Transition metals organometallic compounds

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- Transition metal σ−bonded organometallic compounds like the metal alkyls, aryls and the hydrides derivatives are by far **the most common** organometallic species encountered in the world of chemistry.

- **Ligands** play a vital role in stabilizing transition metal complexes. The stability as well as the reactivity of a metal in its complex form thus depend upon the number and the type of ligands it is bound to.

- Organometallic compounds containing carbon-based ligands exhibit a diverse range of binding modes to metal centers. These binding modes are influenced by the **hybridization** state of the carbon atom bonded to the metal. This versatility allows for the creation of a wide variety of organometallic complexes with unique properties and applications.

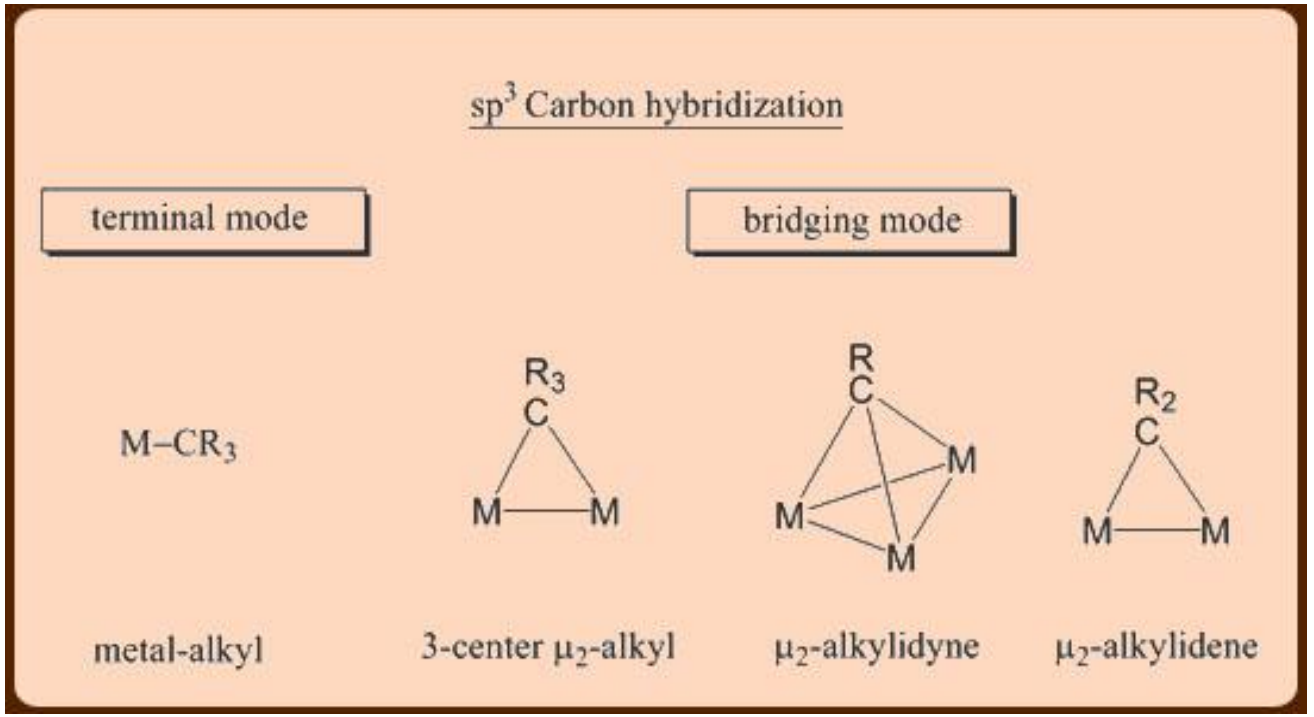
- These ligands can thus bind to a metal in many different ways as depicted below

ligands can either be

a) **purely σ−donor type,** or depending upon the capability of the ligand to form the multiple bonds.

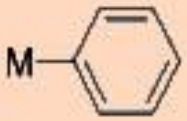
b) **σ−donor/π−acceptor type,** in which the σ−interaction is supplemented by a varying degree of π−interaction.

