Organometallic Chemistry

18-electron rule: Stable electronic configuration

- Irwing Langmuirin (1921) first formulated this rule (extension of octet theory)-rule of thumb
- It states that 'Thermodynamically stable transition metal organometallic compounds are formed when the sum of the metal d-electrons and the electrons conventionally considered as being supplied by the surrounding ligands equals 18'
- Applicable for organometallics with metals (transition) in low oxidation state bearing strong π-acceptor character.
- In octahedral complexes, six bonding interactions are possible. In presence of π-acceptor ligands, bonding combinations with three t_{2g} orbitals also possible leading to nine bonding MOs, and space for a total of 18e.
- Square-planar complex has only eight bonding MOs, thus a 16-electron configuration is energetically favorable
- Complexes with 17e and 19e are paramagnetic in nature
- Complexes with 17 e are strong oxidising agent and complexes with 19 e are strong reducing agent
- No of electrons allows us to predict the stabilities of compounds.
- Two models are used viz. **neutral-atom method** (covalent method) and the **donor-pair method** (oxidation state/ionic method).
- Donor-pair method is more convenient (oxidation numbers can be assigned) to use.

Fewer than 18e	18e	16 or 18e
Sc, Ti, V	Cr, Mn, Fe	Co, Ni
Y, Zr, Nb	Mo, Tc, Ru	Rh, Pd
La, Hf, Ta	W, Re, Os	Ir, Pt

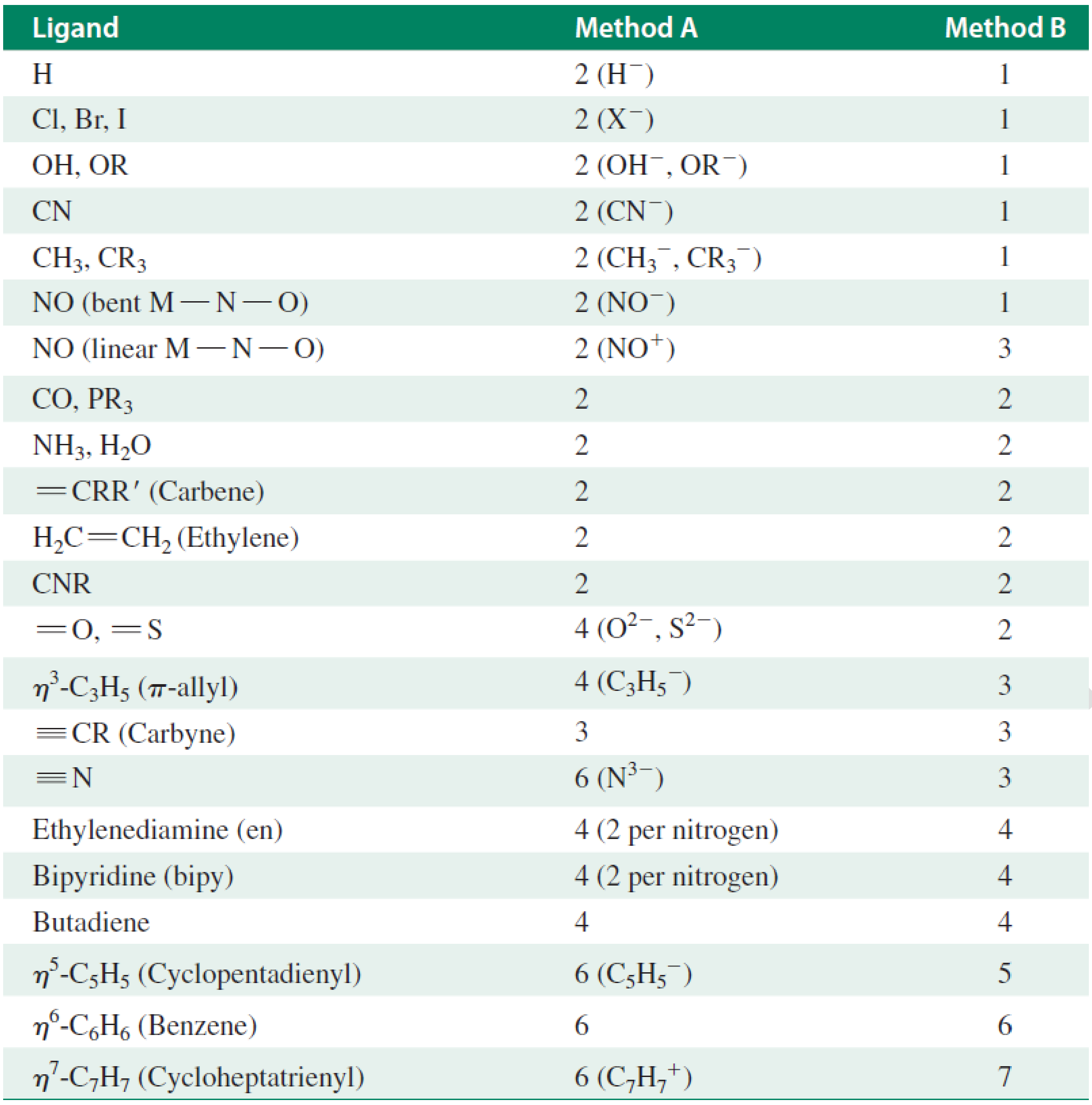
Neutral-ligand method

- All ligands are treated as neutral and are categorized according number of electrons they donate.
- Metal atom is also treated as neutral, considers all valence electrons of the metal.
- For charged complex, add/subtract the appropriate number of electrons to the total
- Count 1e for every covalent bond to another atom and count 2e for every dative bond from another atom. Three- and four-center bonds need special treatment
- Delocalized carbon fragments: usually 1e per C-atom (hapticity)
- TEC is the sum of electrons contributed by metal and all ligands.
- **Advantage:** It is trivial to establish the electron count.
- **Disadvantage:** It overestimates the degree of covalence (underestimates charge)

Donor-pair method/Oxidation state method

- Ligands are considered to donate electrons in pairs (treated as neutral and/or charged)
- Oxidation number of an element is calculated as that for coordination compounds.
- Number of electrons contributed by ligand depend on its nature. CO and PPh_3, are neutral two-electron donors (ON=0), X^-, H^-, and CH_3^- are mono-negative and two-electron donors. Cp treated as $C_5H_5^-$ (ON= -1) a six-electron donor
- Oxidation number of the metal = total charge of complex - charges of ligands.
- Number of electrons the metal provides = Group number - oxidation number.
- TEC is the sum of electrons contributed by metal and all ligands.
- **Advantage**: Both the electron count and the oxidation number may be determined.
- **Disadvantage**: It overestimates the charge on the metal atom

Methods of counting: Oxidation state (A) & Neutral atom (B) method



Ligand	Method A	Method B
H	2 (H^-)	1
Cl, Br, I	2 (X^-)	1
OH, OR	2 (OH^-, OR^-)	1
CN	2 (CN^-)	1
CH_3, CR_3	2 (CH_3^-, CR_3^-)	1
NO (bent M—N—O)	2 (NO^-)	1
NO (linear M—N—O)	2 (NO^+)	3
CO, PR_3	2	2
NH_3, H_2O	2	2
$=CRR'$ (Carbene)	2	2
$H_2C=CH_2$ (Ethylene)	2	2
CNR	2	2
$=O$, $=S$	4 (O^{2-}, S^{2-})	2
η^3-C_3H_5 (π-allyl)	4 ($C_3H_5^-$)	3
$\equiv CR$ (Carbyne)	3	3
$\equiv N$	6 (N^{3-})	3
Ethylenediamine (en)	4 (2 per nitrogen)	4
Bipyridine (bipy)	4 (2 per nitrogen)	4
Butadiene	4	4
η^5-C_5H_5 (Cyclopentadienyl)	6 ($C_5H_5^-$)	5
η^6-C_6H_6 (Benzene)	6	6
η^7-C_7H_7 (Cycloheptatrienyl)	6 ($C_7H_7^+$)	7

Some examples

$Fe(CO)_5$ acquires 18 electrons from the eight valence electrons on the Fe atom and the 10 electrons donated by the five CO ligands.

