Master course in Chemistry

“Principles and Applications of Organometallic Chemistry”

Academic year 2025-2026

Prof. Andrea Biffis

Introduction

Practical Information

Credits: 6 CFU

Lessons: Mondays, 13:30-15:15, hall M
Fridays, 9:30-11:15, hall F

Oral examination (upon arrangement)

Reference textbooks :

- Course slides (available on Moodle)
  https://stem.elearning.unipd.it
  Moodle pwd: metallorganica2025

- C. Elschenbroich, "Organometallics", 3rd ed., Wiley-VCH, Weinheim 2006.

- M. Bochmann, «Organometallics and Catalysis – an Introduction», Oxford University Press 2014

Consultation textbooks (available in the Chemistry Library or in the professor's office):

R. H. Crabtree, "*The Organometallíc Chemistry of the Transition Metals*", 6th ed., Wiley, New York 2014;
J. F. Hartwig, "*Organotransition Metal Chemistry*", University Science Books, Sausalito, 2010;
D. Astruc, «*Organometallic Chemistry and Catalysis*», Springer, 2007;
"*Comprehensive Organometallic Chemistry 3*", M. P. Mingos, R. H. Crabtree (eds.), Elsevier, Amsterdam 2007;
"*Transition Metals for Organic Synthesis*", M. Beller, C. Bolm (eds.), 2nd ed., Wiley-VCH, Weinheim, 2004;
"*Applied Homogeneous Catalysis with Organometallic Compounds*", B. Cornils, W. A. Herrmann (eds.), 2nd ed.,Wiley-VCH, Weinheim, 2002;
L. S. Hegedus, "*Transition Metals in the Synthesis of Complex Organic Molecules*", University Science Books, Sausalito 1999;

Object of organometallic chemistry (*metalorganic/metal-organic* chemistry?)

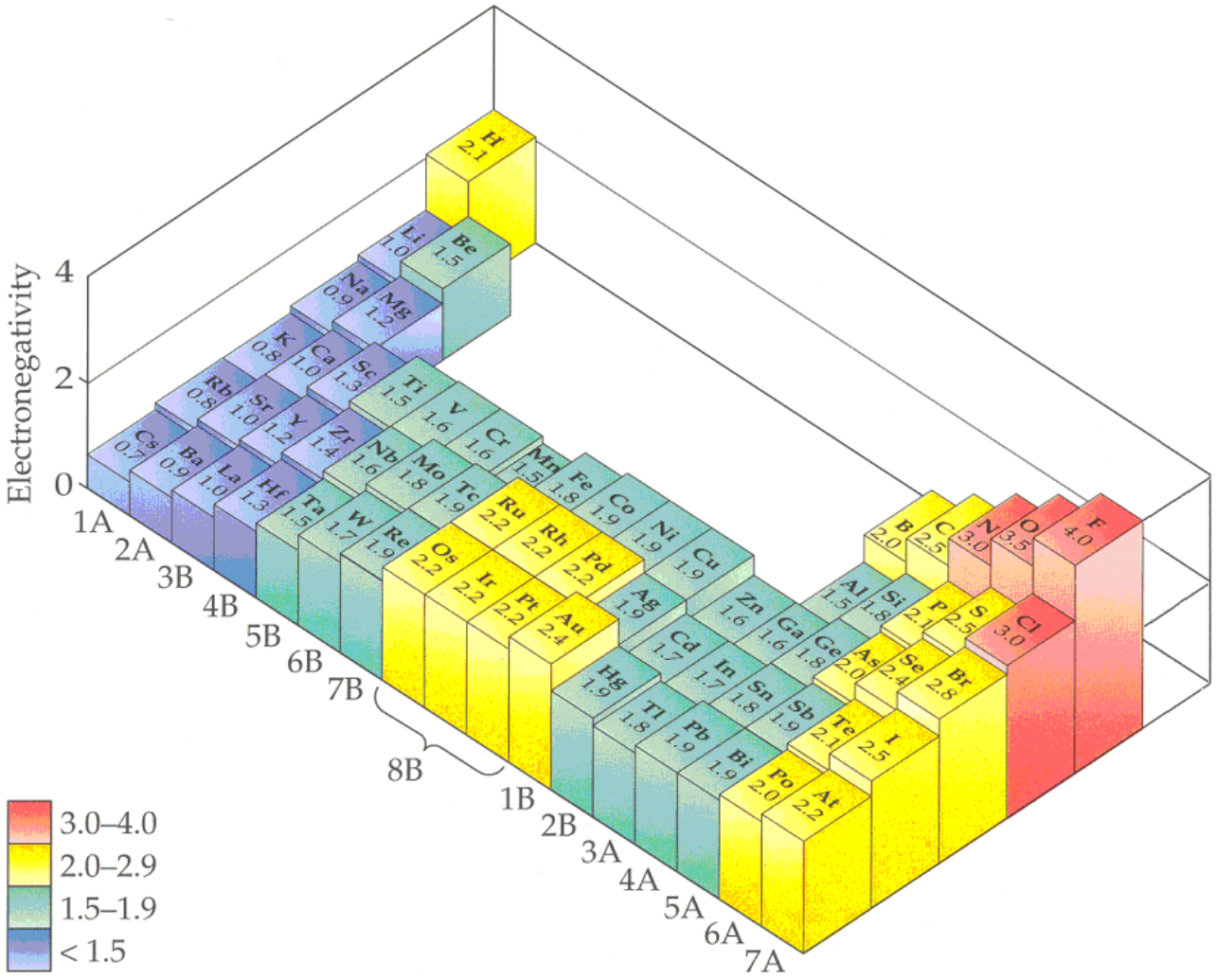
Organoelement compounds: those containing at least 1-bond between C and a less electronegative element (apart H: metals, but also B, Si, P, As, Sb, Se…)

Problem 1: electronegativity not uniquely defined (different electronegativity scales)

Problem 2: elettronegativity of carbon?
$C(sp^3)= 2.50$, $C(sp^2)= 2.75$, $C(sp)= 3.29$

Problem 3: polarization of the C-element bond variable and depending on the element, organic fragment, other fragments bound to element, charge….

Electronegativities of the Elements



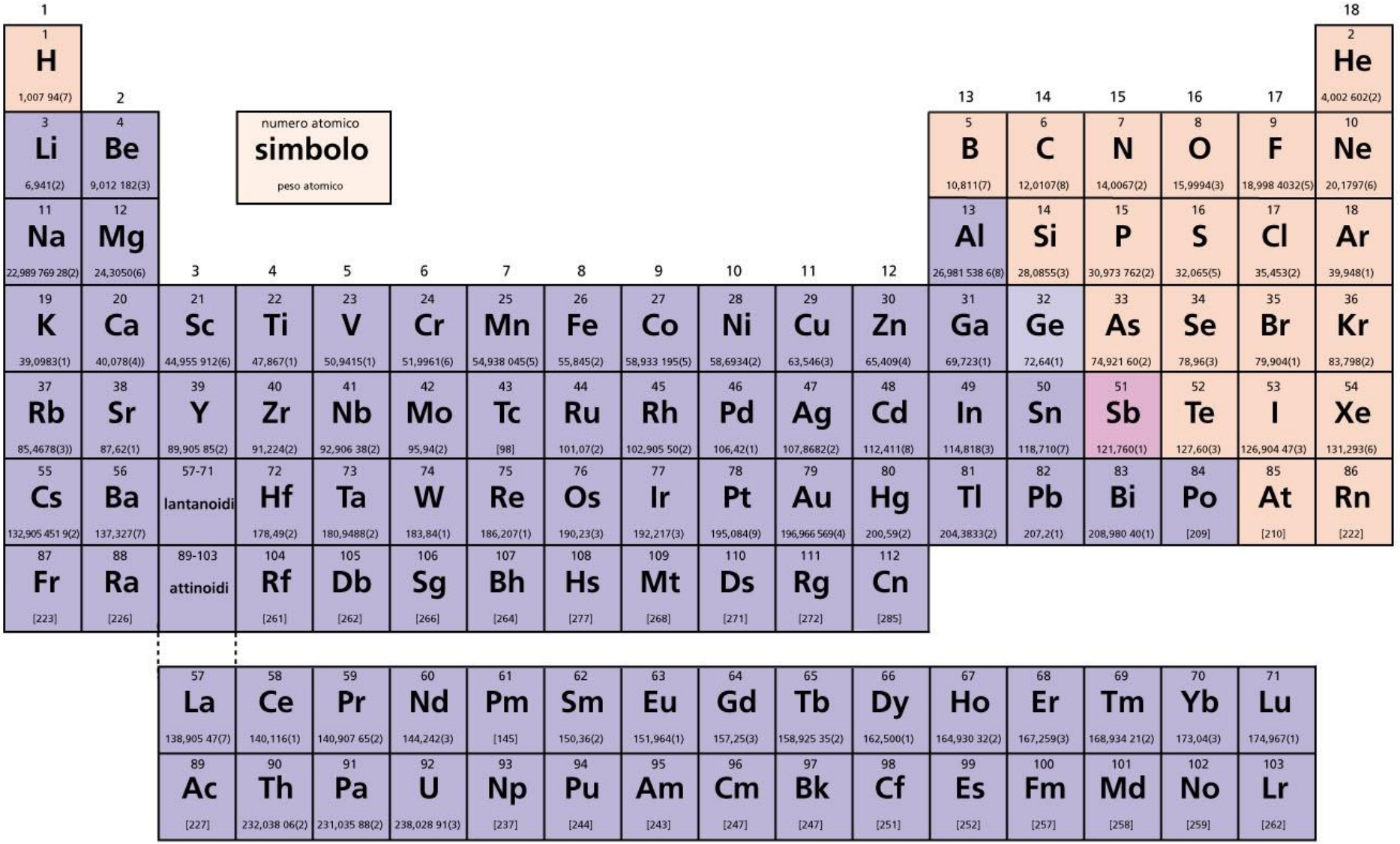
Object of organometallic chemistry

Organometallic compounds: those containing at least one <u>covalent</u> bond between a metal and an “organic” carbon atom (no CN^-, CO_2…)

Exception 1: **CO** (historic and actual significance as C1 building block), R-NC

Exception 2: compounds with nonmetallic elements which behave analogously to organometallic compounds or are nevertheless relevant for organometallic chemistry (**boron**, silicon, *germanium, heavier elements of group 15…)*

Metallic character



Historical development: the beginnings…

1827 Zeise: Na_2PtCl_4 + EtOH → $Na[PtCl_3(C_2H_4)]\cdot H_2O$ + NaCl

1849 Frankland: Et-I + Zn → Et-Zn-I e R_2Zn (and afterwards compounds of Pb, Al, Hg…)

1868 Schützenberger: $[Pt(CO)Cl_2]$

1890 Mond: $Ni(CO)_4$

From **1900** Grignard (Nobel 1912): RMgX

First development (6000 publications by 1935):
- Organometallic compounds as **carbon nucleophiles**
