MSCCH-501

M.Sc I Semester

INORGANIC CHEMISTRY-I

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INORGANIC CHEMISTRY-I *MSCCH-501*

Block I: Stereochemistry and Bonding

UNIT 1 STEREOCHEMISTRY AND BONDING IN MAIN GROUP COMPOUNDS

CONTENTS

1.1.OBJECTIVES

Objectives of this unit are to introduce you with important basic concepts to understand the bonding and structure of inorganic substances. Prerequisites to understand the offerings of this chapter are the concepts of valency, dot structures of inorganic molecules, hybridization and general understanding of structural representation and chemical reactions. At the end of this chapter, you will be able to understand and explain the rather difficult bonding and structures of inorganic molecules.

1.2. INTRODUCTION

There are several models and theories which explain the shapes and geometries of molecules. One of the important theories by G. N. Lewis provided the knowledge of electronic structures of molecules. Many subsequent theories build upon the foundation laid by the Lewis theory of electronic structures of molecules. *Valence Shell Electron Pair Repulsion* (VSEPR) theory is a model used to predict the geometry of a molecule from the number of electron pairs surrounding their central atoms. The theory is also called as Gillespie-Nyholm theory after Ronald Gillespie and Ronald Nyholm who were the main contributors to this theory.

1.3. VALENCE SHELL ELECTRON PAIR REPULSION (VSEPR) THEORY

The VSEPR model which explains the shapes and geometries of polyatomic molecules is based on Lewis model of molecular structures. This theory predicts the shape of molecule from the knowledge of Lewis dot structures. In fact, the VSEPR theory relies on the tendency of the valence electron pairs surrounding an atom to exert repulsion among each other and thereby adoption of geometrical arrangement to minimize this repulsion. It is important to note that repulsion between two lone pairs is stronger than that between a lone pair and a bonding pair of electrons, which in turn is stronger than the repulsion between two bonding pairs of electrons. Hence, the VSEPR theory makes use of positions of different atoms and electrons around a central atom. Complete positioning of bonded and lone electron pairs of electrons determine the shape of the molecule. The final shape is deduced by ignoring the position of lone electron pair of electrons. Although, the VSEPR theory can be applied for a variety of compounds; nevertheless, it excellently explains geometry of simple halides of the p block elements. It is also important to note that the VSEPR models do not take steric factors, i.e., bulkiness of substituent around the central atom into account. Following are the general rules for determining VSEPR geometries of a given molecule.

1. Draw the Lewis structure of the molecule for which geometry has to be evaluated.

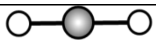
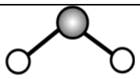
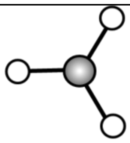
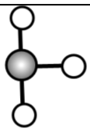
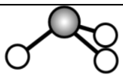
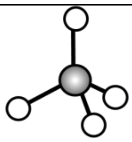
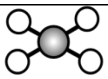
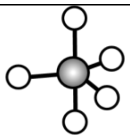
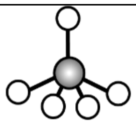
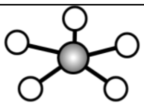
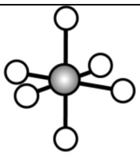
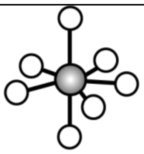
2. Place the lone pairs (lp) and bonding pairs (bp) of electrons around the central atom.

3. Electron–electron repulsions decrease in the sequence: lone pair–lone pair (*lp-lp*) > lone pair–bonding pair (*lp-bp*) > bonding pair–bonding pair (*bp-bp*).

4. If the central atom is connected to a surrounding atom by multiple bonds, then the electron–electron repulsions decrease in the order: triple bond–single bond > double bond–single bond > single bond–single bond.

Possible common shapes for a molecule or ion, AB_n comprising of central atom A surrounded by n atoms of B, are presented in **Table 1.1**.

Table 1.1.*Summary of possible geometry and shapes for simple molecules.*

S. No.	**Molecular formula**	**Coordination number**	**Geometry (Bond Angle)**
1	AB_2	2	 Linear (180°)  Bent
2	AB_3	3	 Trigonal planar (120°)  T shaped (180° / 90°)  Trigonal pyramidal
3	AB_4	4	 Tetrahedral (109.5°)  See-saw shaped  Square planar (90°)
4	AB_5	5	 Trigonal bipyramidal (120° / 90°)  Square pyramidal  Pentagonal planar (72°)
5	AB_6	6	 Octahedral (90°)
6	AB_7	7	 Pentagonal bipyramidal (90° / 72°)

Few worked examples demonstrating distribution of electrons to minimize the electronic repulsion in some selected molecules and the resultant molecular geometries are presented ahead (note that the bonding pair of electrons, i.e., *bp* are depicted as solid lines or flying wedges):

1.3.1. Structure of beryllium chloride ($BeCl_2$)

Beryllium chloride is a white colored hygroscopic solid substance with chemical formula $BeCl_2$. Beryllium chloride has two bonding pairs and no lone pair of electrons around the beryllium atom as depicted in **Figure 1.1**. In order to minimize mutual repulsion, the bonding pairs of electrons orient far from each other which results in the linear geometry of the molecule. As per VSEPR considerations, the Cl-Be-Cl bond angle is 180°

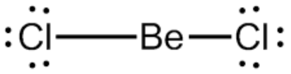


Figure 1.1.*The linear geometry of* $BeCl_2$ *molecule.*

1.3.2. Structure of boron trichloride (BCl_3)

Boron trichloride is a colorless gas with chemical formula BCl_3. This molecule has three bonding pairs of electrons around the boron atom; hence, the molecule assumes trigonal planar geometry with Cl-B-Cl bond angle of 120° (**Figure 1.2**).

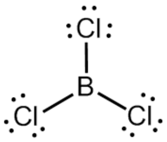
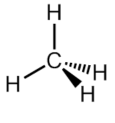
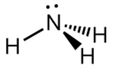


Figure 1.2. *The trigonal planar shape of* BCl_3 *molecule*

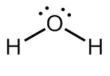
.1.3.3. Structure of water (H_2O), ammonia (NH_3) and methane (CH_4)



4 *bp*, 0 *lp*
Tetrahedral
(109.5°)



3*bp*, 1 *lp*
trigonal pyramidal
(107°)



2 *bp*, 2 *lp*
bent
(104°)

Figure 1.3. *Geometry and structural attributes of methane (left), ammonia (middle) and water (right).*

Each of the water, ammonia and methane molecules has four electron pairs around the respective central atom (**Figure 1.3**). However, the number of bonding and lone pairs of electrons is different. Methane with four bonding pair of electrons has a tetrahedral geometry (H-C-H bond angle = 109.5°). Ammonia has three bonding pairs and a lone pair of electron; therefore, the geometry reduces to trigonal pyramidal. Since, the *lp-bp* repulsion is stronger than the *bp-bp* repulsion; therefore, H-N-H bond angles of ammonia are contracted to 107°. In case of water, there are two lone pairs and two bonding pairs of electrons which surround the oxygen atom. Therefore, the geometry of molecule reduces to bent shape with H-O-H bond angle of 105°.

1.3.4. Structure of nitrate anion (NO_3^-)

The Lewis structure of nitrate anion is presented in **Figure 1.4** where formal charge on the anion is not depicted for the sake of clarity. Central nitrogen atom has one double bonded and two single bonded oxygen atoms around it. There is no lone pair of electron present around nitrogen atom. Hence, VSEPR theory suggests a trigonal planar geometry for nitrate ion (**Figure 1.4**).

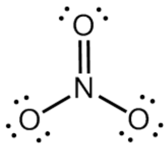


Figure 1.4.*The trigonal planar shape of NO_3^- anion.*

1.3.5. Structure of phosphorous pentachloride (PCl_5)

Phosphorous pentachloride molecule has five bonding pairs of electrons around phosphorous atom and there is no lone pair of electrons on central atom. Therefore, VSEPR theory suggests the structure of PCl_5 to be trigonal bipyramidal (**Figure 1.5**).

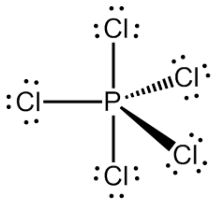
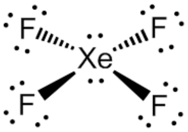


Figure 1.5.*The trigonal bipyramidal shape of PCl_5 molecule.*

1.3.6. Structure of xenon tetrafluoride (XeF_4)

The Lewis structure of xenon tetrafluoride suggests that there are four bonding pairs and two lone pairs of electrons around the central xenon atom. Hence, the octahedral geometry for six coordinated central atom reduces to square planar in case of XeF_4 (**Figure 1.6**).



1.3.7. Limitations of VSEPR theory

The VSEPR theory makes general statements about molecular geometry which is very useful in predicting the geometries of most of the molecules and ions. However, there are limitations to the theory as the predicted structures does not corroborate with those established by physical characterizations in some cases as discussed ahead.

1. IF_7 and TeF_7^- are isoelectronic with seven bonding pairs of electrons around the respective central atoms. Hence, VSEPR predicts pentagonal bipyramidal geometry for both of these structures. VSEPR theory does not predict different bond distances for axial and equatorial positions in pentagonal bipyramidal geometry. Physical characterization establishes that the axial bonds of these structures are slightly shorter than the respective equatorial bonds. Additionally, the geometry of TeF_7^- in their crystallographically characterized salts seems much distorted from the predicted pentagonal bipyramidal geometry as the equatorial fluorine atoms are not coplanar.

2. VSEPR theory successfully predicts the geometry of simple p-block molecules but it is not appropriate to predict structures of the d-block derivatives.

3. VSEPR theory does not take inert pair effect into account. Hence, it does not explain structures of molecules derived from heavy elements of periodic table. Crystallographic analyses have revealed that the species such as $[SeCl_6]^{2-}$, $[TeCl_6]^{2-}$ and $[BrF_6]^-$ possess regular octahedral geometry which is not justifiable using VSEPR theory.

1.4. WALSH DIAGRAMS

Walsh diagrams were first introduced by Prof. A.D. Walsh to rationalize the shapes adopted by polyatomic molecules in the ground state as well as in excited states. Walsh diagrams are graphical representations depicting the calculated orbital binding energies of a molecule plotted against bond angles. These diagrams predict geometries of small molecules and explain why a given molecule is more stable in certain geometry than the other. Walsh's rule states that a molecule will assume a structural geometry which provides most stability to its highest occupied molecular orbital (HOMO).

Walsh diagram is used to explain the regularity in the structures of related molecules having identical number of valence electrons. For example, water (H_2O) and sulphur dioxide (H_2S) exhibit similar structures. Walsh diagram also explains the change in geometry of molecules with the change in their number of electrons or their spin state.

1.4.1. Walsh diagram for tri-atomic molecules

Simplified Walsh diagram for a triatomic molecule is depicted in **Figure 1.7**, which is energy versus bond angle plot. It should be noted that the depicted energy levels are qualitative and for actual system should be calculated by a suitable simulation. MO levels drawn on the left are for the bent configuration with bond angle of 90° whereas those on right are for the linear configuration with bond angle 180°.

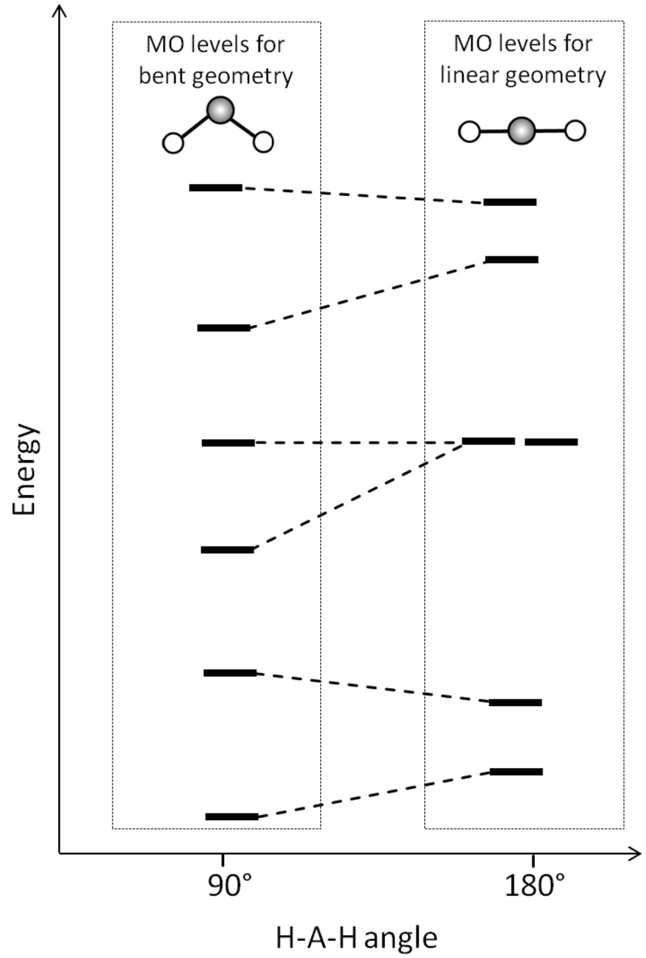


Figure 1.7. *Simplified Walsh diagram for a tri-atomic molecule,* AH_2

The correlation lines joining the energy levels on left and right extreme depict the energy levels for bond angle θ defined by the range $90° \leq \theta < 180°$. The plot offers quick comparison of the energies for bent and linear geometries with a given bond angle, θ. It is evident that the molecule prefers the geometry with lower HOMO levels.

1.4.2. Walsh diagram for penta-atomic molecules

For penta-atomic molecule, an imaginary model AH_4 can be considered which can assume a tetrahedral or square planar geometry. Methane (CH_4) and sulfur tetrafluoride (SF_4) are the real examples for such categories. For instance, for the formation of methane molecule one 2s and three 2p orbitals of carbon and four 1s orbitals, one from each hydrogen atoms get involve in bonding. Above mentioned eight orbitals result in four bonding and four antibonding orbitals out of which bonding orbitals occupy all eight electrons involved in formation of molecule. In case of tetrahedral geometry, significant overlap between the orbitals of carbon and hydrogen is possible which reduces the energy of bonding orbitals whereas in the square planar configuration the extent of overlap is very low which in turn results in orbitals of considerably high energy as depicted in the **Figure 1.8.** Hence, the CH_4 molecule prefers the tetrahedral geometry rather than the square planar or the intermediate distorted geometries.

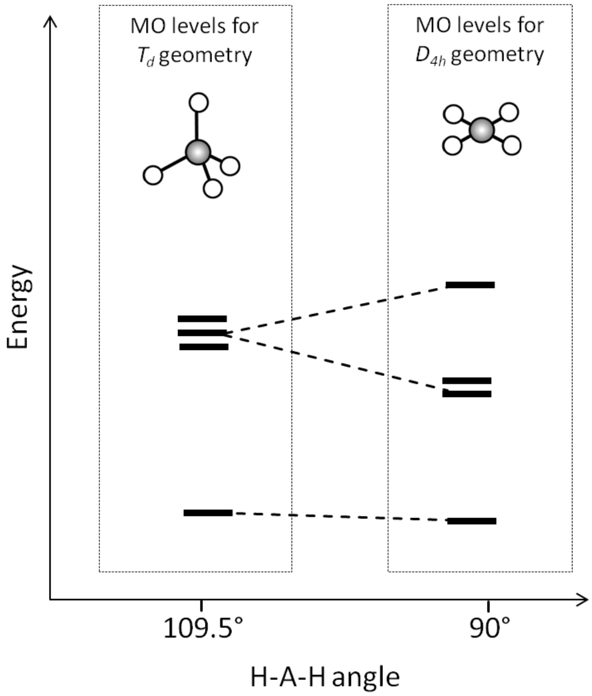


Figure 1.8. *Simplified Walsh diagram for a methane like penta-atomic molecule,* AH_4

1.5. dπ-pπ BOND

Formation of inorganic molecules is different than that of organic molecules in many aspects, one of which is the occurrence of dπ-pπ bonds. Generally, π bonds, as in case of organic molecules, formed by lateral overlapping of p orbitals present on two atoms such as carbon, nitrogen or oxygen. Bonding interactions between two d orbitals resulting in δ bonds in inorganic molecules are also prevalent. However, bonding interactions in inorganic molecules can also make use of suitably available d and

porbitals at once. When a bond forms by lateral overlapping of p (or p*) and d orbitals present on two different atoms, it is called dπ-pπ bond. Such bonds are frequently observed in metal complexes such as carbonyls and nitrosyls. A simple example is sulfur trioxide (SO_3). Main group compounds such as phosphine oxides and disiloxane can also feature the dπ-pπ bonds. Presence of dπ-pπ bonding interactions usually result in shortening of bond length and planar configuration of involved atoms. However, observing such molecular features should not always be attributed to dπ-pπ bonds as several other factors may also be playing role. Hence, a careful evaluation of electronic and orbital symmetries must be made.

Phosphine Oxide ($R_3P = O$) offers an example of dπ-pπ bond in molecules comprising of nonmetallic elements (**Figure 1.9**). In this case, all the p orbitals present on phosphorous are utilized in hybridization and hence, not available for lateral overlapping. Empty d orbital on phosphorous accepts electron density from filled p orbital available with oxygen atom. This dπ-pπ bond causes tighter binding of both involved atoms which is reflected in short bond distance (150 pm) and stability (bond energy 544 kJ/mol) of the bond.

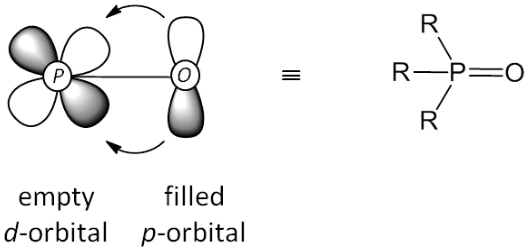


Figure 1.9.*dπ-pπ bond in phosphine oxide.*

Bonding in metal carbonyls is classical example of dπ-pπ bond, where empty π* orbital present of oxygen atom accepts electron density from the filled d orbital of metals which results in the increase in bond order of metal-carbon bond (**Figure 1.10**).

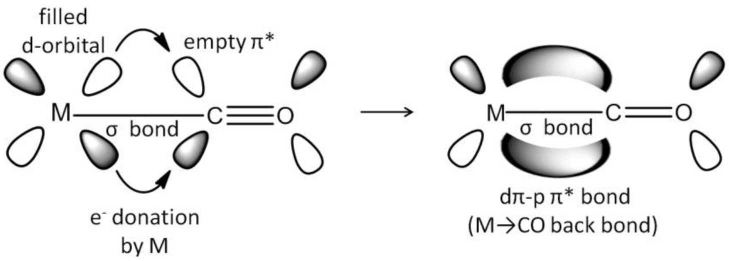


Figure 1.10.*dπ-pπ bond in a typical metal carbonyl system.*

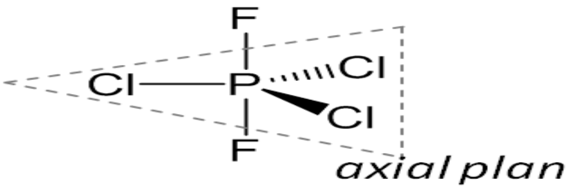
1.6. BENT'S RULE AND ENERGETICS OF HYBRIDIZATION

Hybridization is the concept of mixing of atomic orbitals of different energy and shape to form same number of new hybrid orbitals of equal energies. Hence, hybridization is the energy redistribution of atomic orbitals realized by linear combination of atomic orbitals. As the orbital energies are of the order of magnitude of bond energies, it is important tool to determine the structure of molecules. Bent's rule relates the orbital hybridization of central atom in a molecule with the electronegativities of substituents and was originally stated by Henry Bent as "Atomic s character concentrates in orbitals directed toward electropositive substituents".

Students, you must recall that the 's' orbital has lower energy than the 'p' orbital. Moreover, a hybrid orbital having higher 's' character has lower energy and 's' orbital like shape. On the other hand, higher 'p' character results in higher energy and 'p' orbital like shape of the hybrid orbitals. As the 's' orbitals are closer to the atomic nuclei, it stabilizes the lone pair of electrons than the 'p' orbital does. Hence, it is logical to say that more stable molecular model would allow the orbitals rich in 'p' character for bonding purpose and those rich in 's' character for accommodating the lone pairs of electrons. It can also be stated that, electron density available on 's' rich orbital is closer to the nuclei, hence, less available for bonding. Therefore, electronegative substituents would withdraw electron density from 'p' rich orbitals than the 's' like orbitals.

We can illustrate this using structure and bonding in PCl_3F_2. Formation of this molecule involves mixing of one s, three p and one d orbitals to form five sp^3d orbitals. The five hybrid orbitals are not identical but can be grouped in set of two (axial) and three (equatorial) orbitals (**Figure 1.11**).

The equatorial set is resulted by the mixing of s, p_x and p_y orbitals whereas axial set is resulted by the mixing of p_z and d orbitals. Experimental evidences indicate that the fluorine and chlorine atoms in PCl_3F_2 molecule are situated at axial and equitorial positions respectively, which is in agreement with Bent's rule.



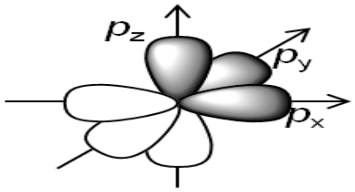


Figure 1.11. *Position of substituents in PCl_3F_2 molecule (left) and the geometry of p-orbitals on phosphorous (right).*

Important implication of Bent's rule and energetic of hybridization can be seen in the significant difference in the bond angles of hydrides of group 15 or 16 elements. As presented in **Table 1.2**, ammonia (hydride of first element in group 15) features a bond angle of 107.2°, whereas the hydrides of subsequent elements down the group, *i.e.*, P. As and Sb feature bond angles closer to 90°. Similar trend can be observed for the group 16 hydrides.

Table 1.2. *Formula and bond angles for group 15 and 16 hydrides.*

S. No.	Group 15 hydride	Bond angle	Group 16 hydride	Bond angle
1	NH_3	107.2°	OH_2	104.5°
2	PH_3	93.8°	SH_2	92°
3	AsH_3	91.8°	SeH_2	91°
4	SbH_3	91.3°	TeH_2	89.5°

The atomic sizes of P, As and Sb are large enough to accommodate three hydrogen atoms around them without steric crowding. Hence, the atomic orbitals of these elements do not undergo energy demanding hybridization while formation of respective hydrides. Thus, the lone pair of central atom in these hydrides remains largely on s-orbital whereas s-orbitals of hydrogen atoms overlap with nearly pure p-orbitals. On the contrary, the nitrogen being small in size, cannot accommodate three bonded hydrogen atoms around it without steric crowding. Evidently, the steric reasons cost much energy in case of ammonia to assume smaller bond angles than the energy required for hybridization. Hence, the atomic orbitals on nitrogen undergo hybridization while formation of ammonia to result in bond angles of 107.2°. Further, the shortening of bond angle from ideal value of 109.5° can be explained on the basis of VSEPR theory. Similar arguments can explain the bond angle trend of group 16 hydrides.

1.7. SOME SIMPLE REACTIONS OF COVALENTLY BONDED MOLECULES

Inorganic reactions are different than the organic ones in many aspects including their structural features. Organic reactions primarily involve sp, sp^2 and sp^3 hybridized carbon centres, therefore, organic reactions usually deal with linear, trigonal planar and tetrahedral geometries. On the contrary, inorganic molecules feature a variety of structural diversity. This poses much concerns pertaining to the structural, configurational and dynamic changes in case of inorganic reactions. Therefore, this section discusses two transformations involving structural changes in inorganic molecules. Subsequent reactions are of environmental and industrial importance.

1.7.1. Atomic inversion

Atomic inversion in molecules is spatial rearrangement of atoms giving rise to the mirror image products. Usually, the molecules involving tri-substituted N and P atoms, *i.e.*, amines and phosphines show such a phenomenon (**Figure 1.12**). It should be noted that the atomic inversion in non-chiral molecules yields product identical to the starting substance. However, a dissymmetric molecule, gives rise to a product with a molecular configuration that is a mirror image of that of the original molecule. The energy barrier for atomic inversion in case for amines is usually so small that the isolation of enantiomers cannot be affected.

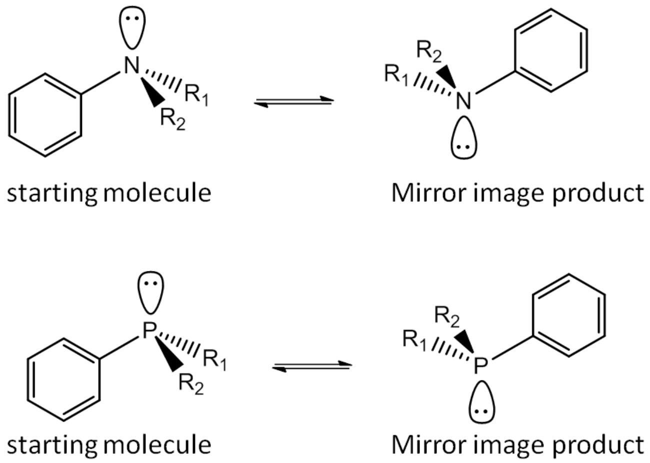


Figure 1.12. *Atomic inversion around nitrogen and phosphorous atoms in dissymmetric amine and phosphine molecules.*

1.7.2. Berry pseudorotation

Fluxional processes are dynamic molecular processes that interchange two or more chemically and/or magnetically different groups in a molecule. Berry pseudorotation in case of phosphorous pentafluoride (PF_5) is classical example of fluxional processes in inorganic substances (**Figure 1.13**). The Berry pseudorotation is a classical mechanism for interchanging axial and equatorial ligands in molecules with trigonal bipyramidal geometry. PF_5 is a trigonal bipyramidal molecule with D_{3h} symmetry. Therefore, bond angles $F_e - P - F_e$ and $F_a - P - F_a$ have the standard values of 120° and 180° respectively, where suffix '*e*' and '*a*' represent equatorial and axial positions. In the Berry pseudorotation, the angle $F_e - P - F_e$ increases from 120° and the angle $F_a - P - F_a$ decreases from 180° at the same rate so that the final positions of equatorial and axial fluorine atoms mutually exchanges. Therefore, the conversion of one trigonal bipyramidal form into other occurs through an intermediate square pyramidal transition state. Any intermediate positions between complete flip of axial and equatorial fluorine atoms are of higher energy, hence are not isolable. Symmetry considerations suggest two separate peaks for equatorial and axial fluorine atoms of PF_5 molecule. However, at room temperature, the ^{19}F-NMR spectrum offers a single peak for the molecule which indicates that the frequency of Berry pseudorotation is higher than the NMR scale.

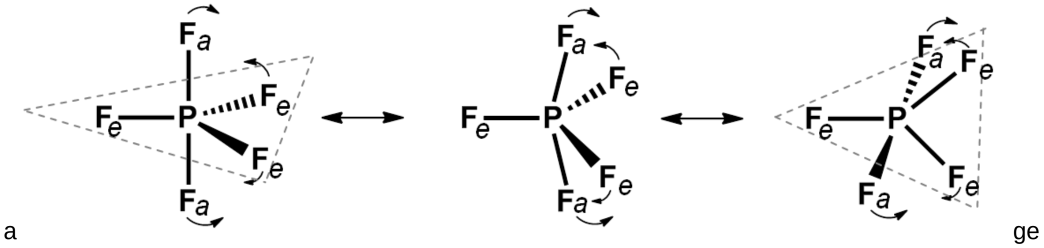


***Figure 1.13**. Schematic depiction of Berry pseudorotation in phosphorous pentafluoride.*

Two trigonal bipyramidal form of PF_5 interconvert *via* square pyramidal transition state. Note that both axial and two of the originally equatorial fluorine atoms in the extreme left structure assume equatorial and axial positions respectively, in the extreme right structure.

1.7.3. Lewis acid-Lewis base adduct formation

Lewis acid is a chemical species capable of accepting an electron pair in their empty orbital, whereas a Lewis base is a species that has an orbital containing electron pair that can be donated to electron deficient species. Hence, Lewis acid can accept electron pair from a Lewis base to form a Lewis adduct. For example, trialkylborane (Lewis acid) accepts electron pair from amines (Lewis base) to form a Lewis adduct. The covalent bond between B and N atoms can also be considered as a dative bond.

$$R_3B + :NR_3 \rightarrow R_3B{-}NR_3$$

1.7.4. Nucleophilic substitution reaction

Hydrolysis or solvolysis is a common reaction of inorganic substances which involves neucleophilic substitution reactions. Hydrolysis of trimethylchlorosilane to yield trimethylsilanol is presented below as an example in **Figure 1.14**. Note that the hydrolysis of a related bifunctional compound, dimethyldichlorosilane is used to synthesize a polymeric silicone material.

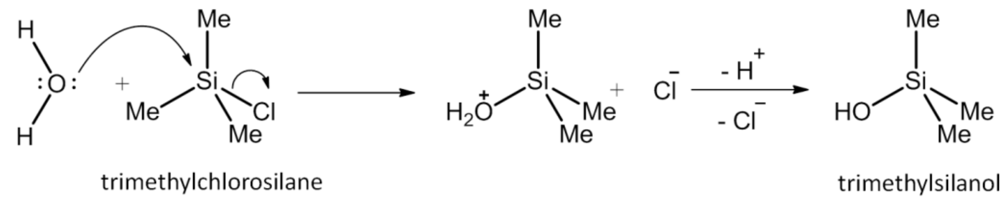


***Figure 1.14**. Synthesis of trimethylsilanol by hydrolysis of trimethylchlorosilane.*

1.7.5. Nitrogen fixation

Nitrogen fixation is a very important reaction involving conversion of natural nitrogen, N_2 (which has a triple bond between two nitrogen atoms) into ammonia. The reaction takes place at ambient temperature and 0.8 atm pressure of nitrogen in the *Rhizobium* bacteria found in the nodules on some plant roots (legumes). The reaction and can be presented as follows:

$$N_2 + 6H^+ + 6e^- \rightarrow 2NH_3$$

The process of nitrogen fixation involves enzymatic catalysis which is not discussed in this book. However, it should be noted that enzymatic processes are highly energy efficient chemical reactions in which various enzymes act as catalysts. It is important to note that the Haber process, an industrial procedure to synthesize ammonia requires high temperature, high pressure and an iron catalyst. Qualitative comparison of nitrogen fixation and Haber process would allow you to assess the superiority of enzymatic processes which are not yet completely understood. The ammonia produced in above reaction is used by plants for formation of essential building blocks of life such as amino acids.

1.7.6. Ozone-oxygen cycle

Ozone (O_3) is found in the stratosphere in large quantities and keeps most of the Sun's ultraviolet radiation from reaching to the earth by absorbing it up there. Ozone molecules (O_3) present in the stratosphere photodissociate to yield oxygen atoms (O) and oxygen molecules (O_2) upon absorption of ultraviolet photons. Simultaneously, ultraviolet photons of appropriate energy also split oxygen molecule (O_2) into two atomic oxygen radicals (O). The atomic oxygen radicals ($O\cdot$) combine with oxygen molecules (O_2) to regenerate ozone (O_3). These cyclic processes continue to occur in

stratosphere and prevent the harmful ultraviolet radiations from reaching the atmosphere.

$$O_3 + \mathrm{h\nu} \rightarrow O^{\cdot} + O_2 \ \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ (1)$$

$$O_2 + \mathrm{h\nu} \rightarrow 2O^{\cdot} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (2)$$

$$O^{\cdot} + O_2 \rightarrow O_3 \ \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (3)$$

The above ozone-oxygen cycle terminates when an atomic oxygen radical (O) combines with ozone molecule (O_3) to yield two oxygen molecules (O_2).

$$O^{\cdot} + O_3 \rightarrow 2O_2 \ \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (4)$$

The cycle can be disrupted by other radicals such as hydroxyl radical (OH·), nitric oxide radical (NO·), chlorine radical (Cl·) and bromine radical (Br·). The above reactions involve photochemical disruption and formation of covalent bond between oxygen atoms in the discussed chemical species.

1.8. SUMMARY

This chapter had discussed some important concepts to understand the bonding and structure of inorganic molecules. VSEPR theory offers a simple yet very useful concept to understand the geometry of simple molecules. Walsh diagram and Bent's rule are relatively intricate topics that complement VSEPR theory towards complete understanding of structures of inorganic molecules. Lastly, some important reactions of inorganic compounds had also been discussed in this unit. The discussion on selected reactions not merely presents the chemical transformations but also touch upon the structural, environmental and industrial importance of the same.

1.9. TERMINAL QUESTIONS

1.9.1. Reasoning based questions

1. Identify the shapes of the following molecules using concepts of VSEPR.

(a) ClF_3

(b) PCl_3

(c) IF_7

(d)XeF_2

2. Draw the Lewis dot structures for each of the following species.

(a) BH_2^-

(b) NI_3

(c) CCl_4

(d) SF_5^-

3. Arrange following in the decreasing order of bond angles:

NO_2 , NO_2^+ , NO_2^-

4. What is the molecular geometry of NCl_3?

5. Which one of the following is the correct bond angle between atoms adopting a trigonal planar geometry?

(a) 90°

(b) 120°

(c) 109.5°

(d) 180°

1.9.2. Short answer type questions

1. Write the statement of the Bent's rule.

2. Write the name of geometry for a molecule with central atom having seven substituents.

3. Write full form of acronym, VSEPR.

4. Central atom in a molecule has two substituents and two lone pair of electrons. Discuss the bond angle that you expect for molecule in question.

5. What are solvolysis reactions?

1.9.3. Long answer type questions

1. Discuss energetic of hybridization with suitable examples.zUttarakhand Open University Page 19

2. Discuss structure of tetrachloromethane (CCl_4) in light of the VSEPR theory.

3. Discuss the dπ-pπ bonding in case of a sulfur compound.

4. Why phosphine oxide exhibits shorter P=O bond length and high stability, explain.

5. Draw and discuss Walsh diagram for methane.

1.10. ANSWERS TO REASONING BASED QUESTIONS

1. Identify the shapes of the following molecules using concepts of VSEPR.

Answer:

(a) ClF_3 …………………. **T-shaped**.

(**Explanation:** Chlorine trifluoride has 10 electrons around the central chlorine atom. This means there are five electron pairs arranged in a trigonal bipyramidal shape with a 175° F-Cl-F bond angle. There are two equatorial lone pairs making the final structure T-shaped.)

(b) PCl_3 …………………….. **trigonal pyramidal**

(**Explanation:** Central phosphorous atom in PCl_3 is sp3 hybridized having three bond pair and one lone pair of electrons. Therefore, four electron pairs arranged in a tetrahedral shape and the final molecular geometry of PCl_3 is trigonal pyramidal.)

(c) IF_7 ………………………… **pentagonal bipyramidal**

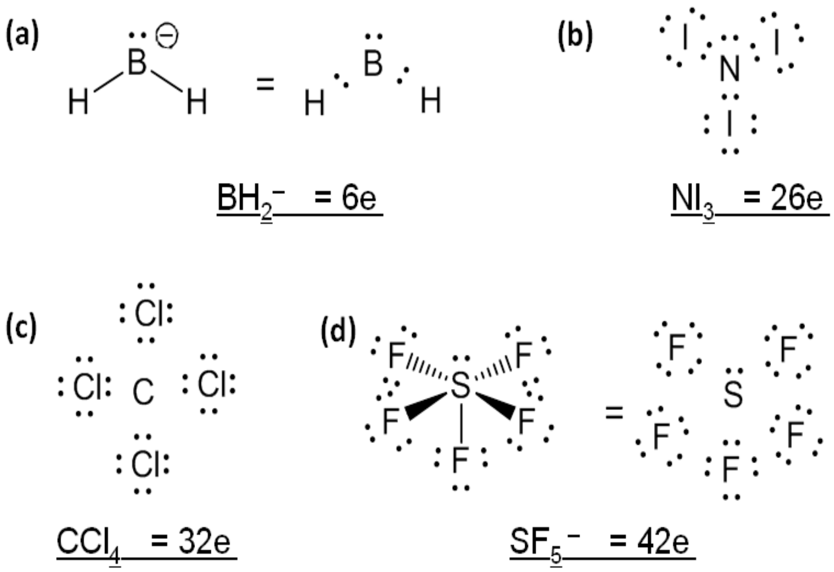
(**Explanation:** Iodine heptafluoride, IF_7, having seven bonding pairs around the iodine atom assumes a pentagonal bipyramidal geometry.)

(d) XeF_2 …………………………. **linear**

(**Explanation:** XeF_2 has three lone pairs and two bonding pairs of electrons. Hence, the electronic structure should assume trigonal bipyramidal geometry. The bonded pairs take the axial position, whereas, the three lone pairs take equitorial position in the molecule in question. Hence, the molecular geometry of XeF_2 is linear.

2. Draw the Lewis Dot Structures for each of the following species.

Answer:



3. Arrange following in the decreasing order of bond angles:

NO_2 , NO_2^+ , NO_2^-

Answer:

$NO_2^+ > NO_2 > NO_2^-$

Explanation:

4. What is the molecular geometry of NCl_3?

Answer: trigonal-pyramidal

5. Which one of the following is the correct bond angle between atoms adopting a trigonal planar geometry?

Answer: (b) 120°

1.11. REFERENCES AND FURTHER STUDIES

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Block I: Stereochemistry and Bonding

UNIT 2 PHOSPHORUS-NITROGEN AND SULFUR-NITROGEN COMPOUNDS

CONTENTS

2.0. OBJECTIVES

Objectives of this unit are to introduce you with the synthesis, structure, bonding and some applications of inorganic compounds of chalcogens (O and S) with their neighbouring group 15 members (N and P). The chapter will deal with phosphonitrilic (phosphorous-nitrogen), phosphorous-sulfur and sulfur-nitrogen compounds. It will help to establish an understanding towards the structure and bonding in these compounds.

2.1. INTRODUCTION

The phosphazenes (phosphonitriles) and sulfur-nitrogen compounds are an important class of inorganic compounds which exhibit interesting structure and bonding. They may present cyclic structural motifs which may be considered as inorganic aromatic analogues.

The reaction chemistry of these compounds is not less interesting than those of boranes. However, the revelation of exact structures for some of the nitrogen sulfur compounds took over hundred years after their discovery. The polymer SN_x was first discovered in 1910 and further investigation revealed that it comprises of only non-metallic elements and behaved as superconductor at 0.26 K. Such a discovery fueled interest in (S–N) chemistry. Their unique structure and properties continue to attract attention of several theoretical chemists who have tried to look into the “aromatic character” of binary S–N systems. The reaction between phosphorous pentachloride and ammonia was described in 1834, the major reaction product was phospham and a small quantity of compound containing, phosphorous, nitrogen and chlorine was also obtained. Later the compound was designated as $N_3P_3Cl_6$. This discovery led to the advent of phophazene chemistry. They have several applications in material chemistry, biochemistry, organic synthesis and polymer chemistry.

2.2. PHOSPHAZENES (PHOSPHONITRILIC / P–N COMPOUNDS)

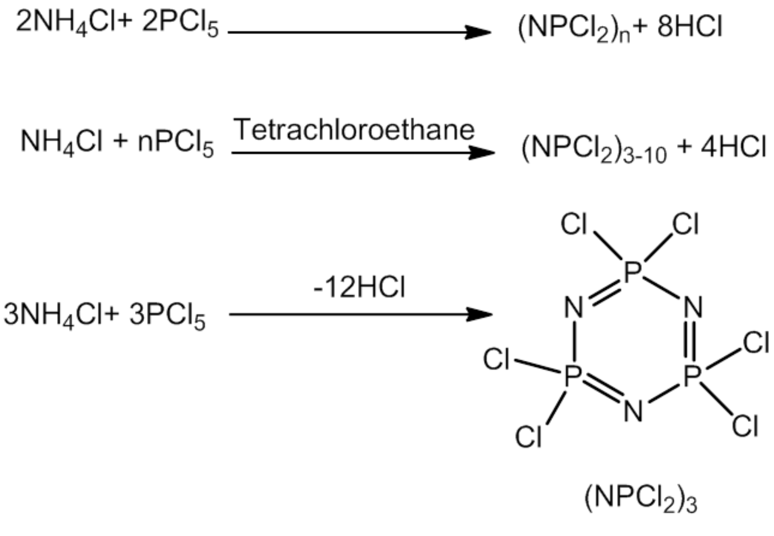
The term phosphazene or phosphonitrile includes those compounds which have phosphorous and nitrogen atom joined alternatively by single or double bonds. Overall, they may constitute a ring or a chain motif in which nitrogen is trivalent and phosphorous is pentavalent. The empirical formula for very first phosphazene $N_3P_3Cl_6$ (white crystalline product obtained by reaction of ammonia with phosphorous pentachloride) was derived after some errors. It was first considered to be $NPCl_2$ but later found out to be a trimer having a cyclic structure (proposed by H.N. Stokes). The trimer on heating yielded an elastomer known as the “inorganic rubber”.

2.3. CYCLOPHOSPHAZENE

The cross linked ‘inorganic rubber ‘was formed by the reaction of $[NPCl_2]_n$ with trace amounts of H_2O. Thus, if the reaction is carried out in the absolute absence of atmospheric moisture, non-cross-linked and soluble macromolecules of $[NPCl_2]_n$ could be prepared.

Reaction of organic nucleophiles with $[NPCl_2]_n$ can result in the replacement of chlorine atom and hence generate stable poly(organo)phosphazenes. A wide range of polymers with mixed substituents having varied properties can be generated if two different nucleophiles are used on the same molecule

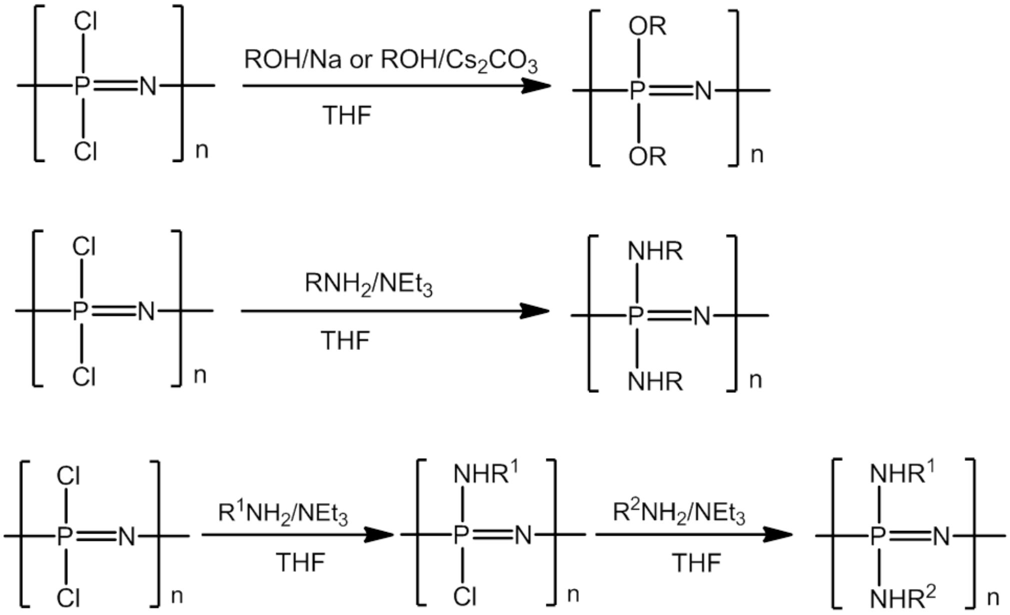
i. Poly(dichloro)phosphazene $[NPCl_2]_n$ is a key precursor in the synthesis of almost all polymeric phosphazenes **(Scheme 1.1)**.



Scheme 1.1. *Synthesis of polymeric phosphazenes*

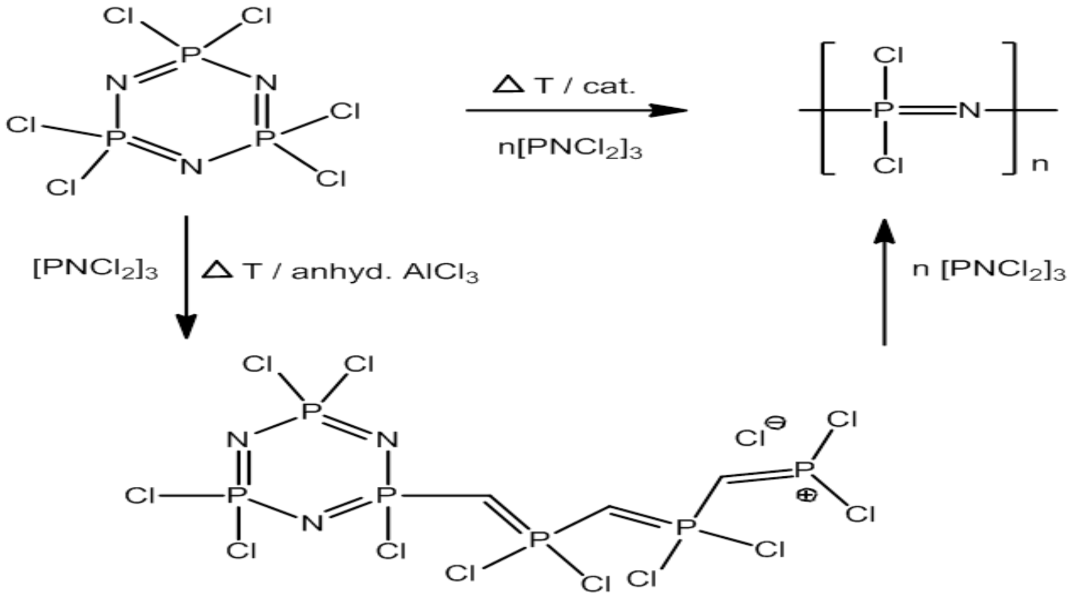
ii. Macromolecular Substitution of $[NPCl_2]_n$

Commonly followed routes of macromolecular substitution to generate poly(organo)phosphazenes are as depicted in **Scheme 1.2**.



Scheme 2.2. *Synthesis of poly(organo)phosphazenes*

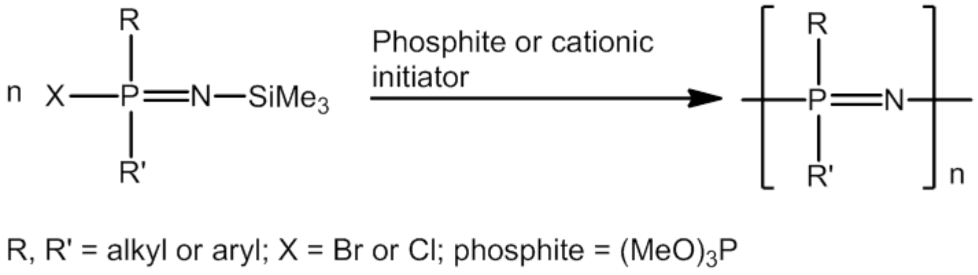
iii. Ring opening polymerization of $[NPCl_2]_3$ (Scheme 2.3)



Scheme 2.3. *Synthesis of cyclophosphazenes by ring opening reaction*

iv. Synthesis of poly(alkyl/aryl)phosphazenes

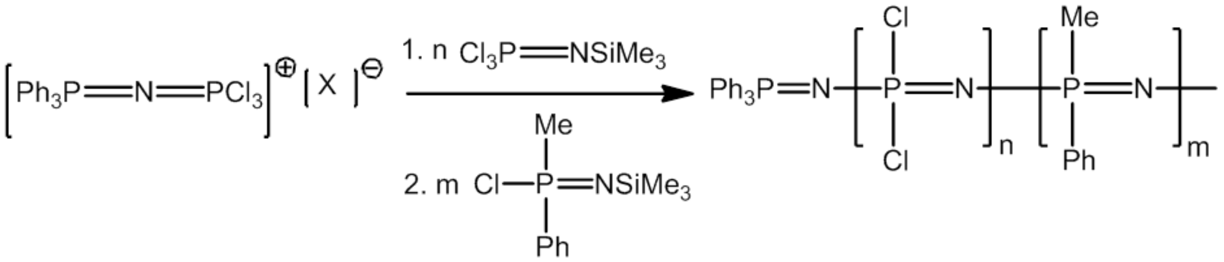
Poly(alkyl/aryl)phosphazenes, $[NPR_2]_n$, are those molecules which have an organic substituent directly attached through a P–C bond **(Scheme 2.4)**.



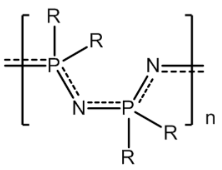
Scheme 2.4. *Synthesis of poly(alkyl/aryl)phosphazenes*

v. Synthesis of block copolymer

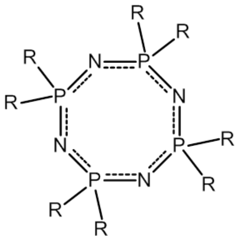
Macromolecular substitution of $[NPCl_2]_n$ gives random copolymers due nonspecific nucleophilic substitution of the chlorine atoms on the polyphosphazene backbone (**Scheme 2.5**). Block copolymers have wider applications and considerable attention is given to their synthesis.



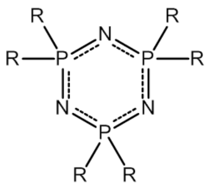
Scheme 2.5. *Synthesis of polyphosphazene block copolymers*



polyphosphazenes



cyclotetraphosphazenes



cyclotriphosphazene

2.4. STRUCTURE AND BONDING IN PHOSPHAZENES

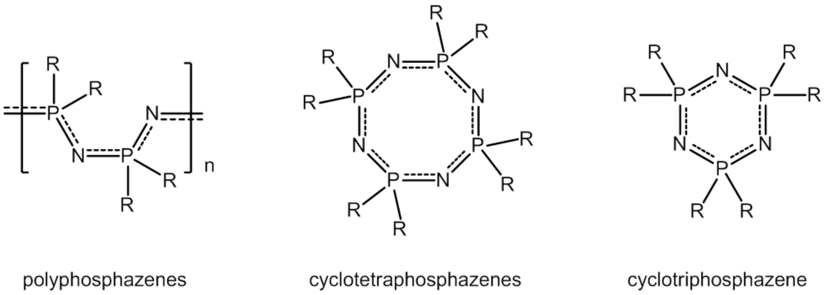

polyphosphazenes cyclotetraphosphazenes cyclotriphosphazene

Figure 2.1. *Structure and bonding in phosphazenes*

The P-N bonds are short in phosphazenes (ca. 1.58 Å) as compared to those in valence saturated phosphazanes (ca. 1.77Å). These short bond lengths and absence of any significant alternation in bond lengths in cyclic phosphazenes and to a lesser extent in polyphosphazanes indicates that these bonds are of multiple bond character (**Figure 2.1**). Initially, Dewar gave the 'island model' according to which delocalization occurs via $d\pi$P-$p\pi$N (3d of P and p of N) overlap resulting in an *island* of electron density spread over P–N–P units with nodes over P centres. But now it is accepted that valence d orbitals do not play a significant role in the bonding of the main group elements. Despite several other works and theories (negative hyperconjugation or group theory analysis) on the structure and bonding in hypervalent compounds, the *island model* still dominates the phosphazene literature.

