Organometallic Chemistry

Inorganic Chemistry Organic Chemistry primarily ionic M-X bonds, dative M-L bonds variable and often

- more or less covalent bonds
- rigid element environments
- fixed oxidation states



Chemistry of Carbon (O, S, Se, N etc.)

Organometallics Chemistry of all elements (metals)

- Direct M-C bond
- more covalent (less ionic)
- than coordination compounds

often less symmetric

Importance

fluxional environments

variable oxidation states

- Easy access to C-C bond
- Catalysis
- Small molecule activation
- New industry
- Around 2000 research article
- Six Nobel Prizes

Edward Frankland

Innocent Ligands: In a metal complex, if the ligands whose oxidation state is clearly known, Eg: O²⁻, Cl⁻

Non-innocent ligands: In a metal complex, if the ligands igands whose oxidation state is not known, Eg: NO

Synthesis of Metal Carbonyls

Direct carbonylation

Ni + 4 CO
$$1 \text{ bar, } 25 \text{ °C}$$
 Ni(CO)₄ pale yellow m.p -17 °C, bp 42 °C
Fe + 5 CO $100 \text{ bar, } 150 \text{ °C}$ Fe(CO)₅ pale yellow m.p -20 °C, bp 103 °C

Reductive carbonylation

From Metal Halides

Reactions of Metal Carbonyls

Reduction: Carbonyl anions

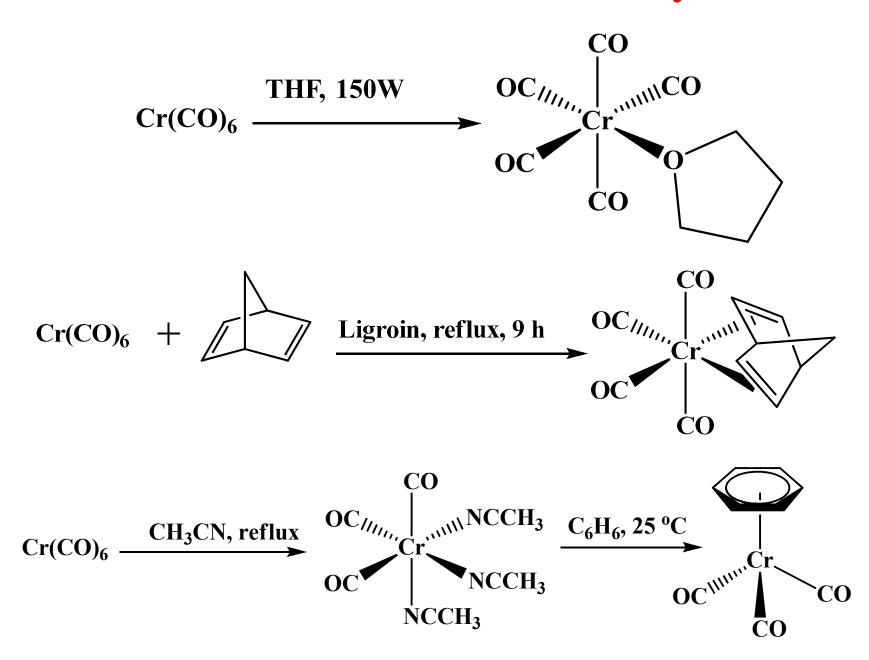
$$V(CO)_6$$
 + Na \longrightarrow Na[$V(CO)_6$]
 $Mn_2(CO)_{10}$ + 2Na \longrightarrow 2 Na[$Mn(CO)_5$]
 $Co_2(CO)_8$ + 2Na \longrightarrow 2 Na[$Co(CO)_4$]
 $Fe(CO)_5$ + Na/Hg \longrightarrow Na $_2Fe(CO)_4$

Oxidation: Iodocarbonyls

$$Mn_2(CO)_{10} + I_2 \longrightarrow 2 Mn(CO)_5 I$$

$$Fe(CO)_5 + I_2 \longrightarrow Fe(CO)_4I_2$$

Activation of metal carbonyls

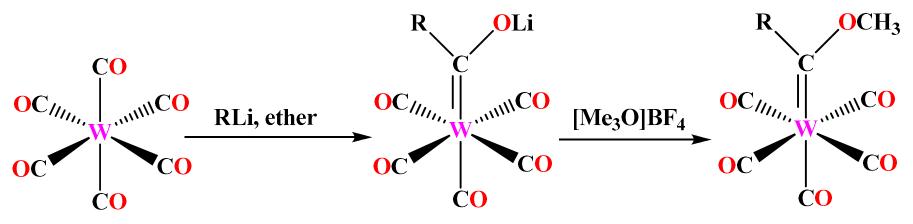


Disproportionation

Some multi-metal carbonyls can undergo disproportionation in the presence of suitable ligands

