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School of Science and Humanities

Department of Chemistry

SCYA5201

Chemistry of Main Group Elements

Unit - 1

Chemistry of Boranes

Structure and bonding in boranes and boron cage compounds- Closo, nido, arachno and carboranes – Styx notation – Wade's rule – Electron count in polyhedral boranes – Synthesis of polyhedral boranes – Isolobal analogy between main group and transition metal fragments– Boron halides – Phosphine- Boron heterocycles – Borazine.

1. Boranes:

Preparation:

Diborane can also be obtained in small quantities by the reaction of iodine with sodium borohydride in diglyme.

$$2NaBH_4 + I_2 \rightarrow B_2H_6 + 2NaI + H_2$$

On heating magnesium boride with HCl a mixture of volatile boranes are obtained.

$$2Mg_3B_2 + 12HCl \rightarrow 6MgCl_2 + B_4H_{10} + H_2$$

$$B_4H_{10} + H_2 \rightarrow 2B_2H_6$$

PHYSICAL PROPERTIES

- Colourless and highly inflammable gas at room temperature.
- At high concentrations, it ignites rapidly in the presence of moist air at room temperature.
- It smells sweet.
- It has boiling point of about 180 K
- It is toxic gas
- It releases huge amount of energy when burnt in the presence of O_2.
- It readily hydrolysed in the water to give hydrogen gas and boric acid.

Chemical Properties:

i) Diboranes reacts with water and alkali to give boric acid and metaborates respectively.

$$B_2H_6 + 6H_2O \rightarrow 2H_3BO_3 + 6H_2$$

$$B_2H_6 + 2NaOH + 2H_2O \rightarrow 2NaBO_2 + 6H_2$$

ii) Action of air:

At room temperature pure diborane does not react with air or oxygen but in impure form it gives B_2O_3 along with large amount of heat.

$B_2H_6 + 3O_2 \rightarrow B_2O_3 + 3H_2O$

$\Delta H = -2165$ KJ mol^{-1}

iii) Diborane reacts with methyl alcohol to give trimethyl Borate.

$B_2H_6 + 6CH_3OH \rightarrow 2B(OCH_3)_3 + 6H_2$

iv) Hydroboration:

Diborane adds on to alkenes and alkynes in ether solvent at room temperature. This reaction is called hydroboration and is highly used in synthetic organic chemistry, especially for anti Markovnikov addition.

$B_2H_6 + 6RCH{=}CHR \rightarrow 2B(RCH\text{-}CH2R)_3$

v) Reaction with ionic hydrides

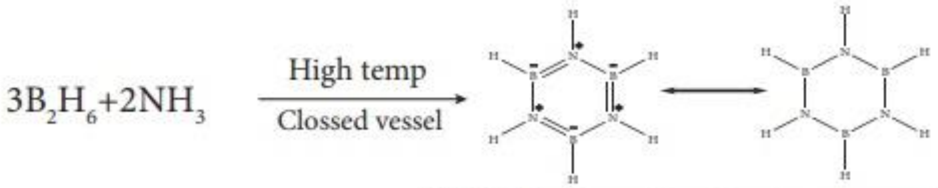
When treated with metal hydrides it forms metal borohydrides

$$B_2H_6 + 2LiH \xrightarrow{\text{Ether}} 2LiBH_4$$
$$B_2H_6 + 2NaH \xrightarrow{\text{Diglyme}} 2NaBH_4$$

vi) Reaction with ammonia:

When treated with excess ammonia at low temperatures diborane gives diboranediammonate. On heating at higher temperatures it gives borazole.

$$3B_2H_6 + 6NH_3 \xrightarrow{-153\text{ K}} 3B_2H_6.2NH_3 \text{ (or) } 3[BH_2(NH_3)_2]^+[BH_4]^-$$



$2B_3N_3H_6$ (Borazole or Borazine - Inorganic benzene)

Structure and Bonding in diborane:

In diborane two BH_2 units are linked by two bridged hydrogens. Therefore, it has eight B-H bonds. However, diborane has only 12 valance electrons and are not sufficient to form normal covalent bonds. The four terminal B-H bonds are normal covalent bonds (two centre - two electron bond or 2c-2e bond).

The remaining four electrons have to be used for the bridged bonds. i.e. two three centred B-H-B bonds utilise two electrons each. Hence, these bonds are three centre- two electron bonds (3c-2e). The bridging hydrogen atoms are in a plane as shown in the figure 2.3. In diborne, the boron is sp^3 hybridised.

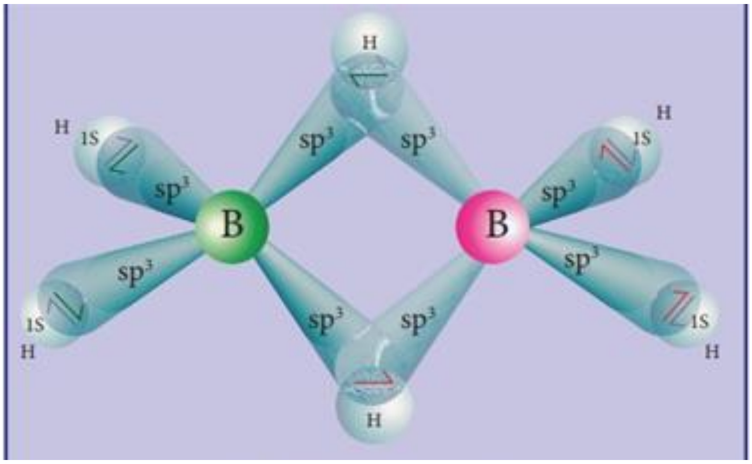


Fig.1. Bonding in diborane

Three of the four sp^3 hybridised orbitals contains single electron and the fourth orbital is empty. Two of the half filled hybridised orbitals of each boron overlap with the two hydrogens to form four terminal 2c-2e bonds, leaving one empty and one half filled hybridised orbitals on each boron. The Three centre - two electron bonds), B-H-B bond formation involves overlapping the half filled hybridised orbital of one boron, the empty hybridised orbital of the other boron and the half filled 1s orbital of hydrogen.

Uses of diborane:

i) Diborane is used as a high energy fuel for propellant
ii) It is used as a reducing agent in organic chemist
iii) It is used in welding torches

2. Borazine:

- Borazine, also known as borazole.
- It is a polar inorganic compound with the chemical formula $B_3H_6N_3$.
- In this cyclic compound, three BH units and three NH units alternate.
- The compound is isoelectronic and isostructural with benzene.
- Borazine has polar hexagonal structure containing 6 membered ring, in which B and N atoms are arranged alternately.

- Because the similarity between the structures of borazine and benzene that borazine is called inorganic benzene.
- In borazine, both Boron and Nitrogen are sp^2 hybridized.
- Each N-atom has an empty p-orbital.
- B-N bond in borazine is dative bond, while arises from the sidewise overlap between the filled p-orbitals of N-atom and empty p-orbitals of B-atom.
- Since borazine is isoelectronic with benzene, both the compounds have aromatic electron cloud.
- Due to greater difference in electronegativity values of B and N - atoms, the electron cloud in B_3N_3 ring of the borazine molecule is partially delocalized. While in the case of benzene ring, the electron cloud is completely delocalized.
- MO calculations have indicated that electron drift from N to B is less than the electron drift from B to N due to the greater electronegativity of the N-atom.
- In benzene molecules, C=C bonds are non-polar, while in case of $B_3H_6N_3$, due to difference in electronegativities between B and N atoms, the B-N bond is polar.
- It is due to the partial delocalization of electron clouds that bonding in the B3N3 ring is weakened.
- N-atoms retain its basicity and B-atoms retain its acidity.
- In borazine, B-N bond length is equal to 1.44 A^o, which is between calculated single B-N bonds (1.54 A^o).
- B=N bond length is 1.36 A^o.
- The angles are equal to 120^o.

Preparation:

$3B_2H_6 + 6NH_3$ —-> $3[BH_2(NH_3)_2][BH_4]$ —heat—> $2B_3N_3H_6 + 12H_2$

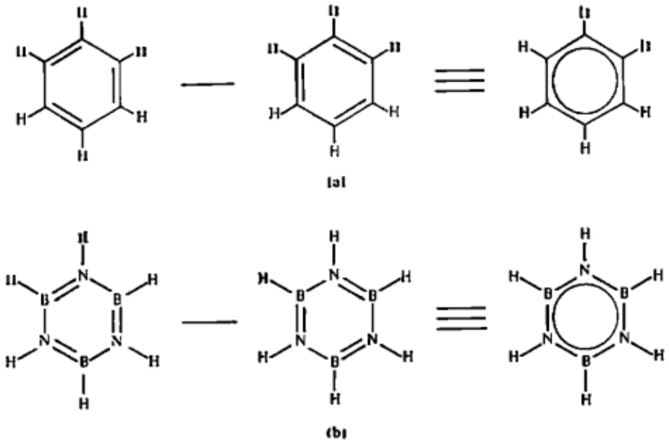
$NH_4Cl + BCl_3$ ——> $Cl_3B_3N_3H_9$ —$NaBH_4$—> $B_3N_3H_6$

$NH_4Cl + NaBH_4$ ——> $B_3N_3H_6 + H_2 + NaCl$

PROPERTIES

- Colorless liquid
- Volatile liquid
- boiling point 84.5 ^0C
- Melting point -58 ^0C
- decomposes at -80 ^0C

Structure:


(a)

(b)

Electronic structures of (a) benzene; (b) borazine.

Chemical properties

$2B_3N_3H_6 + 6HCl \longrightarrow 2Cl_3B_3N_3H_9 \xrightarrow{6NaBH_4} 2B_3N_3H_{12} + 3B_2H_6 + 6NaCl$

USES

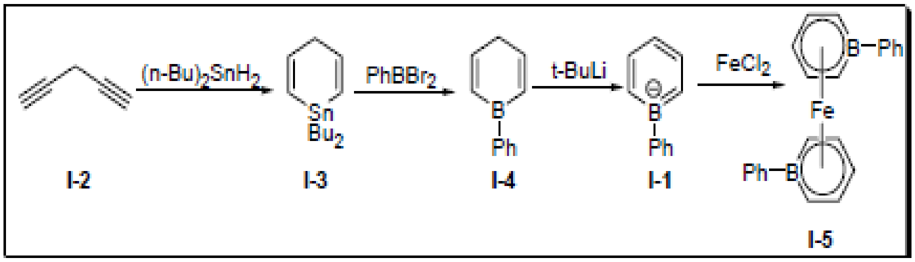
- Borazines are also starting materials for other potential ceramics such as boron carbonides
- Borazine can also be used as precursor to growing boron nitride thin films on surfaces, such as nanomesh structure which is formed on rhodium

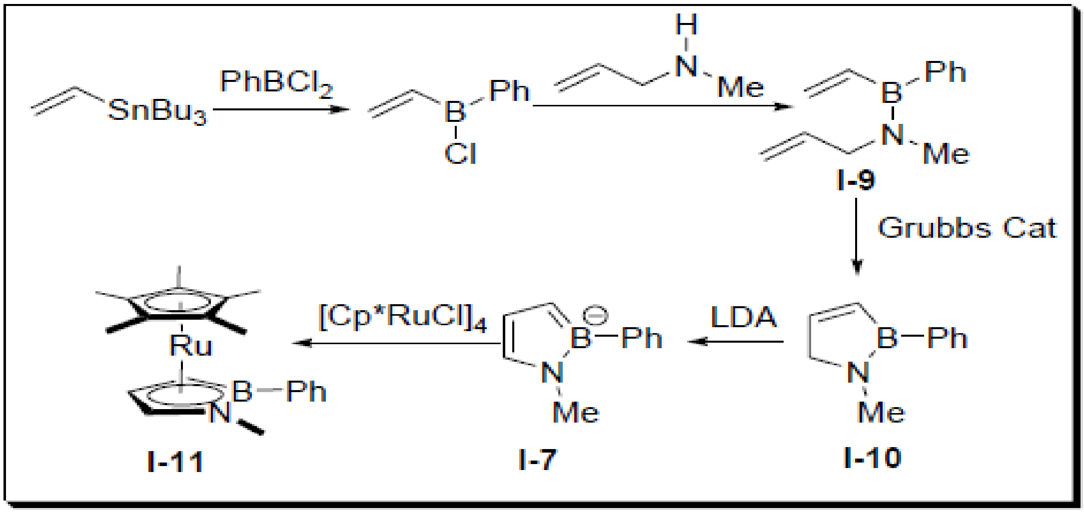
3. BORON HETEROCYCLES

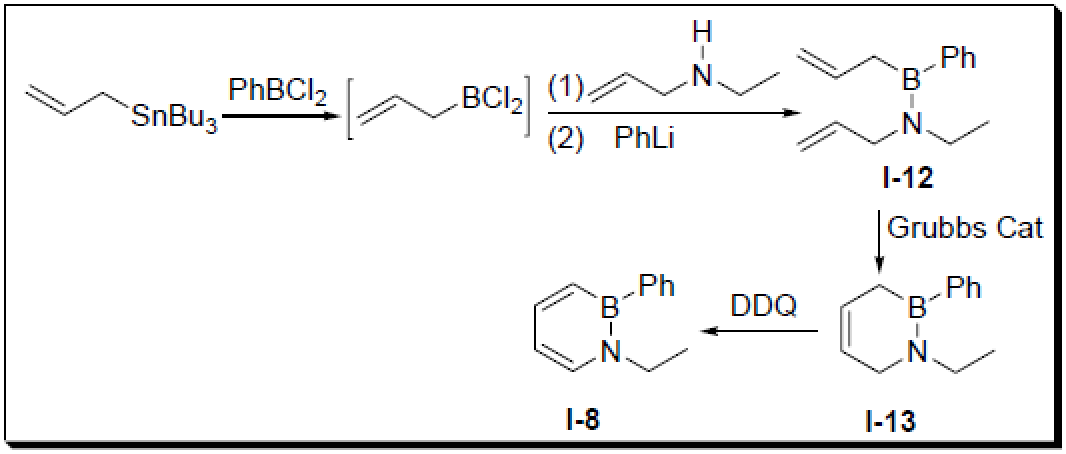
If one or more CH group in Benzene and cyclopentadienyl are replaced by BH group then it is called Boron heterocycles.

PREPARATION

- When stanno-hydration of diethynyl methane with dibutyl tin hydride gives 1,4-dihydro - 1,4-dibutyl stanno benzene . It reacts with renal Boron Bromide to give 1-phenyl-1,4-dihydroxy-bromobenzene.
- When compound is converted to its anion by dipronatio with 3^0-butyl / lithium which on reaction with $FeCl_2$,which gives bis(1-phenyl borate benzene) iron.


(n-Bu)2SnH2
PhBBr2
t-BuLi
FeCl2
Sn
Bu2
B
Ph
B
Ph
B—Ph
Fe
Ph—B
I-2
I-3
I-4
I-1
I-5


SnBu3
PhBCl2
B
Ph
Cl
H
N
Me
B
Ph
N
Me
I-9
Grubbs Cat
LDA
[Cp*RuCl]4
Ru
B—Ph
N
B—Ph
N
Me
B—Ph
N
Me
I-11
I-7
I-10


SnBu3
PhBCl2
BCl2
(1)
H
N
(2) PhLi
B
Ph
N
I-12
Grubbs Cat
DDQ
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B
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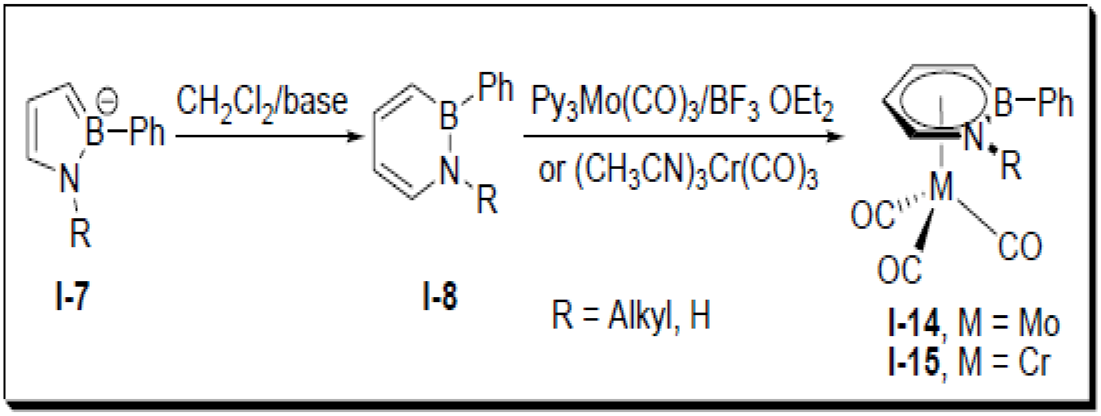
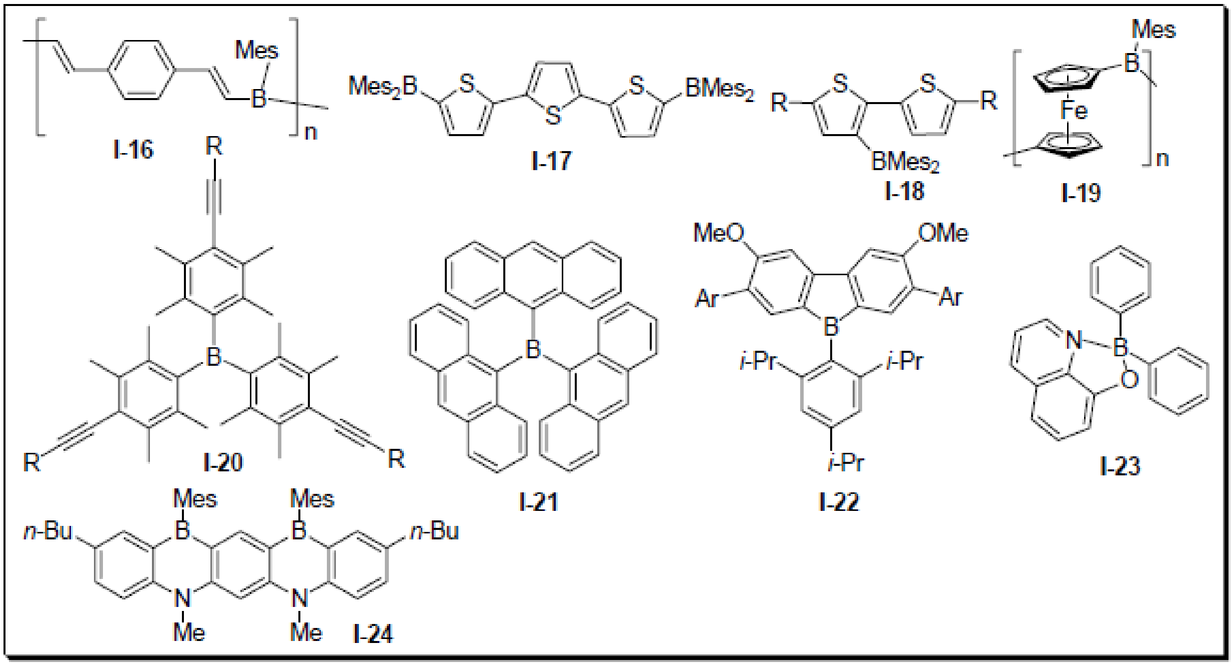
I-8
I-13



- Boron containing π e$^-$ system have recently attracted much attention in research activities.
- 3 coordinate boron is isoelectronic and iso structural with positively carbocation with its vacant Pz orbital.
- Boron is inherently electron deficient with strong e$^-$ acceptor nature allowing conjugation of organic π - systems.
- Hence, it shows unique electronic and physical properties with lewis acid boron forms unique complexes.
- This complex is important for turning the electronic structure of 3 - dimensional molecules.
- Boron takes trigonal planar geometry which can be used as a building block for constructing complex molecules.

