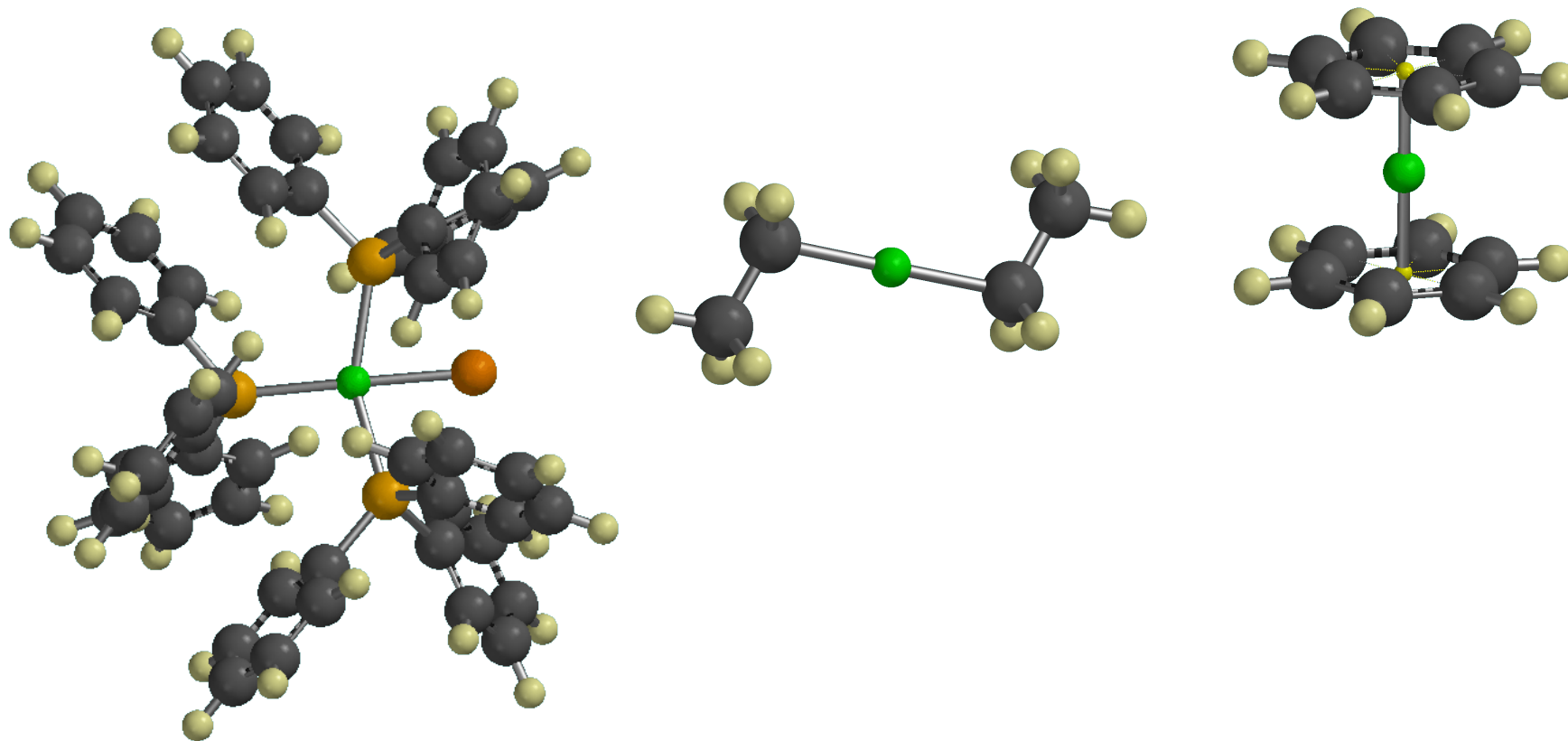


Organometallic Chemistry

between organic and inorganic



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".

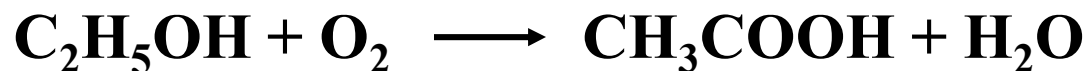
Frontiers in Organometallic Chemistry

- ***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:

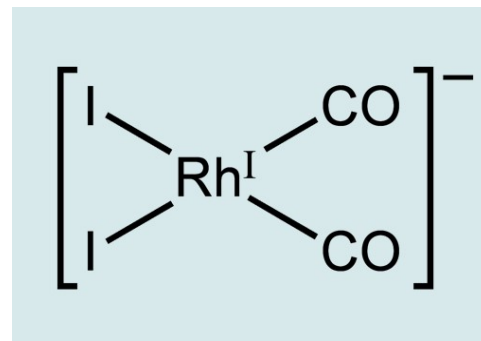


This is *not* a clean and efficient process!

Industrial acetic acid synthesis:



Catalyzed by a rhodium complex.

