INTRODUCTION TO ORGANOMETALLIC CHEMISTRY

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Book: Introduction to Organometallic Chemistry (Ghosh and Balakrishna)

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CHAPTER OVERVIEW

1: Introduction

1.1: Bonding Concepts in Main Group Chemistry

Learning Objectives

In this lecture you will learn the following:

- Lewis structure.
- Limitations of Lewis model.

Organometallic Chemistry of Main Group Elements

Our aim in this course is to introduce one of the important disciplines of inorganic chemistry which bridges the organic compounds with main group and transition elements; organometallic chemistry. Organometallic chemistry is defined as the chemistry of chemical compounds containing one or more metal—carbon bonds which are essentially polar ($M^{\delta+}$—$C^{\delta-}$) in nature. To begin with it is necessary to understand the bonding concepts that explain the structures of both main group and transition elements. The objectives of first few lectures are to give some insight into the various metal—ligand interactions that would later help in planning the synthesis and also eventually looking into their electronic and kinetic stability. The course is divided into four major sections and the first section deals with the various bonding concepts employed for both main group and transition metal compounds. The second and third sections deal with the organometallic chemistry of main group and transition elements, respectively, while the fourth section would be devoted to applications of organometallic compounds with special emphasis to catalysis.

A set of problems along with solutions are presented at the end and also in Chapter 2. In future, it is planned to provide interactive sections as well.
The pertinent literature and books in this and related areas are listed at the end.

Molecular structure and bonding

The chemical properties of the molecules can be directly correlated to their electronic structures. In this lecture attempts are being made to give an overall view of how bonding concept evolved starting from Lewis approach to the development of molecular orbital theory.

1.1.1: Lewis structures

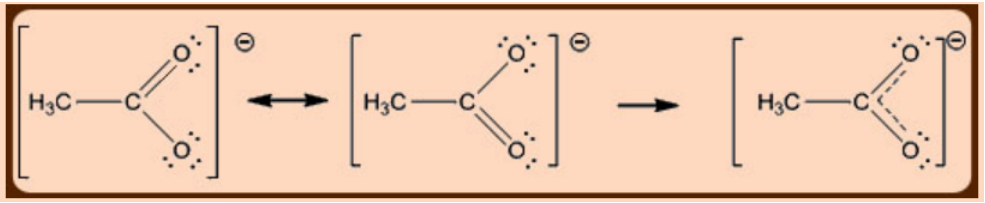
Lewis proposed that when two atoms come close to each other to establish a bond by sharing an electron pair, a covalent bond will be established. One pair of electrons would give a single bond X—Y; two or three pairs of electrons would leads to the formation of double (X=Y) and triple bonds (X≡Y), respectively. The pairs of valence electrons that are not utilized in bonding are called lone pairs of electrons or simply lone pairs. The lone pair of electrons does not participate in bonding; however, they do influence the shape and the geometry of the molecule and their chemical properties as well.

Lewis introduced octet rule which states that each atom shares its valence electrons with neighboring atoms to have a total of eight (s^2p^6) electrons in its valence shell to have noble-gas configuration. An exception to this rule is hydrogen as it can have only two valence electrons in its only shell, 1s.

By simply counting the number of valence electrons present on the central atom and its neighbors, Lewis structures can be written in just three easy steps.

i. Consider the valence electrons of all participating atoms; add an electron for each negative charge and subtract one electron for each positive charge.
ii. Identify the central atom and write the symbols of the atoms around central atom. In majority of polyatomic molecules, the least electronegative one will be the central atom with an exception of hydrides, for example, H_2O, NH_3 or H_2S.
iii. Distribute the electron pairs throughout the molecule to satisfy the octet of all atoms present in the molecule starting from the most electronegative one. Each pair of singly bonded atoms requires one pair of electrons.
iv. Each bonding pair should be represented by a single bond and the net charge is assumed to be possessed by the ion (cation or anion) as a whole and not by an individual atom.

For some molecules, Lewis dot structure differs from the experimentally determined structural observations. For example, in acetate ion both the C—O bonds are identical as per X-ray structure determination but the prediction by the Lewis structure is incorrect. The reason is due to resonance.



Limitations of Lewis model

Molecules with odd number of electrons can never satisfy the octet rule.

Example: NO.

Some atoms with fewer valence electrons can never complete octet without formal charges.

A central atom can have more than 8 electrons. Example: SF_6

Lewis model does not explain paramagnetic nature of O_2.

Geometry and molecular shapes cannot be explained by Lewis model.

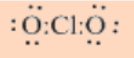
Worked examples

Example 1 : ClO_2^-

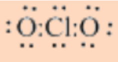
Solution :
ClO_2^- Total number of electrons 7 + 2 x 6 + 1 = 20 = 10 pairs

Identify the central atom and connect the peripheral atoms with a pair of electrons as two dots and count the remaining electron pairs
O : Cl : O 20-4 = 16 electrons left (8 pairs)

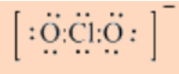
Complete the octet of oxygen atoms and count the remaining electron pairs

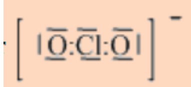

16-12 = 4 electrons

Complete the octet of chlorine atom,


Since all the electrons are utilized and octet is satisfied, no need of any multiple bonds.

The structure is


or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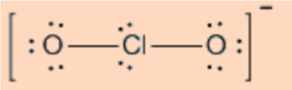
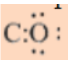


Example 2 : CO

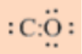
Solution :
CO (carbon monoxide) Total number of electrons 4 + 6 = 10

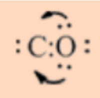
Connect the two atoms with a pair of electrons as two dots and count the remaining electron pairs
C : O 10-2 = 8 electrons left

Complete the octet of oxygen atoms and count the remaining electron pairs


8-6 = 2 electrons

Place the remaining electron pair on carbon atom,


All the electrons are utilized and octet is not satisfied for carbon as there is a shortage of four more electrons.


Drag two electron pairs on oxygen atom in between carbon and oxygen to establish two more bonds so that a triple bond exists between C and O which satisfies the octet of both C and O.

The structure is :C:::O: or :C≡O: or |C≡O|

Problems:

Work out Lewis structures for: BF_4^-, PCl_3, PO_4^{3-}, SO_4^{2-}, O_3, N_2 and SO_2

1.2: VSEPR Theory and its Utility

Learning Objectives

In this lecture you will learn the following

- Definition of VSEPR.
- Hybridization concept.
- Prediction of shapes and geometries of molecules.
- Bent's rule and its application in understanding the structural parameters.

The Valence Shell Electron Pair Repulsion Theory (VSEPR)

VSEPR theory is an improved and extension of Lewis model but predicts the shapes of polyatomic molecules. This model was first suggested by Nevil Sidgwick and Herbet Powell in 1940 and later improved by Ronald Gillespie and Ronald Nyholm.

Prediction of molecular shapes and geometries was made easy by this model through the following simple steps.

1. Draw the Lewis structure.
2. Count the total number of bonds and lone pairs around the central atom. (Each single bond would involve one pair of electrons).
3. Arrange the bonding pairs and lone pairs in one of the standard geometries to minimize the electron-electron repulsion.
    i. Lone pair electrons stay closer to the nucleus and also they spread out over a larger space than bond pairs and hence large angles between lone pairs.
    ii. The repulsion follows the order LP—LP > LP—BP > BP—BP.
4. Multiple bonds should be considered as a single bonding region.

Steric numbers:

Another term called steric number is often used in VSEPR theory.

Steric number (SN) = No. of attached atom + No. of lone pairs. Since the lone pair—lone pair repulsions are maximum, the most stable geometry can be obtained by maximizing the distance between steric numbers on the central atom.

Molecular shapes are eventually determined by two parameters: Bond distance, separation between the nuclei of two bonded atoms in a straight line and the bond angle, the angle between any two bonds containing a common atom.

While mentioning the molecular shapes lone pairs may be ignored, however, while defining the geometry both the lone pairs and bond pairs should be considered.

For example: in water molecule the central oxygen atom is in tetrahedral environment with two lone pairs and two O—H bonds (or two bond pairs). The shape of the water molecule is therefore bent (two lone pairs are ignored).

Similarly, in ammonia, the nitrogen atom is in tetrahedral environment with three bonded pairs (three N—H bonds) and one lone pair. The shape of NH_3 molecule is pyramidal.

Predicting the molecular geometries

To begin with, draw the Lewis structure.

Count the number of bonding pairs and lone pairs around the central atom.

Arrange the bonding pairs and the lone pairs in one of the standard geometries thereby minimizing electron—electron repulsion.

Multiple bonds count as a single bonding region.

What is Bent's rule:
More electronegative substituents 'prefer' hybrid orbitals having less s-character, and more electropositive substituents 'prefer'

orbitals having more s-character.

The bond angles in CH_4, CF_4 and CH_2F_2 can be explained using Bent's rule. While a carbon in CH_4 and CF_4 uses four identical *sp*³ hybrids for bonding, in CH_2F_2 the hybrids used are not identical.

The C-F bonds are formed from sp^{3+x} hybrids, with slightly more *p*-character and less *s*-character than an *sp*³ hybrid, and the hydrogen are bonded by sp^{3-x} hybrids, with slightly less *p*-character and slightly more s-character. Increasing the amount of *p*-character in the C-F bonds decreases the F-C-F bond angle, because for bonding by pure *p*-orbitals the bond angle would be decreased to 90°.

Molecular shapes determined by VSEPR theory

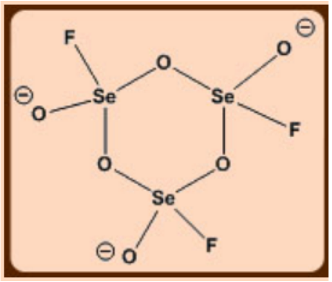
Molecule	Steric Number (Number Electron Pairs) (SN)	Geometry	Example
MA_2	2	Linear	$BeCl_2$
MA_3	3	Trigonal planar	BF_3
MA_4	4	Tetrahedral	SiF_4
MA_5	5	Trigonal bipyramidal	PF_5
MA_6	6	Octahedral	SF_6
MA_7	7	Pentagonal bipyramidal	IF_7

Molecule	SN	Number of lone pairs	Geometry	shape	Example
MA_2	2	0	Linear		CO_2
MA_3	3 3	0 1	Trigonal planar	Trigonal planar angular	SO_3 SO_2
MA_4	4	0 1 2	Tetrahedral	Tetrahedral Trigonal pyramidal Angular	CH_4 NH_3 H_2O
MA_5	5	0 1 2 3	Trigonal bipyramidal	Trigonal bipyramidal Seesaw T-shaped linear	AsF_5 SF_4 ClF_3 XeF_2
MA_6	6	0 1 2	Octahedral	Octahedral Square pyramidal Square planar	SF_6 BrF_5 XeF_4

Problems:

1. Draw the structure and depict the geometry around **Se** atoms in $[Se_3O_6F_3]^{3-}$, which is a symmetric ionic molecule with cyclic structure, using VSEPR model.

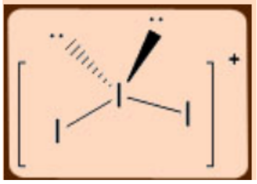
Solution



Apply VSEPR theory to the structure.
Se has six valence electrons. One Se—F and three Se—O (one terminal and two bridging) will add four more electrons to the valence shell of Se, so, 10 e = 5 electron pairs out of which four are bonded pairs and one is a lone pair. A TBP environment is expected.

2. Predict and draw the structure of I_3^+ using VSEPR model.

Solution



Total number of electron at the central I atom is: 7 + 2 -1 (charge) = 8; 2BP + 2LP, should be tetrahedral and angular shape.

3. Which of H_2O and F_2O will have the larger X-O-X bond angle?

Solution:

F is more electronegative than H; therefore the space occupied by the O-H bonding pair in the O valence shell will be greater. Hence, H_2O *will have the larger X-O-X bond angle.*

4. Explain why the X-P-X bond angles for the series of POX_3 molecules decrease from X = Br (104.1°) to X = Cl (103.3°) to X = F (101.3°)

Solution:

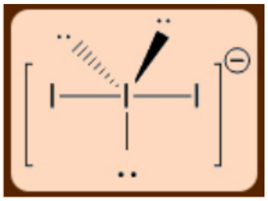
Fluorine is the most electronegative halogen, so it will draw electron density in the P-F bond away from P atom; repulsion of the P-F bonding pairs will be less than the repulsion of P-Cl and P-Br bonding pairs, so the F-P-F bond angle will be the smallest.

5. Show that the following molecules and their corresponding shapes are correct, using VSEPR theory.

BCl_3,	trigonal planar
$[IF5]^{2-}$,	pentagonal planar
$[NH_4]^+$,	tetrahedral
SF_6;	octahedral
XeF_4;	square planar
AsF_5;	trigonal bipyramidal
$Xe(O)F_4$,	square pyramid
IF_7,	pentagonal bipyramidal
$[H_3O]^+$	tetrahedral
H_2Se	tetrahedral

6. Work out the geometry of I_3^- ion using VSEPR model.

Solution



CHAPTER OVERVIEW

2: Organometallic Chemistry of s- and p-block Elements

2.1: General Methods of Preparation

Learning Objectives

In this section you will learn the following

- Various synthetic methodologies to make M—C bonds.
- How to choose an appropriate synthetic method.
- Reaction conditions and the role of solvents

An organometallic compound contains one or more metal-carbon bonds.

Synthesis

General Methods of Preparation

Most organometallic compounds can be synthesized by using one of four M-C bond forming reactions of a metal with an organic halide, metal displacement, metathesis and hydrometallation.

a. Reaction with metal and transmetallation

The net reaction of an electropositive metal M and a halogen-substituted hydrocarbon is

$$2\,\mathrm{M} + \mathrm{RX}(\text{alkyl or aryl}) \longrightarrow \mathrm{MR} + \mathrm{MX}$$

For example

$$8\,\mathrm{Li} + 4\,\mathrm{CH_3Cl} \longrightarrow \mathrm{Li_4(CH_3)_4} + 4\,\mathrm{LiCl}$$

$$\mathrm{Mg} + \mathrm{CH_3Br} \longrightarrow \mathrm{CH_3MgBr}(\text{organometal halide with Mg, Al, Zn})$$

If, one metal atom takes the place of another, it is called transmetallation

$$\mathrm{M} + \mathrm{M'R} \longrightarrow \mathrm{M'} + \mathrm{MR}$$

$$2\,\mathrm{Ga} + 3\,\mathrm{CH_3{-}Hg{-}CH_3} \longrightarrow 3\,\mathrm{Hg} + 2\,\mathrm{Ga(CH_3)_3}$$

Transmetallation is favorable when the displacing metal is higher in the electrochemical series than the displaced metal.

b. Metathesis

The metathesis of an organometallic compound MR and a binary halide EX is a widely used synthetic route in organometallic chemistry.

$$\mathrm{MR} + \mathrm{EX} \longrightarrow \mathrm{ER} + \mathrm{MX}$$

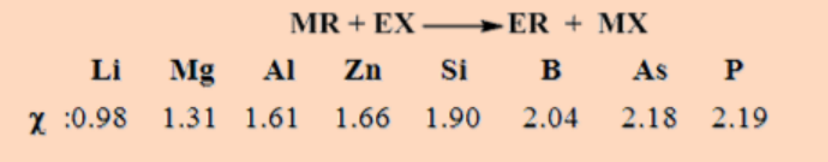
$$\mathrm{Li_4(CH_3)_4} + \mathrm{SiCl_4} \longrightarrow 4\,\mathrm{LiCl} + \mathrm{Si(CH_3)_4}$$

$$\mathrm{Al_2(CH_3)_6} + 2\,\mathrm{BF_3} \longrightarrow 2\,\mathrm{AlF_3} + 2\,\mathrm{B(CH_3)_3}$$

Metathesis reaction can frequently be predicted from electronegativity or hard and soft acid-base considerations.

Hydrocarbon groups tends to bond to the more electronegative element; the halogen favors the formation of ionic compounds with the more electropositive metal.

In brief, the alkyl and aryl group tends to migrate from the less to the more electronegative element [χ = electronegativity].



$$\mathrm{MR} + \mathrm{EX} \longrightarrow \mathrm{ER} + \mathrm{MX}$$

	Li	Mg	Al	Zn	Si	B	As	P
χ	:0.98	1.31	1.61	1.66	1.90	2.04	2.18	2.19

When the electronegativities are similar, the correct outcome may be predicted, with care*, by considering the combination of the softer element with organic group and harder element with fluoride or chloride.

*An insoluble product or reactant may change the outcome, e.g.;

$$\mathrm{SnPh_4(THF) + HgBr_2(THF) \longrightarrow HgPhBr(s) + PhSnBr(THF)}$$

HgPhBr turns out to be insoluble in THF
Metathesis reactions involving the same central element are often referred to as redistribution reactions.

$$\mathrm{SiCl_4 + SiMe_4 \longrightarrow Me_3SiCl + Me_2SiCl_2 + \cdots}$$

$$\mathrm{3\,GeCl_4 + 2\,AlMe_6 \longrightarrow 3\,GeMe_4 + 4\,AlCl_3}$$

Al is more electropositive than Ge, this reaction occurs as it is thermodynamically favorable.

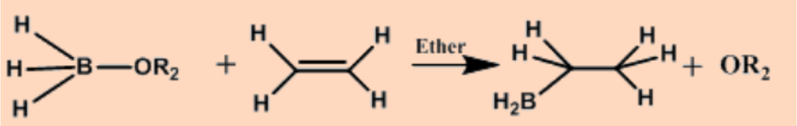
c. Hydrometallation

The net outcome of the addition of a metal hydride to an alkene is an alkylmetal compound.

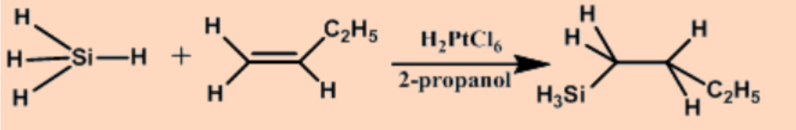
$$\mathrm{EH + H_2C{=}CH_2 \longrightarrow E{-}CH_2{-}CH_3}$$

The reaction is driven by the high strength of E-C bond relative to that of most E-H bonds, and occurs with a wide variety of compounds that contain E-H bonds.

Hydroboration



Hydrosilylation



Ionic and electron-deficient compounds of Group 1, 2

Organometallic derivatives of all Group 1 metals are known. Amongst, the alkyllithium compounds are most thoroughly studied and useful reagents.
Many of them are commercially available.
MeLi is generally handled in ether solution, but RLi compounds with longer chains are soluble in hydrocarbons.

Commercial preparation:

$$\mathrm{M + RX \longrightarrow MR(often\ contaminated\ with\ halide)}$$

The best method would be:

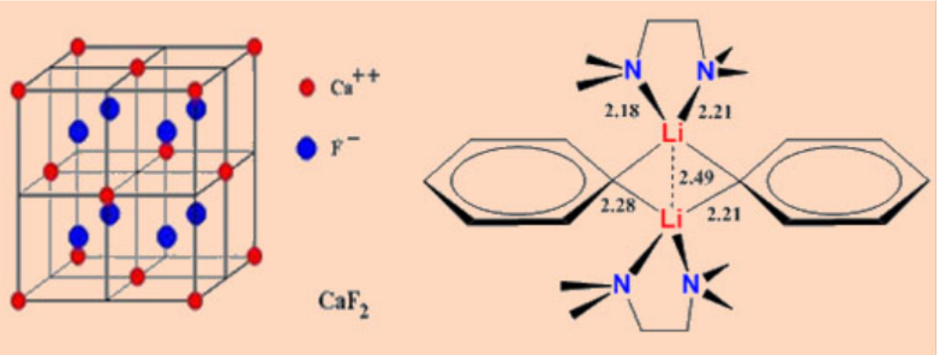
$$\mathrm{HgR_2 + 2\,Li \longrightarrow 2\,LiR + Hg}$$

MeLi exists as a tetrahedral cluster in the solid state and in the solution. Many of its higher homologs exist in solution as hexamers or equilibrium mixture of aggregates ranging up to haxamers.

The larger aggregates can be broken down by Lewis bases, such as, TMEDA.

Common organolithium compounds have one Li per organic group.
Several polylithiated organic molecules containing several lithium atoms per molecule are known.

The simplest example is Li_2CH_2, which can be prepared by the pyrolysis of MeLi which crystallizes in a distorted antifulorite* structure. However, the finer details of the orientation of the CH_2 groups are yet to be established.



*the antifluorite structure is the inverse of the fluorite structure in which the locations ofcations and anions are reversed. Look into the structures of CaF_2 (fluorite structure) and K_2O (antifluorite structure). An fcc array of cations and all the tetrahedral holes are filled with anions.

Radical anion salts

Sodium naphthalide is an example of an organometallic salt with a delocalized radical anion, $C_{10}H_8^{-}$.

Such compounds are readily prepared by reacting an aromatic compound with an alkali metal in a polar aprotic solvent.

Naphthalene dissolved in THF reacts with Na metal to produce a dark green solution of sodium naphthalide.

$$\mathrm{Na(s)} + \mathrm{C_{10}H_8(THF)} \longrightarrow \mathrm{Na[C_{10}H_8](THF)}$$

EPR spectra show that the odd electron is delocalized in an antibonding orbital of $C_{10}H_8$.

Formation of radical anion is more favorable when the π of LUMO of the arene is low in energy.

Simple MOT predicts that the energy of LUMO decreases steadily on going from benzene to more extensively conjugated hydrocarbons.

Sodium naphthalide and similar compounds are highly reactive reducing agents.

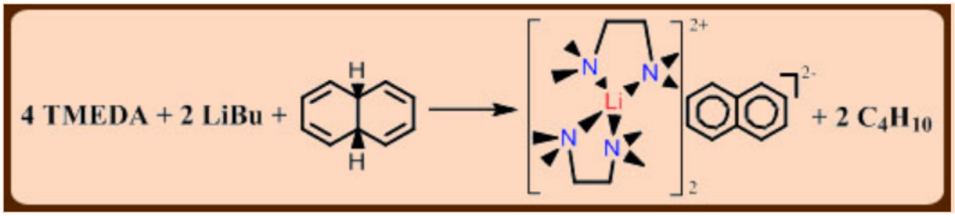
They are preferred to sodium because unlike sodium, they are readily soluble in ethers.

The resulting homogeneous reaction is generally faster and easier to control than a heterogeneous reaction between one reagent in solution and pieces of sodium metal, which are often coated with unreactive sodium oxide or with insoluble reaction products.

The additional advantage is that by proper choice of the aromatic group the reduction potential of the reagent can be chosen to match the requirements of a particular synthetic task.

Alternative route to delocalized anion is the reductive cleavage of acidic C—H bonds by an alkali metal or alkylmetallic compound.

Example:



Problems:

1. Classify the following reactions into, (i) hydrometallation, metal displacement, metathesis OR transmetallation reactions; (ii) give an example for each case in the form of a balanced chemical equation.

Solution

a.

$$\mathrm{M + Mx'R \longrightarrow M' + MR}$$

….Transmetallation

e.g.:

$$\mathrm{2\,Ga + 3\,CH_3{-}Hg{-}CH_3 \longrightarrow 3\,Hg + 2\,Ga(CH_3)_3}$$

b.

$$\mathrm{MR + EX \rightarrow ER + MX}$$

….Metathesis
e.g.:

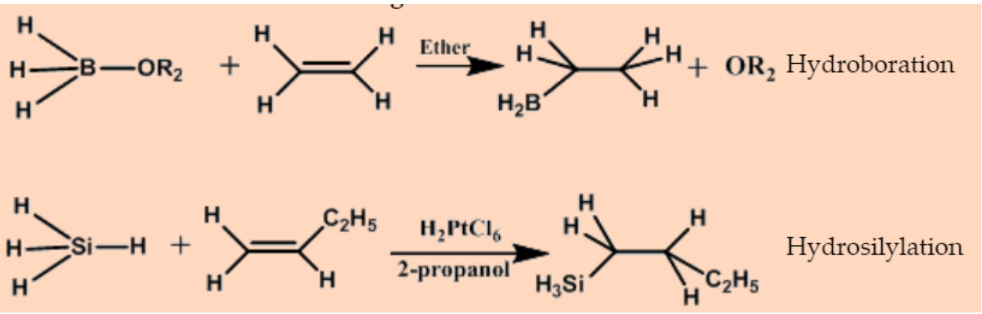
$$\mathrm{Li_4(CH_3)_4 + SiCl_4 \longrightarrow 4\,LiCl + Si(CH_3)_4}$$

or

$$\mathrm{Al_2(CH_3)_6 + 2\,BF_3 \longrightarrow 2\,AlF_3 + 2\,B(CH_3)_3}$$

c. \[\ce{EH + H$_2$C=CH$_2$ -> E—CH$_2$—CH$_3$ } \nonumber \] ….Hydrometallation

e.g.:



Problems:

2. For each of the following compounds, indicate those that may serve as
(1) a good carbanion nucleophile reagent,
(2) a mild Lewis acid,
(3) a mild Lewis base at the central atom,
(4) a strong reducing agent. (A compound may have more than one of these properties)
(a) $Li_4(CH_3)_4$, (b) $Zn(CH_3)_2$, (c) $(CH_3)MgBr$, (d) $B(CH_3)_3$, (e) $Al_2(CH_3)_6$, (f) $Si(CH_3)_4$, (g) $As(CH_3)_3$.

Solution

a. $(MeLi)_4$ - good carbanion nucleophile and strong reducing agent
b. $ZnMe_2$ - reasonable carbanion nucleophile, mild Lewis acid, reducing agent
c. MeMgBr - good carbanion nucleophile
d. BMe_3 - mild Lewis acid
e. Al_2Me_6 - good carbanion nucleophile, strong reducing agent
f. $SiMe_4$ - mild Lewis acid
g. $AsMe_3$ - mild Lewis base

2.2: Organometallic Compounds of Alkali Metals (Sodium and Lithium)

Learning Objectives

In this lecture you will learn the following

- How to synthesize and handle sodium, lithium compounds.
- Structural features.

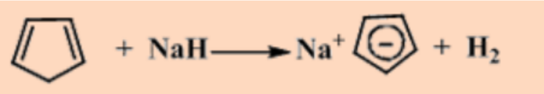
Organometallic compounds of alkaline metals

Organic compounds such as terminal alkynes which contain relatively acidic hydrogen atoms form salts with the alkali metals.

$$2\,\mathrm{Et{-}C \equiv CH} + 2\,\mathrm{Na} \longrightarrow 2\,\mathrm{Na^+[Et{-}C \equiv C]^-} + \mathrm{H_2}$$

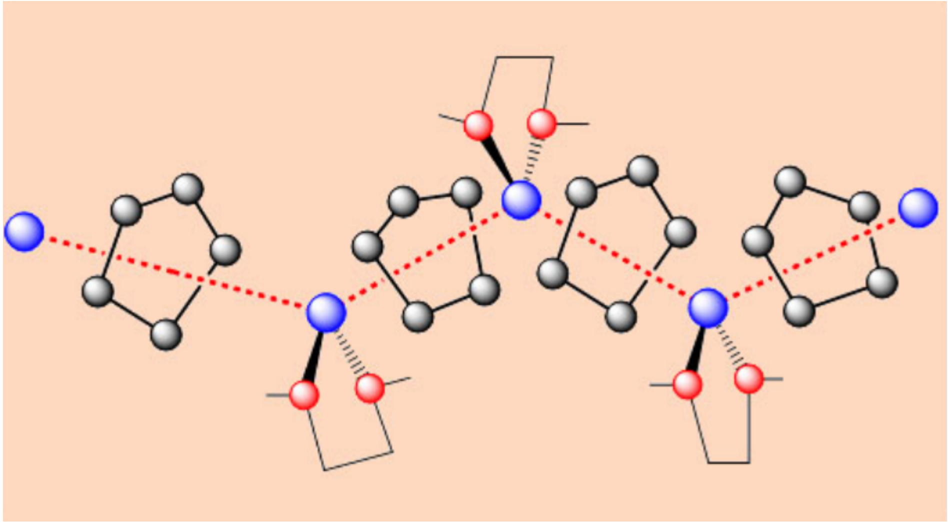
$$\mathrm{Me{-}C \equiv C{-}H} + \mathrm{K[NH_2]} \longrightarrow \mathrm{K^+[Me{-}C \equiv C]^-} + \mathrm{NH_3}$$

$$\mathrm{C_5H_6} + \mathrm{Na} \longrightarrow \mathrm{NaCp} + \tfrac{1}{2}\mathrm{H_2}$$



NaCp is pyrophoric in air, but air-sensitivity can be lessened by complexing the Na^+ with dme.
In the solid state, [Na(dme)][Cp] is polymeric

**Pyrophoric material: is one that burns spontaneously when exposed to air.*



Transmetallation:

$$\mathrm{HgMe_2} + \mathrm{Na} \longrightarrow 2\,\mathrm{NaMe} + \mathrm{Hg}$$

Organolithium compounds:

$$\mathrm{nBuCl} + 2\,\mathrm{Li} \xrightarrow{Hydrocarbon\ Solvent} \mathrm{nBuLi} + \mathrm{LiCl}$$

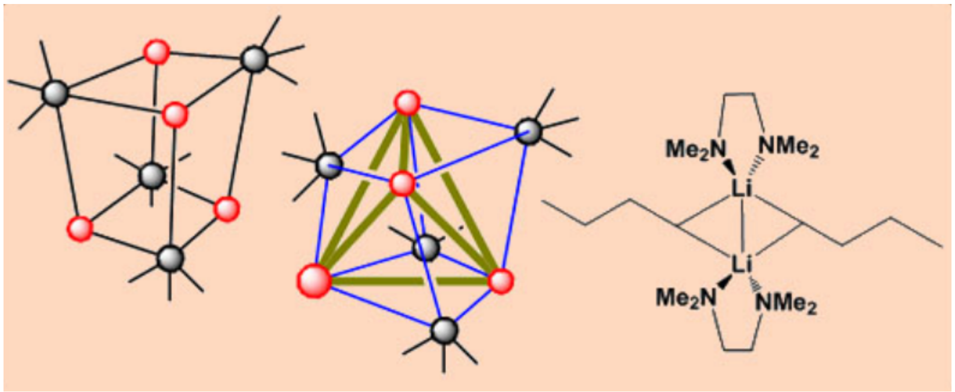
Organolithium compounds are of particular importance among the group 1 organometallics.

Many of them are commercially available as solutions in hydrocarbon solvents.

Solvent choices for reactions involving organometallics of the alkali metals are critical. For example, ^{n}BuLi is decomposed by Et_2O to give ^{n}BuH, C_2H_4 and LiOEt.

Alkali metal organometallics are extremely reactive and must be handled in air- and moisture-free environments; NaMe, for example, burns explosively in air.

Lithium alkyls are polymeric both in solution and in the solid state.



NMR is very useful in understanding the solution structures; ^{6}Li (I = 1), ^{7}Li (I = ½), ^{13}C (I = ½)

The structures of (^{t}BuLi)$_4$ and (MeLi)$_4$ are similar. ^{n}BuLi when mixed with TMEDA, gives a polymeric chain. TMEDA link cubane units together through the formation of Li-N bonds.

Alkyllithium compounds are soluble in organic solvents whereas Na and K salts are insoluble, but are solubilized by the chelating ligand TMEDA. Addition of TMEDA may break down the aggregates of lithium alkyls to give lower nuclearity complexes. E.g. [^{n}BuLi.TMEDA]$_2$

However, detailed studies have revealed that the system is far from simple, and it is possible to isolate crystals of either [^{n}BULi.TMEDA]$_2$ or [(^{n}BuLi)$_4$.TMEDA]$_\infty$.
In the case of (MeLi)$_4$, the addition of TMEDA does not lead to cluster breakdown, and the X-ray structure confirms the composition (MeLi)$_4$.2TMEDA, the presence of both tetramers and the amine molecules in the crystal lattice.

N. D. R. Barnett et al. *J. Am. Chem. Soc.*, 1993, 115, 1573.

Lithium alkyls and aryls are very useful reagents in organic synthesis and also in making corresponding carbon compounds of main group elements.
Lithium alkyls are important catalysts in the synthetic rubber industry for the stereospecific polymerization of alkenes.

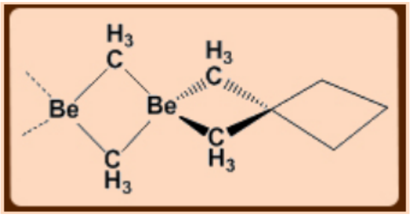
2.3: Organometallic Compounds of Alkaline Earth Metals (Beryllium and Magnesium)

Objectives

In this lecture you will learn the following

- Organometallic compounds of beryllium and magnesium.
- Structural features of alkyl lithium and beryllium sandwich compounds.

Beryllium



$$\mathrm{HgMe_2 + Be \longrightarrow Me_2Be + Hg (at\ 383\ K)}$$

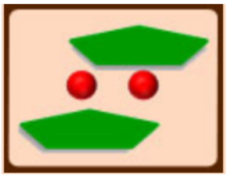
$$\mathrm{2\,PhLi + BeCl_2 \longrightarrow Ph_2Be + 2\,LiCl (in\ diethyl\ ether)}$$

In vapor phase, Me_2Be is monomeric with a linear C—Be—C (Be-C = 170 pm).
The solid state structure is polymeric and resembles that of $BeCl_2$.

$$\mathrm{2\,NaCp + BeCl_2 \longrightarrow Cp_2Be + 2\,NaCl}$$

The X-ray diffraction at 128 K suggested [(η^1-Cp)(η^5-Cp)Be].
However, ^1H NMR spectrum shows that all protons environments are equivalent even at 163 K.

Also, solid state structure shows the Be atom is disordered over two equivalent sites and NMR data can be interpreted in terms of fluxional process in which the Be atom moves between these two sites.
However, Cp^*_2Be possesses a sandwich structure with both the rings are coplanar.



Magnesium

Alkyl and aryl magnesium halides (Grignard reagents, RMgX) are extremely well-known on account of their uses in synthetic chemistry.

$$\mathrm{Mg + Rx \longrightarrow RMgX (in\ diethyl\ ether)}$$

Transmetallation is useful means of preparing pure Grignard reagents.

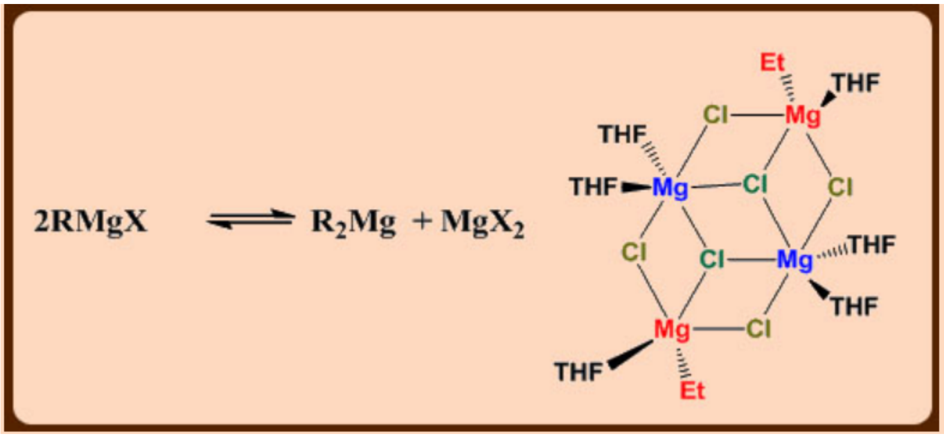
$$\mathrm{Mg + RHgBr \longrightarrow Hg + RMgBr}$$

$$\mathrm{Mg + R_2Hg \longrightarrow Hg + R_2Mg}$$

Two-coordination at Mg in R_2Mg is observed only when the R groups are sufficiently bulky, e.g. $Mg\{C(SiMe_3)_3\}_2$.
RMgX are generally solvated and Mg centre is typically tetrahedral.
e.g. $EtMgBr.2Et_2O$; $PhMgBr.2Et_2O$.

Cp_2Mg has a staggered sandwich structure.

Solutions of Grignard reagent may contain several species, e.g. RMgX, R_2Mg, MgX_2, RMg(μ-X)$_2$MgR, which are further complicated by solvation. The position of equilibrium between these species is markedly dependent on concentration, temperature and solvent; strongly donating solvents favour monomeric species in which they coordinate to the metal centre.

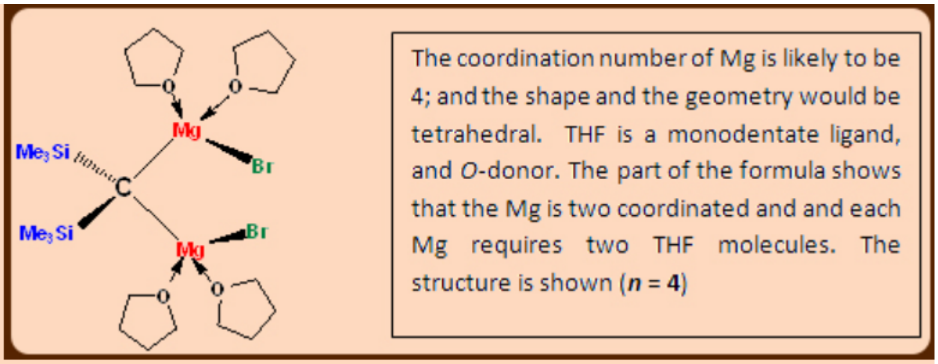


Treatment with dioxane results in the precipitation of $MgCl_2$(dioxane) leaving behind pure R_2Mg in the solution.

Problems:

1. The compound $(Me_3Si)_2C(MgBr)_2$.nTHF is monomeric. Suggest a value of '*n*' and propose a structure for this Grignard reagent.

Solution



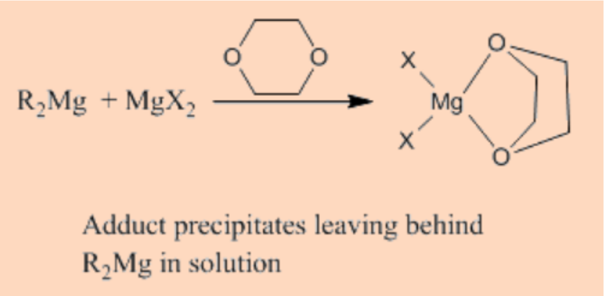
The coordination number of Mg is likely to be 4; and the shape and the geometry would be tetrahedral. THF is a monodentate ligand, and *O*-donor. The part of the formula shows that the Mg is two coordinated and and each Mg requires two THF molecules. The structure is shown (***n*** **= 4**)

2. If a typical Grignard reagent exists as an equilibrium mixture of dialkylmagnesium and magnesium halide, give a method of isolating pure dialkyl magnesium. Your answer should be in the form of balanced chemical equations only.

Solution

$$2\,\mathrm{RMgX} \rightleftharpoons \mathrm{R_2Mg} + \mathrm{MgX_2}$$

Treatment of equilibrium mixture with dioxane results in the precipitation of, say, $MgCl_2$(dioxane) (if, X = Cl), leaving behind pure R_2Mg in the solution.



Adduct precipitates leaving behind R_2Mg in solution

2.4: Structure and Bonding

Learning Objectives

In this lecture you will learn the following

- Solid state structures of nickel-arsenide, alkyl lithium and alkyl aluminium compounds

tructure and bonding

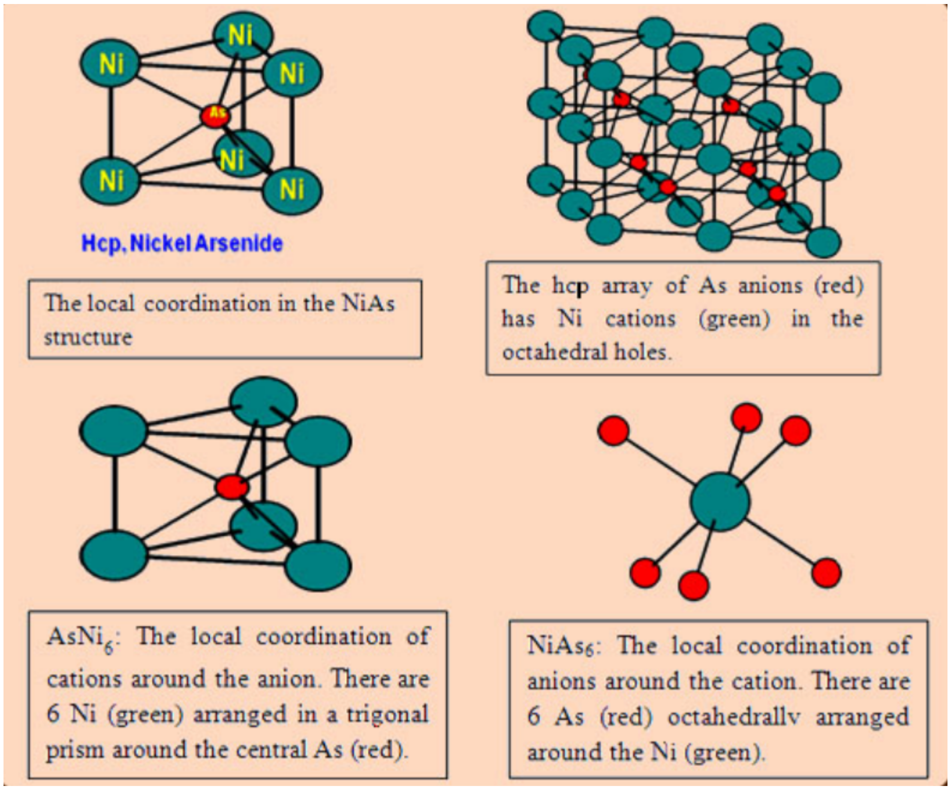
The slight differences that arise between organometallic compounds and binary hydrogen compounds are mainly due to the tendency of alkyl groups to avoid ionic bonding.

The molecular structures of $AlMe_3$and MeLi differ from $AlH_3$and LiH.
Even the more ionic MeK crystallizes in the nickel-arsenide structure rather than the rock-salt structure adopted by KCl.

Nickel-arsenide structure is typical of soft-cation, soft-anion combinations.

Electron deficient compounds such as $AlMe_3$contain 3c-2e bonds analogous to the B—H—B bridges in diborane.

The Nickel-Arsenide, NiAs, Structure



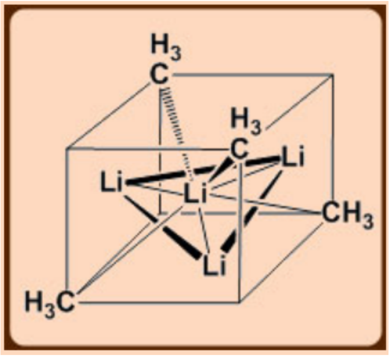
The local coordination in the NiAs structure

The hcp array of As anions (red) has Ni cations (green) in the octahedral holes.

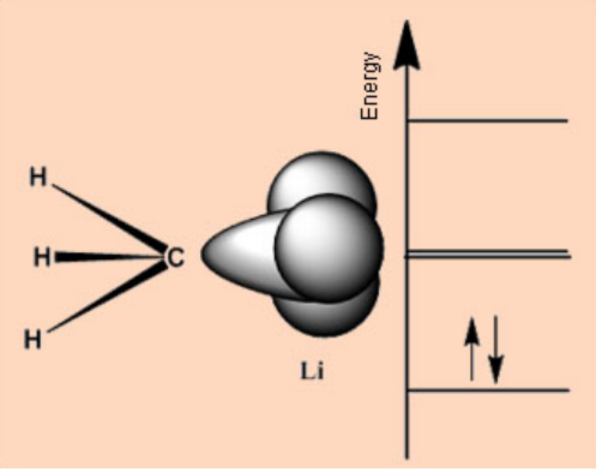
$AsNi_6$: The local coordination of cations around the anion. There are 6 Ni (green) arranged in a trigonal prism around the central As (red).

$NiAs_6$: The local coordination of anions around the cation. There are 6 As (red) octahedrallv arranged around the Ni (green).

MeLi in nonpolar solvents consists of tetrahedron of Li atoms with each face bridged by a methyl group. Similar to Al_2Me_6, the bonding in MeLi consists of a set of localized molecular orbitals. The symmetric combination of three Li 2s orbitals on each face of the Li_4 tetrahedron and one sp^3 hybrid orbital from CH_3 gives an orbital that can accommodate a pair of electron to form a 4c-2e bond.



The lower energy of the C orbital compared with the Li orbitals indicates that the bonding pair of electrons will be associated primarily with the CH_3 group, thus supporting the carbanionic character of the molecule. Some analysis has indicated that about 90% ionic character for the Li-CH_3 interaction.



The interaction between an sp^3 orbital from a methyl group and the three 2s orbitals of the Li atoms in a triangular face of $Li_4(CH_3)_4$ to form a totally symmetric 4c,2e bonding orbital. The next higher orbital is non-bonding and the uppermost is antibonding.

Me_2Be and Me_2Mg exist in a polymeric structure with two 3c,2e-bonding CH_3 bridges between each metal atom.

CHAPTER OVERVIEW

3: Organometallic Chemistry of p-block Elements

3.1: Reactions of Organometallic Compounds

Learning Objectives

In this section you will learn the following

- Chemical properties of organometallic compounds.
- Reactivity patters and their electronic properties.
- Electronic properties verses chemical reactivity.
- Application of alkyl lithium in organic transformations.

Reactions of organometallic compounds

The reactions of organometallic compounds of electropositive elements are dominated by factors such as the carbanion character of the organic moiety and the availability of a coordination site on the central metal atom. Reaction patterns:

a. Oxidation

- All organometallic compounds are potentially reducing agents.
- Those of electropositive elements are in fact very strong reducing agents (many of them are pyrophoric in nature).
- The strong reducing character also presents a potential explosion hazard if the compounds are mixed with larger amount of oxidzing agents.

Why is it so?