DIFFERENT TYPES OF HETEROCYCLES



4. ISOLOBAL ANALOG

Hoffmann developed the concept of isolobal analog to show the connection between an organic or inorganic compound. According to this concept the molecular fragments of a cluster is said to be isolobal when they possess some number of frontier molecular orbital with,

1. Similar shape, Symmetry, Radical extent
2. Approximately same energy
3. Same no of electrons are available for cluster bonding.
4. Isolobal fragments may not be isostructural and isoelectronic.
5. The relationship between isolobal fragments is shown by <r>

FIND OUT THE ISOLOBAL PAIRS FROM THE FOLLOWING

1) Mn$(CO)_5$ →7+10→17
CH_3 →4+3=7 Isolobal

2) Fe$(CO)_4 \rightarrow 8 + 8 \rightarrow 16$
O$\rightarrow 6 \rightarrow 6$ Isolobal

3) CO$(CO)6 \rightarrow 9 + 6 \rightarrow 15$
R_2Si$\rightarrow 2 + 4 \rightarrow 6$ Non Isolobal

4) Mn$(CO)_5 \rightarrow 7 + 10 \rightarrow 17$
Rs$\rightarrow 1 + 6 \rightarrow 7$ Isolobal

5. BORON HALIDES

It is represented as BX_3 where X= F, Cl, Br, I

SYNTHESIS

1.) When B_2O_3 is treated with halogens in presence of carbon, Boron halides are formed.

$$B_2O_3 + 3\ C + 3\ Cl_2 \rightarrow 2\ BCl_3 + 3\ CO$$

2.) It is synthesized by reactions of CaF2 and boric oxide in the presence of H2SO4

$$3\ CaF_2 + B_2O_3 + 3\ H_2SO_4 \rightarrow 2\ BF3 + 3CaSO_4 + 3\ H_2O$$

PROPERTIES

- They are small in size with high charge density.
- They are covalent in nature.
- They act as non- electrolytes in liquid state.

- The boiling point is ranging from 13-300^{0}C and it decreases when the atomic number increases.
- Boron halides are electron deficient because B atom has an incomplete octet structure.
- Boron atom accepts 6 electrons from 3 BX bonds and 2 more electrons from the donor compound.

CHEMICAL PROPERTIES:

i) BCl_3 hydrolyzes readily to give hydrochloric acid and boric acid:

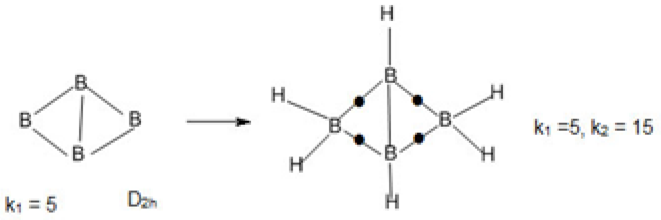
$$BCl_3 + 3\ H_2O \rightarrow B(OH)_3 + 3\ HCl$$

ii) Reduction of BCl_3 to elemental boron is conduct commercially (see below). In the laboratory, when boron trichloride can be converted to diboron tetrachloride by heating with copper metal:[5]

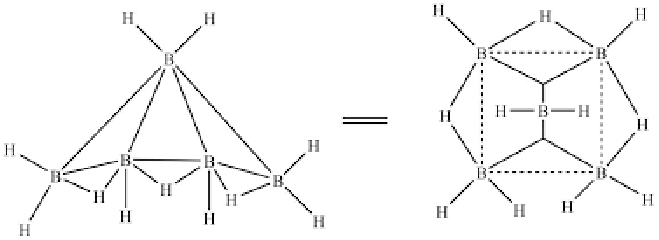
$$2\ BCl_3 + 2\ Cu \rightarrow B_2Cl_4 + 2\ CuCl$$

6. Polyboranes:

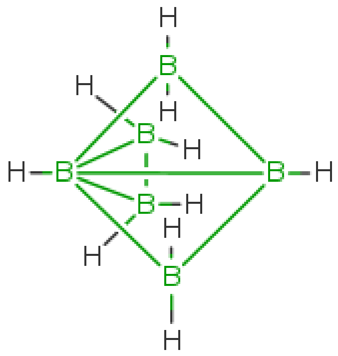
- B_4H_{10}



- B_5H_{11}



- B_6H_{10}



- Wade provided the rule to correlate the no of frame work with e^- with boron, cluster.
- Later, Mingo extended the rule for the transition metal clusters.
- General method for applying wade's rule is as follows
- Determine the total no of the valence electrons from the chemical formula.
- Subtract 2 electrons for each B - H unit.
- Divide the no of remaining electrons by 2 to get the no of skilled electron pairs (SEP)
- A cluster with 'n' vertices and (n+1) SEP for bonding has closo structure.
- A cluster with 'B' atom (n-1) vertices and (n+2) SEP for bonding has Nido structure.
- A cluster with (n-2) vertices (i.e) (n-2) boron atoms and (n+3) SEP for bonding has Arachno structure. (i.e) n-3 Boron atoms with (n+4)

STYX NUMBER OR NOTATION

The overall bonding in boranes can be represented by a 4digit number called Styx number.

s = no.of B-H-B bonds (1st digit)

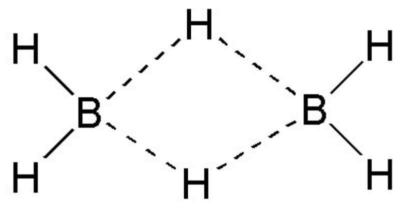
t = no.of B-H-B bonds (2nd digit)

y = no.of B-B bonds (3rd digit)

x = no.of BH_2 group (4th digit)

EXAMPLE

1) B_2H_6(Diborane)



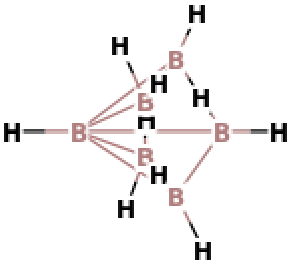
Styx number	Styx Code	Skeletal
s=2	2002	2 x 2 = $4e^-$
t=0		0 x 2 = 0
y=0		0 x 0 = 0
x=2		2 x 2 = $4e^-$
		$8e^-$s

FRAMEWORK ELECTRONS :

The electrons involved in bonding in the formation of Boron cluster in boranes is known as Framework electrons (or) electron

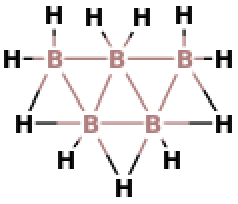
B-H-B	$2e^-$
B-B	$2e^-$
B-B-B	$2e^-$
-BH_2	$2e^-$

3) B_5H_9(Pentaborane 9)



Styx number	Styx Code	Skeletal
s=4(B H B)	4120	9 x 2 = $8e^-$
t=1 (B B B)		1 x 2 = $2e^-$
y=2(B B)		2 x 2 = $8e^-$
x=3(-BH_2)		0 x 2 = 0
		$14e^-s$

4) B_5H_{11}(Pentaborane 11)



Styx number	Styx Code	Skeletal
s=3(B H B)	3203	3 x 2 = $6e^-$
t=2(B B B)		2 x 2 = $4e^-$
y=0(B B)		0 x 2 = 0
x=3(-BH_2)		3 x 2 = $6e^-$
		$16e^-$

WADE’s - MNGO’S RULE :

- This theory provides electrons counting rules to predict the structure of clusters such as boranes & carbones
- In case of transition metal cluster, for each transition metal to additional electrons are subtracted from the total electron count
- This rule is otherwise called as PSEPT theory (Polyhedral skeletal electron pair theory)

$\frac{F}{2} = \frac{Total\ valence\ electrons - 12\ x\ n}{2}$

Eg: $Rh_6(Co)_{16} = \frac{F}{2} = \frac{6\ x\ 9 + 16\ x\ 2 - 12\ x\ 6}{2}$

$= \frac{86 - 72}{2}$

$= 7$

n = 6

n +1 = 7 => closo

$Rh_6(Co)_{16}$ => close (n+1) vertex

References

1.https://www.brainkart.com/article/Diborane_38581/#:~:text=Diborane%20is%20agas%20at%20room,boric%20acid%20and%20metaborates%20respectively.

2. https://edubuzznotes.com/borazine-preparation-properties-structure/

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Chemistry of Main Group Elements

Unit – 2

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Silanes, silicon halides, silicates, germenes and stannenes – Phosphorous halides, oxyacids of phosphorous, phosphazenes – Sulphur halides, oxo acids of sulpur – Structural features and reactivity of reactivity of S-N heterocycles. Interhalogen compounds: Structure and properties of interhalogen compounds [ClF, ICl, ClF3, BrF3, IF3, ClF5, BrF5, IF5] poly halides - pseudohalogens [cyanide,thiocyanate and azide] and Xenon compounds.

1. SILANES:

- It is an inorganic compound with chemical formula, Si H_4.
- It is a colourless, flammable gas with a sharp, repulsive smell.
- It is the silicon analogue of methane.

1.1 PREPARATION:

i) Silane is produced from magnesium silicide and hydrochloric acid:

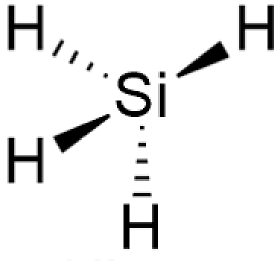
$Mg_2Si + 4\ HCl \rightarrow 2\ MgCl_2 + SiH_4$

ii) It can also be synthesized by the reactions between silicon, hydrogen and silicon tetrachloride:

$Si + 2\ H_2 + 3\ SiCl_4 \rightarrow SiH_4 + SiH_2Cl_2$

iii) A third route includes the reduction of silicon dioxide (SiO_2) in presence of aluminium and hydrogen:

$3\ SiO_2 + 6\ H_2 + 4\ Al \rightarrow 3\ SiH_4 + 2\ Al_2O_3$



Silane

- It has sp^3hybridisation
- The molecular structure of the silanes directly affects their physical and chemical characteristics.
- The Si atoms in silanes are always sp^3 hybridised, that is the valence electrons are said to be in four equivalent orbitals derived from the combination of the 3s orbital and the three 3 p orbitals.
- Three orbitals, which have identical energies and are arranged spatially in the form of a tetrahedron.
- It has 109.5 ° bond angle between the Si - H bonds.

- A silane molecule has only Si- H and Si- Si single bonds.
- Si- H bonds are formed from the overlap of sp^3 orbital of silicon with 1s - orbital of hydrogen.
- Si- Si bonds are formed by the overlap of two sp^3 orbitals on different silicon atoms.
- The bond length is 746.0 pm for a Si- H bond and 233pm for Si- Si bond
- The spatial arrangement of the bonds is similar to that of the four sp^3 orbitals, when they are arranged tetrahedrally with an angle of 109.5 ° between them.

Chemical properties:

i) $SiH_4 + 2O_2 \rightarrow SiO_2 + 2H_2O$

ii) $SiH_4 + O_2 \rightarrow SiO_2 + H_2O$

iii) $2SiH_4 + O_2 \rightarrow 2SiOH_2 + 2H_2$

iv) $SiOH_2 + O_2 \rightarrow SiO_2 + H_2O$

USES

- It is used as coupling agents to adhere glass Fibre to a polymer Matrix for stabilizing the composite material.
- Used to couple a Bio inter layer on a Titanium implant.
- Use as water repellents.

1.2 SILICON HALIDES [Si X_4] [X = Cl, Br, I, F]

SILICON TETRABROMIDE [Si Br_4]

- It is an inorganic compound with the formula Si Br_4
- It is a colourless liquid with suffering odour.
- Undergoes hydrolysis readily with the liberation of HBr
- It resembles closely as Si Cl_4 in all its properties.

Synthesis:

It is synthesized by the reaction of Si with HBr at 6000C.

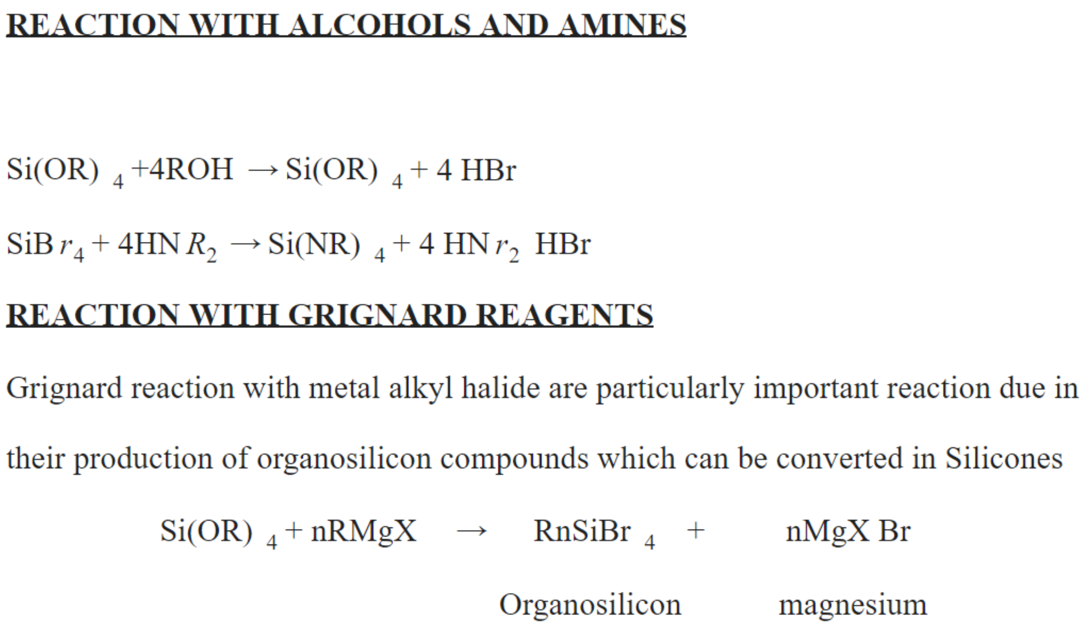
$Si + 4HBr \rightarrow SiBr_4 + 2H_2$

Reactivity:

Reduction:

$SiBr_4$ can be readily reduced by hydrides or complex hydrides.

$4R_2AlH + SiBr_4 \rightarrow SiH_4 + 4R_2AlBr$



REACTION WITH ALCOHOLS AND AMINES

$Si(OR)_4 + 4ROH \rightarrow Si(OR)_4 + 4\ HBr$

$SiBr_4 + 4HNR_2 \rightarrow Si(NR)_4 + 4\ HNr_2\ HBr$

REACTION WITH GRIGNARD REAGENTS

Grignard reaction with metal alkyl halide are particularly important reaction due in their production of organosilicon compounds which can be converted in Silicones

$$\underset{}{Si(OR)_4} + nRMgX \rightarrow \underset{\text{Organosilicon}}{RnSiBr_4} + \underset{\text{magnesium}}{nMgX\ Br}$$

USES

- The pyrolysis of $SiBr_4$ has the advantage of deposition silicon and faster rate.
- Pyrolysis of $SiBr_4$ for followed by treatment with NH_3 yeild Silicon nitride coating a hard compound used for ceramic, scalants and production of many cutting tools.

SiF_4: silicon tetrafluoride:

- It is mainly occur in the volcanic fumes containing significant amount which on hydrolysis forms of hexa fluoro silicic acid

PREPARATION

It is prepared by heating $BaSiF_6$, above 300° C

$BaSiF_6 \rightarrow Si\ F_4 + BaF_2$

Uses

It is used in microelectronics and organic synthesis.

SiI_4: Silicon tetraiodide

$SiH_4 + I_2 \rightarrow SiHI_3$
SiH_2I_2
$SiHI_3 + HI$
SiI_4

Physical properties:

Colourless liquid at room temperature

$SiCl_4$: Silicon tetrachloride

PREPARATION

It is prepared by passing dry Cl_2 over heated amorphous silicon or magnesium silicate (Mg_2Si)

$Si + 2\,Cl_2 \rightarrow SiCl_4$

$Mg_2Si + 4\,Cl_2 \rightarrow SiCl_4 + 2\,MgCl_2$

$2\,SiO_2 + 2C + 2\,Cl_2 \rightarrow SiCl_4 + 2\,CO\uparrow$

It is also prepared by passing a mixture of dry Cl_2 and Si_2Cl_4 on SiO_2

$2\,SiO_2 + 3\,Cl_2 + Si_2Cl_2 \rightarrow 2SiCl_4 + SO_2\uparrow$

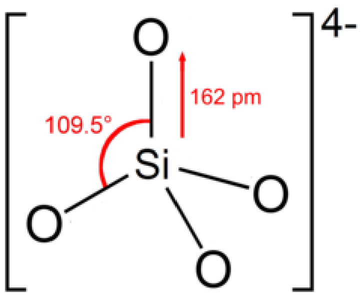
1.3 SILICATES

- They are the largest most interesting and complicated class of minerals than any other minerals.
- Approximately 30% of all minerals are silicates and some geologist estimate that 90% of the earth crust is made up of silicate SiO_4^{4-} base minerals.
- Silicate is based on the basic chemical unit SiO_4^{4-} tetrahedron shaped and anionic group.
- The central Silicon Ion has a charge of positive four which each oxygen has a charge of negative two (-2) and thus Si-O bond is equal to one half the total bond energy of oxygen.
- This condition level the oxygen with the the option of bonding to another silicone ion and therefore linking one SiO_4^{4-} tetrahedron to another.

CLASSIFICATION

- Orthosilicates
- Pyrosilicates
- Ring and chain silicates
- Double chain silicates
- Silicates with sheet structure
- Silicates with 3D fragments

STRUCTURE AND BONDING



- The main structural unit of silicate is Td cluster connecting one silicon and four O atom

- The size of SiO_4^{4-} tetrahedral is relative stable with Si-O Bond length verifying from 0.161 to 0.164nm.
- The strength of Si-O bond is pretty high that provides the thermal stability and chemical resistance of the majority of silicate compound.
- The TetrahedralCluster can be polymerized
  (i.e) linked to each other through the bridging oxygen atoms.
- They are able to form polymers by means of linkage with one, two, three or four neighbouring tetrahedra, forming siloxane, Si - O - Si bonds.
- Other ions can be located in the silicate lattices such as Li^+, Na^+, K^+, $Be2^+$, F^-etc.
- Some cations such as Al, B, Be, are able to isomorphically substitute Si atoms in the Si-O tetrahedral.
- However, most of them are located out of the anionic framework and play the role of “charge balanced cations” and they are all six- coordinates.

Uses

- It is used as thermal insulators.
- Used to make oscillators, used in watches, radios and pressure gages.
- Used to make glass and ceramics.
- Used to form microchips for watches

1.4 SULPHUR - NITROGEN COMPOUNDS

PREPARATION

- $6\ S_2Cl_2 + 16\ NH_3 \rightarrow S_4N_4 + S_8 + 12\ NH_4Cl$

  $4\ NH_4Cl + 6\ S_2Cl_2 \rightarrow S_4N_4 + 16\ HCl + S_8$

- When sulphur reacts with anhydrous liq. NH_3 ,$S_4 N_4$ IS obtain.

  $10s + 4NH_3 \leftrightarrow S_4 N_4 + 6H_2S$

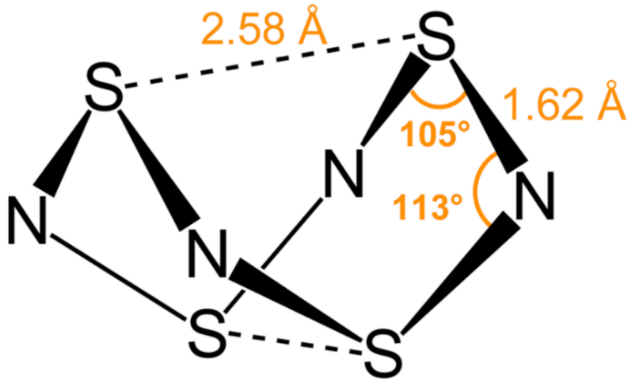
PROPERTIES

- Solid , melting point -178^0 C
- Thermochromic it changes colour with temperature
  At liquid N_2 temp - colourless
  At room temp.orange - yellow
  At 100^{0}C- red
- Crystals are reasonably stable to attack by air, but explosively sensitive to shock and friction.
- $S_4 N_4 + 6NaOH + 3H_2O \rightarrow Na_2 S_2 O_3 + 2Na_2 So_3 + 4NH_3$

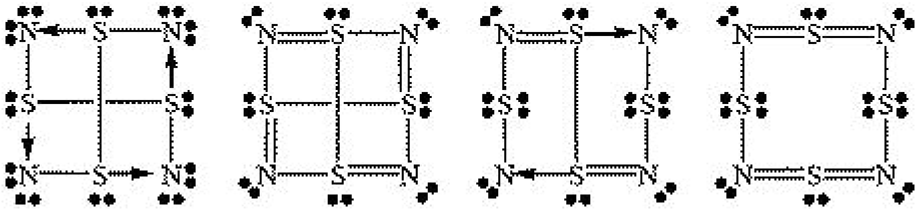
STRUCTURE: Cradle Shaped Structure

1. Average S- N bond length 1.62 Å

2. S-N bond will have partially double bond character
3. All the bonds lengths are equal.
4. Therefore, there is delocalisation.
5. S-S distance is 2.58 Å (weak bonding).



