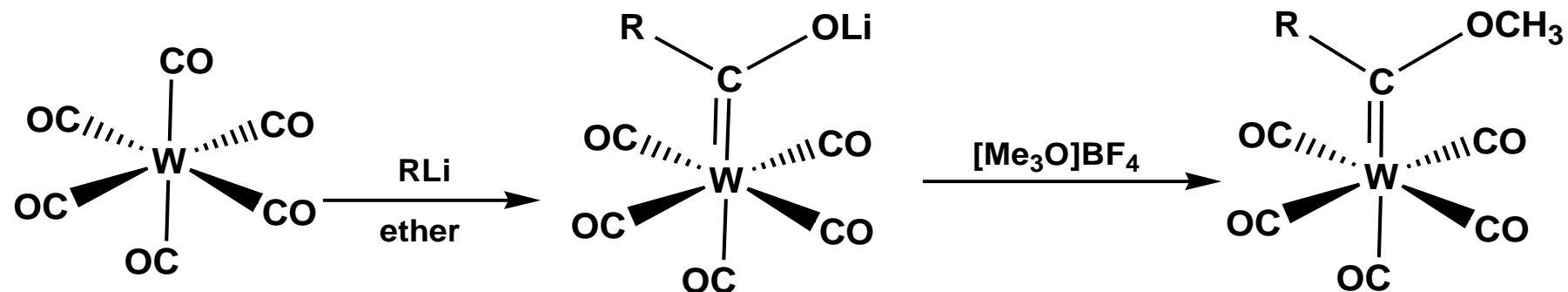


Lecture 8

Reactions of Ferrocene

Reactions of Metal Carbonyls

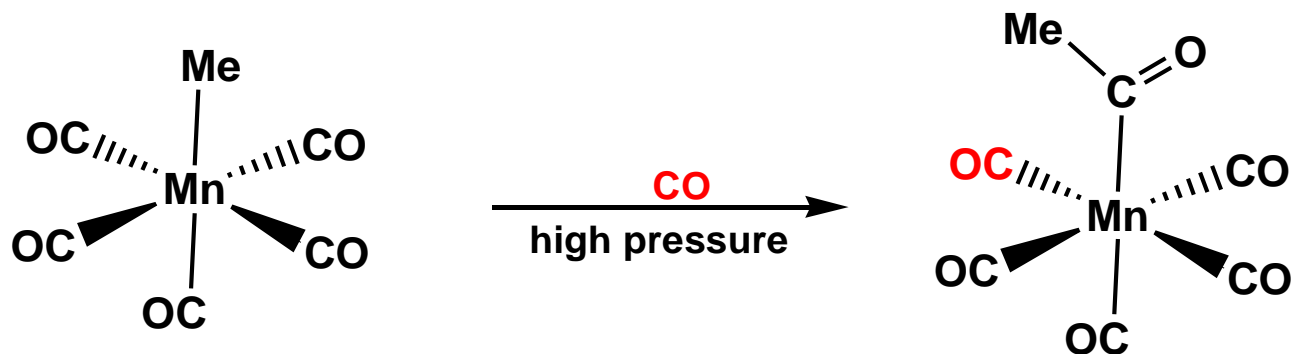
Nucleophilic addition to CO



Fischer Carbene

Carbenes are catalysts for olefin metathesis

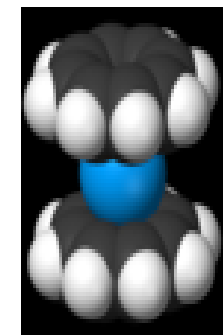
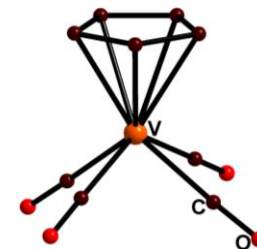
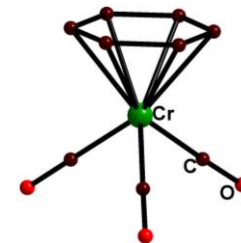
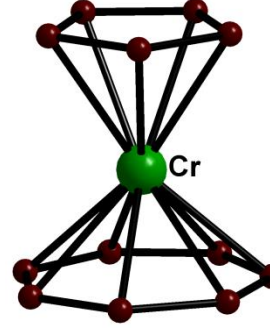
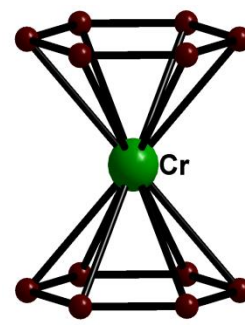
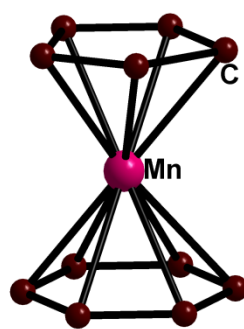
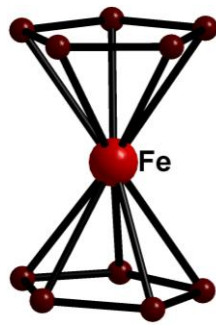
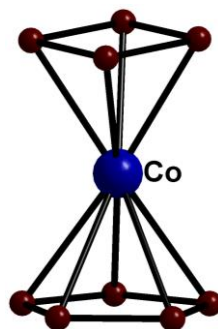
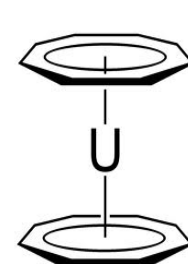
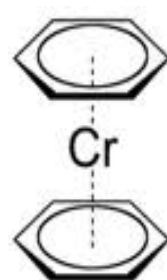
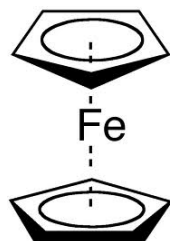
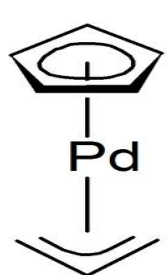
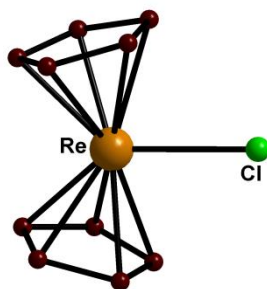
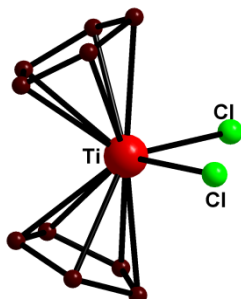
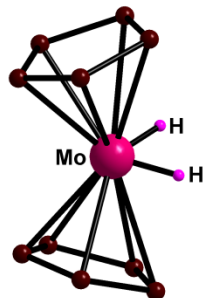
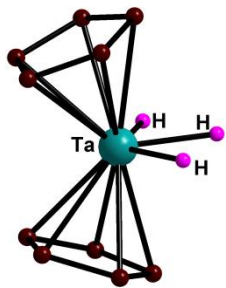
Migratory insertion of CO



