Organometallic Compounds

CC CHE 501 (Inorganic Chemistry)

Unit : II (23 Marks)

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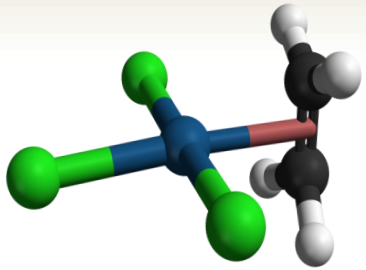
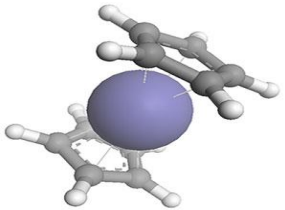
Chemistry Dept'
Science College, Himatnagar

Syllabus

- Definition
- Classification
- Nomenclature
- Structure and Bonding Dihapto & Pentahapto
- OMC of ‘Li’ and ‘Al’





Organometallic Chemistry

References……

1. Organometallic compounds; Dr. Indrajeet Kumar; Pragati Prakashan
2. Organometallic and Bioinorganic Chemistry; 2nd Ed.;Ajai Kumar
3. Organometallic Chemistry; 1st Ed.; Gurudeep Chatwal; Himalaya Publishing house.
4. Organometallic Chemistry; 2nd Ed.; R.C.Mehrotra, A.Singh; New age International limited.
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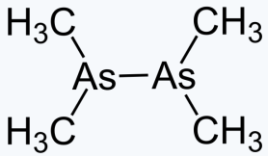
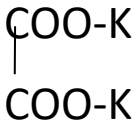
6. Inorganic Chemistry; James E. Huheey, Ekken A.Keuker, Richard L.keuker

first organometallic compound

Cacodyl

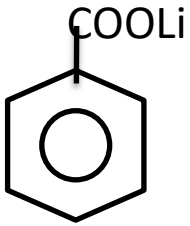
Dimethylarsinous anhdride.

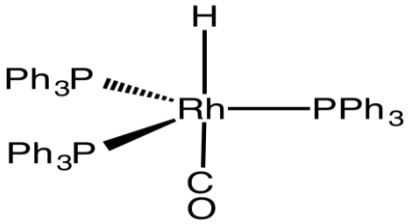


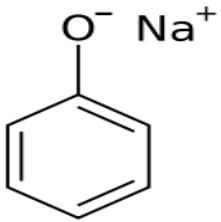


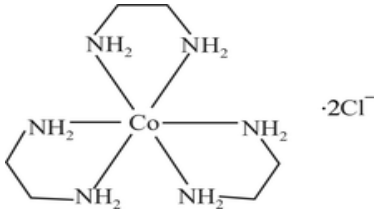
CH_3COONa

CH_3COOK









COMPOUND CONTAIN **METAL + ORGANIC GROUP**

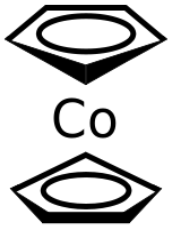
METALO-ORGANIC COMPOUNDS OR ORGANIC DERIVETIVE OF METAL

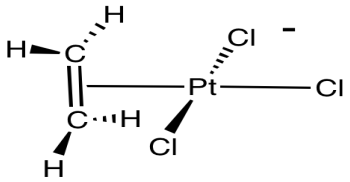
R-Mg-X

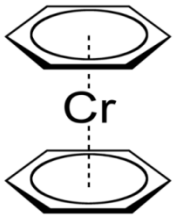
R= ORGANIC GROUP
X = Cl,Br,I…

M(CO)x

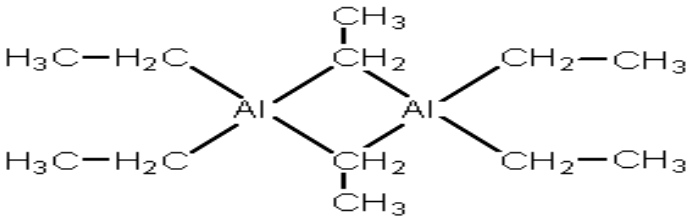
Metalcarbonyl



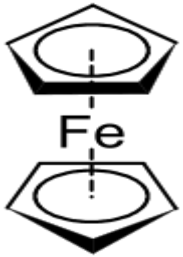


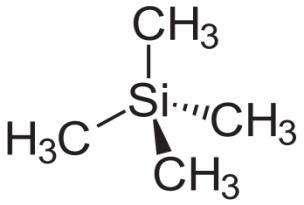


$[Pt(C_2H_4)Cl_3]^-$



topologische Formel





COMPOUND CONTAIN **METAL + ORGANIC GROUP**

METALO-ORGANIC COMPOUNDS OR ORGANIC DERIVETIVE OF METAL

ORGANOMETALLIC COMPOUNDS

1. At least one Metal-Carbon bond.
2. One or More than one Carbone atom of Alkyl, aryl, Saturated, Unsaturated, Heterocyclic etc. organic compound are attached with metal.
3. M-C bond are may be ionic, Covalent (σ *or* π) or *nC-ne* (non classified bond)
4. All metal formed OMC except Noble gases.

ORGANOMETALLIC COMPOUNDS

✓Those metal having electro negativity less then C=2.55 are formed OMC with organic group.

EN of Metals less then 2.55 $M^{+\delta} \longrightarrow C^{-\delta}$

EN of Metals greeter than 2.55 $M^{-\delta} \longleftarrow C^{+\delta}$

H 2.1																
Li 1.0	Be 1.5											B 2.0	C 2.5	N 3.0	O 3.5	F 4.0
Na 0.9	Mg 1.2											Al 1.5	Si 1.8	P 2.1	S 2.5	Cl 3.0
K 0.8	Ca 1.0	Sc 1.3	Ti 1.5	V 1.6	Cr 1.6	Mn 1.5	Fe 1.8	Co 1.9	Ni 1.8	Cu 1.9	Zn 1.6	Ga 1.6	Ge 1.8	As 2.0	Se 2.4	Br 2.8
Rb 0.8	Sr 1.0	Y 1.2	Zr 1.4	Nb 1.6	Mo 1.8	Tc 1.9	Ru 2.2	Rh 2.2	Pd 2.2	Ag 1.9	Cd 1.7	In 1.7	Sn 1.8	Sb 1.9	Te 2.1	I 2.5
Cs 0.7	Ba 0.9	Lu	Hf 1.3	Ta 1.5	W 1.7	Re 1.9	Os 2.2	Ir 2.2	Pt 2.2	Au 2.4	Hg 1.9	Tl 1.8	Pb 1.9	Bi 1.9	Po 2.0	At 2.2

Classification of OMC

- by basis of Composition
- by position of Metal in the Periodic Table
- by Metal-Carbone bond
- By Hapticity

Classification (Type- 1) of Organometallic compounds

OMC Classified by basis of Composition

1. Simple OMC

Only Hydrocarbon organic group

Al(CH3)3; B(CH3)3; $Si(CH_3)_2(C_2H_4)_2$

2. Mixed OMC

Hydrocarbon and Inorganic group

R-Mg-X, $(CH3)_2Sn\ Cl_2$; Zeise's solt

Symmetrical OMC

Only one type organic group

Al(CH3)3; B(CH3)3; Ferrocine

Unsymmetrical OMC

More than one type of organic group

$Si(CH_3)_2(C_2H_4)_2$; $CH_3\ Zn\ C_2H_5$

Classification (Type- 2) of Organometallic compounds

OMC are Classified by position of Metal in the Periodic Table.

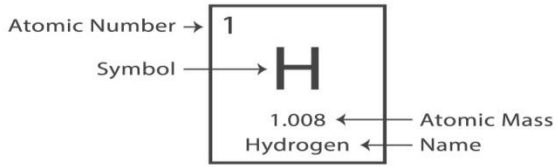
Main group OMC

s-block &
p-block ele.
Ionic
and
σ-covalent
bond

Transition metal group OMC

d & f –block
ele.
π-bond
(N.C.Bond)
nC-ne

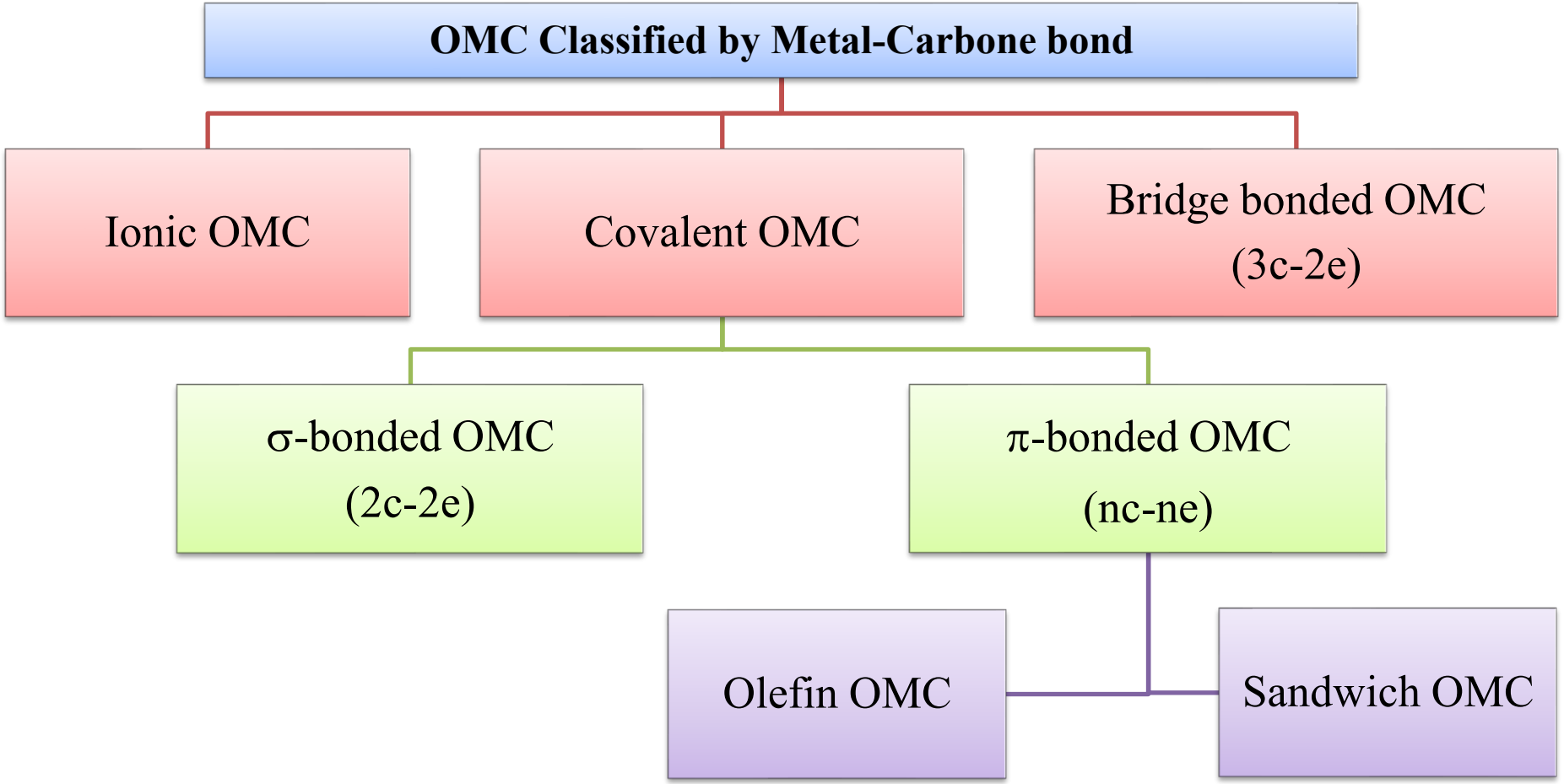
PERIODIC TABLE OF THE ELEMENTS



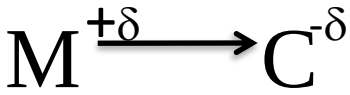
1 H 1.008 Hydrogen																	2 He 4.002602 Helium
3 Li 6.94 Lithium	4 Be 9.0121831 Beryllium											5 B 10.81 Boron	6 C 12.011 Carbon	7 N 14.007 Nitrogen	8 O 15.999 Oxygen	9 F 18.998403163 Fluorine	10 Ne 20.1797 Neon
11 Na 22.98976928 Sodium	12 Mg 24.305 Magnesium											13 Al 26.9815385 Aluminium	14 Si 28.085 Silicon	15 P 30.973761998 Phosphorus	16 S 32.06 Sulfur	17 Cl 35.45 Chlorine	18 Ar 39.948 Argon
19 K 39.0983 Potassium	20 Ca 40.078 Calcium	21 Sc 44.955908 Scandium	22 Ti 47.867 Titanium	23 V 50.9415 Vanadium	24 Cr 51.9961 Chromium	25 Mn 54.938044 Manganese	26 Fe 55.845 Iron	27 Co 58.933194 Cobalt	28 Ni 58.6934 Nickel	29 Cu 63.546 Copper	30 Zn 65.38 Zinc	31 Ga 69.723 Gallium	32 Ge 72.630 Germanium	33 As 74.921595 Arsenic	34 Se 78.971 Selenium	35 Br 79.904 Bromine	36 Kr 83.798 Krypton
37 Rb 85.4678 Rubidium	38 Sr 87.62 Strontium	39 Y 88.90584 Yttrium	40 Zr 91.224 Zirconium	41 Nb 92.90637 Niobium	42 Mo 95.95 Molybdenum	43 Tc 98 Technetium	44 Ru 101.07 Ruthenium	45 Rh 102.90550 Rhodium	46 Pd 106.42 Palladium	47 Ag 107.8682 Silver	48 Cd 112.414 Cadmium	49 In 114.818 Indium	50 Sn 118.710 Tin	51 Sb 121.760 Antimony	52 Te 127.60 Tellurium	53 I 126.90447 Iodine	54 Xe 131.293 Xenon
55 Cs 132.90545196 Caesium	56 Ba 137.327 Barium	57/71	72 Hf 178.49 Hafnium	73 Ta 180.94788 Tantalum	74 W 183.84 Tungsten	75 Re 186.207 Rhenium	76 Os 190.23 Osmium	77 Ir 192.217 Iridium	78 Pt 195.084 Platinum	79 Au 196.966569 Gold	80 Hg 200.592 Mercury	81 Tl 204.38 Thallium	82 Pb 207.2 Lead	83 Bi 208.98040 Bismuth	84 Po 209 Polonium	85 At 210 Astatine	86 Rn 222 Radon
87 Fr 223 Francium	88 Ra 226 Radium	89/103	104 Rf 267 Rutherfordium	105 Db 268 Dubnium	106 Sg 269 Seaborgium	107 Bh 270 Bohrium	108 Hs 269 Hassium	109 Mt 278 Meitnerium	110 Ds 281 Darmstadtium	111 Rg 281 Roentgenium	112 Cn 285 Copernicium	113 Uut 286 Ununtrium	114 Fl 289 Flerovium	115 Uup 289 Ununpentium	116 Lv 293 Livermorium	117 Uus 294 Ununseptium	118 Uuo 294 Ununoctium

