COURSE CODE: SC202(CHEMISTRY)
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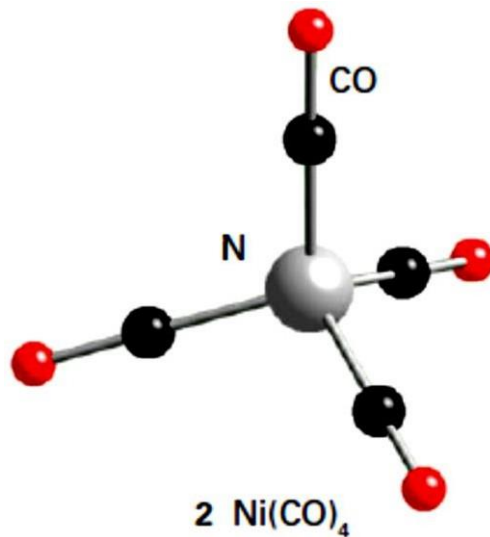LECTURE- ORGANOMETALLIC CHEMISTRY

Organometallic Chemistry

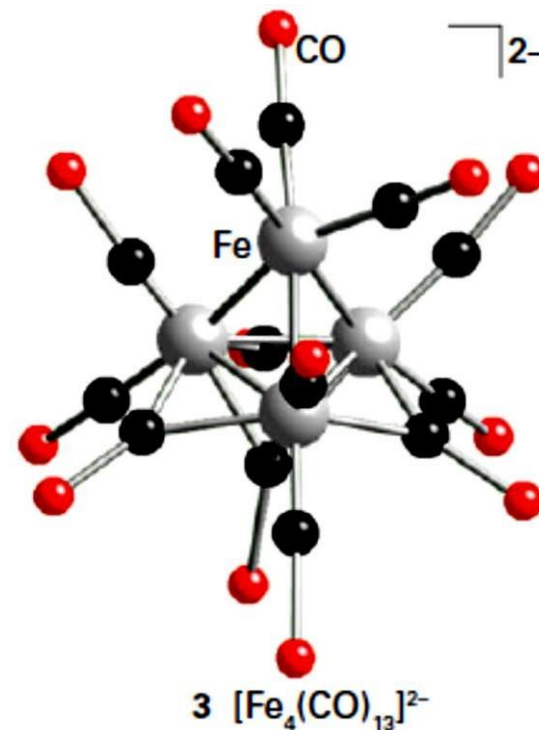**Definition:** Organometallic chemistry is the chemistry of compounds containing metal-carbon bonds.

The first organometallic complex was prepared by W.C. Zeise in 1827, an ethene complex of platinum(II).
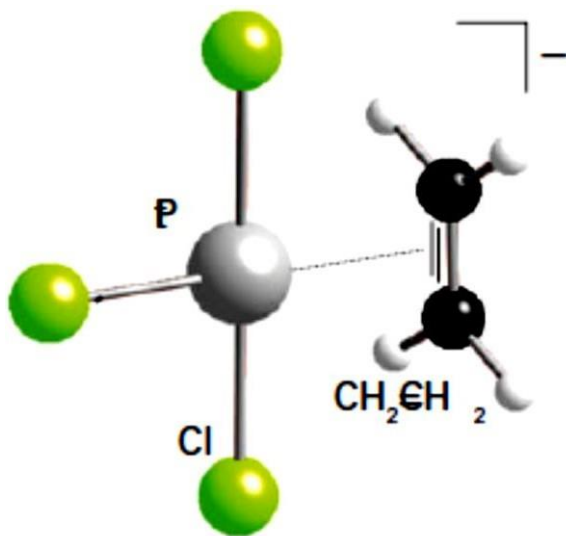
1 $[PtCl_3(C_2H_4)]^-$
Zeise's salt

2 $Ni(CO)_4$

3 $[Fe_4(CO)_{13}]^{2-}$

Classification of organometallic compounds

On the basis of nature of metal-carbon bond organometallic compounds are classified into

➢ **Ionic bonded organometallic compounds:**

The organometallic compounds of alkali, alkaline earth metals, lanthanides and actinides predominantly form ionic compounds. These are generally colourless compounds extremely reactive, and insoluble in organic solvents.

Examples: $Ph_3C^-Na^+$, Cs^+Me^-, Na^+Cp^-.

➢ **Covalent bonded organometallic compounds:**

1) σ- bonded organometallic compounds:

These are the compounds in which carbon atom of the organic ligand is bonded to the metal by a 2 electron, 2 centrered (2e-2c) covalent bond.

Examples: $Ni(CO)_4$, $Fe(CO)_5$

2) π- bonded organometallic compounds:

These are the compounds of metals with alkenes, alkynes, benzene and other ring compounds. In these complexes, the metal and ligand form a bond that involves the π-electrons of the ligand.

Examples:$[(\eta^5\text{-}C_5H_5)_2Fe)]$, $K[PtCl_3(\eta^2\text{-}C_2H_2)]$ (Zeise's salt)

➢ Multicentre bonded organometallic compounds:

The compounds in which a loosely bonded electron deficient species exist with the coordination of metal like Li, Be, Al…etc

Examples: Al_2Me_6

Electron counting and oxidation states

Two models are routinely used to count electrons, the so-called **neutral-ligand method** (sometimes called the *covalent method*) and the **donor-pair method** (sometimes known as the *ionic method*).

(a) Neutral-ligand method

Count all valence electrons of the metal atom and all the electrons donated by the ligands.

If the complex is charged, add or subtract the appropriate number of electrons to the total.

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

Answer (a) We start with the Ir atom (Group 9) which has nine valence electrons, then add in the electrons from the two Br atoms and the CH_3 group (each is a one-electron donor) and finally add in the electrons from the CO and PPh_3 (both are two-electron donors). Thus, the number of valence electrons on the metal atom is $9 + (3 \times 1) + (3 \times 2) = 18$.

(b) In a similar fashion, the Cr atom (Group 6) has six valence electrons, the $\eta^5-C_5H_5$ ligand donates five electrons, and the $\eta^6-C_6H_6$ ligand donates six, so the number of metal valence electrons is $6 + 5 + 6 = 17$. This complex does not obey the 18-electron rule and is not stable.

Table 1:Typical ligands and their electron counts

(a) NeutraHigand method

Ligand	Formula	Designation	Electrons donated
Carbonyl	CO	L	2
Phosphine	PR_3	L	2
Hydride	H	X	1
Chloride	Cl	X	1
Dihydrogen	H_2	L	2
η^1-Alkyl, -alkenyl, -alkynyl, and -aryl groups	R	X	1
η^2-Alkene	$CH_2=CH_2$	L	2
η^2-Alkyne	$RCCR$	L	2
Dinitrogen	N_2	L	2
Butadiene	$CH_2=CH-CH=CH_2$	L_2	4
Benzene	C_6H_6	L_3	6
η^3-Allyl	CH_2CHCH_2	LX	3
η^5-Cyclopentadienyl	C_5H_5	L_2X	5

Table 2: Typical ligands and their electron counts

(b) Donor-pair method*

Ligand	Formula	Electrons donated
Carbonyl	CO	2
Phosphine	PR_3	2
Hydride	H^-	2
Chloride	Cl^-	2
Dihydrogen	H_2	2
η^1-Alkyl, -alkenyl, -alkynyl, and -aryl groups	R^-	2
η^2-Alkene	$CH_2=CH_2$	2
η^2-Alkyne	$RCCR$	2
Dinitrogen	N_2	2
Butadiene	$CH_2=CH-CH=CH_2$	4
Benzene	C_6H_6	6
η^3-Allyl	$CH_2CHCH_2^-$	4
η^5-Cyclopentadienyl	$C_5H_5^-$	6

(b) Donor-pair method

1. Calculation of the oxidation number. *The rules for calculating the oxidation number of an element in an organometallic compound are the same as for conventional coordination compounds.*

a.Neutral ligands, such as CO and phosphine, are considered to be two-electron donors and are formally assigned an oxidation number of 0.

b. Ligands such as halides, H, and CH_3 are formally considered to take an electron from the metal atom, and are treated as Cl^-, H^-, and CH_3^- (and hence are assigned oxidation number -1); in this anionic state they are considered to be two-electron donors. The cyclopentadienyl ligand, C_5H_5(Cp), is treated as $C_5H_5^-$ (it is assigned an oxidation number of -1); in this anionic state it is considered to be a six-electron donor.