2.4.1 Structure of $(NPCl_2)_3$

It has a planar six-membered ring. The bond angles are consistent with sp^2 hybridization (118^0 for P–N–P) of nitrogen and sp^3 hybridization of phosphorous (108^0 for Cl–P–Cl angle). See **Figure 2.2** below in which all bond lengths are reported in angstrom (Å) unit. Two of the sp^2 hybrid orbitals of nitrogen lone pair of electrons. Thus, the remaining one electron is left in the unhybridized p_z orbital.

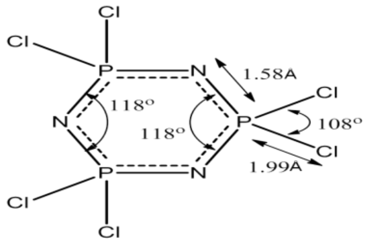


Figure 2.2. *Structural details of $(NPCl_2)_3$*

In case of phosphorous, the four sp^3 hybridized orbitals accommodate four electrons and are used in σ bonding. The remaining one (fifth) electron occupies a vacant d orbital. The resonance structures similar to benzene can also be drawn for $(NPCl_2)_3$. However, the nature of bonding here does not follow the same resonancedelocalization and aromaticity in these inorganic cyclic molecules has been a matter of debate since long. Despite the presence of delocalization in some phosphazenes, not all molecules maintain the planarity of ring. This factor does not make them unstable. The ultra violet spectra of phosphazenes does not show structural features similar to those of aromatic organic compounds and also it is very difficult to reduce their unsaturated bonds. Furthermore, unlike benzene, the π bonds in cyclophosphazene have contribution from both p and d orbitals. Several theories have been suggested for the d_π-p_π bonding. Some of them are discussed below.

a) Craig and Paddock model: The overlap between d_{xz} (gerade) orbital of phosphorous with p_z (ungerade) orbital of nitrogen results in a node due to mismatch in the orbital symmetry and signs of the wave function. The d_{yz} orbital which is perpendicular to the d_{xz} orbital can overlap with the p_z orbital of nitrogen without any nodal surface. Apart from these, there may be π bonding between the nonbonding sp^2 hybrid orbital of nitrogen and d_{xy} or d_{x2-y2} orbitals of phosphorous (**Figure 2.3, a-d**).

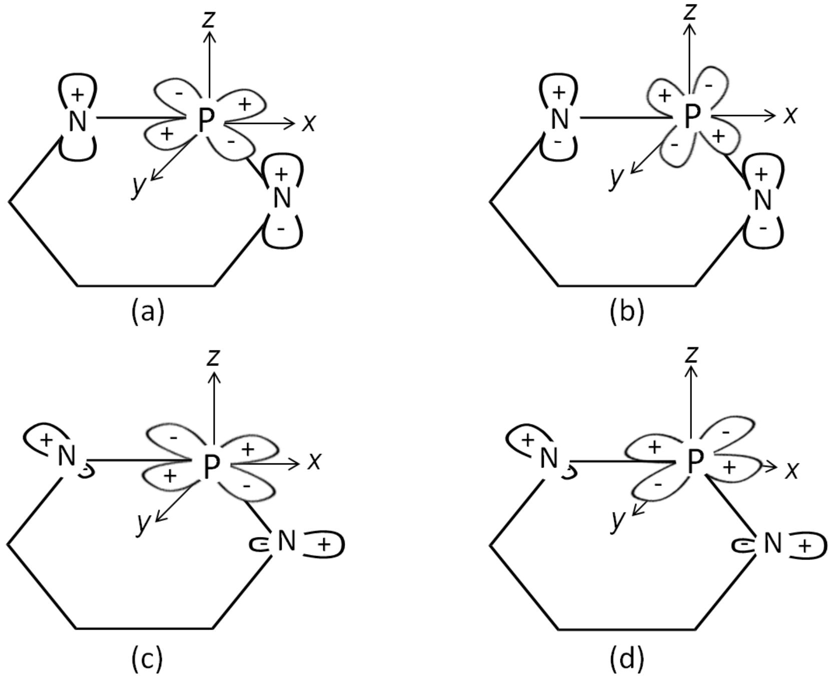


Figure 2.3. *Craig and Paddock model of $(NPCl_2)_3$ structure*

b) Dewar and Coworkers model: As mentioned earlier, they proposed the '*island model*'. It suggested that the d_{xz} and d_{yz} orbitals hybridized to give two hybridized orbitals which are oriented towards the adjacent nitrogen atoms. This gives three centre bonds (P-N-P) about each nitrogen atom having delocalization of electron density over them. Nodes are present over each phosphorous atom because it's two hybrid orbitals are orthogonal to each other (**Figure 2.4**).

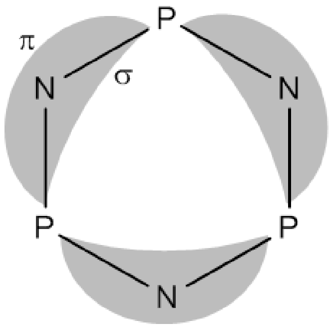
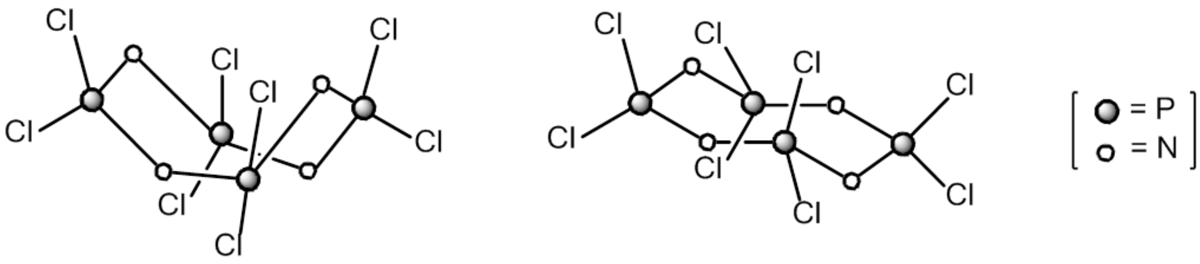


Figure 2.4. *Dewar model of phosphazenestructure*

2.4.2 Structure of tetrameric phosphazenes

Tetrameric phosphazenes have a more flexible structure than their trimeric analogues. They may have a planar structure or tub, boat, chair, crown and saddle conformations. The presence of a definite structure is not very obvious, intermolecular forces play a major role in any structure. The structure of $(NPF_2)_4$ is planar and $(NPCl_2)_4$ is known to exist in two forms. The most stable is the 'chair form' also called as the T form (**Figure 2.5**). The other form has a tub conformation. The nonplanar structures do not prevent extensive delocalization in the rings. Organic analogue of tetrameric phosphazene is the cyclooctatetraene. It is a nonaromatic compound because of lack of planarity and secondly, it does not obey the Hückel's rule of (4n+2)π electrons. Huckle's rule was formulated on pπ-pπ bonding and hold well for organic compounds having n=1 to n=4. Now, these inorganic compounds do not hold organic rules for aromaticity. Here, the d orbitals are involved which overrules the Hückel's rule. The diffused nature of d orbitals is suitable for bonding in nonplanar systems providing greater flexibility to the ring.



Tub conformation of $P_4N_4Cl_8$ Chair conformation of $P_4N_4Cl_8$

Figure 2.5. *Conformations of tetrameric phosphazenes*

2.5. USES OF POLYPHOSPHAZENES

Small changes in the substituents attached can lead to significant changes in the polymer properties. Polyphosphazenes have wide range of applications, such as high performance elastomers due to chain flexibility and high thermal stability. They are used as flame retardants due to their side chain functionality and limiting oxygen indices. Nowadays, they are being explored for such far reaching applications as vaccine delivery, fuel cell membranes, matrices for tissue engineering, drug and gene delivery etc.

Hexachlorotriphosphazene (HCCP): A significant amount of work has been done in the preparation of novel materials and those having high molecular weight by using HCCP, $[NPCl_2]_3$ by coupling the rings with multifunctional nucleophiles. The covalent linkage in HCCP can be used to prepare cyclolinear, cyclomatrix or dendritic structures. In the synthesis of cyclolinear structures, only two reactive sites are used out of the six available in cyclic $[NPCl_2]_3$ unit. Reaction of more than two sites leads to cross-link or cyclomatrix materials.

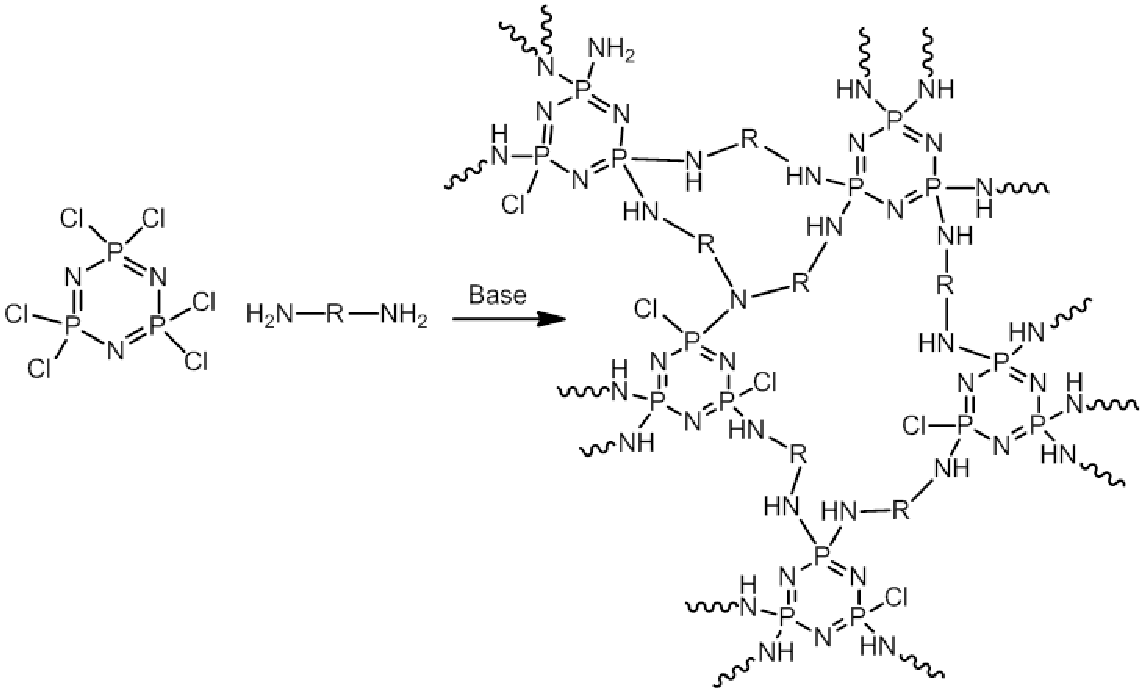


Figure 2.6. *Formation of cyclomatrix phosphazenes*

2.6. PHOSPHORUS-SULFUR COMPOUNDS

2.6.1. Significance

There is much attention directed towards the synthesis of multidentate ligands having different donor atoms and the concept of hemilability. The presence of one strong donor (strongly bonding) and other weak donor (weakly bonding) atom in a molecule finds application in protecting an active site at the metal centre. These molecules serve as interesting ligand systems due to their donor properties which may be altered through chelation. The chelate complexes are quite stable and so, the reactivity of a metal centre for a particular reaction (eg. oxidative addition) can be studied without competing ligand substitution reactions. The P-S compounds are less stable than their oxy-analogues and have lower melting points. They are used as insecticides, lubricating oil additives, flotation and vulcanization accelerators.

2.6.2 Synthesis

Oxygen atoms from phosphorous oxides can be partially or wholly substituted with sulphur atoms to give thio-phosphorous compounds. These may have S as a bridging atom or at terminal positions.

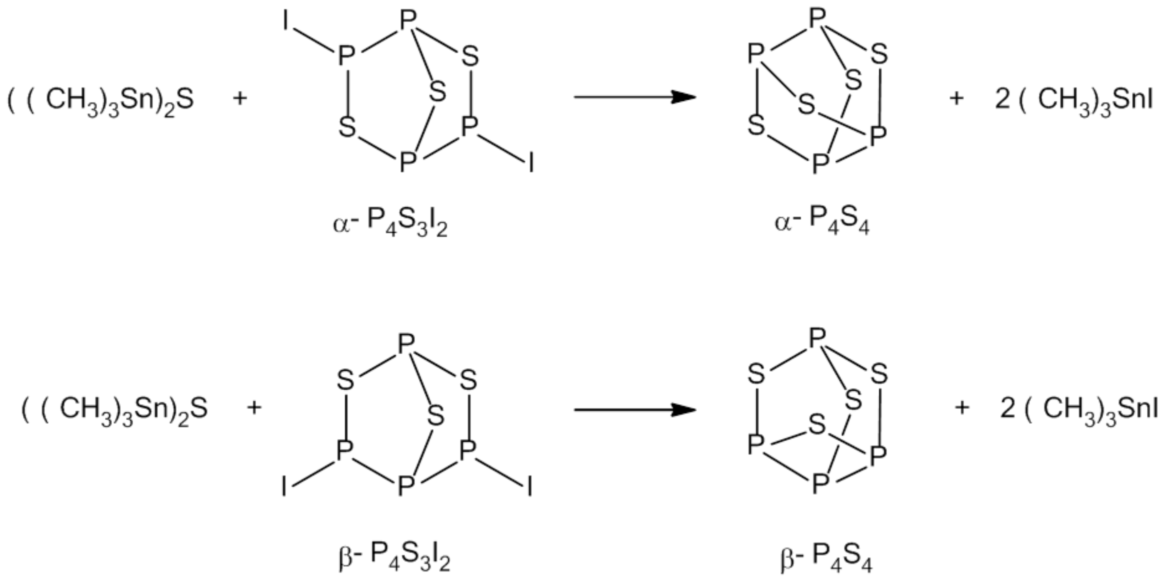
P_4S_{10} and P_4S_9 are isoelectronic and isostructural with phosphorous oxides. P_4S_3 and P_4S_7 can be obtained by using the appropriate stoichiometric quantities of P and S (**Scheme 2.6**).

$$4\ P_4 + 5\ S_8 \longrightarrow 4\ P_4S_{10}$$

$$4\ P_4S_3 + S_8 \xrightarrow{\text{slow oxidation}} 4\ P_4S_5$$

Scheme 2.6. *Synthesis of phosphorus-sulfur compounds*

2.6.3. Synthesis of cage phosphorous sulfides (Scheme 2.7)



Scheme 2.7. *Synthesis of cage phosphorous sulfides*

2.6.4. Structure of cage phosphorous sulfides

Molecular structures of some phosphorous sulfides (P_4S_{10}, P_4S_5, P_3S_3, α and β-P_4S_4) along with some significant bond distances are shown in **Figure 2.7**. These are prepared from P_4 and sulphur atoms which are located at the edges. All distances are reported in angstrom (Å) unit.

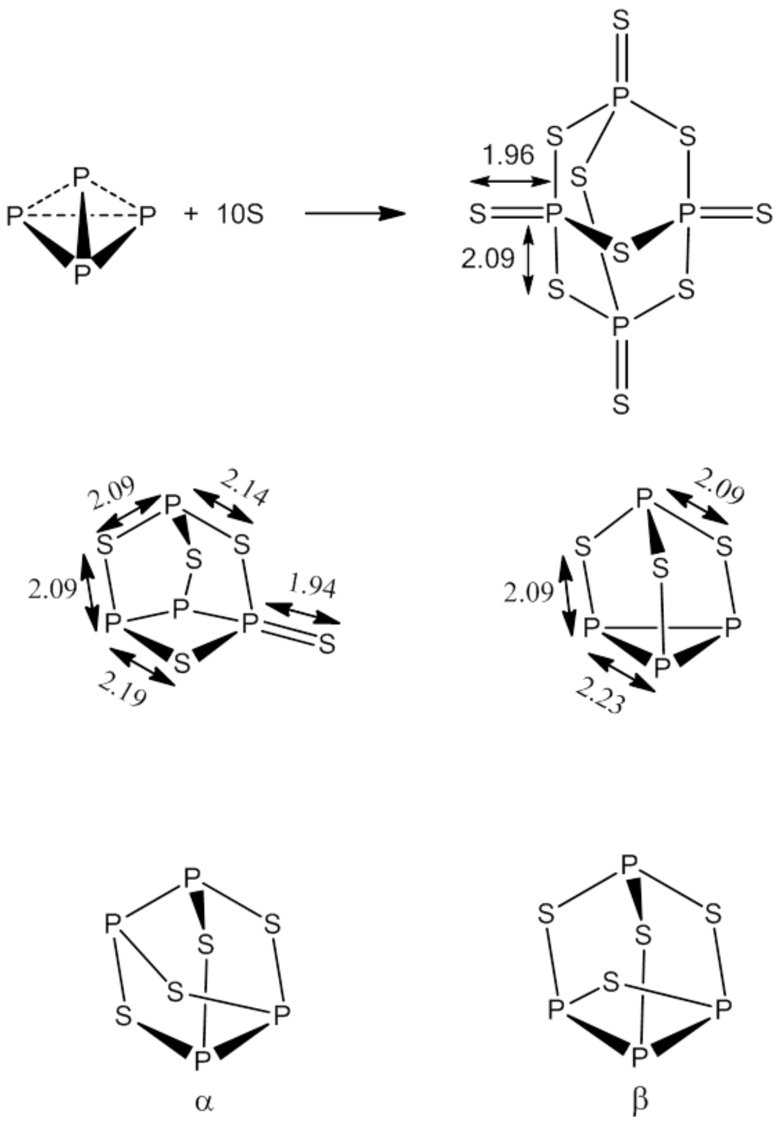


Figure 2.7. Structures of some cage phosphorous sulfides

2.7. SULFUR NITROGEN COMPOUNDS

2.7.1 Significance

The electron rich $(SN)_X$ compounds can serve as donors in charge transfer complexes and unlike phosphonitriles, the cyclic $(SN)_X$ compounds follow Hückel's rule of aromaticity. These factors have attracted much interest to their synthesis, bonding and exploration of their overall chemistry. The S-N compounds have been explored for their bonding with transition metals and also for their magnetic and conducting properties.

A variety of acyclic and cyclic S-N compounds are known. S_2N_2, even though a strained structure, is the smallest homoleptic ring known to exist. It is the most important precursor for the synthesis of several polythiazyl $(SN)_X$.

The synthesis, structure and bonding of some of these compounds is given in **Scheme 2.8**.

$$S_2Cl_2 \xrightarrow{NH_3} S_4N_4 + S_8 + NH_4Cl$$

$$4S + 6\,Cl_2 + 16\,NH_3 \longrightarrow S_4N_4 + 12\,NH_4Cl$$

$$4S + 6\,Cl_2 + 16\,NH_3 \longrightarrow S_4N_4 + 12\,NH_4Cl$$

Scheme 2.8. *Synthesis of sulfur nitrogen compounds*

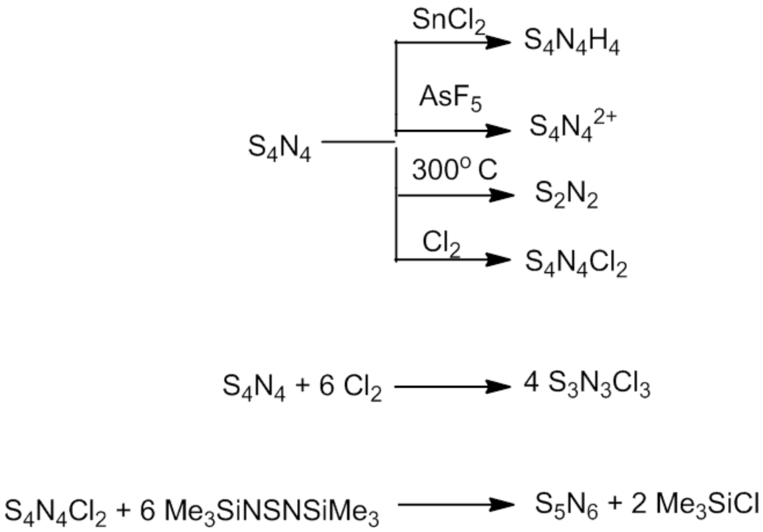
Reaction of silver metal at high temperature and low pressure with S_4N_4 results in thermal decomposition and formation of silver sulfide which catalyses the conversion of remaining S_4N_4 to give cyclic S_2N_2 (**Scheme 2.9**).

$$S_4N_4 + 8\,Ag \xrightarrow[1\text{ mm Hg}]{250\text{-}300^{o}\,C} 4\,Ag_2S + 2\,N_2$$

$$S_4N_4 \longrightarrow 2\,S_2N_2$$

Scheme 2.9. *Synthesis of strained molecule S_2N_2*

S_2N_2 dimerizes rapidly into S_4N_4 in the presence of nucleophiles (**Scheme 2.10**).



Scheme 2.10. *Reactions of sulfur nitrogen compounds*

2.7.3 Structure and bonding

Some S–N compounds show planar ring structure. It has been found that they follow Hückel's rule of $(4n+2)\pi$ electrons. If we consider that in these planar cyclic S–N compounds each atom contributes one electron to the σ bond and two electrons to a lone pair, then sulfur has two π electrons and nitrogen has one π electron. Or we can also explain the electron distribution as follows. At each S–N unit, two electrons are allocated for sigma bonds and two electrons for each S and N atom for non-bonding lone pairs. Thus, one electron at N at two electrons at S are left which can be used in the cyclic π-system of the ring.

Considering these electron's distribution, we can say that S_2N_2 has 6π electrons; $S_3N_3^{-}$ has 10π electrons; $S_4N_3^{+}$ has 10π electrons and $S_5N_5^{+}$ has 14π electrons.

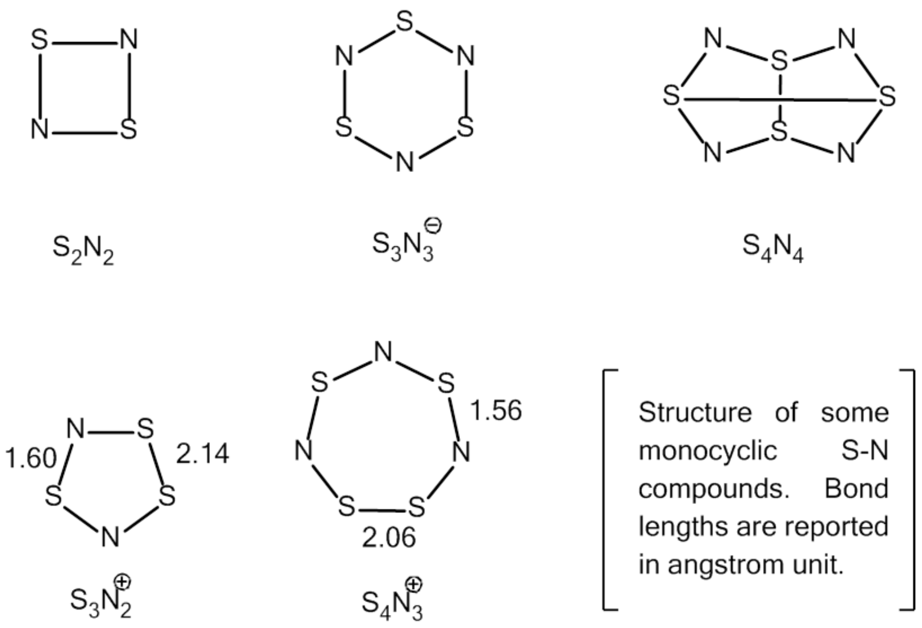
However, in contrast to the stable π-organic molecules, the S–N compounds mentioned above have electrons in the antibonding (π^*) molecular orbitals which has a weakening effect on S–N bond. The stability of these compounds can be ascribed to the following factors:

(a) The higher electronegativity of nitrogen compared to sulfur or oxygen lowers the energy of antibonding (π*) orbitals thus bringing them closer to bonding region.

(b) The longer S–N bond lengths reduces the mutual repulsion between any other pair of electrons, this lowers the energy of the π-system.

i) Disulfur dinitride (S_2N_2): It is cyclic square planar molecule with S–N bond length of 1.65Å. The N–S–N angle is 89.6° while the S–N–S angle is 90.4° (**Figure 2.8**).

ii) Trisulfur trinitride anion ($S_3N_3^-$): The structure of $[nBu_4N]^+[S_3N_3^-]$ is well established. It has a planar six membered ring with S–N bond length in the range 1.58-1.63Å (**Figure 2.8**).



Structure of some monocyclic S-N compounds. Bond lengths are reported in angstrom unit.

Figure 2.8. *Structures of some Sulfur Nitrogen Compounds*

iii) Tetrasulfur tetranitride (S_4N_4): Cradle shape structure belonging to point group D_{2d} (**Figure 2.9**).

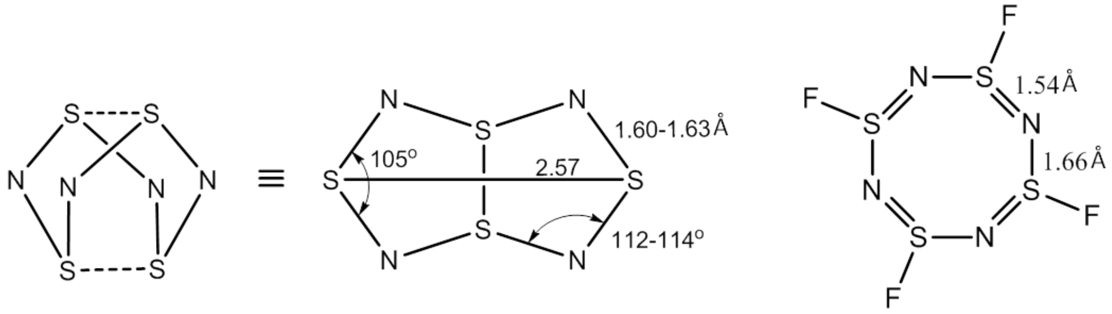


Figure 2.9. *Structures of geometrical features of* S_4N_4 *and* $S_4N_4F_4$

iv) Tetrasulfur dinitride (S_4N_2): It has a nonplanar ring structure (**Figure 2.10**).

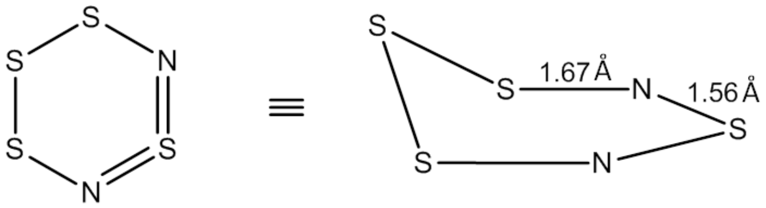


Figure 2.10. *Structures of geometrical features of* S_4N_2

2.8. SUMMARY

This chapter had discussed the important concepts to understand the bonding and structure of some interesting inorganic molecules. Here, we learnt that these class of compounds play an important role in the synthesis of several useful polymeric materials. The P-N and S-N compounds have unique chemistry and bonding and are still an area of active research where new compounds have been synthesized and their structures have been studied. The P-N compounds do not obey Hückel's rule for aromaticity while even though the S-N compounds follow this rule yet cannot be compared to the aromatic organic compounds.

2.9. TERMINAL QUESTIONS

2.9.1. Long answer type questions

Q1. What are phosphonitrilic compounds? Discuss synthesis of cyclophosphazenes.

Q2. Discuss bonding in phosphazenes. Explain the Dewar model in this regard.

Q3. Write a note on hexachlorotriphosphazene discussing its synthesis, structure and uses.

Q4. Explain bonding in S-N compounds explaining why they are not true aromatic compounds.

2.9.2. Short answer type questions

Q1. Give reaction for the synthesis of poly(alkyl/aryl)phosphazene.

Q2. Draw the structure of $(NPCl_2)_3$showing important bond lengths and bond angles.

Q3. What are the two conformations adopted by $(NPCl_2)_4$? Draw their structures.

Q4. Give synthesis and structure of α and β forms of P_4S_4.

Q5. Give reactions for synthesis of S_4N_4 and S_4N_2.

Q6. Draw the structure of S_4N_4 showing important bond angles and bond lengths.

2.9.3. Objective type questions

Q1. The two conformations of $(NPCl_2)_4$ are:

a) Boat and chair (b) crown and chair (c) saddle and tub (d) Tub and chair

Q2. Inorganic benzene is an aromatic compound. True or False?

Q3. Phosphazenes are aromatic but S-N compounds are non-aromatic. True or False?

Q4. Phosphazenes are non-aromatic because they:

(a) are non-planar (b) do not follow Huckle's rule (c) they are not cyclic (d) none of the above

Q5. Some S-N compounds even though planar are not aromatic because they:

(a) lack delocalization (b) do not follow Huckle's rule (c) they are not cyclic (d) have electrons in antibonding (π*) orbitals

Answers: Objective type questions

Q1. (d)

Q2. False

Q3. False

Q4. (b)

Q5. (d)

2.10. REFERENCES AND FURTHER STUDIES

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Block I: Stereochemistry and Bonding

UNIT 3 ORGANOMETALLIC COMPOUNDS OF ALKALI AND ALKALINE EARTH METALS

CONTENTS

3.1. OBJECTIVES

Objectives of this unit are to introduce you with synthesis, properties, structure, bonding and uses of organometallic compounds of alkali and alkali earth metals. Each organometallic compound with its special reactivity, method of synthesis and uses has been described. Their structure bonding relationship has also been provided subsequently. At the end of this unit, students will be able to understand their reactivity and structure along with their uses.

3.2. INTRODUCTION

This chapter provides an introduction to the large area of organometallic chemistry of alkali and alkali earth metals. In an organometallic compound, one or more metal carbon bonds are present. The stability, reactivity and structural properties of each compound depend on periodic properties of the respective metal.

3.3. ORGANOMETALLIC COMPOUNDS OF Li AND Na

3.3.1. Synthesis of organolithium and organosodium compounds

Organolithium compounds having particular importance among the group I organometallics and may be synthesized by the treatment of an organic halide with lithium (**Figure 3.1**) or by following the metallation reactions using n[butyllithium in presence of hydrocarbon (e.g. hexane) as a solvent.

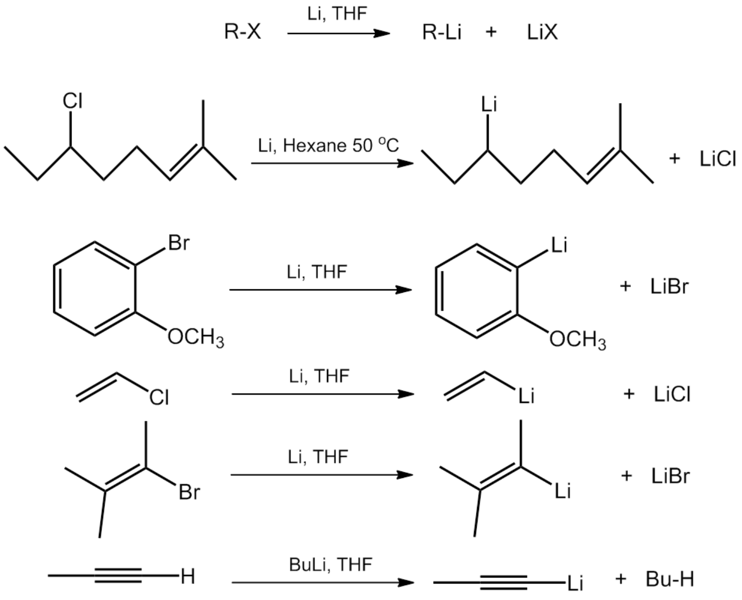


Figure 3.1. *Synthesis of organolithium compounds*

Organolithium can also remove halogen from alkyl and aryl halides proceeding *via* halogen-metal exchange as depicted in **Figure 3.2**.

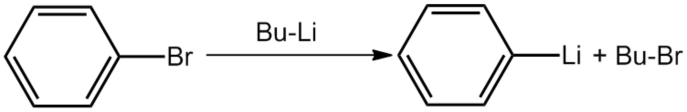


Figure 3.2. *Synthesis of organolithium compounds*

Organic compound having active hydrogen such as acetylic hydrogen form salt with alkali metals.

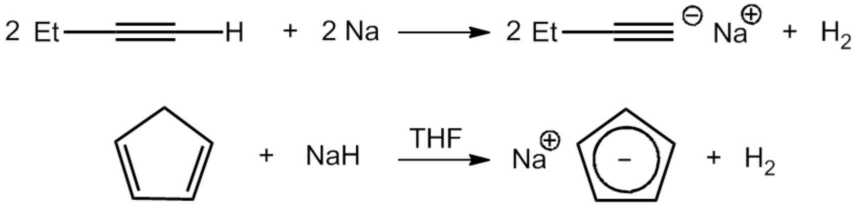


Figure 3.3. *Synthesis of sodium salts of organic compounds possessing active hydrogen.*

Organolithium compounds are more stable than other heavier group alkali metal organo compounds. Sodium and potassium form paramagnetic organometallic compound with many aromatic compounds. This is because of the oxidation of metal in presence of aromatic compound.

3.3.2. Structure and properties of organolithium compounds

Alkyl lithium compounds are polymeric both in solid state and in solution. In a $(RLi)_4$ tetramer, the Li atoms form a tetrahedral unit in ethers, while in case of a $(RLi)_6$ hexamer, the Li atoms define an octahedron. Weiss *et al*. showed that in the structure of $(MeLi)_4$; the average Li-Li bond length is 261pm compared with 267pm in Li_2. It was also established that in the structure of the Li_6C_6-core of $(LiC_6H_{11})_6$ (C_6H_{11} ¼ cyclohexyl); six Li-Li bond distances lie in the range 295-298pm, while the other six bonds are significantly shorter (238–241pm). The presence of such aggregates in the solution is determined by multinuclear NMR spectroscopy. As the organolithium compounds contain a carbon-metal bond, the polarity of a covalent bond between two different elements can be determined by electro negativity difference between them. More the electronegative an element, more it attracts electron density. By virtue of this, partial negative charge remains effective in more electronegative element while partial positive charge remains in electropositive element. In organolithium compounds, the difference in electronegativity is 1.5 as depicted in **Figure 3.4**.

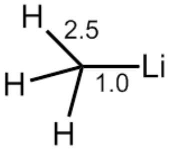


Figure 3.4. *Depiction of electronegativity of carbon and lithium.*

Molecular orbital energy level diagram depicted in **Figure 3.5** represents the C-Li bond having electron density towards more electronegative carbon having less energy are in its atomic orbital. The C-Li sigma bond is closer to energy of sp^3 hybrid orbital of carbon while sigma anti bonding orbital is closer to 2s orbital of lithium.

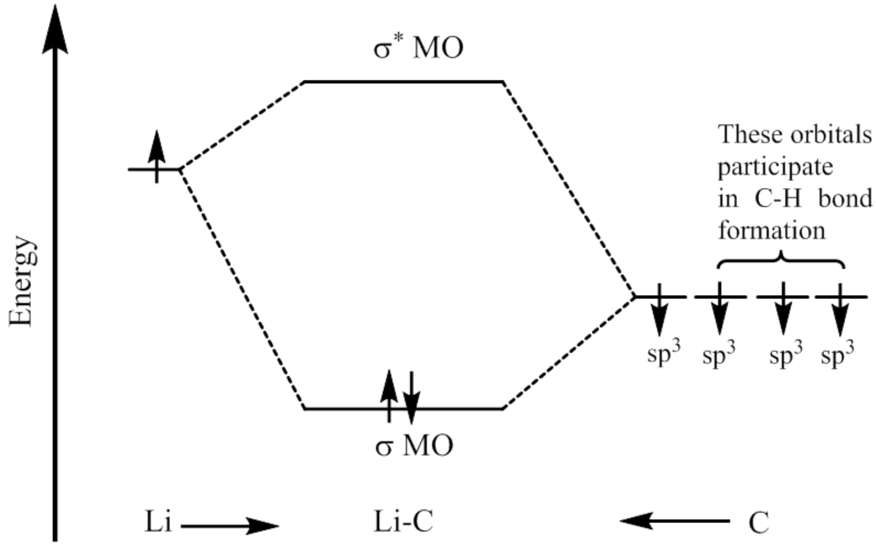


Figure 3.5. *MO diagram of CH_3Li*

3.3.3. Properties and uses of organolithium

Organometallics are very reactive and need to be kept free from moisture. Organometallics act as base and easily get protonated even in the air (**Figure 3.6**).

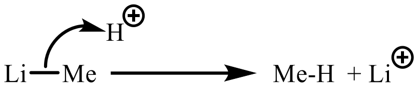


Figure 3.6. *Protonation of organolithium compound.*

Organolithium compounds are of great importance as synthetic reagents. Alkyls and aryls organolithium are used to synthesize to organoboron compounds from boron trihalides having similar reactions with other p-block halides (e.g. $SnCl_4$) (**Figure 3.7**).

$$3BuLi + BCl_3 \longrightarrow Bu_3B + 3LiCl$$

Figure 3.7. *Synthesis of organoboron compound from organolithium compound.*

Lithium alkyls are important catalysts in the synthetic rubber industry for the stereospecific polymerization of alkenes. Metal derivatives of alkynes can react with carbonyl and water to give alcohols (**Figure 3.8**).

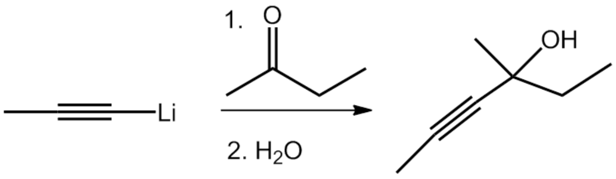


Figure 3.8. *Use of organolithium compound in rubber industry.*

Oraganolithium has advantage over Grignard reagents because Grignard reagents fail to react with highly hindered carbonyl compounds but organolithium reacts normally with such compounds (**Figure 3.9**).

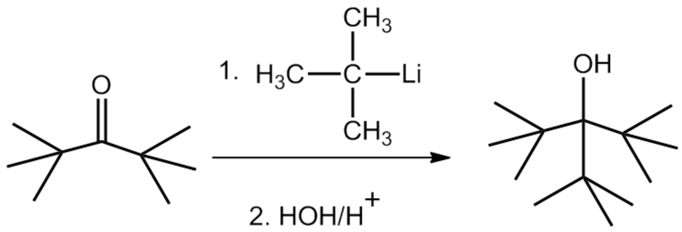


Figure 3.9. Reaction of organolithium compound at highly hindered reaction site.

Addition with ketene and isocyanates give ketone and amide respectively (**Figure 3.10**).

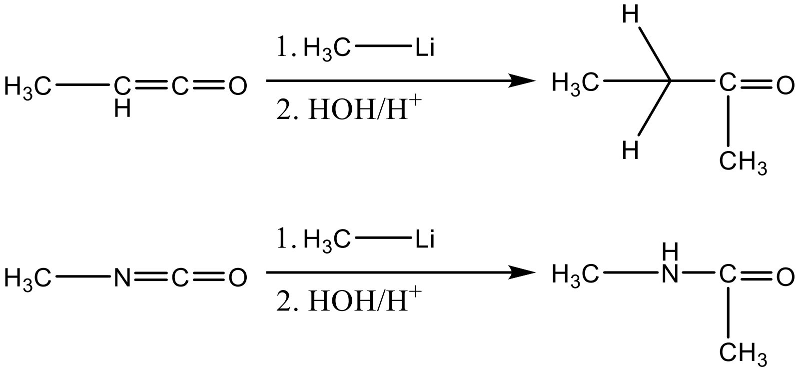


Figure 3.10. Use of organolithium compound for synthesis of ketone and amide.

3.4. ORGANOMETALLIC COMPOUNDS OF Mg: SYNTHESIS, PROPERTIES, STRUCTURE, BONDING AND USES

3.4.1. Synthesis of organomagnesium compounds

Organomagnesium halides were discovered by the French chemist Victor Grignard in 1900. Synthesis of Grignard reagents can be done by reacting magnesium and alkyl halides in ether solvents to form solutions of alkylmagnesium halide (**Figure 3.11**).

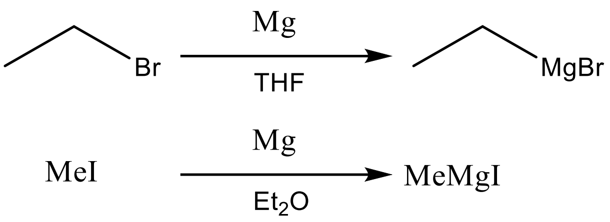


Figure 3.11. *The synthesis of Grignard reagents.*

3.4.2. Structure and bonding

The Grignard reagent only observed as dimer. R_2Mg Can be observed only in solid state when R is bulky (e.g. $Mg\{C(SiMe_3)_3\}_2$ .Grignard reagents are generally solvated, and crystal structure data shows that the Mg centre is typically tetrahedrally sited, for example, in $EtMgBr.2Et_2O$. Examples of 5- and 6-coordination have been observed where the macrocyclic ligand imposes the higher coordination number on the metal centre. Solutions of Grignard reagents may contain several species, e.g. RMgX, R_2Mg, MgX_2, $RMg(m\text{-}X)_2MgR$, which are further complicated by solvation.

3.4.3. Reactions and uses of Grignard reagents

It can act as base to by deprotonating alkynyl proton (**Figure 3.12**).

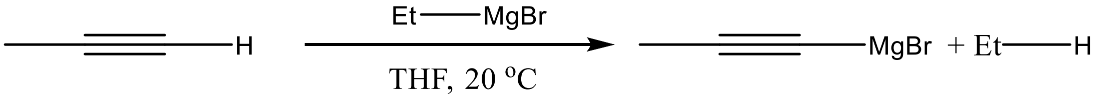


Figure 3.12. *Basic character of Grignard reagent.*

The metal derivative of alkynes can be added to carbonyl double bond; which upon hydrolysis give corresponding alcohols (**Figure 3.13**).

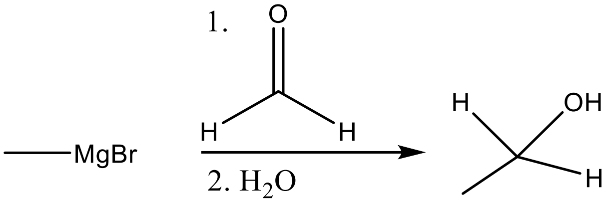


Figure 3.13. *Reaction of RMgX with ketone.*

Similarly, Grignard reagent gives addition product with carbon dioxide which upon hydrolysis gives corresponding acid (**Figure 3.14**).

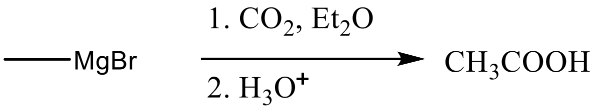


Figure 3.14. *Reaction of RMgX with carbon dioxide.*

Grignard reagents do not react normally with hindered carbonyl compounds (**Figure 3.15**).

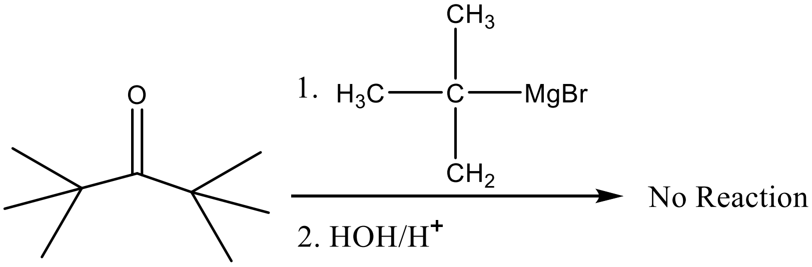


Figure 3.15. *Steric hindrance prevents the reaction of bulky RMgX reagents with bulky substrates.*

Addition to ketene and isocyanates give ketone and amide respectively (**Figure 3.16**).

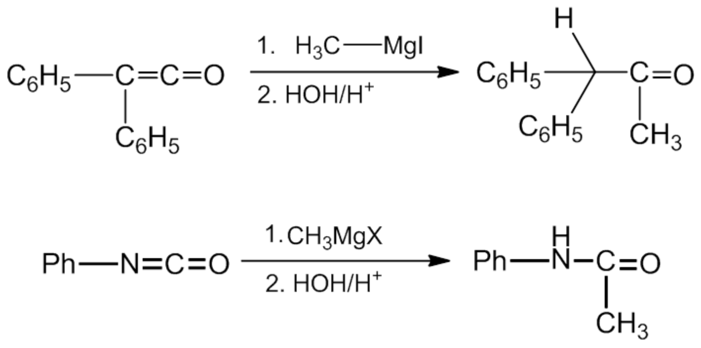


Figure 3.16. Reaction of RMgX reagents with isocyanate and ketene.

3.5. ORGANOMETALLIC COMPOUNDS OF BERYLLIUM AND CALCIUM

Beryllium alkyls and aryls are made by reaction of organopotassium with beryllium chloride in ether medium. They are hydrolysed by water and inflame in air. In the vapour phase, Me_2Be is monomeric, with a linear C-Be-C unit having Be-C bond distance of 170 pm. The solid-state structure is polymeric. However, the bonding in $BeCl_2$ can be described in terms of a localized bonding scheme, there are insufficient valence electrons available in $(Me_2Be)_n$ for an analogous bonding picture. Hence, 3c-2e bonds are predicted as described for BeH_2 (**Figure 3.17**). Higher alkyls are progressively polymerized to a lesser extent, and the tert-butyl derivative is monomeric under all conditions. Beryllium forms a ferrocene like sandwich compound with pi-electron rich ligands such as cyclopentadiene (**Figure 3.18**).

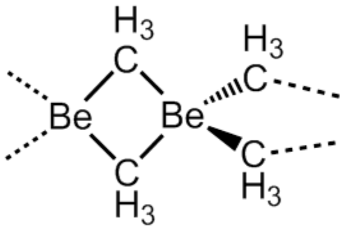


Figure 3.17. Structure of organoberyllium compounds.

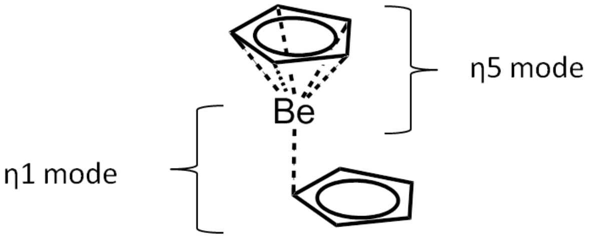


Figure 3.18. *η5 and η1 modes of bonding in sandwich type organoberyllium compounds.*

The heavier group 2 metals are highly electropositive, and metal-ligand bonding is generally considered to be predominantly ionic. While Cp_2Be and Cp_2Mg are monomeric and are soluble in hydrocarbon solvents, Cp_2Ca, Cp_2Sr and Cp_2Ba are polymeric and are insoluble in ethers and hydrocarbons.

3.6. *SUMMARY*

This chapter discussed some important concepts to understand the bonding and structure and uses of organometallic compounds of Li, Na, Mg, Be, and Ca. Synthesis structure bonding and uses of all individual compounds have been discussed.

3.7. TERMINAL QUESTIONS

3.7.1. Multiple choice type questions

1. Which of the following compound is most covalent?

(a) CH_3Li

(b) CH_3Na

(c) CH_3K

2. Which of the following compound is most reactive towards moisture?

(a) CH_3Li

(b) CH_3Na

(c) CH_3K

3. The colour of sodium naphthalene is?

Blue, Red , Orange

4. Oraganolithium compounds are prepared inwhich solvent?

(a) Water, (b) Hexane , (c)THF, (d) both b & c

3.7.2. Short answer type questions

1. Write a short note on structure and properties of organolithium.

2. Draw MO diagram of methyl lithium.

3. Why organometalic compound kept moisture free.

4. Why oraganometallic compound of Na and K are paramagnetic in nature.

5. Why organometallic compound of Na and K are colourful.

6. Draw the structure of Cp_2Mg

7. Why the σ bonding electrons are closer to sp^3 hybrid orbitals of carbon.

8. Draw the structure of $(MeLi)_4$.

9. Metalation reaction is carried in which solvent?

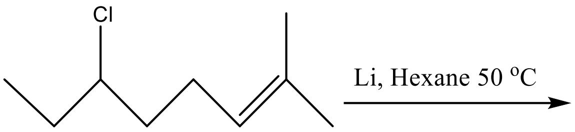
3.7.3. Long answer type questions

1. Discuss the synthesis, structure, MO diagram and uses of organolithium.

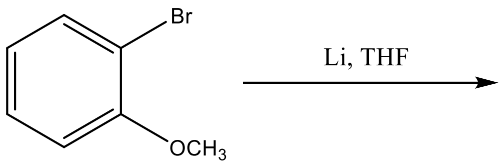
2. Discuss the synthesis, structure and reactions of Grignard reagents.

3. Complete the following reactions.

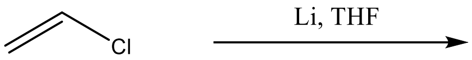
1.


Cl
Li, Hexane 50 °C

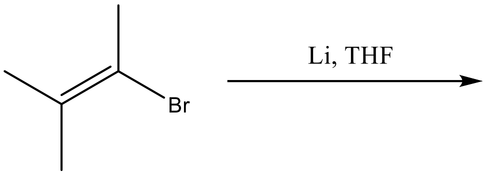
2.


Br
OCH3
Li, THF

3.


Cl
Li, THF

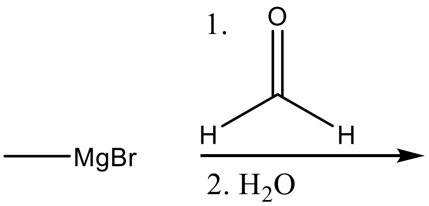
4.