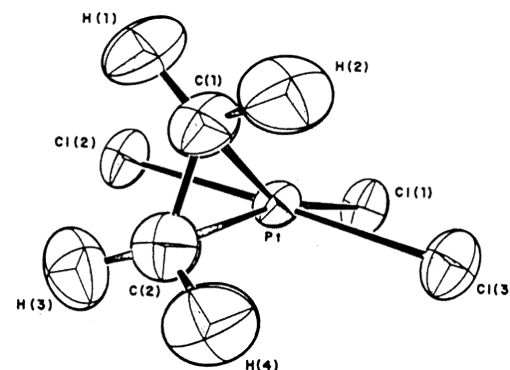
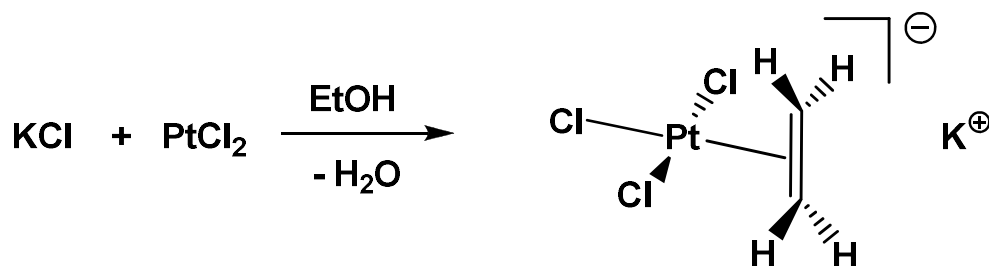


History: first organometallic compounds

- 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) :

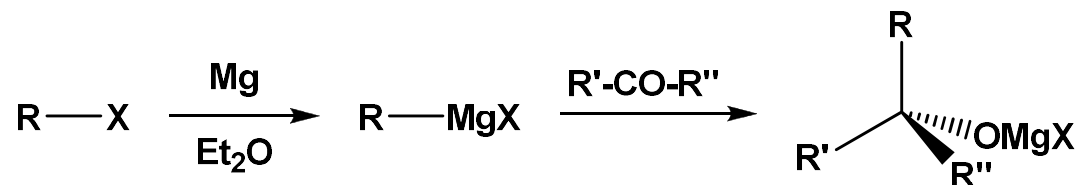


- 1827 Zeise's salt is the first platinum - olefin complex

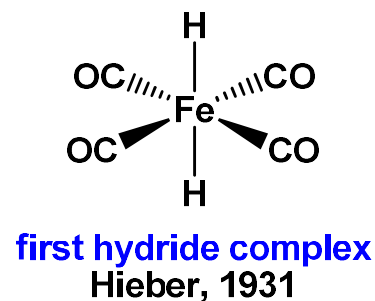
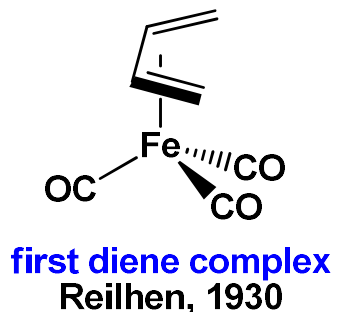


History: 1900 – 1950

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

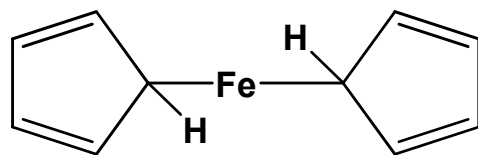


- 1912 Nobel prize Victor Grignard and Paul Sabatier
- 1930 Ziegler and Gilman simplify organolithium preparation, using ether cleavage and alkyl halide metallation, respectively

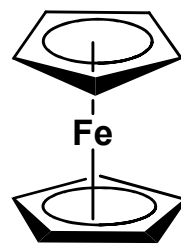


History: 1950 – 1960

- 1951 – 1952 Discovery of ferrocene, $\text{Fe}(\eta^5\text{-C}_5\text{H}_5)_2$



Pauson, 1951



correct structure
Woodward and Wilkinson, 1952

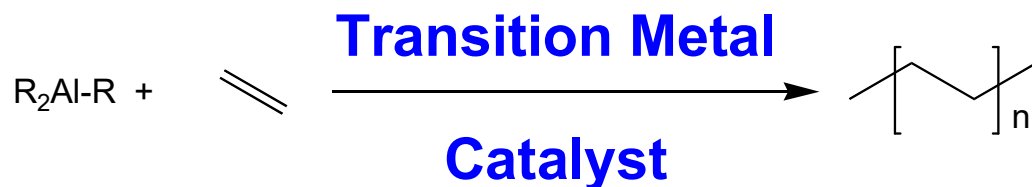
- Originally called “**dicyclopentadienyliron**.”
- x ray analysis proved: ferrocene consisted of an iron(II) ion **sandwiched** between two parallel cyclopentadienyl (Cp) rings.
- The cyclopentadienyl ligand is just one example of many where the pi-system of an organic compound binds directly to a metal atom via a $Md(\pi)\text{-}p(\pi)$ interaction.
- The term ***hapticity***, denoted η , describes the number of ligand atoms coordinated to the central metal atom, e.g. $(\eta^5\text{-Cp})_2\text{Fe}$

History: 1950 – 1960 (continued)

Ziegler/Natta polymerization

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

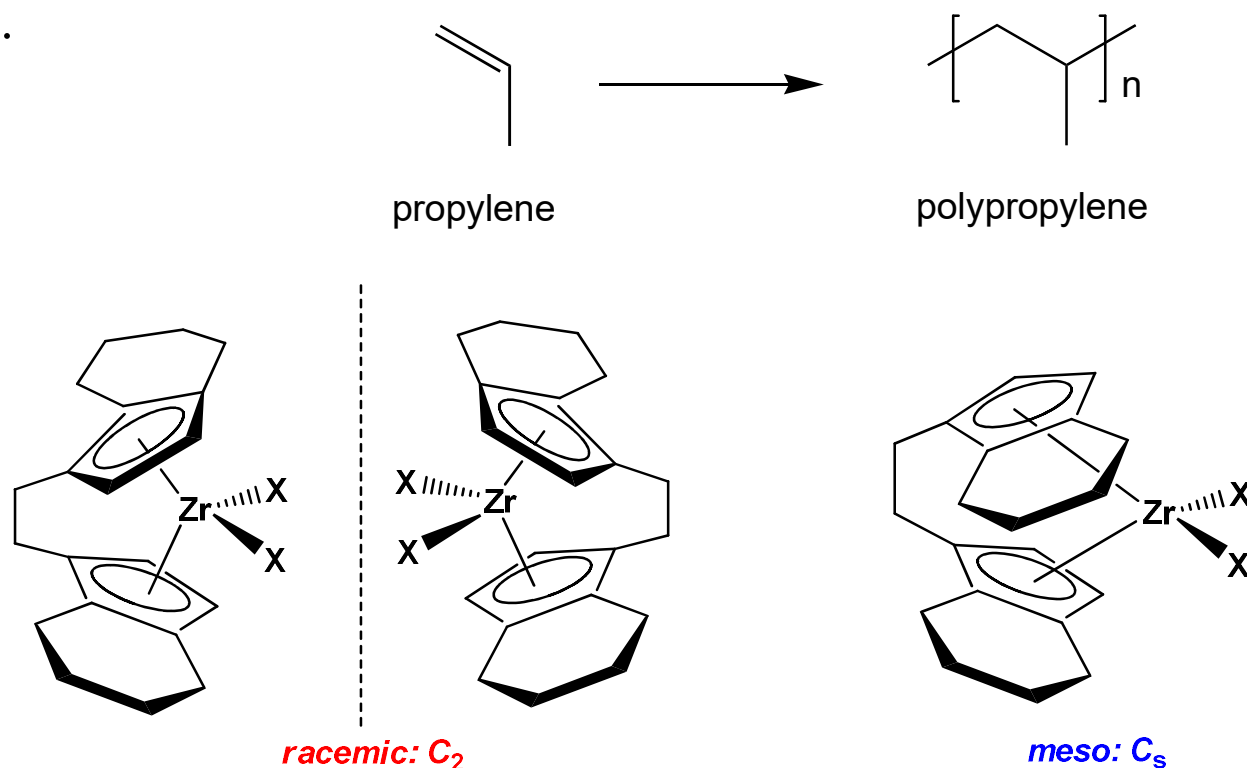
1955 Ziegler and Natta develop olefin polymerization at low pressure using mixed metal catalysts (transition metal halide / AlR_3)



Alkyl-Aluminium compounds
acts as co-catalyst

Ziegler/Natta polymerization

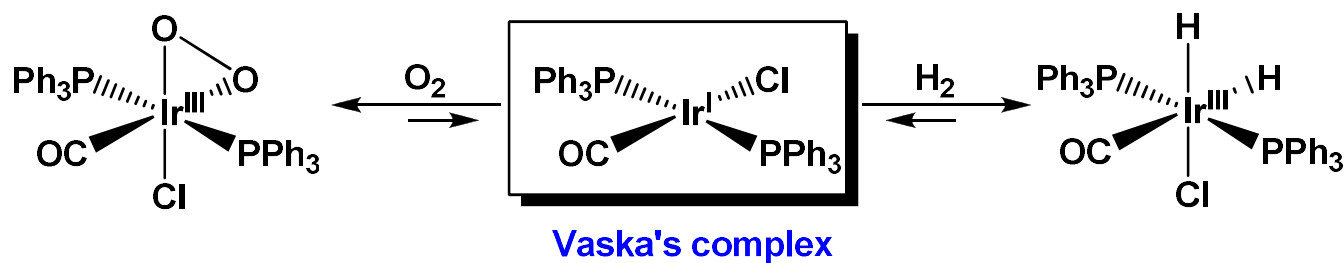
- **Giulio Natta**: Italian chemist, Nobel prize 1963
- Learned of Ziegler's research, and applied findings to other α -olefins such as propylene and styrene.
- Resulting polypropylene was made up of two fractions: amorphous (*atactic*) and crystalline (*tactic*). *Polypropylene is not produced in radical initiated reactions.*