2. The *oxidation number* of the metal atom is the total charge of the complex minus the charges of any ligands.

3. The *number of electrons* the metal provides is its group number minus its oxidation number.

The *total electron count* is the sum of the number of electrons on the metal atom and the number of electrons provided by the ligands.

Question 2: Assign the oxidation number and count the valence electrons on the metal atom in (a) $[IrBr_2(CH_3)(CO)PPh_3)_2]$, (b) $[Cr(\eta^5-C_5H_5)(\eta^6-C_6H_6)]$, and (c) $[Mn(CO)_5]^-$.

Answer (a) We treat the two Br groups and the CH_3 as three singly negatively charged two-electron donors and the CO and the two PPh_3 ligands as three two-electron donors, providing 12 electrons in all. Because the complex is neutral overall, the Group 9 Ir atom must have a charge of 3 (that is, have oxidation number 3) to balance the charge of the three anionic ligands, and thus contributes 9 - 3 = 6 electrons.

This analysis gives a total of 18 electrons for the Ir(III) complex.

(b) We treat the $\eta^5-C_5H_5$ ligand as $C_5H_5^-$ and thus it donates six electrons, with the $\eta^6-C_6H_6$ ligand donating a further six. To maintain neutrality, the Group 6 Cr atom must have a charge of +1 (and an oxidation number of +1) and contributes 6 - 1 = 5 electrons. The total number of metal electrons is 12 + 5 = 17 for a Cr(I) complex.

Hapticity refers to the number of ligand atoms that are considered formally to be bonded to the metal atom. The hapticity is denoted η^n, where n is the number of atoms (and η is eta).

For example, a CH_3 group attached by a single M-C bond is monohapto, η^1, and if the two C atoms of an ethene ligand are both within bonding distance of the metal, the ligand is dihapto, η^2. Thus, three cyclopentadienyl complexes might be described as having η^1 (**4**), η^3 (**5**), or η^5 (**6**) cyclopentadienyl groups.

η^1-Cyclopentadienyl(**4**) η^3-Cyclopentadienyl(**5**)

η^5-Cyclopentadienyl(**6**)

$7[Mo(\eta^6\text{-}C_6H_6)(CO)_3]$

Ref: Shriver & Atkins' Inorganic Chemistry, 5th Ed
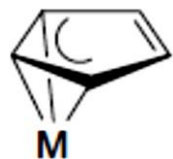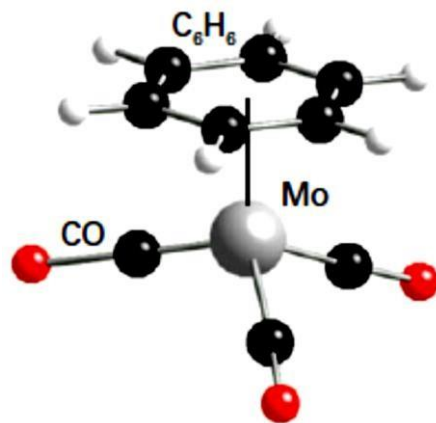
- Some ligands (eg., the hydride ligand, H⁻) can bond to more than one metal atom in the same complex, and are then referred to as **bridging ligands**.

- The Greek letter μ(mu) is used to indicate how many atoms the ligand bridges.

- Thus a μ_2-CO is a carbonyl group that bridges two metal atoms and a μ_3-CO bridges three.

Nomenclature

Ligands are listed in alphabetical order followed by the name of the metal, all of which is written as one word.

The name of the metal should be followed by its oxidation number in parentheses.

For example, $[Mo(\eta^6\text{-}C_6H_6)(CO)_3]$

IUPAC name: benzene(tricarbonyl)molybdenum(0).

$K[PtCl_3(\eta^2\text{-}CH_2\text{=}CH_2)]$ Potassiumtrichloro(ethene)platinate(II)

Question 3: : Give the formal names of (a) ferrocene $[Fe(\eta^5\text{-}C_5H_5)_2$ and (b) $[RhMe(PMe_3)_4]$.

Answer (a) Ferrocene contains two cyclopentadienyl groups that are both bound to the metal atom through all five

carbon atoms, thus both groups are designated $\eta5$. The full name for ferrocene is thus

bis(η^5-cyclopentadienyl)iron(II).

(b) The rhodium compound contains one formally anionic methyl group and four neutral trimethylphosphine

ligands, therefore the formal name is methyltetrakis-(trimethylphosphine) rhodium(I).

Question 4: What is the formal name of $[Ir(Br)_2(CH_3)(CO)(PPh_3)_2]$?

Metal-metal bonding and metal clusters

(a) Structure of clusters

A cluster includes all compounds with metal-metal bonds that form triangular or larger cyclic structures.

$[Co_4(CO)_{12}]$
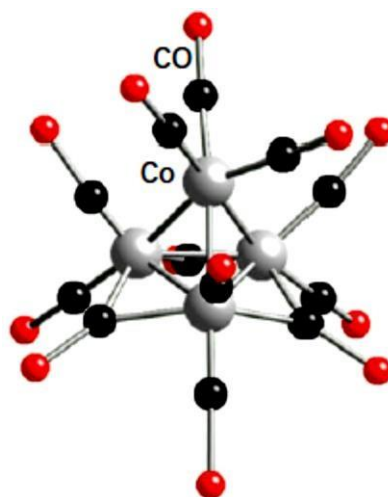
(b) Electron counting in clusters

$Mn_2(CO)_{10}$

Each Mn atom is considered to have 17 electrons (seven from Mn and 10 from the five CO ligands). Mn-Mn bond consists of two electrons shared between the two metal atoms, and hence raises the electron count of each by 1, resulting in two 18-electron metal atoms.

O—O
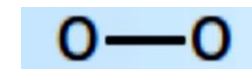
- In $Os_3(CO)_{12}$, each $Os(CO)_4$ fragment has 16 electrons before metal-metal bonding is taken into consideration and three metal-metal bonds, so increasing the number of electrons around each metal to 18, but with a total of only 48 and not 54 electrons

- The bonding electrons are referred to as the **cluster valence electrons** (CVEs), and a cluster of x metal atoms with y metal-metal bonds needs $18x - 2y$ electrons.

