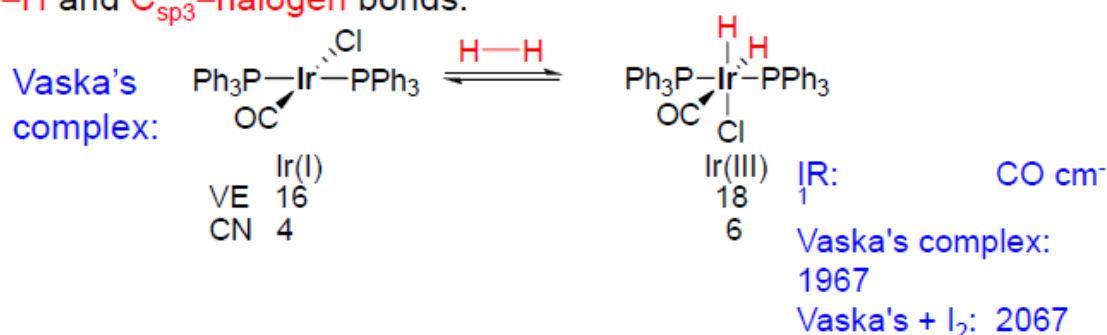


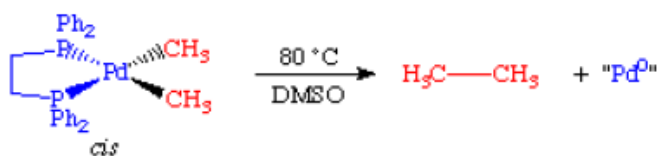
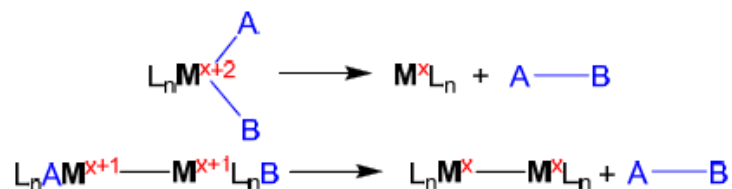
5-3 IMPORTANT TYPES OF REACTIONS

I. Oxidative addition/Reductive elimination

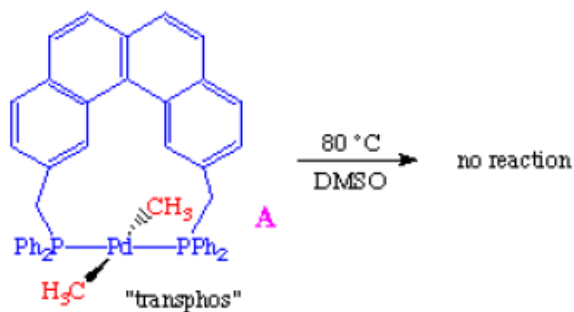
- In oxidative addition, a metal complex with **vacant coordination sites** and a relatively **low oxidation state** is oxidized by the insertion of the metal into a covalent bond (X—Y).
- Both the **formal oxidation state** of the metal and the electron count of the complex increase by two.
- Oxidative additions can occur with the insertion of a metal into many different covalent bonds, they are most commonly seen with **H—H** and **C_{sp3}—halogen** bonds.



A **reductive elimination** involves the elimination or expulsion of a molecule from a transition metal complex. In the process of this elimination, the metal center is reduced by two electrons.



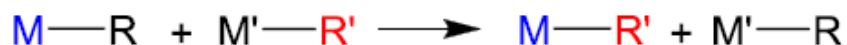
➤ The groups being eliminated must be in a mutually *cis* orientation.



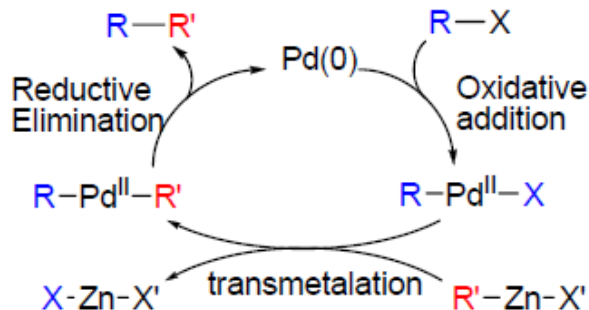
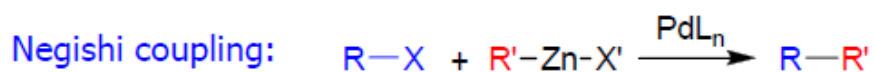
➤ A series of reactions involving an oxidative addition, a rearrangement and then a reductive elimination form the basis for a variety of industrially important catalytic cycles.