- Its structure is not accounted for by simple classical bonding diagram, several canonical structures are possible.



CHEMICAL PROPERTIES

Reduction

$S_4N_4 \xrightarrow{SnCl_2} S_4N_4H_4$

Oxidation

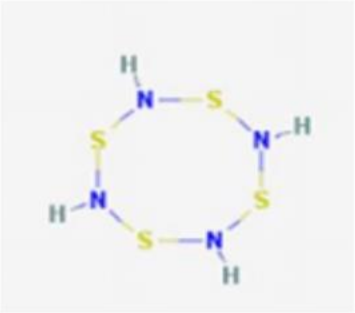
$3S_4N_4 + 6Cl_2 \longrightarrow 4N_3S_3Cl_3$

Fluorination

$S_4N_4 + 2F_2 \longrightarrow S_4N_4F_4$

Hydrogenation

$$S_4N_4 + 2H_2 \rightarrow S_4N_4H_4$$



2-Disulfur dinitride (S_2N_2)

Disulfur dinitride is the chemical compound S_2N_2 with a cyclic square planar structure.

Passing gaseous S_4N_4 over silver metal wool at 250–300 °C at low pressure (1mm Hg) yields cyclic S_2N_2 The silver reacts with the sulfur produced by the thermal decomposition of the S_4N_4 to form Ag_2S, and the resulting Ag_2S catalyzes the conversion of the remaining S_4N_4 into the fourmembered S_2N_2 ring

$$S_4N_4 + 8\,Ag \rightarrow 4\,Ag_2S + 2\,N_2$$

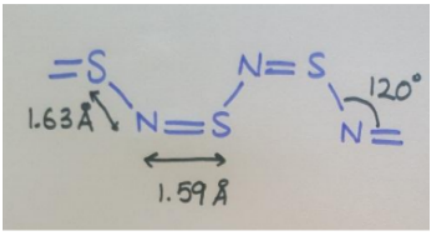
$$S_4N_4 \rightarrow 2S_2N_2$$

PROPERTIES:

- Colourless and Crystalline in nature.
- It has square structure.

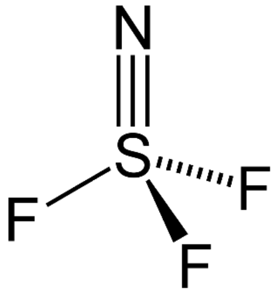
3. POLYTHIAZOLE $(SN)_x$

- Prepared by polymerization of S_2N_2
- Golden brown solid with metallic lustre .
- Zig -Zag planar structure .
- Highly conductive at room temperature .



- Super conductors at 0.26K.
- Delocalization of π electrons takes place .
- Conduction band is formed by overlapping of πAorbital .
- Unpaired electrons on sulphur atom will have half fill bond. Also called as one- dimensional metal.

NSF_3-Thiazyltrifluoride



1.5 GERMENES AND STANNENES

Ge - 32 (p- block)

Electronic configuration : (Ar) $3d^{10} 4s^2 4p^2$

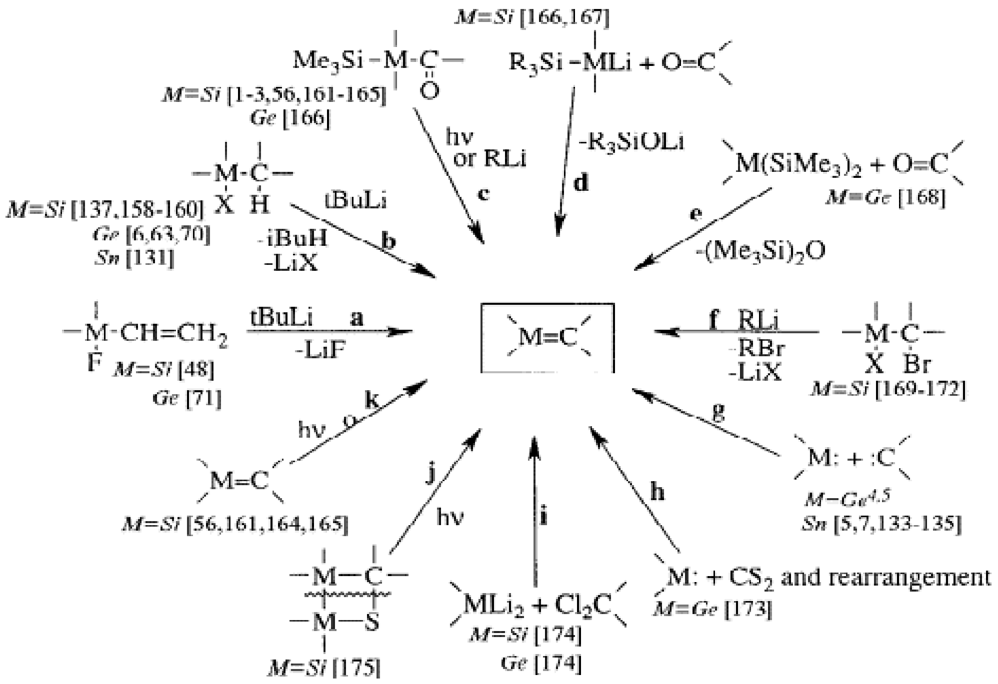
SYNTHESIS

- Fluorodimesitylvinyl germene was prepared in one step from vinyl magnesium bromide and difluoro dimesityl germane.

$$MeS_2\,Ge\,F_2 + CH_2 = CH - MgBr \xrightarrow{THF} Me\,S_2\,\mathit{Ge}\,(\mathit{F})_2\,CH{=}CH_2$$

$$\xrightarrow[Et_2 / -78\ ^0C]{BuLi} MeS_2\,Ge\,(F)\,CH(Li)\,CH2\ .\ t.Bu \xrightarrow[-LiF]{-50\ ^0C} MeS_2\,Ge = CH\,CH_2 + Bu$$

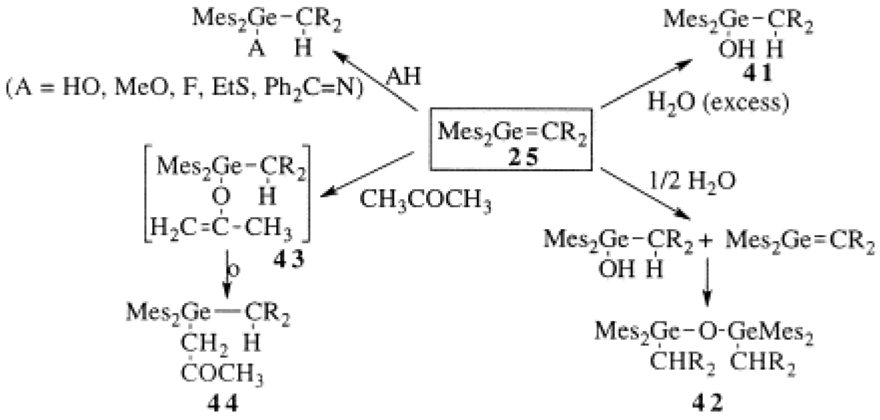
Subsequent addition to compound 1 of a molar equivalent of tert- butyl lithium at -78^0 C gave the - lithiorgermane (2), the elimination of lithium fluoride occurred at -50^0 C with nearly quantitative formation of dimesityl tertiary butyl germene(3)

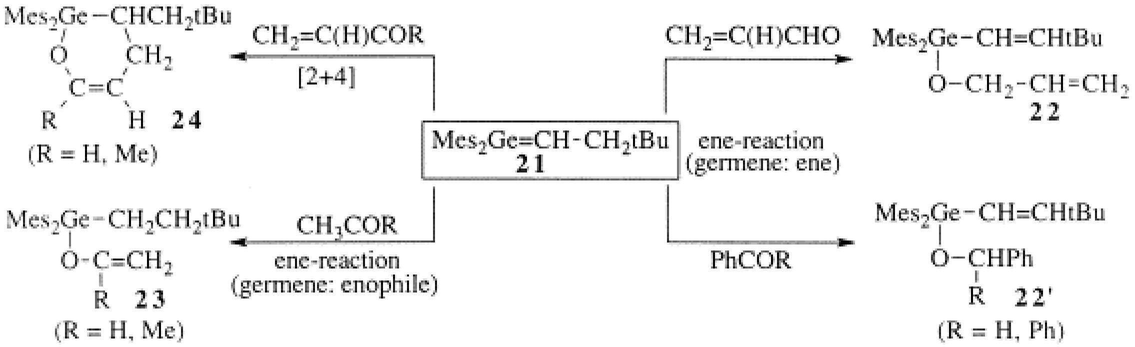


PROPERTIES

- Good thermal stability
- Highly reactive, particularly towards electrophilic or nucleophilic reagents

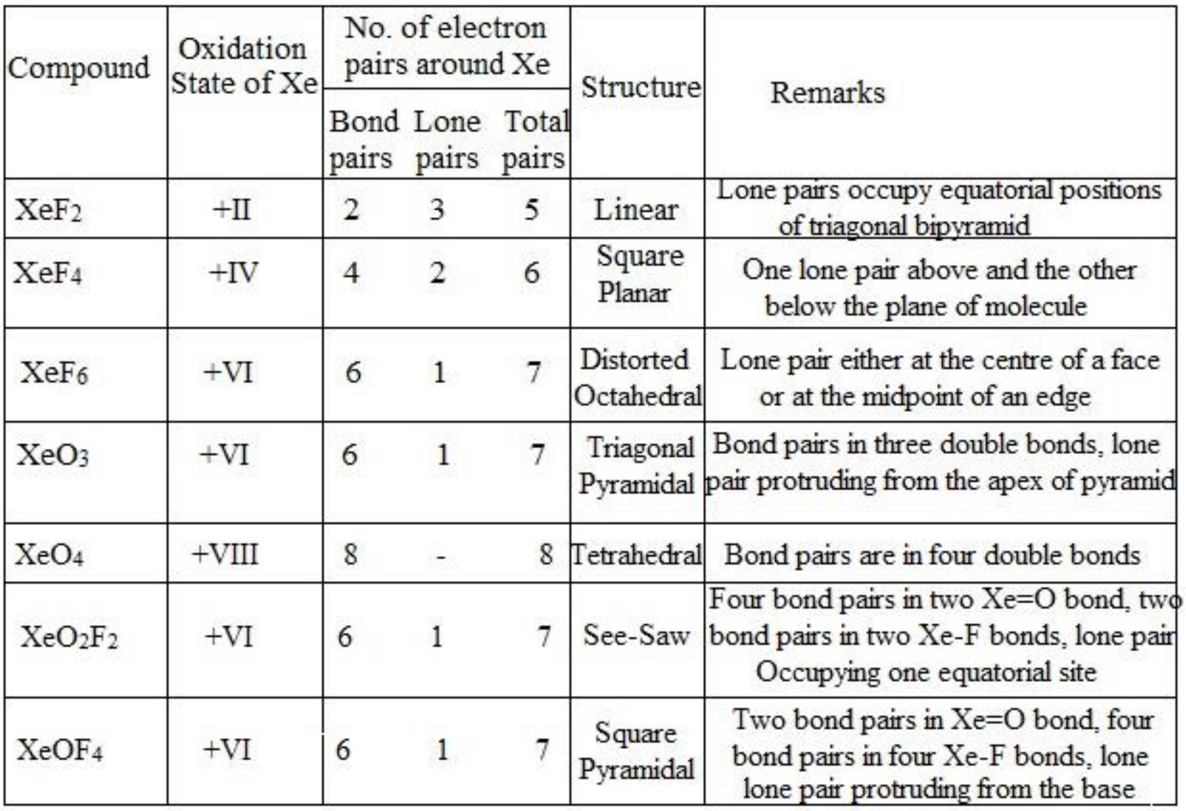
REACTIVITY





1.6 Xenon Compounds:

ELEMENT	**OUTER CONFIGURATION**	**FIRST IONISATION ENTHALPY** (K J mol-1)	**NORMAL BOILING POINT** (K)	**VOLUME IN PERCENTAGE IN ATOM** (x 104)
He^{2}	$1\ s^{2}$	2369	4.2	5.2
Ne^{10}	$2\ s^{2}2\ p^{6}$	2078	27.1	18.2
Ar^{18}	$3\ s^{2}$ 3 p6	1519	87.3	9340.0
Kr^{36}	$4\ s^{2}\ 4\ p^{6}$	1349	120.3	11.4
Xe^{54}	$5\ s^{2}\ 5\ p^{6}$	1169	166.1	0.08
Rn^{86}	$6\ s^{2}\ 6\ p^{6}$	1036	208.2	-



Compound	Oxidation State of Xe	No. of electron pairs around Xe			Structure	Remarks
		Bond pairs	Lone pairs	Total pairs		
XeF_2	+II	2	3	5	Linear	Lone pairs occupy equatorial positions of triagonal bipyramid
XeF_4	+IV	4	2	6	Square Planar	One lone pair above and the other below the plane of molecule
XeF_6	+VI	6	1	7	Distorted Octahedral	Lone pair either at the centre of a face or at the midpoint of an edge
XeO_3	+VI	6	1	7	Triagonal Pyramidal	Bond pairs in three double bonds, lone pair protruding from the apex of pyramid
XeO_4	+VIII	8	-	8	Tetrahedral	Bond pairs are in four double bonds
XeO_2F_2	+VI	6	1	7	See-Saw	Four bond pairs in two Xe=O bond, two bond pairs in two Xe-F bonds, lone pair Occupying one equatorial site
$XeOF_4$	+VI	6	1	7	Square Pyramidal	Two bond pairs in Xe=O bond, four bond pairs in four Xe-F bonds, lone lone pair protruding from the base

Xenon Compounds

1- XeF_2 - Xenon Difuoride

Preparation

(i) $Xe + F_2 \xrightarrow[200\ ^0C]{Ni} XeF_2$

(ii) $Xe + O_2\ F_2 \longrightarrow XeF_2 + O_2$

PROPERTIES

(i) Colourless, crystalline solid

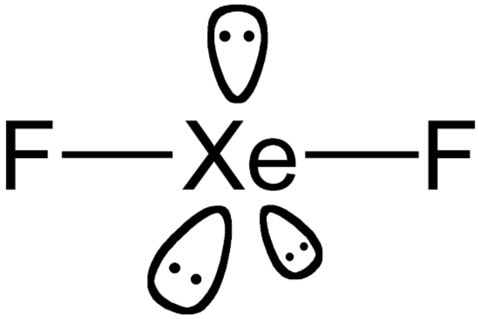
(ii) It reacts with H_2 to give xenon and hydrogen fluoride

$$XeF_2 + H_2 \rightarrow Xe + 2HF$$

(iii) It reacts with water evolving oxygen

$$2\,XeF_2 + 2\,H_2O \rightarrow 2\,Xe + 4HF + O_2$$

STRUCTURE



- 3 lone pair of electrons are present
- Spectroscopy analysis has shown that, XeF_2molecule has linear geometry.
- This is explained by VSEPR theory
- sp^3d hybridisation.

2) Xe F_4 - Xenon Tetraflouride:

Preparation

$$Xe + 2F_2 \xrightarrow[\text{5-6 atm}]{\text{400 °C}} XeF_4$$

Properties

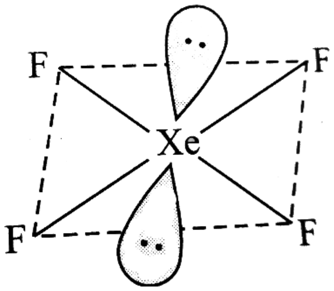
- It is a colourless, crystalline solid
- It dissolves in hydrogen fluoride with out any reaction.
- It reduced by hydrogen at 117°C to give Xe.

  $XeF_4 + 2H_2 \rightarrow Xe + 4HF$

  It reacts with borontrichloride to form boron triflouride

  $2XeF_4 + 4BCl_3 \rightarrow 3Xe + 4BF_3 + 6Cl_2$

STRUCTURE



- 2 lone pair of electrons are present
- Spectroscopy analysis has shown that, XeF_4 molecule has square planar geometry.
- This is explained by VSEPR theory
- sp^3d^2 hybridisation.

3- $XeOF_4$: Xenon oxytetrafluoride

PREPARATION

$$XeF_6 + H_2O \rightarrow XeOF_4 + 2HF$$

PROPERTIES

(i) Colourless compound

(ii) Melting point -4 6^0c

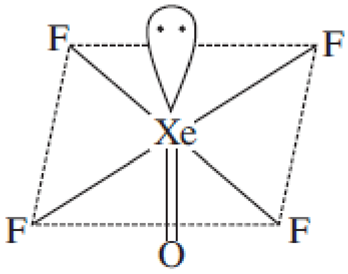
(iii) $XeOF_4 + 3H_2O \rightarrow Xe + H_2O + 4HF$

(iv) $XeOF_4 + H_2O \rightarrow XeOF_2 + 2HF$

Xenon Dioxide fluoride

(v) $2XeOF_4 + SiO2 \rightarrow 2XeO_2F_2 + SiF_4$

STRUCTURE



Square pyramidal

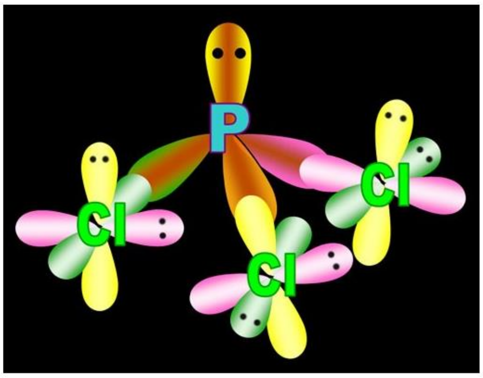
- it has one lone pair of electrons
- it has square planar structure
- SP^2d^2Hybridization
- this is explained by VSEPR theory

1.7 PHOSPHORUS HALIDES

A phosphorus halide is a compound that a phosphorus forms with a halogen. A phosphorus halide is of two types. They are PX_3 and PX_5. Here, we refer X to a halogen. It could be anything from fluorine, chlorine, bromine or iodine. However, the most common phosphorus halide is that of chloride. These chlorides are usually covalent in their nature.

1.7.1 Phosphorus Trichloride PCl_3:

- This is an oily and sleek fluid.
- It is very lethal in nature.
- The shape of this compound is that of a triangular pyramid.
- The atom of phosphorus exhibits sp3hybridization.



- As we can see in the above diagram, phosphorus has its sp3orbitals. It has only one electron and it gives that electron to a p orbital electron from 3 chlorine atoms. The fourth sp3
- Orbital is full. It is a solitary lone pair. Thus, it cannot form a bond. However, it repels alternate bonds. This creates a state of the shape of trigonal pyramidal.

Preparation:

We obtain phosphorus trichloride by passing dry chlorine over heated white phosphorus. The reaction that takes place is as follows:

$$P_4 + 6Cl_2 \rightarrow 4PCl_3$$

We can also obtain this compound by the reaction of thionyl chloride with white phosphorus. Below is the reaction to it.

$$P + 8SOCl_2\ 4SO_2 + 2S_2Cl_2$$

Chemical Properties:

Phosphorus trichloride hydrolysis when we dampen it.

$$PCl_3 + 3H_2O \rightarrow H_3PO_3 + 3HCL$$

It reacts with natural compounds having a –OH group and gives their 'chloro' subsidiaries as products.

Structure of PCl_3:

The phosphorus particle in the centre of PCl_3 exhibits sp3 hybridisation. It has 3 bond sets and 1 lone pair of electrons. Due to this reason, it has a pyramidal shape. It acts as a Lewis base because it has the capacity to donate its lone pair of electrons to other electron-lacking particles or atoms.