- Octahedral M_6 and larger clusters do not conform to this pattern, and the polyhedral skeletal electron pair rules, known as Wade's rules, have been refined by D.M.P. Mingos and J. Lauher to apply to metal clusters. These **Wade-Mingos-Lauher rules** are summarized in Table 3
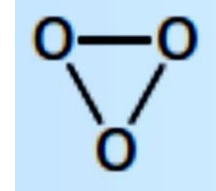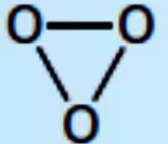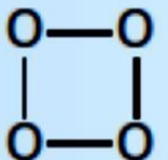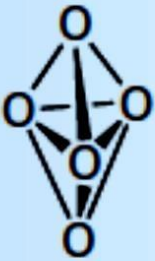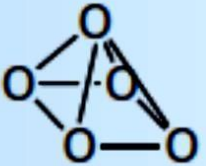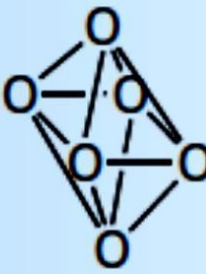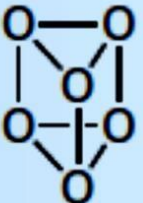
Table 3: Correlation of cluster valence electron (CVE) count and structure

Number of metal atoms	Structure of metal framework		CVE count	Example
1	Single atom	O	18	$Ni(CO)_4$ (2)
2	Linear	O—O	34	$Mn_2(CO)_{10}$
3	Closed triangle		48	$[Co_3(CH)(CO)_9]$
4	Tetrahedron		60	$Co_4(CO)_{12}$ (76)
	Butterfly		62	$[Fe_4(CO)_{12}C]^{2-}$
	Square		64	$Os_4(CO)_{16}$

Ref: Shriver & Atkins' Inorganic Chemistry, 5th Ed

5	Trigonal bipyramid		72	$Os_5(CO)_{16}$
	Square pyramid		74	$Fe_5C(CO)_{15}$
6	Octahedron		86	$Ru_6C(CO)_{17}$
	Trigonal prism		90	$[Rh_6C(CO)_{15}]^{2-}$

Ref: Shriver & Atkins' Inorganic Chemistry, 5th Ed

(c) Synthesis of clusters

Three methods are commonly used to prepare metal clusters:

a.   thermal expulsion of CO from a metal carbonyl,

One example is the synthesis of $[Co_4(CO)_{12}]$ by heating $[Co_2(CO)_8]$:

$$2[Co_2(CO)_8] \rightarrow [Co_4(CO)_{12}] + 4CO$$

In this case, a decrease in valence electrons around the metal resulting from loss of CO is compensated by the formation of M-M bonds.

**b. the condensation of a carbonyl anion and a neutral organometallic complex,**

A widely used and more controllable reaction is based on the condensation of a carbonyl anion and a neutral organometallic complex:

$$[Ni_5(CO)_{12}]^{2-} + [Ni(CO)_4] \rightarrow [Ni_6(CO)_{12}]^{2-} + 4CO$$
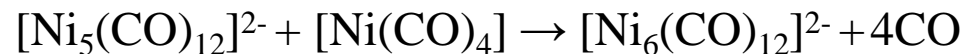
The Ni_5 complex has a CVE of 76 whereas the Ni_6 complex has a count of 86. This type of reactions are called **redox condensation** and are useful for the preparation of anionic metal carbonyl clusters.

c. the condensation of an organometallic complex with an unsaturated organometallic compound.

A third method, pioneered by F.G.A. Stone, is based on the condensation of an organometallic complex containing displaceable ligands with an unsaturated organometallic compound. The unsaturated complex may be a metal alkylidene, L_nMCR_2, a metal alkylidyne, L_nMCR, or a compound with multiple metal-metal bonds:
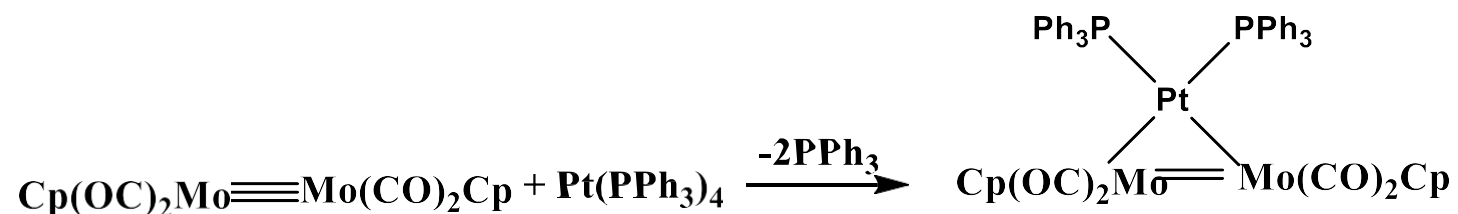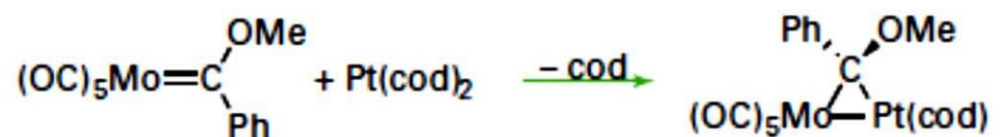
Boron clusters

- B forms several series of neutral and anionic polymeric cage-like boron-hydrogen compounds called borohydrides.

- Borohydrides are formed with up to 12 B atoms and fall into three classes called **closo, nido, and arachno**.

- The borohydrides with the formula $[B_nH_n]^{2-}$ have a **closo structure**, a name derived from the Greek for 'cage'. This series of anions is known for $n = 5$ to 12, and examples include the trigonal-bipyramidal $[B_5H_5]^{2-}$ ion (**8**), the octahedral $[B_6H_6]^{2-}$ ion (**9**), and the icosahedral $[B_{12}H_{12}]^{2-}$ ion (**10**).

8 $[B_5H_5]^{2-}$

9 $[B_6H_6]^{2-}$

10 $[B_{12}H_{12}]^{2-}$
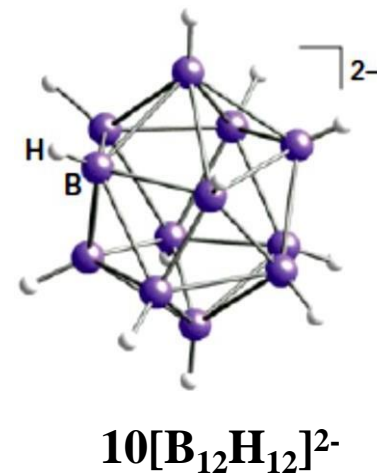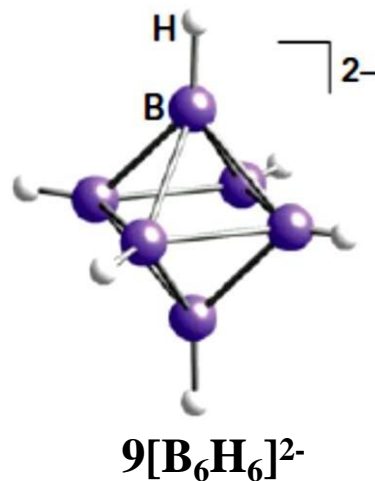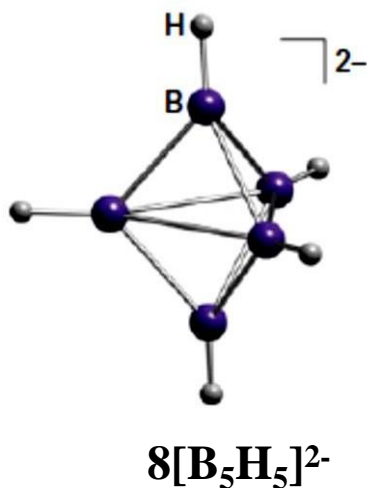
- When boron clusters have the formula B_nH_{n+4} they adopt the ***nido* structure**, a name derived from the Latin for 'nest'. An example is B_5H_9 (**11**).