Lanthanide Series	57 La 138.90547 Lanthanum	58 Ce 140.116 Cerium	59 Pr 140.90766 Praseodymium	60 Nd 144.242 Neodymium	61 Pm 145 Promethium	62 Sm 150.36 Samarium	63 Eu 151.964 Europium	64 Gd 157.25 Gadolinium	65 Tb 158.92535 Terbium	66 Dy 162.500 Dysprosium	67 Ho 164.93033 Holmium	68 Er 167.259 Erbium	69 Tm 168.93422 Thulium	70 Yb 173.054 Ytterbium	71 Lu 174.9668 Lutetium
Actinide Series	89 Ac 227 Actinium	90 Th 232.0377 Thorium	91 Pa 231.03588 Protactinium	92 U 238.02891 Uranium	93 Np 237 Neptunium	94 Pu 244 Plutonium	95 Am 243 Americium	96 Cm 247 Curium	97 Bk 247 Berkelium	98 Cf 251 Californium	99 Es 252 Einsteinium	100 Fm 257 Fermium	101 Md 258 Mendelevium	102 No 259 Nobelium	103 Lr 266 Lawrencium

Classification (Type- 3) of Organometallic compounds



[1] Ionic OMC :



- M-C Bond is Ionic bond. (2C-2e bond)
- Highly electropositive Metals such as Alkali (I-group), Alkaline earth (II-group) and lanthanide and actinide metal.
- Carbone of Organic Compounds is Negative charged (Carbanion ion)
- Example: CH_3K, C_2H_5Na, $Ca(C_2H_5)_2$,

  $C_{10}H_8Na$ (Sodium Naphthalemide) C_6H_6Na.

[2] Covalent OMC :

- M-C Bond is covalent σ OR π bond.
- Bond may be localized or delocalized between one or more Carbone of organic group.
- Sub divided into following types.

(2A) σ-Bonded OMC

(2B) π-Bonded OMC

(2A) σ-Bonded OMC

M-C Bond is covalent bond. (2C-2e)

- Bond may be localized Metal and one Carbone of organic group.
- This OMC are formed by p-Block element

  (Electronegative charge is 1 to 2.5).
- *Some d-block element are also form this type of OMC (W, Mn..)*
- Examples: $B(CH_3)_3$; $Al(CH_3)_3$; $Si(CH_3)_4$; $Pb(CH_3)_4$

(2B) π-Bonded OMC

M-C Bond is π -bond. (*nC-ne*)

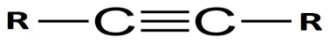
- Bond may be delocalized between Metal and more than two Carbone of organic group.
- This OMC are formed by *d*-Block element.
- Divided into two part by types of organic group.

[2B(i)] Ollifinic π-Bonded OMC

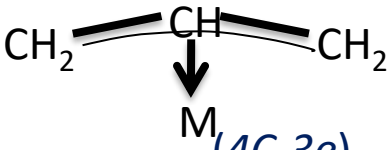
[2B(ii)] Sandwich π-Bonded OMC

[2B(i)] Ollifinic π-Bonded OMC

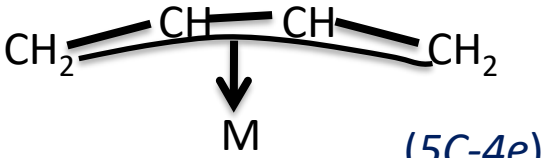
Aliphatic Organic group containing delocalized π- electron formed this type of OMC.

[Containing C=C anc ]

(*3C-2e*)



(*4C-3e*)



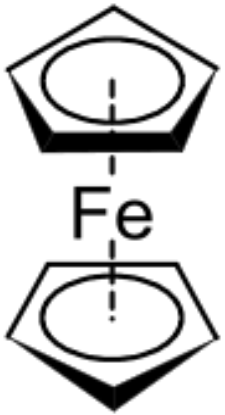
(*5C-4e*)

Zeise's solt $K[Pt(C_2H_4)Cl_3]^-$

[2B(ii)] Sandwich π-Bonded OMC

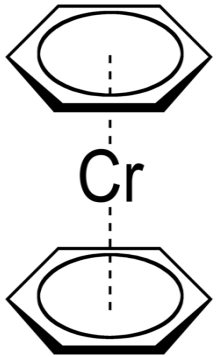
Aromatic Organic group containing delocalized π- electron formed this type of OMC.

Two Aromatic ring attached with one metal to giving delocalized π- electron to the Metal.



(*6C-5e*)

$Fe(C_5H_5)_2$.



(*7C-6e*)

$Cr(C_6H_5)_2$

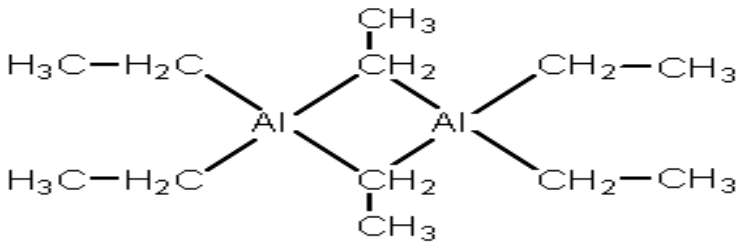
[3] Bridge bonded OMC :

- *3C-2e* bond.
- Alkali or Arial group act as bridging legend.
- Electron deficient OMC.

$Al_2(C_2H_5)_6$
OR
$Al_2(C_2H_5)_4(\mu\text{-}C_2H_5)_2$

$Al_2(C_6H_5)_6$
OR
$Al_2(C_6H_5)_4(\mu\text{-}C_6H_5)_2$

$[Mg(CH_3)_2]_n$
Polymeric dimethylmegnesium



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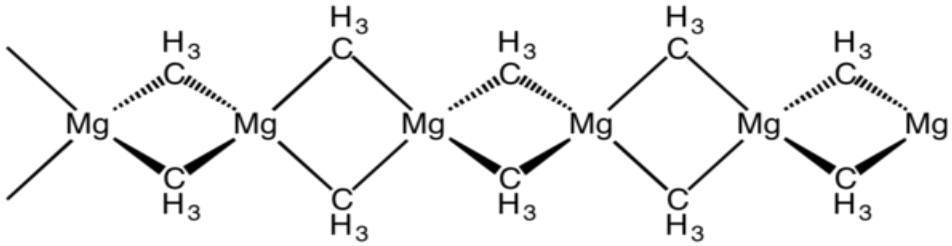


Classification (Type- 4)

OMC Classified by Hapticity

Haptein -
Bind - જોડાવું

Hapticity

Number of Carbone atom of an organic group or molecules which are directly bonded to the Metal

-Indicate by h^n Or η^n ;

where *n*= No. of Carbon atom attached by single bond.

1. Mono-hapto OMC (h^1 Or η^1 –OMC)

• Only one Carbone atom of organic compound is directly bonded with metal is called…..
• Alkanes, alkenes, alkynes, aryls ect. Almost all organic compounds
•Bond of metal- Carbone are Ionic, Covalent, Coordination,
•Type of Metal-Carbone bond is *2C-2e*

•Example:

•Li-CH_3 ; Na-C_6H_5 ; Mg-$CH{=}CH_2$;
•Metal carbonyl $Ni(CO)_4$;$Fe(CO)_5$

2. Di-hapto OMC (h^2 Or η^2 –OMC)

• Only two Carbone atom of organic compound is attached through only bond with metal is called…..

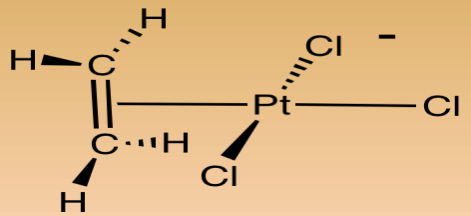
• Unsaturated organic compounds contain π-electron (alkenes, alkynes, aryls) ect.

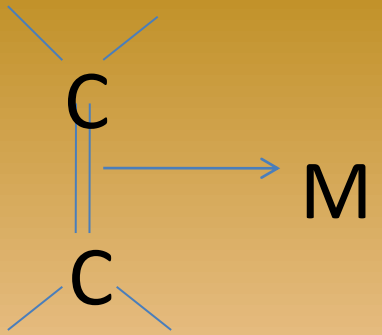
•Bond of metal- Carbone are Non classified π- bond,

•Type of Metal-Carbone bond is *3C-2e*

•Example:

$K[PtCl_3(C_2H_4)]$



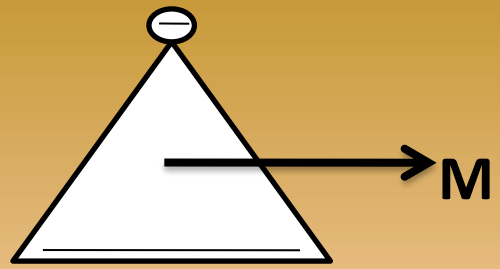


3. Tri-hapto OMC (h^3 Or η^3 –OMC)

- Only three Carbone atom of organic compound is attached through only bond with metal is called…..
- Unsaturated organic comp. contain delocalized π-electron
- Bond of metal- Carbone are Non classified π- bond
- Type of Metal-Carbone bond is *4C-3e*

- Example:

$$CH_2 = CH - CH_2^-$$



$[Mn(\eta^3 - C_3H_5)(CO)_4]$

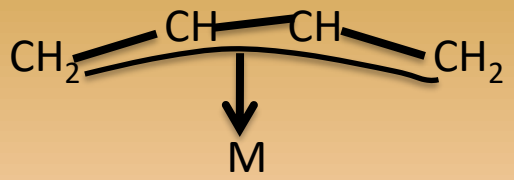
M

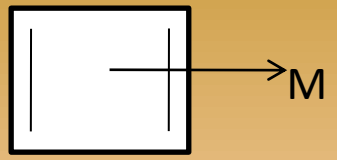
4. Tetra hapto OMC (h^4 Or η^4 –OMC)

- Only four Carbone atom of organic compound is attached through only bond with metal is called…..
- unsaturated organic comp. contain delocalized π-electron
- Bond of metal- Carbone are Non classified π- bond
- Type of Metal-Carbone bond is *5C-4e*

- Example:

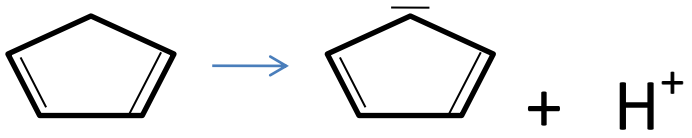
$CH_2 = CH - CH = CH_2$





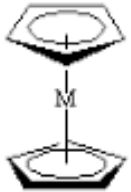
$[Fe(CO)_3(C_4H_4)]$

5. Penta hapto OMC (h^5 Or η^5 –OMC)



$Fe(C_5H_5)_2; ferrocene$

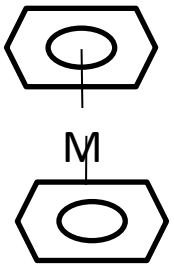
Sandwich π-bonded OMC



6C-5e

6. Hexa hapto OMC (h^6 Or η^6 –OMC)

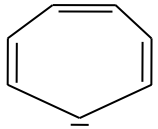
$Cr(C_6H_6)_2; dibenzenecromium$



7C-6e

7. Hepta hapto OMC (h^7 Or η^7 –OMC)

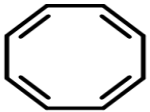
$[Mo(CO)_3(C_7H_7)]BF_4^-$



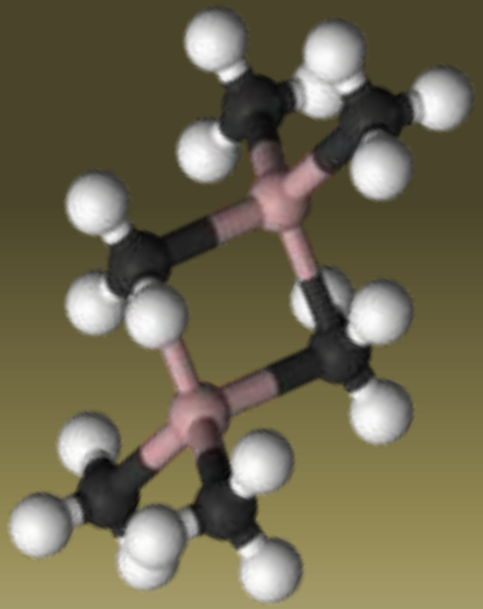
8C-7e

8. Octa hapto OMC (h^8Or η^8 –OMC)

$[U(\eta^8 - C_8H_8)_2]; uranocine$



9C-8e



Nomenclature of **Organometallic Compound** by IUPAC

International Union of Pure and Applied Chemistry

Similar to Coordination compound

Dr.N.I.Patel, Science College, Himatnagar

OMC classified by nature of cation and anion

- Cationic OMC
- Anionic OMC
- Neutral OMC

$[(C_6H_5)Mo(CO)_3]^+ Cl^-$

$K^+ [Pt(C_2H_4)Cl_3]^-$

$[Fe(C_5H_5)_2]$
$[Cr(C_6H_6)_2]$

(1) The cation name first and then the anionic part's name

- Name of simple Cation or Anion (out side of Coordination sphere) is simple as

ion	name	ion	name
K^{+1}	Potassium	Cl^{-1}	Chloride
Na^{+1}	sodium	SO_4^{-2}	Sulphate
NH_4^{+1}	ammonium	SO_3^{-2}	Sulphaite
Li^{+1}	lithium	NO_3^{-1}	Nitrate
Ca^{+2}	Calcium	NO_2^{-1}	Nitrite
Mg^{+2}	Magnesium	CO_3^{-2}	Carbonate
Be^{+2}	Berelium	S^{-2}	Sulphide

(2) Name of OMC (Coordination sphere)

First Name of legend with number and then Metal atom.