Q.1 Do (a) $[IrBr_2(CH_3)(CO)(PPh_3)_2]$ and (b) $[Cr(\eta^5\text{-}C_5H_5)(\eta^6\text{-}C_6H_6)]$ obey the 18-electron rule?

Answer (a) Ir atom (Gr 9) has 9 valence electrons, two electrons from two Br atoms and one electron from CH_3 group (both are one-electron donor), and finally add in the electrons from the CO and PPh_3 (both are two-electron donors). Thus, TEC=18.

(b) In a similar fashion, the Cr atom (Gr 6) has six valence electrons, η^5-C_5H_5 and η^6-C_6H_6 ligands donates five and six electrons respectively, TEC=17.

Q.2 Is $[Mo(CO)_7]$ likely to be stable?

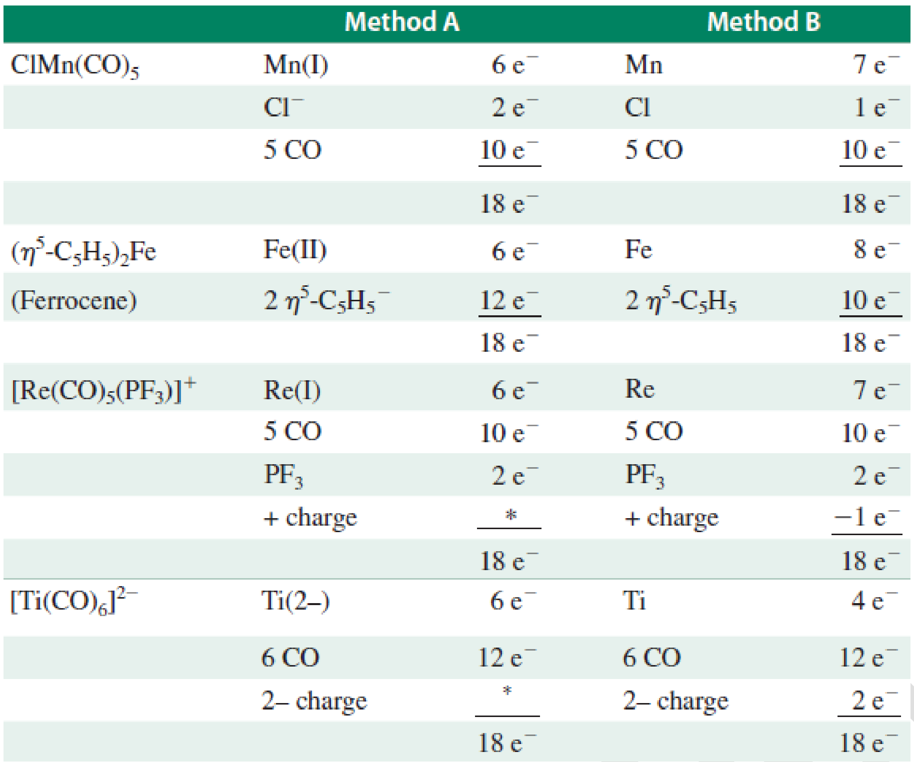
Q.1 Assign the oxidation number and count the valence electrons on the metal atom in (a) $[IrBr_2(CH_3)(CO)(PPh_3)_2]$ and (b) $[Cr(\eta^5\text{-}C_5H_5)(\eta^6\text{-}C_6H_6)]$ and (c) $[Mn(CO)_5]^-$.

Answer: (a) Two Br groups and the CH_3 as three singly negatively charged two-electron donors. CO and the two PPh_3 ligands as three two-electron donors, providing 12 electrons in all. Because neutral, the Group 9 Ir atom must have a charge of +3 to balance the charge of the three anionic ligands, and thus contributes 6 electrons, TVE = 18.

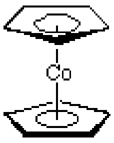
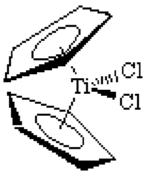
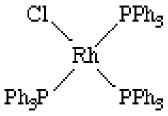
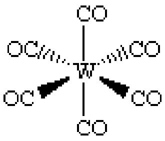
(b) η^5-C_5H_5 ligand is treated as $C_5H_5^-$ and thus it donates six electrons, and η^6-C_6H_6 ligand donates another six. To maintain neutrality, the Group 6 Cr atom must have a charge of 1 and contributes 5 electrons, TVE = 17. This complex does not obey the 18-electron rule and is unlikely to be stable.

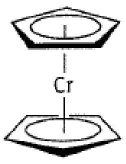
(c) Each CO ligand contributes two electrons, giving 10 electrons. The charge of the complex -1 and the ligands are neutral, the charge should reside Mn atom, giving an OS -1. Thus, Group 7 Mn atom thus contributes 7+1 =8 electrons, TVE =18 (Mn -1 complex).

Comparison of the two methods



	Method A		Method B	
$ClMn(CO)_5$	Mn(I)	6 e^-	Mn	7 e^-
	Cl^-	2 e^-	Cl	1 e^-
	5 CO	10 e^-	5 CO	10 e^-
		18 e^-		18 e^-
$(\eta^5\text{-}C_5H_5)_2Fe$	Fe(II)	6 e^-	Fe	8 e^-
(Ferrocene)	2 $\eta^5\text{-}C_5H_5^-$	12 e^-	2 $\eta^5\text{-}C_5H_5$	10 e^-
		18 e^-		18 e^-
$[Re(CO)_5(PF_3)]^+$	Re(I)	6 e^-	Re	7 e^-
	5 CO	10 e^-	5 CO	10 e^-
	PF_3	2 e^-	PF_3	2 e^-
	+ charge	*	+ charge	−1 e^-
		18 e^-		18 e^-
$[Ti(CO)_6]^{2-}$	Ti(2–)	6 e^-	Ti	4 e^-
	6 CO	12 e^-	6 CO	12 e^-
	2– charge	*	2– charge	2 e^-
		18 e^-		18 e^-

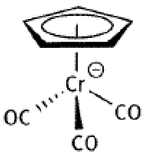
	ionic		covalent	
	Co^{II}	7 e^-	Co	9 e^-
	2 Cp^-	12 e^-	2 Cp•	10 e^-
	Total	19 e^-	**Total**	19 e^-
	Ti^{IV}	0 e^-	Ti	4 e^-
	2 Cl^-	4 e^-	2 Cl•	2 e^-
	2 Cp^-	12 e^-	2 Cp•	10 e^-
	Total	16 e^-	**Total**	16 e^-
	Rh^I	8 e^-	Rh	9 e^-
	Cl^-	2 e^-	Cl•	1 e^-
	3 PPh_3	6 e^-	3 PPh_3	6 e^-
	Total	16 e^-	**Total**	16 e^-
	W^0	6 e^-	W	6 e^-
	6 CO	12 e^-	6 CO	12 e^-
	Total	18 e^-	**Total**	18 e^-



Sandwich complex
Chromocene

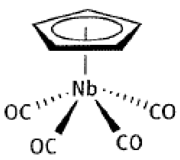
Electron count: Cr d^6
Cp: $2 \times 5 = 10\ e^-$
16 VE

Oxidation state:
2 Cp^- anions per Cr,
overall no charge: Cr(II)



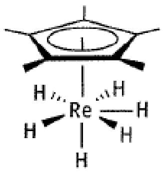
Half-sandwich complex
('Piano stool complex')
Electron count: Cr d^6
Cp: $5\ e^-$
3 CO: $3 \times 2 = 6\ e^-$
Charge $1\ e^-$
18 VE