- Clusters of formula B_nH_{n+6} have an ***arachno* structure**, from the Greek for 'spider' (as they resemble untidy spiders' webs). One example is pentaborane (B_5H_{11}, **12**).
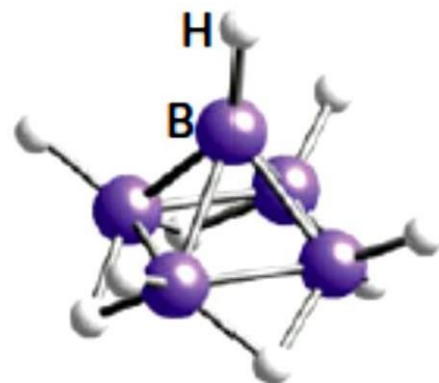
(**11**)B_5H_9
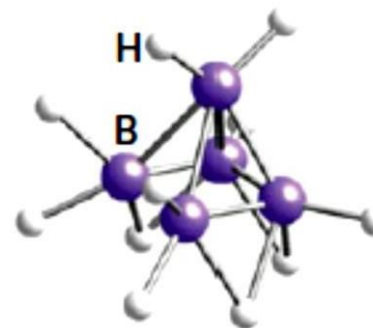
(**12**)B_5H_{11}

Table 4: Classification and electron count of boron hydrides

Type	Formula* pairs	Skeletal electron	Examples
Closo	$[B_nH_n]^{2-}$	$n + 1$	$[B_5H_5]^{2-}$ to $[B_{12}H_{12}]^{2-}$
Nido	B_nH_{n+4}	$n + 2$	B_2H_6, B_5H_9, B_6H_{10}
Arachno	B_nH_{n+6}	$n + 3$	B_4H_{10}, B_5H_{11}
Hypho[†]	B_nH_{n+8}	$n + 4$	None[‡]

Question 6: Count the number of skeletal electrons in B_4H_{10}

Ans: We consider the number of BH units and the number of H atoms.

There are four BH units, which contribute 4 x 2 = 8 electrons, and the six additional H atoms, which contribute a further

six electrons, giving 14 in all.

The resulting seven pairs are distributed as shown in fig:

two are used for the additional terminal B-H bonds,

four are used for the four BHB bridges, and

 one is used for the central B-B bond.

Ref: Shriver & Atkins' Inorganic Chemistry, 5th Ed
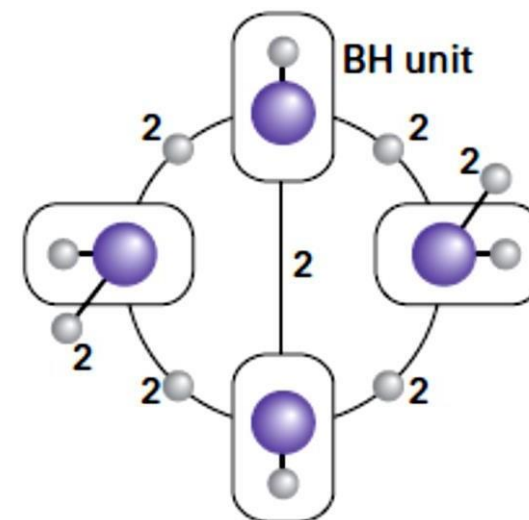
Question 6: *Infer the structure of $[B_6H_6]^{2-}$ from its formula and from its electron count.*

Answer We should note that the formula $[B_6H_6]^{2-}$ belongs to a class of borohydrides having the formula $[B_nH_n]^{2-}$, which is characteristic of a *closo* species.

Alternatively, we can count the number of skeletal electron pairs and from that deduce the structural type. Assuming one B-H bond per B atom, there are six BH units to take into account and therefore 12 skeletal electrons plus two from the overall charge of -2: 6 x 2 + 2 = 14, or seven electron pairs which is $n + 1$ with $n = 6$. This number is characteristic of *closo* clusters. The closed polyhedron must contain triangular faces and six vertices; therefore an octahedral structure is indicated.

Question 7: *How many framework electron pairs are present in B_4H_{10} and to what structural category does it belong? Sketch its structure.*
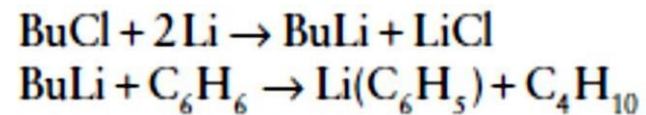
Organometallic compounds of the Group 1 elements

- Group 1 elements form a number of organometallic compounds that are unstable in the presence of water and are pyrophoric in air.

- Sodium and potassium alkyls are produced by a **transmetallation reaction**, which involves breaking a metal-carbon bond and forming a metal-carbon bond to a different metal. For example, methylsodium is produced in the reaction between sodium metal and dimethylmercury in a hydrocarbon solvent:

$$Hg(CH_3)_2 + 2\,Na \rightarrow 2\,NaCH_3 + Hg$$
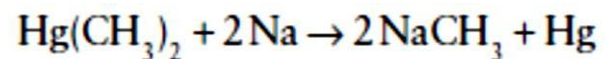
- Organolithiums are the most important Group 1 organometallic compounds. They are liquids or low melting solids, are the most thermally stable of the entire group, and are soluble in organic and nonpolar solvents such as THF.

- They can be synthesized from an alkyl halide and lithium metal or by reacting the organic species with butyllithium, $Li(C_4H_9)$, commonly abbreviated to BuLi.

$$BuCl + 2\,Li \rightarrow BuLi + LiCl$$
$$BuLi + C_6H_6 \rightarrow Li(C_6H_5) + C_4H_{10}$$

- Organolithium compounds are very important in organic synthesis, the most important reactions being those in which they act as nucleophiles and attack, for example, a carbonyl group:

Organometallic compounds of the Group 2 elements

Methylberyllium, $Be(CH_3)_2$ (**13**) , is predominantly a monomer in the vapour phase and in solid it forms polymeric chains in which the bridging CH_3 groups form $3c,2e$ bridging bonds. Bulkier alkyl groups lead to a lower degree of polymerization; ethylberyllium (**14**) is a dimer and t-butylberyllium (**15**) is a monomer.
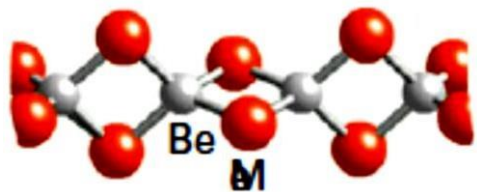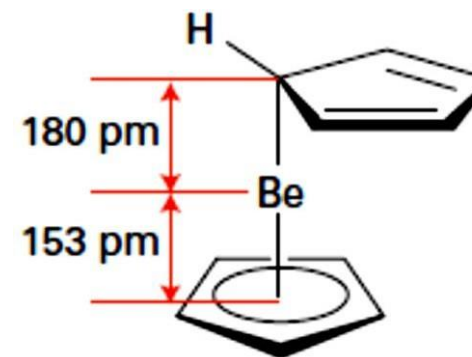