II. Transmetalation

➤ Transmetalation is a general chemical reaction type describing the exchange of ligands between two metal centers. The metal centers need not be the same. The ligands R and R' can be organic or inorganic.

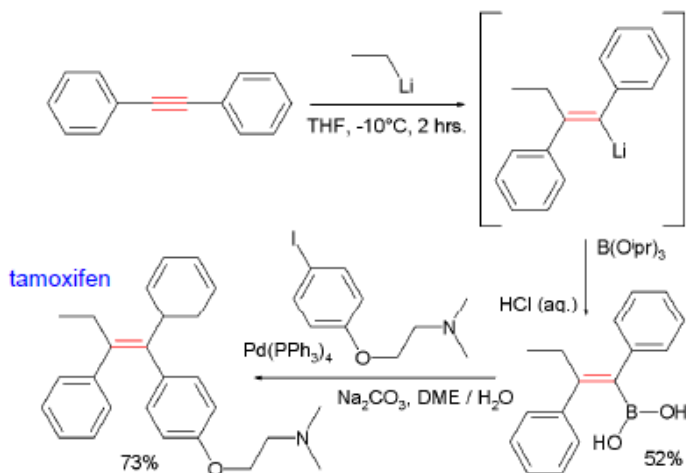
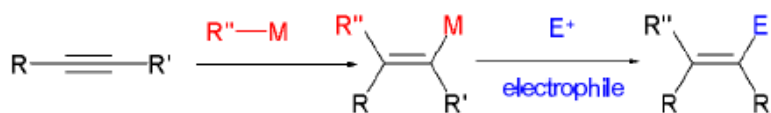


☞ Transmetalation is important in the synthesis of various organometallic compounds. This reaction type also appears frequently in the catalytic cycle of various metal catalyzed organic reactions.



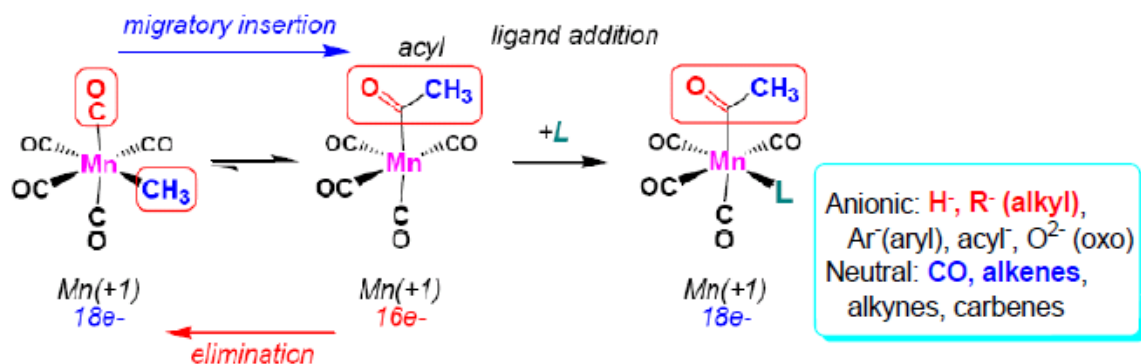
III. Carbometalation

➤ **Carbometalation** is a reaction involving the nucleophilic addition to alkenes and alkynes of a diverse range of organometallic reagents such as **organolithium compounds**, organocopper compounds and Grignard reagents according to the following general alkyne scheme:



IV. Migratory insertion

A **migratory insertion** reaction is when a **cisoidal anionic** and **neutral** ligand on a metal complex couple together to generate a new coordinated **anionic** ligand. This new anionic ligand is composed of the original neutral and anionic ligands now bonded to one another.

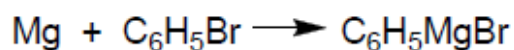


- ☞ No change in formal oxidation state (exception: alkylidenes).
- ☞ The two groups that react must be **cisoidal** to one another.
- ☞ A vacant coordination site is generated by the migratory insertion.
- ☞ Migratory insertions are favored on more electron-deficient metal centers.

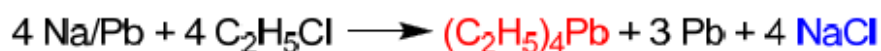
5-4 MAIN-GROUP ORGANOMETALLICS

I. PREPARATION

➤ Direct Synthesis

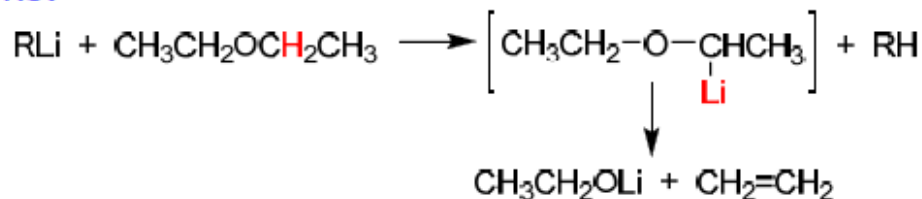


Mixed metal synthesis:



$\Delta H_f^\circ(\text{NaX})$ boosts the driving force.