Metal- Sandwich compounds

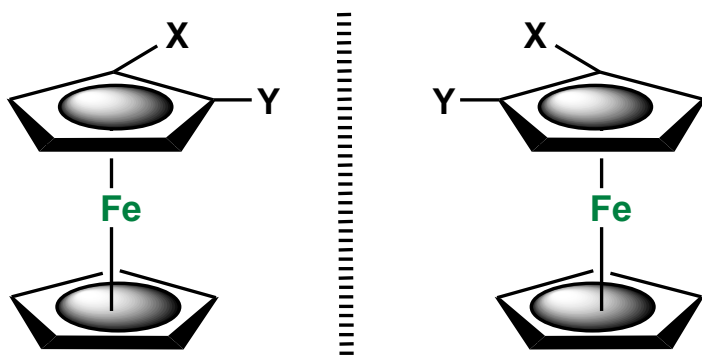
Hapticity of sandwich compounds
varies from 1-8

A transition-metal complex in which a metal atom or ion is
'sandwiched' between two rings of atoms.



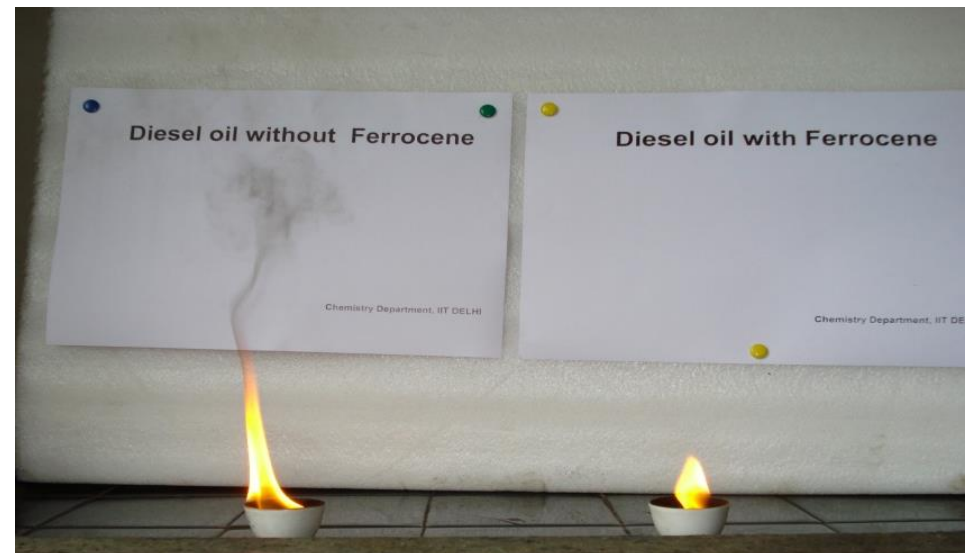
Why metal – sandwich compounds are important?

1. **Transition metal/ metal ion embedded inside an organic matrix:** Makes a metal ion soluble even in hydrocarbon solvents. E.g. Ferrocene is soluble in hexane while Fe^{2+} as such is not. Outcome: a hydrocarbon soluble additive/catalyst
2. Coordination to an electropositive metal often changes the reactivity and electronic properties of the π system bound to it (benzene vs ferrocene)
3. Metal sandwich compounds are excellent substrates to make planar chiral compounds. Applications as chiral catalysts in asymmetric catalysis



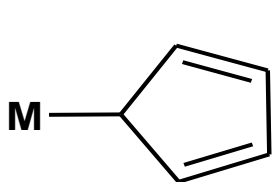
Planar chirality:

Non- super-imposable mirror images

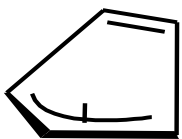


Cyclopentadienyl (Cp–)

- Cyclopentadienyl (Cp–) the most important of all the polyenyl ligands



η^1



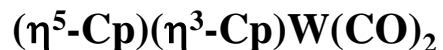
η^3

**Least
common**



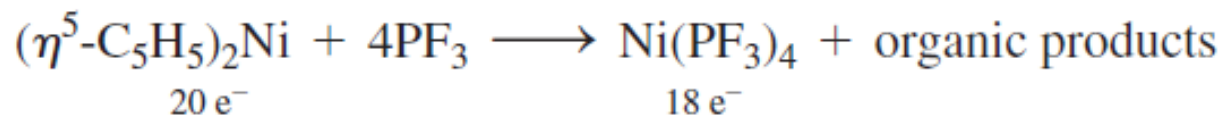
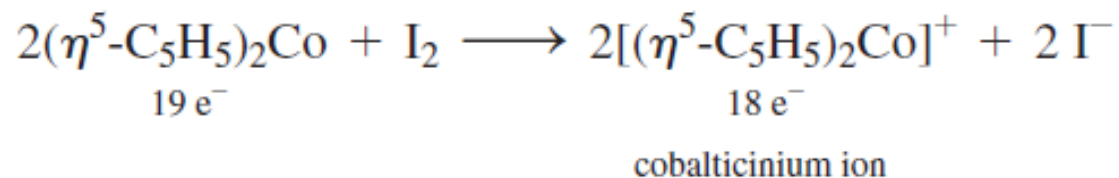
η^5

**most
common**



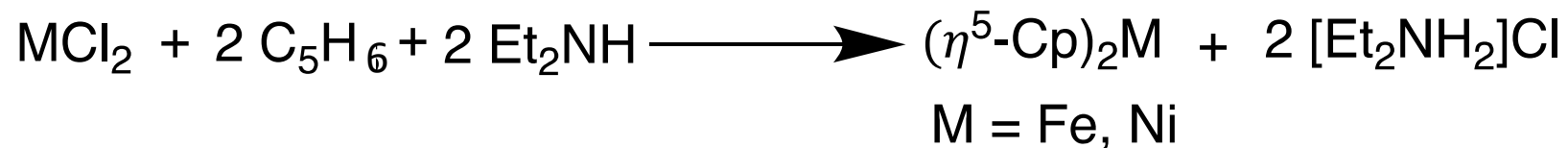
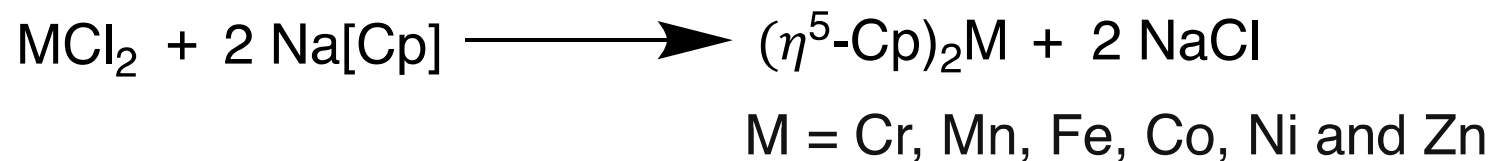
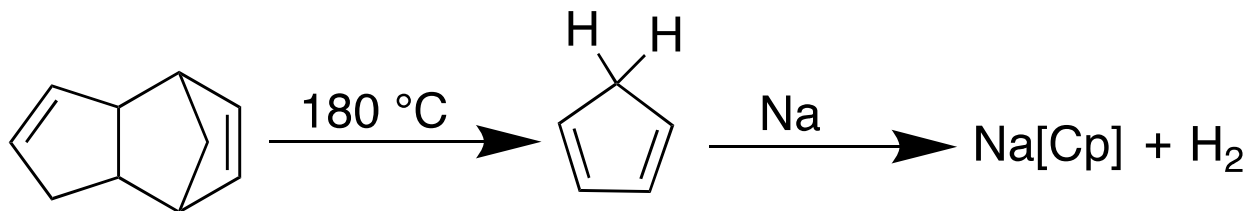
Complex	Electron Count	ΔH for $\text{M}^{2+} \text{-C}_5\text{H}_5^-$ Dissociation (kJ/mol)
$(\eta^5\text{-C}_5\text{H}_5)_2\text{Fe}$	18	1470
$(\eta^5\text{-C}_5\text{H}_5)_2\text{Co}$	19	1400
$(\eta^5\text{-C}_5\text{H}_5)_2\text{Ni}$	20	1320