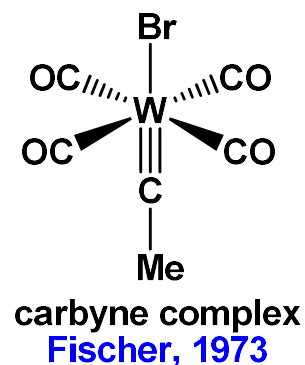
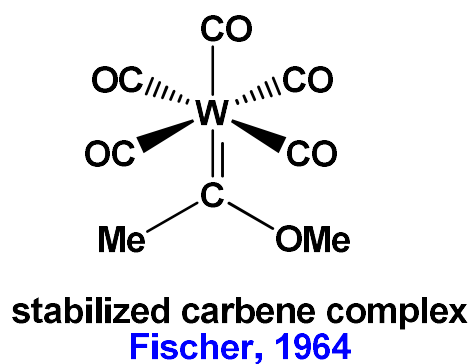
1963 [Nobel prize](#) for [Karl Ziegler](#) and [Giulio Natta](#) on Ziegler-Natta catalysts

History: 1960 – 1980: catalysis

- 1962: Vaska's complex

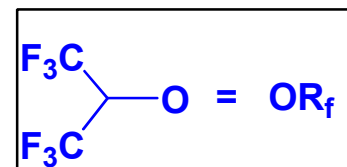
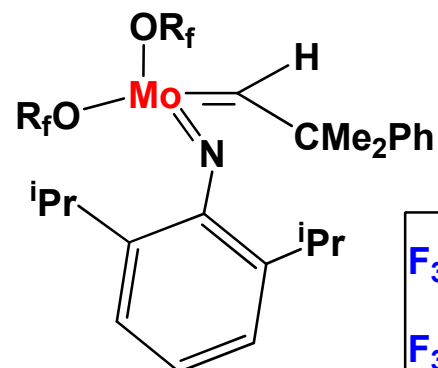
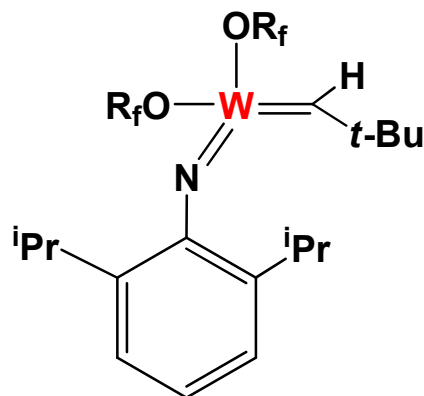


- 1964: Fischer reports the first metal carbene.

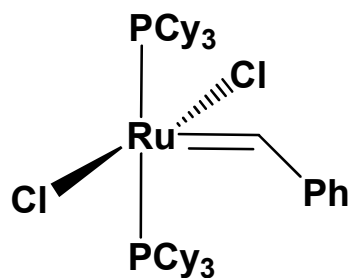
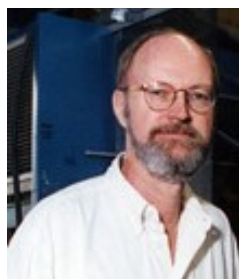