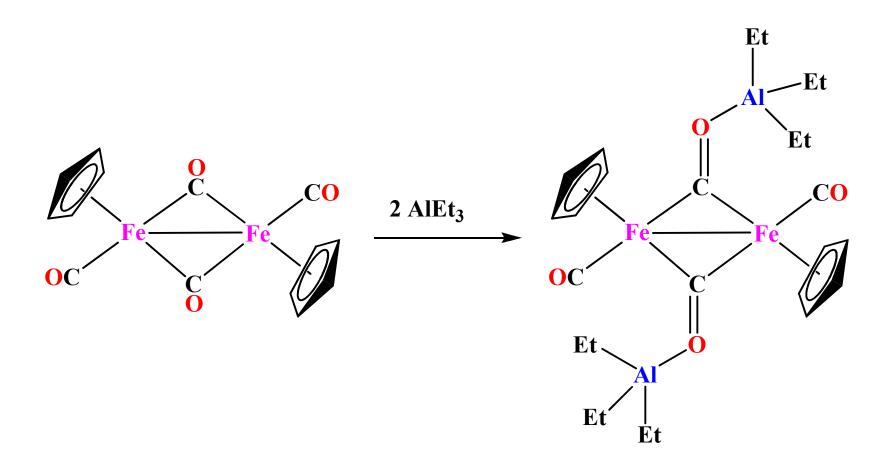
$$3 \text{ Mn}_2(\text{CO})_{10} + 12 \text{Py} \quad \frac{120 \text{ °C}}{-1000} > \quad 2[\text{Mn(Py)}_6]^{2+} + 4[\text{Mn(CO)}_5]^{-1000}$$

Nucleophilic addition to CO



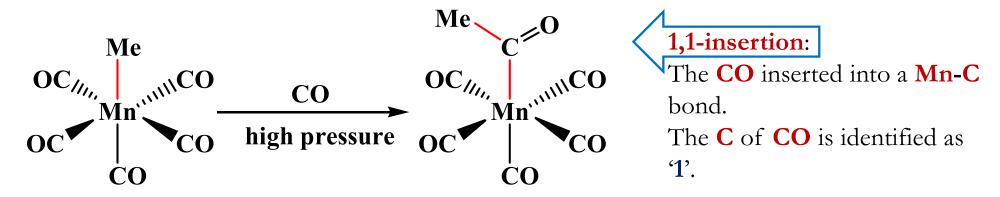
Fischer carbene

Electrophilic addition to the carbonyl oxygen



Migratory Insertion of carbonyls

- The ability of metal carbonyls, especially metal carbonyl anions, to undergo migratory insertion has been utilized in organic synthesis for the preparation of acyl substituted metal carbonyls.
- > These are good precursors for a host of carbonyl containing organic molecules.



Oxidative decarbonylation

$$Mn_2(CO)_{10} + I_2 \longrightarrow 2Mn(CO)_5I \xrightarrow{NaCp} CpMn(CO)_3$$

$$Fe(CO)_5 + I_2 \longrightarrow Fe(CO)_4I_2 + CO$$

Microwave assisted carbonyl substitution

Conventional way
$$[Mo(CO)_{6}] + NaCp \longrightarrow Na[CpMo(CO)_{3}] \xrightarrow{NH_{4}Fe(SO_{4})_{2}} \xrightarrow{OC} \xrightarrow{CO} \xrightarrow{$$

Carbonyl substitution reactions under thermal condition can often be improved by accelerated and simplified by using microwave radiation.

