworkers demonstrated that N-trifluoroacetyl diene 46a underwent smooth RCM with Mo catalyst 2b to afford the dihydropyrrole 47a.

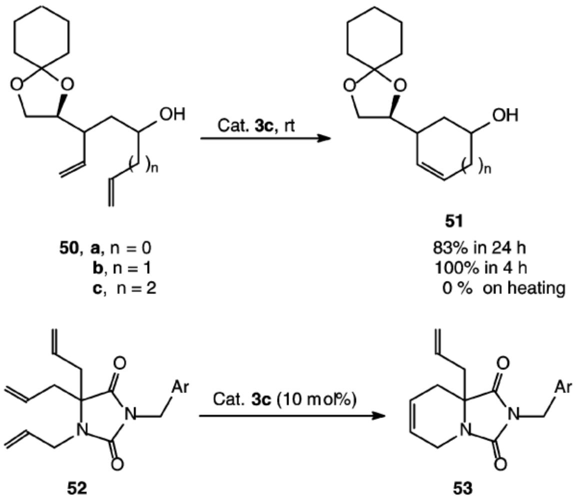
These RCM reactions can also be catalyzed by themRu catalyst 3b. Lewis acids such as $[Ti(OPr)_4]$ facilitate RCM of the diallylamine 48 using the Ru catalyst 9 to afford the pyrrolidine derivative 49.



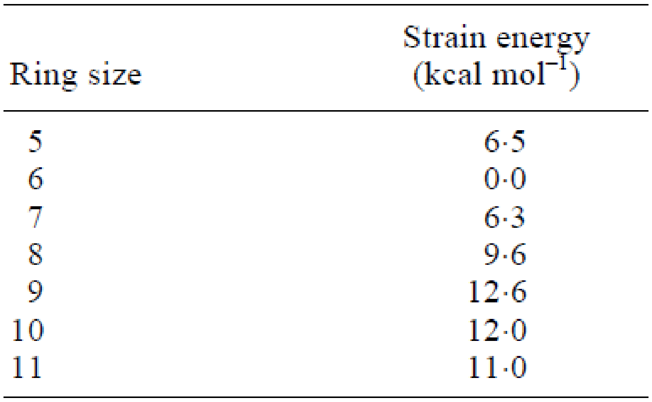


11.12 Size of the ring to be formed

Reactivity in RCM of dienes is influenced to a great extent by the size of the rings to be formed. This is illustrated by the cyclization of the dienes 50a–c. The diene 50a undergoes smooth ring closure in 24h at RT to form the cyclopentenol 51a with Grubbs' catalyst 3c in 83% yield. Under similar conditions, the diene 50b produces the cyclohexenol 51b quantitatively in only 4 h. However, the diene 50c fails to produce the cycloheptenol 51c even on prolonged reaction at RT as well as at elevated temperatures. Thus, as ring size increases it becomes difficult to construct rings through cyclization.



Reactivity in cyclization reaction is influenced by the activation energy in the transition state and the probability of end-to-end encounters (entropy). The activation energy is thought to reflect the strain energy of the ring to be formed and is markedly dependent on ring size, as shown by strain energy data From these data it is clear why the 6- membered ring 50b is easily formed. Although 5-and 7-membered rings have comparable strain energies (higher than 6-membered), it is the entropic factor that prohibits cyclisation of 50c to form the seven membered ring 51c.



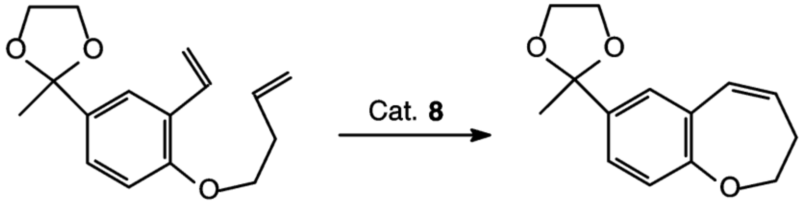
Ring size	Strain energy (kcal mol^{-1})
5	6·5
6	0·0
7	6·3
8	9·6
9	12·6
10	12·0
11	11·0

Formation of medium size rings through RCM requires several features to be installed in the substrate and provide some sort of conformational constraint. This conformationally predisposes the dienes for ring closure. These constraints are achieved either by using a pre-existing ring, i.e. cyclic conformational constraint, or acyclic conformational constraint.

Pre-existing ring as cyclic conformational constraint

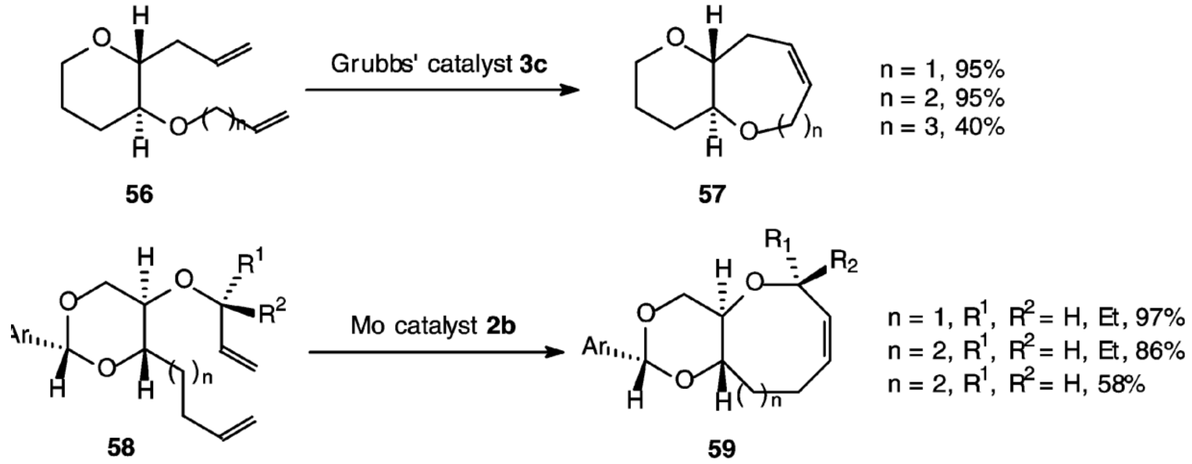
There are several reactions where aromatic rings have been used for cyclic conformational constraint.

For example, RCM of the diene 54 using the catalyst 8 to form the oxepene 55.



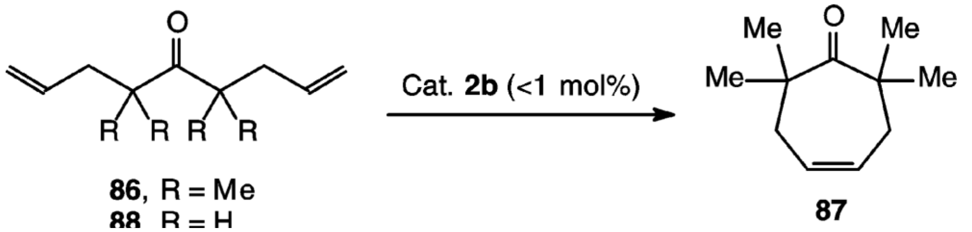
54 **55**

Cyclic ethers also provide very good conformational constraint. For example, the dienes 56 easily cyclise with Grubbs' catalyst 3c to form seven- to nine-membered cyclic ethers 57 in excellent yields. Ring closure of the dienes 58 is achieved with the Mo catalyst 2b to form eight- and nine-membered cyclic ethers 59.



Acyclic conformational constraint

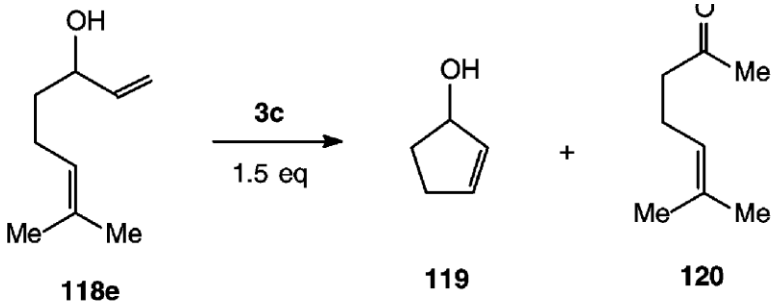
The Thorpe–Ingold effect of the geminal substituents provides conformational constraint to acyclic α,ω-dienes and facilitates RCM. This is nicely demonstrated by smooth ring closure of the diene 86 with the Mo catalyst 2b to form the cycloheptenone 87. In contrast, the diene 88 devoid of geminal substituents fails to produce any cyclised product under identical condition.

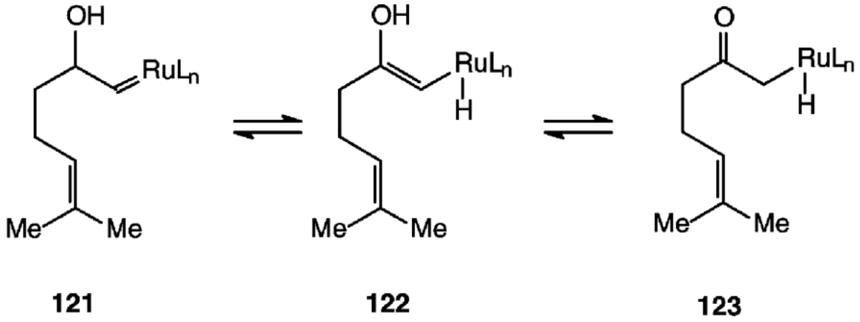


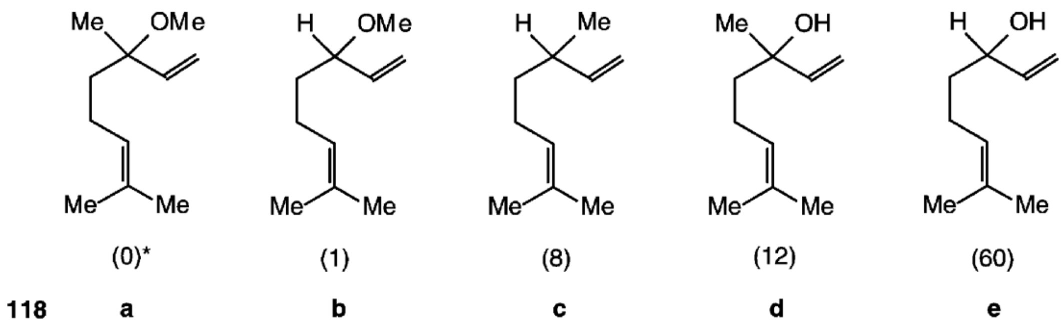
Vicinal stereocentres present on acyclic dienes can lead to conformations where olefinic chains are positioned gauch and help in ring closure.

11.13 Effect of allylic substituents on RCM

Substituent at the allylic position of a substrate greatly influences RCM reactivity. An alkyl substitution at the allylic position retards the reaction of the alkene with metal carbene. Ulman and Grubbs showed that t-butylethylene, containing a fully substituted allylic centre, is inert to reaction with the catalyst3c. In contrast, a hydroxyl group at the allylic position has an accelerating effect on RCM. A systematic investigation by Hoye and Zhao nicely demonstrates the effect of alkyl and hydroxyl substitution on RCM of the dienes 118a–e. One of the alkene units in these substrates is trisubstituted so that metathesis is initiated at the terminal alkene.



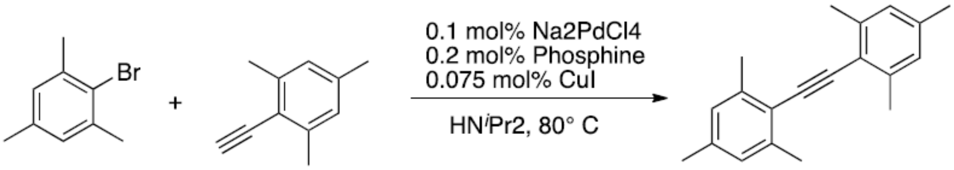




*Number in parentheses shows approximate relative

11.14 Sonogashira Coupling

Kenkichi Sonogashira discovered the Sonogashira Coupling reaction in 1975. The Sonogashira coupling reaction is one of the most widely used methods for the coupling of vinyl or aryl halides with terminal alkynes to form conjugated enynes or aryl alkynes.



There are two catalysts are needed for this reaction: a zerovalent palladium complex and a halide salt of copper(I). Copper(I) salts, such as copper iodide, react with the terminal alkyne and produce a copper(I) acetylide, which acts as an activated species for the coupling reactions. Cu(I) is a co-catalyst in the reaction, and is used to increase the rate of the reaction.

Though the copper co-catalyst is added to the reaction to increase reactivity, the presence of copper can result in the formation of alkyne dimers. This leads to the Glaser coupling reaction, which is an undesired formation of homocoupling products of acetylene derivatives upon oxidation. As a result, when running a Sonogashira reaction with a copper co-catalyst, it is necessary to run the reaction in an inert atmosphere to avoid the unwanted dimerization. Copper-free variations to the Sonogashira reaction have been developed to avoid the formation of the homocoupling products.

11.15 Mechanism

The complete mechanism for the Sonogashira reaction is not completely understood because of the difficulty of isolating and analyzing the organometallic compounds that are present only as intermediates in the reaction.

The mechanism involves the two cycles they are palladium cycle and a copper cycle.

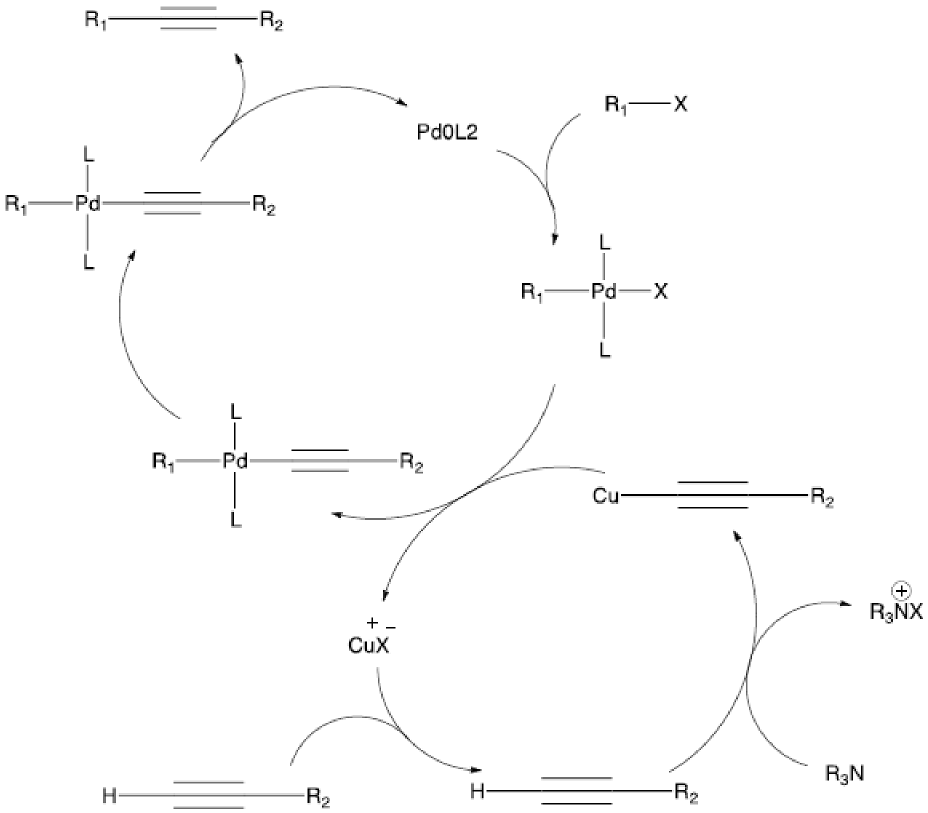
The palladium cycle

This cycle involves following steps

In the first step an inactive palladium [Pd(II)] catalyst is activated by a reduction to the Pd(0) compound. The resulting active palladium catalyst is the 14 electron compound with general formula Pd(0)L_2,

In the second step this compound reacts with the aryl or vinyl halide in an oxidative addition to produce a Pd(II) intermediate. This step is believed to be the rate-limiting step of the reaction.

Palladium(II) intermediate reacts in a transmetallation with the copper acetylide, form a organo copper complex which is produced in the copper cycle, to give palladium acetylide compound by expelling the copper halide. Both organic ligands in palladium acetylide compound are trans oriented and convert to cis isomer by trans-cis isomerisation. In the final step, this cis palladium acetylide compound undergoes reductive elimination to produce the alkyne, with regeneration of the palladium catalyst



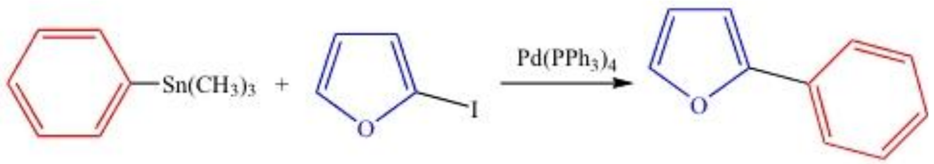
The copper cycle

The organic base present in the reaction media yields a π-alkyne complex which makes the terminal proton on the alkyne more acidic, leading to the formation of the copper acetylide, compound . This compound continues to react with the palladium intermediate, with regeneration of the copper halide. The mechanism is predicted to proceed along the following path.

Recently, a nickel-catalyzed Sonogashira coupling and gold and palladium combined methodology for the Sonogashira coupling also been developed.

11.16 Stille coupling

A coupling reaction between two sp^2 carbons, in which one carbon is bonded to a trialkyltin group, and the other carbon is bonded to a leaving group (chloride, bromide, iodide, or sulfonate) in the p



The Stille Coupling is a versatile C-C bond forming reaction between orano tin compounds (organostannanes) and halides or pseudohalides in presence of palladium [Pd(0) or Pd(II)]. The main drawback of this reaction is the toxicity of the tin compounds used, and their low polarity, which makes them poorly soluble in water. Stannanes are stable, but boronic acids and their derivatives undergo much the same chemistry in what is known as the Suzuki Coupling. Improvements in the Suzuki Coupling may soon lead to the same versatility without the drawbacks of using tin compounds.

In the Stille coupling a Pd° or Pd(II) catalyst is used to couple an electrophile (usually a vinyl or aryl bromide, iodide or triflate) with a vinyl or aryl tin compound. Stille couplings can tolerate a variety of functional groups, including alcohols, ketones, enones, esters, lactones, nitriles, nitro groups and epoxides. In couplings with stereochemically defined alkenyl-X or alkenyl-M species, the olefin stereochemistry is retained.

11.17 Mechanism

The mechanism of the Stille reaction is most extensively studied. Which involves an

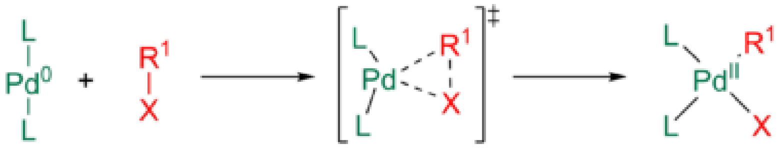
i) Oxidative addition of a halide or pseudohalide to a palladium catalyst

ii) Transmetalation with an organotin reagent and

iii) Reductive elimination to yield the coupled product and regenerated the palladium catalyst

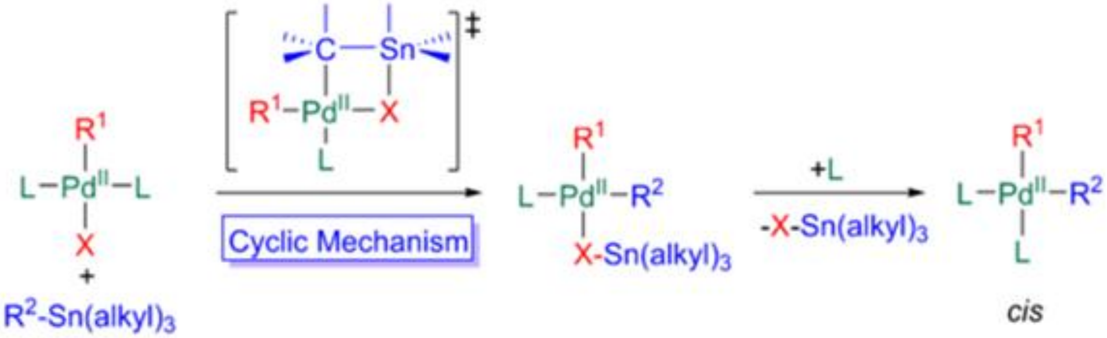
Oxidative Addition

For most sp^2-hybridized organohalides, a concerted three-center oxidative addition to this 14-electron Pd(0) complex is proposed. This process gives the cis-tetravalent 16-electron Pd(II) species. It has been suggested the presence of anionic ligands, such as OAc, accelerate this step by the formation of $[Pd(OAc)(PR_3)_n]^-$, making the palladium species more nucleophillic.



Transmetalation

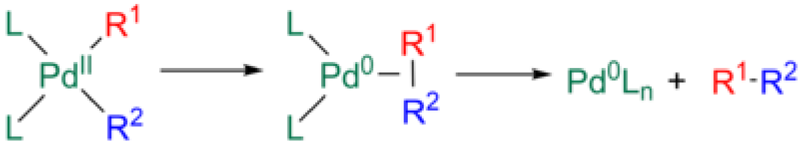
The transmetalation of the trans intermediate from the oxidative addition step is proceed via a variety of mechanisms depending on the substrates and conditions. The most common type of transmetalation for the Stille coupling involves an associative mechanism. In this pathway a tin atom bonded to an allyl, alkenyl, or aryl group in organostannane can coordinate to the palladium via one of double bonds. This produces a fleeting pentavalent, 18-electron species, which can then undergo ligand detachment to form a square planar complex again. This can happens following way the organostannane coordinated to the palladium through the R^2 group, formally transferred to the palladium (the R^2-Sn bond broken), and the X group leave with the tin, completing the transmetalation.



Reductive elimination step

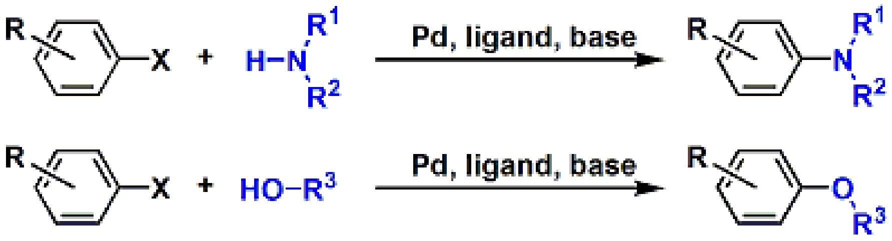
In order make bond between R^1 and R^2 (R^1-R^2) these groups must occupy mutually cis coordination sites on palladium. Any trans-adducts must therefore isomerize to the cis intermediate otherwise the coupling will be frustrated.

First, the 16-electron tetravalent intermediate from the transmetalation step can undergo unassisted reductive elimination from a square planar complex. This reaction occurs in two steps: first, the reductive elimination is followed by coordination of the newly formed sigma bond between R^1 and R^2 to the metal, with ultimate dissociation yielding the coupled product.



11.18 Buchwald reaction

The Buchwald reaction is an organic reaction used to make carbon-nitrogen bonds using organo palladium compound catalyst. This is essentially a cross-coupling reaction of an aryl halide with an amine using palladium as a catalyst in the presence of strong base. The reaction begins by oxidative addition of the aryl halide to the palladium which is followed by coordination of the amine to the palladium. The strong base then abstracts a proton from the amine, forming an amide, which in turn attacks the palladium and kicks out the halide as a leaving group. Reductive elimination then produces the final aryl amine product and regenerates the catalyst.



11.19 Mechanism

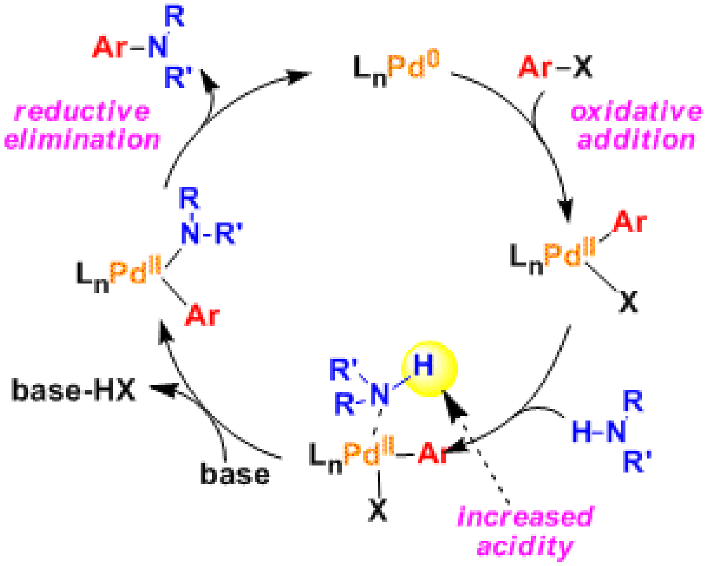
The mechanism of this reaction proceeds through steps similar to other palladium catalyzed C-C coupling reactions. The following steps are involved

i) Oxidative addition of the aryl halide to a Pd(0) species,

ii) Addition of the amine to the oxidative addition complex,

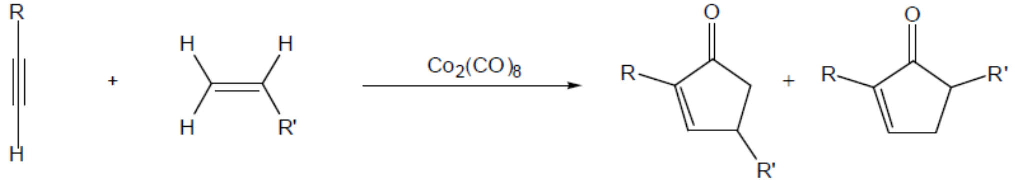
iii) Deprotonation followed by reductive elimination.

An unproductive side reaction can compete with reductive elimination wherein the amide undergoes beta hydride elimination to yield the hydrodehalogenated arene and an imine product. The catalytic cycle proceeds as follows



11.19 Pauson-Khand reaction

The Pauson-Khand reaction is a widely utilized method for making cyclopentenones. The cyclopentenone is formed by cyclization of an alkyne, olefin, and carbon monoxide in the presence of $Co_2(CO)_8$ in a formal [2+2+1] cycloaddition.

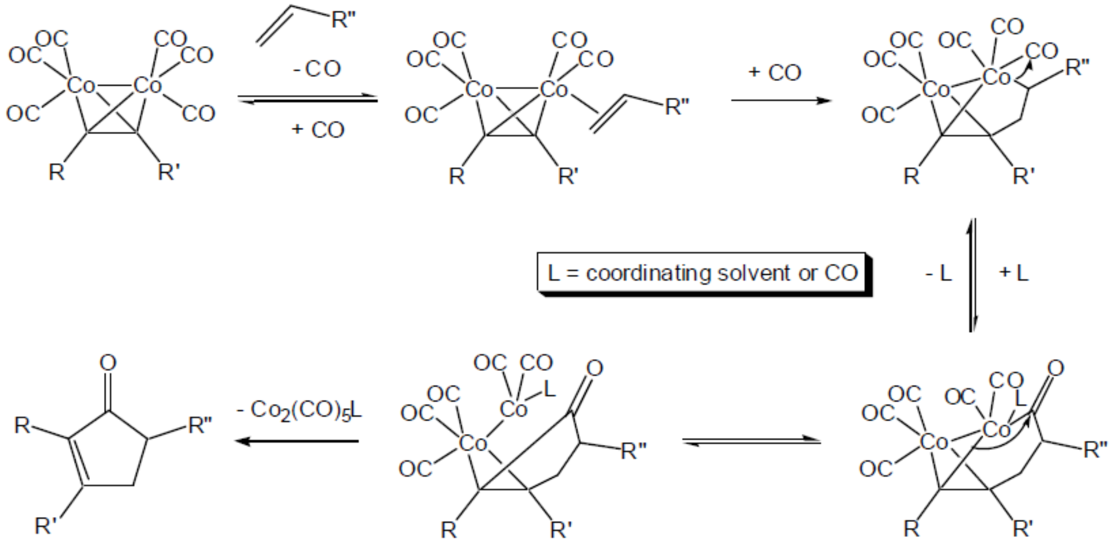


Pauson and Khand first reported this reaction in detail in 1973.2 General reaction conditions involved heating the premade alkyne-$Co_2(CO)_6$ with the alkene to receive moderate yields of cyclopentenones. The Pauson-Khand reaction is tolerant of a wide variety of functionality such as esters, ethers, thioethers, tertiary amines, amides, sulfonamides, nitriles, and alcohols, which makes it an attractive reaction for organic synthesis.