Ferrocene shows much more chemical stability than cobaltocene and nickelocene; many of the chemical reactions of the latter are characterized by a tendency to yield 18-electron products.



Synthesis of ferrocene and other metallocenes

- Neutral cyclopentadiene (C_5H_6) is a weak acid with a pK_a of around 15
- Deprotonated with strong base or alkali metals to generate the anionic Cp^-

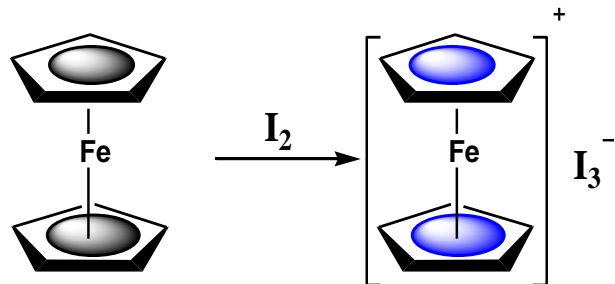


In a sandwich complex, the metal centre lies between two π -bonded hydrocarbon (or derivative) ligands. Complexes of the type $(\eta^5-Cp)_2M$ are called *metallocenes*.

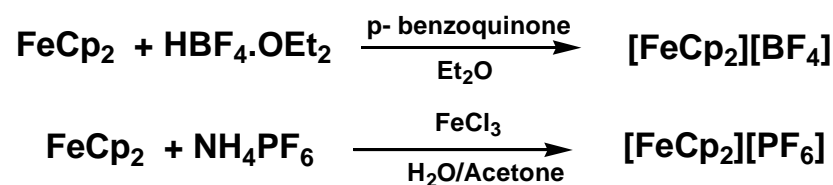
Reactions of Ferrocene

Ferrocene undergoes electrophilic substitution reactions. Many of its reactions are faster than similar reactions of benzene

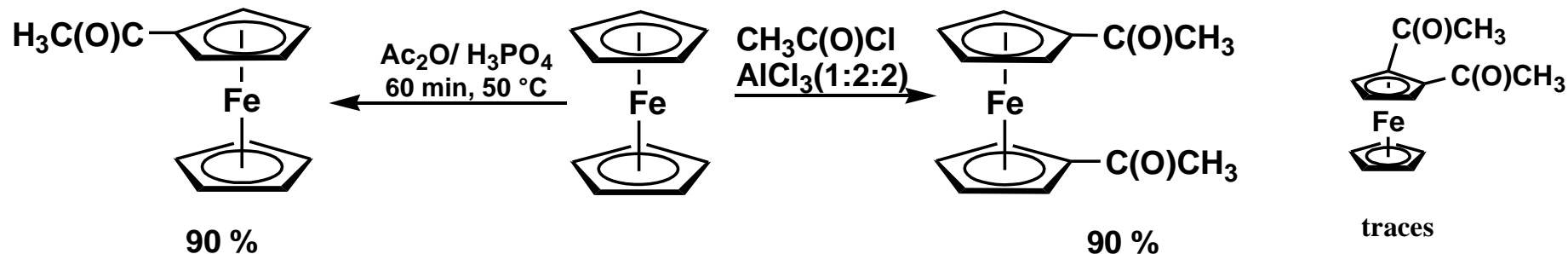
Necessary requirement: The electrophile should not be oxidizing in nature



The oxidized Cp_2Fe^+ , ferrocenium cation, will repel the electrophile away. Therefore direct nitration, halogenation and similar reactions cannot be carried out on ferrocene.

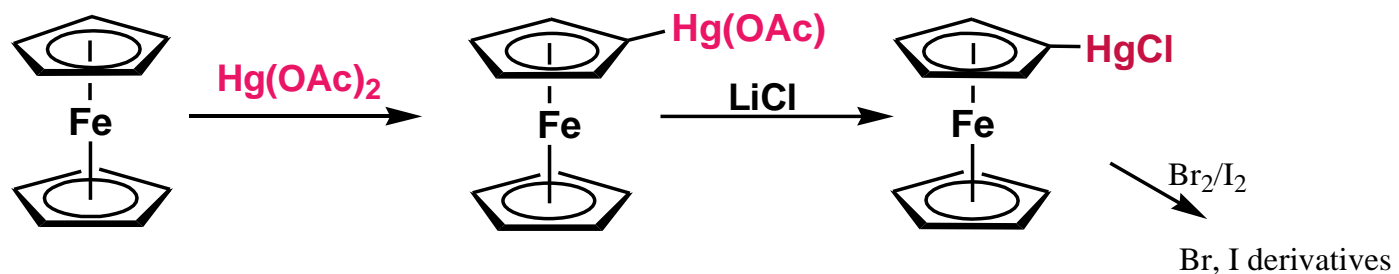


Acetylation



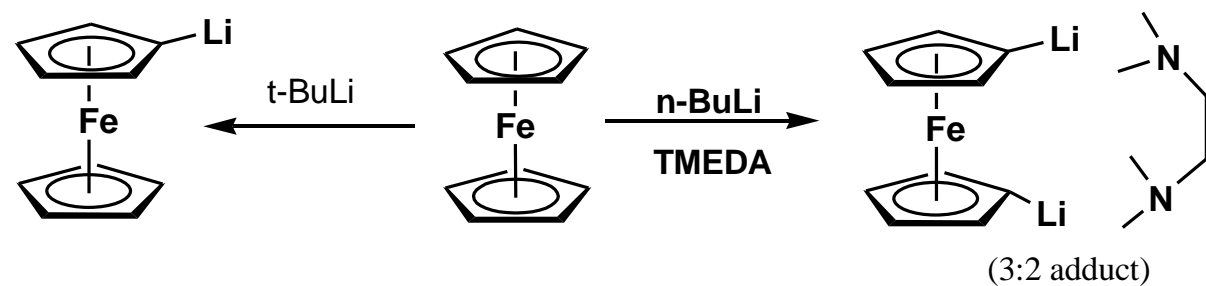
3.3×10^6 times faster than benzene

Chloromercuration (*hazardous*)