All organometallic compounds of the electropositive metals that have unfilled valence orbitals, or that readily dissociate into fragments with unfilled orbitals are pyrophoric,e.g., $\mathrm{Li_4(CH_3)_4}$, $\mathrm{Zn(CH_3)_2}$, $\mathrm{B(CH_3)_3}$ and $\mathrm{Al_2(CH_3)_6}$

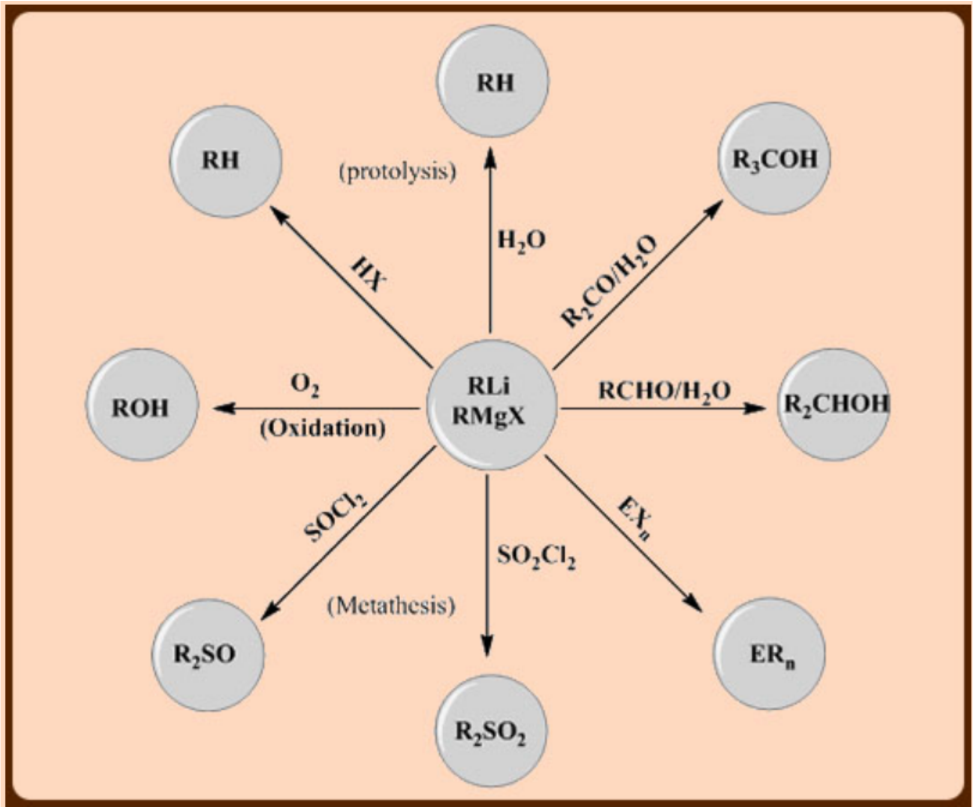
Volatile pyrophoric compounds, such as $\mathrm{B(CH_3)_3}$, may be handled in vacuum line and, inert atmosphere techniques are used for less volatile but air-sensitive compounds. Compounds such as $\mathrm{Si(CH_3)_4}$ and $\mathrm{Sn(CH_3)_4}$ which do not have low-lying empty orbitals, require elevated temperatures to initiate combustion, and can be handled in air.

The combustion of many organometallic compounds takes place by a radical chain mechanism.

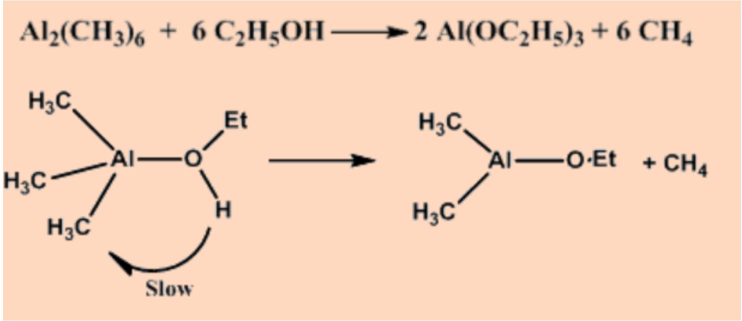
b. Nucleophilic character

The partial negative charge of an organic group attached to an electropositive metal makes it a strong nucleophile and Lewis base. This is referred to as its carbanion character even though the compound itself is not ionic. Alkyllithium and alkylaluminium compounds and Grignard reagents are the most common carbanion reagents in laboratory-scale synthetic chemistry. The carbanion character diminishes for the less metallic boron and silicon.

The carbanion character finds many synthetic applications.



Where X = halide, E = B, Si, Ge, Sn, Pb, As and Sb



c. Lewis acidity

Due to the presence of unoccupied orbitals on the metal atom, electron-deficient organometallic compounds are observed to be Lewis acids.

e.g

$$B(C_6H_5)_3 + LiC_6H_5 \longrightarrow Li[B(C_6H_5)_4]$$

This reaction may be viewed as the transfer of the strong base $C_6H_5^-$ from the weak Lewis acid Li^+ to the stronger acid B(III).

Organometallic species that are bridged by organic groups can also serve as Lewis acids and, in the process, bridge cleavage can take place.

$$Al_2(CH_3)_6 + 2\,N(C_2H_5)_3 \longrightarrow 2\,(CH_3)_3AlN(C_2H_5)_3$$

Electron deficient organometallic species are Lewis acids.

Problems

1. Name each of the following compounds and classify them: (a) $SiH(CH_3)_3$, (b) $BCl(C_6F_5)_2$, (c) $Al_2Cl_2(C_6H_5)_4$, (d) $Li_4(C_4H_9)_4$, (e) $Rb(CH_2H_3)$.

Solution

a. trimethylsilane (tetrahedral monomer, electron-precise);
b. bis(pentafluorophenyl)chloroborane (trigonal monomer, electron-deficient);
c. tetraphenyldichlorodialuminum (two Al-Cl-Al bridges, in this structural form it is electron –precise);
d. butyllithium or more precisely, tetrabutyltetralithium (tetrahedral Li_4 array with a phenyl carbon bridging each face, electron deficient);
e. ethylrubidium, salt-like.

2. Sketch the structures of: (a) methyl lithium, (b) trimethyl boron, (c) hexamethyldialuminum, (d) tetramethylsilane, (e) trimethylarsane, and (f) tetraphenylarsonium.

Solution

a. methyl lithium: Li tetrahedron with each face capped by CH_3 [see chapter 6]
b. trimethyl boron: planar triangular array of B and C
c. hexamethyldialuminum:four terminal CH_3 and two CH_3 bridges in a diborane-like structure
d. tetramethylsilane: tetrahedral
e. trimethylarsane: pyramidal
f. tetraphenylarsonium: pseudotetrahedral

3.2: Organometallic Compounds of Boron and Aluminium

Learning Objectives

In this lecture you will learn the following

- Preparation and reactivity of organoboron and organo aluminium compounds.
- Influence of Lewis acidity on structural features

Organoboron Compounds

BMe_3 is colorless, gaseous (b.p. -22 °C), and is monomeric. It is pyrophoric but not rapidly hydrolyzed by water.

Alkylboranes can be synthesized by metathesis between BX_3 and organometallic compounds of metals with low electronegativity, such as RMgX or AlR_3.

$$BF_3 + 3\,CH_3MgBr \longrightarrow B(CH_3)_3 + 3\,MgBrF(\text{solvent used: dibutyl ether})$$

Why dibutyl ether as a solvent: Has much lower vapor pressure than BMe_3 and as a result the separation by trap-to-trap distillation on a vacuum line is easy.

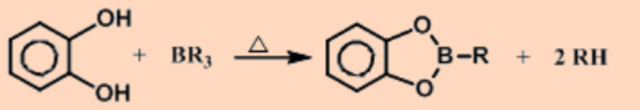
Also, there is a very weak association between BMe_3 and OBu_2($Me_3B{:}OBu_2$).

Although, trialkyl- and triarylboron compounds are mild Lewis acids, strong carbanion reagents lead to anions of the type $[BR_4]^-$.

Example, $Na[BPh]_4$: The bulky anion hydrolyses very slowly in neutral or basic water and is useful for the preparation of large positive cations.

$$Na[BPh]_4 + K^+ \longrightarrow K[BPh]_4$$

$K[BPh]_4$ is insoluble, used for the gravimetric estimation (determination) of potassium, an example of the low solubility of large-cation and large-anion salts in water/



Organohaloboron compounds are more reactive than simple trialkylboron compounds.

Preparation:

$$2\,BCl_3 + 6\,AlR_3 \longrightarrow 3\,R_2BCl + 6\,AlR_2Cl(\text{metathesis})$$

$$2\,BCl_3 + BMe_3 \xrightarrow{(diborane)} 3\,BMeCl_2(\text{redistribution reaction})$$

Reactions: (Protolysis reactions with ROH, R_2NH and other reagents)

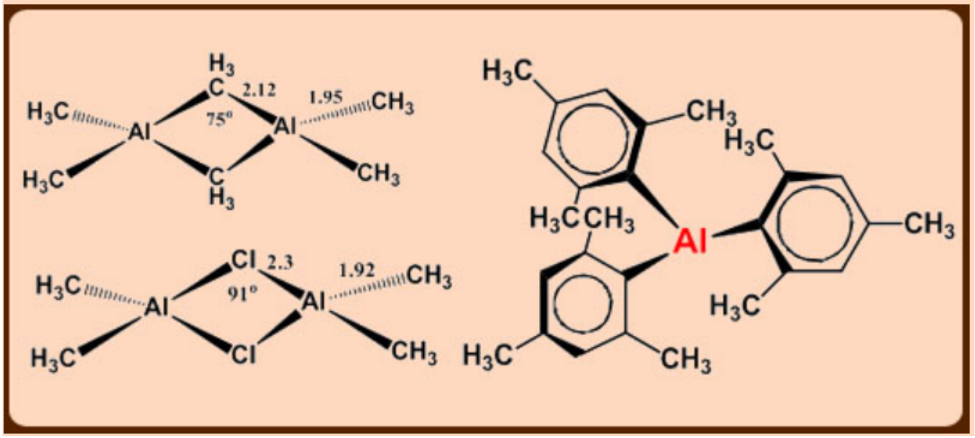
$$3\,BMeCl_2 + 2\,HNR_2 \longrightarrow BMe_2(NR_2) + [R_2NH_2]Cl$$

$$BMe_2Cl + Li(C_4H_9) \longrightarrow BMe_2(C_4H_9) + LiCl$$

Organoaluminium compounds

With less bulky alkyl groups, dimerization occurs and one of the distinguishing features of alkyl bridge is the small Al-C-Al angle, which is ~ 75°.

The 3c,2e bonds are very weak and tend to dissociate in the pure liquid which increases with increase in the bulkiness of the alkyl group.



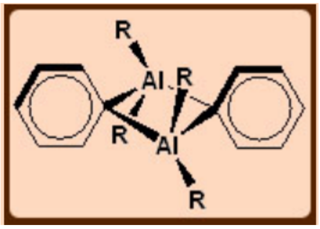
$$Al_2(CH_3)_6 \rightleftharpoons 2\,Al(CH_3)_3$$

K= 1.52 x 10^{-8}

$$Al_2(C_4H_9)_6 \rightleftharpoons 2\,Al(C_4H_9)_3$$

K= 2.3 x 10^{-4}

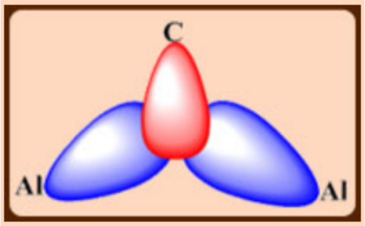
Perpendicular orientation of pheynl groups in Al_2Ph_6
Triphenylaluminium exists as a dimer with bridging η^1-phenyl groups lying in a plane perpendicular to the line joining the two Al atoms.



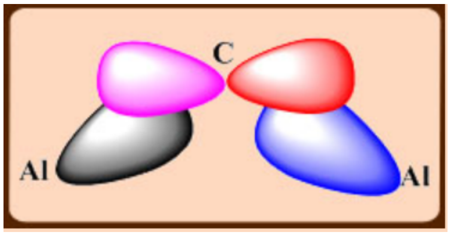
This structure is favored partly on steric grounds and partly by supplementation of the Al-C-Al bond by electron donation from the phenyl π-orbitals to the Al atoms.

Tendency for bridging: X > Ph > alkyl

3c,2e bonds formed by a symmetric combination of Al and C orbitals



An additional interaction between the pπ orbital on C and an antisymmetric combination of Al orbitals.



Synthesis

Very useful as alkene polymerization catalysts and chemical intermediates.
Expensive carbanion reagents for the replacement of halogens organic groups by metathesis.

Laboratory scale preparations involves:

$$2\,\mathrm{Al}+3\,\mathrm{Hg(CH_3)_2}\longrightarrow \mathrm{Al_2(CH_3)_6}+3\,\mathrm{Hg}$$

Commercial method:

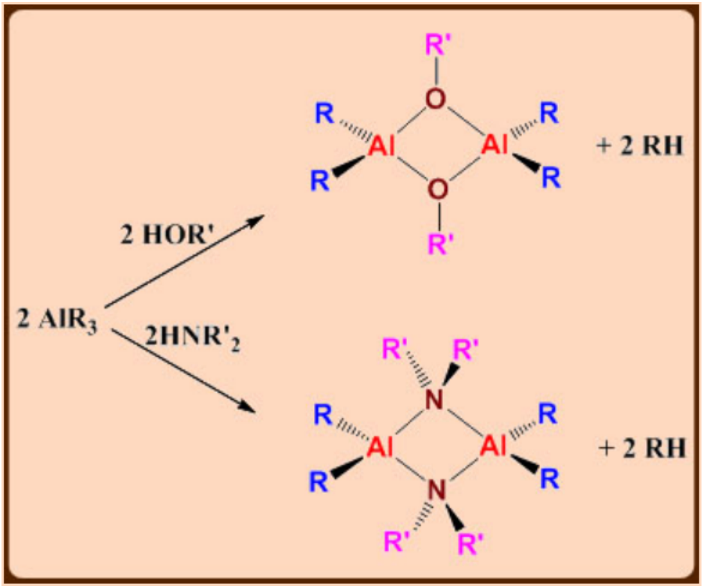
$$2\,\mathrm{Al}+\mathrm{CH_3Cl}\longrightarrow \mathrm{Al_2Cl_2(CH_3)_4}$$

$$\mathrm{Al_2Cl_2(CH_3)_4}+6\,\mathrm{Na}\longrightarrow \mathrm{Al_2(CH_3)_6}+2\,\mathrm{Al}+6\,\mathrm{NaCl}$$

Commercial method for ethylaluminium and higher homologs:

$$2\,\mathrm{Al}+3\,\mathrm{H_2}+6\,\mathrm{RHC{=}CH_2}\xrightarrow[110-200atm]{60-110^{\circ}C}2\,\mathrm{Al_2(CH_2CH_2R)_6}$$

The reaction probably proceeds by the formation of a surface Al—H species that adds across the double bond of the alkene in a hydrometallation reaction.



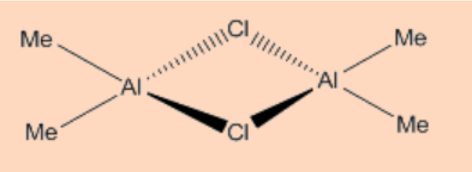
Reactions:

Alkylaluminum compounds are mild Lewis acids and form complexes with ethers, amines and anions. When heated, often β-hydrogen elimination is responsible for the decomposition of ethyl and higher alkylaluminium compounds. E.g. $\mathrm{Al(^{i}C_4H_9)_3}$
Tendency towards bridging structure is: $\mathrm{PR_2^-} > \mathrm{X^-} > \mathrm{H^-} > \mathrm{Ph^-} > \mathrm{R^-}$.

Problems:

1. Propose a structure for $\mathrm{Al_2(Me)_4Cl_2}$.

Solution:
Similar to diborane:



2. For these compounds $\mathrm{(H_3Si)_2O}$ and $\mathrm{(CH_3CH_2)_2O}$, which do you expect to have the lower force constant, Si-O-Si bending or C-O-C bending?

Solution:
Lower force constant for Si-O-Si bending.

3. Explain how the difference in reactivity between Al-C and Si-C bonds with O-H groups leads to the choice of different strategies for the synthesis of aluminum and silicon alkoxides.

Solution

$$\mathrm{Al_2Me_6 + 6\,MeOH \longrightarrow 2\,Al(OMe)_3 + 6\,CH_4}$$

For reaction of Al_2Me_6 with alcohols, see the text book by Shriver and Atkins.
Tetramethylsilane does not react with methyl alcohol. Therefore, the appropriate reagent is tetrachlorosilane and the reaction is:

$$\mathrm{SiCl_3 + 4\,MeOH \longrightarrow Si(OMe)_4 + 4\,HCl}$$

4. Compare formulas of the most stable hydrogen compounds of germanium and arsenic with those of their methyl compounds. Can the differences be explained in terms of the relative electronegativities of C and H?

Solution

GeH_4, GeR_4; AsH_3, AsR_3

The stability of hydrides and alkyls are very similar for each element. This may due to similar H and C electronegativity.

5. To buy from a chemical company, the price of trimethylaluminum is higher than that of triethylaluminum. Is it due to the methods of synthesis? Rationalize the price difference.

Solution:
Triethylaluminum can be made in larger quantities by direct reaction of aluminum, hydrogen gas and ethane gas which is a cheaper method.

$$\mathrm{2\,Al + 3\,H_2 + 6\,RHC{=}CH_2 \xrightarrow[110-200 atm]{60-110^\circ C} 2\,Al_2(CH_2CH_2R)_6}$$

Preparation of trimethyaluminum involves a more expensive route such as MeCl and aluminum to form $Al_2Me_4Cl_2$ followed by treatment with sodium metal. The sodium metal and MeCl are not cheap as compared to ethane and hydrogen gases.

$$\mathrm{2\,Al + CH_3Cl \longrightarrow Al_2Cl_2(CH_3)_4}$$

$$\mathrm{Al_2Cl_2(CH_3)_4 + 6\,Na \longrightarrow Al_2(CH_3)_6 + 2\,Al + 6\,NaCl}$$

3.3: Organometallic Compounds of Gallium and Indium

Learning Objectives

In this section you will learn the following

- Chemistry of gallium and indium.
- *How to stabilize M—M multiple bonds.*

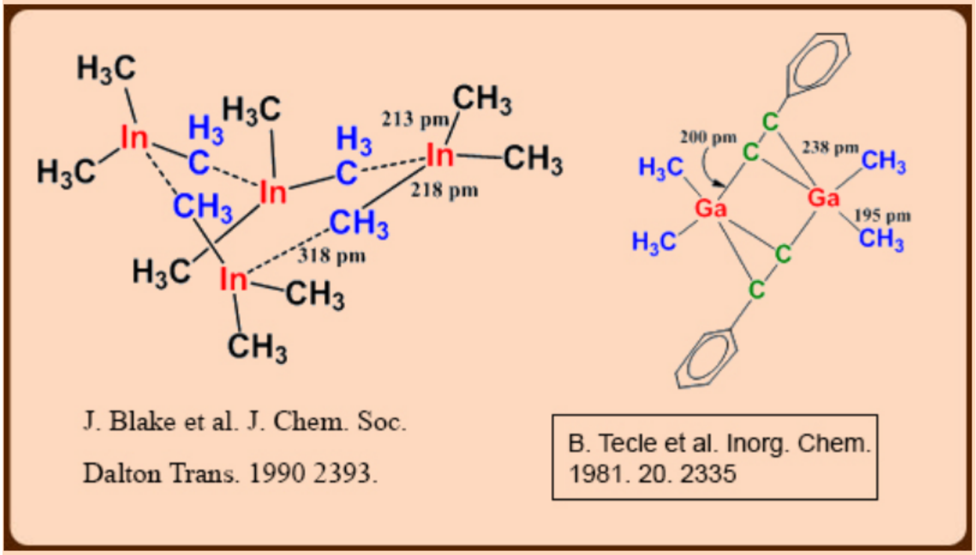
$$3\,Li_4(C_2H_5)_4 + 4\,GaCl_3 \longrightarrow 2\,LiCl + 4\,Ga(C_2H_5)_3$$

Trialkylgallium compounds are mild Lewis acids, so the corresponding metathesis reaction in ether produces the complex $(C_2H_5)_2OGa(C_2H_5)_3$. Similarly excess use of C_2H_5Li leads to the salt, $Li[Ga(C_2H_5)_4]$.

$$Li_4(C_2H_5)_4 + GaCl_3 \longrightarrow 3\,LiCl + Li[Ga(C_2H_5)_4]$$

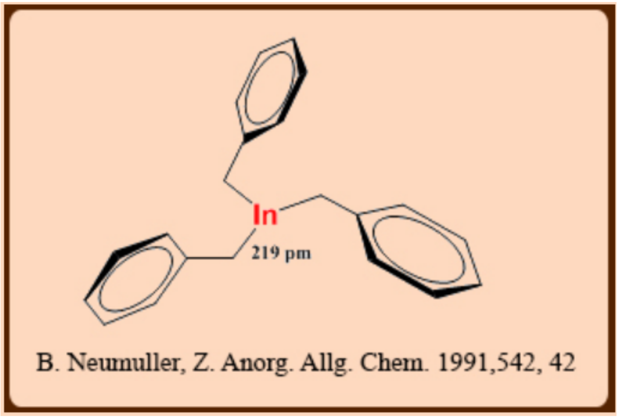
Alkylindium and alkylthalium compounds may be prepared similar to gallium analogs. $InMe_3$ is monomeric in the gas phase and in the solid the bond lengths indicate that association is very weak. Partial hydrolysis of $TlMe_3$ yields the linear $(MeTiMe)^+$ion, which is isoelectronic and isostructural with $HgMe_2$.

CpIn and CoTl exist as monomers in the gas phase but are associated in solids {Inert-pair effect is displayed for In and Tl}. CpTl is useful as a synthetic reagent in organometallic chemistry because it is not as highly reducing as NaCp.



J. Blake et al. J. Chem. Soc. Dalton Trans. 1990 2393.

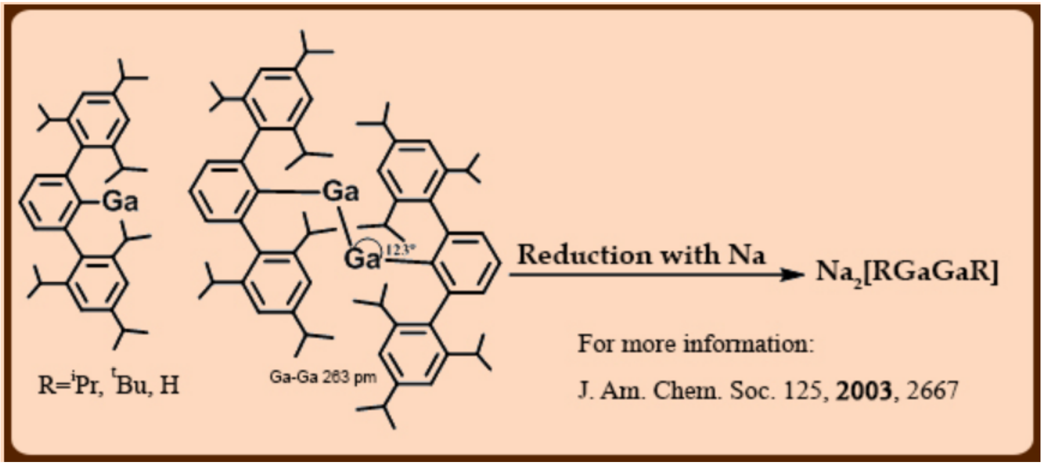
B. Tecle et al. Inorg. Chem. 1981. 20. 2335



B. Neumuller, Z. Anorg. Allg. Chem. 1991,542, 42

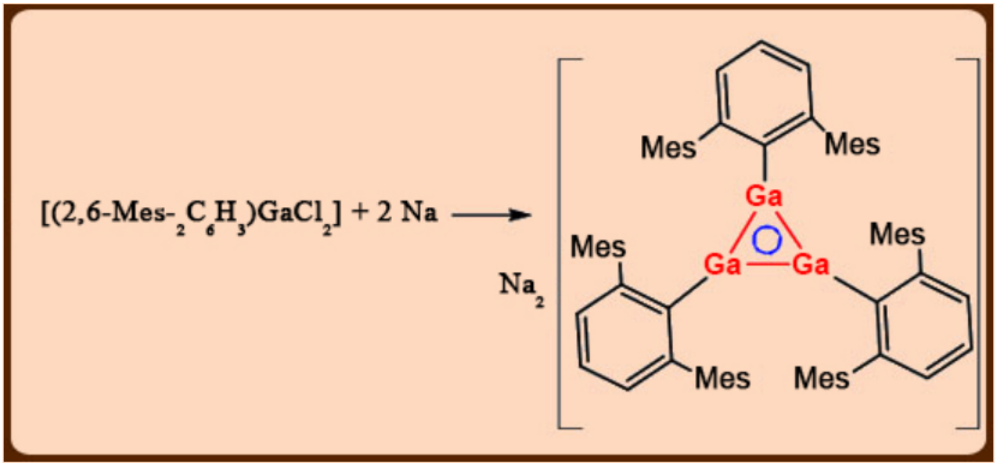
Species of the type R_4E_2(single E-E bond) and $[R_4E_2]^-$ (with E-E bond order of 1.5) can be prepared for Ga and In with bulky R groups (R = $(Me_3Si)_2CH$, 2,4,6-$^iPr_3C_6H_2$), and reduction of $[(2,4,6\text{-}^iPr_3C_6H_2)_4Ga_2]$ to $[(2,4,6\text{-}^iPr_3C_6H_2)_4Ga_2]^-$ is accompanied by a shortening of the Ga—Ga bond from 252-234 pm.

Using even bulkier substituents, it is possible to prepare gallium(I) compounds, RGa starting from GaI. No structural data are yet available for these monomers
(We are working on it).



For more information:
J. Am. Chem. Soc. 125, **2003**, 2667

Crystallized as dimer but reverts to monomer when dissolved in cyclohexane.



Interest in organometallic comounds of Ga, In and Tl is mainly because of their potential use as precursors to semiconducting materials such as GaAs and InP. Volatile compounds can be used in the growth of thin films by MOCVD (metal organic chemical vapor deposition) or MOVPE (metal organic vapor phase epitaxy) techniques. Precursors include appropriate Lewis base adducts of metal alkyls, e.g. $Me_3Ga.NMe_3$ and $Me_3In.PEt_3$. Thermal decomposition of gaseous precursors result in semiconductors (III-V semiconductors) which can be deposited in thin films.

$$\mathrm{Me_3Ga(g) + AsH_3(g) \xrightarrow{1000-1150\mathit{K}} GaAs(s) + 3\,CH_4(g)}$$

III-V semiconductors: Derive their name from the old groups 13 and 15, and include AlAs, AlSb, GaP, GaAs, GaSb, InP, InAs and InSb. Off these GaAs is of the greatest commercial interest. Although Si is probably the most important commercial semiconductor, a major advandage of GaAs over Si is that the charge carrier mobility is much greater. This makes GaAs suitable for high-speed electronic devices.

Another important difference is that GaAs exhibits a fuly allowed electronic transition between valence and conduction bands (i.e. it is direct band gap semiconductor) whereas Si is an indirect band gap semiconductor. The consequence of difference is that GaAs (also other III-V types) are more suited than Si for use in optoelectronic devices, since light is emitted more efficiently. The III-Vs have important applications in light-emitting diodes (LEDs).

Problems:

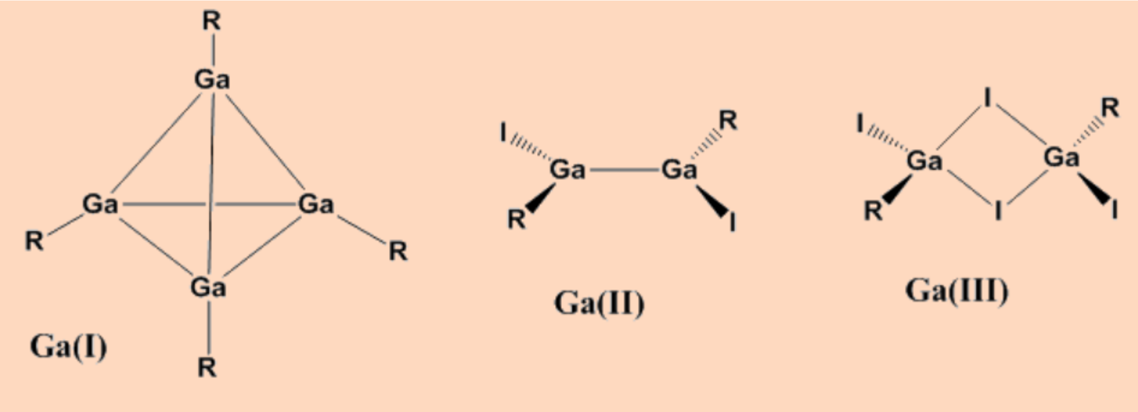
1. Predict the structure of monomeric, Cp_3Ga; polymeric Cp_3In and CpIn.

Solution:

See the articles Organometallics 1985, 4, 751.
Inorg. Chem. 1972, 11, 2832.
Organometallics 1988, 7, 105.

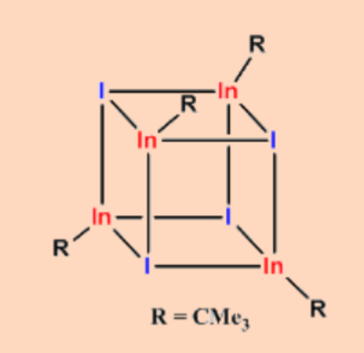
2. The reaction of $[(R_3C)_4Ga_4]$ (R = a bulky substituent) (i) with I_2 in boiling hexane results in the formation of $[(R_3C)GaI]_2$(ii) and $[(R_3C)GaI_2]_2$(iii). Draw the structure and state the oxidation state for (i) - (iii).

Solution:



3. The I_2 oxidation of $[(^tBu\}_4In_4]$ leads to the formation of the In^{II} compound $[(^tBu\}_4In_4I_4]$ in which each indium atom retains a tetrahedral environment. Draw the correct structure.

Solution



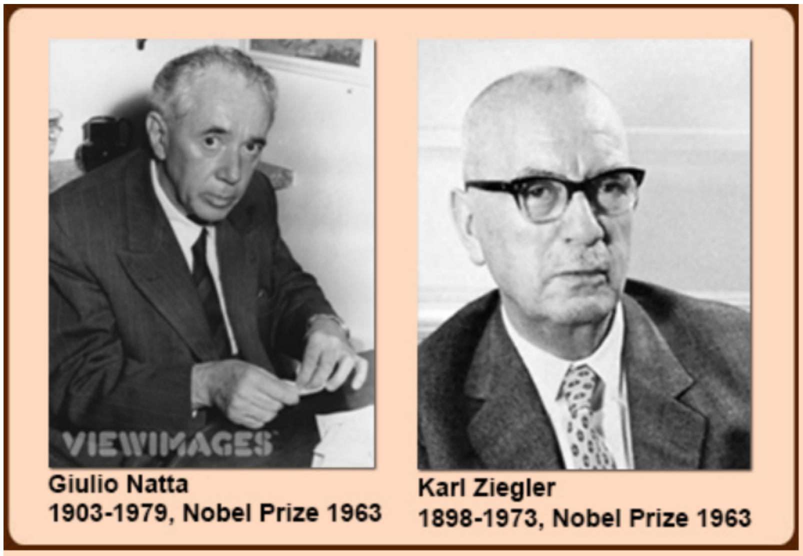
3.4: Zeigler Natta Polymerization Catalysts

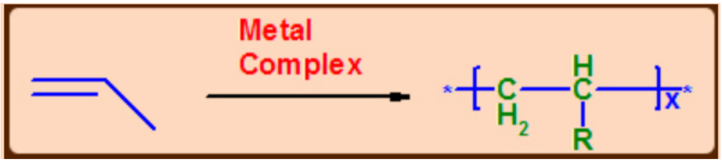
Learning Objectives

In this lecture you will learn the following

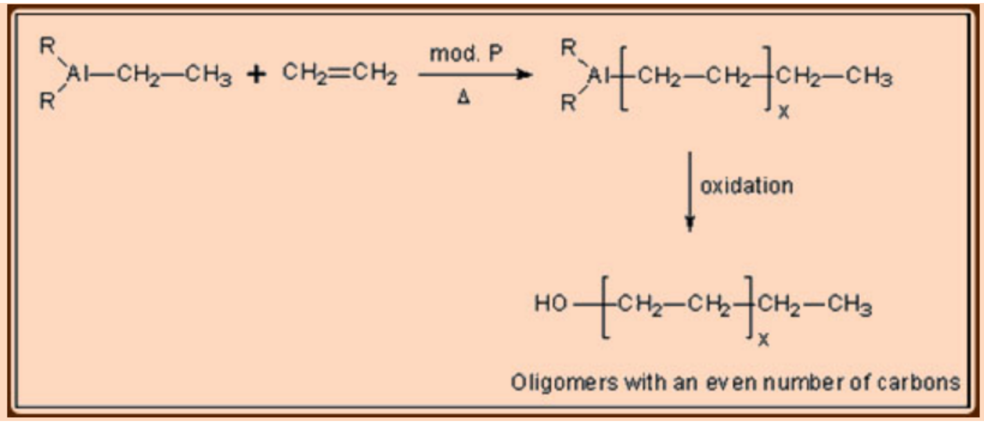
- Olefin polymerization.
- Mechanism involved in polymerization process.

Ziegler Natta Polymerization Catalysts

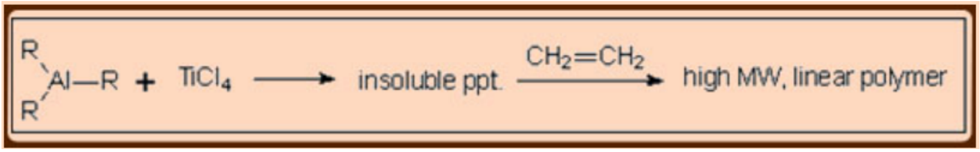




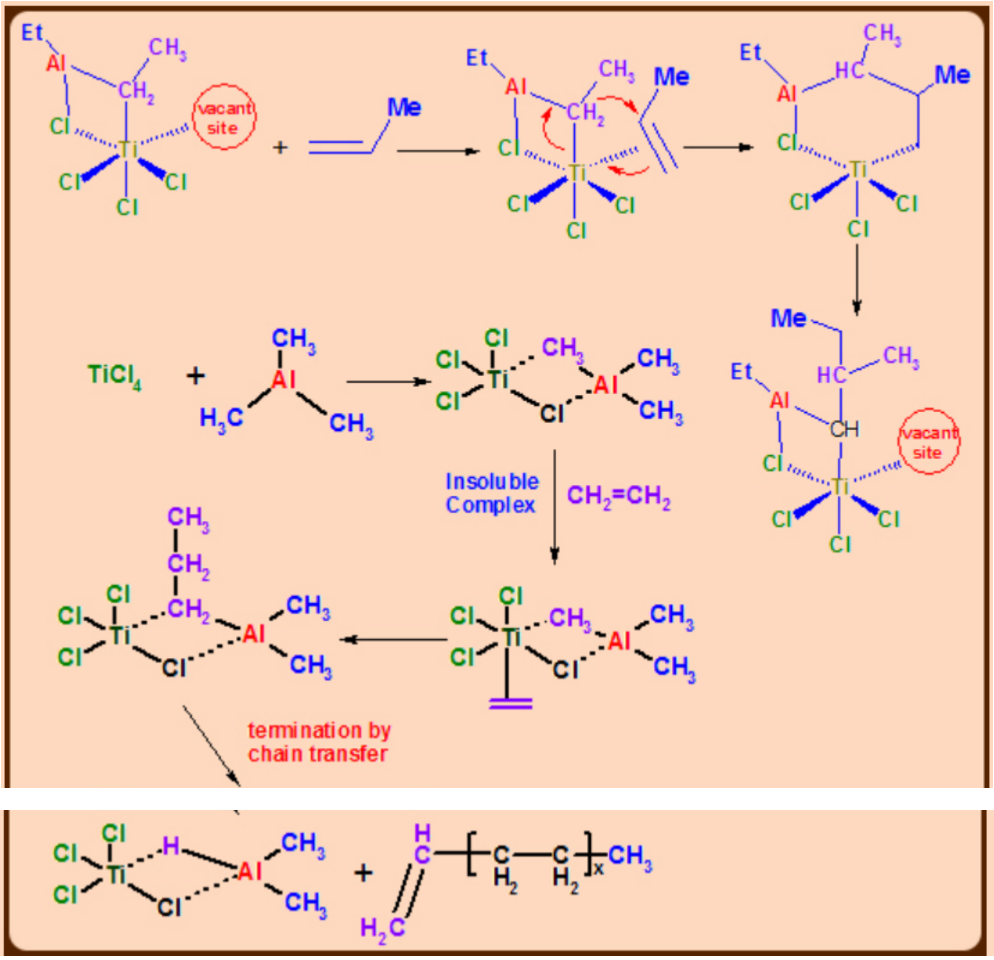
Insertion of aluminum alkyls into olefins was studied by Ziegler. During the systematic investigation of olefin polymerization, Ziegler realized that the most effective catalyst is the combination of $TiCl_4/AlEt_3$which can polymerize ethylene at pressure as low as 1 bar. The application of Ziegler method to the polymerization of propylene and its establishment and the investigation of bulk properties was carried out by Natta and hence the methodology is called Ziegler-Natta process.



Important discovery: R_3Al + Lewis acids.



In the absence of reaction mechanism with solid proof, it is presumed that the reaction is due to the heterogeneous catalysis in which fibrous $TiCl_3$, alkylated on its surface is considered to be the active catalyst species.



This page titled 3.4: Zeigler Natta Polymerization Catalysts is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by M. S. Balakrishna & Prasenjit Ghosh via source content that was edited to the style and standards of the LibreTexts platform.

3.5: Organosilicon and Organogermanium Compounds

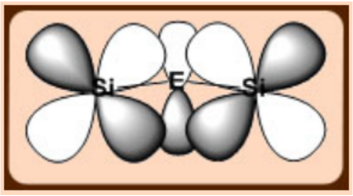
Learning Objectives

In this lecture you will learn the following

- Organosilicon and organogermanium compounds.
- Compounds with Si=Si and Ge=Ge bonds.

Organosilicon and organogermanium compounds

Organosilicon compounds are extensively studied due to the wide range of commercial applications as water repellents, lubricants, and sealants. Many oxo-bridged organosilicon compounds can be synthesized. e.g. $(CH_3)_3Si—O—Si(CH_3)_3$ which is resistant to moisture and air.



The lone pairs on O are partially delocalized into vacant σ*- orbitals of Si, as a result the directionality of the Si-O bond is reduced making the structure more flexible.

This flexibility permits silicone elastomers to remain rubber-like down to very low temperature.

Delocalization also accounts for low basicity of an O atom attached to silicon as the electrons needed for the O atom to act as a base are partially removed.

The planarity of $N(SiH_3)_3$ is also explained by the delocalization of the lone pair on N which makes it very weakly basic.

$$\mathrm{nMeCl + Si/Cu \longrightarrow Me_nSiCl_{4\,-n}}$$

$$\mathrm{SiCl_4 + 4\,RLi \longrightarrow R_4Si}$$

$$\mathrm{SiCl_4 + RLi \longrightarrow RSiCl_3}$$

$$\mathrm{SiCl_4 + 2\,RMgCl \longrightarrow R_2SiCl_2 + 2\,MgCl_2}$$

\[\ce{Me2SiCl2 + tBuBi -> tBuMe2SiCl + LiCl}|]

Si—C bonds are relatively strong (bond enthalpy is 318 kJ mol^{-1}) and R_4Si derivatives possess high thermal stabilities. Et_4Si on chlorination gives $(ClCH_2CH_2)_4Si$, in contrast to the chlorination of R_4Ge or R_4Sn which yields R_nGeCl_{4-n} or R_nSnCl_{4-n}.

Me_2SiCl_2 on hydrolysis produce silicones.

$$\mathrm{Me_3SiCl + NaCp \longrightarrow (\eta^1 - Cp)SiHMe_3}$$

$(\eta^1\text{-}C_5Me_5)\ _2SiBr_2$ on treatment with anthracene/potassium gives $Cp^*{}_2Si$

Solid state structure of $Cp^*{}_2Si$ consists of two independent molecules which differ in the relative orientations of the Cp rings.

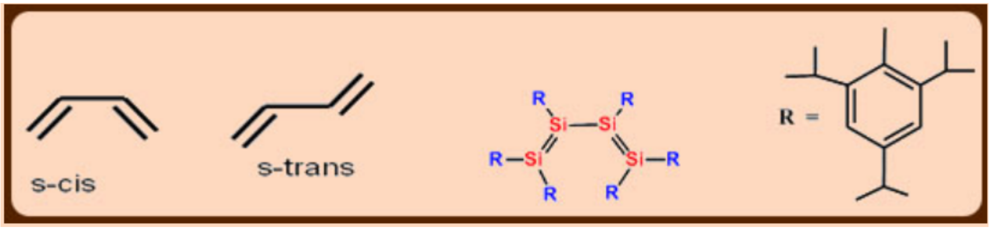
In one molecule, they are parallel and staggered whereas in the other, they are tilted with an angle of 167°at Si.
The reaction between R_2SiCl_2 and alkali metal or alkali naphthalides give cyclo-$(R_2Si)_n$ by loss of $Cl^-$and Si—Si bond formation. Bulky R groups favour small rings [e.g. $(2,6\text{-}Me_2C_6H_3)_6Si_3$ and $^tBu_6Si_3$] while smaller R groups encourage the formation of large rings [$Me_{12}Si_6$, $Me_{14}Si_7$ and $Me_{32}Si_{16}$]

$$[Ph2SiCl2 + Li(SiPh2)5Li - > cyclo - Ph12Si6 + 2LiCl$$

Bulky substituents stabilize $R_2Si{=}SiR_2$ compounds. The sterically demanding 2,4,6-$^iPr_3C_6H_2$ provided first example of compound containing conjugated Si=Si bonds.

Has s-cis configuration in both solution and the solid state.

Similar germanium compounds are also known



*****The spatial arrangement of two conjugated double bonds about the intervening single bond is described as s- cis if synperiplanar and s-trans if antiperiplanar.

3.6: Organotin and Organolead Compounds

Learning Objectives

In this section you will learn the following

- *Organotin and organolead compounds and their preparation.*
- *Bonding in tin compounds with Sn=Sn double bonds.*
- *Uses and environmental issues with tin compounds.*
- Reactivity of tetraethyl lead.
- Structural features of organolead compounds.

Organotin and organolead compounds

Preparation of Sn(IV) derivatives

$$3\,\mathrm{SnCl_3} + 4\,\mathrm{R_3Al} \xrightarrow{R'2O} 3\,\mathrm{R_4Sn} + 4\,\mathrm{AlCl_3}$$

$$\mathrm{R_4Sn} + \mathrm{SnCl_4} \longrightarrow \mathrm{R_3SnCl} + \mathrm{RSnCl_3} \xrightarrow{500K} 2\,\mathrm{R_2SnCl_2}$$

$$\mathrm{SnCl_4} + 4\,\mathrm{RMgBr} \longrightarrow \mathrm{R_4Sn} + 4\,\mathrm{MgBrCl}$$

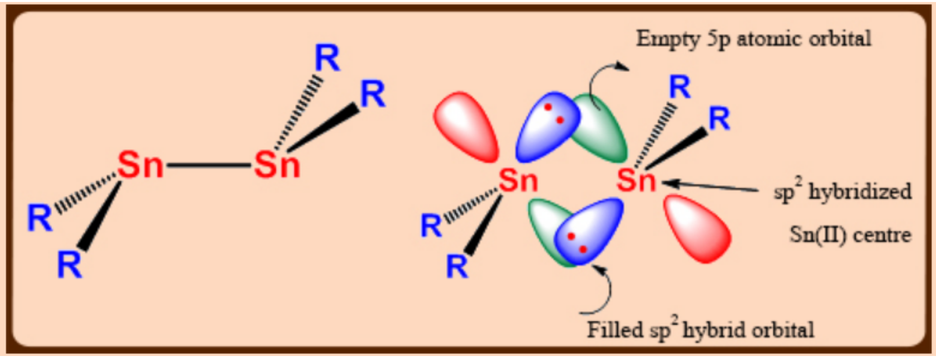
$$\mathrm{SnCl_2} + \mathrm{Ph_2Hg} \longrightarrow \mathrm{Ph_2SnCl_2} + \mathrm{Hg}$$

Tin(II) organometallics of the type R_2Sn, containing Sn-C σ-bonds, are stabilized only if R is sterically demanding.

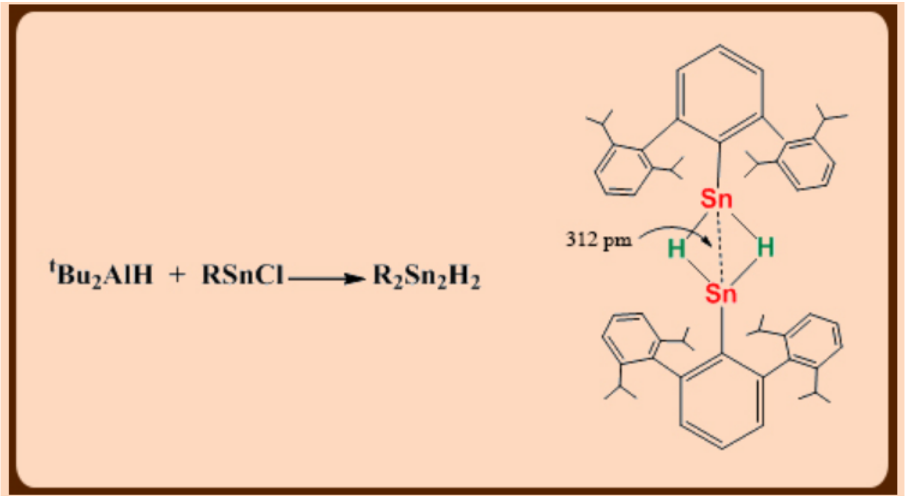
$$\mathrm{SnCl_2} + 2\,\mathrm{Li[(Me_3Si)_2CH]} \longrightarrow \mathrm{[(Me_3Si)_2CH]_2Sn}$$

(monomeric in solution and dimeric in solid state). But the dimer does not possess a planar Sn_2R_4framework unlike an analogous alkene, and Sn—Sn bond distance (267 pm) is shorter than a normal Sn—Sn single bond (276 pm).

Sn_2R_4 has a trans bent structure with a weak Sn=Sn double bond



Look into the reactions of R_3SnCl with various reagents to form useful tin containing starting materials
The first organotin(II) hydride was reported only in 2000.



Shows dimeric structure in the solid state containing hydride bridges (Sn-Sn = 312 pm).

Commercial uses and environmental problems

Organotin(II) compounds find wide range of applications due to their catalytic and biocidal properties.