While the Pauson-Khand reaction was shown to tolerate many functional groups, it also had many limitations. The traditional Pauson-Khand reaction involved a stoichiometric amount of $Co_2(CO)_8$. Also, harsh conditions were employed to effect the transformation, and such high temperatures often led to decomposition of substrates and/or products. Regioselectivity was also a problem. While the reaction is usually selective with respect to substituents on the alkyne, the alkene substituents are not selectively incorporated. Strained olefins were necessary for efficient conversion to product, with the exception of ethylene itself. Internal alkynes were less effective than terminal alkynes, and trisubstituted alkenes were often unreactive. The limitations mentioned sometimes resulted in competition with the formation of aromatic compounds from alkyne trimerization

11.19 Mechanism

There is no solid mechanistic data available for the Pauson-Khand reaction. The mechanism has been proposed based is on regio- and stereochemical observations from many examples. The only intermediate that has been isolated is the initial, stable alkyne-$Co_2(CO)_6$ complex. It is assumed that the next step involves dissociation of a CO ligand and coordination of the alkene. The alkene then irreversibly inserts into one of the cobalt-carbon bonds. This step is thought to be rate-determining as well as product-determining. Migratory insertion of a CO ligand bound to cobalt to form the carbonyl moiety and reductive elimination of the $Co(CO)_3$ fragment follows. Loss of the $Co_2(CO)_5L$ fragment liberates the cyclopentenone product.



11.20 Summary of the unit

The synthesis of ruthenium vinylcarbene complexes allowed the development of well-defined, late transition metal, low oxidation state complexes that catalyze olefin metathesis. Ruthenium carbene complexes are significantly easier to make and handle than the Schrock molybdenum complex. In addition to the metathesis of strained cyclic and exocyclic olefins, the remarkable functional group tolerance (alcohols, aldehydes, carboxylic acids) and stability toward air, water, and acid has made this class of compounds particularly. Mechanistically, the major pathway (>95%) was found to involve phosphine dissociation from the metal center, such that a minor associative pathway in which both phosphines remain bound can be considered to operate only at higher phosphine concentrations. The formation of the 14-electron metallacyclobutane intermediate is the rate-determining step.

11.21 Key words

Olefin metathesis; Ring-Opening Metathesis Polymerization (ROMP); Ring-Closing Metathesis (RCM); Cross Metathesis (CM); *Schrock's Metathesis Catalyst*; *Grubbs' Metathesis Catalyst; First generation Grubbs catalysts*; *Second generation Grubbs catalysts*; Sonogashira Coupling; Stille coupling; Buchwald reaction; Pauson-Khand reaction.

11.22 References for further studies

1) Organometallic Chemistry; R. C. Mehrotra; *New Age International*, **2007**.

2) Organometallic Chemistry of the Transition Elements; Florian P. Pruchnik; *Springer Science & Business Media*, **1990**.

3) Inorganic chemistry; 3rd ed. Gary L. Miessler, Donald A. Tarr *Rex Bookstore, Inc.***2004**.

4) Advanced Inorganic Chemistry: Vollume II. Gurdeep Raj; *Krishna Prakashan Media*, **2010**.

11.23 Questions for self understanding

1) What is olefin metathesis?

2) What are the different types of olefin metathesis? Explain with example

3) Write a note on Ring-Opening Metathesis Polymerization (ROMP)

4) Discuss Ring-Closing Metathesis (RCM)

5) Explain Cross Metathesis (CM)

6) Write the mechanism of olefin metathesis

7) What are the Catalysts used for olefin metathesis?

8) Write a brief notes on
    a) Schrock's Metathesis Catalyst
    b) Grubbs' Metathesis Catalyst

9) Discuss the following
    1) First generation Grubbs catalysts
    2) Second generation Grubbs catalysts

10) Discuss the faactors affecting the olefin metathesis

11) Account for influence of catalyst on RCM

12) Discuss nature of the resulting rings in olefin metathesis (carbocycle or heterocycle)

13) Write a note on size of the ring to be formed in olefin metathesis

14) Explain the effect of allylic substituents on RCM

15) What is Sonogashira Coupling? Explain with example and write the mechanism

16) What is Stille coupling? Explain with example and write the mechanism

17) What is Buchwald reaction? Explain with example and write the mechanism

18) What is Pauson-Khand reaction? Explain with example and write the mechanism

UNIT-12

Structure

12.0 Objective of the unit

12.1 Introduction

12.2 Fluxional molecules

12.3 Rates of rearrangements and techniques of study

12.4 Rate Process and NMR Spectra

12.5 Examples of nonrigid molecules in different coordination geometries

a) Four-coordinate system

b) Trigonal-Bipyramidal Molecules

c) Systems with Coordination Number 6 or Higher

12.6 Classification of fluxional organometallic compounds

12.7 Compounds with Acyclic Alkenes

12.8 Compounds with σ-bonded cyclic alkenes

12.9 Compounds with π-Bonded Cylic Alkenes

12.10 Rotational of Lignds on Metals

12.11 Compounds Involving Ligand Scrambling on Metals

12.12 Summary of the unit

12.13 Key words

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12.15 Questions for self understanding

12.0 Objective of the unit

After studying this unit you are able to

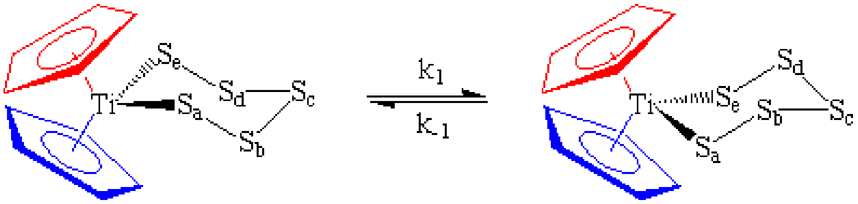
- Explain the Fluxional molecules
- Predict the Rates of rearrangements and techniques of study
- Give the examples of nonrigid molecules in different coordination geometries
- Write the classification of fluxional organometallic compounds
- Identify the compounds with Acyclic Alkenes
- Identify the compounds with σ-bonded cyclic alkenes
- Identify the compounds with π-Bonded Cylic Alkenes

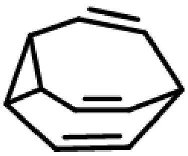
12.1 Introduction

In the earlier chapters the structures of a number of organometallic compounds have been described. In most of the cases these structures are unique and well defined. The atom of molecules is of course continuously involved in approximately harmonic vibrations about their equilibrium position, but in other respects the structure may be considered rigid. As stated in the last-chapter also alkene complexes of transition metals represented a special class of compounds in which the molecules from one type of configuration into another, such molecules have therefore more than one thermally accessible structures which under suitable conditions are interconvertible from one to another fairly rapidly. This phenomenon may be termed as ‘fluxional behaviour’

12.2 Fluxional molecules

Molecules that exhibit rapid intramolecular rearrangements among their component atoms are called Fluxional molecules. As in structural isomerism and tautomerism, fluxional compounds maintain the same number of component atoms. At equilibrium, fluxional molecules may manifest many different isomers and fluctuate rapidly among them for example, bullvalene, which has over 1,200,000 equivalent structures.





Fluxional molecules are generally of two types.

(a) In some cases the non-equivalent of two or more structures results in existence of molecules with different instantaneous identities. Such a process of interconversion is called “tautomerism” and has been known in case of organic molecules. For example

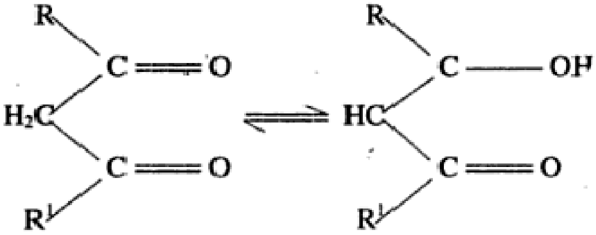


Figure 1: Tautomerism of β-diketones in keto and enol forms

(b)In other cases the two or more configurations are equivalent. Such molecules are called fluxional. An alternate terms “stereochemical non-rigidity’ has suggested for the latter type of ‘fluxional molecules’.

The term ‘stereochemical non-rigidity’ be reversed as a general term for molecules of both the above types i.e tautomeric and fluxional which undergo rapid reversible intramolecular rearrangement.

The first observation of fluxional behavior of organometalllic molecules have been made in 1956 by Piper and Wilkinson in the proton NMR spectra. Only a singlet for Hg(η^1-C_5H_5)$_2$; two singlets for the two cyclopentadienyl ligands at the room temperature in Fe(η^1-C_5H_5) $(CO)_2$ (η^2-C_5H_5) and a singlet for all five ring protons in Cu(η^1-C_5H_5)P(C_2H_5)$_3$:

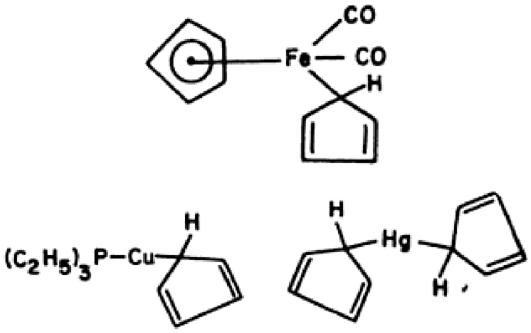


Figure 2: examples of fluxional molecules

These workers explained the appearance of single resonance for all protons in presumably σ-bonded cyclopentadinyl rings in all these compounds to be due to a rapid shifting of metal-carbon bond among the five possible positions.

The next observation was the single ^{13}C peak in the NMR spectrum of $Fe(CO)_5$ which according to the two plausible structure trigonal bipyramid (tbp) and square pyramid(sp) was expected to give two signals in the ratios of 2/3 or ¼ respectively. The observation about the appearance of only single peak wave confirmed by Nyholm and coworkers who believed in the ‘sp’ structure contrary to the ‘tbp’ structure assumed by Cotton and coworkers. Incidentally the structure in the solid state has been established by X-ray crystallography to be the ‘tbp’ type.

The next significance development in the field was the synthesis of cyclooctatetraene complex of iron carbonyl. $Fe(CO)_3$ (η^4-C_8H_8) which again gave only a single line in the PMR spectrum. Dickens and Lipscomb showed that the structure in the crystal involved coordination of two adjacent double bond as had been shown in the case of the corresponding well-known compounds, (1,3-butadieno)$Fe(CO)_3$ to account for the single proton resonance.

Lipscomb and Dikens suggested a dynamical effect amounting to permutation of the carbon atoms of the ring relative to the $Fe(CO)_3$ groups. However as Cotton remarked later that it was doubtful if anyone had correlated this observation with that if Piper and Wilkinson for molecules shown in figure 2.

The concept of fluxional behavior has thus aroused considerable interest in organometallic molecules. However before discussing some of these in greater details it may be appropriate to present some general features of the rates and types rearrangement in the simple fluxional present ion different coordination states and geometries.

12.3 Rates of rearrangements and techniques of study

Out of the difference spectroscopic studies, the NMR technique has proved to be maximum utility in the study of fluxional behavior. For number of system the speed of rearrangements is fast enough at the ambient temperature for the NMR techniques not be able to detect the same but at lower temperatures the rearrangements become slow enough to be detected by NMR spectroscopy.

The choice of a technique suitable for the study of a fluxional system would obviously depend on the rate of rearrangement in a specific case. Form this point of view the spectroscopic techniques could be divided into two broad groups.

(a) In some fast techniques like electronic and vibrational spectroscopy and gas phase electron diffraction the act of observing the molecule is completed in $< 10^{-11}$ sec. process of rearrangement are generally not fast enough to influence these observations. Thus by these techniques

(i) no fluxional behaviour would be expected to be observed if the different configurations are equivalent, and

(ii) for tautomeric or isomeric molecules, both forms will register their presence in the spectrum but to indicated of the interconversations could be possible.

(b) The rearrangement involved in stereochemically non-rigid behaviour is rate processes with activation energies of different magnitudes. When these activation energies are in the range of 25-100 KJ mol^{-1}, the rate of rearrangements can be brought generally between temperatures of $+150^0$ to -150^0C into a range in which the signals due to different fluxional species can be detected separately by NMR technique. Thus by proper choice of temperature, many such rearrangement can be controlled so that they are slow enough ay lower temperature to allow signals due to different fluxional species appearing distinctly and rapid enough at higher temperatures for the signals from the difference configurations or environments to be averaged into a single line at a mean position.

Normally studies of fluxional molecules are carried out with the following two main objectives:

(1) Establishing the instantaneous structure of the molecules

(2) To study the pathway of rearrangement

These targets can be conveniently achieved by NMR line shape analysis and this technique will therefore be discussed in some detail.

12.4 Rate Process and NMR Spectra

If a nucleus is exchanging between two molecular configurations A and B then we have equilibrium.

$$A \Leftrightarrow B$$
$$n_A \quad n_B$$

Where n_A n_B are the mole fractions of A and B. Equilibrium of the type can be generally characterized by two parameters.

(1) The equilibrium position is determined by the free energy of process (ΔG^0) i.e

$$n_A / n_B = \exp(-\Delta G / RT)$$
$$and\, n_A + n_B = 1$$

(2) The free energy of activation (ΔG^0) determines the rate of interconersion i.e rate of reaction (k) for the conversion A→B is given by

$$k = \frac{RT}{Nh}\exp\left(-\Delta G^0 / RT\right)$$

Suppose a nucleus in the molecules in the states A and B exhibits chemical shift δ_A and δ_B respectively with J_A and J_B coupling in Hz. There may be three types of situations which should be considered in this connection.

(a) Slow exchange: when the rate if interconversion of A and B is slow two separate signals representing two non-equivalent sites are observable at V_A and V_B with coupling J_A and J_B

(b) Faster exchange: due to rapid nucleus migration from one site (A) to another (B) the NMR spectrum exhibits one signal in which the chemical shifts and coupling would be the weighted average of the values in A and B and can be represented by

$$V_{av} = n_A v_A + n_B v_B$$
$$J_{av} = n_A j_A + n_B j_B$$

(c) Intermediate rates of exchange. In this case broad signals are observed it may be noted that there are certain other factors which could cause broadening of the NMR signals such as the presence of quadrupolar nuclei and paramagnetic moieties and poor sampling. Besides these easily recognizable features. The presence of broad signals therefore is an indication of an intermediate rate process.

Consider the simplest $Ti(\eta^1\text{-}C_5H_5)_2(\eta^5\text{-}C_5H_5)_2$ which gives rise in its NMR spectrum near the lower temperature limit two equal intensity signals which collapse on raising the temperature (to -36^o) of recording the spectrum into one signal with no coupling present. The temperature at which the two separate signals just merge into one is called the 'coalescence temperature' (Tc). At this temperature true the rate 'k' for exchange between two uncoupled equally populated sites(A and B) is given be the equation.

$$k = \frac{\pi\left(v_A - v_B\right)}{\sqrt{2}}$$

Where $v_A - v_B$ is the separation (in Hz) of the two signal in the absence of exchange

Taking the logarithm of both sides in the equation $k = \frac{RT}{Nh} \exp\left(-\Delta G^0 / RT\right)$ rearranging gives

$$-\Delta G^{\#} = RT \log \frac{RT\sqrt{2}}{Nh\pi} - RT \log K$$

Substituting $k = \frac{\pi \Delta v}{\sqrt{2}}$ and collecting the constant terms gives

$$\Delta G^{\#} = \log \left\{ \frac{R\sqrt{2}}{Nh\pi} + \log \frac{T}{\Delta v} \right\}$$

Finally converting to $\log_{10}$ and substituting values for the constant terms gives the expression

$$\Delta G_T^{\#} = 4.57\,T \left(9.97 + \log_{10} \frac{T}{\Delta v} \right)$$

12.5 Examples of nonrigid molecules in different coordination geometries

Although most of the coordination polyhedral are essential rigid molecules, more and more examples of nonrigidity specially fluxionality in such polyhedra are coming to light. In act with 5 and 7 as well as higher coordination states non-rigidity appears to be quite a common feature.

a) Four-coordinate system

A common feature of fluxional behaviour in such system is the inversion of pyramidal molecules represented by the following figure 3

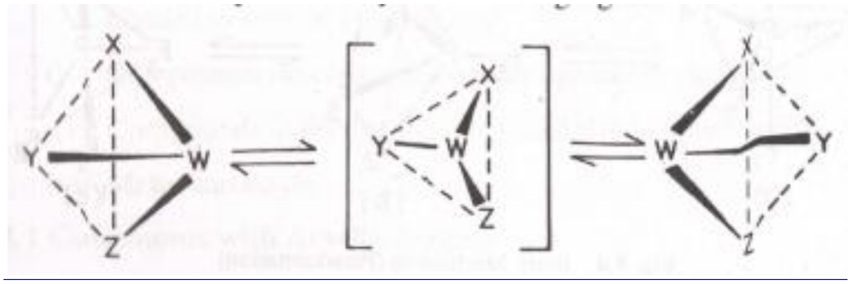


Figure 3: inversion of a pyramidal molecule

The activation energy is quite low in the range of 24-30kj mol^{-1} for ammonia and other noncyclic amines NR_3 resulting in too high a rate of inversion (e.g 2.4 x 10^{10-} sec^{-1} for NH_3) for detecting by n.m.r technique. With phosphines, arines and other species like R_3S^+ and R_2SO the activation energies are higher than 100kj mol^{-1} and inversion are slow enough to allow separation of enantiomers in case of molecules such as $RR'R''P$, $RR'R''As$ and $RR'SO$

Amongst four-coordinate transition metal complexes planar-tetrahedral fluxional changes are quite common e.g

$$\underset{planar}{Ni(R_3P)_2X_2} \xrightarrow{45\,kj\,mol^{-1}} \underset{Tetrahedral}{Ni(R_3P)_2X_2}$$

b) Trigonal-Bipyramidal Molecules

It was in such systems e.g PF_5 and $Fe(CO)_5$ that fluxional behaviour was first detected. In ^{19}F and ^{13}C n.m.r spectra respectively of the above two molecules, only one resonance peak was observed instead of two in the ratio of 3:2

From theoretical consideration it can be concluded that when two nuclei the resonance frequencies o which differ by $(v_1 - v_2) = \Delta v/\sec$ change site at a frequency higher than $(v_1 - v_2)\sec$ then only one resonance peak would be observed at the mean $(v_1 - v_2)2$ position of the two frequencies characteristic of two types of sites between which interchange is occurring In both PF_5 and $Fe(CO)_5$ the dissociative or bimolecular mechanism appears to be ruled out in view of the persistence of ^{31}P-^{19}F and ^{57}Fe-^{13}C coupling although the probability if 1- for -1 exchange in which one equatorial and one axial ligands are involved in each step cannot be ruled out the available experimental evidence appears to favour a 2- for -2 process in which axial ligands exchange simultaneously with two equatorial ones. The most probable mechanism for this type of exchange was suggested by Berry in 1960 as follows.

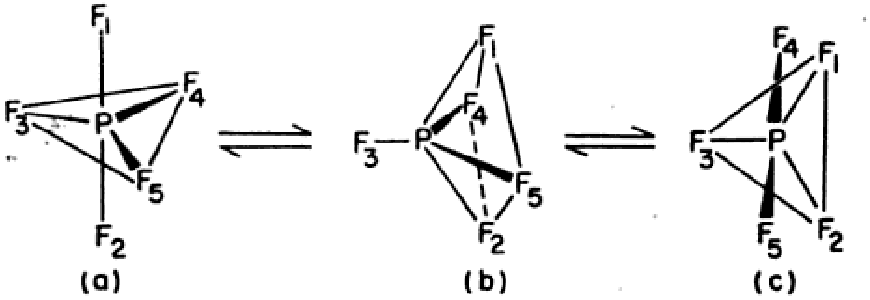


Figure 4: Berry Mechanism (Pseudo rotation)

The exchange process involves change from tbp model to sp intermediate by simultaneous cosign of F^1PF^2 angle form 180^0 and opening of the F^4PF^5 angle from 120^o so that both attain the midway value giving rise to the square set of atoms F_1,F_2,F_3,F_5 all equivalent to one another, the sp configuration (b) could return to the original tbp configutaion (a) or go a step further to attain the new tbp configuration (c) in which the molecules have effectively rotated round the F_3P axis through 90^0. In view of this apparent rotation, berry mechanism is termed ‘pseudirotation’

The first unambiguous evidence for a rapid intramolecular rearrangement in a d^8 pentacoordinate transition metal complex was reported by Udovich and Clark in 1969. The variable low-temperature ^{19}F NMR spectrum of the compound $F_3CCo(CO)_3PF_3$ indicated two equilibrating isomers. Which exchange ligands between axial and equatorial sites.

c) Systems with Coordination Number 6 or Higher

The octahedral configuration is rather rigid and fluxional or tautomeric rearrangement generally does not occur in these except through metal ligand rapture. Amongst the few instances in which fluxional changes have been noticed can be cited: iorn and ruthenium complexes with the composition $MH_2(PR_3)_4$ where M=Fe or Ru. The cis and trans isomers of the former complex have separate well-resolved signals at -50^0 but with increasing temperature these broaden and collapse until at 60^0 C, a sharp line is observed indicating rapid exchange between the two isomeric forms.

For higher coordination states, fluxionality appears to be a normal feature e.g ReF_7, IF_7, $Re\,H_9^{-2}$: ReH_8PR_3 and $ReH_7(PR_3)_2$ all appears to be fluxional molecules with interchange process which have been studied by n.m.r spectroscopic technique.

12.6 Classification of fluxional organometallic compounds

Fluxional organimetallic molecules, which have been studied so for can be divided into the following six major classes.

(1) Compounds with acyclic alkenes.
(2) Compounds with σ-bonded cyclic alkenes.
(3) Compounds with one or more cyclopolyenes π-bonded or σ and π bonded to several metal atoms.
(4) Compounds involving rotation of ligands on metals.
(5) Compounds involving ligands scrambling on metals and
(6) Metal carbonyls.

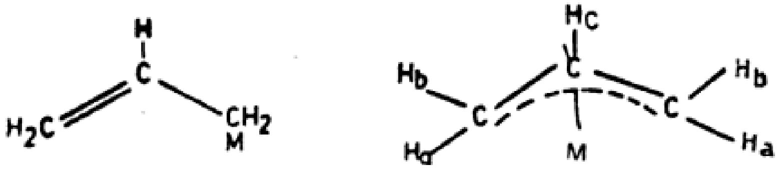
12.7 Compounds with Acyclic Alkenes

The η^3- allyl or π-ally; group is an ubiquitous ligand. A large number of homoeptic as well as heteroleptic π-allyl complexes of both transition and non-transition metals such as

$Pt(\eta^3\text{–}C_3H_5)(\eta^5\text{–}C_5H_5)$; $Co(CO)_3(\eta^3\text{–}C_3H_5)$; $Mn(CO)_4(\eta^3\text{–}C_3H_5)$;
$Zr(\eta^3\text{–}C_3H_5)_4$; $Cr(\eta^3\text{–}C_3H_5)_3$; $Ni(\eta^3\text{–}C_3H_5)_2$;
$Mo(CO)(\eta^3\text{–}CH_2C_6H_5)(\eta^5\text{–}C_5H_5)$; $MgBr(\eta^3\text{–}C_3H_5)$; and

$Zn(\eta^3\text{-}C_3H_5)_2$ are known. In these complexes the instantaneous structure may be represented either by localized σ-bonding or delocalized π-bonding.

In the σ-complex the two hydrogen atoms on α and γ C atoms would be magnetically equivalent to each other. However for η^3-allyl complexes



(a: σ-bonding) (b: π-bonding)

Figure 5: σ and π bonded complexes

Which are rigid on the ^1H n.m.r time-scale the syn and anti hydrogens (H_b and H_a) both exhibit a doublet due to the coupling with the central hydrogen (H_c) which shows a multiplet. Typical NMR parameters observed are H_c δ 6.5-4; H_b δ5-2.5; H_a δ 3-1; J_{bc} -7Hz ; J_{ac} -11 Hz and J_{ab} –Ohz

The π-allyl group often behaves as an electrons-rich moiety but in some of these reactions there appears to be prior dissociation of one terminus to form an intermediate σ-allyl moiety. This kind of system is often reversible and fairly facile leading to fluxional rearrangement on ^1H n.mr timescale.

In the σ-allyl system there is 'free rotation' about the carbon-carbon single bond. So that facile η^3 to η^1 rearrangement provides a mechanism for exchanging the syn and anti groups. It may be noted that the transformation η^3 to η^1 allyl creates a vacant coordination site on the metal as shows in the figure rearrangement of π to σ from undoubtedly accounts for the wide range of reactivities shown by metal allyl complexes.

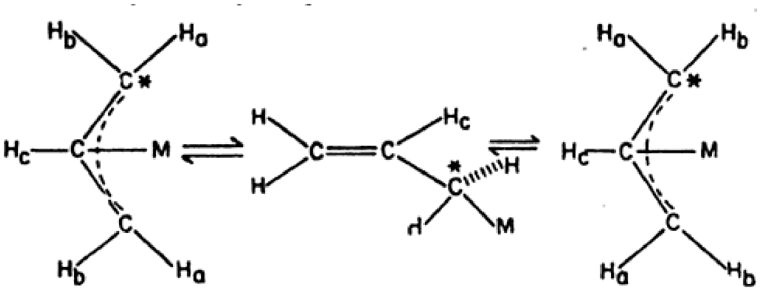


Figure 6: Fluxionality in π-allyl metal complexes.

The complex $Mn(CO)_4$ (η^3-C_3H_5) can exhibit a rigid ^1H n.m.r spectrum such as that shown in figure 7.

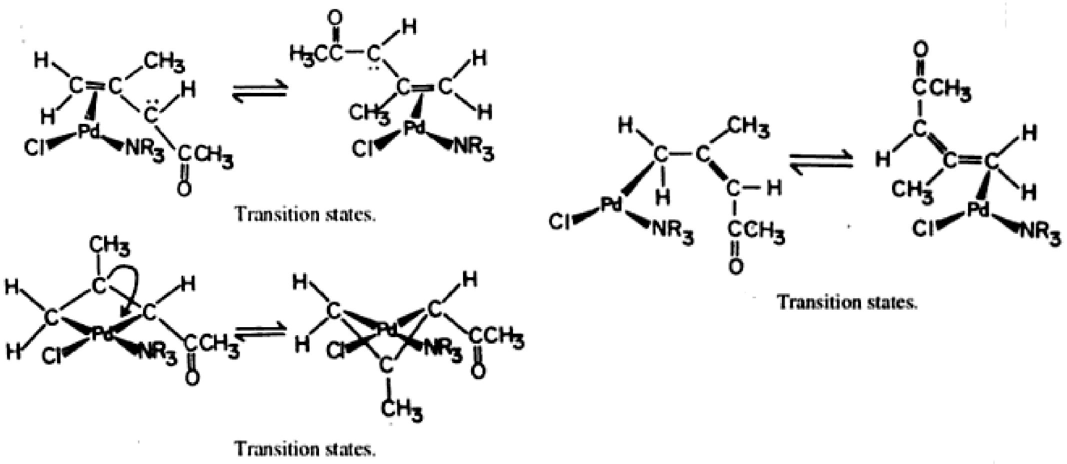
The spectrum shown is of $AA^{'}BB^{'}X$ type where in the case of the η^3-allyl-metal complex, X is the proton on the central carbon atom A and $A^{'}$ are protons and are located anti X and B and $B^{'}$ are protons again quite difference form X but similar to A and $A^{'}$ and located syn to X at elevated temperature or in the presence of a base however this spectrum collapses to a dynamic A_4X spectrum the chief feature of which is the change of doublets for the A and B protons to a single doublet presumably owing to a rapid intermolecular rearrangement that causes $A/A^{'}$(anti) $B/B^{'}$ (syn) protons to have the same chemical shift.

The mechanism of η^3-allyl rearrangement has been extensively examined and a number of pathway for the scrambling of syn and anti protons have been propsed.

Figure 7: ^1H NMR spectrum of (η^3-allyl) tetracarbonylmanganese

For example three of the transition states of intermediates that can lead to syn/anti proton equilibrium in the complex $PdCl(NR_3)(\eta^3$-$CH_2CCH_3CH_2.C(O)\ CH_3)$ are illustrated in figure 8.

Out of the these three schemes the last mechanism appears to be the best to account for proton equilibration in the compound mentioned above and in most other examples which involve a change of a static ^{1}H n.m.r spectrum for a η^3-allyl complexes to a dynamic spectrum.


Transition states.

Transition states.

Transition states.

Figure 8: Transition states

12.8 Compounds with σ-bonded cyclic alkenes

Few examples of this class of compounds are $Fe(\eta^1\text{-}C_5H_5)(CO)_2(\eta^5\text{-}C_5H_5)$; $Cu((\eta^1\text{-}C_5H_5)(PEt_3)$;$Si((\eta^1\text{-}C_5H_5)Me_3$; $Ge(\eta^1\text{-}C_5H_5)_2\ Me_2$, $Sn(\eta^1\text{-}C_5H_5)_4$ $Cr(\eta^1\text{-}C_5H_5)(NO)_2(\eta^5\text{-}C_5H_5)$; $Ti(\eta^1\text{-}C_5H_5)_2\ (\eta^5\text{-}C_5H_5)_2$ $Re(\eta^1\text{-}C_5H_7)(CO)_5$. The compounds Fe $(\eta^1\text{-}C_5H_5)(CO)_2(\eta^5\text{-}C_5H_5)$ represents the one of the first examples of fluxional organometallic molecules. The observation of two singles in the ^{1}H n.m.r spectrum was considered to be highly unusual because one would expect a singlet and a pair of doublets or triplets. Such observations in the ^{1}H n.m.r study of $Fe(\eta^1\text{-}C_5H_5)\ (CO)_2\ (\eta^5\text{-}C_5H_5)$ and for many other similar systems, led to a conjecture about a mechanism for rearrangement reactions which could render all the monohapto bonded cyclopentadienyl protons magnetically equivalent. The variable temperature ^{1}H n.m.r spectrum of this molecule over the range + 30^o C to -100^oC provides valuable information. Some characteristic features of the spectrum are (1) the nature of spectrum over the range -80^0C to -100^0 C is almost unaltered and provides evidence regarding the instantaneous structure in solution and (ii) recognition of rearrangement pathway.

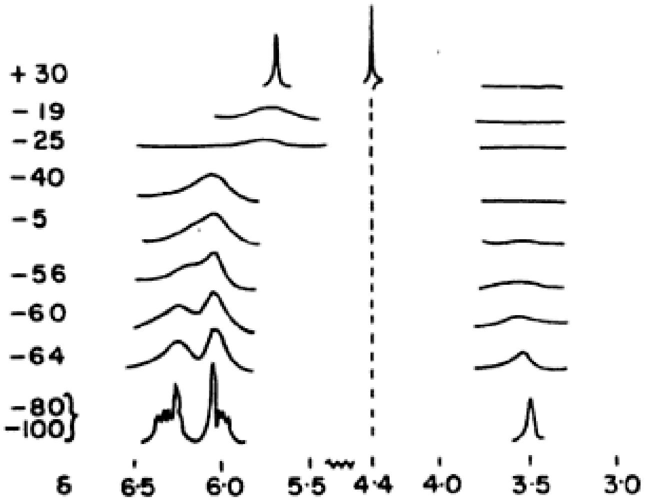


Figure 9: The variable ^{1}H NMR spectra (at 60 MHz) of Fe(η^1-C_5H_5)$(CO)_2$(η^5-C_5H_5) in CS_2.

Although the plausible pathway for proton averaging may involve (1) a dissociative mechanism (ii) random shifts, (iii) 1,2 metal shift a metal atom around the cyclopentadienyl ring from one carbon to the carbon α to 1,3 metal shift yet the experimental evidence favour the 1,2 metal shift as the most appropriate mechanism

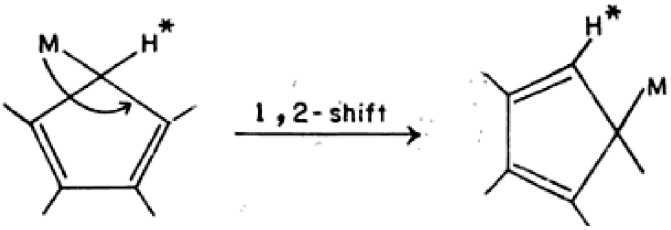


Figure 10: proton averaging by 1,2-metal shift mechanism

For the recognition of the rearrangement pathway generally the following points have been considered to be of great value.

(i) The unsymmetrical collapse of the low field patterns elimination possibilities like random site exchange or a rearrangement process making all the sites equivalent. This type of observation can in fact lead to only two possibilities, e.g 1,2-shifts or 1,3-shifts a close examination of the spectrum permits one to distinguish between the latter two pathway provided the two low-field complex multiple can be assigned.

(ii) Multiplets in the low field may be described as $AA'BB'$ resonance the downfield side of which is broadened more by interaction with allylic H compared to the upfield side; this may be α-H atoms. It may be noted that assignment of α-and β- character on the basis of chemical shifts is highly risky. However magnitudes of coupling constants would be fairly safe to indicate α or β-character of the protons e.g α-protons would be coupled more strongly to allylic H then the β-proton. In view of the above the downfield part of the multiplet which collapses faster than the upfield half may be considered to have predominantly α-character and the rearrangement pathway would involve more frequent in and out movements of protons in the α-environment than ion the β-environments. It is easy to recognize that a succession of 1,2 shifts causes redistribution of protons among α-environment twice as often as among β-environments (whereas 1.3 shift have just the opposite effect)

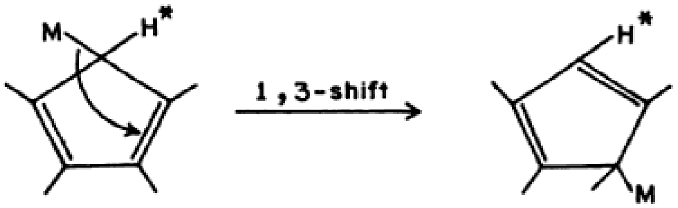


Figure 11: proton averaging by 1,3-metal shift mechanism

A second example of study where ^{1}H NMR has been of assistance is that of metal complex $(C_2H_5)_3PCuC_5H_5$.

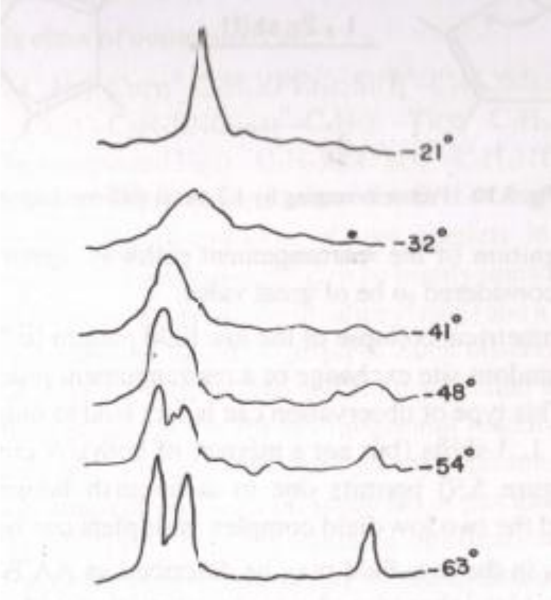
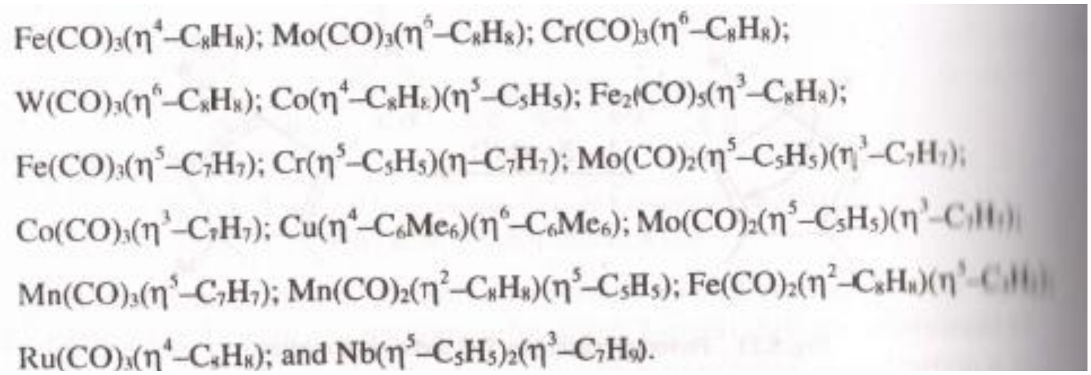


Figure 12: The ^{1}HMR spectrum at several temperatures of Cu (η^1-C_5H_5)$P(C_2H_5)_3$

Form the room temperature down to ~ ~21^{0}C proton spectrum of this compared depicts a singlet only. As the temperature is lowered the singal due to σ-bonded rings broadens and splits into three separates signals corresponding to the three types of protons in the σ-compound . It is worthwhile to mention that the spectral behaviour of the molecules Cu($\eta^1C_5H_5$)P(C_2H_5) at -63^0 is consistent with structure described in section 5.1 however at intermediate temperature the spectral behaviour is quite different from that of ($\eta^1C_5H_5$)Fe(CO)$_2$(η^1 - C_5H_5) e.g the upfield proton of the AA,BB^1 multiple collapses more rapidly thus providing evidence for 1,3-shifts. An alternative explanation involving 1,2-shifts also seems to be plausible.

12.9 Compounds with π-Bonded Cylic Alkenes

A few compounds of cyclic alkenes in which free alkene ligands has more π-electrons available than the number required to satisfy the 18 electron or effective atomic number rule are listed below



$Fe(CO)_3(\eta^4\text{–}C_8H_8)$; $Mo(CO)_3(\eta^6\text{–}C_8H_8)$; $Cr(CO)_3(\eta^6\text{–}C_8H_8)$;
$W(CO)_3(\eta^6\text{–}C_8H_8)$; $Co(\eta^4\text{–}C_8H_8)(\eta^5\text{–}C_5H_5)$; $Fe_2(CO)_5(\eta^3\text{–}C_8H_8)$;
$Fe(CO)_3(\eta^5\text{–}C_7H_7)$; $Cr(\eta^5\text{–}C_5H_5)(\eta\text{–}C_7H_7)$; $Mo(CO)_2(\eta^5\text{–}C_5H_5)(\eta^3\text{–}C_7H_7)$;
$Co(CO)_3(\eta^3\text{–}C_7H_7)$; $Cu(\eta^4\text{–}C_6Me_6)(\eta^6\text{–}C_6Me_6)$; $Mo(CO)_2(\eta^5\text{–}C_5H_5)(\eta^3\text{–}C_7H_7)$;
$Mn(CO)_3(\eta^5\text{–}C_7H_7)$; $Mn(CO)_2(\eta^2\text{–}C_8H_8)(\eta^5\text{–}C_5H_5)$; $Fe(CO)_2(\eta^2\text{–}C_8H_8)(\eta^5\text{–}C_5H_5)$
$Ru(CO)_3(\eta^4\text{–}C_8H_8)$; and $Nb(\eta^5\text{–}C_5H_5)_2(\eta^3\text{–}C_7H_9)$.

It has been shown by n.m.r spectroscopy that in solution these molecules generally undergo rapid intramolecular rearrangement which is recognized by fewer lines in the spectrum then one would expected for the static molecule.

The ^{1}H n.m.r spectrum of Fe(CO$_3$)(($\eta^4C_5H_5$) consists of only a singlet at room temperature which splits to give two broad signals at -145^{0}C. the spectrum is of $A_2H_2M_2X_2$ type with two peaks of almost equal intensity indicating that eight alkenic protons can ve divided into two equal groups of four coordinated and another four uncoordinated ones:

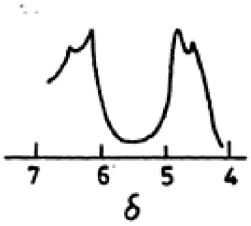


Figure 13: The ^{1}H NMR spectrum of Fe(CO)$_3$(η^4-C_8H_8) at -145^{0}C (60 MHz)

There has been considerable controversy regarding the assignments of the two signals in the above spectrum as well as on the actual instantaneous structure and the rearrangement pathway. An instantaneous structure at low temperature as suggested by Kreiter and coworkers may be represented as below.

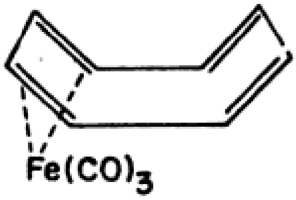


Figure 15: Suggested structure of of $Fe(CO)_3(\eta^4\text{-}C_8H_8)$

This structure has been supported by X-ray structural determination confirming that it is of the (1,3-diene) metal type. Keller and coworkers (1996) have however argued in favour of a dynamic exchange

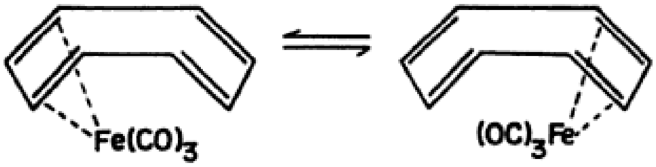


Figure 16: Dynamic exchange in of $Fe(CO)_3(\eta^4\text{-}C_8H_8)$

Cotton and coworkers on the other hand, have suggested a static tub-bonded C_8H_8 structure in which coordinated alkenic protons give rise to the high field signal.

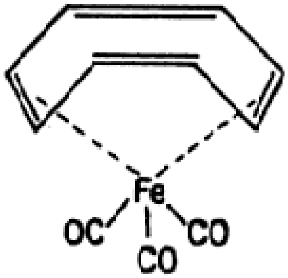


Figure 17: Cotto's Suggestion for structure of $Fe(CO)_3(\eta^4\text{-}C_8H_8)$

Cottons suggestions have received supported form a study of the n.m.r spectrum of methyl-d-cyclooctatetraene-2,3,4,5,6,7-d_6-iron tricarbonyl by Anet and coworkers who showed that the terminal and internal proton of the 1,3-dienen moiety coordination to iron show little difference in chemical shift. In spite of evidence cited above for Cotton's structure some more data have been accumulated favouring structure also. The story therefore is still incomplete and requires more refined and penetrating measurements as well as interpretations.

With the intuition that the behaviour of ruthenium complex would be similar to that of its iron analogue and the rate of rearrangement may be slower. Cotton an coworkers prepared and studied the complex $Ru(CO)_3(\eta^4\text{- }C_5H_5)$. The observation spectra are demonstrated in figure 18.

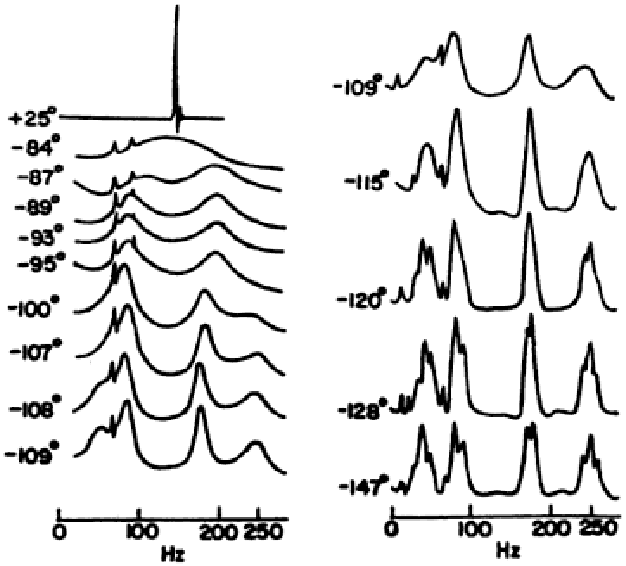


Figure 18: Variable temperature 1H NMR spectra of of $Ru(CO)_3(\eta^4\text{-}C_8H_8)$

The spectra of $Ru(CO)_3(\eta^4\text{- }C_8H_8)$. At the lowest temperatures are essentially limiting spectra and demonstrate fully without anomalies or ambiguities that the instantaneous structure is of the 1,3 diene metal type.

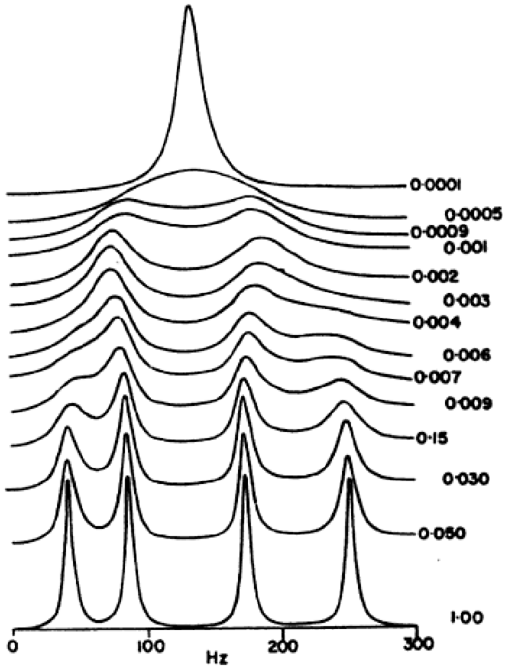


Figure 19: computer – siulated spectra of of $Ru(CO)_3(\eta^4\text{-}C_8H_8)$ assuming a 1,2 shift rearrangement pathway

The technique of computer simulation of spectra was employed to ascertain the rearrangement pathway. Out of various possible pathway (e.g 1,2: 1,3: 1,4 and random shifts) the computed spectra for all expect 1,2 shifts were in gross qualitative disagreement with the observed spectra. For the 1,2 shifts the agreement is very close as comparison

In addition to the $Fe(CO)_3$ (η^4- C_8H_8). And $Ru(CO)_3(\eta^4$- $C_8H_8)$ molecules which have been the target if intensive study and controversy n.m.r studies for stereochemical non-rigidity have been made on several complex products of iron and ruthenium containing more than one metal atom such as $Fe_2(CO)_6(\eta$-$C_8H_8)$, $Ru(CO)_3(\eta^4$- $C_8H_8)$, $Fe_2(CO)_5(\eta$-$C_8H_8)$, and Ru_2 $(CO)_5(\eta^4$- $C_8H_8)$.

12.10 Rotational of Lignds on Metals

The compounds in which flusionality arises due to rotation of ligands on metals can be grouped in various categories such as

(A) Rotational about metal-carbon σ-bonds e.g $ZrMe\{CH(SiMe_3)_2\}(\eta$-$C_5H_5)_2$.

(B) Rotation about metal-carbene bonds e.g $TaCl(CHBu^t)(\eta^5$-$C_5H_5)_2$

(C) Rotation about metal-metal bonds e.g $Mo(CO)_3(\eta^5$-$C_5H_5)_2$

(D) Rotation of coordinated alkenes and alkynes e.g $PtCl_2(PPh_3)(\eta^2$-$C_2H_4)$ and $WMe(CO)(\eta^2$-$C_2H_4)$ $(\eta^5$-$C_5H_5)$ respectively.

(E) Rotation of coordinated π-allyl groups e.g $Mo(CO)_2(\eta^3$-$C_5H_5)$ $(\eta^5$-$C_5H_5)$ and

(F) Rotation of coordinated butadienes e.g $Fe(CO)_3(\eta^4$-$C_8H_8)$ etc.

Followings points may be made

(1) The activation parameters for the rotation about metal-carbon σ-bonds are likely top be affected by the steric demands of bulky ligands such as –$CH(SiMe_3)_2$

(2) The possibilities of particularity the earlier transition metal alkyl bond sassuming some double bond character due to hyperconjugation as illustared below.

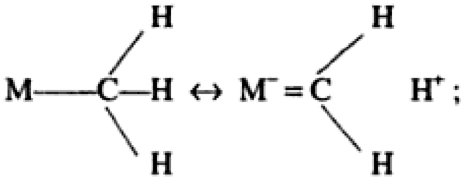


Figure 20: Hyperconjugation of metal-alkyl bond

(3) The activation energies for rotation about metal-metal bonds can generally by dictated by the steric hindrance and multiplicity of the metal-metal bonds and

(4) The activation parameters for the rotation about metal π-alkene bonds can provide information regarded various possible mechanisms.

12.11 Compounds Involving Ligand Scrambling on Metals

Examples of ligand scrambling on metals are widely known in coordination chemistry for various coordination numbers and stereochemistries and rearrangement processes generally involve a cis – trans isomerism in square-planar and octahedral complexes. Fro intarmolecualr rearrangement mechanism such as tetrahedral↔squre-planar interconversion of cis↔trans isomerism in square planar derivatives and trigonal bipyramidal↔squre-pyramidal interconversion are believed to be more probable by the Berry pseudorotation mechanism. There have been insufficient studies for seven coordinate compounds to lead to any conclusive mechanisms.

For organometallic compounds mechanism evidence is weak and it is generally assumed that the compounds are fluxional via the mechanism found for coordination compounds. This assumptions is probably true for compounds involving monodentate ligands, but in the case of π-ligand other mechanism are also possible.

Metal Carbonyls Involving Bridged-Terminal Exchanges and Scrambling of CO Groups

The fluxional behaviour of $Fe(CO)_5$ has already been discussed as one of the first observations of Cotton leadings to a clear realization of the phenomenon itself. It is now generally well known that di and poly nuclear metal carbonyl have a pronounced tendency of exhibiting fluxional interchange which has been more specifically termed of ‘Carbonyl Scrambling’

For example it has been shon in bimolecular carbonyl e.g $Co_2(CO)_8$ that there are a number of structure of the following types

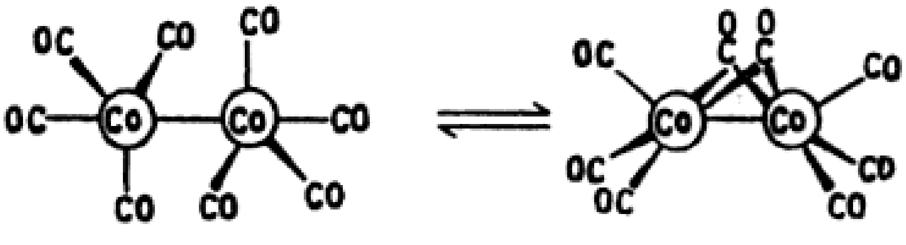


Figure 21: Structure of $Co_2(CO)_8$

These differ in their free energy by only a few (<30) kj mol^{-1}. In such cases a facile interchange of the type represented in the following diagram occurs in which CO(A) passes from the left metal to the right one. While CO(B) is simultaneously making the opposite journey.

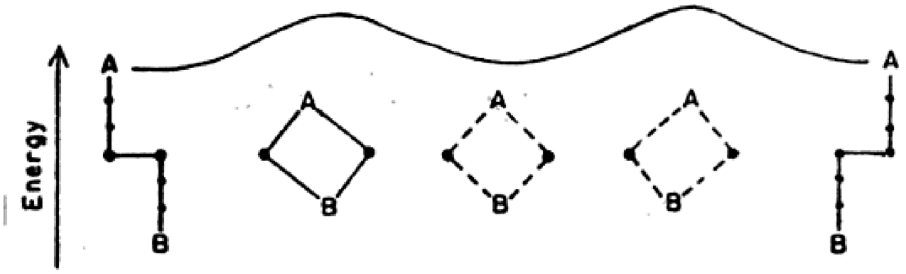
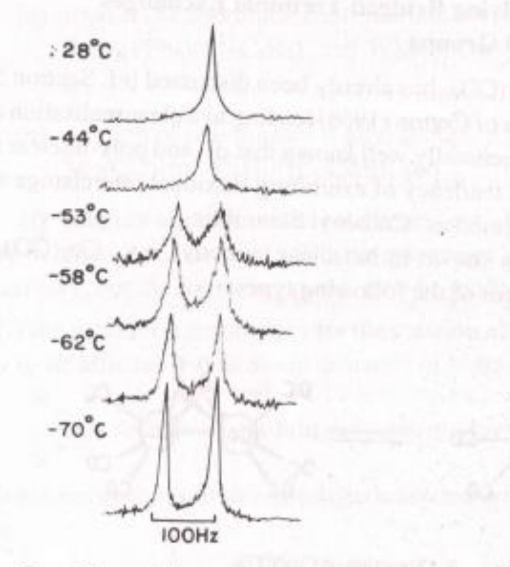


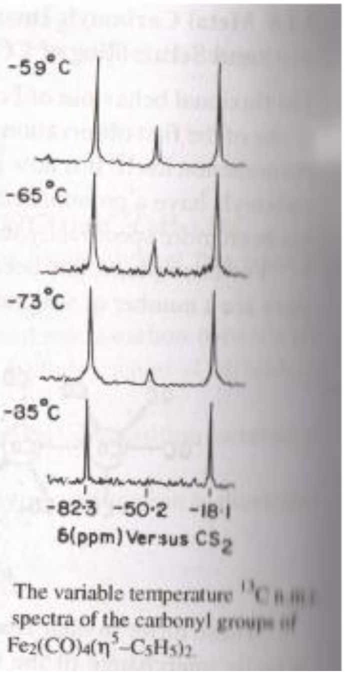
Figure 22: Interchange of CO ligands in metal carbonyls

In this diagram the Co bridged structure is slightly less stable than the terminal one which is the case for $Co_2(CO)_8$ however the opposite position of bridged ones being slightly more stable than the terminal ones are also known

Another interesting example of fluxional behaviour was reported in (η^5-C_5H_5)$_2$ $Fe_2(CO)_4$ moleules the ^{1}H n.m.r spectrum of which in solution showed at -70^0 C the proton resonance at two positions but these gradually coalesced when the temperature is raised giving only one sharp signal at +28^0 C



The variable temperature H n.m.r. spectra of the cis- and trans- [η^5–$C_5H_5Fe(CO)_2$]$_2$.



The variable temperature ^{13}C n.m.r spectra of the carbonyl groups of $Fe_2(CO)_4(\eta^5$–$C_5H_5)_2$.

The ^{13}C n.m.r spectrum of $Fe_2(CO)_4(\eta^5-C_5H_5)_2$ shows that the following cis-trans exchange is accompanied by the interchange of the CO groups between bridging and terminal positions.

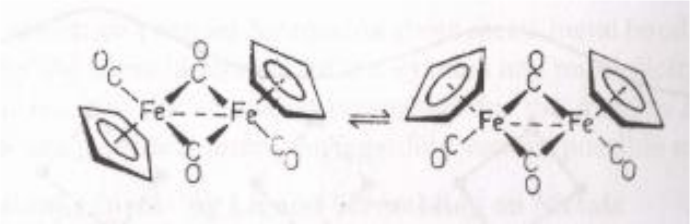


Figure 23: The *cis-trans* exchange of CO and C_5H_5 groups

It appears that the CO bridges open in a concerted way to give a non-bridged $C_5H_5(CO)_2Fe-Fe(CO)_2C_5H_5$ intermediate in which rotation about the Fe-Fe bond takes place.

12.12 Summary of the unit

Molecules that undergo rapid intramolecular rearrangements among equivalent structures in which the component atoms are interchanged are called fluxionals. The general class of fluxional' organometallic molecules includes both sigma and pi types. The experimental investigation of such molecules generally consists in a study of the way in which their nuclear magnetic resonance (NMR) spectra change with temperature. Usually, the first objective is to record the limiting low-temperature spectrum (hereafter called, simply, the limiting spectrum). This is the spectrum at a temperature sufficiently low that the rate of the intramolecular rearrangement process is insufficient to alter significantly the spectrum given by the molecule in one of its nuclear configurations of minimum free energy (hereafter called the instantaneous structure of the molecule).

12.13 Key words

Fluxional molecules; Nonrigid molecules in different coordination geometries; Rotational of Lignds on Metals; Compounds Involving Ligand Scrambling on Metals

12.14 References for further studies

1) Organometallic Chemistry; R. C. Mehrotra; *New Age International*, **2007**.

2) Organometallic Chemistry of the Transition Elements; Florian P. Pruchnik; *Springer Science & Business Media*, **1990**.

3) Inorganic chemistry; 3rd ed. Gary L. Miessler, Donald A. Tarr *Rex Bookstore, Inc.***2004**.

4) Advanced Inorganic Chemistry: Vollume II. Gurdeep Raj; *Krishna Prakashan Media*, **2010**.

12.15 Questions for self understanding

1) What are fluxional molecules? Give examples
2) Write anotes on
a) Rates of rearrangements and
b) techniques of study for fluxional molecules
3) Explain the rate process and NMR Spectra in study of fluxional molecules
4) Give the examples of nonrigid molecules in following different coordination geometries

a) Four-coordinate system

b) Trigonal-Bipyramidal Molecules

c) Systems with Coordination Number 6 or Higher

5) Discuss the classification of fluxional organometallic compounds

6) Write a note on following

a) Compounds with Acyclic Alkenes

b) Compounds with σ-bonded cyclic alkenes

c) Compounds with π-Bonded Cylic Alkenes

7) Discuss the rotational of Lignds on Metals in fluxional molecules

8) Discuss the compounds Involving Ligand Scrambling on Metals

UNIT-13

Structure

13.0 Objectives of the unit

3.1 Introduction

13.2 Inorganic chains

13.3 General Properties of Inorganic Polymers.

13.4 Catenation

13.5 Hetero catenation

13.6 Polysiloxanes

13.7 Polysilanes

13.8 Preparation

13.9 Properties

13.10 Silicate Minerals

13.11 Classification of Silicates

i*) Ortho Silicates*

ii) Pyrosilicates

iii) Cyclic Silicates

iv) Chains Silicates

v) Sheet Silicates

13.12 Intercalation

13.13 One dimension conductors

13.14 Summary of the unit

13.15 Key words

13.16 References for further studies

13.17 Questions for self understanding

13.0 Objectives of the unit

After studying this unit you are able to

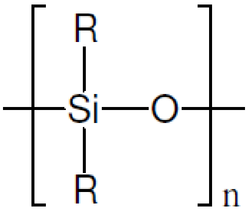
- Identity the general properties of inorganic polymers.
- Explain the Catenation
- Explain the Hetero catenation
- Explain the different types of silicate Minerals
- Identity the application of Intercalation
- Explain the one dimension conductors

3.1 Introduction

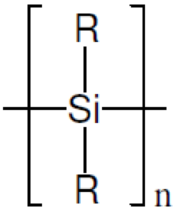
Some non- metals have the tendency to resemble carbon in certain properties. This chapter discusses one such property of nonmetals. Nonmetals other than carbon have also the tendency to form chains, rings and cages. Most metals show less tendency to form compounds of this type, and the length of the chains and size of the rings thus formed are restricted. However, the ease with which both metals and nonmetals and combinations of the two form clusters has only been recognized in the last decade. This branch of chemistry has seen a rapid growth.

13.2 Inorganic chains

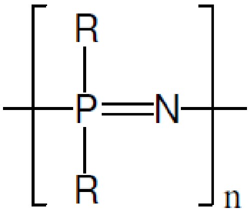
In addition to polymers that contain only carbon or other ‘organic’ atoms in the chain, polymers containing ‘inorganic’ atoms can also be formed. These compounds are of interest because they offer the opportunity to develop new technological applications due to their reactivity, structure, and physical properties. Many are now known. The most widely developed contain silicon as polysiloxanes and polysilanes. Another common class are the polyphosphazenes.



$$\left[\overset{R}{\underset{R}{\mathrm{Si}}} - \mathrm{O} \right]_n$$



$$\left[\overset{R}{\underset{R}{\mathrm{Si}}} \right]_n$$



$$\left[\overset{R}{\underset{R}{\mathrm{P}}} = \mathrm{N} \right]_n$$

13.3 General Properties of Inorganic Polymers.

1. With a few exception (such as sulphur) inorganic polymers fail to burn. They only soften or melt at high temperature.
2. Inorganic polymers which are having cross linked structure with a high density of covalent bonds are generally stiffer and harder than the inorganic polymers.

3. The chain segments between cross links in polymers having cross linked structure are generally short and stiff. Consequently these structure are not flexible enough to allow intercalation of solvent molecules.
4. Usually the inorganic polymers are built up of highly repeat units. These polymers would therefore dissolve only in polar solvents.

   Most of these polymers however react with the solvents. There are thus only a few inorganic polymers which actually dissolve in appropriate solvents.
5. Inorganic polymers are usually much less ductile than the organic polymers. Thus while organic polymers such as polyethylene can extend by about 20 per cent or more before fracture inorganic polymers break even when extended by about 10 per cent.
6. Inorganic polymers may be obtained in pure crystalline as well as in pure amorphous forms. Organic polymers on the other hand have structures which are partly crystalline and partly amorphous.
7. Inorganic polymers are generally stronger, harder and more brittle than the organic polymers.

13.4 Catenation

Carbon has the ability to form successively two other C-atoms to form chains of varying lengths and shapes. This property of carbon is called "Catenation". Catenation is responsible for the variety and a large number of organic compounds. Due to catenation carbon forms long chains, branched chains, rings, ring and chain structured compounds.

This phenomenon is not common in the remainder of the periodic table. Silicon and related non-metals have the tendency of form chains, to a limited extent. There is no thermodynamic barrier to the formation of long chain silanes, $Si_{(n)}H_{(2n+2)}$. Their synthesis ad characterizations are difficult tasks. Si-Si bonds are weaker than C-C bonds. Silanes are very highly reactive. At 400°C, Si_2H_6 decomposes much faster than C_2H_6.

$2Si_2H_6 + 7O_2 \rightarrow 4SiO_2 + 6H_2O$. This reaction is kinetically favoured. Compounds of silanes from n=1 to n=8 have been isolated, including both straight chain and branched-chain compounds. A number of Polysilane polymers have been isolated. The chemistry of germanes is similar to silanes. Nitrogen, phosphorous and Sulphur form chains. Chain length up to 8 atoms of nitrogen are known. They are highly explosive. In the case of sulphanes, chains up to 8 sulphur atoms have been obtained. P_2H_6 is well known P_3H_5 is well characterized. Oxygen forms no chains longer than three atoms, O_3 and its anion O_3 and a few compounds are known, for e.g., bis (perfluoroalkyl) trioxides such as $F_3C000CF_3$. Allotropes of both 'S' and 'Se', are known in which helical chains of great length are present.

Sulphur chains are instable with respect to S_8 (Cyclic). The chain form of 'Se' is stable. Red 'P' is polymeric and is thought to have chains of pyramidal 'P' atoms. Polyhalide ions are stable, for e.g., I_3.

13.5 Hetero catenation

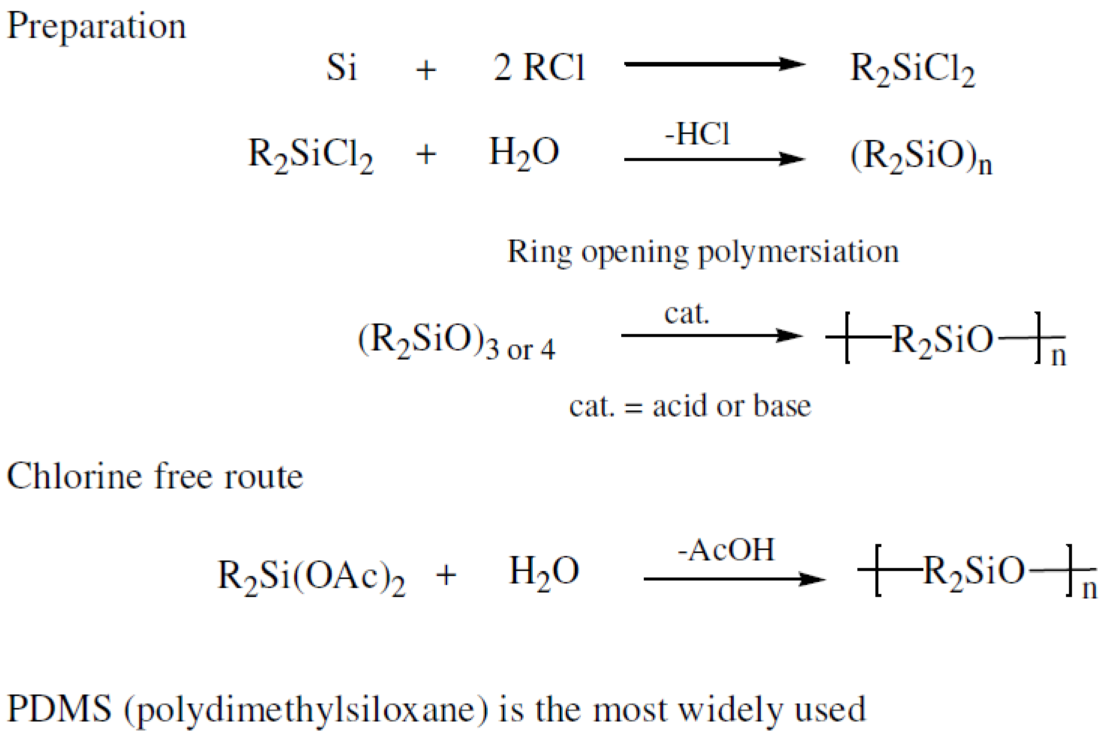
The phenomenon of hetero catenation or chains built up of alternating atoms of different elements is well known. Silicons, $(R_2SiO)_n$ and polyphosphazenes $(PN(OR)_2)_n$ are hetero catenated polymers, having wide application. *The simplest hetero catenated compounds are those formed by the dehydration of acids or their salts*. Simple acid phosphate salts on heating give rise to pyrophosphates, for e.g., $(P_2O_7)^{-4}$. The general formula of polyphosphate may be given as : $(PnO_{3n+1})^{(n+2)-}$; n = 2, it is known as diphosphate, n =3- triphosphate etc., melt/100l

$$5Na_3PO_4 + P_4O_{10} \xrightarrow{Metal/100l} 3Na_5P_3O_{10}$$

condensed poly phosphates such as sodium triphosphates, are largely used as detergents.

13.6 Polysiloxanes

Most important inorganic polymers have large commercial applications. In medical field, this polymer is used as prosthetics, catheters, contact lenses, drug delivery capsules. And in non medical field, this polymer is used as. elastomers, adhesives, lubricants, water repellents, molds and cosmetics.



13.7 Polysilanes

The polymer backbone contains only silicon atoms. A silicon chain allows electron delocalisation of sigma electrons. Many uses of polysilanes derive from the electron mobility. Most uses are in the electronics industry as photoresists and precursors to silicon containing materials.

13.8 Preparation

There are two general methods are employed for synthesis of these polymers they are

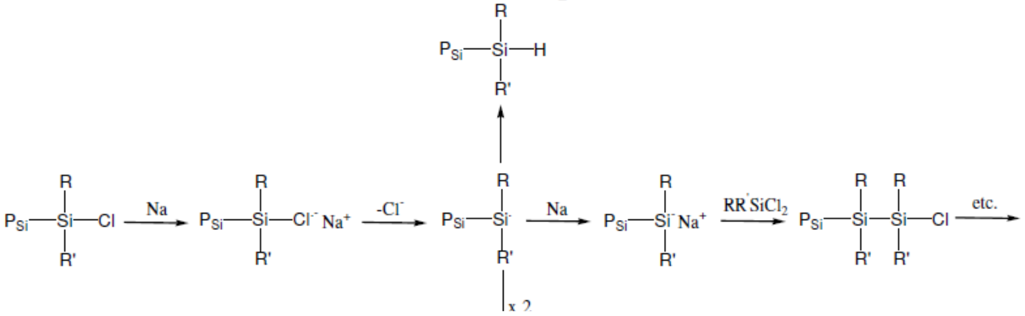
1) Condensation of dichlorosilanes with alkali metals

2) Dehydrogenative coupling of silanes

Condensation of dichlorosilanes with alkali metals

$$RR'SiCl_2 \xrightarrow[> 100\ ^{o}C]{Na,\ toluene} (RR'Si)_n$$

Product distribution indicates radicals are important intermediates

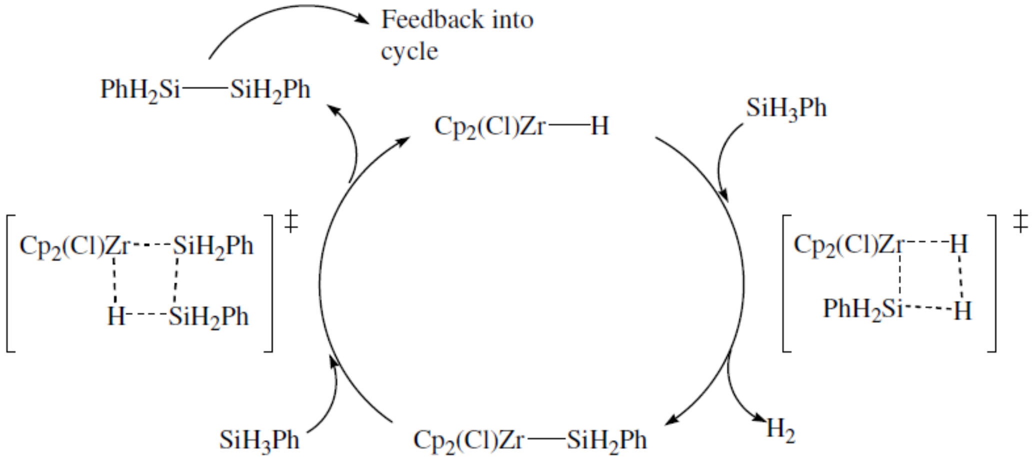


Dehydrogenative coupling of silanes

$$n\ RR'SiH_2 \xrightarrow{catalyst} H(SiRR')_nH + (n-1)\ H_2$$

Two proposed mechanisms

σ-bond metathesis



Mechanism involved in this reaction is step growth polymerisation. The Si-Si bond formation can occur via σ-bond metathesis or via a silylene if a hydride and a-hydrogen are present

13.9 Properties

σ-electron delocalisation is present in polysilanes that contrasts to organic polymers (e.g. polyacetylene) that have π-electron delocalisation. Physcial properties arising from delocalisation including strong electronic absorption, conductivity, photoconductivity and photosensitivity. σ-electron delocalisation occurs primarily because of the good overlap of Si-Si bonds and lower electronegativity of Si relative to carbon.

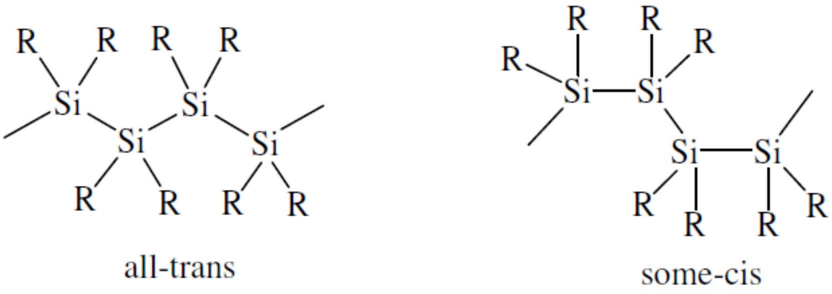
For conduction to occur a band must be partially filled. One can do this by

1. Adding electrons to the conduction band by reaction with a reducing agent.
2. Removing electrons from the valence band by reaction with an oxidising agent.
3. Promoting electrons from the filled valence band to the empty conduction band using heat or light.

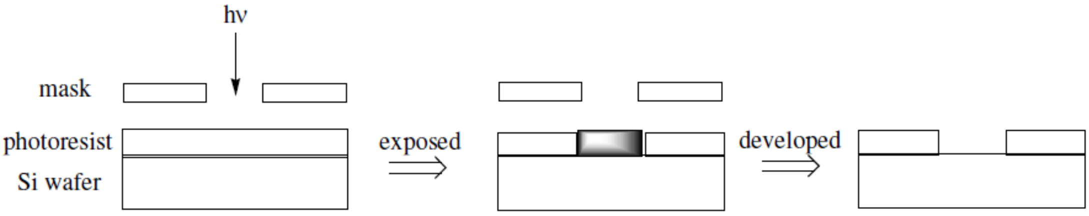
In polysilanes the band gap is such that 300-400nm light can excite electrons from valence band into conduction band.

The band gap is sensitive to

1. Chain length. Band gap decreases and absorption wavelength increases (lower energy). Reaches limit at ~ 30 Si atoms.
2. Conformation of polymer chain: trans conformation leads to absorption at lower wavelengths (better overlap) because less steric strain.



Conformation dependent on temperature that leads to strong theormochromism (colour change with temperature) Polysilanes can be used as photoresists



13.10 Silicate Minerals

Silicon forms a very large number of compounds containing heterocatenated anions. The silicates make up of various minerals. About three fourths of the earth crust is silicon and oxygen. The majority of silicate minerals are insoluble, because they have an infinite ionic structure and because of the Si-O bond. Silicate structures have been solved by X-ray crystallographic methods:

i) The electro negatively difference between 'Si' and 'O' is equal to 1.7. This suggests that the bonds are 50% ionic and 50% covalent.

ii) The structure may be considered both by ionic and covalent methods. The radius ratio of Si^{+4} : O^{-2} is 0.29, which suggests that 'Si' is four co ordinate. It is surrounded by four oxygen atoms at the corners of a tetrahedron. 'Si' in $(SiO_4)^{-4}$ may be assumed to be SP_3 hybridized (3s and three 3P orbitals) and hence silicates are based on $(SiO_4)^{-4}$ tetrahedral units.

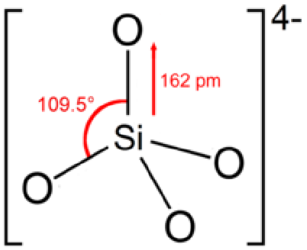
iii) The SiO_4 tetrahedra may exists as discrete units or may polymerize into larger units by sharing corners, i.e., by sharing oxygen atoms.

iv) The 'O' atoms are often close packed or nearly close packed. Close packed structures have tetrahedral and octahedral holes and metal ions can occupy either tetrahedral or octahedral sites depending on their size. Al^{3+} can fit into either octahedral or tetrahedral site. Thus Al can replace either octahedral or tetrahedral site. Thus Al can replace either a metal in one of the holes or a silicon atom in the lattice. This is particularly important in the aluminosilicates.

13.11 Classification of Silicates

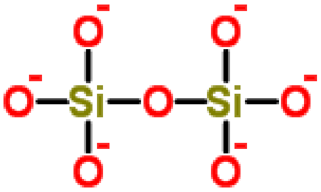
i*) Ortho Silicates*

A wide variety of minerals contain discrete $(SiO_4)^{4-}$ tetrahedra. They have the general formula $M_2(SiO_4)$ (M=Be, Mg, Fe, Mn or Zn). $M(SiO_4)$ M- Zr. These silicates share no corners. In Zn_2SiO_4 (Willemite) and Be_2SiO_4 (Phenacite) Zn and Be have a 'CN' of 4; Zn and Be occupy tetrahedral holes. In Mg_2SiO_4, Mg has a CN of 6 and occupies octahedral holes. ZrSiO4 is a gem stone. Zr has a CN of 8. The structure is not close packed. The garnents are minerals with discrete tetrahedra; are used as red gem stones. Its formula is $M_3M_2(SiO_{4)3}$ M(II) = Mg, Ca or Fe (II); Me(III) may be Fe(III), Cr or Al. These are 8 coordinate.



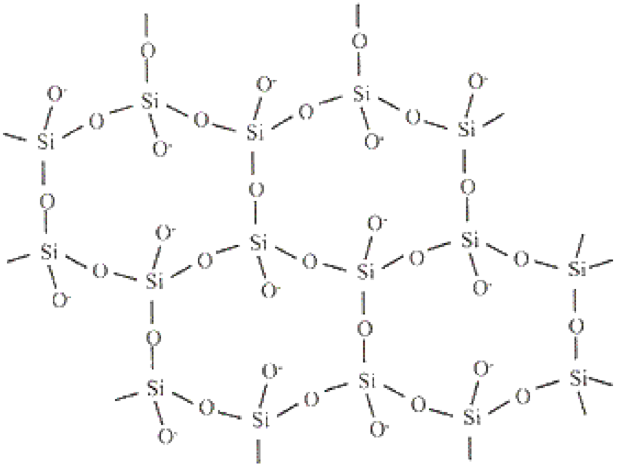
ii) Pyrosilicates

Two tetrahedral units are joined by sharing the 'O' at one corner and the unit is $(Si_2O_7)^{6-}$. This is the simplest of the condensed silicate ions. The name pyro comes from the similarity in structure with pyrophosphates like $Na_4P_2O_7$. Pyrosilicates are rare, for e.g., Thortveitite $(Sc_2(Si_2O_7)$ Si-O-Si bond angle is 180^o in this compound and it changes upto 133^o. The co ordination number of the metal changes from 6 to 7 and then to 8, with increase in size of the metal. Structural studies show no difference in the lengths of the bridging and terminal Si-O bonds.



iii) Cyclic Silicates

If two oxygen atoms per tetrahedron are shared, ring structures of formula $(SiO_3)_n^{2n-}$ may be formed. Rings containing, three, four, six and eight tetrahedral units are known. But those with three and six are the most. The cyclic ion $Si_3O_9^{6-}$ occurs in wollastonite, $Ca_3(Si_3O_9)$. The $Si_6O_{18}^{12-}$ occurs in beryl, $Be_3Al_2(Si_6O_{18})$. In beryl the Si_6O_{18} units are aligned one above the other, leaving channels. Na^+, Li^+ and Cs^+ are commonly found in these channels, and because of the channels the mineral is permeable to gases consisting of small atoms or molecules e.g., helium. Beryl and emerald are gemstones. Beryl is found with granite and usually forms pale green crystals, which are six sided prisms. Emerald has the same formula as beryl, but it contains 1-2%Cr, which gives it a strong green colour.



iv) Chains Silicates

Pyroxenes are simple chain silicates. These are formed by the sharing of oxygen atoms on two corners of each tetrahedron, with other tetrahedra. This gives the formula $(SiO_3)_n^{2n-}$. A large number of important minerals form chains, but there are a variety of different structures formed because the arrangement of tetrahedra in space may vary and thus affect the repeat distance along the chain. The most common arrangement repeats after every second tetrahedron for e.g., in spodumene, $LiAl[(SiO_3)_2]$, enstatite $Mg_2[(SiO_3)_2]$ and diopsite, $CaMg[(SiO_3)_2]$. $Ca[(SiO)_3]$ has a repeat of three, and others are known with repeat units 4,5,6,7,9 and 12. Double chains can be formed when two simple chains are joined together by shared oxygens. These minerals are amphiboles. They have different formulae, due to several ways of forming double chains, for e.g.,$[(Si_2O_5)_n{}^{2n-}$, $[(Si_4O_{11})_n{}^{6n-}$, $[(Si_6O_{17})_n{}^{10n-}$etc., Asbestos minerals are the best known amphiboles . These have the structural units $(Si_4O_{11})_n{}^{6n-}$. Amphiboles always contain – OH groups, which are attached to the metal ions. The Si-O bonds in the chains are strong and directional. Adjacent chains are held together by metal ions present. Pyroxenes and amphiboles cleave readily parallel to the chains, forming fibres. For this reason, they are called fibrous minerals. The cleavage angles for pyroxenes and amphiboles are different.

Example are tremolite $Ca_2Mg_5([(Si_4O_{11})_2](OH)_2$ and crocidolite $Na_2Fe_3Fe_2$ $([(Si_4O_{11})_2]$ $(OH)_2$ (. (blue asbestos). The mineral chrysatile $Mg_3(OH)_4($ $Si_2O_5)$ is white asbestos and is a sheet silicate. Asbestos causes lung cancer.

v) Sheet Silicates

When SiO_4 units share three corners the structure formed is an infinite two dimensional sheet of empirical formula $(Si2O_5)_n{}^{2n-}$ within the Si-O sheet bonds are strong but much weaker forces hold each sheet to the next one. These sheets cleave into thin sheets. These consist of two or three layers joined together. Examples are

(i) Clay minerals (Kaolinite)

(ii) White asbestos

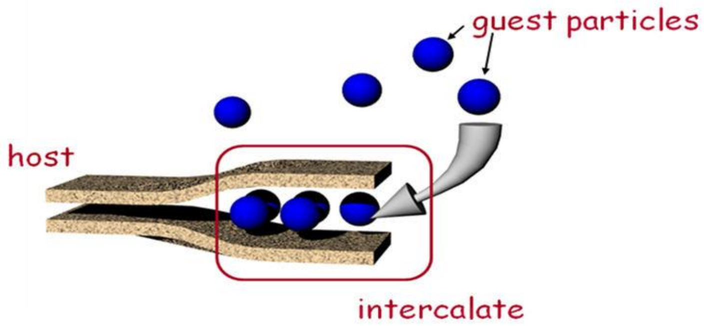
(iii) Micas (Muscovite)

(iv) Montmorillonites (fullers earth, bentonite).

Consider the formation of a two layer structure. If a Si_2O_5 layer is placed alongside a layer of $Al(OH)_3$, then many of the 'O' atoms will coincide. The 'OH' groups in $Al(OH)_3$ can be removed and an electrically neutral two layer structure is formed. These double layers stacked parallel give the mineral kaolinite, which has the formula $Al_2(OH)_4(Si_2O_5)$. It is a white solid and formed by the decomposition of granite.

13.12 Intercalation

The term intercalation denotes a process in which a molecule or an ion (guest) is placed into a host lattice. The structure of the host remains unchanged or is only slightly altered in the guest-host complex that is in the intercalation compound (intercalate).



A compound formed when a guest molecule, atom, or or ion is inserted into cavities or other spaces, particularly between layers, in a host compound, resulting in little change of structure in the host compound. For example, graphite intercalation compounds consist of (largely intact) graphite layers with guest molecules or atoms are located in between.

The intercalation reaction is usually chemically or thermally reversible. Other terms like insertion, inclusion or topotactic reaction, are often used for the intercalation reactions, but all of them correspondto the above given definition. Intercalation chemistry is one of the field of supramolecular chemistry. Intercalation reactions offer the way for the synthesis of new solids and allow controlled systematic changes of their physical properties. These materials have many applications, for instance as catalysts, sorbents, electrochromic displays, electrodes for secondary batteries (Li-ion batteries) and components for fuel cells.

Graphite consists of hexagonal carbon planes stacked along c-axis by weak van der Waals force. Therefore, many substances, what is called intercalates, can enter into the gallery of the graphite to form graphite intercalation compounds (GICs). The GICs have a unique stage structure. Stage is defined as number of graphene layer between intercalates. When some atoms or molecules enter into graphite at every two layers, the GIC possess the stage 2 structure. In the higher stage GICs, intercalates are regarded as a pseudo two dimensional structure, and therefore, much work has been done on the GICs in terms of transport properties, magnetic properties, lattice dynamics, etc

Due to these properties, GICs can be expected to act as effective thermoelectric materials. Thermoelectric materials have the ability to directly convert thermal energy into electricity. They have recently attracted considerably interest as promising materials for clean power generators. An excellent thermoelectric material should have a high electricalconductivity (σ) to minimize Joule heating, a low thermal conductivity (κ) to prevent thermal shorting, and a large Seebeck coefficient (α) for the maximum conversion of heat to electrical power.

There are many advantages of using GICs as thermoelectric materials, such as the light weight of the materials, high selectivity of their shapes (plate, sheet, fiber, powder, etc.), and their harmless nature.

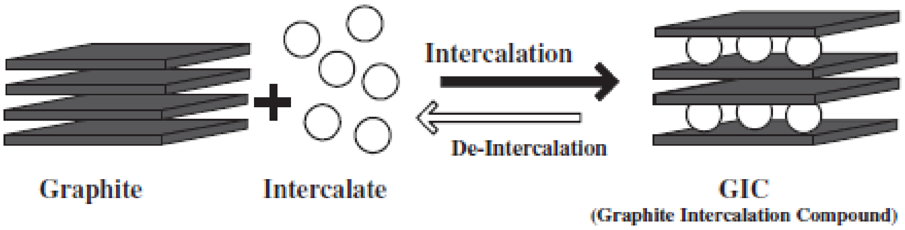


Fig. 1 Illustration of intercalation reaction.

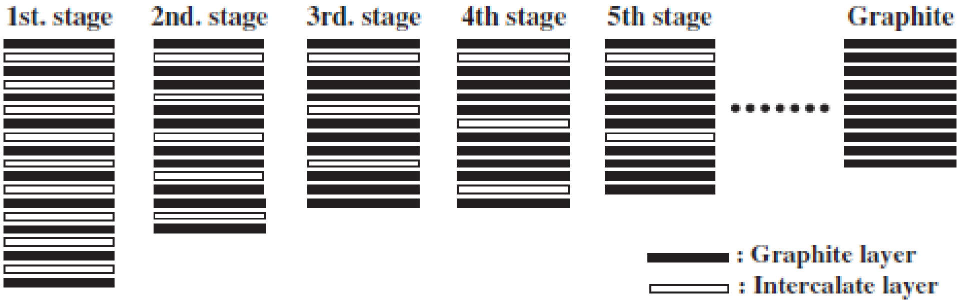


Fig. 2 Models of stage structure.

The type of carrier in GICs changes with the intercalated species. Therefore, we can fabricate both p and n-type GICs that are necessary to construct thermoelectric power generators. In the GICs, the electrical conductivity is governed mainly by the electrical carriers, while the thermal conductivity is governed mainly by the phonon transport. Therefore, it may be possible to control the electrical conductivity and the thermal conductivity independently.

13.13 One dimension conductors

There is, at present, a great interest in compounds possessing new and unique electronic properties, because the successful application of these compounds may lead to devices with as large an impact on technology as the silicon and germanium devices of the last two decades. One class of compound at present being studied in several laboratories throughout the world is that possessing structural and electronic properties which suggest the possibility of one-dimensional metallic conduction. Two main series of compounds which appear capable of development to give this type of behaviour are being investigated. One series consists of organic charge-transfer compounds containing the TCNQ (tetracyanoquinodimethane, see Fig. la) molecule and the other series contains some partially oxidised transition metal complexes.

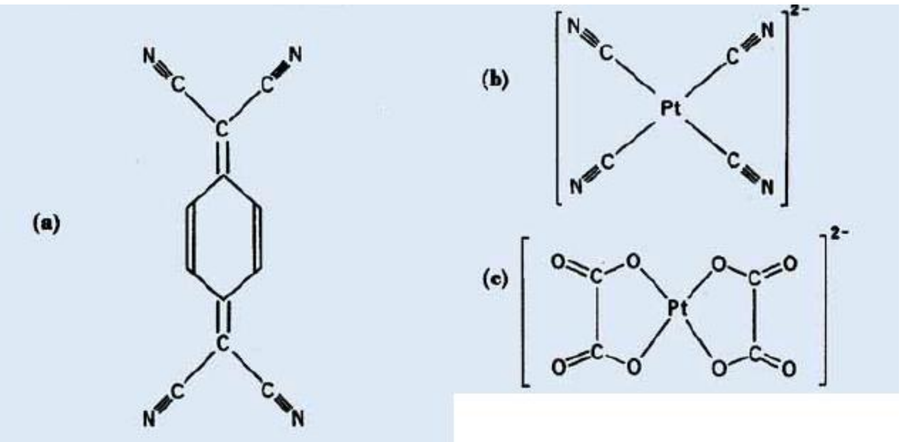


Fig. 1 Two series of compounds appear capable of development as one-dimensional metallic conductors. 1a shows the TCNQ (tetracyanoquinodimethane) molecule included in the series of organic charge-transfer compounds. 1b shows the cyano-complex ion $[Pt(CN)_4]^{2-}$ and 1c the oxalato-complex ion $[Pt(C_2O_4)_2]^{2-}$, on which the series of partially oxidised complexes are based

The transition metal complexes which appear to be capable of development as one dimensional metallic conductors are those in which the metal atom is surrounded by a square-coplanar arrangement of ligands and in which the square-coplanar units are stacked above one another to form a chain of metal atoms running throughout the crystal (see Fig. 2). This type of complex is mainly limited to nickel(II), palladium(II), and platinum(I1).

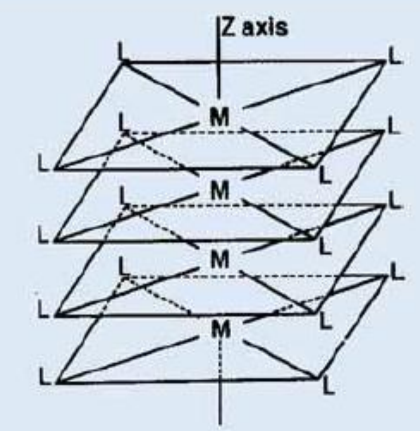


Fig. 2 Transition metal complexes capable of development as one-dimensional metallic conductors contain the metal atom M surrounded by a square-coplanar arrangement of ligands L. The square-coplanar units are stacked above one another to form a chain of metal atoms running through the crystal

The electrical conduction properties of several examples of this type of complex have been studied (e.g. Ni(dmg), where dmg is dimethylglyoxime, $Pt(NH_3)_4PtC1_4$, and $K,Pt(CN)_4.xH_2O$ and they have been found to behave as semiconductors with the conductivity in the direction of the metal atom chain ranging from 10^{-4} to 10^{-l0} ohm-lcm-l at room temperature.

In this type of complex it has been suggested that the outermost p_z, and d_z^2 orbitals (Fig. 3), or a combination of these orbitals, on adjacent metal atoms may overlap to form a d_z^2 band and, at higher energy, a p_z band. In the case o€ nickel(II), palladium(I1) and platinum(I1) complexes, each d_z^2 orbital contains two electrons, while the p_z orbital is empty, and therefore the d_z^2 band is completely full and the p_z band is completely empty (Fig. 4).

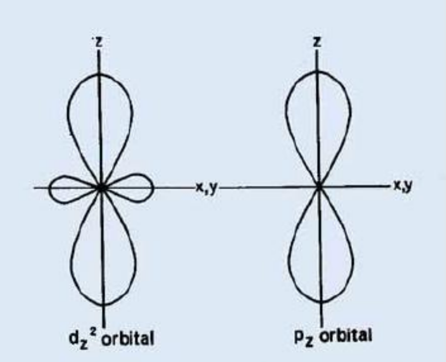


Fig. 3 Orbitals used in the formation of a band structure

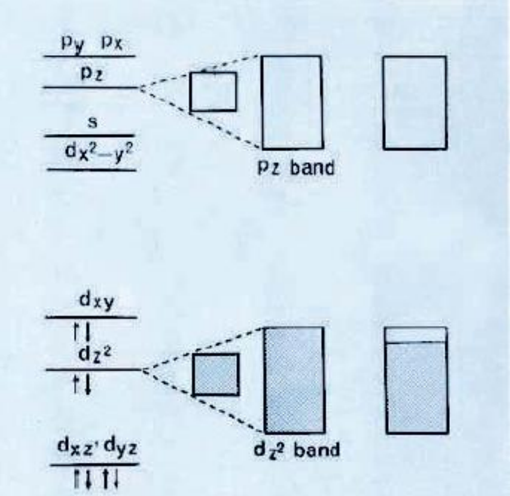


Fig. 4 Diagrammatic representation of the band structure in d^8 metal-atom chain compounds showing the effect of: (a) decreasing intermetallic distance, (b) partial oxidation. Dotted portion indicates filled band

The semiconduction properties of these compounds can therefore be understood in terms of promotion of electrons from the filled d_z^2 band to the empty p, band. Alternatively, the observed conductivity may result from electrons “hopping” from one square coplanar complex to the next one in the chain, the hopping process being thermally activated.

13.14 Summary of the unit

The silicates are the largest, the most interesting and the most complicated class of minerals than any other minerals. Approximately 30% of all minerals are silicates and some geologists estimate that 90% of the Earth's crust is made up of silicates, SiO_4^{4-} based material. Thus, oxygen and silicon are the two most abundant elements in the earth's crust. ilicates is based on the basic chemical unit SiO_4^{4-}, tetrahedron shaped anionic group. The central silicon ion has a charge of positive four while each oxygen has a charge of negative two (-2) and thus each silicon-oxygen bond is equal to one half (½) the total bond energy of oxygen. This condition leaves the oxygens with the option of bonding to another silicon ion and therefore linking one SiO_4^{4-} tetrahedron to another.

13.15 Key words

Inorganic polymers; Catenation; Hetero catenation; silicate Minerals; Intercalation; One dimension conductors

13.16 References for further studies

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2) Cyclic Polymers; E.R. Semlyen; *Springer Science & Business Media*, **2007**.

3) Concise Inorganic chemistry – J.D.Lee 5th edition

4) Inorganic chemistry – Huhecy et al Pearson Education – Asia.

13.17 Questions for self understanding

1) What are the general properties associated with inorganic polymers?

2) What is catenation? Explain with example

3) What is meant by hetero catenation?

4) Write a note on polysiloxanes

5) Explain different types of polysilanes and their preparation

6) What are the general properties associated with polysilanes?

7) What are silicate minerals?

8) Discuss the classification of Silicates

9) Write a note on followings

i) Ortho Silicates

ii) Pyrosilicates

iii) Cyclic Silicates

iv) Chains Silicates

v) Sheet Silicates

10) What are Intercalations? Explain their applications

11) What are one dimension conductors? Explain their uses.

UNIT-14

Structure

14.0 Objectives of the unit

14.1 Introduction

14.2 Molecular species containing B-N bonds

14.3 Borazines

14.4 Synthesis of borazines

14.6 Phosphazenes

14.7 Structure

14.8 Bonding in chain

14.9 Phosphazene polymers

14.10 Sulphur nitrogen compounds

14.11 Synthesis of S_4N_4

14.12 Structural studies of S-N compounds

14.13 Summary of the unit

14.14 Key words

14.15 References for further studies

14.16 Questions for self understanding

14.0 Objectives of the unit

After studying this unit you are able to

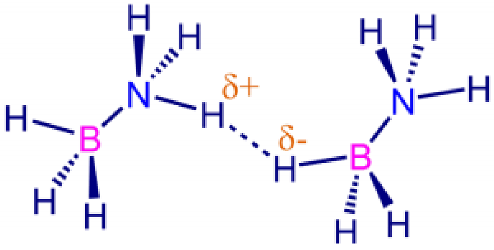
- Identify the molecular species containing B-N bonds
- Explain the synthesis structure of borazines
- Explain the synthesis structure phosphazenes
- List out the uses of phosphazene polymers
- Identity the sulphur nitrogen compounds
- Explain the structural studies of S-N compounds

14.1 Introduction

Polymers have revolutionized human civilization. Carbon forms polymers most extensively on account of its unparalleled catenation property (tendency to form chains). Although to a limited extent, catenation is exhibited by some other elements in Group 14 and Group 15. For example, in Group 14, the catenation tendency follows the sequence C >> Si > Ge~Sn >> Pb. In Group 15, the N-N single bond is so weak that its chain length does not go beyond 3 (in N_3 ion). The chain length in case of phosphorus is up to 2 (e.g. in P_2H_4).Silicon in Group 14 forms polymeric silanes with difficulty. In conjugation with oxygen however, it makes extensive Si-O-Si linkages forming silicones. Similarly, in conjugation with nitrogen, phosphorus shows unique capability of forming extensive — N =P — bonds in what are called phosphazenes. These two classes of polymers established Si and as the second and the third most extensively polymer-forming elements, respectively and, have revolutionized polymer science on account of their oxidative, thermal and radiation stabilities. The C = C and C – H bonds in C-based polymers are susceptible to oxidation and the C-C bonds are prone to cleavage, but these two classes of silicones and phosphazenes are free from these lacunae. Their good dielectric properties, excellent water repellency, antistick & antifoamproperties, solvent resistance, flame resistance, sometimes physiological inertness and similar other properties have brought out remarkable versatility in their applications from engineering goods to items in medical sciences.

14.2 Molecular species containing B-N bonds

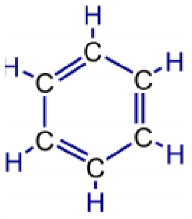
Aminoboranes, $R_3B–NR_3$, are isoelectronic with hydrocarbons, $R_3C–CR_3$. H_3N-BH_3 is a solid at room temperature, polar molecule H_3C-CH_3 is a gas that condenses at –89 °C, nonpolar.

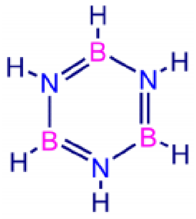


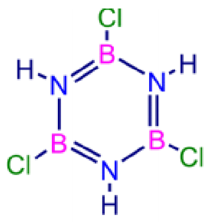
The striking difference in the properties is due to hydrogen bonding between H_3BNH_3 molecules (recall that strongly hydrogen bonded H_2O is a liquid under normal conditions, whereas H_2S is a gas, because of weaker H-bonding).

14.3 Borazines

Borazine is an inorganic compound with the chemical formula $(BH)_3(NH)_3$. In this cyclic compound, the three BH units and three NH units alternate. The compound is isoelectronic and isostructural with benzene. Like benzene, borazine is a colourless liquid. For this reason borazine is sometimes referred to as "inorganic benzene". Borazine, $B_3N_3H_6$ is a colorless liquid with an aromatic odor and physical properties that resemble those of benzene, C_6H_6


benzene


borazine


trichloroborazine

14.4 Synthesis of borazines

Stock synthesized borazine by heating the adduct of diborane with ammonia.

$$3B_2H_6+6NH_3 \longrightarrow 3\,(BH_2(NH_3)_2)\,(BH_4) \xrightarrow{\Delta} 2B_3N_3H_6+12H_2$$

More efficient of syntheses are

$$NH_4Cl + Bcl_3 \longrightarrow Cl_3B_3N_3H_3 \xrightarrow{NaBH_4} B_3N_3H_6$$

$$NH_4Cl + NaBH_4 \longrightarrow B_3N_3H_6+H_2 + NaCl$$

N or B substituted borazines may be made by appropriate substitution on the starting materials prior to the synthesis of the ring or substitution after the ring has formed

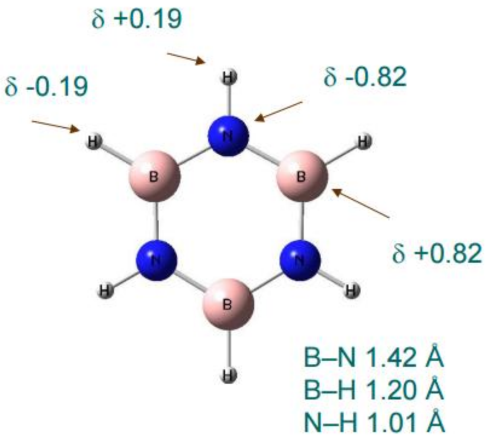
$$(R\,NH_3)\,cl + BCl_3 \longrightarrow Cl_3B_3N_3R_3 \xrightarrow{NaBH_4} H_3B_3N_3R_3$$

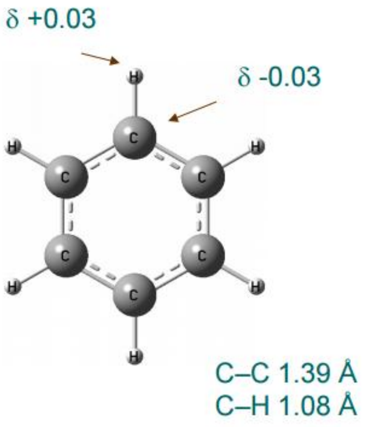
$$Cl_3B_3N_3R_3 + 3LiR' \longrightarrow R_3'B_3N_3R_3 + 3LiCl$$

Borazine is isoelectronic with benzene, as B=N is with C=C. Physical properties of borazine and benzene are similar. The physical properties of alkyl-substituted derivatives of benzene and borazine are remarkably similar. For example the ratio of the absolute boiling points of the substituted borazines to those of similarly substituted benzene is constant. This similarity led to a labeling of borazine as "Inorganic Benzene". This is a misnomer because the chemical properties of borazine and benzene are different

14.5 Structure and properties of borazine

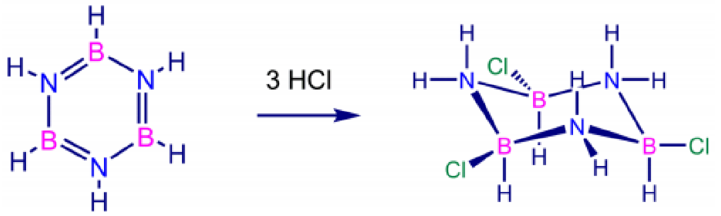
In both benzene and borazine the P electrons are delocalized over all of the ring atoms. Because of the electro negativity difference between Boron and Nitrogen, more electron density is located on the nitrogen atoms. Due to this partial localization, the π bonding is weakened in the ring. Each nitrogen receives more σ -electron density from the neighboring boron than it gives away as a π-donor.





In borazine, the difference in electronegativities of boron (2.0) and nitrogen (3.0) leads to a charge distribution which makes the B and N atoms susceptible to a nucleophilic and an electrophilic attack, respectively. Thus Borazine is much more reactive than benzene. The following are representative reactions of borazine.

1. $(HBNH)_3 + 3HCl \rightarrow (ClHBNH_2)_3$ *addition reaction*



borazine cyclotrichlorotriborazane

2. $2(ClHBNH_2)_3 + 6NaBH_4 \rightarrow 2(H_2BNH_2)_3 + 6NaCl + 3B_2H_6$ *'reduction'*

It is of interest to note that borazine resembles benzene in forming arene – metal complexes, thus the hexa methyl borazine complex- $B_3N_3(CH_3)_6Cr(CO)_3$ has been reported and closely resembles, $C_6(CH_3)_6Cr(CO)_3$ but is thermally less stable. The ring metal dissociation energy of the borazine complex is about one half that of the arene complex.

Borazine analogues of naphthalene and related hydrocarbons have been made by pyrolyzing borazine or by passing it through a silent discharge. Related four membered rings $R_2B_2M_2R_2$ and $R_4B_4M_4R_4$ are also known boron nitride ceramics has been synthesized from borazine derivative $(CH_2{=}CH)B_3N_3H_5$, which is polymarised and decomposed to give boron nitride

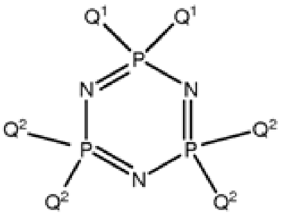
$$CH_2{=}CH\ B_3N_3H_5 \xrightarrow[125^\circ C]{\text{Borazine}} \left[CH_2-CH-B_3N_3H_5 \right]_n \xrightarrow[NH_3]{1000^\circ C} BN$$

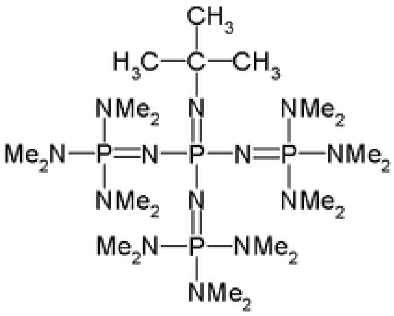
Benzene may be hydrogenated to give cyclohexane. But hydrogenationof borazine results in polymeric materials of indefinite composition. Cycloborazine $B_3N_3H_{12}$ is obtained by the reduction of the chloro derivative.

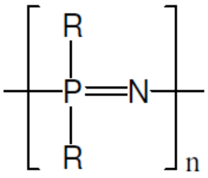
$$2\ B_3N_3H_6+6Hcl \longrightarrow 2cl_3B_3N_3H_9 \xrightarrow{6NaBH4} 2B_3N_3H_{12}+3B_2H_6+6Nacl$$

14.6 Phosphazenes

The Phosphazenes are cyclic or chain compounds that contain alternating phosphorus and nitrogen atoms with two substituents on each phosphorus atom. The three main structural types are cyclic trimer, cyclic tetramer and the oligomer or high polymer. A few cyclic pentamers and hexamers are also known. The alternating single and double bouds in the figures are written for convenience but should not be taken literally







$$\left[-\overset{R}{\underset{R}{P}}=N- \right]_n \quad n > 15000$$

Hexachlorocyclotriphosphazene $(NPCl_2)_3$, is a key intermediate in the synthesis of many other phosphazenes and is manufactured commercially on either a large or a small scale, it is readily prepared by the reaction.

$$nPcl5 + nNH_4\,cl \xrightarrow{\text{in } C_2H_2cl_4} (N\,PCl2)_n + 4n\ Hcl$$

This reaction produces a mixture of $(NPCl_2)_n$ species with n = 3,4,5 and low polymeric linear species. Favorable conditions give 90% yields of the n = 3 or 4 species, which can be separated easily

.

$$(NP\,cl_2)_3 + 6Na\ OR \text{ —— } (NP(OR)_2)_3 + 6Nacl$$

$$(NP\,cl_2)_3 + 6Na\ SCN \text{ —— } (NP(NCS)_2)_3 + 6Nacl$$

$$(NP\,F2)_3 + 6Ph\ Li \text{ —— } (NP\,Ph_2)_3 + 6Li\ F$$

The compound $(NPCl_2)_3$ undergoes substitution reactions with groups like, OH, OR, NR_2, NHR, or R, to give fully or partially substituted derivatives. Largest class of inorganic polymers because of ease of side group modification

$$P\,Br_5 \xrightarrow[\text{Excess } Br_2]{NH_4\,Br} (N\,PBr_2)_3$$

The mechanisms of these reactions are not fully understood, but in general they appear to involve S_N2 attack on 'P' by an anion. Bromo compounds may be prepared in the same manner

$$(NPCl_2)_3 + 6\ NaF \text{ —— } (NPF_2)_3 + 6Nacl$$

The fluoride may be prepared indirectly by fluorination of the chloride

14.7 Structure

Backbone comprises alternate P and N atoms. Side groups (R) can be organic inorganic or organometallic. Method of synthesis allows modification of side groups. Uses include solid electrolytes (batteries), advanced elastomers (elastic at low temperature). Aerospace and automobile applications because of resistance to hydrocarbon solvents and oils, and flame resistance. Textiles.

The halide trimers consist of planar six membered rings. The bond angles are consistent with sp^2 hybridization of the nitrogen and approximately sp^3 hybridization of the phosphorous. Two of the sp^2 or bital of nitrogen, containing one electron each, are used for 'σ' bonding and the third contains a lone pair of electron. This leaves one electron for the unhybridised p_z orbital.

The four sp^3 hybrid orbital (containing four electrons) of phosphorous are used for 'σ' bonding leaving a fifth electron to occupy a 'd' orbital. Resonance structures can be drawn like benzene ring indicating aromaticity (Fig 1.5a). The Planarity of the ring, the equal P-N bond distances and the shortness of the P-N bonds, and the stability of the compounds suggest delocalisation. All phosphazenes are not planar. This does not make them less stable. Phosphazenes are much more difficult to reduce. Unlike in benzene π-bonding in cyclophosphazenes involves d and p orbitals Craig and Paddock suggested the following model. The d_{xz} orbital of the phosphorous atom overlaps with the p_z orbital of the nitrogen atom adjacent to it (Fig 1.6a). As a result of the ‘g’ symmetry of the ‘d’ orbitals an inevitable mismatch in the signs of the wave functions occur on the trimer, resulting in a node which reduces the stability of the dolocalished molecular orbital. The d_{yz} orbital which is perpendicular to the d_{xz}, can also overlap with the pz orbital of nitrogen, but in this case no nodal surface results (Fig 1.6b). There may be in plane π-bonding between the sp^2 non bonding orbital of nitrogen and the d_{xy} and for $dx -y^2$ orbital of the phosphorous (fig 1.6c and 1.6d).

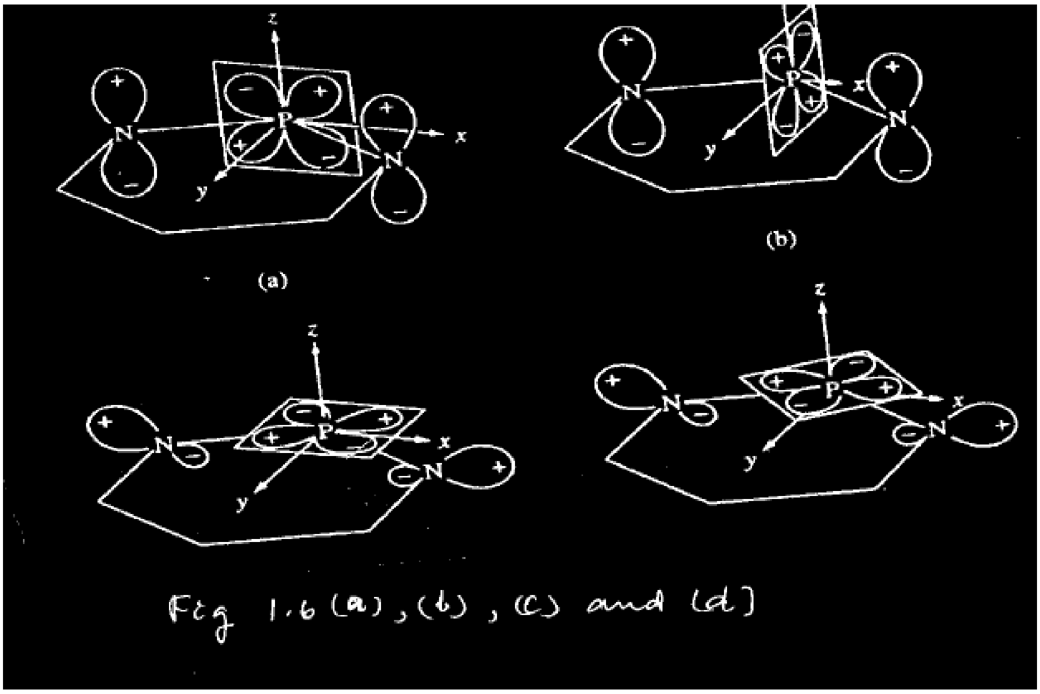


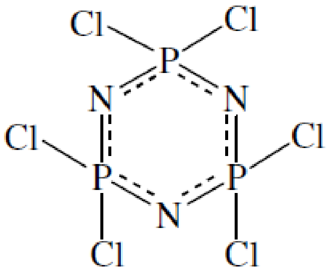
Fig 1.6 (a), (b), (C) and (d]

The structure of tetrameric phosphoazenes is more flexible than these of the trimers. The structure of $(NPF_2)_4$ is planar, but others are found in a variety of conformations (tub, boat, chair, crown, saddle and structures in between). Inter molecular forces play a major role in these structures. The use of ‘d’ orbital removes the restrictions of the Huckel rule $(4n+2)\pi$ electrons for aromaticity. Thus the model due to Craig predicts that the tetramer is stabilized by delocalisation unlike cyclo, octatetraene).

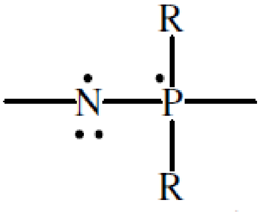
14.8 Bonding in chain

Cis and trans conformers exist and barrier to rotation about the P-N bond is very small. However, the bonding in phosphazenes is still not well understood although theories have been discussed since 1960.

Empirical observations: Phosphazenes do not exhibit alternating bond lengths but the bond length is much less than a single P-N bond (multiple bond character). This means hypervalent P.

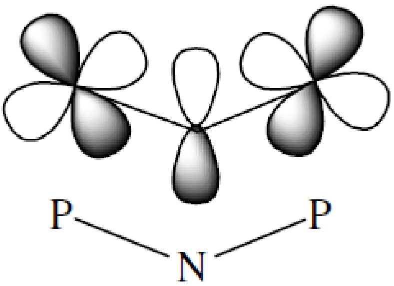


Polyphosphazenes are not coloured and do not conduct electricity that is characteristic of extensive conjugation.

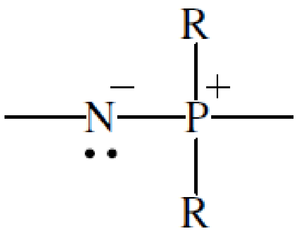


σ-framework

The problem is distribution of the remaining valence electrons. Original Dewar proposed that Phosphorus-3d orbitals are involved in bonding to give P-N-P ‘islands’ where N $2p_z$ overlap P 3d orbitals.

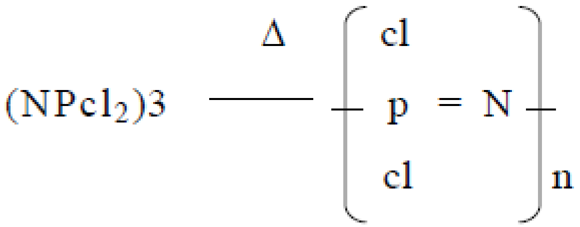


Rotation about P-N bond is low energy because N $2p_z$ can retain overlap with 3d orbitals on rotation. More recent calculations suggest ionic bonding appears to be dominant.



14.9 Phosphazene polymers

Phosphozenes can be polymerized. Their polymers have advantages overcarbon-based polymers polyolefin's and polyesters. However commercial application is not well developed as silicones $(R_2SiO)_n$. Trimericchloro phosphazenes can be polymerized thermally.



$$(NPcl_2)3 \xrightarrow{\Delta} \left[\begin{array}{c} cl \\ -p = N- \\ cl \end{array} \right]_n$$

If this is done carefully, extensive cross linking does not take place and the polymer (n = 15,000) remains stable in organic solvents, similarly

$$(PNcl_2)_n + 2n\ NaOR \longrightarrow [PN(OR)_2]_n + 2Nacl$$

$$(PNcl_2)_n + 2n\ R_2NH \longrightarrow [PN(NR_2)_2]_n + 2n\ Hcl$$

can be obtained. By varying the nature of the side chain 'R' various elastomers, Plastics, films and fibres have been obtained. They are flexible at low temperatures and water and fire resistant. Some R groups like R= CH_2CF_3 in OR group in the above reactions are water repellant and do not interact with living and promise to be useful in fabrications of artificial blood vessels and prosthetic devices.

14.10 Sulphur nitrogen compounds

Compounds which contain sulphur- nitrogen rings were known in the last century, but many new ones have been prepared in the last decade. It is currently an area of considerable interest

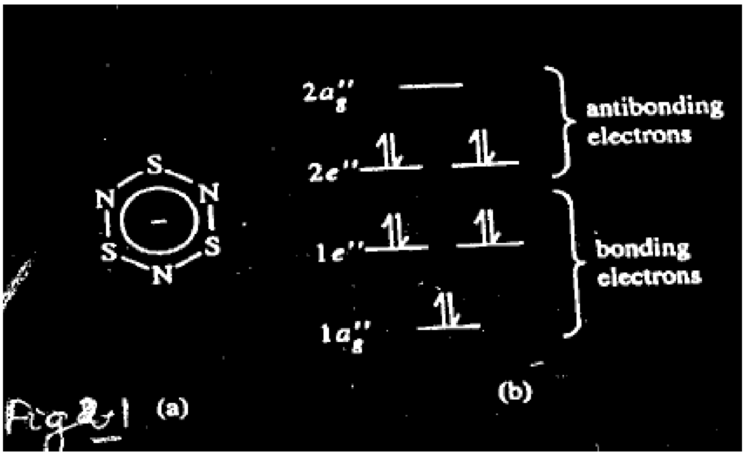
14.11 Synthesis of S_4N_4

The ammonolysis of S_2Cl_2, either in solution or in an inert solvent or heated over solid ammonium chloride yields tetra- sulphur, tetra- nitride

$$S2cl_2 \overset{NH_3}{\overline{\qquad}} S_4N_4+S_8 + NH_4cl$$

The product is a bright orange solid insoluble in water but soluble in some organic solvents. The crystals are reasonable stable to attack by air,

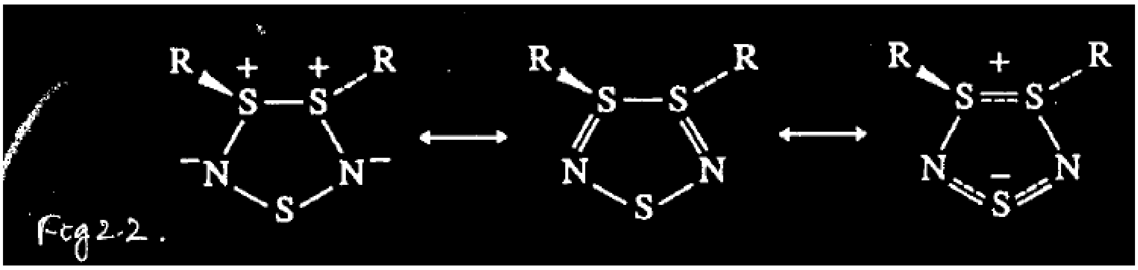
They are explosively sensitive to shock or friction. Reduction of S_4N_4 with metallic potassium or sodium oxide gives S_3N_3 (Fig 2.1a).