1.7.2 Phosphorus Pentachloride PCl_5:

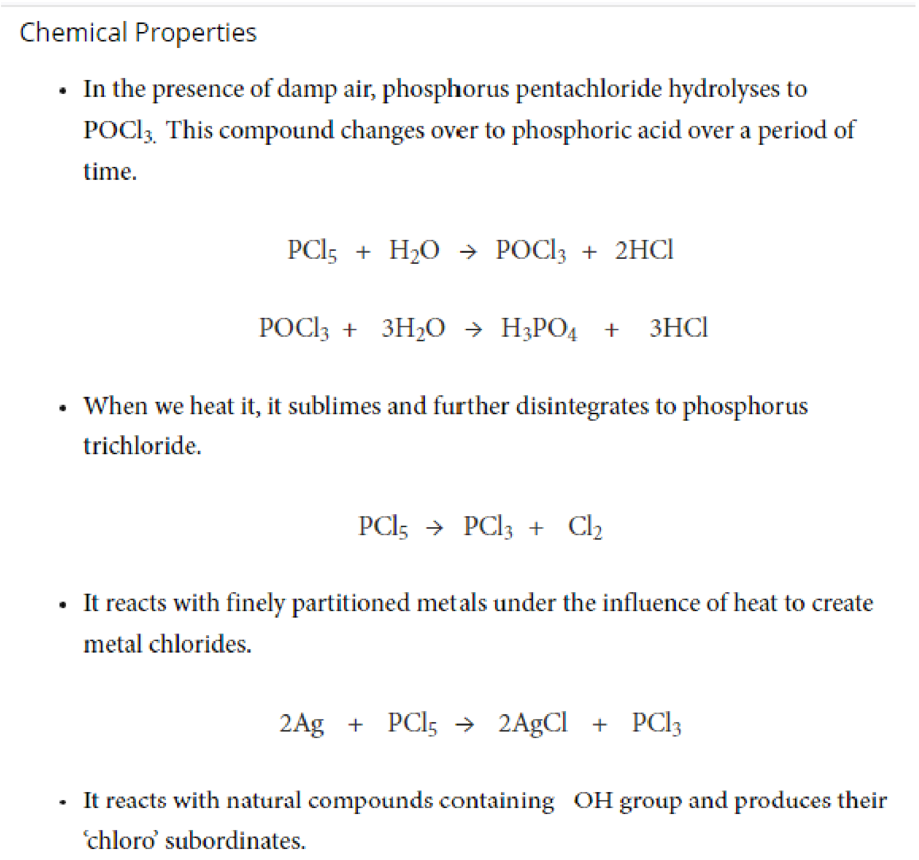
It is yellowish-white in colour. Phosphorus Pentachloride is a very water delicate solid. It dissolves in organic solvents like carbon tetrachloride, benzene, carbon disulphide, diethyl ether. Its structure is that of a trigonal bi-pyramid. We find this structure primarily in vaporous and fluid stages. In the solid state, we can find it as an ionic solid, $[PCl4]^+[PCl6]^-$. Here, the cation, $[PCl4]^+$ is tetrahedral and the anion, $[PCl6]^-$ is octahedral. We must know that the molecule has three tropical P-Cl bonds and two pivotal P-Cl bonds. Due to the more prominent repulsion at hub positions as compared to the central positions, we see that the two axial bonds are longer than tropical bonds.

Preparation:

i)We can produce pentachloride by the reaction with an excess of dry chlorine.

$$P_4 + 10Cl_3 \rightarrow 4PCl_5$$

ii) We can also produce it by the reaction of SO_2Cl_2 and phosphorus.



Chemical Properties

- In the presence of damp air, phosphorus pentachloride hydrolyses to $POCl_3$. This compound changes over to phosphoric acid over a period of time.

$$PCl_5 + H_2O \rightarrow POCl_3 + 2HCl$$

$$POCl_3 + 3H_2O \rightarrow H_3PO_4 + 3HCl$$

- When we heat it, it sublimes and further disintegrates to phosphorus trichloride.

$$PCl_5 \rightarrow PCl_3 + Cl_2$$

- It reacts with finely partitioned metals under the influence of heat to create metal chlorides.

$$2Ag + PCl_5 \rightarrow 2AgCl + PCl_3$$

- It reacts with natural compounds containing OH group and produces their 'chloro' subordinates.

$$P_4 + 10SO_2Cl_2 \rightarrow 4PCl_5 + 10SO_2$$

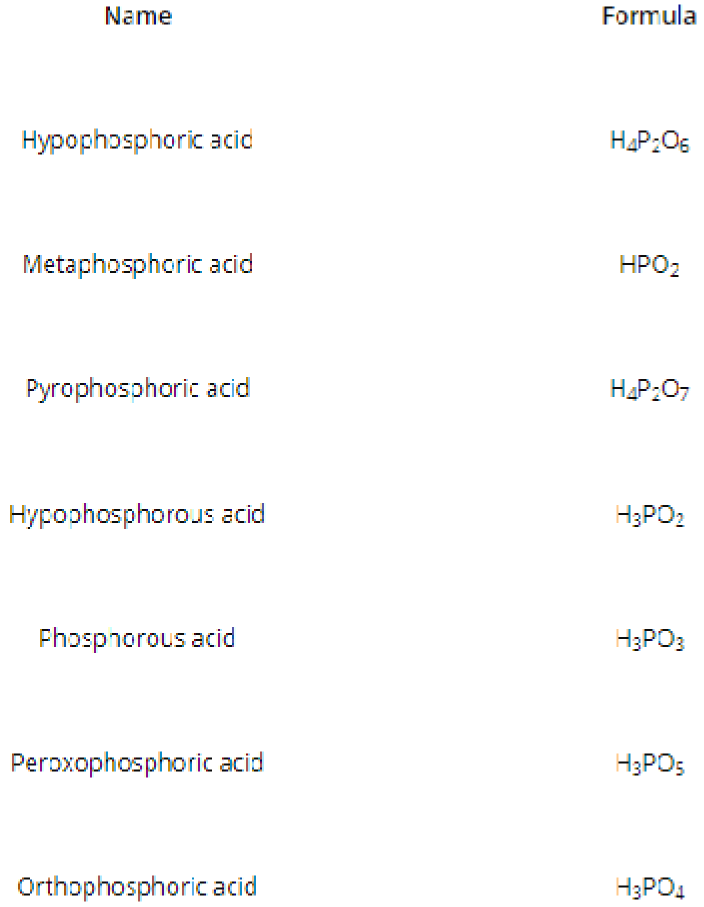
Structure of PCl_5

As we discussed earlier, the central phosphorus atom in phosphorus pentachloride experiences SP^3d hybridisation. All the five electrons combine in these hybrid orbitals as bond sets. The molecular shape of the particle is trigonal bipyramidal.

After the five electrons get hybridised, we get five electrons of equivalent size and shape. Three of them frame a triangle (120° partition) in the centre. One bond is above and one is underneath those three.

1.8 Oxoacids of Phosphorus

Few Popular Oxoacids of Phosphorus
In this section, we will look at some of the most important and popular oxoacids of phosphorus.

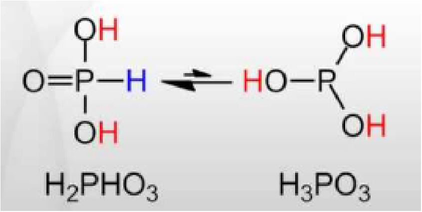


Name	Formula
Hypophosphoric acid	$H_4P_2O_6$
Metaphosphoric acid	HPO_3
Pyrophosphoric acid	$H_4P_2O_7$
Hypophosphorous acid	H_3PO_2
Phosphorous acid	H_3PO_3
Peroxophosphoric acid	H_3PO_5
Orthophosphoric acid	H_3PO_4

1) Phosphorus acid, H_3PO_3

Phosphorous acid is a diprotic acid. This means that it ionizes two protons. We can describe it in a better manner by the structural formula $HPO(OH)_2$. We can prepare phosphorous acid by the hydrolysis of phosphorus trichloride with acid or steam.

$$PCl3 + 3H_2O \rightarrow HPO(OH)_2 + 3HCl$$



2) Phosphoric acid, H_3PO_4

Phosphoric acid is a triprotic acid. This means that it can ionise three protons. It is a non-toxic acid, when pure. It is solid at the room temperature and pressure. We can prepare phosphoric acid by adding sulfuric acid to tricalcium phosphate rock:

$$Ca_5(PO_4)_3X \quad + \quad 5H_2SO_4 \quad + \quad 10H_2O \rightarrow 3H_3PO_4 \quad + \quad 5CaSO_4.2H_2O \quad + \quad HX$$

(X can be F, Cl, Br, and OH).

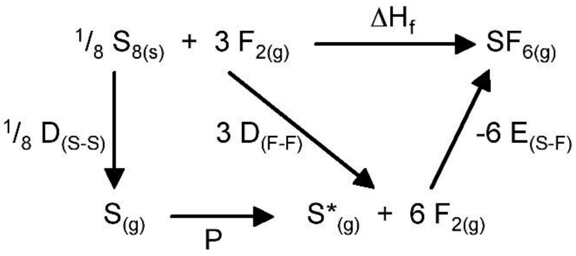
1.9 Sulfur Halides:

1.9.1 Sulfur hexafluoride:

Sulfur hexafluoride (SF_6) is a gas at standard temperature and pressure (25 °C, 1 atm). The most common synthesis involves the direct reaction of sulfur with fluorine yields SF_6.

$$S + 3\,F_2 \rightarrow SF_6$$

It should be noted that while SF_6 is highly stable, SCl_6 is not formed. The explanation of this difference may be explained by a consideration of the Born-Haber cycle shown in Figure. A similar cycle may be calculated for SCl_6; however, a combination of a higher dissociation energy for Cl_2 and a lower S-Cl bond energy (Table) provide the rational for why SCl_6 is not formed.



Born-Haber cycle for the formation (ΔH_f) of SF_6: where $D_{(X-Y)}$ = dissociation energy for X-Y bond, $E_{(S-F)}$ = S-F bond energy, and S* indicates 6 coordinate sulfur.

Comparison of diatomic bond dissociation and S-X bond energy for the fluorine and chlorine analogs.

Bond dissociation energy	**kJ/mol**	**Bond energy**
$D_{(F-F)}$	158	$E_{(S-F)}$
$D_{(Cl-Cl)}$	262	$E_{(S-Cl)}$

The S-F bond length (1.56 Å) is very short and consistent with π-bonding in addition to σ-bonding. Like SiF_6^{2-}, SF_6 is an example of a hypervalent molecule.

Molecular orbital bonding in SF_6.

Sulfur hexafluoride is an unreactive, non-toxic compound. Its inert nature provides one of its applications, as a spark suppressor. The hexafluoride is generally resistant to chemical attack, e.g., no reaction is observed with potassium hydroxide (KOH) at 500 °C. The low reactivity is due to SF_6 being kinetically inert due to:

- Coordination saturation precluding associative reactions with nucleophiles.
- Strong S-F bond (360 kJ/mol) limiting dissociative reactions.

Thermodynamically SF_6 should react with water ($\Delta H = -460$ kJ/mol), but the rate factors are too great. Sulfur hexafluoride can be reduced with sodium in liquid ammonia, Equation, or with $LiAlH_4$. In each of these reactions the mechanism involves the formation of a radical, Equation. The reaction with sulfur trioxide yields SO_2F_2, Equation, however, the reactions with carbon or CS_2 only occur at elevated temperatures (500 °C) and pressure (4000 atm).

$$SF_6 + 8\,Na \rightarrow Na_2S + 6\,NaF$$

$$SF_6 + e^- \rightarrow SF_6^{\cdot -}$$

$$SF_6 + 2\,SO_3 \xrightarrow{250\ ^\circ C} 3\,SO_2F_2$$

2. INTERHALOGEN COMPOUND

- An interhalogen compound is a molecule which contains two or more different halogen atoms
- (fluorine, chlorine, bromine, iodine, or astatine) and no atoms of elements from any other group.
- Most interhalogen compounds known are binary (composed of only two distinct elements)
- The common interhalogen compounds include Chlorine monofluoride, bromine
- trifluoride, iodine pentafluoride, iodine
- heptafluoride, etc

Interhalogen compounds into four types, depending on the number of atoms in the particle. They are as follows:
XY
XY3
XY5
XY7

X is the bigger (or) less electronegative halogen.
Y represents the smaller (or) more electronegative halogen.

All are of the type XX'n where n = odd nos. X' is
always the lighter halogen
since the smaller halogen X' are bonded around the larger X. As the
ratio of the radius of X to that of X' increases, n also increases

Properties of Interhalogen Compounds

- A lot of these compounds are unstable solids or fluids at 298K. A few other compounds are gases as well. As an example, chlorine monofluoride is a gas. On the other hand, bromine trifluoride and iodine trifluoride are solid and liquid respectively.
- These compounds are covalent in nature.
- These interhalogen compounds are diamagnetic in nature. This is because they have bond pairs and lone pairs
- Interhalogen compounds are very reactive. One exception to this is fluorine. This is because the A-X bond in interhalogens is much weaker than the X-X bond in halogens, except for the F-F bond.

2.1 Pseudohalogens:

Compounds that resemble the halogen elements, X_2, in their chemistry.

E.g. $(CN)_2$ cyanogen, $(SCN)_2$ thiocyanogen, ICN iodine cyanide.

Certain ions that have sufficient resemblance to halide ions are sometimes referred to as pseudohalide ions.

E.g. N^{3-}, SCN^{-}, CN^{-}.

It is formed by the combination of two or more P block elements with a negative charge CN- cyanide group a combination of carbon and nitrogen with uni-negative charge. They are called pseudohalogens as they form covalent compounds, complexes similar to the halogens. They differ from halogens as they are able to polymerize unlike halogens and their complexes are not paramagnetic.

The anions $CN^{–}$, $CNO^{–}$, $N^{3–}$, $OCN^{–}$, and $SCN^{–}$ can be coined classical linear pseudohalides. A small species can be classified as a classical pseudohalogen when it fulfills the following criteria with respect to a halogen-like chemical behaviour: A pseudohalogen (X) forms

- a strongly bound (linear) univalent radical (X×),
- a singly charged anion ($X^{–}$),
- a pseudohalogenhydrogen acid of the type HX,
- salts of the type M(X)n with silver, lead and mercuric salts of low solubility,
- a neutral dipseudohalogen compound (X–X) which disproportionates in water and can be added to double bonds, and
- interpseudohalogen species (X–Y).

While many linear pseudohalogens (e.g. CN, OCN, CNO, N_3, SCN) are known, often the corresponding pseudohalide acids, dipseudohalogens, and interpseudohalogens are thermodynamically highly unstable (e.g. HN_3, OCN–NCO, NC–SCN) with respect to N_2/CO elimination or polymerisation or indeed, remain unknown (e.g. N_3–N_3).

PROPERTIES OF PSEUDOHALOGENS

- These are volatile.
- Pseudohalogens, like the halogens, add at ethylenic double bond linkage.
- Pseudohalogens , like the halogens, react with alkalies.
- Pseudohalogens form covalent pseudohalides.

Eg : Thiocyanogen $(SCN)_2$

PREPARATION:

It is prepared by $Pb(SCN)_2$ with Br_2 in the real solution at 0 ◦C.

$Pb(SCN)_2 + Br_2 \rightarrow (SCN)_2 + Pb\,Br_2$

PROPERTIES:

- It is yellow solid
- Insoluble in water.
- It oxidises Cu(I) salts to Cu(II) salts.
- Sulphur is precipitated from H_2S.

USES OF PSEUDOHALOGEN COMPOUNDS

- Used as an oxidising agent.
- Used for the determination of unsaturation in organic compound.

https://www.schulz.chemie.uni-rostock.de/forschung/halogenpseudohalogen-chemistry/

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Chemistry of Main Group Elements

UNIT 3

ORGANO METALLIC REAGENTS AND MACROCYCLES

Synthesis and reactivity of organo-lithium, beryllium and magnesium compounds. Macrocyclic Ligands: Calixarines, cryptands and crown ethers-structure and applications in complexation chemistry.

1. Organolithium Reagents:

Organolithium reagents are organometallic compounds that contain carbon – lithium bonds. These reagents are important in organic synthesis, and are frequently used to transfer the organic group or the lithium atom to the substrates in synthetic steps, through nucleophilic addition or simple deprotonation.

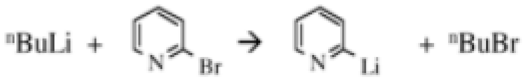
Synthesis:

The best general method for RLi synthesis involves the reaction of an alkyl or aryl chloride with lithium metal in benzene or an aliphatic hydrocarbon (e.g., hexane)

$$RCl + 2\,Li \rightarrow RLi + LiCl$$

Metal-hydrogen exchange reactions

$$RH + R'Li \rightarrow R'H + RLi$$



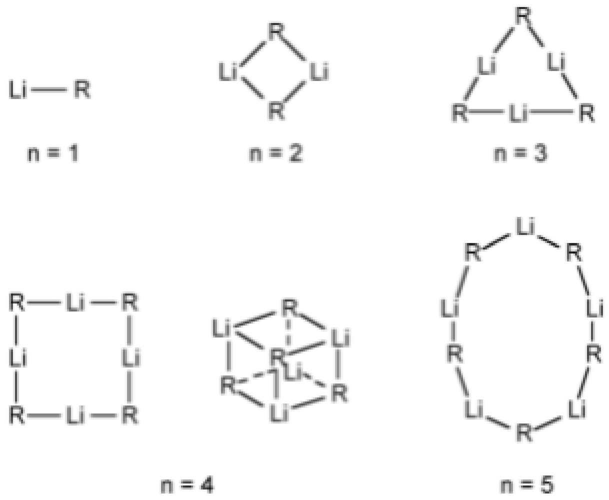
$$2\,Li + R_2Hg \rightarrow 2\,RLi + Hg$$

Properties:

- Alkyl lithium compounds are either low melting solids or liquids, with high volatility (depending on the substituent) due to the covalent nature of the bonding.
- They are soluble in aliphatics, aromatics, and ethers.
- Organolithium compounds react rapidly with air and water (both vapor and liquid).

Structure:

The structure of organolithium compounds is dominated by their highly oligomeric nature as a result of 3-center 2-electron bridging bonds. In all cases the extent of oligomerization is dependant on the identity of the alkyl (or aryl) group. The alkyl-bridged bond is similar to those found for beryllium and aluminum compounds. In the vapor phase any particular organolithium derivative show a range of oligomeric structures. For example, the mass spectrum of EtLi shows ions associated with both tetramers (e.g., $[Et_3Li_4]^+$) and hexamers (e.g., $[Et_5Li_6]^+$). The structures of the different oligomers have been predicted by molecular orbital calculations



Chemical Properties:

Hydrolysis:

Organolithium compounds react with water to give the hydrocarbon and lithium hydroxide. Lithium alkyls also react with other hydroxylic compounds such as alcohols and carboxylic acids.

$$CH_3Li + H_2O \rightarrow CH_4 + LiOH$$

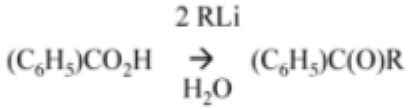
$$CH_3Li + HOR \rightarrow CH_4 + LiOR$$

Reaction with carbonyls:

Organolithium compounds react with organic carbonyls (aldehydes, ketones, and esters) to yield the alcohol on hydrolysis. This synthetic route is particularly useful since lithium reagents are far more reactive than the analogous Grignard, allowing reactions to be carried out at lower temperatures and minimizing enolization side reactions.

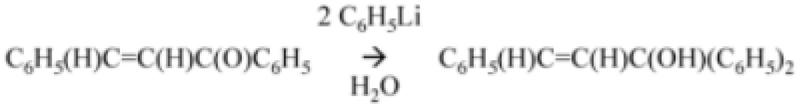
$$MeLi + (^tBu)_2C{=}O \rightarrow (^tBu)_2MeCOLi \xrightarrow{H_2O} (^tBu)_2MeCOH + LiOH$$

The high reactivity of alkyl lithium compounds means that they react with carboxylic acids to yield the ketone rather than the lithium carboxylate.