Br
Li, THF

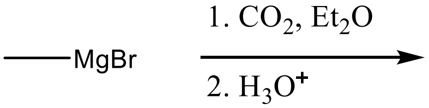
5.


H
BuLi, THF

6.


MgBr
1.
O
H
H
2. H2O

7.


MgBr
1. CO2, Et2O
2. H3O+

3.8. ANSWERS TO MULTIPLE CHOICE TYPE QUESTIONS

1. Which of the following compound is most covalent.

Answer:

(a) CH_3Li

(**Explanation:** The electropositive character increasing as Li<Na<K so K form most ionic compound

2. Which of the following compound is most reactive towards moisture?

Answer: CH_3K

(**Explanation:** The electropositive character increasing as Li<Na<K so K form most ionic compound. Further reactivity of organometallic compounds as nucleophile and as base depends mainly on electropositive character of C-M bond. Thus, more will be electropositive character higher will be the reactivity of organometallic compounds.

3. The colour of sodium naphthalene is:

Blue, Red , Orange

Answer: Blue

Explanation: This is because of more electropositive character of Na because Na easily give its electron to benzene and act as base to form ionic adduct which is colourful.

4. Oraganolithium compounds are prepared inwhich solvent?

(a) Water, (b) Hexane , (c)THF, (d) both b & c

Answer: (d) both b & C

Explanation: This is because Organolithium compounds highly basic in nature and are very reactive with water to give back reaction.

3.9. REFERENCES AND FURTHER STUDIES

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Block I: Stereochemistry and Bonding

UNIT 4 ALKYLS AND ARYLS OF TRANSITION METALS

CONTENTS

4.1. OBJECTIVES

The objectives of this unit are to introduce you with the synthesis, properties, structure, bonding and uses of organometallic compounds of transition metals. Each organometallic compound with its special reactivity, method of synthesis and uses has been described. You will understand the role played by ligands in stabilizing the organometallic compounds and certain factors which destabilize these compounds.

4.2. INTRODUCTION

Organometallic chemistry is the chemistry of compounds containing metal-carbon bonds. Metal carbonates and metal carboxylates are not counted as organometallic compounds because they do not have metal-carbon bonds. Metal cyanides and metal carbides have metal-carbon bond but they are not organic compounds so not considered as organometallic compounds. The organometallic chemistry of the d and f blocks has been developed much more recently. In nineteenth century, few d-block organometallic compounds were synthesized and partially characterized. One example is prepared by W.C. Zeise in 1827, with the first metal carbonyls. Later on in 1868, $[PtCl_2(CO)_2]$ being reported by P. Schutzenberger. The next major discovery was tetracarbonylnickel, which was synthesized by L. Mond, C. Langer, and F. Quinke in 1890. The discovery of the remarkably stable organometallic compound ferrocene, $Fe(C_5H_5)_2$, occurred in 1951 when IR and NMR techniques were available. The ‘sandwich’ structure of ferrocene was soon correctly inferred from its IR spectrum and then determined unambiguously by X-ray crystallography.

In general, the distinctions between the coordination compounds and organometallic compounds are: *1.* Coordination complexes normally are charged, with variable d-electron count, and are soluble in water; *2.* While organometallic compounds are often neutral, with fixed d-electron count, and are soluble in organic solvents such as tetrahydrofuran. Most organometallic compounds have properties that are much closer to organic compounds than inorganic salts, with many of them having low melting points.

Metal alkyls and aryls are very simple organometallic compounds. Their transition metal complexes came to be known somewhat later.

4.3. TRANSITION METAL ALKYLS AND ARYLS

Metal alkyls are formed by bonding between metal and alkyl radicals however, metal aryls are formed by bonding between metal ion and aryl radical. Transition metal alkyls play an important role in numerous organic synthesis reactions. Lithium alkyl compounds are one of the most widely used organic reagents. The advent of organometallic chemistry was rather dramatic when a cadet accidently synthesized very foul smelling $Me_2As\text{-}O\text{-}AsMe_2$ from As_2O_3 and CH_3COOK. In another incident Edward Frankland wanted to synthesize free ethyl radicals from metallic zinc and ethyl iodide. However, instead of the desired radicals, he obtained a colorless liquid which was found out to be diethyl zinc. Thus, $ZnEt_2$ is the first organometallic compound synthesized and Frankland is known as the father of organometallic chemistry. Later it was Victor Grignard who discovered alkyl magnesium halide (RMgX) compounds and known as the Grignard reagent.

4.3.1. Stability and bonding

The stability and reactivity of a metal complex depends on the number and type of coordinating ligands. The ligands can bind to metal in various bonding modes. They may be only sigma donor type or if they are capable of forming multiple bonds, they may be σ donor/π acceptor type. Alkyls can also bridge two metals centres which is well established in Al alkyl complexes, eg. Al_2Me_6. The various bonding modes in metal alkyls are depicted in **Figure 4.1** below.

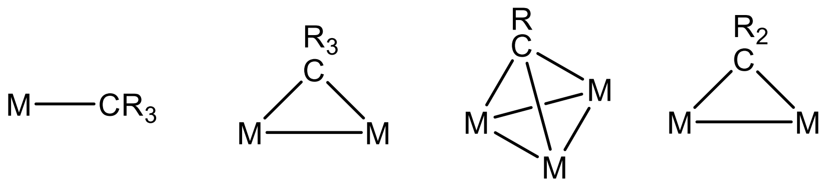


Figure 4.1. *Various bonding modes in metal alkyls*

On the basis of their stability and the phenomenon leading to their decomposition, metal alkyls can be classified under following heads and their salient features are also discussed.

4.3.2. Alkyls of early transition metals

Alkyls of early transition metals such as Ti or Zr are very air and moisture sensitive but moving right and down the periodic table, the M–C bond becomes much stable and less reactive. The overall stability of the alkyl complexes also depends upon the inherent stability of the alkyl group attached. For example, as we move from sp^3 CH_3^- to sp^2 $C_6H_5^-$ to sp hybridized $RC{\equiv}C^-$; the lone pair of the anion is stabilized by increasing '*s*' character and hence, reactivity decreases.

Much difficulty was found in the synthesis of stable transition metal complexes with *d* block metals as compared to the main group metal alkyl complexes. It was found that the difficulty arose from the existence of several decomposition pathways which made the M–C bond in transition metal-alkyls unstable. Since, the metal carbon bond in these compounds are strong enough having E = 30-65 kcal/mol, the instability might be due to kinetic factors rather than thermodynamic factors. Thus, if we know the factors causing thermodynamic instability, they can be countered by making certain changes in the structure of the organometallic complex. This is much easier to handle than increasing the bond strength if the instability was due to kinetic factors. Here, we first discuss the factors causing thermodynamic instability in these complexes.

4.3.2.1. β-Elimination

β-Elimination is the major factor behind the decomposition of metal alkyls into hydridometal alkene complex. For β-elimination to occur, the following conditions should be fulfilled:

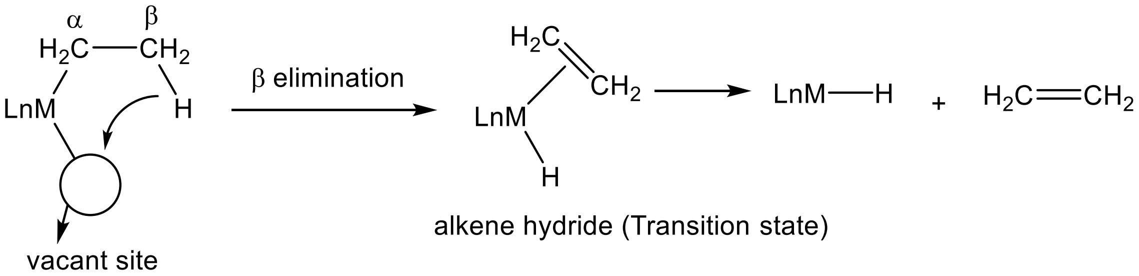
i) The β-carbon of the complex should bear a β-hydrogen substituent.

ii) The orientation of the M–C–C–H should be nearly coplanar so that the β-hydrogen is in proximity with the metal atom.

iii) The metal should have a vacant site for interacting with the hydrogen atom. The term vacant site has a wider meaning than simply implying at the gap in the coordination sphere of the metal atom to accommodate the incoming ligand. The metal must also have an empty orbital to accept the β-H or to say a pair of electrons which will make up the β C–H bond. So, the product alkene hydride has 2e$^-$ more than the alkyl starting material.

iv) The phenomenon of β-elimination is found to be more prominent in case of d^2 system than in d^0 and main group metal alkyls.

Factors (i) and (iii) play an important role in the generation of metal hydride from metal alkyl. Thus, the overall geometry should be such that the vacant site on the metal should be *cis* to the -R group on the metal and M–C–C–H in the ligand should be coplanar. The mechanism is concerted that is the breaking C–H bond and formation of M–C and M–H bonds occur simultaneously (**Scheme 4.1**).



Scheme 4.1. *Schematic reperesentation of β elimination*

Some main group alkyls also show elimination but the process is much slow. This is because the *d*-block metals stabilize the transition state. Sometimes β-elimination can be reversible as shown in example below (**Figure 4.2**).

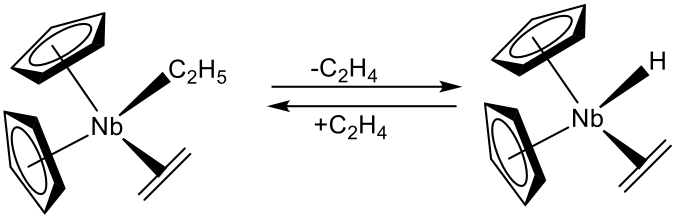


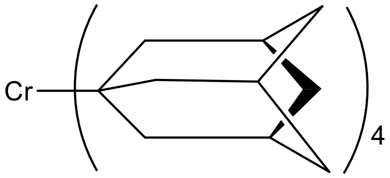
Figure 4.2. *Nb complex as an example of reversible β-elimination*

4.3.2.2. Stable alkyls: blocking β-elimination

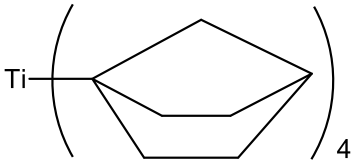
To have stable transition metal alkyls, the phenomena of β-elimination can be blocked by following ways;

1. Using alkyls having no β-hydrogen. Examples: $W(Me)_6$, $Ti(CH_2Ph)_4$, $Pt(C\equiv CCF_3)_2L_2$, $TaCl_2(CH_2CMe_3)_3$, $C_2F_5Mn(CO)_5$ etc.

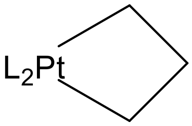
2. Alkyls in which β-hydrogen is unable to reach the metal centre due to the bulk of the ligand or the geometry of the ligand is such that it hinders proximity between β-hydrogen and metal. eg. $PtH(C\equiv CH)L_2$, $PdPh_2L_2$, $Cr(CMe_3)_4$, $Cr(CHMe_2)_4$



$[Cr(1\text{-adamantyl})_4]$



$Ti(6\text{-norbornyl})_4$



$L_2Pt(CH_2)_3$

3. Alkyls having structure such that the M–C–C–H unit cannot become syn-coplanar.

4. Metal alkyl having 18 electrons with firmly bound ligands (see cobalt complex below) will not dissociate easily to generate an open coordination site and hence, the phenomena of β-elimination can not occur. In the Ti(IV) complex as depicted below, there are no *d* electrons that is d^0 configuration at the metal centre makes β-elimination extremely slow (**Figure 4.3**).

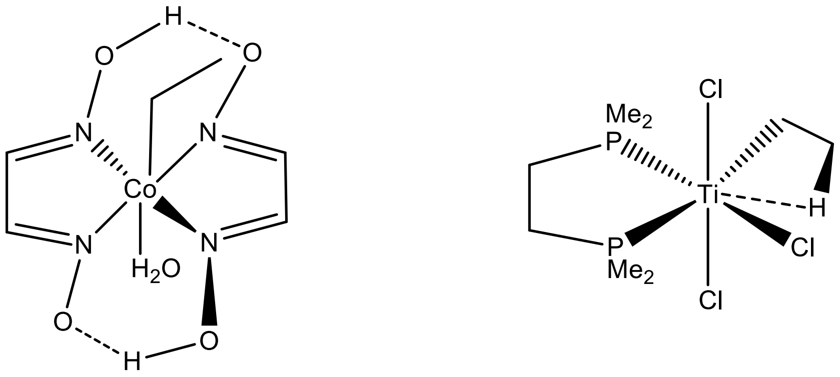


Figure 4.3. *Co complex,example of an 18 electron system; Ti(IV) complex example of a* d^0 *system*

4.3.3. Agostic alkyls

Intramolecular interaction (weak bonding) of C–H proton with metal centre is known as agostic interaction. In certain metal alkyl complexes, it appears that β-elimination should occur however, they do not undergo the process. One such example is the $Ti(PMe_2)_2(CH_2CH_3)Cl_3$. Here, the β C-H bond appears to approach the metal effectively for β-elimination but the reaction does not occur. It happens because d^0 Ti has no electron density for back donation into σ* orbital of the C–H bonds. This back donation is important for breaking C–H bond similar to the process of oxidative addition. Agostic interaction of C–H proton with the metal centre also imparts stability to the complex having a vacant coordination site. Thus, we now know that for β-elimination, we not only need a vacant $2e^-$ site on *d* orbital (an empty d orbital) but we also need a filled *d* orbital (an available electron pair) for breaking C–H bond. Most common organometallic reactions require a σ acidic and π base bifunctional character. Transition metals with their partially filled d orbitals fulfill these conditions and hence, give β-elimination reactions readily.

4.3.4. Reductive elimination

Another very common decomposition pathway shown by metal alkyls is reductive elimination (**Figure 4.4**). This results in the decrease of electron count and oxidation state by two. This phenomena can occur in any metal alkyl (d^0 or $18e^-$) in which the metal can exist in the oxidation state two units lower than that in the original complex. Metal alkyl complexes having a halide functional group do not undero reductive elimination because the equilibrium lies on the left in the reaction due to their thermodynamic stablility.

$$\underset{18e}{L_nM(Me)X} \xrightarrow{\text{red. elimination}} \underset{16e}{L_nM + MeX}$$

If X=H, then reductive elimination is kinetically facile and thermodynamically favourable. If X=CH_3, the elimination may still occur but it is not very favourable kinetically. The elimination reaction is most favourable when X=H because H has only 1s electrons which are bonding and capable of making or breaking bonds in any direction in the transition state. The CH_3 has sp^3 orbitals directed in space which may not be favourably oriented to give efficient overlap in the transition state.

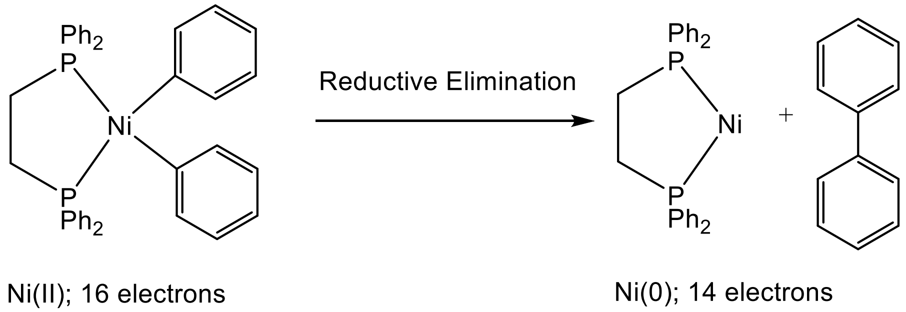


Figure 4.4. *An example of reductive elimination*

4.3.5. Halide elimination

Similar to β-elimination of H, metal alkyls having halide substituents may also undergo β-elimination of halide. Fluoro alkyls of early transition metals, lanthanides and actinides are not very stable due to high M–F bond strength undergo β-elimination of halide. However, late transition metals have weaker M–F bond and form stable fluoro alkyls. The M–C bond strengths are very high. CF_3 acts as π acceptor through the σ* orbitals of the C–F bond which contributes to the strengthening of M–C bond for the π basic late transition metals. Eg. C_6F_5 forms very stable alkyls with late transition metals. Here π* orbitals act as electron acceptor.

4.3.6. Stability from bulky substituents

It has been well known that bulky substituents can be used to stabilize several kinds of metal complexes with organic ligands ranging from alkyls to carbenes. Decomposition pathways occuring through association of the organometallic complex with solvent or with another molecule of the complex are also known specially with 16e$^-$ metals. These can be suppressed by introducing bulky coligands. eg. The diphenyl nickel(II) complex is less stable than its p-tolyl analogue (**Figure 4.5**). This is because the square planar Ni(II) complex is more vulnerable to attack from other species in the 'z' direction perpendicular to the plane of the molecule. Bulky alkyl groups such as adamantyl, norbornyl, neopentyl ($–CH_2CH_3$) or trimethylsilylmethyl ($–CH_2Si(CH_3)_3$) are commonly used in organometallic chemistry.

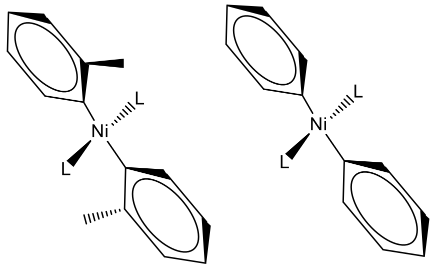


Figure 4.5. *Structure of diphenyl nickel(II) and p-tolyldiphenyl nickel(II) complex*

The above listed reasons inhibit β-elimination however, there is sometimes possibility of α-elimination. This leads to the formation of carbenes having M=C bonds. For example, in thermal decomposition of Ti(CH_2*t*-Bu)$_4$, the first step is α-elimination leading to the formation of Ti(=CH*t*-Bu)(CH_2*t*-Bu)$_2$. The synthesis of complex Ta(CH_2*t*-Bu)$_5$ intead led to the formation of carbene complex t-Bu(CH)=Ta(CH_2t-Bu)$_3$.

4.4. SYNTHESIS OF METAL ALKYLS

4.4.1. Metathesis

Reaction of metal halides with organomagnesium, organolithium, organotin, organozinc and organoaluminium reagents. Grignard or organolithium reagents react with metal halide or cationic metal complex to give an alkyl usually by nucleophilic attack on the metal. Transfer of alkyl group from one metal to another transition metal is known as transmetalation.

$$ZrCl_4 + 4\ PhCH_2MgCl \xrightarrow{Et_2O} Zr(CH_2Ph)_4$$

$$WCl_6 + LiCH_3 \longrightarrow W(CH_3)_6 + LiCl$$

$$NbCl_5 + Zn(CH_3)_2 \longrightarrow Nb(CH_3)_2Cl_3 + ZnCl_2$$

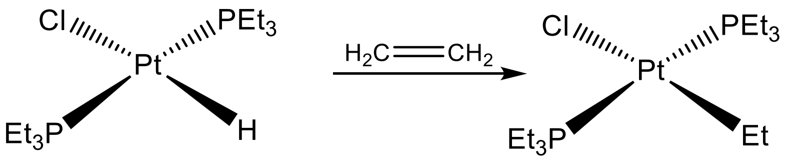
4.4.2. Electrophilic attack on metal

$$Mn(CO)_5^- \xrightarrow{CF_3COCl} CF_3COMn(CO)_5 \xrightarrow{-CO} CF_3Mn(CO)_5$$

$$Mn(CO)_5^- \xrightarrow{CH_3I} CH_3Mn(CO)_5 + I^-$$

4.4.3. Alkene insertion or hydrometallation

In this type of reaction insertion takes place between metal hydride and alkene. They are useful in certain homogeneous catalytic processes.



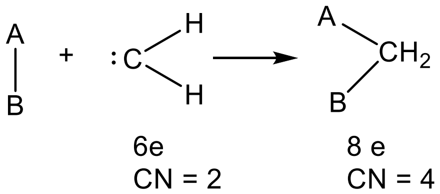
4.4.4. Oxidative addition

In the process of oxidative addition, a A–B bond is broken followed by insertion of metal fragment L_xM into A–B bond. AB could be any group such as CH_3–H, H_2, RCO–Cl, CH_3–I etc. Thus, if ML_n has M in zero oxidation state, coordination number (CN) is ‘n’ and has 16 electrons, the complex after insertion of AB will have M in +2 oxidation state, coordination number of ‘n+2’ and becomes a 18 electron system.

$$IrCl(CO)(PPh_3)_2 \xrightarrow{CH_3I} MeIrCl(CO)(PPh_3)_2$$

$$Pt(PPh_3)_4 \xrightarrow{CH_3I} CH_3PtIL_2$$

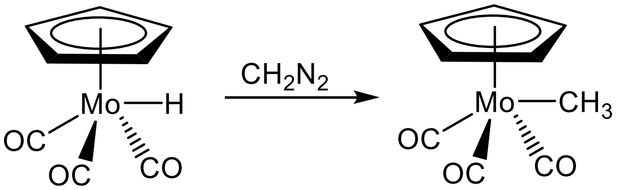
The insertion of AB is analogous to some carbene insertion such as CH_2 into C–H, Si–H and O–H bonds. This can be understood on the basis of isolobal principle.



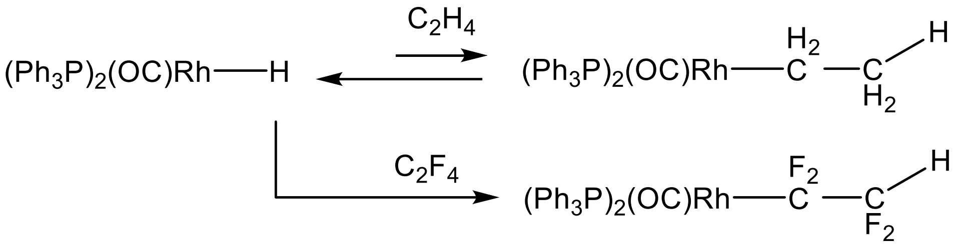
4.4.5. Insertion

The process of insertion is useful in making an alkyl from an alkene and metal hydride. Olefin insertion is the reverse of β-elimination.

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

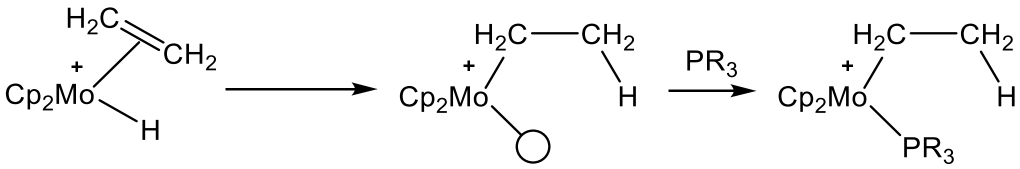


As we had mentioned earlier that alkyls having β-hydrogen are kinetically unstable and it might look improbable to make alkyls in this way. Thus, it is observed that usually a small equilibrium concentration of alkyl is obtained through insertion reaction. This amount is enough to help a catalytic reaction to proceed if the alkyl formed is trapped rapidly by some method. For example, in catalytic hydrogenation, the alkyl group is trapped by reductive elimination with a second hydride to give the product alkane. On the contrary, if the alkene is a fluorocarbon, the product obtained from insertion is fluoroalkyl which in turn is thermodynamically very stable (as mentioned earlier). Thus, the C_2H_4 insertion undergoes reversibly whereas C_2F_4 insertion product forms irreversibly because of high M–C bond strength in the latter case (**Scheme 4.2**).



Scheme 4.2. *Depiction of difference in insertion reaction when done with C_2H_4 and C_2F_4*

Another way to capture alkylmetal complex is to fill the vacant site on the metal that is formed during insertion with another ligand as depicted in **Scheme 4.3** below:



Scheme4.3. *Depicting capturing alkyl metal complex by using a different ligand at the vacant site generated on metal.*

Oxidative addition can be viewed as insertion of LnM into A–B, but the term "insertion" in organometallic chemistry is reserved for insertion of ligand into a M–X bond.

4.5. ORGANOCOPPER COMPOUNDS IN ORGANIC SYNTHESIS

Organocopper complexes are the class of organometallic compounds in which copper is bonded to the carbon atom. The isolation of a phenyl copper compound although impure from phenyl Grignard reagent and copper iodide can be called as the start of organocopper chemistry. The importance of organocopper complexes in synthetic organic chemistry was highlighted by Gilman in 1936. It was observed that catalytic amounts of organocopper reagents favor 1,4-addition over 1,2-addition in the reaction between Grignard reagents and α, β-unsaturated ketones gave impetus to further interest and development of these reagents. In present time, organocuprates are the most frequently used reagents in synthetic organic chemistry.

Oxidation states of copper: Copper belongs to group 11 along with silver and gold. Copper can exhibit following oxidation states: Cu (0), Cu (I), Cu (II), Cu (III) and Cu (IV), out of these Cu (0) and Cu (IV) species are rare. In inorganic and coordination chemistry, Cu (II) state is the most abundant. However, in the synthesis of organocopper compounds Cu (II) reduced to Cu(I). Thus, the oxidation of state of copper in organocuprates is Cu (I).

Stability of organocopper compounds: Organolithium compounds are more reactive than organocuprates. Organocopper compounds are intrinsically thermally unstable. The R in organocuprates acts as nucleophiles and attacks the various organic electrophiles.

Alkyl copper compounds decompose below 0^0 C. The stability of these compounds is generally found to follow the following order, alkyl < aryl ≈ alkenyl < alkynyl. Thermal stability of organocopper compounds can be increased by, (i) substitution of hydrogen atoms by fluorine in the organic moiety (ii) addition of other ligands such as phosphines or amines, and (iii) use of substituents having heteroatoms which can provide additional intramolecular coordination sites to the metal. These complexes are generally found to possess linear, trigonal or T-shaped geometries however, they may be some other possible geometries too.

4.5.1. Synthesis of organocopper reagents

4.5.1.1. Gilman reagent

It is a lithium and copper containing reagent. The methods of preparation and their use in coupling reactions are depicted in **Scheme 4.4** below

$$\underset{\text{Alkyl lithium}}{2RLi} + \underset{\substack{\text{Cu(I) halide}\\ \text{(X= Cl, Br, I)}}}{CuX} \xrightarrow[]{\substack{\text{diethyl ether}\\ \text{or THF}}} \underset{\text{Lithium dialkylcuprate}}{R_2CuLi} + \underset{\text{Lithium halide}}{LiX}$$

$$\underset{\substack{\text{Lithium dialkyl}\\ \text{cuprate}}}{R_2CuLi} + \underset{\text{Alkyl halide}}{R'X} \longrightarrow \underset{\text{Alkane}}{R\text{-}R'} + \underset{\text{alkylcopper}}{RCu} + \underset{\text{Lithium halide}}{LiX}$$

$$\underset{\substack{\text{Lithium dimethyl}\\ \text{cuprate}}}{(CH_3)_2CuLi} + \underset{\text{1-Iododecane}}{(CH_3)(CH_2)_8CH_2I} \xrightarrow{\substack{\text{diethyl ether}\\ 0^{\circ}\text{ C}}} \underset{\text{Undecane}}{(CH_3)(CH_2)_8CH_2CH}$$

$$\underset{\substack{\text{Lithium diphenyl}\\ \text{cuprate}}}{(C_6H_5)_2CuLi} + \underset{\text{1-Iodooctane}}{ICH_2(CH_2)_6CH_3} \xrightarrow{\text{diethyl ether}} \underset{\text{1-Phenyloctane}}{C_6H_5CH_2(CH_2)_6CH_3}$$

Scheme 4.4. *Synthesis and uses of Gilman's Reagent*

The method has some limitations such as it works well for mostly methyl and primary alkyl halides, vinyl and aryl halides. Elimination occurs with secondary and tertiary alkyl halides.

4.5.1.2. Synthesis of homocuprate reagents

The resultant organocuprates are thermally labile and hence prepared at low temperature.

$$\underset{\text{M= Li, MgX}}{RM} + CuBr / CuI \xrightarrow[\text{- MBr / MI}]{Et_2O\text{ or THF}} R(Cu)_n \underset{}{\overset{RM}{\rightleftharpoons}} R_2CuM$$

4.5.1.3. Synthesis of heterocuprate reagents

These cuprates are thermally more stable and less prone to β-elimination.

$$RLi + Me_3SiCH_2Li + CuI \longrightarrow [(Me_3SiCH_2)CuR]\ Li$$

4.5.1.4. Higher order organocuprate reagents (Lipshutz reagents)

Cyanocuprates or Lipshutz reagents possess the reactivity of homocuprates and thermal stability of heterocuprates. The cyanocuprates are particularly useful for substitution reactions of secondary halides and epoxides.

$$\text{CuCN} + 2\ \text{RLi} \xrightarrow[-78^{o}\ \text{C to } 0^{o}\ \text{C}]{\text{Et}_2\text{O or THF}} \text{R}_2\text{Cu(CN)Li}_2$$

4.5.2. Uses of organocuprates

Organocopper compounds are used in cross-coupling reactions to form higher alkanes. Cross coupling reactions are those in which two different alkyls R and R′ couple to form a new alkane R–R′. This type of reaction is used to make new C–C bonds between alkyl groups. Organocopper reagents offer efficient methods for coupling of two different carbon moieties. Copper is less electropositive than Li and Mg thus the C–Cu bond is less polarized than Li–C or Mg–C bonds. This difference brings in the following changes in reactivity:

(i) organocopper reagents react with alkyl, alkenyl and aryl halides to yield alkylated products.

(ii) organocopper reagents are more selective and they can be acylated with acid chlorides without attacking ketones, alky halides and esters.

(iii) In reaction with α, β-unsaturated carbonyl compounds, the organocopper reagents prefer 1,4-addition over 1,2-addition.

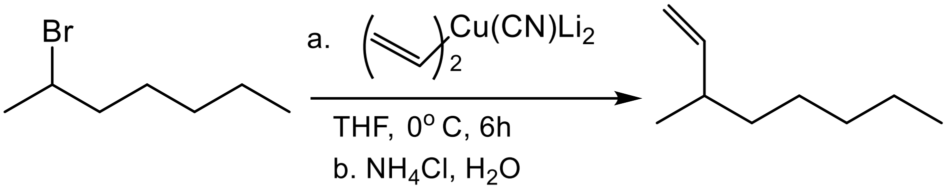
4.5.2.1. Substitution of alkyl halides

Coupling of alkyl halide with homocuprate is more economical than with heterocuprate.

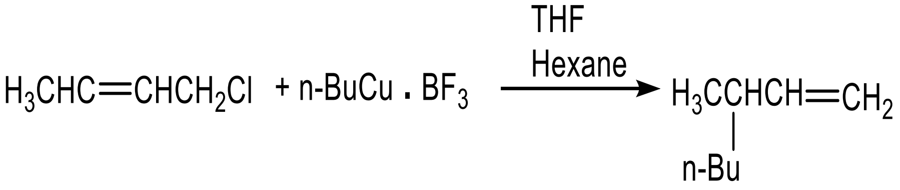
$$\text{Me}_2\text{CuLi} \xrightarrow[\text{b. H}_3\text{O}^+]{\substack{\text{a. n-C}_7\text{H}_{15}\text{I} \\ \text{Et}_2\text{O, -20}^{o}\ \text{C}}} \text{n-C}_9\text{H}_{20}$$

$$[\text{MeCuNR}_2]\text{Li} \xrightarrow[\text{b. H}_3\text{O}^+]{\substack{\text{a. n-C}_8\text{H}_{17}\text{I} \\ \text{Et}_2\text{O, rt}}} \text{n-C}_9\text{H}_{20}$$

The homocuprates have a limitation that is they do not couple well inactivated secondary halides. They readily undergo substitution reactions at primary positions. However, cyanocuprates undergo substitution reactions even at inactivated secondary carbon centres.

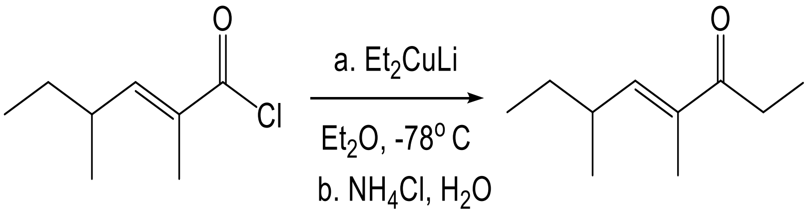


4.5.2.2. Substitution of allylic halides

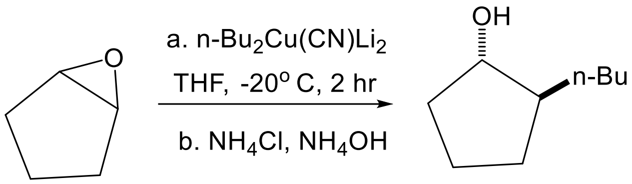


$$H_3CHC{=}CHCH_2Cl + n\text{-}BuCu \cdot BF_3 \xrightarrow{\substack{\text{THF}\\ \text{Hexane}}} H_3C\underset{\substack{|\\ \text{n-Bu}}}{C}HCH{=}CH_2$$

4.5.2.3. Acylation



4.5.2.4. Epoxide cleavage reactions



4.6. SUMMARY

The role of ligands is extremely vital in determining the stability of organometallic compounds. There are several methods to synthesize these complexes. The two main phenomena which control the stability of these compounds are β-elimination and bimolecular decomposition reactions. Thus, designing of such complexes in which these factors are minimised, can be achieved by altering the substituents and some other factors discussed above. The role of organocopper complexes is extremely widespread in synthetic organic chemistry. These complexes can be synthesized by various methods as discussed.

4.7. TERMINAL QUESTIONS

4.7.1. Short answer type questions

Q1. In which direction would you expect a late transition metal hydride to undergo insertion with $CH_2=CF_2$ to give the most stable alkyl product?

Q2. Suggest an efficient method for preparing $IrMe_3L_3$ from $IrClL_3$, LiMe, and MeCl.

Q3. Give product of the reaction between $Cp(CO)_2Fe(H)$ and 1,3-butadiene. Here Cp stands for cyclopentadiene ring.

Q4. Give product of the reaction between $Cp(CO)_3Mo(H)$ and CH_2N_2 (diazomethane). Here Cp stands for cyclopentadiene ring.

Q5. What is Gilman Reagent? Give one example

Q6. Write short note on role of bulky substituents in increasing the stability of metal alkyl/aryl complexes.

Q7. Write short note on reductive elimination

4.7.2. Long answer type questions

Q1. Discuss in brief factors causing thermal instability in transition metal alkyl complexes.

Q2. What factors are necessary for β-elimination and what factors can reduce the possibility of β-elimination in metal alkyls?

Q3. What are agostic alkyls and why don't they undergo β-elimination?

4.8. ANSWERS

4.8.1. Short answer type questions

A 1. $M{-}CF_2{-}Me$ (*σ*-acceptor substituents, especially F strongly stabilize an alkyl).

A 2. Oxidative addition of MeCl, followed by reaction of the product with LiMe, which acts as a Me− donor and replaces the Ir−Cl by Ir−Me.

A3. $Cp(CO)_2Fe(CH_2CH{=}CH{-}CH_3)$

A4. $Cp(CO)_3Mo{-}CH_3$

A5. It is a lithium and copper containing organometallic reagent. Eg. Lithium dimethylcuprate.

4.9. REFERENCES AND FURTHER STUDIES

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2. J. E. Huheey, E. A. Keiter and R. L. Keiter, (1993), "Inorganic chemistry: Principles of Structure and Reactivity", fourth ed., HarperCollins College Publishers, New York.

3. J. T. B. H. Jastrzebski and G. van Koten, (2002), "Modern Organocopper Chemistry"; Chapter 1,pp. 1-44, (N. Krause, Eds.), John Wiley & Sons, Inc.

Block II: Metal pi-Complexes and Metal Clusters

UNIT 5 METAL–π COMPLEXES – I

CONTENTS

5.1. OBJECTIVES

Objectives of this unit are to introduce you with important and basic concepts to understand the bonding and structure of inorganic metal complexes with some very important small molecules such as the carbonyl, nitrosyl, dinitrogen, dioxygen and tertiary phosphines as ligands. They are neutral ligands and are extensively used in the synthesis of inorganic complexes in conjunction with other ligands. This chapter will take you through the detailed chemistry of metal carbonyls including their electronic structure, bonding, synthesis and some applications. The chapter will also provide you with the general understanding of other mentioned neutral ligands and their inorganic complexes.

5.2. INTRODUCTION

Coordination complexes of transition metals with carbon monoxide (CO) ligand are called ‘metal carbonyls’. Technically, any coordination complex that has at least one carbon monoxide (CO) ligand in its coordination sphere is termed as metal carbonyl. Carbon monoxide is a weak Lewis base, even then it forms stable complexes with transition metals. Stability of metal carbonyls relies on the existence of back-bonding between the metal and the carbon monoxide ligand. Since, the ability of metal to participate in back bonding is directly related to availability of electron density in its orbitals, hence, the stable metal carbonyls often comprise metals in their lower oxidation states.

Metal carbonyls are used as homogeneous catalysts in organic syntheses and as precursors for the synthesis of other organometallic complexes. Mononuclear metal carbonyls, *i.e.*, those containing only one metal centre are usually colorless or pale yellow volatile liquids or solids that are flammable and toxic. Hence, skin contact, inhalation or ingestion of metal carbonyls must be avoided while in laboratory by employing adequate laboratory techniques and safety equipments.

Nitric oxide or nitrosyl (N≡O) ligand binds to metals in a very different manner than that of carbonyl. It is interesting to study the structure, bonding and catalytic reactivity of metal nitrosyl complexes. They find applications as homogeneous catalysts in dimerization reactions, olefin disproportionation and hydrogenation reactions.

Furthermore, tertiary phosphine (PR_3) ligands are one of the favorite ligands of inorganic chemists. This is because of the strong σ donor and π acceptor properties in their complexes with transition metals. The electronic and steric properties of phosphines and hence, their metal complexes can be altered as per need by varying the –R group on PR_3. They are capable of stabilizing transition metal complexes in low oxidation states and hence, constitute an important class of homogeneous catalysts.

We know that both N_2 and O_2 are present in abundance in the atmosphere and hence, they have become important raw materials for large scale industrial synthesis of compounds. In the production of ammonia through nitrogen fixation, nitrogen is reduced while reduction of oxygen gives energy. The electronic distribution, geometries and bonding modes of these molecules as ligands in metal complexes has been extensively studied and discussed in literature.

5.3. CLASSIFICATION OF METAL CARBONYLS

The metal carbonyls are a class of organometallic compounds where the metal atom is bound to the carbon atom of CO which is a small molecule acts as a neutral ligand in these complexes. There are several schemes to classify various metal carbonyls, some of which are illustrated ahead:

5.3.1. Classification on the basis of type of ligands

Metal carbonyls are classified as homoleptic or heteroleptic on the basis of type of ligands present in the coordination sphere of the metal.

5.3.1.1.Homoleptic carbonyls

The metal complexes those contain only one type of ligands are called homoleptic complexes. Hence, homoleptic carbonyls are those having only carbon monoxide (CO) molecules as ligands. For example, $Ni(CO)_4$, $Fe(CO)_5$, $Cr(CO)_6$, $Co_2(CO)_8$ etc.

5.3.1.2. Heteroleptic carbonyls

The metal complexes those contain more than one type of ligands are called heteroleptic complexes. Hence, heteroleptic carbonyls are those having carbon monoxide (CO) as well as other molecules as ligands. For example, $Ni(CO)_3(PPh_3)$, $Cr(CO)_3(NO)_2$ etc.

5.3.2. Classification on the basis of number of metal atoms

Metal carbonyls are classified as mononuclear or polynuclear on the basis of number of ligands present in the coordination sphere of the metal.

5.3.2.1. Mononuclear carbonyls

The metal carbonyl complexes those contain only one atom of metal are called mononuclear carbonyls. For example, $Ni(CO)_4$, $Fe(CO)_5$, $Cr(CO)_6$ etc.

5.3.2.2. Polynuclear carbonyls

The metal carbonyl complexes those contain two or more than two atoms of metal are called polynuclear carbonyls. For example, $Mn_2(CO)_{10}$, $Fe_2(CO)_9$, $Co_2(CO)_8$, $Fe_3(CO)_{12}$, $MnCo(CO)_4$ etc. The CO ligand can be bridging or terminal. The bridging CO has a bond order of nearly two which is similar to the carbonyl in organic compounds whereas the terminal CO has a bond order of three. The IR stretching frequency of free CO is 2143 cm^{-1}, for terminal carbonyl, it is 2125-1850 cm^{-1} and for bridging CO, it lies between 1850-1700 cm^{-1}.

Polynuclear carbonyls are further classified as homonuclear metal carbonyls or heteronuclear metal carbonyls depending on whether the complex contains only one kind of metal or more than one kind of metal. For example, $MnCo(CO)_9$ is a heteronuclear carbonyl complex because it contains two types of metals, *viz.*, Mn and Co.

5.4. PREPARATION OF METAL CARBONYL

5.4.1. From CO gas

Treatment of carbon monoxide with metals or their simple salts under the conditions of high pressure and high temperature yields corresponding carbonyl complexes. Few examples are presented below:

$$Fe \xrightarrow{CO,\ 200\ atm,\ 200°C} Fe(CO)_5$$

$$Ni \xrightarrow{CO,\ 1\ atm,\ 30°C} Ni(CO)_4$$

$$Co \xrightarrow{CO,\ 1\ atm,\ 30°C} Co_2(CO)_8$$

$$NiI_2 + 4CO \longrightarrow Ni(CO)_4 + I_2$$

$$Ni(CN)_2 + 4CO \longrightarrow Ni(CO)_4 + C_2N_2$$

5.4.2. Reductive carbonylation (reducing agent plus CO gas)

Treatment of carbon monoxide with simple metal salts in the presence of reducing agent such as hydrogen gas yields corresponding carbonyl complexes. Few examples are presented below:

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

$$3Ru(acac)_3 + H_2 + 12CO \xrightarrow{200\ atm,\ 150°C\ ,\ MeOH} Ru_3(CO)_{12}$$

$$CrCl_3(s) + Al(s) + 6CO(g) \xrightarrow{AlCl_3,\ Benzene} Cr(CO)_6(sol.)$$

$$2MnI_2 + 2Mg + 10CO(g) \xrightarrow{210\ atm,\ 25°C\ ,\ EtOEt} Mn_2(CO)_{10} + 2MgI_2$$

$$2CoS + 4Cu + 8CO(g) \xrightarrow{200\ atm,\ 200°C} Co_2(CO)_8 + 2CuS$$

$$2CoI_2 + 4Cu + 8CO(g) \xrightarrow{210\ atm,\ 25°C} Co_2(CO)_8 + 4CuI$$

$$2FeI_2 + 2Cu + 5CO(g) \xrightarrow{210\ atm,\ 25°C} Fe(CO)_5 + Cu_2I_2$$

$$2CoCO_3 + 2H_2 + 8CO(g) \xrightarrow{250-300\ atm,\ 125°C} Co_2(CO)_8 + 2CO_2 + 2H_2O$$

$$MoCl_5 + 5Na + 6CO(g) \xrightarrow{diglyme} Mo(CO)_6 + 5NaCl$$

There are some reports where CO acts as carbonylating as well as reducing agent. Few examples:

$$OsO_5 + 5CO(g) \xrightarrow{350\ atm,\ 250\ °C} Os(CO)_5 + 2O_2$$

$$Re_2O_7(s) + 17CO(g) \xrightarrow{350\ atm,\ 250\ °C} Re_2(CO)_{10}\,(s) + 7CO_2$$

5.4.3. From iron pentacarbonyl

The carbonyl group in iron pentacarbonyl are labile and can be replaced by chloride to give a different metal carbonyl.

$$MoCl_6(s) + 3Fe(CO)_5 \xrightarrow{EtOEt,\ 110\ °C} Mo(CO)_6 + 3FeCl_2 + 9CO$$

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

5.4.4. Dinuclear carbonyls from mononuclear carbonyls

Photolysis or thermolysis of mononuclear carbonyls yields bi- and multimetallic carbonyls such as diiron nonacarbonyl ($Fe_2(CO)_9$). On further heating, the products decompose eventually into the metal and carbon monoxide.

$$2FeCO_5 \xrightarrow{h\vartheta} Fe_2(CO)_9 + CO$$

$$2OsCO_5 \xrightarrow{h\vartheta} Os_2(CO)_9 + CO$$

Synthesis of higher osmium carbonyl clusters such as $Os_4(CO)_{13}$, $Os_6(CO)_{18}$ up to $Os_8(CO)_{23}$ can be achieved from the thermal decomposition of triosmium dodecacarbonyl ($Os_3(CO)_{12}$).

5.4.5. Mixed-metal carbonyls by salt metathesis reaction

$$4\ KCo(CO)_4 + [Ru(CO)_3Cl_2]_2 \longrightarrow 2Ru(Co)_2(CO)_{11} + 4KCl + 11CO$$

5.5. PROPERTIES OF METAL CARBONYLS

5.5.1. General properties

Metal carbonyls are coordination complexes of transition metals with carbon monoxide. They are also classified as organometallic compounds since they contain a metal-carbon bond. Most metal carbonyls are volatile liquids or solids. They are colorless or pale yellow and are flammable. Vanadium hexacarbonyl (17 e metal carbonyl) is a bluish-black solid. Di- and polymetallic carbonyls are darker in color. Triiron dodecacarbonyl ($Fe_3(CO)_{12}$) crystals are deep green in colour. Metal carbonyls are soluble in carbon tetrachloride, benzene, acetone, ether and glacial acetic acid.

5.5.2. Toxicity

They are toxic by inhalation, ingestion or skin contact. They carbonylate haemoglobin to form carboxyhaemoglobin and it loses its ability to bind oxygen and form oxyhaemoglobin. They are carcinogenic over long-term exposure.

5.5.3. Magnetic properties

All metal carbonyls except vanadium hexacarbonyl are diamagnetic. Metals having even atomic number form mononuclear carbonyls having all paired electrons. Dinuclear metal carbonyls comprising of metals with odd atomic number have metal-metal bonds that utilize the unpaired electrons.

5.5.4. Thermodynamic stability

Metal carbonyls are thermodynamically unstable. When exposed to air, they undergo oxidation at different rates. Some are oxidized in air when heated.

5.6. STRUCTURE AND BONDING IN METAL CARBONYLS

It is important to notice that there are not many ligands those form homoleptic complexes like the carbon monoxide. Moreover, carbon monoxide is a neutral ligand with weak Lewis basic character that forms stable complexes with metals, usually in their low oxidation state. In order to understand the structure of and the nature of bonding in metal carbonyls, it is very important to understand the structure of carbon monoxide. **Figure 5.1** represents a schematic molecular orbital diagram for the carbon monoxide molecule, where the middle shaded part represents the molecular orbitals of the CO molecule whereas 2s and 2p orbitals of carbon and that of oxygen are presented on the left and right hand side of the central shaded portion respectively. Note that the 2s and the 2p orbitals of oxygen are drawn at slightly lower energy levels than the respective orbitals of oxygen atoms which is attributed to the difference in their electronegativity. It is evident from the **Figure 5.1** that the highest occupied molecular orbital (HOMO) of the CO is closer to the 2p orbitals of the carbon. Hence, the CO ligand coordinates through the molecular orbital (MO) primarily localized on the carbon atom which suggests that the carbon monoxide ligand connects through its carbon atom with the metal centre. Additionally, the MO diagram also reveals that there are vacant antibonding molecular orbitals (top three anti bonding orbitals) available on the CO molecule which may accept electron density from suitable electron rich species.

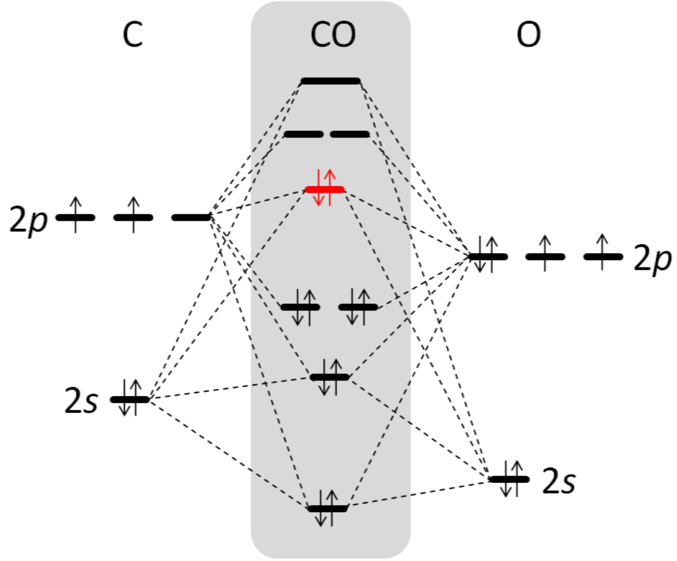


__Figure 5.1.__ Molecular orbital (MO) diagram of carbon monoxide molecule.

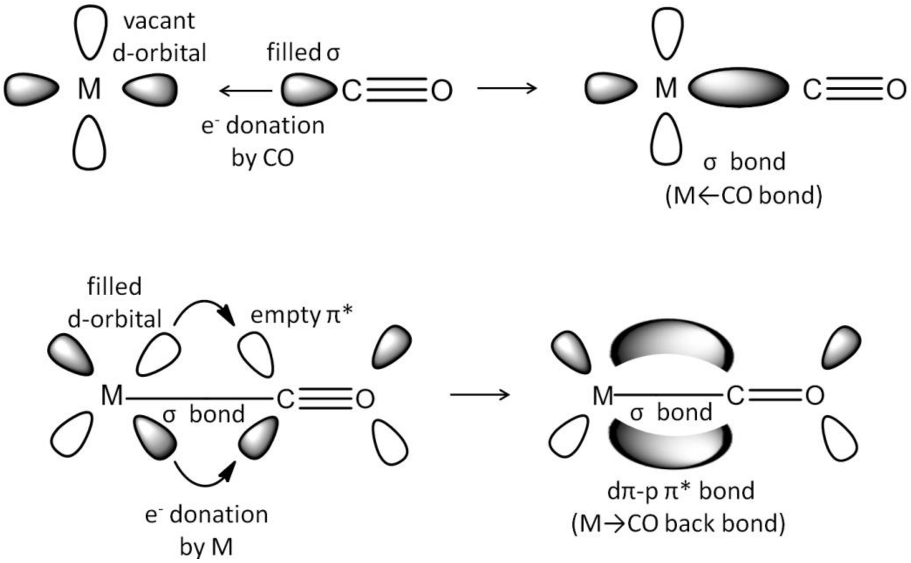


__Figure 5.2.__ Molecular orbital (MO) diagram of carbon monoxide molecule.

Figure 5.2 depicts the formation of sigma and pi bonds between metal atom or ion and a carbonyl ligand. The upper half of the figure shows that the overlapping of HOMO localized on carbon with a suitable vacant orbital present on the metal centre, resulting in a L to M sigma bond. It is interesting fact that the formation of ML sigma bond allows close proximity between the vacant anti bonding orbitals of carbonyl molecule and the filled d-orbitals available with metal center. Such proximity facilitates transfer of electron density from filled d-orbitals to the vacant ligand antibonding orbitals resulting in the formation of M to L back-bond. Transfer of any electron density from ligand to metal causes strengthening of L to M bond and makes metal centre rich in electron density which in turn allows transfer of more electron density from filled d-orbitals to the vacant anti-bonding orbitals situated on ligand and thus, resulting in the strengthening of M to L back-bond. This phenomenon is called 'synergistic effect' and eventually causes mutual strengthening of L to M bond as well as M to L back-bond. M to L back-bond is an example of dπ-pπ* overlap attributable to the nature of overlapping orbitals.