Oxidation state: one Cp^-
overall 1− charge: Cr(0)



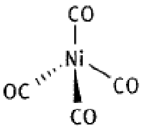
Half-sandwich complex
(7-coordinate)
Electron count: Nb d^5
Cp: $5\ e^-$
4 CO: $4 \times 2 = 8\ e^-$
18 VE

Oxidation state: one Cp^-
anion no overall charge:
Nb(I)



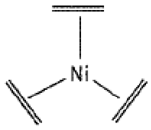
Half-sandwich complex
(9-coordinate)
Electron count: Re d^7
Cp: $5\ e^-$
6 H: $6 \times 1 = 6\ e^-$
18 VE

Oxidation state: Cp^-
plus 6 H^-, no overall
charge: Re(VII)



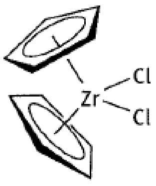
Nickel tetracarbonyl
tetrahedral
Electron count: Ni d^{10}
4 CO = + $4 \times 2 = 8\ e^-$
18 VE

Oxidation state:
neutral ligands,
no overall charge: **Ni(0)**



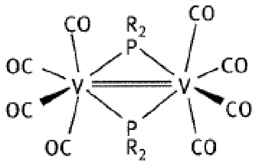
Tris(ethylene)nickel
trigonal-planar
Electron count: Ni d^{10}
3 C_2H_4: $3 \times 2 = 6\ e^-$
16 VE

Oxidation state:
neutral ligands,
no overall charge: **Ni(0)**



Bent metallocene
Electron count:
Zr d^4
2 Cl: $2\ e^-$
Cp: $2 \times 5 = 10\ e^-$
16 VE

Oxidation state:
2 Cp^- anions, 2 Cl^-
anions, overall no
charge: Zr(IV)



Electron count: V d^5
shared electrons
from V=V bond: $2\ e^-$
4 CO = $4 \times 2 = 8\ e^-$
bridging PR_2: $3\ e^-$
18 VE

Oxidation state: 2 PR_2^-,
no overall charge: **V(I)**

Problems for practice

Q.1 Confirm that the Cr center in $[(\eta^6\text{-}C_6H_6)Cr(CO)_3]$ obeys the 18-electron rule, but Rh in $[(CO)_2Rh(\mu\text{-}Cl)Rh(CO)_2]$ does not.

Q. 2 Confirm that the Fe centers in $H_2Fe(CO)_4$ and $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]^-$ obey the 18-electron rule.

Q. 3 Show that $Fe(CO)_4(\eta^2\text{-}C_2H_4)$, $HMn(CO)_3(PPh_3)_2$ and $[\eta^5\text{-}(C_6H_5Br)Mn(CO)_3]^+$ contain 18-electron metal centres.

Q. 4 Show that $[Rh(PMe_3)_4]^+$ contains a 16-electron metal center. Comment on whether violation of the 18-electron rule is expected

Q. 5 Metal–metal bonding in multinuclear species is not always clear-cut. Solely on the basis of the 18-electron rule, suggest whether $(\eta^5\text{-}Cp)Ni\ )(\mu\text{-}PPh_2)_2Ni(\eta^5\text{-}Cp)$ might be expected to contain a metal–metal bond

Q. 6 Show that an M-M single bond is expected in $M_2(CO)_{10}$ (M = Mn, Tc, Re) on the basis of the 18-electron rule.

Q. 7 The presence of an Fe-Fe bond in the compound$(\eta^5\text{-}Cp)(CO)Fe(\mu\text{-}CO)_2Fe\ (CO)(\eta^5\text{-}Cp)$ has been a controversial topic. Solely on the basis of the 18-electron rule, show that an Fe-Fe bond is expected. What does your conclusion depend on? Are your assumptions infallible?

Q. 8 What is the electron count for and oxidation number of platinum in the anion of Zeise's salt,$[Pt(CH_2CH_2)Cl_3]$? Treat CH_2CH_2 as a neutral two-electron donor.

Q. 9 Show that both (a) $[Mo(\eta^6\text{-}C_7H_8)(CO)_3]$ and (b) $[Mo(\eta^7\text{-}C_7H_7)(CO)_3]$ are 18-electron species.

Exceptions to the 18-electron rule

- Square planar organometallic complexes of the late transition metals (16e).
- Some organometallic complexes of the early transition metals like Cp_2TiCl_2, WMe_6, Me_2NbCl_3, $CpWOCl_3$ [Reason: Some of the orbitals of these complexes are too high in energy for effective interaction or the ligands are mostly σ-donors]
- Some high valent d^0 complexes have a lower electron count than 18.
- Sterically demanding bulky ligands force complexes to have less than 18 electrons.
- The 18-electron rule fails when bonding of organometallic clusters of moderate to big sizes (6 Metal atoms and above) are considered.
- Not applicable to organometallic compounds of main group metals as well as to those of lanthanides and actinides.

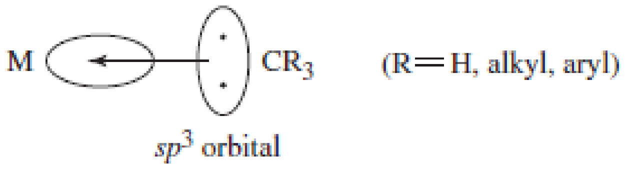
Metal Alkyls

- E. Frankland prepared the first σ-bonded organometallic compound-Diethyl zinc in 1848 by the reaction,

$$3C_2H_5I + 3Zn \rightarrow (C_2H_5)_2Zn + C_2H_5ZnI + ZnI_2$$

- W. J. Pope reported the first transition metal alkyl $PtMe_3I$ in 1907
- Alkyl groups bonded via covalent σ-interaction between the metal atom and the C -atom of the organic fragment.
- Alkyl groups with a H-atom on C-atom adjacent to the one that bonds to the metal are prone to decompose by a process known as β-hydrogen elimination.
- Choice of alkylating agent can affect the course of the reaction

- Transition metal alkyl complexes important for catalysts *e.g.* olefin polymerization and hydroformylation
- Problem is their weak kinetic stability



Methyl lithium:

Preparation

Organolithium compounds are of particular importance among the group 1 organometallics. Many of them are commercially available as solutions in hydrocarbon solvents.

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

Lithium alkyls are polymeric both in solution and in the solid state. The structures of $(t\text{-BuLi})_4$ and $(MeLi)_4$ are similar. Alkyl lithium compounds are soluble in organic solvents. Lithium alkyls and aryls are very useful reagents in organic synthesis and in making corresponding carbon compounds of main group elements. Lithium alkyls are important catalysts in the synthetic rubber industry for the stereospecific polymerization of alkenes. The molecular structures of $AlMe_3$ and MeLi differ from AlH_3 and LiH.

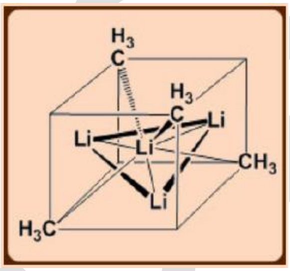
Structure and bonding

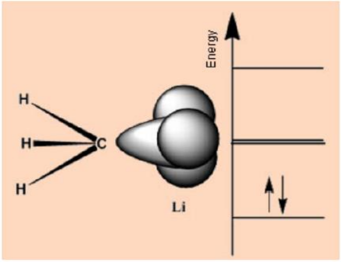
MeLi in nonpolar solvents consists of tetrahedron of Li atoms with each face bridged by a methyl group. Like Al_2Me_6, the bonding in MeLi consists of a set of localized molecular orbitals. The symmetric combination of three Li 2s orbitals on each face of the Li_4 tetrahedron and one sp hybrid orbital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

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

The interaction between a sp^3 orbital from a methyl group and the three 2s orbitals of the Li atoms in a triangular face of $Li(CH_3)_3$ to form a totally symmetric 4c, 2e bonding orbital. The next higher orbital is non-bonding and the uppermost is antibonding.