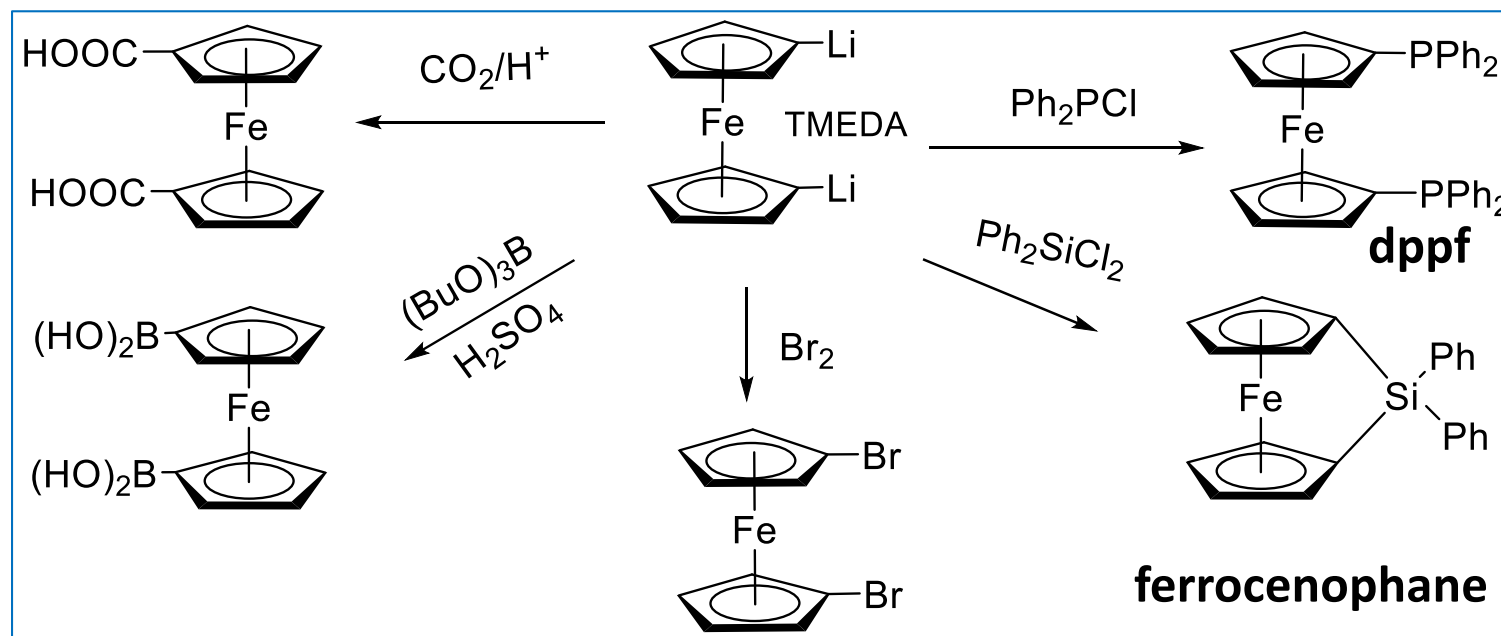
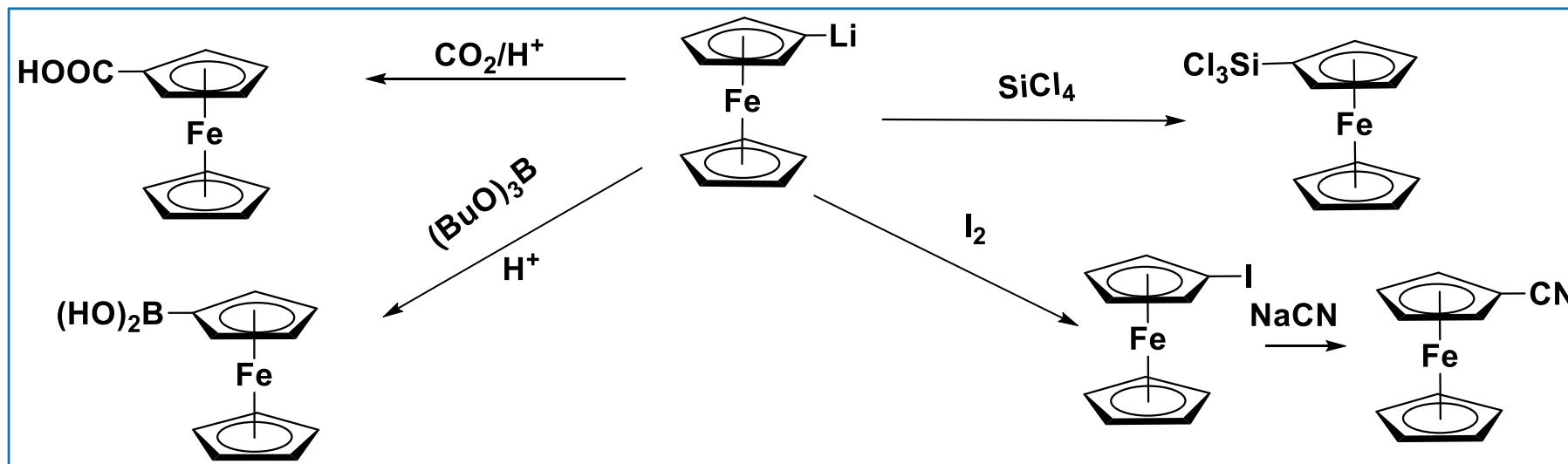
109 times faster than benzene