5.6.1. Effective Atomic Number (EAN) Rule

The rule states that "total number of electrons on the zero valent metal atom including those gained after sigma donation of electron pairs by CO molecules becomes equal to the atomic number of the next closest inert gas."

Thus,

$$EAN = a + 2b$$

Where *a* equals to the total number of electrons or atomic number of the metal atom and *b* equals to the total number of sigma bonds between metal atom and CO groups or ligands present in the complex. It is multiplied by 2 since, each CO or other ligand contributes to 2 electrons. Some examples are as follows:

(i) $Cr(CO)_6$: 24 + 2x6 = 36 [Kr]

(ii) $Fe(CO)_5$: 26 + (2x5) = 36 [Kr]

(iii) $W(CO)_6$: 74 + (2x6) = 86 [Rn]

(iv) $Ru(CO)_5$: 44 + (2x5) = 54 [Xe]

(v) $Mn_2(CO)_{10}$: (25x2) + (2x10) + 2 (for 1 M-M bond contributes 2 e) = 72; EAN of each metal atom = 72/2 = 36 [Kr]

Remember that the mononuclear metal carbonyl having odd atomic number do not follow EAN rule. Examples:

(vi) $V(CO)_6$: 23 + (2 x 6) = 35

(vii) $Mn(CO)_5$: 25 + (2 x 5) = 35

(viii) $Co(CO)_4$: 27 + (2 x 4) = 35

5.6.2. The 18 Electron Rule

The 18 electron rule was postulated to categorize stable metal complexes. Those complexes which have 18 outer shell electrons or where the sum of *d* electrons, electrons donated by ligands and overall charge on the complex is equal to 18 are considered to follow this rule and are expected to be stable in nature. However, it has been found in several examples which do not follow the rule and several exceptions do exist. Complexes with 14 or 16 electron count were also found to be stable. The stability of an octahedral complex weather following this rule or not can be rationalized by looking into their molecular orbital description. The most stable arrangement will correspond to a fully occupied bonding molecular orbitals (a_{1g}, t_{1u}, e_g and t_{2g}) and vacant anti bonding molecular orbitals (**Figure 5.3**). Thus, these nine MOs will require a total of eighteen electrons. The antibonding orbitals will be vacant when the energy gap (Δ_o) between the highest bonding MO and the lowest antibonding MO is large which makes occupation of antibonding e_g* unfavorable. Such complexes will follow the 18 electron rule, particularly the second and third row transition metals, which do not have more than 18 electrons beyond the core MOs. The largest Δ_o splitting is also consistent with strong σ donor and π acceptor ligands such as CO, PF_3, olefins and arenes which are located at the upper end of electrochemical series.

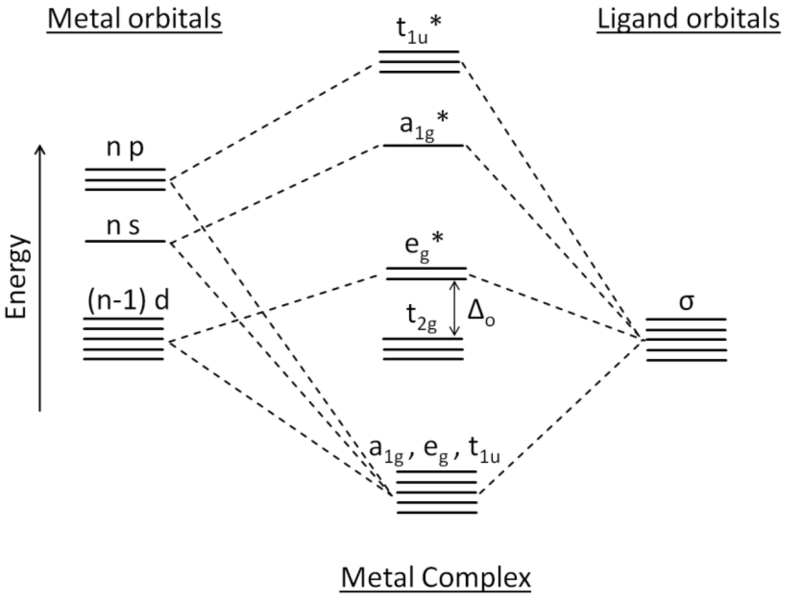


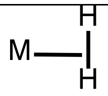
***Figure 5.3**. Simplified MO diagram for an octahedral transition metal complex depicting sigma interactions only.*

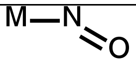
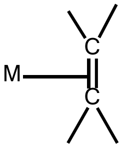
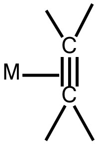
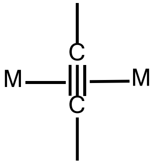
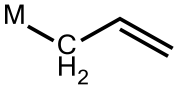
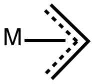
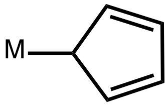
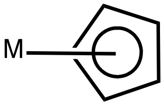
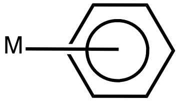
There are complexes having less than 18 electrons where the ligands (such as Cl, F) do not contribute in extra stabilization of t_{2g} orbitals by π bonding. Example: $[WCl_6]^{2-}$ has 14 electrons, $[TcF_6]^{2-}$ has 15 electrons, $[OsCl_6]^{2-}$ has 16 electrons and $[PtF_6]^{-}$ has 17 electrons. We know in spectrochemical series CO and NO lie at the higher end as they are good π acceptors and hence stabilize the t_{2g} orbitals. This in turn increases the (Δ_o) value and hence, octahedral complexes with CO and NO ligands are mostly found to follow the 18 electron rule. Generalizing, we can say that electron rich or metals in low oxidation states and ligands that are good π acceptors adhere to the 18 electron rule. Having more than 18 electrons in certain complexes can be attributed to small Δ_o and so occupation of e_g* orbitals is probable. Examples: $\{[Co(H_2O)_6]^{2+}\}$ has 19 electrons, $\{[Ni(en)_3]^{2+}\}$ has 20 electrons, $\{[Cu(NH_3)_6]^{2+}\}$ has 21 electrons and $\{[Zn(NH_3)_6]^{2+}\}$ has 22 electrons.

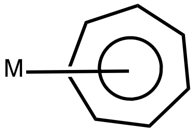
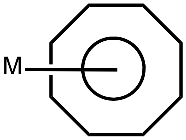
5.6.3. Counting of electrons in complexes

To count the number of electrons in the complexes, there are two popular methods *viz.* neutral atom method and oxidation state method. Here, we will be discussing only the neutral atom method as it is easier to follow. For this, we need to know the number of electrons each ligand donates to the metal in the complex (**Table 5.1**). Metal is taken as in *zero oxidation* state in this method and overall charge on the complex is also considered; an overall positive charge say *+x* will be subtracted whereas a negative overall charge of say *–y* will be subtracted from the total electron count.

Table 5.1. *Electrons donated by various ligands.*

	Ligand	**Electrons Donated**
1.	Carbonyl (M–CO)	2
2.	μ–CO (Bridging Carbonyl) (M–CO–M)	2
3.	Carbene ($M=CR_2$)	2
4.	Phosphine ($M–PR_3$)	2
5.	μ Phosphide ($M–PR_2–M$)	3
6.	Amine ($M–NR_3$)	2
7.	Amide (($M–NR_2$)	1
8.	μ Amido ($M–(NR_2)–M$)	3
9.	Hydrogen (M–H)	1
10.	Dihydrogen; 	2
11.	Dinitrogen; (M–N=N)	2
12.	Isocyanide; (M–CNR)	2
13.	Halide (M–X)	1
14.	μ Halide (M–X–M)	3
15.	Alkyl (M–R)	1
16.	Aryl (M–Ar)	1
17.	Thiolate (M–SR)	1
18.	Alkoxide (M–OR)	1
19.	μ Alkoxide (M–(OR)–M)	3

20.	Acyl (M–C(O)–R)	1
21.	Nitrosyl (Linear; M–N≡O)	3
22.	Nitrosyl (Bent) 	1
23.	 Alkene (sidewise); η^2	2
24.	 Alkyne (sidewise); η^2	2 or 4 if it functions as π electron donor
25.	μ-alkyl (M–CR_3–M)	1
26.	 μ-alkyne(bridging);	4
27.	 η^1allyl	1
28.	 η^3allyl	3
29.	 η^1 cyclopentadienyl	1
30.	 η^5cyclopentadienyl	5
31.	 η^6benzene	6

32.	 η^7 cycloheptatrienyl	7
33.	 η^8cyclooctatetraenyl	8

Note: μ = Indicates bridging ligand; η = indicates hapticity of the ligand

5.6.4. Determination of total number of M-M bonds in a cluster

First determine the total number of valence electrons in the complex that is the number of valence electrons in the metal plus the electrons from each ligand plus the charge (**Table 5.2**). Say it comes out to be '*x*'. Now, suppose '*n*' is the number of metals in the complex. Subtract '*x*' from *n**18 *i.e.* (*n**18)-*x*; suppose the value comes out to be '*y*'. The '*y*' divided by 2 *i.e.* (*y/2*) gives the number of *metal-metalbonds* in the complex. '*x*' divided by '*n*' gives the number of *electronsper metal atom*. Now if this number comes out to be 18 it implies there are no metal-metal bonds; for 17, there will be one metal-metal bond and if it is 16, there will be two metal-metal bonds and so on.

Table 5.2. *Stepwise determination of number of M-M bonds*

Example	**number of metal atoms (n)**	**Total Valence Electrons (x)**	**y = (n*18)-x**	**M-M bonds (y/2)**	**No of bonds per metal atom (18 – x/n)**	**Theoretical Structure**
$Fe_3(CO)_{12}$	3	8X3 + 12*2 = 48	(18*3)-48 = 6	3	18 - 48/3 = 2	Fe—Fe \ / Fe
$[\eta^5\text{-CpMo(CO)}_2]_2$	2	(5+6+4)*2 = 30	(18*2-30) = 6	3	18 - 30/2 = 3	Mo≡Mo
$(\eta^4\text{-}C_4H_4)_2(Fe_2(CO)_3$	2	4*2 + 8*2 + 2*3 = 30	(18*2-30) = 4	2	18 - 30/2 = 3	Fe≡Fe

Note: asterisk mark (*) represents mathematical operation of multiplication.

The 18 electron rule allows predicting the number of M-M bonds; it however does not give any information about bridging or terminal carbonyl. Structures of some common metal carbonyl complexes are depicted in **Figure 5.4**.

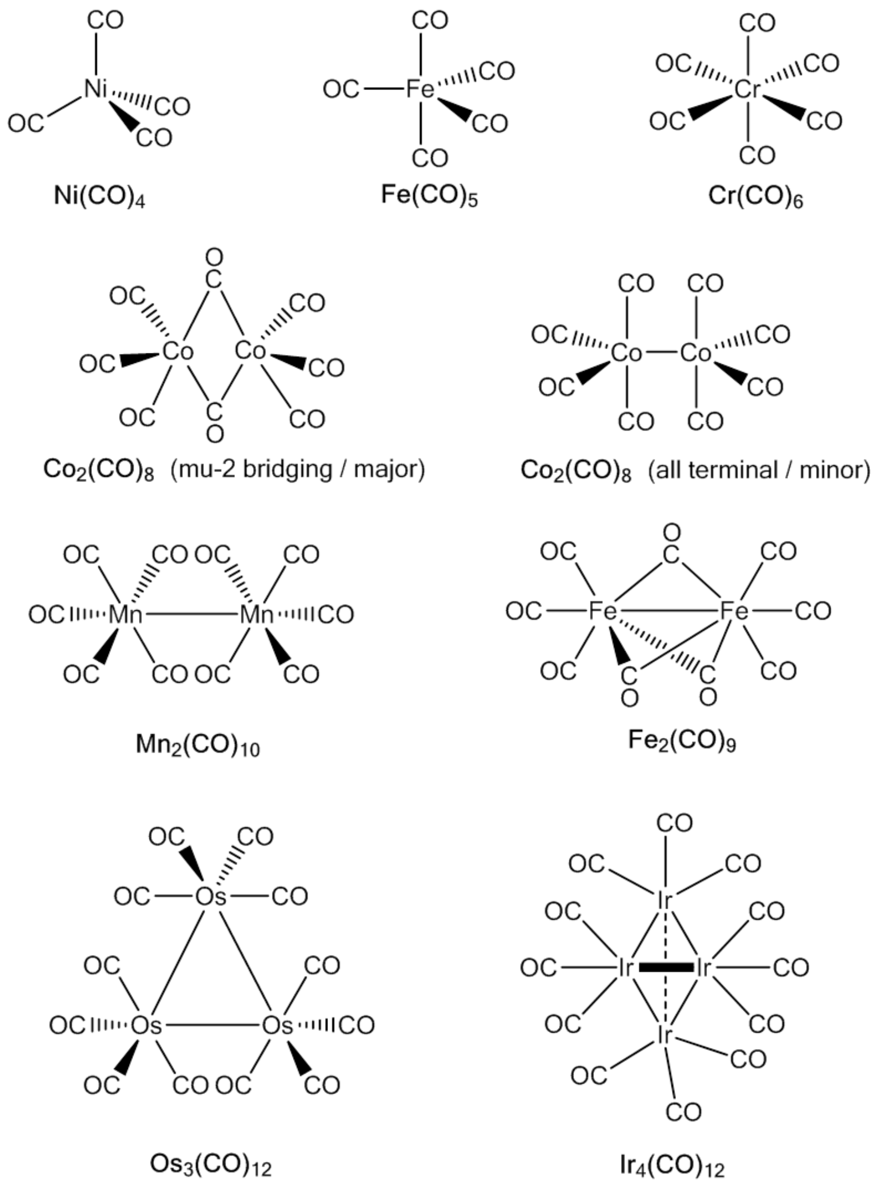


Figure 5.4. *Chemical structures of some common metal carbonyl complexes.*

5.7. *VIBRATIONAL SPECTRA OF METAL CARBONYLS*

Vibrational spectroscopy is one of the most commonly used method of characterizing metal carbonyls. Infrared (IR) spectroscopy or vibrational spectroscopy deals with the absorption of energy in the infrared region of the electromagnetic spectrum. The C–O vibration of a carbonyl group is denoted as ν_{CO} and is observed at 2143 cm^{-1} in the free CO molecule. This frequency of absorption changes as the CO coordinates with a metal atom; it may shift upwards or downwards. The change in the frequency directly depends upon the C–O bond strength (bond order) and inversely varies with the strength of π back bonding between metal and carbon. The acceptance of electrons in π* orbitals has a significant effect and decreases the bond order and hence, the bond strength. Here are some of the factors which effect the number of CO bands observed and ν_{CO}.

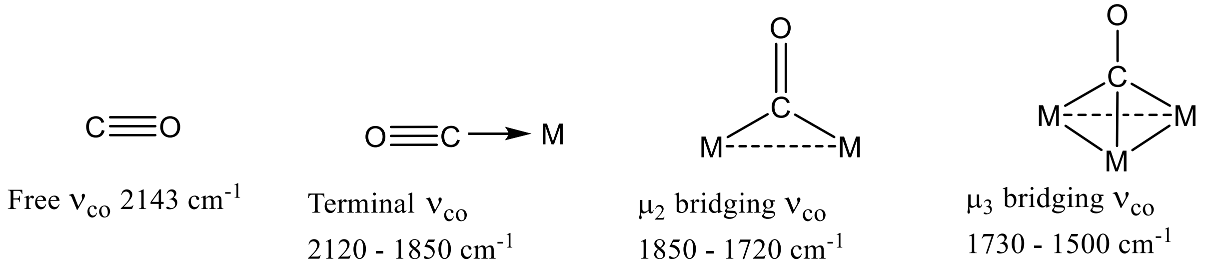
(i) Charge on the metal centre and role of other ligands: A negative charge on metal centre or presence of another ligand with greater σ donation and poor π accepting behavior will decrease the CO stretching frequency whereas the increase of a positive charge on metal centre and poor σ donation and strong π accepting behavior will increase the CO stretching frequency. As the electron density on metal increases, more π back bonding to the CO ligand(s) takes place. As more electron density goes into the formally empty π* antibonding orbital the C–O bond further weakens but M–CO bond strengthens making it more double bond like in nature (**Table 5.3**). **Examples:** $[Ag(CO)]^+$ has ν_{CO} = 2204 cm^{-1}, $[Ni(CO)_4]$ has ν_{CO} = 2060 cm^{-1} and $[Co(CO)_4]^-$ has ν_{CO} = 1890 cm^{-1}.

Table 5.3. *Vibrational frequencies of CO ligand in some common complexes*

Compound	$[Ti(CO)_6]^{2-}$	$[V(CO)_6]^{1-}$	$[Cr(CO)_6]$	$[Mn(CO)_6]^{1+}$	$[Fe(CO)_6]^{2+}$
ν_{CO} (cm^{-1})	17481	1859	2000	2095	2204

The coordination of CO to metal itself decreases its vibrational frequency from 2143 cm^{-1} that is for free CO due to the π back bonding between empty metal orbitals of π symmetry with antibonding (π*) orbitals of CO. This results in increase of M–CO bond but a decrease in C–O bond. The coordination of other ligands which compete with CO for π back bonding will decrease ν_{CO}.

(ii) Bonding Modes: The number and intensity of carbonyl bands observed depends on the number of CO ligands present and symmetry of complex. As the CO bonding is shifted from terminal to bridging, μ_2 or $\mu_3$bridging, the ν_{CO} goes on decreasing (**Figure 5.5**).



Free ν_{co} 2143 cm^{-1}

Terminal ν_{co} 2120 - 1850 cm^{-1}

μ_2 bridging ν_{co} 1850 - 1720 cm^{-1}

μ_3 bridging ν_{co} 1730 - 1500 cm^{-1}

Figure 5.5. *Depiction of various bonding modes exhibited of carbonyl ligand.*

(iii) Ligand donation effects: As mentioned before, the ability of ligands to donate electron density to metal has significant effect on the overall electron density about the metal centre which in turn affects the CO stretching frequency. For example, two *trans*π back bonding ligands will compete for the same d orbital electron density thus, weakens the M–L π back bonding by each one of them. If both *trans* ligands are carbonyls, they will make equally strong bonds with the metal. If the *trans* ligand is a σ donor, it will increase the M–CO bond strength also allowing for CO π back bonding. For example, the pyridine and amines are not strong σ donor but they are even poor π back bonding ligands. Thus, we can generalize that if any ligand say L is *trans* to CO and is weak π accepting ligand (such as pyridine), most of the electron density will be taken up by the CO and hence the stretching frequency will be lower. If the ligand (L) *trans* to CO is a strong π donor such as the PPh_3, the competition for π electron density increases and hence, ν_{CO} will increase slightly. If the *trans* ligand is PF_3, the ν_{CO} is almost same as that of the complex having all CO ligands. This implies that π accepting nature of PF_3 and CO are similar (**Figure 5.6**).

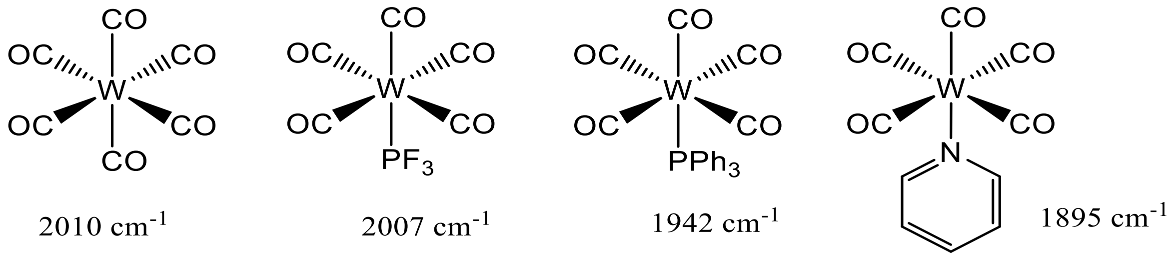


Figure 5.6. *Depiction of ligand donation effect in terms of vibrational frequencies.*

5.8. IMPORTANT REACTIONS OF METAL CARBONYLS

Metal carbonyls serve as precursors in the formation of other carbonyl compounds. Some of the significant reactions are summarized below:

5.8.1. Substitution reactions

The carbonyl ligands can be substituted by other mono- and bidentate ligands under thermal or photochemical conditions. Ligands that can be used to substitute carbonyl are phosphines, cyanide (CN^-), N-donating ligands, chelating ligands and ethers.

Substitution reactions occur via dissociative mechanism except 17 electron metal carbonyls which proceed via associative mechanism. The later mechanism is rare and incorporates a 19 electron intermediate species.

Dissociative mechanism

$$M(CO)_n \longrightarrow M(CO)_{n-1} + CO$$

$$M(CO)_{n-1} + L \longrightarrow M(CO)_{n-1}L$$

Associative mechanism

$$M(CO)_n + L \longrightarrow M(CO)_nL$$

$$M(CO)_nL \longrightarrow M(CO)_{n-1}L + CO$$

Some examples

$$Fe(CO)_5 + 2\,CNR \longrightarrow Fe(CO)_3(CNR)_2 + 2\,CO$$

$$Ni(CO)_4 + 4\,CNR \longrightarrow Ni(CNR)_4 + 4\,CO$$

$$Mn_2(CO)_{10} + PR_3 \longrightarrow 2\,Mn(CO)_4(PR_3) + 2\,CO$$

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

Bidentate ligands can replace carbonyl in multiples of two. Some bidentate ligands and their reactions with metal carbonyls are given below. Please note that o-phenylene-bis(dimethyl arsine) and o-phenanthroline ligands are abbreviated as diars and o-phen respectively.

$$Mo(CO)_6 + diars \longrightarrow Mo(CO)_4(diars) + 2\,CO$$

$$Ni(CO)_4 + O-phen \longrightarrow Ni(CO)_2(O-phen) + 2\,CO$$

$$Cr(CO)_6 + 2\,diars \longrightarrow Cr(CO)_2(diars)_2 + 4\,CO$$

5.8.2. Reduction

Metallic sodium or sodium amalgam are used to reduce metal carbonyls to give carbonylate anions.

$$Mn_2(CO)_{10} + 2Na \longrightarrow 2\,Na[Mn(CO)_5]$$

$$Fe(CO)_5 + 2Na \longrightarrow Na_2[Fe(CO)_4] + CO$$

$$Cr(CO)_6 + 2Na \longrightarrow Na_2[Cr(CO)_5] + CO$$

In above reactions Mn(0), Fe(0), Cr(0) are oxidized to Mn(I), Fe(II) and Cr(II) oxidation states respectively.

5.8.3. Nucleophilic reactions

In the reaction of carbonyl compounds with sodium hydroxide, the hydroxide anion (nucleophile) attacks the CO ligand to form a metallacarboxylic acid which is followed by release of carbon dioxide to give metal hydrides or carbonylmetalates. This reaction is known as Hieber base reaction.

$$Fe(CO)_5 + NaOH \longrightarrow Na[Fe(CO)_4\,COOH]$$

$$Na[Fe(CO)_4\,COOH] + NaOH \longrightarrow Na[HFe(CO)_4] + NaHCO_3$$

Protonation of hydrido anion gives the neutral compound.

$$Na[HFe(CO)_4] + H^+ \longrightarrow H_2Fe(CO)_4 + Na^+$$

5.8.4. Reaction with electrophiles

Metal carbonyls are relatively unreactive towards electrophiles even though they exist in low oxidation states. They do not react with alkylating agents, weak acids and weak oxidizing agents. However, they have been found to react with halogens as shown in some of the reactions given below.

$$Fe(CO)_5 + X_2 \longrightarrow Fe(CO)_4X_2 + CO$$

$$Mo(CO)_6 + Cl_2 \longrightarrow Mo(CO)_4Cl_2 + 2\,CO$$

Some polynuclear carbonyls undergo metal-metal bond cleavage in presence of halogens.

$$Mn(CO)_{10} + Cl_2 \longrightarrow 2\,Mn(CO)_5Cl$$

5.8.5. Reaction with nitric oxide

Metal carbonyls react with nitric oxide to give metal nitrosyls.

$$Fe(CO)_5 + 2NO \xrightarrow{95^\circ C} Fe(CO)_2NO_2 + 3CO$$

$$Co_2(CO)_8 + 2NO \xrightarrow{40^\circ C} 2\;Co(CO)_3NO + 2CO$$

5.8.6. Reaction with hydrogen

Metal carbonyls can be reduced to hydrides upon reaction with hydrogen to give metal hydrides.

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

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

Even though the above neutral compounds are called hydrides. They have been found to act as proton donors thus, behaving as acids.

$$Mn(CO)_5H \xrightarrow{165^\circ C\ ,200\ atm} Mn(CO)_5]^- + H^+$$

$$Co(CO)_4H \longrightarrow Co(CO)_4]^- + H^+$$

The anionic hydrides such as $[HFe(CO)_4]^-$ behave as true hydrides (reducing agents) and can reduce the alkyl halides.

$$RX + [HFe(CO)_4]^- \longrightarrow RH + [XFe(CO)_4]^-$$

5.9. TRANSITION METAL NITROSYLS

The chemistry of transition metal nitrosyls though gained significant attention somewhat later to that of metal carbonyls but in present times, the work done in this field runs parallel to that of metal carbonyls. Nitric oxide or the nitrosyl ligand can bind to the metal in a manner quite different from that of carbonyls. The two common binding modes of NO can be represented as shown below (**Figure 5.7**):

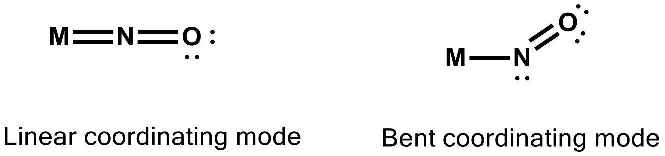


Figure 5.7. *Depiction of linear and bent coordination modes of nitrosyl ligand.*

In the linear binding mode, the N behaves as a three electron donor in NO^+ and M–N has a multiple bond character. It donates one electron to the metal before donating an electron pair for the formation of coordinate covalent bond. The nitrosyl NO^+ is isoelectronic with CO ligand. It is the most common bonding observed. In the bent coordination mode, the N acts as a single electron donor towards the metal and the M–N–O bond angle is 120°. Here, the M–N bond is longer than that in the linear bonding mode, it is still somewhat shorter than the single σ M–N bond distance. In most of the nitrosyl complexes, NO^+ (nitrosyl or nitrosonium ion) acts as the ligand by donating a pair of electrons. In some complexes, nitric oxide is also known to exist as anion NO^- such as in $[Co^{+3}(CN)_5(NO)]^{-3}$ and $[Co^{+3}(NH_3)_5(NO)]^{+2}$.

The free nitric oxide has an IR stretching frequency of 1870 cm^{-1}. The nature of other ligands present in the complex, charge and structure of the complex affect the NO stretching frequency (ν_{NO}). The nitrosyl ligand is linear when it coordinates as NO^+ and ν_{NO} is observed in the range 1720-1400 cm^{-1}. The role of metal nitrosyls has been much explored as homogeneous catalysts. They find their biggest application in olefin disproportionation reactions.

5.10. DINITROGEN COMPLEXES

Transition metal coordination compounds containing dinitrogen molecules (N_2) as ligands are called dinitrogen complexes. Such complexes are of interest because dry air in earth's atmosphere contains nearly 78% nitrogen by volume that reflects reluctance of dinitrogen towards chemical reactions in ordinary conditions. Dinitrogen is converted to its organic and inorganic derivatives *via* a process called 'nitrogen fixation', which primarily involves the binding of dinitrogen to metal centers present in the enzyme nitrogenase followed by a series of other steps. Ruthenium complex, $[Ru(NH_3)_5(N_2)]^{2+}$ is the first synthetic complex that contains a dinitrogen ligand. It is an octahedral paramagnetic complex in which five of the hexacoordinated sites are occupied by ammine ligands and the sixth position is occupied by dinitrogen molecule, N_2. The presence of N_2 as a ligand in these compounds cause a strong vibrational band in the FTIR spectra of the compound around 2170–2100 cm^{-1}.

Alike acetylene (C_2H_2) and carbon monoxide (CO) molecules, dinitrogen (N_2) also possess a triple bond. Similar to these acetylene and carbonyl ligands, dinitrogen also offers mononuclear (terminal) and bridging bonding modes. If the N_2 molecule is shared by two or more metal centers in a complex, the manner of bonding is termed as the bridging modes. Based on the geometric relationship between the N_2 molecule and the metal center, the complexes are also differentiated to have end-on or side-on modes (**Figure 5.8**). In the end-on bonding mode of transition metal-dinitrogen complexes, the N-N vector can be considered in line with the metal ion center, whereas in the side-on modes, the metal-ligand bond is known to be perpendicular to the N-N vector.

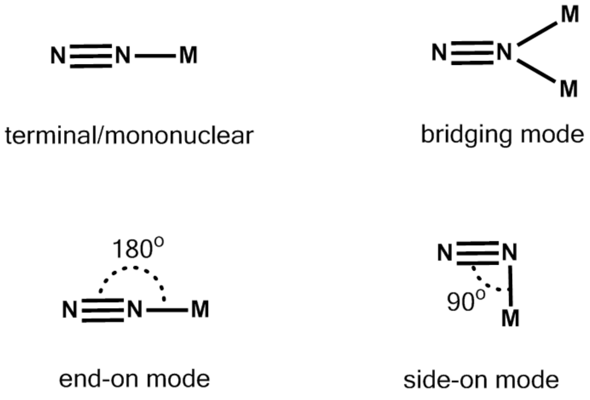


Figure 5.8. *Depiction of various coordination modes of dinitrogen ligand.*

5.11. DIOXYGEN COMPLEXES

Transition metal coordination compounds containing dioxygen molecules (O_2) as ligands are called dioxygen complexes. As the biological process of 'nitrogen fixation' motivated the study of synthetic dinitrogen complexes, biological oxygen carrier proteins including myoglobin, hemoglobin, hemerythrin, and hemocyanin has inspired the studies pertaining to the transition metal complexes of dioxygen molecules. These proteins reversibly bind with the oxygen molecules. Hence, reversibly bound oxygen containing transition metal complexes are of particular interest for their capability to mimic natural respiratory systems. The first synthetic oxygen complex was reported in 1938 with cobalt (II) complex reversibly bound O_2. O_2 ligand can bind to a single metal center through two coordination modes namely, "end-on" (η^1-) where the ligand is connected to metal center at one point only and the other one is "side-on" (η^2-) mode, where the ligand connects to the same metal centre through two sites, *i.e.*, forms η^2- chelates (**Figure 5.9**).

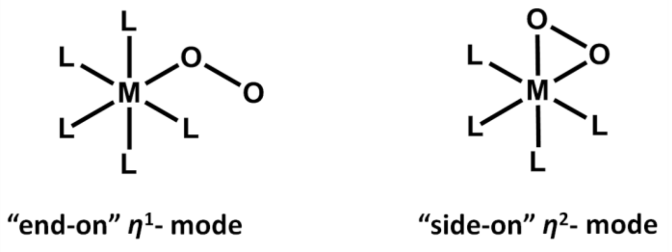


Figure 5.9. *Depiction of various coordination modes of dioxygen ligand.*

Dioxygen derivatives of cobalt (II) and iron (II) complexes of porphyrin (and related anionic macrocyclic ligands) usually exhibit η^1-bonding mode. On the other hand, η^2-bonding mode is the most common motif through which dioxygen ligand coordinates to the metal centres. Reacting low-valent metal complexes with oxygen yields η^2-adducts. For example, Vaska's complex reversibly binds O_2 as presented below (**Figure 5.10**):

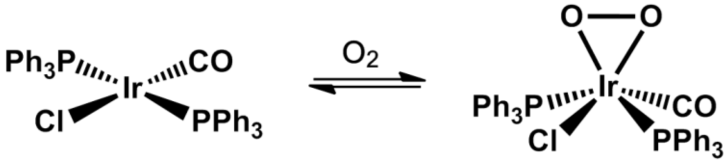


Figure 5.10. *Binding of dioxygen ligand with Vaska's complex.*

Dioxygen ligand can also bridge two metal centres at once as in case of the hemocyanin. Each of the oxygen atom of bridging dioxygen ligand can bind either to one metal center each or η^2-chelate the metal centers. Hence, there are three possible bonding modes namely, μ_2-η^1,η^1-, μ_2-η^1,η^2- and μ_2-η^2,η^2-. The exact bonding mode is often characterized by the x-ray crystallographic studies (**Figure 5.11**).

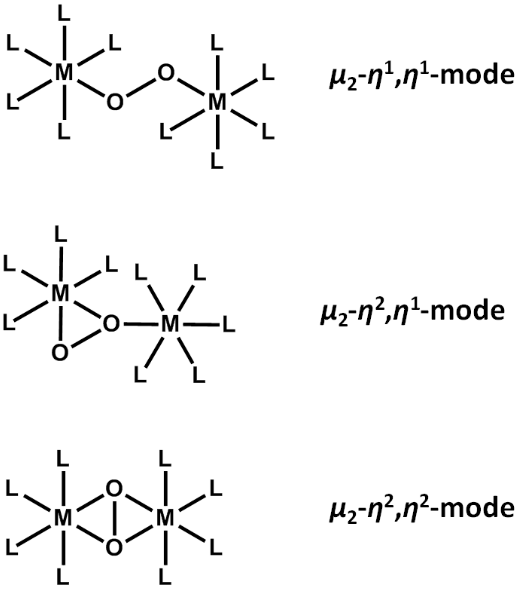
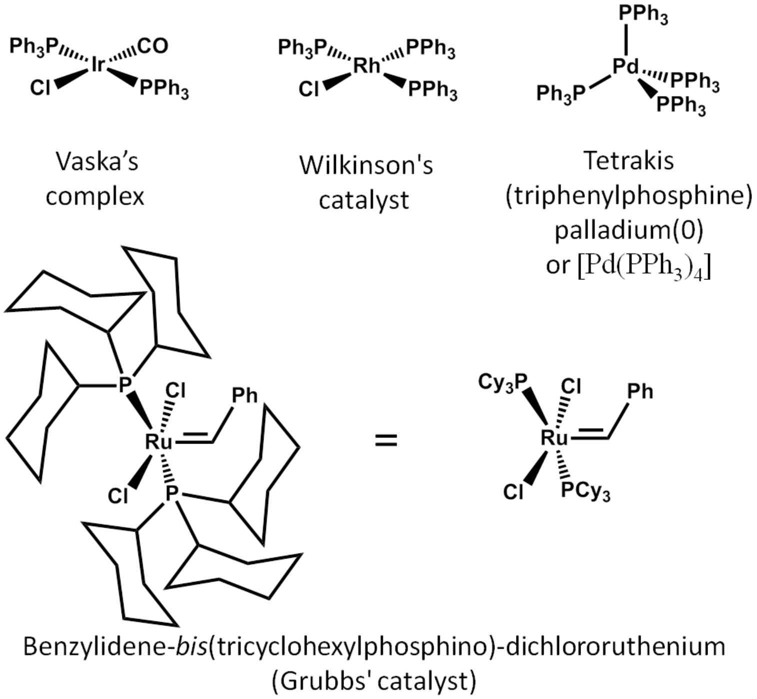


Figure 5.11. *Various binding modes of dioxygen ligand.*

5.12. TERTIARY PHOSPHINE AS LIGAND

Phosphines are two electron donor ligands which coordinate through the lone pair of electrons available on the phosphorous atom. Phosphine ligands, particularly triphenylphosphine is an excellent ligand as it shows good solubility in organic solvents and tend to bind with transition metals in a range of oxidation states. Important examples of triphenylphosphine containing metal complexes include Vaska's complex, Wilkinson's catalyst ($Rh(PPh_3)_3Cl$), Grubbs' catalyst, and $[Pd(PPh_3)_4]$ (**Figure 5.12**).



Vaska's complex

Wilkinson's catalyst

Tetrakis (triphenylphosphine) palladium(0) or $[Pd(PPh_3)_4]$

Benzylidene-*bis*(tricyclohexylphosphino)-dichlororuthenium (Grubbs' catalyst)

Figure 5.12. *Some important transition metal complexes comprising phosphine ligands.*

Triphenyl phosphine complexes are prepared by the treatment of metal halides with triphenylphosphine as depicted below for the synthesis of bis(triphenylphosphine)palladium(II) chloride.

$$[PdCl_2]_n + \ 2n\, PPh_3 \rightarrow n\, PdCl_2(PPh_3)_2$$

As stated earlier, phosphine molecules are two electron donors, *i.e.*, Lewis bases which interact with metal centres as σ donor ligands. Additionally, phosphorous atoms possess empty d orbitals as well as the σ* anti-bonding orbitals those can accept electron density from filled d orbitals available with metal centre. This back-bonding causes tighter binding of metal and phosphine ligand (**Figure 5.13**).

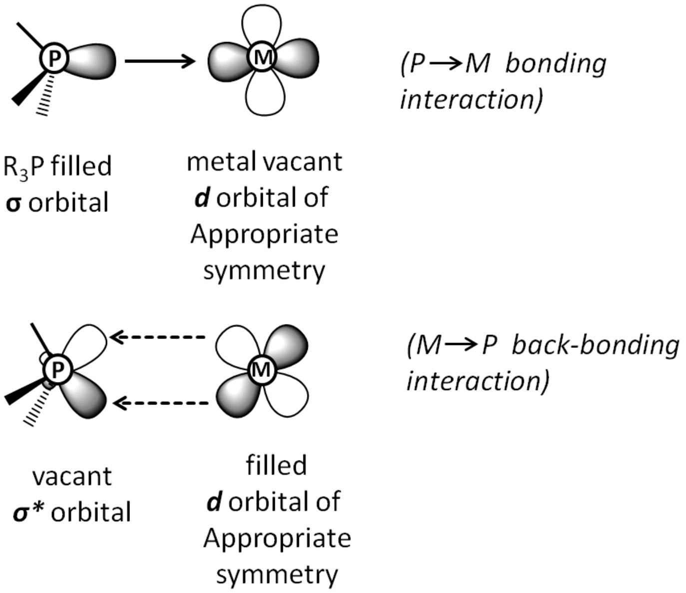


Figure 5.13. *Schematic depiction of bonding and back-bonding interactions in transition metal complexes comprising phosphine ligands.*

Phosphine complexes are mainly used as catalysts for organic conversations. Wilkinson's catalyst is used for hydrogenation of olefins with molecular hydrogen. The mechanism of hydrogenation of olefins catalyzed by Wilkinson's catalyst involves initial dissociation of one or two PPh_3 ligands to give 14- or 12-electron complexes, respectively. The initial step is the oxidative addition of H_2 to the metal center which further followed by π-complexation of alkene, migratory insertion and reductive elimination yielding the formation of the alkane as depicted in **Figure 5.14**.

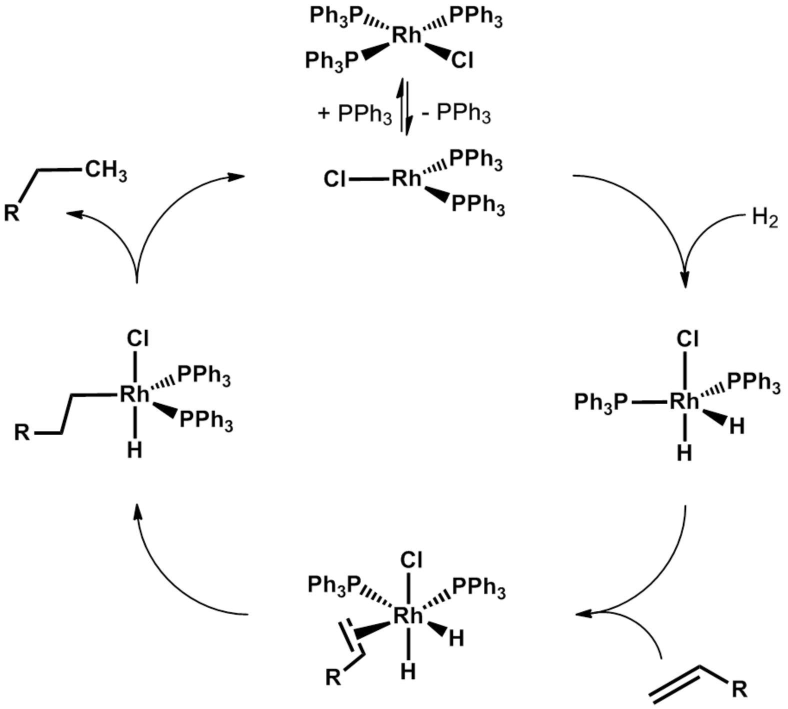


Figure 5.14. *Schematic depiction of mechanism of hydrogenation of alkenes catalyzed by Wilkinson's catalyst.*

5.13. SUMMARY

This chapter provides an account of important aspects of organometallic chemistry particularly in context of metal carbonyls. Several methods of synthesis and chemical reactions or carbonyls are presented in this unit. Molecular and electronic structural aspects have been discussed to make students understand the basics of bonding in carbonyl and other organometallic complexes. Detailed account and implications of effective atomic number rule and 18 electron rules are also presented. Later sections of the chapter elucidate the important aspects of transition metal complexes of nitrosyl, dinitrogen, dioxygen, and triphenyl phosphine ligands.

5.14. TERMINAL QUESTIONS

5.14.1. Long answer type questions

Q1. What are carbonyl compounds? Discuss synthesis of metal carbonyls.

Q2. Discuss bonding in carbonyls. Explain using MO theory why only the carbon atom of the ligand CO donates electrons in metal carbonyls.

Q3. Write a note on chemical properties of metal carbonyls.

Q4. Explain back-bonding in transition metal complexes of triphenyl phosphenes.

5.14.2. Short answer type questions

Q1. Give two methods for the synthesis of metal nitrosyl complexes.

Q2. Draw structure of Vaska's complex.

Q3. What are the uses of Wilkinson's catalyst? Explain with a reaction.

Q4. Give schematic account of μ_2-η^1,η^1-, μ_2-η^1,η^2- and μ_2-η^2,η^2- bonding modes of dioxygen.

Q5. What are side-on and end-on bonding modes of dioxygen ligand.

Q6. Draw two bonding modes of dinitrogen ligand.

Q7. Calculate the oxidation state of the metal centre and the total valence electron count of the following species. (i) TiF_6^{2-}; (ii) $Ni(en)_3^{2+}$ (iii) $Cu(NH_3)_6^{2+}$ (iv) $W(CN)_8^{4-}$ (v) $CH_3Co(CO)_4$.

[*Hint*: Q7. (i) +4 and 12; (ii) +2 and 20; (iii) +2 and 21; (iv) +4 and 18; (v) 0 and 18]

5.14.3. Objective type questions

Q1. State the oxidation state of the metal and the total valence electron count of the complex, $V(C_2O_4)_3^{3-}$.

(a) +3 and 14 (b) +3 and 16 (c) +5 and 17 (d) 0 and 18

Q2. State the oxidation state of the metal and the total valence electron count of the complex, $Mn(acac)_3$.

(a) +3 and 14 (b) +3 and 16 (c) +5 and 17 (d) 0 and 18

Q3. State the oxidation state of the metal and the total valence electron count of the complex, $W(CN)_8^{3-}$.

(a) +3 and 14 (b) +3 and 16 (c) +5 and 17 (d) 0 and 18

Q4. State the oxidation state of the metal and the total valence electron count of the complex, $CpMn(CO)_3$.

(a) +3 and 14 (b) +3 and 16 (c) +5 and 17 (d) 0 and 18

Q5. State the oxidation state of the metal and the total valence electron count of the complex, $Fe_2(CO)_9$.

(a) +3 and 14 (b) +3 and 16 (c) +5 and 17 (d) 0 and 18

5.15. ANSWERS TO OBJECTIVE TYPE QUESTIONS

Q1. (a)

Q2. (b)

Q3. (c)

Q4. (d)

Q5. (d)

5.16. REFERENCES AND FURTHER STUDIES

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Block II : METAL π-COMPLEXES AND METAL CLUSTERS

UNIT 6 METAL π-COMPLEXES

CONTENTS

6.1. OBJECTIVES

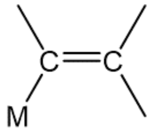
In this chapter, synthesis, bonding, structure, reactions and various structural aspects of organometallic compounds with various σ donor/ π acceptor ligands will be discussed. These types of ligands are alkenyl, allyl, aryl, akynyl, diene, cyclopentadiene etc. This chapter will first cover some basic concepts and terminologies of organometallic chemistry and proceed to organometallic complexes, their synthesis, reactions and properties. The chapter aims to provide an insight into the structure and bonding of metal atoms with π molecular orbitals of the organic ligands such carbene, carbyne and carbide along with some other relevant aspects.

6.2. INTRODUCTION

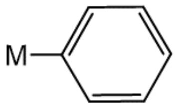
It is the study of organometallic compounds. These compounds contain metal element bond of largely covalent character. It is a combined aspect of organic and inorganic chemistry.

Organometallic compounds: Compounds of metal ions with organic ligands in which metal is bound to the ligand via metal-carbon bond are known as organometallic compounds. The bonding interaction in these complexes is defined, as it must be "ionic or covalent, localized or delocalized between one or more carbon atoms of an organic group or molecule and a transition, lanthanide, actinide, or main group metal atom. This M—C bond may be single, double or triple bonded (M—C, M═C, M ≡ C). The study on metal carbon single bonds was one of the earliest starting in about nineteenth century when compounds such as the Grignard reagent were in focus. Organometallic compounds have acted as a connecting link between organic and inorganic chemistry. These complexes have found wide range of applications in the field of catalysis.

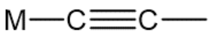
This chapter will deal with metal alkenyl, allyl, aryl, akynyl, diene and cyclopentadiene complexes along with some arene and alicyclic ligand complexes covering their synthesis, stability, chemical reactivity, nomenclature, applications and some other aspects.



Alkenyl complexes



Aryl complexes



Alkenyl complexes

6.3. HAPTICITY

The term hapticity describes the manner in which group of contiguous atoms of a ligand are coordinated to the metal center. It is indicated by Greek letter eta (η). In the symbol η^x, x represents the number of contiguous atoms of the ligand that are coordinated to the metal. The term is usually employed to describe ligands having extended π-conjugation. eg. Ferrocene: bis(η^5-cyclopentadienyl)iron, Zeise's salt: $K[PtCl_3(\eta^2-C_2H_4)].H_2O$

6.4. THE 18-ELECTRON RULE

This rule helps in predicting the stability of metal complexes. In thermodynamically stable transition metal complexes, the sum of number of *'d'* electrons and the electrons provided by the conventional ligands should equal 18. The rule is generally found to be followed by electron rich metal center (low oxidation state) and π-accepting ligand.

Method of counting electrons using neutral atom method

Ligand	**Neutral atom electron count**
Amine ($M-NR_3$)	2
Amide ($M-NR_2$)	1
μ-amido ($M–(NR_2)–M$; bridging $–NR_2$	3
Alkene (sidewise; η^2)	2
Alkyne (sidewise; η^2)	2
Alkoxide (M–OR)	2

μ-alkoxide (M–(OR)–M; bridging –OR	3
η^1-allyl	1
η^3-allyl	3
μ-alkyne	4
μ-alkyl	1
η^3-Allenyl	3
η^2-Butadiene	2
η^4-Butadiene	4
Alkyl (M–R)	1
Aryl (M–Ar)	1
acyl (M–C(O)–R	1
Carbonyl (M-CO)	2
η^1-cyclopentadienyl	1
η^5-cyclopentadienyl	5
η^6-benzene	6
η^2-Benzene	2
η^7-cycloheptatrienyl	7
η^8-Cyclooctatetraenyl	8
Carbene ($M=CR_2$)	2
Carbyne (M≡CR	3
μ-CO (M–(CO)–M); bridging	2
Hydrogen (M-H)	1
μ-H; bridging	1
Halogen (M–X)	1
μ-X (M–X–M); X = bridging halogen	3

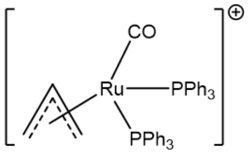
Phosphine (M-PR_3)	2
µ-phosphido (M–(PR_2)–M	3
Nitrosyl bent	1
Nitrosyl linear	3
Thiolate (M–SR)	1

Some examples:

In neutral atom method, metal is taken in zero oxidation state and any positive or negative charge on the coordination sphere is added if positive and subtracted if negative.

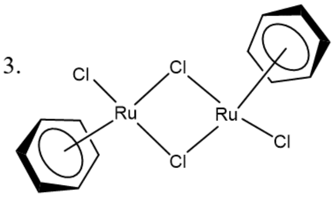
1. $Fe(Cp)_2(CH_2NMe)_2$: (Fe; 8 e) + (2 η^5- Cp; 10 e) = 18 electrons

2.



Ru 8 e; η^3 – allyl 3 e; $2PPh_3$ 4 e; charge -1 = 16 e

3.