13$(BeMe_2)_n$, $Me = CH_3$
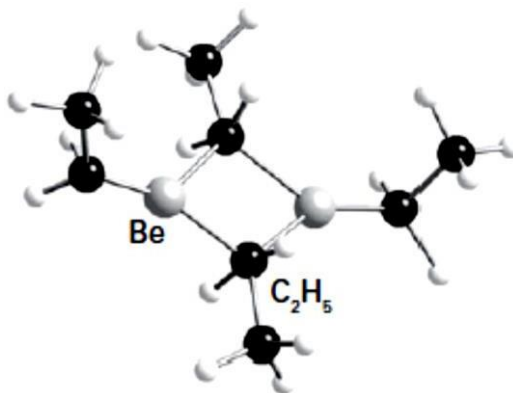
14$(BeEt_2)_2$
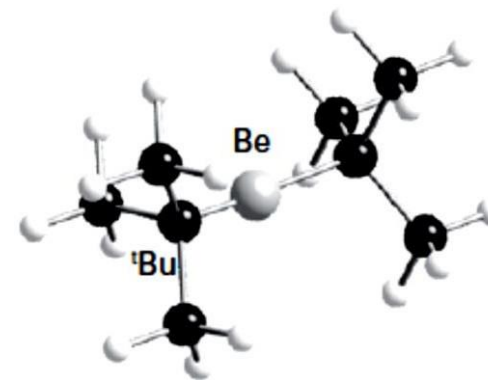
15$BetBu_2$, $^tBu = (CH_3)_3C$

An interesting organoberyllium compound is beryllocene, **16**$(C_5H_5)_2Be$, in which the Be atom is positioned directly above the centre of one cyclopentadienyl ring and below a single C atom on the other ring.

**16**$BeCp_2$, $Cp = C_5H_5$

Alkyl- and arylmagnesium halides are very well known as **Grignard reagents** and are widely used in synthetic organic chemistry where they behave as a source of R$^-$. The reaction to produce the Grignard reagents is carried out in ether or tetrahydrofuran:

$$Mg(s) + RBr(sol) \rightarrow RMgBr(sol)$$
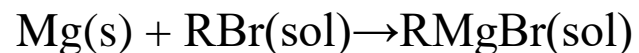
Grignard reagents are widely used in the synthesis of organometallic compounds of other metals, as in the formation of alkylberyllium compounds. They are also widely used in organic synthesis. One reaction is **organomagnesiation**, which involves addition of the Grignard reagent to an unsaturated bond:

$$R_1MgX \text{ (sol)} + R_2R_3C{=}CR_4R_5(sol) \rightarrow R_1R_2R_3C{=}CR4R5MgX \text{ (sol)}$$
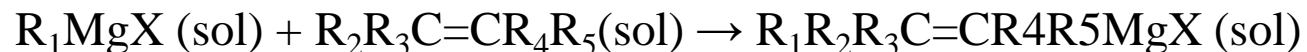
Organometallic compounds of the Group 13 elements

The most important organometallic compounds of the Group 13 elements are those of B and Al.

(a) **Organoboron compounds**

- Organoboranes of the type BR_3 can be prepared by hydroboration of an alkene with diborane.

$$B_2H_6 + 6CH_2{=}CH_2 \longrightarrow 2B(CH_2CH_3)_3$$
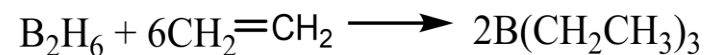
- Like other B compounds, the organoboron species are electron deficient and consequently act as Lewis acids and form adducts easily.

(b) **Organoaluminium compounds**

- Alkylaluminium compounds can be prepared on a laboratory scale by transmetallation of a mercury compound:

$$2Al + 3Hg(CH_3)_2 \longrightarrow Al_2(CH_3)_6 + 3Hg$$

17 $Al_2(CH_3)_6$
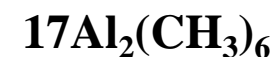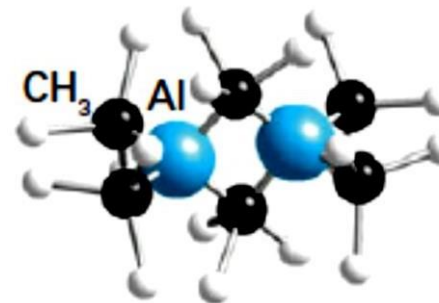
- In the dimeric halides, the bridging Al-Cl-Al bonds are $2c,2e$ bonds, that is each Al-Cl bond involves an electron pair. In the alkylaluminium dimers the Al-C-Al bonds are $3c,2e$ bonds, with one bonding pair shared across the Al-C-Al unit.

- Triethylaluminium and higher alkyl compounds are prepared from the metal, an appropriate alkene, and hydrogen gas at elevated temperatures and pressures.

$$2Al + 3H_2 + 6CH_2{=}CH_2 \xrightarrow[\text{10-20MPa}]{\text{60-110°C,}} Al_2(CH_2CH_3)_6$$
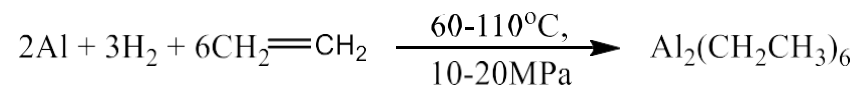
Triethylaluminium, often written as the monomer $Al(C_2H_5)_3$, is used in the ZieglerNatta polymerization catalyst.

Organometallic compounds of Group 14

Tin and lead form tetravalent organo compounds; organotin compounds are used as fungicides and pesticides.
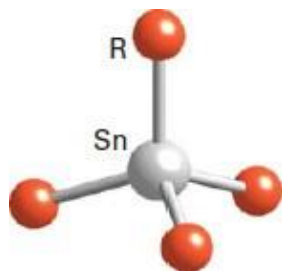

- The structures of R_4Sn compounds are all similar, with a tetrahedral tin atom.
- The halide derivatives, R_3SnX, often contain SnXSn bridges and form chain structures. The presence of bulky R groups may affect the shape. For example, in $(SnFMe_3)_n$ **(18)** , the SnFSn backbone is in a zig-zag arrangement
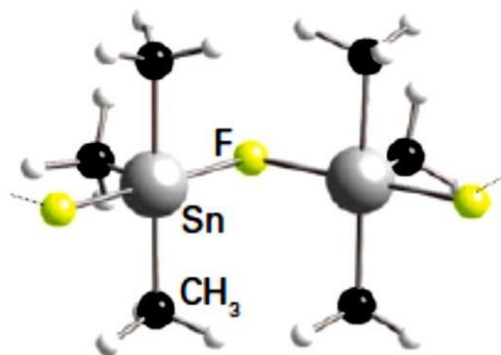

18$(SnFMe_3)_n$, Me $= CH_3$

Tetraethyl lead used to be made on a huge scale as an antiknock agent in petrol.