Some examples are given below with different hybridization of carbon

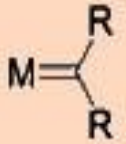


sp^2 Carbon hybridization

terminal mode

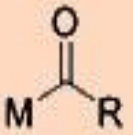


metal-aryl



metal-alkylidene

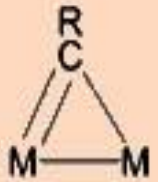
metal-vinyl



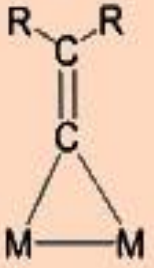
metal-acyl

bridging mode

3-center μ_2–aryl



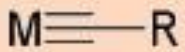
μ_2-alkylidyne



μ_2-vinylidene

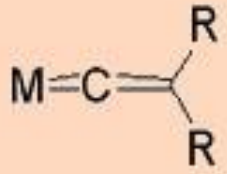
sp Carbon hybridization

terminal mode



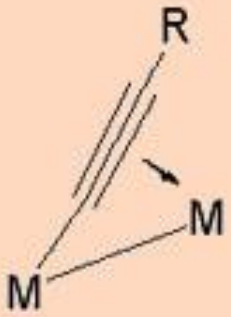
metal-alkylidyne

metal-alkynyl

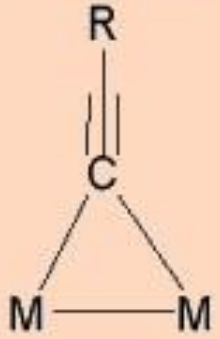


metal-vinylidene

bridging mode



$\mu 2$ (σ,π)-alkynyl



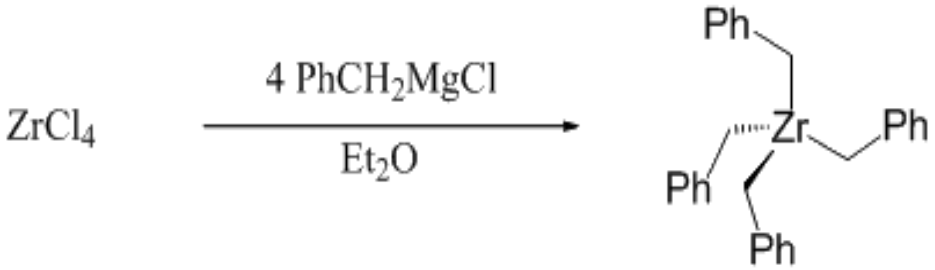
3-center μ_2-alkynyl

Preparation of transition metal-alkyl and transition metal-aryl complexes

- The transition metal−alkyl and transition−metal aryl complexes are usually prepared by the following routes discussed below:

Metathesis ("salt metathesis“)

- Metathesis: This involves the reaction of metal halides with organometallic reagents, such as organolithium, organomagnesium, organoaluminum, organotin, and organozinc compounds.
- Example: The reaction provides an example of a metathesis reaction between zirconium tetrachloride ($ZrCl_4$) and benzylmagnesium chloride (PhCH2MgCl).
- The products of this reaction are zirconium tetraphenyl ($ZrPh_4$) and magnesium chloride ($MgCl_2$).

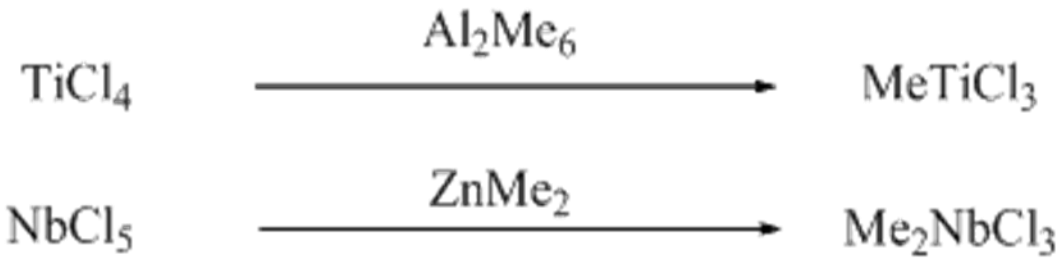


The Carbanionic Nature Of Organometallic Compounds And Their Reactivity In Halide Exchange Reactions.

- **Carbanionic nature:** Organolithium and organomagnesium compounds are strongly carbanionic (R:-), meaning the carbon atom attached to the metal has a significant negative charge. This makes them highly reactive nucleophiles.

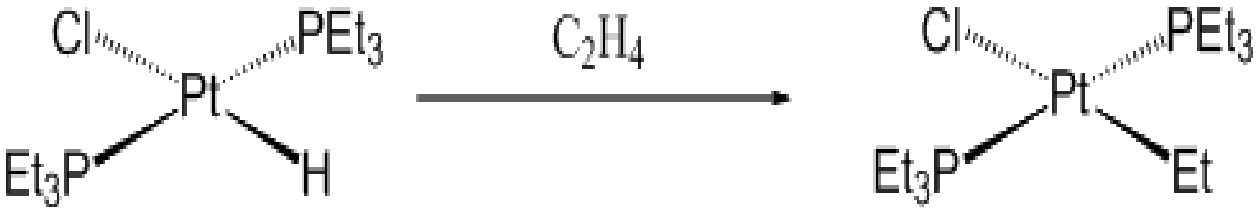
- **Reduced carbanionic nature:** Other main group organometallics, such as organoalkyl, organozinc, and organotin compounds, are less carbanionic in nature. This means they are less reactive and have weaker nucleophilic properties.