2Ru 16 e; 2(μ – Cl) 6 e; 2(Terminal Cl) 2 e; 2 (η^6 – C_6H_6) = 12 e
Total 36 e; 18 e per Ru metal centre

Determination of total number of metal-metal bonds

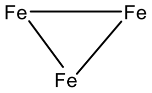
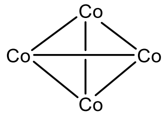
i. First determine the total number of valence electrons (VE) in the molecule that is the valence electrons contributed by the metal plus valence electrons from each ligand plus the charge suppose it comes out to be X.

ii. Now subtract this number (X) from the product of (n x18), where n=total number of metal atoms in the complex, say {(n x 18)-X} comes out to be Y.

iii. Y divided by 2 gives the total number of M-M bonds.

iv. X divided by n gives total number of electrons per metal atom. If the total number of electrons come out to be 18 that implies there are no M-M bonds; if it comes out to be 17, this indicates presence of 1 M-M bond; if it is 16 it would indicate 2 M-M bonds and so on.

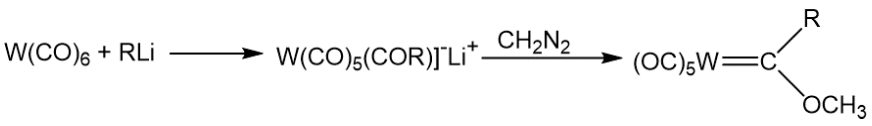
Some examples:

Complex	**TVE (X)**	**(18 x n)-X = Y**	**M-M bonds (Y/2)**	**Bonds per metal (X/n)**	**Geometry about metal**
$Fe_3(CO)_{12}$	48	(18 x 3)-48 =6	6/2=3	48/3 = 16; 2 bonds per metal	
$Co_4(CO)_{12}$	60	72-60 =12	12/2=6	60/4=15; 3	
$(\eta^4\text{-}C_4H_4)_2Fe_2(CO)_3$	30	36 – 30 = 6	6/2 = 3	30/2 = 15; 3	Fe≡Fe

6.5. ORGANOMETALLIC CARBENE, CARBYNE, CARBIDO COMPLEXES

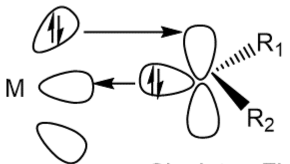
6.5.1. Transition metal carbene complexes (structure, synthesis and reactions)

Transition metal carbene complexes are those which show bonding with divalent organic ligand known as the carbene ($M=CR_2$). One of the most initial class of compounds containing metal carbon double bonds are carbene complex, first reported by Fischer and Maasböl in 1964. Hexacarbonyltungsten reacts with methyl or phenyl lithium followed by reaction with diazomethane generates metal carbene complex.

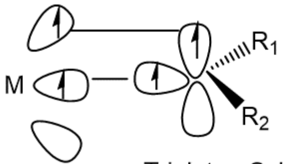


$$W(CO)_6 + RLi \longrightarrow W(CO)_5(COR)]^-Li^+ \xrightarrow{CH_2N_2} (OC)_5W{=}C(R)(OCH_3)$$

Carbenes are those species, which contain a neutral divalent carbon having only six electrons. Out of these, two electron pairs are involved in bonding with other substituents while the remaining electron pair is nonbonding. This lone pair of electrons may be paired (singlet) or unpaired (triplet) giving rise to singlet and triplet forms respectively. Singlet carbenes are also known as Fischer carbenes. In both types of carbene, carbon is sp^2 hybridized.

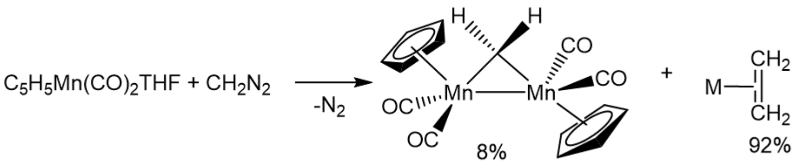


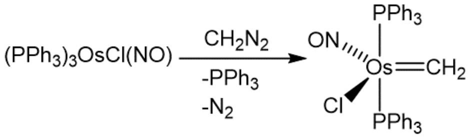
Singlet or Fischer carbene



Triplet or Schrock carbene

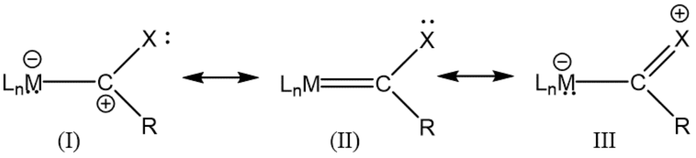
6.5.1.1. Synthesis of complexes



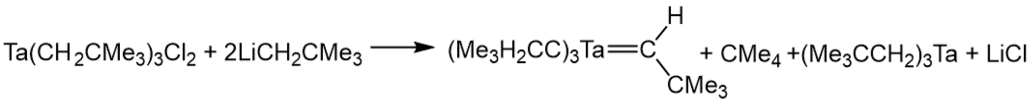


6.5.1.2. Structure and bonding

The metal-carbon bond can be represented by several resonance structures as shown below.



The coordinated carbene is sp^2hybridized and has trigonal planar geometry. The pair of electrons in sp^2orbital may participate in the formation of metal carbon sigma bond, and the empty $p_z$orbital may participate in accepting pi-electron density. Metal carbon double bonds may result if the filled metal d orbitals donate electrons to the empty p_z orbital of carbene. Fischer carbenes are found with low oxidation state metal centres usually middle and late transition metals such as Fe(0), Mo(0), Cr(0), W(0), π-electron acceptor metal and π-donor substituents on carbon such as alkoxide and amino groups. Later, Schrock discovered second type of carbenes, which are nucleophilic in nature (see reaction below). These were called “Schrock” carbenes to differentiate them from Fischer carbenes.



$$Ta(CH_2CMe_3)_3Cl_2 + 2LiCH_2CMe_3 \longrightarrow (Me_3H_2CC)_3Ta{=}C(H)(CMe_3) + CMe_4 + (Me_3CCH_2)_3Ta + LiCl$$

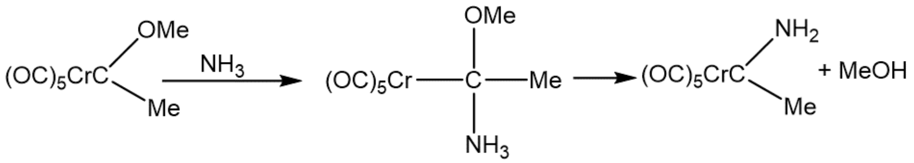
These carbenes are found with early transition metal complexes existing in high oxidation states, non-π accepting auxiliary ligands and non-π donating substituents on carbon. Schrock carbenes have two unpaired electrons existing in triplet state. Each unpaired electron of carbene overlaps with two metal orbitals, which provide an electron. The role of carbene carbon in accepting or donating electrons depends directly on the extent of π bonding involving metal and substituents present on carbon. The IR data reveals that the carbene carbon is weak π-acceptor and stronger σ-donor than carbonyl.

6.5.1.3. Reactions of transition metal carbenes

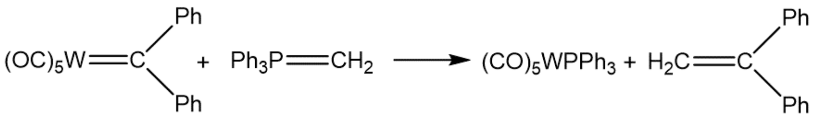
1. The nucleophilic nature of Fischer carbene is shown in the reaction given below. The functionalized Ru Fischer-type complexes are used in a variety of olefin metathesis reactions.

$$(\eta^5\text{-}C_5H_5)_2MeTa{=}CH_2 + AlMe_3 \longrightarrow (\eta^5\text{-}C_5H_5)_2MeTa\text{–}CH_2AlMe_3$$

2. Electrophilic nature of Fischer carbene is shown in the reaction given below. Here, NH_3 acts as a nucleophile forming the intermediate and eliminates a molecule of methanol in the product. The reaction is favorable because electronegativity of nitrogen is less than oxygen also; the π-electron donor capability is more than oxygen.

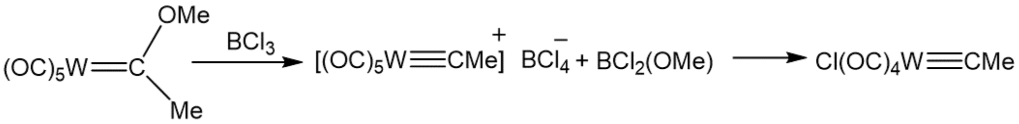


3. Carben metal complexes can undergo reaction similar to Wittig reaction

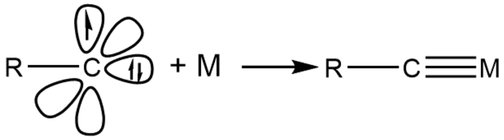


6.5.2. Transition metal carbyne complexes (structure, synthesis and reactions)

After a decade of discovery of metal-carbon double bonds, first report of a metal-carbon triple bond was published.

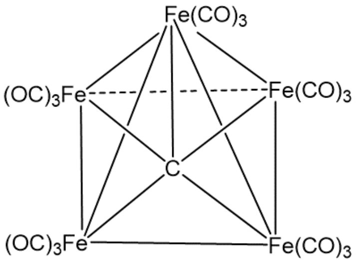


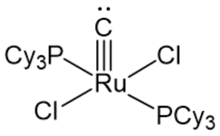
The carbyne ligand is considered as a three electron donor having a pair of electron in a *sp* hybridized orbital and a single electron in *p* orbital. These *sp* electrons are donated to form the σ-bond while the *p* electrons pair up with one metal atom to form the π-bond respectively. The second π-bond is formed by the donation of an electron pair from the metal atom to the empty *p* orbital of the ligand. They exhibit almost linear geometry. The M—C bond is shorter than those found in metal carbene complexes.

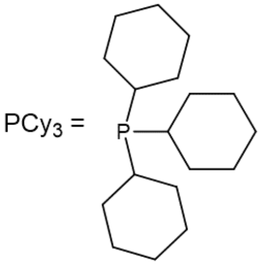


6.5.3. Transition metal carbido complexes (structure, synthesis and reactions)

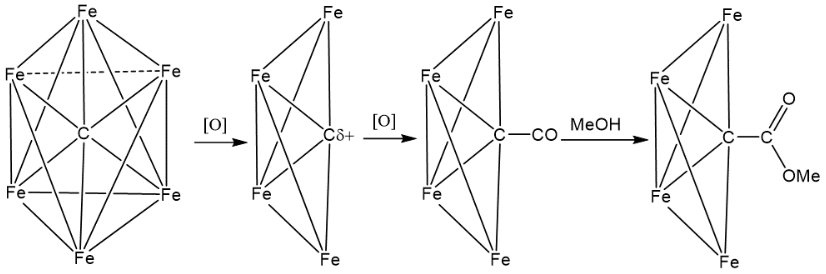
In carbido complexes, atomic carbon functions as a ligand. Carbon bound solely to metal atoms are called carbido complexes. As such, these complexes are not very reactive however, if one or more metal atom(s) is/are removed exposing the carbon atom, it becomes a highly reactive species. They are useful in the synthesis of more complicated carbides. In $[Fe_6C(CO)_{16}]^{2-}$ oxidation causes removal of two Fe^{2+} ions exposing the carbon atom which can react with nucleophiles such as carbon monoxide. The carbido complexes are used as precursors for the synthesis of carbides and other organic synthesis. $RuC(PCy_3)_2Cl_2$ is an example of terminal carbide complex with Ru–C distance lying in the range of metal carbon triple bond. Here, PCy is tricyclohexylphosphine ligand. Some examples of metal carbide complexes are shown below.







The carbon atom in carbide complexes is inert but when it is exposed after removal of one or more metal atoms, it becomes reactive. An example explaining this, is given below.



6.6. TRANSITION METAL π-COMPLEXES

Transition metal π complexes are frequently observed with alkene, allyl, diene and arene ligands. These ligands have unsaturation and hence, rich in π electrons which have the ability to participate in various types of bonding; σ donation, π donation or π back bonding. The formation of metal ligand bond with these unsaturated ligands changes their properties greatly which plays a crucial role in their important synthetic applications. The metal π complexes can be divided into various types on the basis of their electron donor capability.

i. Alkenyl and alkynyl complexes; alkene and alkyne-two electron donors

ii. Allylic complexes: Allyl - three electron donor

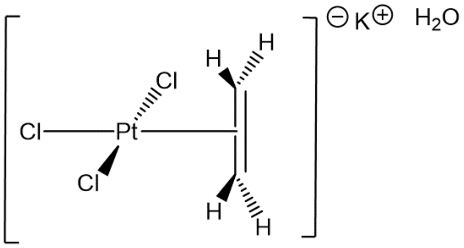
iii. Dienyl complexes: Diene - four electron donor

iv. Cyclopentadienyl complexes - five electron donor

v. Arene complexes – Aryl - six electron donor

6.6.1. Transition metal alkene complexes (structure, synthesis and reactions)

The first metal olefin complex was synthesized by Danish chemist Zeise. The complex $K[PtCl_3(C_2H_4)]\cdot H_2O$ is known as Zeise's salt. Here, the metal Pt is bound to ethylene.

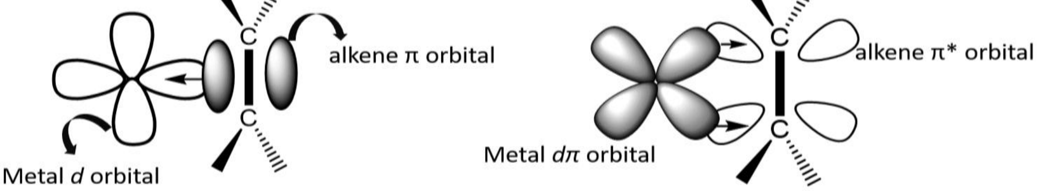


Zeise's salt

Alkenes are neutral two electron donors (per C=C double bond). Due to the presence of empty π* antibonding orbitals, there is the possibility of some π-backbonding. Alkenes are weakly coordinating ligands and important substrates for catalytic reactions. The metal-olefin bonding interaction can be explained by Dewar Chatt model.

6.6.1.1. Structure and bonding

The π bond in alkene (two electron donor) binds in a σ fashion to the metal. The Dewar Chatt model takes into account two mutually opposing electron donation. One sigma donation occurs from C=C π-electrons to an empty d_π metal orbital of metal followed by π-back donation from filled metal d_π orbital into empty C=C π^* orbital. Thus, it is obvious that metal with d^0 configuration will not form metal-olefin complexes. This type of electron donation mentioned above affects the C=C bond of the olefinic moiety bound to metal bringing about a change in hybridization as well as in the C−C bond distance. The amount of π back bonding depends upon how electron rich the metal center is and whether or not electron withdrawing groups are present on alkene so as to increase its electron accepting capability. For example, in the complex shown below the presence of electron withdrawing fluorine groups make it a better π acceptor. This results in weakening of C=C bond but strengthening of alkene metal bond. $[Rh(Cp)(\eta^2\text{-}F_2C=CF_2)_2$



In case of smaller metal to ligand π−back donation compared with the ligand to metal σ−donation, lengthening of the C−C bond in the metal bound olefin moiety is observed. This happens because 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. Also, as the metal to ligand π−back donation increases, the electron donation from the filled metal *dπ* orbital to the π* orbital of the metal which is bound to olefin moiety increased. This results in an increase in the C=C bond length. This lengthening of the C=C bond in the olefin bound to the metal can be correlated to the π−basicity of the metal. For example, for a weak π−basic metal, C=C bond lengtheningis expected to be small while that for a strong π−basic metal, C=C bond lengthening would be significant.

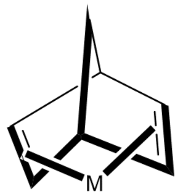
As a result of ligand−metal π−back donation, change of hybridization at olefinic carbon is observed. The sp^2 olefinic carbon in complexes with no metal to ligand π−back donation changes to sp^3 carbon in complexes having metal to ligand π−back donation. This change in hybridization can be easily detected by ^{1}H and ^{13}C NMR spectroscopy. Electronic effects in alkenes can be easily monitored by using IR spectroscopy. The greater the π−back bonding, the weaker the C=C double bond and the lower the C=C stretching frequency in the IR. Note that both σ−donation and π−back bonding weaken the C=C bond and lower the stretching frequency, but π−back bonding has a more pronounced effect.

The metal to ligand π−back donation is also responsible for stronger binding of strained olefin system to the metal centre such as observed in the case of cyclopropane and norbornene. The stronger bonding of these systems arises from the relief in strain achieved upon binding to the metal. In the metal-olefin complexes having insignificant π−back bonding, the chemical reactivity of the olefin bound to the metal is reverse to the free olefin. A free olefin is electron rich due to the presence of π−electrons in its outermost valence orbital and hence, it undergoes electrophilic attack. But in the olefin bound to the metal (olefin-metal complex), the complex has significant σ−donation of the olefinic π−electrons and metalto-ligand π−back donation is negligible, the olefinic C becomes positively charged and hence, undergoes a nucleophilic attack. This nature of reversal of olefin reactivity is called umpolung character.

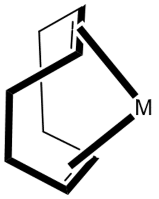
Overall, the thermodynamic stability of alkene complexes depends on nature of alkene and metal.

1. Electron withdrawing groups on alkene generally increase the strength of metal alkene bond while electron donating groups decrease the stability.

2. If an alkene can form *cis* and *trans* isomers in almost all cases, the *cis*-alkene forms the more stable complex.
3. Metal complexes with strained ring alkene system (eg. cyclopropene) exhibit higher stability. The ring strain raised the energy of cycloalkene ring system making it a better donor to metal centre.
4. Chelating dienes show better stability due to the chelate effect such as norbornadiene and cyclooctadiene. These can be easily substituted at the metal centre by phosphines.
5. Third row metals form the strongest bonds and most stable complexes.



Norbornadiene complex

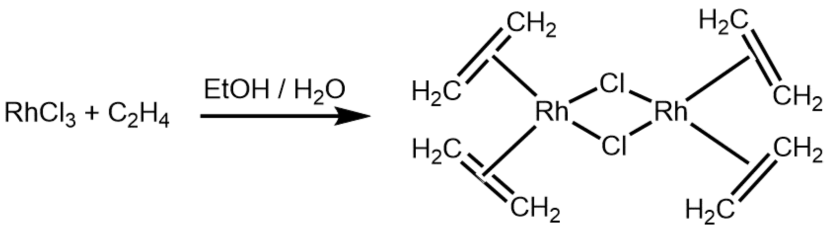


Cyclooctadiene complex

6.6.1.2. Synthesis

Metal alkene complexes are synthesized by the following methods:

1. Reduction of metal in presence of olefin

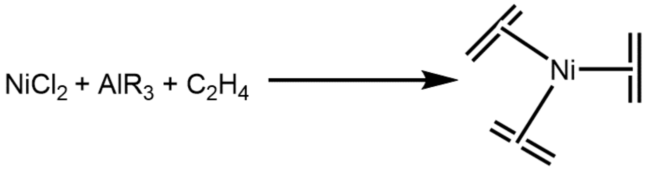


2. Substitution

$$K_2PtCl_4 + C_2H_4 \xrightarrow[\text{60 Bar}]{\text{Dil. HCl}} K[C_2H_4PtCl3].H_2O + KCl$$

$AlCl_3$

3. Reduction in presence of an olefin



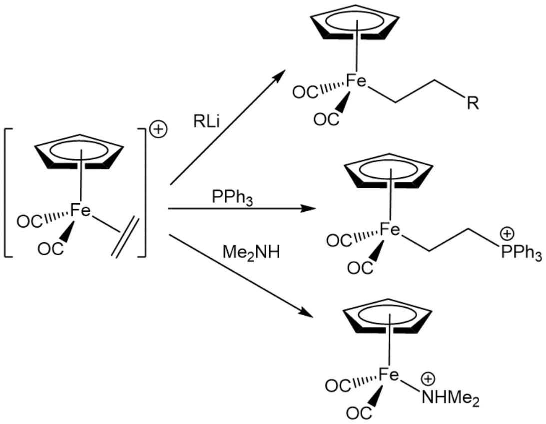
6.6.1.3. Reactions

1. Insertion reactions

Alkenes insert into M-X bonds where X is any other atom. The reaction is most common when X is hydrogen. For other atoms, the reaction becomes rare. Alkenes with strained system also undergo insertion reactions readily.

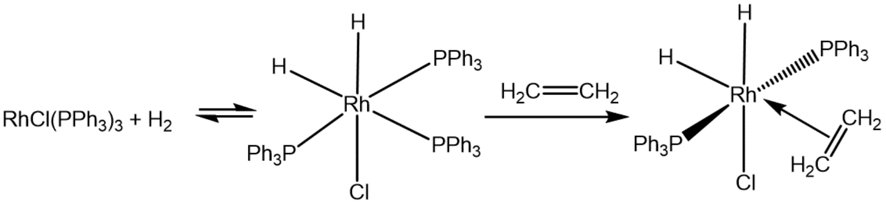
$$PtHCl(PEt_3)_2 + C_2H_4 \rightleftharpoons PtEtCl(PEt_3)_2$$

2. Nucleophilic atta

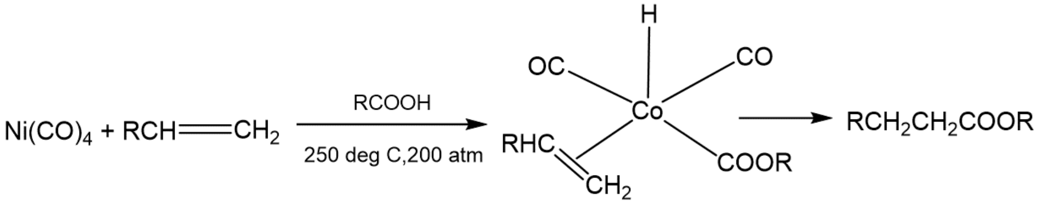


3. Hydrogenation

This reaction is useful in the role played by olefins in catalytic reactions.

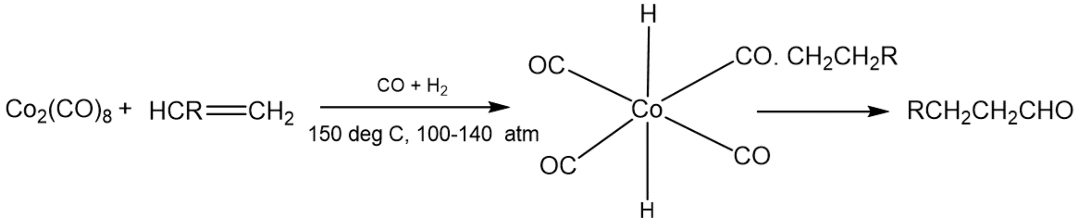


4. Carboxylation



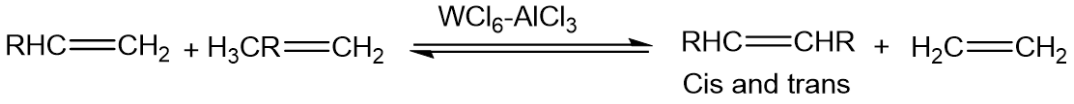
5. Hydroformylation (oxo reaction)

Conversion of alkenes to aldehydes RCH_2CH_2CHO (major) and RCH(CHO)R (minor) in presence of cobalt catalyst.



6. Olefin metathesis

Alkene metathesis or alkene dismutation are reactions in which carbon-carbon double bond is broken and rearranged in a statistical manner to give new products

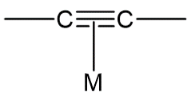


6.6.2. Transition metal alkynyl complexes (structure, synthesis and reactions)

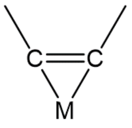
Alkynes differ from alkenes in having an extra pair of pi electrons. They can act as two or four electron donors depending on the need of the metal involved. The extra pair of pi electrons make them excellent bridging ligands.

6.6.2.1. Structure and bonding

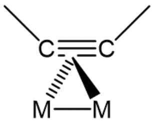
Alkynes can combine as sigma bonding (η^1) and /or π bonding (η^2) giving rise to many coordination modes. Transition-metal alkynyl complexes can be regarded as complexes of the $HC{\equiv}C^-$ ligand, which is isoelectronic with CN^-, CO and N_2. Alkynes are categorized as strong-field ligands in spectrochemical series and good σ and π donors and poor π acceptors, compared to other ligands in the series. Alkynes are better donors than alkenes and coordinate more readily to metal for steric and electronic reasons. They are also more reactive towards undergoing C-C coupling among other reactions. Whenever, alkynes act as bridging ligands as they almost always bridge parallel to M-M axis. They can bridge more than two metals in cluster compounds.



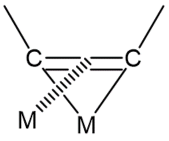
Monodentate



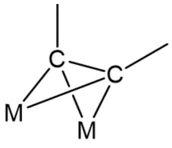
Bidentate



Bidentate

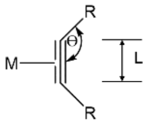


Tridentate

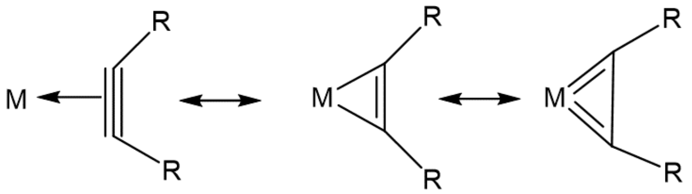


Quadridentate

After coordination, substantial changes are seen in the structure of alkyne moiety such as distortion from linearity (change in angle theta ϴ) and increase in carbon–carbon bond length (L).



Here also, the bonding can be understood based on Dewar Chatt Duncanson model. That is the ligand to metal electron donation takes place via interaction of filled π bonding alkyne orbital with a suitable acceptor orbital on metal. And electron back donation from filled metal d orbital into π* antibonding of alkyne which causes weakening of C≡C bond. The ligand to metal electron donation predominates in high oxidation metal ions and electron rich alkynes. Whereas, the back donation occurs in low oxidation state metals and electron poor alkynes. The net effect of these two electron donating phenomenon is the decrease in carbon–carbon bond order and gives multiple bond character to metal-alkyne linkage. Thus, they are sometimes represented as metallocyclopropenes.



In case of electron deficient metals, the metal alkyne linkage is additionally strengthened by secondary-(π)-alkyne to metal interactions, resulting in alkyne acting as four electron donor.

6.6.2.2. Synthesis

1. From metal carbonyls

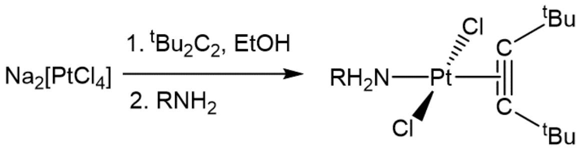
$$M(CO)_6 + RC{\equiv}CR' \xrightarrow{UV} M(CO)_5\,(RC{\equiv}CR') + CO$$

(M= Mo, W)

$$Fe(CO)_5 + RC{\equiv}CR \longrightarrow Fe(CO)_5\,(\eta^2{-}RC{\equiv}CR) + CO$$

$$V(CO)_4(\eta^5{-}C_5H_5)_2 + RC{\equiv}CR \longrightarrow V(CO)_2\,(\eta^2{-}RC{\equiv}CR)(\eta^5{-}C_5H_5)_2 + 2CO$$

2. From transition metal halide salts



3. From alkali metal or alkaline earth metal salts of alkyne

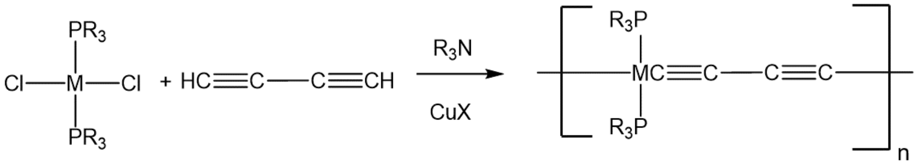
Until recently, most of σ-alkynyl complexes were prepared by the interaction of either an alkali-metal or an alkaline-earth-metal alkynyl complex (M =Li, Na, Mg, etc.) with a transition-metal halide L_nM X (X=Cl, Br, I), or the neutral alkyne itself with a transition-metal complex. The first method is of displacement reaction, in which the alkynyl anion acts as a nucleophile and the metal center as an electrophilic substrate.

$$RC{\equiv}CM + L_nM'X \longrightarrow (RC{\equiv}C)L_nM' + MX$$

(M = Li, Na. Mg; M’= transition metals, X = Cl, Br, I, L_n= any neutral ligand)

4. Dehydrohalogenation

In this process, a cuprous halide is used as a catalyst. Dehydrohalogenation occurs between di-terminal alkynes and transition metal halides. Amine acts as an acid acceptor and solvent.

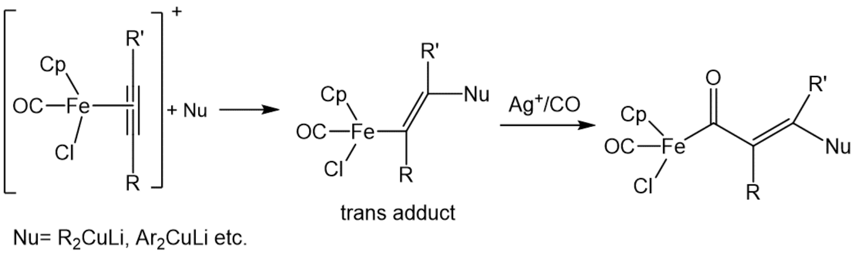


6.6.2.3. Reactions

A. Reactions at C−C triple bond

Nucleophilic addition

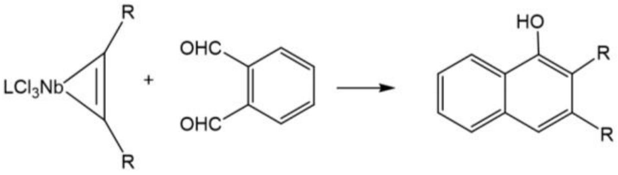
This type of reaction may result in the formation of *cis* or *trans* adduct when direct attack of nucleophile (Nu) occurs at alkyne. It is observed with coordinatively saturated nonlabile complexes. Formation of *cis* adduct probably occurs via initial attack at the metal or at some auxiliary ligand followed by migration of Nu to alkyne. In the reaction shown below, the *trans* adduct is formed which then undergoes oxidative carbonylation.



Electrophilic addition

These types of reactions result in formation of metal-vinyl complexes or final formation of substituted olefins. Because of net electron withdrawal by organometallic fragment, metal alkyl complexes are less reactive than free alkynes towards electrophilic attack.

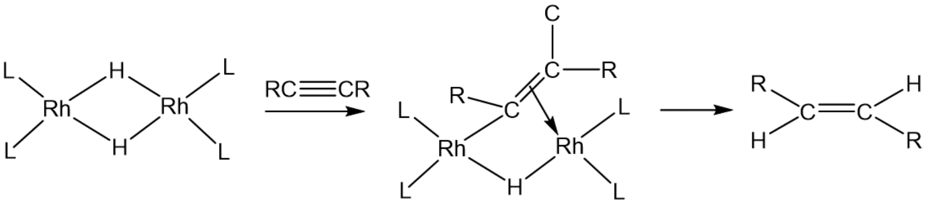
1. A good exception is found in the complex $NbCl_3(THF)_2$(alkyne) owing to its strong nucleophilic character. It reacts with 1,2-aryldihalides in a regioselective manner to yield 2,3-disubstituted-1-naphthols



2. $Pt(PPh_3)_2(\eta^2\text{-}PhC{\equiv}CPh) \xrightarrow{HCl} Pt(PPh_3)_2Cl + PhCH{=}CHPh$

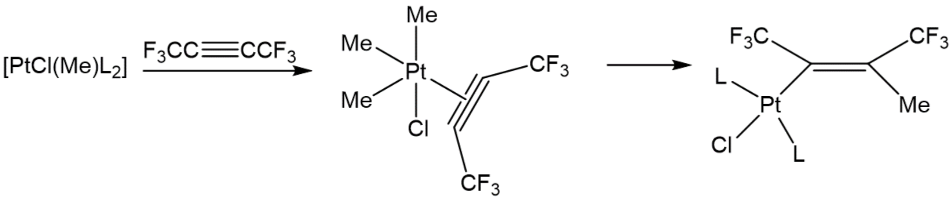
M-H addition / hydrogenation

Trans-hydrogenation of alkynes proceeds via a vinyl species



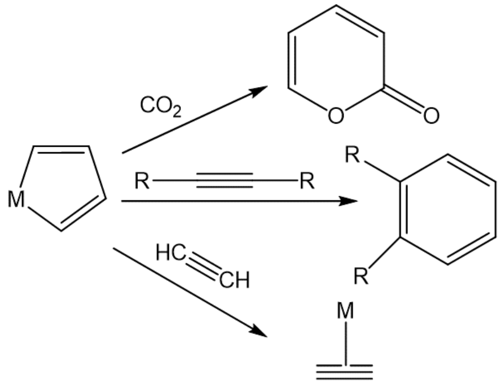
M−C addition

In the reaction of $L_2PtClMe$ with electrophilic alkynes, *cis*-M−C addition is observed.



Coupling reactions with other unsaturated molecules

Alkynes undergo several metal assisted coupling reactions with olefins, alkynes and other unsaturated species leading to cyclization, oligomerization and polymerization. Some of the most common metal-assisted intermolecular cyclo coupling reactions with various species are shown below.



Displacement reactions

Displacement of one alkyne by another has been used for synthesis of new alkyne complexes.

$$Pt(PR_3)_2(HC{\equiv}CH) + RC{\equiv}CH \longrightarrow Pt(PR_3)_2(RC{\equiv}CH) + HC{\equiv}CH$$

Displacement reaction is shown by some other ligands also such as the phosphines.

$$Pt(PR_3)_2(HC{\equiv}CH) + 2PPh_3\ (excess) \longrightarrow Pt(PR_3)_4 + HC{\equiv}CH$$

Reactions on π bond of alkyne

$$HC{\equiv}CH + H_2O \xrightarrow[150^{o}C,\ 130\ atm]{Ni(CO)_4} H_2C{=}CHCOOH$$

$$HC{\equiv}CH + CO + MeOH \xrightarrow[O_2]{PdCl_2\ /\ thiourea} MeOOCHC{=}CHCOOMe$$

6.7. TRANSITION METAL ALLYL COMPLEXES

Metal allyl complexes can be classified as σ allyl (σ-C_3H_5) complexes, π allyl (π-C_3H_5) complexes and allyl bridged (μ-C_3H_5) complexes. In σ allyl complexes (η^1, monohapto form), the allyl radical ($CH_2=CHCH_2^{\cdot}$) contributes only one electron to the metal-allyl bond giving a conventional carbon-metal electron-pair linkage. Whereas in π allyl complexes (η^3, trihapto form), the allyl radical contributes three electrons to metal-allyl bond. This results in a stronger metal-allyl bond in σ complexes. There are some reports where allyl ligand binds in a bridging manner.

6.7.1. σ−Allyl transition metal complexes (structure, synthesis and reactions)

6.7.1.1. Synthesis

These complexes can be synthesized via following methods.

i. Treatment of sodium salt of desired metal carbonyl with allyl halide gives σ allyl complexes

$$Na^+[Mn(CO)_5]^- + ClCH_2CH=CH_2 \longrightarrow (CO_5)Mn(\sigma\text{-}C_3H_5) + NaCl$$

ii. Addition of metal hydrides to conjugated dienes

$$\pi\text{-}C_5H_5Fe(CO)_2H + CH_2=CHCH=CH_2 \longrightarrow \pi\text{-}C_5H_5Fe(CO)_2(\sigma\text{-}CH_2CH=CHCH_3)$$

6.7.1.2. Reactions

σ-allyl complexes are generally yellow oils insoluble in water but soluble in polar solvents.

i. Exposure of σ-allyl metal carbonyl complexes to UV light results in the displacement of carbon monoxide from the metal and formation of a π-ally1 derivative.

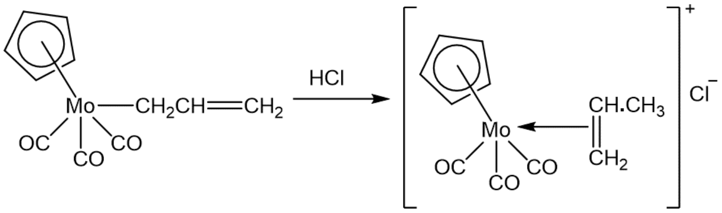
$$(CO_5)Mn(\sigma\text{-}C_3H_5) \underset{\text{Pressure}}{\overset{\text{UV}}{\rightleftharpoons}} (CO_4)Mn(\pi\text{-}C_3H_5) + CO$$

ii. Carbonyl insertion

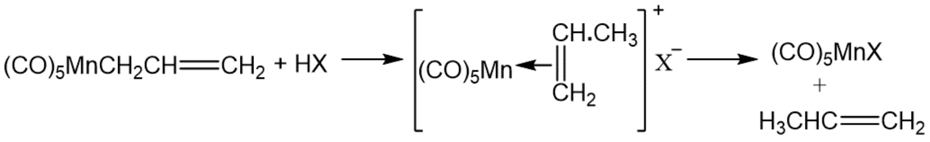
$$CH_2=CHCH_2Co(CO)_4 \underset{+CO}{\overset{-CO}{\rightleftharpoons}} CH_2=CHCH_2COCo(CO)_3 \xrightarrow{PPh_3} CH_2=CHCH_2COCo(CO)_3PPh_3$$

iii. Protonation with acids gives π-ethylenic metal complexes.

(a)



(b)



6.7.2 π−Allyl transition metal complexes (structure, synthesis and reactions)

The structure of π−allyl transition metal complexes was revealed by X ray diffraction studies on π−allylpalladium dichloride (π-$C_3H_5PdCl)_2$. It revealed that the terminal carbons are equivalent, having equal C−C bond length and the three carbons are in plane facing the metal. The molecular orbitals of allyl ligand (Ψ_1, Ψ_2, Ψ_3) interact with the metal in metal allyl complex. The energy of these orbitals increases with increase in number of modes. Usually Ψ_1, and Ψ_2 molecular orbitals participate in ligand to metal σ-donation, where Ψ_1 is involved in dative L-type bonding and Ψ_2 is involved in covalent bonding with metal *d*-orbitals.

6.7.2.1. Synthesis

Experimental precautions in the synthesis of these complexes are essential such as exclusion of air from reaction mixture.

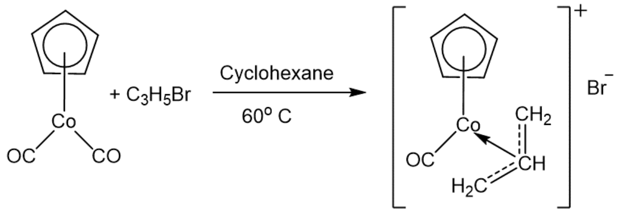
1. Reaction of salts of transition metal carbonyls with allyl halides similar to the one discussed for σ-allyl complexes can be used to obtain π-allyl complexes.

$$Na[Mn(CO)_5] + CH_2{=}CH{-}CH_2{-}Br \longrightarrow (CO)_5Mn(\eta^1\text{-}C_3CH_5) + NaBr$$

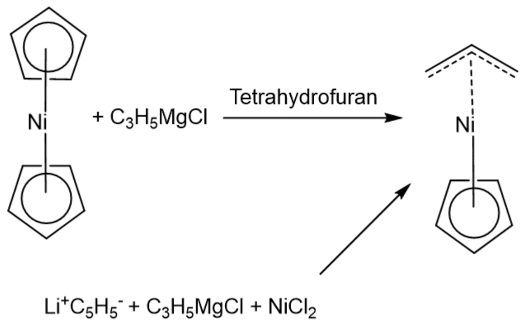
2. Direct reaction between an allyl halide or alcohol and a metal halide or a metal carbonyl.

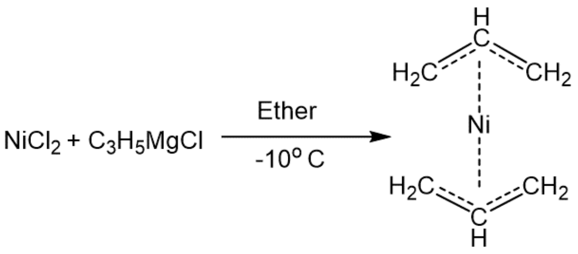
$$H_2C{=}CHCH_2OH + Na_2PdCl_4 \xrightarrow[50^{o}\ C]{50\%\ \text{acetic acid}} [\pi\text{-}C_3H_5PdCl]_2 + Pd^0 + \text{propylene}$$

$$Ni(CO)_4 + C_3H_5Br \xrightarrow[70\ -\ 80^{o}\ C]{\text{Benzene}} [\pi\text{-}C_3H_5NiBr]_2$$



3. Reaction of allyl Grignard reagents with metal salts

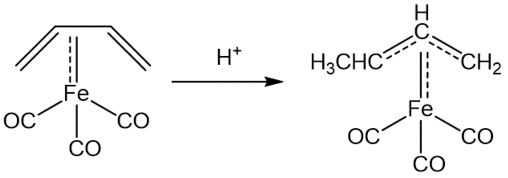




4. Reaction of olefins or allenes (eg. $CH_2{=}C{=}CH_2$) with metal salt also result in formation of allyl complexes. The reaction is believed to proceed via olefin-metal complex intermediate.

$$2MCl_2 + 2C_xH_y \xrightarrow{\text{Low temperature}} \underset{\text{Intermediate olefin complex}}{[MCl_2C_xH_y]_2} \longrightarrow \underset{\pi\text{-allylic complex}}{[MClC_xH_{y-1}]_2} + HCl$$

5.Protonation of diene metal complexes



6.7.2.2. Reactions

The stability of π−allyl transition metal complexes varies greatly. Some palladium complexes are stable above 200 deg C while some are very unstable. Most of these complexes undergo oxidation; some are highly sensitive (such as bis(π-allyl)nickel) and ignite in air.

1. Hydrolysis

$$[\pi\text{-}C_3H_5PdCl]_2 \xrightarrow{H_2O} H_2C{=}CHCHO + H_2C{=}CHCH_3 + Pd^0 + 2HCl$$

2. Displacement reactions

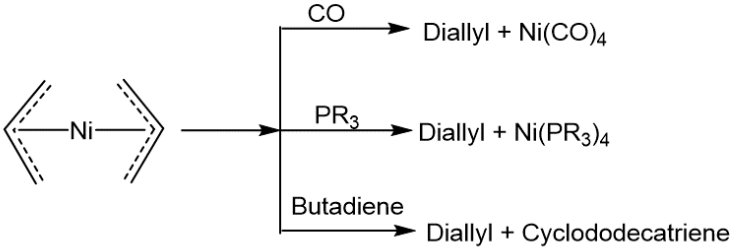
π-allyl groups can be displaced by other ligands such as tertiary phosphines, carbon monoxide, alkenes etc. However, the allyl complexes offer varied degree of resistance to displacement by other ligands.

$$\pi\text{-}C_3H_5Co(CO)_3 + 2(C_6H_5)_3P \longrightarrow \pi\text{-}C_3H_5Co(CO)_2[(C_6H_5)_3P]$$

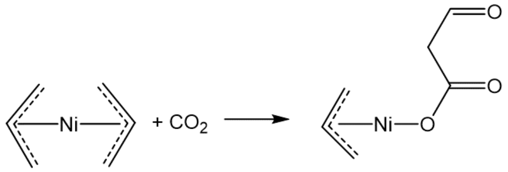
In a similar nickel complex, $[\pi\text{-}C_3H_5NiCl]_2$the π-allyl system is not displaced by triphenylphosphine instead $(NiCl)_2$ bridge is cleaved

$$[\pi\text{-}C_3H_5NiCl]_2 + 2(C_6H_5)_3P \longrightarrow 2\pi\text{-}C_3H_5NiCl[(C_6H_5)_3P]$$

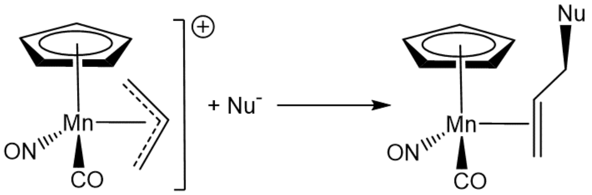
In contrast bis(π-allyl)Ni is very reactive and undergoes displacement of both π-allyl groups.



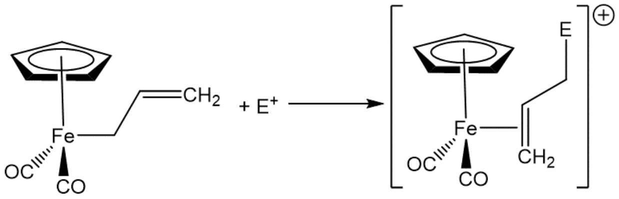
3. Insertion reaction



4. Reaction with nucleophile

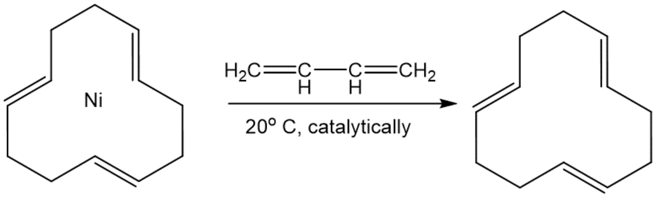


5. Reaction with Electrophile



6. Catalytic properties of π-allyl nickel complexes

The 16 electron complex of cyclododecatrienyl-nickel reacts catalytically with butadiene at 20 C. Here, cyclotrimerization of diene results in the formation of cis and trans isomers of cyclododecatriene. The cyclododecatriene ligand readily “slips-off” nickel.



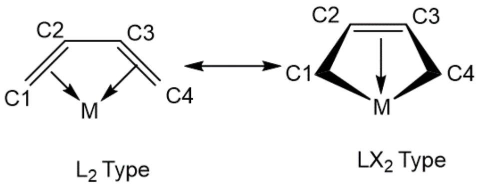
6.7.3 Bridging / μ-allyl metal complexes

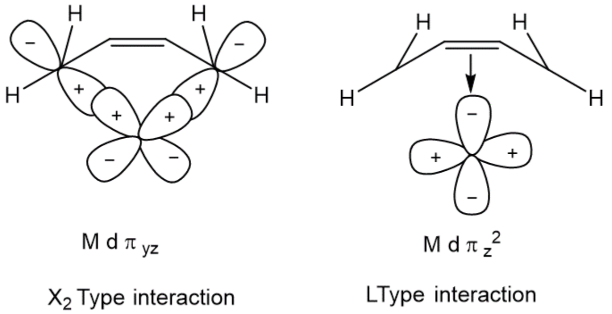
Murdoch and Weiss found on the basis of proton magnetic resonance studies that the complex $C_3H_5Fe(CO)_3I$ exists as in a monomer-dimer equilibrium in solution. It was then suggested that the dimeric species involved bridging allyl groups. However, it is not yet certain that bridging allyl complexes exist but still there is a strong possibility of their existence.

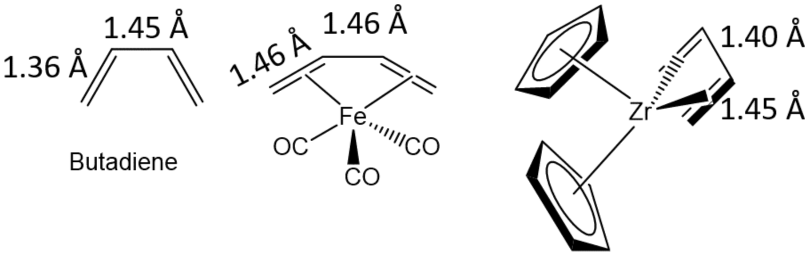
6.8. TRANSITION METAL BUTADIENE COMPLEXES (STRUCTURE, SYNTHESIS AND REACTIONS)

6.8.1. Structure and bonding

The diene ligands discussed here are 4 (hapticity η^4) electron donors. The most studied complexes are of 1,3-butadiene which is a 4-electron donor. It binds to the metal in a cis manner. The Dewar-Chatt model predicts that the ligand may bind to metal as L_2 (π_2) donor type (eg. (butadiene)$Fe(CO)_3$), similar to alkene or as LX_2 ($\sigma_2\pi$) donor type. The L_2 type bonding is less common than LX_2 type. As a consequence of LX_2 type of bonding, C2-C3 bond length (1.45 Å) becomes shorter (1.40 Å)

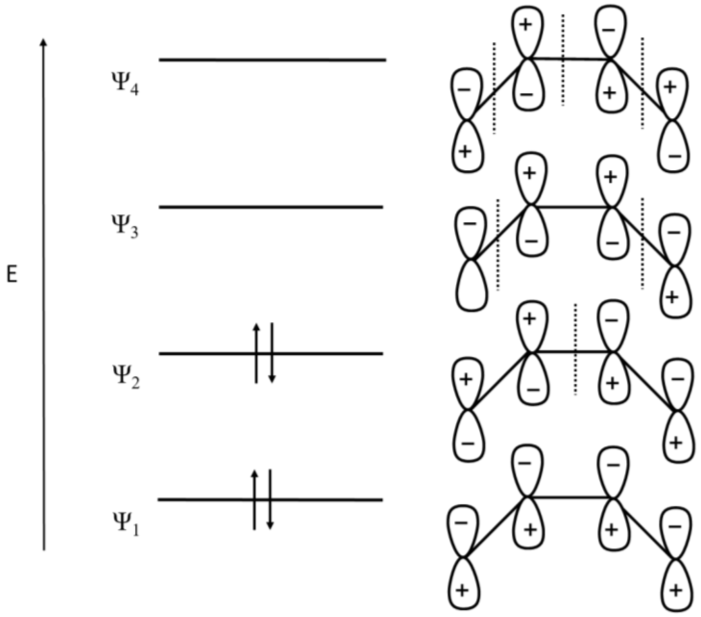






In the above complexes, it can be observed that π back donation from iron (in Fe(η^4-C_4H_6)$(CO)_3$) and σ donation from alkenes to iron weaken and lengthen the C=C bond (becomes 1.46 Å from 1.36 Å). But in the zirconium complex (Cp_2(η^4-$C_4H_6$$(CO)_3$), an interesting reversal is observed. Here the single bond across the back of the butadiene is shortened (becomes 1.40 Å from 1.45 Å). This happens here because Zr is in low +2 oxidation state (it prefers +4 oxidation state) and thus, electron rich; so, it transfers its two electrons to butadiene via π−back donation.

