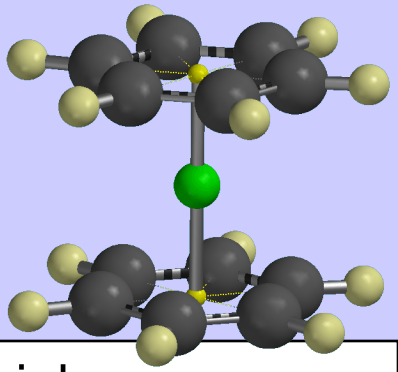
CHIMICA METALLORGANICA E CATALISI OMOGENEA

6 CF

LUNEDI ORE 11,30 -13,30 **silvia.bordoni@unibo.it**

MARTEDI ORE 11 -13,30 AULA 2



Esame scritto con 5 domande aperte (risposte coincise 10-15 righe
e **orale** ***Your own presentations***
presentazione discussione con in 10-12 diapo ppt
di un articolo recente scelto tra una rosa proposta e domande inerenti

What ? ***Organometallic Chemistrybetween organic and inorganic***

Why? ***To infer the role of the metal in homogeneous catalysis and to exploit the mechanisms in catalyzed processes***

What for?

To learn the strategy to design novel single site catalyst, To synthesize complexes for new material (light harvesting, MOF),

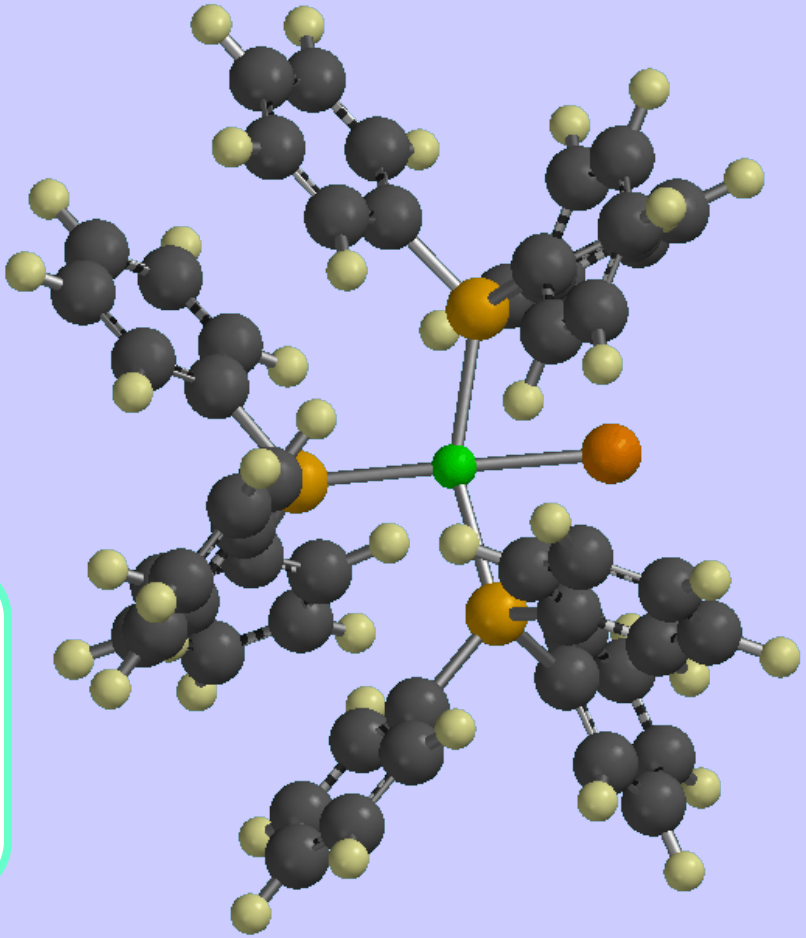
to study C-C, C-H, H_2 and CO_2 activation, new complexes for medicinal chemistry

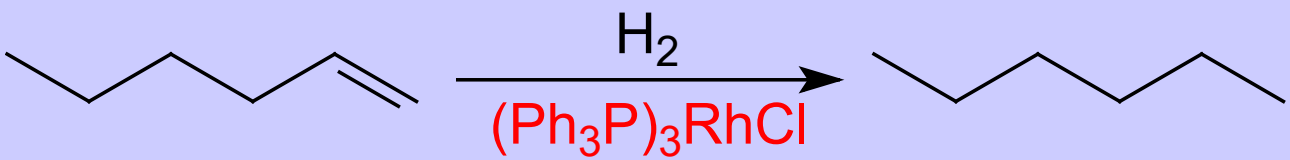
What is organometallic chemistry ?