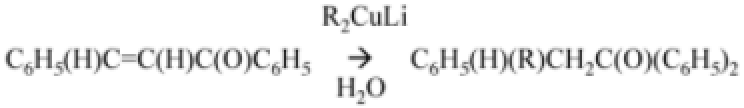
$$(C_6H_5)CO_2H \xrightarrow[H_2O]{2\ RLi} (C_6H_5)C(O)R$$

Organolithium compounds generally react with α,β-unsaturated ketones to give the 1,2-addition product. However, lithium dialkylcuprates, which are formed from the alkyl lithium and copper(I) iodide, add exclusively by the 1,4-addition.



$$C_6H_5(H)C{=}C(H)C(O)C_6H_5 \xrightarrow[H_2O]{2\ C_6H_5Li} C_6H_5(H)C{=}C(H)C(OH)(C_6H_5)_2$$

$$2\ RLi + CuI \rightarrow R_2CuLi + LiI$$



$$C_6H_5(H)C{=}C(H)C(O)C_6H_5 \xrightarrow[H_2O]{R_2CuLi} C_6H_5(H)(R)CH_2C(O)(C_6H_5)_2$$

Transmetallation:

One of the most useful methods of preparing organometallic compounds is the exchange reaction of one organometallic compound with a salt of a different metal, Equation. This is an equilibrium process, whose equilibrium constant is defined by the reduction potential of both metals. In general the reaction will proceed so that the more electropositive metal will form the more ionic salt (usually chloride).

$$RM + M'X \rightleftharpoons RM' + MX$$

Lithium reagents may be used to prepare a wide range of organometallic compounds.

$$4\ n\text{-}C_4H_9Li + SnCl_4 \rightarrow Sn(C_4H_9)_4 + 4\ LiCl$$

2. Grignard Reagent: RMgX

Organomagnesium compounds are less reactive than the corresponding organolithium ones because, due to the higher electronegativity of magnesium compared to lithium, the carbon–magnesium bond is less polarized than the carbon–lithium one.

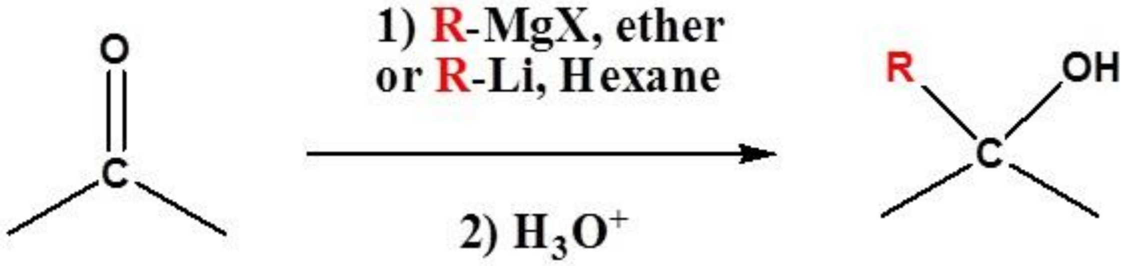
Preparation:

$R_3C{-}X + Mg \rightarrow R_3C{-}MgX$

Halide reactivity in these reactions increases in the order: Cl < Br < I and Fluorides are usually not used. The alkyl magnesium halides described in the second reaction are called Grignard Reagents after the French chemist, Victor Grignard, who discovered them and received the Nobel prize in 1912 for this work.

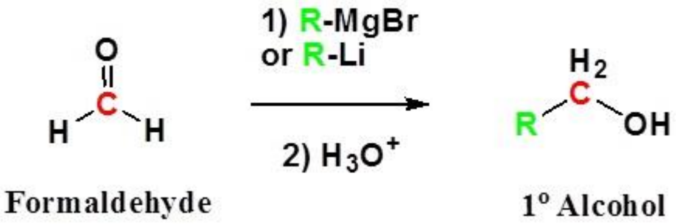
Reaction of Organometallic Reagents with Various Carbonyls:

Because organometallic reagents react as their corresponding carbanion, they are excellent nucleophiles. The basic reaction involves the nucleophilic attack of the carbanionic carbon in the organometallic reagent with the electrophilic carbon in the carbonyl to form alcohols.

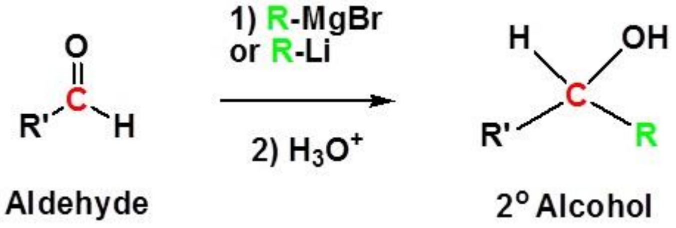


Grignard and Organolithium Reagents will perform these reactions:

Addition to formaldehyde gives 1° alcohols

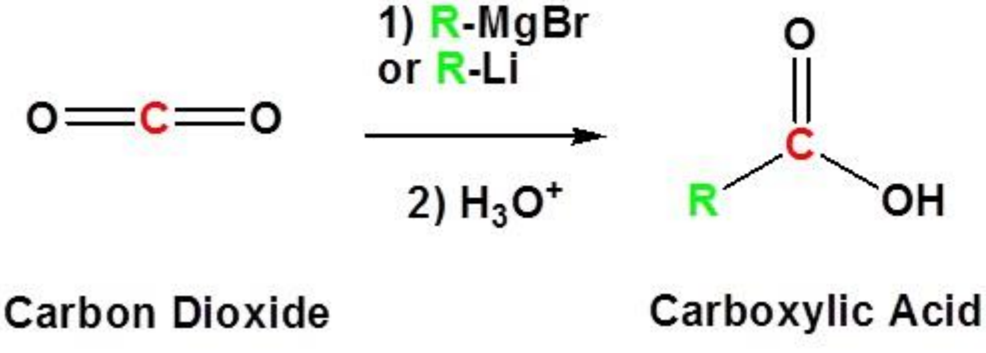


Addition to aldehydes gives 2° alcohols



Addition to ketones gives 3° alcohols

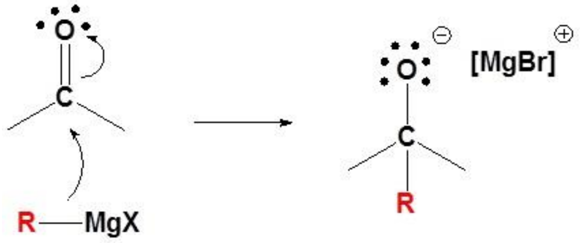
Addition to carbon dioxide (CO_2) forms a carboxylic acid



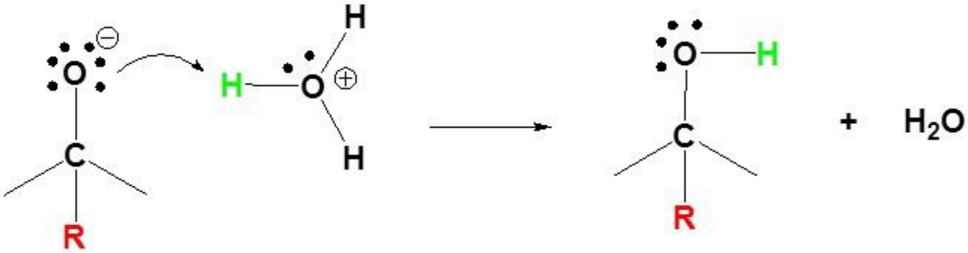
Mechanism for the Addition to Carbonyls

The mechanism for a Grignard agent is shown; the mechanism for an organometallic reagent is the same.

1) Nucleophilic attack

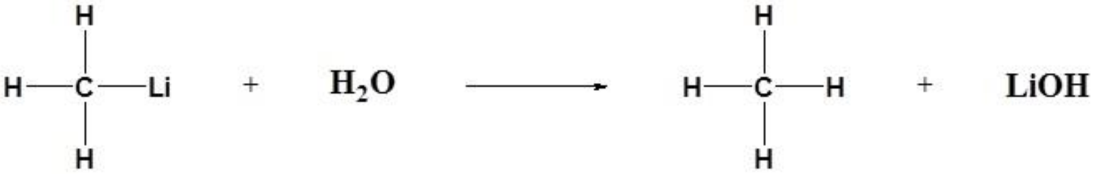


2) Protonation

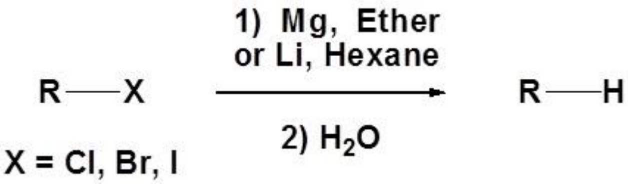


Organometallic Reagents as Bases

These reagents are very strong bases (pKa's of saturated hydrocarbons range from 42 to 50). Although not usually done with Grignard reagents, organolithium reagents can be used as strong bases. Both Grignard reagents and organolithium reagents react with water to form the corresponding hydrocarbon. This is why so much care is needed to insure dry glassware and solvents when working with organometallic reagents.



In fact, the reactivity of Grignard reagents and organolithium reagents can be exploited to create a new method for the conversion of halogens to the corresponding hydrocarbon (illustrated below). The halogen is converted to an organometallic reagent and then subsequently reacted with water to from an alkane.

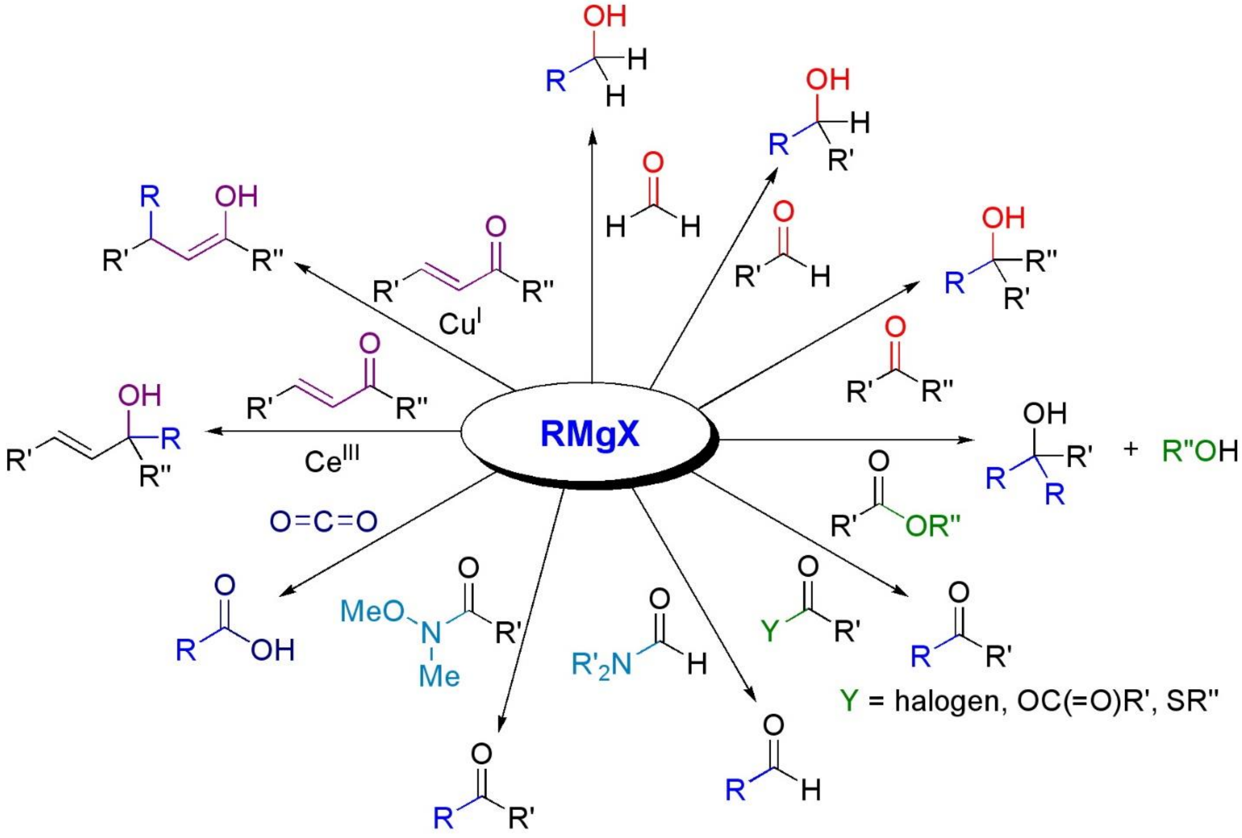


Grignard reagents react with oxygen, sulfur, and halogens to form substances containing C−OC−O, C−SC−S, and C−XC−X bonds, respectively:

$$\mathrm{RMgX + O_2 \longrightarrow R{-}O{-}O{-}MgX \xrightarrow{RMgX} 2ROMgX \xrightarrow{H_2O,\ H^{\oplus}} 2ROH}$$

$$\mathrm{RMgX + \tfrac{1}{8}S_8 \longrightarrow RSMgX \xrightarrow{H_2O,\ H^{\oplus}} RSH}$$

$$\mathrm{RMgX + I_2 \longrightarrow RI + MgXI}$$



3. Organoberyllium Compounds:

Organoberyllium compounds are more difficult to prepare and are less nucleophilic than their magnesium counterparts. These features, together with their high toxicity, have limited their utility.

Organoberyllium compounds are best prepared via transmetallation reactions or by reaction of beryllium halides with other organometallic compounds.

$$\mathbf{HgMe_2 + Be \rightarrow Me_2Be + Hg\ at\ 383K}$$

$$\mathbf{2\ PhLi + BeCl_2 \rightarrow Ph_2Be + 2\ LiCl}$$

In the vapour phase Me_2Be is monomeric but in the solid state it is polymeric and the bonding is considered electron deficient with 3 centre - 2 electron bonds. With higher alkyls the amount of polymerisation decreases and the tert-butyl derivative is monomeric and linear in both solid and vapour phases.

$$2NaCp+BeCl_2 \longrightarrow Cp_2Be+2NaCl$$

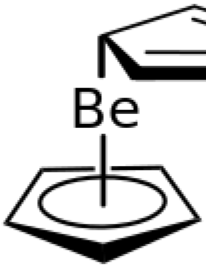
Beryllocene:

The reaction of NaCp with beryllium chloride leads to beryllocene (Cp_2Be)

$$2K[C_5Me_5]+BeCl_2 \rightarrow (C_5Me_5)_2Be+2KCl$$

reaction is carried out in an ether/toluene mix at 388K.

The solid state structure suggests that the two rings are bound to the Be differently such that 1 is designated η^5 and the other η^1.



Structure of $(\eta1-Cp)(\eta5-Cp)Be(\eta1-Cp)(\eta5-Cp)Be$ *also called Beryllocene*

The experimental ^1H NMR spectrum adds to the confusion of the bonding since even at 163 K the protons all appear equivalent. This is accounted for by fluxional processes. Some variations of the compound have been prepared to see how general this effect is, for example, 4 protons on each ring replaced by methyl groups and all 5 protons replaced by methyl groups, $(meCp)_2Be$, and even 4 on one ring and 5 on the other replaced with methyl groups. In the first case the fluxional process was observed down to 183K and in the second case the two rings were found to be coparallel and staggered. (Note that the structure of ferrocene is described as eclipsed when prepared at very low temperatures or in the gas phase but when formed at higher temperatures it is disordered and more staggered and since the barrier to rotation of the two rings is quite low, at 298 K in the solid state there is motion). However, Cp^*_2Be possesses a sandwich structure with both the rings are coplanar.

4. Macrocyclic ligands:

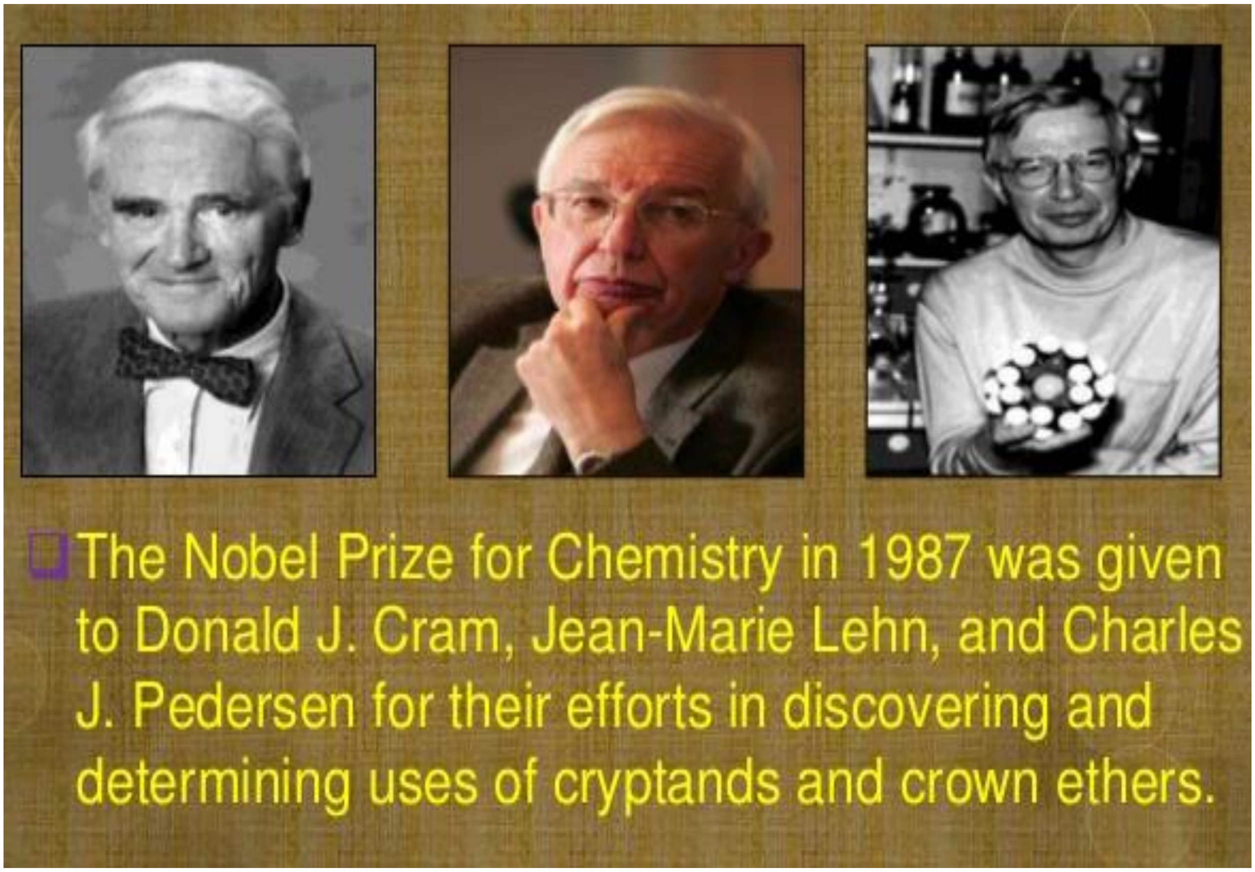
A macrocyclic ligand is a macrocycle with a ring size of atleast nine or three donor sites

Eg: crown ethers

Porphyrins

Cryptands

Calixarenes, etc.



- The Nobel Prize for Chemistry in 1987 was given to Donald J. Cram, Jean-Marie Lehn, and Charles J. Pedersen for their efforts in discovering and determining uses of cryptands and crown ethers.

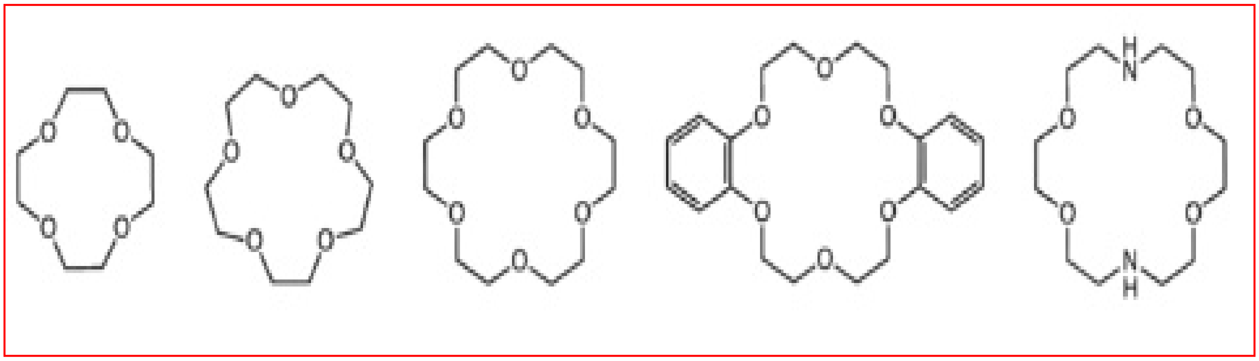
What is the need to study these molecules

- They are exceptionally versatile.
- selectively binding a range of metal ions and also a variety of organic neutral and ionic species.
- Crown ethers are currently being studied and used in many applications beyond their traditional place in chemistry.