2005 Nobel prize in chemistry

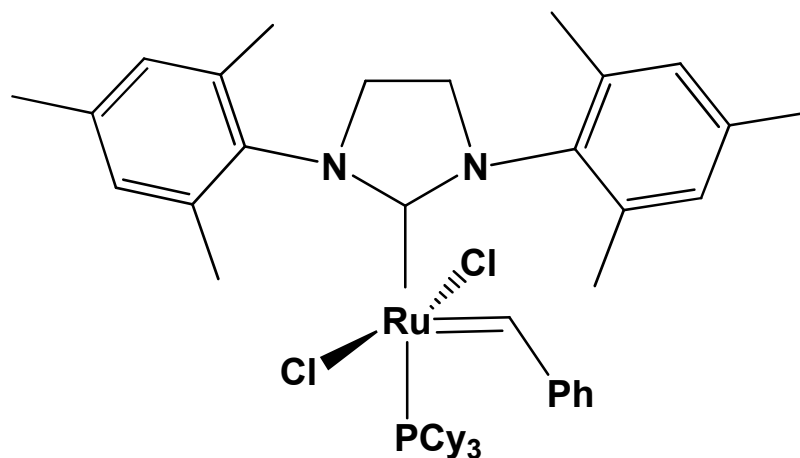
Schrock catalysts



Grubbs catalysts

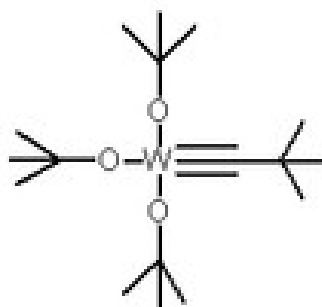


1st generation

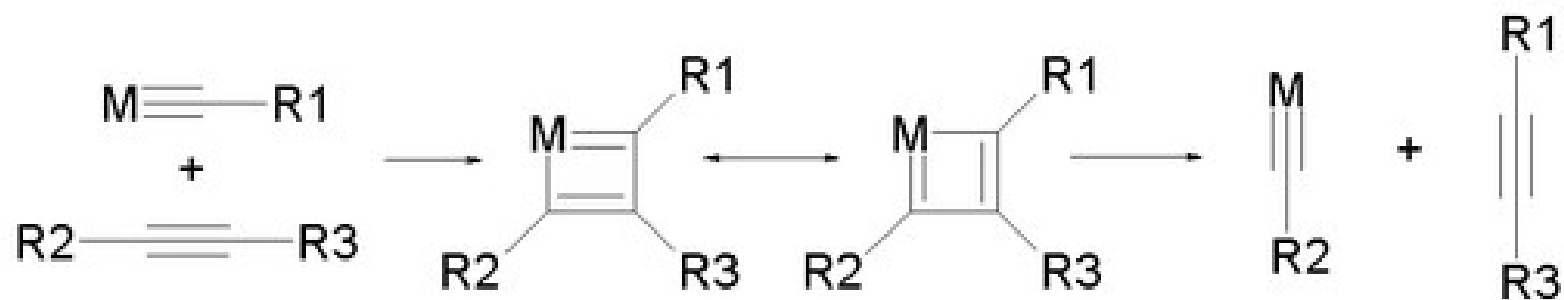


2nd generation

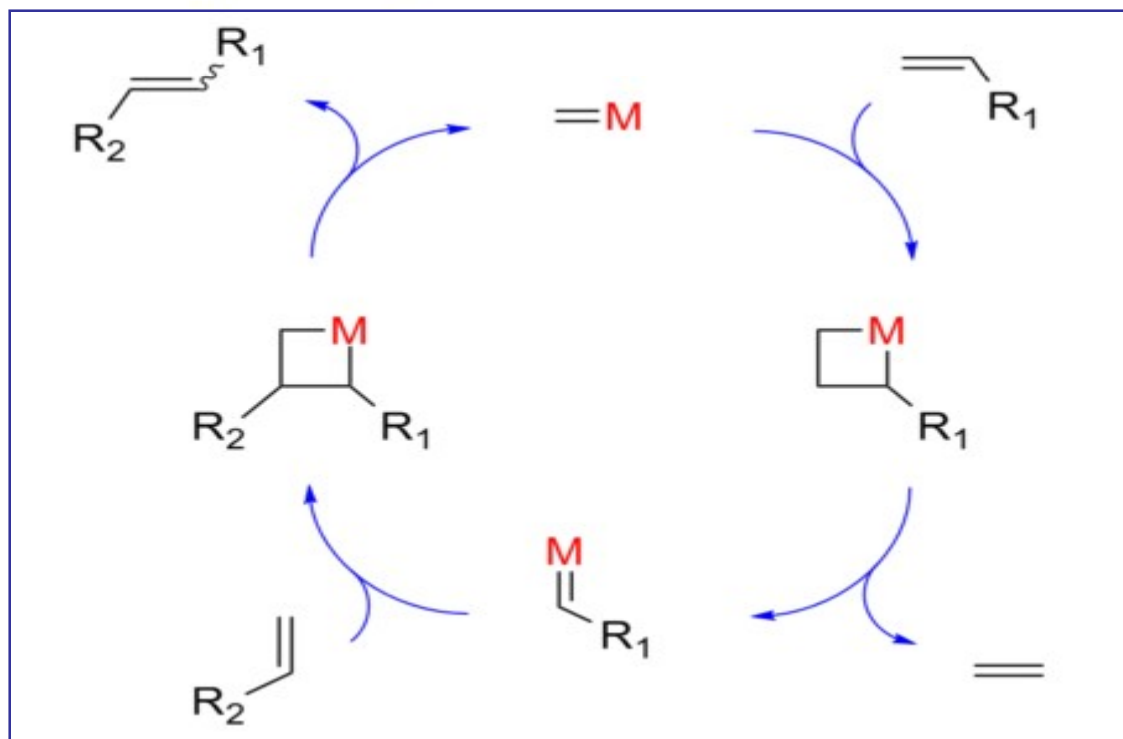
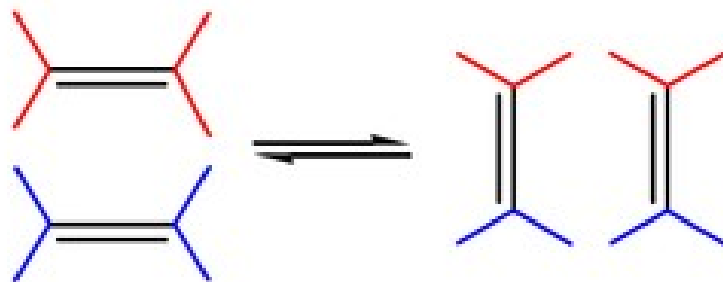
SCHROCK CATALYST AND ALKYNE METATHESIS