- **Alkylating power (the ability of compounds to transfer alkyl groups to molecules):** The reduced carbanionic nature of organoalkyl, organozinc, and organotin reagents results in lower alkylating power. This means they are less effective at transferring alkyl groups to other molecules.
- **Halide exchange:** However, the reduced alkylating power of these reagents can be advantageously used in partial exchange of halide ligands. This involves replacing some of the halide ligands (such as Cl or Br) in a metal complex with alkyl groups.

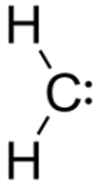


Alkene insertion or Hydrometallation

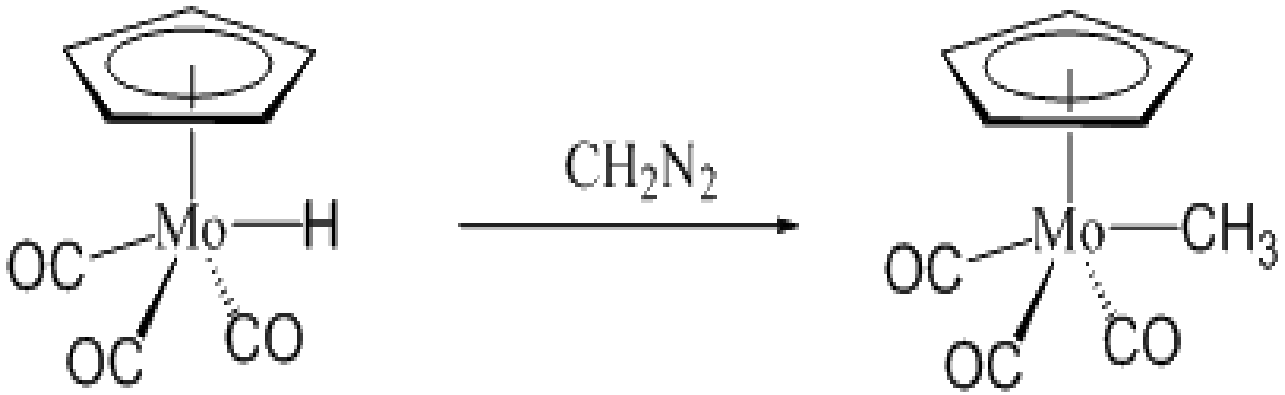
- As the name implies, this category of reaction involves an insertion reaction between **metal hydride** and alkene as shown below.
- These type reactions are relevant to certain homogeneous catalytic processes in which insertion of an olefin to M−H bond is often observed.



Carbene insertion



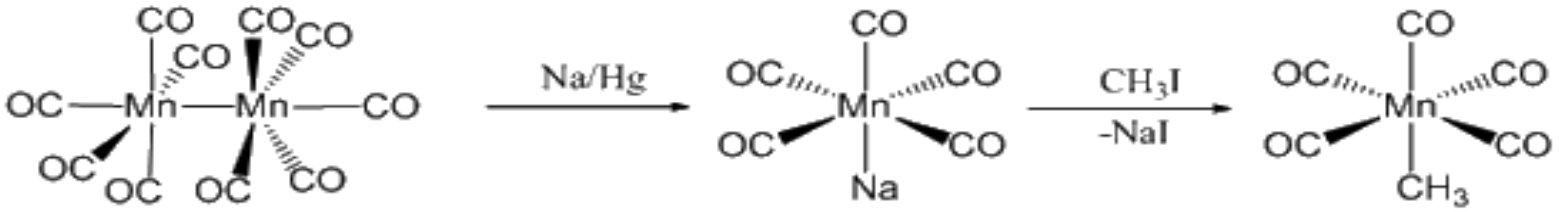
This category represents the reaction of metal hydrides with carbenes.



- **Reactants:** The starting material is a molybdenum complex containing a cyclopentadienyl ligand (Cp), three carbonyl ligands (CO), and a hydride ligand (H).
- **Reaction type:** Substitution reaction, where a methyl group (CH_3) replaces a hydride ligand (H) in the molybdenum complex.
- **Role:** The methyl group acts as a nucleophile, attacking the metal center and forming a new bond, so The hydride ligand acts as a leaving group, dissociating from the metal center and being replaced by the methyl group.

Metallate alkylation reaction

This reaction involves the interaction of carbonylate anions(CO) with alkyl halides.