4.1 Crown Ethers

- It is a type of cyclic ether consisting of a ring of carbon and oxygen atoms, with two or more carbon atoms between each oxygen atom.
- Crown ethers are cyclic chemical compounds that consist of a ring containing several ether groups.

- Crown – resemblance between the structure of a crown ether bound to a cation and a crown sitting on a person’s head.



Nomenclature

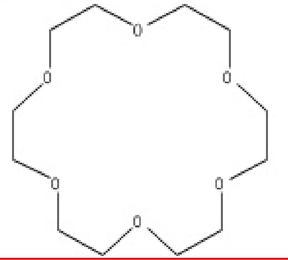
- The crown ethers are designated as per IUPAC nomenclature and also by Pederson’s crown nomenclature.
- It is always represented by notations.
- They are named as M-crown-N,

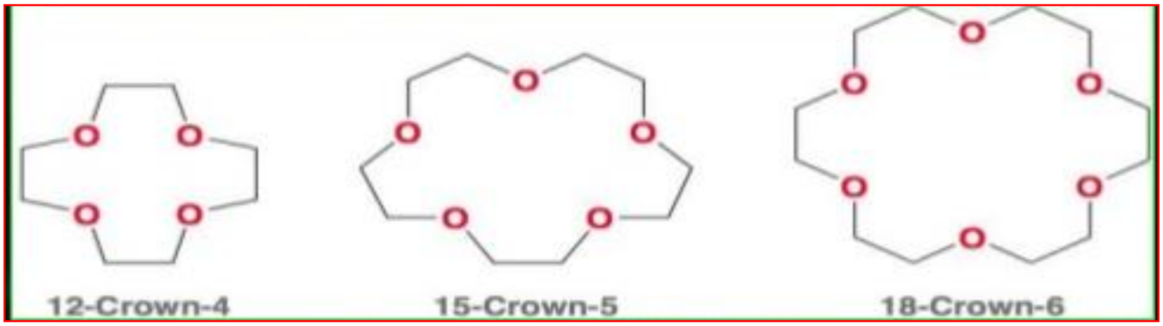
where M = total no. of atoms in the in cycle,

N = total no. of oxygen atoms.

Eg:

(18)-crown-6.



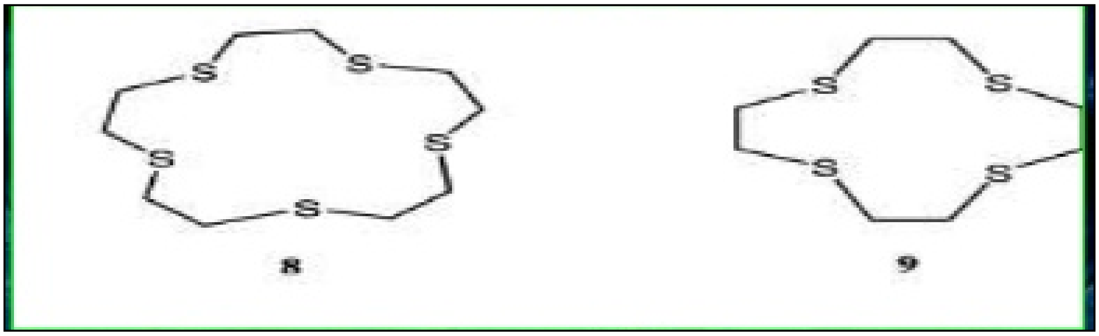


12-Crown-4 15-Crown-5 18-Crown-6

- Its inner side is hydrophilic (reacts with water)
- Outer part is hydrophobic in nature (repelled by water)

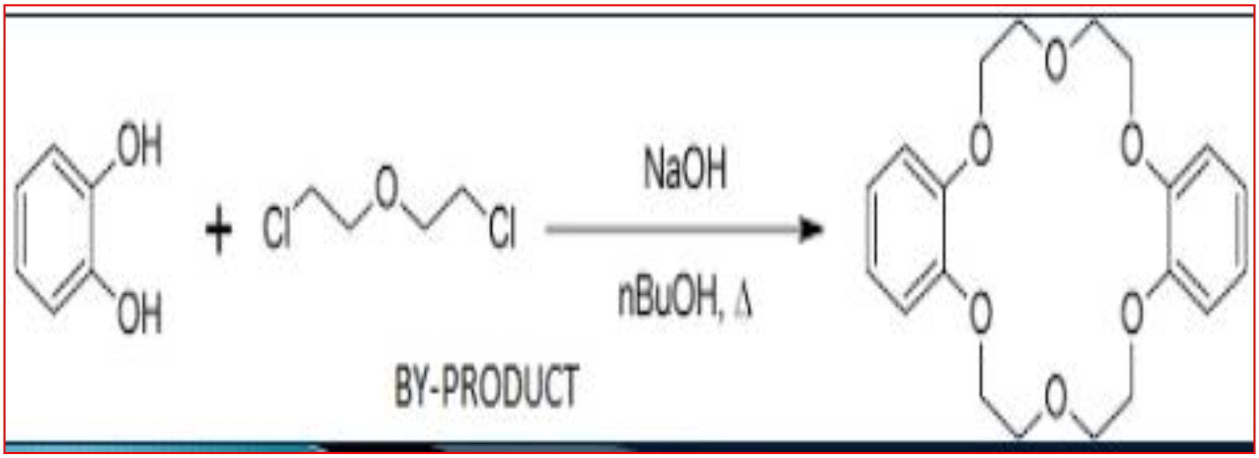
Thiacrowns:

It’s a special type of crown ether where the sulphur atoms takes the position of oxygen.



Synthesis of Crown ethers:

- Pederson synthesized the crown ethers by ionization of the phenolic hydroxyls.



Applications

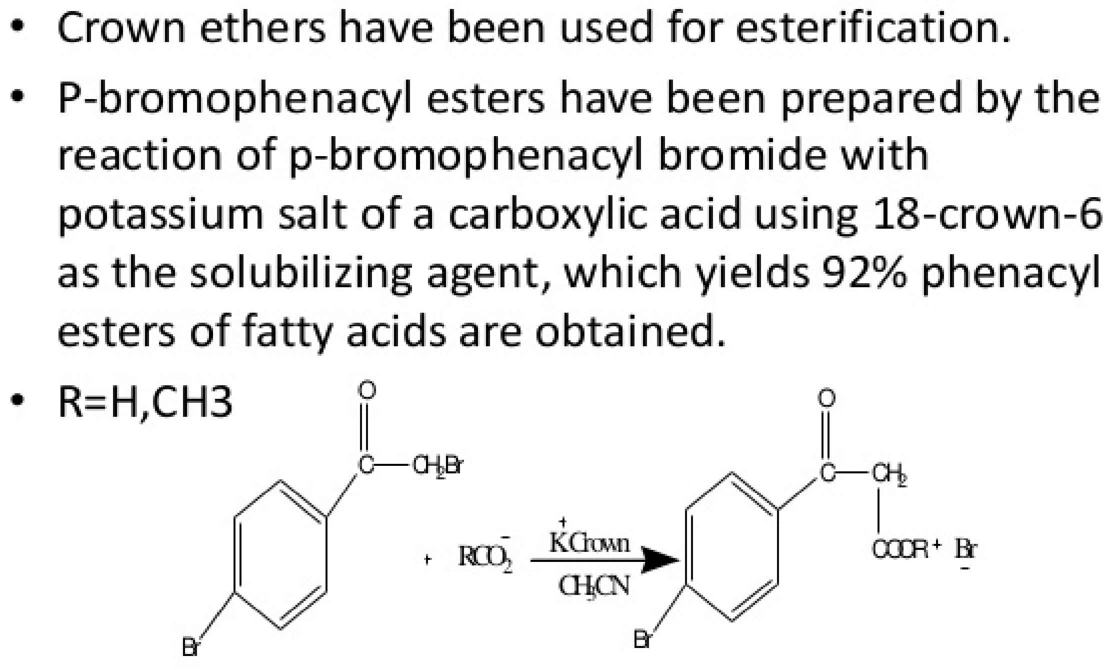
- Synthetic application
- Analytical application

Synthetic application

- Esterification
- Saponification
- Anhydride Formation
- Potassium Permanganate Formation
- Aromatic substitution reaction

- Elimination Reactions
- Displacement reactions
- Generation of carbenes
- Formation of superoxide anion
- o,c,n-alkylations etc.

Esterification



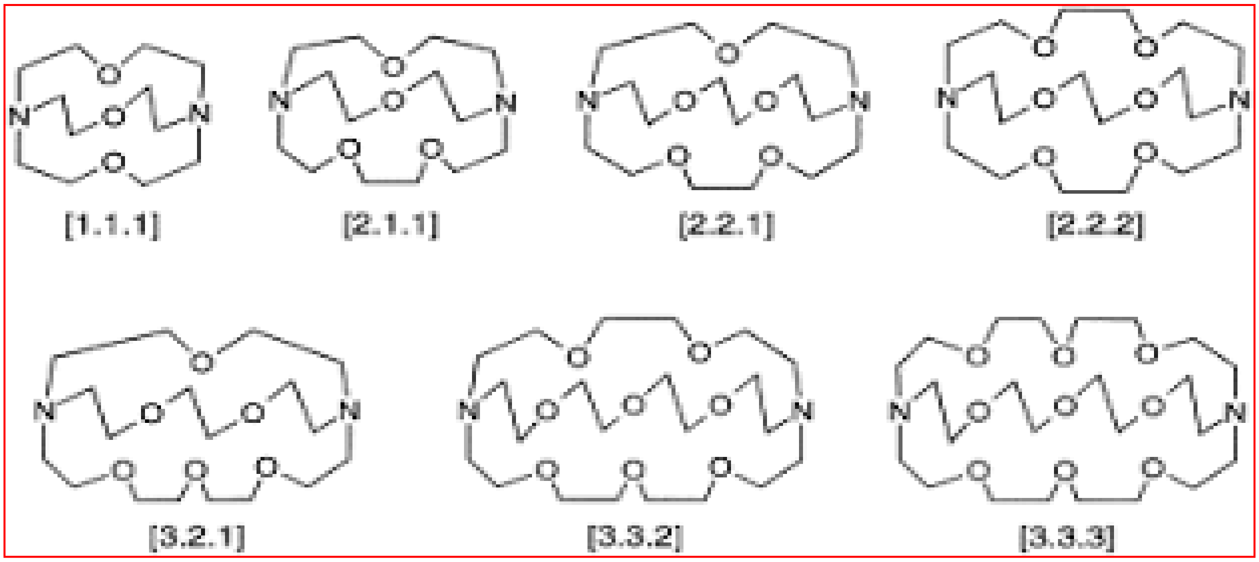
- Crown ethers have been used for esterification.
- P-bromophenacyl esters have been prepared by the reaction of p-bromophenacyl bromide with potassium salt of a carboxylic acid using 18-crown-6 as the solubilizing agent, which yields 92% phenacyl esters of fatty acids are obtained.
- R=H,CH3

Analytical Application:

- Determination of gold in geological samples.
- Supercritical fluid extraction of trace metal from solid and liquid materials.
- Oxidation and determination of aldehydes.
- Used in the laboratory as phase transfer catalyst.

4.2 Cryptands:

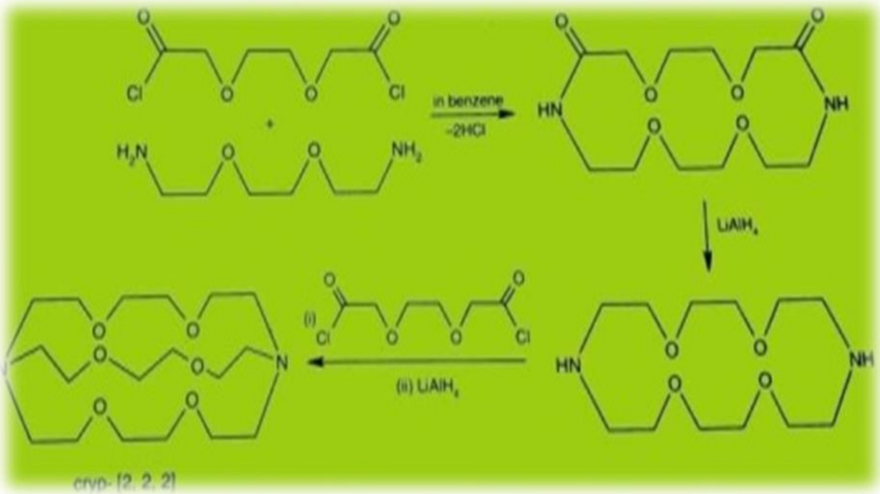
- These materials were first reported in 1969.
- Cryptands are a family of bicyclic and polycyclic multidentate ligands for a variety of cations.
- Cryptand means this ligand binds substrate in a crypt interring the guest in a burial.



- The most common and most important cryptand is $N[CH_2CH_2OCH_2CH_2OCH_2CH_2]_3N$. The formal IUPAC name for this compound is 1,10-diaza-4,7,13,16,21,24-hexaoxabicyclo[8.8.8]hexacosane.
- This compound is termed as [2,2,2] cryptand.
- The number indicates the number of ether oxygen atoms (binding sites) in each of the three bridges between the amino nitrogen "caps".

Synthesis:

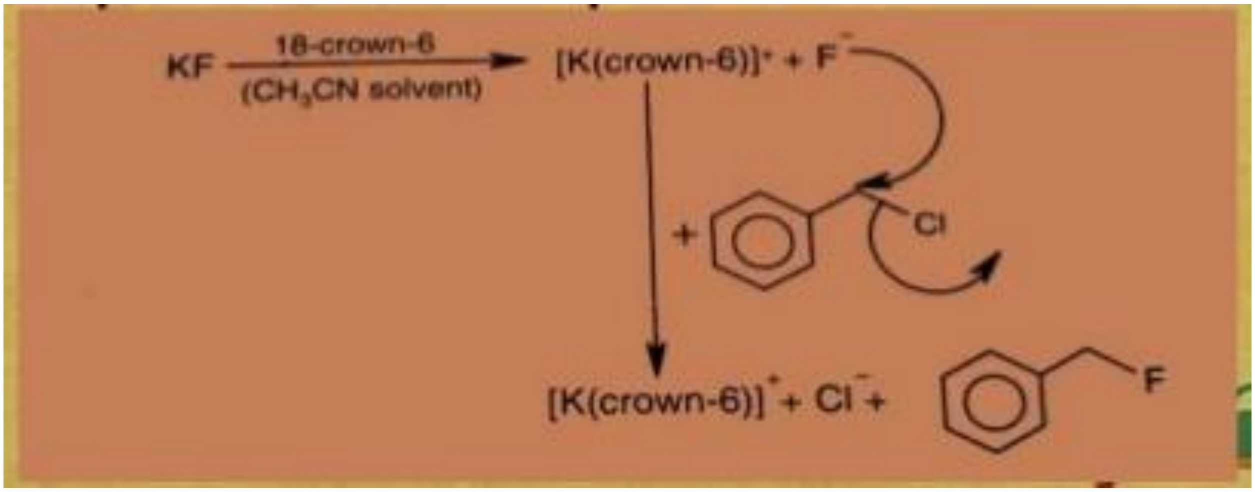
- The cryptand can be synthesized by the following method for [2,2,2] cryptand.



Applications

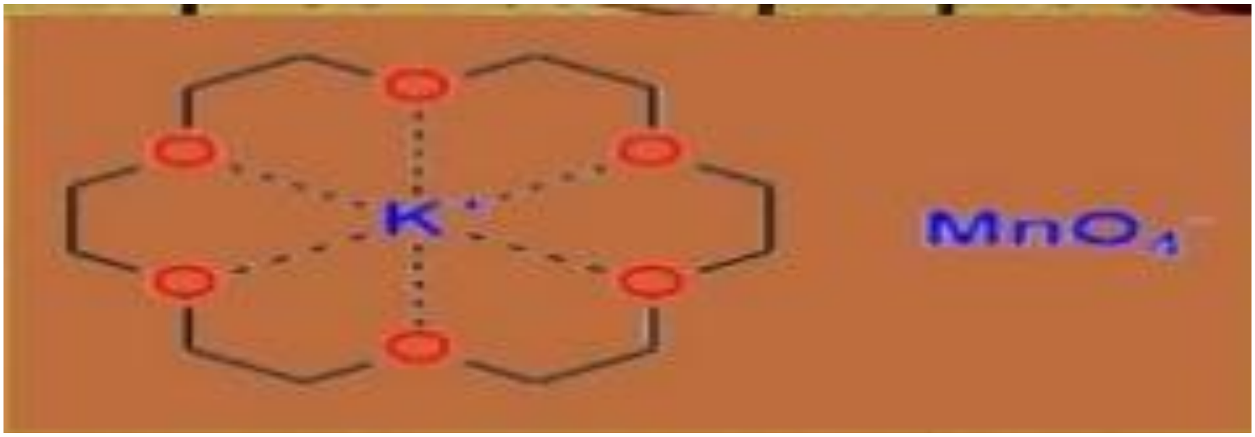
- Used as phase transfer catalyst.

Eg when KF is solubilized in the presence of 18-crown-6 or [2,2,2]cryptand, K^+ ion is stabilized as $[K(macrocycle)]^+$ and the unsolvated F^- ion acts as a poweful nucleophile.

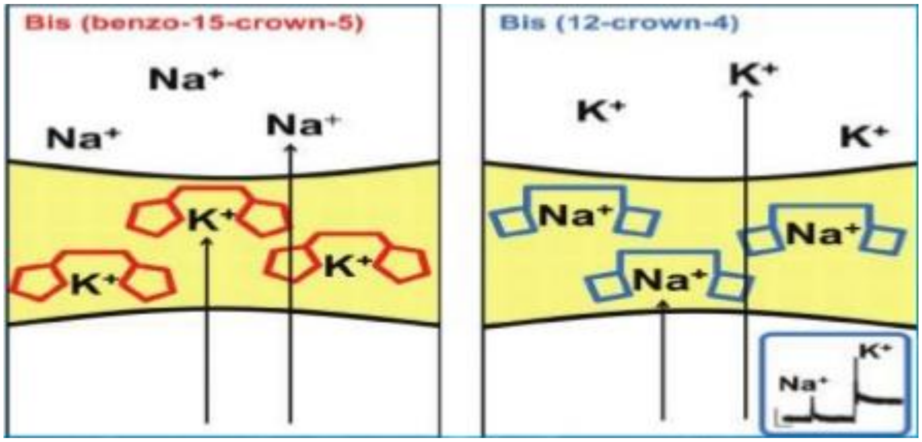


- They are able to bind insoluble salts into organic solvents.

Eg when $KMnO_4$ solubilized in benzene in presence of crown-6 or suitable cryptand produces a purple solution called purple benzene.



- Used in crystallization process.
- Used for selecting the ion selective electrodes.



- Used for seperation of chemically similar metals ions based on size factor (eg., lanthanides, alkali metal ions etc.,)

4.3 Calixarenes:

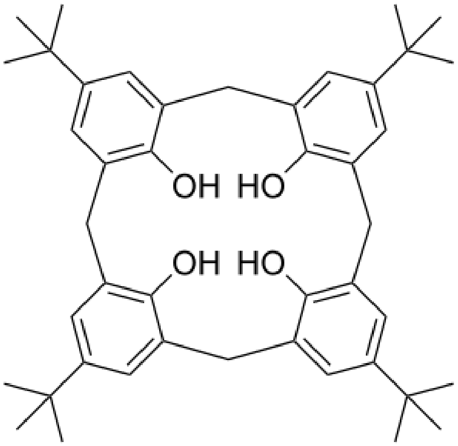
- It is a macrocycle or cyclic oligomer obtained from hydroxyalkylation product of phenol and aldehyde.
- Calixarenene- calix or chalice which means it resembles like a vase

arene means aromatic building block.

- It have hydrophobic cavity that can hold smaller molecules or ions like cryptands.
- Its nomenclature states that by counting the no. of repeating units in the ring.