Tris(t-butoxy)(2,2-dimethylpropylidyne)(VI)tungsten

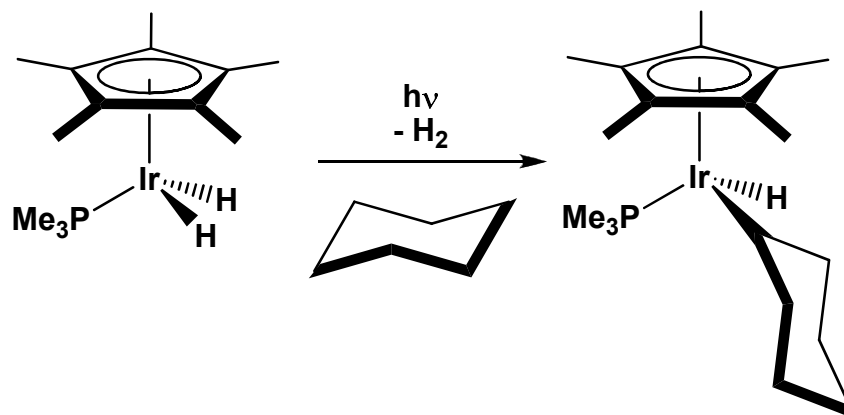


GRUBB'S CATALYST is used in organic synthesis to achieve olefin cross-metathesis, ring-opening metathesis polymerization (ROMP), acyclic diene metathesis polymerization (ADMET), and ring-closing metathesis.