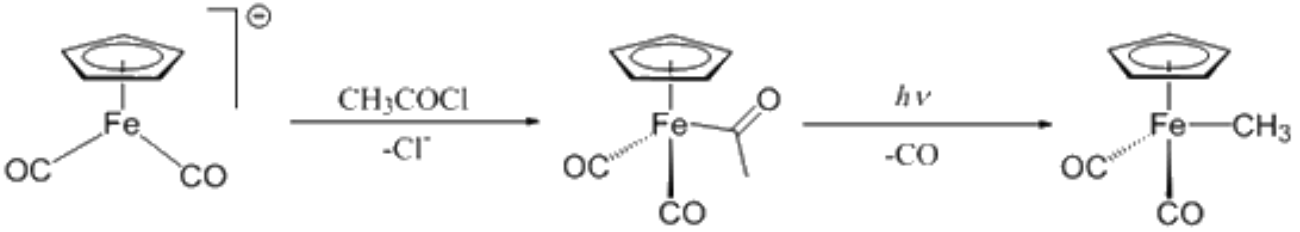


Preparation of transition **metal-alkyl** and transition **metal-aryl complexes** (contd..)

Reaction: The carbonylate anion acts as a nucleophile, attacking the carbon atom of the alkyl halide and displacing the halide ion. This results in the formation of a new carbon-metal bond and the release of a halide salt.

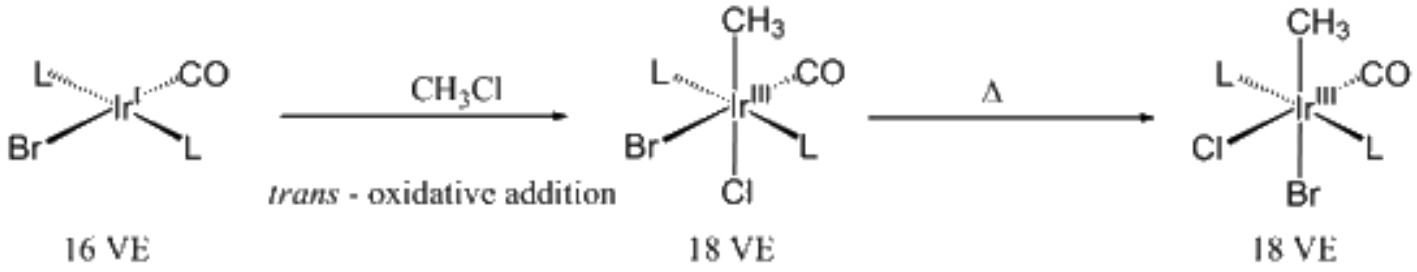
Metallate acylation reaction

This category involves the reaction of carbonylate anions with acyl halides.



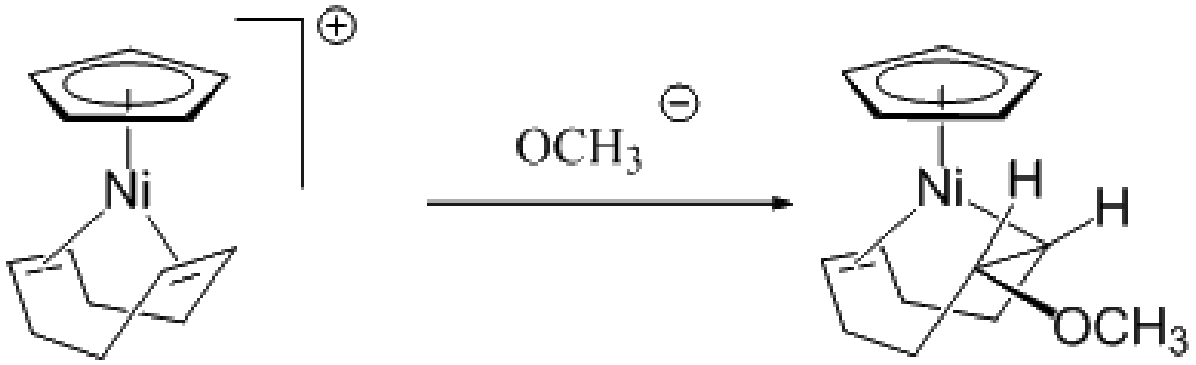
Oxidative addition reaction

Many unsaturated 16 VE (Valance Electrons) transition metal complexes having d^8 or d^{10} configuration undergo oxidative addition reactions with alkyl halides. The oxidative addition reactions proceed with the oxidation state as well as coordination number of **the metal increasing by +2**.



Addition reaction

This category involves the reaction of an activated metal bound olefin complex with a nucleophile as shown below.



Cyclopentadienyl complex

- A **cyclopentadienyl complex** is a metal complex with one or more cyclopentadienyl groups ($C_5H^-_5$, abbreviated as Cp^-).

