ALMA MATER STUDIORUM
UNIVERSITÀ DI BOLOGNA

Chimica Metallorganica e Catalisi Omogenea cf 6
When? Who knows?

What is?

Is the Thermodynamic and Kinetic Study of Metal sites bound to coordinated ligands made of organic fragments to activate towards further reactions

What for?

Is useful for fine comprehension of fixing elusive organic fragment; to explore Catalytic Mechanisms and new catalysts, pharmaceuticals or new materials by finely modulating the tunable M-Ln system

Silvia Bordoni

We recall previously acquired inorganic concepts such as

- Crystal field theory versus molecular orbital theory
- LX ligand classifications

- We will learn

Definition: At least one M-C bond
commonly Low-Valent Transition Metal but also Main Elements

- Electrons Counting
  to satisfy the inert gas rule → 18 electron rule of MLn systems

- Designation of Formal Oxidation State of Metal to estimate the real Metal d^n electrons

- Low valent metals → covalent binding
- Flexible Geometry
  (ruled by VSEPR but interligand attraction H-bonding or π–π stacking)
- Multiple Oxidation States
- Acid-base behavior
- Synergistic effects (push-pull electron density)

Weak interactions

- Intramolecular bonding (agostic) M---H----C
- or Intermolecular M—H···H—O—C--M
- H_2 , sp^3 C-H , CO_2 activation

Metal triggers
the reactivity of the ligands
devoted to important industrial Reactions in Processes as

Isomerization ,
Hydrogenation ,
Hydroformylation ,
Acetic acid production ,
Metathesis ,
Oligomerization or Polymerization

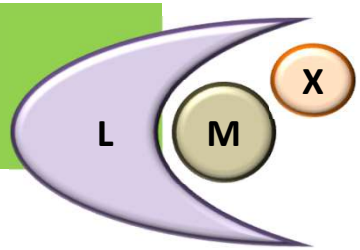
Ambitious Targets are
Sustainable C-H activation of alkanes ,
CO_2 activation ,
use of C1 building block by using Lighter Metals,
as Nature does

A question for you: in the contest of sustainibility
Describe the nature for a desirable efficient catalyst :

- 1 Cheap,
- 2 robust
- 3 long-lived
- 4 Low toxicity

- 5 Lewis Acid Metal Centre – Lewis Base Ligands

- 6 At least one vacant coordinative unsaturation

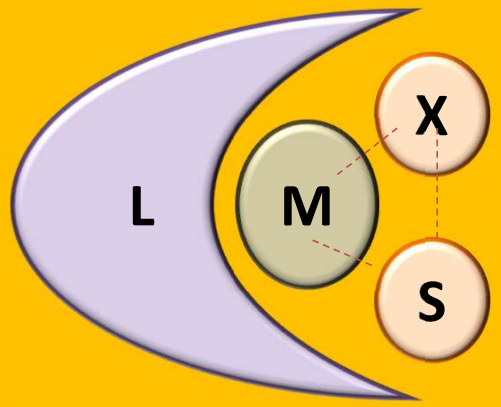


- 7 multiple oxidation states

- 8 Flexible metal-based HOMO-LUMO frontier orbitals for energy and shape

Large ligands (Ln) are often used to **stabilize** coordinative (and electronic) unsaturation,
Necessary to make the catalyst reactive and **fast** reactive

Ln bonds are binding M
by a composed mixture of orbitals,



then M also use a
variety of orbitals
to bind a substrate S
to make it react with activated X

Catalysis requires a responsive (reactive + adaptive)
metal + ligands system

Frontier MOs (HOMO + LUMO) to M-Ln bonds

The substrate S may be
activated causing
umpolung = charge inversion

Organic alkenes are prone to electrophilic addition
M-alkene is subjected by nucleophilic attack

Other topics will be
Metals in medicine (anticancer) or
Toxicology of metals thought as less harmful (Al or Se)

4 hours per week for 6 credits proposed
with a blended methodology

EXAM
2 different PPT slides presentations (MAX 12) and questions about

1) a SUBJECT treated in the CLASS
2) a free choice RECENT RESEARCH PAPER

on Organometallic Chemistry
selected along the proposed publications

For any questions
doubts
elucidations
or curiosity
about the program

please feel free of conctacting me writing
by email address at

silvia.bordoni@unibo.it