Lithiation reaction

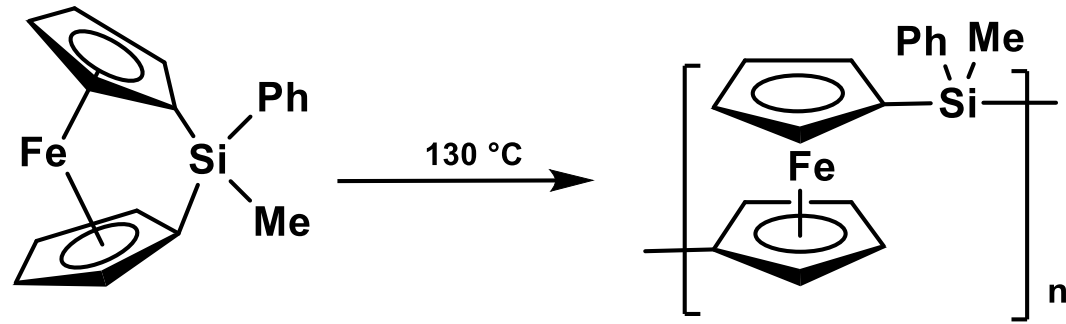


Does not happen with benzene;
only with bromobenzene

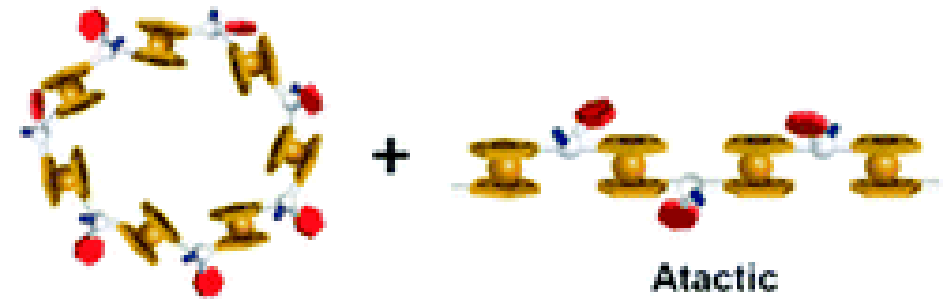
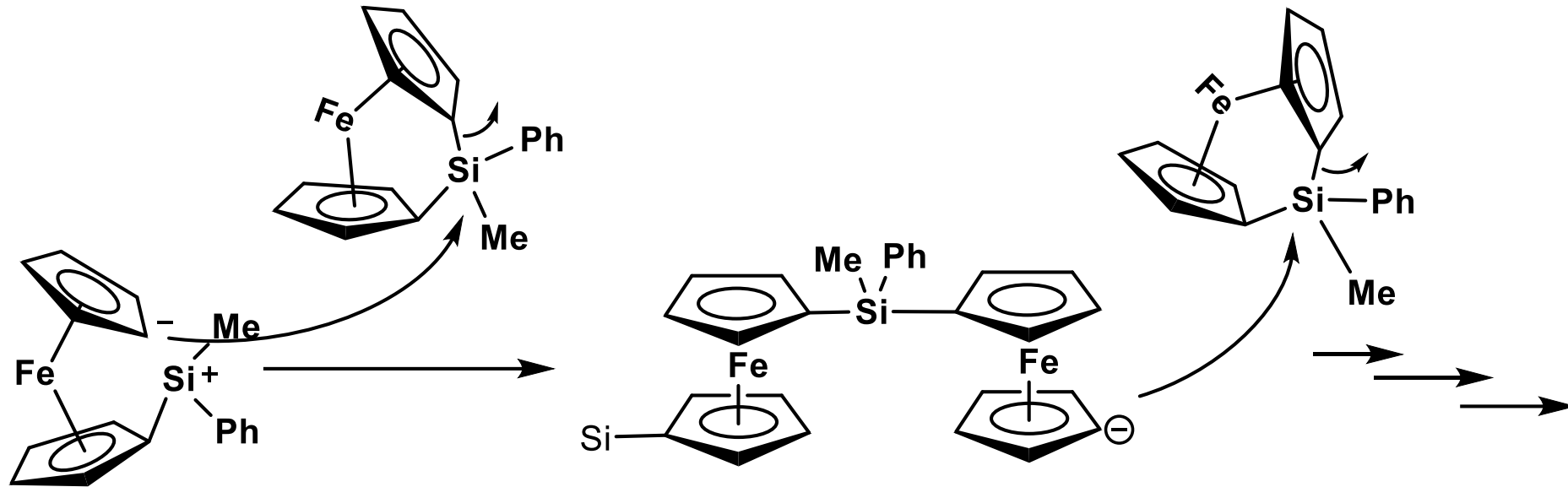
Lithiation and 1,1'-di-lithiation – access to range of new derivatives



Polymers with ferrocene in the backbone

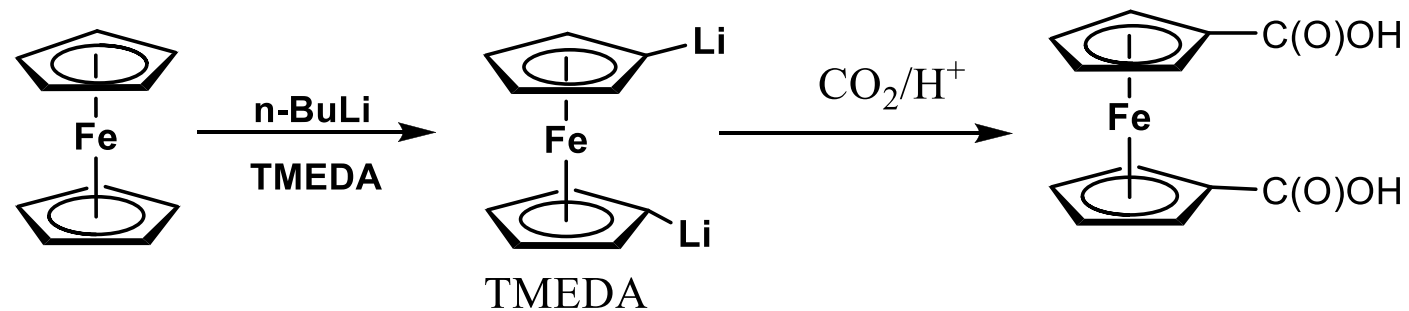


M. Wt: 3.4×10^5



Problem solving - synthesis

Starting from ferrocene show minimum number of steps for preparing 1,1'-ferrocene dicarboxylic acid



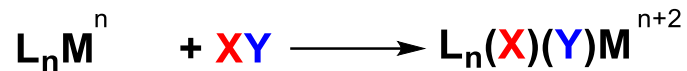
Organometallic Reaction Mechanism

Common paths in organometallic reactions

1. **Oxidative addition**
2. **Reductive elimination**
3. **Migratory Insertion**
4. **β -hydrogen elimination**
5. **σ -bond metathesis**

Oxidative addition

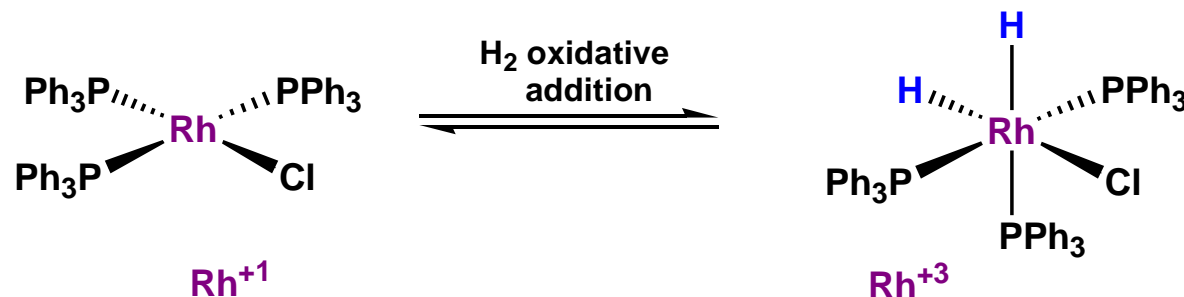
When addition of ligands is accompanied by oxidation of the metal, it is called an oxidative addition reaction