Alkyllead compounds, R_4Pb, can be made in the laboratory by using a Grignard reagent or an organolithium compound:

$$2PbCl_2 + 4RLi \longrightarrow R_4Pb + 4LiCl + Pb$$

$$2PbCl_2 + 4RMgBr \longrightarrow R_4Pb + Pb + 4MgBrCl$$
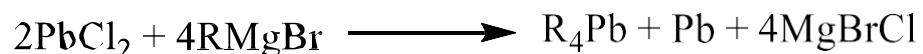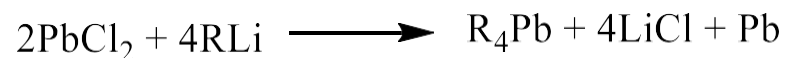
They are all monomeric molecules with tetrahedral geometry around the Pb atom. The halide derivatives may contain bridging halide atoms to form chains. Monomers are favoured by more bulky organic substituents. For example, $Pb(CH_3)_3Cl$ exists as a chain structure with bridging Cl atoms whereas the mesityl derivative $Pb(Me_3C_6H_2)_3Cl$ is a monomer.
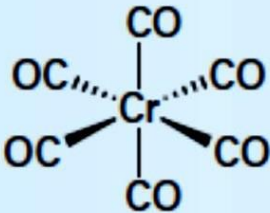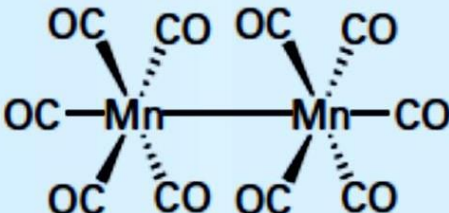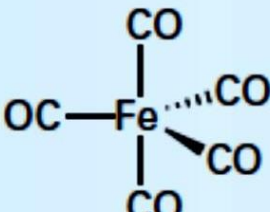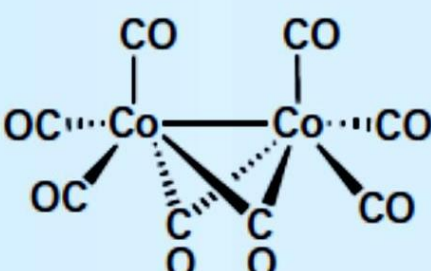

19$(PbClMe_3)_n$
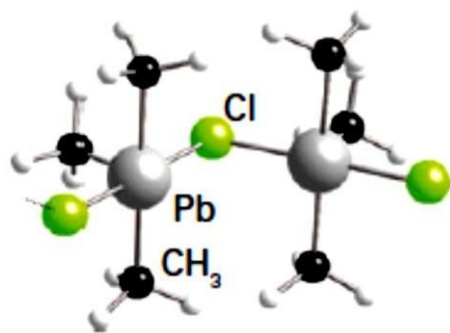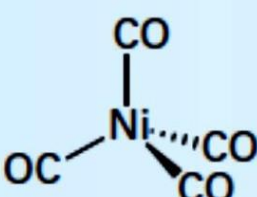
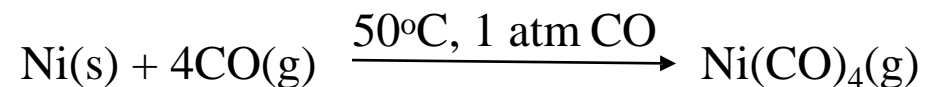**d-Block carbonyls**

Homoleptic carbonyls
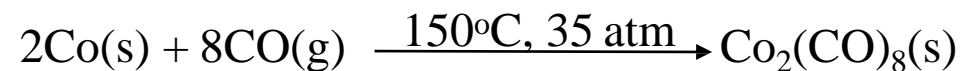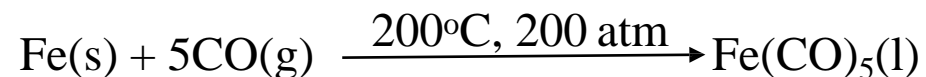
- A **homoleptic complex** is a complex with only one kind of ligand.

- The simple **vanadium carbonyl $V(CO)_6$ is an exception as it only has 17 valence electrons and is too sterically crowded to dimeriz**e; it is, however, readily reduced to the 18-electron $V(CO)_6$ anion.

- The Group 6 hexacarbonyls are octahedral, pentacarbonyliron(0) is trigonal bipyramidal, tetracarbonylnickel(0) is tetrahedral, and decacarbonyldimanganese(0) consists of two square-pyramidal $Mn(CO)_5$ groups joined by a metal-metal bond.

Group formula		Valence electrons		Structure
6	Cr(CO)$_6$	Cr	6	
		6(CO)	12	
		Total	18	
7	Mn$_2$(CO)$_{10}$	Mn	7	
		5(CO)	10	
		M–M	1	
		Total	18	
8	Fe(CO)$_5$	Fe	8	
		5(CO)	10	
		Total	18	
9	Co$_2$(CO)$_8$	Co	9	
		4(CO)	8	
		M–M	1	
		Total	18	
8	Ni(CO)$_4$	Ni	10	
		4(CO)	8	
		Total	18	

In 1890 Mond, Langer, and Quinke discovered that the direct combination of nickel and carbon monoxide produced tetracarbonylnickel(0), $Ni(CO)_4$, a reaction that is used in the **Mond process** for purifying nickel

$$Ni(s) + 4CO(g) \xrightarrow{50°C, \ 1 \ atm \ CO} Ni(CO)_4(g)$$

$Fe(CO)_5$, are synthesized at high pressures and temperatures

$$Fe(s) + 5CO(g) \xrightarrow{200°C, \ 200 \ atm} Fe(CO)_5(l)$$

$$2Co(s) + 8CO(g) \xrightarrow{150°C, \ 35 \ atm} Co_2(CO)_8(s)$$

**Synthesis and reactivity of cyclopentadienyl compounds**

Cyclopentadiene itself is acidic enough that potassium hydroxide will deprotonate it in solution and, for example, ferrocene can be prepared as follows:

$$2KOH + 2C_5H_6 + FeCl_2 \longrightarrow Fe(C_5H_5)_2 + 2H_2O + 2KCl$$
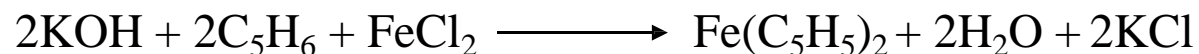
Because of their great stability, the 18-electron Group 8 compounds ferrocene maintain their ligand-metal bonds under rather harsh conditions, and it is possible to carry out a variety of transformations on the cyclopentadienyl ligands. For example, they undergo reactions similar to those of simple aromatic hydrocarbons, such as FriedelCrafts acylation:
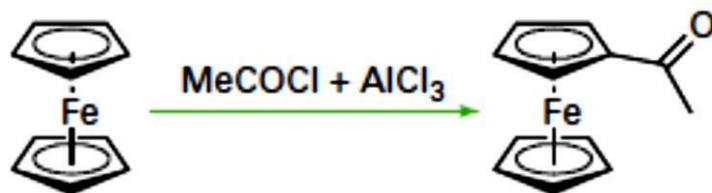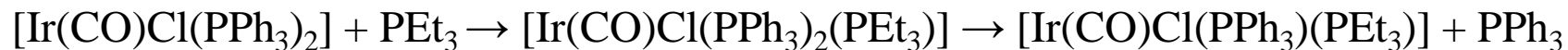