Oxidative addition & Reductive elimination

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

$$L_{n}M + X-Y \longrightarrow L_{n}(X)(Y)M$$

$$d^{n}$$

$$d^{n-2}$$

$$Ph_{3}P \longrightarrow CI$$

$$Ph_{3}P \longrightarrow CI$$

$$Rh^{+1}$$

$$Rh^{+3}$$

$$Ph_{3}P \longrightarrow CI$$

- Oxidation state of the metal increase by 2
- Coordination number of the metal increase by 2
- 2 anions get coordinated to the metal

Conditions to be satisfied by metal

- 1. Availability of non-bonded electron density
- 2. Availability of 2 vacant coordination sites
- 3. Stable oxidation states separated by 2

■ Elimination of ligands are accompanied by reduction of the metal, it is called an reductive elimination reaction

$$L_{n}(X)(Y)M \longrightarrow L_{n}M + X-Y$$

$$d^{n-2} \qquad d^{n}$$

$$Ph_{3}P \longrightarrow Ir \longrightarrow Ph_{3}P$$

$$CI \longrightarrow PPh_{3} \qquad Ph_{3}P \longrightarrow Ir \longrightarrow PPh_{3} \qquad + CH_{3}I$$

$$(+3) \qquad (+1)$$

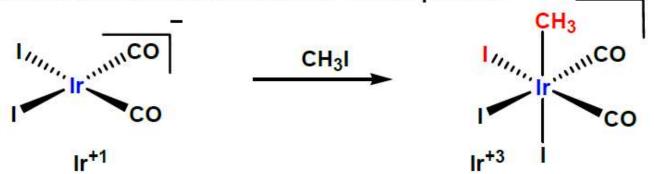
- Oxidation state of the metal decrease by 2
- Coordination number of the metal decrease by 2
- 2 *cis* oriented anionic ligands form a **obond** and leave the metal

Requirements

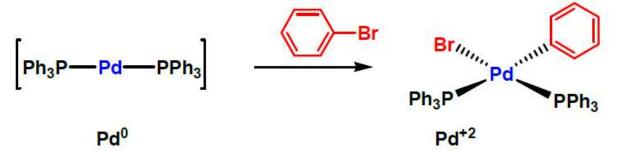
- 1. High formal positive charge on the metal
- 2. Presence of bulky groups on the metal
- 3. Electronically stable product

Oxidative addition: examples

Methanol to acetic acid conversion- Cativa process



Pd catalyzed Cross coupling of Ar-B(OH)2 and Ar-X - Suzuki Coupling



Oxidative addition involving C-H bonds

Reductive elimination: examples

Hydroformylation (conversion of an alkene to an aldehyde)

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

Cativa Process (Methanol to Acetic acid)

$$\begin{array}{c} H_3C \\ \hline \\ I_{M,n} \\ \hline \\ CO \end{array} \longrightarrow \begin{array}{c} H_3C - C - I \\ \hline \\ CO \end{array} \longrightarrow \begin{array}{c} I_{M,n} \\ \hline \\ CO \end{array}$$

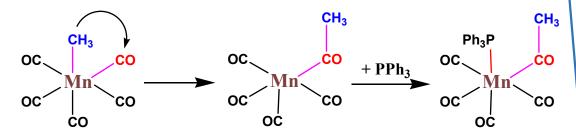
Migratory insertion & β -hydride elimination

Migratory insertion

A reaction in which a ligand or a group of atoms cis to one another migrate to the other, and forms a bond with an atom of the other group

Features

- o No change in oxidation state of the metal
- o A vacant coordination sites is created
- o The vacant site is occupied by a ligand
- o The ligand/groups involved, must be *cis* to each other