Side reactions:

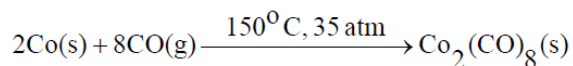
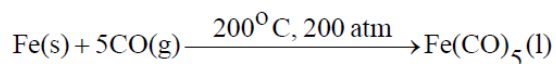
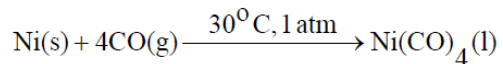


2. SYNTHESIS OF METAL CARBONYLS

Following are some of the general methods of preparation of metal carbonyls.

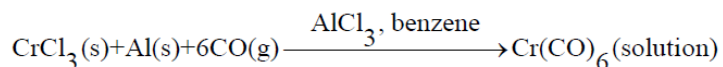
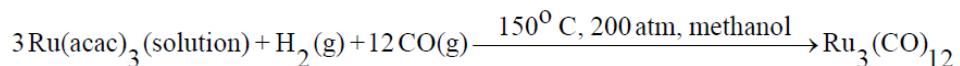
Direct Combination:

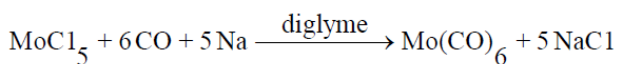
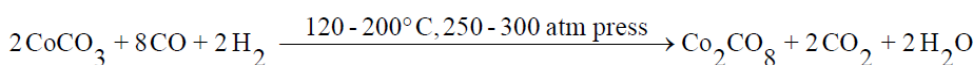
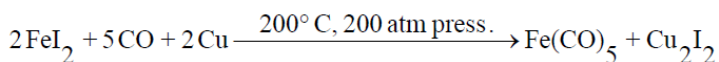
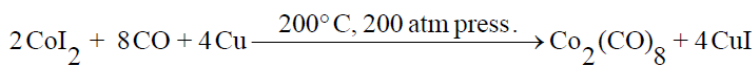
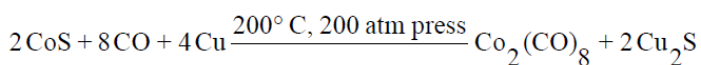
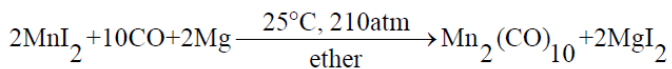
Only $\text{Ni}(\text{CO})_4$ and $\text{Fe}(\text{CO})_5$ and $\text{Co}_2(\text{CO})_8$ are normally obtained by the action of carbon monoxide on the finely divided metal at suitable temperature and pressure.



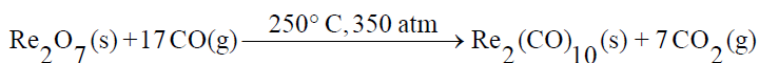
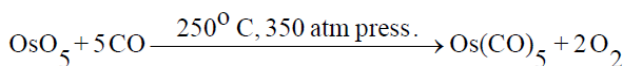
Reductive carbonylation:

Many metallic carbonyls are obtained when salts like $\text{Ru}(\text{acac})_3$, CrCl_3 , Re_2O_7 , VCl_3 , CoS , $\text{Co}(\text{CO})_3$, CoI_2 etc. are treated with carbon monoxide in presence of suitable reducing agent like Mg , Ag , Cu , Na , H_2 , AlLiH_4 etc.

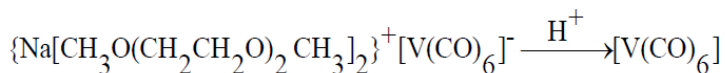
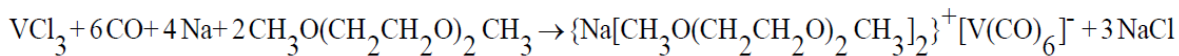




Sometimes CO acts as a carbonylating and reducing agent as under.