Reduction of S_4N_4 with Sn(II) chloride produces tetrasulphur tetraimide isoelectronic with S_8. When S_4N_4 is heated under pressure in a solution of CS_2, containing sulphur S_4N_2 is formed.

14.12 Structural studies of S-N compounds

It is impossible to write a simple Lewis structure for S_4N_4. A cage structure for S_4N_4 has been suggested. This structure contains two pairs of non-bonding sulphur atoms at a distance of about only 258pm, considerably shorter than the sum of the vanderwall's radii (360pm). All of the S-N bond distances within the ring are approximately equal (162pm) and has 12π electrons and this indicates considerable delocalisation. The molecule S_4N_2 has half-chair conformation. The molecule $S_3N^-_3$ has a planar six membered ring. It has 10π electrons instead of six (Fig 2.1b).



Still the Huckel rule is obeyed (4n+2) rule and the system is expected to be aromatic. Four of the π electrons occupy antibonding orbitals and this weakens the S-N bond. Sulphur – nitrogen compounds have often unpredictable structures, for example the compound Ph SN =

S = NSPh is considered to have resonance structures (Fig 2.2). This is based on the fact that the separation between end sulphur atoms is only 329pm (compared to vanderwal's sum of 360pm).

Polymeric sulphur nitride (also called polythiazyl), $(SN)_x$ has some physical properties of a metal. It is prepared from S_4N_4.

$$S_4N_4 \xrightarrow{Ag} S_2N_2 \longrightarrow (SN)_x.$$

The S_4N_4 is pumped in a vacuum line over silver wool at 220°C, where it polymerize slowly to a lustrous golden material. It has conductivity near that of mercury at room temperature and it becomes a super conductor at low temperatures below (O.26K). X- rays studies indicate that the SN chains have the structure shown in Fig (2.3a). This chain can be generated from adjacent square planar S_2N_2 molecules. The S-N bonds in this starting material have a bond length of 165.4pm, intermediate between single (174pm) and double (154 pm) S-N bonds.

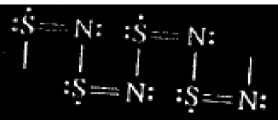


Fig 2.3 (b)

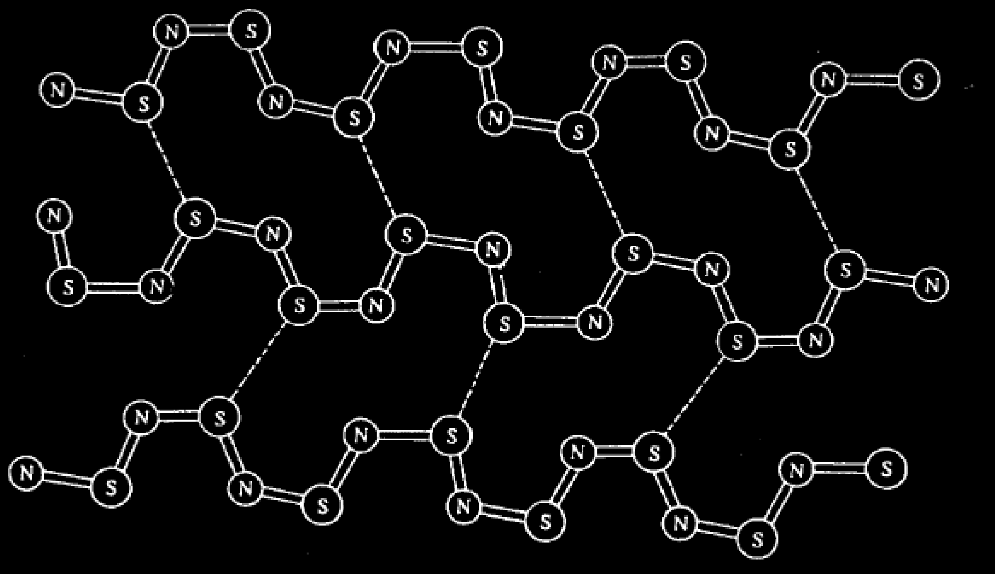
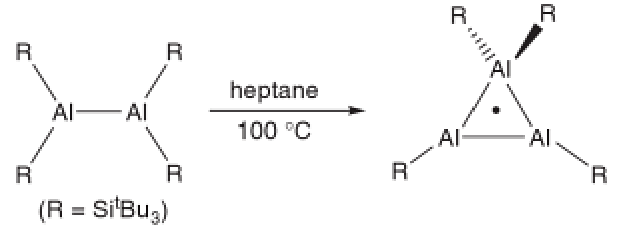
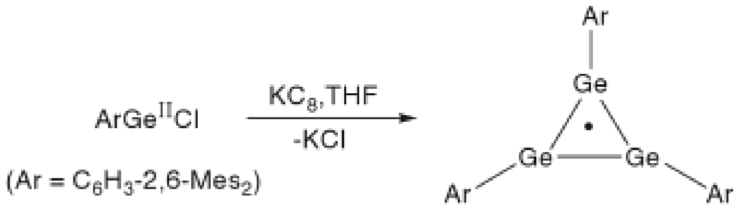


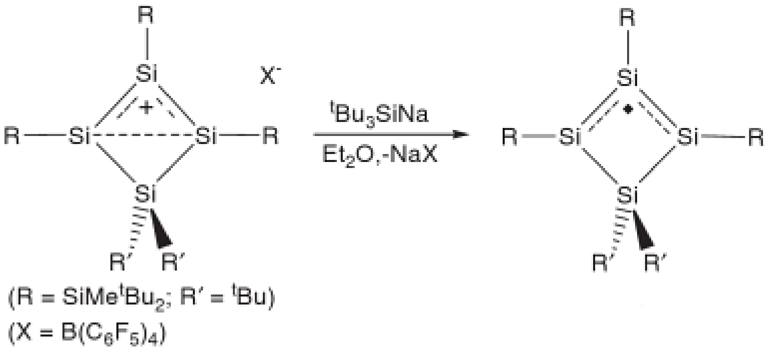
Fig 2.3(a) $(SN)_x$ chains in one layer of polymers sulphurnitride

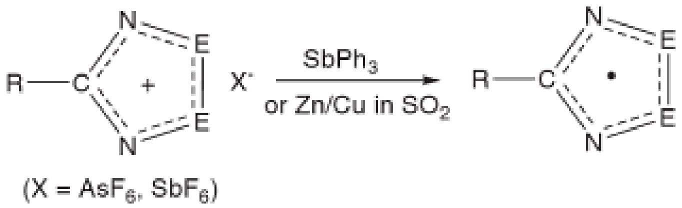
For the $(SN)_x$ chain many resonance structures can be drawn. The single structure (Fig 2.3 b) has single bond double bond resonance system, with nine electrons on each sulphur atom. Every S-N unit has thus one antibonding π* electron. The half filled over lapping π*orbitals will combine to form a half- filled conduction band in much the same way as half- filled 2s orbitals on a mole of Lithium atoms, form a conduction band. This conduction band lies only along the direction of the $(SN)_x$ fibres, the polymer is thus a one dimensional conductor

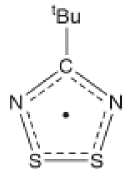
The three membered ring $[Al_3R_3]$ (R = Si $^tBu_3$) provides an example of ability of bulky substituents to stabilize cyclic radicals of the main group elements in ring



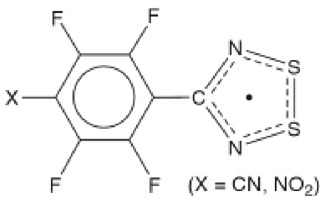








Paramagnetic liquid



Ferromagnetic

14.13 Summary of the unit

Silicones contain Si–O–Si linkages and Si–C bonds. Naturally, the synthetic routes involve formation of one or both of the two. Formation of Si–O–Si linkage is simple and is achieved through condensation of two Si–OH bonds (as in the case of formation of silicates from hydrolysis product of $SiCl_4$). The first step in synthesis of silicones naturally, involves putting 'R' groups (R = – CH_3, –C_6H_5) on the tetrahedral Si atom. Care is taken to have at least one 'X' (X = Cl) on this atom so that it could be substituted by hydrolysis. Subsequent condensation through Si–OH bonds generate Si–O–Si linkage. Phosphazenes were initially termed phosphonitrilic polymers. Later on, the new term was used to represent phosphorus, nitrogen (= azo) and P = N double bonds (= ene) which are always present in these polymers. They are thus 'unsaturated PN compounds' containing phosphorus, mostly in +V state. As is usual with polymers, they may have cyclic or chain structure. Their polymers differ in substitution on phosphorus and on the nature of those substitutents besides the way and the extent, to which polymerization has taken place. Their water repellent, solvent resistant and flame resistant properties have found new applications and these have led to many technological innovations during the last few decades. They are usually classified on the basis of number of phosphazene units that are incorporated in the structure.

14.14 Key words

Borazines; Phosphazenes; Sulphur nitrogen compounds; Synthesis of S_4N_4

14.15 References for further studies

1) Inorganic Rings and Polymers of the P-block Elements: From Fundamentals to Applications; Tristram Chivers, Ian Manners; *Royal Society of Chemistry (Great Britain);* **2009.**

2) Cyclic Polymers; E.R. Semlyen; *Springer Science & Business Media*, **2007**.

3) Concise Inorganic chemistry – J.D.Lee 5th edition

4) Inorganic chemistry – Huhecy et al Pearson Education – Asia.

14.16 Questions for self understanding

1) How are different types of phosphazenes syntherised?

2) Compare the properties of borazine and benzene, on the basis of their structures.

3) How would $B_3P_3(Ph)_3$ react with Br_2?

3) Write a note on molecular species containing B-N bonds

4) What are borazines?

5) Explain the different methods of synthesis of borazines

6) Discuss the structure borazines

7) What are phosphazenes?

8) Discuss the structure phosphazenes

9) What type of bonding is presesen in phosphazenes chain?

10) Write a note on phosphazene polymers

11) Write a note on sulphur nitrogen compounds

12) Explain the different methods for Synthesis of S_4N_4

13) Discuss the structural studies of S-N compounds

UNIT-15

Structure

15.0 Objectives of the unit

15.1 Introduction

15.2 cages

15.3 Boron cages

15.4 Carboranes

15.5 Metallo carborane

15.6 Synthesis of Metallo carborane

15.7 Examples of Metallo carborane

15.8 Comparison of Metallo carborane with Metallocenes

15.9 Summary of the unit

15.10 Key words

15.11 references for further study

15.12 Questions for self understanding

15.0 Objectives of the unit

After studying this unit you are able to

- Identity the elements which form cages
- Explain the different boron cages
- Explain the synthesis and applications of carboranes
- Explain the applications of metallo carborane
- Explain the synthesis of Metallo carborane

15.1 Introduction

Boron clusters with more than 12 vertices showing a very rich and diverse chemistry were confined to the 13- and 14-vertex metallacarboranes until 2003. Very recently, significant progress in the syntheses of 13- and 14-vertex carboranes has been made, leading to the preparation of 15-vertex metallacarboranes. These studies open up new possibilities for the development of polyhedral clusters of extraordinary size.

15.2 cages

The bonding and structures of boranes are of great interest. They are different from all other hydrides. These compounds are electron deficient. Diborane (B_2H_6) has 12 valency electrons (3 from B and 6 from H atoms). Electron diffraction studies indicate that the compound has B-H-B bridges. The two bridging H-atoms are in a plane perpendicular to the rest of the molecule, and prevent rotation between the two 'B' atoms. Specific heat measurements confirm that the rotation is hindered. Four of the H- atoms are in a different environment than the other two. This is confirmed by Raman spectra and by the fact that diborane cannot be methylated beyond $Me_4B_2H_2$, without breaking the molecule into BMe_3. The terminal B- H distances are the same. These are assumed to be normal covelant bonds. These are (2C-2e) two centre- two electron bonds. The structure is shown in fig 1. Each of the bridging B-H- B linkages then involves a delocalised three centre bonds. Each 'B' is sp^3 hybridised.

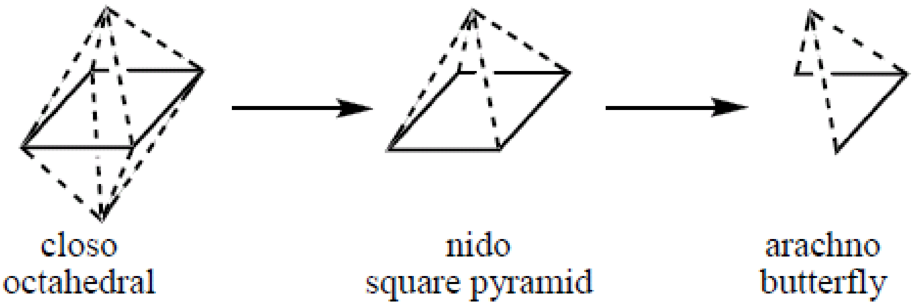
15.3 Boron cages

The boron atoms will form a shape by occupying vertices on a polyhedron (e.g. for 4 B atoms the polyhedron can be a tetrahedron), whether or not the boron atoms are actually bound to each other. This arrangement is frequently called a "cage." .

Closo- refers to the most symmetrical possible arrangement, a closed polyhedron (e.g. 6 B atoms form an octahedron, see figure below).

Nido- comes from the next higher *closo*- polyhedron with the most highly connected boron vertex removed (e.g. for 5 B atoms, an octahedron less any one vertex to yield a square pyramid). *Arachno*- comes from the next higher *nido*- structure with the most highly connected boron vertex on the open face removed (e.g. for 4 B atoms, a square pyramid less any basal vertex to yield a butterfly structure).

The words *closo*-, *nido*-, and *arachno*- are derived from words meaning "closed" (Greek), "nest" (Latin), and "spider's web" (Greek). A large number of examples are shown on p. 799 of Huheey, Keiter, and Keiter.



15.4 Carboranes

Carboranes are cage compounds composed of two carbons (the dots) and 10 borons (the other vertices of the cage). In the parent carborane there is a hydrogen (or another substituent) on every vertex.

$$B_{10}H_{14} + R\text{-}C \equiv C\text{-}R \text{ —— } R_2C_2B_{10}H_{10} + 2H_2$$

This molecule in question is called 1,2-dehydro-o-carborane and is the carborane version of benzyne or 1,2-dehydrobenzene. Two hydrogens have been removed to make a strained high energy pi bond. Henry Gingrich came up with the following synthesis (following a route I thought had little chance).

$$\text{closo} - C_2B_9H_{11} + 2e \text{ —— } [\text{nido} - C_2B_9H_{11})^{2-}$$

$$[\text{nido} - C_2B_9H_{11}]^{2-} \text{ —— } [\text{closo} - C_2B_9H_{11}) + 2e$$

The systems $C_2B_{10}H_{12}$ is isoelectronic with $[B_{12}H_{12})^{2-}$ and can be synthesized from decarborane and alkynes using diethyl sulphide as solvent

$$2[C_2B_9H_{11}]^{2-} + Fecl_2 \text{ —— } [(C_2B_9H_{11})_2Fe]^{2-} + 2cl\text{-}$$

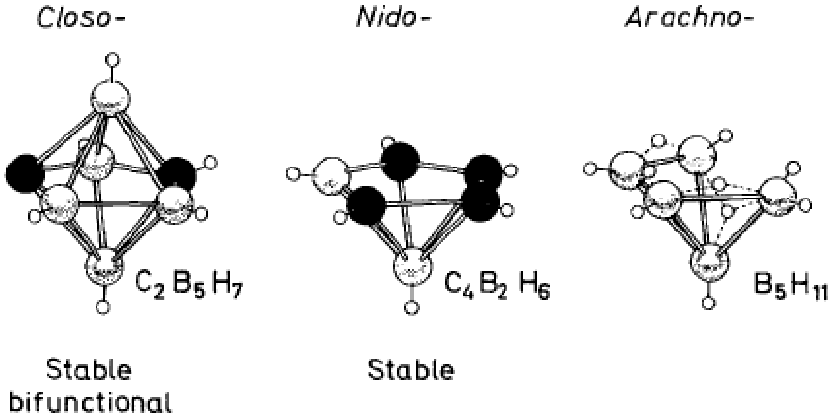
The acetylene may be unsubstituted or substituted, in which case, the compound is known as 1,2 –dicarba-closo-dodeca borane or orthocarborane and is isoelectronic and iso structural with $[B_{12}H_{12})^{2-}$. It is stable to both heat and air, but it isomerises at high temperatures to the 1,7 (meta or 'neo' isomer) and the 1,12 (Para isomer). The mono carboranes are known in closo, nido and arachno structures. In the anion $[C_2B_9H_{11}]^{2-}$, each of the three 'B' atoms and the two carbon atoms on the open face of the cage directs an orbital (sp^3) toward the apical position occupied formerly by the 12th boron atom. Further these orbitals contain a total of six electrons.

Hence this anion $[C2B_9H^{11}]^{2-}$ has a resemblence to cyclopentadiendeanion. This anion could be considered isoelectronic with C_5H_5 - and should be capable of acting as a π ligand in metallocene compounds. Hawthorne succeeded in synthesizing metalla carboranes

This has structure similar to ferrocene

The field of carborane (including borane) chemistry may be divided into three parts, *closo* carboranes, *nido*-carboranes, and *arachno*-carboranes which may be generalized as

$C_{0-2}B_nH_{n+2}$, $C_{0-4}B_nH_{n+4}$ and $C_{0-6}B_nH_{n+6}$ with respect to their empirical formulae



Examples of the three carborane classes.

15.5 Metallo carborane

Supramolecular systems composed of organic or metal-organic building-block units that are connected by strong covalent bonds are of interest because of their potential for creating “designer materials” having tailorable electronic, optical, magnetic, catalytic, or other properties. Metal-containing supramolecular systems are particularly interesting, since the metal centers may function as tunable electrophores or chromophores. Metallacarboranes are a “natural” for this kind of designer chemistry, given their oxidative and thermal stability, and the small systems (six-vertex nido-MC_2B_3 and seven-vertex closo-MC_2B_4clusters) offer certain additional advantages: They are similar in steric requirement to metallocenes and hence can more easily replace metal-cyclopentadienyl moieties in organometallic systems; the presence of only three or four boron vertices limits the number of possible isomers of B-functionalized derivatives, simplifying the directed synthesis and isolation of specified target compounds;nido-MC_2B_3. In these compounds the metal and the polyhedral boranes can either be connected by direct bonding or ionic. A lot of them have similar sompund structure as the carboranes.

Most metal derivatives of carborane have he metal directly bonded to the boron atom some polyhedral derivatives will do as well. It is usually the nido structures that bond with metal. Metallocarborane system is usually more stable tahe metallocene system. Metal derivatives of polyhedral borane and carborane have wide applications in catalysis chemistry, organic synthesis and medicine etc…

15.6 Synthesis of Metallo carborane

A. Coordination using nido-caborane anion as ligands (1965)

$$2C_2B_9H_{11}{}^{2-} + Fe^{2+} \xrightarrow{\text{thf}} \underset{(82)}{[Fe^{II}(\eta^5\text{-}C_2B_9H_{11})_2]^{2-}}$$

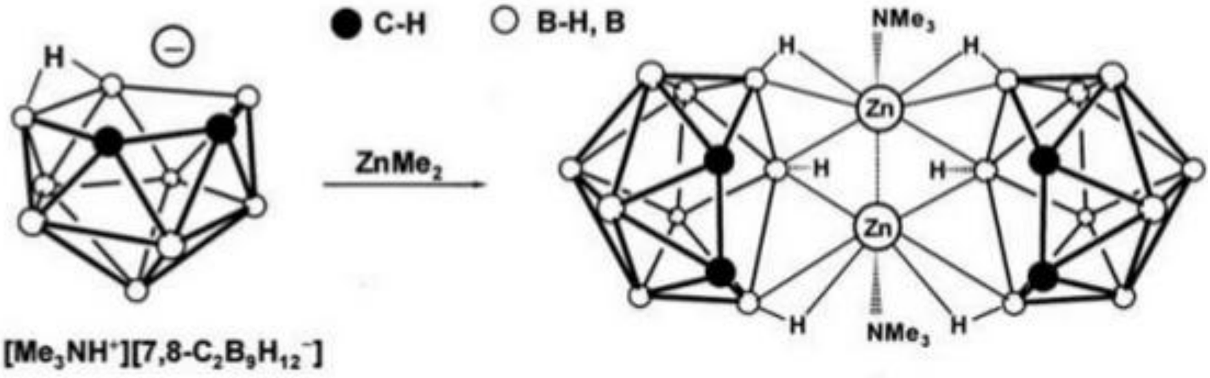
$$\underset{+e^-}{\overset{\text{air}}{\rightleftharpoons}} [Fe^{III}(\eta^5\text{-}C_2B_9H_{11})_2]^-$$

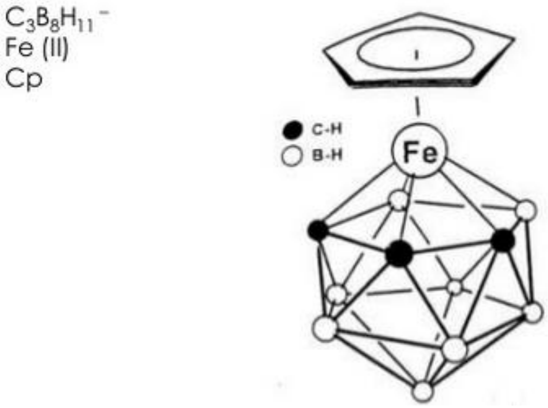
A. Polyhedral Expansion

$$2[\mathit{closo}\text{-}C_2B_{n-2}H_n] \xrightarrow[\text{thf}]{4Na/C_{10}H_8} 2[\mathit{nido}\text{-}C_2B_{n-2}H_n]^{2-}$$

$$\xrightarrow{M^{m+}} [M(C_2B_{n-2}H_n)_2]^{(m-4)+}$$

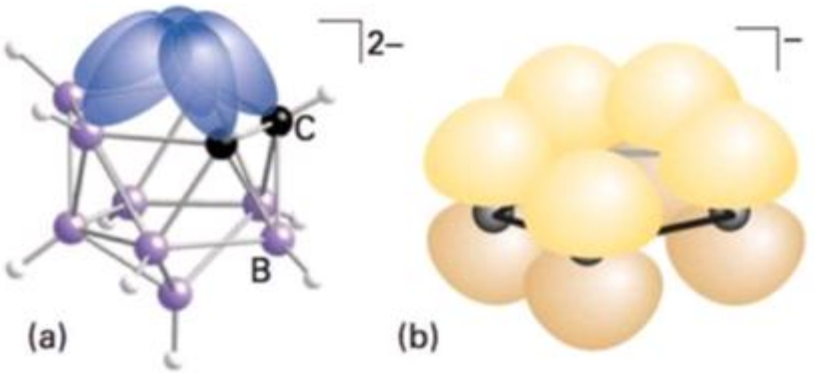
15.7 Examples of Metallo carborane





15.8 Comparison of Metallo carborane with Metallocenes

It is generally accepted that the anion a usually works much more efficiently than anion b. Therefore the bonding in metalocarbenes are stronger than in metallocenes and thus more stable than in metallocenes and thus more stable than metallocences



a. $C_2B_9H_{11}{}^{2-}$ anion

b. $C_5H_5^-$

15.9 Summary of the unit

A carborane is a cluster composed of boron, carbon and hydrogen atoms. Like many of the related boranes, these clusters are polyhedra and are similarly classified as closo-, nido-, arachno-, hypho-, etc. based on whether they represent a complete (closo-) polyhedron, or a polyhedron that is missing one (nido-), two (arachno-), or more vertices.

Interesting examples of carboranes are the extremely stable icosahedral closo-carboranes. These boron-rich clusters exhibit unique organomimetic properties with chemical reactivity matching classical organic molecules, yet structurally similar to metal-based inorganic and organometallic species.

A prominent example is the charge-neutral $C_2B_{10}H_{12}$ or o-carborane with the prefix o derived from ortho, which has been explored for use in a wide range of applications from heat-resistant polymers to medical applications. The electronic structure of these compounds is best described by Wade-Mingos rules for cluster molecules. Another important carborane is carborane acid, a chlorinated superacid $H(CHB_{11}Cl_{11})$, which has an anion structure.

15.10 Key words

Cages; Boron cages; Carboranes; Metallo carborane

15.11 references for further study

1) Inorganic Rings and Polymers of the P-block Elements: From Fundamentals to Applications; Tristram Chivers, Ian Manners; *Royal Society of Chemistry (Great Britain);* **2009.**

2) Cyclic Polymers; E.R. Semlyen; *Springer Science & Business Media*, **2007**.

3) Concise Inorganic chemistry – J.D.Lee 5th edition

4) Inorganic chemistry – Huhecy et al Pearson Education – Asia.

15.12 Questions for self understanding

1) What are cages
2) Explain the bonding in different types of boron cages
3) What are carboranes
4) Discuss the different method of synthesis of carboranes
5) Mention the applications of carboranes
6) What are metallo carborane
7) Explain the synthesis of Metallo carborane
8) Compare the Metallo carborane with Metallocenes

15.9 Summary of the unit

UNIT-16

Structure

16.0 Objectives of the unit

16.1 Introduction

16.2 inter halogen compounds

16.3 Types of inter halogen compounds

16.4 Diatomic interhalogens

16.5 Tetra-atomic interhalogens

16.6 Hexa-atomic interhalogens

16.7 Octa-atomic interhalogens

16.8 Preparations of Interhalogen compounds

16.9 Structures of interhalogen compounds

16.10 Polyhalide ions

16.11 Halogen oxides

16.12 Halogen Oxoacids and Oxoanions

16.13 Pesudohalides and Pseudohalogens

16.14 Similarities between halide ions and pseudohalide ions.

16.15 Dissimilarities between halide ions and pseudohalide ions

16.17 Similarities between halogens and Pseudohalogens.

16.18 Dissimilarity between halogens and Pseudohalogens

16.19 Summary of the unit

16.20 Key words

16.21 References for further studies

16.22 Questions for self understanding

16.0 Objectives of the unit

After studying this unit you are able to

- Recognize the Inter halogen compounds
- Identify the types of inter halogen compounds
- Explain the preparations of interhalogen compounds
- Write the structures of interhalogen compounds
- Recognize the polyhalide ions
- Recognize the halogen oxides
- Recognize the pesudohalides and Pseudohalogens

16.1 Introduction

The compounds which are formed by the union of two different halogens are called inter halogen compounds. There are never being a more than two types of halogen in a molecule. Inter halogen compounds are of 4-types.

AX- type : ClF, BrF, BrCl, ICl, IBr,

AX3-type: ClF_3, BrF_3, $(ICl_3)_2$,

AX5-type: ClF_5, BrF_5, IF_5,

AX7-type: IF_7.

The inter halogen compounds of type AX and AX_3 are formed between the halogen having very low electronegative difference. Examples: ClF, ClF_3.

The inter halogen compounds of type AX_5 and AX_7 are formed by larger atoms having low electronegativity with the smaller atoms having high electronegativity . This is because it is possible to fit the greater number of smaller atom around a larger one. Examples: BrF_5, IF_7.

The inter halogens are generally more reactive than halogens except F. This is because A-X bonds in inter halogen compounds are weaker than X-X bond in halogen molecules. Reaction of inter halogens are similar to halogens. Hydrolysis of interhalogen compounds give halogen acid and oxy-acid.

16.2 inter halogen compounds

Interhalogen compounds are the derivatives of halogens. Compounds containing two different types of halogens are called interhalogen compounds. Example,chlorine monofluoride, bromine trifluoride, iodine pentafluoride, iodine heptafluoride…etc

The halogens react with each other to form interhalogen compounds. The general formula of most interhalogen compounds is XYn, where n = 1, 3, 5 or 7, and X is the less electronegative of the two halogens. They are all prone to hydrolysis, and ionise to give rise to polyatomic ions

16.3 Types of inter halogen compounds

Depending on the number of atoms in the molecule interhalogens are classified into four types.

They are

- i) AX
- ii) AX_3
- iii) AX_5
- iv) AX_7

A' is larger (or) less electronegative halogen and 'X' is smaller (or) more electronegative halogen. Number of atoms in a molecule can be known with the radius ratio. (Radius Ratio = Radius of larger halogen atom / Radius of smaller halogen atom). As the radius ratio increases the number of atoms per molecule also increases. So among interhalogen compounds Iodine heptafluoride has largest no of atoms per molecule as it has highest radius ratio.