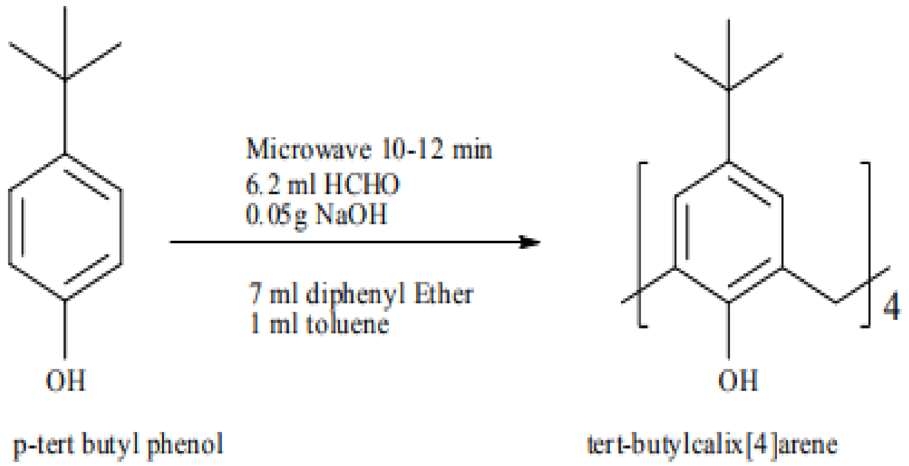
Eg. Calix[4]arene has 4 units in the ring.

Calix[6]arene has 6 units in the ring.



Calix[4]arene with tert-butyl substitution.

Synthesis:



Applications:

- Applied in enzyme mimetics.
- Used as ion selective electrodes or sensors.
- Used a selective membranes in ourifying technology.
- Used in non-linear optics.
- Used as stationary phase in HPLC.
- Used as scaffolds in cancer immunotheraphy.

References:

1. Text book of organic synthesis special techniques-vk ahulwalia, renu Aggarwal.
2. Analytical applications of crown ethers, G.S. Vasilikiotis, I.N. papadoyannis, and Th. A. Kouimtzis
3. Synthesis of Thiacrown and Azacrown ethers based on the spiroacetal framework by, Marica Nikac University of Western Sydney.
4. https://chem.libretexts.org/Bookshelves/Organic_Chemistry/Map%3A_Organic_Chemistry_(Smith)/Chapter_20%3A_Introduction_to_Carbonyl_Chemistry_Organometallic_Reagents_Oxidation_and_Reduction/20.09_Organometallic_Reagents.
5. https://cnx.org/contents/9G6Gee4A@25.3:gjp7zkI5@2/Organolithium-Compounds
6. https://chem.libretexts.org/Bookshelves/Organic_Chemistry/Map%3A_Organic_Chemistry_(Bruice)/11%3A_Organometallic_Compounds/11.01%3A_Organolithium_and_Organomagnesium_Compounds

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Chemistry of Main Group Elements

UNIT 4

ORGANYLS

Preparation and reactivity of aluminium organyls – Carbalumination, hydroalumination – Chemistry of Ga(I) and In(I) – Reduction of Al, Ga and In organyls – Germanium, tin and lead organyls.

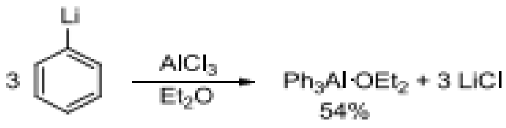
1. Introduction:

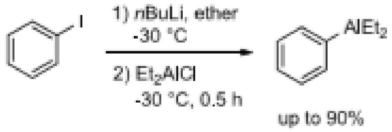
Organoaluminium compounds are known for more than 150 years. Following the groundbreaking experiments of Frankland (1849) on the preparation of dialkylzinc reagents by the reaction of zinc with alkyl iodides

1.1 Preparation methods of Organoaluminium Compounds:

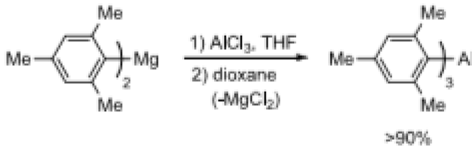
1.1.1 Transmetallation:

The most widely employed synthesis of organoaluminium compounds on laboratory scale is the transmetallation reaction (salt metathesis), using organometallics and an aluminium salt. The driving force of this reaction is the formation of a thermodynamically more stable carbon-metal bond, which is usually the more covalent bond.

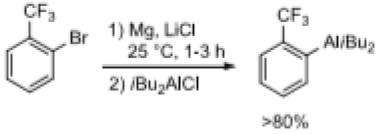




The reaction of organomagnesium reagents with AlCl3 has been investigated thoroughly as well. Since early attempts41 this procedure has developed to a powerful synthetic methodology. Thus, for example starting from dimesitylmagnesium, sterically hindered organoaluminiums can be prepared easily

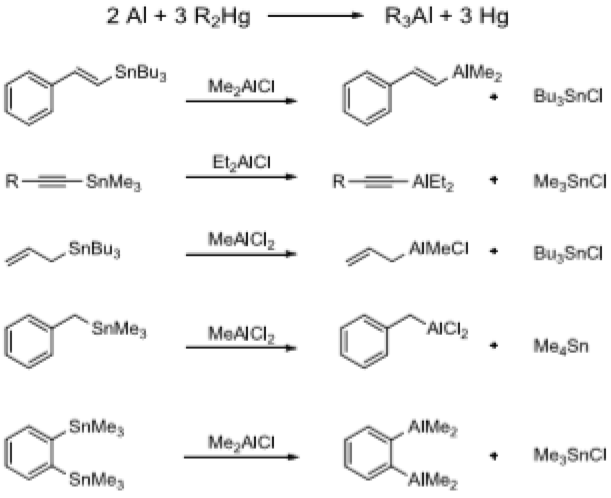


Even functionalized organoaluminiums have been prepared recently by the reaction of functionalized organomagnesium reagents with aluminium salts under Barbier conditions

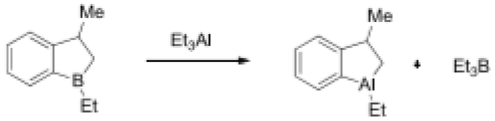


1.1.2 Metal-Exchange Reaction:

The preparation of organoaluminium compounds has been achieved starting from mercury organyls (Scheme 6).49 Of course, because of the use of toxic mercury this approach is not applicable nowadays anymore. Such an exchange is not only occurring when the metal is used in its elemental state, but also between two organometallic compounds. Thus, several groups have demonstrated that organoaluminiums can be prepared by a Sn-Al exchange and alkenyl-, alkynyl-, allyl-, benzyl- and arylaluminiums have been synthesized using alkylaluminium chlorides (Scheme 7).50



Organoboron reagents are relatively stable and most important, far less toxic than organomercury or organotin compounds. Of course, because of the similarity between boron and aluminium, exchange reactions between these two elements have been investigated.51 Thus, treatment of triethylaluminium with triphenylboron at 140 °C leads rapidly to an exchange of ligands (Scheme 8).49e. equilibrium has to be shifted by removal of volatile reaction products, such as Et3B, to obtain high exchange rates.54 Remarkably, this exchange has also been achieved using boracycles in which case aluminium heterocycles are generated.



1.1.3 Hydrolalumination:

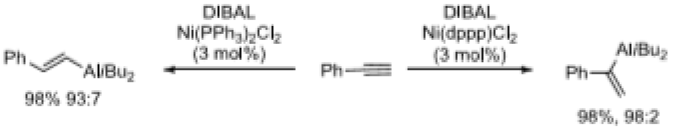
The addition of aluminium hydrogen bonds to unsaturated compounds such as alkenes and alkynes is referred to as hydroalumination. The hydroalumination reaction was recognized by Ziegler51, 67 and has found application in one of the most important industrial syntheses of triorganoaluminiums: the "Ziegler direct process" (Scheme 15).68 Two observations are combined in one process: First, Al reacts with hydrogen in the presence of AlR3 leading to aluminium hydrides (increase) and secondly the Al-H bond can react with alkenes (attachment). In summary, R3Al has been synthesized from Al, H2 and alkene, the process therefore is referred to as "direct synthesis".

$$Al + 1.5\,H_2 + 2\,Et_3Al \xrightarrow[100 - 200\text{ bar}]{80 - 160\text{ °C}} 3\,Et_2AlH \quad \text{"increase"}$$

$$3\,Et_2AlH + 3\,C_2H_4 \xrightarrow[1 - 10\text{ bar}]{80 - 110\text{ °C}} Et_3Al \quad \text{"attachment"}$$

$$Al + 1.5\,H_2 + 3\,C_2H_4 \longrightarrow Et_3Al$$

The hydroalumination of alkynes and alkenes has developed to a general method for the preparation of various alkenylaluminium and alkylaluminium reagents.70 Most recently it could be shown that the use of Ni-salts catalyses the hydroalumination. Remarkably, by changing the Ni-catalyst, regioselectivity of the hydrolalumination can be achieved.



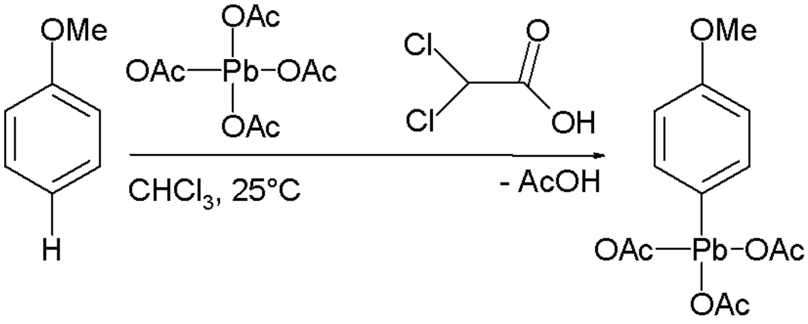
2. Lead Organyls:

Organolead compounds are chemical compounds containing a chemical bond between carbon and lead. The first organolead compound was hexaethyldilead ($Pb_2(C_2H_5)_6$), first synthesized in 1858.

Synthesis:

Organolead compounds can be derived from Grignard reagents and lead chloride. For example, methylmagnesium chloride reacts with lead chloride to tetramethyllead, a water-clear liquid with boiling point 110 °C and density 1.995 g/cm³. Reaction of a lead(II) source with sodium cyclopentadienide gives the lead metallocene, plumbocene.

Certain arene compounds react directly with lead tetraacetate to aryl lead compounds in an electrophilic aromatic substitution. For instance anisole with lead tetraacetate forms 'p-methoxyphenyllead triacetate in chloroform and dichloroacetic acid



Other compounds of lead are organolead halides of the type $R_nPbX_{(4-n)}$, organolead sulfinates ($R_nPb(OSOR)_{(4-n)}$) and organolead hydroxides ($R_nPb(OH)_{(4-n)}$). Typical reactions are:[4]

$R_4Pb + HCl \rightarrow R_3PbCl + RH$
$R_4Pb + SO_2 \rightarrow R_3PbO(SO)R$
$R_3PbCl + 1/2Ag_2O\ (aq) \rightarrow R_3PbOH + AgCl$
$R_2PbCl_2 + 2\ OH^- \rightarrow R_2Pb(OH)_2 + 2\ Cl^-$

$R_2Pb(OH)_2$ compounds are amphoteric. At pH lower than 8 they form R_2Pb^{2+} ions and with pH higher than 10, $R_2Pb(OH)_3^-$ ions.

Derived from the hydroxides are the plumboxanes:

$2\ R_3PbOH + Na \rightarrow (R_3Pb)_2O + NaOH + 1/2\ H_2$
$(R_3Pb)_2O + R'OH \rightarrow 1/n\ (R_3PbOR')_n - n\ H_2O$

Organolead compounds form a variety of reactive intermediates such as lead free radicals:

$Me_3PbCl + Na\ (77\ K) \rightarrow Me_3Pb^{\cdot}$
$Me_3Pb\text{-}Pb\text{-}Me_3 \rightarrow [Me_2Pb]$
$[Me_2Pb] + (Me_3Pb)_2 \rightarrow Me_3Pb\text{-}Pb(Me)_2\text{-}PbMe_3$
$Me_3Pb\text{-}Pb(Me)_2\text{-}PbMe_3 \rightarrow Pb(0) + 2\ Me_4Pb$

3. Tin organyls:

Organotin compounds or stannanes are chemical compounds based on tin with hydrocarbon substituents. Organotin chemistry is part of the wider field of organometallic chemistry. The first organotin compound was diethyltin diiodide ($(C_2H_5)_2SnI_2$), discovered by Edward Frankland in 1849.

Preparation:

i) Organotin oxides and hydroxides are common products from the hydrolysis of organotin halides. Unlike the corresponding derivatives of silicon and germanium, tin oxides and hydroxides often adopt structures with penta- and even hexacoordinated tin centres, especially for the diorgano- and monoorgano derivatives. The group Sn-O-Sn is called a stannoxane. Structurally simplest of the oxides and hydroxides are the triorganotin derivatives.

$$R_3SnOH \rightleftharpoons R_3SnOSnR_3 + H_2O$$

ii) The reaction of a Grignard reagent with tin halides.

$$4EtMgBr + SnCl_4 \rightarrow Et_4Sn + 4\ MgClBr$$

Properties:

iii) The symmetrical tetraorganotin compounds, especially tetraalkyl derivatives, can then be converted to various mixed chlorides by redistribution reactions.

$$3\ R_4Sn + SnCl_4 \rightarrow 4\ R_3SnCl$$
$$R_4Sn + SnCl_4 \rightarrow 2\ R_2SnCl_2$$
$$R_4Sn + 3\ SnCl_4 \rightarrow 4\ RSnCl_3$$

iv) The mixed organo-halo tin compounds can be converted to the mixed organic derivatives, as illustrated by the synthesis of dibutyldivinyltin.

$$Bu_2SnCl_2 + 2\ C_2H_3MgBr \rightarrow Bu_2Sn(C_2H_3)_2 + 2\ MgBrCl$$

References

1. Main Group Metals in Organic Synthesis Yamamoto, Hisashi / Oshima, Koichiro (eds.) 2004 ISBN 3-527-30508-4
2. Synthesis of Organometallic Compounds: A Practical Guide Sanshiro Komiya Ed. 1997
3. Caseri, Walter (2014). "Initial Organotin Chemistry". Journal of Organometallic Chemistry. 751: 20–24. doi:10.1016/j.jorganchem.2013.08.009

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School of Science and Humanities

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SCYA5201

Chemistry of Main Group Elements

Unit 5

LANTHANIDES & ACTINIDES

Lanthanides: lanthanide series, abundance and natural isotopes - lanthanide contraction, similarity in properties, occurrence, oxidation states - chemical properties of Ln(III) cations - magnetic properties, colour and electronic spectra of lanthanide compounds - separation of lanthanides, solvent extraction, ion exchange method.

Actinides: actinide series, abundance and natural isotopes, occurrence, preparation of actinides - oxidation states - general properties, the later actinide elements, uranium-occurrence, metallurgy; chemical properties of hydrides, oxides, and halides - complexes of lanthanides and actinides - term symbols

1. Actinides:

The two series of elements in the f block derive from the filling of the seven 4f and 5f orbitals, respectively. This occupation of f orbitals from f1 to f14 corresponds to the elements cerium (Ce) to lutetium (Lu) in Period 6 and from thorium (Th) to lawrencium (Lr) in Period 7. The 4f elements are collectively the lanthanoids (formerly and still commonly ‘the lanthanides’, but this terminology is potentially confusing as the suffix -ide generally refers to an anionic form of an element) and the 5f elements are the actinoids (still commonly the ‘actinides’). The lanthanoids are sometimes referred to as the ‘rare earth elements’. That name, however, is inappropriate because they are not particularly rare, except for promethium, which has no stable isotope. A general lanthanoid is represented by the symbol Ln and an actinoid by An.

1.1CHARACTERISTICS OF THE LANTHANIDES

The lanthanides exhibit a number of features in their chemistry that differentiate them from the d-block metals. The reactivity of the elements is greater than that of the transition metals, akin to the Group II metals:

1. A very wide range of coordination numbers (generally 6–12, but numbers of 2, 3 or 4 are known).
2. Coordination geometries are determined by ligand steric factors rather than crystal field effects.
3. They form labile ‘ionic’ complexes that undergo facile exchange of ligand.
4. The 4f orbitals in the Ln^{3+} ion do not participate directly in bonding, being well shielded by the $5s^2$ and $5p^6$ orbitals. Their spectroscopic and magnetic properties are thus largely uninfluenced by the ligand.
5. Small crystal-field splitting and very sharp electronic spectra in comparison with the d-block metals.
6. They prefer anionic ligands with donor atoms of rather high electronegativity (e.g. O, F).
7. They readily form hydrated complexes (on account of the high hydration energy of the small Ln^{3+} ion) and this can cause uncertainty in assigning coordination numbers.
8. Insoluble hydroxides precipitate at neutral pH unless complexing agents are present.
9. The chemistry is largely that of one (3+) oxidation state (certainly in aqueous solution).
10. They do not form Ln=O or Ln≡N multiple bonds of the type known for many transition metals and certain actinides.

11. Unlike the transition metals, they do not form stable carbonyls and have (virtually) no chemistry in the 0 oxidation state.

1.2 THE OCCURRENCE AND ABUNDANCE OF THE LANTHANIDES:

The lighter lanthanides are more abundant than the heavier ones; secondly, that the elements with even atomic number are more abundant than those with odd atomic number. Overall, cerium, the most abundant lanthanide on earth, has a similar crustal concentration to the lighter Ni and Cu, whilst even Tm and Lu, the rarest lanthanides, are more abundant than Bi, Ag or the platinum metals. The abundances are a consequence of how the elements were synthesized by atomic fusion in the cores of stars with heavy elements only made in supernovae. Synthesis of heavier nuclei requires higher temperature and pressures and so gets progressively harder as the atomic number increases. The odd/even alternation (often referred to as the Oddo–Harkins rule) is again general, and reflects the facts that elements with odd mass numbers have larger nuclear capture cross sections and are more likely to take up another neutron, so elements with odd atomic number (and hence odd mass number) are less common than those with even mass number. Even-atomic-number nuclei are more stable when formed.

1.3 THE LANTHANIDE CONTRACTION:

As the series La–Lu is traversed, there is a decrease in both the atomic radii and in the radii of the Ln^{3+} ions, more markedly at the start of the series. The 4f electrons are ‘inside’ the 5s and 5p electrons and are core-like in their behaviour, being shielded from the ligands, thus taking no part in bonding, and having spectroscopic and magnetic properties largely independent of environment. The 5s and 5p orbitals penetrate the 4f subshell and are not shielded. The Lanthanides – Principles and Energetics increasing nuclear charge, and hence because of the increasing effective nuclear charge they contract as the atomic number increases. Some part (but only a small fraction) of this effect has also been ascribed to relativistic effects. The lanthanide contraction is sometimes spoken of as if it were unique. It is not, at least in the way that the term is usually used. Not only does a similar phenomenon take place with the actinides (and here relativistic effects are much more responsible) but contractions are similarly noticed on crossing the first and second long periods (Li–Ne; Na–Ar) not to mention the d-block transition series. However, as will be seen, because of a combination of circumstances, the lanthanides adopt primarily the (+3) oxidation state in their compounds, and therefore demonstrate the steady and subtle changes in properties in a way that is not observed in other blocks of elements. The lanthanide contraction has a knock-on effect in the elements in the 5d transition series. It would naturally be expected that the 5d elements would show a similar increase in size over the 4d transition elements to that which the 4d elements demonstrate over the 3d metals. However, it transpires that the ‘lanthanide contraction’ cancels this out, almost exactly, and this has pronounced effects on the chemistry, e.g., Pd resembling Pt rather than Ni, Hf is extremely similar to Zr.

1.4 CAUSE OF LANTHANIDE CONTRACTION:

As we move along the lanthanide series from Ce to Lu, the addition of electrons takes place to the 4f-orbitals, one at each step. The mutual shielding effect of f-electrons is very little, being even smaller than that of d-electrons, due to the scattered or diffused shape of these orbitals. However, the nuclear charge (i.e. atomic number) goes on increasing by one unit at each step (i.e., each next element). Thus, the attraction between the nucleus and the outermost shell electrons also goes on increasing gradually at each step. The 4f-electrons are not able to shield effectively the attraction of the nucleus (i.e. inward pull) for the electrons in the outer most shell as the atomic number of lanthanide elements increases. This results in the increased inward pull of the outer most electrons by the nucleus, finally causing the reduction in the atomic or ionic size of these elements. The sum of the successive reductions gives the total lanthanide contraction. It may be concluded that the lanthanide contraction among the 4f-sereies elements and their ions takes place due to the poor shielding effect of 4f-electrons and gradual increase in the nuclear charge.