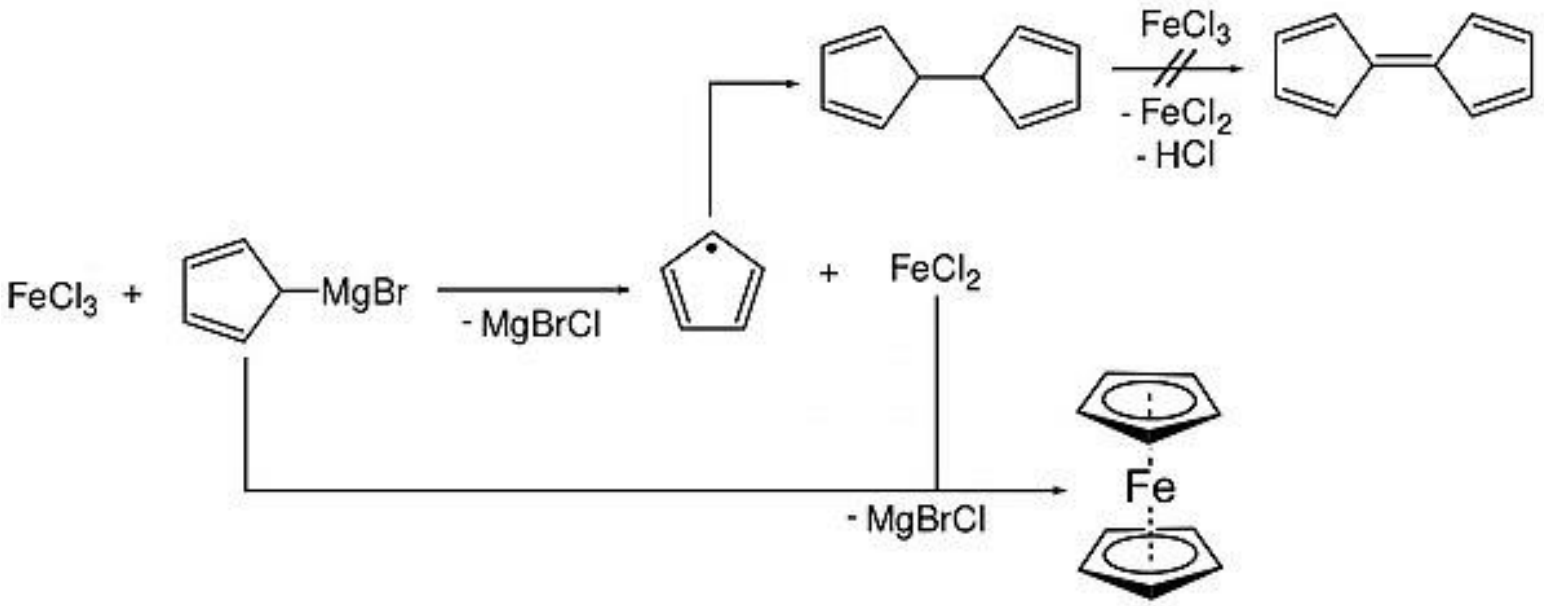
- Cyclopentadienyl ligands almost invariable bind to metals as pentahapto (η^{5-}) bonding mode. The metal–cyclopentadienyl interaction is typically drawn as a single line from the metal center to the center of the Cp ring.

- Biscyclopentadienyl complexes are called **metallocenes**. A famous example of this type of complex is ferrocene ($FeCp_2$), which has many analogues for other metals, such as chromocene ($CrCp_2$), cobaltocene ($CoCp_2$), and nickelocene ($NiCp_2$). When the Cp rings are mutually parallel the compound is known as a sandwich complex.

Ferrocene

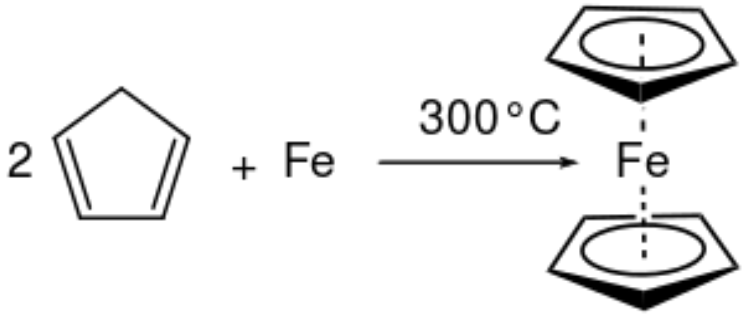
- Ferrocene is an organometallic compound with the formula $Fe(C_5H_5)_2$. The molecule consists of **two cyclopentadienyl** rings bound on opposite sides of a central iron atom.
- It is a orange solid with a camphor-like odor, that sublimes above room temperature, and is soluble in most organic solvents. It is remarkable for its stability:
- it is unaffected by air, water, strong bases, and can be heated to 400 °C without decomposition.
- In oxidizing conditions it can reversibly react with strong acids to form the ferrocenium cation $Fe(C_5H_5)_2^+$.