The molecular orbitals of butadiene comprise of two filled Ψ_1 (HOMO-1) and Ψ_2 (HOMO) orbitals and two vacant Ψ_3 (LUMO) and Ψ_4 (LUMO+1) orbitals. In their metal complexes, ligand to metal σ-donation occurs from the filled Ψ_2 orbital of the 1,3-butadiene while the π-back donation occurs from metal to the empty Ψ_3 orbital of butadiene.

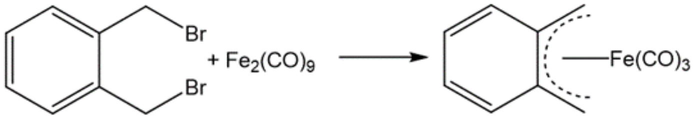


Metal-diene interaction

As mentioned above, the cisoid form is more prevalent in 1,3-butadiene complexes however, few transoid forms are also known such as in dinuclear $Os_3(CO)_{10}C_4H_6$ andmononuclear complexes $Cp_2Zr(C_4H_6)$, shown above.

6.8.2. Synthesis of butadiene metal complexes

1.



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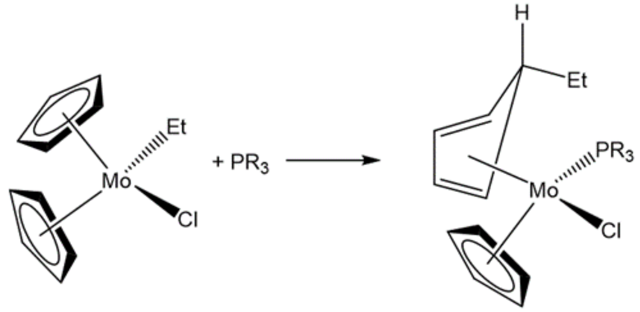


3. $Fe(CO)_5 + CH_2{=}CH{-}CH{=}CH_2 \xrightarrow{\text{Pressure}} Fe(CO)_3(\eta^3\text{-}C_4H_6) + 2CO$

4. $Fe(CO)_5 + CH_2{=}CH{-}CH{=}CH_2 \xrightarrow{\text{UV}} Fe(CO)(\eta^4\text{-}C_4H_6)_2 + 4CO$

5. Using metal vapour

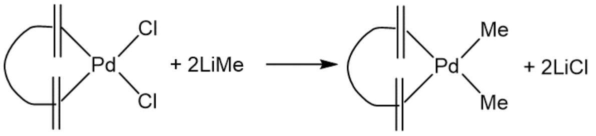
$Cr + CH_2{=}CH{-}CH{=}CH_2 \xrightarrow{4CO} Cr(CO)_4(\eta^4\text{-}C_4H_6)$

6.8.3. Reactions of diene complexes

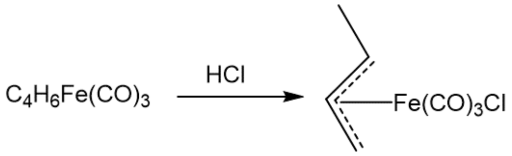
1. Substitution

$Fe(CO)_5 + CH_2{=}CH{-}CH{=}CH_2 \xrightarrow{\text{UV}} Fe(CO)(\eta^4\text{-}C_4H_6)_2 + 4CO$

2. Substitution/addition reactions with nucleophile

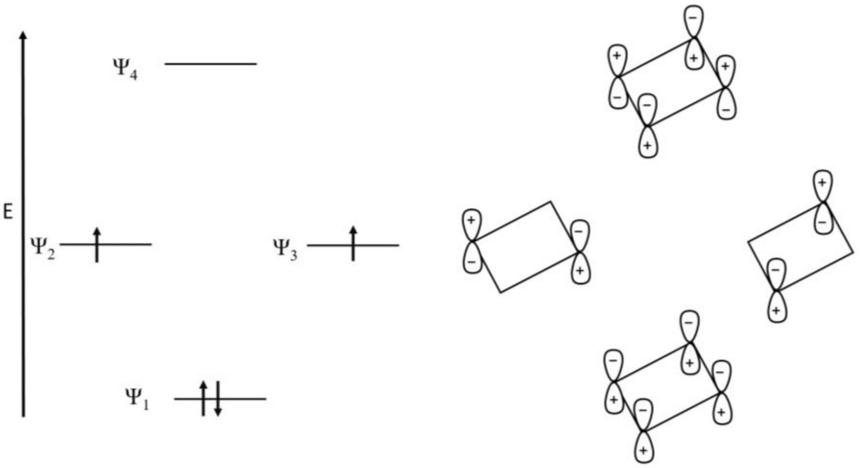


3. Addition of proton (electrophilic addition)



6.9. TRANSITION METAL CYCLOBUTADIENE COMPLEXES (STRUCTURE AND BONDING)

Cyclobutadiene ligand shows interesting behavior because its neutral form is anti-aromatic (4π electrons) and so, unstable as a free molecule. But its dianionic form is stable because it now becomes aromatic having 6π electrons. Electronic structure of cyclobutadiene ligand is shown below.

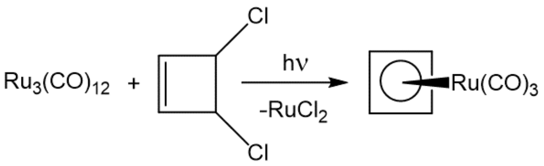


The cyclobutadiene ligand is stabilized by significant π-back donation from metal orbitals to vacant ligand orbitals. It must be remembered that complexation between cyclobutadiene and metal will occur when both the metal and ligand orbitals have similar energies along with matching signs of their wave functions. On complexation, cyclobutadiene acquires a square planar shape.

6.9.1. Synthesis

The first cyclobutadiene complex synthesized is $[\{NiCl(\mu\text{-}Cl)(\eta^4\text{-}C_4Me_4)\}_2]$, since then a large number of complexes have been synthesized.

1.



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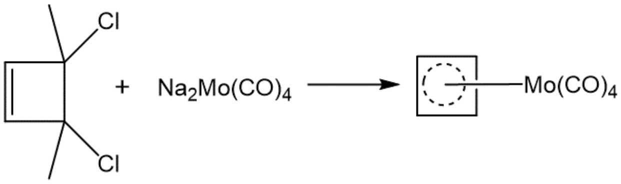

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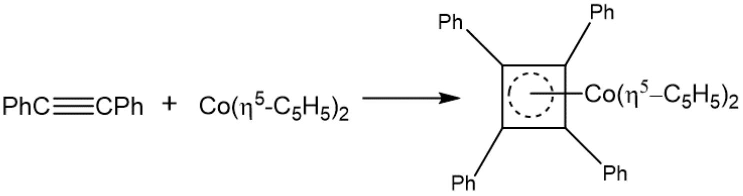
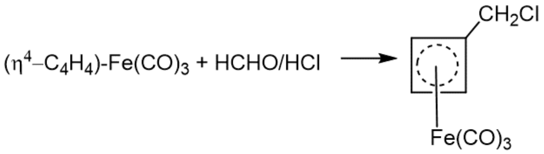


6.9.2. Reactions

Cyclobutadiene in itself is highly reactive and unstable species. Some of the reactions of its metal complexes are shown below.

1.



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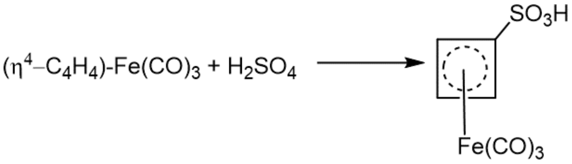

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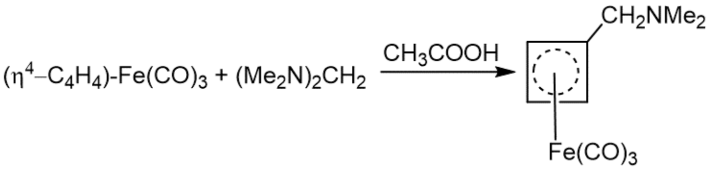

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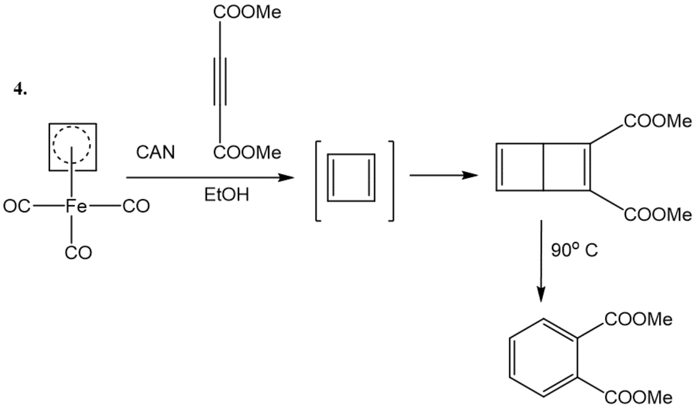
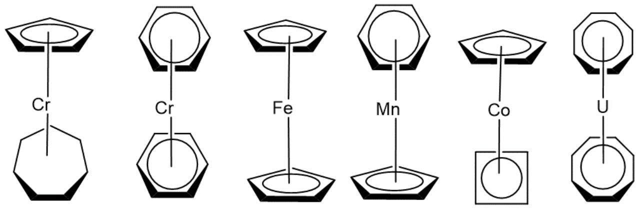


6.10. TRANSITION METAL CYCLOPENTADIENYL COMPLEXES

Dienyl ligands formally contribute five electrons in bonding to transition metals. The most common dienyl is cyclopentadienyl (C_5H_5) abbreviated as Cp. This ligand comprises a wide variety of organometallic compounds. It is inert to most nucleophiles and electrophiles and stabilizes the organometallic complexes. They may be “piano-stool”$CpML_n$ (n= 2, 3 or 4), metallocene Cp_2M type, bent metallocene Cp_2MX_n(n= 1, 2 or 3). In the “piano-stool” structure the Cp ring is designated as the “seat” of the stool and the remaining ligands as its legs. Some other metallocenes are called “sandwich” compounds where the metal atom is present between two carbocyclic rings.

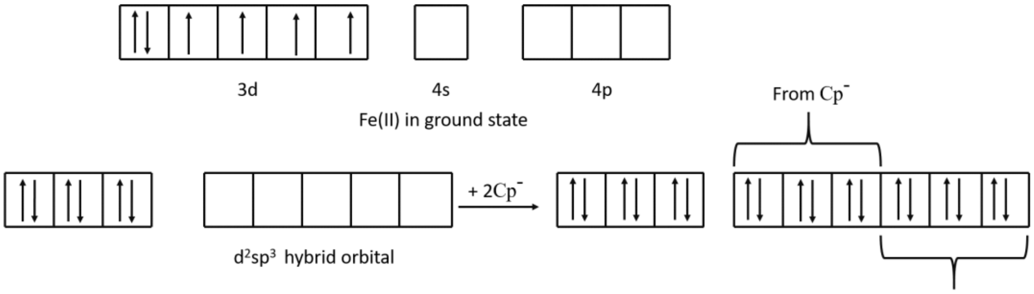
The common binding form to metal is in η^5 form but some lower hapticities are also seen such as η^3 in (η^5-Cp)(η^3-Cp)$W(CO)_2$ and η^1 (monohapto) binding in (η^5-Cp)(η^1-Cp)$Fe(CO)_2$ which are rare. The binding modes of Cp are also ascertained by ^1H NMR spectroscopy. A singlet is observed between 5.5-3.5 ppm for Cp-protons. The complex $(\pi\text{-}C_5H_5)_2Fe$ is commonly called as ferrocene and other similar transition metal complexes are called by their trivial name analogous to ferrocene. The name arose because they participated in reactions similar to those of aromatic compounds. Out of several metallocenes, only ferrocene shows high thermal stability of up to 500^0 C and does not oxidize in air. Some examples of known metallocenes are presented below.



6.10.1 Structure and bonding in ferrocene

In 1952, G. Wilkinson and R. B. Woodward deduced the sandwich structure of ferrocene: two anionic cyclopentadienyl (Cp) rings each donating 6 π electrons to the Fe^{2+} cation between them. The structure of ferrocene as revealed by single crystal X ray diffraction studies confirm iron to be sandwiched between two cyclopentadiene rings. These rings are arranged in an eclipsed manner. All C−C distances are in the range 1.40±0.02 Å. The pentagonal ring of Cp is analogous to hexagonal ring of benzene having sp^2 hybridized carbon. Five electrons from five carbons and one electron from the formation of Cp^- contribute total of six electrons which are present in three of the five π-bonding orbitals while the remaining two π-bonding orbitals are vacant. In the Fe complex, ferrocene, Fe(II) is d^2sp^3 hybridized, each Cp^- coordinates giving three electron pairs. Below is a depiction of electron filling in hybridized orbitals of ferrocene.

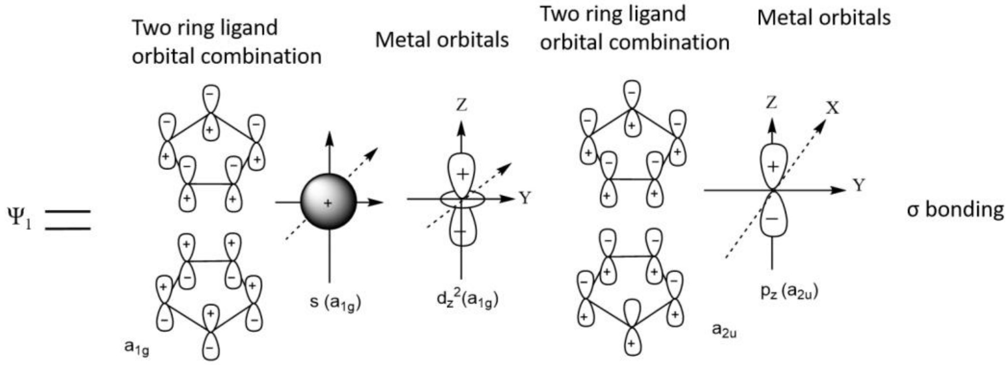
The filled t_{2g} orbitals of Fe(II) are involved in π-back bonding with vacant π^* orbitals of the ligand Cp^-. Thus, each Cp^- acts as a π-donor and π-acceptor in the formation of a sandwich compound.

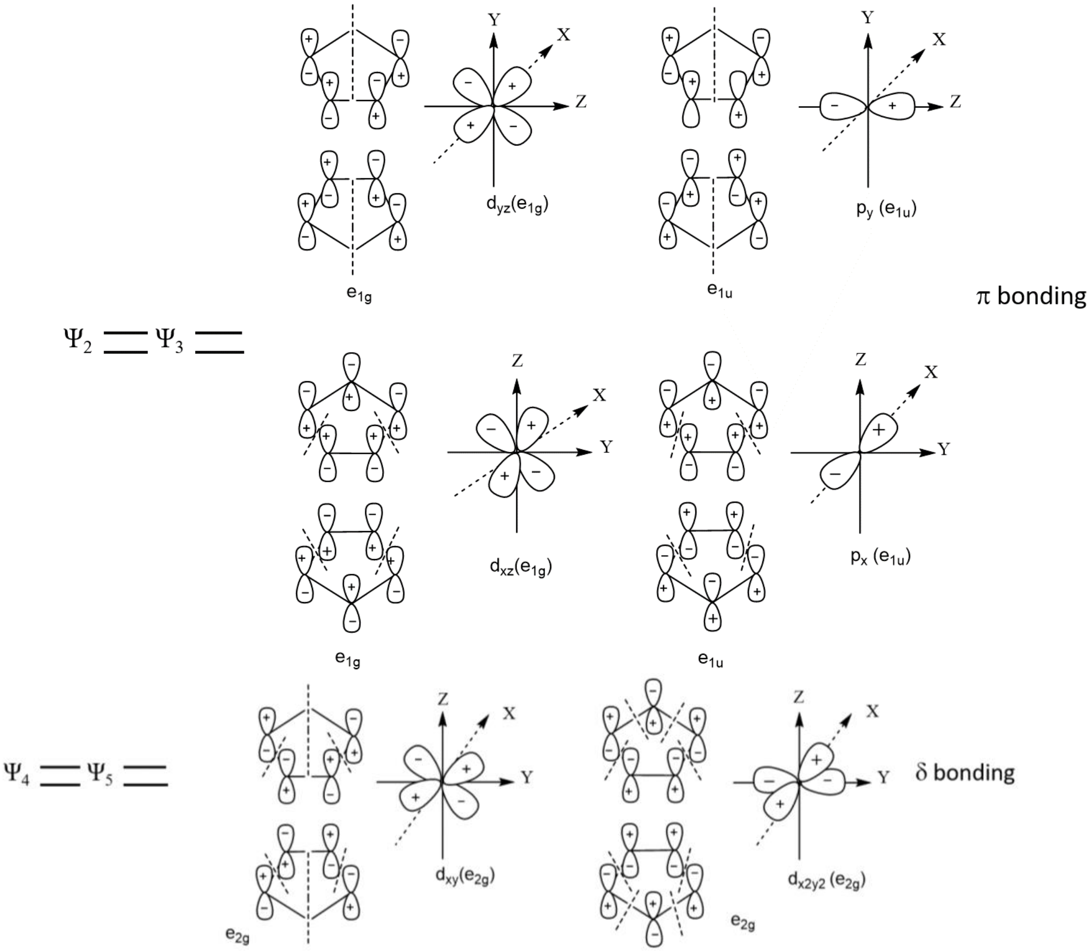


6.10.2. Cyclopentadienyl-metal interaction in ferrocene

The frontier molecular orbitals (FMO) of cyclopentadienyl ligand contain five orbitals (Ψ_1-Ψ_5) distributed within three energy levels. The lowest energy state (Ψ_1)does not contain any node and so represented by a_1 state. Following a_1, the next higher energy states are Ψ_2 and Ψ3 which are doubly degenerate and represented as e_1 states. They have one nodal plane containing the principal axis. Above them lie doubly degenerate Ψ_4 and Ψ_5, designated as e_2 states which have two nodal planes and are even higher in energy. This pattern of doubly degenerate orbitals of increasing energy and nodal planes continues until the number of molecular orbitals is equal to the number of atomic *p* orbitals that is the number of carbon atoms in the ring. If this number is odd, the highest antibonding orbital is degenerate and if it is even then the highest anti bonding orbital is non degenerate.

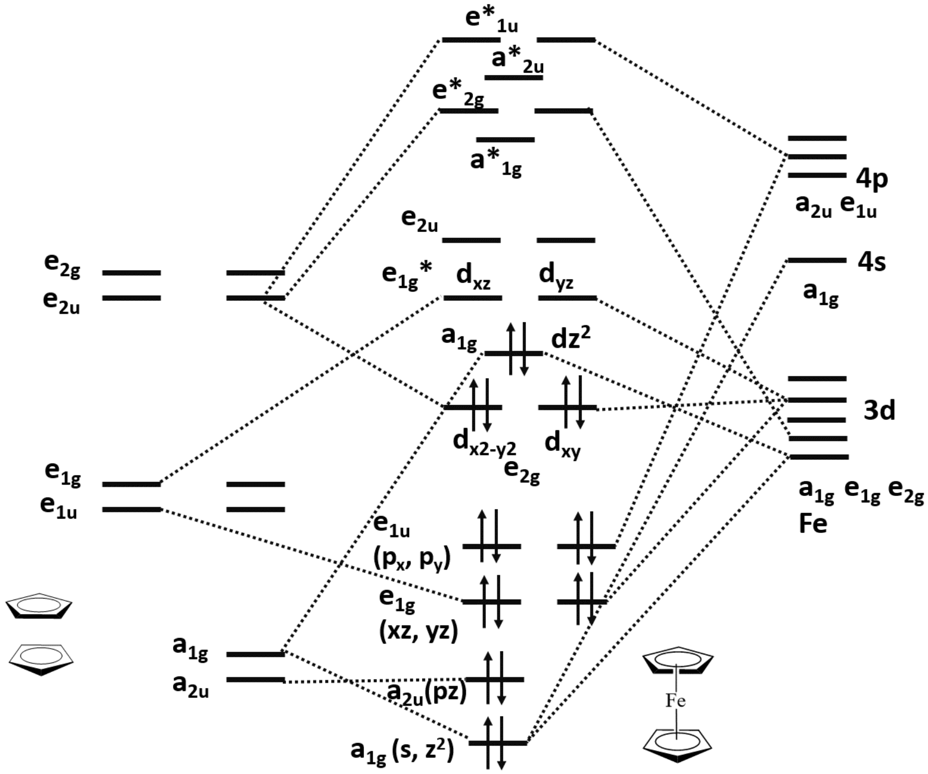
The orbitals on two ligands may interact in addition or in subtraction giving rise to ligand group orbitals (LGO). The wave functions (Ψ) of these five molecular orbitals are derived from the linear combination of the five pπ atomic orbitals wave function (ϕ) of the $C_5H_5^-$ ring. These combine with atomic orbitals of matching symmetry on the metal to form the molecular orbitals (MO). For better understanding, consider the lowest energy ligand bonding orbital. If the wave function of this orbital from the two ligand metallocene rings are added, a gerade ligand group orbital having symmetry (a_{1g}) similar to atomic *s* orbital is formed. Conversely, if the two wave functions are subtracted, an ungerade LGO is produced having same symmetry as that of an atomic *p* orbital (a_{2u}). Thus, in a similar fashion, other LGOs can be constructed by adding or subtracting the higher MOs of the two rings. Overall molecular correlation diagram of Cp_2M type of complexes is generated from the orbitals which subsequently interact with the metal orbitals as shown below.





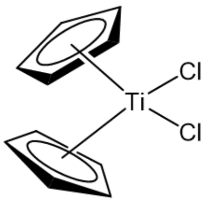
The Cp_2M type complexes are formed by the entire first row of transition metal ions fromSc to Zn. The number of unpaired electrons correspond to the number of unpaired electrons present in the valence orbitals of the metal.

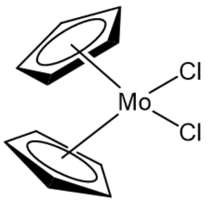
From the first-row transition metal metallocenes, manganocene exists in two forms. First, is a high spin form having five unpaired electrons as in Cp_2Mn and the second is a low spin form with one unpaired electron as in Cp_2^*Mn in which Cp^* has higher field strength. Cobaltocene, Cp_2Co has 19 valence electrons and thus gets oxidized to diamagnetic Cp_2Co^+ which now has 18 valence electrons. Similarly, Cp_2Fe is also diamagnetic with 18 valence electrons. MO diagram of ferrocene is shown below. A total of 18 electrons are filled coming from Fe(II) (6 electrons) and from two $C_5H_5^-$ rings (2x6=12). $Fe(C_5H_5)_2$ is more stable than $Co(C_5H_5)_2$ and $Ni(C_5H_5)_2$ having 19 and 20 electrons respectively. This is due to the fact that in ferrocene there are no electrons in antibonding molecular orbitals (ABMO) whereas in cobaltocene there is one electron and in nickelocene there are two electrons in antibonding molecular orbitals. These electrons are easily removed and thus, cobaltocene and nickelocene are easily oxidized. Similarly, $Cr(C_5H_5)_2$and $V(C_5H_5)_2$ have 16 and 15 electrons respectively thus they have empty bonding molecular orbital-nonbonding molecular orbitals which makes them susceptible to being reduced.



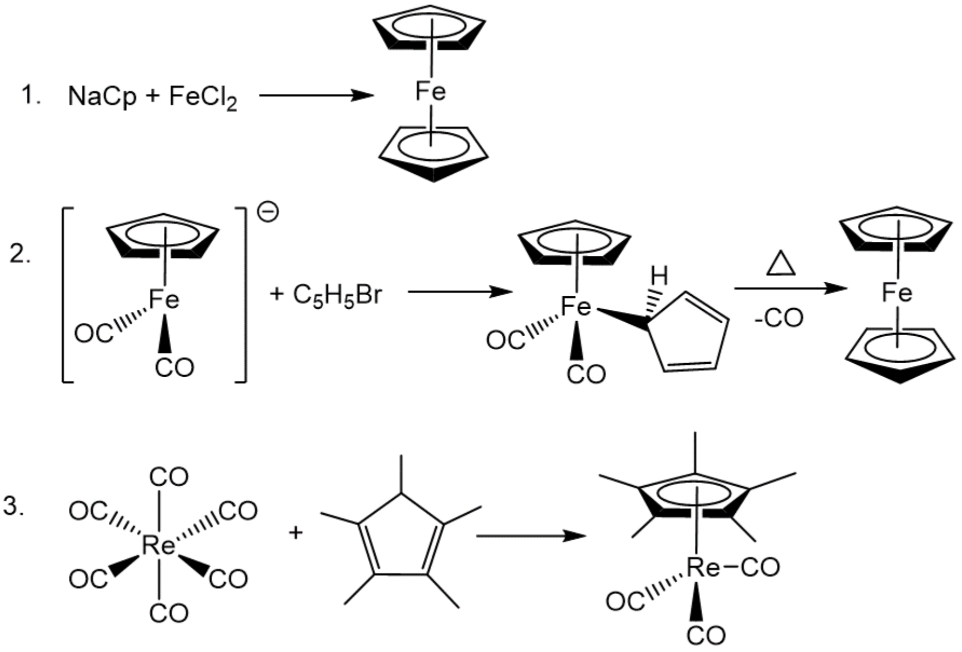
6.10.3. BENT METALLOCENES (Cp_2MX_n)

These are called bent metallocenes since the two Cp rings are bent at an angle and X represents some other auxiliary ligand. They are generally formed by members of group 4 and heavier members of group 5-7. Here frontier doubly degenerate e_{2g} orbitals of Cp_2M moiety interact with the filled lone pair orbitals of the ligand.





6.10.4. Synthesis of cyclopentadienyl metal complexes



4. $2C_5H_5MgBr + FeCl_2 \longrightarrow Fe(C_5H_5)_2 + 2MgBrCl$

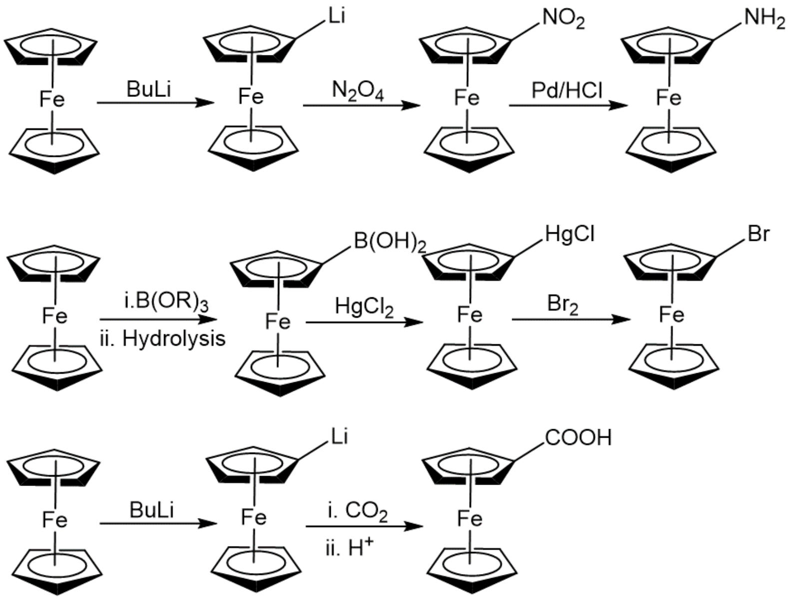
5. $Fe(CO)_5 + 2C_5H_6(g) \longrightarrow Fe(C_5H_5)_2 + 5CO\ (g) + H_2(g)$

6.10.5. Reactivity and properties of cyclopentadienyl metal complexes

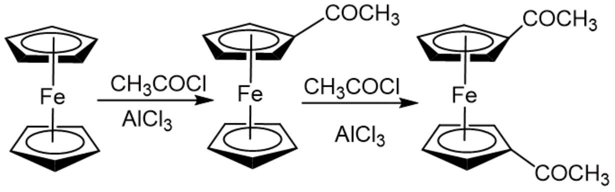
6.10.5.1. Reactions on C_5H_5 rings

The reactions on Cp ring of ferrocene are indicative of its aromatic properties. These include electrophilic substitution reactions and Friedel Crafts reactions.

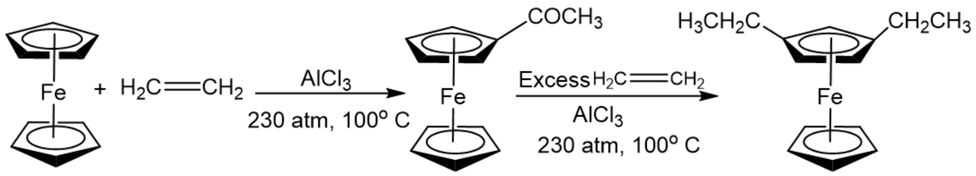
(a) Electrophilic substitution reactions: These include nitration, halogenation carboxylation etc.



(b) Friedel Crafts reactions

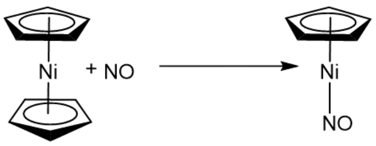


Acetylation

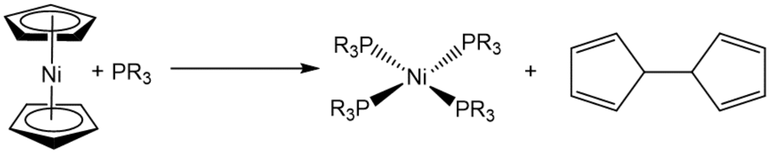


Alkylation

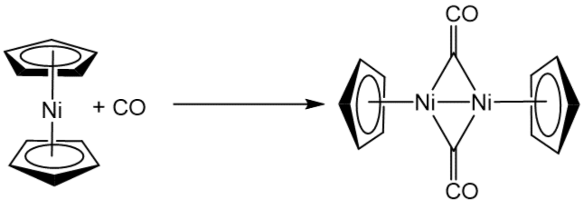
2. Reaction with NO



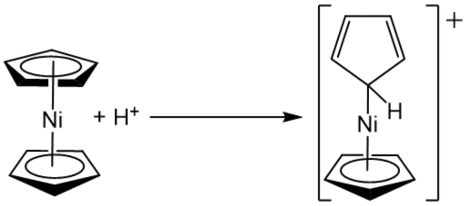
3. Reaction with PR$_3$



4. Reaction with CO



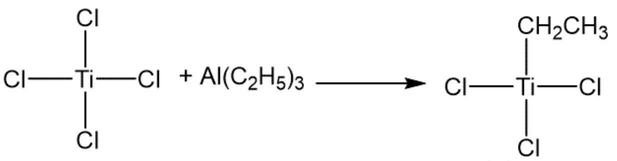
5. Reaction with H$^+$



6.11. SOME OTHER ORGANOMETALLIC COMPLEXES

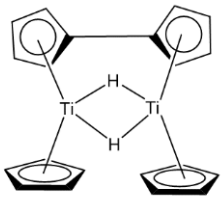
Among other organometallic compounds, those of Ti, Cr, Nb and Mo are well known. Some important ones are discussed here.

The Zeigler Natta catalyst is an organometallic compound of titanium. When $TiCl_4$ is added to triethylaluminium {$Al(C_2H_5)_3$} in hexane, it yields the catalyst which is employed in conversion of ethane to its straight chain polymer polyethene.



Zeigler Natta Catalyst

Titanocene was discovered in 1956 by Wilkinson group as a bright green paramagnetic solid which soon turned brown. But they could not establish its structure correctly. It was much later that the correct structure of titanocene was established as a dimer having Ti−H bonds which were bridging. The structure is shown below.



Some of the known compounds of Nb, Ta with Cp rings are [$Nb(C_5H_5)_2Cl_2$], [$Nb(C_5H_5)_2Cl_3$] and [$Ta(C_5H_5)_2Cl_2$].

6.12. TRANSITION METAL ARENE COMPLEXES

6.12.1 Dibenezene complexes

The arene ligands discussed here are mostly benzene and substituted benzene which are 6 electrons donor (exhibiting hapticity η^6). They form sandwich compounds where the arene ring acts as the flat π-system between which a metal atom is present. These complexes are soluble in organic solvents and are stable upto 200-300^0 C.

Preparation and properties of dibenzene chromium

Dibenzene chromium is a black solid which melts at 280^0 C. Chromium is d^2sp^3 hybridized. Dibenzene chromium was first synthesized by using Grignard reagent. PhMgBr was made to react with $CrCl_3$ to form mono-hapto complex [$CrPh_3(Et_2O)_3$] which rearranges to form $[Cr(\eta^6\text{-}C_6H_6)_2]^+$ along with some other products.

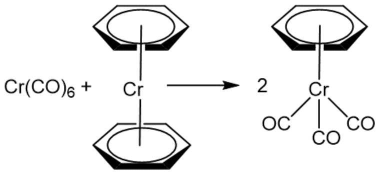
Fischer-Hafner method of arene complex synthesis is adapted more frequently. Here, aluminum is used to reduce the metal salt and $AlCl_3$ is used to assist binding of chromium to benzene. The cation $[Cr(\eta^6\text{-}C_6H_6)_2]^+(AlCl_4)^-$ formed in first step is reduced to dibenzyl chromium with sodium dithionate

($Na_2S_2O_4$). The Fisher-Hafner method has some limitations and does not work well for all metals such as manganese and vanadium. The limitation also extends to substituted benzene. If the substituent has lone pair of electrons such as in chloride or amino group, the lone pair complexes with $AlCl_3$ and stops the reaction.

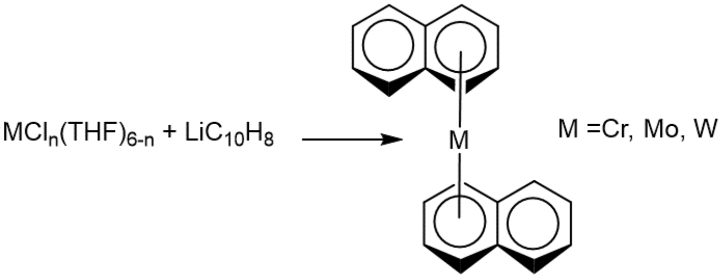
$$3CrCl_3 + 2Al + AlCl_3 + 6C_6H_6 \longrightarrow 3[Cr(\eta^6\text{-} C_6H_6)_2]^+ [AlCl_4]^-$$

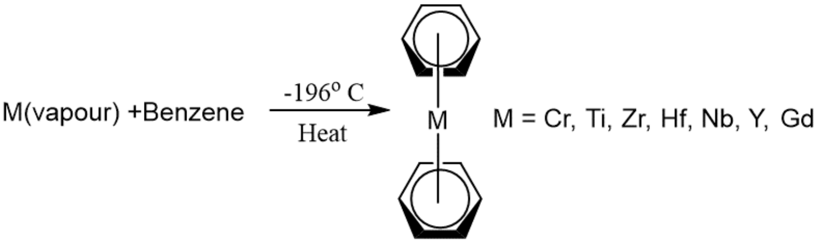
$$2[Cr(\eta^6\text{-} C_6H_6)_2]^+ [AlCl_4]^- + Na_2S_2O_4 + 4NaOH \longrightarrow 2[Cr(C_6H_6)_2] + 2Na_2SO_3 + 2NaCl + 2AlCl_3 + 2H_2O$$

Complexes of dibenzene with Cr, Mo and W are air sensitive. The benzene rings in these complexes are eclipsed and have small rotational barrier that is their orientation can be altered easily. Furthermore, these rings are labile and so can be substituted easily which is unlike Cp rings in ferrocene. The reaction shown below also holds for dibenzene Mo and W complexes.



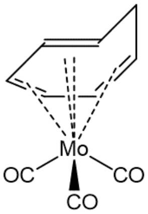
6.12.2. Synthesis of some other arene complexes



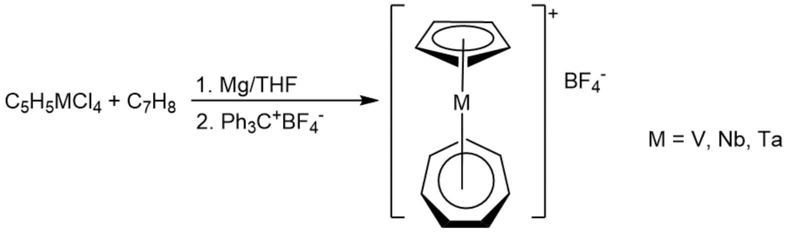


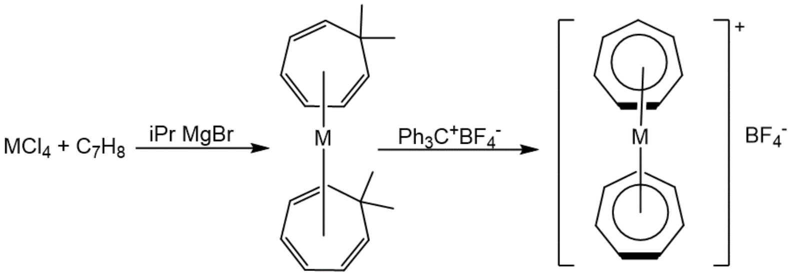
6.13. CYCLOHEPTATRIENE COMPLEXES

Cycloheptatriene is also six electrons donor similar to benzene but differs in delocalization of electrons in C_7H_8. It is non aromatic since it lacks planarity. In $C_7H_8Mo(CO)_3$, the double bonds are arranged trans to carbonyl ligands.



Synthesis of some cycloheptatrienyl complexes





6.14. CYCLOOCTATETRAENE COMPLEXES

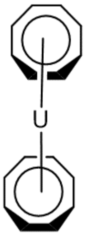
Cyclooctatetraene or Cot has four π-bonds and hence, total of 8 eight electrons. Since, it does not follow Huckel's rule of (4n+2) electrons and is non planar, it is non aromatic compound. Cot is twisted into a "tub-shape" which is 18 kcal more stable than the flat anti-aromatic form. However, its dicationic form is planar and aromatic.

$$2K + C_8H_8 \longrightarrow 2K^+ + (C_8H_8)^{2-}$$

Cyclooctatetraene "tub-shape"(8 π electrons) Cyclooctatetraene dianion (10 π electrons)

The Cot dianion like Cp^- anion reacts with actinides in their tetrapositive state (U^{4+}, Np^{4+}, Th^{4+}, Pu^{4+}) and forms neutral metallocenes. The sandwich compound with uranium was the first metallocene synthesized with Cot^{2-} and called as uranocene.

$$UCl_4 + 2Cot^{2-} \longrightarrow U(Cot)_2$$



6.15. SUMMARY

This chapter provides understanding of a very important area of inorganic chemistry that is organometallic chemistry. The unit builds the concept of synthesis, bonding and chemical reactivity of organometallic complexes. It brings about a connection between organic and inorganic chemistry. The concept of σ-bonding and π-back donation is the highlight of many organometallic complexes. The study of these compounds is crucial because they play an important role in as catalysts in many organic synthetic reactions.

6.16. TERMINAL QUESTIONS

Q1. The………….. of C−C bond distance in the metal bound olefin moiety is observed as a result of ligand to metal …………

Q2. What is the oxidation state of Pt in Zeise's salt?

Q3. Mention the type of orientations displayed by butadiene ligands for binding to metal

Q4. The number of π−electrons present in the cyclobutadiene moiety of a metal cyclobutadiene complex.

Q5. What different hapticitiesare exhibited by cyclopentadienyl ligand?

Q6. Specify the hapticities of the cyclopentadienyl ligands in $Cp_2W(CO)_2$

Q7. Specify the hapticity of the cyclopentadienyl ligands in $CpRh(CO)_2(PMe_3)$

Q8. What is the hybridization of carbon in carbene.

Q9. Give the formal oxidation state of the metal and the number of d-electrons in$(\eta^6\text{-}C_6H_6)_2Cr$

Q10. Calculate and suggest if the given compounds follow 18 electron rule.

(i) $[ReCl(H_2C{=}CH_2)(dppe)_2]^+$; [dppe = $Ph_2PCH_2CH_2PPh_2$]

(ii) $CpMo(PMe_3)_2(C{\equiv}CMe)(CO)$

(iii) $Cp_2Rh_2(\mu\text{-}NHMe)_2$

6.17. ANSWERS

A1. lengthening, σ− donation

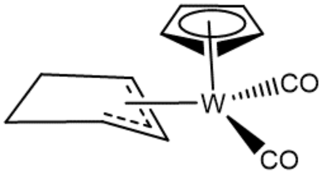
A2. Pt(II)

A3. Cisoid (common) and transoid (rare).

A4. Six

A5. 1, 3, and 5

A6. 5 and 3

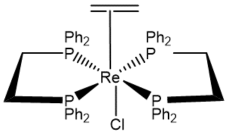


A7. 3

A8. sp^2

A9. Cr(0), d^4

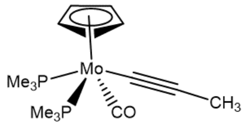
A10.(i) Re(+2) = 5e; Cl^- = 2e; $CH_2{=}CH_2$ = 2e; 2dppe= 8e



Total= 17 electrons

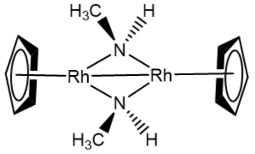
(ii) Mo(+2)= 4e; Cp^{-}= 6e; CCR^{-}= 2e; CO= 2e; 2PR3= 4e

Total= 18 electrons



(iii)Rh(+2)= 6e; Cp^{-}= 6e; 2μ-$NHMe^{-}$= 4e; Rh-Rh= 1e

Total= 18 electrons



6.18. REFERENCES

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Block II : METAL π-COMPLEXES AND METAL CLUSTERS

UNIT 7 METAL CLUSTERS

CONTENTS

7.1. OBJECTIVES

The chapter covers boranes, carboranes, metalloboranes, metallocarboranes along with various aspects of isopoly and heteropoly acids. This chapter aims at providing a good understanding of metal cluster compounds with respect to their synthesis, structure and properties. Types of boranes, carboranes, their synthesis and various bonding aspects in these class of compounds will be focused. Metal clusters have multiple metal atoms which have extensive coordination environment. It draws the attention of the reader towards the change in chemistry of these materials from that of the bulk metal.

7.2. INTRODUCTION

Clusters are a collection of atoms or molecules which are intermediate in size between a molecule and bulk solid. They may have varied nuclearities and stoichiometry and can be considered as link between atoms, molecules and bulk material. The properties of clusters change with size. Metal clusters have metal-metal bonds. This chapter first deals with boron compounds and then gradually leads to clusters such carboranes, metalloboranes, metallocarboranes and isopoly-heteropoly acids. These complex materials find various applications in the synthesis of various organic derivatives and industry.

7.3. BORANES

7.3.1. Boron

Boron occurs naturally as *borax* $Na_2B_4O_5(OH)_4.8H_2O$ and as *kernite* $Na_2B_4O_5(OH)_4.2H_2O$. Some other ores of boron are Colemanite, Urexite and Kernite. Borate minerals contain trigonal BO_3 or tetrahedral BO_4 units. Boron has two stable isotopes, $^{5}B_{11}$ (80.4% abundance) and $^{5}B_{10}$ (19.6%), of which $^{5}B_{10}$ has a very high neutron absorption cross section. Boron is a non-metal belonging to group 13 (III A) whereas the other elements of this group show metallic properties. Thus, the chemistry of boron is quite different from other elements of the group. Boron resembles carbon and silicon in its tendency to form covalent compounds using its sp^2 hybridized orbitals. No ionic compounds containing B^{3+} cations are formed because the energy of ionization is very high. All BX_3 compounds are coordinatively unsaturated and behave as Lewis acids with Lewis bases generally forming adducts.

7.3.2. Boron hydrides or boranes

Boron forms several hydrides known as *Boranes*, composed solely of boron and hydrogen bonds and may be neutral or ionic. They are electron deficient species possess fewer valence electrons than are required for a localized bonding scheme. Their chemistry was first studied by Alfred Stock. Typical boranes are B_2H_6, B_4H_{10}, $B9H_{15}$, $B_{10}H_{14}$, and $B_{20}H_{16}$.

7.3.2.1. Nomenclature

The nomenclature of boranes is somewhat simple. As mentioned before boranes exist as neutral and ionic species.

Neutral Boranes**:** For neutral boranes, prefix di, tri etc. are used before 'borane' to indicate the number of boron atoms. The number of hydrogen atoms are indicated by writing the Arabic numeral in the parentheses at the end. For example:

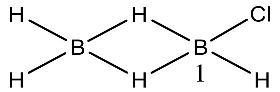
BH_3	borane (3)
B_2H_6	diborane (6)
B_3H_7	triborane (7)
B_4H_{10}	tetraborane (10)
B_5H_9	pentaborane (9)
B_5H_{11}	pentaborane (11)
B_6H_{10}	hexaborane (10)
$B_{10}H_{14}$	decaborane (14)
$B_{10}H_{16}$	decaborane (16)
$B_{20}H_{16}$	icosaborane (16)

It is to be noted that these names are based on the molecular formula and not on their structures. Generally, the numbers in the bracket are not written.

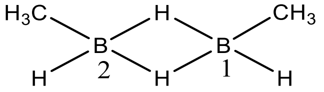
***Anionic Boranes*: For anions the name ends with ‘ate’ and the number of hydrogen and boron atoms are specified along with the charge. Example:

$Na[B_2H_7]$	sodium heptahydrodiborate(1 -)
$Na_2[B_2(C_6H_5)_6]$	sodium hexaphenyldiborate(2 -)
$Ca[B_3H_8]_2$	calcium octahydrotriborate(1 -)
$Na_2[B_{10}Cl_{10}]$	sodium decachlorodecaborate(2-)
$Na_2[B_{10}H_{10}]$	sodium decahydrodecaborate(2-)
$Na[B_{10}H_9NH_3]$	sodium amminenonahydrodecaborate(1-)
$B_{10}H_8(NH_3)_2$	diammineoctahydrodecaboron
$[B_{10}H_7(NH_3)_3]^+$	triammineheptahydrodecaboron(1+) ion
$[B_{10}H_8(COOH)_2]^{2-}$	dicarboxyoctahydrodecaborate(2-) ion
$Na_2B_4O_7$	sodium heptaoxotetraborate(2-) or sodium tetraborate

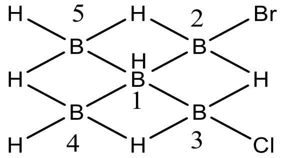
Certain prefixes such as ‘closo, nido and arachno are used. This classification will also be discussed. Eg. $Na_2[B_{10}H_{10}]$ sodium decahydro-*closo*-decaborate(2-), [$B_{12}H_{11}$Clchloroundecahydro dodecaborate(2-)ion.



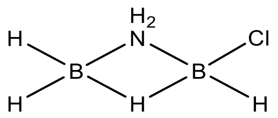
1-chlorodiborane (6)



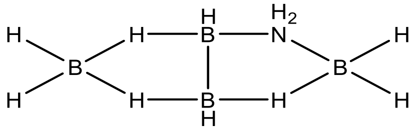
1,2-dimethyldiborane (6)



2-bromo-3-chloropentaborane (9)



μ–aminodiborane (6)



1,2-μ-aminotetraborane (10)

Substituted Boranes

7.3.2.2. Classification

Higher boranes or borane clusters possess deltahedral structures which are somewhat complex in terms of their 3c-2e bonding (**Figure 7.1**). A deltahedron is a polyhedron that possesses only triangular faces, e.g., an octahedron. The boranes are mainly classified as:

1. ***closo***-B_nH_{n+2} (*closo*-Greek for cage), *Closo* pertains to the most symmetrical form that is a closed polyhedra

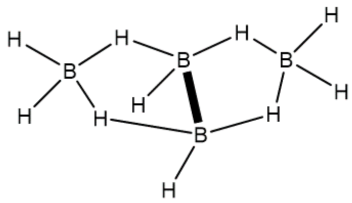
2. ***nido***-B_nH_{n+4} (*nido*-Greek for nest), *nido* has one of the vertexes removed from a regular polyhedral; (n + 1)-cornered polyhedron.

3. ***arachno***-B_nH_{n+6} (*arachno*-Greek for spider web). *Arachno* is a higher version of *nido*, with most highly connected boron vertex on the open face removed. Thus, the *arachno* form has two vertices missing; (n + 2)-cornered polyhedron.

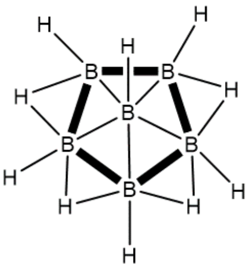
4. ***Hypho***- B_nH_{n+8} (Greek: net like): They have the most open clusters in which the B atoms occupy n corners on an (n + 3)-cornered polyhedron.

5. ***Conjuncto***- B_nH_{n+10} (Latin: join together): They have structures formed by linking together of two or more of the above-mentioned type of clusters.

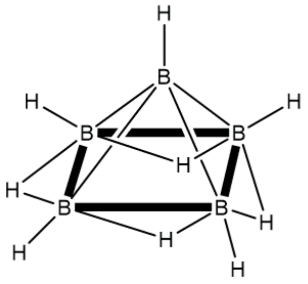
They can also be written as having the general formula $B_nH_n^{2-}$, $B_nH_n^{4-}$, $B_nH_n^{6-}$, $B_nH_n^{8-}$, $B_nH_n^{10-}$ for closo, nido, arachno, hypho and conjuncto respectively. That is formally subtracting the number of H^+ ions from the formula to make the number of boron and hydrogen atoms equal.