Strictly speaking, the chemistry of compounds containing low-valent M ***at least one metal-carbon bond***.

Metal hydrides are often included, H being considered as the "smallest organic group" (as in propyl, ethyl, methyl, hydride).

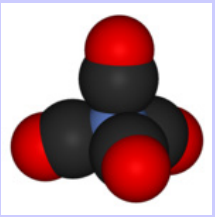
Metal-carbon bonds are often formed ***temporarily*** or ***potentially***, so in practice many compounds are included that do not actually contain metal-carbon bonds.

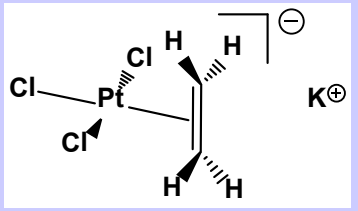




Un po' di storia

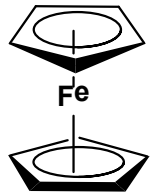
NOBEL PRIZES



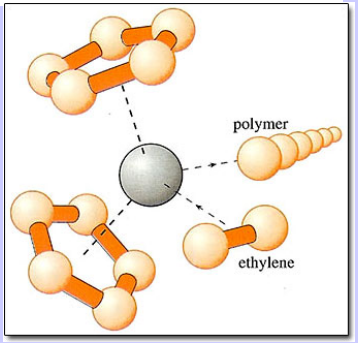


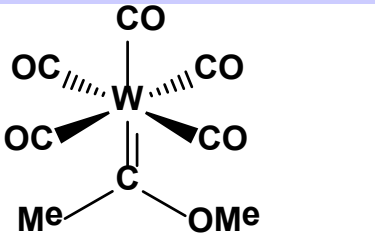
- **1912 Victor Grignard and Paul Sabatier**
- **1917 Schlenk prepares Li alkyls via transalkylation from R_2Hg**
- **1827 Zeise** Pt olefin salt
- **1930 Ziegler and Gilman** organolithium
- **1951 – 1952 Ferrocene, $Fe(\eta^5\text{-}C_5H_5)_2$**
  - **Keally, Pauson, and Miller** synthesis
  - **Wilkinson and Woodward** correct structure
- **1973 Geoffrey Wilkinson**
- **and Ernst Otto Fischer on sandwich compounds**
- **1955 Ziegler and Natta olefin polymerization**
- **1962: Vaska's complex**
- **1964: Fischer carbyne and carbene**
- **1981 R.Hoffman K. Fukui on isolobal analogy**
- **2001 Sharpless, Knowles Noyori Asymmetric catalysis**
- **2010 Heck Negishi Suzuki Pd-catalyzed C-C coupling**