16.4 Diatomic interhalogens

The interhalogens of form XY have physical properties intermediate between those of the two parent halogens. The covalent bond between the two atoms has some ionic character, the less electronegative element, X, being oxidised and having a partial positive charge. Most combinations of F, Cl, Br and I are known, but not all are stable.

Chlorine monofluoride (ClF)

The lightest interhalogen compound is ClF. It is a colorless gas with a normal boiling point of -100^0C.

Bromine monofluoride (BrF)

BrF has not been obtained pure becuase it dissociates into the trifluoride and free bromine quickly

Iodine monofluoride (IF)

IF is unstable and decomposes at 0^0C, disproportionating into elemental iodine and iodine pentafluoride.

Bromine monochloride (BrCl)

A red-brown gas with a boiling point of ^0C.

Iodine monochloride (ICl)

Red transparent crystals which melt at 27.2^0C to form a choking brownish liquid (similar in appearance and weight to bromine). It reacts with HCl to form the strong acid $HICl_2$. The crystal structure of iodine monochloride consists of puckered zig-zag chains, with strong interactions between the chains.

Iodine monobromide (IBr)

Made by direct combination of the elements to form a dark red crystalline solid. It melts at 42^0C and boils at 116^0C to form a partially dissociated vapour.

16.5 Tetra-atomic interhalogens

Chlorine trifluoride (ClF_3)

It is a colourless gas which condenses to a green liquid, and freezes to a white solid. It is made by reacting chlorine with an excess of fluorine at 250^0C in a nickel tube. It reacts more violently than fluorine, often explosively. The molecule is planar and T-shaped. It is used in the manufacture of uranium hexafluoride.

Bromine trifluoride (BrF_3)

It is a yellow green liquid which conducts electricity Å it ionises to form $[BrF_2^+]+[BrF_4^-]$. It reacts with many metals and metal oxides to form similar ionised entities; with some others it forms the metal fluoride plus free bromine and oxygen. It is used in organic chemistry as a fluorinating agent. It has the same molecular shape as chlorine trifluoride.

Iodine trifluoride (IF_3)

It is a yellow solid which decomposes above -28^0C. It can be synthesised from the elements, but care must be taken to avoid the formation of IF_5. F_2 attacks I_2 to yield IF_3 at -45^0C in CCl_3F. Alternatively, at low temperatures, the fluorination reaction $I_2 + 3XeF_2 \rightarrow 2IF_3 + 3Xe$ can be used. Not much is known about iodine trifluoride as it is so unstable.

Iodine trichloride (ICl_3)

It forms lemon yellow crystals which can be melted under pressure to a brown liquid. It can be made from the elements at low temperature, or from iodine pentoxide and hydrogen chloride. It reacts with many metal chlorides to form tetrachloriodides, and hydrolyses in water. The molecule is a planar dimer, with each iodine atom surrounded by four chlorine atoms.

16.6 Hexa-atomic interhalogens

Chlorine pentafluoride (ClF_5)

It is a colourless gas, made by reacting chlorine trifluoride with fluorine at high temperatures and high pressures. It reacts violently with water and most metals and nonmetals.

Bromine pentafluoride (BrF_5)

It is a colourless fuming liquid, made by reacting bromine trifluoride with fluorine at 200^{0}C. It is physically stable, but reacts violently with water and most metals and nonmetals.

Iodine pentafluoride (IF_5)

It is a colourless liquid, made by reacting iodine pentoxide with fluorine, or iodine with silver fluoride. It is highly reactive, even slowly with glass. It reacts with elements, oxides and carbon halides. The molecule has the form of a tetragonal pyramid.

16.7 Octa-atomic interhalogens

Iodine heptafluoride (IF_7)

It is a colourless gas. It is made by reacting the pentafluoride with fluorine. IF_7 is chemically inert, having no lone pair of electrons in the valency shell; in this it resembles sulphur hexafluoride. The molecule is a pentagonal bipyramid. This compound is the only interhalogen compound possible where the larger atom is carrying seven of the smaller atoms.

All attempts to form bromine heptafluoride have met with failure; instead, bromine pentafluoride and fluorine gas are produced.

Fluorine being smallest than all other halogens can't act as the center. Majority of Inter halogen compounds are formed by Br and I, which combine with small size atoms such as fluorine, since it is possible to associate more small size atoms around a large central atom. Your text book is right, more electronegative atoms are smaller in size, as like fluorine.

16.8 Preparations of Interhalogen compounds

These compounds are prepared by two methods.

By direct combination of Halogens and by reaction of Halogens with lower Interhalogen compounds.

(i) Halogen molecules react directly to form interhalogen compound

Ex: Equal volumes of chlorine and fluorine combine at 473K to form chlorine monofluoride.

(ii) A halogen molecule reacts with a lower interhalogen to form a new interhalogen compound.

Ex: Fluorine reacts with iodine pentafluoride at 543K to form Iodine Heptafluoride

Physical properties

Interhalogen compounds exist in gaseous state, liquid state (or) solid state. Most of these compounds are volatile solids (or) liquids at 298K while remaining are gases.

For example chlorine monofluoride is gas while bromine trifluoride and iodine trifluoride are existing in liquid and solid state respectively.

All these compounds are covalent in nature due to less electronegativity difference between bonded atoms.

Ex: Chlorine monofluoride, Bromine trifluoride , Iodine heptafluoride are covalent.

All these compounds are Diamagnetic in nature as they have only lone pairs and bond pairs.

Interhalogen compounds are more reactive than constituent halogens (except fluorine). This is because A-X bond in interhalogens is weaker than X-X bond in halogens except F-F bond.

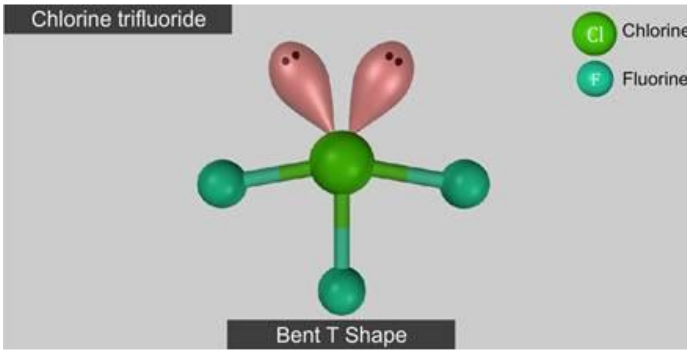
16.9 Structures of interhalogen compounds

Structures of these different types of inter halogens are different from one another which can be explained using V.S.E.P.R Theory.

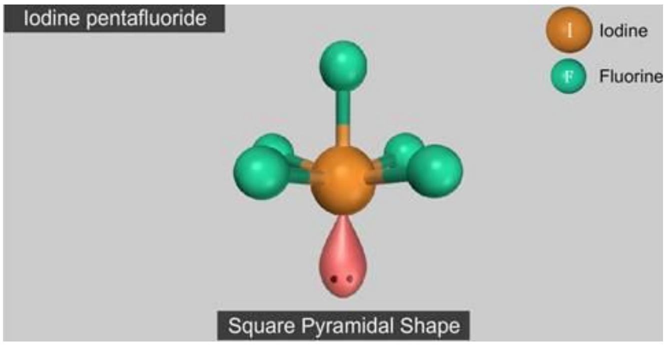
In chlorine trifluoride the central atom chlorine has seven electrons in the valence shell. Three of these will form three bondpairs with three fluorine atoms leaving four electrons.

According to V.S.E.P.R theory these will occupy corners of trigonal bipyramid. The lone pairs will occupy the equatorial positions while bond pairs will occupy the other three positions.

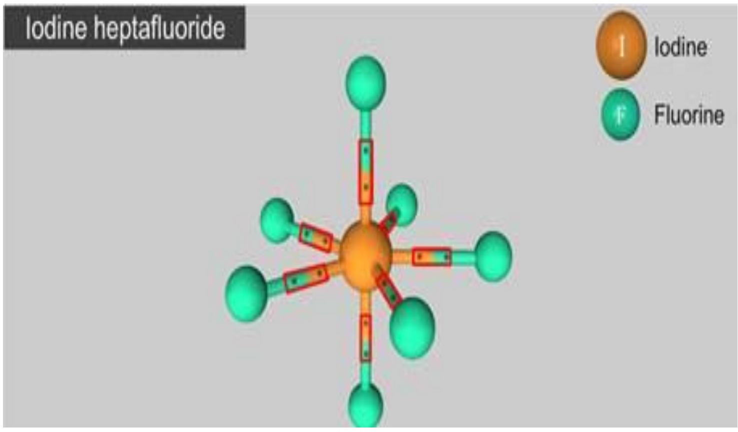
To minimize the lone pair- lone pair repulsions the axial bond pairs will bend towards the equatorial positions. Hence its shape is bent T-shape.



In Iodine pentafluoride the central atom has five bond pairs and one lone pair hence shape is square pyramidal



In Iodine heptafluoride the central atom has seven bond pairs so it has pentagonal bipyramidal shape



16.10 Polyhalide ions

Halogens or interhalogens combine with halide ions to form polyhalide ions. The most common example of polyhalide ion formation is furnished by the increase in solubility of iodine in water in the presence of which is due to the formation of tri iodide ion, I^{-3}

$$I^{-} + I^{2} \longrightarrow I^{-3}$$

Many other examples of polyhalides ions are

(i) Cl^{3-}, Br_3^-, ICI_2^-, IBr_2^- including I^{3-}. In these ions, one of the halogen atoms (in case of similar atoms) or halogen atom larger in size undergoes sp_3d-hybridization giving a linear shape with three lone pairs at equatorial positions.

(ii) Cl_3^+, Br_3^+, I_3^+, ICI_3^+, IBr_2^+ Here we find central atom sp^3 hybridized giving a bent shape with two lone pairs of electrons on the central atom.

(iii) ICI_4^-, BrF_4^-, I_3^-. Here central atom involves sp^3d^2 hybridization giving square planar shape with two lone pairs of electrons on axial positions.

(iv) ICI_4^-, BrF_4^-, I_5^-. In these ions central atom involves sp^3d hybridization giving a distorted tetrahedral structure with one lone pair of electrons on equatorial position.

(v) I_7^-, IF_6^+. The central I atom undergoes sp^3d^3 hybridization giving a distorted octahedral structure with one lone pair of electrons.

(vi) I_7^+, Here central I atom involves sp^3d^2 hybridization giving an octahedral structure.

Fluorine due to its highest electronegativity (and only –1 oxidation state) does not form polyhalide ions where it acts as a central atom.

16.11 Halogen oxides

The halogens form a range of compounds with oxygen, but many of these are unstable. Oxides are formed in the range E_2O to E_2O_7. Oxoacids are formed in the range HOE to $HOEO_3$ (there is only HOF with fluorine). Oxoanions are formed in the range EO^- to EO_4^- Fluorine forms two compounds with oxygen.

Oxygen difluoride, OF_2

It is formed from the reaction of F_2 with hydroxide ions, and has the C_{2v} structure of water as predicted by VSEPR. *Dioxygen difluoride, FOOF*

It is produced by photolysis of a mixture of F_2 and O_2, and is a very good fluorinating agent, example, in the fluorination of Plutonium.

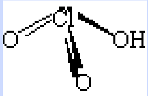
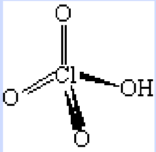
reparation of OF_2: $2F_{2\,(g)} + 2OH^-_{(aq)} \rightarrow OF_{2\,(g)} + 2F^-_{(aq)} + H_2O_{(l)}$

Oxidation of Plutonium: $Pu_{(s)} + 3O_2F_{2\,(g)} \rightarrow PuF_{6\,(g)} + 3O_{2\,(g)}$

ClO_2 is used as a bleaching agent and disinfectant when used in dilute solutions. The oxidizing properties of Cl^{IV} make it useful for these purposes.

16.12 Halogen Oxoacids and Oxoanions

The structure of the oxoacids of the halogens can be used to predict their acidities, using Pauling's rule, ie. $pK_a = 8\text{-}5p$ for the acid $(O)_pE(OH)_q$. The usefulness of this relationship can be seen in the oxoacids of chlorine.

HOCl	**hypochlorite**	Cl—OH	**p = 0:** 8-5p = 8	**pK_a = 7.53**
HOClO	**chlorite**		**p = 1:** 8-5p = 3	**pK_a = 2.00**
$HOClO_2$	**chlorate**		**p = 2:** 8-5p = -2	**pK_a = -1.2**
$HOClO_3$	**perchlorate**		**p = 3:** 8-5p = -7	**pK_a = -10**

The pKa of HIO_6 is only 3.29, and this seems high, but if one looks at the structure, we see that it is $(HO)_5IO$, and so p =1 and the pKa is predicted to be 3. The rule is therefore fairly accurate, and can also be used as a tool for predicting the structure.

It can be seen that $HClO_4$ is a very strong acid, and so the conjugate base, ClO_4^-, is a very weak base. It is also a very poor Lewis base, and does not form complexes. However, it is also a strong oxidizing agent, and solid perchlorate compounds can form metastable complexes which are explosive. The oxidizing power of the halogen oxoanions leads to the instability of HOF. Above -40°C, it reacts with water to give HF and hydrogen peroxide. The XO^- ion is also prone to disproportionation.

$$HOF + H_2O \rightarrow HF + H_2O_2$$

$$3XO^- \rightarrow XO_3^- + 2X^-$$
$$4XO_3^- \rightarrow 3XO_4^- + X^-$$

16.13 Pesudohalides and Pseudohalogens

There are certain uni-negative groups (e.g CN^-, OCN^-, N_3^- etc) which are made up of two or more electronegative atoms and resembles halide ions in some respects. These uni-negative groups or ions are called pseudohalide ions. Examples of some important pseudohalide ions are: Cyanide ion (CN^-), isocyanide ion (NC^-), fulminate ion (ONC^-), cyanate or oxy-cyanide ion (OCN^-), isocyanate ion (NCO^-), thiocyanate ion (SCN^-), isothiocyanate ion (NCS^-), tellurocyanate ion ($TeCN^-$), selenocyanate ion ($SeCN^-$), isoselenocyanate ion ($NCSe^-$), azide ion (N_3^-), azidothiocarbonate ion or azido carbondisulphide ion ($SCSN^-_3$). The salt (ionic compounds) containing pseudohalide ions (e.g AgCN, Pb $(CNS)_2$ etc.) are called Pseudohalides.

As the dimers of halide ions are called halogens the covalent dimers of the pseudohalide ions are called Pseudohalogens or halogenoids. So for only a limited number of Pseudohalogens, has been isolated and characterised. Examples of some pseudohalogen or halogenoids are cyanogen, $(CN)_2$: oxy-cynogen $(OCN)_2$; thiocynogen $(SeCN)_2$; azidocarbon disulphide $(SCSN_3)_2$.

16.14 Similarities between halide ions and pseudohalide ions.

Following are important similarities between halide ions and pseudohalide ions:

1. **Formation of ionic as well as covalent compounds.** Like halide ions, pseudohalide ions also from ionic as well as covalent compounds. Ionic compounds are given by these ions with metals while covalent compounds are given by the combinations of these ions with non metals or metalloids. Examples are

Ionic compounds : AgCl (AgCl), $PbCl_2$ [$Pb(CNS)_2$], AgCl (HgCNS).

Covalent Compounds: ICl(ICN), $SiCl_4$[$Si(NCS)_4$] $COCl_2$[$CO(N_3)_2$], SO_2Cl_2[$SO_2(N_3)_2$ ions

2. **Oxidation of hydracids.** HX acids (X=Cl^-, Br^-, I^-) can be oxidised to free halogen (X_2). Similarly HY acids (Y=SCN CN etc.) can also be oxidised to free Pseudohalogens (Y_2). For example:

$4HCl+MnO_2 \rightarrow MnCl_2+H_2O+Cl_2$; $4HSCN+MnO_2 \rightarrow Mn(SCN)_2+2H_2O+(SCN)_2$

3. **Thermal decomposition of Pb (IV) salts.** On heating some of the Pb (IV) salts of halide ions (e.g $PbCl_4$) decompose to give Pb(II) salts and free halogen molecule. Similarly some Pb (IV) salts of pseudohalide ions [e.g $Pb(SCN)_4$, $Pb(SeCN)_4$] decompose to give Pb(II) salts and free psedohalogens. For example

$$PbCl_4 \xrightarrow{\Delta} PbCl_2 + Cl_2 \quad Pb(SCN)_4 \xrightarrow{\Delta} Pb(SCN)_2 + (SCN)_2$$

4. **Formation of complex ions.** Like halide ions, psedohalide ions also form complex ions with transition metal ions. Example are given below:

   Complex ions given by halide ions: $[FeF_6]^{3-}$, $[CoCl_4]^{2-}$, $[HgI_4]^{2-}$

   Complex ions given by pseudohalide ions: $Fe(CN)_6]^{3-}$, $[Co(SCN)_4]^{2-}$, $[Hg(CN)_4]^{2-}$.

5. **Formation of interpseudohalogen and interhalogen compounds.** Halide ions can combine together to form interhalogen compounds like CIF, ICl, IBr etc. similarly pseudohalide ions can also combine together to form interpseudohalogen compounds like $CN.N_3$, CN.SCN etc.

6. **Formation of monobasic hydracids.** Like halide ions, psedohalide ions also combine with H_2 to form monobasic hydracids.

   $H_2+2Cl^- \rightarrow 2HCl+2e^-$ $H_2+2CN^- \rightarrow 2HCN+2e.$

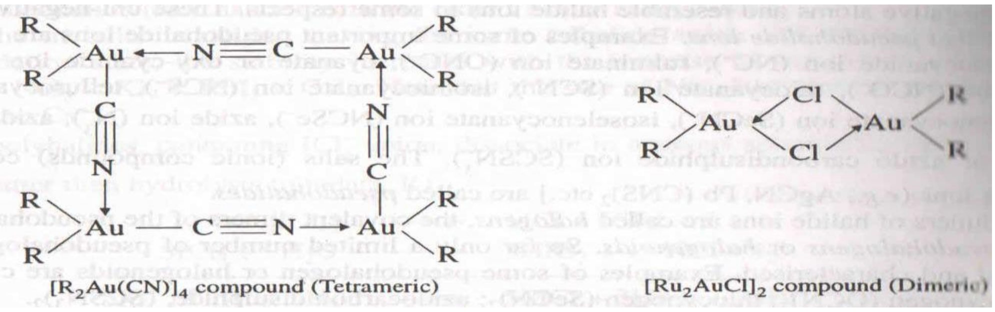
7. **Formation of insoluble salts.** Like halide ions, pseudohalide ions give insoluble salts with Ag^+, Pb^{2+} and Hg^+ cations.

   $Ag^+ + Cl^- \rightarrow AgCl$
   $Ag^+ + CN^- \rightarrow AgC$

   $Pb^{2+} + 2Cl^- \rightarrow PbCl_2\downarrow$
   $Pb^{2+} + 2CNS^- \rightarrow Pb(CNS)_2\downarrow$

   $Hg^+ + Cl^- \rightarrow HgCl\downarrow$
   $[g^+ + CNS^- \rightarrow HgCNS\downarrow$

8. **Acting as bridging Ligands.** Like halide ions pseudohalide ions also have more than one pair of electrons and hence can co ordinate with two metal ions simultaneously. Consequently like halide ions, pseudohalide ions also can act as bridging ligands. For example in $[R_2Au(CN)]_4$ which is a tetrameric compound, four CN^- ions act as bridging ligands. Similarly in $[R_2AuCl]_2$ which is a diametric compound two Cl^- ions act as bridging ligands.



$[R_2Au(CN)]_4$ compound (Tetrameric) $[Ru_2AuCl]_2$ compound (Dimeric)

Note that in each of the above compounds the geometry of Au atoms is square planar

16.15 Dissimilarities between halide ions and pseudohalide ions.

The differences between the two classes of ions are given as follows.

1. The hydracids, formed by the pseudohalide ions on combination with hydrogen are relatively weaker than the analogous hydracids formed by the halide ions. For example

HCN is a very weak acid, while HCl is a very strong acid in aqueous medium. The weak nature of hydracids given by pseudohalide ions may be due to the poor electronegativity of the Pseudohalogens.

2. Pseudohalide ions are stronger coordinating ligands than the halide ions and hence the complexes formed by pseudohalide ions are low spin (i.e inner-orbital involving d^2sp^3 hybridisation whnile those formed by the halide ions are high spin(outer orbital involving sp^3 d^2 hybridisation). For example $[Fe(CN)_6]^{3-}$ is low spin complex while $[FeF_6]^{3-}$ is a high spin complex.

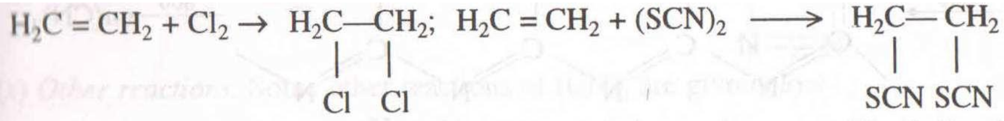
That the pseudohalide ions are stronger ligands than the halide ions is due to tha ability of the electron deficient pseudohalides to form σ-bound (from the pseudohalide to the metal) as well as π-bound (from the metal to pseudohalide).

3. Pseudohalide ions. Being made up of two hetero atoms can function as ambidentate ligands. For example class a metals from isothiocyanate complexes like $[Co\ (NCS)_4]^{2-}$ in which N-atoms is coordinated Co^{2+} ion while class B metals from thiocyanate complexes like $[Pb(SCN)_4]^{2-}$ in which S atoms is bounded to Pb^{2+} ion. halide ions have no tendency to act as ambidentate ligands.

16.17 Similarities between halogens and Pseudohalogens.

Following are the points showing the similarities between the two classes of compounds:

1. **Volatile and diametric nature.** Like halogens, Pseudohalogens are also diametric and fairly volatile (with the exception of polymeric thiocynogen) in the free state.
2. **Isomorphous nature.** Pseudohalogens are isomorphous to halogens when in the free or solid state. For example Cl_2 is isomorphous to $(CN)_2$ and similarly Br_2 is isomorphous with $(SCN)_2$.
3. **Addition to ethylenic double bond**. Like halogens Pseudohalogens also add to ethylenic double bond linkage for example.



$$H_2C=CH_2+Cl_2\rightarrow \underset{Cl}{\underset{|}{H_2C}}-\underset{Cl}{\underset{|}{CH_2}};\quad H_2C=CH_2+(SCN)_2\longrightarrow \underset{SCN}{\underset{|}{H_2C}}-\underset{SCN}{\underset{|}{CH_2}}$$

4. **Reaction with alkalies.** Like halogens, pseudohaloen also react with alkalies. For example (i) $(SCN)_2$+2KOH(cold and dilute) → KSCN+KOSCN+H_2O

   Cl_2+2KOH(cold and dilute) →KCI+KOCl+H_2O .

   (ii) $3(SCN)_2$+6KOH(hot and concentrated) →5KSCN+$KSCNO_2$+$3H_2O$

   $3Cl_2$+6KOH(hot and concentrated) → 5KCl+$KClO_3$+$3H_2O$

5. **Formation of monobasic hydracids.** Like halogen Pseudohalogens also combine with H_2 to form monobasic hydracids.

$Cl_2+H_2 \rightarrow 2HCl$; $(CN)_2+H_2 \rightarrow 2HCN$

16.18 Dissimilarity between halogens and Pseudohalogens

Pseudohalogens undergo polymeristaion and form polymerized series for example

$$n(CN)_2 \xrightarrow{500^0 C} 2(CN)_n; \qquad n(SCN)_2 \xrightarrow{Roomtemp} 2(SCN)_n$$

Halogens have no tendency to undergo polymerisation.

Some Pseudohalogens

1. Cynogen $(CN)_2$ or C_2N_2

This compound was discovered by Gay-Lussac in 1815

Preparation.

(i) It is formed by heating the cyanides of Hg (II), Ag(I) and Au (III). Hg $(CN)_2$ is heated to dull redness in a hard glass tube to get $(CN)_2$ gas which is collected over Hg.

$$Hg(CN)_2 \rightarrow Hg+(CN)_2$$

The yield of $(CN)_2$ obtained in this way is not quantitative, since $(CN)_2$ formed polymerises (at 500^0C) to insoluble paracynogen $(CN)_x$

$$X(CN)_2 \xrightarrow[500^0]{\text{Polvmeristaio}} 2(CN)x$$

$(CN)_2$ is set free at a lower temperature and is obtained in better yield by heating a mixture of $Hg(CN)_2$ and $HgCl_2$.

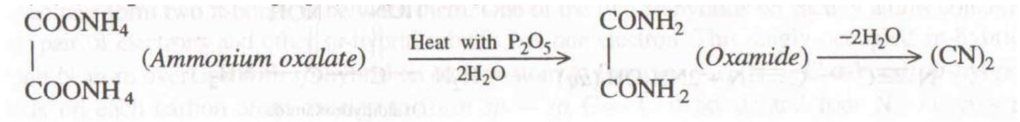
$$Hg(CN)_2+HgCl_2 \rightarrow Hg_2Cl_2+(CN)_2$$

(ii) $(CN)_2$ can also be prepared by the action of KCN on $CuSO_4$ solution. The reaction proceeds as :

$CuSO_4$(solution) $+2KCN \rightarrow K_2SO_4+Cu(CN)_2$

$2Cu(CN)_2 \rightarrow 2CuCN+(CN)_2$

(iii) $(CN)_2$ can also be prepared by heting ammonium oxalate with P_2O_5



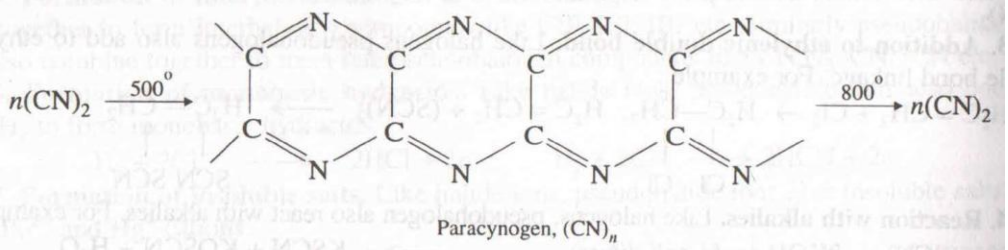
Properties.

(i) It is a colourless extremely poisonous, flamable gas (boiling point =-21.2^0) and freezes to a solid (melting point =-27.9^0). it has a smell of bitter almonds.

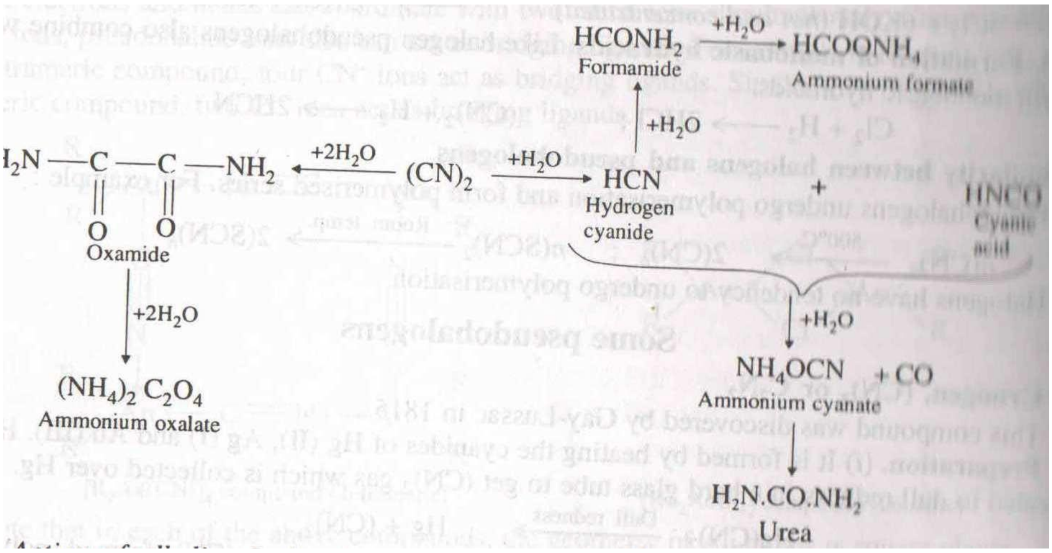
(ii) **Burning in air.** It burns in air with a violet coloured flame to give CO_2 and N_2. During this reaction explosion takes place.

$(CN)_2 + 2O_2 \rightarrow 2CO_2 + N_2$

(iii) **Polymerisation.** Although pure $(CN)_2$ is stable the pure gas undergoes polymerisation on heating to 500^0 to an insoluble solid paracyanogen $(CN)_n$ which at 800^0 reagenerates $(CN)_2$ but decomposes above this temperature.



(iv) **Hydrolysis.** It is soluble in water and undergoes slow hydrolysis to give a number of products the main products being ammonium formate urea, oxamide and ammonium oxalate.