(a) How to Name of Legend ?

First write number of legend and then name of legend

1. Name of Anionic legends:

-ide,(આઇડ)-ite,(આઇટ)-ate (એટ) suffix Replaced by –'o'.(ઓ)

Example:	Cl^-,	Chloride, -Chloro;	SO_3^{-2} Sulphite -sulphito
	NO_3^-,	Nitrite, -Nitro;	SO_4^{-2} Sulphate - sulpheto
	NO_2^-	Nitriate,-Nitrieto	

2. Name of Neutral legends :

Example:

	Special Name
H_2O,	Aquo;
NH_3,	Ammine;
CO,	Carbonyl;
NO,	Nitrosyl
OH,	Hydroxyl

3. Name of Organic legends

-ane (એન) Or –e (એ) suffix replaced by '–yl' (આઈલ)

Example:

CH_4-	Methane,	Methyl,
C_4H_9,	Butane ,	Butyl,
$CH_2=CH_2$,	Ethene,	Ethenyl ,
$CH_2=CH-CH_3$	Propyne,	Propynyl
C_6H_5	Benzene ,	Phenyl

Indication of Number of Legends

For simple legends-

-di, tri, tetra, penta, hexa, hepta, octa….

For Complex legend,

(aromatic organic group, bridge bonding group)

– bis, tris, tetrais, pentais, hexais…..

Indication of Hapticity:

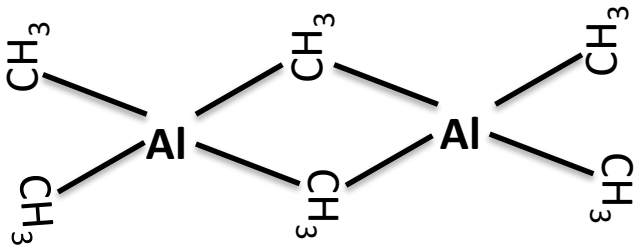
The hapticity of and organic ligand is denoted by the symbol 'η' 'eta' with appropriate numerical superscript to No. of 'C' attached with Metal. η^2 η^3 η^4

$K[PtCl_3(C_2H_4)]$

Potassium trichloro(η^2-ethenyl)platinate(II)

- **If there is bridge ligand prefix 'μ' before name of ligand.**

$Al \cdot \mu - (CH_3)_2(CH_3)_4$



Bis -μ-methyl teramethyl alluminium

- *If there are two or more different kind of legends, they are written in the **alphabetical order** irrespective of the number of legends.*

$[PtBrCl.NH_3(\eta^2 - C_2H_4)]$

TriAmminebromochloro (η^2-ethenyl)platinum

$[PtBr_2Cl.(\eta^2 - C_2H_4)]$

Dibromochloro (η^2-ethenyl)platinum

(b) Name Of Metal ion:

Anionic OMC:

Ligands are name first and then the metal ion.

To name the metal ion, the suffix –ate(એટ) is added to its name and to indicate the oxidation state in Roman Number in bracket of the metal ion.

Example:

Fe^{+2}: Ferrate(II); Ni^{+2} : Nickelate(II)

Co^{+3}; Cobaltate(III) ; Pt^{+4} :Platinate(IV)

Cationic OMC:

To simple name of metal ion with indication oxidation state in Roman Number in bracket.

Special Name Of Metal:

The name of Neutral OMC contained p-block element may be named as following….

Symbol	Name	OMC Name
Pb	Plumbs	Plumbane
B	Boron	Borane
Sb	Antimony	Stibine
Si	Silicone	Silane
Ge	Germanium	Germane
As	Arsenate	Arsine
PH_3	Phosphate	Phosphaine
Sn	Tin	Stannane

Name Of Metal In Neutral & Mixed OMC:

Ligands are name first in Alphabetical order then the metal ion.

OR

First name of Organic ligand and then metal and last inorganic ligand(simple name).

$(CH_3)_2SnBr_2$

1.Dibromo dimethyl stannane

2.Dimethyl tin dibromide

$(C_2H_5)Pb(CH_3)_3(CO)_2$

Dicarbonyl ethyal trimethyl plumbane

$(C_6H_5)Ge(C_6H_5)$

Diphynyl germane.

$(CH_3)As(C_2H_5)$

Ethyl methyl arsine.

$[Fe(\eta^4 - C_4H_4)_2(CO)_2]$ *Dicarbonylbis(η^4-cyclobutadienyl)iron*

$[Mn(\eta^5 - C_5H_5)_2(CO)_3]$

Tricarbonyl bis(η^5-cyclopentadinyl)manganese

$Cr(C_6H_6)_2$ *Bis(η^6 –phenyl)chromium*

$Fe(C_5H_5)_2$ *Bis(η^5-cyclopentadienyl)iron(0)*

$[Ni(\eta^3 - C_3H_5)_2]$ Bis(η^3-allyl(propynyl))nickel

$[PtBrCl.NH_3(\eta^2 - C_2H_4)]$

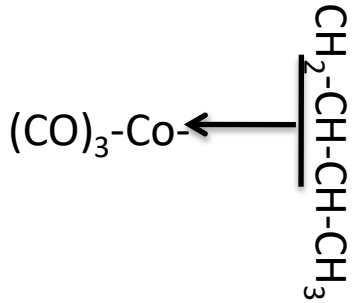
Amminebromochloro (η^2-ethenyl)platinum

$(CO)_3Fe(\mu - CH_3)_3Fe(CO)_3$ Di(Tris(μ-methyl) tricarbonyl iron)

$Al_2(CH_3)_4(\mu\text{-}CH_3)_2$. trimethylaluminium, *Bis -μ-methyl teramethyl alluminium*

$K[Sb(C_6H_6)(Cl)_5]$

Potassiumpentachlorophenylantimonate(IV)



Tricarbonyl(1-3 η^3-butenenyl) cobalt.

$K[B(C_6H_5)_4]$ Ptassium tetraphenyl borate(III)

$[B(CH_2\text{-}CH_3)_3]$ Triethyl borane

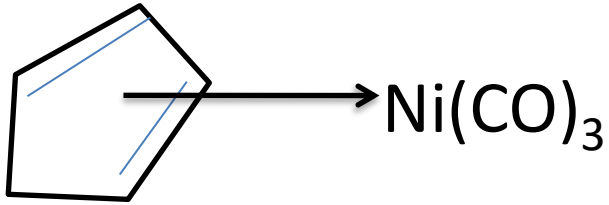
$[Co(\pi\text{-}C_3H_5)(CO)_3]$ (η^3-allyl) tricarbonyl cobalt.

$[Fe(C_4H_6)(CO)_3]$ (η^4-butadinene) tricarbonyl iron.

$Li(n\text{-}C_4H_9)$ n-butyl lithium.

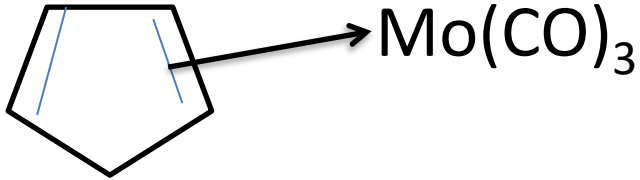
$K[Sb(C_6H_5)(Cl)_5]$ Potassium pentachloro(phenyl)atimonate.

$[Ni(\eta^4\text{-}C_5H_5)(CO)_3]$



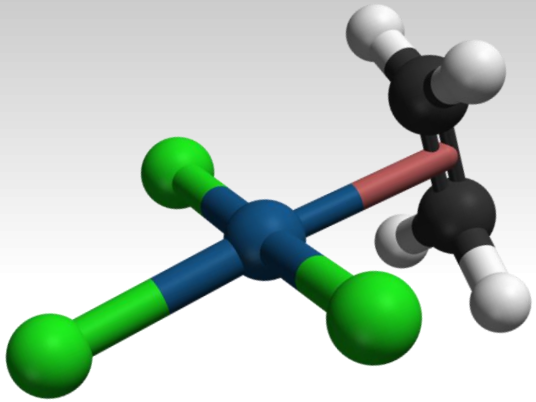
Tricarbonyl(1-4 η^4-cyclopentadinyl) nickel.

$[Mo(\eta^2\text{-}C_5H_5)(CO)_3]$



Tricarbonyl(η^2-cyclopentadinyl) mollybledum.

Di-hpto OMC or Ollifinic OMC



- ડાઈ-હેપ્ટો કાર્બધત્વિક સયોજનો સમજાવો
- ઓલિફીનીક કાર્બધત્વિક સયોજનો નોધ લખો
- Zeise's સોલ્ટ ની બનાવટ, ગુણધર્મો અને બંધારણ-બંધન સમજાવો.
- "Zeise's સોલ્ટ" નોધ લખો

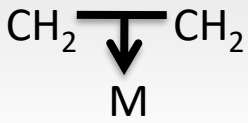
Zeise's salt $K[Pt\ Cl_3(C_2H_4)]\cdot H_2O.$

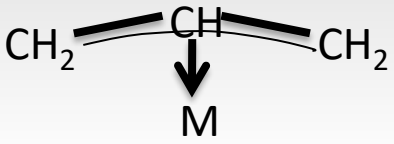
Potassium trichloro(η^2-ethenyl)platinate(II)

Ollifinic OMC

Aliphatic, Unsaturated hydrocarbon organic group like Alkain, alkaline etc.. containing delocalized π- electron are attached with metal (σ and π bond) and Gives Ollifinic OMC.

More than two "c' atom bonding with metal
and gives *di, tri, tera…hapto* OMC

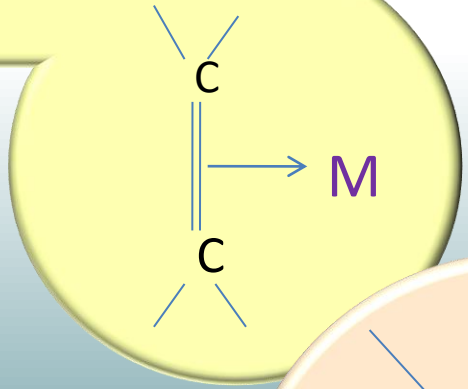


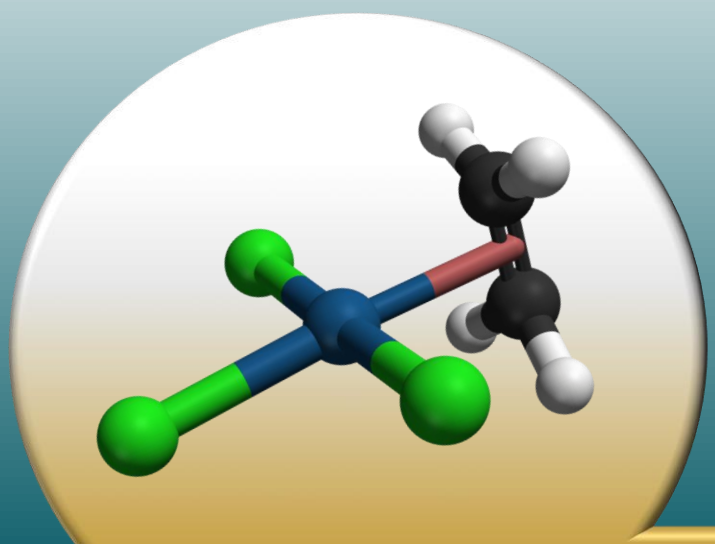


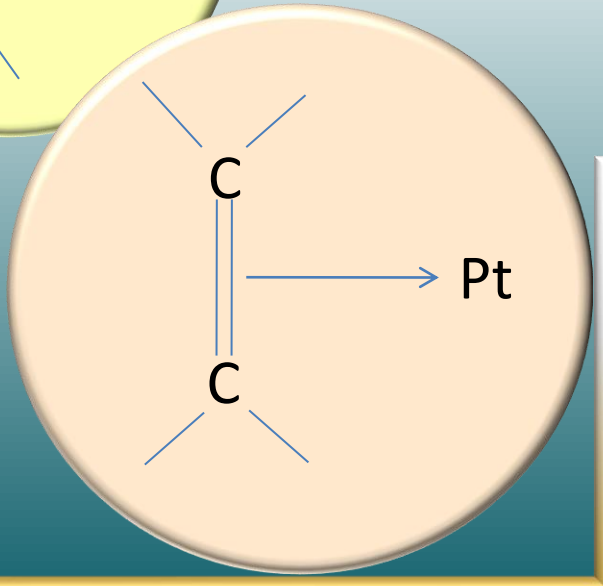
Metals are
Pt(II); Ag(I); Pd(II); Hg(II); Cu(I)

Di-hpto ollifinic OMC

η^2 -OMC





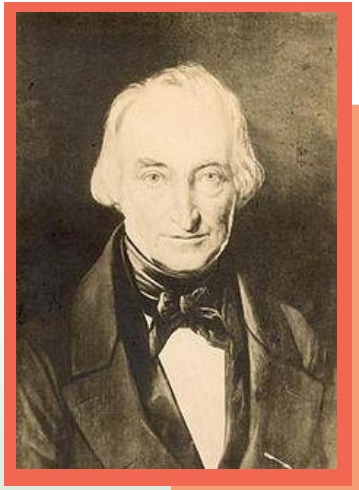


The zeise ion :

$K^+ + [PtCl_3(C_2H_4)]^-$

Zeise's solt is a example of **Di-hpto ollifinic OMC**

air-stable, yellow, coordination complex contains an η^2-ethylene ligand.



History

Zeise's salt was one of the first Organometallic compounds to be reported.

It was discovered by William Christopher Zeise, who prepared this compound in 1830 while investigating the reaction of $K_2[PtCl_4]$ with boiling ethanol.

$$K_2[PtCl_4] + C_2H_4OH \longrightarrow K[Pt(C_2H_4)Cl_3].H_2O + KCl$$

Preparation

This compound is commercially available as a mono hydrate.

$$K[Pt(C_2H_4)Cl_3] \cdot H_2O$$

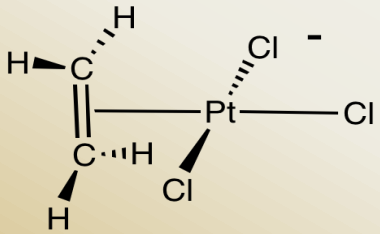
The hydrate is commonly prepared from $K_2[PtCl_4]$ and ethylene in the presence of a catalytic amount of $SnCl_2$. And than extraction with ether.

$$K_2[PtCl_4] + C_2H_4 \xrightarrow{SnCl_2} K[Pt(C_2H_4)Cl_3] + KCl$$

Properties

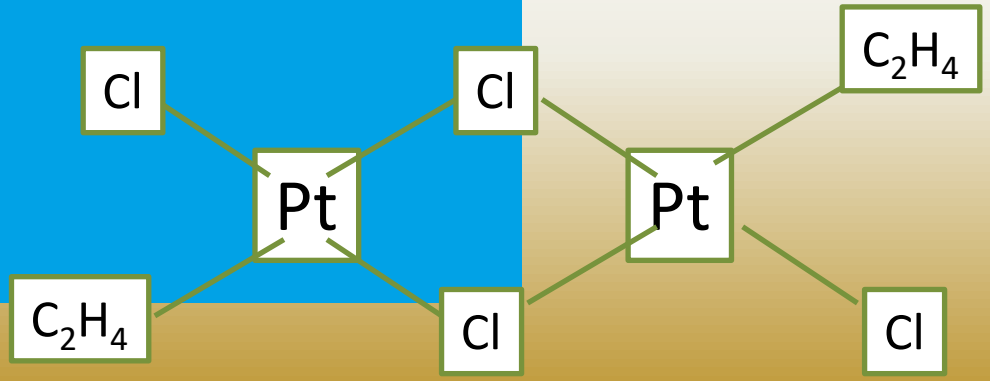
- Yellow color, solid substance
- Soluble in Benzene and Chloroform.
- Decomposed at 125°C to 130°C.
- Reaction with Pyridine , 3Cl are substituted.

$$K[Pt(C_2H_4)Cl_3] + Py \longrightarrow [Pt(C_2H_4)Py_3]$$



Properties

•Reaction with Ethonolic solution of Zeise's solt with con.HCl gives dimmer form of salt . (orange colour salt)

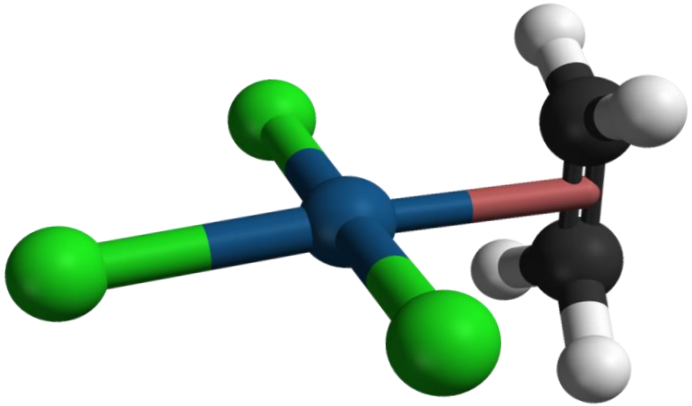


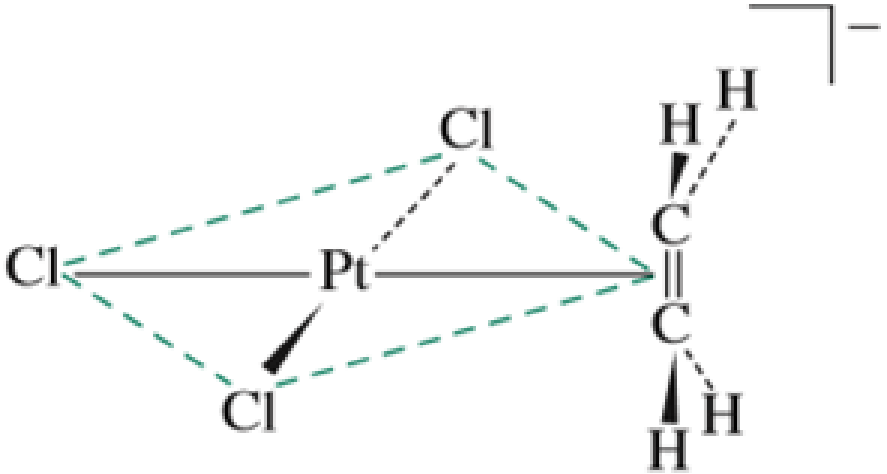
$$2K[Pt(C_2H_4)Cl_3] + Con.HCl \xrightarrow{C_2H_4OH} [Pt_2(C_2H_4)_2Cl_4] + 2KCl$$

Structure

The zeise ion structure is square planar geometry.

The alkene C=C bond is approximately perpendicular to the $PtCl_3$ plane.



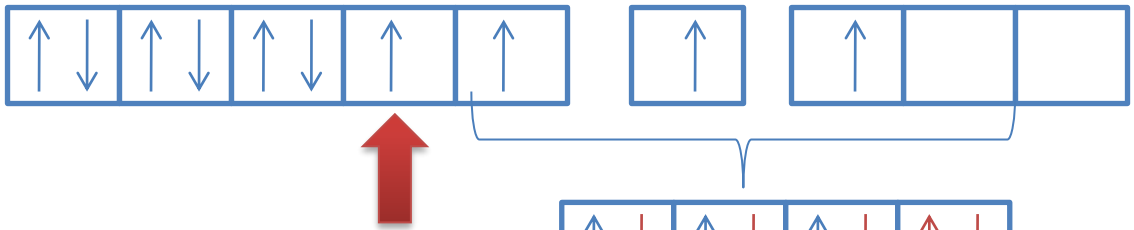


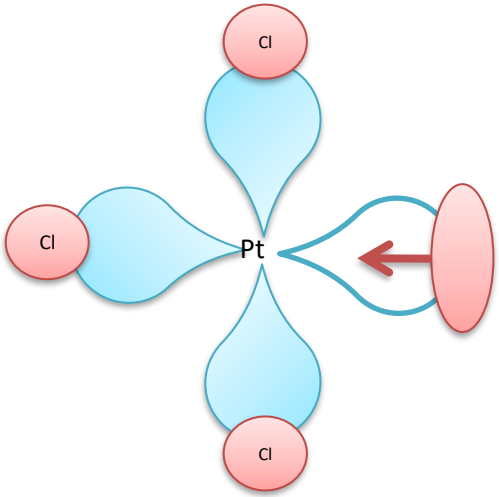
X-Rays. Bond Length C=C is 1.40 A to 1.47 A

Bonding

$Pt_{z=78}: [Xe]^{54}; 4f^{14}, 5d^{8}, 6S^{2}.$

$Pt^{*}{}_{z=78}: [Xe]^{54}; 4f^{14}, 5d^{8}, 6S^{1}, 6P^{1}.$



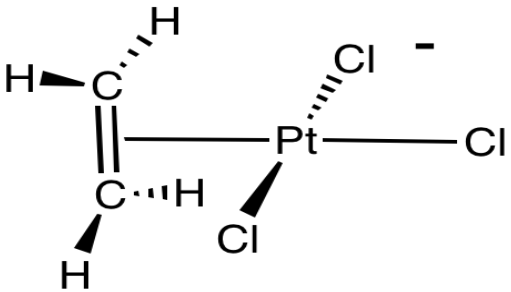


dsp^2 hybrid orbital

$K^{+} + [PtCl_3(C_2H_4)]^{-}$

Cl^{-} Cl^{-} Cl^{-}

C2H4

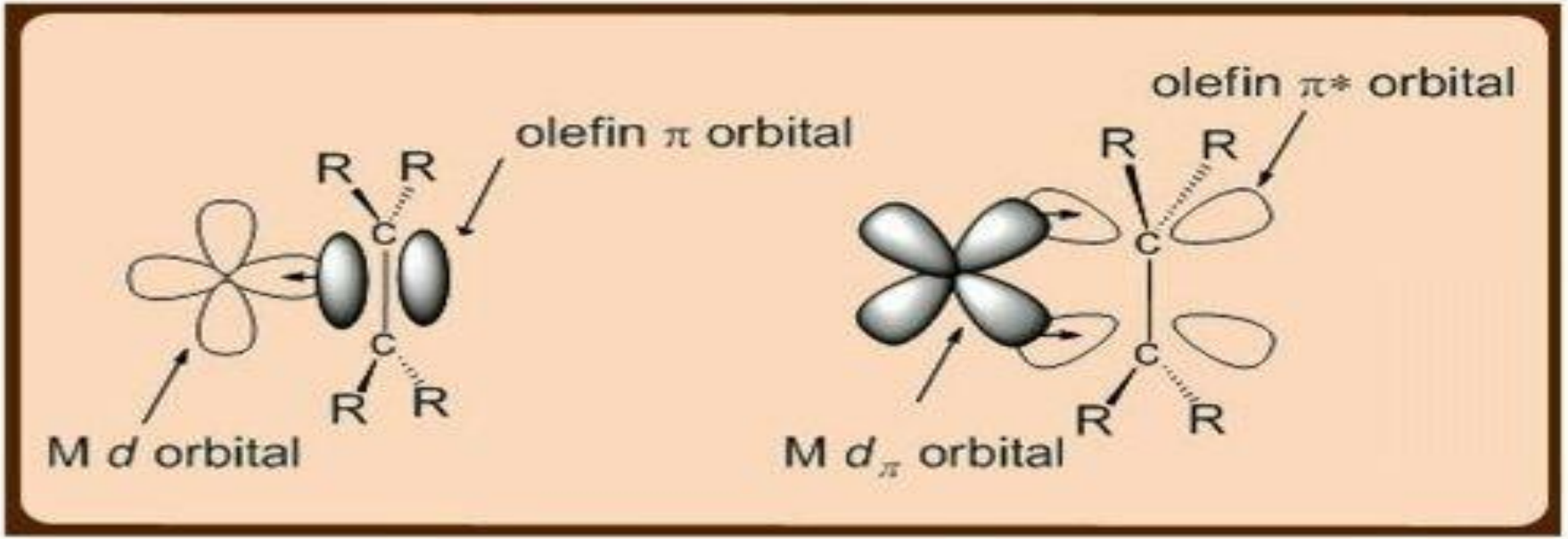


Square planer geometry

X-Rays. Bond Length C=C is 1.40 A to 1.47 A why ?

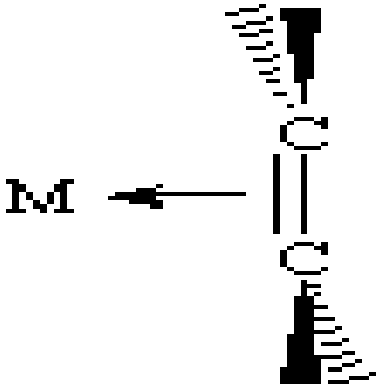
In common organic compounds

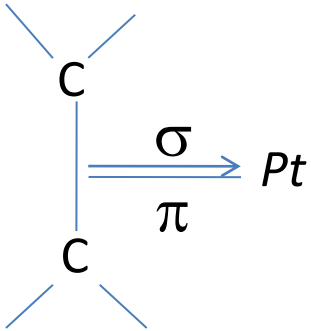
Bond length of –C-C- is 1.54 A, And –C=C- is 1.34 A

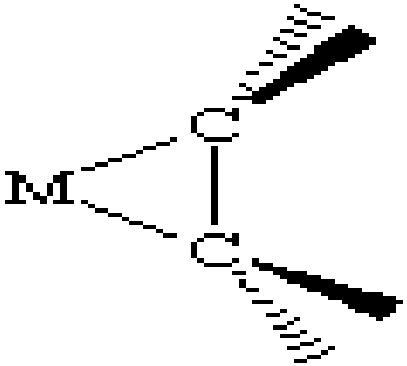


Back bonding -Back donation- dπ-pπ bonding

X-Rays. Bond Length C=C is 1.40 A to 1.47 A why ?





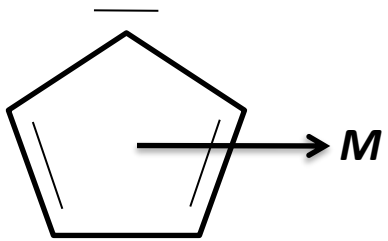


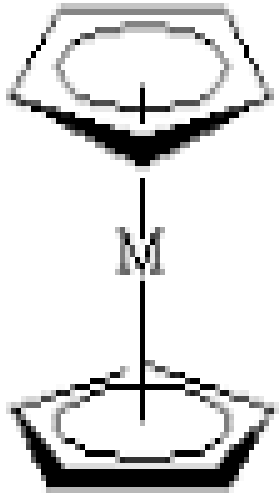
Bond Type OR nature : $d\pi$-$p\pi$

Bond order : Pt ═══ C_2H_4

Metalocene, Ferrocene, *η^{5}-OMC, Sandwich bonded OMC*

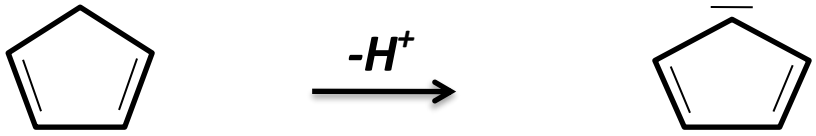
1. મેટલોસીન સયોજનો ઉપર નોધ લખો.
2. ફેરોસીન ની બનાવટ, ગુણધર્મ અને બંધારણ સમજાવો.
3. ફેરોસીન ઉપર નોધ લખો





Metallocene

✓Cyclopentadine ion having 5π delocalized electron.

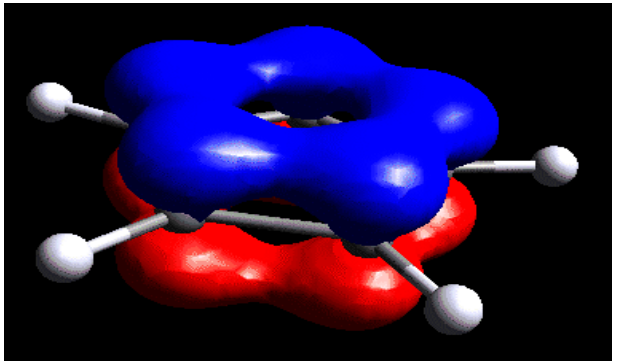


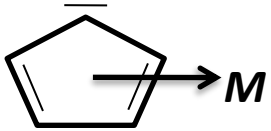
Cyclopentadien

4π localized electron

Cyclopentadien ion

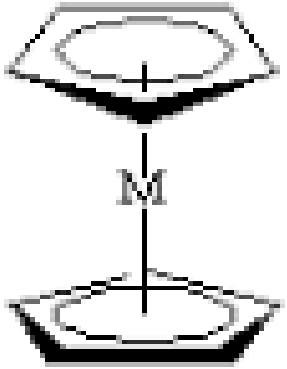
5π delocalized electron





✓CP attached with Metal to *6C-5e* bond.
✓*CP is η^5 legend make η^5OMC*

η^5 (pentahapto) sandwich structure.

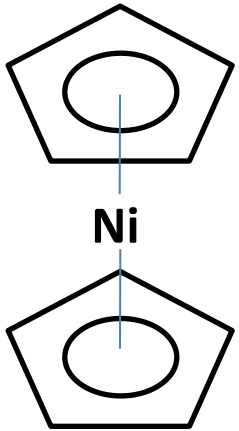


Metallocene consisting of two cyclopentadienyl rings bound on opposite sides of a central metal atom and give sandwich structure.

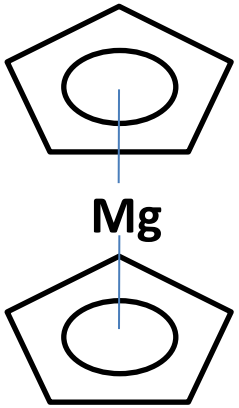
M= Mg, Ti, V, Cr, Mn, Fe, Co, Ni

η^5 (pentahapto) sandwich structure.

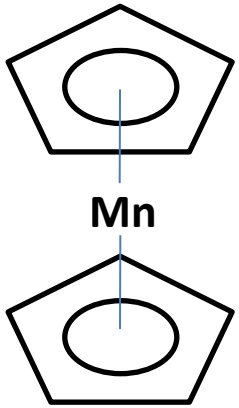
M= Mg, Ti, V, Cr, Mn, Fe, Co, Ni



Nickelocene



Magnocene



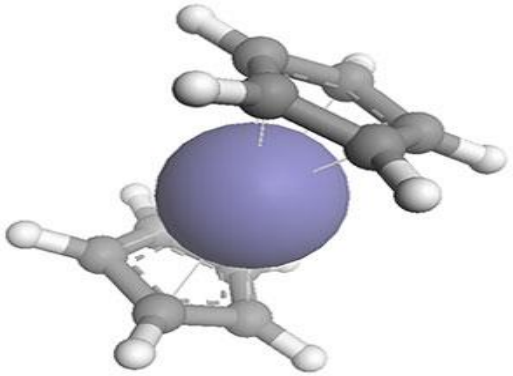
Manganocene

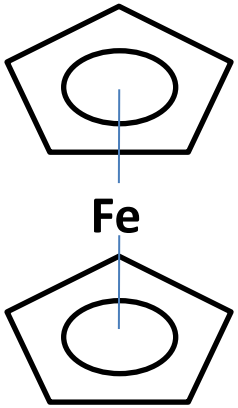
Such OMC are also known as sandwich bonded compounds.

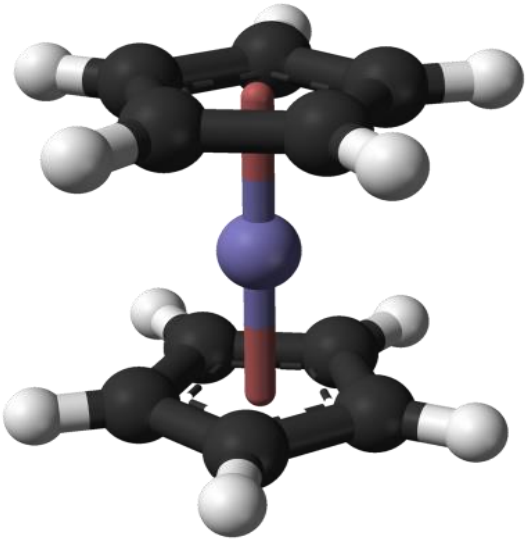
Ferrocene

[Discover in 1951]
[Important example of Metallocene]

Formula $Fe(C_5H_5)_2$.







bis(η^5-cyclopentadienyl)iron(0)

dicyclopentadienyl iron

Synthesis

[1] Synthesis of ferrocene using the Grignard reagent **cyclopentadienyl magnesium bromide**, add Iron(III) chloride is then suspended in anhydrous diethyl ether.

$$6\ C_5H_5MgBr + 2\ FeCl_3 \rightarrow 2\ Fe(C_5H_5)_2 + 6\ MgBrCl + 2\ \mathbf{(C_5H_5)_2}$$

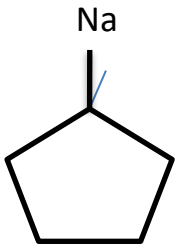
[2] The direct reaction of gas-phase cyclopentadiene with metallic iron at 300 °C or with iron pentacarbonyl

$$Fe_{(s)} + 2\ C_5H_6(g) \rightarrow Fe(C_5H_5)_2 + H_2(g)$$

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

[3] **Trans metalation;** Using commercially available sodium cyclopentadienide react with ferrous chloride:

$$2\ NaC_5H_5 + FeCl_2 \rightarrow Fe(C_5H_5)_2 + 2\ NaCl$$

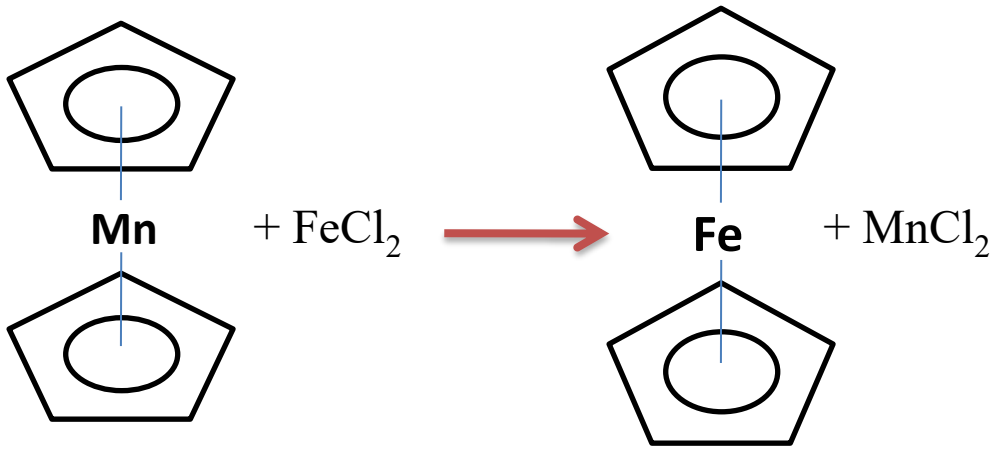


[4] Some amine bases can be used for the preparation of ferrocene.

$$2\ C_5H_6 + 2\ (CH_3CH_2)_2NH + FeCl_2 \rightarrow Fe(C_5H_5)_2 + 2\ (CH_3CH_2)_2NH_2Cl$$

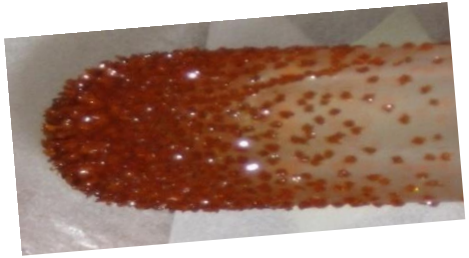
[5] Direct transmetalation can also be used to prepare ferrocene from other metallocenes, such as manganocene:

$$FeCl_2 + Mn(C_5H_5)_2 \rightarrow MnCl_2 + Fe(C_5H_5)_2$$



Properties:

- Crystals of ferrocene yellowish-orange colour.
- Camphor like order
- Ferrocine is soluble in normal organic solvents, such as benzene, but is insoluble in water.
- Crystals of ferrocene after purification by vacuum sublimation



- Ferrocene is an air-stable solid
- It is stable to temperatures as high as 400 °C.
- Diamagnetic (no unpaired ele.; $\mu = 0$)

Structure

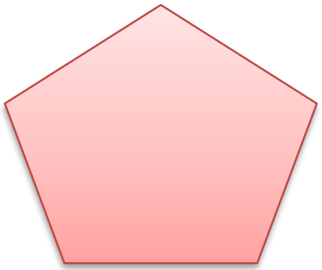
Between value of 1.33 to 1.54 A

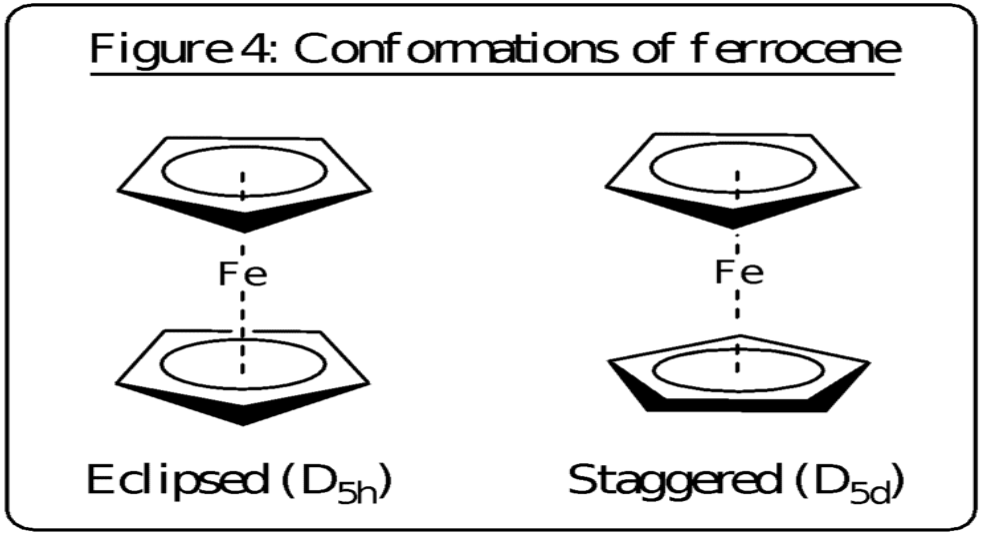
According to X-ray crystallography

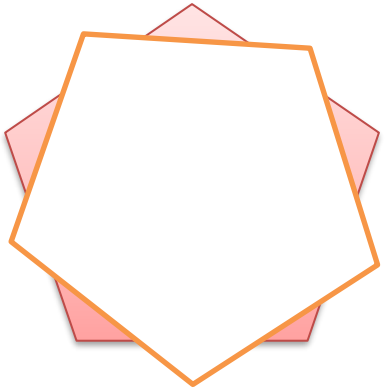
: The bond distances C-C are 1.39 Å In CP rings, Fe–C is 2.04 Å.

: η^5 (pentahapto) sandwich structure.

: The CP rings being in a staggered and eclipsed conformation,



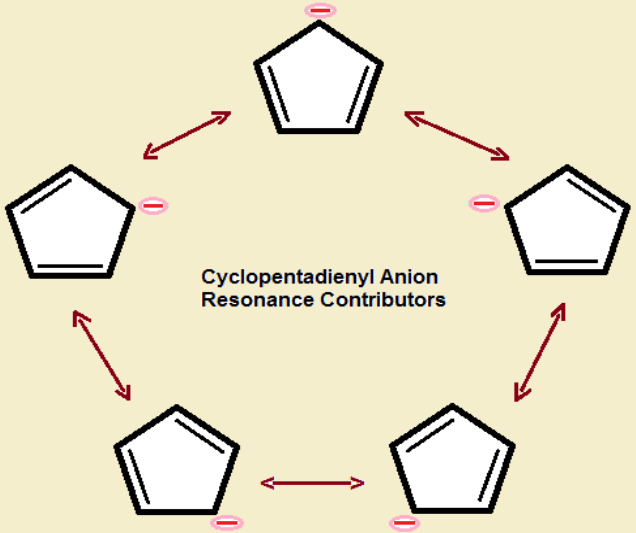




In gas phase.

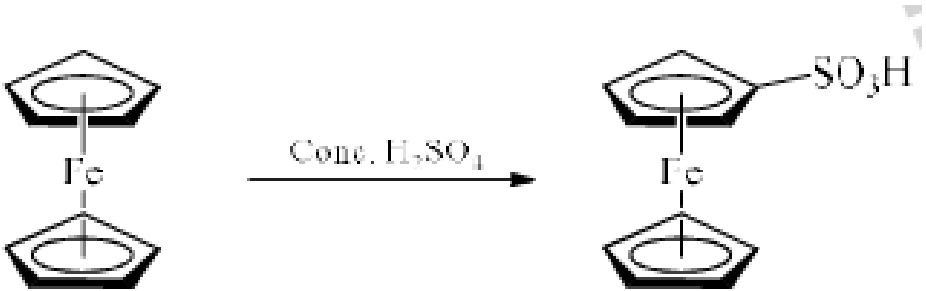
In crystal

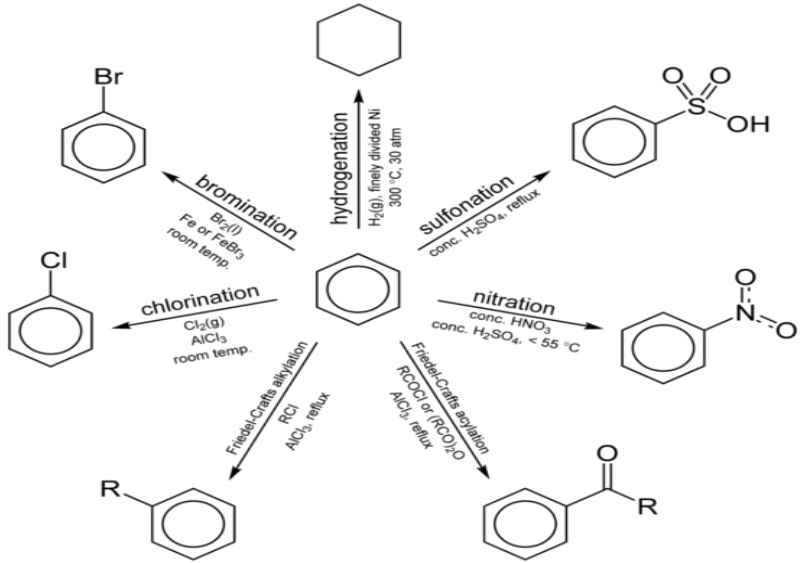
Each cyclopentadienyl (CP) ring is then allocated a single negative charge, bringing the number of delocalized 5π-electrons and thus making them aromatic.



In ferrocene C-C bond length is 1.39 A
Between value of 1.33 to 1.54 A

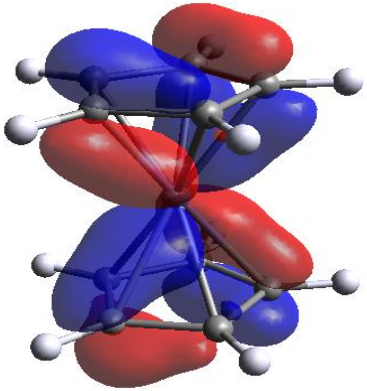
Ferrocene is aromatic in nature, so it gives reaction like benzene. Sulphonation, alkailation, halogination, nitration..ect….

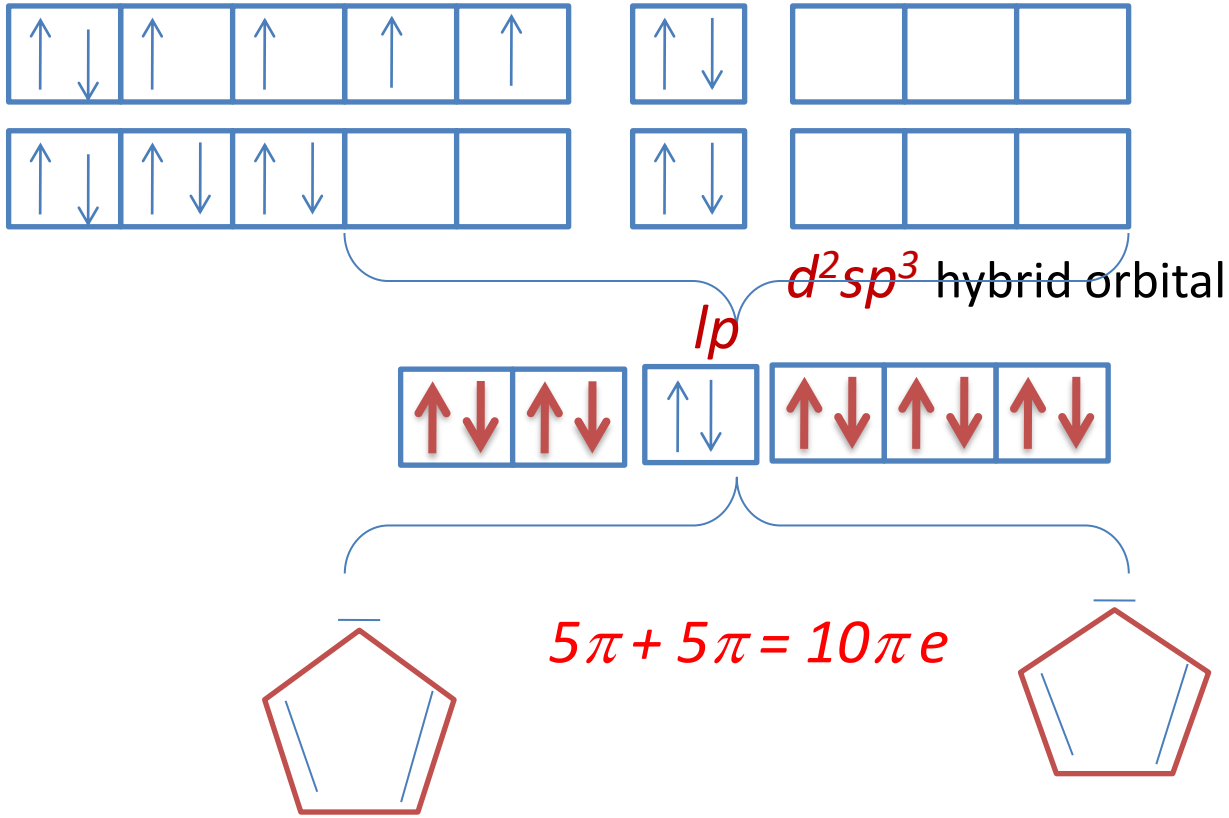




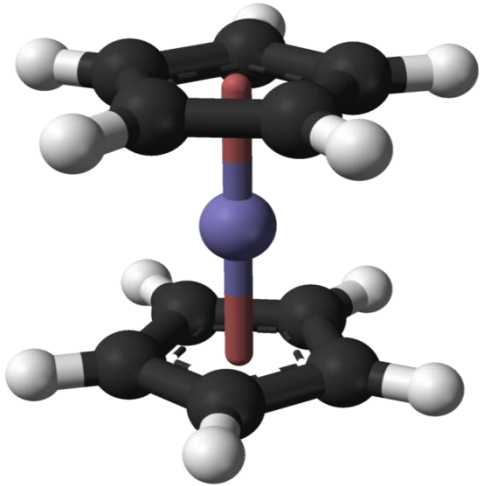
Bonding in Ferrocene

$Fe_{z=26}: [Ar]^{18}; 3d^6, 4S^2, 4P^0.$





$Fe_{z=26}: [Ar]^{18}; 3d^6, 4S^2, 4P^0.$



EAN rules

EAN= T.Fe's ele.+ accepted ele.

= 26 + 2(5)

=36 (Kr)

18^{th} electron rules,

EAN= Fe's velence ele.+ accepted ele.

= 08 + 2(5)

=18 ele.(Ar)

Conclusion: Ferrocene is stable compound

Organolithium compounds

contain

Carbon – lithium bonds.

પ્રશ્ન: ૧, કાર્બલીથીયમ સંયોજનો ઉપર નોધ લખો.

પ્રશ્ન: ૨, કાર્બલીથીયમ સંયોજનોની બનાવટ, ગુણધર્મો, ઉપયોગ સમજાવો.

પ્રશ્ન: ૩, આલ્કાઈલલીથીયમ સંયોજનોની સંરચના સમજાવો.

Dr.Naresh I.Patel
Chemistry Dept.
Science College, Himatnagar

Li- is first alkaline metal

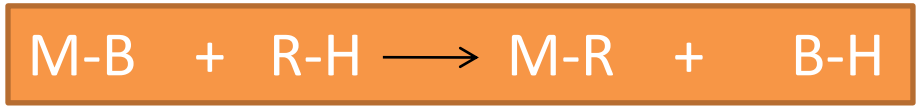
(Li:Z=3; $1S^2;2S^1$), *Electron deficient atom,*

Lithium alkyl [R-Li] is important Organolithium compounds

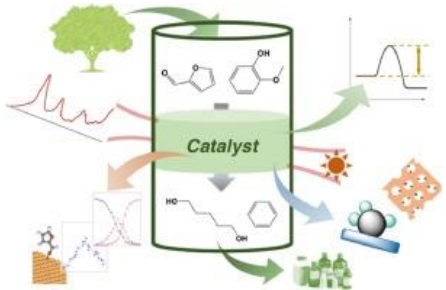
Wher, R=CH_3, ; C_2H_5.

Importance:

It is found that in comparison with Grignard reagents, organolithium reagents can often perform the same reactions with *increased rates and higher yields*, such as in the case of **metalation**.



$C_2H_5Na + C_6H_6 = C_6H_5Na + C_2H_6$



Preparation [1] Reaction with lithium metal

***Reduction** of alkyl or aryl halide with metallic lithium can afford simple alkyl and aryl organolithium reagents.*

Laboratory Preparation

$$2Li_{(s)} + R - X \xrightarrow{ether} R - Li + LiX$$

$$2Li_{(s)} + Ar - X \xrightarrow{ether} Ar - Li + LiX$$

$$X = Cl, Br, I$$

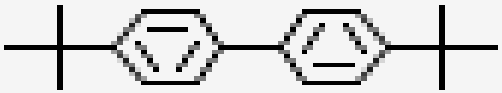
Industrial preparation

Organolithium compound is achieved by treating *the alkyl chloride with metal lithium* containing 0.5-2% sodium. The sodium *increases the rate and Product.*

$$2Li_{(s)} + C_4H_9Cl \xrightarrow{Na_{(s)}+Ether} \underset{n-Butyllithium}{Li-C_4H_9} + LiX + E$$

The conversion is highly exothermic .

Sometimes, lithium metal in the form of fine powders are used in the reaction with certain catalysts such as ***naphthalene*** ***or 4,4'-di-t-butyl biphenyl (DTBB).***



Preparation [2] Metalation (*lithium hydrogen exchange*).

This is the most common method for preparing ***alkynyllithium****, because the terminal hydrogen bound to the* ***sp*** *carbon is very acidic and easily* ***deprotonated.***

In Acetylene compounds 'H' atom is Acidic nature. The relative acidity of hydrogen atoms define the position of lithium.

$$C_6H_5Li + C_6H_5 - C \equiv C^-H^+ \longrightarrow C_6H_6 + C_6H_5 - C \equiv C^-Li^+$$

2-phynyl ethyane (acetylene)

Preparation [3] Lithium halogen exchange

✓***tert*-butyllithium or *n*-butyllithium** are the most commonly used reagents for generating new organolithium species through lithium halogen exchange.

✓Lithium-halogen exchange is mostly used to convert ***R-X or Ar-X (X= Br, I)*** with sp^2 carbons to the corresponding organolithium compounds.

✓The reaction is extremely fast, and often proceed at -60 to -120 °C.
✓Crystal Phenyllithium is prepared by this method.

$$C_4H_9Li + C_6H_5I \rightarrow C_4H_9I + C_6H_5Li_{(s)}$$

Preparation [4] Transmetalation

This method can be used for preparing vinyllithium.

Vinyllithium is prepared by Metal exchange in ***Phenyllithium and tetra vinyltin.***

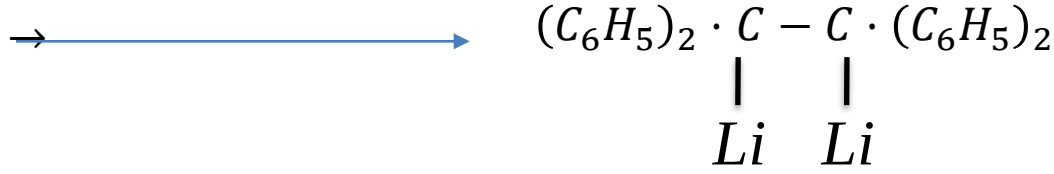
$$4C_6H_5Li + (CH_2 = CH_2)_4Sn \xrightarrow{Diethylether} (C_6H_5)_4Sn + \underset{\text{soluble}}{4(CH_2 = CH_2)Li}$$

Phenyltin is less soluble then vinyllithium so it is easily separate from mixture.

$$(C_6H_5)_2Hg + 3Li_{(s))} \xrightarrow{Murcuration+ether} 2(C_6H_5)Li + \underset{Alloy}{Li - Hg}$$

Preparation [5] Addition reaction

$$(C_6H_5)_2C = C(C_6H_5)_2 + 2Li_{(s)} \rightarrow$$



1,2 tetra phenyl ethene

Tetra phenyl ethanyl dilithium

Properties:

- Organolithium compounds are ***highly reactive*** species and require *specialized handling techniques.*
- Reactions are conducted using air free techniques.
- They are often ***corrosive, flammable,*** and sometimes ***spontaneous ignition*** when presence of ***oxygen or moisture***.
- Organolithium reagents are stored below 10°C.
- Organolithium reagents react with ethers, which are often used as solvents.
- Organolithium compounds are highly ***volatile***.
- ***Sublimation*** in vacuum.
- ***Decomposed*** at normal room Temperature.

$$CH_3 \cdot CH_2 \cdot Li \xrightarrow{Air \cdot \Delta} Li - H + CH_2 = CH_2$$

- ***Li-CH_3 is Most stable*** Organolithium compound.

  - ✓ It is Collourless, Crystal solid compound.
  - ✓ It is decomposed at *200 C*.
  - ✓ Soluble in Non-poler organic solvent.
    Benzene, Carbone tetrachloride.

Structure and Bonding

- *Organolithium structures have been elucidated by NMR spectroscopy and X-ray diffraction analysis.*

- *Alkyllithium R-Li species are often represented as **monomer or polymers**.*
- *Their structures depend on the nature of organic substituent, Solvent and the presence of other ligands.*

- *Methyl Lithium and Ethyl litihium are tetramer.*
- *$[Li\text{-}CH_3]_4$; $[Li\text{-}C_2H_5]_4$*

Compound	Solvent	Structure
methyllithium	THF	tetramer
methyllithium	ether	tetramer
n-butyllithium	pentane	hexamer
n-butyllithium	ether	tetramer
n-butyllithium	THF	tetramer-dimer
sec-butyllithium	pentane	hexamer-tetramer
isopropyllithium	pentane	hexamer-tetramer
tert-butyllithium	pentane	tetramer
tert-butyllithium	THF	monomer
phenyllithium	ether	tetramer-dimer
phenyllithium	ether/HMPA	dimer

Bonding and Structure

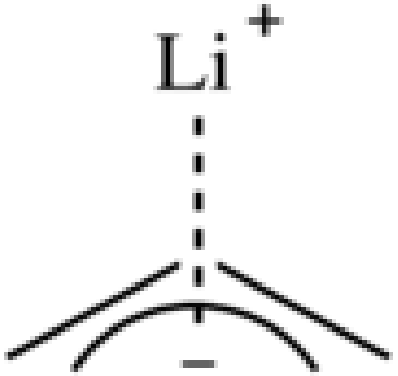
Nature of carbon-lithium bond

The relative electro negativities of carbon and lithium suggests that the C-Li bond will be highly polar.
The C-Li bond to be essentially ionic, a small covalent character.