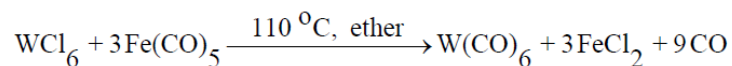
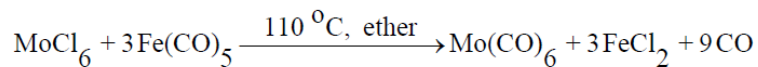


A solution of vanadium chloride in diethylene glycol dimethyl ether, which is acidified by phosphoric acid, gives vanadium hexacarbonyl

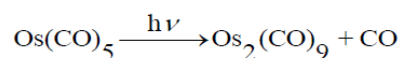
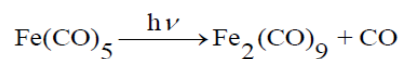
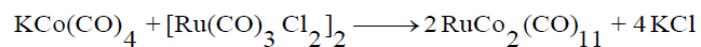


Preparation of mononuclear carbonyls from iron pentacarbonyl:

The labile carbonyl groups in iron pentacarbonyl can be replaced by chloride to give a different metal carbonyl. These reactions are characterized by low yield, which can be improved using high pressure.

**Preparation of dinuclear carbonyls from mononuclear carbonyls:**

When a cold solution of $\text{Fe}(\text{CO})_5/\text{Os}(\text{CO})_5$ in glacial CH_3COOH is irradiated with ultra-violet light, $\text{Fe}_2(\text{CO})_9/\text{Os}_2(\text{CO})_9$ are obtained.

**Preparation of mixed-metal carbonyls by metathesis reaction**

5. BONDING IN METALLIC CARBONYLS

Carbon monoxide:

In order to understand the bonding in metal carbonyls, let us first see the MO diagram of carbon monoxide.

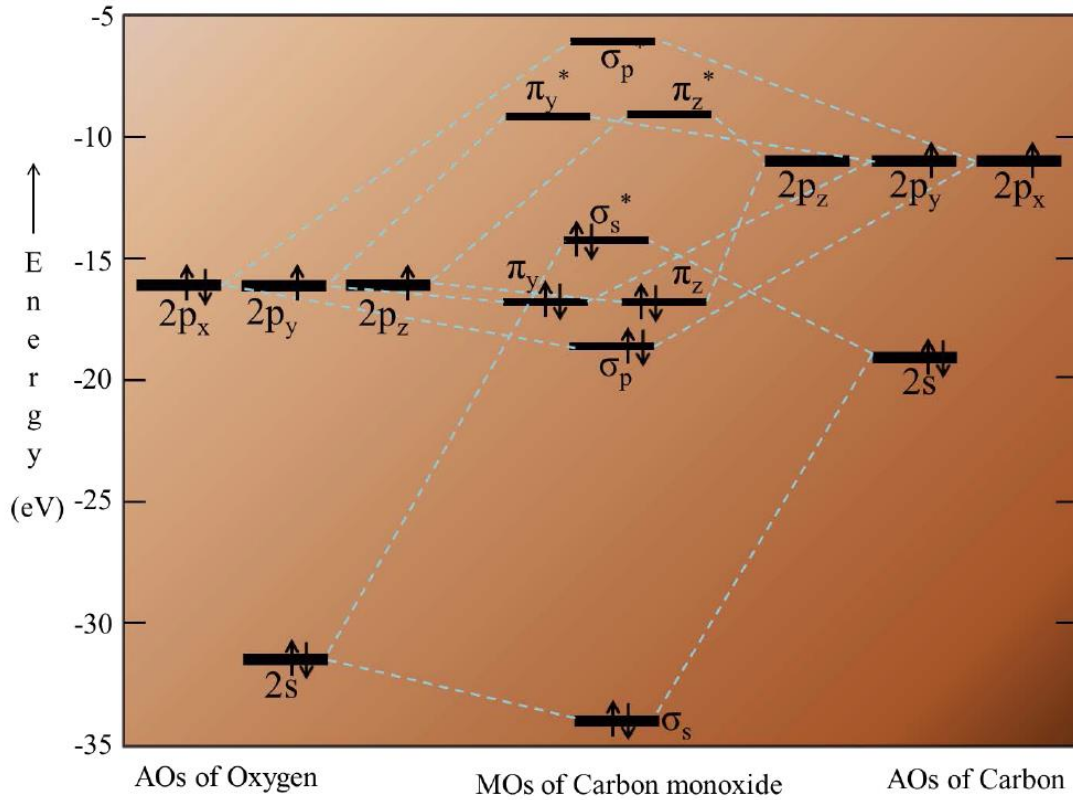


Figure: Molecular Orbital Energy Level Diagram of Carbon Monoxide

The order of energy of the molecular orbitals and the accommodation of ten electrons of the carbon monoxide can be shown as: