

**P.G. SEMESTER-IV**

**Elective Course-1a**

**Inorganic Chemistry Special**

**Unit -1 (a) Alkyl and Aryl Transition Metal Complexes**

**Topic: Routes of Synthesis of Alkyl and Aryl Transition Metal Complexes Part-2**

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## Nucleophilic Attack On Coordinated Ligand

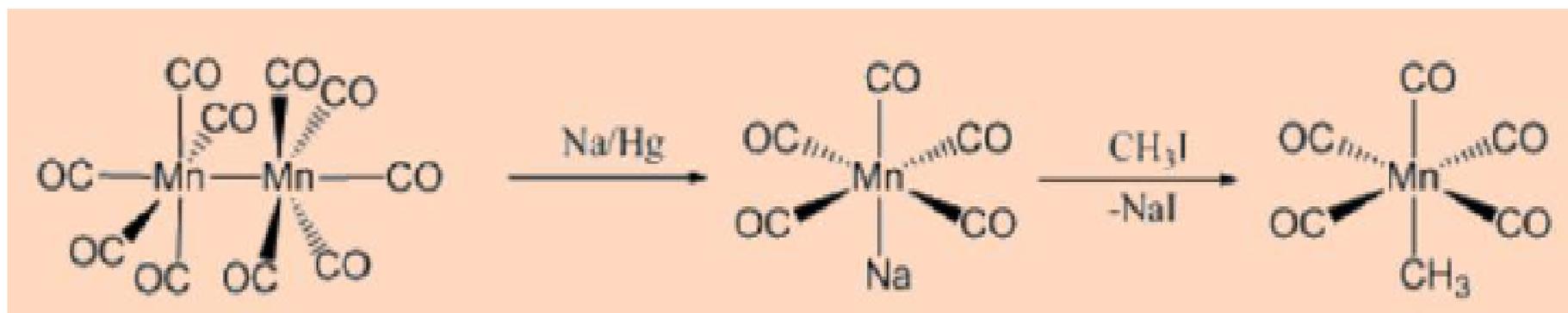
Instead of the metal acting as a nucleophile, a coordinated unsaturated ligand is attacked by an external nucleophile.

- **Process:** Attack on a coordinated alkene or CO by a carbanion or hydride.
- **Example:** Attack of an alkoxide on a coordinated CO to form a metal-ester complex.
- **General Scheme:**



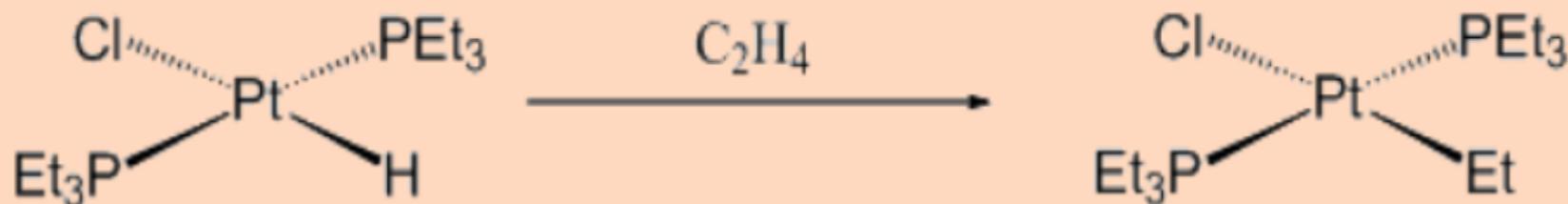
## Metallate alkylation reaction

This category represents the reaction of carbonylate anions with alkyl halides as shown below.



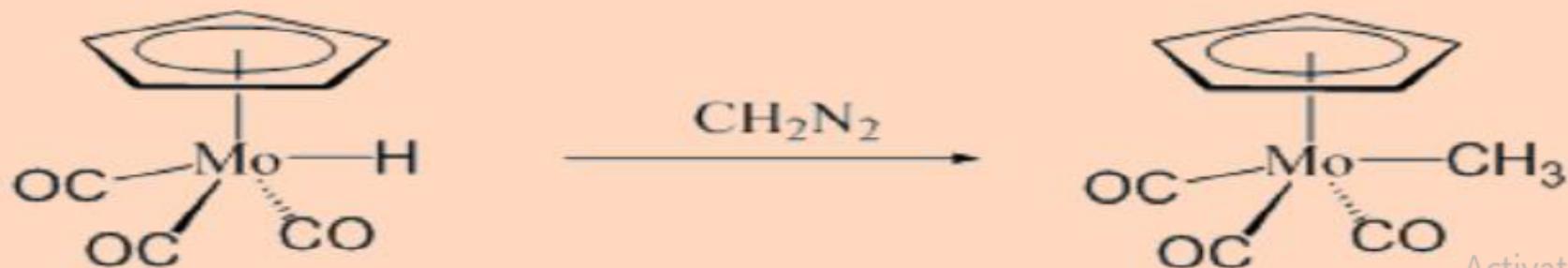
### Alkene insertion or Hydrometallation

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.



## Metallation (C-H Activation)

Direct replacement of a hydrogen atom on an organic molecule by a metal.

- **Orthometallation:** A specific type where a ligand already attached to the metal undergoes C-H activation at the *ortho* position of an aromatic ring, forming a chelate ring.
  - **Example:** Reaction of  $[PdCl_4]^{2-}$  with azobenzene to form a cyclometallated product.
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### Key Stability Factors

When synthesizing these complexes, two "death traps" must be avoided:

1.  **$\beta$ -Hydrogen Elimination:** The most common decomposition path where a hydrogen on the  $\beta$ -carbon transfers to the metal, releasing an alkene.
  - *Solution:* Use alkyls like  $-CH_2SiMe_3$  or  $-C(Me)_3$  which lack  $\beta$ -hydrogens.
2. **Reductive Elimination:** The reverse of oxidative addition, where the alkyl group and another ligand leave the metal.

## Comparison of Methods

Method	Starting Materials	Change in Ox. State	Best For
<b>Metathesis</b>	Metal Halide + R-Li/R-MgX	No change	Bulk synthesis
<b>Oxidative Addition</b>	Low-valent Metal + R-X	+2	Catalytic cycles
<b>Insertion</b>	M-H/M-R + Alkene/CO	No change	Polymerization
<b>Metallation</b>	Metal Salt + Hydrocarbon	Variable	Chelate complexes