The crystal structure of methyl lithium in body centred cubic with the $Li_4(CH_3)_4$ units at each lattice site. Each unit is a tetramer in which the four Li-reside at the corner of a tetrahedron and the triply bridging methyl groups are located above the centres of the triangular faces.





Trialkyl aluminium:

Preparation

Laboratory scale preparations involves:

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

Commercial method:

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

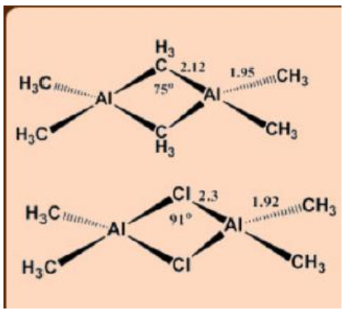
$$\mathrm{Al_2Cl_2(CH_3)_4 + 6\,Na \longrightarrow Al_2(CH_3)_6 + 2\,Al + 6\,NaCl}$$

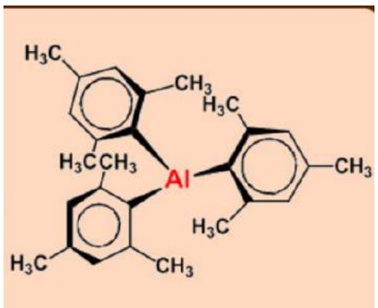
Commercial method for ethylaluminium and higher homologs:

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

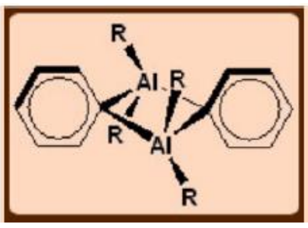
Structure

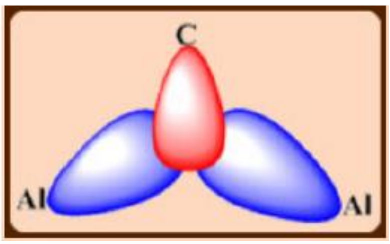
With less bulky alkyl groups, dimerization occurs and one of the distinguishing features of alkyl bridge is the small Al-C-Al angle, which is ~ 75°. The 3c,2e bonds are very weak and tend to dissociate in the pure liquid which increases with increase in the bulkiness of the alkyl group.

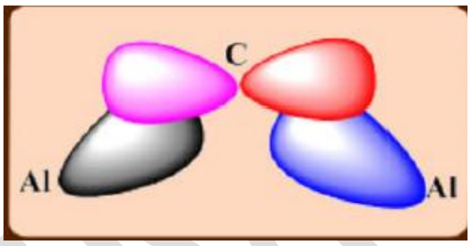




Perpendicular orientation of phenyl groups in Al_2Ph_6. Triphenylaluminium exists as a dimer with bridging η-phenyl groups lying in a plane perpendicular to the line joining the two Al atoms. This structure is favoured partly on steric grounds and partly by supplementation of the Al-C-Al bond by electron donation from the phenyl π-orbitals to the Al atoms. 3c-2e bonds formed by a symmetric combination of Al and C orbitals. An additional interaction between the pπ orbital on C and an antisymmetric combination of Al orbitals.



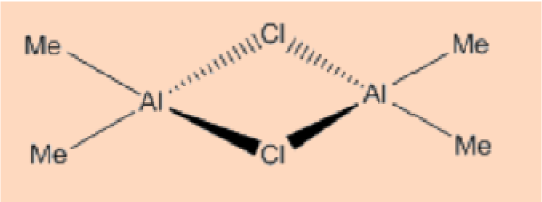




1. Propose a structure for $Al_2(Me)_4Cl_2$.

Solution:

Similar to diborane:

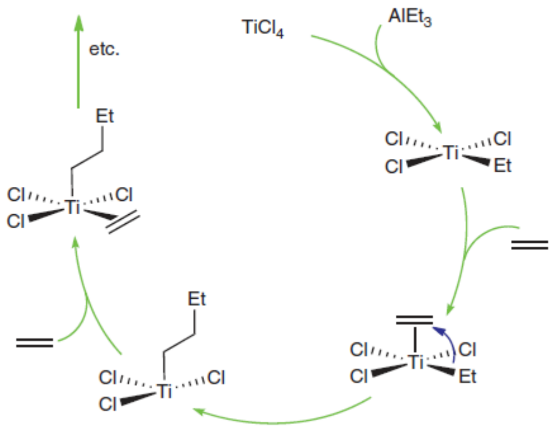


Ziegler-Natta Catalysis (Polymerization of olefins – Noble Prize 1963)

- K. Ziegler (Germany) discovered in 1953 that when $TiCl_4(s)$ and $AlEt_3$ are combined they produced an extremely active **heterogeneous catalyst** for the polymerization of ethylene at atmospheric pressure.
- G. Natta (Italy) extended the method to other olefins like propylene and developed variations of the Ziegler catalyst based on his findings on the mechanism of the polymerization reaction.
- The Ziegler-Natta catalyst family includes halides of titanium, chromium, vanadium, and zirconium, typically activated by alkyl aluminum compounds

Mechanism

- Details of the mechanism of Ziegler-Natta catalysis are still uncertain
- Cossee–Arlman mechanism is regarded as highly plausible
- The catalyst is prepared from $TiCl_4$ and $Al(C_2H_5)_3$, which react to give polymeric $TiCl_3$ mixed with $AlCl_3$ in the form of a fine powder.
- The alkylaluminium alkylates a Ti atom on the surface of the solid and an ethene molecule coordinates to the neighboring vacant site.
- In the propagation steps for the polymerization, the coordinated alkene undergoes a migratory insertion reaction.
- This migration opens another neighboring vacancy, and so the reaction can continue and the polymer chain can grow.
- The release of the polymer from the metal atom occurs by β-hydrogen elimination, and the chain is terminated.
- Some catalyst remains in the polymer, but the process is so efficient that the amount is negligible.
- Three different steps in polymerization
- **Initiation** (generation of active catalyst from less active or precursor),
- **Propagation** (polymer chain growth over repeated steps) and
- **Termination** (stops the polymer chain growth)



Function of aluminium alkyl

1. Alkylate the transition metal
2. Acts as Lewis acid and create a vacant coordination site by abstracting a halide or alkyl ligand from the transition metal
3. Acts as cleaning role, by mopping up impurities from the monomer and the reaction medium
4. The active species has a pseudo-tetrahedral structure with vacant site suitable for alkene coordination

Metal alkenes

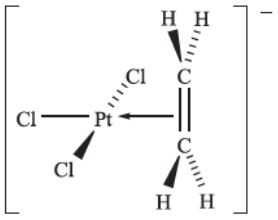
- Alkene complexes of metals constitute one of the important classes of coordination compounds.
- The metals are found in low oxidation states owing to the more favorable interaction with the soft π-electron donors
- Most metal alkene complexes contain other ligands. However, complexes with only the metal and organic ligands (olefins) are also known.
- Alkene complexes are often made by displacement of CO or halide ion by an alkene.
- **Zeise's salt,** the first synthesized organometallic compound, W. C. Zeise, 1827
- **Zeise's method:** By dehydration of ethanol. The dimer $[Pl(C_2H_4)Cl_2]_2$ is obtained first and the original salt is obtained by treating the concentrated dimer with KCl.