OX state of metal increases by 2 units

Coordination number increases by 2 units

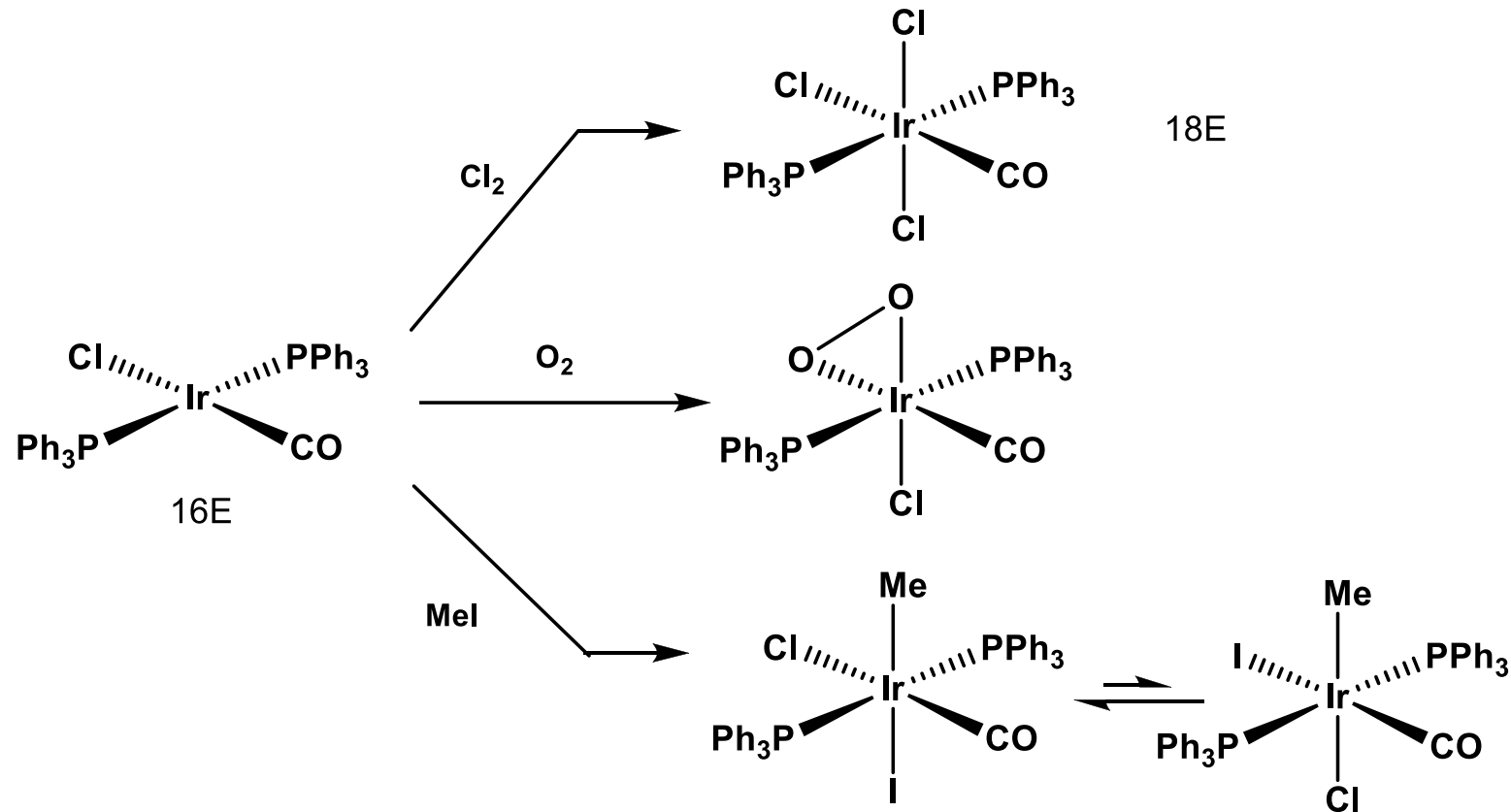
2 new anionic ligands are added to the metal



Requirements for oxidative addition

- Availability of nonbonded electron density on the metal
- Two vacant coordination sites on the reacting complex (L_nM), that is, the complex must be coordinatively unsaturated
- A metal with stable oxidation states separated by two units; the higher oxidation state must be energetically accessible and stable.

Examples of Oxidative addition : Cis or trans ?

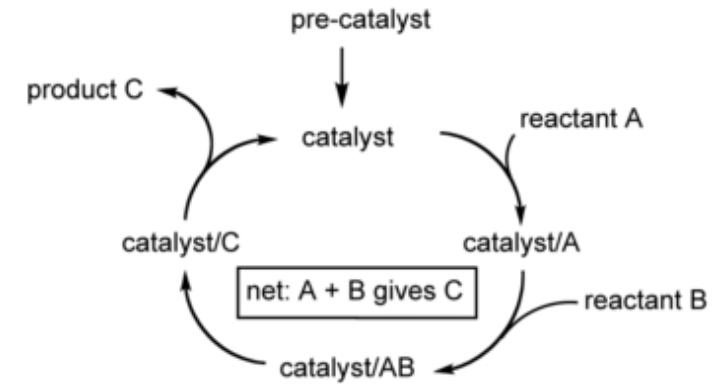
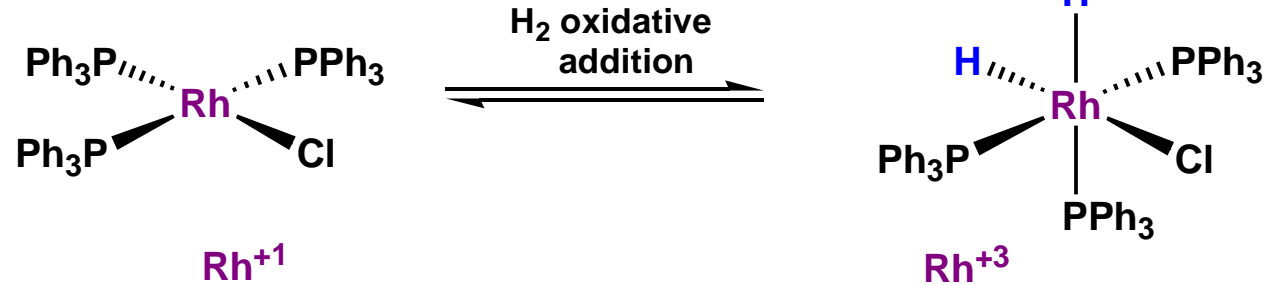