It also is possible to replace H on a C_5H_5 ring by Li:
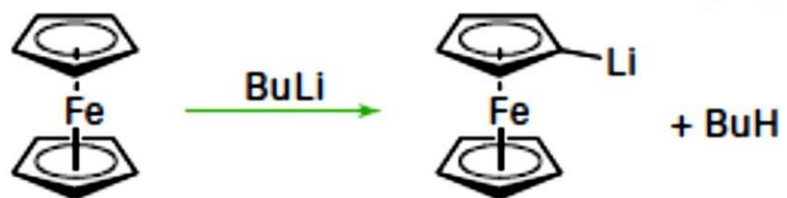
Reactions

a. *Ligand substitution*

The substitution of ligands in organometallic complexes is very similar to the substitution of ligands in coordination complexes, with the additional constraint that the valence electron count at the metal atom does not increase above 18.

$$[Ir(CO)Cl(PPh_3)_2] + PEt_3 \rightarrow [Ir(CO)Cl(PPh_3)_2(PEt_3)] \rightarrow [Ir(CO)Cl(PPh_3)(PEt_3)] + PPh_3$$

$$[V(CO)_5(NO)] + PPh_3 \rightarrow [V(CO)_4(NO)(PPh_3)] + CO$$

$$[Re(\eta 5\text{-}Cp)(CO)_3] + PPh_3 \rightarrow [Re(\eta^3\text{-}Cp)(CO)_2(PPh_3)] + CO$$

## b. *Oxidative addition and reductive elimination*

Oxidative addition reactions result in two more ligands bound to the metal with an increase in the total electron count at the metal of 2. Thus oxidative addition reactions normally require a coordinatively unsaturated metal centre, and are particularly common for 16-electron square-planar metal complexes:


16e Pt(II)   18e Pt(IV)

The oxidative addition of hydrogen is a concerted reaction: dihydrogen coordinates to form a σ-bonded H_2 ligand, and then backbonding from the metal results in cleavage of the H-H bond and the formation of *cis* dihydrides:

Four-coordinate   Five-coordinate   Six-coordinate
16e Rh(I)   18e Rh(I)   18e Rh(III)
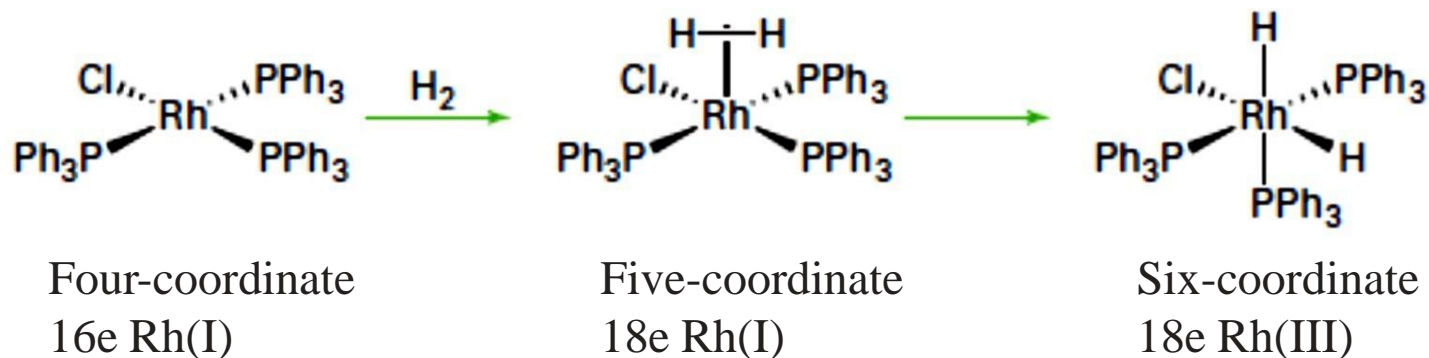
- In an S_N2 oxidative addition reaction, a lone pair on the metal attacks the XY molecule displacing Y, which subsequently bonds to the metal:
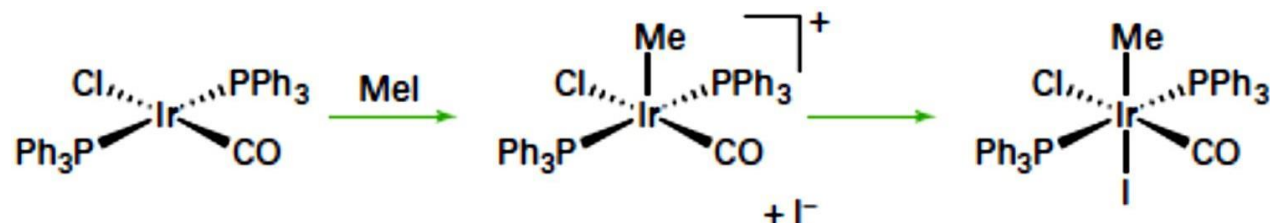

- There are two stereochemical consequences of this reaction. First, the two incoming ligands need not end up *cis* to each other and, second, unlike the concerted reaction, any chirality at the X group is inverted. An S_N2-type oxidative addition is common for polar molecules such as alkyl halides.

- The opposite of oxidative addition, where two ligands couple and eliminate from a metal centre, is known as **reductive elimination**:
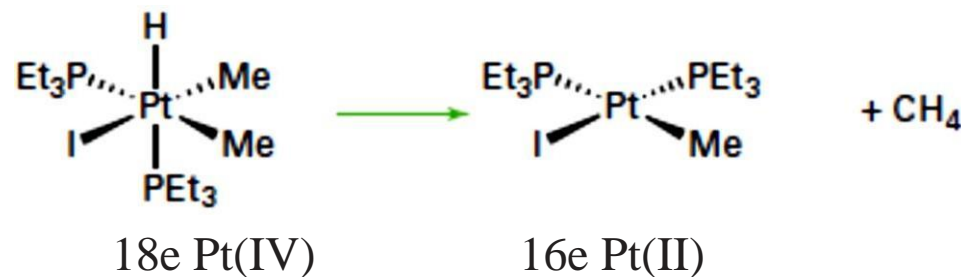
- Reductive elimination reactions require both eliminating fragments to be *cis* to each other.

c. σ-Bond metathesis

- A reaction sequence that is exchange of two species is known as σ-**bond metathesis**.

- σ-Bond metathesis reactions are common for early d-metal complexes where there are not enough electrons on the metal atom for it to participate in oxidative addition.