B_4H_{10} arachno



B_6H_{10} nido



B_5H_9 nido

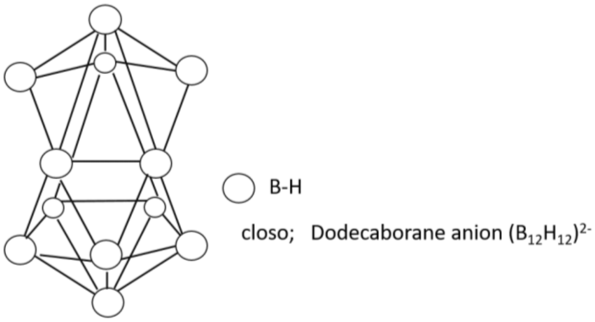


Figure 7.1. *Structure of various types of boranes*

7.3.2.3. STYX number

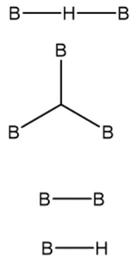
The Styx rules were given by Lipscomb to determine what type of bonds are possible for a given formula of boron hydride. It is assumed that one B–H bond is present for each boron atom.

i. The centre 3c-2e, B–H–B bond is labelled as ‘S’

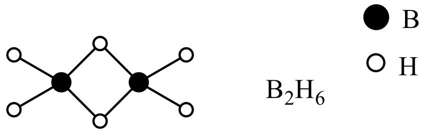
ii. Closed or open 3c-2e B–B–B bond is labelled as ‘T’

iii. The 2c-2e B–B bond is labelled as ‘Y’

iv. The B–H terminal bond (2c-2e) labelled as ‘X’ or simply we can say number of BH_2units

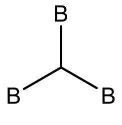


The B–B–B bond may be open or closed but it is the closed bonds that are always considered.



Total valence electrons two B and six H = 12
STYX number is 2002

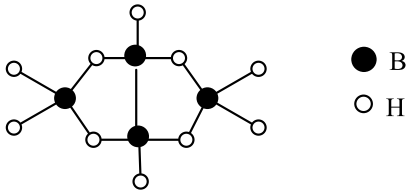
B—H—B (Bridging) Electrons used = 2x2 = 4; S = 2



T = 0

B—B Y = 0

B—H Four terminal BH bonds, electrons used = 4x2=8
Extra BH X = 2

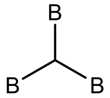


B_4H_{10}

Total valence electrons; four B and ten H, total = 12 + 10 = 22

STYX number is 4012

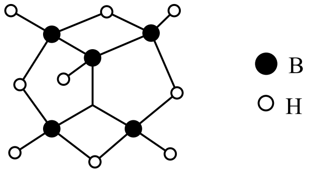
B—H—B (Bridging) Electrons used = 4x2= 8; S = 4



T = 0

B—B One B-B bond; electrons used = 2; Y = 1

B—H Six terminal BH bonds, electrons used = 6x2 = 12; X = 2

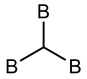


B_5H_9

Total valence electrons; five B and nine H, total = 15 + 9 = 24

STYX number is 4120

B—H—B (Bridging) Electrons used = 4x2 = 8; S = 4



One closed B-B-B bond; 3c-2e; electrons used = 2; T = 1

B—B Two B-B bond; 2c-2e; electrons used = 4; Y = 2

B—H Five B-H bonds, electrons used = 5x2 = 10; X = 0

7.3.2.4. Diborane(6)

Synthesis

Diborane(6), B_2H_6 is a gas and like most boranes it is air-sensitive and catches fire. It is spontaneously hydrolyzed by water into hydrogen and boric acid.

One of the simplest methods is hydride abstraction from BH_4^-.

$$BH_4^- + BX_3 \longrightarrow \tfrac{1}{2} B_2H_6 + HBX_3^- \ (X = Cl, Br)$$

$$3\ NaBH_4 + 4\ BF_3 \xrightarrow{\text{Ether}} 2\ B_2H_6 + 3\ NaBF_4$$

$$2\ NaBH_4 + I_2 \xrightarrow{\text{Diglyme}} B_2H_6 + 2\ NaI + H_2$$

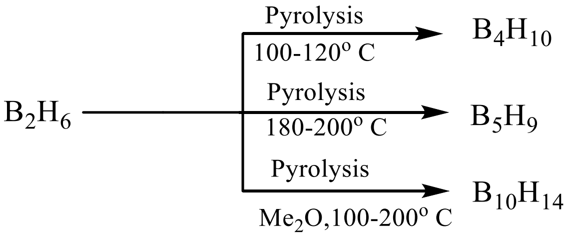
At industrial scale, diborane is prepared by reduction of BF_3 with sodium hydride

$$2\ BF_3 + 6\ NaH \longrightarrow B_2H_6 + 6\ NaF$$

Diborane acts as a very versatile reagent in synthesis of organoboranes. It also acts as a reducing agent for certain functional groups such as nitriles and aldehydes.

Synthesis of some higher borane and their ions

Most of the higher boranes can be prepared from diborane by controlled pyrolysis reactions.



$$B_{10}H_{14} + R_3N \xrightarrow{150^oC} 2(R_3NH)^+ + B_{10}H_{10}^{2-} + H_2$$

$$6\ B_2H_6 + R_3N \xrightarrow{150^oC} 2(R_3NH)^+ + B_{12}H_{12}^{2-} + 11\ H_2$$

7.3.2.5.Structure and bonding

In the earliest stages of decoding the structure of diborane, many errors and contradictions led to the establishment of the structure known today. The imminent deficiency of electrons in their structural formula indicates that there cannot be conventional 2c-2e (two center-two electron, two electrons are shared between two atoms) bonds. Thus, in the efforts to rationalize the structure of boranes, earliest concepts of multicenter bonding were developed. Languet-Higgins proposed the theory of 3c-2e (three center-two electron) bonds which greatly helped in the understanding of bonding in boranes. This implies that a pair of electrons can share more than two atomic centers.

The simplest borane i.e. diborane B_2H_6, is two electron short species for bonding when compared with its electron-precise analogue C_2H_6. Thus, diborane is two electron short of conventional 2c-2e bonding. It was proposed that BH_3 exists as dimer to form B_2H_6. This was later confirmed by X-ray diffraction studies. These studies revealed the presence of *terminal* and *bridging* hydrogen atoms. The two-terminal hydrogen atoms present on each boron atom form the conventional 2c-2e bonds; thus, utilizing eight electrons out of the total of 12 electrons. The remaining two H atoms are bridging in nature. They link together the two boron centers (B-H-B) as shown in **Figure 7.2**. The bridging bonds are electron deficient utilizing only 4 electrons and form 3c-2e bonds. Thus, the deficiency of two electrons is compensated by the formation of the electron deficient B–H_μ–B bridging bonds (**Figure 7.2**). The higher boranes acquired a deltahedral structure and involve formation of several 3c-2e bonds.

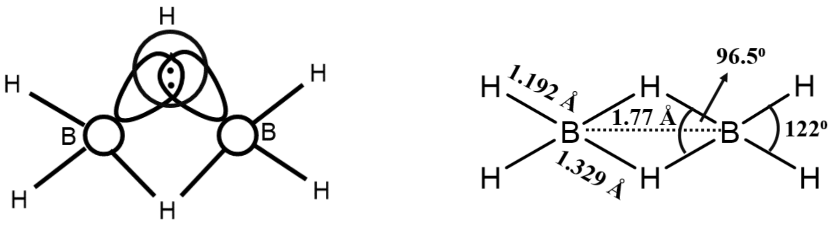
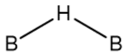
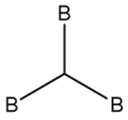
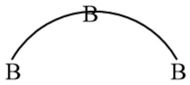


Figure 7.2. *Bonding of diborane*

Various types of bonds found in boranes are shown below.

	2c-2e boron-hydrogen bond
	3c-2e bridging boron-hydrogen-boron bond
	2c-2e boron-boron bond
	3c-2e closed boron bond
	3c-2e open B-B-B bond

7.3.2.6. Reactions

Diborane

1. Reaction with oxygen

$$B_2H_6 + 3\,O_2 \longrightarrow B_2O_3 + 3\,H_2O;\ \text{Exothermic reaction } \Delta H = -2160\ \text{kJ/mol}$$

2. Reaction with water

$$B_2H_6 + 6\,H_2O \longrightarrow 2\,B(OH)_3 + 6\,H_2$$

3. Reaction with acids

- Diborane is hydrolyzed by weak acids such as alcohols.

$$B_2H_6 + 6\,ROH\ \text{(weak acid)} \longrightarrow 2\,B(OR)_3 + 6\,H_2$$

- With HCl, a terminal hydrogen is replaced with chlorine

$$B_2H_6 + HCl \longrightarrow B_2H_5Cl + H_2$$

4. Reaction with chlorine

$$B_2H_6 + 6\,Cl_2 \longrightarrow 2BCl_3 + 6\,HCl$$

5. Reaction with nucleophile

The electron deficient 3c-2e B-H-B sites are prone to attack by nucleophiles such as NH_3, $(CH_3)_2NH$, CH_3NH_2

$$B_2H_6 + 2\,NH_3 \longrightarrow [H_2B(NH_3)_2]^+[BH_4]^-$$

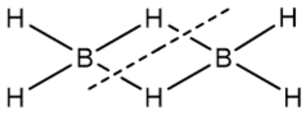
- Boronium ions formed above of the type $[H_2BL_2]^+$ undergo substitution by other bases such as PR_3

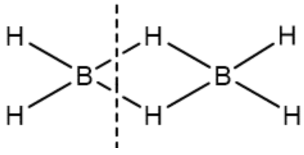
$$[H_2B(NH_3)_2]^+ + 2\,PR_3 \longrightarrow [H_2B(PR_3)_2]^+ + 2\,NH_3$$

- Large amines cause symmetrical cleavage of diborane giving Lewis base adducts of BH_3

$$B_2H_6 + 2\,N(CH_3)_3 \longrightarrow 2H_3B \longleftarrow N(CH_3)_3$$

- Reactions with NH_3 and $N(R)_3$ reveal that Soft Lewis bases induce symmetrical cleavage of diborane, while hard Lewis bases induce asymmetrical cleavage.





5. Reduction

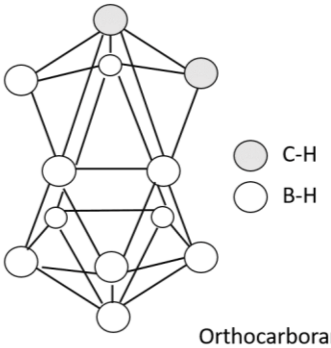
$$2\ B_2H_6 + 2\ Na \longrightarrow NaBH_4 + NaB_3H_8$$

$$B_2H_6 + NaBH_4 \longrightarrow NaB_3H_8 + H_2$$

$$5\ B_2H_6 + 2\ NaBH_4 \longrightarrow Na_2B_{12}H_{12}$$

7.4. CARBORANES

Carboranes are large family of clusters which contain boron and carbon atoms. They are mixed hydrides of carbon and boron having electron deficient molecular structure. The carboranes are considered to be derived from $BnHn^{2-}$ by replacement of BH^{-} unit(s) with isoelectronic (since C atom has one more electron than B so CH moiety is isoelectronic with BH^{-}) and isostructural CH unit(s).



Orthocarborane ($C_2B_{10}H_{12}$)

Each C-H group is regarded as donating 3 electrons to the framework electrons. So, a replacement of two BH^{-} will give a neutral molecule having general formula $B_{n-2}C_2H_n$. Carboranes having n =5 to n = 12 are known. They have delocalized electrons in the boron framework having one or more carbon atoms. Carboranes with higher boron content are dominant. The most studied boranes are $B_{10}H_{10}^{2-}$ and $B_{12}H_{12}^{2-}$;thus, for carboranes, the best studied system is $C_2B_{10}H_{12}$ that is isoelectronic with $[B_{12}H_{12}]^{2-}$. Some other boranes and their corresponding carboranes are listed below:

Pentaborane(5) $B_5H_5^{2-}$ [$C_2B_3H_5$], Hexaborane(6)$B_6H_6^{2-}$ [$C_2B_4H_6$]

Heptaborane(7) $B_7H_7^{2-}$ [$C_2B_5H_7$], Octaborane(8) $B_8H_8^{2-}$ [$C_2B_6H_8$],

Nonaborane(9)$B_9H_9^{2-}$ [$C_2B_7H_9$] , Decaborane(10) $B_{10}H_{10}^{2-}$[$C_2H_8H_{10}$]

Dianions $B_{11}H_{11}^{2-}$ [$C_2B_9H_{11}$].

Similar to boranes, carboranes are also classified as *closo*, *nido* and *arachno* which can be regarded as derivatives of B_nH_{n+2} (or related anion $B_nH_n^{2-}$), B_nH_{n+4} and B_nH_{n+6} respectively.

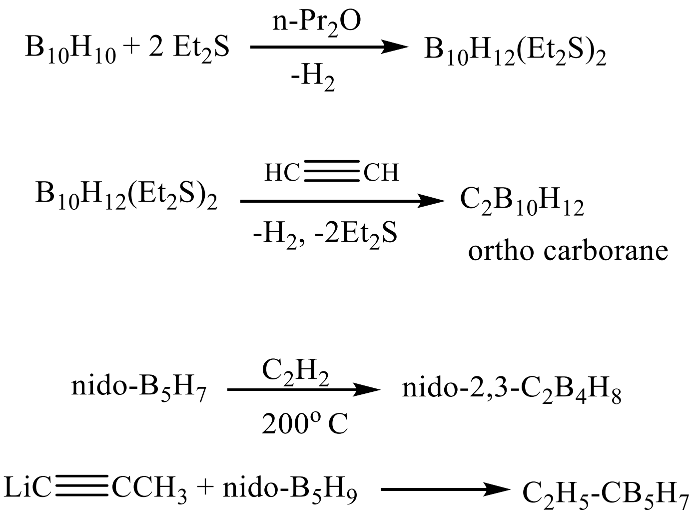
i. *Closocarboranes*: General formula is $C_xB_{n-x}H_{n-x+2}$ bonded by n+1 skeletal pair of electrons. Eg. Most common with x=2, $C_2B_{n-2}H_n$. One or both C atoms can be replaced by isoelectronic B^- ion to give $CB_{n-1}H_{n+1}$.

ii. *Nidocarboranes*: General formula is $C_xB_{n-x}H_{n-x+4}$ bonded by n+2 skeletal pair of electrons. Here also C can be replaced by B^- or BH to give compounds that have their skeleton isostructural with B_nH_{n+4}

iii. *Arachnocarboranes*: General formula is $C_xB_{n-x}H_{n-x+6}$ bonded by n+3 skeletal pair of electrons. These are structurally related to B_nH_{n+6} (i.e. x =0); for example $C_2B_7H_{13}$ is related to B_9H_{15} and $B_9H_{14}^-$

7.4.1. Synthesis and reactions

7.4.1.1. Synthesis



$$B_{10}H_{10} + 2\,Et_2S \xrightarrow[-H_2]{n\text{-}Pr_2O} B_{10}H_{12}(Et_2S)_2$$

$$B_{10}H_{12}(Et_2S)_2 \xrightarrow[-H_2,\ -2Et_2S]{HC\equiv CH} \underset{\text{ortho carborane}}{C_2B_{10}H_{12}}$$

$$\text{nido-}B_5H_7 \xrightarrow[200^{o}\,C]{C_2H_2} \text{nido-2,3-}C_2B_4H_8$$

$$LiC\equiv CCH_3 + \text{nido-}B_5H_9 \longrightarrow C_2H_5\text{-}CB_5H_7$$

7.4.1.2. Reactions

1. Pyrolysis

$$C_2B_nH_{n+4} \longrightarrow C_2B_nH_{n+2} + H_2$$

$$C_2B_nH_{n+4} \longrightarrow C_2B_{n-1}H_{n+1} + C_2B_{n+1}H_{n+3} + 2\,H_2$$

$$\begin{aligned}\text{1,2-Me}_2\text{-nido-B}_5\text{H}_7 \longrightarrow\ & \text{closo-1,5-C}_2\text{B}_3\text{H}_5 + \text{closo-1-CB}_5\text{H}_7 + \text{nido-2-CB}_5\text{H}_9 \\ & \text{3-Me-nido-2-CB}_5\text{H}_8\end{aligned}$$

2. Cluster Expansion

$$\text{closo-1,7-C}_2\text{B}_6\text{H}_8 + 1/2\text{B}_2\text{H}_6 \longrightarrow \text{closo-1,6-C}_2\text{B}_7\text{H}_9 + \text{H}_2$$

$$\text{closo-1,6-C}_2\text{B}_7\text{H}_9 + 1/2\text{B}_2\text{H}_6 \longrightarrow \text{closo-1,6-C}_2\text{B}_8\text{H}_{10} + \text{H}_2$$

7.4.1.3. Carborane ligands

The carborane anion or dicarbollide anion $[B_9C_2H_{11}]^{2-}$ has been used as ligand and numerous studies have been done on its derivatives. This anion forms sandwich compounds with many metal ions known as bis(dicarbollides). When the 1,2-and 1,7-dicarba-closo-dodecaboranes are heated with alkoxide ions, degradation of parent carborane occurs to form isomeric *nido*carborane anions $(B_9C_2H_{12})^-$.

$$C_2B_{10}H_{12} + MeO^- + MeOH \xrightarrow{85^o\ C} [C_2B_9H_{12}]^- + H_2 + B(OMe)_3$$

$$[C_2B_9H_{12}]^- + NaH \longrightarrow [C_2B_9H_{11}]^{2-} + H_2 + Na^+$$

$$\text{nido 7,8- }[C_2B_9H_{11}]^{2-} + FeCl_2 \longrightarrow \eta^5[7,8\text{-}(C_2B_9H_{11})]_2Fe$$

The $(B_9C_2H_{12})^-$ anions are very strong bases and readily acquire H^+ to give $B_9C_2H_{11}^{2-}$ anion which can be further protonated to give neutral *nido-carboranes* $B_9C_2H_{13}$. The $B_9C_2H_{13}$ is a strong acid which on heating gives *closo*-carborane $(B_9C_2H_{11})$ with loss of hydrogen.

$$[C_2B_9H_{11}]^{2-} \xrightleftharpoons{H^+} [C_2B_9H_{12}]^- \xrightleftharpoons{H^+} C_2B_9H_{13}$$

7.5. WADE'S RULE

A set of rules were laid down by Kenneth Wade to predict the shape of boron clusters. These rules correlate skeletal structures of boranes, carboranes, heteroboranes and their anions (closo, nido, arachno, hypho) with the number of skeletal electron pairs present in them.

According to the rule, suppose a cluster has say 'n' skeletal atoms (that is the vertices) then it will adopt *closo* structure if it contains n+1 skeletal bonding electron pairs. Similarly, *nido* if n+2, *arachno* if n+3 and *hypho* if n+4 skeletal bonding electron pairs respectively and so on.

To determine this, one needs to know the number of skeletal electron pairs in a cluster which can be determined by following the electron count for various donating units as given below.

Each BH unit gives 2 skeletal bonding electrons.

B as such gives three skeletal electrons.

Each C-H unit of a carboranecontributes 3 skeletal bonding electrons.

Each additional H furnishes 1 skeletal bonding electron.

Ionic charges must be included in the electron count.

For borane clusters with other hetero-elements,

C, Si, Ge and Sn of a cluster is replaced with a BH unit;

N, P and As with a BH_2 unit and

S andSe with a BH_3 unit for counting purpose

Examples:

B_5H_9	**$B_2H_7^-$**	**$C_2B_{10}H_{12}$**	**$C_2B_9H_{11}^{2-}$**
5 BH = 5x2 =10e	2 BH = 2x2 = 4e	2 CH= 3x2 = 6e	2 CH= 2x3= 6e
4 H = 4x1 = 4e	5 H = 5x1 = 5e	10 BH= 2x10 = 20e	9 BH= 9x2 =18e
14 e = 7pair	1(-) = 1e	26e = 13 pair	2(-) = 2e
n = 5; n+2 = *nido*	10 e = 5 pair	n= 12; n+1 = *closo*	26 e = 13 pair
	n = 2; n+3= *arachno*		n= 11; n+2 = *nido*

$(MeSi)_2B_{10}H_{10}$

2 MeSi = 2x3 = 6e

10 BH = 10x2 = 20e

26 e = 13 pair

n = 12; n+1 = *closo*

$CPB_{10}H_{11}$

Consider $C \equiv BH$; $PB_{11}H_{12}$

Consider $P \equiv BH_2$; $B_{12}H_{14}$

12BH = 12x2= 24e

2H = 2e

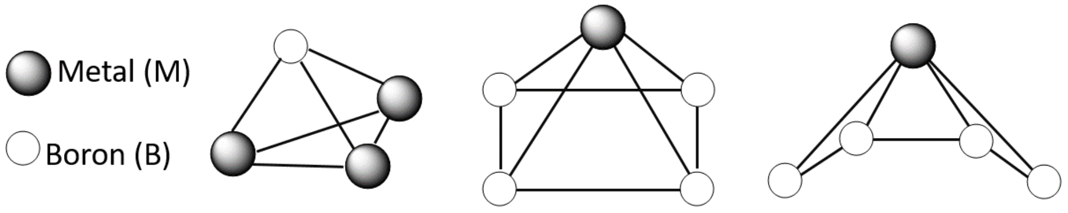
26e = 13 pair; n= 12; n+1= *closo*

7.6. METALLOBORANES

Compounds in which metal atom bound with boron hydride group form the class of compounds known as metalloboranes. They can be classified into following categories:

1. Ionic hydroborates: Such as $NaBH_4$, $Ba(BH_4)_2$
2. Metal hydroborates: Contain hydrogen bridge bonds, M–H–B. Eg: $Al(BH_4)_3$, $(Ph_3P)_2CuBH_4$.
3. Metal Carbaboranes: Include π-bonded ‘sandwich compounds’.
4. Compounds containing metal-boron bonds except those in the above category (3).

Like boranes and carboranes, metalloboranes can also be structurally classified as *closo*, *nido*, *arachno*, *crypto* and *commo*. Some of them are depicted below.



closo-M_3B nido-1-MB_4 arachno-1-MB_4

7.6.1. Synthesis

1. Metathesis of borane anion

$$B_5H_9 + KH \xrightarrow[-H_2]{} B_5H_8^{\,-} \xrightarrow[-I^-]{Fe(\eta^5\text{-}C_5H_5)(CO)_2I} [2\text{-}\{Fe(\eta^5\text{-}C_5H_5)(CO)_2\}(\eta^1\text{-}B_5H_8)]$$

$$B_5H_9 + KH \xrightarrow[-H_2]{} B_5H_8^{\,-} \xrightarrow[-Cl^-,\ -PPh_3^-]{[CuCl(PPh3)3]} [\mu^{2,3}\text{–}\{Cu(PPh_3)_2\}(\eta^2\text{-}B_5H_8)]$$

2. Polyhatpto coordination complexes which may or may not have cluster arrangement

$$B_{10}H_{14} + 2\ TMND + cis\text{-}[PtCl_2(PMe_2Ph)_2 \longrightarrow [Pt(\eta^4\text{-}B_{10}H_{12})(PMe_2Ph)_2] + 2\ TMNDHCl$$

N, N, N', N'-tetramethylnaphthalene-1,8-diamine (TMND also known as "proton sponge") is an excellent Bronsted base (proton acceptor) but a very weak nucleophile (Lewis base) towards boron.

$$B_3H_8^- + cis\text{-}[PtCl_2(PR_3)_2] + NEt_3 \longrightarrow Pt(\eta^3\text{-}B_3H_7)(PR_3)_2 + Et_3NHCl + Cl^-$$

3. Oxidative insertion of metal leading to formation of expanded cluster

$$KB_5H_8^- + trans\text{-}[Ir^{+1}(CO)Cl(PPh_3)_2] \longrightarrow nido\text{-}2,\ 2,\ 2\text{-}(CO)(PPh_3)_2\ \text{-}\ 2Ir^{+3}B_5H_8] + KCl$$

$$TlB_3H_8^- + trans\text{-}[Ir^{+1}(CO)Cl(PPh_3)_2] \xrightarrow{C_6H_6} Ir^{+3}\eta^3\text{-}B_3H_7(CO)H(PPh_3)_2] + TlCl$$

4. Partial degradation of borane anion

$$[B_9H_{14}]^- + cis\text{-}[PtCl_2(PMe_2Ph)_2] \longrightarrow arachno\text{-}[7,\ 7\text{-}(PMe_2Ph)_2\text{-}7\text{-}PtB_8H_{12}$$

$$[B_{10}H_{10}]^{2-} + trans\text{-}[Ir(CO)Cl(PPh_3)_2] \xrightarrow{CH_3OH} \text{several metalloborane products having 4-10 boron atoms}$$

5. Deprotonation of metalloborane followed by metallation

$$Pt\ (\eta^3\text{- }B_8H)\ (PMe_2Ph)_2 + cis\text{-}[PtCl_2(PMe_2Ph)_2] \xrightarrow{2KH} arachno\text{-}[6,6,9,9\text{-}(PMe_2Ph)_4\text{-}6,9\text{-}Pt_2B_8H_{10}$$

6. Borane as a 2-electron ligand

$$B_6H_{10} + [Fe_2(CO)_9] \xrightarrow{r.t.} [\mu^{5,6}\text{- }\{Fe(CO)_4\}B_6H_{10}] + Fe(CO)_5$$

$$B_6H_{10} + K[Pt\ (\eta^2\text{-}C_2H_4)Cl_3 \xrightarrow{r.t.} trans\text{- }[Pt\ (\eta^2\text{-}B_6H_{10})_2Cl_2] + KCl + C_2H_4$$

7. Borane as a bronsted Acid

$$2\ B_{10}H_{14} + 2\ CdEt_2 + 4\ Et_2O \longrightarrow [\{(Et_2O)_2Cd(\eta^2,\ \eta^2\text{-}B_{10}H_{12})\}_2]$$

8. Reaction of boron with atomized metal

$$B_5H_9 + \text{Co (atomic)} + C_5H_6 \longrightarrow \text{closo-1,2,3-}(\eta^5\text{-}C_5H_5)_3\text{-1,2,3-}Co_3B_5H_5] + \text{other products}$$

9. Oxidative addition of B–H to Ir^{+1}

$$[B_{10}H_9] + \text{trans-}[Ir(CO)Cl(PPh_3)_2] \longrightarrow \text{nido-}[2\text{-}Ir(CO)ClH(PMe_3)_2\}B_5H_8]$$

10. Cluster expansion using diborane

$$1/2\ B_2H_6 + [\mu^{5,6}\text{-}\ \{Fe(CO)_4\}B_6H_9]^- \longrightarrow [Fe(\eta^2\text{-}B_7H_{12})(CO)_4]^-$$

11. Synthesis of small clusters from mononuclear units

$$3\ BH_3.THF + [Fe(CO)_4]^{2-} \longrightarrow [\mu\text{-}\{Fe(CO)_4\}B_2H_5]^- + BH_4^- + 3THF\ ; \quad THF= \text{tetrahydrofuran}$$

12. Metathesis of halogen containing polyboranes with anionic metal complexes

$$2\text{-}C1B_5H_8 + Na[Mn(CO)_5] \longrightarrow \text{nido-}[2\text{-}\{Mn(CO)_5\}B_5H_8]$$

13. Thermally or photolytically induced cluster isomerization of a previously synthesized metalloborane cluster

$$\text{closo-}[2\text{-}(\eta^5\text{-}C_5H_5)\text{-}2\text{-}NiB_9H_9](\text{red}) \xrightarrow[\text{or } h\nu]{\text{warm}} \text{closo-}[\eta^1\text{-}(5\text{-}C_5H_5)\text{-}1\text{-}NiB_9H_9]\ (\text{yellow})$$

14. Ligand exchange reactions

$$[Pd(B_{10}H_{12})(PPh_3)_2] + 1,10\text{-phen} \longrightarrow [Pd(B_{10}H_{12})(\text{phen})] + 2\ PPh_3$$

1,10-phen = 1,10-phenanthroline

$$[Pd(B_{10}H_{12})(PPh_3)_2] + 2\ CN^- \xrightarrow{\text{MeCN}} [Pd(B_{10}H_{12})(CN)_2]^{2-} + 2\ PPh_3$$

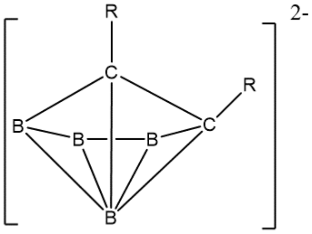
15. Cluster expansion (reaction of a borane anion with a metal halide in the presence of a ligand)

$$NaB_5H_8 + NiBr_2 + NaC_5H_5 \longrightarrow \text{closo-}[1,6\text{-}(\eta^5\text{-}C_5H_5)_2\text{-}1,6\text{-}Ni_2B_8H_8] + \text{closo-}[1,7(\eta^5\text{-}C_5H_5)_2\text{-}1,7\text{-}Ni_2B_{10}H_{10}]$$

7.7. METALLACARBORANES

Metallacarboranes or metallacarboboranes are metal complexes where carboranes or heteroboranes act as ligands with at least one metal atom incorporated in the cage framework. They are inorganic polyhedral clusters which contain carbon, boron, hydrogen and metal ion in different combinations. Hawthorne and co-workers first synthesised metallacarboranes in the mid-1960s. A typical example of metallacarborane is the $[C_2B_9H_{11}]^{2-}$ (dicarbollide) cluster having a metal atom sandwiched between two dicarbollide units. Here, the dicarbollide, binds as η^5 and thus, considered to be isolobal with cyclopentadienyl ligand, somewhat similar to ferrocene. Hawthrone suggested that $[C_2B_9H_{11}]^{2-}$is isoelectronic with $C_5H_5^-$ and therefore, it should be capable of acting as the π ligand in similar metallocenes compounds.

The other highly investigated metallacarborane is *nido*-$[2,3\text{-}R_2C_2B_4H_4]_2$(R=H or a cage carbon substituents), having pentagonal bipyramidal structure.



[nido-2,3-$R_2C_2B_4H_4]^{2-}$

There are two different types of metallacarboranes, endo- and exo. In endo- type, the metal centre is sandwiched between two carborane clusters. Whereas, in exo- type, a metal fragment is linked to the periphery of the carborane skeleton, generally through B-H···M interactions.

Synthesis

1. Preparation of $[C_2B_9H_{11}]^{2-}$ (dicarbollide)

$$C_2B_{10}H_{12} + MeO^- + 2\ MeOH \longrightarrow [C_2B_9H_{12}]^- + H_2 + B(OMe)_3$$

$$[C_2B_9H_{12}]^- + NaH \xrightarrow{\text{thf}} [C_2B_9H_{11}]^{2-} + H_2 + Na^+$$

2. Preparation of metallacarboranes

$$2[C_2B_9H_{11}]^{2-} + FeCl_2 \longrightarrow [(C_2B_9H_{11})_2Fe]^{2-} + 2Cl^-$$

$$[C_2B_9H_{11}]^{2-} + C_5H_5^- + FeCl_2 \longrightarrow [C_2B_9H_{11}FeC_5H_5]^- + 2Cl^-$$

$$[C_2B_9H_{11}]^{2-} + BrMn(CO)_5 \longrightarrow [C_2B_9H_{11}Mn(CO)_3]^- + Br^- + 2CO$$

7.8. COMPOUNDS WITH METAL-METAL MULTIPLE BONDS

Metal clusters are those compounds which have metal-metal bonds. They are as old as chemistry itself. The halide and oxide metal clusters will be discussed here. In these clusters, the metal ion is in higher formal oxidation state +2 to +3 and frequently comprise of transition metals on the left side of periodic table (early second row and third row of transition metals). Such as Zr, Nb, Tc, Ru, Rh, Hf, Ta, W, Re, Os, Ir and Pt.

The *d* orbitals play a crucial role in the formation of these clusters since effective overlap of *d* orbitals is necessary for the stability of metal cluster. Contraction of *d* orbitals will cause destabilizing effect on the cluster. It is owing to these reasons that the transition metals of first row even in +2 or +3 oxidation states are unable to extend the *d* orbitals sufficiently for effective overlap.

7.8.1. Dinuclear compounds

A typical example of dinuclear metal compound is $[Re_2X_8]^{2-}$ ion. It can be synthesized as shown below. Reducing agents such as H_2, H_3PO_2 or PhCOCl can be used. The ion is formed as a royal blue colored product.

$$2\ ReO_4^- \xrightarrow[H_3PO_2]{HX} [Re_2X_8]^{2-} \qquad X = Cl, Br, I, NCS$$

These compounds show two very interesting structural features. Firstly, the Re-Re distance in the compound is 224 pm which is shorter than the average Re-Re distance in rhenium metal (at 275 pm) or in Re_3Cl_9 (248 pm). Secondly, the chlorine atoms are present in eclipsed configuration at 330 pm from Re which less than the sum of their van der Waals radii (340-360 pm). So, in such situation, a staggered form would be preferable. Both the above features were explained by F. A. Cotton by proposing a quadruple bond.

Cotton suggested that the metal-metal bonds lay about the *z* axis and each Re atom was bonded to four chlorine atoms in an almost square planar arrangement. The Re-Cl bonds are dsp^2 hybridized utilizing the $dx^2\text{-}y^2$ orbitals. He proposed that the metal $\boldsymbol{dz^2}$ and $\boldsymbol{p_z}$ orbitals lie along the bond axis and may be hybridized. One of the corresponding hybridized orbitals is directed towards the rhenium atom and the second orbital directed in the opposite direction. The former makes an **σ bond** with the orbital of similar symmetry on the second rhenium atom while the latter hybridized orbital forms an approximately nonbonding orbital. The **d_{xz}** and **d_{yz}** orbitals of each metal atom are obliquely oriented towards their counterpart on the other rhenium atom. These orbitals overlap to form **two π bonds**; one in the *xz* plane and other in the *yz* plane. The fourth bond that is a **δ bond** is formed by the sideways overlap of the two **d_{xy} (or $d_{x^2-y^2}$)** orbitals on each rhenium atom. The overlap of d_{xy} orbitals is possible only when the chlorine atoms are eclipsed. In case they are staggered the metal d_{xy} orbitals will also be staggered resulting in zero overlap.

The Re-Cl bonds are regarded as dative bonds between the Re^{3+} and Cl^- ions. Overall, the eight *d* electrons from two metal atoms are involved in an σ bond, two π bonds and a δ bond to constitute the overall quadruple bond. Hence, the complex is diamagnetic. This model also explains the short metal-metal distance and eclipsed orientation of chlorine atoms (**Figure 7.3**).

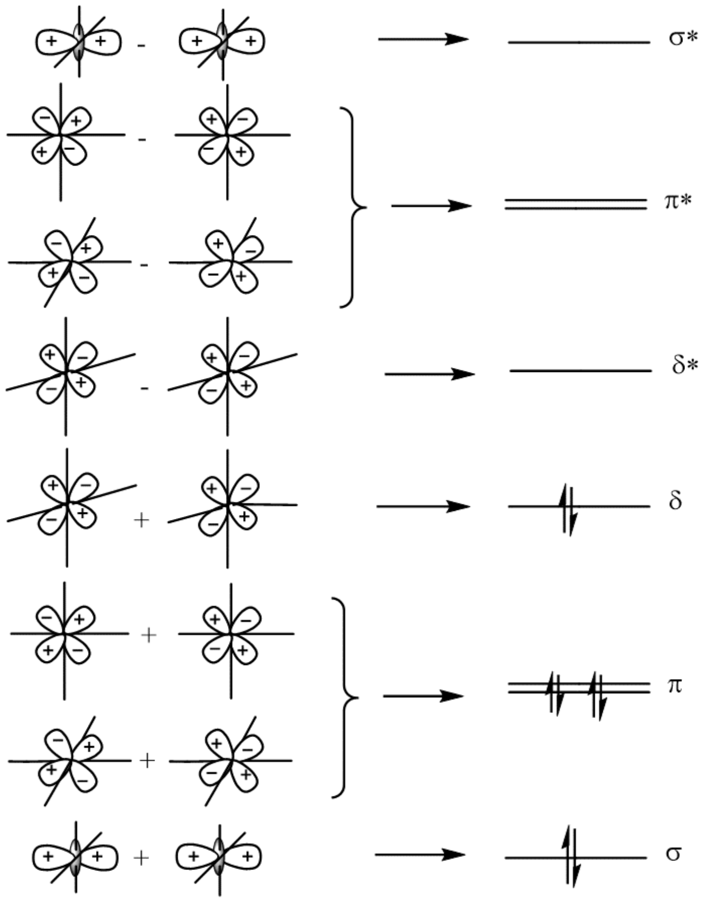


***Figure 7.3.** Bonding of $[Re_2X_8]^{2-}$ ion*

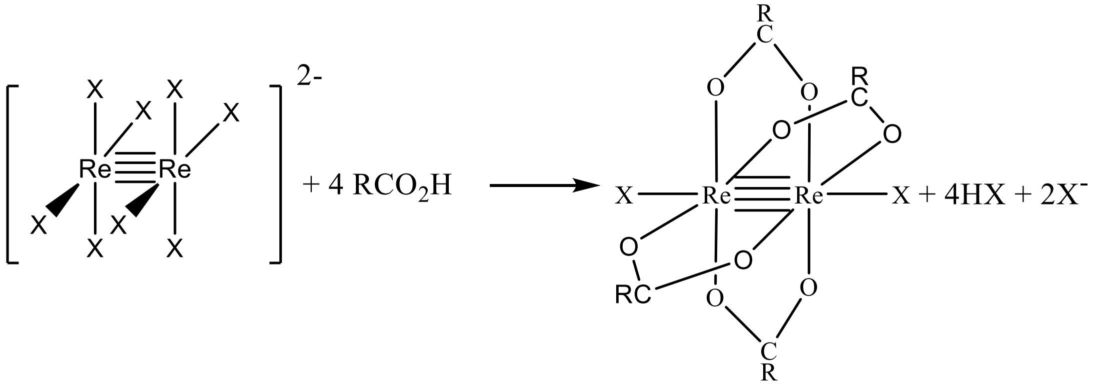
$[Mo_2Cl_8]^{2-}$ is isoelectronic with and has structure similar to the $[Re_2X_8]^{2-}$ ion. Both of them form a large series of carboxylate complexes with carboxylic acids.

$$[Re_2Cl_8]^{2-} + 2\ MeCOOH \longrightarrow Re_2(MeCO)_2Cl_4 + 4Cl^- + 2H^+$$

$$[Re_2Cl_8]^{2-} + 4\ MeCOOH \longrightarrow Re_2(MeCO)_4Cl_2 + 6Cl^- + 4H^+$$

$$Re_2(MeCO)_4Cl_2 + 4PhCOOH \longrightarrow Re_2(PhCOO_2)_4Cl_2 + 4MeCOOH$$

$$2Mo(CO)_6 + 4MeCOOH \longrightarrow Mo_2(MeCO_2)_4 + 12CO + 2H_2$$



7.8.2. Some other metal clusters

7.8.2.1. Dinuclear clusters with metal-metal triple bonds

Other examples of metal-metal quadruple bonding are dinuclear complexes of tungsten and molybdenum of the type $[M(OR)_6]$ (M= Mo, W). The alkoxide functions as the stabilizing ligand for 12 electron clusters. It has two filled p orbitals which can donate π electron density to metal centers. These complexes are coordinatively unsaturated and contain metal-metal triple bonds which are somewhat analogous to carbon-carbon triple bonds. The isolobality of CR and $W(OR)_3$ is eminent from the synthesis of $(t\text{-}BuO)_3W\equiv WCR$. This is clear from the reactions given below.

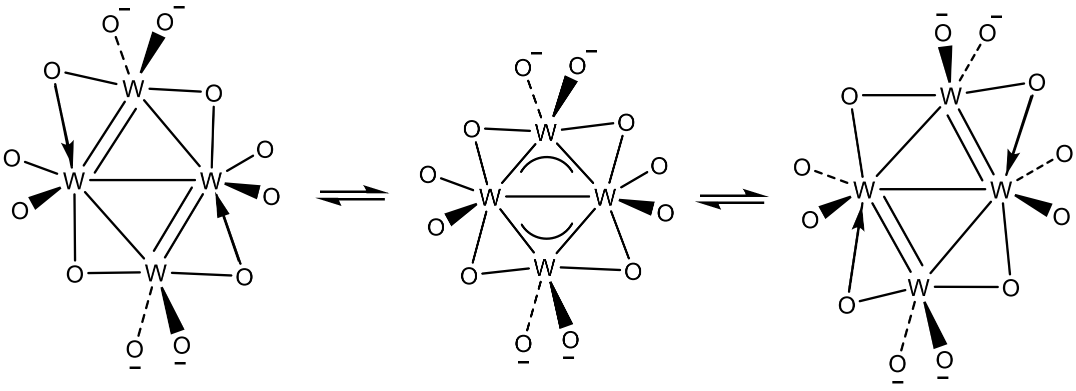
$$(RO)_3W{\equiv}W(OR)_3 + 2\,X_2 \longrightarrow (X)_2(RO)_3W{-}W(OR)_3(X)_2 \qquad (X = Cl, Br, I)$$

$$(i\text{-}Pr)_3Mo{=}Mo(O\text{-}i\text{-}Pr)_3 + i\text{-}PrOO\text{-}i\text{-}Pr \longrightarrow (i\text{-}PrO)_4Mo{=}Mo(OPr\text{-}i)_4$$

$$(t\text{-}BuO)_3W{\equiv}W(OBu\text{-}t)_3 + RC{\equiv}CR \longrightarrow 2(t\text{-}BuO)_3W{\equiv}CR$$

It has been found that $W_2(O\text{-}i\text{-}Pr)_6$ shows dimerization existing in equilibrium with $W_4(O\text{-}i\text{-}Pr)_{12}$, having structure which may be thought of as cyclobutadiene analogue. The cluster resonates about the symmetrical rhomboidal core known as "*The Bloomington Shuffle*".

$$W_4(OPr^i)_{12} \rightleftharpoons 2W_2(OPr^i)_6$$



Reactions:

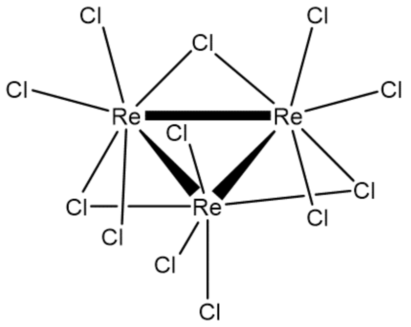
$$M_2(NMe_2)_6 + 6Bu^tOH \xrightarrow[\text{Hexane}]{22^oC} M_2(OBu^t)_6 + 6HNMe_2$$

$$W_2(NMe_2)_6 + CO_2(\text{excess}) \xrightarrow[\text{Toluene}]{22^oC} W_2(O_2CNMe_2)_6$$

$$Cp_2W_2Cl_4 + H_2 \overset{22^oC}{\rightleftharpoons} Cp_2W_2(H)_2Cl_4$$

7.8.2.2. Trinuclear clusters

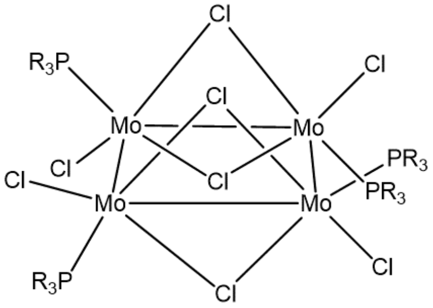
A typical example of noncarbonyl cluster containing three metal atoms is $[(ReCl_3)_3]$ and its derivatives. Each Re (III) has a d^4 configuration. The complexes are diamagnetic and not paramagnetic which would have been the case if each Re atom was singly bonded to other Re atoms. Since, the metal atoms are engaged in double bonds to the neighboring metal atom the complexes are paramagnetic.



7.8.2.3. Tetranuclear clusters

One of the typical examples is the dimer $W_4(O\text{-}i\text{-}Pr)_{12}$ of $W_2(O\text{-}i\text{-}Pr)_6$, the structure of which is shown above. $W_4(OR)_{16}$ has also been synthesized having W–W single bonds. It can be considered as the saturated version of $W_4(OR)_{12}$. Quadruply bonded dinuclear compounds can dimerize to form tetranuclear clusters.

$$2\,K_4Mo_2Cl_8 + R_3P \longrightarrow Mo_4(PR_3)_4Cl_8 + KCl$$



The above cluster has alternating single and triple Mo–Mo bonds.

7.8.2.4. Hexanuclear clusters

Transition metals such as molybdenum, niobium, and tantalum along with rhenium are known to form extensive metal clusters with multiple metal-metal bonds. Eg. $[Mo_6Cl_8]Cl_4$, six metal atoms coordinated with eight chloride ions on each face of an octahedron. Each Mo(II) atom can use its four electrons to form four bonds with neighboring metal atoms and are engaged in dative bonds with the four chloride ions.

7.9. POLYOXOMETALATES (ISOPOLY AND HETEROPOLY ACIDS)

Acid catalysis is an important area of heterogeneous catalysis. Among several acid catalysts, polyoxometalates (POM) also known as heteropoly acids (HPAs) hold an important position owing to their catalytic properties. HPAs are used as catalysts in different reactions as acid, redox and bifunctional catalysts in homogeneous and heterogeneous reaction systems owing to their high solubility in polar solvents and thermal stability. They are also used as heterogeneous and homogeneous catalyst in medicine as antiviral and antitumoral agents.

Polyoxometallates is a generalized term used for a large number of nanosizedanionic clusters which are built from transition metal oxoanions linked via shared oxide ions. Most of the polyoxometalates are polyoxoanions of transition metals such as V, Mo and W. The POMs can be classified into large group of anions based on their composition namely (i) isopolyoxometalates and (ii) heteropolyoxometalates. The isopolyoxometalates consist of metal-oxide cluster with d^0 metal ions such as Mo^{6+}, W^{6+}or V^{5+} having general formula $[M_mO_y]^{p-}$. These do not contain any additional heteroatom. The heteropolyoxometalates include additional p, d or f block elements along with the metal-oxide framework. They have the general formula $[X_xM_mO_y]^{q-}$ and here $x \leq m$.

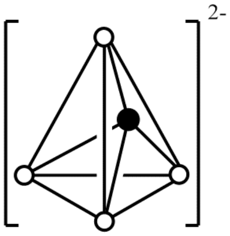
7.9.1. The isopolyoxometalates or isopoly acids

Some important isopolymetalates are discussed in this section. The basic unit of isopolychromate is CrO_4 tetrahedra. They exist both in solution & as solids. Chromates are stable only at high pH, on lowering the pH protonation and dimerization occurs and $(Cr_2O_7)^{2-}$. In acidic solution $(Cr_2O_7)^{2-}$, predominates whereas in basic solution $(CrO_4)^{2-}$ predominates.

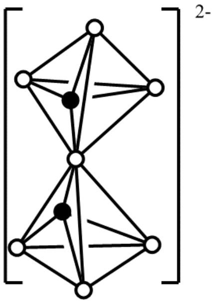
$$\underset{\text{Basic solution}}{2(CrO_4)^{2-} + H^+} \rightleftharpoons 2[CrO_3\text{-}OH]^- \rightleftharpoons \left[O_3Cr—O—CrO_3\right]^{2-} + H_2O$$

$$n/2\ Cr_2O_7^{2-} + n\ H^+ \longrightarrow (CrO_3)_n + n/2\ H_2O$$

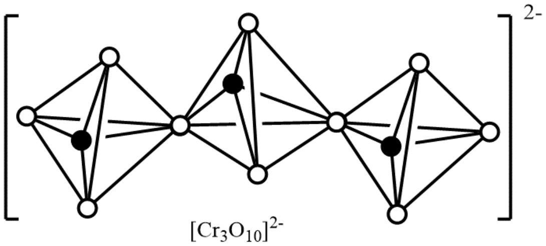
The CrO_3 structure consists of infinite linear chains of CrO_4 tetrahedra.



$[CrO_4]^{2-}$



$[Cr_2O_7]^{2-}$



$[Cr_3O_{10}]^{2-}$

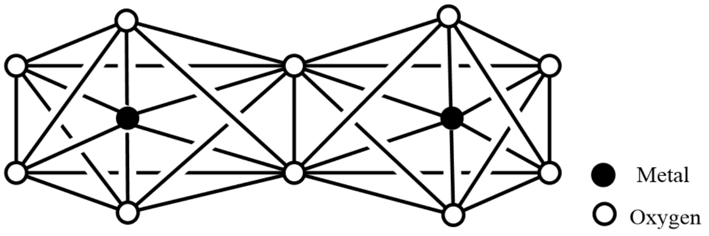
There are certain reports of polymerization such as the Tri chromates $(Cr_3O_{10})^{2-}$ and tetra chromates $(Cr_4O_{13})^{2-}$. Polymerization does not go beyond $(Cr_4O_{13})^{2-}$. These anions as well as dichromate ion are formed by corner sharing CrO_4^{2-}tetrahedra. The tendency for Cr to form large number of polyacids is limited. The small size of Cr^{6+} evidently limits it to the tetrahedral rather than octahedral coordination with oxygen.

The vanadate anion VO_4^{3-} exists in strongly alkaline solution. On lowering the pH, protonation occurs. Protonation and dehydration occur as pH is reduced from 13 to 8 in more concentrated solutions forming $[V_2O_7]^{4-}$ and higher vanadates. Polymerization continues at low pH resulting in precipitation of hydrous V_2O_5. At about pH 6,decavanadate $[V_{10}O_{28}]^{6-}$ is formed. The ion is protonated to $[HV_{10}O_{28}]^{5-}$ and $[[H_2V_{10}O_{28}]^{4-}$ as the pH is lowered to 3.5. Alkali salts of isopolyvanadates nay be colourless or coloured. The salts with alkali metal to vanadium ratio at least unity are usually colourless, while salts with alkali metal to vanadium ratio less than unity are coloured.

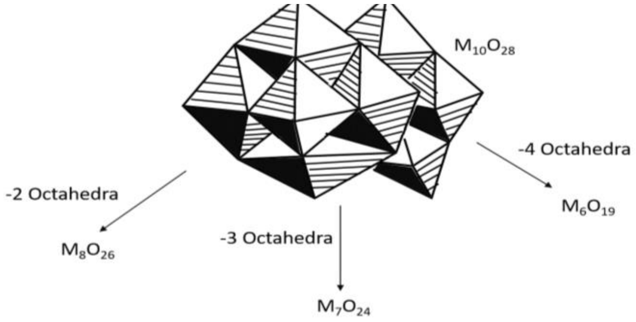
Tetrahedral $[MoO_4]^{2-}$ is formed when the trioxide of molybdate is dissolved in aqueous alkali. Under strongly acidic pH, precipitate of yellow molybdic acid $MoO_3.2H_2O$ is obtained. The first stable isopolymolybdate is $[Mo_7O_{24}]^{6-}$, the heptamolybdate or paramolybdate. When this solution is further acidified to pH of about 1.8 – 2.9, the octamolybdate ion $[Mo_8O_{26}]^{4-}$is obtained.

