# CH103: Introductory Chemistry



# Organometallic Chemistry

# Why should you care ?

- Organometallic chemistry is the basis of *homogeneous catalysis*, which is the method of choice for clean and efficient synthesis of fine chemicals, pharmaceuticals and many larger-scale chemicals.

- Many *plastics* (polythene, polypropene, butadiene rubber, ...) and *detergents* are made via organometallic catalysis.

- Organometallic chemistry is also the basis for understanding important steps in *heterogeneous catalysis* reactions such as olefin hydrogenation and CO oxidation.

- Organometallic compounds are used on a large scale as precursors for *generation of semiconductors* (AlN, GaAs, etc).

- *Silicone rubbers* are one of the few classes of organometallic compounds used as "final products".

# Frontiers in Organometallic Chemistry

- *Definition* of organometallic chemistry: transformations of organic compounds using metals.

- Organometallic chemistry is at the interface between inorganic and organic chemistry.
  - Inorganic: subset of coordination chemistry
  - Organic: subset of synthetic methods

- Other interdisciplinary areas
  - Bioorganometallic chemistry
  - Surface organometallic chemistry
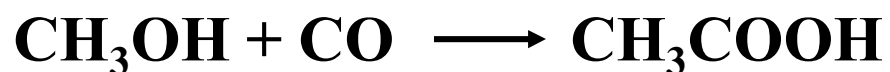
# Real life Example: Acetic Acid synthesis

Acetic acid is an important industrial chemical.

The traditional synthesis uses bio-oxidation of ethanol obtained via fermentation:
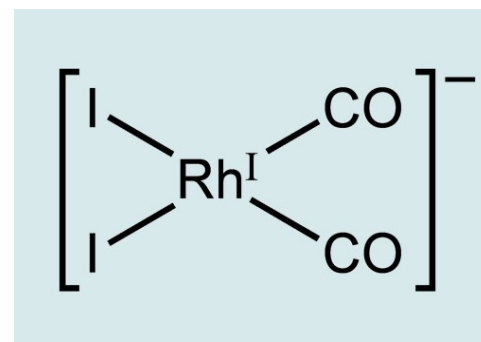
$$C_6H_{12}O_6 \longrightarrow 2\ C_2H_5OH + 2\ CO_2$$

$$C_2H_5OH + O_2 \longrightarrow CH_3COOH + H_2O$$
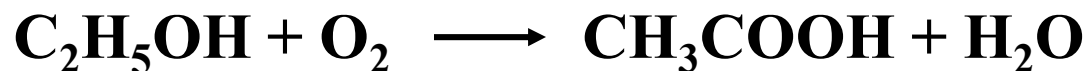
This is *not* a clean and efficient process!

Industrial acetic acid synthesis:

$$CH_3OH + CO \longrightarrow CH_3COOH$$

Catalyzed by a rhodium complex.

# History: first organometallic compounds

- **1760 Louis Claude Cadet de Gassicourt (Paris) investigates inks based on cobalt salts and isolates cacodyl from cobalt minerals containing arsenic ($CoAs_2$ and $CoAsS_2$) :**
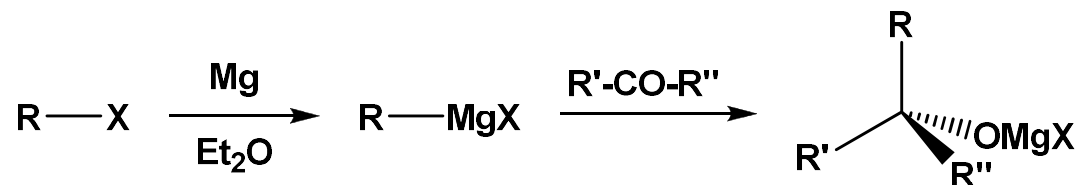
  $$As_2O_3 + 4\ CH_3COOK \rightarrow [AsMe_2]_2O + 2K_2CO_3 + 2CO_2 \ \textit{first}$$
  *organometallic compound*

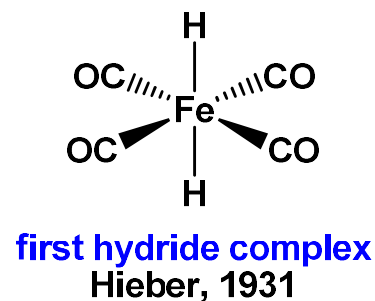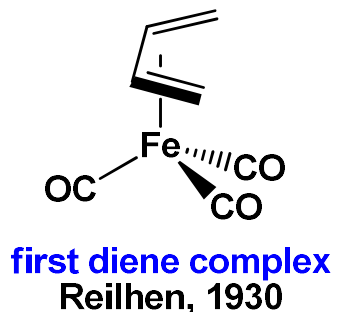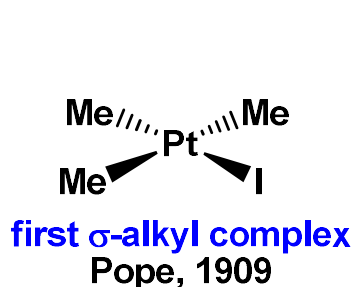- **1827 Zeise's salt is the first platinum - olefin complex**
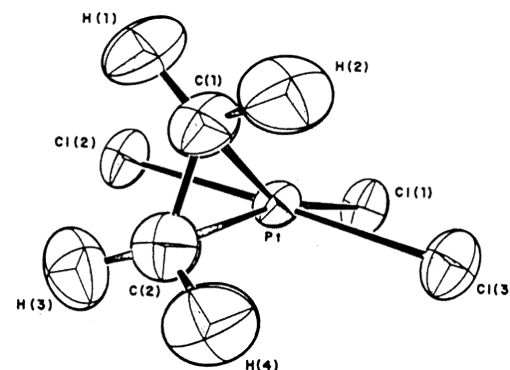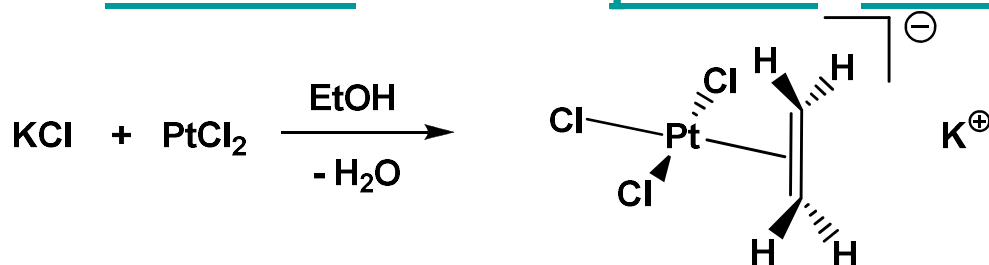
# History: 1900 – 1950

- 1863 Charles Friedel and James Crafts prepared organochlorosilanes
- 1893 Alfred Werner develops the modern ideas of coordination chemistry
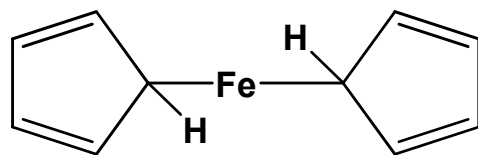- 1899 introduction of Grignard reagents

$$R-X \xrightarrow[Et_2O]{Mg} R-MgX \xrightarrow{R'-CO-R''} \underset{R''}{\overset{R}{R'{\overset{|}{\underset{}{C}}}}}OMgX$$