- $^{n}Bu_3SnOAc$ is an effective fungicide and bactericide and also a polymerization catalyst.
- $^{n}Bu_2Sn(OAc)_2$ is used as a polymerization catalyst and a stabilizer for PVC.
- $^{n}Bu_3SnOSn^{n}Bu_3$ is algicide, fungicide and wood-preserving agent.
- $^{n}Bu_3SnCl$ is a bactericide and fungicide.
- Ph_3SnOH used as an agricultural fungicide for crops such as potato, sugar beet and peanuts.
- The cylic compound $(^{n}Bu_2SnS)_3$ is used as a stabilizer for PVC.

Tributyltin derivatives have been used as antifouling agents, applied to the underside of ships' hulls to prevent the build-up of, for example, barnacles.

Global legislation now bans or greatly restricts the use of organotin-based anti-fouling agents on environmental grounds. Environmental risks associated with the uses of organotin compounds as pesticides, fungicides and PVC stabilizers are also a cause for concern.

*A barnacle is a type of arthropod belonging to infraclass Cirripedia in the sub-phylum Crustacea, and is hence related to crabs and lobsters.

Organolead compounds

Tetraethyllead

$$4\,\mathrm{NaPb} + 4\,\mathrm{EtCl} \longrightarrow \mathrm{Et_4Pb} + 3\,\mathrm{Pb} + 4\,\mathrm{NaCl}[at\ 373K\ in\ an\ autoclave]$$

Laboratory Scale,

$$2\,\mathrm{PbCl_3} + 4\,\mathrm{RMgBr} \xrightarrow[-4MgBrCl]{Et2O} 2\,(\mathrm{R_2Pb}) \longrightarrow \mathrm{R_4Pb} + \mathrm{Pb}$$

Thermolysis leads to radical reactions.

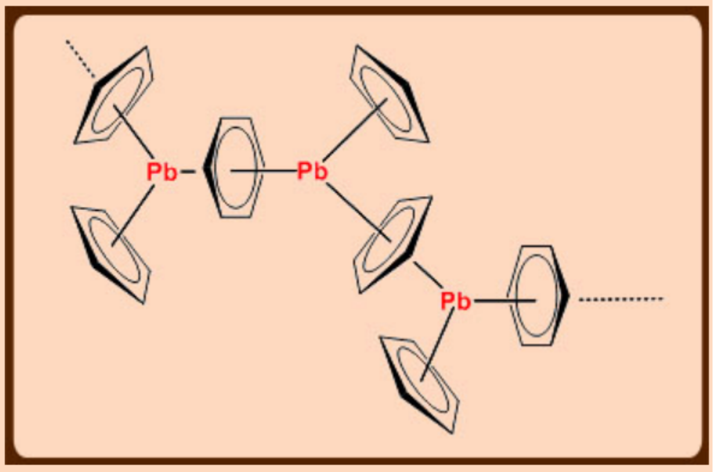
$$\mathrm{Et_4Pb} \longrightarrow \mathrm{Et_3Pb} + \mathrm{Et}$$

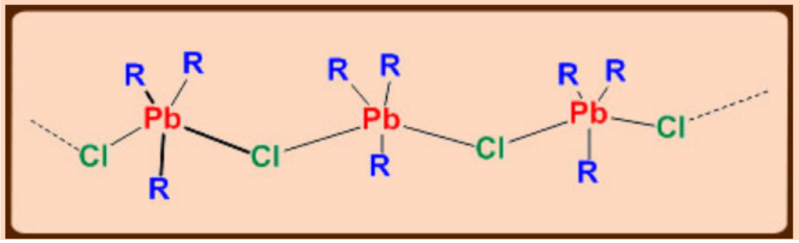
$$2\,\mathrm{Et} \longrightarrow \mathrm{n{-}C_4H_{10}}$$

$$\mathrm{Et_3Pb} + \mathrm{Et} \longrightarrow \mathrm{C_2H_4} + \mathrm{Et_3PbH}$$

$$\mathrm{Et_3Pb} + \mathrm{Et_4Pb} \longrightarrow \mathrm{H_2} + \mathrm{Et_3Pb} + \mathrm{Et_3PbCH_2CH_2}$$

Tetraalkyl and tetraaryl lead compounds are inert with respect to attack by air and water at room temperature. WHY ????





Me_3PbCl consists of linear chain
Solid state structure of Cp_2Pb shows polymeric nature, but in the gas phase, discrete Cp_2Pb molecules are present which possess the bent structure similar to silicon analogue.
$R_2Pb{=}PbR_2$ are similar to analogues tin compounds

Problems

1. Find out the structures of $(Me_3SiCH_2)_3SnF$ and Me_2SnF_2

Solution: use VSEPR theory

CHAPTER OVERVIEW

4: Organoelement Compounds of Group 15

4.1: Organometallic Compounds of As(V) and Sb(V)

Learning Objectives

In this section you will learn the following

- Organoaresnic and organoantimony compounds.
- Preparation and reactivity of pentavlent As and Sb compounds.

Organic chemistry of non-metal phosphorus, metalloids such as arsine and antimony along with metallic element bismuth is termed as organoelement chemistry. The importance given to organoarsenic compounds earlier due to their medicinal values was waded out after antibiotics were discovered and also their carcinogenic and toxic properties were revealed. Also, the synthetically important organometallic compounds of group 13 and 14 masked the growth of group 15 elements. However, the organoelement compounds of phosphorus, arsenic and antimony find usefulness as ligands in transition metal chemistry due to their σ-donor and π-acceptor abilities which can be readily tuned by simply changing the substituents. These donor properties are very useful in tuning them as ligands to make suitable metal complexes for metal mediated homogeneous catalysis. Although organoelement compounds can be formed in both +3 (trivalent and tricoordinated) and +5(pentavalent and tetra or pentacoordinated) oxidation states, trivalent compounds are important in coordination chemistry.

For organoelement compounds of group 15, the energy of E—C bond decreases in the order, E = P > As > Sb > Bi, and in the same sequence E—C bond polarity increases.

Organometallic compounds of As(V) and Sb(V)

Due to the strong oxidizing nature of pentahalides, the direct alkylation or arylation to generate ER_5 is not feasible, but can be prepared in two steps.
A few representative methods of preparation are given below:

$$\mathrm{Me_3As} \xrightarrow{Cl2} \mathrm{Me_3AsCl_2} \xrightarrow[Et2O]{MeLi} \mathrm{Me_5As}$$

$$\mathrm{Ph_3Sb} + \mathrm{PhI} \longrightarrow \mathrm{Ph_4SbI} \xrightarrow[-LI]{PhLi} \mathrm{Ph_5Sb}$$

$$\mathrm{Ph_3Bi} \xrightarrow[-SO2]{SO2Cl2} \mathrm{Ph_3BiCl_2} \xrightarrow[-MgXCl]{PhMgX} \mathrm{Ph_5Bi}$$

Structures and properties

Pentaalkyl or pentaaryl derivatives are moderately thermally stable. On heating above 100°C, they form trivalent compounds as shown below:

$$\mathrm{Me_5As} \xrightarrow{T>100^\circ} \mathrm{Me_3As} + \mathrm{CH_4} + \mathrm{CH_2CH_2}$$

$$\mathrm{Ph_5Sb} \xrightarrow{T>200^\circ} \mathrm{Ph_3Sb} + \mathrm{Ph{-}Ph}$$

Reaction with water,

$$\mathrm{Me_5As}^{+}\mathrm{H_2O} \longrightarrow \mathrm{Me_4AsOH} + \mathrm{MeH}$$

Pentavalent compounds readily form “tetrahedral onium” cations and “octahedral and hexacoordinatged ate” anions.

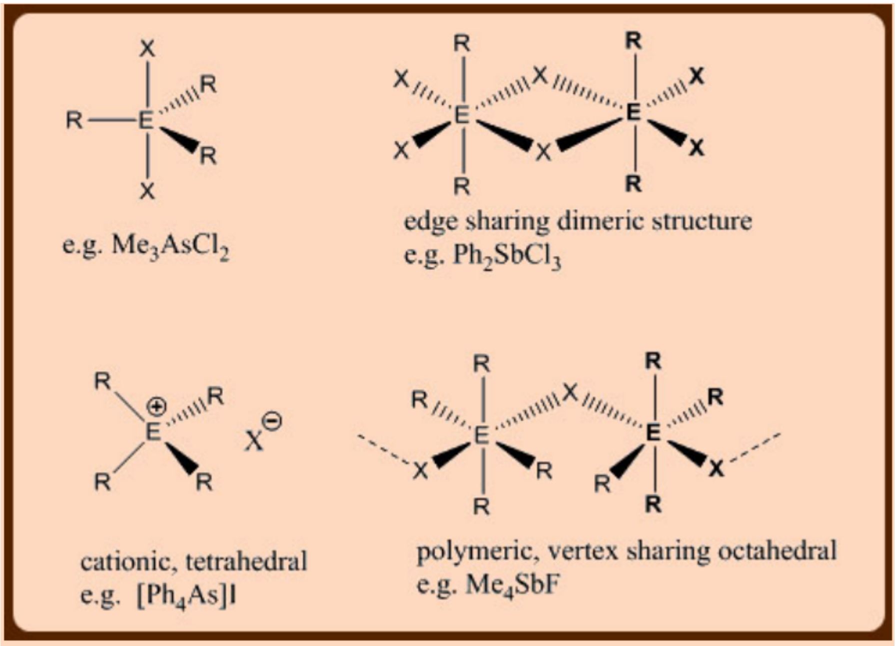
$$\mathrm{Ph_5E} + \mathrm{BPh_3} \longrightarrow [\mathrm{Ph_4E}][\mathrm{BPh_4}](E = As, Sb, Bi)$$

$$\mathrm{Ph_5E} + \mathrm{LiPh} \longrightarrow \mathrm{Li}[\mathrm{EPh_6}]$$

In solid state, Ph_5As adopts trigonal bipyramidal geometry, whereas Ph_5Sb prefers square based pyramidal geometry although the energy difference between the two is marginal.

The salts of the type $[R_4E]^+$ adopt tetrahedral geometry, whereas hexacoordinated anions $[R_6E]^-$assume octahedral geometry.

Mixed organo-halo compounds of the type R_nEX_{5-n} adopt often dimeric structures due to the presence of lone pairs of electrons on X which can readily coordinate to the second molecule. The following structural types can be anticipated.



The thermal stability of R_nEX_{5-n} decreases with decreasing ‘n’. Thermal reactions are essentially the reverse reactions of addition reactions used in the preparation of R_5E.

$$R_3SbX_2 \xrightarrow{\Delta T} R_2SbX + RX$$

$$Ph_3AsCl_2 \xrightarrow[100^\circ C]{CO_2} Ph_2AsCl + Cl_2$$

$$Me_2AsCl_3 \xrightarrow{50^\circ C} MeAsCl_2 + MeCl$$

4.2: Organometallic Compounds of As(III) and Sb(III)

Learning Objectives

In this lecture you will learn the following

- Preparation of trivalent compounds.
- Mono and bis derivatives.
- Reaction of organo arsenic and antimony compounds.
- Structural features of organolead compounds.

Organometallic compounds of As(III) and Sb(III)

Direct synthesis

Mono- derivatives

$$2\,\mathrm{As} + 3\,\mathrm{MeBr} \xrightarrow[Cu]{\Delta T} \mathrm{Me_2AsBr} + \mathrm{MeAsBr_2}$$

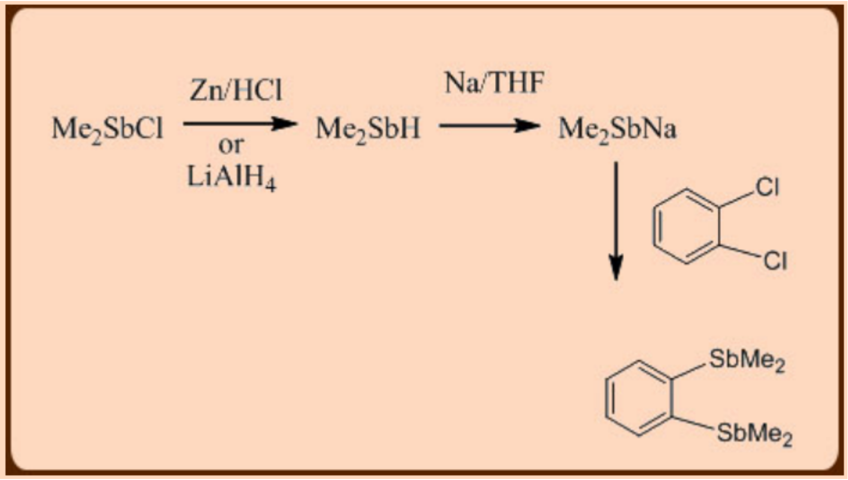
$$\mathrm{Me_2AsBr} + \mathrm{PhLi} \longrightarrow \mathrm{Me_2AsPh}$$

$$\mathrm{MeAsBr_2} + 2\,\mathrm{PhLi} \longrightarrow \mathrm{MeAsPh_2}$$

$$\mathrm{EX_3} + 3\,\mathrm{RMgX} \longrightarrow \mathrm{R_3E} + 3\,\mathrm{MgX_2}$$

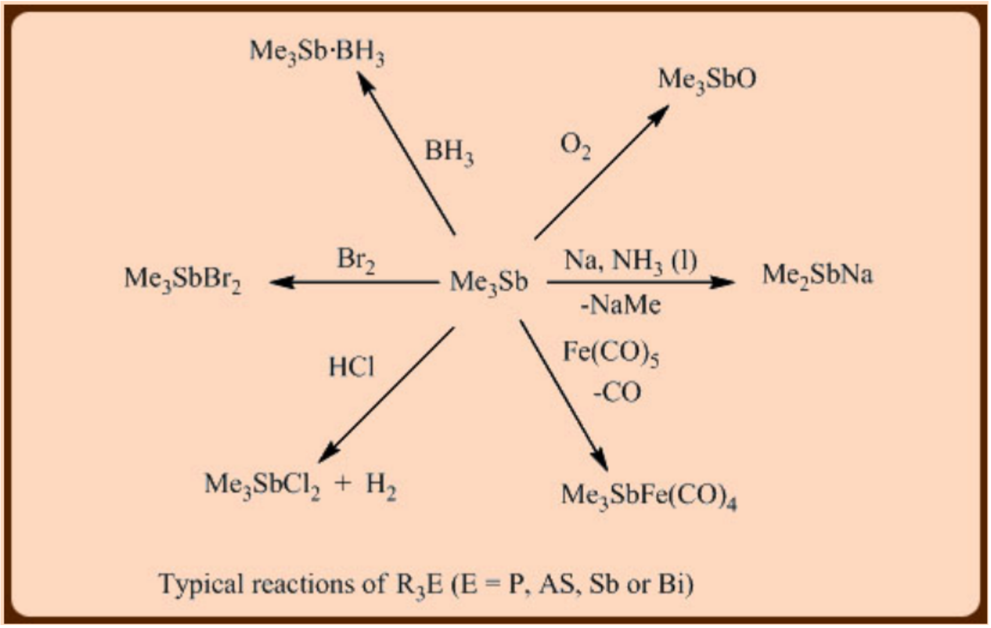
$$\mathrm{EX_3} + 3\,\mathrm{RLi} \longrightarrow \mathrm{R_3E} + 3\,\mathrm{LiX}$$

Bis derivatives:



In a similar way, a variety of bisphosphines and arsines can be generated.

Reactions of trialkyl derivatives, R_3E



Typical reactions of R_3E (E = P, AS, Sb or Bi)

The transition metal chemistry of R_3E, phosphines, arsines or stibines has been extensively studied because of their distinct donor and acceptor properties. Among them, the phosphines or tertiary phosphines (R_3P) are the most valuable ligands in metal mediated homogeneous catalysis. Interestingly, the steric and electronic properties can be readily tuned by changing the substituents on phosphorus atoms. Chapter 16 is fully dedicated to the chemistry of phosphines.

Properties

Trialkyl derivatives are highly air-sensitive liquids with low boiling points and some of them are even *pyrophyric*. Triphenyl derivatives are solids at room temperature and are moderately stable and oxidizing agents such as $KMnO_4$, H_2O_2 or TMNO are needed for oxidation to form $Ph_3E{=}O$.

Cyclic and acyclic derivatives containing E—E bonds

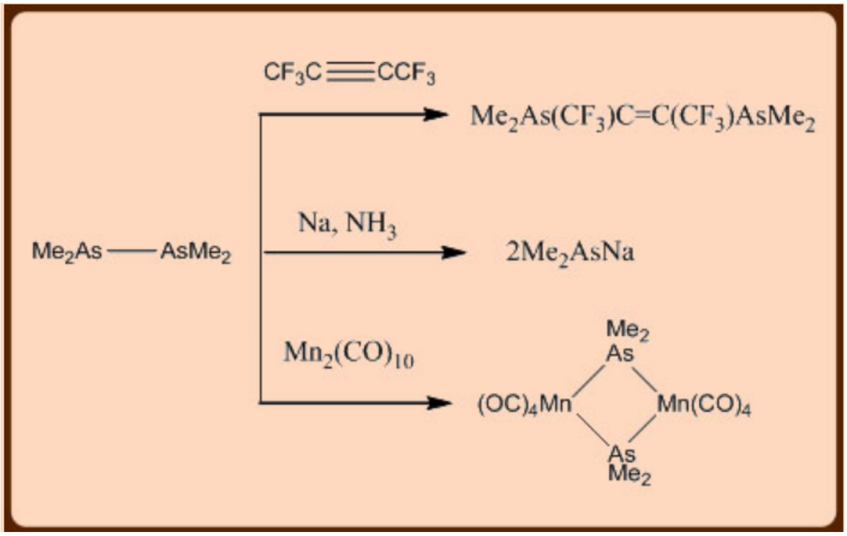
E—E single bonds:

The E—E bond energies suggest that they do not have greater stability and the stability decreases down the group.
The simplest molecules include $Ph_2P{-}PPh_2$, $Me_2As{-}AsMe_2$ prepared by coupling reactions:

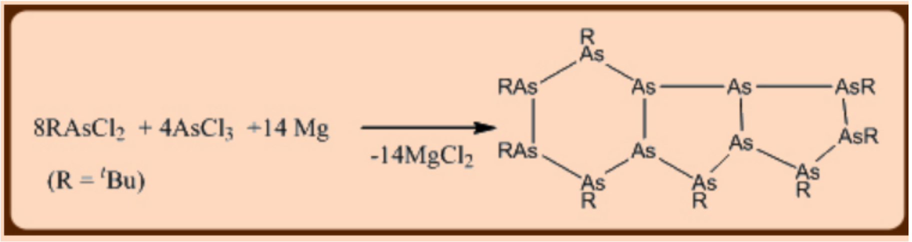
$$\mathrm{Me_2AsH + Me_2AsCl \xrightarrow[-HCl]{} Me_2As{-}AsMe_2}$$

$$\mathrm{2\,Ph_2BiCl \xrightarrow{Na,NH3} Ph_2Bi{-}BiPh_2}$$

The weakness of E—E bonds accounts for many interesting reactions and a few of such reactions are listed below:



Cyclic and polycyclic derivatives can be prepared by employing any of the following methods:



Problems:

1. Confirm that the octahedral structure of $[Ph_6Bi]^-$ is consistent with VSEPR theory.

Solution:
Octahedral similar to PF_6^-
5 (Bi valence electrons) + 6 (each Ph) + 1 (-ve charge) = 12 electrons

i.e. six pairs, octahedral geometry

2. Comment on the stability of $BiMe_3$ and $Al_2(^iBu)_6$ with respect to their thermal decomposition and give chemical equations for their decomposition.

Solution:
Similar to other heavy p-block elements, Bi—C bonds are weak and readily undergo homolytic cleavage. The resulting methyl radicals will react with other radicals or form ethane.

$$2\,\mathrm{BiMe_3} \longrightarrow 2\,\mathrm{Bi} + 3\,\mathrm{CH_3{-}CH_3}$$

The $Al_2(^iBu)_6$ dimer readily dissociates. At elevated temperature dissociation is followed by β-hydrogen elimination. This type of elimination is common for organometallic compounds that have alkyl groups with β-hydrogens, can form stable M—H bonds, and can provide a coordination site on the central metal.

The decomposition reaction is:

$$\mathrm{Al_2(iBu)_6} \xrightarrow{\Delta} 2\,\mathrm{Al(iBu)_3} \longrightarrow [\Delta\Delta]\,\mathrm{Al(iBu)_2H} + \mathrm{(CH_3)_2C{=}CH_2}$$

3. Using a suitable Grignard reagent, how would you prepare (i) MeC(Et)(OH)Ph; (ii) $AsPh_3$.

Solution

i. Add a Grignard reagent to a C=O bond, then acidify.

Several possibilities, e.g.

$$\mathrm{Me{-}C(O){-}Et + PhMgBr \longrightarrow Me{-}C(OMgBr)(Et)(Ph) \longrightarrow MeC(Et)(OH)Ph\ or\ Me{-}C(O){-}Ph + EtMgBr \longrightarrow etc}$$

ii. $$\mathrm{AsCl_3 + 3\,PhMgBr \longrightarrow AsPh_3 + 3\,MgBrCl}$$

4.3: Phosphines

Learning Objectives

In this lecture you will learn the following

- Classification of ligands.
- Nature of bonding in phosphines.
- Steric and electronic properties of phosphines.
- Bonding in phosphines and CO.
- Cone angle and its application in catalysis.

Classification of Ligands by donor atoms

Ligand is a molecule or an ion that has at least one electron pair that can be donated. Ligands may also be called Lewis bases; in terms of organic chemistry, they are ‘nucleophiles’.

Metal ions or molecules such as BF_3 (with incomplete valence electron shells (electron deficient) are called Lewis acids or electrophiles).

Why do molecules like H_2O or NH_3 give complexes with ions of both main group and transition metals. E.g $[Al(OH_2)_6]^{3+}$ or $[Co(NH_3)_6]^{3+}$

Why other molecules such as PF_3 or CO give complexes only with transition metals.

Although PF_3 or CO give neutral molecules such as $Ni(PF_3)_4$ or $Ni(CO)_4$ or $Cr(CO)_6$.

Why do, NH_3, amines, oxygen donors, and so on, not give complexes such as $Ni(NH_3)_4$.

Classical or simple donor ligands

Act as electron pair donors to acceptor ions or molecules, and form complexes of all types of Lewis acids, metal ions or molecules.

Non-classical ligands, π-bonding or π-acid ligands: Form largely with transition metal atoms.

In this case special interaction occurs between the metals and ligands

These ligands act as both σ-donors and π-acceptors due to the availability of empty orbitals of suitable symmetry, and energies comparable with those of metal t_{2g} (non-bonding) orbitals.

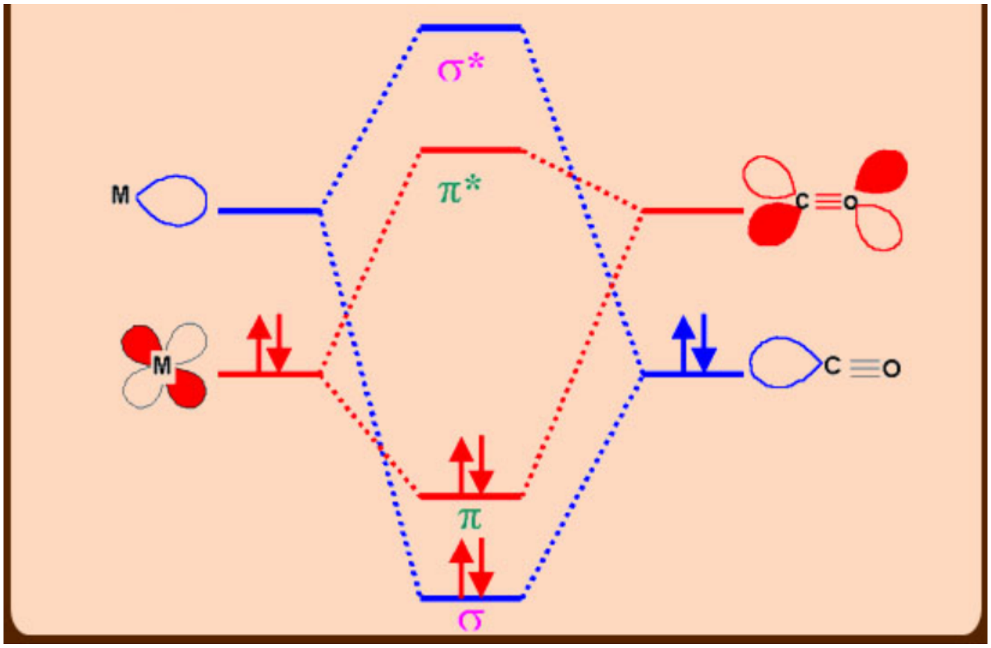
e.g. Consider PR_3 and NH_3: Both can act as bases toward H^+, but P atom differs from N in that PR_3 has σ* orbitals of low energy, whereas in N the lowest energy d orbitals or σ* orbitals are far too high on energy to use.

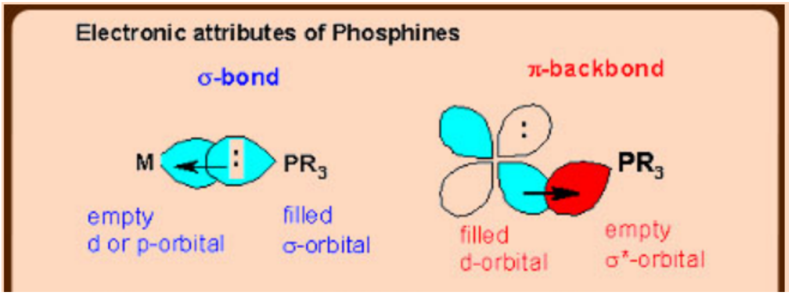
Consider CO that do not have measurable basicity to proton, yet readily reacts with metals like Ni that have high heats of atomization to give compounds like $Ni(CO)_4$.

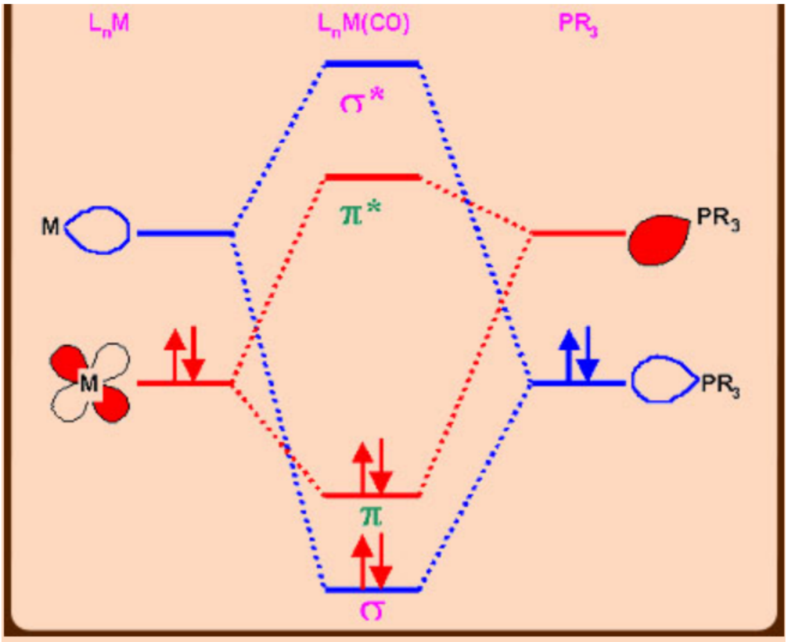
Ligands may also be classified electronically depending upon how many electrons that they contribute to a central atom. Atoms or groups that can form a single covalent bond are one electron donors.

EXAMPLES: F, SH, CH_3 etc.,
Compounds with an electron pair are two-electron donors

EXAMPLE: NH_3, H_2O, PR_3 etc.,

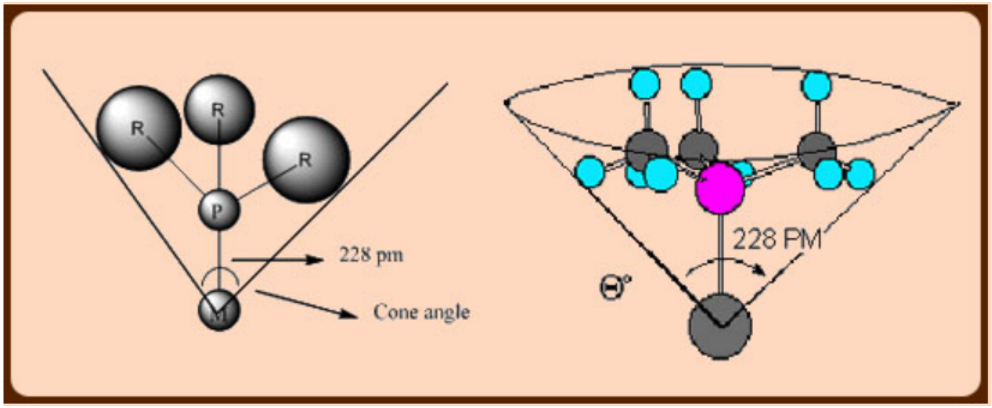

σ*
π*
M
C≡O
M
C≡O
π
σ


Electronic attributes of Phosphines
σ-bond
π-backbond
M
PR$_3$
PR$_3$
empty
d or p-orbital
filled
σ-orbital
filled
d-orbital
empty
σ*-orbital


L$_n$M
L$_n$M(CO)
PR$_3$
σ*
π*
M
PR$_3$
M
PR$_3$
π
σ

Steric factors in phosphines (Tolman's cone angle)

Cone angle is very useful in assessing the steric properties of phosphines and their coordination behavior.



The electronic effect of phosphines can be assessed by IR and NMR spectroscopic data especially when carbonyls are co-ligands. In a metal complex containing both phosphines and carbonyl, the ν(CO) frequencies would reveal the σ-donor or π–acceptor abilities of phosphines. If the phosphines employed are strong σ-donors, then more electron density would move from M (t_{2g} orbitals)- π*(CO) and as a result, a lowering in the ν(CO) is observed. In contrast, if a given phosphine is a poor σ-donor but strong π -acceptor, then phosphine(σ*-orbitals) also compete with CO for back bonding which results in less lowering in ν(CO) frequency.

Another important aspect is the steric size of PR_3 ligands, unlike in the case of carbonyls, which can be readily tuned by changing R group. This is of great advantage in transition metal chemistry, especially in metal mediated catalysis, where stabilizing the metals in low coordination states is very important besides low oxidation states. This condition can promote oxidative addition at the metal centre which is an important step in homogeneous catalysis. The steric effects of phosphines can be quantified with Tolman's cone angle.

Cone angle can be defined as a solid angle at metal at a M—P distance of 228 pm which encloses the van der Waal's surfaces of all ligand atoms or substituents over all rotational orientations. The cone angles for most commonly used phosphines are listed in the following table.

Phosphine	***Cone Angle (°)***
PH_3	***87***
PF_3	***104***
$P(OMe)_3$	***107***
PMe_3	***118***
PMe_2Ph	***122***
PEt_3	***132***
PPh_3	***145***
PCy_3	***170***
$P(Bu^t)_3$	***182***
$P(mesityl)_3$	***212***

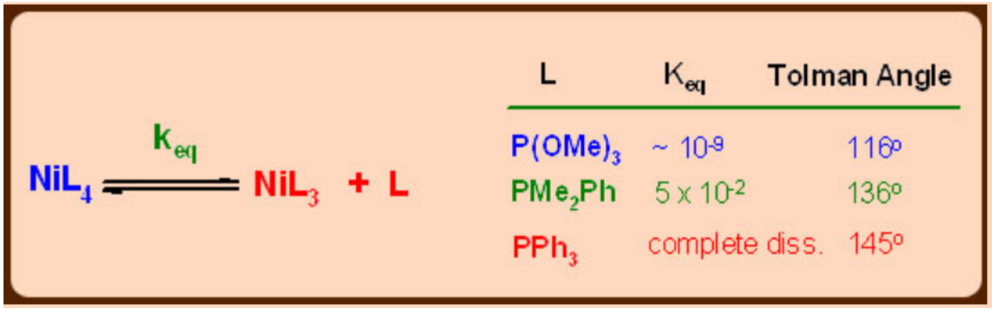
Phosphines with different cone angles versus coordination number for group 8 metals:

ML_4	***ML_3***	***ML_2***
$(Me_3P)_4Ni$		
$(Me_3P)_4Pd$		

$(Me_3P)_4Pt$	***$(Ph_3P)_3Pt$***	***$(tert\text{-}Bu_3P)_2Pt$***

Tolman Angle and Catalysis

Sterically demanding phosphine ligands can be used to create an empty coordination site (16 VE complexes) which is an important trick to fine tune the catalytic activity of phosphine complexes.



$$NiL_4 \overset{k_{eq}}{\rightleftharpoons} NiL_3 + L$$

L	K_{eq}	Tolman Angle
$P(OMe)_3$	~ 10^{-9}	116°
PMe_2Ph	5×10^{-2}	136°
PPh_3	complete diss.	145°

CHAPTER OVERVIEW

5: Group 12 Elements

5.1: Organometallic Compounds of Zinc and Cadmium

Learning Objectives

In this section you will learn the following

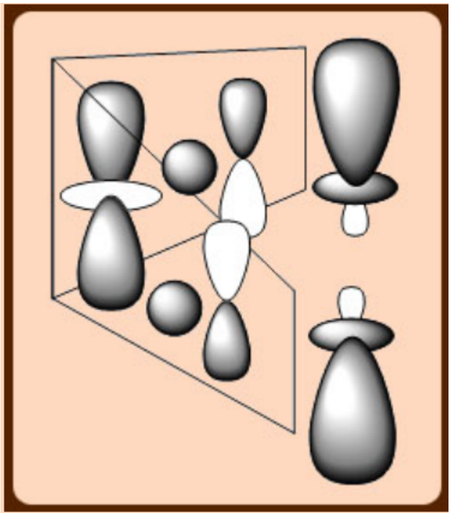
- Organometallic compounds of zinc and cadmium.
- Structural features of organozinc compounds

Organometallic compounds of zinc and cadmium

Dialkyl compounds of Zn, Cd and Hg do not associate through alkyl bridges.
Dialkylzinc compounds are only weak Lewis acids, organocadmium compounds are even weaker, and organomercury compounds do not act as Lewis acids except under special circumstances.

The Group 12 metals form linear molecular compounds, such as $ZnMe_2$, $CdMe_2$ and $HgMe_2$, that are not associated in solid, liquid or gaseous state or in hydrocarbon solution.

They form 2c, 2e bonds. Unlike Be and Mg analogs, they do not complete their valence shells by association through alkyl bridges. The bonding in these molecules are similar to d^{10} metals such as Cu^I, Ag^I and Au^I with linear geometry ($[N\equiv C\text{-}M\text{-}C\equiv N]^-$, M = Ag or Au). This tendency is sometimes rationalized by invoking *pd* hybridization in the M^+ ion, which leads to orbitals that favor linear attachment of ligands (similar to *spd* hybridization).



The preference for the linear coordination may be due to the similarity in energy of the outer n*s*, n*p* and (n-1)*d* orbitals, which permits the formation of collinear *spd* hybrids.

The hybridization of *s*, p_z and d_z2 with the choice of phases shown here produces a pair of collinear orbitals that can be used to form strong σ-bonds.

Organozinc and organocadmium compounds

Convenient route is metathesis with alkylaluminium or alkyllithium compounds.
With alkyllithium compounds it is the electronegativity which is decisive, whereas between Al and Zn it is hardness considerations correctly predict the formation of softer $ZnCH_3$ and harder AlCl pairs.

$$\mathrm{ZnCl_2 + Al_2Me_6 \longrightarrow ZnMe_2 + Al_2Cl_2Me_4}$$

Alkylzinc compounds are pyrophoric and readily hydrolyzed, whereas alkylcadmium compounds react more slowly with air. Due to mild Lewis acidity, dialkylzinc and dialkylcadimum compounds form stable complexes with amines, especially with chelating amines.
The Zn—C has greater carbanionic character than the Cd—C bond.

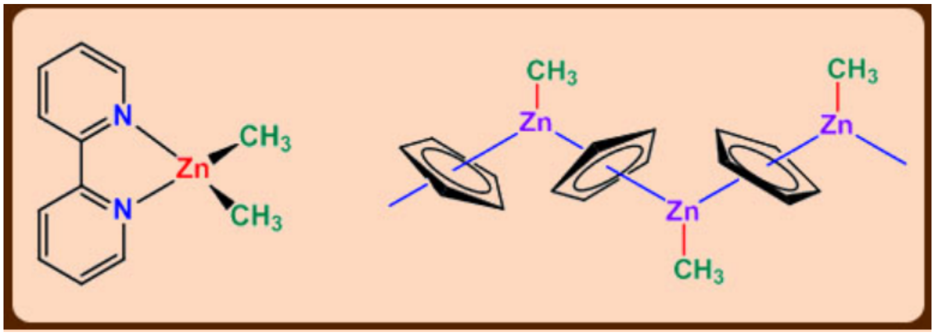
For example, addition of alkylzinc compounds across the carbonyl group of a ketone:

$$\mathrm{ZnMe_2 + (CH_3)_2C{=}O \longrightarrow (CH_3)_2C{-}O{-}ZnCH_3}$$

This reaction do not proceed with the less polar alkylcadmium or alkylmercury compounds, but organolithium, organomagnesium and organoaluminium compounds can promote this reaction readily since all of which contain metals with lower electronegativity than zinc.

Interestingly, the cyclodipentadienyl compounds are structurally unusual. CpZnMe is monomeric in the gas phase with a pentahapto Cp group.

In the solid state it is associated in a zig-zag chain, each Cp group being pentahapto with respect to two Zn atoms.



Problems:

1. Do you think that the following reaction proceeds? If so, why and how?

$$\mathrm{ZnCl_2 + Al_2Me_6 \longrightarrow ZnMe_2 + Al_2Cl_2Me_4}$$

Solution

Al_2Me_6 being an electron deficient molecule readily exchanges two methyl groups with zinc for two chloride ions. Since chloride ions have sufficient electron in their valence shell act as four electron donor through bridging coordination mode. $Al_2Cl_2Me_4$ is no longer an electron deficient molecule.

5.2: Organometallic Compounds of Mercury

Learning Objectives

In this section you will learn the following

- Dialkymercury preparation.
- Mercury toxicity.
- Mercury poisoning.

Consider this reaction that proceeds due to both electronegativity and hardness considerations.

$$2\,\mathrm{RMgX} + \mathrm{HgX_2} \longrightarrow \mathrm{HgR_2} + \mathrm{MgX_2}$$

Dialkylmercury compounds are very versatile starting materials for the synthesis of many organometallic compounds of more electropositive metals by transmetallation. However, owing to high toxicity of alkylmercury compounds, other synthons are preferred. In striking contrast to the high sensitivity of dimethylzinc to oxygen, dimethylmercury survives exposure to air.

Mercury Toxicity

The toxicity of mercury arises from the very high affinity of the soft Hg atom for sulfhydryl (—SH) groups in enzymes. Simple mercury-sulfur compounds have been studied as potential analogs of natural systems. The Hg atoms are most commonly four-coordinated, as in $[Hg_2(SMe)_6]^{2-}$.

Mercury poisoning was a serious concern even from early days. Issac Newton, Alfred Stock worked in the early 20th century. Later in 60s awareness came following the incidence of brain damage and death it caused among the inhabitants in Minamata, Japan. Mercury from a plastic company was allowed to escape into a bay where it found its way into fish that were later eaten. Research has shown that bacteria found in sediments are capable of methylating mercury, and that species such $HgMe_2$ and $[HgCH_3]^+$ enter the food chain because they readily penetrate cell walls. The bacteria appear to produce $HgMe_2$ as a means of eliminating toxic mercury ions through their cell walls and into the environment.

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CHAPTER OVERVIEW

6: General Properties of Transition Metal Organometallic Complexes

6.1: 18 Valence Electron Rule

Learning Objectives

In this section you will learn the following

- Have an insight about the stability of the transition metal complexes with respect to their total valence electron count.
- Be aware of the transition metal complexes that obey or do not obey the 18 Valence Electron Rule.
- Have an appreciation of the valence electron count in the transition metal organometallic complexes that arise out of the metal-ligand orbital interactions.

The transition metal organometallic compounds exhibit diverse structural variations that manifest in different chemical properties. Many of these transition metal organometallic compounds are primarily of interest from the prospectives of chemical catalysis. Unlike the main group organometallic compounds, which use mainly *ns* and *np* orbitals in chemical bonding, the transition metal compounds regularly use the $(n-1)d$, *ns* and *np* orbitals for chemical bonding (Figure 6.1.1). Partial filling of these orbitals thus render these metal centers both electron donor and electron acceptor abilities, thus allowing them to participate in σ-donor/π-acceptor synergic interactions with donor-acceptor ligands like carbonyls, carbenes, arenes, isonitriles and etc,.

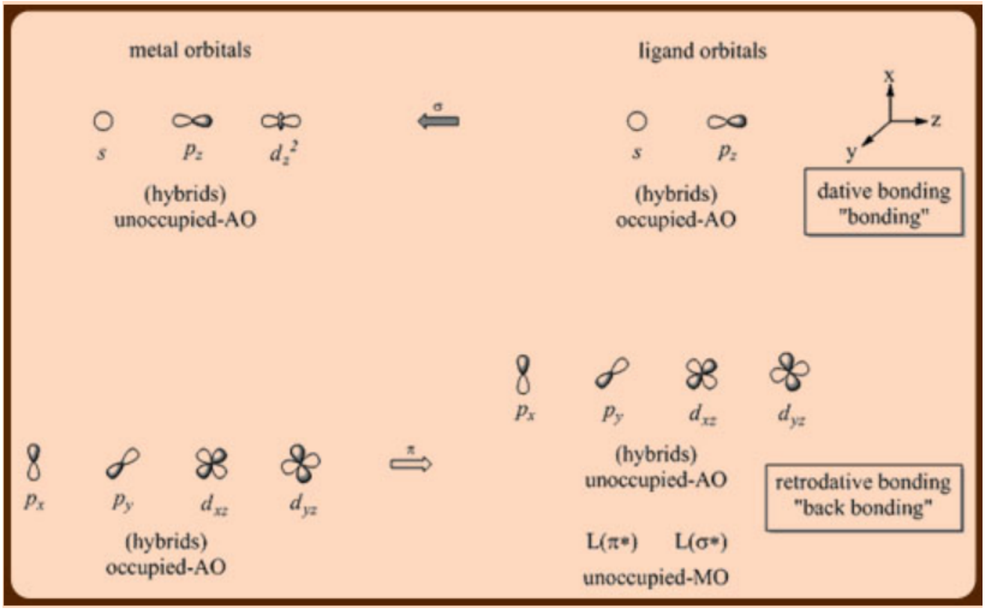
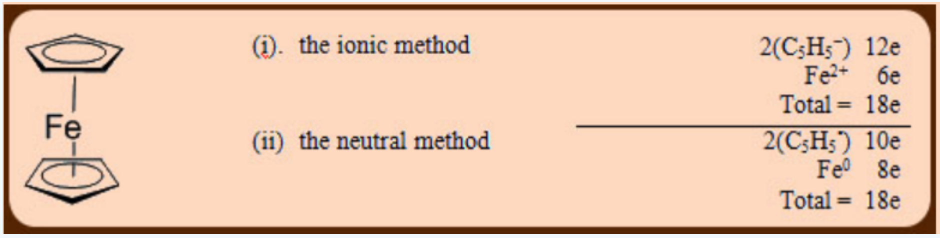


Figure 6.1.1

The 18 Valence Electron (18 VE) Rule or The Inert Gas Rule or The Effective Atomic Number (EAN) Rule: The 18-valence electron (VE) rule states that thermodynamically stable transition metal compounds contain 18 valence electrons comprising of the metal *d* electrons plus the electrons supplied by the metal bound ligands. The counting of the 18 valence electrons in transition metal complexes may be obtained by following either of the two methods of electron counting, (*i*). the ionic method and (*ii*). the neutral method. Please note that a metal-metal bond contributes one electron to the total electron count of the metal atom. A bridging ligand donates one electron towards bridging metal atom.

Example 6.1.1

Ferrocene $Fe(C_5H_5)_2$



(i). the ionic method

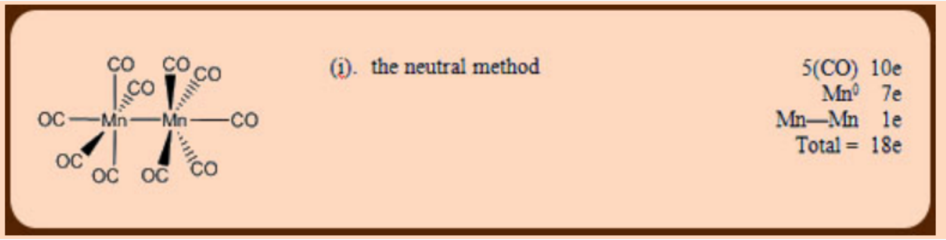
$2(C_5H_5^-)$ 12e
Fe^{2+} 6e
Total = 18e

(ii) the neutral method

$2(C_5H_5^{\cdot})$ 10e
Fe^0 8e
Total = 18e

Example 6.1.2

$Mn_2(CO)_{10}$



(i). the neutral method

5(CO) 10e
Mn^0 7e
Mn—Mn 1e
Total = 18e

Transition metal organometallic compounds mainly belong to any of the three categories.

a. **Class I** complexes for which the number of valence electrons do not obey the 18 VE rule.
b. **Class II** complexes for which the number of valence electrons do not exceed 18.
c. **Class III** complexes for which the valence electrons exactly obey the 18 VE rule.

The guiding principle which governs the classification of transition metal organometallic compounds is based on the premise that the antibonding orbitals should not be occupied; the nonbonding orbitals may be occupied while the bonding orbitals should be occupied.