Homonuclear systems (H_2 , Cl_2 , O_2 , C_2H_2) Cis

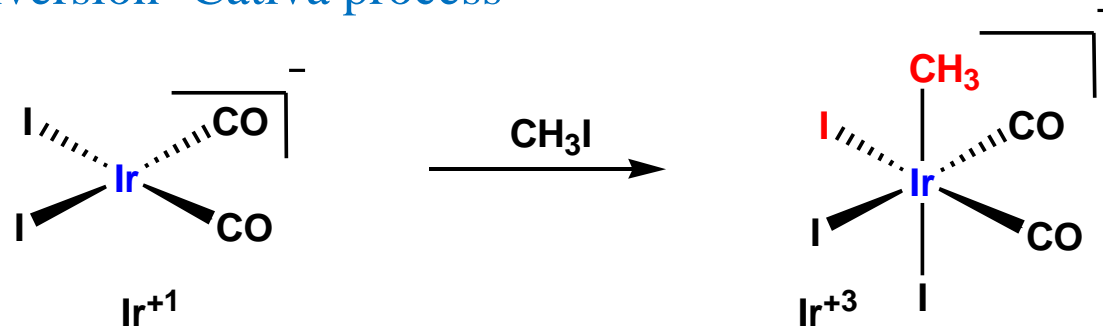
Heteronuclear systems (MeI) Cis or trans

An important step in many homogeneous catalytic cycles

Hydrogenation of alkenes- Wilkinson catalyst

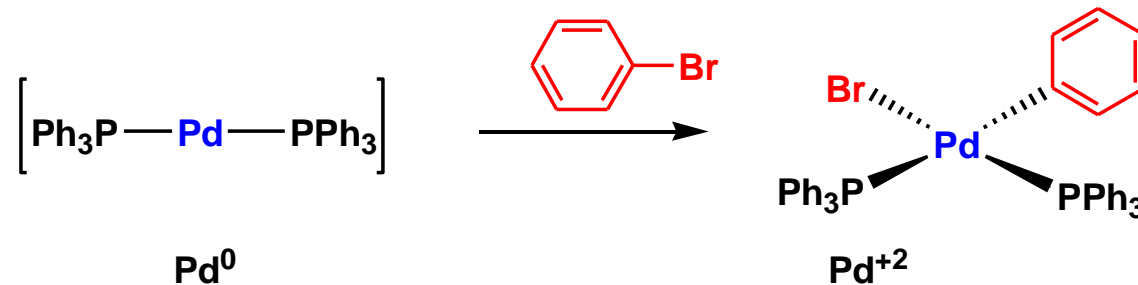


Methanol to acetic acid conversion- Cativa process



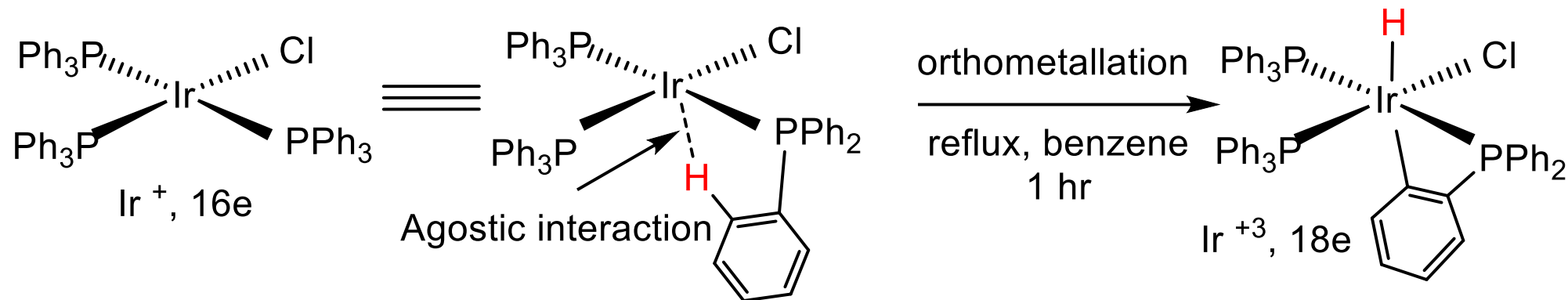
Often the first step of the mechanism

Pd catalyzed Cross coupling of Ar-B(OH)_2 and Ar-X – Suzuki Coupling



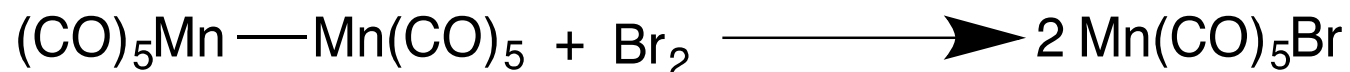
The more electron rich the metal, more easy is the oxidative addition

Oxidative addition involving C-H bonds and cyclo/ortho metallation



Orthometallations, oxidative additions in which an *ortho* position of an aromatic ring becomes attached to the metal, are quite common.

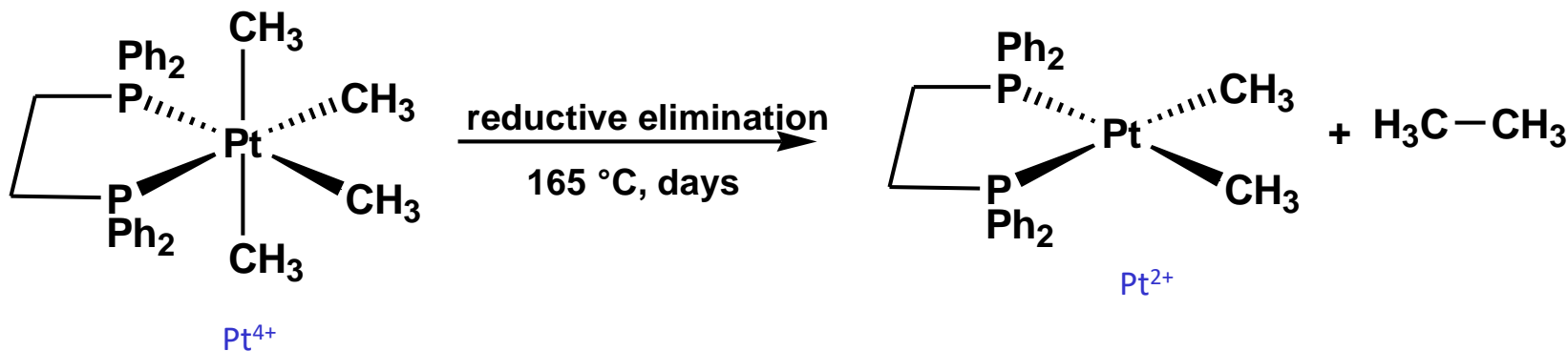
Oxidative addition at a binuclear complex



For a binuclear complex oxidative addition increases oxidation state of metal by one each.