- 1912 *Nobel prize* Victor Grignard and Paul Sabatier

- 1930 Ziegler and Gilman simplify organolithium preparation, using ether cleavage and alkyl halide metallation, respectively
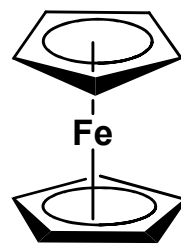
first σ-alkyl complex
Pope, 1909

first diene complex
Reilhen, 1930

first hydride complex
Hieber, 1931

# History: 1950 – 1960

- 1951 – 1952 Discovery of ferrocene, $Fe(\eta^5\text{-}C_5H_5)_2$



**Pauson, 1951**

**correct structure**
**Woodward and Wilkinson, 1952**

- Originally called "**dicyclopentadienyliron**."
- x ray analysis proved: ferrocene consisted of an iron(II) ion **sandwiched** between two parallel cyclopentadienyl (Cp) rings.
- The cyclopentadienyl ligand is just one example of many where the pi-system of an organic compound binds directly to a metal atom via a M*d* (pi)-*p*- (pi) interaction.
- The term *hapticity*, denoted n, describes the number of ligand atoms coordinated to the central
metal atom, e.g. $(\eta^5\text{-}Cp)_2Fe$

# History: 1950 – 1960 (continued)

1955     Ziegler and Natta develop olefin polymerization at low pressure using mixed metal catalysts (transition metal halide / $AlR_3$)

**1963 *Nobel prize* for Karl Ziegler and Giulio Natta on Ziegler-Natta catalysts**

➢ The catalysts used in coordination polymerization are transition metal organic compounds.

➢ A typical Ziegler-Natta catalyst is a combination of $TiCl_4$ and $(CH_3CH_2)_2AlCl$, or $TiCl_3$ and $(CH_3CH_2)_3Al$.

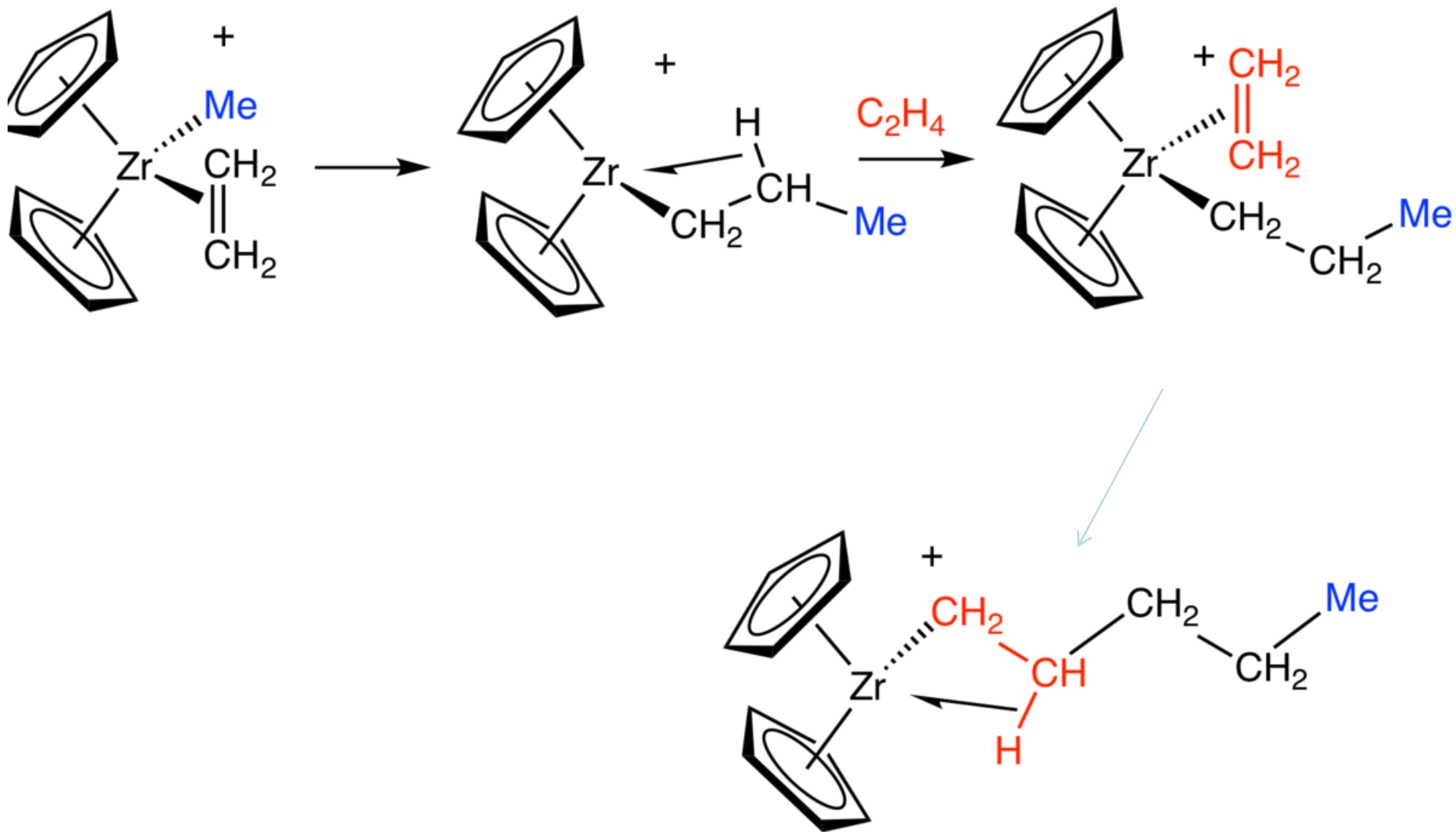➢ Many Ziegler-Natta catalyst combinations include a metallocene.
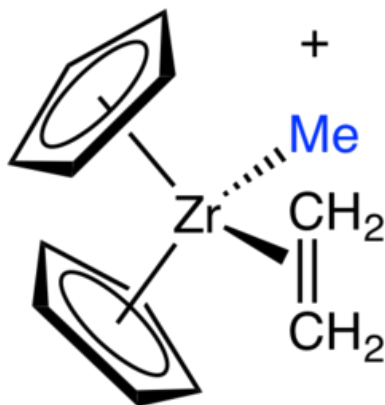
# Zieglar-Natta Catalyst
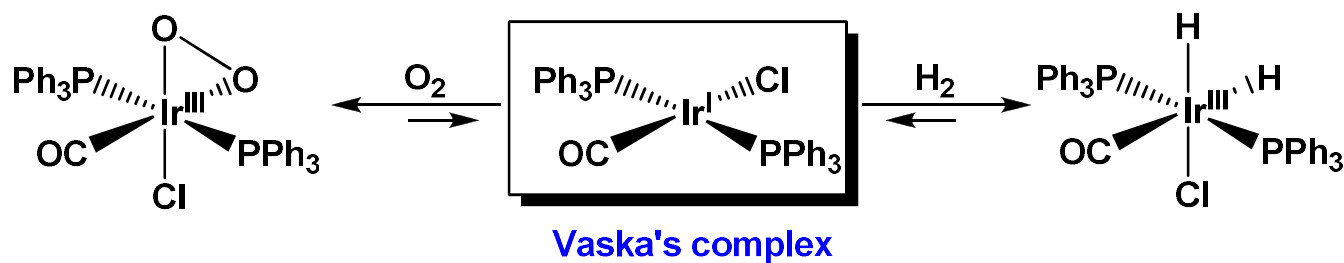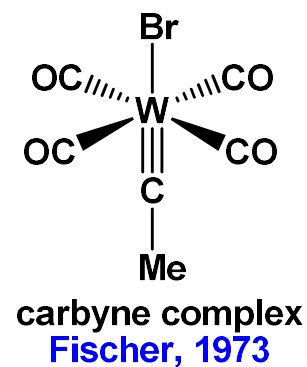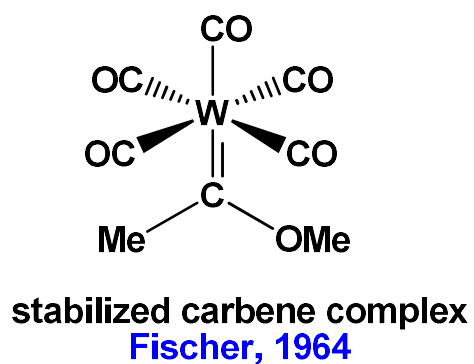
Polyethylene Polymerization
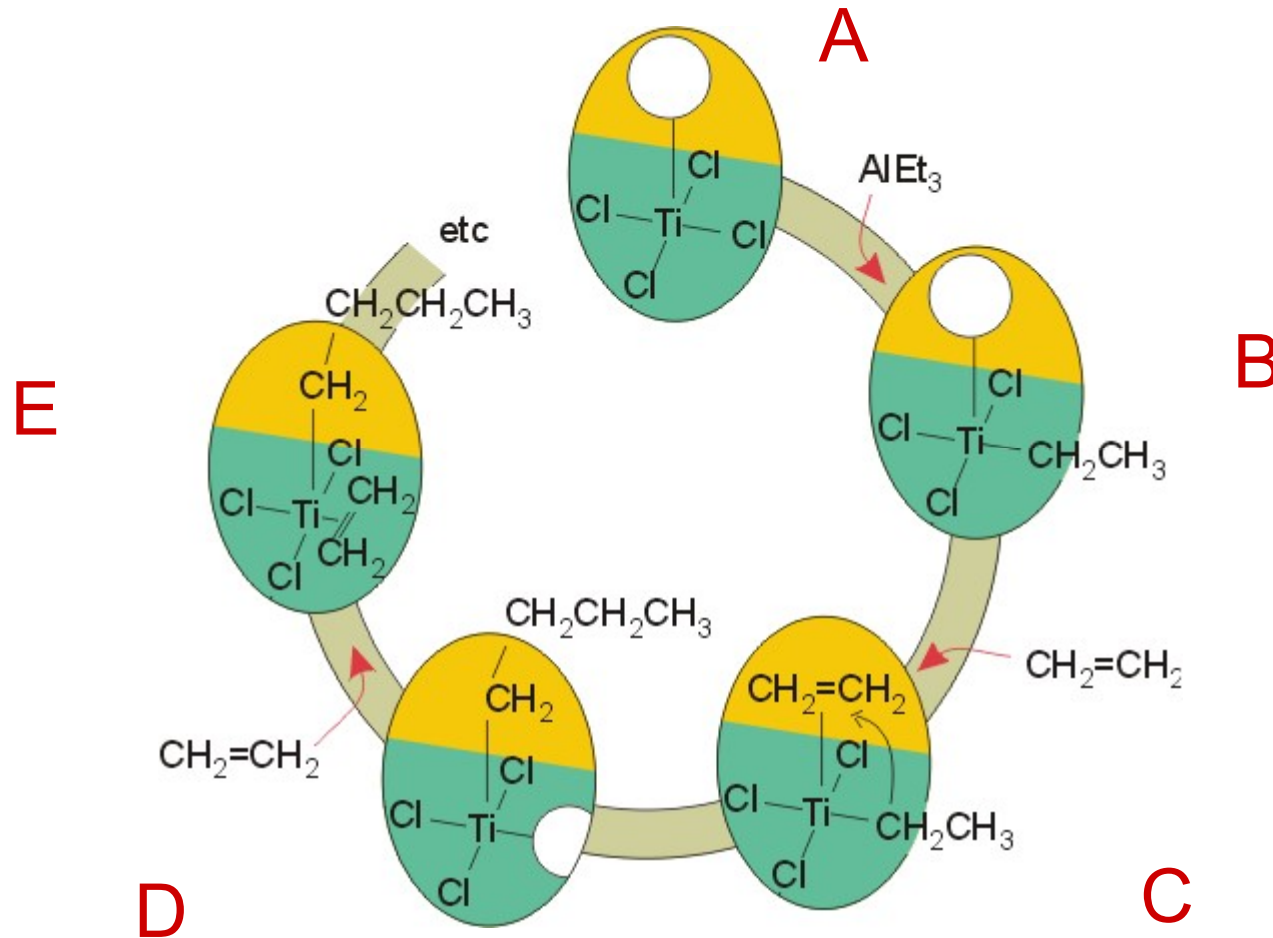
# Zieglar-Natta Catalyst

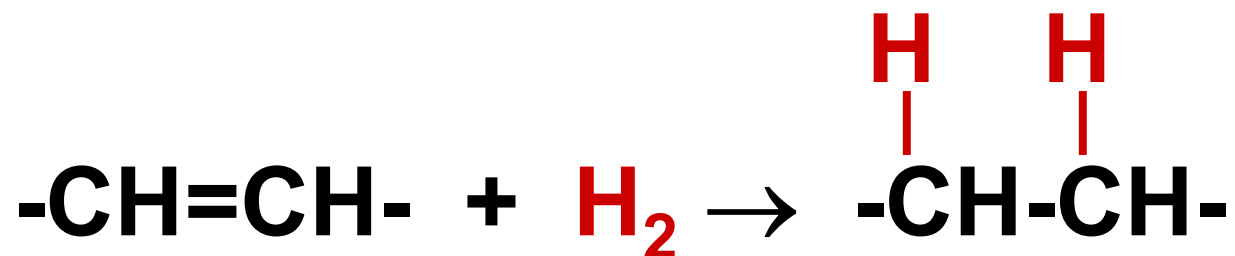# History: 1960 – 1980: catalysis

- 1962: Vaska's complex



**Vaska's complex**

- 1964: Fischer reports the first metal carbene.



stabilized carbene complex
**Fischer, 1964**

carbyne complex
**Fischer, 1973**

# Hydrogenation of Unsaturated Hydrocarbons

1973 *Nobel prize* Geoffrey Wilkinson and Ernst Otto Fischer on sandwich compounds

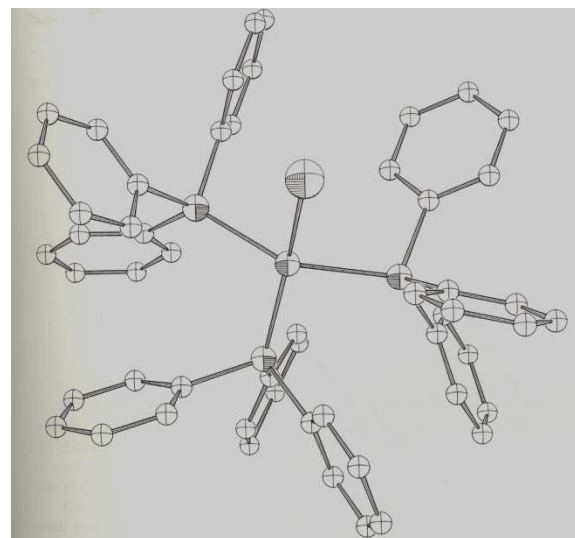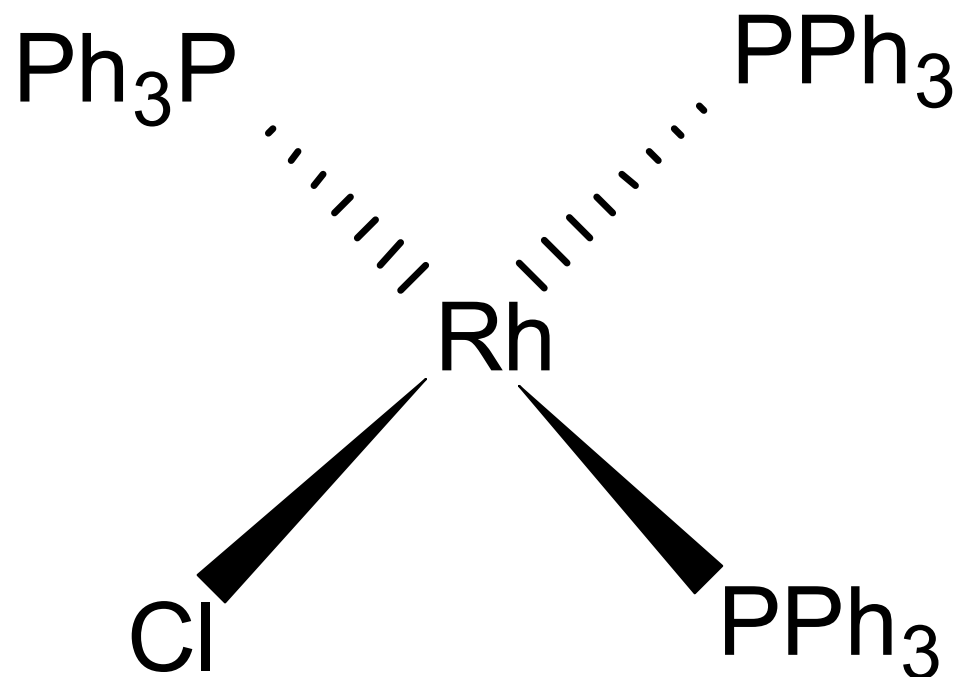$$-CH=CH- \; + \; H_2 \rightarrow \; \overset{\displaystyle H \quad\; H}{\underset{\textstyle}{\overset{|\quad\;\; |}{-CH-CH-}}}$$

The most common catalyst

⇓

Wilkinson's Catalyst, [RhCl(PPh$_3$)$_3$]

# Wilkinson's Catalyst (WC)

Ph$_3$P ........ PPh$_3$

Rh

Cl ........ PPh$_3$
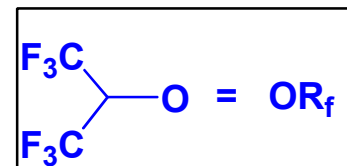
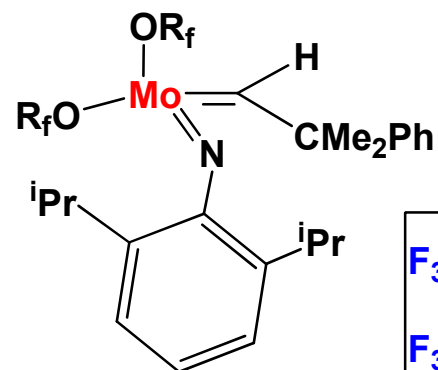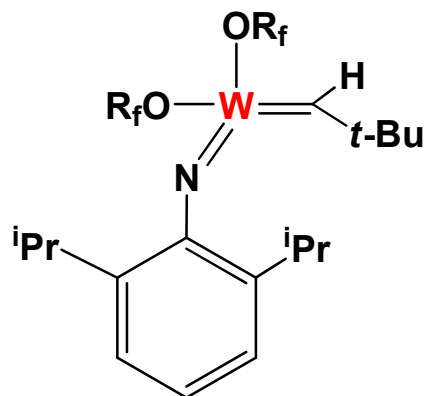**Chlorotris(triphenylphosphine)rhodium(I)**