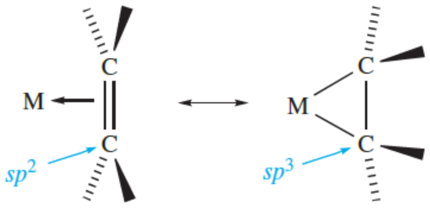
$$K_2[PtCl_4] + C_2H_5OH \rightarrow K[PtCl_3(\eta^2\text{-}C_2H_4)]$$

- **Smoother condition:** By treating $K_2[PtCl_4]$ with ethylene in presence of catalytic amount of $SnCl_2$, with $[PtCl_3(SnCl_3)]^{2-}$ being the intermediate.

$$K_2[PtCl_4] + C_2H_4 \xrightarrow{SnCl_2} K[PtCl_3(C_2H_4)] + KCl$$

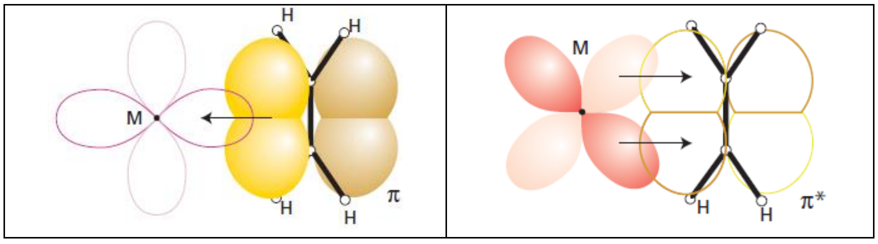
- **Structure of Zeise's salt**
- $[PtCl_3(\eta^2\text{-}C_2H_4)]^-$ ion contains a square planar (or pseudo-square planar) Pt(II) center and in the solid state, the ethene ligand lies perpendicular to the coordination 'square plane', thereby minimizing steric interactions.
- Pt-Cl bond trans to C_2H_4 (234 pm) is longer than the cis Pt-Cl bonds (~230 pm)
- Pt-C bonds are equidistant from Pt atom (~213pm).
- The C-C distance, 137 pm, is slightly longer than in free ethylene (134 pm), indicating some dπ-pπ* back-bonding.
- Back-bonding is also indicated by a bending of the four hydrogen atoms away from the Pt atom

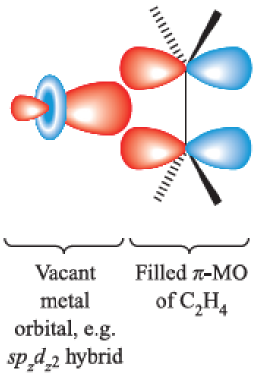
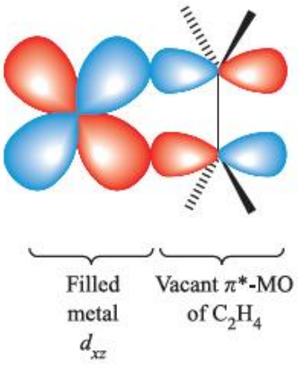




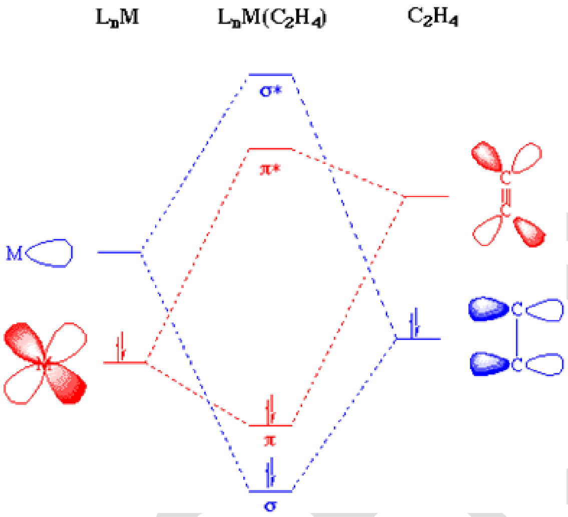
Bonding in metal-alkene/Zeise's salt (Dewar Chatt Duncanson model)

- Alkenes (C_2H_4) normally bond side-on to a metal atom (Pt) with equidistant C-atoms and other groups on the alkene (C_2H_4) lying perpendicular to metal (Pt) plane and two C-atoms.
- The electron density of the C=C π-bond can be donated to a suitable empty orbital (d_{x2-y2}) on the metal (Pt) atom to form a σ-bond.
- Simultaneously, a filled metal d orbital (d_{yz}, T_{2g}) can donate electron density back to the empty π* orbitals of the alkene to form a π-bond (Dewar Chatt Duncanson model).
- These effects tend to reduce the C-C bond order (elongated C-C distance) and rehybridizing C-atoms to sp^3, indicated by the bending of H-atoms away from the metal (Pt).



$Pt(d_{x2-y2}) \leftarrow \pi(C_2H_4)$	$Pt(d_{yz}) \rightarrow \pi^*(C_2H_4)$
	

- ➢ Greater the electron density back-donated into the π* orbital on the alkene, the greater the reduction in the C=C bond order



MO diagram of Metal-alkene complex

Grignard reagent

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

$$Mg + RX \longrightarrow RMgX \text{ (in diethyl ether)}$$

- ➢ Transmetallation is useful means of preparing pure Grignard reagents.

$$Mg + RHgBr \longrightarrow Hg + RMgBr$$
$$Mg + R_2Hg \longrightarrow Hg + R_2Mg$$

- ➢ RMgX are generally solvated and Mg centre is typically tetrahedral. For example, $EtMgBr.2Et_2O$; $PhMgBr.2Et_2O$
- ➢ Solutions of Grignard reagent may contain several species, e.g. RMgX, R_2Mg, MgX_2, $RMg(\mu\text{-}X)_2MgR$, which are further complicated by solvation.
- ➢ After its formation, the Grignard reagent is most of the time in dynamic equilibrium between the monomer, the dimer, sometimes the polymer and the species resulting from dismutation, i.e. MgR_2 and MgX_2.
- ➢ The equilibrium established between different species of Grignard reagent in ether solution is known as **Schlenk equilibrium**.

$$2RMgX \leftrightarrow R_2Mg + MgX_2$$

- ➢ The position of equilibrium between these species is markedly dependent on concentration, temperature and solvent; strongly donating solvents favour monomeric species in which they coordinate to the metal centre.
- ➢ Treatment with dioxane results in the precipitation of $MgCl_2$(dioxane) leaving behind pure R_2Mg in the solution.

Metallocenes

- ➢ Bonding theory proposed to be in between a metal and π-orbitals of ligand.
- ➢ Metallocene name come from their similarities with aromatic molecules.
- ➢ These complexes have two Cp rings with metal sandwiched between the two rings, formally known as metallocene, $(Cp)_2M$, 18e rule is not mandatory.
- ➢ All the C-C bond lengths in each of these bound ligands are identical, ligands are aromatic.
- ➢ First row Metallocenes are known for V(II), Cr(II), Mn(II), Fe(II), Co(II) and Ni(II),
- ➢ All except $(\eta^5\text{-}C_5H_5)_2V$, where the starting chloride is VCl_3 can be synthesized by using $Na[C_5H_5]$ precursor prepared as follows. Sodium cyclopentadienide can then be used to react with d-metal halides to produce Metallocenes

$$2\,Na + 2\,C_5H_6 \xrightarrow{THF} 2\,Na[C_5H_5] + H_2$$
$$MCl_2 + 2Na[Cp] \longrightarrow (\eta^5\text{-}Cp)_2M + 2NaCl$$
$$M = Cr, Mn, Fe, Co, Ni$$

Ferrocene

- $(Cp)_2Fe$ is the best-known cyclopentadienyl complex
- It is a diamagnetic, orange solid (MP 393 K) and obeys 18-electron rule
- In the gas phase, the two cyclopentadienyl rings are eclipsed
- The structure of $(\eta^5\text{-}C_5H_5)_2Fe$ in the solid state, originally believed to be staggered, is now viewed to be nearly eclipsed with rotational angle of 9° between the Cp rings.
- In case of substituted Cp rings, the barrier to rotation is higher, and staggered orientation is favored in both gas and solid states.

Preparation

- The Fe(III) is first reduced by the Grignard reagent to Fe(II) which then reacts to form ferrocene

$$Fe^{3+} \xrightarrow{CpMgX} Fe^{2+} \xrightarrow{CpMgX} (n^5\text{-}C_5H_5)_2Fe$$

- Cyclopentadiene itself is acidic enough so that potassium hydroxide will deprotonate it in solution and then reaction with $FeCl_2$ leads to the formation of $(\eta^5\text{-}C_5H_5)_2Fe$

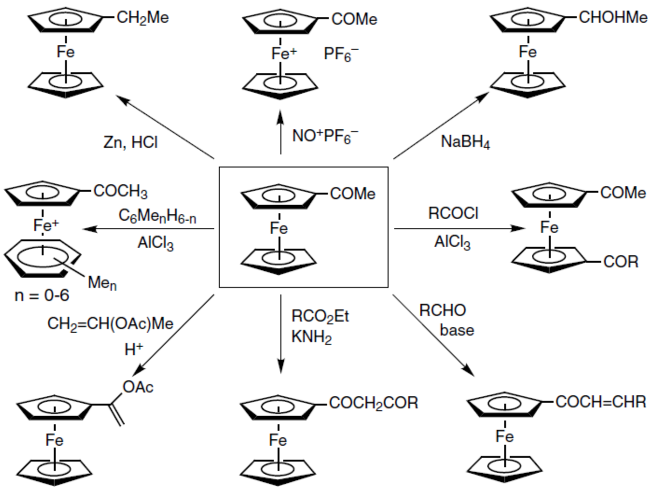
$$2\,KOH + 2\,C_5H_6 + FeCl_2 \xrightarrow{DMSO} Fe(C_5H_5)_2 + 2\,H_2O + 2\,KCl$$

- Alternatively., $(\eta^5\text{-}C_5H_5)_2Fe$ can be synthesized by

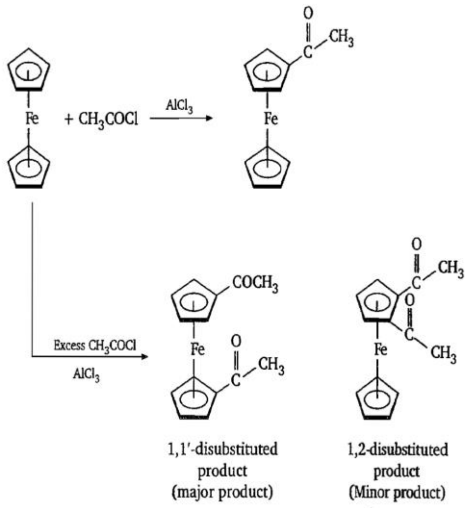
$$MCl_2 + 2C_5H_6 + 2Et_2NH \longrightarrow (\eta^5\text{-}Cp)_2M + 2[Et_2NH_2]Cl$$

$$(M = Fe, Ni)$$

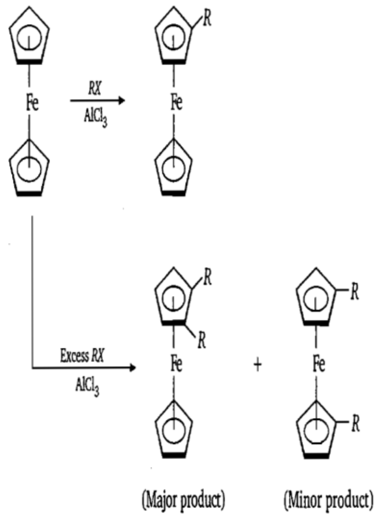
Reactions:



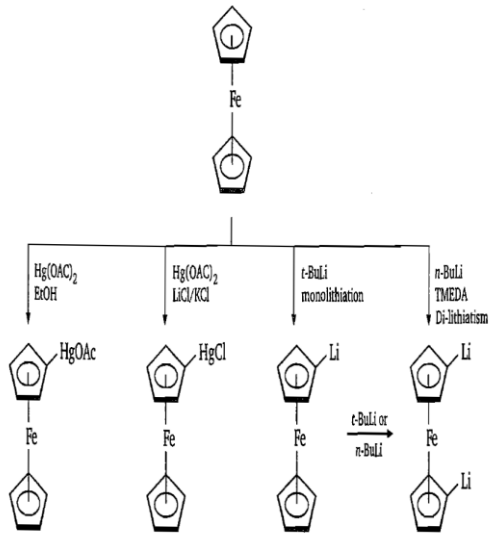
- Ferrocene behaves like an aromatic compound
- Ferrocene is more electron rich than benzene; Friedel-Crafts acylation reaction is faster (10^6 times) than benzene. It undergoes acylation using RCOCl and $AlCl_3$. $AlCl_3$ reacts with RCOCl to produce electrophile $R\text{-}C^+{=}O$. $1,1^/$-disubstituted product is the major product.



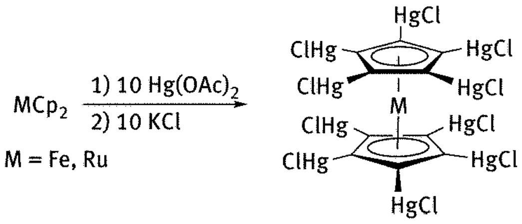
- It is also possible to introduce the RCO group by the reaction of acetic anhydride with H_3PO_4 as catalyst. In this reaction only monosubstituted product is formed.
- Ferrocene undergoes alkylation using RX and AlCl3 on one ring to give monosubstituted alkyl derivative. The presence of alkyl group (electron donating) activates the ring for further substitution resulting in disubstituted derivative (in the same ring) as major product. Herein, $AlCl_3$ reacts with RX to generate the electrophile R^+.



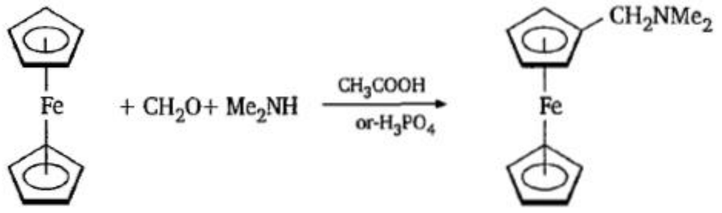
- The introduction of metal into the ring is called a metallation. Metallation reactions of ferrocene are useful for synthesizing other derivatives.



- The Cp ring can be lithiated and the resulting $CpFe(C_5H_4Li)$ behaves like a conventional lithium aryl in its reactions with electrophiles. Mono lithiated ferrocene is formed by the reaction of ferrocene with t-BuLi.
- Metallation of the Cp ligands in ferrocene can also proceed with complete substitution of all 10 H-atoms. This can be achieved by electrophilic mercuration with $Hg(OAc)_2$ or $Hg(O_2CCF_3)_2$.