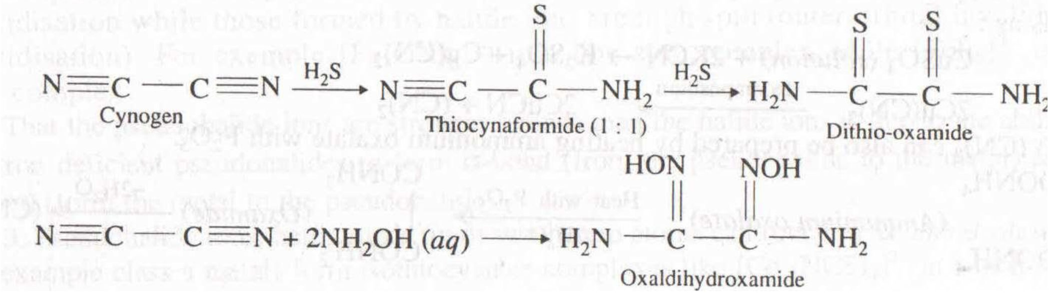
(v) **Action of alkalies.** It dissolves in alkalies (e.g KOH) to form the cyanide (KCN) and oxy-cyanide (KCNO).

$(CN)_2 + 2KOH \rightarrow KCN + KCNO + H_2O$

(vi) **Action of alkali metals.** It combines directly with alkali metals to form their cyanides.

$2K + (CN)_2 \rightarrow 2KCN$

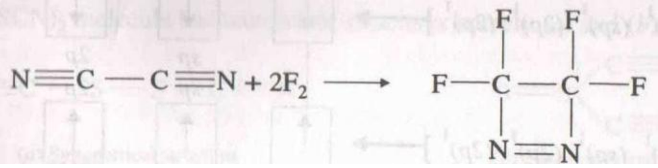
(vii) **Addition reactions.** A number of reactions of $(CN)_2$ involve addition across one or both of the multiple bonds in its molecule. Thus H_2S gives thiocynaformide and dithio-oxamide while aqueous NH_2OH gives oxaldihydroxamide.



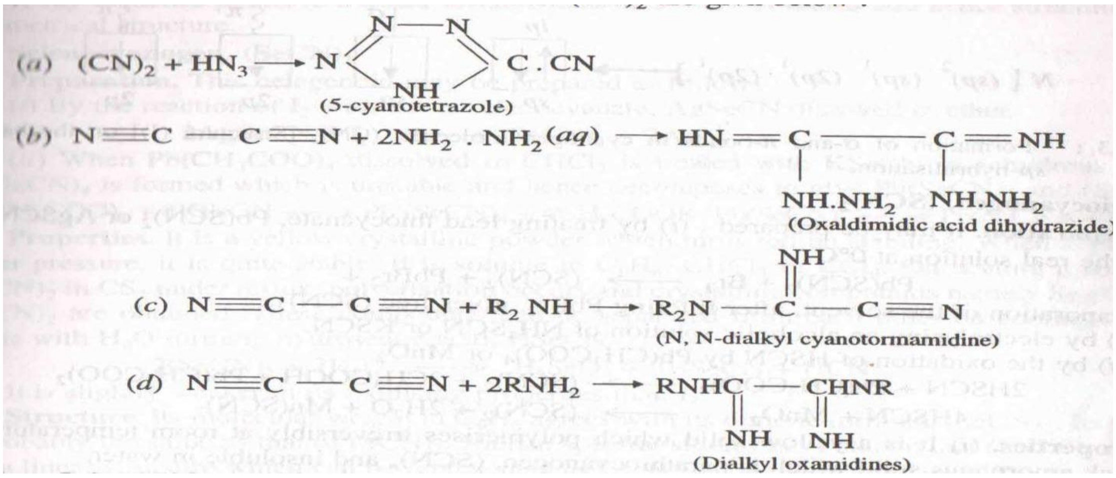
(viii) **Reduction by hydrogen**. When $(CN)_2$ is reduced by H_2 both the triple bonds are converted into single bonds by taking up hydrogen atoms and thus ethylebediamine $H_2N\text{-}CH_2\text{-}CH_2\text{-}NH_2$ is formed.

$$N \equiv C - C \equiv N + 4H_2 \longrightarrow H_2N - CH_2 - CH_2 - NH$$

(ix) **Flourination.** When $(CN)_2$ is fluorinated by AgF_2 at ≈ 110^0 it gives $CF_2(N)_2$ (I) although other products may also be obtained

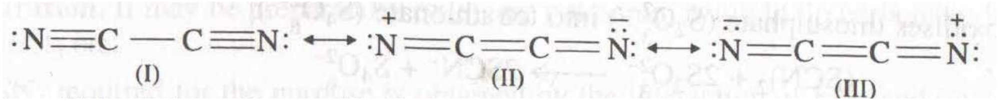


(x) Other reactions. Some other reactions of $(CN)_2$ are given below.

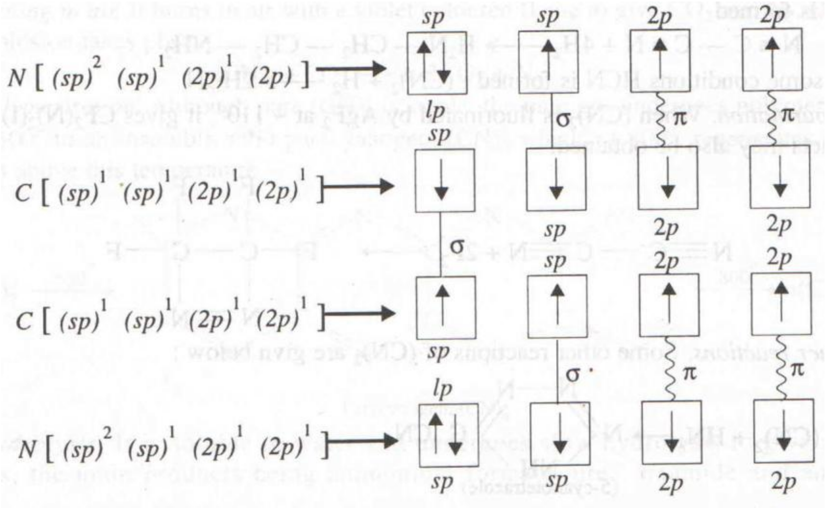


Uses. It is used in organic synthesis and as poisonous gas in wars

Structure. The vapour density of the gas is 26 which shows that its formula is C_2N_2. The formation of ethylene diamine $H_2N\text{-}CH_2\text{-}CH_2\text{-}NH_2$ on reduction and of oxamide during the hudrolysis shows that the order of atoms in cyanogens molecule should be N-C-C-N which is linear and symmetrical. Thus the structure of $(CN)_2$ is N≡C-C≡N. the N-C and C-C bond lengths which are equal to 1.16Å and 1.37 Å respectively shows that the true structure of the molecules is best represented as a resonance hybrid of the following three structures, structure (I) being the most contributing form.



In structure (I) both the carbon and both the nitrogen atoms are sp hybridized and each carbon and nitrogen pair from two π-bounds in between them. One of the two sp-hybrids on each N atoms contains a lone pair of electrons and other sp-hybrid on carbon atom to form sp-sp N-C σ-bond. Sp-hybrid orbitals on each carbon atom overlap to form sp-sp C-C σ-bonds and four N-C p-p π-bonds as shown in figure. Each N atoms has a lone pair of electrons residing in one of the two sp-hybrid orbitals.



2. **Thiocyanogen $(SCN)_2$**

Preparation. It may be prepare

(i) By treating lead thiocyanate, $Pb(SCN)_2$ or AgSCN with Br_2 in the real solution at 0^0C

$Pb(SCN)_2 + Br_2 \rightarrow (SCN)_2 + PbBr_2\downarrow$

Evaporation of the solvent after filtering $PbBr_2$ gives free $(SCN)_2$

(ii) By electrolyzing an alcoholic solution of NH_4SCN or KSCN

(iii) By the oxidation of HSCN by $Pb(CH_3COO)_4$ or MnO_2

$2HSCN + Pb(CH_3COO)_4 \rightarrow (SCN)_2 + 2CH_3COOH + Pb(CH_3COO)_2$

Properties.

(i) It is yellow solid which polymerises irreversibly at room temperature to a red-brick amorphous solid which is parathiocyanogen, $(SCN)_n$ and insoluble in water.

(ii) It is most stable in CCl_4 or CH_3COOH solution in which it exits NCSSCN.

(iii) It is rapidly hydrolysed by water to form thiocyanic acid (HSCN) and hydrocyanic acid (HCN).

(iv) Following reactions of $(SCN)_2$ indicate its oxidising property and similarities with halogens.

(a) A solution $(SCN)_2$ in ether or in CS_2 liberates I_2 from an iodide.

$(SCN)_2 + 2I^- \rightarrow 2SCN^- + I_2$

(b) It oxidises Cu (I) salts to Cu (II) salts

$(SCN)_2 + 2CuSCN \rightarrow 2Cu^{2+} + 4SCN^-$

(c) It combines with metals to form metallic salts

$(SCN)_2 + M(M=0) \rightarrow M(SCN)_2\ (M=+2)$

(d) It oxidises thiosulphate ($S_2O_3^{2-}$) into tetrathionate ($S_4O_6^{2-}$)

$(SCN)_2 + S_2O_3^{2-} \rightarrow 2SCN^- + S_4O_6^{2-}$

(e) Sulphur is precipitated from H_2S

$(SCN)_2 + H_2S \rightarrow 2H^+ + 2SCN^- + S\downarrow$

(f) Arsenite (AsO_3^{3-}) is oxidised to arsenate (AsO_4^{3-}).

$(SCN)_2 + AsO_3^{3-} + H_2O \rightarrow 2SCN^- + 2H^+ + AsO_4^{3-}$

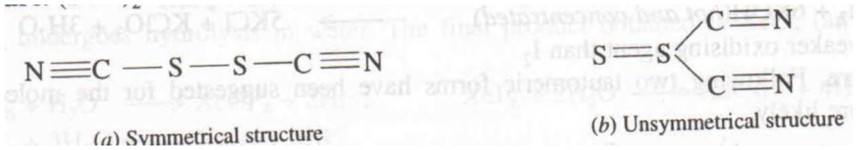
(v) Some order reactions shown by $(SCN)_2$ can be represented by the following chemical equation.

(a) Cold solution of $(SCN)_2 + NO \rightarrow NO.SCN$(Nitrosyl thiocyanate)

(b) IM cold solution of $(SCN)_2 \rightarrow (SCN)_2.2HCl \rightarrow (SCN)_2.H_2O$(Monohydrate)

Uses. $(SCN)_2$ is used (i) as an oxidising agent. (ii) for the determination of unsaturation in organic compounds.

Structure. $(SCN)_2$ molecule has tautomeric structure namely (a) and (b) shown below



(a) Symmetrical structure (b) Unsymmetrical structure

X-ray evidence points to a linear of S-C-N atoms and hence structure (a) is a symmetrical structure.

3. Selenocyanogen $(SeCN)_2$

Preparation. This helegenoid may be prepared as follows :

(i) By the reaction of I_2 with silver selenocyanate, AgSeCN dissolved in ether.

$2AgSeCn + I_2 \rightarrow (SeCN)_2 + 2AgI\downarrow$

(ii) When $Pb(CH_3COO)_4$ dissolved in $CHCl_3$ is treated with KSeCN in anhydrous acetone, $Pb(SeCN)_4$ is formed which is unstable and hence decomposes to give $Pb(SeCN)_2$ and $(SeCN)_2$.

$Pb(CH_3COO)_4 + 4\ KSeCN \rightarrow Pb(SeCN)_4 + 4CH_3COOH$.

$Pb(SeCN)_4 \rightarrow Pb(SeCN)_2 + (SeCN)_2$.

Properties. It is yellow crystalline powder which turns red on standing. When kept dry and under pressure, it is quite stable. It is soluble in C_6H_6, $CHCl_3$ or CCl_4. On heating a solution of $(SeCN)_2$ in CS_2 under reflux, polyerisation occurs and crystalline compounds namely $Se_3(CN)_2$ and $Se(CN)_2$ are obtained. These compounds can be separated from each other on cooling $(SeCN)_2$ reacts eith H_2O forming hydrosentic acid HSeCN.

$2(SeCN)_2 + 3H_2O \rightarrow H_2SeO_3 + 3HSeCN + HCN$

It is slightly weaker in its oxidising properties than I_2.

Structure. Its molecular weight in C_6H_6 agrees with its dimetric formula $(SeCN)_2$. Its structure is probably the same as that of $(SCN)_2$. Raman spectral studies have shown that $(SeCN)_2$ molecules has a linear structure which can be represented as.

4. Oxy-Cyanogen $(OCN)_2$

Preparation.

(i) Lidov prepared it by the action of H_2O_2 , CuO or sodium hypobromite on KOCN.

$4KOCN + 2H_2O_2 \rightarrow 2K_2CNO_2 + (OCN)_2 + 2H_2O$

(ii) $(OCN)_2$ can also be prepared by the action of AgOCN on I_2 in CS_2 or CCl_4 solution

$2AgOCN + I_2 \rightarrow 2AgI + (OCN)_2$

(iii)$(OCN)_2$ can also be prepared by the action of cyanogens bromide (CN**Br**) on Ag_2O

2 CN**Br+** $Ag_2O \rightarrow 2AgBr + (OCN)_2$

Properties

$(CNO)_2$ shows typical properties of Pseudohalogens. It liberates I_2 from an iodide solution reacts with metals, forms interpseudohalogen compounds.

5. Azido carbon disulphide $(SCSN_3)_2$

Preparation. It may be prepared by oxidising potassium azidodithio carbonate $KSCSN_3$ with $H_2O_2I_2$, $FeCl_3$

$KSCSN_3$ required for the purpose is obtained by the interaction of KN_3 and CS_2 at 40^0C.

$KN_3 + CS_2 \rightarrow KSCSN_3$

$2\ KSCSN_3 + H_2O_2 \rightarrow (SCSN_3)_2 + 2KOH$

$2KSCSN_3 + I_2 \rightarrow (SCSN_3)_2 + 2KI$

$2KSCSN_3+2FeCl_3\rightarrow(SCSN_3)_2+2FeCl_2+2KCl$

Properties. It is white crystalline solid slightly soluble in water. It is unstable and decompose violently automatically to give N_2 , sulphur and $(SCN)_2$

$(SCSN_3)_2\rightarrow2N_2+2S+(SCN)_2$

It reacts slowly with dilute acid and rapidly with concentrated acids to liberate sulphur. However with HNO_3 no sulphur is precipitated.

In reaction with an alkali is resembles Cl_2 as shown below:

(a) $(SCSN_3)_2+2KOH$(cold and dilute) $\rightarrow KSCSN_3+KOSCSN_3+H_2O$

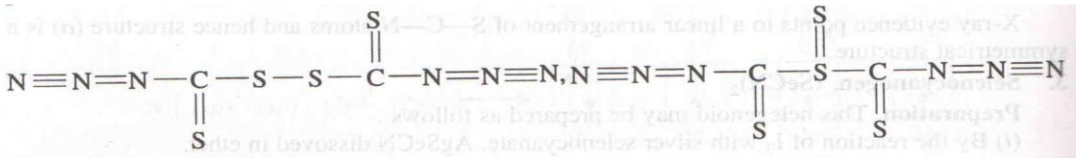
Cl_2+2KOH (cold and dilute) $\rightarrow KCI+KOCl+H_2O$

(b) $2(SCSN_3)_2+6KOH$(Hot and concentrated) $\rightarrow5KSCSN_3+KSCSN_3O_3+3H_2O$

$3Cl_2+6KOH$(hot and concentrated) $\rightarrow5KCl+KClO_3+3H_2O$

It is weaker oxidising agent then I_2

Structure. Following two tautomeric forms have been suggested for the molecule (I) is probably more likely.



$$N\equiv N=N-\underset{\underset{S}{\|}}{C}-S-S-\overset{\overset{S}{\|}}{C}-N=N\equiv N,\quad N\equiv N=N-\underset{\underset{S}{\|}}{C}-\overset{\overset{S}{\|}}{S}-\underset{\underset{S}{\|}}{C}-N=N\equiv N$$

(I) (II)

Fluorides of xenon

The stable fluorides formed by xenon are xenon difluoride (XeF_2) xenor tetrafluoride (XeF_4) and xenon hexafluoride (XeF_6).XeF_2 and XeF_4 are more stable than XeF_6 . in this fluorides Xe is in +2, +4 and +6 oxidation state respectively.

Preparation of xenon fluorides

(i) These are generally prepared by mixing Xe and F_2 in different ratio in different condition for example.

$$\underbrace{Xe + F_2}_{2:1\text{ ratio}} \xrightarrow[\text{tube }(400^{\circ}C)]{\text{Sealed Ni}} XeF_2\ ;\quad \underbrace{Xe + F_2}_{2:1\text{ ratio}} \xrightarrow[\text{discharge}]{\text{Electric}} XeF_2$$

$$Xe + F_2 \xrightarrow[(Hg\text{ vapours})]{\text{Photochemical combination}} XeF_2\ ;\quad \underbrace{Xe + 2F_2}_{1:5\text{ ratio}} \xrightarrow[400^{\circ}C,\ 5\text{-}6\text{ atm}]{\text{Ni tube}} XeF_4$$

$$\underbrace{Xe + 2F_2}_{1:2\text{ ratio}} \xrightarrow[-80^{\circ}C]{\text{Electric discharge}} XeF_4\ ;\quad \underbrace{Xe + 3F_2}_{1:20\text{ ratio}} \xrightarrow[250\text{-}300^{\circ}C,\ 50\text{-}60\text{ atm}]{\text{Ni vessel}} XeF_6$$

$$\underbrace{Xe + 3F_2}_{1:3\text{ ratio}} \xrightarrow[\text{low temp.}]{\text{Electric discharge}} XeF_6$$

(ii) The fluoride can also be prepared by the fluorination methods, for example

(a) XeF_2 can be prepared by the fluorination of Xe by oxygen monofluoride, O_2F_2 at -178^{0}C

$Xe+O_2F_2 \rightarrow XeF_2+O_2$

(b) XeF_6 can also be prepared by the fluorination of XeF_4 by O_2F_2 or by F_2 under pressure.

$XeF_4+O_2F_2 \rightarrow XeF_6+O_2$; $XeF_4+F_2 \rightarrow XeF_6$

Properties of fluorides

(i) **Physical state**. All the three fluorides are colourless crystalline solides whose melting points. Are as XeF_2=140^{0}C . XeF_4=117.1^{0}C , XeF_6=49.5^{0}C. XeF_4 sublimes readily.

(ii) Hydrolysis

(a) XeF_2 is reduced by H_2O to Xe and H_2O is oxidised to O_2

$2XeF_2+2H_2O \rightarrow 2Xe+4FH+O_2$

XeF_2 is rapidly hydrolysed by an aqueous solution of a base.

$2\ XeF_2+4\ OH^- \rightarrow 2Xe+4F^-+2H_2O+O_2$

(b) XeF_4 undergoes disproportionation in water giving XeO_3 which is a highly explosive solid

$2\ XeF_4+3H_2O \rightarrow Xe(g)+XeO_3(s)+6HF\ (aq)+F_2(g)$

If the reaction is carried out at -80^{0}C XeF_2 is formed. In this reaction slow and partical hydrolysis of XeF_4 takes place

$XeF_4+H_2O \rightarrow XeOF_2+2HF$

(c) XeF_6 undergoes hydrolysis in water. The final product obtained is XeO_3 (an explosive solid)

$XeF_6+H_2O \rightarrow XeOF_4+2HF$

$XeF_6+3H_2O \rightarrow XeO_3+6HF$

$XeF_6+2H_2O \rightarrow XeO_2F_2+4HF$

In strongly basic solution the reaction proceeds as :

$$XeF_6 + 7OH^- \rightarrow 6F^- + 3H_2O + HXeO^-_{4\,(xenateIon)} \xrightarrow{+2OH^-} \frac{6}{4}H_2O + \frac{1}{4}Xe + \frac{3}{4}XeO^{-4}_{6\,(persxenate\ ion)}$$

In acidic solution the main species is $XeOF_4$ (Xe=+6) and H_6XeO_6(Xe=+6) H_6XeO_6 is called xenic acid.

(iii)Fluorinating properties.

(a) XeF_2 is a mid fluorinating agent. Thus it react with C_6H_6 to give C_6H_5F.

(b) XeF_4 is a stronger fluorinating agent than XeF_2 thus it converts Hg to HgF_2 Pt to PtF_4, NO to NOF, NO_2 to NO_2F, SF_4 to SF_6 BCl_3 to BF_3 etc.

$2Hg+XeF_4\rightarrow Xe+2HgF_2$; $Pt+XeF_4\rightarrow Xe+PtF_4$

$2SF_4+XeF_4\rightarrow Xe+2SF_6$; $4BCl_3+3XeF_4\rightarrow 3X_3+4BF_3+6Cl_2$

(iv) Oxidising properties. All the three fluorides can oxidise many substance and are themselves reduced to xenon. For example

(a) $XeF_2+H_2\rightarrow Xe+2HF$; $2XeF_2+2H_2O\rightarrow 2Xe+4HF+O_2$

$$XeF_2+I_2\xrightarrow{BF_3}Xe+2IF;$$

$XeF_2+2SO_3\rightarrow Xe+S_2O_6F_2$

$XeF_2+2HCl\rightarrow Xe+2HF+Cl_2$; $XeF_2+2Ce^{3+}\rightarrow 2Ce^{4+}+Xe+2F^-$

(b) $XeF_4+2H_2\rightarrow Xe+4HF$; $3XeF_4+4BCl_3\rightarrow 3X_3+4BF_3+6Cl_2$

$XeF_4+4I^-\rightarrow Xe+4F^-+2I_2$

(c) $XeF_6+3H_2\rightarrow Xe+6HF$

XeF_6 can also oxidise NH_3(N=-3) to N_2 (N=0) and HCl (Cl=-1) to Cl_2 (Cl=0) in these reaction XeF_6 is reduced to Xe

$XeF_6+8NH_3\rightarrow Xe+6NH_4F+N_2$; $XeF_6+6HCl\rightarrow X_3+7HF+3C_{12}$

(v) **Formation of adducts.** All the three fluorides give adducts (addiction compounds) with F^- ion acceptor like PF_5, AsF_5, SbF_5 etc.

(a) In BrF_3 solution XeF_2 forms adducts with MF_5 molecules (M=P, As, Sb)

$XeF_2+MF_5\rightarrow XeF_2.MF_5$; $XeF_2+2MF_5\rightarrow XeF_2.2MF_5$

$2XeF_2+MF_5\rightarrow 2XeF_2.MF_5$.

(b) XeF_4 dissolves in molten SbF_5 and gives the addition compound $XeF_4.SbF_5$ which is an ionic compound and hence is represented as $[XeF_3]^+[SbF_6]^-$

$XeF_4+SbF_5\rightarrow XeF_4.SbF_5\rightarrow[XeF_3]^+[SbF_6]^-$

XeF_4 dissolves in molten TaF_5 giving a straw coloured compound, $Xe(TaF_6)_2$ which is described as an addition compound $XeF_2.2TaF_5+F_2$

(c) XeF_6 gives addition compound with AsF_5 and SbF_5 molecules

$XeF_6+MF_5\rightarrow XeF_6.MF_5\rightarrow[XeF_5]^+[MF_6]^-$ (M=As,Sb)

In these reactions XeF_6 molecule acts as F^- ion donor while MF_5 molecule behaves as F^- ion acceptor

XeF_6 also reacts with alkali metal fluorides (except LIF) and gives species containing XeF_7^- and XeF_8^{2-} ions. Thus in these reactions XeF_6 molecule acts F^- ion acceptor and MF molecule (M=Na, K,Rb, (s) behaves as F^- ion donor.

$XeF_6+2MF \rightarrow M_2XeF_8$ (Octafluoro-xenate)

(M=Na,K)

$$XeF_6+2RbF \xrightarrow{200^0C} 2Rb\ XeF_7 \xrightarrow{50^0C} Rb_2\ XeF_8+XeF_6$$

Molten (Heptafuroroxenate) (Octafluoroxenate)

(vi) **Action of HF.** XeF_2 and XeF_4 both dissolve in HF. On the other hand XeF_6 dissolves in HF, giving a solution which is a good conductor of electricity. The electrical conductivity of the solution is because of the formation of XeF_5^+ and HF_2^-

$$XeF_6+HF \rightarrow XeF_5^+ + HF_2^-$$

(vii) **Heat of formation,** Δ Hf. All the three fluorides are exothermic compounds and have (excepting XeF_2) large negative ΔH*f* value as shown XeF_2=-125.5 kJ mol$^-$ XeF_4=-410.0 kJ mol^{-1}, XeF_6=-401.7 kJ mol^{-1} .

(viii) Some more properties of XeF_6. (a) XeF_6 is the most volatile of all the fluorides. Its vapours have a greenish yellow colour. (b) XeF_6 is extremely reactive. It cannot be stored in a glass or quarts vessels, since it readily reacts with SiO_2 present in glass as one of its constituents. With SiO_2, XeF_6 gives dangerously explosive XeO_3 as a final product

$2XeF_6+3SiO_2 \rightarrow 2XeO_3+3SiF_4$

Structure and geometry of Xenon fluorides.

The structure and shape (geometry) of XeF_2, XeF_4 and XeF_6 molecules . have a pentagonal bipyramidal structure

Oxy-fluorides of xenon

Xenon forms the following oxy-fluorides. $XeOF_2$ (xenon oxy-difluoride), $XeOF_4$ (xenon oxy-tetrafluoride), XeO_2F_2 (xenon dioxy-difluoride), XeO_3F_2 (xenon trioxy-difluoride) and XeO_2F_4 (xenon dioxy-tetrafluoride)

1. **Xenon oxy-difluoride,** $XeOF_2$ (Xe=+4)

   It is formed by the partial and slow hydrolysis of XeF_4 at -80^{0}C.

$$XeF_4+\ H_2O \xrightarrow{-80^0C} XeOF_2+2HF$$

   It is not a very stable compound.

2. **Xenon oxy-tetrafluoride,** $XeOF_4$ (Xe=+6)

   It is obtained by the partial hydrolysis of XeF_6 with H_2O and by its action on SiO_2.

   $XeF_6+H_2O \rightarrow XeOF_4+2HF$; $2XeF_6+SiO_2 \rightarrow XeOF_6+SiF_4$

Properties.

(i) It is colour less volatile liquid which solidifies at about 245K

(ii) It reacts with SiO_2 forming XeO_2F_2.

$2XeOF_4+SiO_2\rightarrow XeO_2F_2+SiF_4$

It is due to this reaction that $XeOF_4$ is not kept in glass vessels but in nickel vessels.

(iii) It is reduced to Xe by H_2

$XeOF_4+3H_2\rightarrow Xe+H_2O+4HF$

(vi) $XeOF_4$ reacts with H_2O giving XeO_3 as the final product

$XeOF_4$ (Xe=+6) + $2H_2O\rightarrow XeO_3$(Xe=+6)+4HF

3. **Xenon dioxy-difluoride XeO_2F_2 (Xe=+6)**

It is prepared by the action of SiO_2 on $XeOF_4$ or by hydrolysis it

$2XeOF_4+SiO_2\rightarrow 2XeO_2F_2+SiF_4$; $XeOF_4+H_2O\rightarrow XeO_2F_2+2HF$

XeO_2F_2 is a colour less solid and melts at 29.8^0C. it is easily hydrolysed by H_2O giving XeO_3.

$$XeO_2F_2+H_2O\rightarrow XeO_3+2HF$$

Structure of xenon oxy-fluorides

The structure/geometry of $XeOF_2$, $XeOF_4$, XeO_2F_2, XeO_3F_2 and XeO_2F_4 molecules has

16.19 Summary of the unit

Compounds formed with bonds between different Halogen atoms are known as interhalogen compounds. The binary compounds have formulae XY, XY_3, XY_5 and XY_7 (where X is the heavier halogen atom). Ternary species are also formed, and the species can be neutral, cations or anions. All the interhalogens are thermodynamically stable with respect to decomposition to the elements, though the low valency compounds are unstable with respect to disproportionation.

16.20 Key words

Inter halogen compounds; Types of inter halogen compounds; Polyhalide ions; Halogen oxides; Pesudohalides and Pseudohalogens

16.21 References for further studies

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16.22 Questions for self understanding

1) What are Inter halogen compounds?

2) What are the different types of inter halogen compounds are present?

3) Write notes on

a) Diatomic interhalogens

b) Tetra-atomic interhalogens

c) Hexa-atomic interhalogens

d) Octa-atomic interhalogens

4) Discuss the method of Preparations of Interhalogen compounds

5) Discuss the Structures of interhalogen compounds

6) What are Polyhalide ions

7) What are Halogen oxides

8) Explain synthesis and reactions of halogen oxoacids and oxoanions

9) What are Pesudohalides?

8) Write the similarities between halide ions and pseudohalide ions.

9) List the dissimilarities between halide ions and pseudohalide ions

10) Write the similarities between halogens and Pseudohalogens.

11) List the dissimilarity between halogens and Pseudohalogens