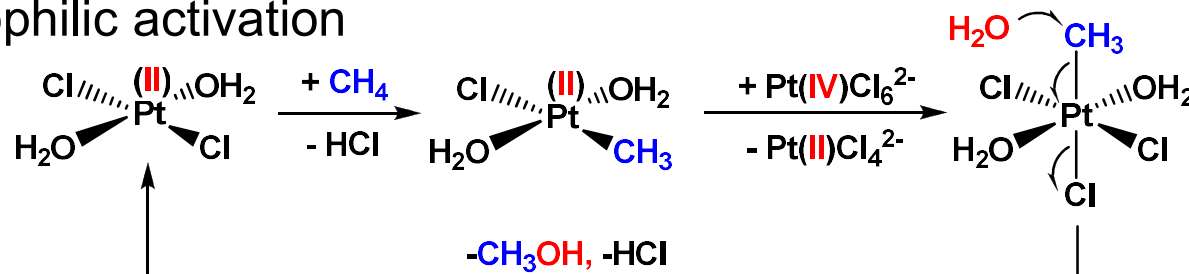
C-H activation

- Oxidative addition



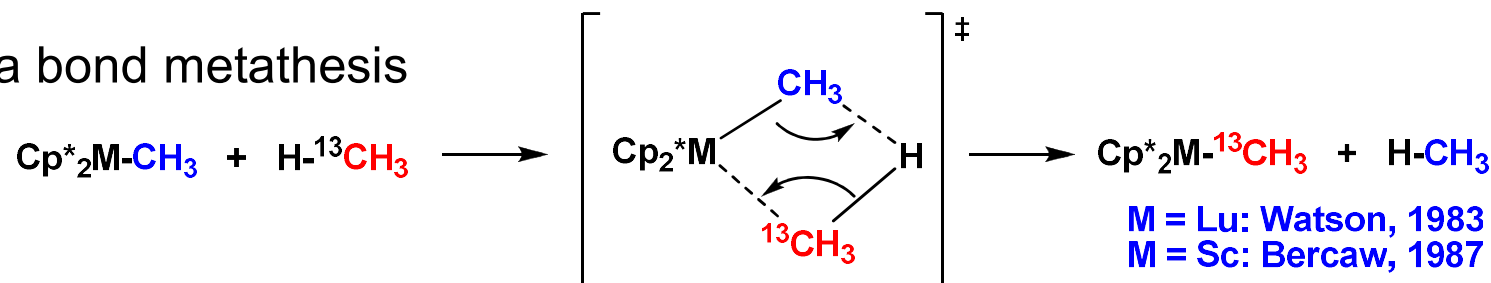
1982
Bergman
Graham

- Electrophilic activation

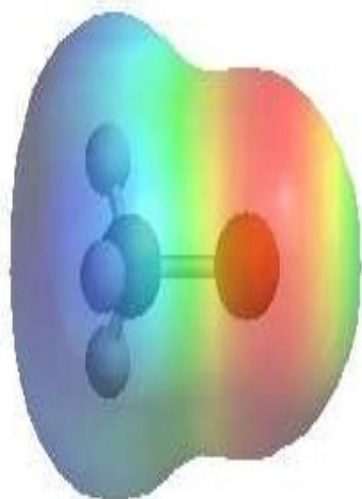


Shilov, 1972

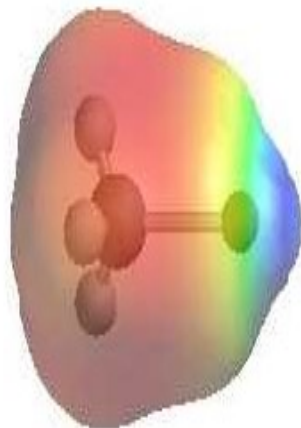
- Sigma bond metathesis



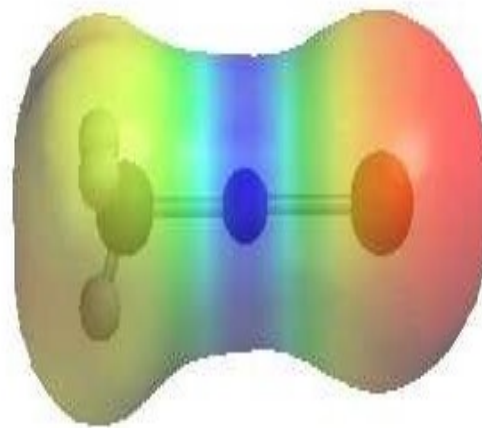
C-H activation requires very reactive species.



methyl chloride
 CH_3Cl



methyl lithium
 CH_3Li



methyl magnesium bromide
 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 than 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 $\text{R}^- \text{M}^+$

Organolithium Compounds

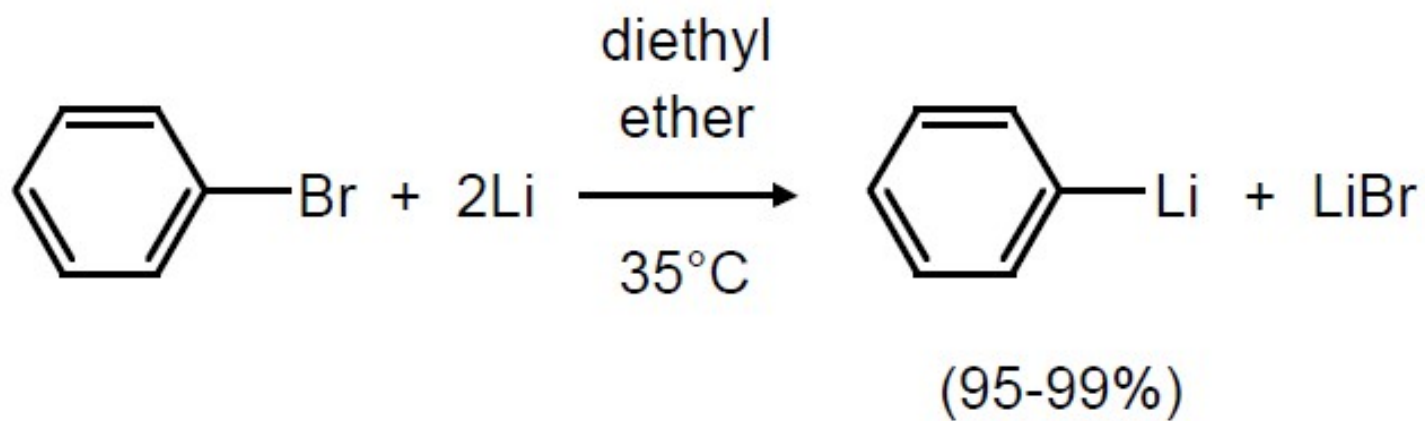
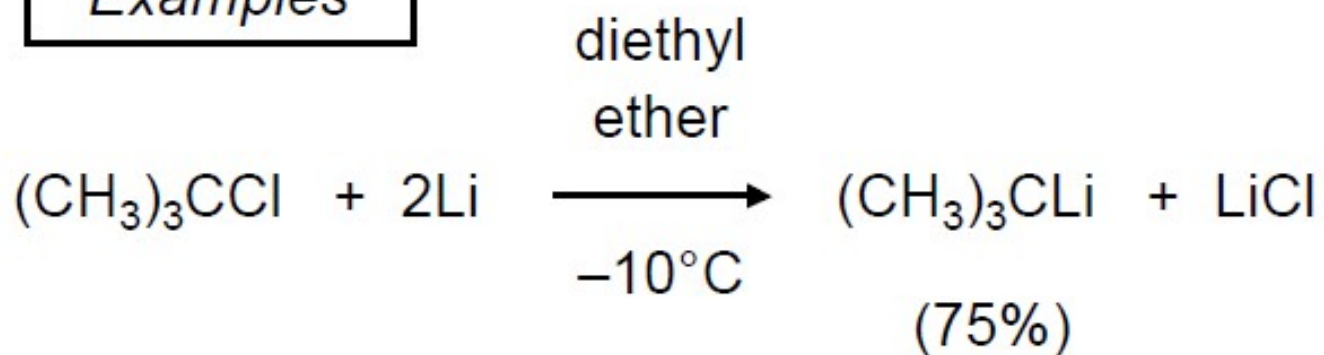
normally prepared by reaction of alkyl halides
with lithium