- Pauson and Kealy synthesized ferrocene using iron(III) chloride and a Grignard reagent and cyclopentadienyl magnesium bromide. Iron(III) chloride is suspended in anhydrous diethyl ether and added to the Grignard reagent.
- A redox reaction occurs, forming the cyclopentadienyl radical and iron(II) ions. Dihydrofulvalene is produced by radical-radical recombination while the iron(II) reacts with the Grignard reagent to form ferrocene.



Gas-metal reaction

- The other early synthesis of ferrocene was by Miller et al., who reacted metallic iron directly with gas-phase cyclopentadiene at elevated temperature.



An approach using iron pentacarbonyl was also reported.

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

Modern modifications of Pauson and Kealy's original Grignard approach are known:

- Using sodium cyclopentadienide:

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

- Using freshly-cracked cyclopentadiene:

$$FeCl_2 \cdot 4H_2O + 2\ C_5H_6 + 2\ KOH \rightarrow Fe(C_5H_5)_2 + 2\ KCl + 6\ H_2O$$

- Using an iron(II) salt with a Grignard reagent:

$$2\ C_5H_5MgBr + FeCl_2 \rightarrow Fe(C_5H_5)_2 + 2\ MgBrCl$$

- Even some amine bases (such as diethylamine) can be used for the deprotonation, though the reaction proceeds more slowly than when using stronger bases:

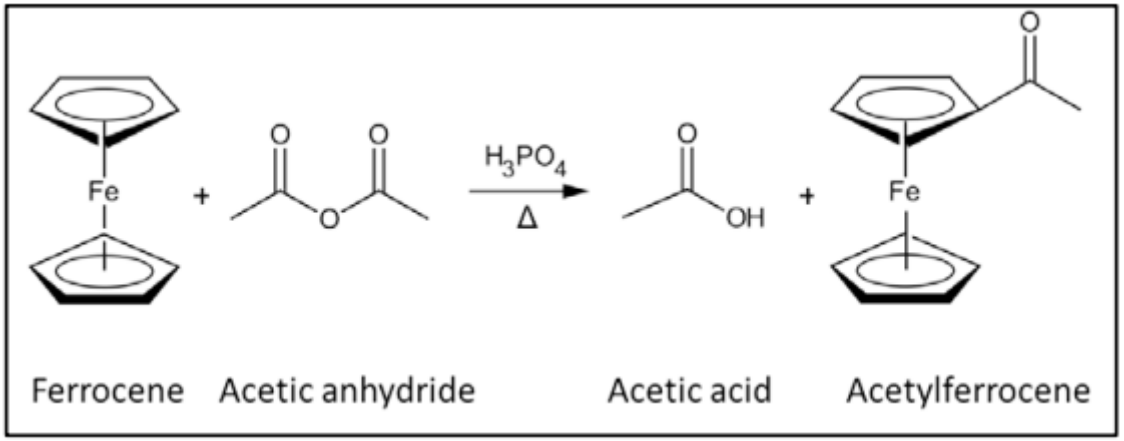
$$2\ C_5H_6 + 2\ (CH_3CH_2)_2NH + FeCl_2 \rightarrow Fe(C_5H_5)_2 + 2\ (CH_3CH_2)_2NH_2Cl$$