Electronegativity

Carbone : 2.55

Lithium : 0.98

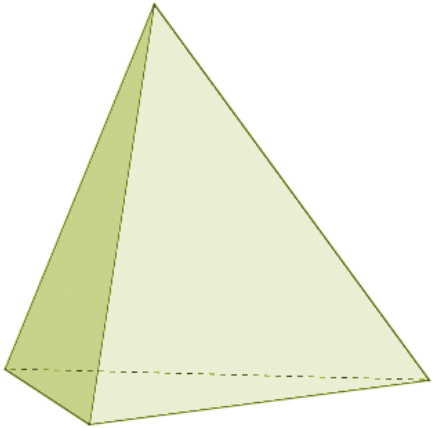


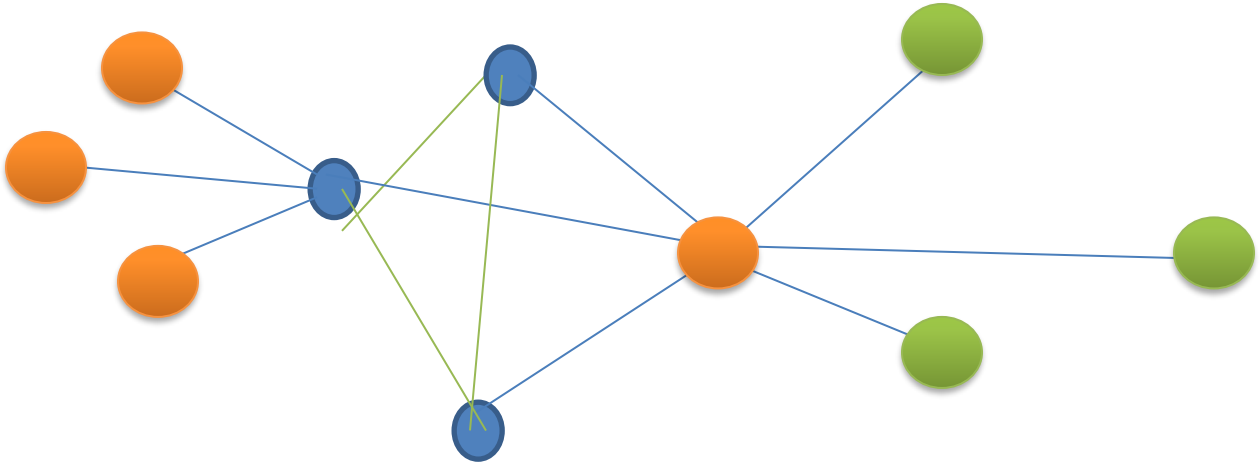
- In Alkyl lithium (R-Li),

$C_{Z=6}: 1S^2; 2S^2; 2P^2$

$Li_{Z=3}: 1S^2; 2S^1;$

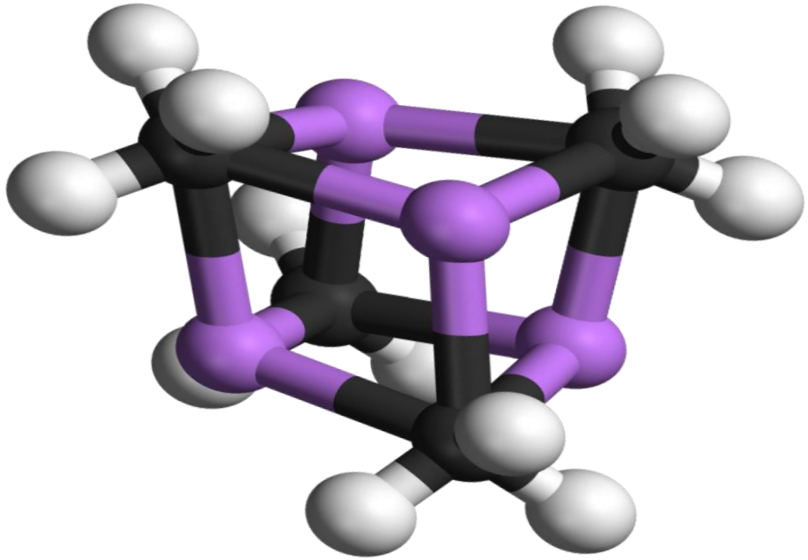
- Sp^3 Hybridization of Li and C atom.
- Geometry of Li and C atom is Tetrahedron.
- One C attached to 3H and 3Li. Coordination No.of C=6
- One Li attached to 4 C, Coordination No.of Li=4

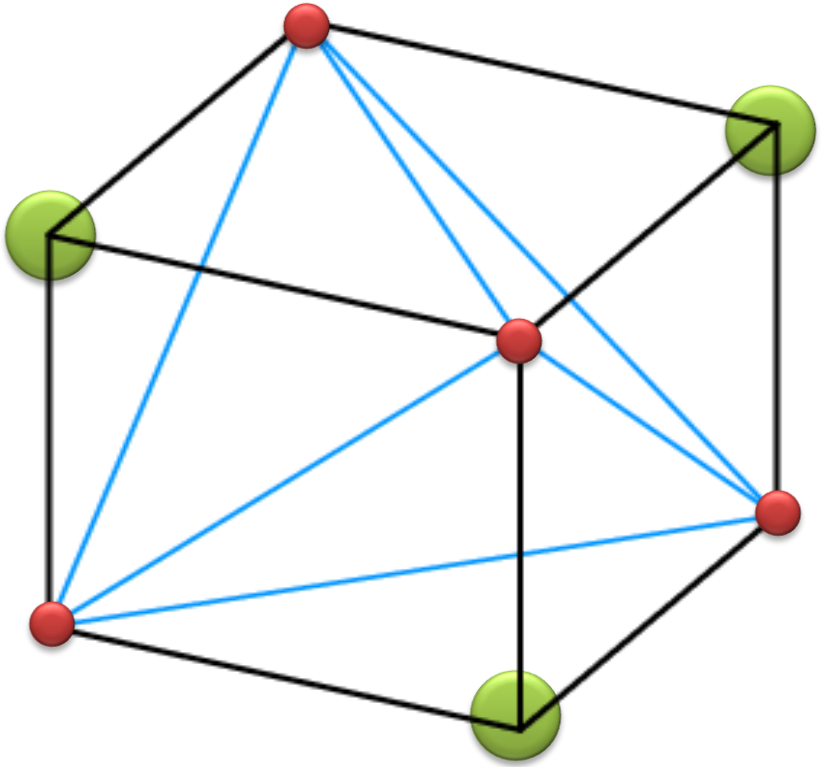


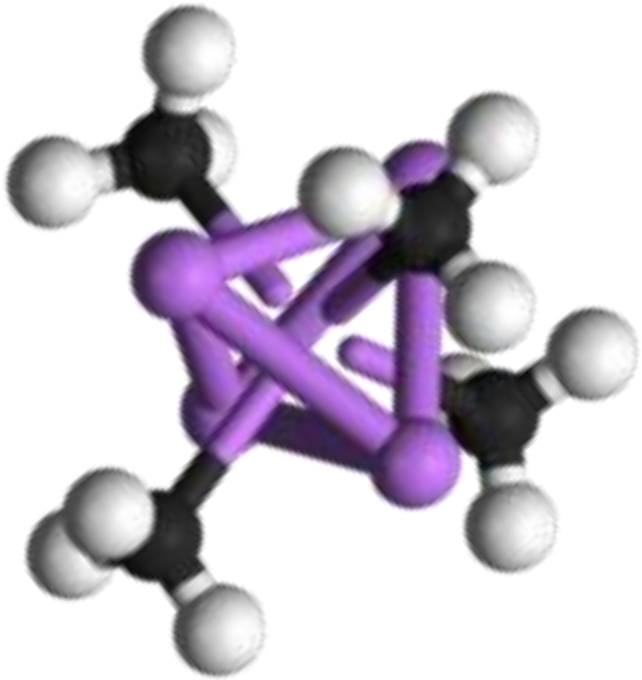


Structure of $[Li\text{-}CH_3]_4$

Li lies on the angle of tetrahedron
CH_3 lies on the face of tetrahedron.







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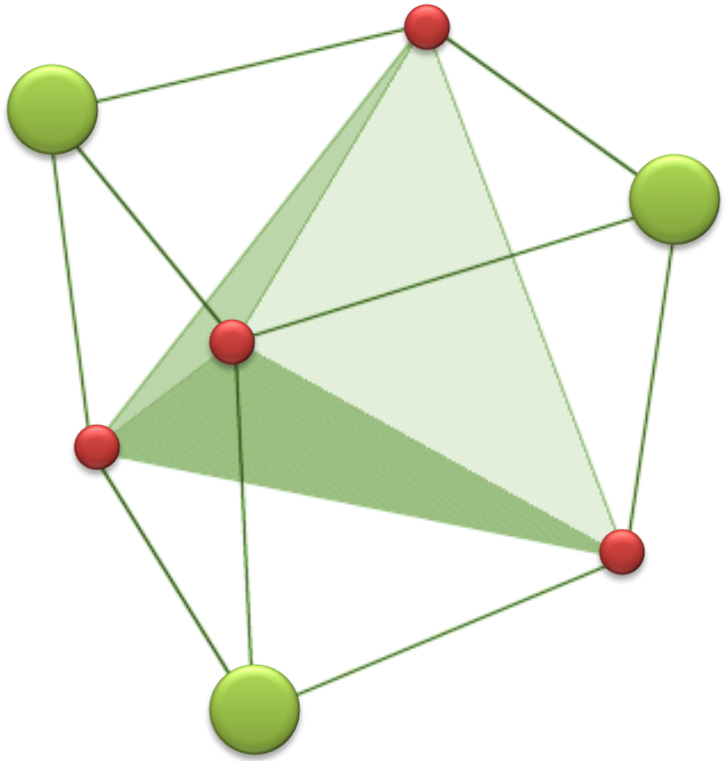


Uses of Organolithium Compounds

Highly reactable so limited used of Organolithium compounds.

- *They are important reagents in organic synthesis, and are frequently used in* ***nucleophilic addition, simple deprotonation and metalation.***

- *Used in* ***Polymerization*** *as a catalyst (Butyl lithium)*
- *To prepred* ***Ollifin and cyclopropen****. (alkyl lithium)*
- *Use in Industrial synthesis of* ***Vitamin-A****.*[retinol/retinal/retinoic acid] *(Acetylene lithium)*
- *As a* ***Tranquilizer drugs in Placidyl****.(Acetylene lithium)*
- *To* ***adding a phenyl group*** *in organic compounds. (Phenyl lithium)*

Organoaluminium compound

Compounds containing bonds between carbon and aluminum bond.

Illustrative organoaluminium compounds are the dimer **trialkylaluminium**, $[R_3\text{-}Al]_2$

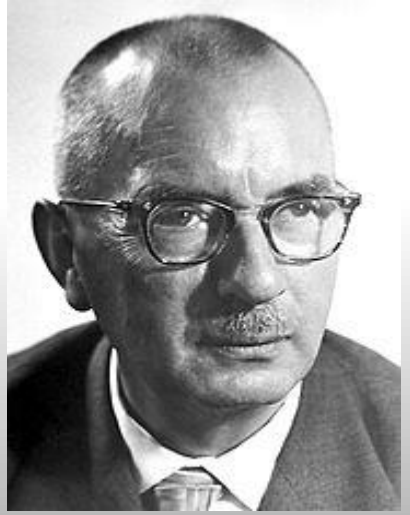
These compounds are mainly used for the production of polyolefins

History

The first organoaluminium compound $(C_2H_4)_3Al_2I_3$ was discovered in 1859.

In 1950s, Karl Ziegler and Colleagues discovered of **trialkylaluminium** $[R_3\text{-}Al]_2$ compounds and applied these compounds as catalytic in olefin polymerization.

(Nobel Prize to Ziegler.)

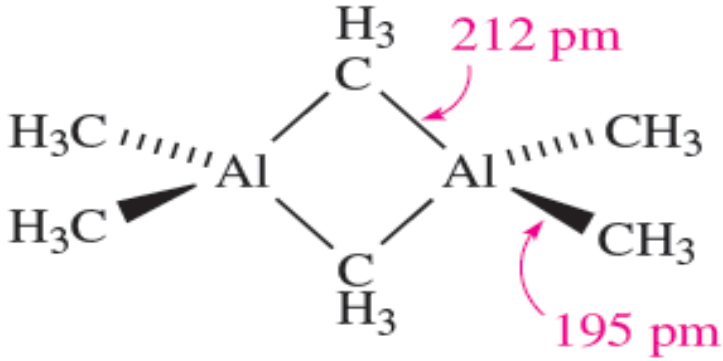


Karl Waldemar Ziegler
(November 26, 1898 – August 12, 1973) was a German chemist who won the Nobel Prize in Chemistry in 1963,

Trialkylaluminium compounds

The **trialkylaluminium** compounds are thus usually ***dimeric*** with a pair of bridging (3C-2e bond) alkyl legends,

Monomer : $Al(CH_3)_3$; $Al(C_2H_5)_3$



Dimer :
$Al_2(CH_3)_4(\mu\text{-}CH_3)_2$. trimethylaluminium,
contains two Al centres, and six Methyl groups.

$Al_2(C_2H_5)_4(\mu\text{-}C_2H_5)_2$. triethylaluminium,
contains two Al centres, and six ethyl groups.