- Dimethylamine and formaldehyde undergo a Mannich reaction with ferrocene to give dimethylaminomethylferrocene. This product is used for the preparation of many other derivatives. Formaldehyde and dimethylamine react to generate the electrophile $^{+}CH_2\text{-}NMe_2$ and it attacks on the Cp ring to give the product

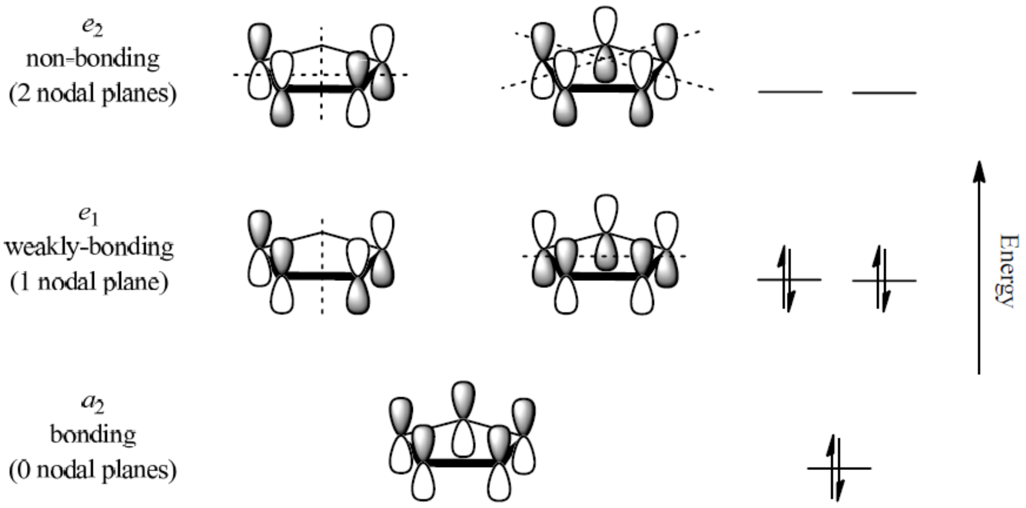


Structure and bonding

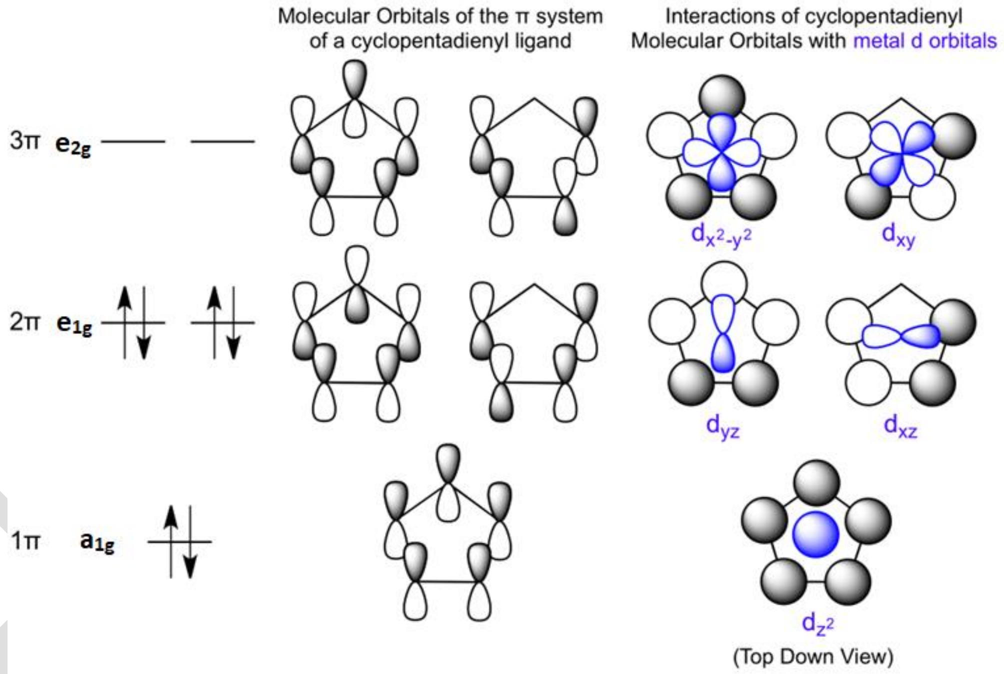
- The two cyclopentadienyl (Cp) rings of ferrocene may be orientated in the two extremes of either an eclipsed (D_{5h}) or staggered (D_{5d}) conformation
- Ground state structures of ferrocene may be either D_{5h} or D_{5d} (energy barrier of rotation about Fe-Cp axis is very small)
- The primary orbital interactions occur between d-orbitals of Fe and π-orbitals of the Cp ligand
- The D_{5d} point group representations simplify the symmetry matching of ligand molecular orbitals and metal atomic orbitals.
- In D_{5d} symmetry, there is a center of symmetry and there will be centro-symmetric (g) and anti-symmetric (u) combinations

- The five p-orbitals on the planar Cp^- ring (D_{5h} symmetry) can be combined to produce five molecular orbitals.
- X-ray crystallographic and electronic diffraction studies in the gas phase indicate an eclipsed conformation
- For $(\eta^5\text{-}Cp)_2M$, such as ferrocene, the π-orbitals of the two Cp ligands are combined pairwise to form the symmetry-adapted linear combination of molecular orbitals (SALC's), resulting in three different Ligand Group Orbitals (LGOs)

1. A low-lying filled bonding pair of a_{1g} and a_{2u} symmetry
2. A filled weakly bonding pair of e_{1g} and e_{1u} symmetry
3. An empty anti-bonding pair of e_{2g} and e_{2u} symmetry.

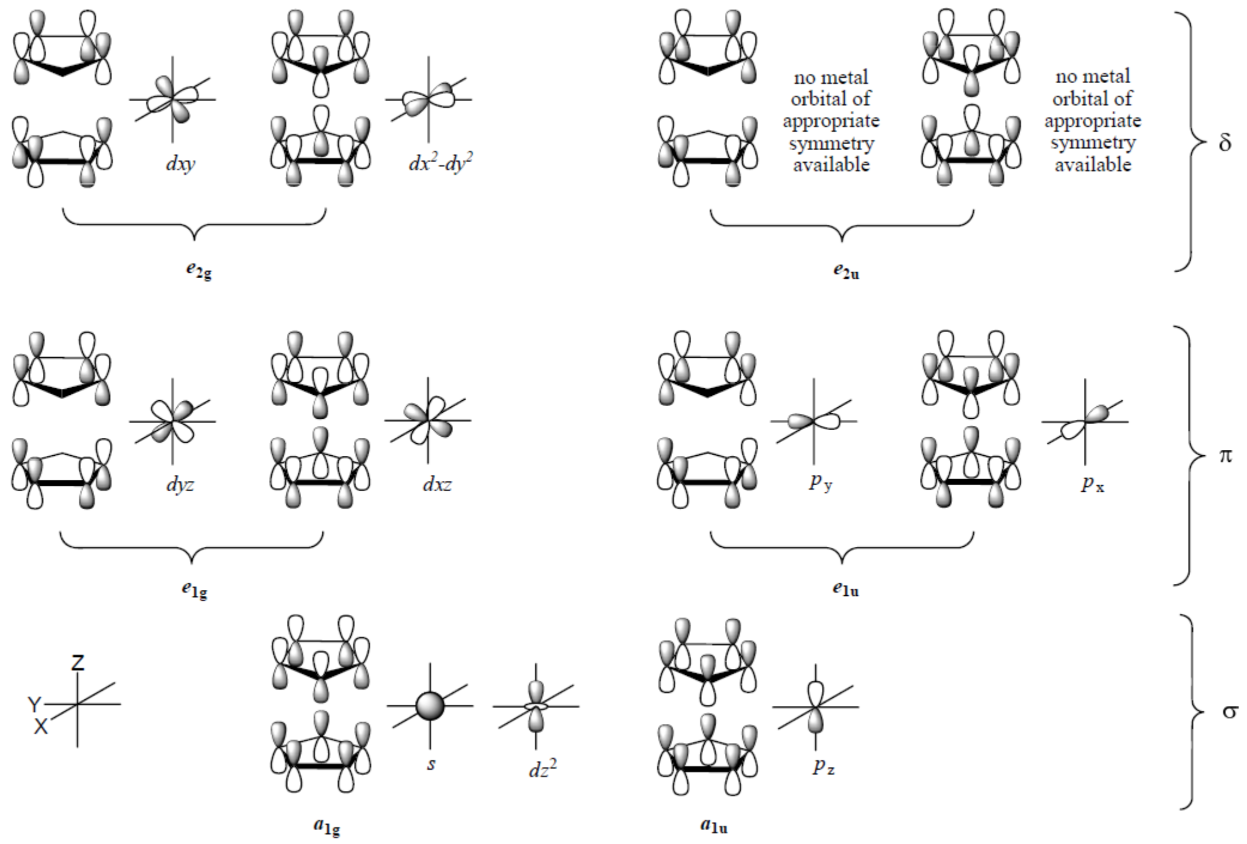


The π-molecular orbitals of the cyclopentadienyl ring (D_{5h})