Square planar    d$^8$ configuration

# Wilkinson's Catalyst (WC) Mechanism
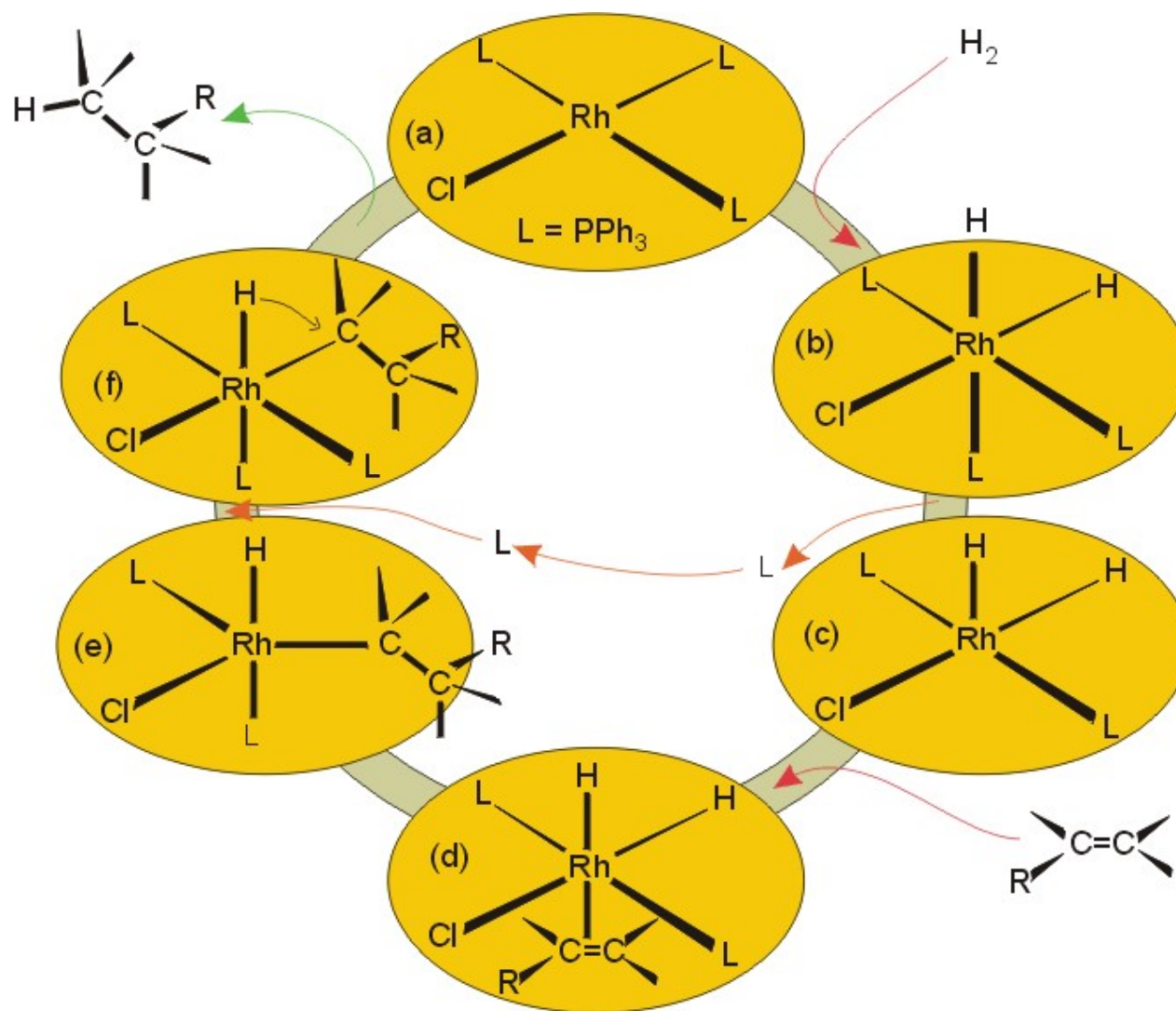
# 2005 Nobel prize in chemistry

**Schrock catalysts**



**Grubbs catalysts**
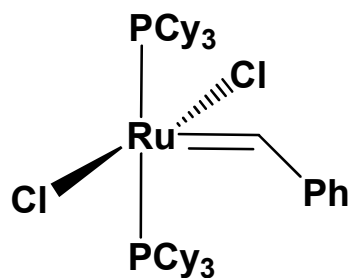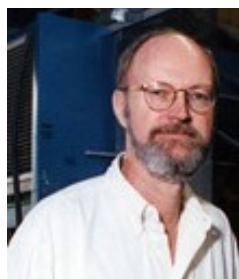
*1st generation*
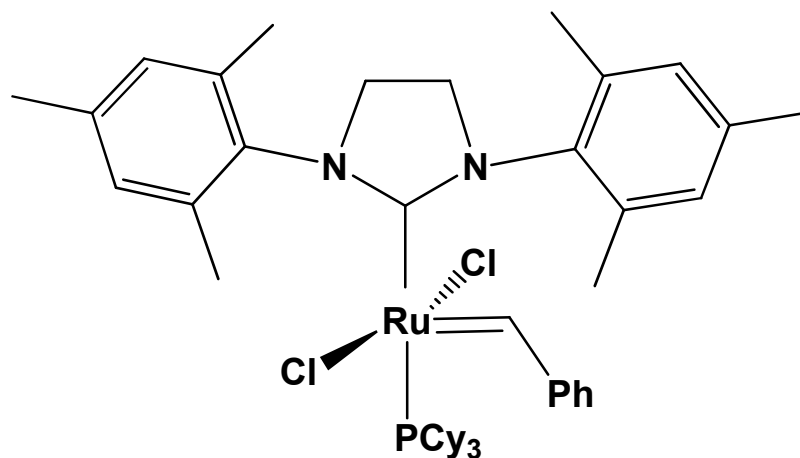
*2nd generation*

# SCHROCK CATALYST AND ALKYNE METATHESIS
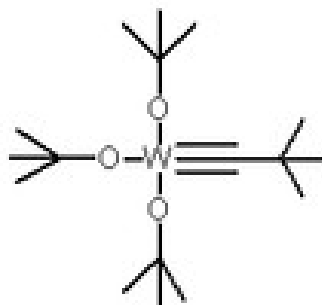


**Tris(t-butoxy)(2,2-dimethylpropylidyne)(VI)tungsten**
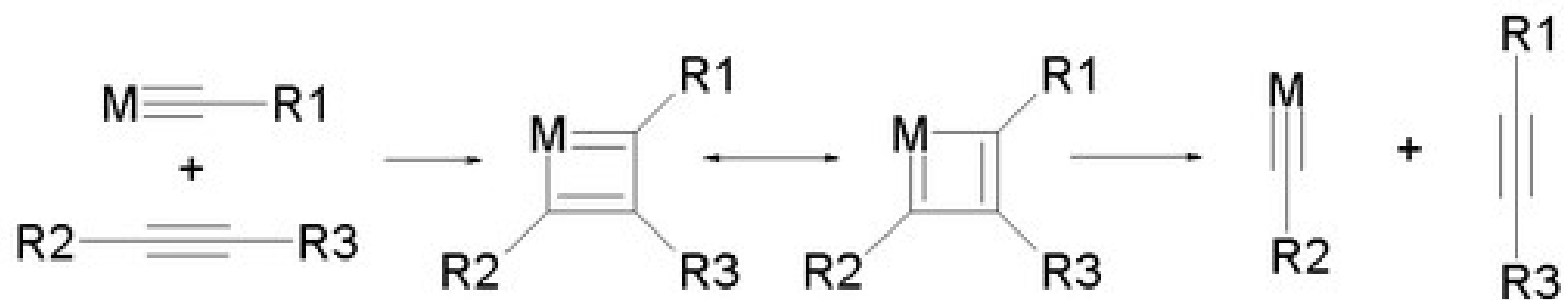
**GRUBB'S CATALYST** is used in organic synthesis to achieve olefin cross-metathesis , ring-opening metathesis polymerization (ROMP), acyclic diene metathesis polymerization (ADMET), and ring-closing metathesis.
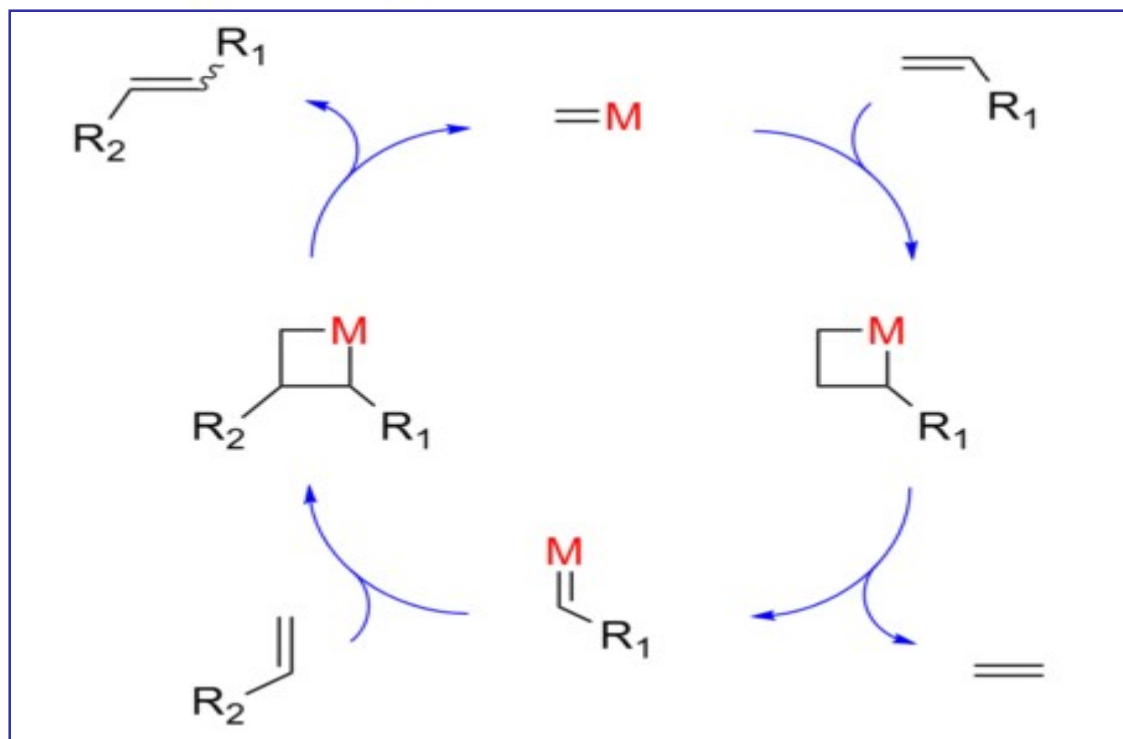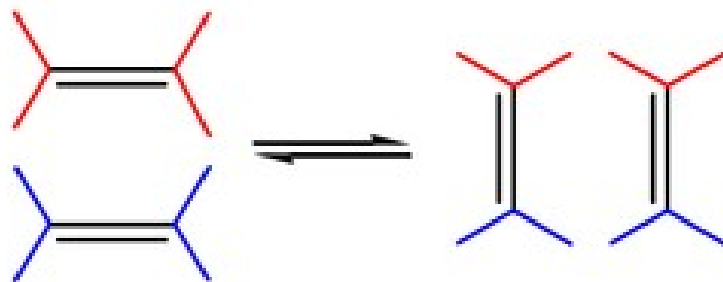
# C−H activation



- Oxidative addition

  $h\nu$
  $- H_2$
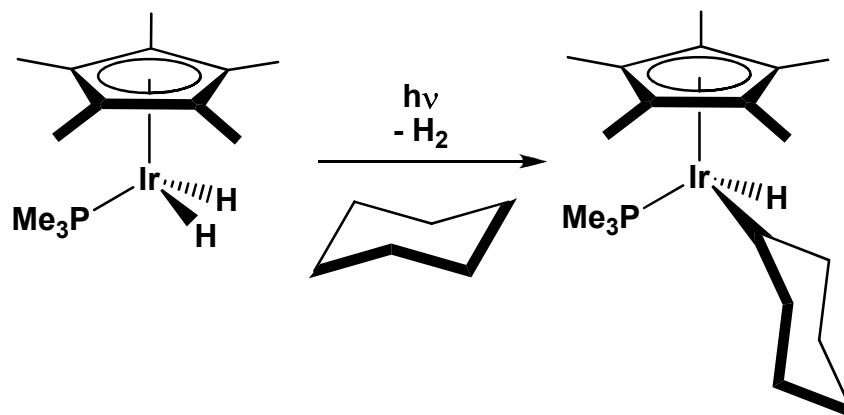
  1982
  Bergman
  Graham

- Electrophilic activation

  Shilov, 1972

  $H_2O$  $CH_3$

  $+ CH_4$
  $- HCl$

  $+ Pt(IV)Cl_6^{2-}$
  $- Pt(II)Cl_4^{2-}$

  $-CH_3OH$, $-HCl$

- Sigma bond metathesis

  $Cp^*_2M\text{-}CH_3$ + $H\text{-}^{13}CH_3$ ⟶ $\left[\ Cp_2^*M \cdots \substack{CH_3 \\ ^{13}CH_3} \cdots H\ \right]^{\ddagger}$ ⟶ $Cp^*_2M\text{-}^{13}CH_3$ + $H\text{-}CH_3$

  M = Lu: Watson, 1983
  M = Sc: Bercaw, 1987
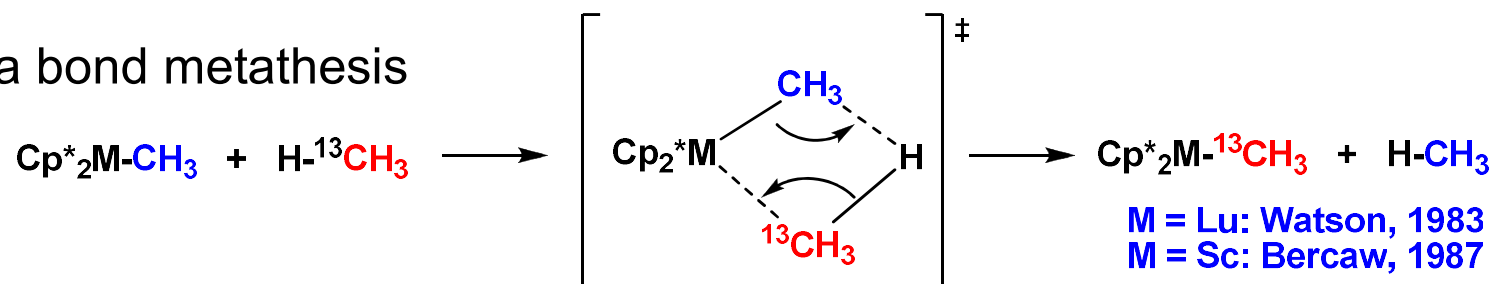
*C-H activation requires very reactive species.*
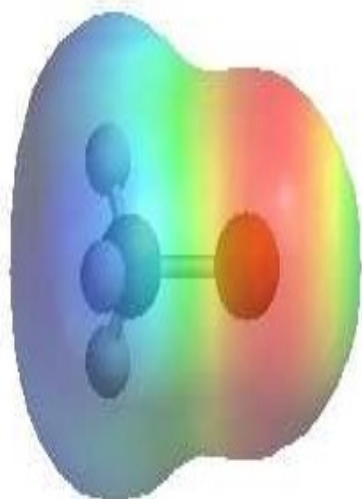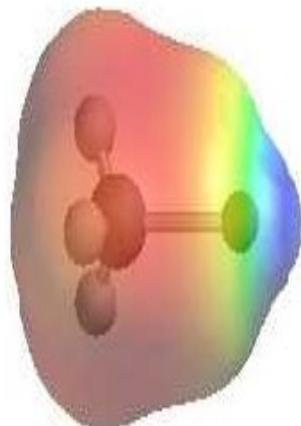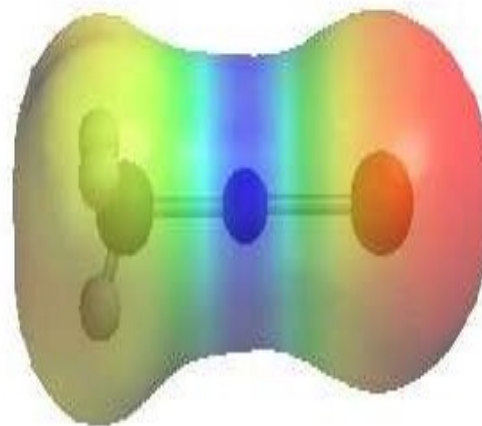
| methyl chloride | methyl lithium | methyl magnesium bromide |
| $CH_3Cl$ | $CH_3Li$ | $CH_3MgBr$ |

The images show the electrostatic potentials for methyl chloride, methyl lithium and methyl magnesium bromide.

The more **red** an area is, the higher the electron density and the more **blue** an area is, the lower the electron density.

- In the alkyl halide, the methyl group has lower electron density (**blue**), and is an **electrophile**.
- In methyl lithium, the methyl group has higher electron density (**red**) and is a **nucleophile**.
- In methyl magnesium bromide, the methyl group is less electron rich that methyl lithium.

Therefore, organometallic compounds react as electron rich or anionic carbon atoms *i.e.* as carbanions, which means they will function as either **bases** or **nucleophiles**.

It is reasonable to think of these organometallic compounds as $R^- M^+$

## Organolithium Compounds

normally prepared by reaction of alkyl halides with lithium

$$R-X + 2Li \longrightarrow R-Li + LiX$$

same for Ar—X

is an oxidation-reduction reaction: carbon is reduced

$$(CH_3)_3CCl \ + \ 2Li \ \xrightarrow[-10°C]{\text{diethyl ether}} \ (CH_3)_3CLi \ + \ LiCl$$

(75%)



diethyl ether, 35°C

(95-99%)
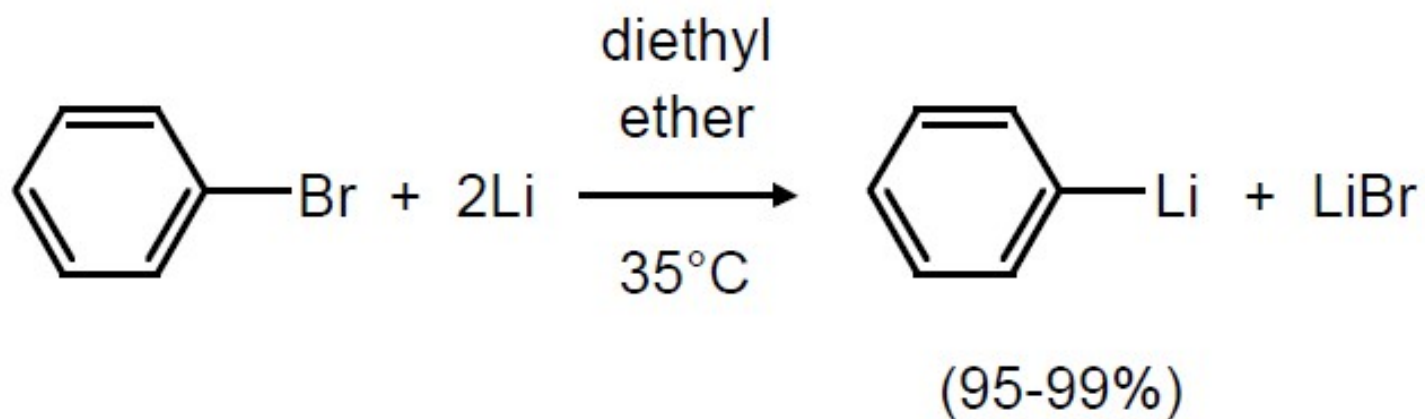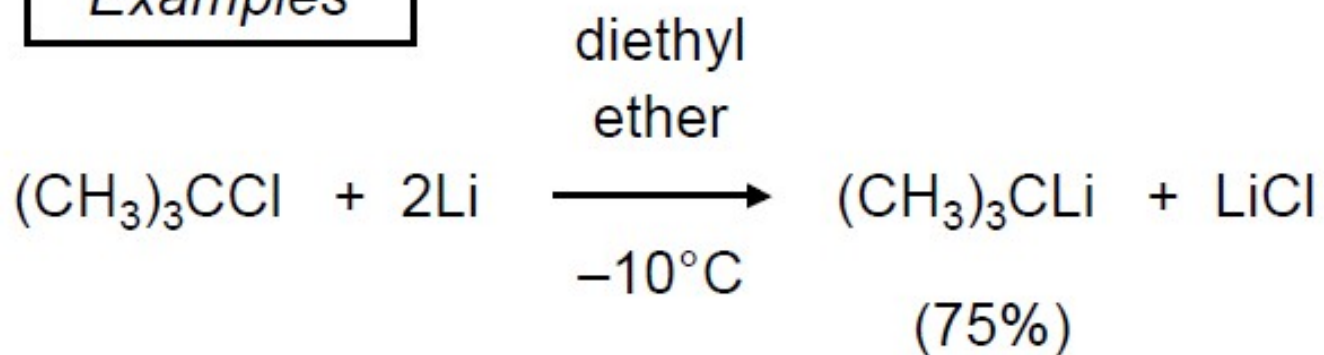
prepared by reaction of alkyl halides
with magnesium

$$R-X + Mg \longrightarrow RMgX$$

same for Ar—X

Diethyl ether is most often used solv
Tetrahydrofuran is also used.

**Examples**



diethyl
ether
—Cl + Mg $\longrightarrow$ —MgCl
−10°C
(96%)

diethyl
ether
—Br + Mg $\longrightarrow$ —MgBr
35°C
(95%)
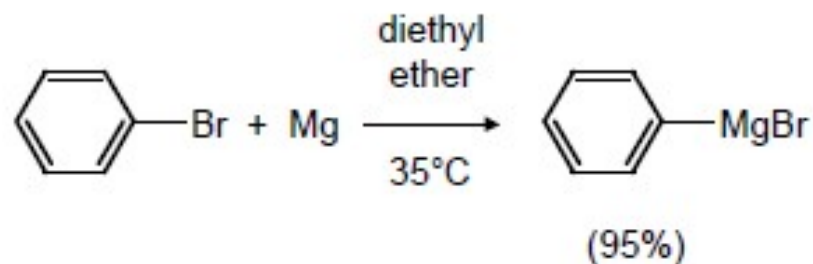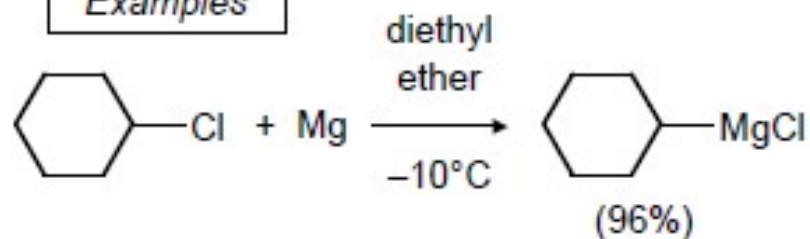
Grignard reagents act as nucleophiles toward the carbonyl group

diethyl ether

two-step sequence gives an alcohol as the isolated product
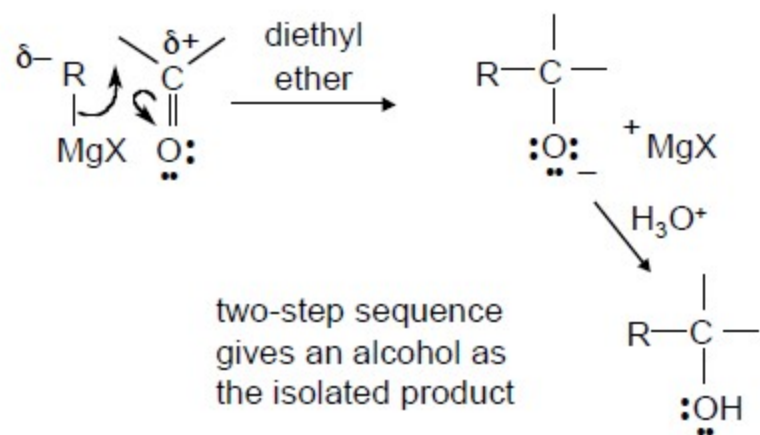
Grignard reagents react with:

formaldehyde to give primary alcohols

aldehydes to give secondary alcohols

ketones to give tertiary alcohols

esters to give tertiary alcohols

# Ligands in organometallic chemistry

- **Cationic 2e donor**: $NO^+$ (nitrosyl)

- **Neutral 2e donors**: $PR_3$ (phosphines), CO (carbonyl), $R_2C=CR_2$ (alkenes), $RC\equiv CR$ (alkynes, can also donate 4e), $N\equiv CR$ (nitriles)

- **Anionic 2e donors**: $X^-$ (halide), $CH_3^-$ (methyl), $CR_3^-$ (alkyl), $Ph^-$ (phenyl), $H^-$ (hydride). *The following can also donate 4e if needed, but initially count them as 2e donors (unless they are acting as bridging ligands):* $OR^-$ (alkoxide), $SR^-$ (thiolate), $NR_2^-$ (inorganic amide), $PR_2^-$ (phosphide)

- **Anionic 4e donors**: $C_3H_5^-$ (allyl), $O^{2-}$ (oxide), $S^{2-}$ (sulfide), $NR^{2-}$ (imide), $CR_2^{2-}$ (alkylidene) *and from the previous list:* $OR^-$ (alkoxide), $SR^-$ (thiolate), $NR_2^-$ (inorganic amide), $PR_2^-$ (phosphide)

- **Anionic 6e donors**: $Cp^-$ (cyclopentadienyl), $O^{2-}$ (oxide)
- **Z ligands: do not bring e to the metal:** $BR_3$, $AlR_3$