SIMILARITY IN PROPERTIES:

There is very small change in the radii of lanthanides and hence their chemical properties are quite similar. This makes the separation of these elements using the usual physical and chemical methods difficult. Consequently, new methods like ion exchange technique, solvent extraction etc. have now been used for their separation which are based on slight difference in the properties like hydration, complex ion formation, etc.

OXIDATION STATES:

The characteristic oxidation state of the lanthanide elements is ± 3. The universal preference for this oxidation state together with the notable similarity in size led to great difficulties in the separation of the elements prior to the development of chromatographic methods. Despite their propensity to form stable +3 cations. the lanthanides do not closely resemble transition metals such as chromium or cobalt. The free lanthanide metals are more reactive and in this respect are more similar to the alkali or alkaline earth metals than to most of the transition metals. They all react with water with evolution of hydrogen. The oxidation state (+III) is ionic and Ln^{+3} dominates the chemistry of these elements. The Ln^{2+} and Ln^{4+} ions that do occur are always less stable than Ln^{3+}. In the same way as for other elements the higher oxidation states occur in the fluorides and oxides and the other halides. Particularly bromides and iodides. Oxidation numbers (+II) and (+IV) do occur. Particularly when they lead to:

1. A noble gas configuration
2. A half-filled f shell
3. A completely filled f shell

The (+III) state is always the most common and most stable. The only (+IV) and (+II) states which have any aqueous chemistry are Ce^{4+}, Sm^{2+}, Eu^{2+} and Yb^{2+}. The lanthanide elements resembles each other much more closely than do a horizontal row of the transition elements. This is because the lanthanides effectively have only one stable oxidation state, (+III). Thus in this series it is possible to compare the effects of small change in the size and nuclear charge on the chemistry of these elements.

1.5 SPECTRAL PROPERTIES OF LANTHANIDES:

Most lanthanoid ions are only weakly coloured because their absorptions in the visible region of the spectrum are commonly f-f transitions which are symmetry forbidden. The spectra of their complexes generally show much narrower and more distinct absorption bands than those of d-metal complexes. Both the narrowness of the spectral features and their insensitivity to the nature of coordinated ligands indicate that the f orbitals have a smaller radial extension than the filled 5s and 5p orbitals. The 5s and 5p orbitals are expected to shield the 4f electrons from the ligands. f-orbitals are relatively deep inside the atom and overlap only weakly with ligand orbitals. Hence, as a first approximation, their electronic states (and therefore electronic spectra) can be discussed in the free-ion limit and the Russell-Saunders coupling scheme remains a reasonable approximation despite the elements having high atomic numbers. the visible spectra of lanthanoids usually consist of a large number of sharp, low intensity peaks that are barely affected by changing the coordination environment of the central metal ion.

The spectra of the lanthanoid ions are normally characterized by the following properties:
1. Numerous absorptions due to the large number of microstates. Weak absorptions due to lack of orbital mixing. Molar absorption coefficients(ε) are typically
2. 10 $dm^3\ mol^{-1}\ cm^{-1}$ compared with d metals (close to 100 $dm^3\ mol^{-1}\ cm^{-1}$).
3. Sharp absorptions due to the weak interaction of the f orbitals with the ligand vibrations.
4. Spectra that are to a large degree independent of the ligand type and coordination number

1.6 MAGNETIC PROPERTIES:

Magnetism is a property associated with unpaired electrons. La^{3+} (f0), Ce^{4+} (f0), Yb^{2+} (f14) and Lu^{3+}(f 14) have no unpaired electron, hence they are diamagnetic. Other lanthanide ions have unpaired electron in 4f orbital, so they are paramagnetic. Magnetic behaviour in case of lanthanides arises due to the contribution of both spin moment as well as orbital magnetic moment, unlike the d-block elements where magnetic moment corresponds to spin only values [μ = n(n+2), n = no. of unpaired electrons]. Because in case of inner-transition f-block elements, the 4f orbitals are quite shielded from the surroundings and do not interact strongly with the ligands surrounding the metal ion. Consequently, the orbital motion of 4f orbitals are not restricted (not quenched). Therefore, in case of lanthanides, the magnetic effect arising from the orbital motion of the electron, as well as that arising from the electrons spinning on its axis, contributes to the total magnetic moment. Therefore, magnetic moments of lanthanides are calculated by taking into consideration spin as well as orbital contributions and a more complex formula:

$\mu = 4S (S+1) + L (L+1)$ is used,

where L = orbital quantum no. and S = spin quantum no. In case of lanthanides, the spin contribution (S) and orbital contribution (L) couple together to give a new quantum no. J, called total angular momentum quantum no.

$J = L - S$, when the orbital is less than half full
$J = L + S$, when the orbital is less than half full
Magnetic moment values for lanthanides in Bohr Magneton (BM) is given by:
$\mu = g J (J + 1)$
Where g is called Lande splitting factor and is given by:

1.7 SEPARATION OF LANTHANIDES BY ION-EXCHANGE METHOD:

This is the most rapid and most effective method for the isolation of individual lanthanide elements from the mixture. An aqueous solution of the mixture of lanthanide ions (Ln^{3+}aq) is introduced into a column containing a synthetic cation exchange resin such as DOWAX-50 [abbreviated as HR (solid)]. The resin is the sulphonated polystyrene containing-SO3H as the functional group. As the solution of mixture moves through the column, Ln^{3+}aq ions replace H^+ions of the resin and get themselves fixed on it:

$Ln^{3+}aq + 3H\text{-resin} \rightarrow Ln(resin)_3 + 3H^+ aq$

The H^+ aq ions are washed through the column. The Ln^{3+}aq. ions are fixed at different positions on the column. Since, Lu^{3+}aq. is largest (Lu^{3+} anhydrous is smallest and is hydrated to the maximum extent) and Ce^{3+}aq. is the smallest, Lu^{3+}aq. ion is attached to the column with minimum firmness remaining at the bottom and Ce^{3+}aq. ion with maximum firmness remaining at the top of the resin column. In order to move these Ln^{3+}aq. ions down the column and recover them, a solution of anionic ligand such as citrate or 2-hydroxy butyrate is passed slowly through the column (called elution). The anionic ligands form complexes with the lanthanides which possess lower positive charge than the initial Ln^{3+}aq ions. These ions are thus displaced from the resin and moved to the surrounding solutions as eluant- Ln complexes. For example, if the citrate solution (a mixture of citric acid and ammonium citrate) is used as the eluant, during elution process, NH^{4+} ions are attached to the resins replacing Ln^{3+}aq. ions which form Ln-citrate complexes:

$Ln(resin)_3 + 3NH_4^+ \rightarrow 3NH_4\text{- resin} + Ln^{3+}aq$
$Ln^{3+}aq + \text{citrate ions} \rightarrow \text{Ln-citrate complex}$

As the citrate solution (buffer) runs down the column, the metal ions get attached alternately with the resin and citrate ions (in solution) many times and travel gradually down the column and finally pass out of the bottom of the column as the citrate complex. The Ln^{3+}aq cations with the largest size are, eluted first (heavier Ln^{3+}aq ions) because they are held with minimum firmness and lie at the bottom of the column. The lighter Ln^{3+}aq ions with smaller size are held at the top of the column (with maximum firmness) and are eluted at last. The process is repeated several times by careful control of concentration of citrate buffer in actual practice.

1.8 LANTHANIDE SEPERATION BY SOLVENT EXTRACTION:

Solvent extraction has come to be used for the initial stage of the separation process, to give material with up to 99.9% purity. In 1949, it was found that Ce^{4+} could readily be separated from Ln^{3+} ions by extraction from a solution in nitric acid into tributyl phosphate $[(BuO)_3PO]$. Subsequently the process was extended to separating the lanthanides, using a non-polar organic solvent such as kerosene and an extractant such as $(BuO)_3PO$ or bis (2-ethylhexyl) phosphinic acid $[[C_4H_9CH(C_2H_5)]2P{=}O(OH)]$ to extract the lanthanides from aqueous nitrate solutions. The heavier lanthanides form complexes which are more soluble in the aqueous layer. After the two immiscible solvents have been agitated together and separated, the organic layer is treated with acid and the lanthanide extracted. The solvent is recycled and the aqueous layer put through further stages. For a lanthanide Ln_A distributed between two phases, a distribution coefficient D_A is defined:

$D_A = [Ln_A \text{ in organic phase}] / [Ln_A \text{ in aqueous phase}]$

For two lanthanides Ln_A and Ln_B in a mixture being separated, a separation factor $\beta^A{}_B$ can be defined, where,

$\beta^A{}_B = D_A/D_B$
β is very close to unity for two adjacent lanthanides in the Periodic Table (obviously, the larger β is, the better the separation). In practice this process is run using an automated continuous counter-current circuit in which the organic solvent flows in the opposite direction to the

aqueous layer containing the lanthanides. An equilibrium is set up between the lanthanide ions in the aqueous phase and the organic layer, with there tending to be a relative enhancement of the concentration of the heavier lanthanides in the organic layer. Because the separation between adjacent lanthanides in each exchange is relatively slight, over a thousand exchanges are used. This method affords lanthanides of purity up to the 99.9% purity level and is thus well suited to large-scale separation, the products being suited to ordinary chemical use. However, for electronic or spectroscopic use ('phosphor grade') 99.999% purity is necessary, and currently ion-exchange is used for final purification to these levels. The desired lanthanides are precipitated as the oxalate or hydroxide and converted into the oxides (the standard starting material for many syntheses) by thermal decomposition. Various other separation methods have been described, one recent one involving the use of supercritical carbon dioxide at 40°C and 100 atm to convert the lanthanides into their carbonates whilst the quadrivalent metals (e.g. Th and Ce) remain as their oxides.

2. ACTINIDES:

2.1 CHARACTERISTICS:

Early in the actinide series, electrons in the 6d orbitals are lower in energy than there is 5f orbitals. This is clear from the ground-state electronic configurations of the atoms, which show that the 6d orbitals are filled before 5f. The 5f orbitals are starting to be filled at protoactinium, and with the exception of curium, the 6d orbitals are not occupied again. The 5f orbitals are not shielded by the filled 6s and 6p subshells as the 4f orbitals of the lanthanides are (by the corresponding 5s and 5p subshells). Moreover, the energy gap between $5f\,n\ 7s^2$ and $5f\,n{-}1\ 6d\ 7s^2$ configurations is less than for the corresponding lanthanides. Not only are the 5f orbitals less 'inner orbitals' in the sense that the 4f orbitals are for the lanthanides, and thus more perturbed in bonding, but the near-degeneracy of the 5f, 6d, and 7s electrons means that more outer-shell electrons can be involved in compound formation (and a wider range of oxidation states observed). Thus, the first four ionization energies of Th are 587, 1110, 1978, and 2780 kJ mol^{-1} compared with respective values for Zr of 660, 1267, 2218, and 3313 kJ mol^{-1}. So, for the earlier actinides, higher oxidation states are available and, as for the d block, several are often available for each metal [relativistic effects may also be important. However, as the 5f electrons do not shield each other from the nucleus effectively, the energies of the 5f orbitals drop rapidly with increasing atomic number, so that the electronic structures of the later actinides and their ions become more and more like those of the lanthanides, whose chemistry they thus resemble.

OXIDATION STATES:

The important oxidation states exhibited by actinides are compiled below in the tabular form. Some of them are stable but most of these oxidation states are unstable. It may be seen from these oxidation states that the +2 state is shown by Th and Am only in the few compounds like $ThBr_2$, ThI_2, ThS, etc. The +3 oxidation state is exhibited by all the elements and it becomes more and more stable as the atomic number increases. The +4 oxidation state is shown by the elements from Th to Bk, the +5 oxidation state by Th to Am, the +6 state by the elements from U to Am and the +7 state is exhibited by only two elements, viz., Np and Pu. Np in the +7 state acts as an oxidising agent. The principal cations given by actinide elements are M^{3+}, M^{4+} and oxo-cations such as MO^{2+} (oxidation state of M = + 5) and $MO2^{2+}$ (oxidation state of M = +6). The examples of oxo-cations are UO^{2+}, PuO^{2+}, $UO2^{2+}$ and $PuO2^{2+}$ which are stable in acid and aqueous solutions. Most of the M^{3+} ions are more or less stable in aqueous solution. Np^{3+} and

Pu^{3+} ions in solution are oxidized to Np^{4+} and Pu^{4+} by air. The latter ions are further oxidized slowly to $UO2^{2+}$ and $PuO2^{2+}$ by air. The lighter elements up to Am show variable oxidation states, the maximum being for Np, Pu and Am, but the heavier elements show oxidation state of +2 or +3.

2.2 MAGNETIC AND SPECTRAL PROPERTIES:

It has already been mentioned that the paramagnetic nature of the substances is due to the presence of unpaired electrons. The actinide elements like lanthanides show paramagnetism in the elemental and ionic states. Tetravalent thorium (Th4+) and hexavalent uranium (U6+) ions are diamagnetic due to the absence of unpaired electrons. Th4+ = U6+ = Rn (Z= 86) structure (diamagnetic, paired electrons). Since, actinides constitute second f-series, it is natural to expect similarities with lanthanides (the first f series) in their magnetic and spectroscopic properties. But there are some differences between the lanthanides and actinides. Spin-orbit coupling is strong (2000-4000cm-1) in the actinides as happens in the lanthanides but because of the greater exposure of the 5f-electrons, crystal field splitting is now of comparable magnitude and J is no longer such a good quantum number. It is also noted that 5f and 6d subshells are sufficiently close in energy for the lighter actinides to make 6d levels accessible. As a result, each actinide compound has to be considered individually. This must allow the mixing of J levels obtained from Russel-Saunders coupling and population of thermally available excited levels. Accordingly, the expression $\mu = g\ J(J+1)$ is less applicable than for the lanthanides and magnetic moment values obtained at room temperature are usually lower and are much more temperature dependent than those obtained for compounds of corresponding lanthanides. The electronic spectra of actinide compounds arise from the following three types of electronic transitions:

(a) ***f-f transitions***: These are Laporte (orbitally) forbidden but the selection rule in relaxed partially by the action of crystal field in distorting the symmetry of the metal ion. Because the actinides show greater field, hence the bands are more intense. These bands are narrow and more complex, are observed in the visible and UV regions and produce the colours in aqueous solutions of simple actinide salts.

(b) ***5f-6d transitions***: These are Laporte and spin allowed transitions and give rise to much more intense bands which are broader. They occur at lower energies and are normally confined to the UV region hence do not affect the colours of the ions.

(c) ***Metal to ligand charge transfer***: These transitions are also fully allowed and produce broad, intense absorptions usually found in UV region, sometimes trailing in the visible region. They produce the intense colours which are characteristic of the actinide complexes. The spectra of actinide ions are sensitive to the crystal field effects and may change from one compound to another. It is not possible to deduce the stereochemistry of actinide compounds due to complexity of the spectra. Most of the actinide cations and salts are coloured due mainly to f-f transitions. Those with f0, f7 and f14 configurations are colourless. The colours of some of the compounds in different oxidation states are given below:

$NpBr_3$: green; NpI_3 : brown; $NpCl_4$: red-brown; NpF_6 : brown
PuF_3 : purple; $PuBr_3$: green; PuF_4 : brown; PuF_6 : red brown
AmF_3 : pink; AmI_3 : yellow; AmF_4 : dark tan.

The coordination chemistry of actinides is more concerned with aqueous solutions. Because of the wider range of oxidation states available in actinides, their coordination chemistry is more varied. Most of the actinide halides form complex compounds with alkali metal halides. For example, $ThCl_4$ with KCl forms complexes such as $K[ThCl_5]$ and $K_2[ThCl_6]$, etc. $ThCl_4$ and $ThBr_4$ also form complexes with pyridine, e.g. $ThCl_4$.py Chelates are formed by the actinides with multidentate organic reagents such as oxine, EDTA, acetyl acetone, etc. The actinides with small size and high charge have the greatest tendency to form complexes. The degree of complex formation for the various ions decreases in the order: $M^{4+} > MO2^{2+} > M^{3+} > MO^{2+}$.
The complexing power of different anions with the above cations is in the order:
Monovalent anions : F- > NO^2 - > Cl-   Bivalent anions : $CO_3^{2-} > C_2O_4^{2-} > SO_4^{2-.}$

2.3 SYNTHESIS:

Apart from thorium, protactinium, and uranium, the actinides are obtained by a bombardment process of some kind. Thus for actinium (and also protactinium):

226Ra + 1 n → 227Ra + γ ;   227Ra → 227Ac + β− 230
Th + 1 n → 231Th + γ ;   231Th → 231Pa + β−

Similarly, for the elements directly beyond uranium:

238U + 1 n → 239U + γ ;   239U → 239Np + β−;   239Np → 239Pu + β−
and 238U + 1 n → 237U + 21 n;   237U → 237Np + β−

For obvious reasons, this route is not likely to be followed in the future; instead, heavy ion-bombardment, using particles such as 11B, 12C, and 16O, will be used, though more recently heavier ones like 48Ca and 56Fe have been utilized. This route is reliable but has the twin drawbacks (from the point of view of yield) of requiring a suitable actinide target and also being an atom-at-a-time route. Examples include:
244Cm + 4 He → 247Bk + 1 H
253Es + 4 He → 256Md + 1 n
248Cm + 18O → 259No + 3 1 n + 4 He
249Cf + 12C → 255No + 2 1 n + 4 He
248Cm + 15N → 260Lr + 3 1 n
249Cf + 11B → 256Lr + 4 1 n

HALIDES

The compounds known are summarized in Table 10.1. The only compound of an early actinide in the +2 state is ThI2, a metallic conductor which is probably Th4+ (e−)2 (I−)2. Certain heavier actinides form MX_2 (Am, Cf, Es), which usually have the structure of the corresponding EuX_2 and are thus genuine M2+ compounds. All four trihalides exist for all the actinides as far as Es, except for thorium and protactinium. Tetrafluorides exist for Th–Cm and the other tetrahalides as far as NpX_4 (and in the gas phase in the case of PuCl4). Pentahalides are only known for Pa, U, and Np; whilst there are a few MF_6 (M = U–Pu), uranium is the only actinide to form a hexachloride. The known actinide halides are generally stable compounds; most are soluble in (and hydrolysed by) water.

SIMILARITIES BETWEEN LANTHANIDES AND ACTINIDES

- In the atoms of the elements of both the series, three outermost shells are partially filled and remaining inner shells are completely filled but the additional or differentiating electron enters (n-2) f-subshell.
- The elements of both series exhibit +3 oxidation state which is prominent and predominant state.
- Like Lanthanide contraction found in the lanthanide elements, there occurs contraction in size in the actinide elements called actinide contraction. Both the contractions are due to poor shielding effect produced by f-electron with increasing nuclear charge.
- The elements of both the series are quite reactive and are electropositive.
- The electronic absorption bands of the elements of both the series are sharp and appear like lines. These bands are produced due to f-f transitions within (n-2)f-subshell though such transitions are orbital forbidden.
- Most of the lanthanide and actinide cations are paramagnetic.
- The nitrates, perchlorates and sulphates of trivalent lanthanide and actinide elements are soluble while the hydroxides, fluorides and carbonates of these elements are insoluble.
- The lanthanide and actinide elements show similarity in properties among their series though the lanthanides are closer among them sieves in properties as compared to actinides.

DIFFERENCES BETWEEN LANTHANIDES AND ACTINIDES

Lanthanides	Actinides
1. From left to right along 4f series, the decrease of atomic size is nor regular with increase in atomic number. But decrease of ionic radius is regular	1. From left to right along 5f series, the decrease of atomic size and ionic radius is regular.
2. Along with +3 oxidation state, +2 and +4 oxidation state are also observed.	2. Along with +3 oxidation state, +4, +5, +6 and +7 oxidation state are also observed.
3. Lanthanide compounds are less basic.	3. Actinide compounds are more basic.
4. Ability to form complex compound is low.	4. Ability to form complex compound is high.
5. They does not form oxocation.	5. They form oxocation.
6. Except Pm, other lathanides are non-radioactive.	6. All actinides are radioactive

References:

1. Textbook of Inorganic chemistry by J.D. Lee.