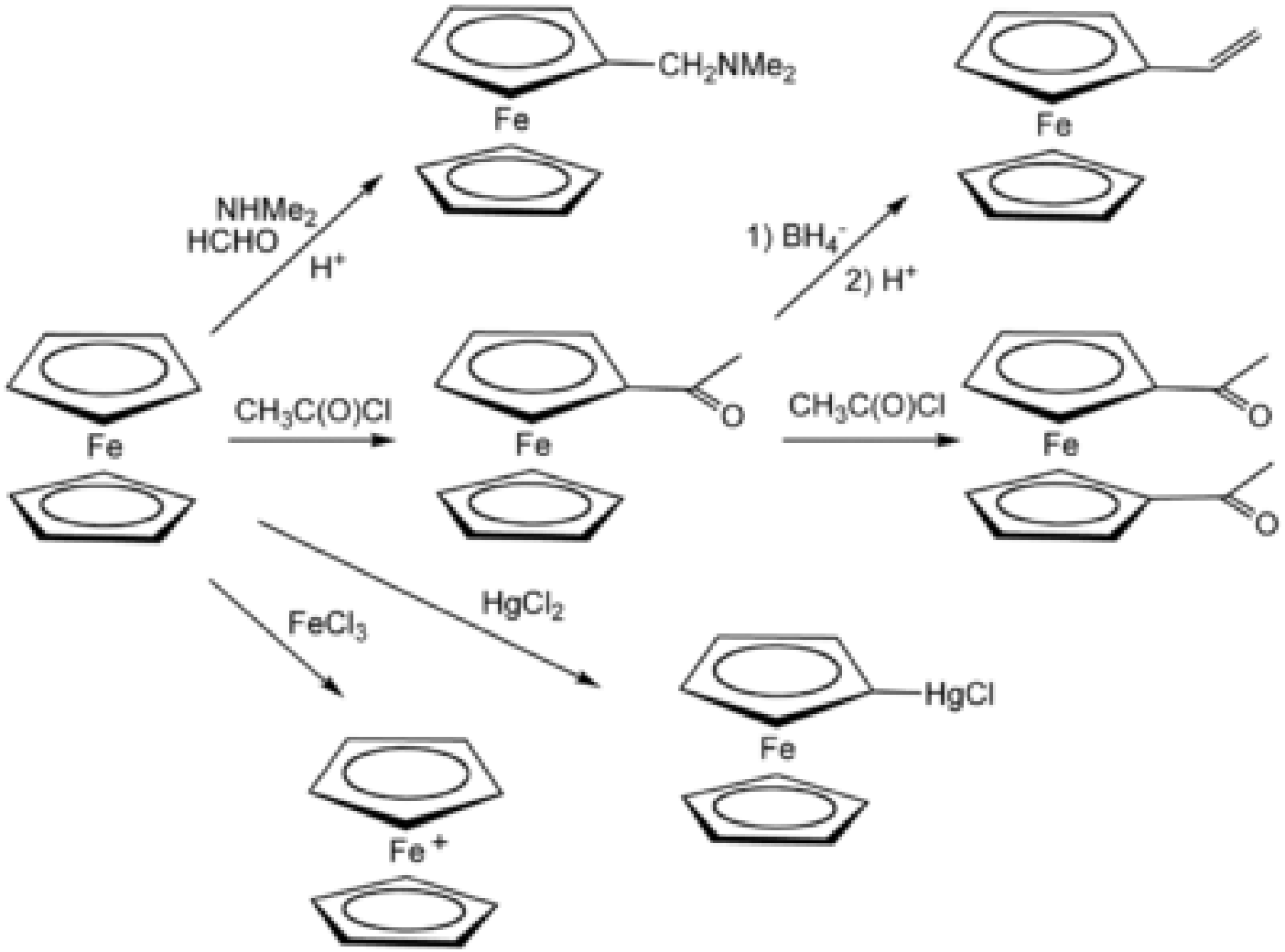
- Direct transmetalation can also be used to prepare ferrocene from other metallocenes, such as manganocene:

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

Reactions With electrophiles

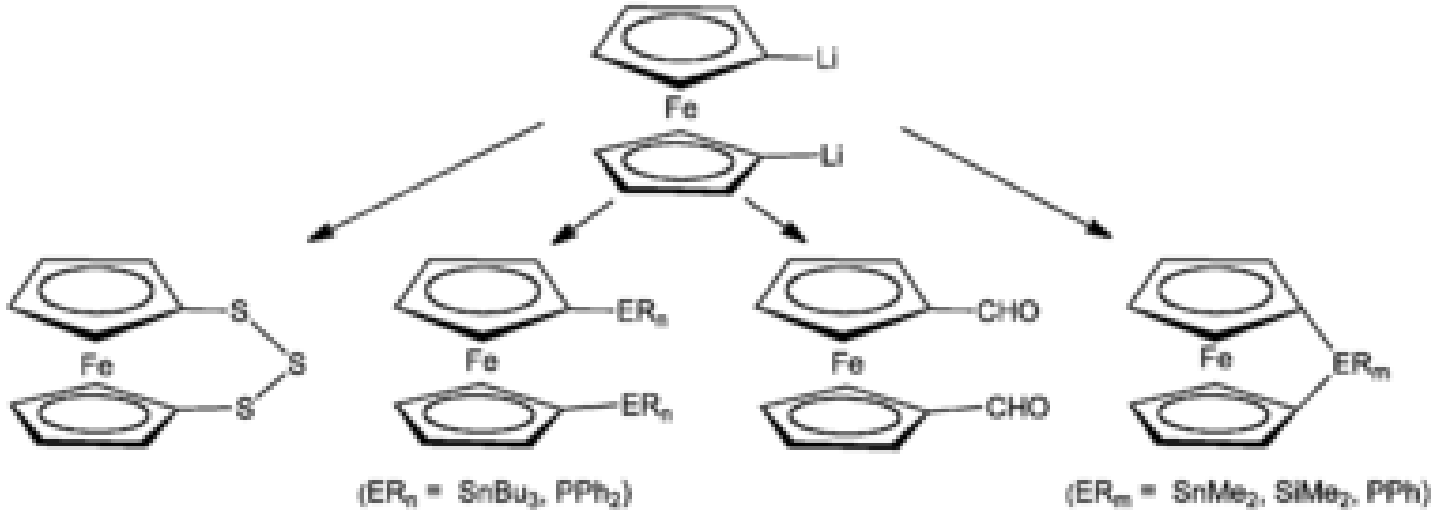
- Ferrocene undergoes many reactions characteristic of aromatic compounds, enabling the preparation of substituted derivatives.
- A common undergraduate experiment is the Friedel–Crafts reaction of ferrocene with acetic anhydride (or acetyl chloride) in the presence of phosphoric acid as a catalyst.