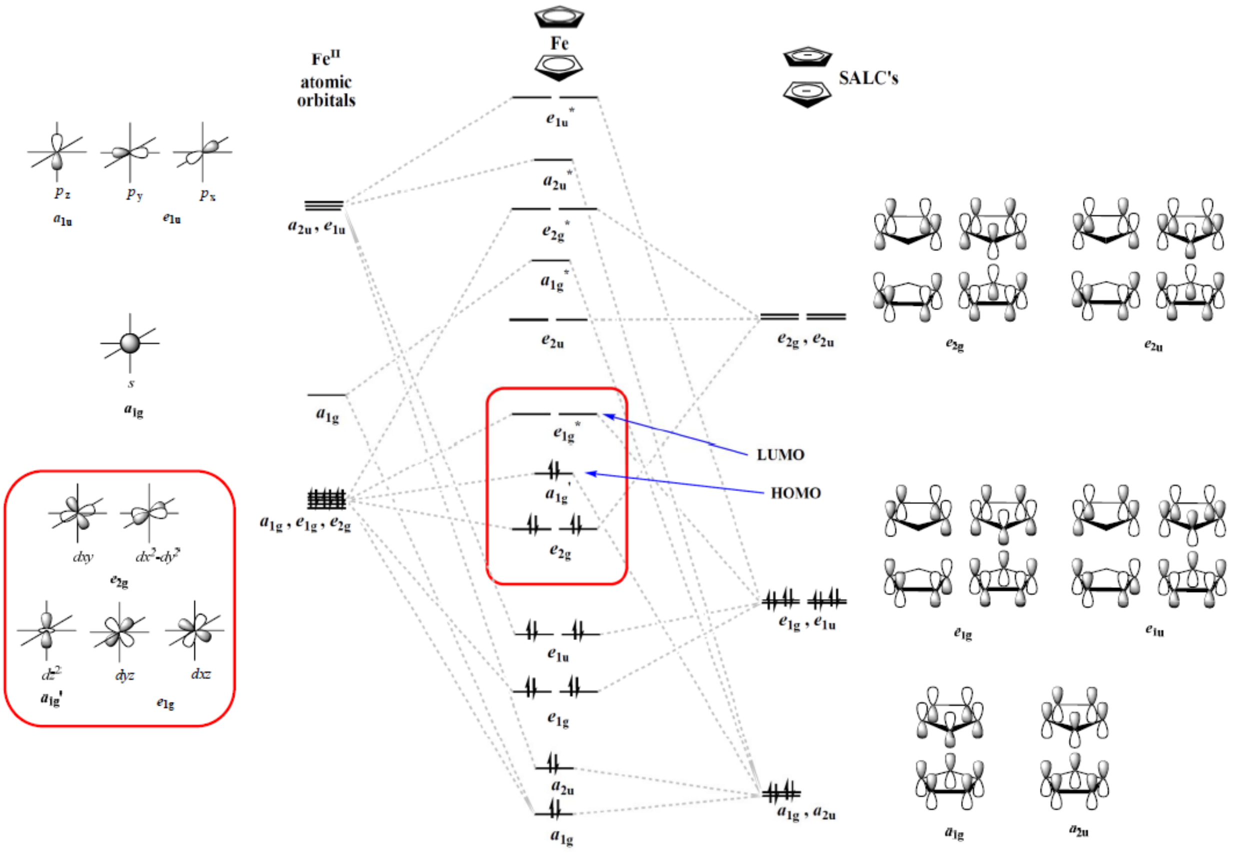
- a_{1g} (σ) orbitals are very stable & interact very little, poor σ-donor
- Only e_{1g} orbitals of ligand matches with 3d orbitals (d_{yz}, d_{zx}) that form two strong π-bonds
- e_{2g} (π) orbitals are very high in energy & interact and interact little, poor π-acceptor
- Metal orbitals of suitable symmetry interact with SALC orbitals and give MOs of $(\eta^5\text{-}Cp)_2Fe$.

Symmetry matching of SALC orbitals with the metal atomic orbitals

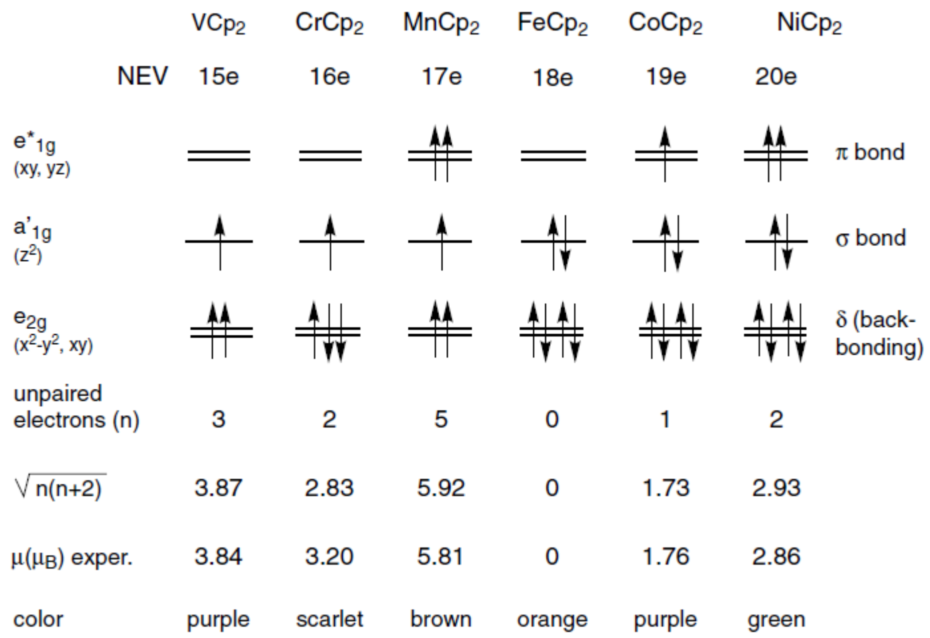


- a_{1g} (σ) orbitals are very stable & interact very little, poor σ-donor
- Only e_{1g} orbitals of ligand matches with 3d orbitals (dyz, dzx) that form two strong π-bonds
- e_{2g} (π) orbitals are very high in energy & interact and interact little, poor π-acceptor.
- e_{1u} and a_{2u} (4p) orbitals on Fe are at a high energy, do not contribute much to bonding
- no metal d-orbitals have appropriate symmetry with e_{2u}

A qualitative molecular orbital diagram for ferrocene (D_{5d})



- LUMO (e_{1g}) is not significantly antibonding so addition of e does not impart notable impact on the stability
- HOMO (e_{2g} and a_{1g}) is slightly bonding and therefore removing e from them does not greatly destabilize the complex



	VCp_2	$CrCp_2$	$MnCp_2$	$FeCp_2$	$CoCp_2$	$NiCp_2$	
NEV	15e	16e	17e	18e	19e	20e	
e^*_{1g} (xy, yz)			↑↑		↑	↑↑	π bond
a'_{1g} (z^2)	↑	↑	↑	↑↓	↑↓	↑↓	σ bond
e_{2g} (x^2-y^2, xy)	↑↑	↑↓↓	↑↑	↑↓↑↓	↑↓↑↓	↑↓↑↓	δ (back-bonding)
unpaired electrons (n)	3	2	5	0	1	2	
$\sqrt{n(n+2)}$	3.87	2.83	5.92	0	1.73	2.93	
$\mu(\mu_B)$ exper.	3.84	3.20	5.81	0	1.76	2.86	
color	purple	scarlet	brown	orange	purple	green	

Structure and aromaticity. Comparison of aromaticity and reactivity with that of benzene