same for Ar—X

is an oxidation-reduction reaction: carbon
is reduced

Examples



Grignard Reagents

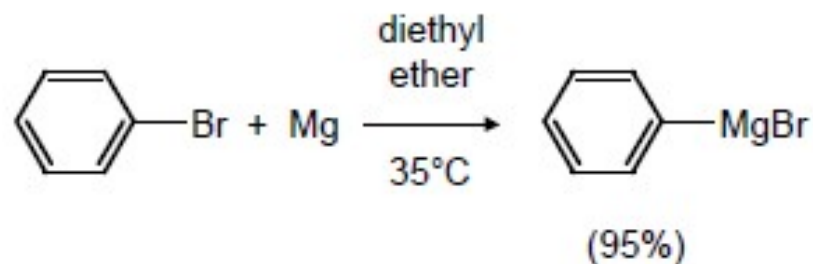
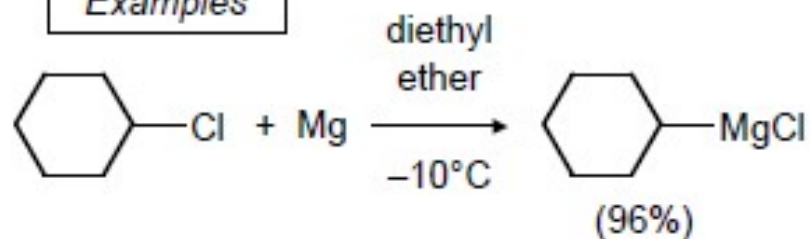
prepared by reaction of alkyl halides
with magnesium



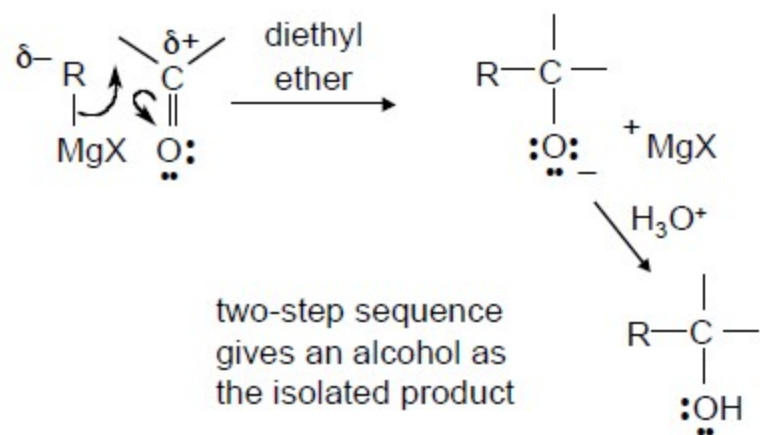
same for Ar—X

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

Examples



Grignard reagents act as nucleophiles toward the carbonyl group



Grignard reagents react with:

formaldehyde to give primary alcohols

aldehydes to give secondary alcohols

ketones to give tertiary alcohols

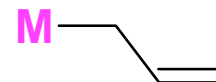
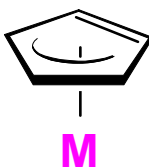
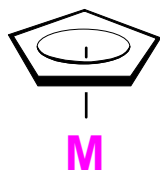
esters to give tertiary alcohols

Ligands in organometallic chemistry

- **Cationic 2e donor:** NO^+ (nitrosyl)
- **Neutral 2e donors:** PR_3 (phosphines), CO (carbonyl), $\text{R}_2\text{C}=\text{CR}_2$ (alkenes), $\text{RC}\equiv\text{CR}$ (alkynes, can also donate 4e), $\text{N}\equiv\text{CR}$ (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

η^x



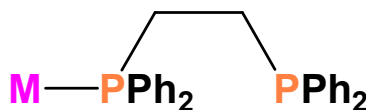
$\eta^5\text{-Cp}$

$\eta^3\text{-Cp}$

$\eta^3\text{-allyl}$

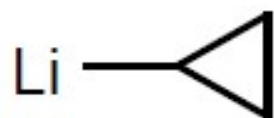
$\eta^1\text{-allyl}$

κ^x

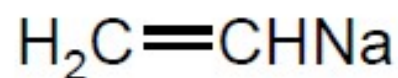


$\eta^1\text{-dppe} / \kappa^1\text{-dppe}$

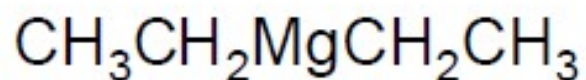
Metal is the parent



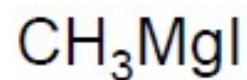
Cyclopropyllithium



Vinylsodium



Diethylmagnesium



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.