CH2NMe2
Fe
NHMe2
HCHO
H+
1) BH4-
2) H+
Fe
Fe
CH3C(O)Cl
O
Fe
CH3C(O)Cl
O
Fe
O
FeCl3
HgCl2
HgCl
Fe
Fe+

Lithiation

- Ferrocene reacts with butyllithium to give 1,1′-dilithioferrocene, which is a versatile nucleophile.
- Tert-Butyllithium produces monolithioferrocene.
- Dilithioferrocene reacts with S8, chlorophosphines, and chlorosilanes.
- The strained compounds undergo ring-opening polymerization.



Chromocene

- **Chromocene**, formally known as bis(η^5- cyclopentadienyl)chromium(II), is a chemical compound with the condensed structural formula **[$Cr(C_5H_5)_2$]**.
- Each molecule contains an atom of chromium bound between two planar systems of five carbon atoms known as cyclopentadienyl (Cp) rings in a sandwich arrangement, which is the reason its formula is often abbreviated as Cp_2Cr.
- It is an organometallic compound as it has (haptic) covalent chromium–carbon bonds.
- Chromocene is structurally similar to ferrocene, the prototype for the metallocene class of compounds; however, as it has only 16 valence electrons, it does not follow the 18-electron rule

- Ernst Otto **Fischer**, who shared the 1973 Nobel Prize in Chemistry for his work on sandwich compounds, was the first to report a synthesis for chromocene. One simple method of preparation involves the reaction of chromium(II) chloride with sodium cyclopentadienide:

$$CrCl_2 + 2\ NaC_5H_5 \rightarrow Cr(C_5H_5)_2 + 2\ NaCl$$

- Such syntheses are typically conducted in THF; decamethylchromocene, $Cr[C_5(CH_3)_5]_2$, can be prepared analogously from $LiC_5(CH_3)_5$.
- Chromocene can also be prepared from chromium(III) chloride in a redox process:

$$2\ CrCl_3 + 6\ NaC_5H_5 \rightarrow 2\ Cr(C_5H_5)_2 + C_{10}H_{10} + 6\ NaCl$$

- The chromium(0) organometallic complex chromium hexacarbonyl can be oxidised by cyclopentadiene in the presence of diethylamine to produce chromocene, the removed protons being reduced to produce hydrogen gas.

$$Cr(CO)_6 + 2\ C_5H_6 \rightarrow Cr(C_5H_5)_2 + 6\ CO + H_2$$

Cobaltocene

- **Cobaltocene**, known also as **bis(cyclopentadienyl)cobalt(II)** or even "bis Cp cobalt", is an organocobalt compound with the formula $Co(C_5H_5)_2$.
- It is a darkpurple solid that sublimes readily slightly above room temperature. Cobaltocene was discovered shortly after ferrocene, the first metallocene.
- Due to the ease with which it reacts with oxygen, the compound must be handled and stored using air-free techniques.
- Cobaltocene is prepared by the reaction of sodium cyclopentadienide (NaC_5H_5) with anhydrous cobalt(II) chloride in THF solution. Sodium chloride is cogenerated, and the organometallic product is usually purified by vacuum sublimation.

Nickelocene

- **Nickelocene** is the organonickel compound with the formula Ni(η5-$C_5H_5)_2$.
- Also known as bis(cyclopentadienyl)nickel or $NiCp_2$, this bright green paramagnetic solid is of enduring **academic interest**, although it does not yet have any known practical applications.
- Preparation Nickelocene was first prepared by E. O. Fischer in 1953, shortly after the **discovery of ferrocene**, the first metallocene compound.
- It has been **prepared** in a one-pot reaction, by deprotonating cyclopentadiene with ethylmagnesium bromide, and adding anhydrous nickel(II) acetylacetonate.
- A modern synthesis entails treatment of anhydrous sources of $NiCl_2$ (such as hexaamminenickel chloride) with sodium cyclopentadienyl:

$$[Ni(NH_3)_6]Cl_2 + 2\ NaC_5H_5 \rightarrow Ni(C_5H_5)_2 + 2\ NaCl + 6\ NH_3$$

Half sandwich compounds

- Half sandwich compounds are organometallic complexes that feature a **cyclic polyhapto** ligand bound to an MLn center, where L is a unidentate ligand.
- Thousands of such complexes are known. Well known examples include Cyclobutadieneiron tricarbonyl and $(C_5H_5)TiCl_3$.
- Commercially useful examples include $(C_5H_5)Co(CO)_2$, which is used in the synthesis of substituted pyridines, and methylcyclopentadienyl manganese tricarbonyl, an antiknock agent in petrol.