# Nomenclature

$\eta^x$
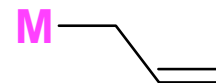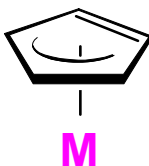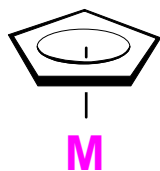
| $\eta^5$-Cp | $\eta^3$-Cp | $\eta^3$-allyl | $\eta^1$-allyl |
|---|---|---|---|

$\kappa^x$
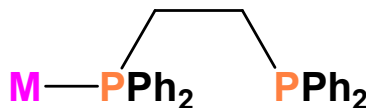
M—PPh$_2$     PPh$_2$     $\eta^1$-dppe / $\kappa^1$-dppe

Metal is the parent

Li—△

Cyclopropyllithium

$H_2C\!\!=\!\!CHNa$

Vinylsodium

$CH_3CH_2MgCH_2CH_3$
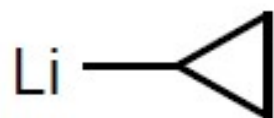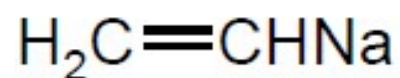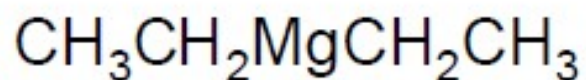
Diethylmagnesium

$CH_3MgI$
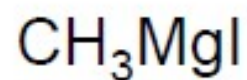
Methylmagnesium
iodide

# 18 electron rule

❖ Used for predicting formulas for stable metal complexes.

❖ Valence shells of a transition metal consists of nine valence orbitals, which collectively can accommodate 18 electrons either as nonbinding electron pairs or as bonding electron pairs.

❖ Alternatively, combination of nine atomic orbitals with ligand orbitals gives rise to nine molecular orbitals which are either metal-ligand bonding or non-bonding.

❖ When a metal complex has 18 valence electrons, it is said to have achieved the same electron configuration as the noble gas at the end of the period.

# Neutral counting

■ In period 2: B, C, N, O, and F have 3, 4, 5, 6, and 7 valence electrons, respectively.

■ In period 4: K, Ca, Sc, Ti, V, Cr, Fe, Ni have 1, 2, 3, 4, 5, 6, 8, 10 valence electrons respectively.

■ Add one for every halide or other anionic ligand.

■ Add two for every lone pair bonding to the metal (e.g. each Lewis base binds with a lone pair). Unsaturated hydrocarbons such as alkenes and alkynes are considered Lewis bases. Similarly Lewis and Bronsted acids (protons) contribute nothing.

■ Add one for each homoelement bond.

■ Add one for each negative charge, and subtract one for each positive charge.

# Ionic counting

- ■ Calculate the number of electrons of the element, assuming an oxidation state e.g. for a $Fe^{2+}$ has 6 electrons, $S^{2-}$ has 8 electrons.

- ■ Add two for every halide or other anionic ligand which binds to the metal through a sigma bond.

- ■ Add two for every lone pair bonding to the metal (e.g. each phosphine ligand can bind with a lone pair). Similarly Lewis and Bronsted acids (protons) contribute nothing.

- ■ For unsaturated ligands such as alkenes, count the number of carbon atoms binding to the metal. Each carbon atom provides one electron.

# 18 electron rule : How to count electrons

Methods of counting: Neutral atom method & Oxidation state method

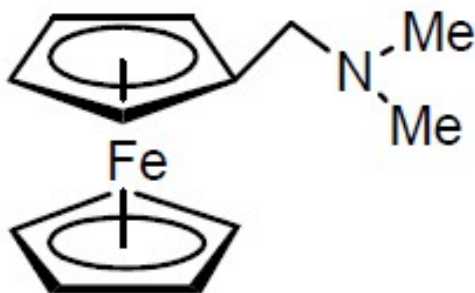| Ligand | Neutral atom | Oxidation state | | Ligand | Neutral atom | Oxidation state | |
|---|---|---|---|---|---|---|---|
| | | Electron contribution | Formal charge | | | Electron contribution | Formal charge |
| Carbonyl (M–CO) | 2 | 2 | 0 | Halogen ( M–X) | 1 | 2 | –1 |
| Phosphine (M–PR$_3$) | 2 | 2 | 0 | Alkyl (M–R) | 1 | 2 | –1 |
| Amine (M–NR$_3$ ) | 2 | 2 | 0 | Aryl (M–Ar) | 1 | 2 | –1 |
| Amide (M–NR$_2$ ) | 1 | 2 | –1 | acyl (M–C(O)–R) | 1 | 2 | –1 |
| Hydrogen (M–H) | 1 | 2 | –1 | $\eta^1$-cyclopentadienyl | 1 | 2 | –1 |
| Alkene (sidewise) $\eta^2$- | 2 | 2 | 0 | $\eta^1$-allyl | 1 | 2 | –1 |
| Alkyne (sidewise) $\eta^2$- | 2 | 2 | 0 | $\eta^3$-allyl | 3 | 4 | –1 |
| $\eta^2$-C$_{60}$ | 2 | 2 | 0 | $\eta^5$-cyclopentadienyl | 5 | 6 | –1 |
| Nitrosyl bent | 1 | 2 | –1 | $\eta^6$-benzene | 6 | 6 | 0 |
| Nitrosyl linear | 3 | 2 | +1 | $\eta^7$-cycloheptatrienyl | 7 | 6 | +1 |
| Carbene (M=CR$_2$) | 2 | 4 | –2 | Carbyne (M≡CR) | 3 | 6 | –3 |
| Alkoxide (M–OR) | 1 | 2 | –1 | Thiolate (M–SR) | 1 | 2 | –1 |
| μ-CO (M–(CO)–M) | 2 | 2 | 0 | μ-H | 1 | 2 | –1 |
| μ-alkyne | 4 | 4 | 0 | μ-X (M–X–M) X = halogen | 3 | 4 | –1 |
| μ-alkyl | 1 | 2 | –1 | μ-amido (M–(NR$_2$)–M | 3 | 4 | –1 |
| μ-phosphido (M–(PR$_2$)–M | 3 | 4 | –1 | μ-alkoxide (M–(OR)–M | 3 | 4 | –1 |

# 18 electron rule : How to count electrons
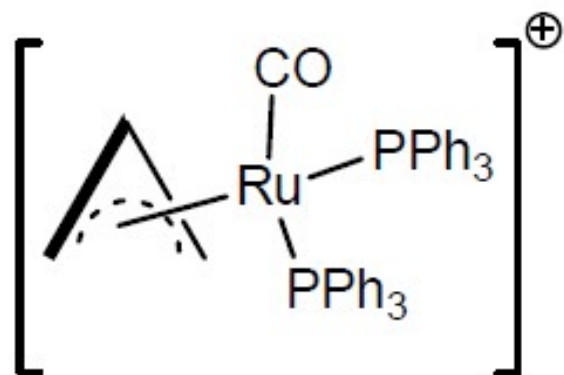


| | neutral atom method | oxidation state method |
|---|---|---|
| Ru | 8 | 6 (Ru +2) |
| $\eta^3$ - allyl | 3 | 4 |
| 2 PPh$_3$ | 4 | 4 |
| CO | 2 | 2 |
| charge | -1 | not required |
| | 16 | 16 |
| Fe | 8 | 6 (Fe +2) |
| 2 $\eta^5$-Cp | 10 | 12 |
| | 18 | 18 |

<u>16 electron compounds:</u>  Square-planar low-spin $d^8$ metal Ions are Rh(I), Ir(I), Ni(II), Pd(II), and Pt(II)

# 18 electron rule : How to count electrons