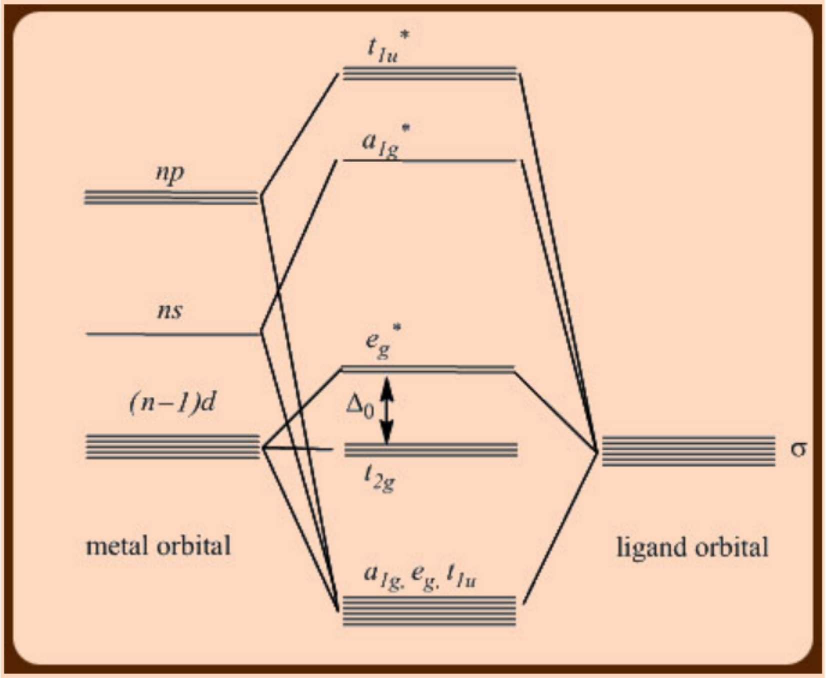


Figure 6.1.2: A simplified molecular orbital diagram for an octahedral transition metal complex showing σ−interactions only.

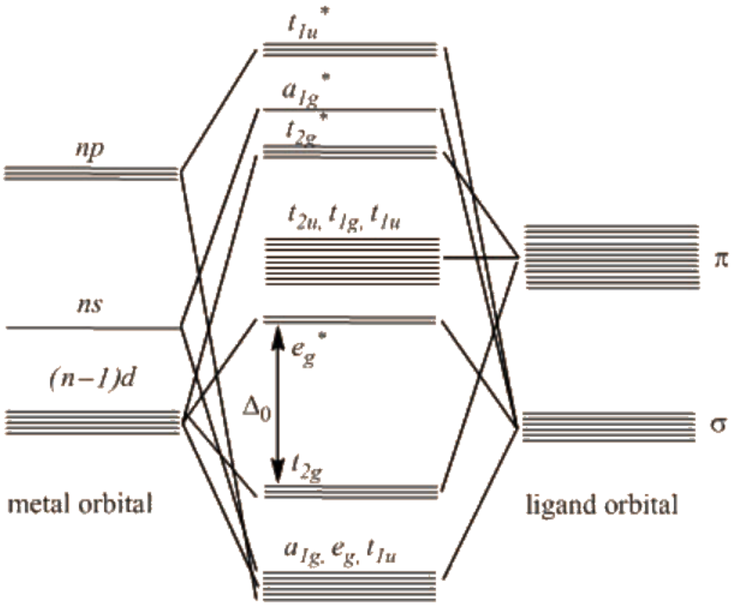


Figure 6.1.3: A simplified molecular orbital diagram for an octahedral transition metal complex showing σ−and π−interactions only.

Class I

In **class I** complexes, the Δ_o splitting is small and often applies to *3d* metals and σ ligands at lower end of the spectrochemical series. In this case the t_{2g} orbital is nonbonding in nature and may be occupied by 0−6 electrons (Figure 6.1.2). The e_g* orbital is weakly antibonding and may be occupied by 0−4 electrons. As a consequence, 12−22 valence electron count may be obtained for this class of compounds. Owing to small Δ_{tetr} splitting energy, the tetrahedral transition metal complexes also belongs to this class.

Class II

In **class II** complexes, the Δ_o splitting is relatively large and is applicable to *4d* and *5d* transition metals having high oxidation state and for σ ligands in the intermediate and upper range of the spectrochemical series. In this case, the t_{2g} orbital is essentially nonbonding in nature and can be filled by 0−6 electrons (Figure 3). The e_g* orbital is strongly antibonding and is not occupied at all. Consequently, the valence shell electron count of these type of complexes would thus be 18 electrons or less.

Class III

In **class III** complexes, the Δ_o splitting is the largest and is applicable to good σ donor and π acceptor ligands like CO, PF_3, olefins and arenes located at the upper end of the spectrochemical series.

The t_{2g}orbital becomes bonding owing to interactions with ligand orbitals and should be occupied by 6 electrons. The e_g* orbital is strongly antibonding and therefore remains unoccupied.

Problems

State the oxidation state of the metal and the total valence electron count of the following species.

1. $V(C_2O_4)_3{}^{3-}$

Ans: +3 and 14

2. $Mn(acac)_3$

Ans: +3 and 16

3. $W(CN)_8{}^{3-}$

Ans: +5 and 17

4. $CpMn(CO)_3$

Ans: 0 and 18

5. $Fe_2(CO)_9$

Ans: 0 and 18

Self Assessment test

State the oxidation state of the metal and the total valence electron count of the following species.

1. TiF_6^{2-}

Ans: +4 and 12

2. $Ni(en)_3^{2+}$

Ans: +2 and 20

3. $Cu(NH_3)_6^{2+}$

Ans: +2 and 21

4. $W(CN)_8^{4-}$

Ans: +4 and 18

5. $CH_3Co(CO)_4$

Ans: 0 and 18

Summary

The transition metal complexes may be classified into the following three types.

i. The ones that do not obey the 18 valence electron rule are of class I type
ii. The ones that do not exceed the 18 valence electron rule are of class II and
iii. The ones that strictly follow the 18 valence electron rule.

Depending upon the interaction of the metal orbitals with the ligand orbitals and also upon the nature of the ligand position in spectrochemical series, the transition metal organometallic compounds can form into any of the three categories.

6.2: Synthesis and Stability

Learning Objectives

In this lecture you will learn the following

- Understand the role lead by ligands in stabilizing organometallic transition metal complexes.
- Know about various synthetic methods available for preparing the organometallic transition metal complexes.
- Understand the various factors like β-elimination and other bimolecular decomposition pathways that contribute to the observed instability of the organometallic transition metal complexes.
- Obtain insight about making stable organometallic transition metal complexes by suppression of the destabilizing factors mentioned.

Ligands play a vital role in stabilizing transition metal complexes. The stability as well as the reactivity of a metal in its complex form thus depend upon the number and the type of ligands it is bound to. In this regard, the organometallic carbon based ligands come in diverse varieties displaying a wide range of binding modes to a metal. In general, the binding modes of the carbon-derived ligands depend upon the hybridization state of the metal bound carbon atom. These ligands can thus bind to a metal in many different ways as depicted below. Lastly, these ligands can either be of *(a)* purely σ−donor type, or depending upon the capability of the ligand to form the multiple bonds may also be of *(b)* a σ−donor/π−acceptor type, in which the σ−interaction is supplemented by a varying degree of π−interaction.

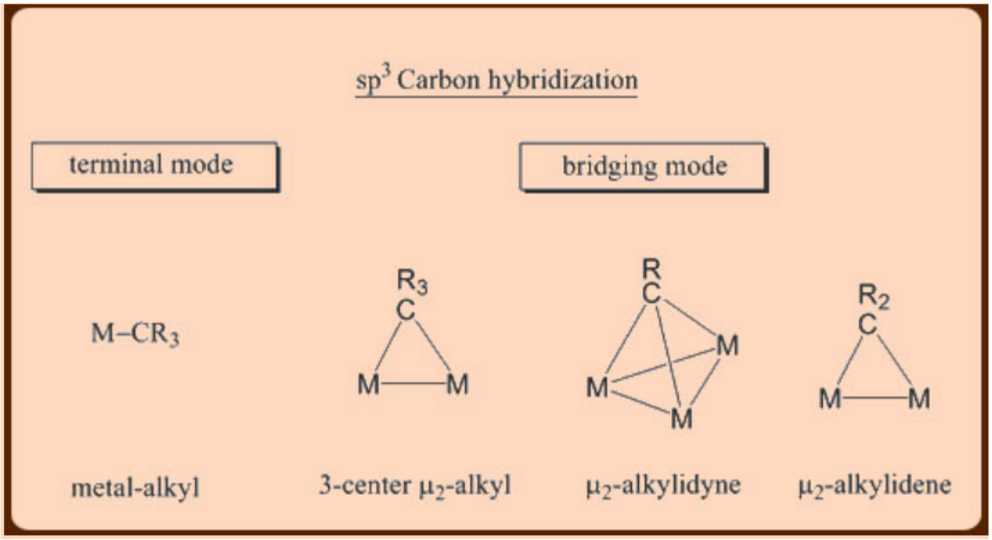


Figure 6.2.1

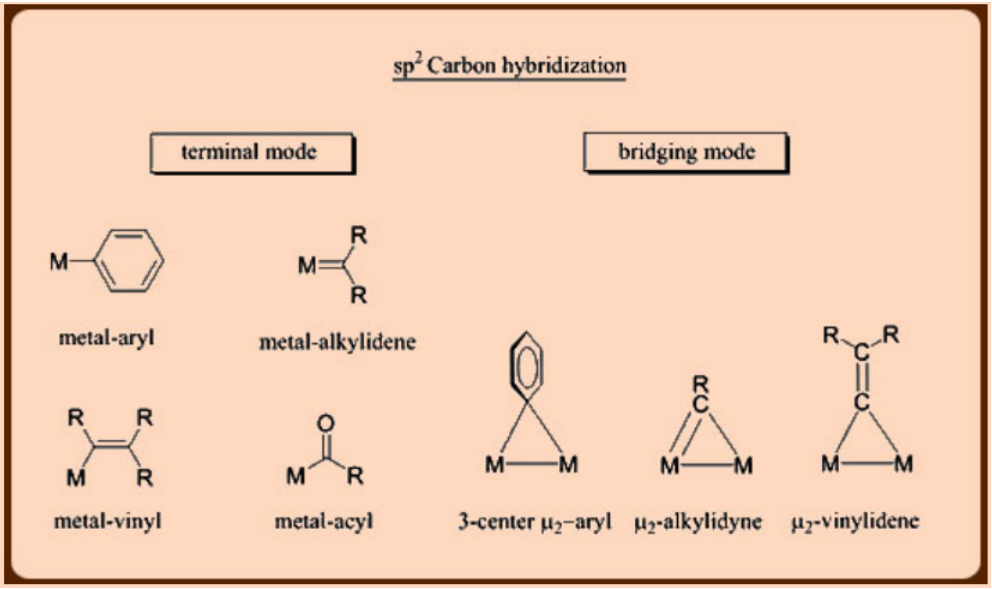


Figure 6.2.2

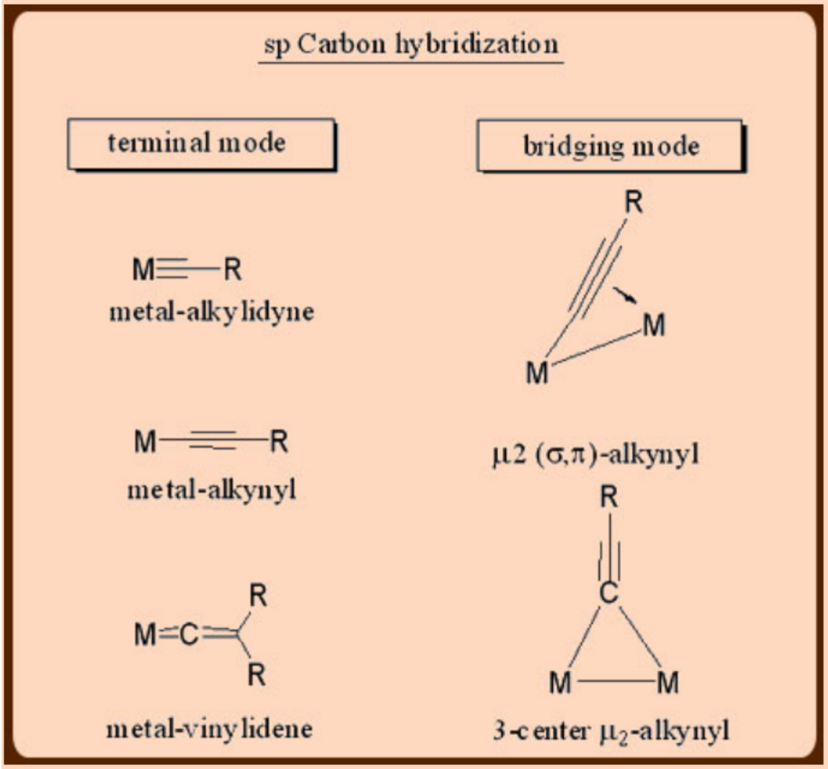


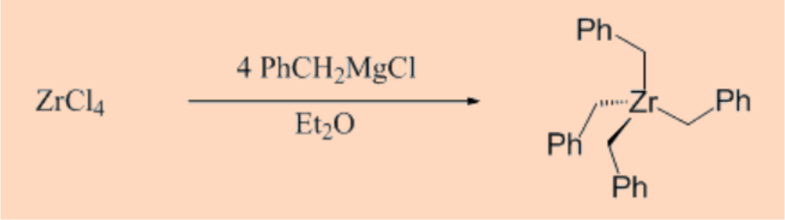
Figure 6.2.3

Preparation of transition metal-alkyl and transition metal-aryl complexes

The transition metal−alkyl and transition−metal aryl complexes are usually prepared by the following routes discussed below,

a. Metathesis

This involves the reactions of metal halides with organolithium, organomagnesium, organoaluminium, organotin and organozinc reagents.



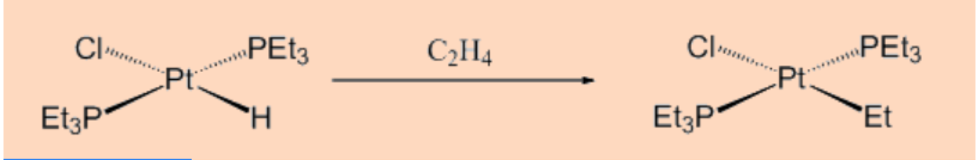
Of the different organoalkyl compounds listed above, the organolithium and organomagnesium compounds are strongly carbanionic while the remaining main group organometallics like the organoalkyl, organozinc and organotin reagents are relatively less carbanionic in nature. Thus, the main group organometallic reagents have attenuated alkylating power, that can be productively used in partial exchange of halide ligands.

$$TiCl_4 \xrightarrow{Al2Me6} MeTiCl_3$$

$$NbCl_5 \xrightarrow{ZnMe2} Me_2NbCl_3$$

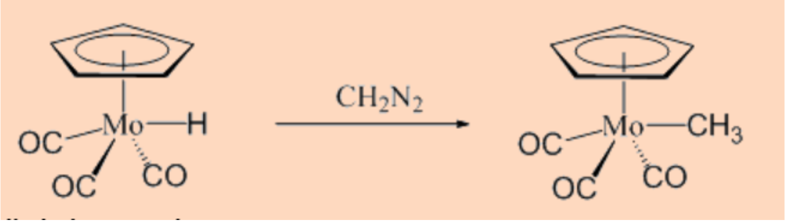
b. Alkene insertion or Hydrometallation

As the name implies, this category of reaction involves an insertion reaction between metal hydride and alkene as shown below. These type reactions are relevant to certain homogeneous catalytic processes in which insertion of an olefin to M−H bond is often observed.



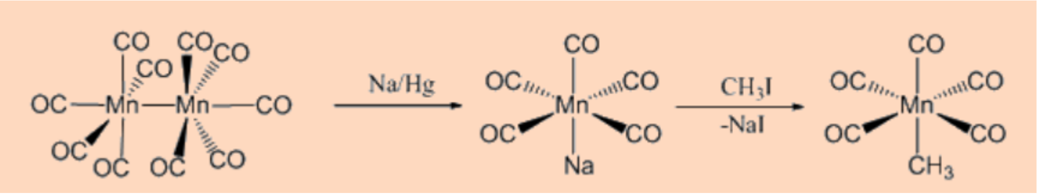
c. Carbene insertion

This category represents the reaction of metal hydrides with carbenes.



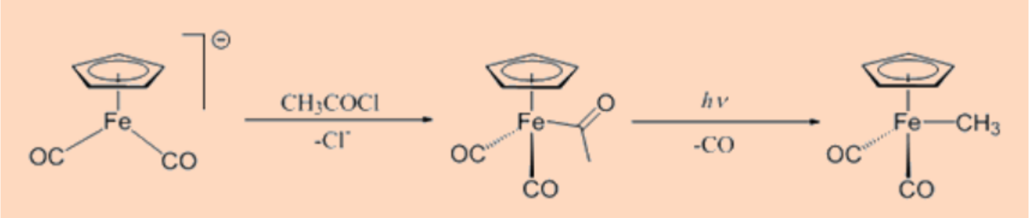
d. Metallate alkylation reaction

This category represents the reaction of carbonylate anions with alkyl halides as shown below.



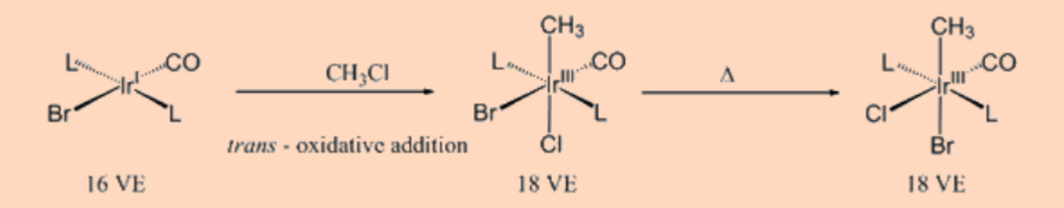
e. Metallate acylation reaction

This category involves the reaction of carbonylate anions with acyl halides



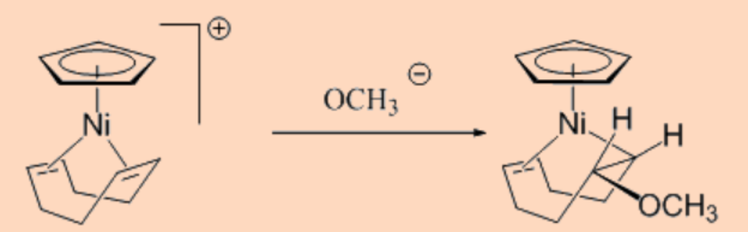
f. Oxidative addition reaction

Many unsaturated 16 VE transition metal complexes having d^8 or d^{10} configuration undergo oxidative addition reactions with alkyl halides. The oxidative addition reactions proceed with the oxidation state as well as coordination number of the metal increasing by +2.



g. Addition reaction

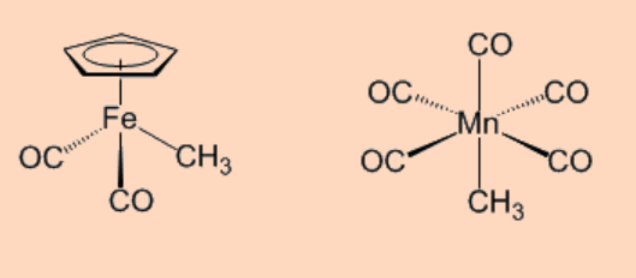
This category involves the reaction of an activated metal bound olefin complex with a nucleophile as shown below.



Thermodynamic Stability and Kinetic Lability

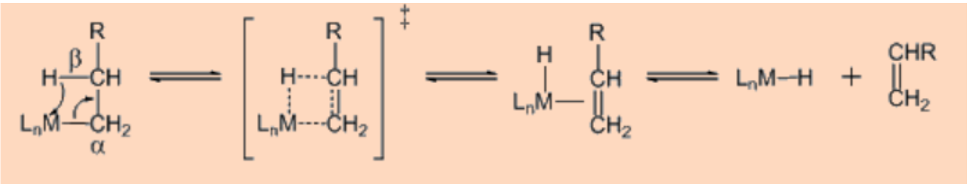
The transition metal organometallic compounds are often difficult to synthesize under ordinary laboratory conditions and require stringent experimental protocols involving the exclusion of air and moisture for doing so. As a consequence, many homoleptic binary transition metal−alkyl and transition metal−aryl compounds like, Et_2Fe or Me_2Ni cannot be made under normal laboratory conditions. More interestingly, most of the examples of transition metal−aryl and transition metal−alkyl compounds, known in the literature, invariably contain additional ligands like η^5-C_5H_5, CO, PR_3 or halides.

For example,

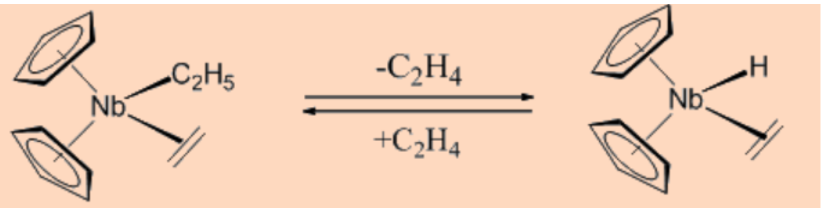


Transition metal−carbon (TM−C) bond energy values are important for understanding the instability of transition metal organometallic compounds. In general, the TM−C bonds are weaker than the transition metal−main group element (TM−MGE) bonds (MGE = F, O, Cl, and N) and more interestingly so, unlike the TM−MGE bond energies, the TM−C bond energy values increase with increasing atomic number. The steric effects of the ligands also play a crucial role in influencing the TM−C bond energies and thus have to be given due consideration.

Contrary to the popular belief, the difficulty in obtaining transition metal−aryl and transition metal−alkyl complexes does primarily arise from the thermodynamic reasons but rather the kinetic ones. β−elimination is by far the most general decomposition mechanism that contribute to the instability of transition metal organometallic compounds. β−elimination results in the formation of metal hydrides and olefin as shown below.



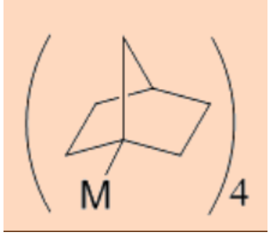
β−elimination can also be reversible as shown below.



The instability of transition metal organometallic compounds can arise out of kinetic lability like in the case of the β−elimination reactions that trigger decomposition of these complexes. Thus, the suppression of the decomposition reactions provides a viable option for the stabilization of the transition metal organometallic complexes. The β−elimination reactions in transition metal organometallic complexes may be suppressed under any of the following three conditions.

a. Formation of the leaving olefin becomes sterically or energetically unfavorable

In the course of β−elimination, this situation arises when the olefinic bond is formed at a bridgehead carbon atom or when a double bond is formed with the elements of higher periods. For instance, the norbornyl group is less prone to decomposition by β−elimination because that would require the formation of olefinic double bond at a bridgehead carbon atom in the subsequent olefin, *i.e*. norbornene, and which is energetically unfavorable.

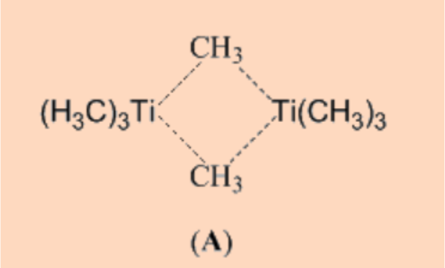


b. Absence of β−hydrogen atom in organic ligands

Transition metal bound ligands that do not possess β−hydrogen cannot decompose by β−elimination pathway and hence such complexes are generally more stable than the ones containing β−hydrogen atoms. For example, the neopentyl complex, $Ti[CH_2C(CH_3)_3]_4$ (m.p 90 °C), and the benzyl complex, $Zr(CH_2Ph)_4$ (m.p. 132 °C), exhibit higher thermal stability as both of the neopentyl and benzyl ligands lack β−hydrogens.

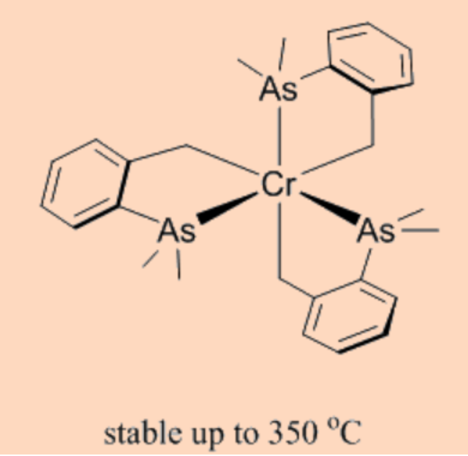
c. Central metal atom is coordinatively saturated

Transition metal organometallic complexes in which the central metal atom is coordinatively saturated tend to be more stable due to the lack of coordination space available around the metal center to facilitate β−elimination reaction or other decomposition reactions. Thus, the absence of free coordination sites at the metal is crucial towards enhancing the stability of the transition metal organometallic complexes. For example, $Ti(Me)_4$, which is coordinatively unsaturated can undergo a bimolecular decomposition reaction *via* a binuclear intermediate (**A**), is unstable and exhibits a decomposition temperature of –40 °C. On the contrary, $Pb(Me)_4$, that cannot undergo decomposition by such bimolecular pathway, is more stable and distills at 110 °C at 1 bar atmospheric pressure.



The Ti(Me)$_4$ decomposes by dimerization involving the formation of Ti−C (*3c−2e*) bonds. For Pb(Me)$_4$, such bimolecular decomposition pathway is not feasible, as being a main group element it has higher outer *d* orbital for extending the coordination number. If the free coordination site of Ti(Me)$_4$ is blocked by another ligand, as in [(bipy)Ti(Me)$_4$], then the thermal stability of the complex, [(bipy)Ti(Me)$_4$], increased significantly. Other bidentate chelating ligands like *bis*(dimethylphosphano)ethane (dmpe) also serve the same purpose.

Coordinative saturation thus brings in kinetic stabilization in complexes. For example, Ti(Me)$_4$is extremely reactive as it is coordinatively unsaturated, while W(Me)$_4$ is relatively inert for reasons of being sterically shielded and hence, coordinatively saturated. Thus, if all of the above discussed criteria for the suppression of β-elimination are taken care of, then extremely stable organometallic complexes can be obtained like the one shown below.



Problems

1. Arrange the following compounds in the order of their stability.

a. Ti(Et)$_4$
b. Ti(Me)$_4$ and
c. Ti(6-norbornyl)$_4$

Ans: Ti(Et)$_4$ < Ti(Me)$_4$ < Ti(6-norbornyl)$_4$

2. Predict the product of the reaction given below.

$$\text{(BuP)CuCH}_2\text{CD}_2\text{C}_2\text{H}_5 \longrightarrow$$

Ans: Equi molar amounts of (Bu$_3$P)CuD and CH$_2$=CDC$_2$H$_5$

3. Will the compound β-eliminate,

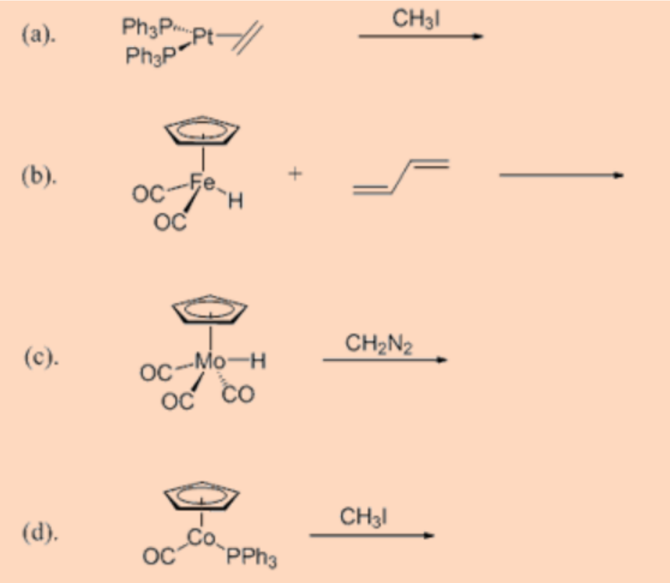
$$\text{PtH(C}\equiv\text{CH)L}_2 \xrightarrow{\text{\textbackslash Beta}-elimination}$$

(a). readily, (b). slowly and (c). not at all.
Explain your answer with proper reasoning.

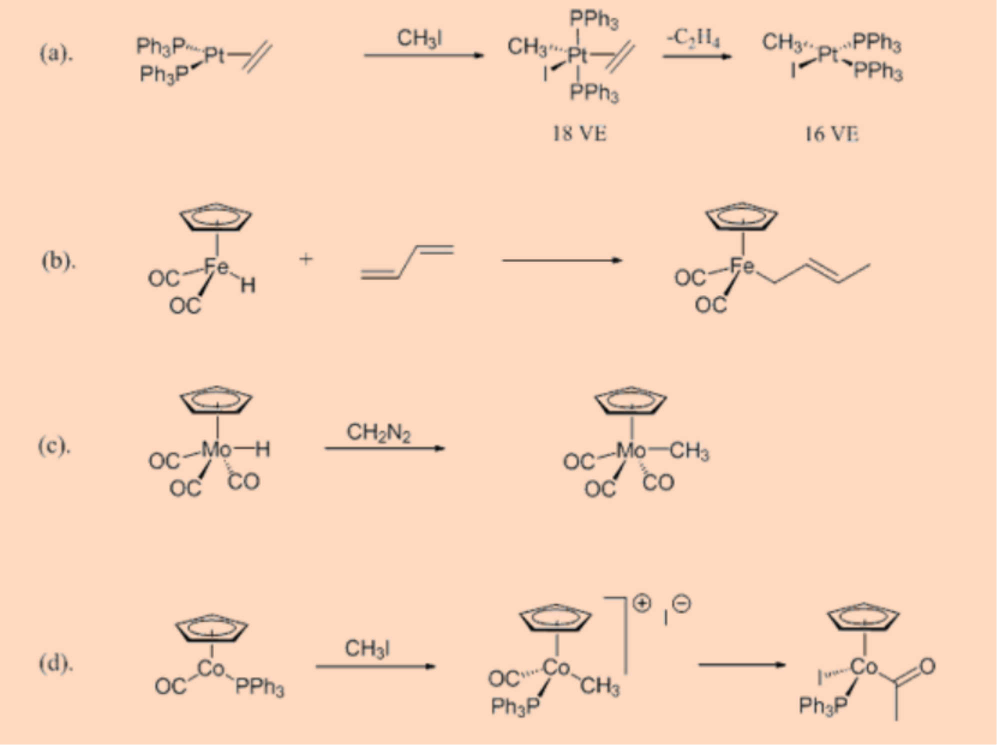
Ans: Not at all as the ß-hydrogens are pointing away from the metal and cannot participate in ß-elimination recation.

Self Assessment test

1. Write the product(s) of the reactions.



Ans:



Summary

Ligands assume a pivotal role in the stabilization of the organometallic transition metal complexes. There are several methods available for the preparation of the organometallic transition metal complexes. The observed instability of the organometallic transition metal complexes can be attributed to two main phenomena namely β-elimination and bimolecular decomposition reaction that severely undermine the instability of these complexes. The suppression of these decomposition pathway thus pave way for obtaining highly stable organometallic transition metal complexes.

CHAPTER OVERVIEW

7: Metal Alkyls and Metal Hydrides

7.1: Transition Metal Alkyl Complexes

Learning Objectives

In this lecture you will learn the following

- Get a general prospective on the historical background of transition metal organometallic compounds with particular emphasis on metal alkyls.
- Know more about stable metal alkyls.
- Get introduced to transition metal agostic alkyls.
- Develop an understanding of reactions of relevance to metal alkyls like the reductive eliminations, oxidative additions and the halide eliminations.

Transition metal σ−bonded organometallic compounds like the metal alkyls, aryls and the hydrides derivatives are by for the most common organometallic species encountered in the world of chemistry. Yet, these compounds remained elusive till as late as the 1960s and the 1970s.

Historical background

Metal alkyls of the main group elements namely, Li, Mg, Zn, As and Al, have been known for a long time and which over the years have conveniently found applications in organic synthesis whereas development on similar scale and scope in case of the transition metal counterparts were missing till only recently. The origin of the organometallic compounds traces back to 1757, when Cadet prepared a foul smelling compound called cacodyl oxide from As_2O_3 and CH_3COOK, while working in a military pharmacy in Paris. Years later in 1840, R. W. Bunsen gave the formulation of cacodyl oxide as $Me_2As{-}O{-}AsMe_2$. The next known transition metal organometallic compound happens to be Et_2Zn, which was prepared serendipitously in 1848 from the reaction of ethyl iodide (EtI) and Zn with the objective of generating free ethyl radical. Frankland further synthesized alkyl mercury halides like, CH_3HgI, from the reaction of methyl iodide (CH_3I) and Hg in sunlight. It is important to note that the dialkyl mercury, R_2Hg, and the dialkyl zinc, R_2Zn, have found applications as alkyl transfer reagents in the synthesis of numerous main group organometallic compounds.

Another notable development of the time was of the preparation of Et_4Pb from ethyl iodide (EtI) and Na/Pb alloy by C. J. Lowig and M. E. Schweizer in 1852. They subsequently extended the same method for the preparation of the Et_3Sb and Et_3Bi compounds. In 1859, aluminumalkyliodides, R_2 AlI, were prepared by W. Hallwachs and A Schafarik from alkyl iodide (RI) and Al. The year 1863 saw the preparation of organochlorosilanes, $RmSiCl_{4-m}$, by C. Friedel and J. M. Crafts while the year 1866 saw the synthesis of halide-free alkyl magnesium compound, Et_2Mg, by J. A. Wanklyn from the reaction of Et_2Hg and Mg. In 1868, M. P. Schutzenberger reported the first metal−carbonyl complex in the form of $[Pt(CO)Cl_2]_2$. In 1890, the first binary metal−carbonyl compound, $Ni(CO)_4$ was reported by L. Mond, who later founded the well−known chemical company called ICI (Imperial Chemical Industries). In 1909, W. J. Pope reported the first σ−organotransition metal compound in the form of $(CH_3)_3PtI$. In 1917, the alkyllithium, RLi, compounds were prepared by W. Schlenk by transalkylation reactions. In 1922, T. Midgley and T. A. Boyd reported the utility of Et_4Pb as an antiknock agent in gasoline. A. Job and A. Cassal prepared $Cr(CO)_6$ in 1927. In 1930, K. Ziegler showed the utility of organolithium compounds as alkylating agent while in the following year in 1931, W. Heiber prepared $Fe(CO)_4H_2$ as the first transition metal−hydride complex. O. Roelen discovered the much renowned hydroformylation reaction in 1938, that went on to become a very successful industrial process worldwide.

The large scale production and the use of silicones were triggered by E. G. Rochow, when he reported the ‘direct synthesis’ from methyl chloride (CH_3Cl) and Si using Cu catalyst at 300 °C in 1943. The landmark compound, ferrocene $(C_5H_5)_2Fe$, known as the first sandwich complex was obtained by P. Pauson and S. A. Miller in 1951. H. Gilman introduced the important utility of organocuprates when he prepared $LiCu(CH_3)_2$, in 1952. In the subsequent year 1953, G. Wittig found a new method of synthesizing olefins from phosphonium ylides and carbonyl compounds that fetched him a Nobel prize in 1979. The year 1955 turned out to be a year of path breaking discoveries with E. O. Fischer reporting the rational synthesis of bis(benzene)chromium, $(C_6H_6)_2Cr$ while K. Ziegler and G. Natta announcing the ground breaking polyolefin polymerization process that subsequently gave them the Nobel prizes, E. O. Fischer sharing with G. Wilkinson in 1973 while K. Ziegler and G. Natta shared the same in 1963. In 1956, H. C. Brown reported hydroboration for which he too received the Nobel prize in 1979. In 1963, L. Vaska reported the famous Vaska’s complex, *trans*−$(PPh_3)_2Ir(CO)Cl$, that reversibly binds to molecular oxygen. In 1964, E. O. Fischer reported the first carbene complex, $(CO)_5WC(OMe)Me$. In 1965, G. Wilkinson and R. S. Coffey reported the Wilkinson catalyst, $(PPh_3)_3RhCl$, for the hydrogenation of alkenes. In 1973, E. O. Fischer synthesized the first carbyne complex, $I(CO)_4Cr(CR)$.

After the early 1970s, there were tremendous outburst in activity, in the area of transition metal organometallic chemistry leading to phenomenal developments having far-reaching consequences in various branches of the main stream and interfacial chemistry. Several Nobel prizes that have been awarded to the area in recent times fully recognized the significance of these efforts with Y. Chauvin, R. R. Schrock, and R. H. Grubbs winning it in 2005 for olefin metathesis and Akira Suzuki, Richard F Heck and E. Negishi receiving the same for the Pd catalyzed C−C cross-coupling reactions in organic synthesis in 2010.

Metal alkyls

In day to day organic synthesis, particularly from the application point of view, the metal alkyls are often perceived as a source of stabilized carbanions for reactions with various electrophiles. The extent of stabilization of alkyl carbanions in metal alkyl complexes depend upon the nature of the metal cations. For example, the alkyls of electropositive metals like that of Group 1 and 2, Al and Zn are regarded as polar organometallics as the alkyl carbanions remain weakly stabilized while retaining strong nucleophilic and basic character of a free anion. These polar alkyls are extremely air and moisture sensitive as in their presence they often get hydrolyzed and oxidized readily. Similar high reactivity was also observed in case of the early transition metal organometallic compounds particularly of Ti and Zr. On the contrary the late transition metal organometallic compounds are much less reactive and stable. For example, the Hg−C bond of $(Me{-}Hg)^+$ cation is indefinitely stable in aqueous H_2SO_4 solution in air. Thus, on moving from extremely ionic Na alkyls to highly polar covalent Li and Mg alkyls and to essentially covalent late−transition metal alkyls, a steady decrease in reactivity is observed. This trend can be correlated to the stability of alkyl carbanions that also depended on the nature of hybridization of the carbon center, with sp^3 hybridized carbanions being the least stable and hence most reactive, followed by the sp^2 carbanions being moderately stable while the *sp* carbanions being the least reactive and most stable. The trend also correlates well with the respective p*K*a values observed for CH_4 (p*K*a = ~50), C_6H_6 (p*K*a = ~43) and RC≡CH (p*K*a = ~25).

Stable alkyls

As has been mentioned earlier, that the β−elimination is a crucial destabilizing influence on the transition metal organometallic complexes. Hence, inhibition of this decomposition pathway leads to increased stabilities of organometallic compounds. Thus, many stable alkyl transition metal complexes do not possesses β−hydrogens like, $W(Me)_6$ and $Ti(CH_2Ph)_4$. In some cases despite the presence of the β−hydrogens the organometallic complexes are stable as the β−hydrogens are deposed away from the metal center like in, $Cr(CHMe_2)_4$, and $Cr(CMe_3)_4$. In this category of stable transition metal organometallic compounds also falls the ones that contain β−hydrogens but cannot β−eliminate owing to the formation of a olefinic bond at a bridgehead, which is unfavorable, like in $Ti(6{-}norbornyl)_4$ and $Cr(1{-}adamantyl)_4$. Lastly, some 18 VE metal complexes are stable, again despite having β−hydrogens, for reasons of being electronically as well as coordinatively saturated at the metal center owing to attaining the stable 18 electron configuration.

Agostic alkyls

Agostic alkyls are extremely rare but very interesting species that represents a frozen point in a β−elimination pathway that have fallen short of the completion of the decomposition reaction. Thus, these agostic alkyl complexes can be viewed as snap shots of a β−elimination trajectory thereby providing valuable mechanistic understanding of the decomposition reaction. The agostic interaction has characteristic signatures in various spectroscopic techniques as observed from the decreasing J_{C-H}coupling constant values in the ^1H NMR and the ^{13}C NMR spectra and the lowering of the ν_{C-H}stretching frequencies in the IR spectroscopy. The agostic alkyl complexes can be definitively proven by X−ray diffraction or neutron diffraction studies. The agostic alkyls thus have activated C−H bonds which are of interest for their utility in chemical catalysis. Quite interestingly, many d^0 Ti agostic alkyl complexes do not β−eliminate primarily for the metal center being too electron deficient to donate electron to the σ* C−H orbital as required for the subsequent β−elimination process.

Reductive elimination

Reductive elimination represents a major decomposition pathway of the metal alkyls. Opposite of oxidative addition, the reductive elimination is accompanied by the decrease in the oxidation state and the valence electron count of the metal by two units. The metal alkyl complexes may thus reductively eliminate with an adjacent hydrogen atom to yield an alkane, (R−H) or undergo the same with an adjacent alkyl group to give an even larger alkane (R−R) as shown below.

$$L_nMRH \longrightarrow R{-}H + L_nM$$

$$L_nMR_2 \longrightarrow R{-}R + L_nM$$

The reductive elimination is often facilitated by an electron deficient metal center and by sterically demanding ligand systems. Often d^8 metals like Ni(II), Pd(II), and Au(III) and d^6 metals in high oxidation state like, Pt(IV), Pd(IV), Ir(III), and Rh(III) exhibit reductive elimination.

Oxidative addition

Unlike the reductive elimination that represents a decomposition pathway of metal alkyls, the oxidative addition reaction represents a useful method for the formation of the metal alkyl complexes. The oxidative addition thus leads to increase in valence electron count and the oxidation state of the metal center by two units. The oxidative addition reactions are often facilitated by low valent electron rich metal centers and by less sterically demanding ligands.

Halide elimination

β−halide elimination is observed for the early transition metals and the *f*−block elements resulting in the formation of stable alkyl halides. The phenomenon is mostly seen in case of the metal fluorides and arise owing to the very high alkyl−fluoride bond strengths that favor the halide elimination.

Problems

1. Who elucidated the structure of cacodyl oxide?

Ans: R. W. Bunsen in 1840

2. Give the example of the first olefin bound transition metal complex?

Ans: Zeise's salt, $Na[PtCl_3(C_2H_4)]$

3. Who discovered olefin polymerization?

Ans: K. Ziegler and G. Natta

4. What kind of metal center promotes oxidative addition reactions?

Ans: Electron rich

5. The 18 VE complex would favor/disfavor oxidative addition reactions?

Ans: Disfavor

Self Assessment test

1. O. Roelen discovered which famous reaction?

Ans: Hydroformylation

2. What is the first binary metal−carbonyl complex?

Ans: $Ni(CO)_4$

3. Who discovered the hydroboration reaction?

Ans: H. C. Brown

4. Reductive elimination reaction is favored by what kind of ligands?

Ans: Sterically demanding

5. β−halide elimination is mainly observed for what type of metal halide complexes?

Ans: Metal fluorides

Summary

A broader outlook on metal alkyls is obtained from the study of its historical background thus dispelling many myths about these compounds like them being inherently unstable. It also establishes newer founding principles like these compounds indeed being thermodynamically stable under certain experimental conditions and thus facilitating further attempts to take up the synthesis of these compounds. Another important class of transition metal organometallic compounds are the agostic alkyls, which can be viewed as the ones that have proceeded along but have fallen short of the final sequence of the β−elimination step. While oxidative addition reaction remains a key method for synthesizing metal alkyls, the complementary reaction, *i.e*, the reductive elimination, represents a decomposition reaction of these compounds. β−halide elimination reactions are observed for early transition metal elements and *f*−block elements.

7.2: Metal Hydrides

Learning Objectives

In this lecture you will learn the following

- Know about metal hydrides, their synthesis, characterization and their reactivity.
- Know about σ−complexes and their properties.
- Know about transition metal dihydrogen complexes.

Metal hydrides occupy an important place in transition metal organometallic chemistry as the M−H bonds can undergo insertion reactions with a variety of unsaturated organic substrates yielding numerous organometallic compounds with M−C bonds. Not only the metal hydrides are needed as synthetic reagents for preparing the transition metal organometallic compounds but they also are required for important hydride insertion steps in many catalytic processes. The first transition metal hydride compound was reported by W. Heiber in 1931 when he synthesized $Fe(CO)_4H_2$. Though he claimed that the $Fe(CO)_4H_2$ contained Fe−H bond, it was not accepted until 1950s, when the concept of normal covalent M−H bond was widely recognized.

The metal hydride moieties are easily detectable in ^{1}H NMR as they appear high field of TMS in the region between 0 to 60 ppm, where no other resonances appear. The hydride moieties usually couple with metal centers possessing nuclear spins. Similarly, the hydride moieties also couple with the adjacent metal bound phosphine ligands, if at all present in the complex, exhibiting characteristic *cis* (J = 15 − 30 Hz) and *trans* (J = 90 − 150 Hz) coupling constants. In the IR spectroscopy, the M−H frequencies appear between (1500 − 2200) cm^{-1} but their intensities are mostly weak. Crystallographic detection of metal hydride moiety is difficult as hydrogen atoms in general are poor scatterer of X−rays. Located adjacent to a metal atom in a M−H bond, the detection of hydrogen atom thus becomes challenging and as a consequence the X−ray crystallographic method systematically underestimates the M−H internuclear distance by ~ 0.1 Å. However, better data could be obtained by performing the X−ray diffraction studies at a low temperature in which the thermal motion of the atoms are significantly reduced. In light of these facts, the neutron diffraction becomes a powerful method for detection of the metal hydride moieties as hydrogen scatters neutrons more effectively and hence the M−H bond distances can be measured more accurately. A limitation of neutron diffraction method is that large sized crystals are required for the study.