Pauson, 1951

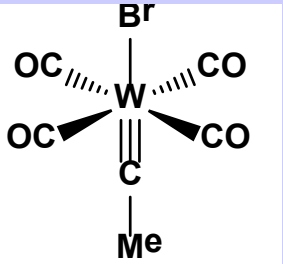


correct structure
Woodward and Wilkinson, 1952

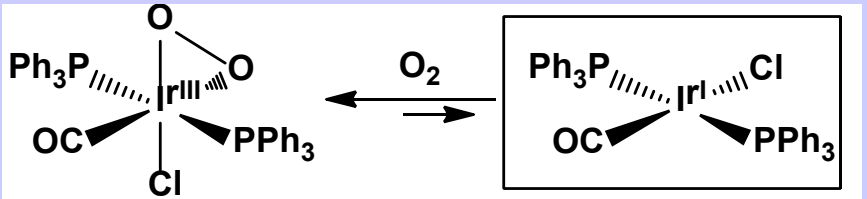




stabilized carbene complex
Fischer, 1964



carbyne complex
Fischer, 1973



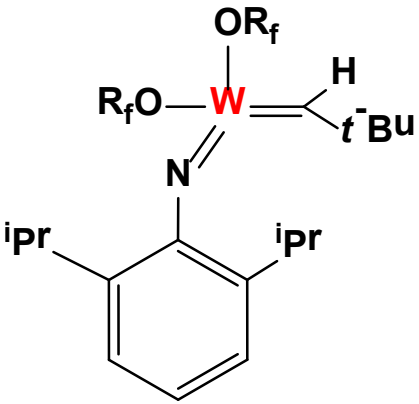
Vaska's complex

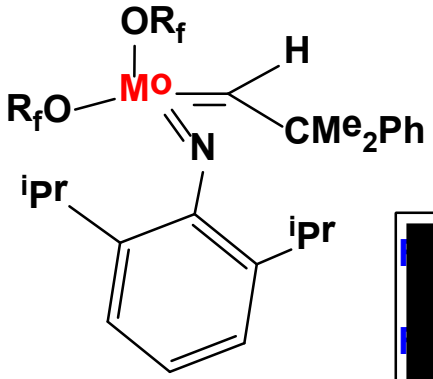
Yves Chauvin mechanism

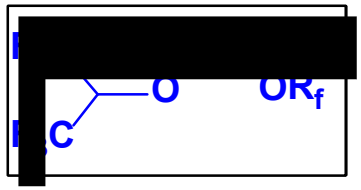
2005 Nobel prize in chemistry on olefin metathesis

Metatesi

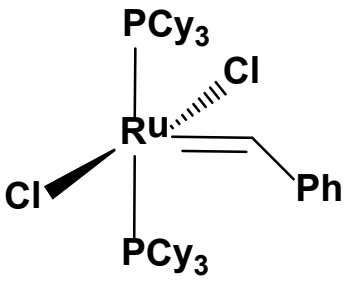
Schrock catalysts



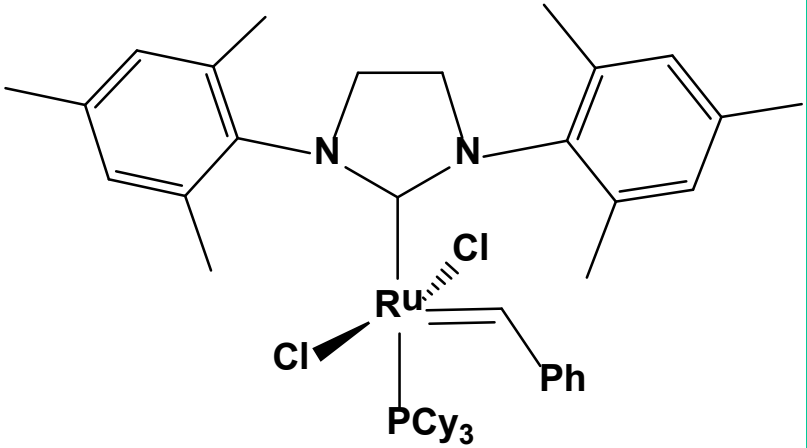




Grubbs catalysts



1st generation



2nd generation

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Course Roadmap

- 1-Introduction: what is organometallic chemistry, and why should you care?
- 2-Electron counting: the basis for understanding structure and reactivity
- 3-An overview of Transition metal chemistry organometallic systems electron count and molecular orbitals
- 4-Transition metal chemistry: overview of common ligands
- 5-Ligand bonding nature of **Fisher and Schrock carbenes**
- 6-Ligand substitution: thermodynamic and kinetic rules
- **7-Migratory Insertion** and elimination
- 8- Oxidative insertion and reductive elimination Migratory Insertion
- 9-Applications in catalysis: **asymmetric hydrogenation** synthesis
- 10-A real example: **the Monsanto-Cativa Acetic Acid processes**
- 11-Intermezzo: characterization of organometallic compounds
- 12-New strategies on **C-H activation and CO2 reduction**
- 13-Strategies to sustainable organometallic for green chemistry applications