Preparation [1] From alkyl halides and aluminium

Industrially, simple aluminum alkyls of the type Al_2R_6 (R = Me, Et) are prepared in a two-step process beginning with the *alkylation of aluminum powder:*

$$2\ Al + 3\ CH_3CH_2Cl \rightarrow (CH_3CH_2)_3Al_2Cl_3$$

The product, $(CH_3CH_2)_3Al_2Cl_3$, can be converted to the trialkyl aluminum derivatives by reduction:

$$\mathbf{2\ (CH_3CH_2)_3Al_2Cl_3 + 6\ Na \rightarrow (CH_3CH_2)_6Al_2 + 2\ Al + 6\ NaCl}$$

This method is used for production of trimethylaluminum and triethyl aluminium.

Preparation [2] Hydroalumination

Aluminum powder reacts directly with certain alkenes in the presence of hydrogen. The process entails two steps,

The first producing dialkylaluminium hydrides at 80^0C Temperatures

$$3\ Al + 3/2\ H_2 + 6\ CH_2{=}CH2 \rightarrow [HAl(CH_2CH)_2]_3$$

In a subsequent step, these hydrides are treated with more alkenes to effect hydro alumiunation:

$$2\ [HAl(CH_2CH)_2]_3 + 6\ CH_2{=}CH2 \rightarrow 3\ [Al_2(CH_2CH_3)_6]$$

Preparation[3] Trans metalation

(Laboratory preparations) (Buktone and Odaling Method)

The synthesis in the laboratory, including metathesis or transmetalation methods.

Metathesis of aluminium trichloride with R-Li gives the trialkylalluminium:

$$AlCl_3 + 3\ R\text{-}Li \rightarrow R_3Al + 3\ LiCl \qquad R=Me,\ Et,\ Bu,$$

•Trans metalation at 80 to 90 C

$$2\ Al + 3\ Hg(CH_3)_2 \rightarrow [Al(CH_3)_3]_2 + 3\ Hg$$

Preparation [4] From Alluminium Alloy

Synthesis of alkylaluminium by reaction of Megnesium -Alluminium alloy with Alkylhalide.

$$Al_2\text{-}Mg_3 + 6\ R\text{-}Cl \rightarrow 2\ R_3Al + 3\ MgCl_2$$

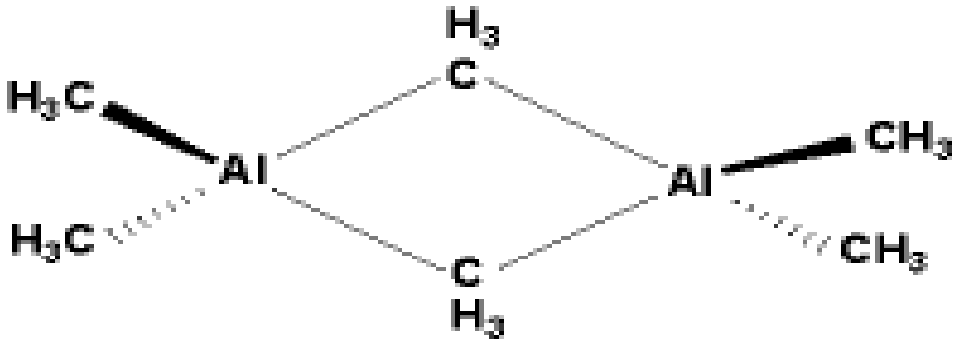
R=Me, Et,

Properties:

- Colorless liquid
- Trimethyl alluminium is dimar, $Al_2(CH_3)_4(\mu\text{-}CH_3)_2$
- Soluble in Benzene solvant.
- Liquid at room Temperature.
- M.P.=15 C. and B.P.=126 C.
- Spontaneously inflammable but reactive liquid.
- Reaction with air and water gives Hydrides and Oxides.

Bonding and Structure

$Al_2(CH_3)_4(\mu\text{-}CH_3)_2$. Dimer trimethylaluminium,



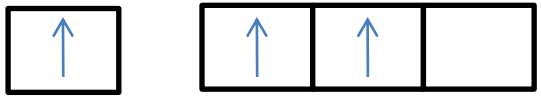
Contains
two aluminium centres,
and
six Methyl groups.

Two methyl are bridge bonded.

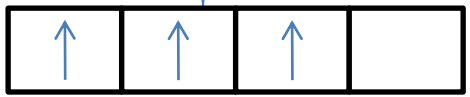
- *In these structures, each Al is* ***sp³*** *hybridized and is bonded to four C atoms, but there are not enough electrons to assign a pair of electrons per chemical bond. Here, Al-C-Al is 3C-2e bridge bond.*
- *The four-coordinate Al prefers to be tetrahedral.*

$Al_{(z=13)}: 1S^2; 2S^2; 2P^6; \underline{3S^2; 3P^1}$

Al*:

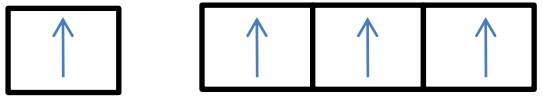


SP^3 H.O.:

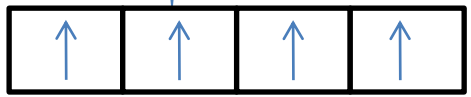


$C_{(z=6)}: 1S^2; \underline{2S^2; 2P^2}$

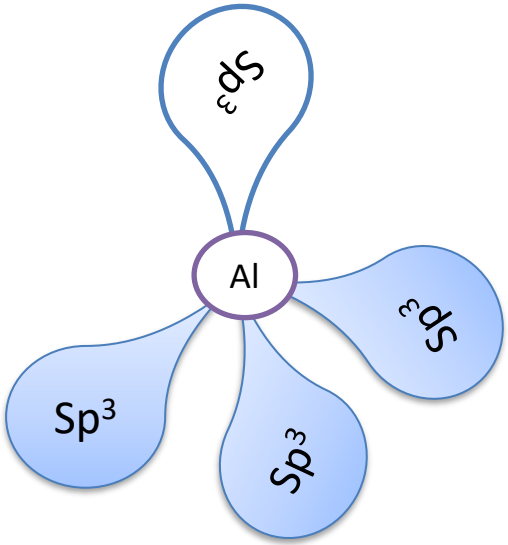
C*:

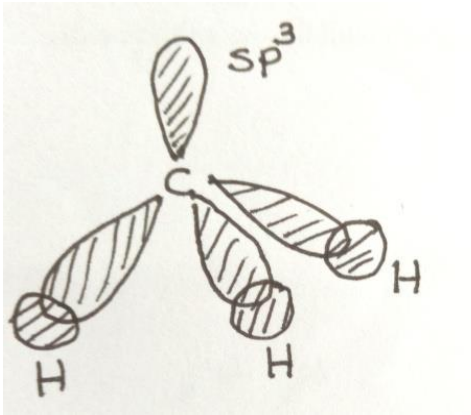


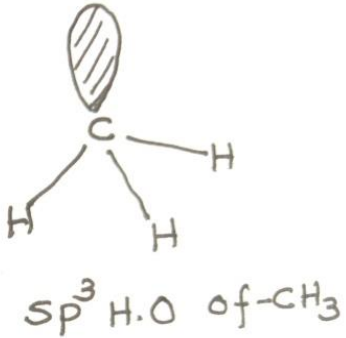
SP^3 H.O.:

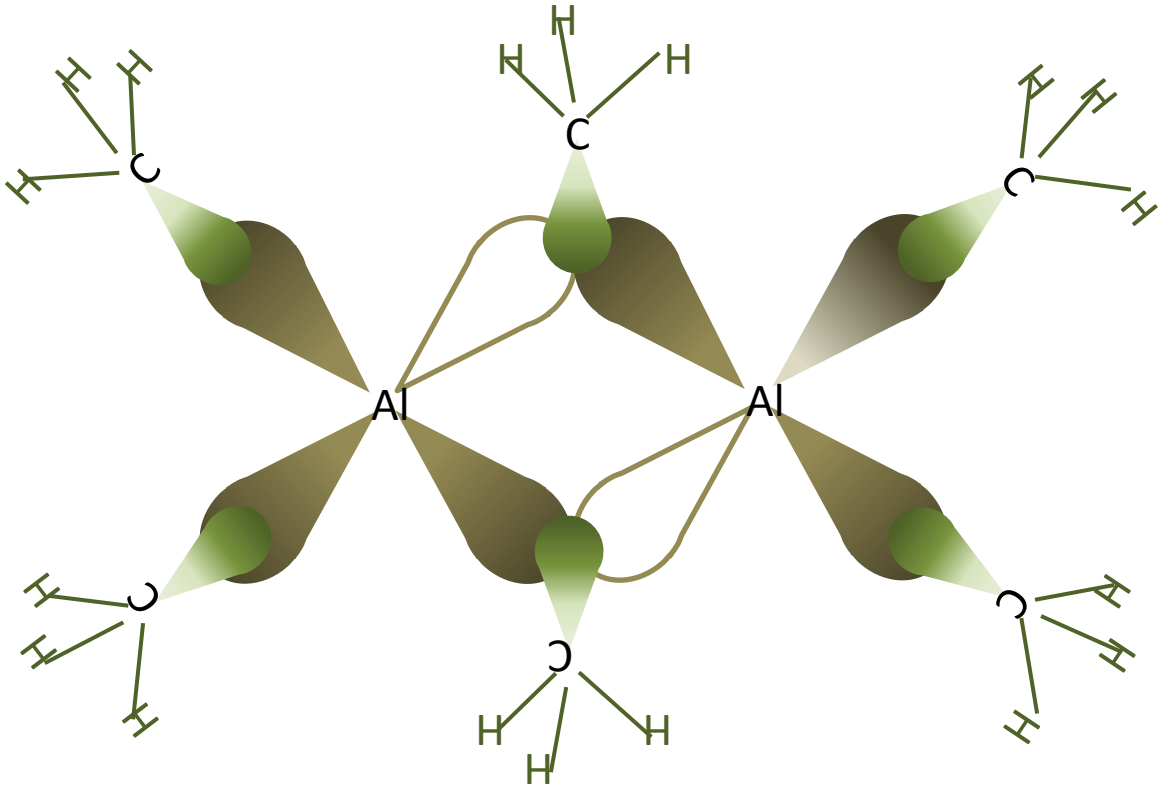


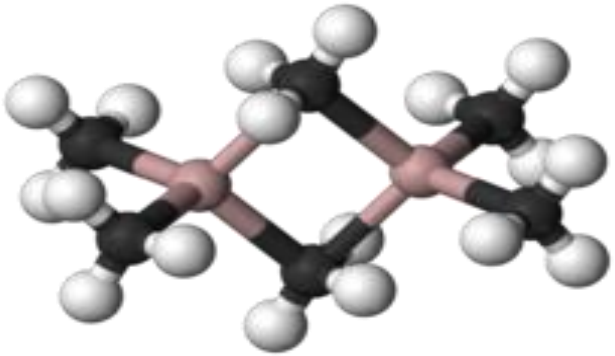
SP^3 Hybridization



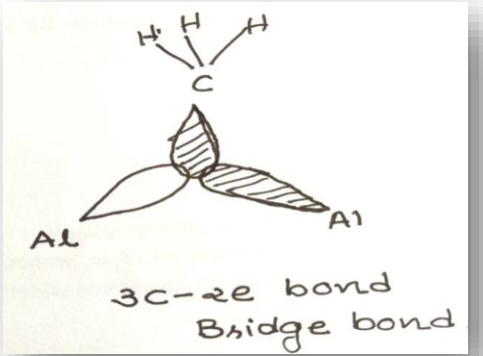


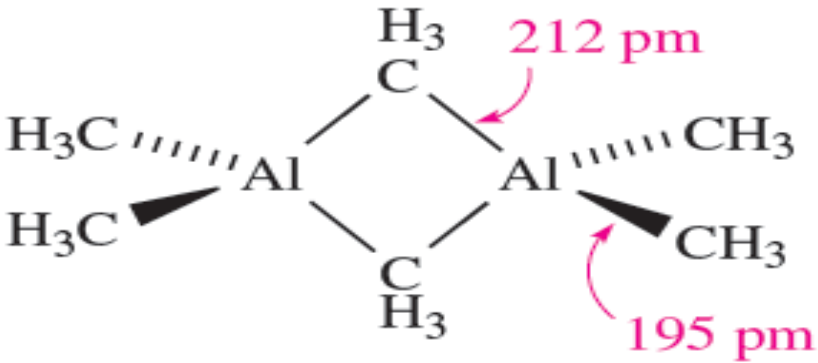




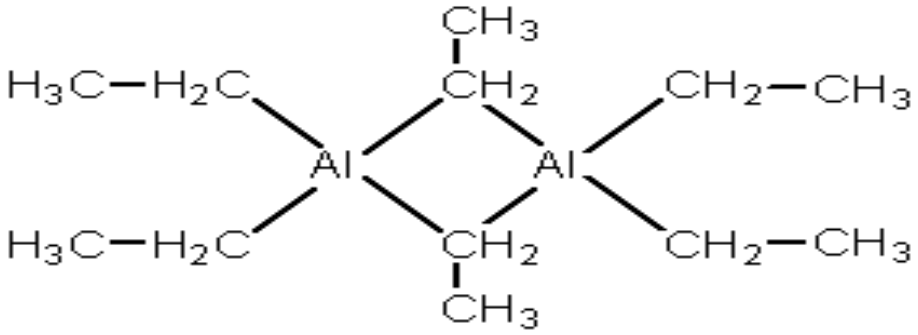


Sp^3 Hybrid orbitals of 'Al' and 'C'





$Al_2(CH_3)_4(\mu\text{-}CH_3)_2$. trimethylaluminium



topologische Formel

$Al_2(C_2H_5)_4(\mu\text{-}C_2H_5)_2$. triethylaluminium,

Uses of Alkyllalluminium:

- Al_2Et_6 and Al_2Me_6 used in Jet-fuels with Hydrocarbone.
- Al_2Bu_6 is used in Alkene exchange reaction.
- Al_2Et_6 is used as Catalyst (Ziegler) in Polymerization (poly olefins)
- For Preparation of Polithene and Alkoxi polimer.