- For instance, the 16-electron compound [ZrHMe(Cp)$_2$] cannot react with H$_2$ to give a trihydride as all its electrons are involved in bonding to the existing ligands. A four-membered transition state is proposed in such cases, and a concerted bond-making and bond-breaking step results in elimination of methane:
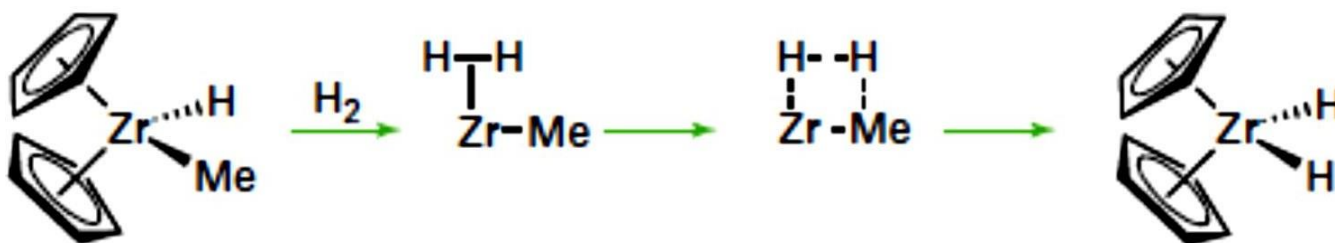
d. *1,1-Migratory insertion reactions*

A **1,1-migratory insertion reaction** is exemplified by reactions of the η^1-CO ligand, where the following change can take place:
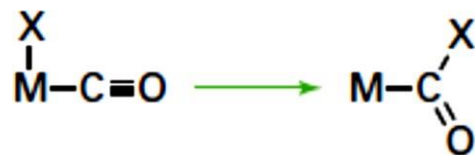
- 1,1-Migratory insertion reactions result from the migration of a species such as a hydride or alkyl group to an adjacent ligand such as carbonyl to give a metal complex with two fewer electrons on the metal atom..

- The overall reaction results in a decrease in the number of electrons on the metal atom by 2, with no change in the oxidation state. It is therefore possible to induce 1,1-migratory insertion reactions by the addition of another species that can act as a ligand:
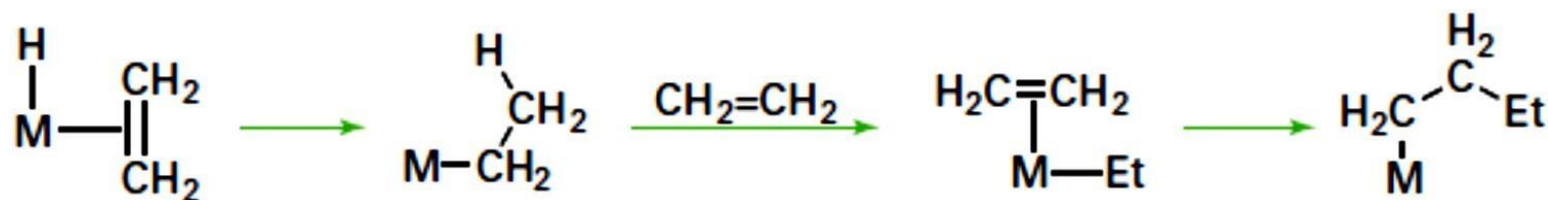
$$[Mn(CH_3)(CO)_5] + PPh_3 \rightarrow [Mn(CH_3CO)(CO)_4PPh_3]$$
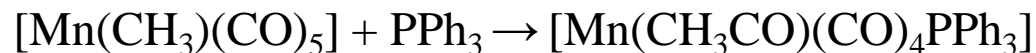
e. *1,2-Insertions and β-hydride elimination*

1,2-Insertion reactions are commonly observed with η^2-ligands, such as alkenes and alkynes, and are exemplified by the reaction:
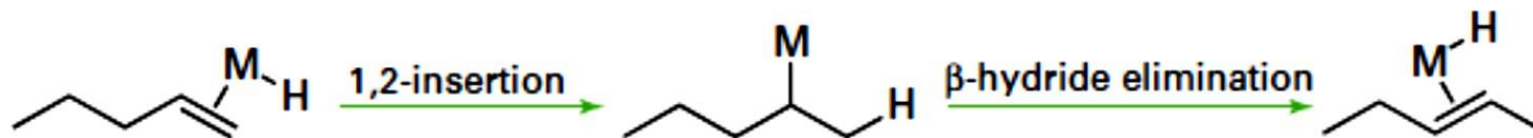
1,2-Insertion reactions result in the formation of an η^1 ligand with no change in oxidation state of the metal

Repetition of this process gives polyethene.

β-hydride elimination is the reverse of 1,2-insertion. The 1,2-insertion reaction, coupled with the β-hydride elimination, can also provide a low-energy route to alkene isomerization:

## f. α-, γ-, and δ-Hydride eliminations and cyclometallations

α -Hydride eliminations are occasionally found for complexes that have no β-hydrogens and the reaction gives rise to a carbene that is often highly reactive:

$$M-CH_3 \xrightarrow{\text{α-H elimination}} M=CH_2 \quad (\overset{H}{\underset{|}{M}}=CH_2)$$
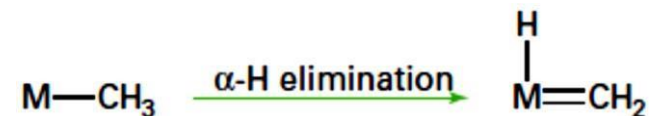
γ-Hydride and δ-hydride eliminations are more commonly observed. Because the product contains a **metallocycle**, a cyclic structure incorporating a metal atom, these reactions are normally described as **cyclometallation** reactions:
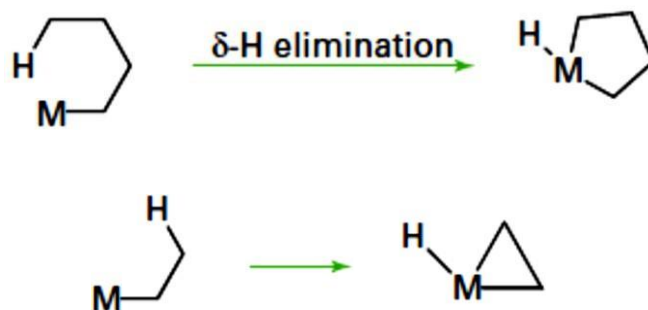
Identify the reaction type

a.

b.
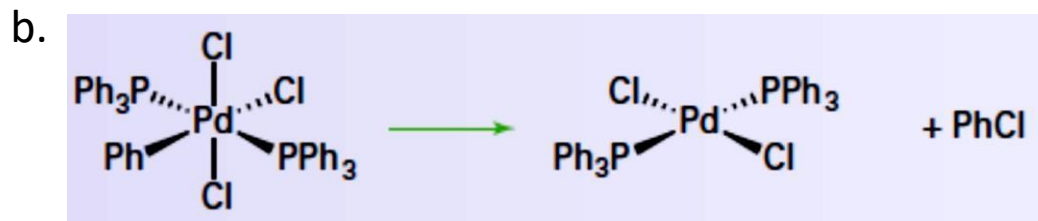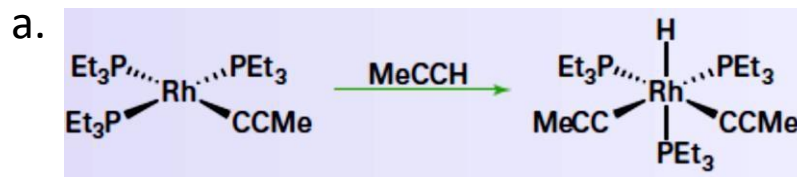
a. oxidative addition reaction

In order to identify this reaction, we need to establish the valence electron counts and oxidation states of both the starting material and the product. The four-coordinate squareplanar Rh starting material contains an η^1-alkynyl ligand as well as three neutral phosphine ligands; it is therefore a 16-electron Rh(I) species. The six-coordinate octahedral product contains two η^1-alkynyl ligands, a hydride ligand, and three neutral phosphine ligands; it is therefore an 18-electron Rh(III) species. The increase in both coordination number and oxidation number by 2 identifies it as an oxidative addition.