Reductive elimination

Almost the exact reverse of Oxidative Addition



Oxidation state of metal decreases by 2 units

Coordination number decreases by 2 units

2 cis oriented anionic ligands form a stable σ bond and leave the metal

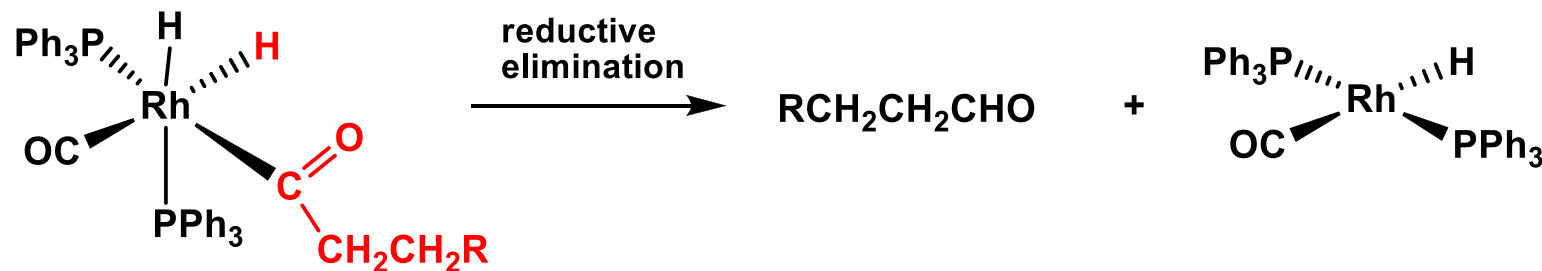
Factors which facilitate reductive elimination

- A high formal positive charge on the metal,
- The presence of bulky groups on the metal, and
- An electronically stable organic product.

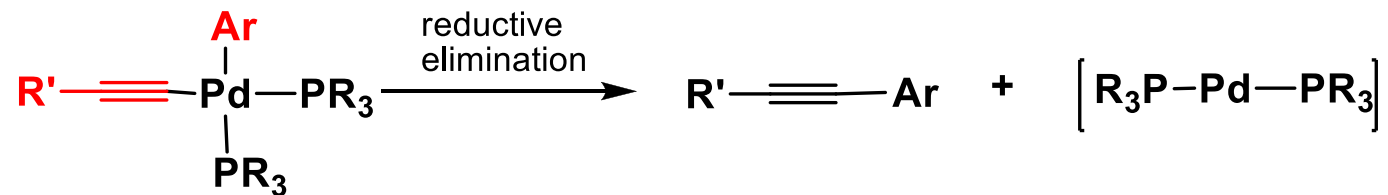
Cis orientation of the groups taking part in reductive elimination is a MUST

Final step in many catalytic cycles

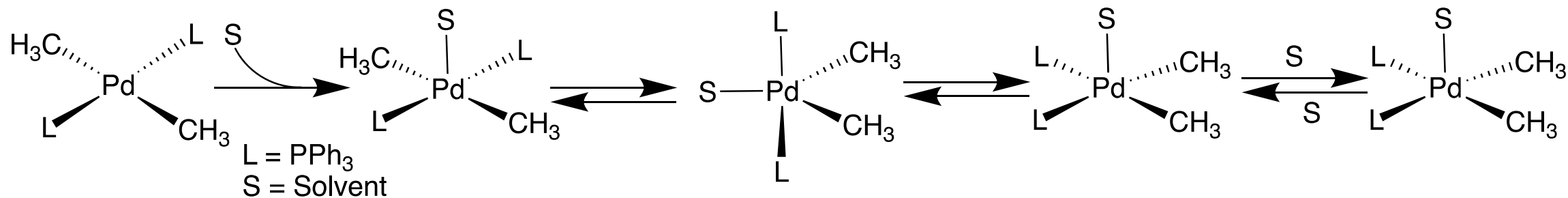
Hydroformylation (conversion of an alkene to an aldehyde)



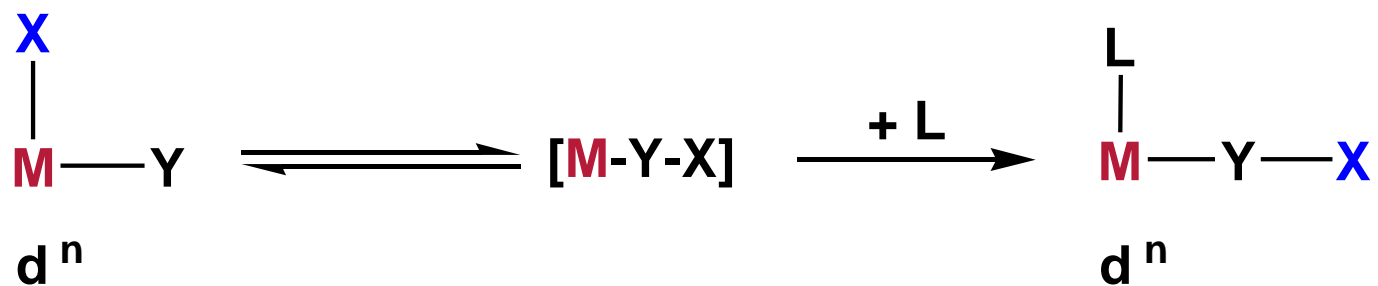
Sonogashira Coupling (coupling of a terminal alkyne to an aryl group)



Mechanism of *trans* to *cis* conversion



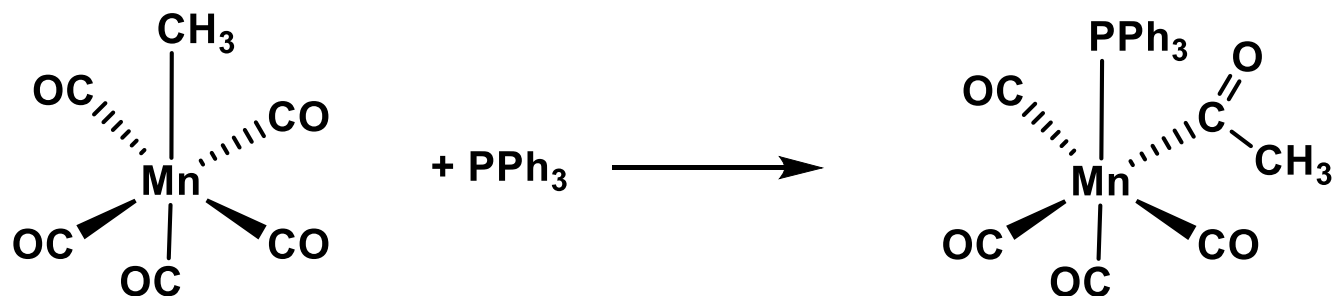
Migratory Insertion



No change in the formal oxidation state of the metal

A vacant coordination site is generated during a migratory insertion (*which gets occupied by the incoming ligand*)

The groups undergoing migratory insertion **must be *cis*** to one another



These reactions are enthalpy driven and although the reaction is entropy prohibited the large enthalpy term dominates

Types of Migratory Insertion