The polymerization of vanadate, molybdate and tungstate ions forms the isopoly anions whereby the coordination number of metal ion may vary from four to six. The basic building unit is an octahedron of six oxygen atoms surrounding each metal ion. The octahedra may link sharing an apex or edge but rarely a face. The larger octahedral motif provides relaxation to the electrostatic repulsions. Some common edge sharing polyanions are $[V_{10}O_{28}]^{6-}$, $[Mo_8O_{26}]^{4-}$, $[W_6O_{19}]^{2-}$, $[W_7O_{24}]^{6-}$, $[Nb_6O_{19}]^{8-}$ and $[Ta_6O_{19}]^{8-}$. To form larger polyanions, edge sharing is converted to apex sharing. The isopoly anions may be considered as a closed packed array of oxide ions with metal ions present in the octahedral holes. In the edge sharing array of $[V_{10}O_{28}]^{6-}$, ten octahedral are stacked in an edge sharing manner. The sharing of edges between MO_6 octahedra causes repulsion between the metal ions which is reduced partially by displacement of M from the centre of the octahedra. The repulsion increases with increase in the ionic radius viz. $V^{5+} > Mo^{6+} > W^{6+} > Nb^{6+} > Ta^{6+}$.

It is noteworthy that polymerization ceases for isopoly anions. A possible explanation for which lies in the position of oxygen atoms. A terminal oxygen atom is strongly π bonded to the transition metal (such as Mo (VI), W(VI)). These terminal oxygen atoms are never located trans to one another which prevents their competition for the same vacant t_{2g} orbital. Instead, they are present opposite to a bridging or internal oxygen. This results in the metal ion being displaced towards the terminal oxygen and away from the oxygen opposite to it which is what we encounter in *trans* effect. On the contrary, metal ions such as Al (III) or Ga (III) are poor π acceptors. Thus, they do not stabilize their terminal oxygen atoms which can therefore attack other units and result in continuing polymerization.



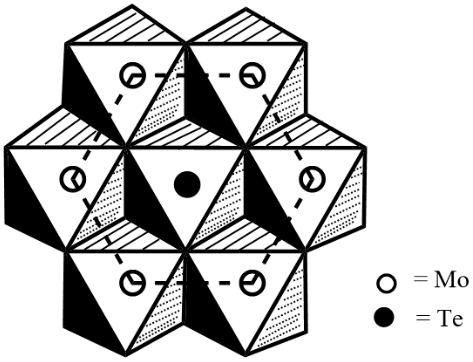
Edge sharing distorted octahedra



7.9.2. The heteropolyoxometalates

Their general formula is $[X_xM_mO_y]^{n-}$($x \leq m$); M isusually Mo or W and sometimes V, Nb or Ta. X is the heteroatom which may be located at the centre of polyanion. The heteroatom can be any element in the periodic table some of the most frequently encountered ions are P^{5+}, As^{5+}, Si^{4+}, Ge^{4+}, B^{3+} etc.

Heteropolyanions are very important for catalysis and other applications hence, they are discussed in detail. Molybdenum and tungsten polyoxometalates are extensively studied and most easily formed because of the accessibility of their *d* orbitals forming metal-oxygen π bonds. The structure of the related phosphotungstate anion was determined in 1934, and is generally called the Keggin structure after its discoverer. In the period following thisother fundamental structures, e.g. the Wells-Dawson ion, were discovered, and their chemistry and applications as catalysts were determined.



6-molybdotellurate anion ; $[TeMo_6O_{24}]^{6-}$

7.9.3. Classification of polyoxometalates on the basis of structure

The first example of POM is ammonium phosphomolybdate containing the $[PMo_{12}O_{40}]^{3-}$ ion. The polyoxometalates are classified taking into account a few highly symmetrical 'parent' polyanions and on the basis of these many other polyoxometalate structures can be considered as their derived forms. Broadly, the three such parent structures can be as a tetrahedron, an octahedron and an icosahedron polyhedron XO_n (n = 4, 6 or 12) placed at the centre. These structures are discussed below:

1. Keggin structure (Td symmetry): This type of structure is most stable and easily available and very important for catalysis. The Kegginheteropoly anions are represented by the formula $[XM_{12}O_{40}]^{x-8}$;here

X is the heteroatom (eg. P), x is the oxidation number. The M^{6+} ion can be Mo^{6+} or W^{6+}, one or more of these can be substituted by V^{5+}, Co^{2+}, Zn^{2+}. The type of structure contains a central XO_4 tetrahedron surrounded by twelve edges and corners sharing metal-oxygen MO_6 octahedra which are arranged in four M_3O_{13} groups. Each group is formed by three MO_6 octahedra sharing edges and having a common oxygen atom which is also shared with the central tetrahedron XO_4.

A complete structure contains forty oxygen atoms which are of four types: twelve terminal M=O, twelve edge-bridging angular M-O-M shared by the octahedra within a M_3O_{13} group, twelve corner-bridging quasi-linear M-O-M connecting two different M_3O_{13} groups and four internal X-O-M. These different types of oxygen atoms were revealed by ^{17}O NMR spectroscopy. Rotation of M_3O_{13} groups by 60^0 about the three-fold axis leads to the formation of the geometrical isomers. Rotation of oneM_3O_{13} group produces β isomer and rotation of two, three or all four M_3O_{13} groups produces the γ, δ and ε isomers respectively. If one or more metal atoms are removed, lacunary derivatives of Keggin anions are formed.

The examples of Keggin type heteropoly acids are:
$H_3PMo_{12}O_{40}$- 12-phosphomolybdic acid
$H_3PW_{12}O_{40}$- 12-phosphotungstic acid
$H_4SiMo_{12}O_{40}$- 12-silicomolybdic acid
$H_4SiW_{12}O_{40}$- 12-silicotungstic acid

2. The Well-Dawson structure: The dimeric Well-Dawson heteropoly anion is $[X_2M_{18}O_{62}]^{2x-16}$. Here M = Mo^{6+} or W^{6+}; X = P^{5+} or As^{5+}; x = charge on 'X' atom. This anion has two trivacant lacunary Keggin species. The Well-Dawson structure contains two M_3O_{13} groups. Rotation of one of these groups by 60° about the 3-fold axis gives the β-isomer. The molybdenum anion is chiral because of a displacement of the molybdenum atoms within their MoO_6 octahedral unit. However, the tungsten complex does not exhibit chirality probably because of the greater rigidity of thetungsten framework.

3. The Anderson-Evans structure: This is another structural type with an octahedron as the central polyhedral. This structure is adopted by the 6-heteropoly anions such as $[TeMo_6O_{24}]^{6-}$. This structure contains six coplanar edges sharing MO_6 octahedra arranged in closed ring. The heteroatom is present in the octahedra at the centre of the ring.

4. The Dexter-Silverton structure: Somewhat less common, containing 12 heteropoly anions $[XM_{12}O_{42}]^{x-12}$; where M = Mo^{6+}; X = Ce^{+4}, U^{+4}, Th^{+4}. In this anion, the central atom is surrounded by twelve O atoms. Thus, an icosahedron forms the central polyhedron. MO_6 polyhedra are arranged in face-sharing fashion unlike edge sharing in other types of structures.

7.9.4. Nomenclature of heteropolyoxometalates

A systematic nomenclature scheme for polyoxometalates has been developed. It uses a labelling system for the metal atoms and sometimes for the oxygen atoms to avoid ambiguity. The resulting names, however, are too long and complicated; these are practically never used for routine purposes.

The current nomenclature that treats polyoxometalates (also referred to as heteropoly anions, heteropoly compounds, polyoxoanions or polyanions) as quasi coordination complexes.

i. The heteroatom, if present is considered as the central atom of the complex and the addenda as the ligands.
ii. The heteroatoms are placed before the heteroatoms
iii. Heteropoly anion is placed in square brackets and thus separated from the countercation
iv. *Examples:* $[SiW_{12}O_{40}]^{4-}$12-tungstosilicate or dodecatungstosilicate
$H_3[PMo_{12}O_{40}]$: 12-molybdophosphoric acid
$Na_5[PMo_{10}V_2O_{40}]$: Sodium decamolybdodivanabdophosphate

7.9.5 Detailed structure of Keggin type polyoxometalate

I) Primary structure: The heteropoly acids are ionic crystals in solid state consisting of large polyanions linked together. The α-type Keggin structure has a tetrahedral (Td) symmetry and consists of a centrally located XO_4 tetrahedral structure which is surrounded by twelve edges and corners sharing MO_6 octahedra (M = addenda atom). These octahedrals are arranged on four M_3O_{13} groups. Each of these groups is composed of three octahedral sharing their edges and having a common O atom which is also shared with the central tetrahedral XO_4.

The oxygen atoms in Keggin structure are classified into four classes on the basis of symmetry equivalence. (i) $X–O_a–M$, $M–O_b–M$: act as inter-bridges between corner sharing octahedral; (ii)

M–O_c–M: 'intra-bridges' between edge sharing that is within a M_3O_{13} unit; (iii) M–O_d: these are the terminal oxygen atoms (M is the addenda atom and X is the central atom).

II) Secondary structure: The overall three-dimensional structure composed of large polyanions, cations, water of crystallization and other molecules constitutes the secondary structure of HPAs. The acid form of heteropoly anions in the solid state contains counterprotons or cations. These play an important role in linking the neighbouring heteropoly anions. For example, in $H_3PW_{12}O_{40}.6H_2O$, the protons are present as $H_5O_2^+$ species, these link the four neighbouring heteropoly anions via hydrogen bonding with the terminal W–O_d. Secondary structure may also contain organic molecules.

III) Tertiary Structure: The complete assembled structure of the heteropoly acid (HPA) constitutes the tertiary structure. That is, it includes size of the particles, pore structure and distribution of protons.

7.9.6. Properties of heteropoly acids

The general characteristics of heteropoly ions are as following:

i) Heteropoly acids are usually very strong acids.
ii) They are highly soluble in water and often very soluble in organic solvents.
iii) The lattice energies of heteropoly compounds are low thus the solvation energies of heteropolyanions are also less. The solubility of the HPAs depends on the solvationenergy of the cation.
iv) In aqueous medium, they are stable at lower pH values but undergo hydrolysis at higher pH values.
v) Heteropoly anions are multi electron oxidants. Those having Mo and V are relatively stronger oxidants. Heteropolymolybdates are strong oxidizing agents and are readily converted to their reduced form called 'heteropoly blues'.

Acidic properties of heteropoly acids: The aqueous solution of heteropoly acids behave as strong acids. They are sometimes called as 'super-acids' because they are stronger than the commonly found mineral acids such as H_2SO_4, HCl, HNO_3, etc. This can be attributed to the presence of 'mobile protons' in the secondary structure of HPAs. Also, in HPAs the negative charge is spread over much larger anions as compared with mineral acids. The acidity is generally determined by dissociation constants and the Hammet acidity function.

The acid strength depends upon the structure of polyanion, the constituent elements as well as the extent of hydration and reduction. The acid strength of crystalline heteropoly acids decrease in the order

$H_3PW_{12}O_{40}$>$H_4SiW_{12}O_{40}$> $H_3PMo_{12}O_{40}$> $H_4SiMo_{12}O_{40}$. HPAs containing tungsten are more acidic than those having molybdenum.

7.9.7. Catalytic applications of heteropoly acids

The application of HPAs as catalysts is determined by several factors such as size, mass, electron and proton transfer and storage ability, thermal stability, mobility of lattice oxygen and Bronsted acidity. The catalytic reactions can be performed in homogeneous as well as heterogeneous (gas-solid, liquid-solid orbiphasic liquid-liquid) systems. HPAs can serve as efficient catalysts owing to the following properties.

i) Their multifunctionality and structural mobility.

ii) They are strong Bronsted acids as well as efficient oxidants exhibiting fast reversible multi-electron redox transformations under mild conditions.

iii) Their acid-base properties can be tuned by varying their chemical composition

iv) Solid heteropoly compounds possess a discrete solid state ionic structure unlike the network of zeolites or metal oxides. The structure of heteropoly compounds is not disturbed upon substitution or after undergoing oxidation/reduction and exhibits high proton mobility.

v) The HPAs are highly soluble in polar solvents and have high thermal stability in solid state.

HPAs have been used as catalysts in different types of reactions, such as formation of carboxylic acids from the corresponding aldehydes, as well as the dehydrogenation of alcohols, aldehydes and carboxylic acids to form C=C and C=O bonds. HPAs have been developed and commercialized for oxidation of methacrolein to methacrylic acid, hydration of olefins such as propene and butene, polymerization of tetrahydrofuran etc. In the oxidation of alkenes and the coupling of aromatics (Wacker process), molybdovanadates are employed as catalysts. Polyoxomolybdates are widely used in hydrodesulfurization and hydrodenitrification of fossil fuels.

7.10. SUMMARY

This chapters provide a good understanding of metal clusters those involving boron hydrides, their transition metal derivatives i.e. metalloboranes also including carboranes and metallacarboranes. Their synthesis, nomenclature and structural details give an important understanding of metal clusters. Another aspect of metal clusters is the unique multiple bonds between metal atoms in certain transition metal clusters. The chapter deals with polyoxometallates which brings the focus on isopoly and heteropoly acids of chromium, molybdenum and tungsten having potential applications in catalysis.

7.11. TERMINAL QUESTIONS

Q1. Sketch the molecule B_2H_6 and show the different bonding between the hydrogen and boron atoms?

Q2. Which structures (closo, nido, arachno) do the molecules B_5H_8, $B_4H_4^{2-}$ and $B_{10}H_{14}$ have?

Q3. What are boron hydrides or boranes? Write a short note on the classification of boranes with examples.

Q4. What are metal clusters? Explain the structure of $[Re_2X_8]^{2-}$ ion.

Q5. Give some examples of metal clusters having metal-metal multiple bonds. Draw structure of any two.

Q6. What are polyoxometallates? Write short note on isopoly and heteropolyoxometallates.

Q7. Explain why polymerization stops in isopoly acids?

Q8. Write short note on Keggin type polyoxometalate.

7.12. ANSWERS

Q2.

B_5H_8	**$B_4H_4^{2-}$**	**$B_{10}H_{14}$**
Count valence electrons	Count valence electrons	Count valence electrons
5x3e (B) = 15 e	4x3e (B) = 12 e	10x3e (B) = 30 e
8x1 (H) = 8 e	4x1 (H) = 4 e	14x1 (H) = 14 e
	+ 2 charge	
Total =23 e	Total =18 e	Total =44 e
4n+3= *nido*	4n+2= closo	4n+4= arachno
Here n=5 (no. of B atoms	Here n=4 (no. of B atoms	Here n=10 (no. of B atoms)

Q7. It is noteworthy that polymerization ceases for isopoly anions. A possible explanation for which lies in the position of oxygen atoms. A terminal oxygen atom is strongly π bonded to the transition metal {such as Mo(VI), W(VI)}. These terminal oxygen atoms are never located *trans* to one another which prevents their competition for the same vacant t_{2g} orbital. Instead, they are present opposite to a bridging or internal oxygen. This results in the metal ion being displaced towards the terminal oxygen and away from the oxygen opposite to it which is what we encounter in *trans* effect. On the contrary, metal ions such as Al(III) or Ga(III) are poor π acceptors. Thus, they do not stabilize their terminal oxygen atoms which can therefore attack other units and result in continuing polymerization.

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Block II: METAL π-COMPLEXES AND METAL CLUSTERS

UNIT 8 METAL-LIGAND EQUILIBRIA IN SOLUTION

CONTENTS

8.1. OBJECTIVES

After going through this unit, you will be able to answer the following questions:

What is thermodynamic and kinetic stability?

Chelate effect.

Factors affecting stability of complexes.

Different methods for the determination of stability constants.

8.1. INTRODUCTION

Addition of metal ions to an aqueous solution containing other species such as ligands with which the metal ions can interact lead to the formation of complexes. These complexes bear metal ligand bonds and several weak and strong intra-intermolecular interactions. After a certain time lapse, the system attains equilibrium between the reactants and new species formed. It is important to study such metal-ligand systems and their equilibrium because they play a vital role in bio-organic, bio-inorganic systems, industrial processes etc.

In order to understand chemical behavior of systems in solution, where an assumption is made that the system is in equilibrium (equilibrium exists between various chemical species in the system), it becomes pertinent to know about the equilibrium constants. In a system involving formation of complexes in metal ligand solution, these are called stability constants or formation constants.

8.3. STEPWISE AND OVERALL FORMATION CONSTANTS AND RELATION BETWEEN THEM

When referring to the stability of compounds, it implies that the compound exists in a stable condition under suitable conditions and can be stored for appreciable time. The stability constant (formation constant, binding constant) is an estimate of the strength of interaction between metal and ligands leading to the formation of the complex. The formation of complexes in solution can be understood qualitatively in terms of kinetic and thermodynamic stability.

8.3.1. Thermodynamic stability

It is the measure of the extent to which formation of complex occurs or the extent of transformation under a given set of condition at equilibrium. Thermodynamic stability depends on the strength of bond between metal and ligand. The strength of bond between metal and ligand shows great variation. For example, in $[Co(SCN)_4]^{2+}$, the strength of bond metal and thiocyanate is very weak and breaks immediately in aqueous solution. On the contrary, in $[Fe(CN)_6]^{3-}$,the bond between ferric ion and nitrile anions is very strong and does not break in aqueous solution. Thus, thermodynamic stability deals with metal ligand bond energy and other thermodynamic parameters. Tetracyanonickelate(II) $\{[K_2Ni(CN)_4]\}$ ion is a good example of a thermodynamically stable complex but kinetically labile whereas hexa amine cobalt(III) cation $[Co(NH_3)_6]^{3+}$ in acid solution is kinetically inert and thermodynamically unstable.

$$[Co(NH_3)_6]^{3+} + 6H_3O^+ \rightarrow [Co(H_2O)_6]^{3+} + 6NH_4^+$$

Stability and inertness can be expressed thermodynamically in terms of free energies of reaction $\Delta G°$. A stable complex has large negative $\Delta G°$. The following relation relates the standard enthalpy change $\Delta H°$ for the reaction to equilibrium constant β_n:

$$\Delta G° = -RT \ln \beta_n$$

$$\Delta G° = \Delta H° - T\Delta S°$$

$\Delta S°$ values for similar complexes of metal ions of a particular transition series with a particular ligand will not differ significantly and hence, $\Delta H°$ value will be related to β_n values. Therefore, order of values of $\Delta H°$ will be order of β_n values.

8.3.2. Kinetic stability

Kinetic stability refers to the reactivity or ligand substitution in general. It is the speed with which transformation of reactants occurs leading to attainment of equilibrium. Thus, substitution may take place rapidly with some ligands while slowly with others. The former type is called labile ligands and the latter are known as inert. In kinetic studies, time factor plays an important role in deciding the stability of the complex. It deals with rate and mechanism of complex formation.

8.3.3. Stepwise and overall/cumulative formation constants

The formation of complex can be considered as a type of acid base equilibrium existing between the competing species M^{n+} ion, ligand (L) and H^+ ions

Thus, two equilibria have to be considered

$$H + L \rightleftharpoons HL$$

$$M + L \rightleftharpoons ML$$

Moreover, to consider stability constant for complex formation the equation can be represented as:

$$M + nL \rightleftharpoons ML_n$$

8.3.4. Stepwise formation constant

It is considered that complex formation is a stepwise process occurring by a series of stages. For example, the stepwise formation constant of ML_n can be expressed as

$$M + L \rightleftharpoons ML \qquad K_1 = \frac{[ML]}{[M][L]} \qquad \text{So, } [ML] = K_1 [M] [L] \qquad (a)$$

$$ML + L \rightleftharpoons ML_2 \qquad K_2 = \frac{[ML_2]}{[ML][L]} \qquad \text{So, } [ML_2] = K_2 [ML] [L] \qquad (b)$$

$$ML_2 + L \rightleftharpoons ML_3 \qquad K_3 = \frac{[ML_3]}{[ML_2][L]} \qquad \text{So, } [ML_3] = K_3 [ML_2] [L] \qquad (c)$$

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$$ML_{n-1} + L \rightleftharpoons ML_n \qquad K_n = \frac{[ML_n]}{[ML_{n-1}][L]} \qquad \text{So, } [ML_n] = K_n [ML_{n-1}] [L] \qquad (n)$$

Here, K_1, K_2, K_3 and K_n are stepwise equilibrium constants with respect to the formation of the complexes one step at a time, M denotes metal ion and L denotes a monodentate ligand. The overall formation constant (K_f) of complex from reagents in terms of stepwise constant is given as

$$K_f = K_1 \text{ x } K_2 \text{ x } K_3 \ldots K_n$$

8.3.5. Cumulative or overall formation constant

Cumulative or overall formation constant is represented by symbol β. It can be represented as the product of stepwise formation constants.

$$M + L \rightleftharpoons ML \qquad \beta_1 = \frac{[ML]}{[M][L]}$$

$$M + 2L \rightleftharpoons ML_2 \qquad \beta_2 = \frac{[ML_2]}{[M][L]^2}$$

$$M + 3L \rightleftharpoons ML_3 \qquad \beta_3 = \frac{[ML_3]}{[M][L]^3}$$

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$$M + n L \rightleftharpoons ML_n \qquad \beta_n = \frac{[ML_n]}{[M][L]^n}$$

Here, β_1, β_2, β_3 stand for overall stability constant for each stage of complex formation and β_n stands for n^{th} overall (or cumulative) formation constant. Usually, K_n decreases with each subsequent step. This can be reasoned as follows. As ligand is added to the metal ion M^{n+}, ML forms first, with the addition of more ligand $[ML_2]$ rises sharply and [ML] drops. With further addition of L, $[ML_2]$ drops and $[ML_3]$ rises and so on. Addition of ligand to form a new complex is always reversible and formation of ML_n progresses with greater n values for L. Thus, there is probability of more ligands to fall back off as there are fewer places to put the new ligands in the coordination sphere, so it is expected that stepwise K_n's will drop. For example, the formation of $[Cd(NH_3)_4]^{2+}$ depicted below, the drop in equilibrium constant with added L groups is evident.

$$Cd^{2+} + NH_3 \rightleftharpoons [Cd(NH_3)]^{2+} \qquad K_1 = 10^{2.65}$$

$$[Cd(NH_3)_3]^{2+} + NH_3 \rightleftharpoons [Cd(NH_3)_4]^{2+} \qquad K_4 = 10^{0.93}$$

8.3.6. Relation between stepwise and overall stability constants

A stepwise constant can be expressed as the quotient of two or more overall constants

$$\beta_1 = K_1$$

$$\beta_2 = K_1 \times K_2$$

$$\beta_3 = K_1 \times K_2 \times K_3$$

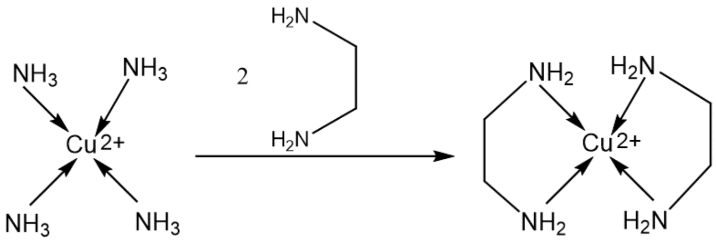
$$\beta_n = K_1 \times K_2 \;.... \qquad K_n = \sum_{i=1}^{i=n} K_i$$

From above, it can be stated that overall stability or formation constant (β_n) is the product of stepwise stability or formation constants (K_1, K_2, ... K_n). It is always suitable to define each stability constant with reference to an equilibrium expression.

8.4. FACTORS AFFECTING THE STABILITY OF METAL COMPLEXES WITH REFERENCE TO THE NATURE OF METAL ION AND LIGAND.

8.4.1 Chelate effect

The formation of a closed ring in an inorganic metal complex by attachment of a ligand to metal ion at two points is called a chelate. Minimum of a bidentate ligand is required for formation of a chelate. Alternatively, we can say that chelate complexes are formed by multidentate ligands. The name chelate is derived from the Greek word ‘Chela’ means ‘Claw of lobster or crab’. A series of experiments revealed that the stability of inorganic chelate metal complexes was greater than those having no chelating ligands in their structure. However, there are several other factors, which shall be considered while deciding stability of complexes, discussed below. An example is the complex ion formed between ethylene diamine (en) and cupric ion, $[Cu(NH_2CH_2NH_2)_2]^{2+}$.



Consider for example, a reaction vessel containing cupric ions, NH_3 and en (ethylene diamine) given the condition that cupric ions are equally available to both the ligands and concentration of NH_3 is twice that of en ligand. The bidentate en ligand forms chelate complex with copper resulting in five-membered ring whereas in the other copper complex formed with NH_3 ligand, the two en ligands are replaced by four NH_3 ligands. Under given set of conditions, it is found that the concentration of complex **1** is greater than that of **2**. This can be attributed to the additional stability provided by chelation of **en** ligand in complex **1**.

$$Cu^{2+} + 2en \rightleftharpoons [Cu(en)_2]^{2+} \qquad 1$$

$$Cu^{2+} + 4NH_3 \rightleftharpoons [Cu(NH_3)_4]^{2+} \qquad 2$$

8.4.1.1. Factors influencing stability due to chelation

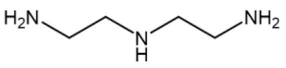
Ring size

The stability of a chelate complex depends on the size of the ring. That is the number of atoms constituting the ring. For example, a four membered ring is unstable whereas a five and six membered ring complexes are more stable. The instability of four membered chelate is attributed to internal strain because of the small inter-bond angle in the ring. The order can be generalized as,

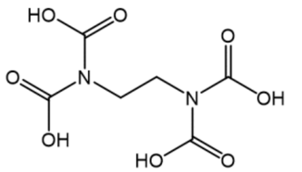
Five membered > Six membered > Seven membered

The stability of metal chelates decreases by increasing the chelate size. This is because larger rings are less rigid so less entropy is lost in their formation.

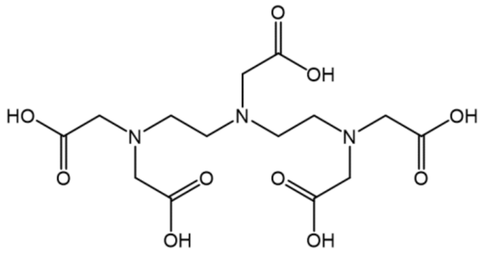
Apart from ethylenediamine (en), other multidentate ligands which form chelate complexes are diethylenetriamine (dien), EDTA (ethylenediaminetetraacetic acid) and DTPA (Diethylenetriaminepentaacetic acid).



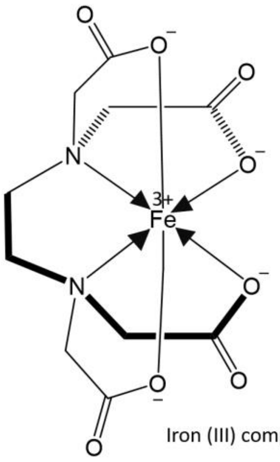
Diethylenetriamine



Ethylene diamine tetra acetic acid



Diethylenetriaminepentaacetic acid



Iron (III) complex with EDTA

The non-protonated form of EDTA forms a hexacoordinate complex with iron bearing five membered chelates. DTPA has eight donor atoms hence forms complexes with metals with large atomic size such as lanthanide or actinide, which form 8 or 9 coordinate complexes.

Number of rings

In general, it is observed that the stability of the complex increases with increase in the number of donor atoms available for coordination. Increase in number of rings increases the stability of the compound. The complex $[Ni(en)_3]^{2+}$ having three chelate rings is approximately 10^{10} times more stable than complex having no chelation such as $[Ni(NH_3)_6]^{2+}$. Schwarzenbach has referred to this increase in stability with the dentate character of the ligand as the chelate effect. This effect is larger for the transition metal ions.

Steric effect

This effect comes into play when the groups present on coordinating ligands obstruct each other; thus, distorting bond angles and decrease in stability. The phenomenun is called F-strain. As steric effect decreases, stability of complex increases. For example Ni(II) complexes with 2-methyl 8-hydroxy quinoline are less stable than complexes with 8-hydroxy quinoline. Similarly, complexes of ethylene diamine are more stable than its tetramethyl derivatives. The later compounds have greater steric repulsion due to the presence of four additional methyl groups.

8.4.1.2. Chelate effect and its thermodynamic origin

We know that greater stability of chelate complexes is called the chelate effect. The additional stability due to chelation can be explained considering the thermodynamic aspects of this phenomenon. It is believed that there is difference in entropy between chelate and non-chelate complex reactions. The formation of chelate complexes results in greater disorder because of the formation of a larger number of free particles in the products whereas there is negligible change in the number of particles in the formation of comparable nonchelate complexes. This fact can be illustrated with the following example. The stability of a complex with bidentate ligand such as ethylenediamine is significantly greater than the complex of the same metal ion with monodentate ligands having comparable donor ability such as ammonia.

$$[Cu(OH_2)_4]^{2+} + en \rightleftharpoons [Cu(OH_2)_2(en)]^{2+} + 2\,H_2O$$

$$\Delta H = -54 \text{ kJ mol}^{-1}, \Delta S = 23 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$[Cu(OH_2)_4]^{2+} + 2\,NH_3 \rightleftharpoons [Cu(OH_2)_2(NH_3)_2]^{2+} + 2H_2O$$

$$\Delta H = -46 \text{ kJ mol}^{-1}, \Delta S = -8.4 \text{ J K}^{-1} \text{ mol}^{-1}$$

8.4.2. Macrocyclic effect

It is observed that stability of complexes with macrocyclic ligands is higher than the corresponding complexes formed with open chain ligands. The phenomenun is called “macrocyclic effect” and both entropy and enthalpy changes are considered. An important factor with macrocyclic ligands is that they bind with specific metal ions only depending on the size of the cavity in them. Hence, they show selectivity with metal ions unlike open chain (chelating) ligands. For example, the crown ether 18-crown-6 forms much stronger complexes with the potassium ion, K^+ than with the smaller sodium ion, Na^+.

8.4.3. Nature of central metal ion

8.4.3.1. Class A and B metals

According to Ahrland, Chatt and Davies, metal complexes can be put in class A if they form stronger complexes with ligands having N, O or F as donor atoms whereas those which form stable complexes with ligands having P, S or Cl can be put in class B. For example Ni(II) forms stable complexes with amine ligands whereas Pt(II) forms stable complexes with phosphine ligands where donor atom is phosphorous. Later, Pearson’s Hard and Soft Acid Base theory (HSAB) classified metals as hard and soft where class A metals are hard acids whereas class B metals are soft acids.

Type of Acid/Base	Characteristic Features	Examples
Hard acids	Atomic centers of small ionic radii. High positive charge. Empty orbitals in their valence shells. Low electronegativity and low electron affinity. Likely to be strongly solvated. High energy LUMO.	H^+, Li^+, Na^+, K^+, Be^{2+}, Mg^{2+}, Ca^{2+},Sr^{2+}, $Sn^{2+}Al^{3+}$, Ga^{3+}, In^{3+}, Cr^{3+}, Co^{3+}, Fe^{3+},Ir^{3+}, La^{3+}, Si^{4+}, Ti^{4+}, Zr^{4+}, Th^{4+},VO^{2+} , UO_2^{2+}, BF_3, BCl_3, $B(OR)_3$, $AlMe_3$
Soft acids	Large radii. Low or partial positive charge. Completely filled orbitals in their valence shells.	Cu^+, Ag^+, Au^+, Hg^+ , Cs^+ , Tl^+ , Hg^{2+} , Pd^{2+}, Cd^{2+} , Pt^{2+} Metal atoms in zero oxidation states

	Intermediate electronegativities Low energy LUMO's with large magnitude of LUMO coefficients.	
Border line acids		Fe^{2+} , Co^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+} , Pb^{2+} , $B(CH_3)_3$, SO_2, NO^+
Hard bases	Small radii and highly solvated. Electronegative atomic centres Weakly polarizable. Difficult to be oxidized. High energy HOMO.	H_2O, OH^-, F^-, Cl^-, CH_3CO^{2-}, $PO4^{3-}$, SO_4^{2-}, CO_3^{2-}, NO_3^-, ClO_4^-, ROH,RO^-, R_2O, NH_3, RNH_2, N_2H_4
Soft bases	Large atoms with intermediate electronegativity High polarizability Easily undergo oxidation. Low energy HOMO's but large magnitude HOMO coefficients	RSH, RS^-, R_2S, I^-, CN^-, SCN^-, $S_2O_3^-$, R_3P, R_3As $(RO)_3P$, RNC, CO, C_2H_4, C_6H_6, R^-, H
Borderline bases		Aniline, pyridine, N_3^-, Br^-, NO_2, SO_3^{2-}, N_2

In general, hard acids form stronger complexes with hard bases and vice versa. Hard-hard interactions are predominantly electrostatic in nature while soft-soft interactions are covalent in nature. The hardness of metal ions increases with increase in oxidation state. This is evident from the fact that Fe^{2+} forms stable complexes with N donor ligands while Fe^{3+} forms stable complexes with O donor ligands.

8.4.3.2. Ionic radius of metal ions

In 1953, Irving and Williams suggested that first row transition metal ions could be arranged in order of their ligand binding affinities. Thus, they designed a series arranging octahedral divalent first transition metal ion complexes in order (shown below) of their stability known as the Irving-Williams series.

$$Mn < Fe < Co < Ni < Cu > Zn$$

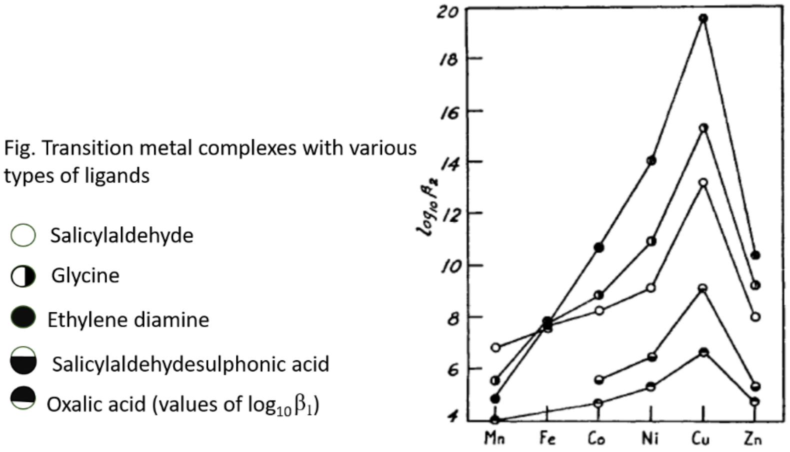
The order was found to hold true for a variety of ligands and it can be explained as follows.

(i) The ionic radius is found to decrease from Mn to Zn as a general periodic trend hence accounts for increase in stability.

(ii) The crystal field stabilization energy (CFSE) increases from zero for Mn^{2+} to maximum for Ni^{2+} complexes and again falls to zero for Zn^{2+}. Even though CFSE for Cu^{2+} is lesser than that for Ni^{2+} octahedral complexes, still Cu^{2+} complexes are more stable due to the Jahn Teller distortion.

The plot shown below from the original publication shows variation of overall stability constant of transition metal complexes with different ligands.

Fig. Transition metal complexes with various types of ligands



Reference paper: H. Irving and R. J. P. Williams, *J. Chem. Soc.*, **1953**, 3192

8.4.4. Nature of the ligand

8.4.4.1. Size and charge

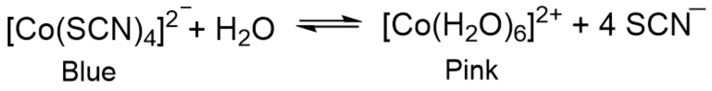
Ligands with less charge and greater size form less stable complexes as compared to ligands with more charge and smaller size.

8.4.4.2. Basic character

Higher the basic character of the ligand that is the tendency to donate electrons to the central metal ion, higher is the stability of the complexes formed. Eg. Aromatic amines form less stable complexes as compared to aliphatic amines because of the weak electron donating tendency of the aromatic amines. Ligands such as NH_3 and CN^- are more basic in nature and hence form stable complexes.

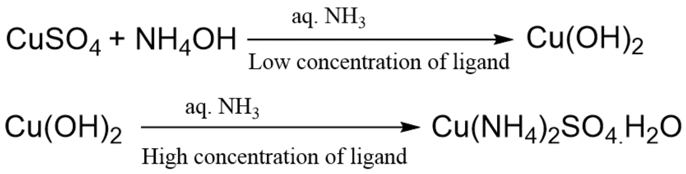
8.4.4.3. Ligand concentration

Some complexes can exist in aqueous solution only when the concentration of coordinating ligand is high. This is because in some cases water molecules behave as a better coordinating ligand. For eg. Co^{2+} can exist as stable blue coloured solution of $[Co(SCN)_4]^{2-}$ only in presence of high concentration of thiocyanate (SCN^-) ions. But on dilution in aqueous solution a stable pink colored complex of $[Co(H_2O)_6]^{2+}$ is formed but on further addition of SCN^- the pink color disappears to give blue color solution. The phenomena shows that there is a competition between the SCN^- and H_2O ligands in formation of complex with Co(II) ion..



$$\underset{\text{Blue}}{[Co(SCN)_4]^{2-}} + H_2O \rightleftharpoons \underset{\text{Pink}}{[Co(H_2O)_6]^{2+}} + 4\,SCN^-$$

Similarly, reaction of cupric sulfate at lower concentration of ammonia forms copper hydroxide whereas at higher concentration of ligand forms ammonium cupric sulfate monohydrate.



$$CuSO_4 + NH_4OH \xrightarrow[\text{Low concentration of ligand}]{\text{aq. }NH_3} Cu(OH)_2$$

$$Cu(OH)_2 \xrightarrow[\text{High concentration of ligand}]{\text{aq. }NH_3} Cu(NH_4)_2SO_4.H_2O$$

8.5. METHODS OF DETERMINING THE BINARY FORMATION/STABILITY CONSTANTS

The study of formation of metal complexes in aqueous solutions in last couple of decades has shifted from the more basic purposes of interpreting the mechanism of formation and correlating stability constant data to numerous applied fields such as the formation of complexes in biological fluids to the treatment of sewage. An interesting example of application of these studies is seen in determining the toxicity of cadmium to the grass shrimp (Palaemonetes pugio) in the presence of chloride ion and the chelating ligand, nitrilotriacetic acid (NTA). By studying both chloride and NTA complexes of the metal ion, it was shown that the degree of toxicity was directly related to the activity of the free cadmium ion. In examples such as above, stability data are used as tools to investigate systems or processes or to understand the mechanism of biological and other reactions.

The stability constant of complex in the solution is usually determined by measurement of equilibrium constants (K) for complex forming reaction. The knowledge of stability constant is crucial to rationalize the understanding of the behaviors of metal complexes in the solution. Also, the study of stability or formation constants is useful because most of the properties and utility of the complexes depend on it. Many physical and chemical properties can be employed to detect the formation of complexes in solution and to measure the stability constants. The detection of the complexes and the determination of the stability constants are very closely related. Some of the methods of finding binary stability constants are discussed below.

8.5.1. Potentiometric method

In this method, association between the metal ion M^{m+} and the ligand as an anion of the weak acid H_nL is studied. Here, the nature and concentration of all the species present in solution have to be determined such as pH of buffer solution containing H_nL, base (NaOH, KOH) and metal ion generally used as perchlorate salt (generalized here as MX_m).

To calculate the stability constants from potentiometric pH titration data, we need equations on the mass balance and charge balance conditions.

The total concentration of the metal ion may be written:

8.5.1. 1. Bjerrum method

Bjerrum designed this method to determine the stability constant using pH meter to measure H^+ ion concentration based on the fact that formation of a ligand-metal complex is a type of acid-base reaction equilibrium where there is competition for the ligand between M^{n+} ion and H^+ ions. Thus, the following two equilibria operate

$$H + L \rightleftharpoons HL$$

$$M + L \rightleftharpoons ML$$

Thus, by titrating a mixture of M and HL with a base concentration of H^+ can be followed. With the help of prior knowledge of acid dissociation constant K_a of HL, stability constant for the formation of complex ML can be determined.

Consider the equilibrium in which an acid, metal ions and a basic ligand are present. Thus,

$$L + H^+ \longrightarrow HL^+;\ Ka = \frac{[HL^+]}{[L]\,[H^+]}$$

$$L + M^+ \longrightarrow ML^+;\ Kf = \frac{[ML^+]}{[L]\,[M^+]}$$

Here, K_a and K_f are acid dissociation constant and formation constant of complex respectively.

If, C_H, C_M and C_L are the concentration of acid, metal and ligand in moles/litre, their concentration can be expressed in terms of following equations:

$$C_H = [H^+] + [HL^+]$$

$$C_L = [L] + [ML^+] + [HL^+]$$

$$C_M = [M^+] + [ML^+]$$

Using above three equations and equation for K_a, we can derive equations for $[ML^+]$, $[M^+]$ and [L] as shown below:

$$C_L - C_H = [L] - [H^+] + [ML^+]$$

$$[ML^+] = C_L - C_H + [H^+] - [L]$$

Using value of [L] from the K_a expression, we get

$$[ML^+] = C_L - C_H + [H^+] - [HL^+]/Ka\,[H]$$

or

$$[ML^+] = C_L - C_H + [H^+] - \{(C_H - [H^+])/(Ka\,[H])\}$$

$$[M^+] = C_M - [ML^+]$$

$$[L] = [HL^+]/Ka\,[H^+]$$

or

$$[L] = C_H - [H^+]/Ka\,[H^+]$$

Thus, using the values of $[ML^+]$, $[M^+]$ and $[L]$ from above equations and substituting in $K_f = [ML^+]/[M^+]\,[L]$, K_f can be calculated. The values of C_H, C_L, C_M, Ka and $[H^+]$ are generally determined potentiometrically using a pH meter.

Drawbacks: It should be noted that if two or more solution species have identical charges and same number of metal ions and ligand molecules, only the sum of the concentrations could be determined potentiometrically. Thus, the two forms of glycine $NH_3^+CH_2COO^-$ and NH_2CH_2COOH, complex species such as $[FeEDTA]^{-1}$ and $[Fe(OH)(H.EDTA)]^{-1}$, configurational and conformational isomers and inner- and outer sphere complexes cannot be distinguished by this method. Other methods such as spectrophotometry may be more suitable in these cases.

8.5.1.2 Irving-Rossotti method

Irving and Rossotti method is based on the method devised by Bjerrum. They explained that the formation curve of a system of metal ligand complex could be calculated directly from pH-meter readings during a titration, without knowledge of the hydrogen ion concentration or activity. They derived simple general equations, which can be used for all ligands that are conjugate bases or weak acids and illustrated the application of that equation to specific systems. The Irving-Rossotti titration curves for the same volumes of alkali, the ligand formation curve is positioned in two different ways, with respect to the acid curve in two different regions of pH. At low pH, the ligand titration curve shows higher values of pH than the acid titration curve indicating that it contains less number of titrable hydrogen ion. At higher pH, it exhibits lower pH value than the acid titration curve showing more number of titrable hydrogen ions due to dissociation of -COOH group and thus, behaves as an acid. From the displacement of these two curves, $\bar{n}_H$ can be calculated.

Further, metal complexes formed by reaction of the type,

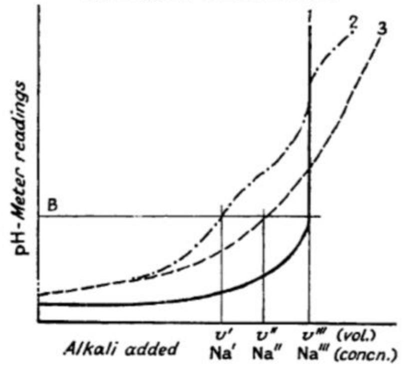
$$M^{2+} + LH \rightleftharpoons ML^+ + H^+$$

The ligand on coordination with metal releases H^+ ion in the solution and hence the metal + ligand solution contains some titrable hydrogen ions and thus the metal titration curve, shows lower pH value for the same amount of alkali than the ligand curve. Thus, ¯n factor can be computed from the difference in the volume of alkali required to produce the same pH in the metal and ligand titration.

The formation curves: Irving-Rossotti method involves pH-titration of the following three sets of mixtures (keeping total volume constant) against a carbonate free standard alkali:

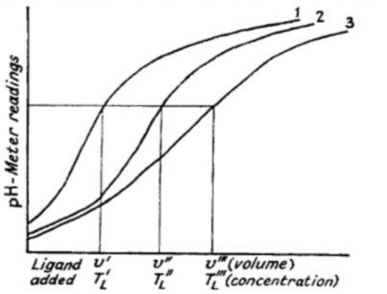
(i) Mineral acid (ii) Mineral acid + Ligand solution (iii) Mineral acid + Ligand solution + Metal ion solution. The ionic strength and temperature of solution is kept constant.

Fig 1. Typical titration curves



Curve 1. Mineral acid alone
Curve 2. Mineral acid plus ligand
Curve 3. Mineral acid plus ligand plus metal

Fig 2. Titrations with a solution of the ligand



Curves 1 and 2: Mineral acid at two different concentrations
Curve 3: Mineral acid and metal ions

Reference paper: H.M. Irving, and H.S. Rossotti, *J. Chem. Soc.*, **1954**, 2904-2910

8.5.2. Spectrophotometric method

Spectrophotometric methods are highly sensitive. The deciding factor in this technique is that the species involved in chemical equilibria must absorb light and give different spectral response. Thus, concentration of species involved in equilibrium and new species formed can be measured directly from UV-visible spectra.

The method is based on the Beer-Lambert Law where log (I_0/I) = εcd (I_0/I is the ratio of incident light to transmitted light, c is the molar concentration of the absorbing solute, d is the light path length in centimeters and ε is the absorptivity). Some precautions must be considered while measuring absorbance such as prevention of any contamination of the solution or cell faces. In addition, the spectrophotometer should be used to record small differences in optical density having inaccuracy in the absorbance of the instrument is negligible.

When only two species are present such as the ionization of monobasic acids, measurement of absorbance as a function of wavelength at different pH values can be used to calculate the equilibrium constant. This may be useful for compounds whose solubility is poor, direct titration can be done since absorptivities are often large enough to allow study of solutions having concentration upto l0^{-5} mol dm^{-3}.

Drawback: For a complex which is too stable or too weak the K value cannot be determined spectrophotometrically. In addition, if the ligand or metal absorb at the chosen wavelength, the measured absorbances must be corrected.

8.5.2.1. Job's method

Using the stoichiometry of the complex, the value of K (the stability constant) can be determined form the expression given below, if the value of m and n are known:

$$K = \frac{m^{n-1} \times n^{m-1} \times (P-1)^{m+n-1} [n-(m+n)x]}{C_1^{m+n-1} \times P^{n-1} [P(m+n)^{x-1}]^{m+n}}$$

where, K = stability constant, 1/K = dissociation constant of the complex, P = ratio of the concentration of the ligand to the concentration of metal, C_1= molar concentration of metal solution, X = concentration of ligand for which the concentration of complex is maximum, m = the number of moles of a metal required to combine with "n" moles of ligand for (1:1) metal ligand ratio in the complex having m = n = 1, the stability constant K can be calculated from the equation given below.

$$K = \frac{(P-1)(1-2x)}{C_1 \times [(P+1)(x-1)]^2}$$

8.6. TERMINAL QUESTIONS

Q1. Arrange $[Co(NH_3)_6]^{3+}$, $[CoF_6]^{3-}$, and $[Co(en)_3]^{3+}$ in order of decreasing stability.

Q2.Arrange $[Cr(en)_3]^{3+}$, $[CrCl_6]^{3-}$, $[CrF_6]^{3-}$, and $[Cr(NH_3)_6]^{3+}$ in order of increasing stability.

Q3. Based on the given values, rank the following complex ions from most to least stable.

$[Cr(OH)_4]^-$ $K_f = 8.0\times10^{29}$; $[Ni(CN)_4]^{2-}$ $K_f = 2.0\times10^{31}$; $[Co(NH_3)_6]^{3+}$ $K_f = 4.5\times10^{33}$; $[Cu(CN)_4]^{3-}$ $K_f = 2.0\times10^{30}$

Q4.Among, $[Ni(en)_3]^{2+}$, $[Ni(EDTA)]^{2-}$, and $[Ni(NH_3)_6]^{2+}$which would you expect to have the largest and smallest K_f value? Explain.

8.7. ANSWERS

Q1. $[Co(en)_3]^{3+} > [Co(NH_3)_6]^{3+} > [CoF_6]^{3-}$

Q2. Here the metal ion is the same all the complexes i.e. Cr^{3+}. Therefore, we must consider the properties of the ligands to decide the stability of the complexes. We know that the stability of a metal complex increases as the basicity of the ligands increases; we need to determine the relative basicity of the four ligands. By our understanding of acid–base properties, we can say that ammonia and ethylenediamine, with nitrogen donor atoms, are the most basic ligands. The fluoride ion is a stronger base (it has a higher charge-to-radius ratio) than chloride, so the order of stability based on ligand basicity is

$[CrCl_6]^{3-} < [CrF_6]^{3-} < [Cr(NH_3)_6]^{3+} \approx [Cr(en)_3]^{3+}$.

Another reason is the chelate effect, so we expect ethylenediamine to form a stronger complex with Cr^{3+} than ammonia. Thus, the likely order of increasing stability is

$[CrCl_6]^{3-} < [CrF_6]^{3-} < [Cr(NH_3)_6]^{3+} < [Cr(en)_3]^{3+}$.

A3.$[Co(NH_3)_6]^{3+}$>$[Ni(CN)_4]^{2-}$>$[Cu(CN)_4]^{3-}$>$[Cr(OH)_4]^{-}$

A4. Ethylenediamine (en) is a bidentate ligand and forms one chelate while EDTA is a six dentate ligand and forms five chelate rings and ammonia is a monodentate non chelating ligand. We know that complexes with greater number of rings are more stable. Hence, $[Ni(EDTA)]^{2-}$ will have highest Kf value since it has five rings, followed by $[Ni(en)_3]^{2+}$ which has three rings and $[Ni(NH_3)_6]^{2+}$ has no rings hence it will have smallest K_f value among the above three complexes.

8.8. REFERENCES

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