Example: Acetic Acid synthesis

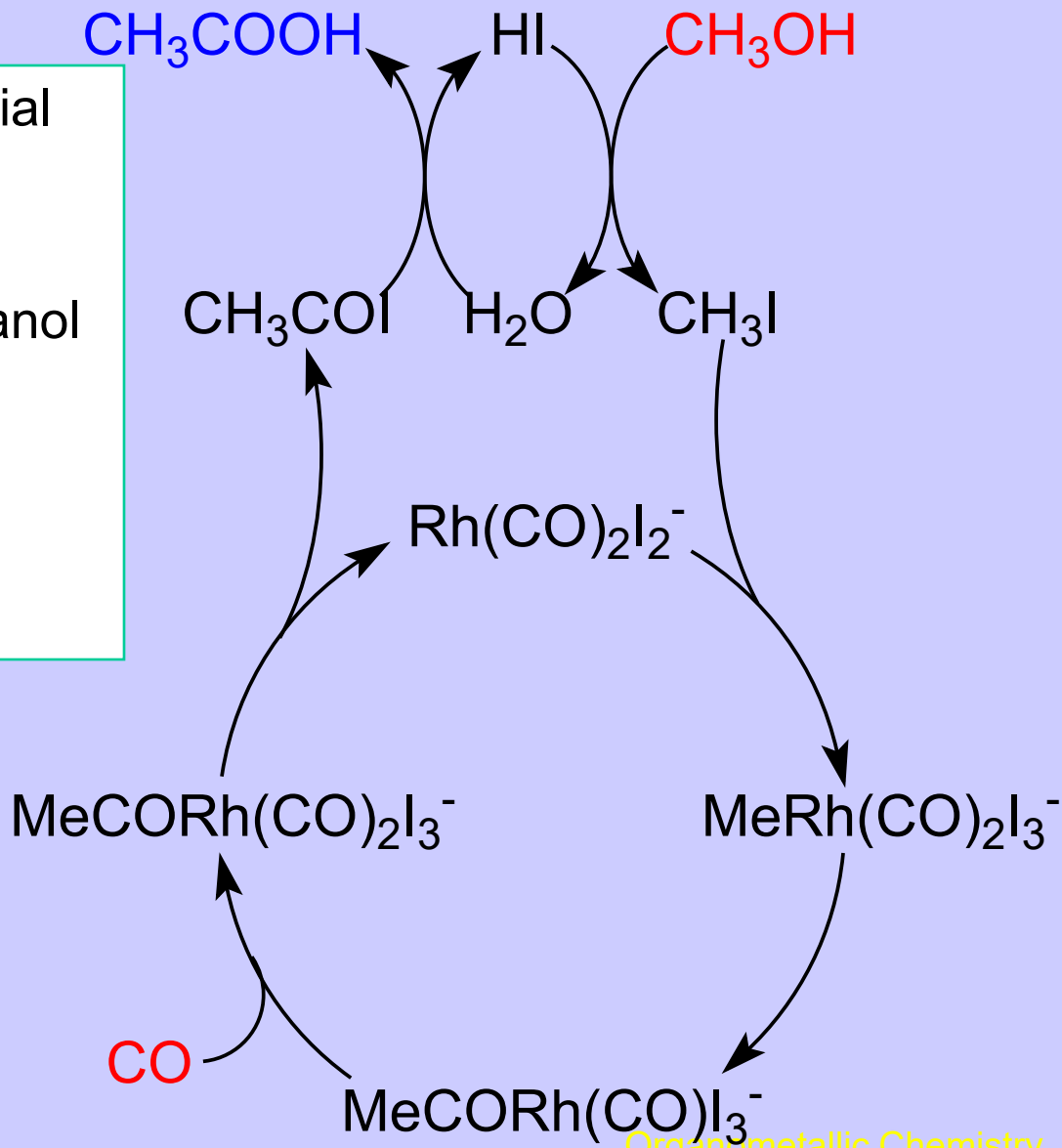
Acetic acid is an important industrial

Intermediate and product, and industrially the synthesis

implies the carbonylation of methanol

$CH_3OH + CO \rightarrow CH_3COOH$

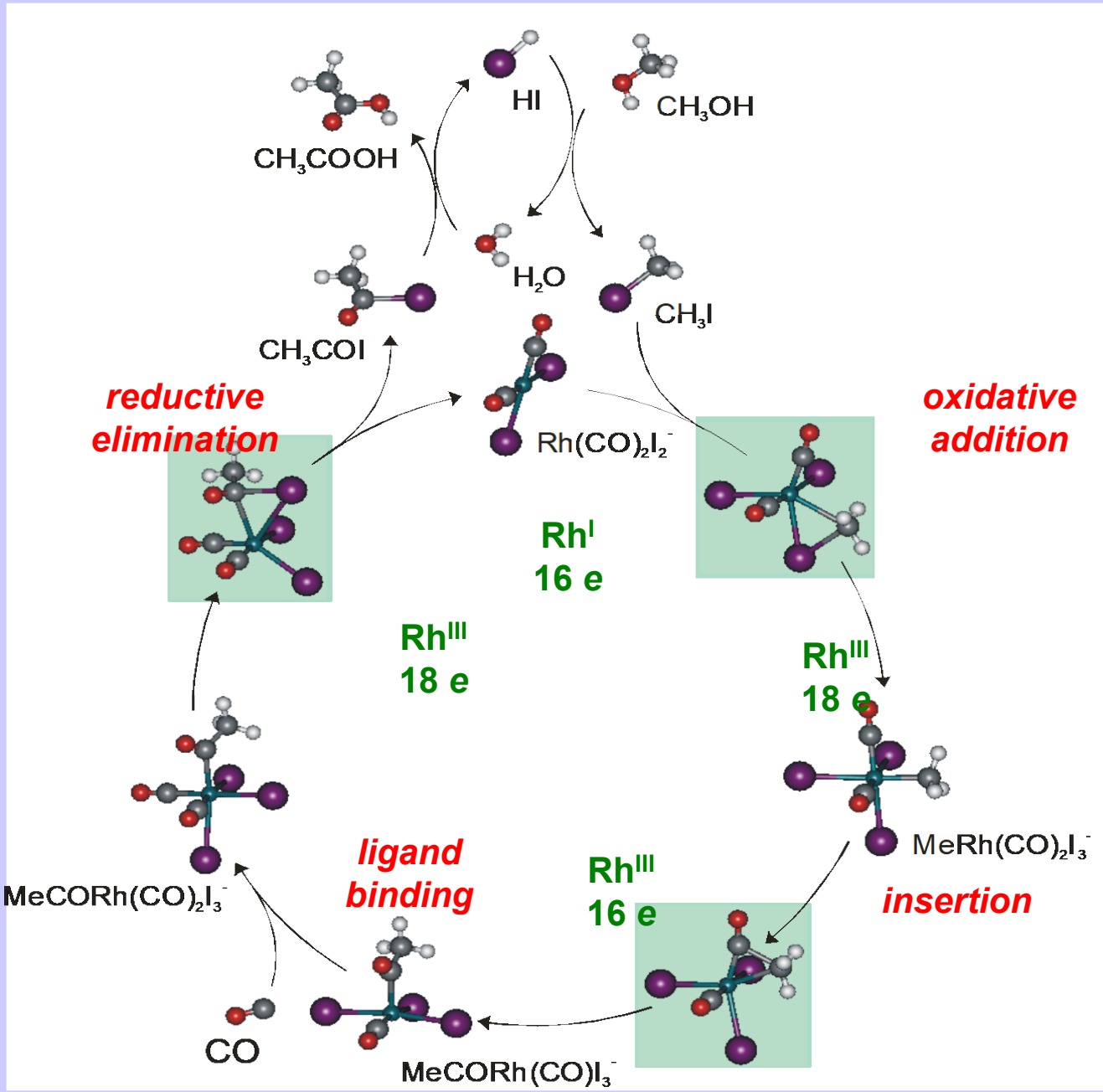
Catalyzed by a rhodium or iridium complexes



Acetic Acid synthesis

This cycle is known in considerable detail:

To understand it, you need to be familiar in electron counting and common reaction types



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 (L-DOPA) and many larger-scale intermediate chemicals.

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

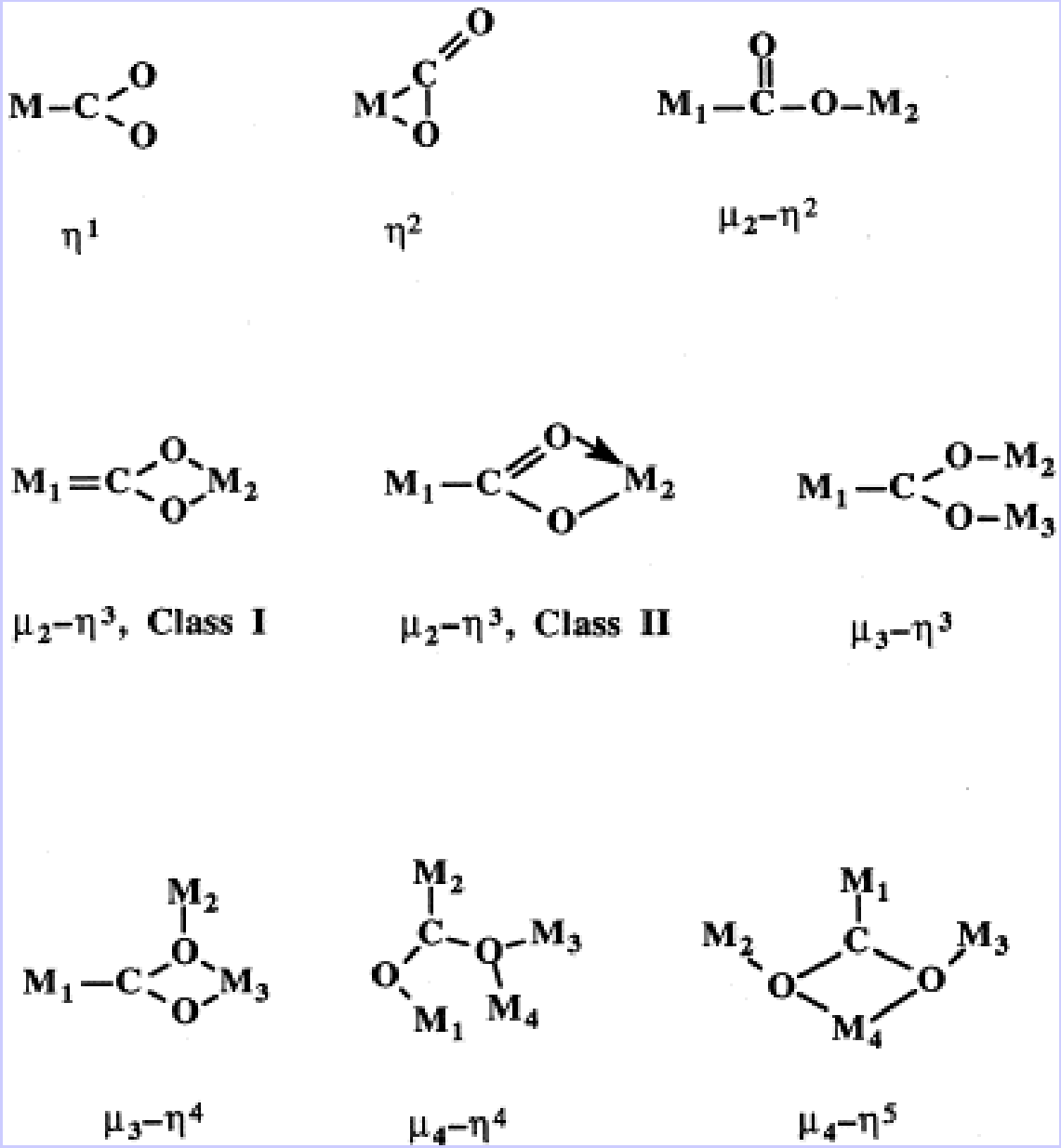
Many ***plastics*** (as polythene, polypropene) and ***detergents*** are made via organometallic catalysis .

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

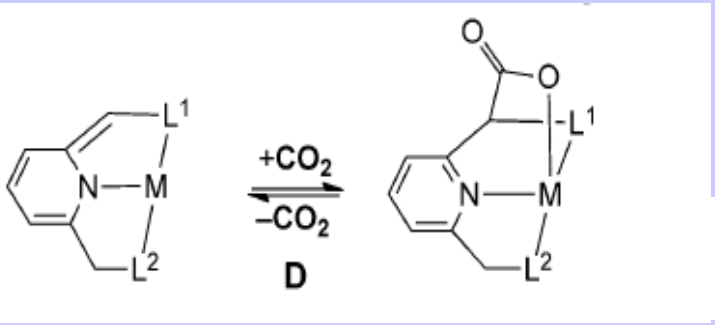
Organometallic compounds are used on a large scale as precursors for ***generation of materials*** *as MOF, light harvesting nanocatalysts or semiconductors*

- **CO_2 activation requires multipurpose mechanism and fexible hapticity**

•Sigma and π–coordination



Gibson 2019



Pincer chemistry: Milstein (Weissman Institute Israel 2019)

Course Objectives

By the end of this course, you should be able to:

- Make an educated guess about stability and reactivity of a given compound, based on electron counting rules
- Propose reasonable mechanisms, based on "standard" organometallic reaction steps, for many metal-catalyzed INDUSTRIAL reactions
- Use steric and electronic arguments to predict how changes in reactants, metal or ligands affect the outcome of reactions
- Read a current research literature paper, understand and explain its content and significance with a scientific criticism