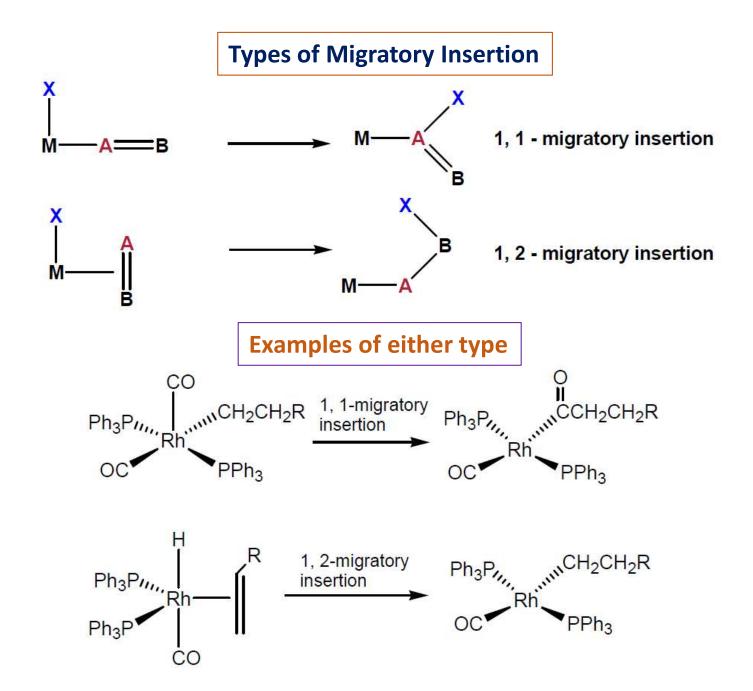
β-hydride elimination

A reaction in which an alkyl group having a β -hydrogen, σ -bonded to the metal is converted to metal bonded hydride and π -bonded alkene.

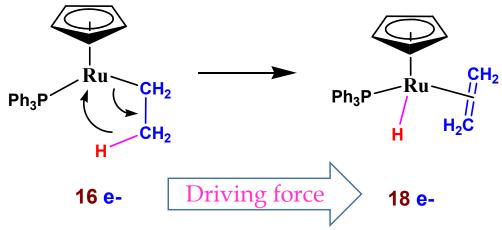
Condition

- o The alkyl group should have a β-hydrogen
- O A vacant site cis to the σ-bonded alkyl group
- o If the alkyl is CH_3 , it wont. But ethyl, propyl, butyl having β-hydrogen do.

Migratory insertion: examples

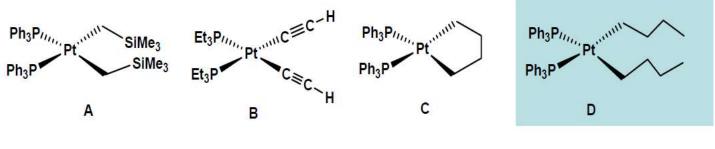


β -hydride elimination: examples



β-hydrogen elimination does not occur if,

- The alkyl group does not have a β-hydrogen. Eg.:-CH₂Ph, -CH₂-C(CH₃)₃, -CH₂Si(CH₃)₃
- β-hydrogen on the alkyl is unable to approach the metal. Eg.: -C≡CH
- The M-C-C-H unit is not in the same plane
 Select the most unstable from the following. Justify your choice.



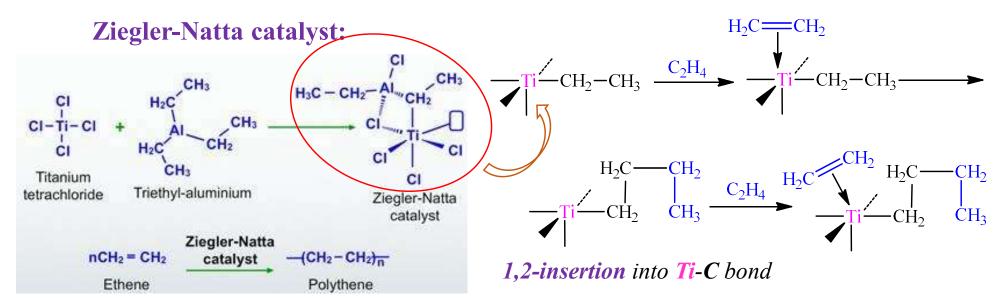
No β-H

β-H unable to approach M

MCCH unit will not be coplanar

Hydroformylation

Ziegler-Natta catalysis



- Isotactic polymer is formed by stereo-regular polymerization
- Polymerized product is released by β-hydride elimination a) from polymer,
 b) by Hydride transfer to monomer c) by hydrogenation

$$(\eta^{5}-Me_{5}C_{5})_{2}LuCH_{3} \xrightarrow{H_{2}C = CH(CH_{3})} \underbrace{1,2\text{-insertion into } \textbf{Lu-C bond}}_{1,2\text{-insertion into } \textbf{Lu-C bond}}$$

$$(\eta^{5}-Me_{5}C_{5})_{2}LuCH_{2}CH(CH_{3})_{2} \xrightarrow{1,2\text{-insertion into } \textbf{Lu-C bond}}_{1,2\text{-insertion into } \textbf{Lu-C bond}}$$

$$(\eta^{5}-Me_{5}C_{5})_{2}LuCH_{2}CH(CH_{3})CH_{2}CH(CH_{3})_{2}$$