Synthesis

Following reactions are employed for synthesizing metal hydrides.

i. Protonation reactions
For this reaction to occur the metal center has to be basic and electron rich.

$$[\mathrm{Fe(CO)_4}]^{-2} \xrightarrow{H+} [\mathrm{HFe(CO)_4}]^{-} \xrightarrow{H+} \mathrm{H_2Fe(CO)_4}$$

ii. From hydride donors
Generally for this method, a main group hydride is reacted with metal halide.

$$\mathrm{WCl_6 + LiBEt_3H + PR_3 \longrightarrow WH_6(PR_3)_3}$$

iii. Using dihydrogen (H_2) addition
This method involves oxidative addition of H_2 and thus requires metal centers that are capable of undergoing the oxidative addition step.

$$\mathrm{WMe_6 + PMe_2Ph} \xrightarrow{H_2} \mathrm{WH_6(PMe_2Ph)_3}$$

iv. From a ligand
This method takes into account the β−elimination that occur in a variety of metal bound ligand moieties, thereby yielding a M−H bond.

$$\mathrm{RuCl_2(PPh_3)_3 + KOCHMe_2 + PPH_3 \longrightarrow RuH_2(PPh_3)_4 + Me_2CO + KCl}$$

Reactions of metal hydrides

Metal hydrides are reactive species kinetically and thus participate in a variety of transformations like the ones discussed below.

i. Deprotonation reactions
The deprotonation reaction can be achieved by a hydride moiety resulting in the formation of H_2gas as shown below.

$$\mathrm{WH_6(PMe_3)_3 + NaH \longrightarrow Na[WH_5(PMe_3)_3] + H_2}$$

ii. Hydride transfer and insertion
In this reaction a hydride transfer from a metal center to formaldehyde resulting in the formation of a metal bound methoxy moiety is observed as shown below.

$$\mathrm{Cp_2 \cdot ZrH_2 + CH_2O \longrightarrow Cp_2 \cdot Zr(OMe)_2}$$

iii. Hydrogen atom transfer reaction

An example of hydrogen atom transfer reaction is given below.

$$\mathrm{[Co(CN)_5H]^{3-} + PhCH{=}CHCOOH \longrightarrow [Co(CN)_5]^{3-} + PHCH{-}CH_2COOH}$$

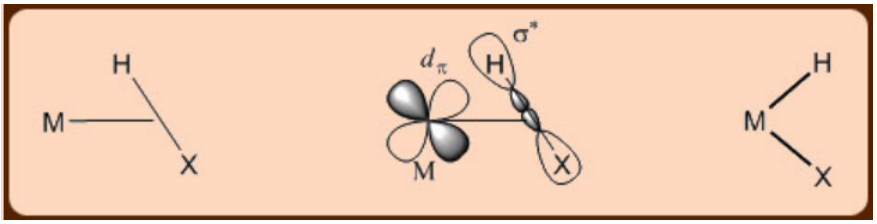
It is interesting to note that the nature of hydrogen atom in a M−H bond can vary from being protic in nature, when bound to electron deficient metal centers as in metal carbonyl compounds, to that of being hydridic in nature, when bound to more electropositive early transition metals. In the latter case, the hydride moieties tend to be basic and exhibit hydride transfer reactions with electrophiles like aldehydes or ketones. Furthermore, the protonation of these basic metal hydrides leads to the elimination of dihydrogen (H_2) gas along with the generation of a vacant coordination site at the metal center.

Bridging hydrides

The metal hydrides usually show two modes of binding, namely terminal and bridging. In case of the bridging hydrides, the hydrogen atom can bridge between two or even more metal centers and thus, the bridging hydrides often display bent geometries.

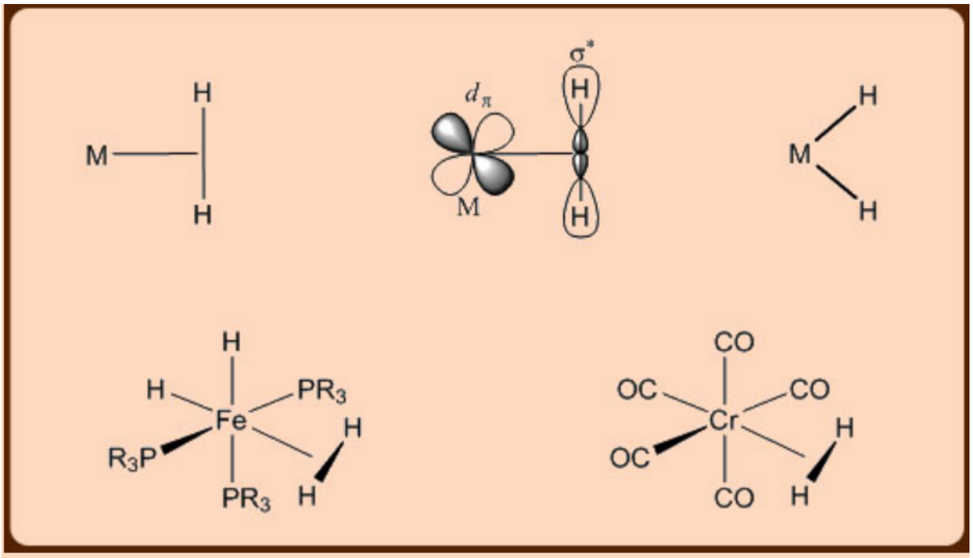
σ−complexes

σ−complexes are rare compounds, in which the σ bonding electrons of a X−H bond further participate in bonding with a metal center (X = H, Si, Sn, B, and P). The σ complexes thus exhibit an askewed binding to a metal center with the hydrogen atom, containing no lone pair, being more close to the metal center and thereby resulting in a side−on structure. Many times if the metal center is electron rich, then further back donation to the σ* orbital of the metal bound X−H moiety may occur resulting in a complete cleavage of the X−H bond.

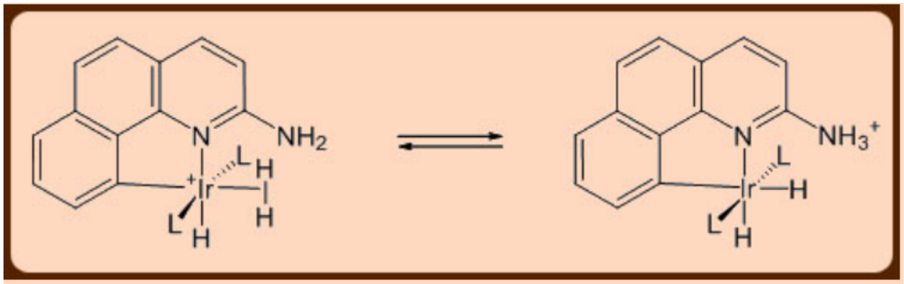


Metal dihydrogen complexes

The simplest variant of a σ−complex contains a dihydrogen ligand. The first dihydrogen complex was isolated by Kubas, after which many new ones were reported.



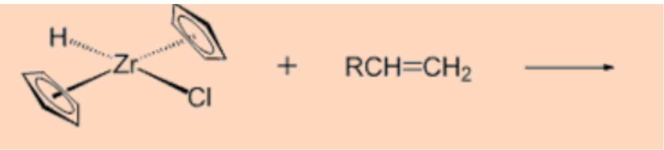
Quite expectedly, the dihydrogen moiety bound to a metal in a σ−complex is found to be more acidic (p*K*a = 0 − 20) when compared to the free dihydrogen molecule (p*K*a = 35). It is interesting to note that the p*K*a change associated with the binding of dihydrogen to a metal in a σ−complex relative to that of the free H_2 molecule is significantly larger than the change associated with binding of H_2O to metal. Owing to this inherent acidity, the deprotonation of the metal bound dihydrogen moiety by a base can thus be appropriately employed for heterolytic activation of the dihydrogen moiety as illustrated below.



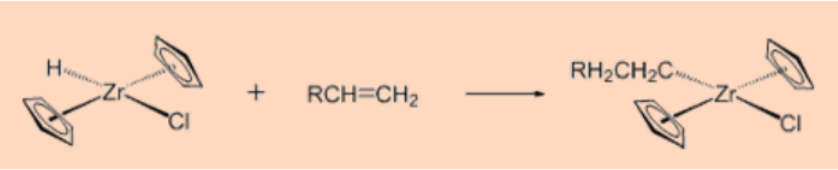
The dihydrogen complexes of metals are often referred to as nonclassical hydrides. The electron rich π basic metals are anticipated to split the metal bound dihydrogen moieties resulting in classical dihydride complexes. Along the same line of thinking, the electron deficient and less π basic metal would tend to stabilize a dihydrogen complex. The dihydrogen complexes can also be characterized by the X ray diffraction as well as neutron diffraction methods. In IR spectrum, the metal bound H−H stretch appear in the range (2300 − 2900) cm^{-1} while in the ^1H NMR spectrum the same appear between 0 to −10 ppm as a broad peak. The dihydrogen complexes are often characterized by isotopic labeling studies of metal bound H−D moiety that shows a coupling constant of 20 – 34 Hz as supposed to 43 Hz observed in case of the free H−D molecule.

Problems

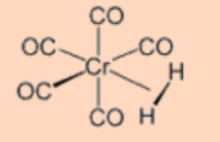
1. Predict the product of the reaction.



Ans:



2. Give the oxidation state and total valence electron count of the metal center.



Ans: Oxidation state 0 and 18 VE

3. What kind of metal centers would stabilize metal dihydrogen complexes?

Ans: Electron deficient and less π basic ligands

4. Specify whether the nature of hydrogen moiety in the complex, $HCo(CO)_4$ is acidic or basic?

Ans: Acidic

5. Where do the M−H stretching bands appear in the IR spectrum of metal hydride complexes?

Ans: 1500 to 2200 cm^{-1}

Self Assessment test

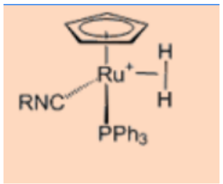
1. Predict the product of the reaction.

$$\mathrm{IrCl(Co)(Pph_3)_2} \xrightarrow{H_2}$$

Ans:

$$\mathrm{IrCl(CO)(PPh_3)_2} \xrightarrow{H2} \mathrm{IrH_2Cl(CO)(PPh_3)_2}$$

2. Give the oxidation state and total valence electron count of the metal center.



Ans: Oxidation state +2 and 18 VE

3. What kind of metal centers would stabilize classical dihydride complexes?

Ans: Electron rich and more p basic ligands

4. Specify whether the nature of hydrogen moiety in the complex, $IrH_5(PCy_3)_2$ is acidic or basic?

Ans: Basic

5. Between X−ray diffraction and neutron diffraction, which is a better method for the characterization of the M−H moiety?

Ans: Neutron diffraction

Summary

Metal hydrides are important compounds in the overall scheme of organometallic chemistry as they are involved in many crucial steps of numerous catalytic reactions. Apart from metal hydrides another important class of compounds are transition metal σ−complexes whose simplest variant are the metal dihydrogen complexes. These σ−complexes and the metal dihydrogen complexes are important for the heterolytic activations of the respective metal bound H−heteroatom and the H−H bonds.

CHAPTER OVERVIEW

8: Carbonyls and Phosphine Complexes

8.1: Metal Carbonyls

Learning Objectives

In this lecture you will learn the following

- The historical background of metal carbonyl complexes.
- The CO ligand and its binding ability to metal.
- Synergism between the ligand to metal forward σ–donation and the metal to ligand backward π–donation observed in a metal-CO interaction.
- The synthesis, characterization and their reactivity of the metal carbonyl compounds.

Metal carbonyls are important class of organometallic compounds that have been studied for a long time. Way back in 1884, Ludwig Mond, upon observing that the nickel valves were being eating away by CO gas in a nickel refining industry, heated nickel powder in a stream of CO gas to synthesize the first known metal carbonyl compound in the form $Ni(CO)_4$. The famous Mond refining process was thus born, grounded on the premise that the volatile $Ni(CO)_4$ compound can be decomposed to pure metal at elevated temperature. Mond subsequently founded the Mond Nickel Company Limited for purifying nickel from its ore using this method.

The carbonyl ligand (CO) distinguishes itself from other ligands in many respects. For example, unlike the alkyl ligands, the carbonyl (CO) ligand is unsaturated thus allowing not only the ligand to σ−donate but also to accept electrons in its π* orbital from d_π metal orbitals and thereby making the CO ligand π−acidic. The other difference lies in the fact that CO is a soft ligand compared to the other common σ−and π−basic ligands like H_2O or the alkoxides (RO−), which are considered as hard ligands.

Being π−acidic in nature, CO is a strong field ligand that achieves greater d−orbital splitting through the metal to ligand π−back donation. A metal−CO bonding interaction thus comprises of a CO to metal σ−donation and a metal to CO π−back donation (Figure 8.1.1). Interestingly enough, both the spectroscopic measurements and the theoretical studies suggest that the extent of the metal to CO π−back donation is almost equal to or even greater than the extent of the CO to metal σ−donation in metal carbonyl complexes. This observation is in agreement with the fact that low valent−transition metal centers tend to form metal carbonyl complexes.

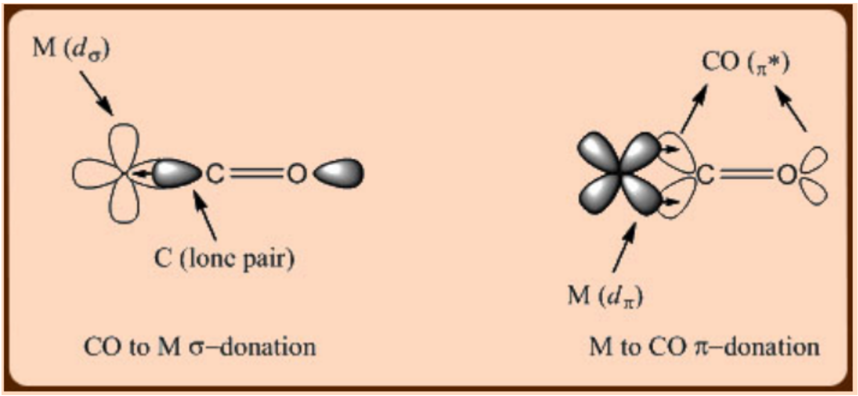


Figure 8.1.1: Orbital diagram showing ligand to metal forward σ-donation and the metal to ligand backward π-donation in metal-CO interaction.

In the metal carbonyl complexes, the direct bearing of the π−back donation is observed on the M−C bond distance that becomes shorter as compared to that of a normal M−C single bond distance. For example, the $CpMo(CO)_3CH_3$ complex, exhibits two kind of M−C bond distances that comprise of a longer $Mo{-}CH_3$ distance (2.38 Å) and a much shorter Mo−CO distance (1.99 Å) arising out of a metal to ligand π−back donation. It becomes thus apparent that the metal−CO interaction can be easily characterized using X−ray crystallography. The infrared spectroscopy can also be equally successfully employed in studying the metal−CO interaction. Since the metal to CO π−back bonding involves a π−donation from the metal d_π orbital to a π* orbital of a C−O bond, significant shift of the ν(CO) stretching frequency towards the lower energy is observed in metal carbonyl complexes with respect to that of free CO (2143 cm^{-1}).

Preparation of metal carbonyl complexes

The common methods of the preparation of the metal carbonyl compounds are,

i. Directly using CO

$$\mathrm{Fe} \xrightarrow{CO,\ 200atm,\ 200^{\circ}C} \mathrm{Fe(CO)_5}$$

The main requirement of this method is that the metal center must be in a reduced low oxidation state in order to facilitate CO binding to the metal center through metal to ligand π−back donation.

ii. Using CO and a reducing agent

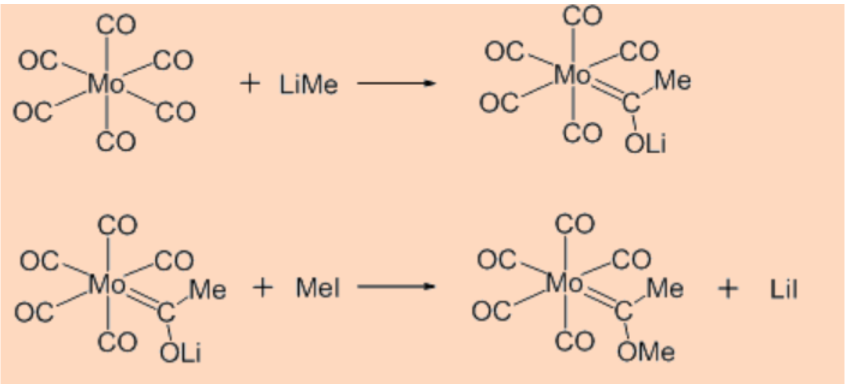
$$\mathrm{NiSO_4 + CO + S_2O_4^{2-} \longrightarrow Ni(CO)_4}$$

This method is commonly called reductive carbonylation and is mainly used for the compounds having higher oxidation state metal centers. The reducing agent first reduces the metal center to a lower oxidation state prior to the binding of CO to form the metal carbonyl compounds.

iii. From carbonyl compounds
This method involves abstraction of CO from organic compounds like the alcohols, aldehydes and CO_2.

Reactivities of metal carbonyls

i. Nucleophilic attack on carbon



The reaction usually gives rise to carbene moiety.

ii. Electrophilic attack at oxygen

$$\mathrm{Cl(PR_3)_4Re{-}CO + AlMe_3 \longrightarrow Cl(PR_3)_4Re{-}CO \longrightarrow AlMe_3}$$

iii. Migratory insertion reaction

$$\mathrm{MeMn(CO)_5 + PMe_3 \longrightarrow (MeCO)Mn(CO)_4(PMe_3)}$$

The metal carbonyl displays two kinds of bindings in the form of the terminal and the bridging modes. The infrared spectroscopy can easily distinguish between these two binding modes of the metal carbonyl moiety as the terminal ones show ν(CO) stretching band at *ca*. 2100-2000 cm^{-1} while the bridging ones appear in the range 1720−1850 cm^{-1}. The carbonyl moiety can bridge between more than two metal centers (Figure 8.1.2).

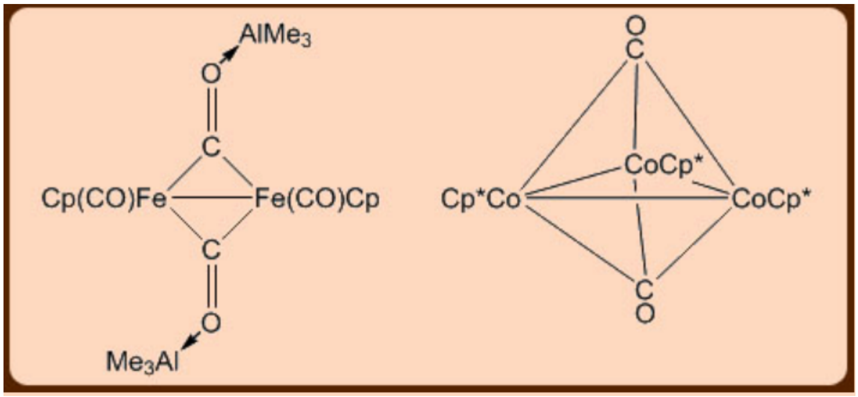


Figure 8.1.2: Different bridging modes of the carbonyl binding to a metal is shown.

Problems

1. How many lone pairs are there in the CO molecule?

Ans: Three (one from carbon and two from oxygen).

2. Despite O being more electronegative than C, the dipole moment of CO is almost zero. Explain.

Ans: Because of the electron donation from oxygen to carbon.

3. What type of metal centers form metal carbonyl complexes?

Ans: Low−valent metal centers.

4. What are the two main modes of binding exhibited by CO ligand?

Ans: Terminal and bridging modes of binding.

Self Assessment test

1. Predict the product of the reaction?

$$\mathrm{Ni} + \mathrm{CO}_{\mathrm{Excess}} \longrightarrow$$

Ans: Three (one from carbon and two from oxygen).

2. Upon binding to a metal center the C−O stretching frequency increases/decreases with regard to that of the free CO?

Ans: Decreases.

3. Explain why do low−valent metal centers stabilize CO binding in metal carbonyl complexes?

Ans: Because metal to ligand π−back donation.

4. Give an example of a good σ−donor and π−donor ligand?

Ans: Alkoxides (RO^-).

Summary

CO is a hallmark ligand of organometallic chemistry. The metal carbonyl complexes have been studied for a long time. The CO ligands bind tightly to metal center using a synergistic mechanism that involves σ−donation of the ligand lone pair to metal and followed by the π−back donation from a filled metal *d* orbital to a vacant σ* orbital of C−O bond of the CO ligand. The metal carbonyl complexes are prepared by several methods. The metal carbonyl complexes are usually stabilized by metal centers in low oxidation states.

8.2: Metal Phosphines

Learning Objectives

In this lecture you will learn the following

- Know about metal phosphine complexes.
- Have an understanding of the steric and electronic properties of the phosphine ligands.
- Obtain a deeper insight about the metal phosphine interactions.
- Be introduced to other π−basic ligands.

Phosphines are one of the few ligands that have been extensively studied over the last few decades to an extent that the systematic fine tuning of the sterics and electronics can now be achieved with certain degree of predictability. Phosphines are better spectator ligands than actor ligands. Tolman carried out pioneering infrared spectroscopy experiments on the $PR_3Ni(CO)_3$ complexes looking at the $\nu_{(CO)}$stretching frequencies for obtaining an insight on the donor properties of the PR_3 ligands. Thus, a stronger σ−donor phosphine ligand would increase the electron density at the metal center leading to an enhanced metal to ligand π−back bonding and thereby lowering of the $\nu_{(CO)}$ stretching frequencies in these complexes. Another important aspect of the phosphine ligand is its size that has significant steric impact on its metal complexes. Thus, unlike CO ligand, which is small and hence many may simultaneously be able to bind to a metal center, the same is not true for the phosphine ligands as only a few can bind to a metal center. The number of phosphine ligands that can bind to a metal center also depends on the size of its R substituents. For example, up to two can bind to a metal center in case of the PCy_3 or $P(i{-}Pr)_3$ ligands, three or four for PPh_3, four for Me_2PH, and five or six for PMe_3. The steric effect of phosphine was quantified by Tolmann and is given by a parameter called *Cone Angle* that measures the angle at the metal formed by the PR_3 ligand binding to a metal (Figure 8.2.1).

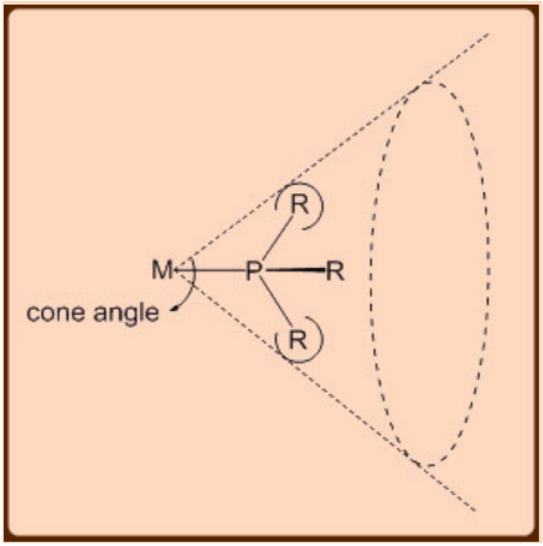


Figure 8.2.1: Cone Angle in metal−phosphine complexes.

The *Cone Angle* criteria has been successfully invoked in rationalizing the properties of a wide range of metal phosphine complexes. One unique feature of the phosphine ligand is that it allows convenient change of electronic effect without undergoing much change in its steric effects. For example, PBu_3 and $P(O^iPr)_3$ have similar steric effects but vary in their electronic effects. The converse is also true as the steric effect can be easily changed without undergoing much change in the electronic effect. For example, PMe_3 and $P(o{-}tolyl)_3$ have similar electronic effect but differ in their steric effects. Thus, the ability to conveniently modulate the steric and the electronic effects make the phosphine ligands a versatile system for carrying out many organometallic catalysis.

Structure and Bonding

Phosphines are two electron donors that engage a lone pair for binding to metals. These are thus considered as good σ−donors and poor π−acceptors and they belong to the same class with the aryl, dialkylamino and alkoxo ligands. In fact they are more π−acidic than pure σ−donor ligands like $NH_3$and, more interestingly so, their π−acidity can be varied significantly by systematic incorporation of substituents on the P atom. For example, PF_3 is more π−acidic than CO. Analogous to what is observed in case of the benchmark π−acidic CO ligand, in which the metal d_π orbital donates electron to a π* orbital of a C−O bond, in the case of the phosphines ligands, such π−back donation occurs from the metal d_π orbital occurs on to a σ* orbital of a P−R bond (Figure 8.2.2). In phosphine ligands, with the increase of the electronegativity of R both of the σ and the σ* orbitals of the P−R bond gets stabilized. Consequently, the contribution of the atomic orbital of the P atom to the σ*−orbital of the P−R bond increases, which eventually increases the size of the σ* orbital of the P−R bond. This in turn facilitates better overlap of the σ* orbital of the P−R bond with the metal d_π orbital during the metal to ligand π−back donation in these metal phosphine complexes.

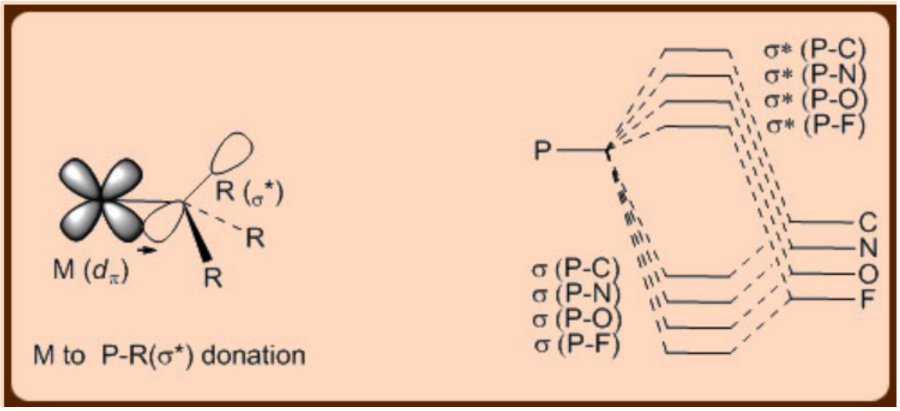


Figure 8.2.2: Back donation from the metal d_π orbital to a σ* orbital of a P−R bond.

Starting from CO, which is a strong π−acceptor ligand, to moving to the phosphines, which are good σ−donors and poor π−acceptor ligands, to even going further to other extreme to the ligands, which are both good σ−donors as well as π−donors, a rich variety of phosphine ligands thus are available for stabilizing different types of organometallic complexes. In this context the following ligands are discussed below.

π-basic ligands

Alkoxides (RO^-) and halides like F^-, Cl^- and Br^- belong to a category of π−basic ligands as they engage a second lone pair for π−donation to the metal over and above the first lone pair partaking σ−donation to the metal. Opposite to what is observed in the case of π−acidic ligands, in which the π* ligand orbital stabilizes the d_π metal orbital and thereby affecting a larger ligand field splitting, as consistent with the strong field nature of these ligands (Figure 3), in the case of the π−basic ligands, the second lone pair destabilizes the d_π metal orbitals leading to a smaller ligand field splitting, which is in agreement with the weak field nature of these ligands. The orbitals containing the lone pair of the ligands are usually located on the more electronegative heteroatoms and so they are invariably lower in energy than the metal d_π orbitals. Hence, the destabilization of the metal d_π orbitals occurs due to the repulsion of the filled ligand lone pair orbital with the filled metal d_π orbitals. In case of the situations in which the metal d_π orbitals are vacant, like in d^0 systems of Ti^{4+} ions, the possibility of the destabilization of the metal d_π orbitals do not arise but instead stabilization occurs through the donation of the filled ligand lone pair orbital electrons to the empty metal d_π orbitals as seen in the case of TiF_6 and $W(OMe)_6$. Thus, this scenario in π−basic ligands is opposite to that observed in case of the π−acidic ligands, for which the empty π* ligand orbitals are higher in energy than the filled metal d_π orbitals.

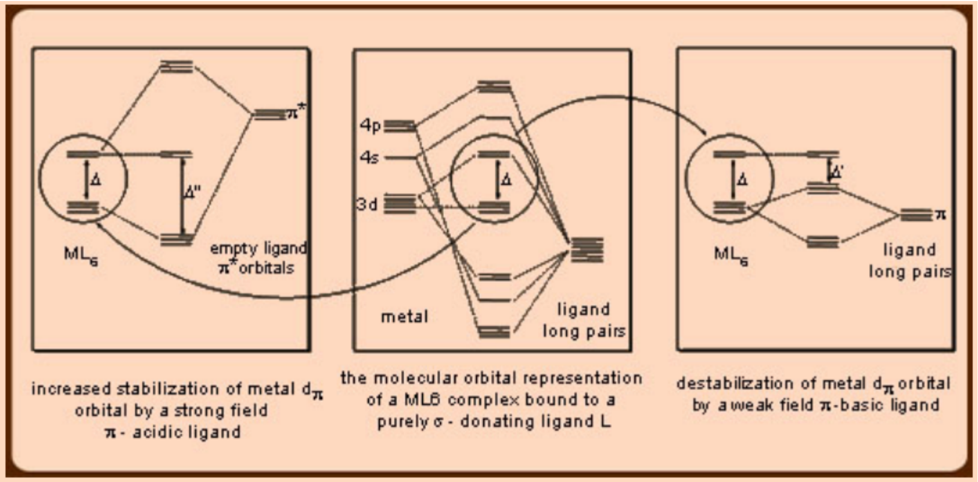


Figure 8.2.3: Orbital interactions in the presence of the π−acceptor, (pure) σ−donor and π−basic ligands are shown.

CHAPTER OVERVIEW

9: Complexes of π−bound Ligands

9.1: Metal Alkene Complexes

Learning Objectives

In this lecture you will learn the following

- The metal alkene complexes.
- The metal−olefin bonding interactions.
- The synthesis and reactivities of the metal−olefin complexes.
- The *umpolung* reactivities of olefins in the metal alkene complexes.

Though the first metal olefin complex dates back a long time to the beginning of 19th century, its formulation was established only a century later in the 1950s. While reacting K_2PtCl_4 with EtOH in 1827, the Danish chemist Zeise synthesized the famous **Zeise's salt** $K[PtCl_3(C_2H_4)] \bullet H_2O$ containing a Pt bound ethylene moiety and which incidentally represented the first metal−olefin complex (Figure 9.1.1).

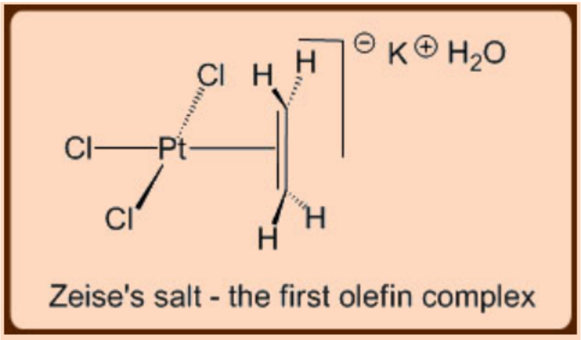


Figure 9.1.1: Zeise's salt

The metal−olefin bonding interaction is best explained by the *Dewar−Chatt* model, that takes into account two mutually opposing electron donation involving σ−donation of the olefinic C=C π−electrons to an empty d_π metal orbital followed by π−back donation from a filled metal d_π orbital into the unoccupied C=C π* orbital. Quite understandably so, for the d^0 systems, the formations of metal−olefin complexes are not observed. The extent of the C=C forward π-donation to the metal and the subsequent π−back donation from the filled d_π orbital to the olefinic C=C π* orbital have a direct bearing on the C=C bond of the metal bound olefinic moiety in form of bringing about a change in hybridization as well as in the C−C bond distance (Figure 9.1.2).

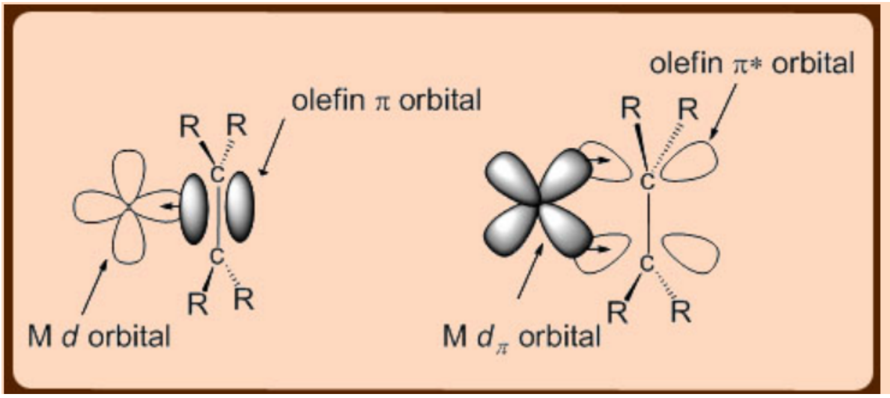


Figure 9.1.2: Metal olefin bonding interactions.

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

Another implication of ligand−metal π−back donation is in the observed change of hybridization at the olefinic C atoms from pure *sp*^{2}, in complexes with no metal to ligand π−back donation, to *sp*^{3}, in complexes with significant metal to ligand π−back donation, is observed. The change in hybridization from *sp*^{2} to *sp*^{3} centers of the olefinic carbon is accompanied by the substituents being slightly bent away from the metal center in the final metalacyclopropane form (Figure 9.1.3). This change in hybridization can be conveniently detected by ^{1}H and ^{13}C NMR spectroscopy. For example, in case of the metalacyclopropane systems, which have strong metal to ligand π−back donation, the vinyl protons appear 5 ppm (in the ^{1}H NMR) and 100 ppm (in the ^{13}C NMR) high field with respect to the respective position of the free ligands.

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

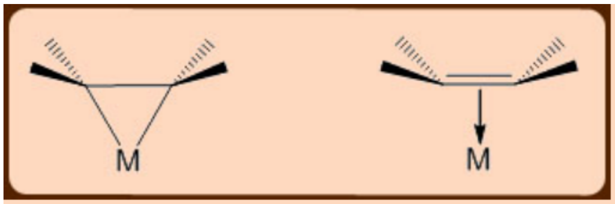


Figure 9.1.3: Metalacyclopropane system and *Dewar−Chatt* model

Synthesis

Metal alkene complexes are synthesized by the following methods.

i. Substitution in low valent metals

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

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

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

iii. From alkyls and related species

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

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

Reaction of alkenes

The metal alkene complexes show the following reactivities.

i. Insertion reaction

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

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

ii. *Umpolung* reactions

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

iii. Oxidative addition

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

Exercise 9.1.1

Predict the product of the reaction.

$$\text{AuMe(PPh}_3) + \text{CF}_2\text{=CF}_2 \longrightarrow \text{A} \longrightarrow \text{B}$$

Answer

A = $\{(CF_2=CF_2)AuMe(PPh_3)\}$ and

B = $Au(CF_2\text{-}CF_2Me)(PPh_3)$

Exercise 9.1.2

Specify whether the lengthening/shortening of the C−C bond distance in the metal bound olefin moiety is observed as a result of metal to ligand π−back donation?

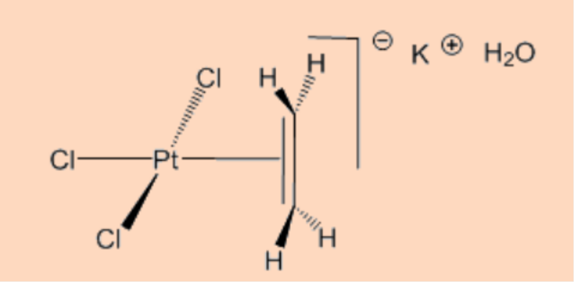
Answer

Lengthening

Exercise 9.1.3

Draw the structure of Zeise's salt.

Answer



Exercise 9.1.4

The change in hybridization at the olefinic C from sp^2 to sp^3 primarily arise due to?

Answer

Metal-ligand π-back donation.

Self Assessment test

1. Predict the product of the reaction.

$$\text{PtCl}_2^- + \text{C}_2\text{H}_4 \longrightarrow$$

Ans: $[PtCl_3(C_2H_4)]^-$ and Cl^-

2. Specify whether the lengthening/shortening of the C−C bond distance in the metal bound olefin moiety is observed as a result of ligand to metal σ− donation?

Ans: Lengthening.

3. Metalacyclopropane intermediate in a metal bound olefin complex is primarily formed due to which kind of interaction?

Ans: Metal−ligand π−back donation

4. The oxidation state of Pt in Zeise's salt is?

Ans: Pt^{II}

Summary

Alkenes are an important class of unsaturated ligands that bind to a metal by σ−donating its C=C π−electrons and also accepts electrons from the metal in its π* orbital of C=C bond. These symbiotic σ−donation and π−back donation in metal bound olefin complexes have a significant impact on their structure and reactivity properties. Quite importantly, the structural manifestations arising out of these forward σ−donation and π−back donation can be characterized by using ^1H, ^{13}C NMR and IR spectroscopic methods.

9.2: Metal Allyl and Diene Complexes

Learning Objectives

In this lecture you will learn the following

- The metal−allyl complexes.
- The metal−diene complexes.
- The metal−cyclobutadiene complexes.
- The respective metal−ligand interactions.

The allyl ligand is often referred to as an “actor” ligand rather than a “spectator” ligand. It binds to metals in two ways *i.e.* in a η^1 (monohapto) form and a η^3 (trihapto) form (Figure $9.2.1$). (*i*). In its monohapto (η^1) form, it behaves as an anionic *1e−donor* X type of a ligand analogous to that of a methyl moiety while (*ii*) in a trihapto (η^3) form, it acts as an anionic *3e−donor* LX type of a ligand.

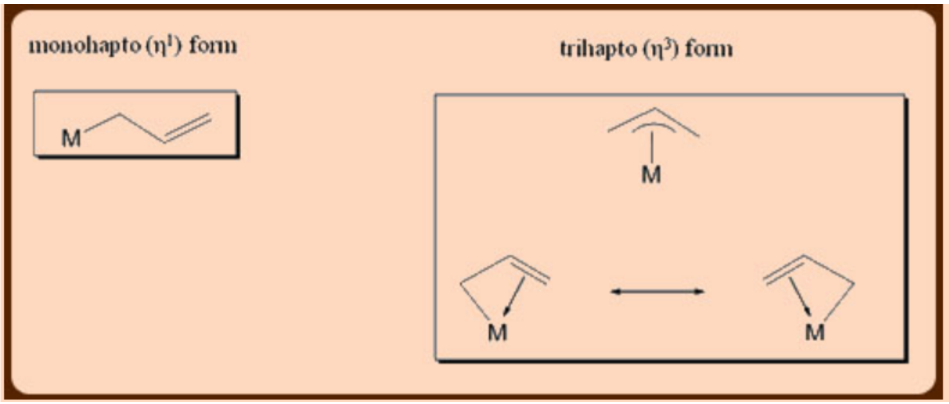


Figure $9.2.1$: Metal−allyl interaction.

Metal−allyl interaction

Of particular interest are the molecular orbitals namely Ψ_1, Ψ_2 and Ψ_3 of the allyl ligand that interact with the metal in a metal allyl complex. The energy of these molecular orbitals increase with the increase in the number of nodes. Of the three, the Ψ_1 and Ψ_2 orbitals usually engage in ligand to metal σ−donation, with Ψ_1 involving in a dative L−type bonding and Ψ_2 participating in a covalent X−type bonding with the metal *d* orbitals (Figure $9.2.2$).

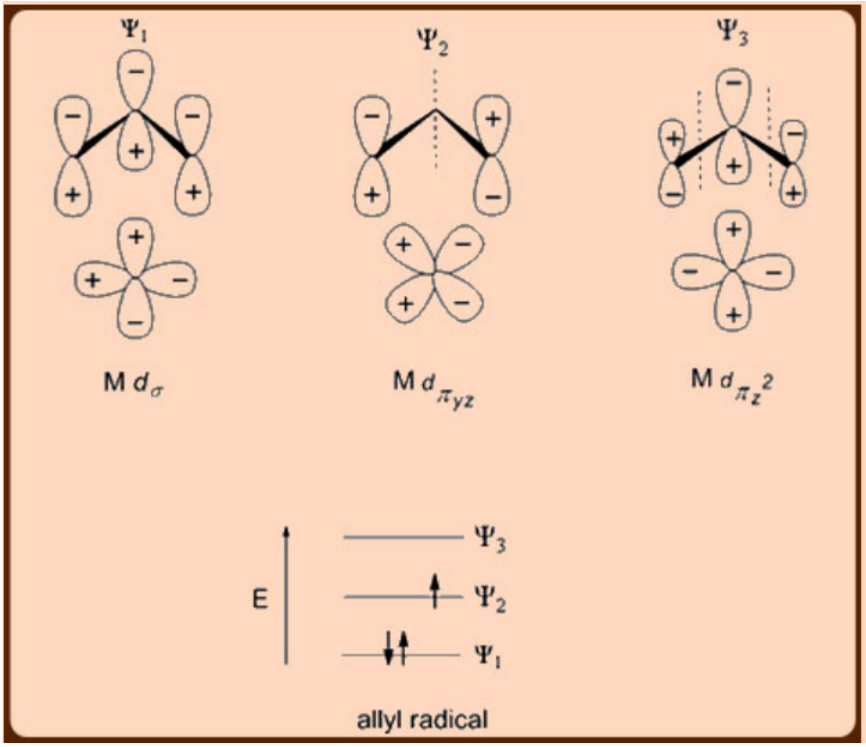


Figure 9.2.2: Metal−allyl interactions.

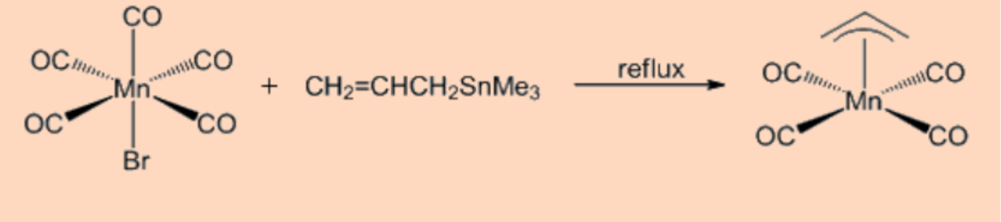
Synthesis of the metal allyl complexes

The metal allyl complexes are synthesized by the following methods.

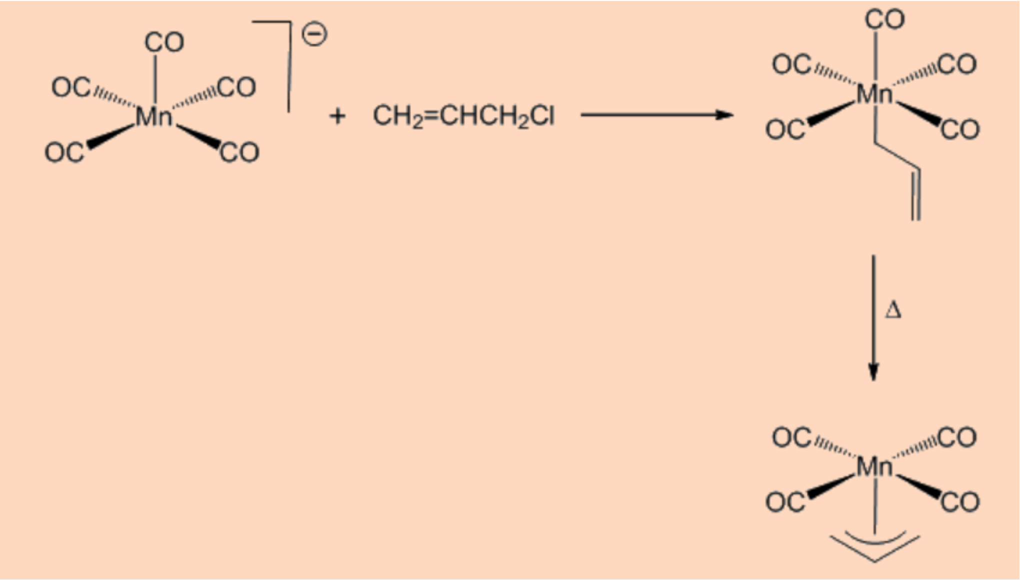
i. From an alkene complex as shown below.

$$\mathrm{Mo(dpe)_2(\eta 2-propene) \rightleftharpoons Mo(dpe)_2(\eta 3-allyl)H}$$

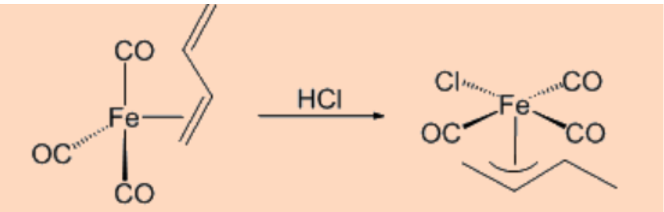
ii. By a nucleophilic attack of an allyl compound as shown below.



iii. By an electrophilic attack of an allyl compound as shown below.



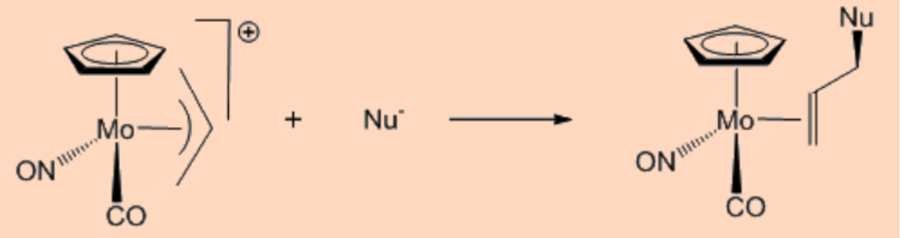
iv. From a diene complex as shown below.



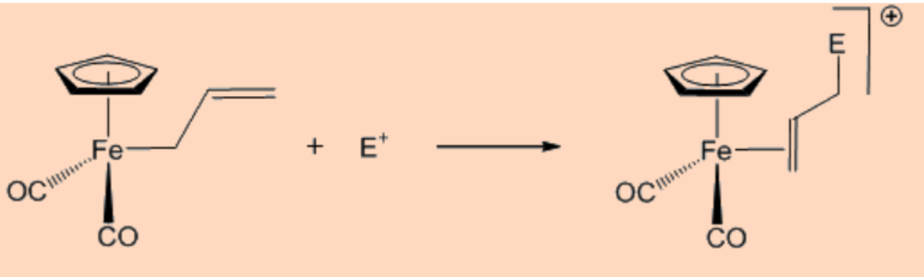
Reactions of metal allyl complexes

The reactivities of the metal allyl complexes toward various species are illustrated below.

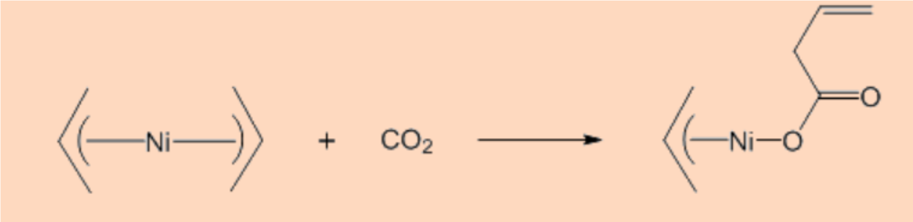
i. Reaction with nucleophiles



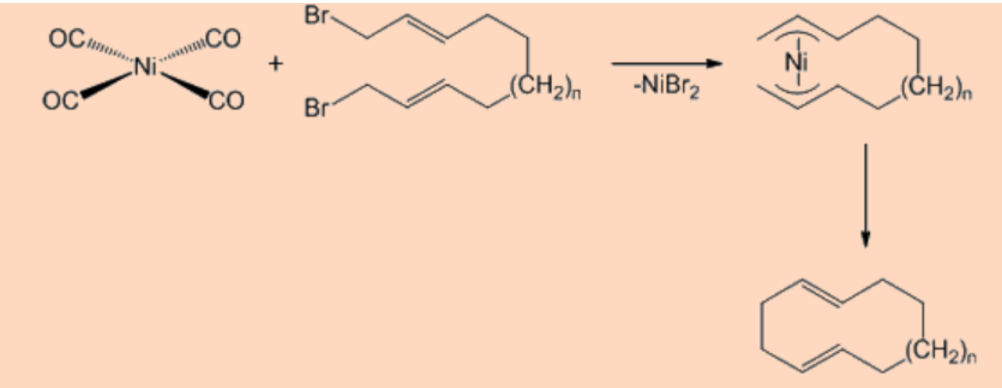
ii. Reaction with electrophiles



iii. Insertion reaction



iv. Reductive elimination



Diene complexes

1,3−Butadiene is a *4e−donor* ligand that binds to a metal in a *cisoid* conformation. The *Dewar−Chatt* model, when applied to 1,3−butadiene, predicts that the ligand may bind to metal either as a L_2 (π_2) donor type, similar to that of an alkene, or as an LX_2 ($\sigma_2\pi$) donor type, similar to that of a metalacyclopropane form. The L_2 binding of 1,3−butadiene is rare, *e.g.* asin (butadiene)$Fe(CO)_3$, while the LX_2 type binding is more common, *e.g.* as in $Hf(PMe_3)_2Cl_2$. An implication of the LX_2 type binding is in the observed shortening of the $C_2{-}C_3$ (1.40 Å) distance alongside the lengthening of the $C_1{-}C_2$(1.46 Å) and $C_3{-}C_4$ (1.46 Å) distances (Figure 9.2.3).

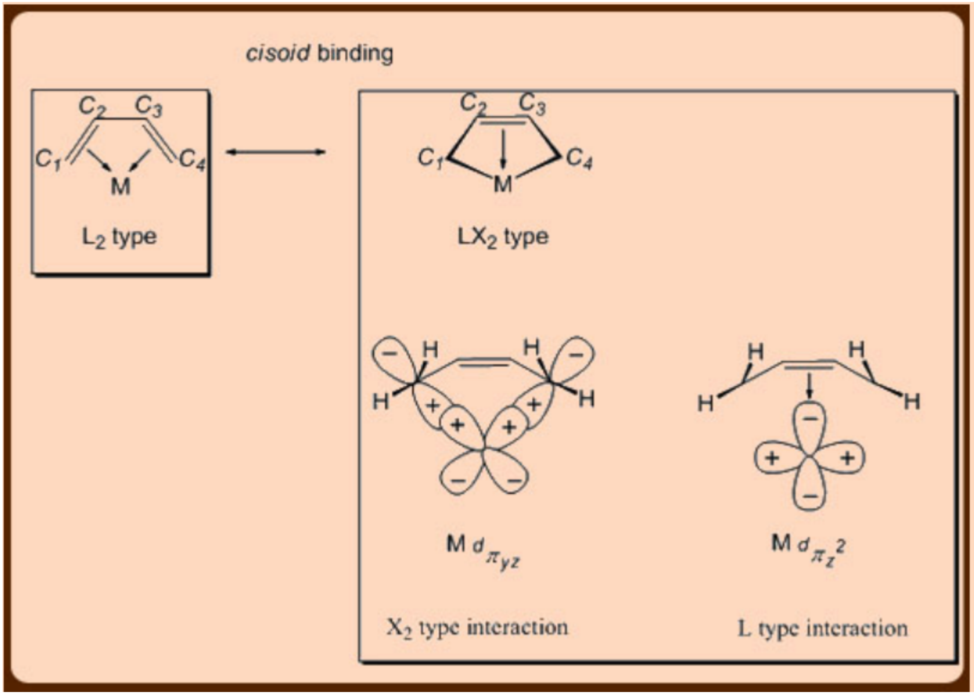


Figure 9.2.3: Metal−diene interaction in *cisoid* binding.

The molecular orbitals of the 1,3−butadiene ligand comprises of two filled Ψ_1 (HOMO−1) and Ψ_2(HOMO) orbitals and two empty Ψ_3 (LUMO) and Ψ_4 (LUMO+1) orbitals. In a metal−butadiene interaction the ligand to metal σ−donation occurs from the filled Ψ_2

orbital of the 1,3−butadiene ligand while the metal to ligand π−back donation occurs on to the empty Ψ_3 orbital of the 1,3−butadiene ligand (Figure 9.2.4).

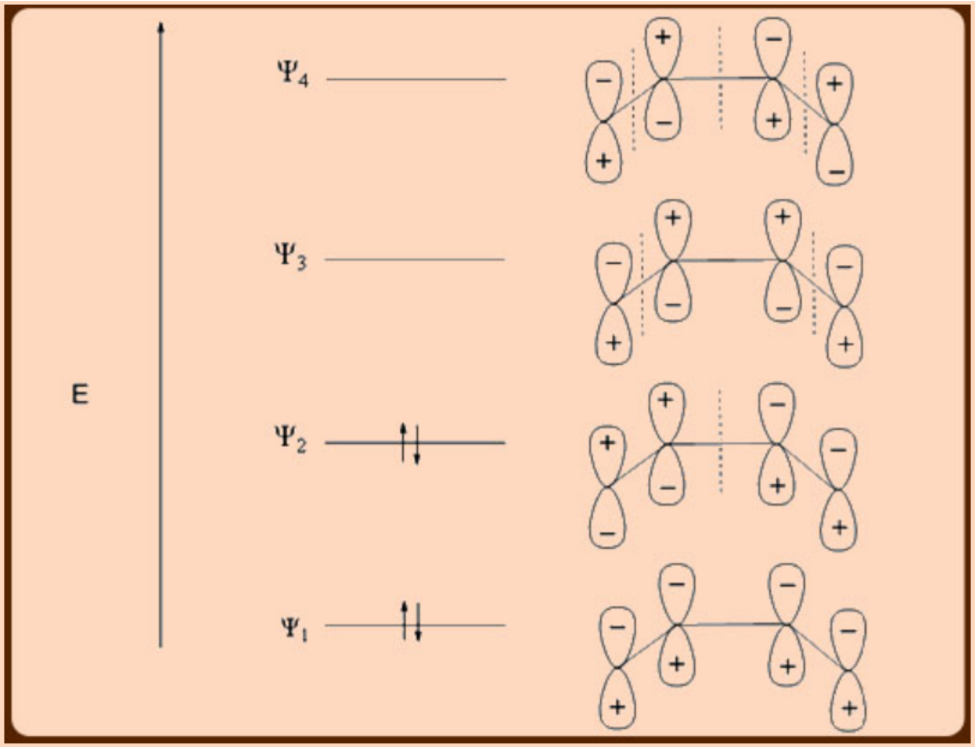


Figure 9.2.4: Metal−diene interaction.

Though *cisoid* binding is often observed in metal butadiene complexes, a few instances of *transoid*binding is seen in dinuclear, *e.g.* as in $Os_3(CO)_{10}(C_4H_6)$, and in mononuclear complexes *e.g.* as in $Cp_2Zr(C_4H_6)$ (Figure 9.2.5).

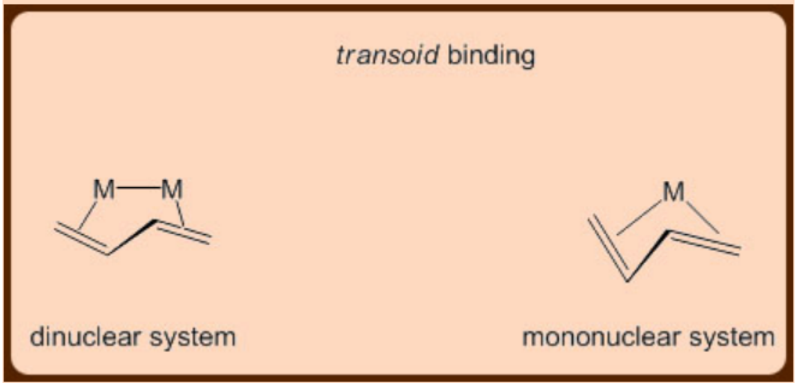
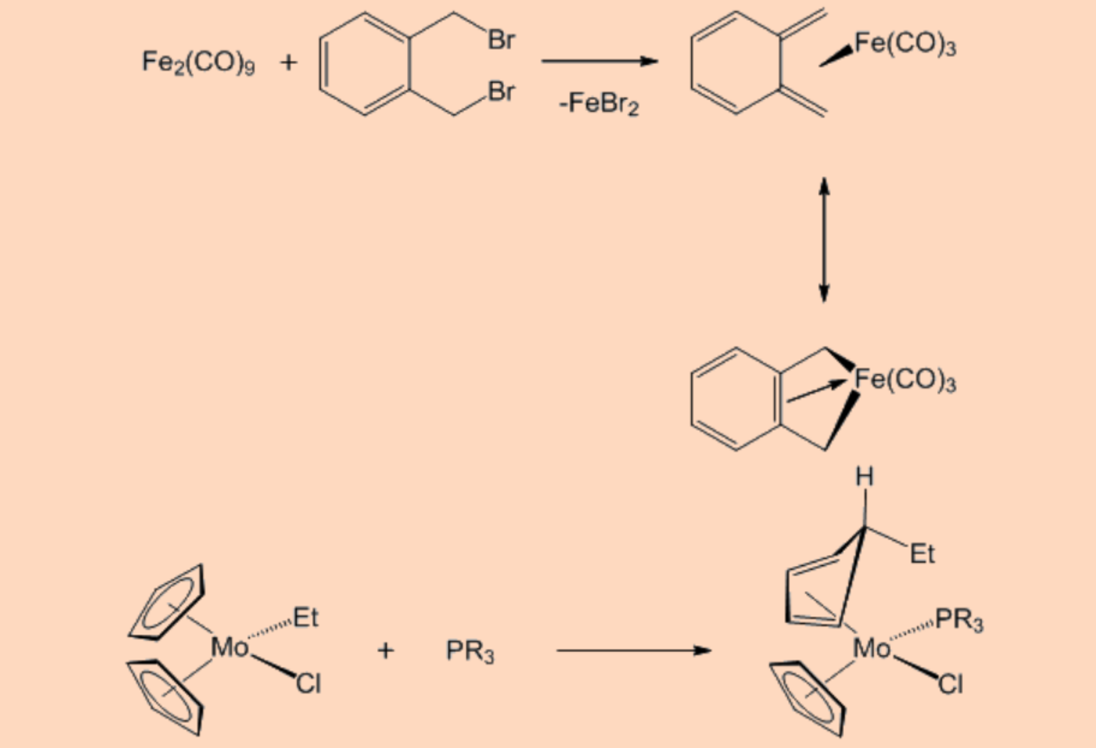


Figure 9.2.5: Metal−diene interaction in *transoid* binding.

Synthesis of metal butadiene complex

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



Metal cyclobutadiene complexes

Cyclobutadiene is an interesting ligand because of the fact that its neutral form, being anti−aromatic (4π−electrons), is unstable as a free molecule (Figure 9.2.6), but its dianionic form is stable because of being aromatic (6π−electrons). Consequently, the cyclobutadiene ligand is stabilized by significant metal to ligand π−back donation to the vacant ligand orbitals.

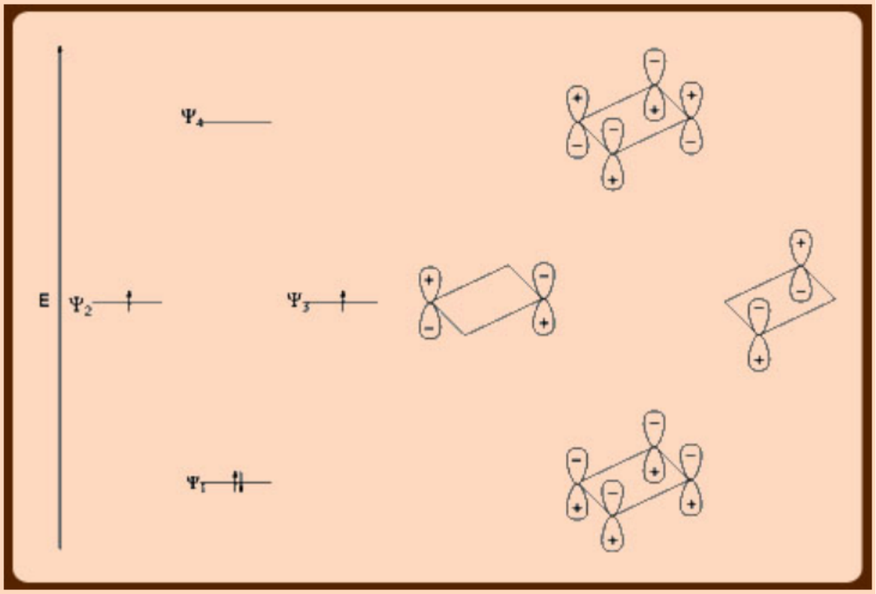
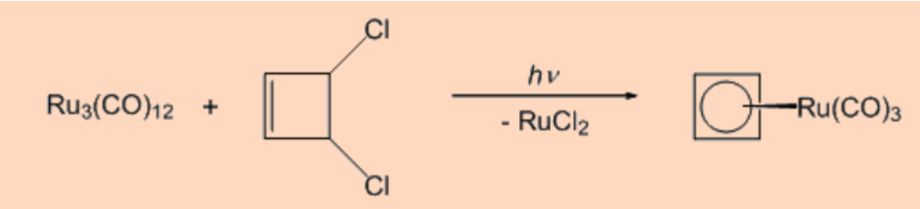


Figure 9.2.6: Electronic structure of cyclobutadiene ligand.

A synthetic route to metal cyclobutadiene complex is shown below.



Problems

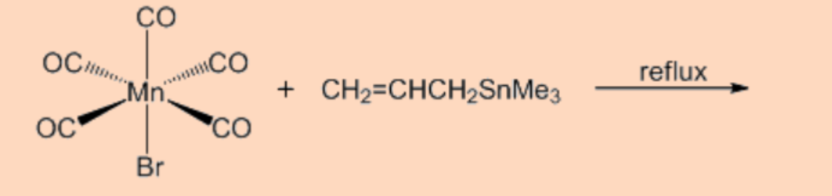
1. The hapticities displayed by an allyl moiety in binding to metals are?

Ans: 1 and 3.

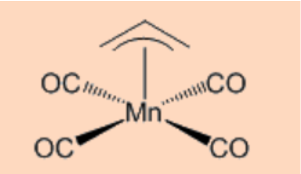
2. Identify which molecular orbitals of an allyl moiety engage in σ−interaction with a suitable *d* orbital of a metal in a η^3−metal allyl complex?

Ans: Ψ_1 and Ψ_2.

3. Predict the product of the reaction.



Ans:



4. Identify which molecular orbitals of a butadiene moiety engage in σ−interaction with a suitable *d*orbital of a metal in a η^4−metal butadiene complex?

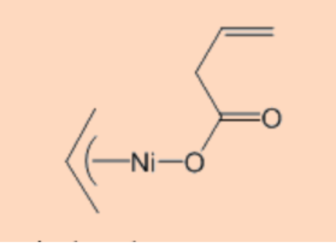
Ans: Ψ_2.

Self Assessment test

1. Predict the product of the reaction.

$$<(--\mathrm{Ni}--)>+\mathrm{CO_2}\longrightarrow$$

Ans:



2. Identify which molecular orbitals of a butadiene moiety engage in π−interaction with a suitable *d*orbital of a metal in a η^4−metal allyl complex?

Ans: Ψ_3.

3. Mention the type of orientations displayed by butadiene ligands for binding to metal.

Ans: Cisoid (common) and transoid (rare).

4. Comment on the number of π−electrons present in the cyclobutadiene moiety of a metal cyclobutadiene complex.

Ans: 6 π−electrons.

Summary

Allyl, 1,3−butadiene and cyclobutadiene together constitute an important class of σ−donor/π−acceptor ligands that occupy a special place in organometallic chemistry. The complexes of these ligands with metals are important intermediates in many catalytic cycles and hence an understanding of their interaction with metal is of significant importance. In this context, the synthesis, characterization and the reactivities of the organometallic complexes of these ligands are described alongside the respective metal−ligand interactions.

9.3: Metal Cyclopentadienyl Complexes

Learning Objectives

In this lecture you will learn the following

- The cyclopentadienyl ligands.
- The synthesis and reactivity of metal−cyclopentadienyl complexes.
- The metal−cyclopentadienyl interaction.

Cyclopentadienyl moiety acts as an important “spectator” ligand and is quite ubiquitous in organometallic chemistry. It remains inert to most nucleophiles and electrophiles and solely engages in stabilizing organometallic complexes. The cyclopentadienyl ligands form a wide array of organometallic compounds exhibiting different formulations that begin with the so-called “piano stool” $CpML_n$ (n = 2,3 or 4) type ones and extends to the most commonly observed “metallocene” Cp_2M type ones to even go beyond further to the “bent metallocene” Cp_2MX_n (n = 1,2 or 3) type ones. In the “piano stool” $CpML_n$ structure, the cyclopentadienyl (Cp) ligand is regarded as the “seat” of the piano stool while the remaining L ligands are referred to as the “legs” of the piano stool. Though the cyclopentadienyl ligand often binds to metal in a η^5 (pentahapto) fashion, *e. g.* as in ferrocene, the other form of binding to metal at lower hapticities, like that of the η^3 (trihapto) binding *e. g.* as in $(\eta^5{-}Cp)(\eta^3{-}Cp)W(CO)_2$ and that of the η^1 (monohapto) binding *e. g.* as in $(\eta^5{-}Cp)(\eta^1{-}Cp)Fe(CO)_2$, are also seen on certain rare occasions.

The binding modes of the cyclopentadienyl ligand in metal complexes can be ascertained to a certain degree by ^1H NMR in the diamagnetic metal complexes, in which the Cp−protons appear as a singlet between 5.5−3.5 ppm while the β and γ hydrogens come at 7−5 ppm.

Cyclopentadienyl−metal interaction

The frontier molecular orbital of the cyclopentadienyl ligand contains 5 orbitals (Ψ_1−Ψ_5) residing in three energy levels (Figure 9.3.1). The lowest energy orbital Ψ_1 does not contain any node and is represented by an a_1 state, followed by a doubly degenerate e_1 states that comprise of the Ψ_2 and $\Psi_3$orbitals, which precede another doubly degenerate e_2 states consisting of Ψ_4 and Ψ_5 orbitals.

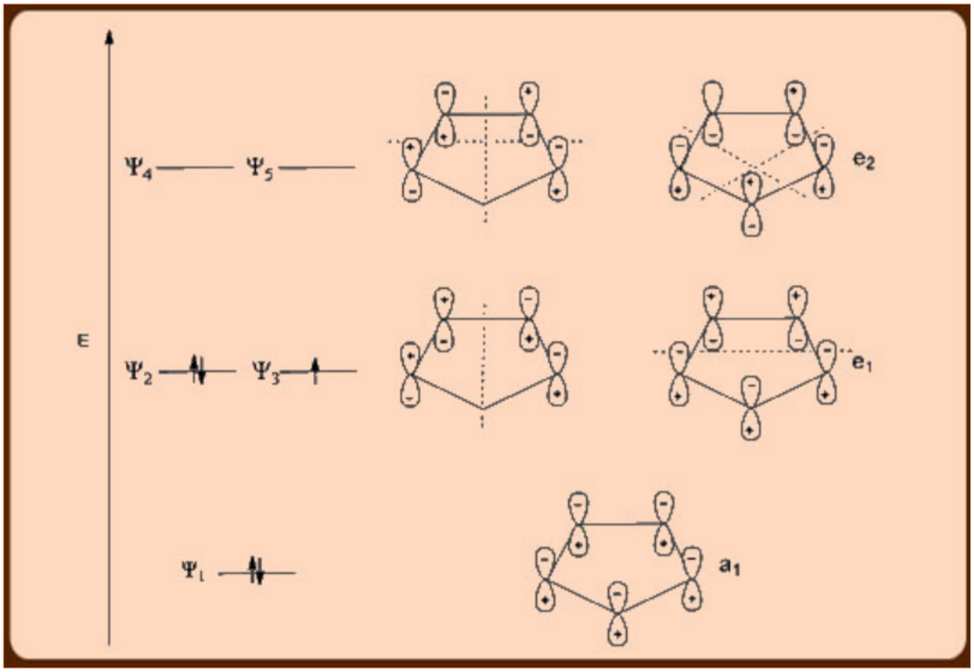


Figure 9.3.1 : Molecular orbital diagram of cyclopentadienyl ligand.

The above frontier molecular orbital diagram becomes more intriguing on moving over to the metallocenes that contain two such cyclopentadienyl ligands. Specifically, in the Cp_2M system, (*e. g.* ferrocene) each of these above five molecular orbital of the two cyclopentadienyl ligands combines to give ten ligand molecular orbitals in three energy levels (Figure 9.3.2). Of these, the orbitals that subsequently interact with the metal orbitals to generate the overall molecular orbital correlation diagram for the Cp$_2$M type of complexes are shown below (Figure 9.3.3).

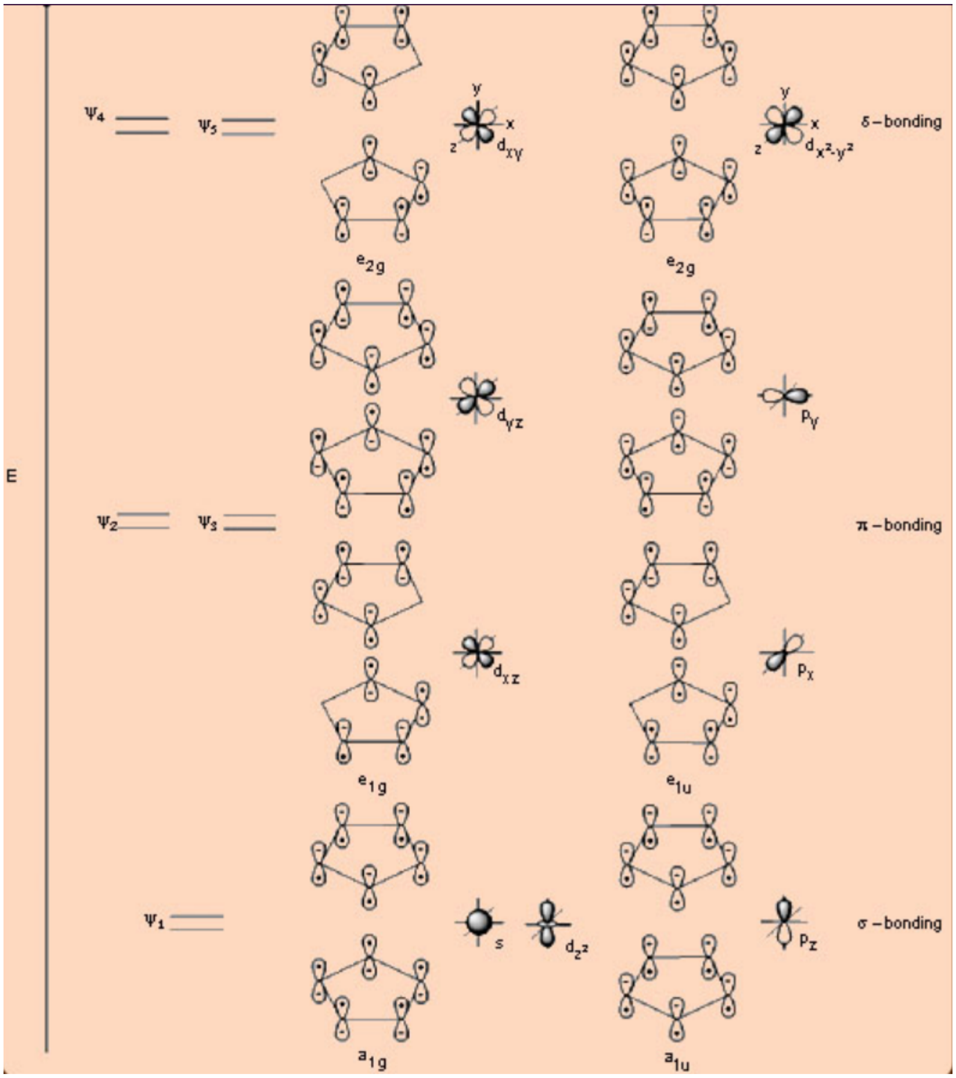


Figure 9.3.2 : Metal−cyclopentadienyl Bonding interactions.

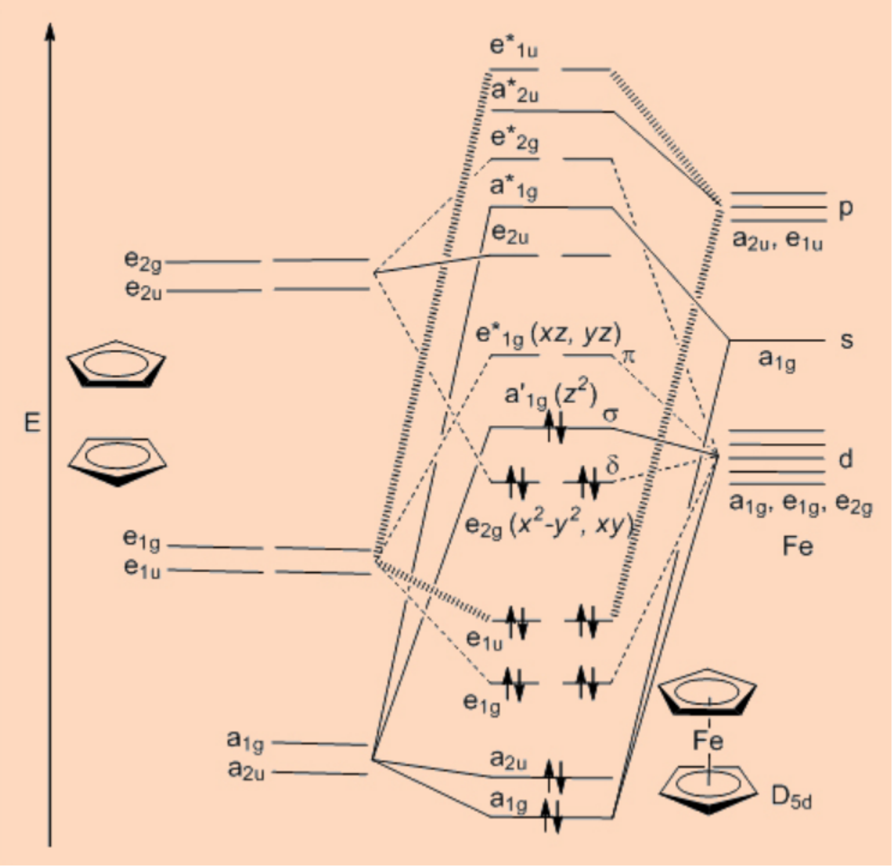


Figure 9.3.3 : MO diagram of ferrocene.

Generic metallocene Cp_2M type complexes are formed for many from across the 1st row transition metal series along Sc to Zn. The number of unpaired electrons thus correlates with the number unpaired electrons present in the valence orbital of the metal (Figure 4). Of the complexes of the 1st row transition metal series, the manganocene exists in two distinct forms, one in a high-spin form with five unpaired electrons, *e.g.* as in Cp_2Mn and the other in a low-spin form with one unpaired electron, *e.g.* as in $Cp^*{}_2Mn$ owing to the higher ligand field strength of the Cp* ligand. Cobaltocene, Cp_2Co, has 19 valence electrons (VE) and thus gets easily oxidized to the diamagnetic 18 VE valence electron species, Cp_2Co^+. Of these metallocenes, the much-renowned ferrocene, Cp_2Fe is a diamagnetic 18 VE complex, whose molecular orbital diagram is shown above (Figure 9.3.3).

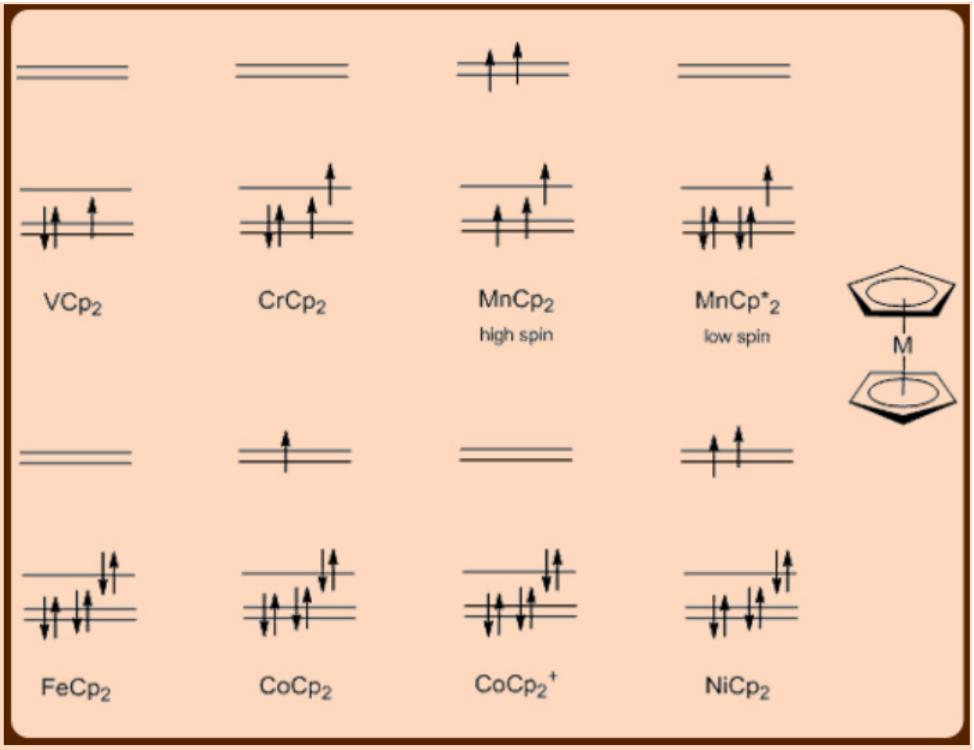


Figure 9.3.4 : Metallocene

Bent metallocenes

Bent metallocenes are Cp_2MX_n type complexes formed of group 4 and the heavier elements of groups 5−7. In these complexes the frontier doubly degenerate e_2g orbitals of Cp_2M fragment interacts with the filled lone pair orbitals of the ligand (Figure 9.3.5).

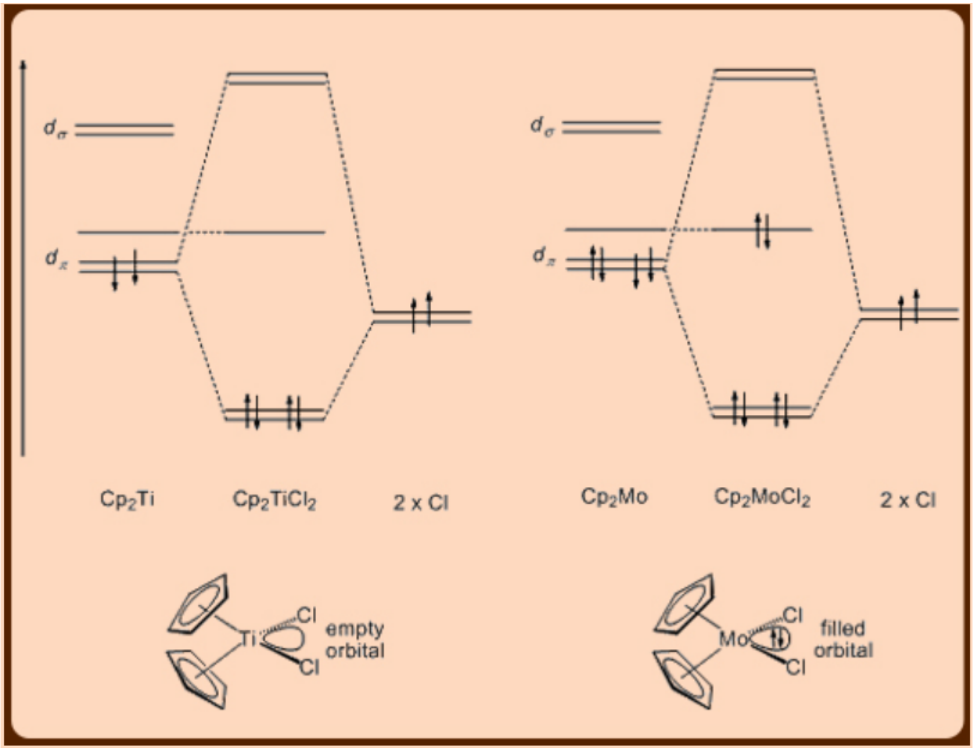
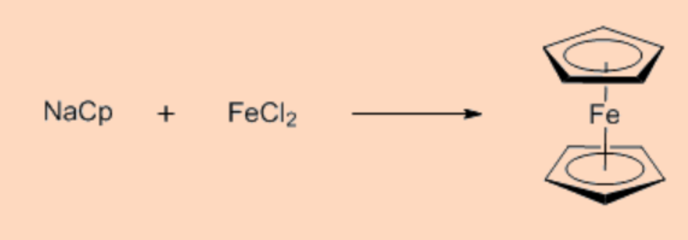


Figure 9.3.5 : Bent metallocene.

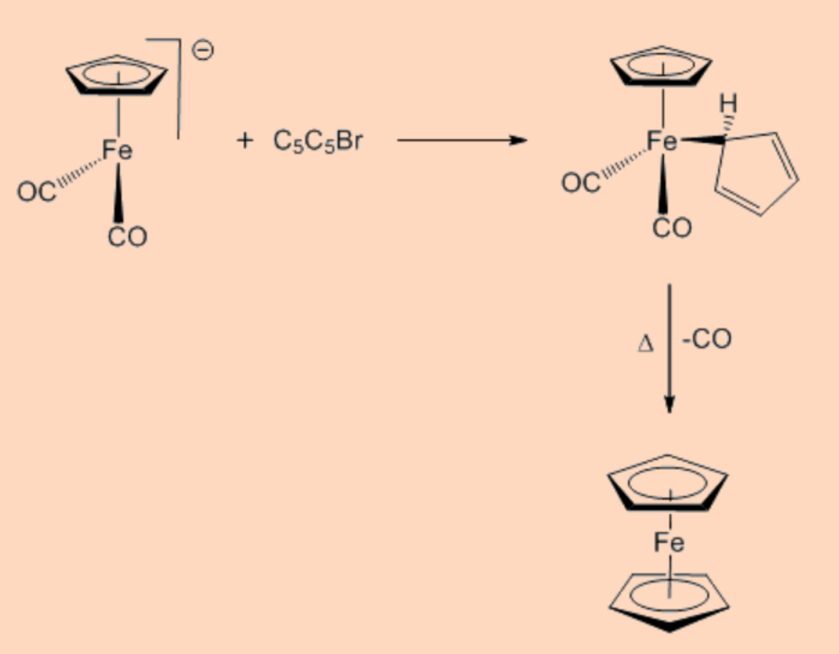
Synthesis of cyclopentadienyl-metal complexes

The metal−cyclopentadienyl complexes are synthesized by the following methods.

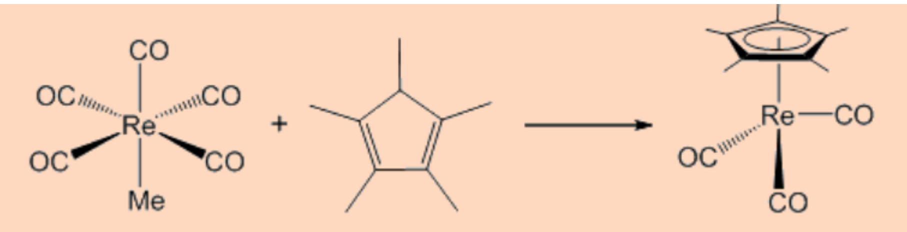
i. from Cp−



ii. from Cp+



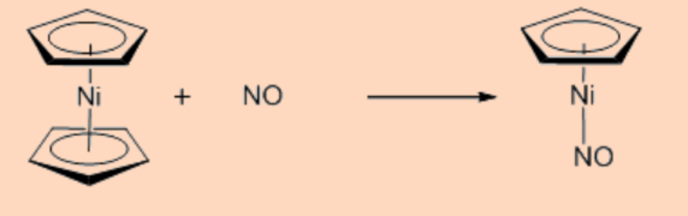
iii. from hydrocarbon



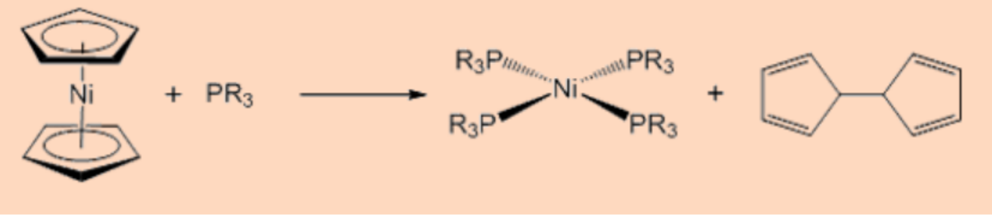
Reactivity of cyclopentadienyl-metal complexes

The reactivity of cyclopentadienyl−metal complexes of the type Cp$_2$M is shown for a representative nickellocene complex.

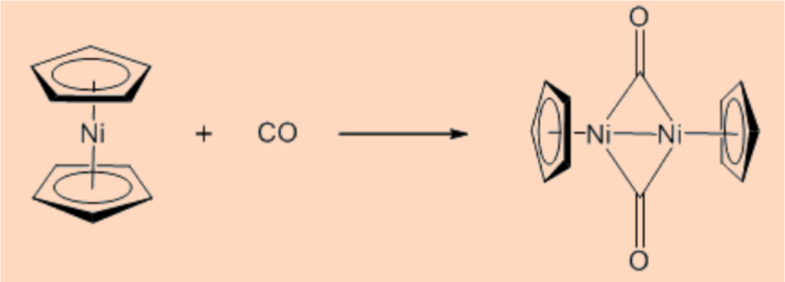
i. reaction with NO



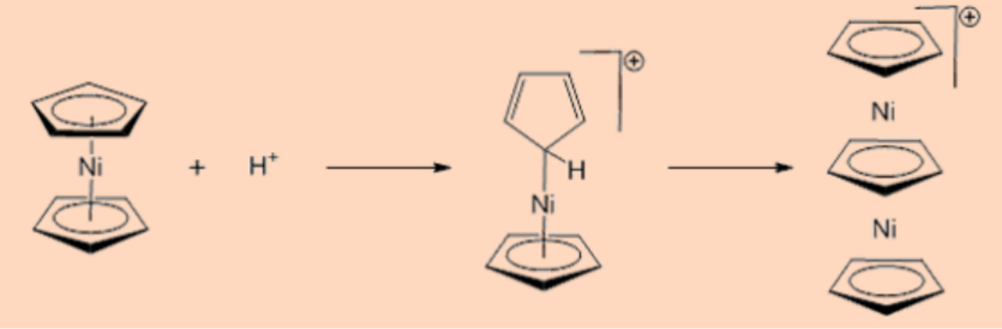
ii. reaction with PR_3



iii. reaction with CO



iv. reaction with H^+



Problems

1. Comment on the p−acceptor property of the cyclopentadienyl ligand.

Ans: The ligand being anionic shows very little π-acceptor properties.

2. Give the total valence electron count at the metal in a nickellocene complex.

Ans: 20 electrons.

3. Explain why the metal center in cobalticene gets easily oxidized.

Ans: 19 electrons cobalticene gets easily oxidized to 18 electron Cp_2Co^+.

4. Specify the number unpaired electrons present in chromocene.

Ans: 2

Self Assessment test

1. Specify the number of unpaired electron present in vanadocene.

Ans: The ligand being anionic shows very little π-acceptor properties.

2. What different hapticities are exhibited by cyclopentadienyl ligand?

Ans: 1, 3, and 5.

3. Specify the hapticities of the cyclopentadienyl ligands in $Cp_2W(CO)_2$.

Ans: 5 and 3.

4. Specify the hapticity of the cyclopentadienyl ligands in $CpRh(CO)_2(PMe_3)$.

Ans: 3.

Summary

Cyclopentadienyl moiety is almost synonymous with the transition metal organometallic complexes as the ligand played a pivotal role at the early developmental stages of the field of organometallic chemistry in the 1960s and 1970s. An important quality of the cyclopentadienyl ligand is that it behaves as an extremely good “spectator” ligand being inert to nucleophiles and electrophiles and displays uncanny ability towards stabilizing metal complexes of elements from across the different parts of the periodic table. Cyclopentadienyl moiety thus forms several types of complexes of different formulations like that of the “piano stool” $CpML_n$ (n = 2,3 or 4) types, the metallocene Cp_2M types and the bent metallocene Cp_2MX_n (n = 1,2 or 3) types. Cyclopentadienyl metal complexes make valuable catalysts for many chemical transformations of interest to academia and industries alike. The cyclopentadienyl moiety participates in a complex interaction with the metal involving ligand frontier molecular orbitals and the metal valence orbitals. Cyclopentadienyl metal complexes can be accessed by many methods.

CHAPTER OVERVIEW

10: Reaction Mechanisms

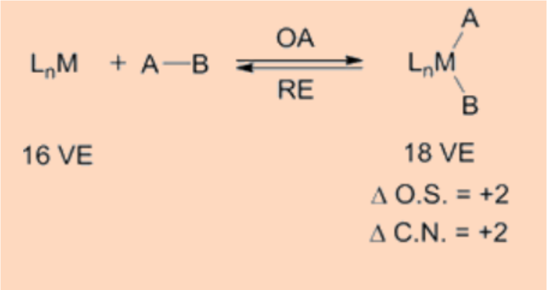
10.1: Oxidative Addition and Reductive Elimination

Learning Objectives

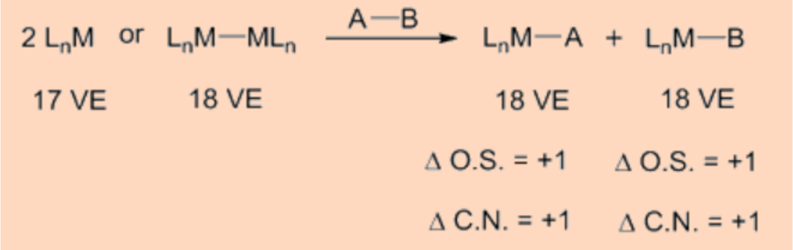
In this lecture you will learn the following

- The oxidative addition reactions.
- The reductive elimination reactions.
- Various mechanistic pathways prevalent for these reactions.

Oxidative addition (OA) is a process that adds two anionic ligands *e. g.* A and B, that originally are a part of a A-B molecule, like in H_2 or Me−I, on to a metal center and is of significant importance from the perspective of both synthesis and catalysis. The exact reverse of the same process, in which the two ligands, A and B, are eliminated from the metal center forming back the A−B molecule, is called the reductive elimination (RA). As A and B are anionic X type ligands, the oxidative addition is accompanied by an increase in the coordination number, valence electron count as well as in the formal oxidation state of the metal center by two units. The oxidative addition step may proceed by a variety of pathways. It requires the metal center to be both coordinatively unsaturated and electron deficient.

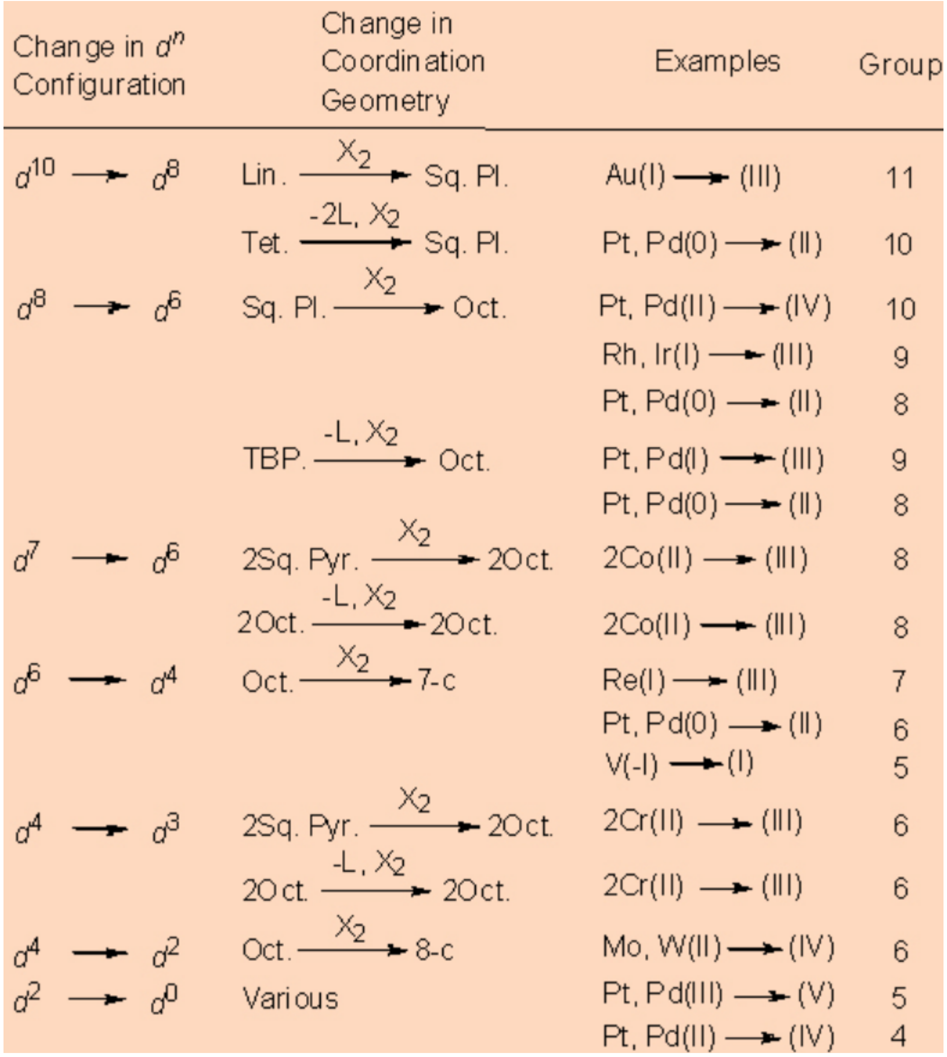


Oxidative addition transfers a single mononuclear metal center having 16 VE to a 18 VE species upon oxidative addition. Another frequently observed pathway is that a 18 VE complex looses a ligand to become a 16 VE species which then undergoes an oxidative addition. Apart from above two types, another possible pathway for oxidative addition proceeds as a binuclear oxidative addition in which each of the two metal centers undergo change in oxidation state, electron count and coordination number by one unit instead of two. This type of a binuclear oxidative addition is observed for a 17 VE metal complex or for a binuclear 18 VE metal complex having a metal−metal bond and, for which the metal has a stable oxidation state at a higher positive oxidation state by one unit.



It is interesting to note that in the oxidative addition the breakage of A−B σ−bond occurs as a result of a net transfer of electrons from the metal center to a σ*−orbital of the A−B bond, thus resulting in the formation of the two new M−A and M−B bonds. The oxidative addition is facilitated by electron rich metal centers having low oxidation state whereas the reductive elimination is facilitated by metal centers in higher oxidation state.

Table 10.1.1. Common types of oxidative addition reactions.



Change in d^n Configuration	Change in Coordination Geometry	Examples	Group
$d^{10} \rightarrow d^8$	Lin. $\xrightarrow{X_2}$ Sq. Pl.	Au(I) → (III)	11
	Tet. $\xrightarrow{-2L,\ X_2}$ Sq. Pl.	Pt, Pd(0) → (II)	10
$d^8 \rightarrow d^6$	Sq. Pl. $\xrightarrow{X_2}$ Oct.	Pt, Pd(II) → (IV)	10
		Rh, Ir(I) → (III)	9
		Pt, Pd(0) → (II)	8
	TBP. $\xrightarrow{-L,\ X_2}$ Oct.	Pt, Pd(I) → (III)	9
		Pt, Pd(0) → (II)	8
$d^7 \rightarrow d^6$	2Sq. Pyr. $\xrightarrow{X_2}$ 2Oct.	2Co(II) → (III)	8
	2Oct. $\xrightarrow{-L,\ X_2}$ 2Oct.	2Co(II) → (III)	8
$d^6 \rightarrow d^4$	Oct. $\xrightarrow{X_2}$ 7-c	Re(I) → (III)	7
		Pt, Pd(0) → (II)	6
		V(-I) → (I)	5
$d^4 \rightarrow d^3$	2Sq. Pyr. $\xrightarrow{X_2}$ 2Oct.	2Cr(II) → (III)	6
	2Oct. $\xrightarrow{-L,\ X_2}$ 2Oct.	2Cr(II) → (III)	6
$d^4 \rightarrow d^2$	Oct. $\xrightarrow{X_2}$ 8-c	Mo, W(II) → (IV)	6
$d^2 \rightarrow d^0$	Various	Pt, Pd(III) → (V)	5
		Pt, Pd(II) → (IV)	4

Abbreviations: Lin. = linear, Tet. = tetrahedral, Oct. = octahedral, Sq. Pl. = square planar, TBP = trigonal bipyramidal, Sq. Pyr. = square pyramidal: 7-c, 8-c = 7- and 8-coordinate.

In principle, the oxidative addition is the reverse of reductive elimination, but in practice one may dominate over the other. Thus, the favorability of one over the other is depends on the position of equilibrium, which is further dependent on the stability of the two oxidation states of the metal and on the difference of bond strengths of A−B versus that of the M−A and M−B bonds. For example, metal hydride complexes frequently undergo reductive elimination to give alkanes but rarely an alkane undergoes oxidative addition to give an alkyl hydride complex. Along the same line, alkyl halides frequently undergo oxidative addition to a metal giving metal−alkyl halide complexes but these complexes rarely reductively eliminate to give back alkyl halides. Usually the oxidative addition is more common for 3rd row transition metals because they tend to possess stronger metal ligand bond strengths. The oxidative addition is also favored by strong donor ligands, as they stabilize the higher oxidation state of the metal. The oxidative addition reaction can expand beyond transition metals as observed in the case of the Grignard reagents as well as for some main group elements.

Oxidative addition may proceed by several pathways as discussed below.

Concerted oxidative addition pathway

Oxidative addition may proceed by a **concerted 3−centered associative mechanism** involving the incoming ligand with the metal center. Specifically, the addition proceeds by the formation of a σ−complex upon binding of an incoming ligand say, H_2, followed by the cleavage of the H−H bond as a result of the back donation of electrons from the metal to the σ*−orbital of the H−H bond. Such type of addition is common for the H−H, C−H and Si−H bonds. As expected these proceed by two steps (*i*) the formation of a σ−complex and (*ii*) the oxidation step. For example, the oxidative addition of H_2 to Vaska's complex $(PMe_3)_2Ir(CO)Cl$ proceeds by this pathways.

S_N2 pathway

This pathway of oxidative addition is operational for the polarized AB type of ligand substrates like the alkyl, acyl, allyl and benzyl halides. In this mechanism, the L_nM fragment directly donates electrons to the σ*−orbital of the A−B bond by attacking the least electronegative atom, say A, of the AB molecule and concurrently initiating the elimination of the most electronegative atom of the AB molecule in its anionic form, B^-. These reactions proceed *via* a polar transition state that is accompanied by an inversion of the stereochemistry at the atom of attack by the metal center and are usually accelerated in polar solvents.

Radical pathway

This type of oxidative addition proceeds *via* a by radical pathway that generally are vulnerable to the presence of impurities. The radical processes can be of non−chain and chain types. In a non−chain type of mechanism, the metal (M) transfer one electron to the σ*−orbital of the RX bond resulting in the formation of a radical cation $M^{+\bullet}$ and a radical anion $RX^{-\bullet}$. The generation of the two radical fragments occurs by the way of the elimination of the anion X^- from the radical anion $RX^{-\bullet}$ leaving behind the radical $R^\bullet$ while the subsequent reaction of X^- anion with the radical cation $M^{+\bullet}$ generates the other radical $MX^\bullet$ in the course of the reaction. Such type of non−chain type of oxidative addition is observed for the addition of the alkyl halide to $Pt(PPh_3)_3$ complexes.

$$\mathrm{PtL_3} \xrightarrow{fast} \mathrm{PtL_2}$$

$$\mathrm{PtL_2} + \mathrm{RX} \longrightarrow {}^\bullet\mathrm{PtL_2} + {}^{\bullet -}\mathrm{RX} \xrightarrow{slow} {}^\bullet\mathrm{PtXL_2} + {}^\bullet\mathrm{R}$$

$$ {}^\bullet\mathrm{PtXL_2} + {}^\bullet\mathrm{R} \xrightarrow{fast} \mathrm{RPtXL_2}$$

The other type in this category is the chain radical type reaction that is usually observed for the oxidative addition of EtBr and $PhCH_2Br$ to the $(PMe_3)_2Ir(CO)Cl$ complex. For this process a radical initiator is required and the reaction proceeds along a series of known steps common to a radical process.

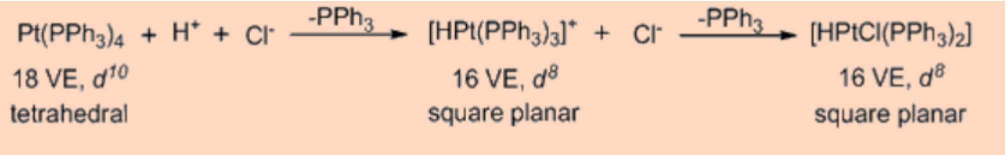
$$\mathrm{R}^\bullet + \mathrm{IR^ICl(CO)L_2} \longrightarrow \mathrm{RIr^{II\bullet}Cl(CO)L_2}$$

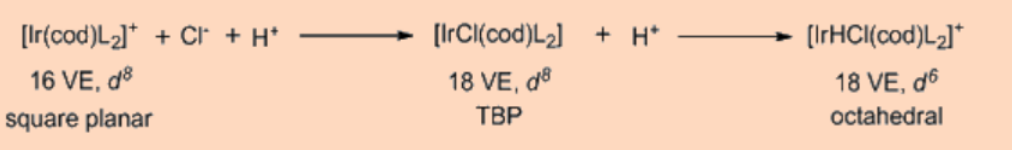
$$\mathrm{RIr^{II\bullet}Cl(CO)L_2} + \mathrm{RX} \longrightarrow \mathrm{RXIr^{III}Cl(CO)L_2} + \mathrm{R}^\bullet$$

$$2\,\mathrm{R}^\bullet \longrightarrow \mathrm{R_2}$$

Ionic pathway

This is kind of pathway for the oxidative addition reaction is common to the addition of hydrogen halides (HX) in its dissociated H^+ and X^- forms. The ionic pathways are usually of the following two types (*i*) the ones in which the starting metal complex adds to H^+ prior to the addition of the halide $X^-$and (*ii*) the other type, in which the halide anion X^- adds to the starting metal complex first, and then the addition of proton H^+ occurs on the metal complex.





Reductive Elimination

The r**eductive eliminations** are reverse of the oxidative addition reactions and are accompanied by the reduction of the formal oxidation state of the metal and the coordination numbers by two units. The reductive eliminations are commonly observed for d^8 systems, like the Ni(II), Pd(II) and Au(III) ions and the d^6 systems, like the Pt(IV), Pd(IV), Ir(III) and Rh(III) ions. The reaction may proceed by the elimination of several groups.

$$\mathrm{L_nMRH \longrightarrow L_nM + R{-}H}$$

$$\mathrm{L_nMR_2 \longrightarrow L_nM + R{-}R}$$

$$\mathrm{L_nMH(COR) \longrightarrow L_nM + RCHO}$$

$$\mathrm{L_nMR(COR) \longrightarrow L_nM + R_2CO}$$

$$\mathrm{L_nMR(SiR_3) \longrightarrow L_nM + R{-}SiR_3}$$

Binuclear Reductive Elimination

Similar to what has been observed in the case of binuclear oxidative addition, the binuclear reductive elimination is also observed in some instances. As expected, the oxidation state and the coordination number decrease by one unit in the binuclear reductive elimination pathway.

$$\mathrm{2\,MeCH{=}CHCu(PBu_3)} \xrightarrow{heat} \mathrm{MeCH{=}CHCH{=}CHMe}$$

$$\mathrm{ArCOMn(CO)_5 + HMn(CO)_5 \longrightarrow ArCHO + Mn_2(CO)_{10}}$$

Problems

1. What kind of metal centers favor oxidative addition?

Ans: Electron rich low valent metal centers.

2. Complete the sentence correctly.

(a) Reductive elimination is frequently observed in coordinatively saturated/unsaturated metal complexes.
(b) Reductive elimination is accompanied by increase/decrease in the oxidation state of the metal.
(c) Oxidative addition is accompanied by increase/decrease in the coordination number of the metal

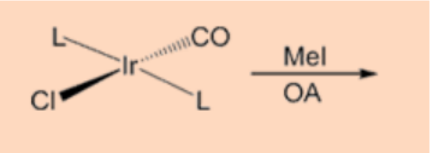
Ans:

(a) Saturated.
(b) Decrease in the oxidation state by two units.
(c) Increase in the coordination number by two units

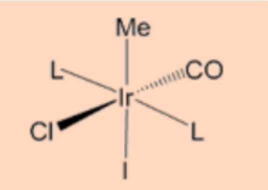
3. State the various mechanistic pathways involved in oxidative addition reactions.

Ans: Concerted oxidative addition, S_N2 mechanism, radical and ionic mechanism.

4. Complete the reaction.



Ans:



Self Assessment test

1. What kind of metal centers favor reductive elimination?

Ans: Electron deficient high valent metal centers

2. Complete the sentence correctly.

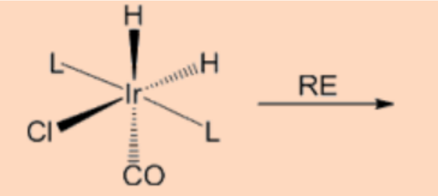
(a) Oxidative addition is frequently observed in coordinatively saturated/unsaturated metal complexes.
(b) Oxidative addition is accompanied by increase/decrease in the oxidation state of the metal.
(c) Reductive elimination is accompanied by increase/decrease in the coordination number of the metal.

Ans:
(a) Unsaturated.
(b) Increase in the oxidation state by two units.
(c) Decrease in the coordination numbers by two units.

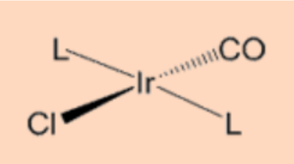
3. How does the geometry of the square planar complexes change upon oxidative addition reactions?

Ans: Square planar to octahedral.

4. Complete the reaction.



Ans:



Summary

The oxidative addition and the reductive elimination reactions are like the observe and reverse of the same coin. The oxidative addition is generally observed for metal centers with low oxidation state and is usually accompanied by the increase in the oxidation state, the valence electron count and the coordination number of the metal by two units. Being opposite, the reductive elimination is seen in the case of the metal centers with higher oxidation state and is accompanied by the decrease in the oxidation state, the valence electron count and the coordination number of the metal by two units. The oxidative addition may proceed by a variety of pathways that involve concerted, ionic and the radical based mechanisms. More interestingly, the oxidative addition and reductive elimination reactions are not solely restricted to the mononuclear metal complexes but can also be observed for the binuclear complexes.

10.2: Insertion and Elimination Reactions

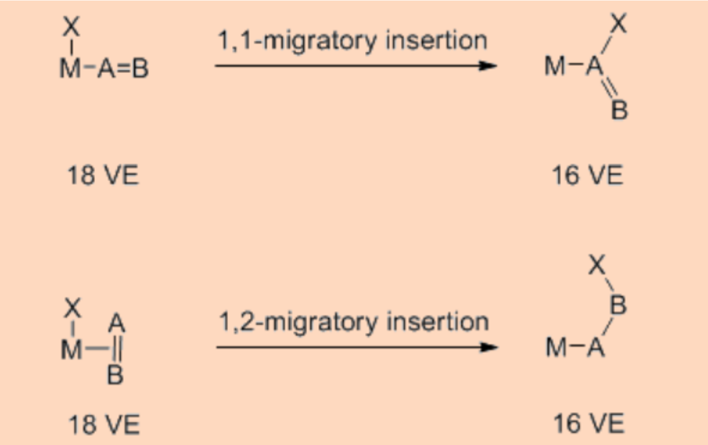
Learning Objectives

In this lecture you will learn the following

- The insertion and elimination reactions.
- The various mechanistic pathways by which these reactions proceed.
- Their relevance in some important catalytic cycles.

Unlike what we have learned about the oxidative addition and the reductive elimination reactions, that facilitate the addition or removal of 1−electron and 2−electron ligands on to a metal center, the insertion and the elimination reactions perform the subsequent transformation of these ligands from within the same coordination sphere of a metal. Thus, in an insertion reaction a metal bound 2 electron A=B type of a ligand can insert on to a M−X bond resulting in a new metal bound 1−electron ligand like, M−A−B−X, which is formed as a result of the formations of the M−A and B−X bonds. The insertion reaction thus leads to the generation of one vacant site created at the initial metal bound A=B site. Thus a primary requirement for reverse elimination reaction to occur is the presence of a *cis* vacant site.

Insertions are of two types, 1,1−insertion and 1,2−insertion. In 1,1−insertion both the metal M and the ligand X of the M−X bond end up on the same atom like in the M−A(X)−B moiety formed after the insertion of the A=B molecule in the M−X bond, whereas in the 1,2−insertion, these end up on the adjacent atoms like in the M−A−B−X moiety formed after the insertion of the A=B molecule in the M−X bond. The type of insertion depends on the type of the ligand undergoing the insertion like η^1−ligand showing 1,1−insertion and η^2−ligands showing 1,2−insertion. For example, the CO ligand exclusively undergoes 1,1−insertion while the C_2H_4 ligand undergoes 1,2−insertion. The SO_2 ligand remains the only exception as it can bind by both η^1−(by S−donor site) and η^2−(by S− and O−donor sites) modes and thus shows both type of insertions.

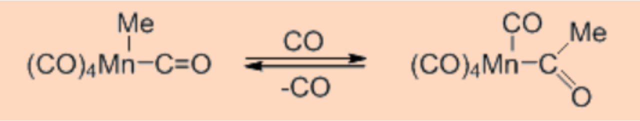


Though the insertion and the elimination reactions are mutually reversible, owing to the thermodynamical reasons one is favored over the other. For example, SO_2 is known to insert into the M−R bond with no report of its elimination is known of it, while for N_2 ligand, no report of its insertion is known but it’s elimination from a M−N=N−R bond is known.

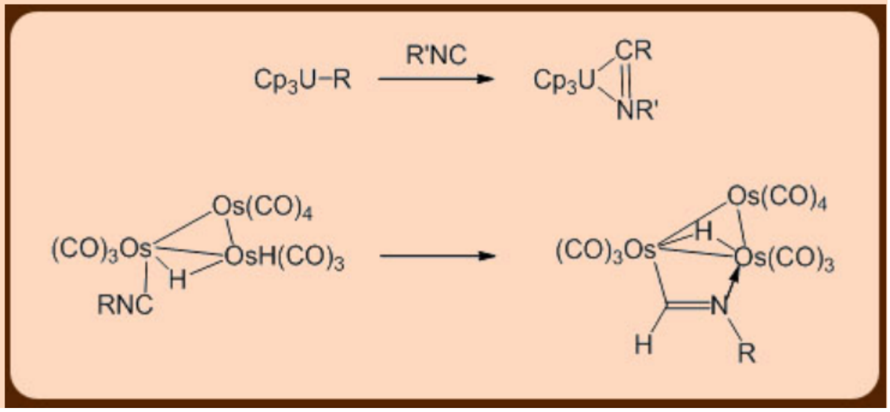
$$\mathrm{M{-}R + SO_2 \longrightarrow M{-}SO_2R}$$

$$\mathrm{M{-}N{=}N{-}Ar \longrightarrow M{-}Ar{=}N_2}$$

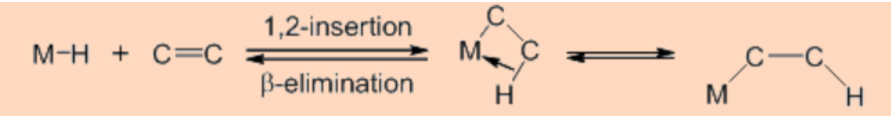
The CO ligand inserts readily into a metal−alkyl bond. Sterically demanding substituents (R) is found to accelerate the reaction as a bulky R group in an acyl moiety in the final M−CO−R bond is far removed from the metal center than that in the starting M−R bond.



Isonitriles readily insert into M−R and M−H bonds giving η^2-bound iminoacyls.

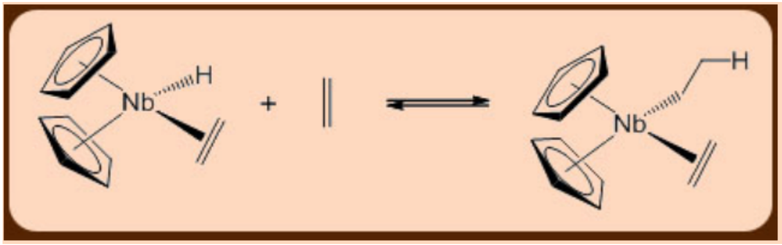


Olefins usually inserts across a M−H bond and such insertions are of relevance to the commercially important olefin polymerization process. In certain cases the 1,2−insertions of olefins give species exhibiting agostic insertions.



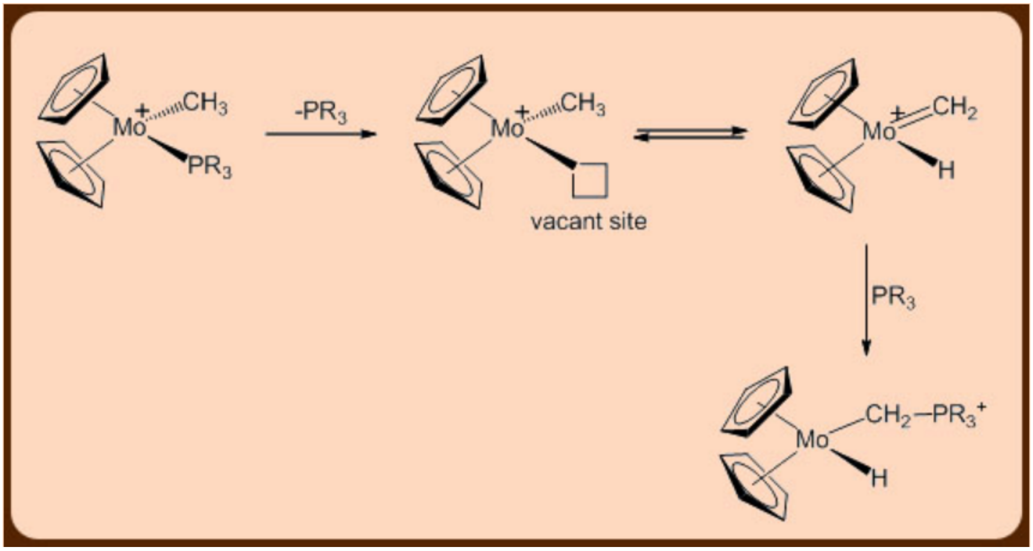
ß-Elimination

β−elimination is just a reverse of 1,2−insertion and is a major cause of decomposition of metal alkyl bond having a b−hydrogen atom. A pre-requisite for the β−elimination reaction to occur is the presence of an adjacent vacant site next to the metal alkyl bond undergoing the β−elimination. The β−elimination step results in the formation of a metal hydride species that also contain a metal bound olefin moiety.



α-elimination

In absence of a β−hydrogen, a metal bound alkyl moiety may undergo the cleavage of a C−H bond at the α, γ and δ positions. For example, a methyl moiety may α−eliminate to give a metal bound methylene hydride moiety.



Problems

1. Give an example of a ligand that undergo 1,1−insertion.

Ans: CO

2. Give an example of a ligand that undergo 1,2−insertion.

Ans: C_2H_4

3. Give an example of a ligand that undergo both the 1,1−insertion and the 1,2−insertion reactions.

Ans: C_2H_4

Self Assessment test

1. On what type of bonds does CO insertion usually occur?

Ans: Metal−alkyl (M−R) bonds.

2. On what type of bonds does isonitrile insertion usually occur?

Ans: Metal-alkyl (M-R) and the metal-hydride (M-H) bonds.

3. On what type of bonds does C_2H_4 insertion usually occur?

Ans: Metal-hydride (M-H) bonds.

4. State an important requirement for the occurrence of an elimination reaction.

Ans: The presence of an adjacent vacant site.

Summary

Insertion and elimination reactions are important sequences that carryout transformation of the metal bound ligands to the corresponding product from within the same coordination sphere of the metal center and thus together represent key steps of an overall catalytic cycle. The insertions are highly ligand dependent and may proceed by 1,1−insertion and 1,2−insertion mechanisms. Elimination reactions are just reverse of the insertion reactions and they too may proceed by several pathways. The two pathways that are commonly observed are the β−elimination and the α−eliminations, even though other type of elimination pathways exists.

10.3: Nucleophilic and Electrophilic Addition and Abstraction

Learning Objectives

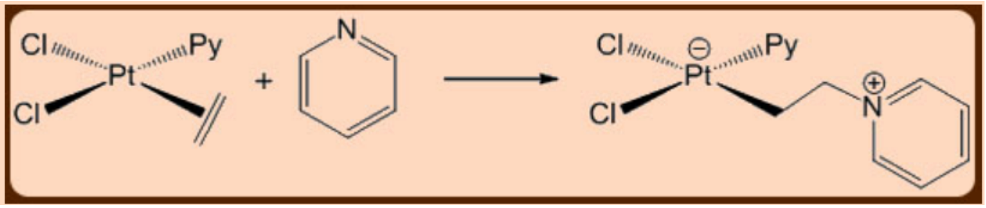
In this lecture you will learn the following

- Ligand activation by metal that leads to a direct external attack at the ligand.
- Nucleophilic addition and nucleophilic abstraction reactions.
- Electrophilic addition and electrophilic abstraction reactions.

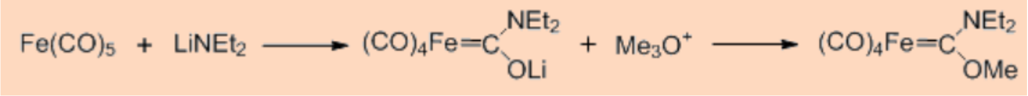
The nucleophilic and electrophilic substitution and abstraction reactions can be viewed as ways of activation of substrates to allow an external reagent to directly attack the metal activated ligand without requiring prior binding of the external reagent to the metal. The attacking reagent may be a nucleophile or an electrophile. The nucleophilic attack of the external reagent is favored if the L_nM fragment is a poor π−base and a good σ−acid *i.e.*, when the complex is cationic and/or when the other metal bound ligands are electron withdrawing such that the ligand getting activated gets depleted of electron density and can undergo an external attack by a nucleophile Nu^-, like LiMe or OH^-. The attack of the nucleophiles may result in the formation of a bond between the nucleophiles and the activated unsaturated substrate, in which case it is called nucleophilic addition, or may result in an abstraction of a part or the whole of the activated ligand, in which case it is called the nucleophilic abstraction. The nucleophilic addition and the abstraction reactions are discussed below.

Nucleophilic addition

An example of a nucleophilic addition reaction is shown below.



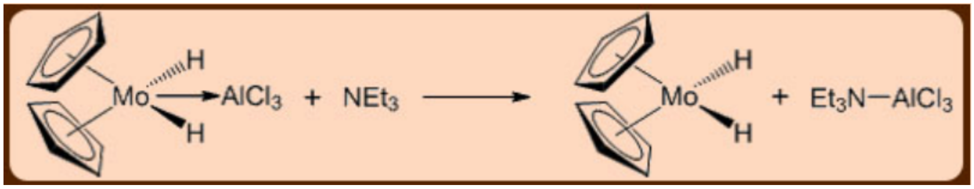
Carbon monoxide (CO) as a ligand can undergo nucleophilic attack when bound to a metal center of poor π−basicity, as the carbon center of the CO ligand is electron deficient owing to the ligand to metal σ−donation not being fully compensated by the metal to ligand π−back donation. Thus, activated CO ligand undergoes nucleophilic attack by the lithium reagent to give an anionic acyl ligand, which upon alkylation generates the famous Fischer carbene complex.



$$Fe(CO)_5 + LiNEt_2 \longrightarrow (CO)_4Fe{=}C\genfrac{}{}{0pt}{}{NEt_2}{OLi} + Me_3O^+ \longrightarrow (CO)_4Fe{=}C\genfrac{}{}{0pt}{}{NEt_2}{OMe}$$

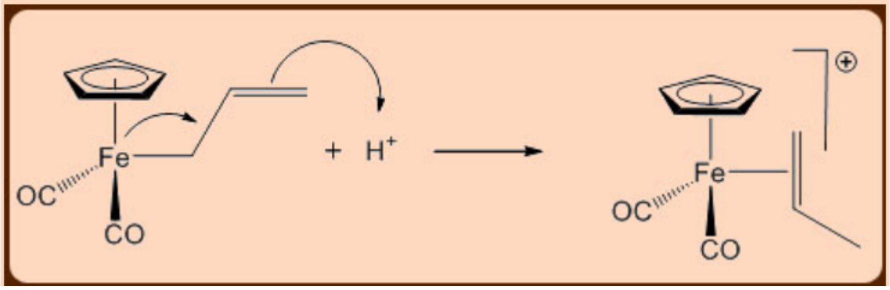
Nucleophilic abstraction

An example of a nucleophilic abstraction reaction is shown below.



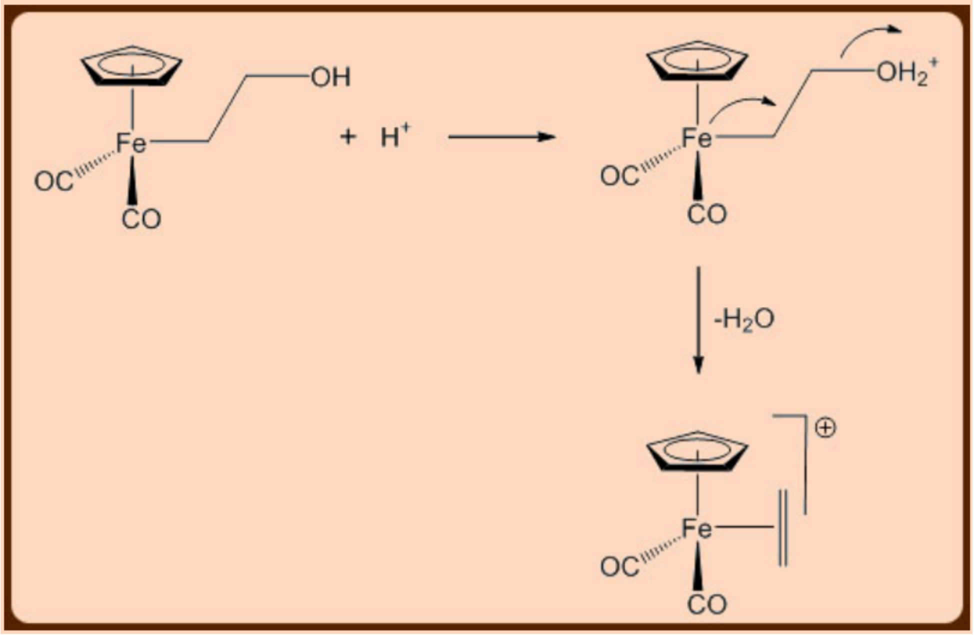
Electrophilic addition

Similar to the nucleophilic addition and abstraction reactions, the electrophilic counterparts of these reactions also exist. An electrophilic attack is favored if the L_nM fragment is a good π−base and a poor σ−acid *i.e.*, when the complex is anionic with the metal center at low−oxidation state and/or when the other metal bound ligands are electron donating such that the ligand getting activated becomes electron rich from the π−back donation of the metal center and thus can undergo an external attack by an electrophile E^+ like H^+ and CH_3I. The attack of the electrophiles may result in the formation of a bond between the electrophile and the activated unsaturated substrate, in which case it is called electrophilic addition, or may result in an abstraction of a part or the whole of the activated ligand, in which case it is called the electrophilic abstraction.



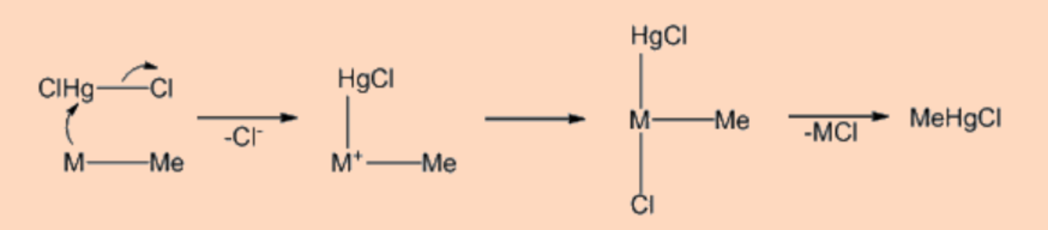
Electrophilic abstraction

An example of an electrophilic abstraction reaction is shown below.



Alkyl abstractions are often achieved by Hg^{2+} that can proceed in two ways, (*i*) by an attack at the α−carbon of a metal alkyl bond leading to an inversion of configuration at the alkyl carbon and (*ii*) by an attack at the metal center leading to retention of configuration at the alkyl carbon. The inversion of configuration proceeds by the following pathway.

The retention of configuration proceeds by the following pathway.



CHAPTER OVERVIEW

11: Applications

11.1: Homogeneous Catalysis - I

Learning Objectives

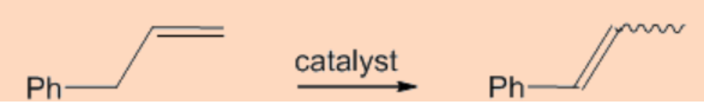
In this lecture you will learn the following

- The application of organometallic complexes in homogeneous catalysis.
- Alkene isomerization.
- Alkene and the arene hydrogenations.
- Transfer hydrogenation.

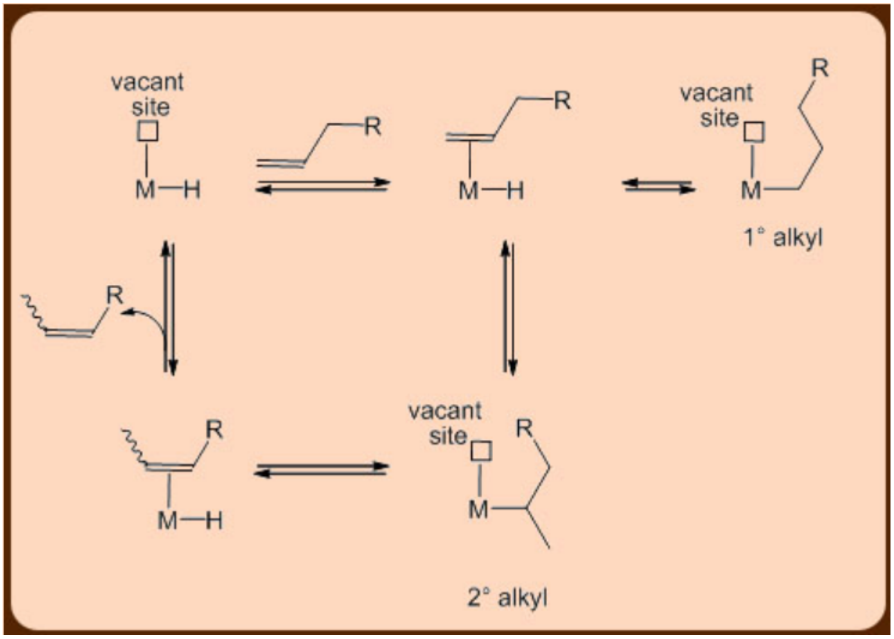
One of the most important exploits of the organometallic chemistry is its application in the area of homogeneous catalysis. The field has now expanded its territory to accommodate in equal measures many large-scale industrial processes as well as numerous small scale reactions of the day-to-day organic synthesis. A few representative examples of organometallic catalysis are outlined below.

Alkene Isomerization

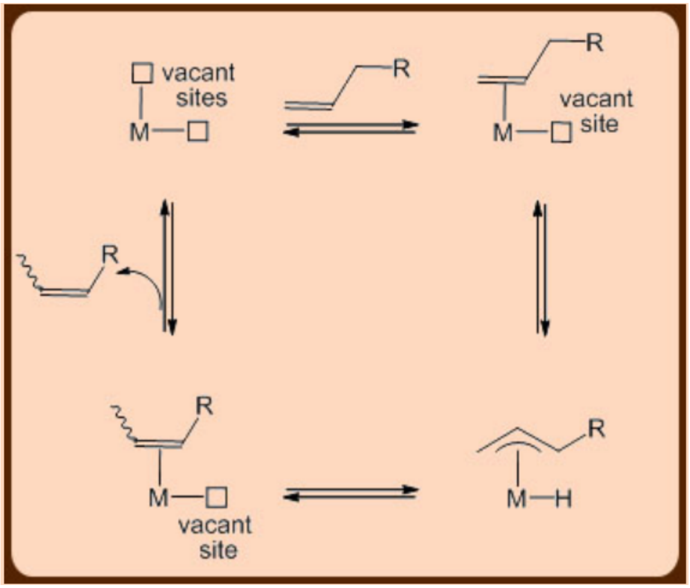
Alkene isomerization is a transformation that involve a shift of a double bond to an adjacent position followed by 1,3−migration of a H atom. The isomerization reaction is transition metal catalyzed.



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.



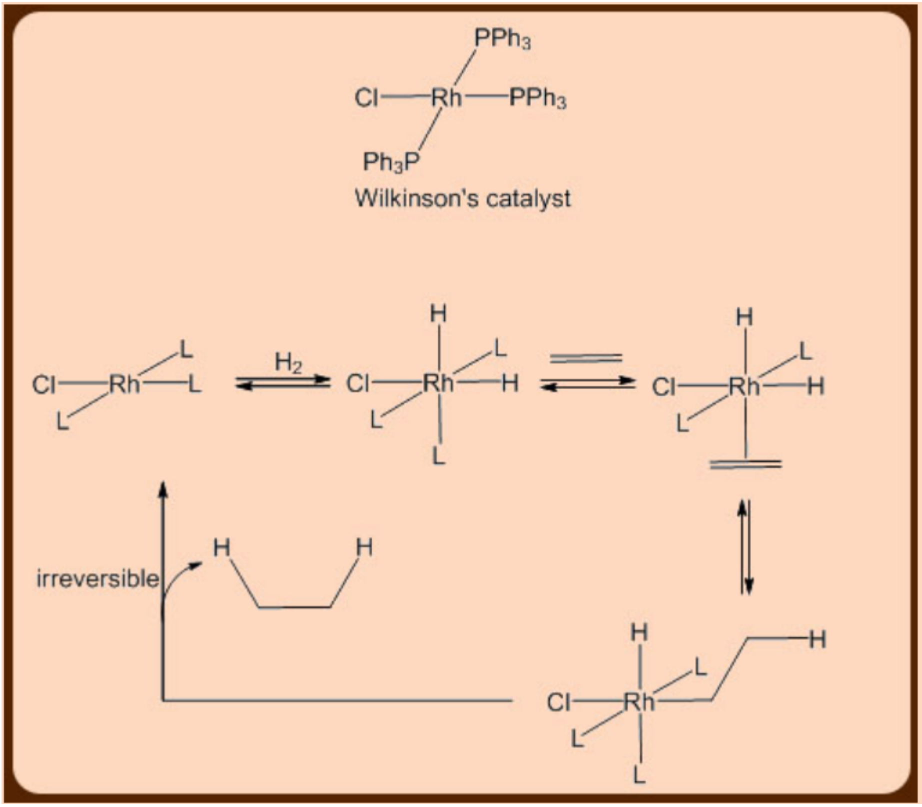
The η^3−allyl mechanism requires the presence of two vacant sites. This mechanism goes through a η^3−allyl intermediate formed by a C−H activation at the allylic position of the olefin formed after binding to the metal and alongside leads to the formation of a M−H bond. Subsequent H transfer from the metal back to the η^3−allyl moiety leads to the alkene isomerized product.



Alkene Hydrogenation

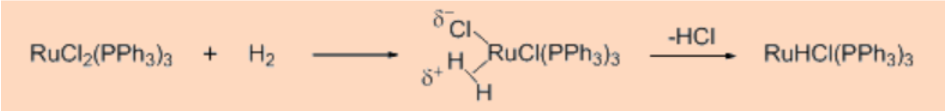
The transition metal catalyzed alkene hydrogenation reactions are of significant industrial and academic interest. These reactions involve the H_2 addition on a C=C bond of olefins to give alkenes. The alkene hydrogenation may proceed by three different pathways namely the (*i*) oxidative addition (*ii*) heterolytic activation and (*iii*) the homolytic activation of the H_2 molecule.

The oxidative addition pathway is commonly observed for the Wilkinson's catalyst $(PPh_3)_3RhCl$ and is the most studied among all of the three pathways that exist. The catalytic cycle initiates with the oxidative addition of H_2 followed by alkene coordination. The resultant species subsequently get converted to the hydrogenated product.

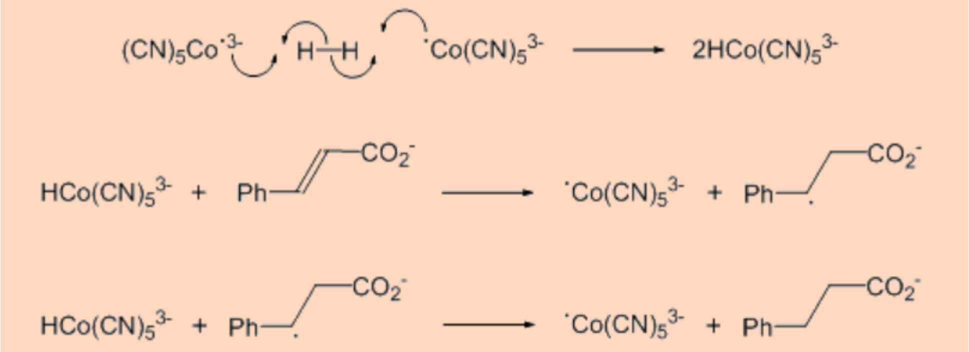


The second pathway proceeds by the heterolytic activation of the H_2 molecule and requires the presence of a base like NEt_3, which facilitates the heterolytic cleavage by abstracting a proton from the H_2 molecule and leaving behind a hydride H^- ion that participates in the hydrogenation reaction. This type of mechanism is usually followed by the $(PPh_3)_3RuCl_2$ type of complexes.

$$X-Y+M-Z \longrightarrow M-X+Y-Z$$

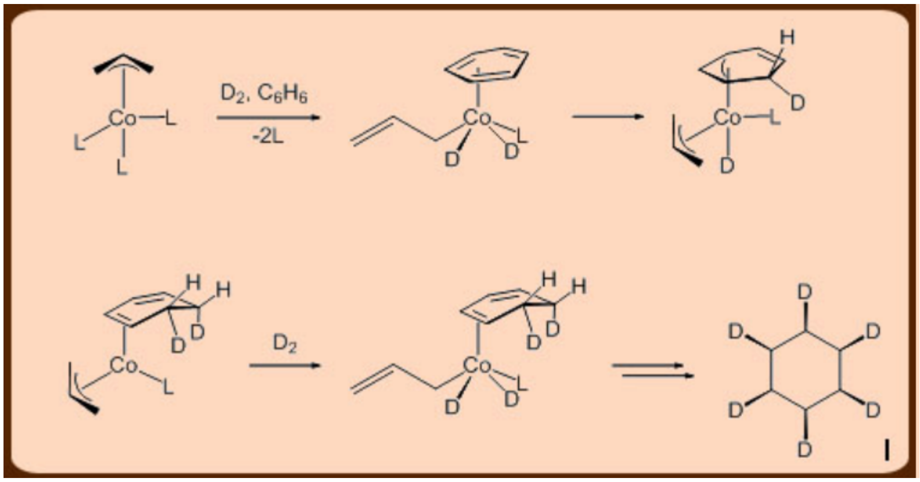


Homolytic cleavage of H_2 is the third pathway for the alkene hydrogenation. It is the rarest of all the three methods and proceeds mainly in a binuclear pathway. Paramagnetic cobalt based $Co(CN)_5^{3-}$ type catalysts carries out alkene hydrogenation by this pathway *via* the formation of the $HCo(CN)_5^{3-}$species.



Arene hydrogenations

Examples of homogeneous catalysts for arene hydrogenation are rare though it is routinely achieved using catalysts like Rh/C under the heterogeneous conditions. A representative example of a homogeneous catalyst of this class is $(\eta^3-allyl)Co[P(OMe)_3]_3$ that carry out the deuteration of benzene to give the all-*cis*-$C_6H_6D_6$ compound.



Transfer hydrogenation

This is a new kind of a hydrogenation reaction in which the source of the hydrogen is not the H_2molecule but an easily oxidizable substrate like isopropyl alcohol. The method is particularly useful for the reduction of ketones and imines but not very effective for the olefins.

$$Me_2CHOH + RCH{=}CH_2 \longrightarrow Me_2C{=}O + RCH_2CH_3$$

Summary

The applications of organometallic compounds in homogeneous catalysis have transcend the boundaries of industry to meet the day-to-day synthesis in laboratory scale reactions. The alkene isomerization is one such application of homogeneous catalysis by the transition metal organometallic complexes. The hydrogenation reactions of alkene, arene, ketone and imine substrates are achieved by several types of the transition metal organometallic catalysts. They also proceed by different mechanisms involving oxidative addition, heterolytic and homolytic cleavages of the H−H bond. The transfer hydrogenation reaction uses easily oxidizable substrates like $i-$PrOH instead of H_2 as the hydrogenation source.

11.2: Homogeneous Catalysis - II

Learning Objectives

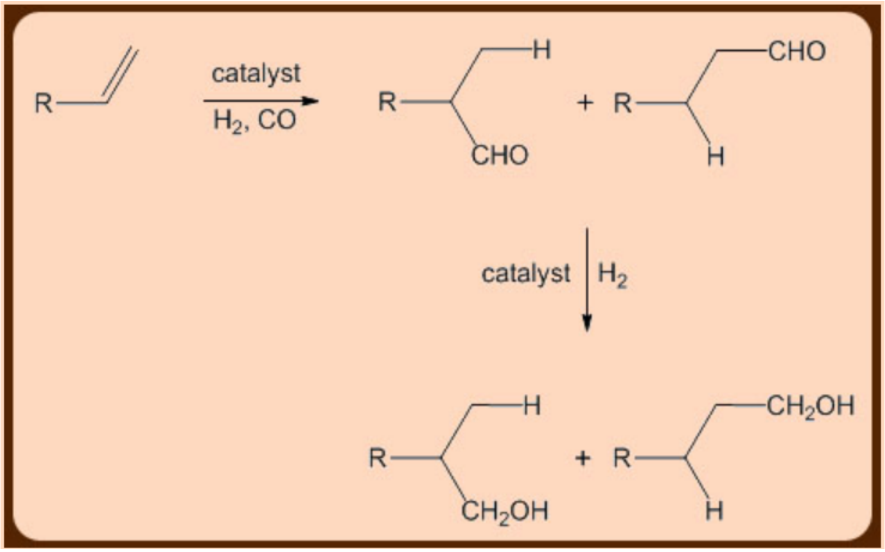
In this lecture you will learn the following

- The hydroformylation reaction and its mechanism.
- The C−C cross-coupling reactions and their mechanisms.

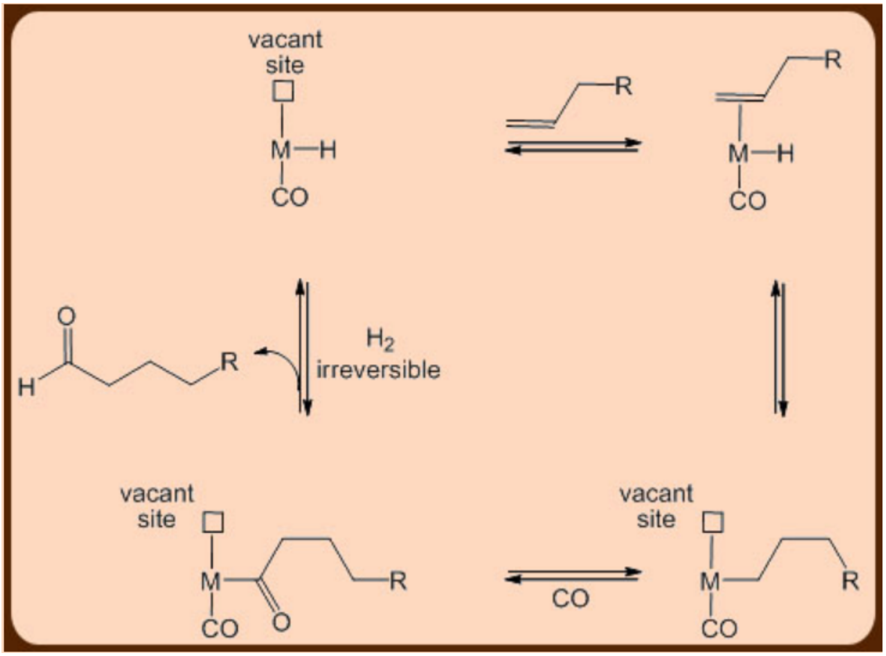
It is truly an exciting time for the field of organometallic chemistry as its potentials in homogeneous catalysis are being realized in an unprecedented manner. The growth in the field organometallic chemistry has been rightly acknowledged by the award of three Nobel prizes in over a decade in the areas of asymmetric hydrogenation (Nyori and Knowles in 2001), olefin metathesis (Grubbs, Schrock and Chauvin in 2006) and palladium mediated C−C cross coupling reactions (Suzuki, Negishi and Heck, 2010). A few representative examples of such landmark discoveries of homogeneous catalysis by organometallic compounds are discussed below.

Hydroformylation reaction

Hydroformylation, popularly known as the "oxo" process, is a Co or Rh catalyzed reaction of olefins with CO and H_2 to produce the value-added aldehydes.



The reaction, discovered by Otto Roelen in 1938, soon assumed an enormous proportion both in terms of the scope and scale of its application in the global production of aldehydes. The metal hydride complexes namely, the rhodium based $HRh(CO)(PPh_3)_3$ and the cobalt based $HCo(CO)_4$ complexes, catalyzed the hydroformylation reaction as shown below.



C−C cross-coupling reactions

The palladium catalyzed cross-coupling reactions are a class of highly successful reactions with applications in the organic synthesis to have emerged recently. The reactions carry out a coupling of the aryl, vinyl or alkyl halide substrates with different organometallic nucleophiles and as such encompasses a family of C−C cross-coupling reactions that are dependent on the nature of nucleophiles like that of the B based ones in the Suzuki-Miyuara coupling, the Sn based ones in the Stille coupling, the Si based ones in the Hiyama coupling, the Zn based ones in the Negishi coupling and the Mg based ones in the Kumada coupling reactions (Figure 11.2.1).

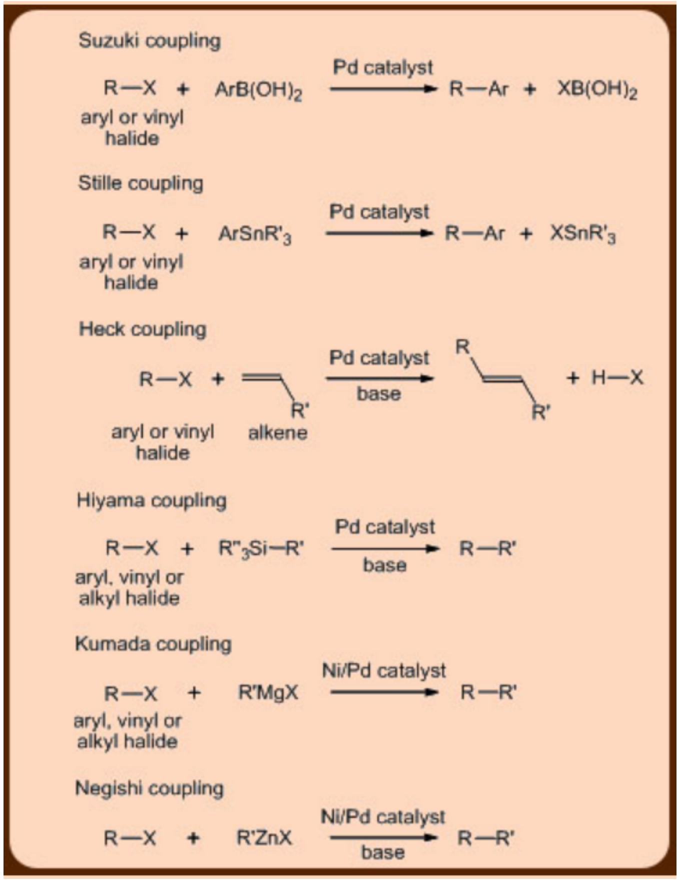


Figure 11.2.1: Various types of the palladium mediated C−C cross-coupling reactions.

An unique feature of these reactions is the exclusive formation of the cross-coupled product without the accompaniment of any homo-coupled product. Another interesting feature of these coupling reactions is that they proceed *via* a common mechanism involving three steps that include the oxidative addition, the transmetallation and the reductive elimination reactions (Figures 11.2.2 and 11.2.3).

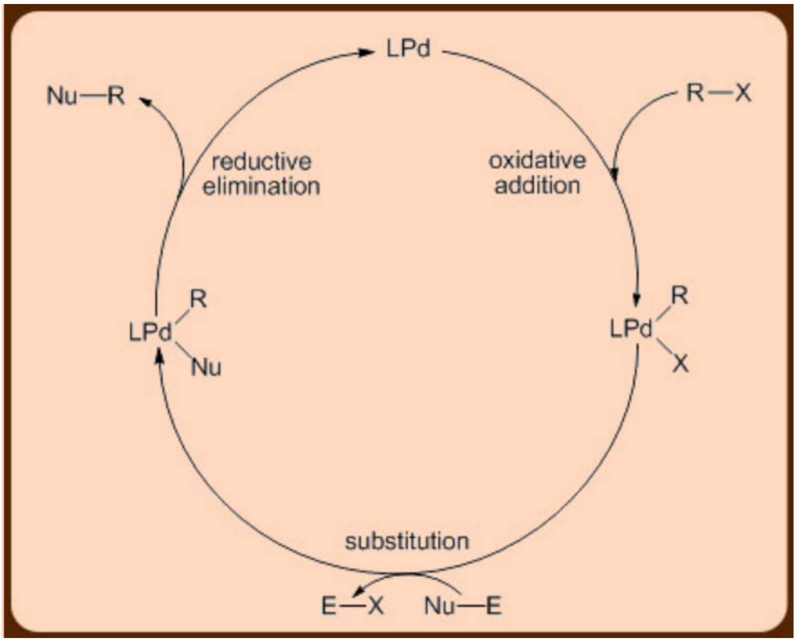


Figure 11.2.2: A general catalytic cycle for the palladium mediated C−C cross-coupling reactions.

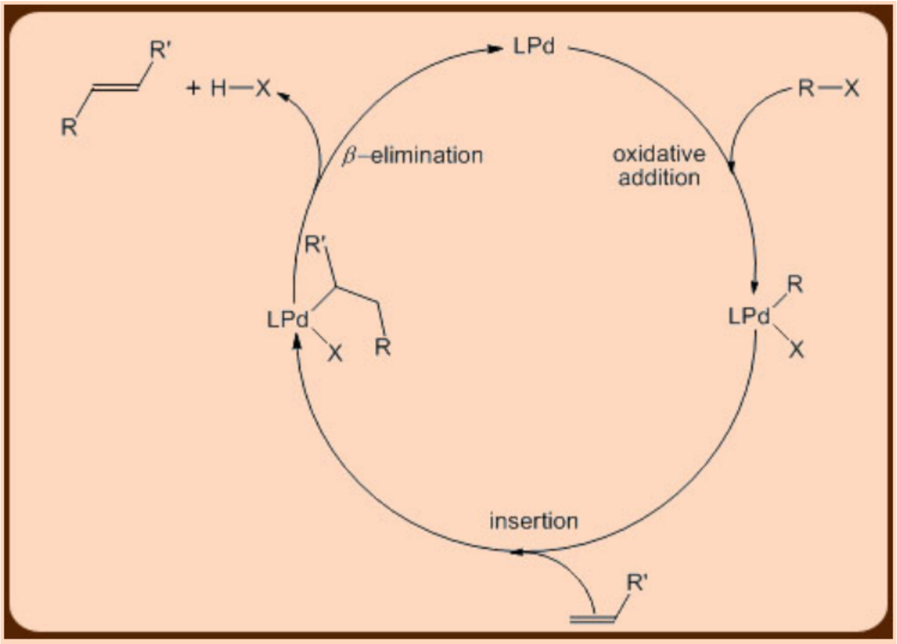


Figure 11.2.3: A catalytic cycle for the palladium mediated Heck coupling reaction.

Summary

Organometallic complexes play a pivotal role in several successful homogeneous catalysis reactions like that of the hydroformylation and the C−C cross-coupling reactions. These reactions are important because of the fact that both of the hydroformylation and the C−C cross-coupling reactions give more value added products compared to the starting reactants. The palladium catalyzed C−C cross-coupling reactions are a class of highly successful reactions that have permanently impacted the area of organic synthesis in a profound way to an extent that the 2010 Nobel prize has been conferred on one of these reactions thereby recognizing the importance of the C−C cross-coupling recations.

CHAPTER OVERVIEW

12: Physical Methods in Organometallic Chemistry

12.1: Characterization of Organometallic Complexes

Learning Objectives

In this lecture you will learn the following

- The characterization techniques of organometallic compounds.
- The NMR analysis of these compounds.
- The IR analysis of these compounds.
- The X-ray single crystal diffraction studies of these compounds.

The characterization of an organometallic complex involves obtaining a complete understanding of the same right from its identification to the assessment of its purity content, to even elucidation of its stereochemical features. Detailed structural understanding of the organometallic compounds is critical for obtaining an insight on its properties and which is achieved based on the structure-property paradigm.

Synthesis and isolation

Synthesis and isolation are two very important experimental protocols in the overall scheme of things of organometallic chemistry and thus these needs to be performed carefully. The isolation of the organometallic compounds is essential for their characterization and reactivity studies. Fortunately, many of the methods of organic chemistry can be used in organometallic chemistry as the organometallic compounds are mostly nonvolatile crystalline solids at room temperature and atmospheric pressure though a few examples of these compounds are known to exist in the liquid [$(CH_3C_5H_4Mn(CO)_3$] and even in the vapor [$Ni(CO)_4$] states. The organometallic compounds are comparatively more sensitive to aerial oxygen and moisture, and because of which the manipulation of these compounds requires stringent experimental skills to constantly provide them with anaerobic environment for their protection. All of these necessities led to the development of the so-called special Schlenk techniques, requiring special glasswares and which in conjunction with a high vacuum line and a dry box allow the lab bench-top manipulation of these compounds. Successful isolation of organometallic compounds naturally points to the need for various spectroscopic techniques for their characterizations and some of the important ones are discussed below.

1H NMR spectroscopy

The ^1H NMR spectroscopy is among the extensively used techniques for the characterization of organometallic compounds. Of particular interest is the application of ^1H NMR spectroscopy in the characterization of the metal hydride complexes, for which the metal hydride moiety appear at a distinct chemical shift range between 0 ppm to -40 ppm to the high field of tetramethyl silane (TMS). This upfield shift of the metal hydride moiety is attributed to a shielding by metal $d-$electrons and the extent of the upfield shift increases with higher the d^n configuration. Chemical shifts, peak intensities as well as coupling constants from the through-bond couplings between adjacent nuclei like that of the observation of $J_{P\text{-}H}$, if a phosphorous nucleus is present within the coupling range of a proton nucleus, are often used for the analysis of these compounds. The ^1H NMR spectroscopy is often successfully employed in studying more complex issues like fluxionality and diastereotopy in organometallic molecules (Figure $12.1.1$).

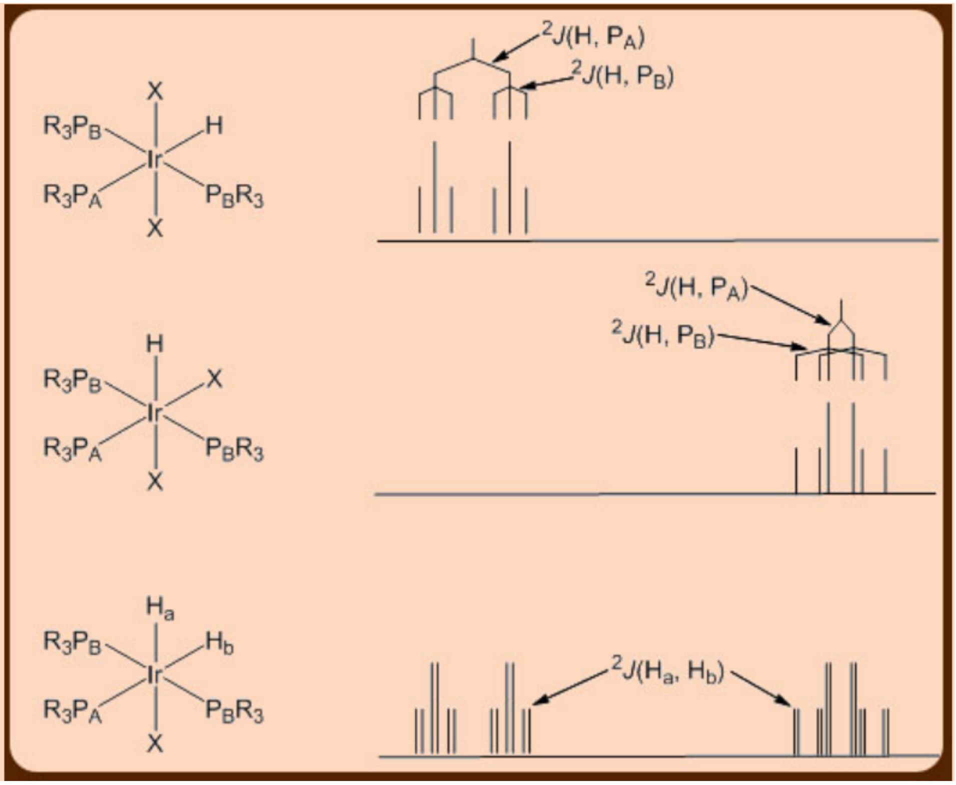


Figure 12.1.1: Different phosphorous-proton coupling patterns in various iridium hydride complexes.

The paramagnetic organometallic complexes show a large range of chemical shifts, for example, $(\eta^6{-}C_6H_6)_2V$ exhibits proton resonances that extend even up to 290 ppm.

13C NMR spectroscopy

Although the natural abundance of NMR active ^{13}C (I = ½) nuclei is only 1 %, it is possible to obtain a proton decoupled ^{13}C{^{1}H} NMR spectra for most of the organometallic complexes. In addition, the off−resonance ^{1}H decoupled ^{13}C experiments yield $^1J_{C\text{-}H}$ coupling constants, which contain vital structural information, and hence are very critical to the ^{13}C NMR spectral analysis. For example, the $^1J_{C\text{-}H}$ coupling constants directly correlate with the hybridization of the C−H bonds with *sp* center exhibiting a $^1J_{C\text{-}H}$ coupling constant of ~250 Hz, a sp^2 center of 160 Hz and a sp^3 center of 125 Hz. Similar to what is seen in ^{1}H NMR, a phosphorous−carbon coupling is also observed in a ^{13}C NMR spectrum with the *trans* coupling (~100 Hz) being larger than the *cis* coupling (~10 Hz).

^{31}P NMR spectroscopy

The ^{31}P NMR spectroscopy, which in conjunction with ^{1}H and ^{13}C NMR spectroscopies, is a useful technique in studying the phosphine containing organometallic complexes. The ^{31}P NMR experiments are routinely run under ^{1}H decoupled conditions for simplification of the spectral features that allow convenience in spectral analysis. Thus, for this very reason, many mechanistic studies on catalytic cycle are conveniently undertaken by ^{31}P NMR spectroscopy whenever applicable.

IR spectroscopy

Qualitative to semi-quantitative analysis of organometallic compounds using IR spectroscopy are performed whenever possible. In general the signature stretching vibrations for chemical bonds are more conveniently looked at in these studies. The frequency (ν) of a stretching vibration of a covalent bond is directly proportional to the strength of the bond, usually given by the force constant (k) and inversely proportional to the reduced mass of the system, which relates to the masses of the individual atoms.

$$\nu = \frac{1}{2\pi C}\sqrt{\frac{k}{m_r}}$$

$$m_r = \frac{m_1 m_2}{m_1 + m_2}$$

The organometallic compounds containing carbonyl groups are regularly studied using IR spectroscopy, and in which the CO peaks appear in the range between 2100−1700 cm^{-1} as distinctly intense peaks.

Crystallography

The solid state structure elucidation using single crystal diffraction studies are extremely useful techniques for the characterization of the organometallic compounds and for which the X-ray diffraction and neutron diffraction studies are often undertaken. As these methods give a three dimensional structural rendition at a molecular level, they are of significant importance among the various available characterization methods. The X-ray diffraction technique is founded on Bragg's law that explains the diffraction pattern arising out of a repetitive arrangement of the atoms located at the crystal lattices.

$$2d\sin\theta = n\lambda$$

A major limitation of the X-ray diffraction is that the technique is not sensitive enough to detect the hydrogen atoms, which appear as weak peaks as opposed to intense peaks arising out of the more electron rich metal atoms, and hence are not very useful for metal hydride compounds. Neutron diffraction studies can detect hydrogens more accurately and thus are good for the analysis of the metal hydride complexes.

Summary

Along with the synthesis, the isolation and the characterization protocols are also integral part of the experimental organometallic chemistry. Because of their air and moisture sensitivities, specialized experimental techniques that succeed in performing the synthesis, isolation and storage of these compounds in an air and moisture-free environment are often used. The organometallic compounds are characterized by various spectroscopic techniques including the ^{1}H NMR, ^{13}C NMR and IR spectroscopies and the X-ray and the neutron diffraction studies.

CHAPTER OVERVIEW

13: Multiply-Bonded Ligands

13.1: Metal-Carbenes

Learning Objectives

In this lecture you will learn the following

- The metal−ligand multiple bonding and their relevance in.
- The Fischer type carbene complexes.
- The Schrock type carbene complexes.

The organometallic compounds containing metal−ligand multiple bonds of the types, M=X and M≡X (X = C, N, O) are of current interest as they are valuable intermediates in many important catalytic cycles. In this regard, considerable attention has been paid towards developing an understanding of the metal−ligand multiply bonded systems like that of the metal carbene $L_nM{=}CR_2$ type complexes and of the metal carbyne $L_nM{\equiv}CR$ type complexes. A detailed account of the metal−carbene complexes is presented in this chapter.

Metal carbene complexes

Carbenes are highly reactive hexavalent species that exist in two spin states, *i.e.* (*i*) in a singlet form (═), in which two electrons are paired up and (*ii*) in a triplet form (═), in which the two electrons remain unpaired. Of the two, the singlet form is the more reactive one. The instability of carbene accounts for its unique reactivity like that of the insertion reaction, which has aroused significant interest in recent years. The singlet carbene and the triplet carbene bind differently to metals, with the singlet one yielding Fischer type carbene complexes while the triplet one yielding Schrock type carbene complexes (Figure 13.1.1).

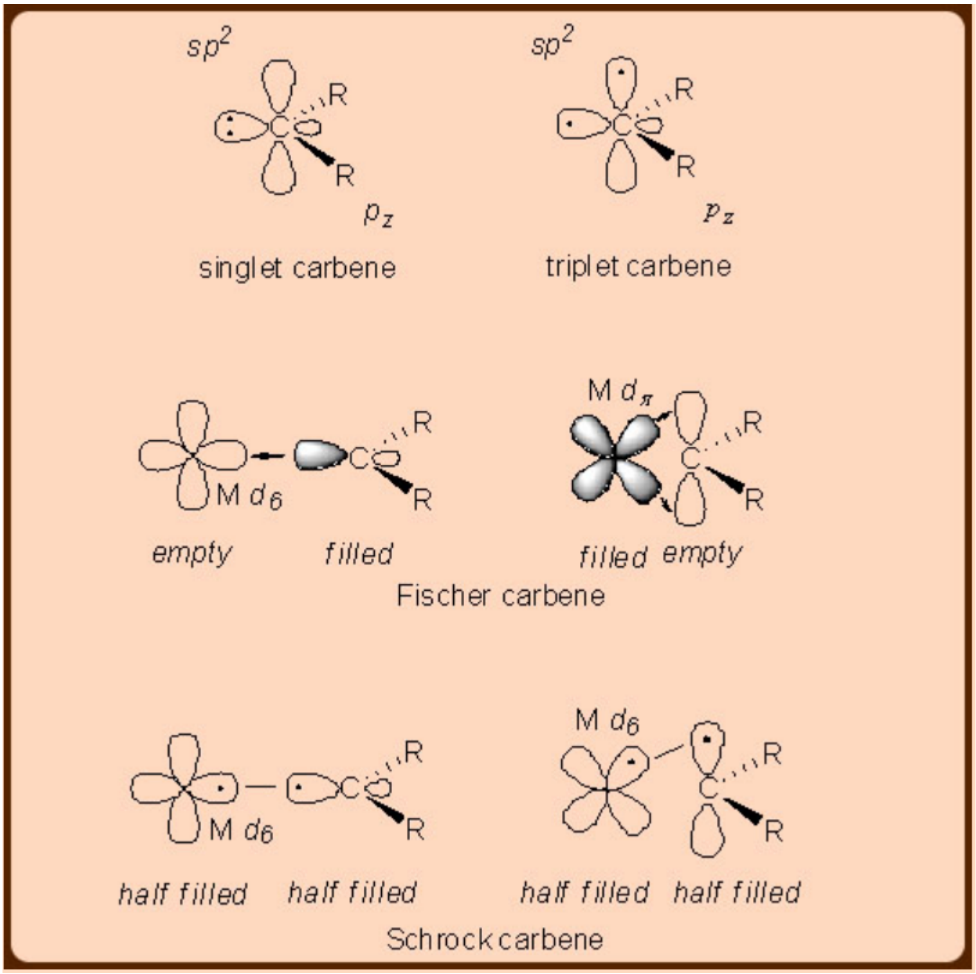


Figure 13.1.1: Metal−ligand multiple bonding in the Fischer and Schrock carbene system.

The $L_nM=CR_2$ type Fischer carbene complexes comprise of two dative covalent interactions that include (*i*) a $L_nM \leftarrow CR_2$ type ligand to metal σ−donation and (*ii*) a $L_nM \rightarrow CR_2$ type metal to ligand π−back donation. The Fischer type carbene complexes are usually formed with metal centers at a low oxidation state. These are also commonly observed for the more electron rich late−transition metals that participate in the $L_nM \rightarrow CR_2$ type metal to ligand π−back donation. Another characteristic of the Fischer type carbene complex is the presence of the heteroatom substituents like R = OMe or NMe_2 on the carbene CR_2 moiety which makes the carbene carbon significantly cationic (δ^+) to facilitate the $L_nM \rightarrow CR_2$ type metal to ligand π−back donation.

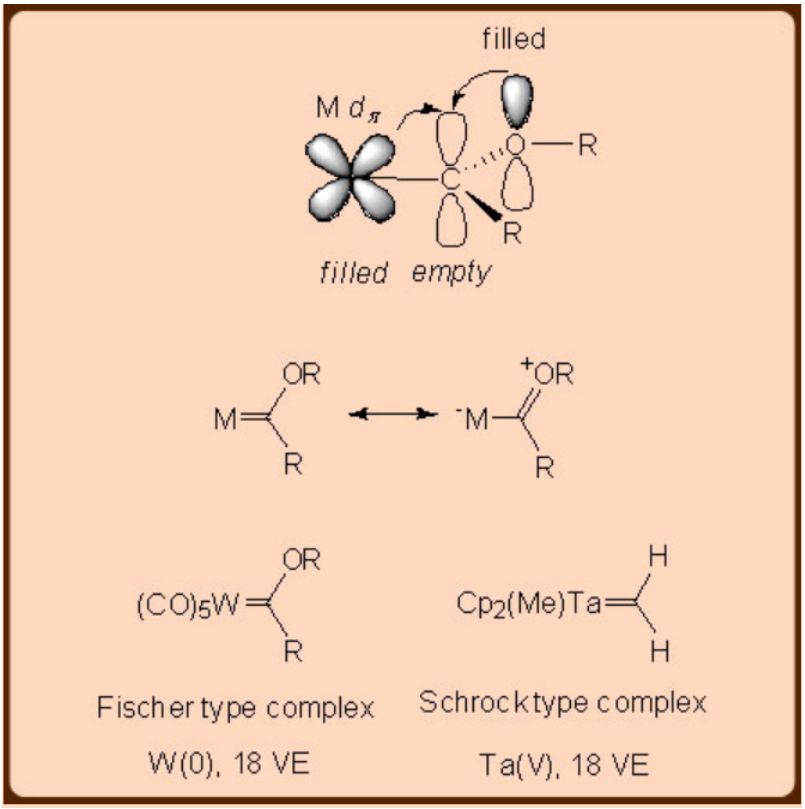
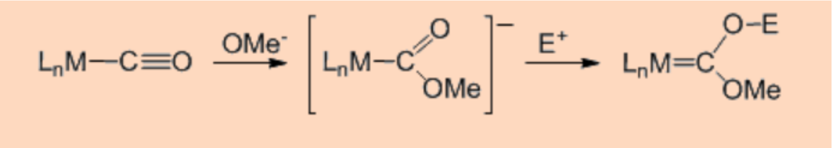


Figure 13.1.2: Fischer and Schrock type complexes.

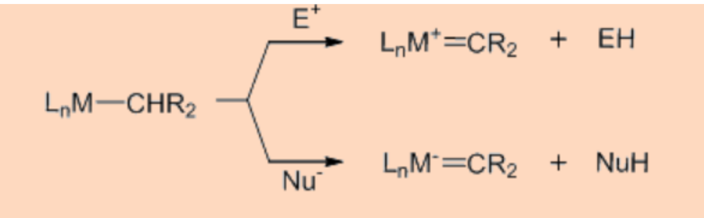
Similarly, the $L_nM=CR_2$ type Schrock carbene complexes comprise of two covalent interactions that involve one electron donation towards the σ−bond from each of the metal L_nM and the carbene CR_2fragments. Schrock carbene complexes are thus formed with the metal centers having high oxidation state and are usually observed for electron deficient early−transition metals (Figure 13.1.2).

Carbene complexes can be prepared by the following methods.

i. by the reaction with electrophiles



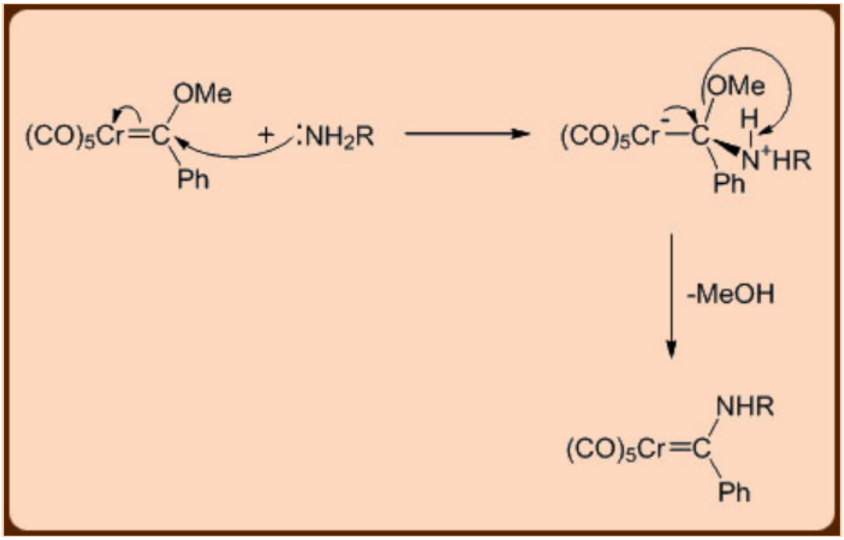
ii. by H^-/H^+ abstraction reactions as shown below



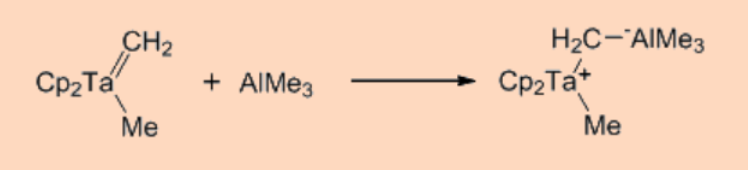
iii. from low−valent metal complexes

$$L_nM + CH_2N_2 \longrightarrow L_nMCH_2 + N_2$$

Because of the electronically different metal−ligand interaction that exist between the L_nM and the carbene CR_2 moiety, the reactivity of Fischer and Schrock carbene complexes are completely different. For example, the Fischer type carbene complexes undergo attack by nucleophiles at its carbene−C center.



The Schrock type carbene complexes on the other hand undergo attack by electrophiles at its carbene−C center.



Summary

The metal−ligand multiple bonding is of significant interest as many of the compounds containing such bonds are important intermediates in various catalytic cycles. The metal−ligand doubly bonded carbene systems can exist in two varieties like the Fischer type and the Schrock type carbene complexes. Due to their different electronic structures, the reactivities of these Fischer type and the Schrock type carbene complexes differ significantly, with the former undergoing nucleophilic attack while the later undergo electrophilic attack at their respective carbene−C centers.

13.2: Metal-Carbynes

Learning Objectives

In this lecture you will learn the following

- The metal−ligand multiple bonding and their relevance in.
- The Fischer type carbyne complexes.
- The Schrock type carbyne complexes.

The metal−ligand multiply bonded systems even extended beyond the doubly bonded Fischer and the Schrock carbenes to the triply bonded $L_nM{\equiv}CR$ type Fischer carbyne and the Schrock carbyne complexes. Similar to carbene that exists in a singlet and a triplet spin state, the carbyne also exists in two other spin states *i.e* in a doublet and a quartet form.

Upon binding to the metal in its doublet spin state as in the Fischer carbene system, the carbyne moiety donates two electrons *via* its *sp* hybridized lone pair containing orbital to an empty metal *d* orbital to yield a $L_nM \leftarrow CR$ type ligand to metal dative bond. It also makes a covalent π−bond through one of its singly occupied p_z orbital with one of the metal *d* orbitals. The carbyne−metal interaction consist of two ligand to metal interactions namely a dative one and a covalent one that together makes the carbyne moiety a LX type of a ligand. In addition to these two types of ligand to metal bonding interactions, there remains an empty p_y orbital on the carbyne−C atom that can accommodate electron donation from a filled metal *d* orbital to give a metal to ligand π−back bonding interaction (Figure 13.2.1).

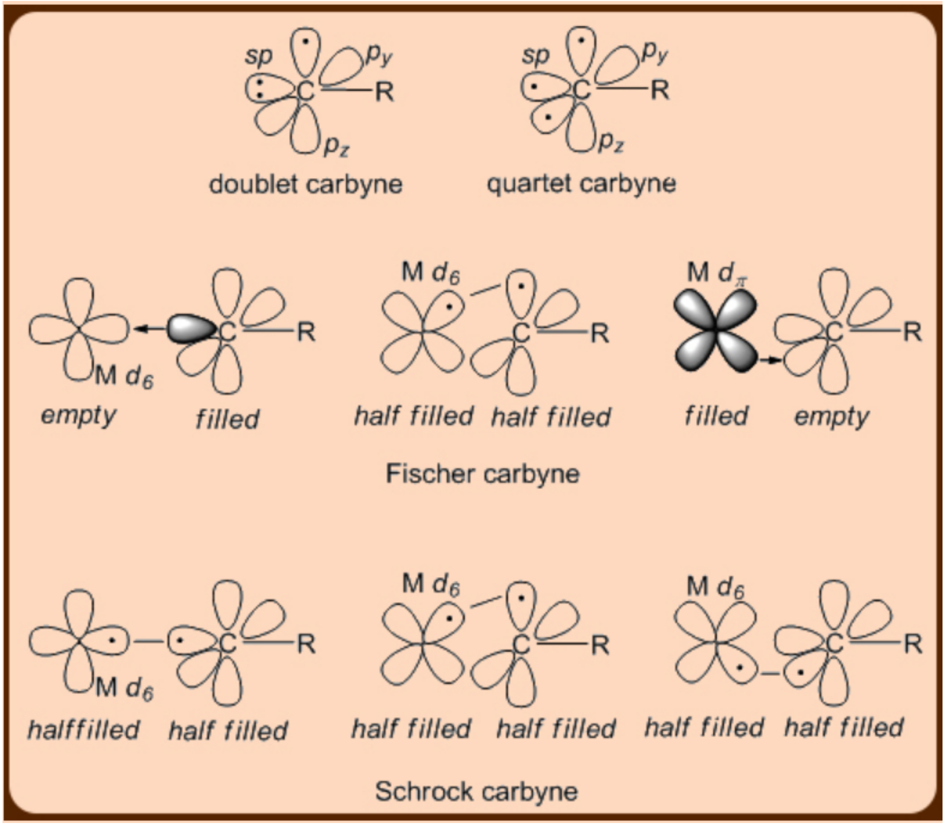


Figure 13.2.1: Metal−ligand multiple bonding in the Fischer and Schrock carbyne system

Analogously, in the quartet carbyne spin state in the Schrock carbyne systems three covalent bonds occur between the singly occupied *sp*, $p_y$and p_z orbitals of carbyne−C moiety with the respective singly occupied metal *d* orbitals (Figure 13.2.1).

Similar to what has been observed earlier in the case of the Fischer carbenes and Schrock carbenes, the Fischer carbyne complexes are formed with metal centers in lower oxidation states for *e.g.* as in $Br(CO)_4W{\equiv}CMe$, while the Schrock carbyne complexes are formed with metals in higher oxidation state, *e.g.* as in $(t{-}BuO)_3W{\equiv}Ct{-}Bu$.

Carbyne complexes can be prepared by the following methods.

i. The Fischer carbyne complexes can be prepared by the electrophilic abstraction of a methoxy group from a methoxy methyl substituted Fischer carbene complex.

$$\mathrm{L(CO)_4M{=}C(OMe)Me + 2\,BX_3 \longrightarrow [L(CO)_4M \equiv CMe]^+BX_4^- + BX_2(OMe) \longrightarrow X(CO)_4M \equiv CMe}$$

ii. Schrock carbynes can be prepared by the deprotonation of a α−CH bond of a metal−carbene complex.

$$\mathrm{CPCl_2Ta{=}CHR} \xrightarrow[(ii)Ph3P=CH2]{(i)PMe3} \mathrm{Cp(PMe_3)ClTa \equiv CR}$$

iii. by an α−elimination reaction on a metal−carbene complex

$$\mathrm{Cp \cdot Br_2Ta{=}CHt{-}Bu} \xrightarrow[(ii)Na/Hg]{(i)dmpe} \mathrm{Cp \cdot (dmpe)HTa \equiv Ct{-}Bu}$$

iv. by metathesis reaction

$$\mathrm{(t{-}BuO)_3W \equiv W(Ot{-}Bu)_3 + t{-}BuC \equiv Ct{-}Bu \longrightarrow 2\,(t{-}BuO)_3W \equiv Ct{-}Bu}$$

The reactivities of Fischer and the Schrock carbynes mirror that of the Fischer and Schrock carbenes. For example, the Fischer carbyne undergo nucleophilic attack at the carbyne−C atom while the Schrock carbyne undergo electrophilic attack at the carbyne−C atom.

Summary

The theme of metal−ligand multiple bonding extends beyond the doubly bonded Fischer and the Schrock carbene systems to even triply bonded Fischer and the Schrock carbyne systems. The carbyne moieties in these Fischer and the Schrock carbyne systems respectively exist in a doublet and a quartet spin state. The carbyne complexes are generally prepared from the respective carbene analogues by the abstraction of alkoxy (OR), proton (H^+), hydride (H^-) moieties, the α−elimination reactions and the metathesis reactions. The reactivity of the Fischer and the Schrock carbyne complexes parallel the corresponding Fischer and the Schrock carbene counterparts with regard to their reactivities toward electrophiles and nucleophiles.

CHAPTER OVERVIEW

14: Metathesis

14.1: Catalytic Applications of Organometallic Compounds- Alkene Metathesis

Learning Objectives

In this lecture you will learn the following

- The alkene metathesis reactions and their different variants.
- The application of metal carbenes in alkene metathesis reactions.
- The functional group tolerance, air and moisture sensitivity and high efficiency as important catalyst attributes for the alkene metathesis reactions.

The application of organometallic chemistry in homogenous catalysis is progressively increasing with the fast pace of discovery of new catalysts in the area. The benefits of organometallic catalysis have now percolated to all facets of the chemical world that span from the confines of the industry to the day-to-day small scale use in organic synthesis in academic laboratories. Quite a few of these applications of organometallic complexes in homogeneous catalysis have made a permanent imprint on the ever going developmental process that is constantly transforming our day-to-day life. An example of such a success story is of alkene metathesis, which is described in this chapter.

Alkene metathesis

Alkene metathesis reactions are gaining wide popularity in synthesizing unsaturated olefinic compounds as well as the unsaturated polymeric counterparts. Central to this catalysis is a metal carbene intermediate that reacts with olefins to give different olefinic compounds or even the unsaturated olefinic polymers depending upon the reaction conditions of the metathesis reaction. Metathesis is an unusual transformation in which a C=C is broken and also formed during catalysis to generate new unsaturated olefins.

$$\mathrm{RCH{=}CHR + R'CH{=}CHR' \rightleftharpoons 2\,RCH{=}CHR'}$$

Though a large variety of metal−carbene catalysts have been developed for the metathesis reaction, only a few have been found to be functional group tolerant. Thus a critical step in broadening the utility of metathesis reaction has been in developing catalysts that are functional group tolerant. In this regard, the early-transition metal based carbene catalysts like that of the Ti based ones are highly oxophilic and hence are intolerant to the functional groups. On the other hand, the more electron-rich Mo and W based catalysts are of intermediate character. Finally, the late-transition metal based Ru catalysts are found to be exceptionally tolerant toward functional groups but all the while exhibiting high reactivity toward olefinic bonds. In this context notable are the Grubb's Ru catalyst, which is easy to handle, and the Schrock's Mo catalyst, which display high activity.

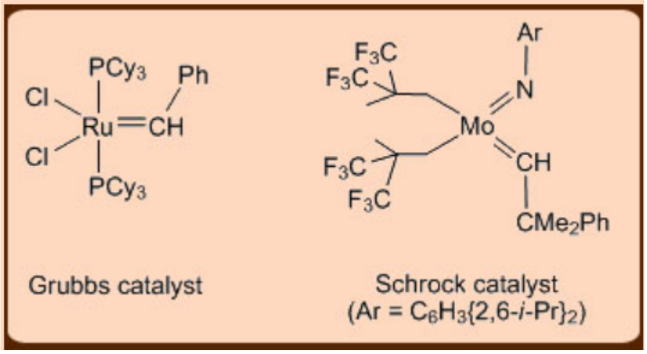
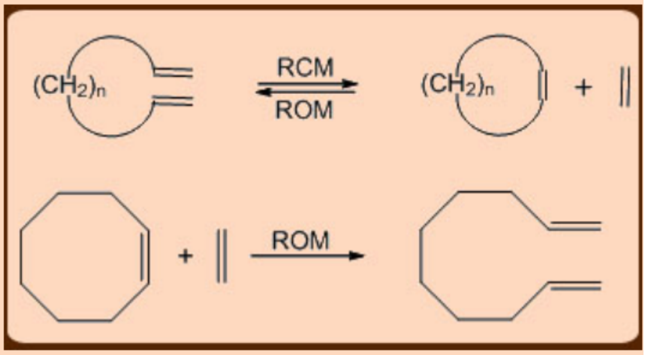


Figure 14.1.1: The Grubb's and the Schrock's catalyst.

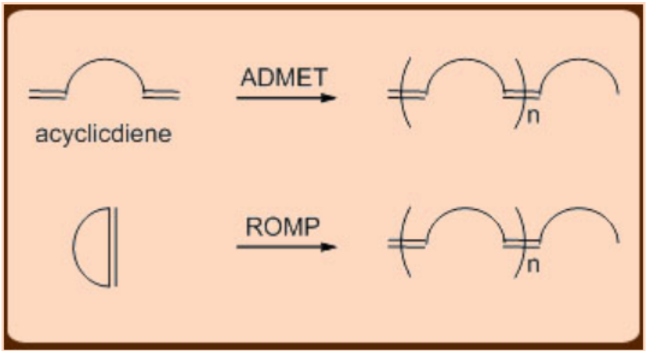
The metathesis reaction as such stands for a family of related reactions all of which involve a "cutting and stitching" of olefinic bonds leading to different unsaturated products. When two different olefin substrates are used, the reaction is called the "cross metathesis" owing to the fact that the olefinic ends are exchanged.

$$\mathrm{RCH{=}CHR + R'CH{=}CHR' \rightleftharpoons 2\,RCH{=}CHR'}$$

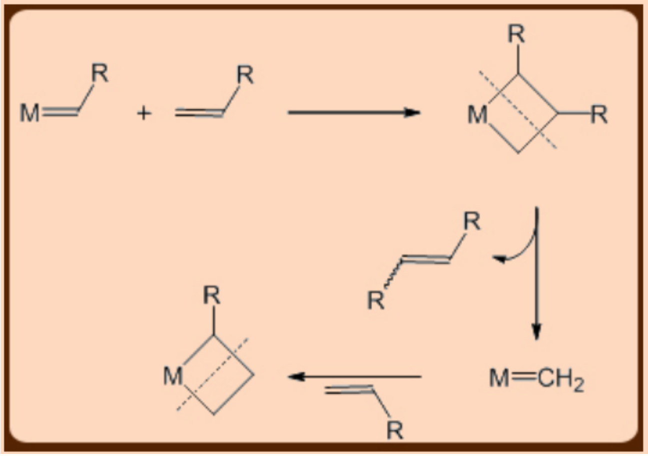
The metathesis reactions can even extend further to the conjugated dienes that can undergo Ring Closing Metathesis (RCM) in systems where the ring strain is not too high in the final product. The reverse of Ring Closing Metathesis (RCM) is called the Ring Opening Metathesis (ROM), and which is usually favored in the presence of large excess of C_2H_4.



The variants of metathesis often used in producing polymers are, (*i*) the Acyclic Diene Metathesis (ADMET) and (*ii*) the Ring Opening Metathesis Polymerization (ROMP), in which the relief of ring-strain of cycloalkenes drives the polymerization reaction forward. Both of these reactions, produce long chain polymers in a living fashion and as a result of which these reactions are useful for producing block copolymers −(AAABBBB) $_n$−.



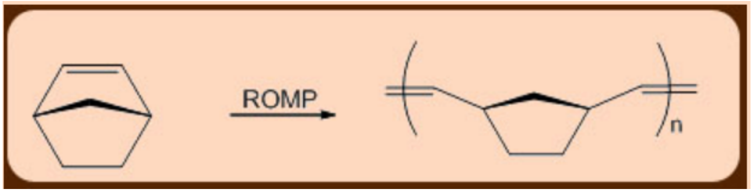
Though several possibilities have been debated for the mechanism of the metathesis reaction, the one proceeding *via* a metalacyclobutane intermediate has gained credence.



Several important industrial applications have emerged out of the metathesis reaction like that of the commercial synthesis of the housefly pheromone.

$$\mathrm{Me(CH_2)_7CH{=}CH_2 + Me(CH_2)_{12}CH{=}CH_2 \longrightarrow Me(CH_2)_7CH{=}C(CH_2)_{12}Me[housefly\ pheromone] + C_2H_4 +}$$
$$\text{other products}$$

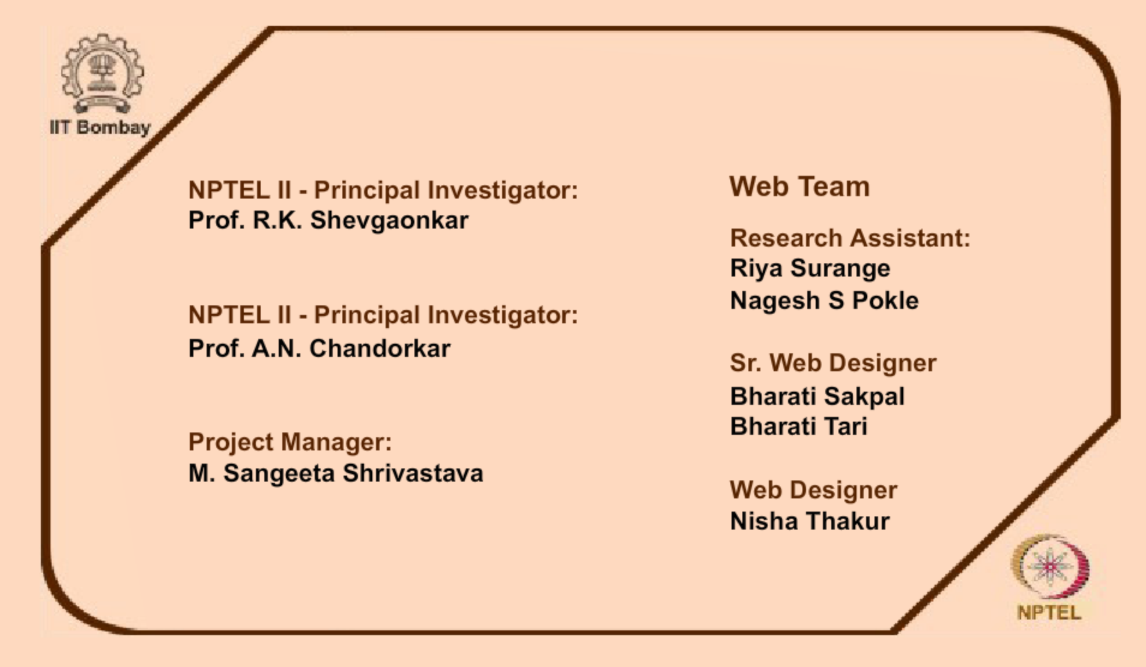
Similarly, the polycyclopentadiene polymer, which is formed from the Ring Opening Metathesis Polymerization (ROMP) of dicyclopentadiene substrate, is used for bullet proof related applications because of its exceptional strength owing to its cross-linked nature.



Summary

Alkene metathesis represents a distinct class of related chemical reactions that involve the “cutting and stitching” of olefinic bonds to give unsaturated organic products. Depending upon the nature of the product formed, different type of alkene metathesis reactions exist like the alkene metathesis, cross-metathesis, Ring Closing Metathesis (RCM), Ring Opening Metathesis (ROM), Acyclic Diene Metathesis (ADMET), and the Ring Opening Metathesis Polymerization (ROMP). A commonality that runs through all of these different varieties of the metathesis reaction is its mechanism that involves a catalytically active metal−carbene species. The mechanism is said to be proceed *via* a 4−membered metalacyclobutane intermediate. The alkene metathesis has found important applications in organic synthesis as well as in the chemical industry.

14.2: Credits



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