- **Applications of transition metal metallocarbonyls** (Ni purification, hydroformylation, Reppe carbonylation…)

Historical development: after WW2…

From **1947** Ziegler: **olefin polymerization** (Nobel 1963 with Natta)

From **1951** Discovery and determination of the **structure of ferrocene** (Wilkinson and Fischer, Nobel 1973)

From **1959** **Wacker process** (ethylene → acetaldehyde)

Enormous successive development, particularly for transition metals (TM):

G. E. Coates “Organometallic Compounds” :
1st Edition (1956) less than 200 pages, less than 25 on TM;
2nd Edition (1960) 260 pages
3rd Edition: (1971) 950 pages (2 volumes)

Historical development: the XXI century

2001 Nobel to Knowles, Noyori and Sharpless (asymmetric catalysis)

2005 Nobel to Chauvin, Grubbs and Shrock (olefin metathesis)

2010 Nobel to Heck, Negishi and Suzuki (Heck and cross-coupling reactions)

2018 Nobel to Frances Arnold for her studies on the directed evolution of biocatalysts (enzymes/cells): biocatalysts can perform abiotic *organometallic* reactions!

2022 Nobel to Sharpless, Meldal and Bertozzi for their studies on click and bio-orthogonal (*organometallic*) reactions

Current impact of Organometallic Chemistry

Thousands of **publications** per year in dedicated journals: Organometallics (ACS), Journal of Organometallic Chemistry (Elsevier), Applied Organometallic Chemistry (Wiley)…

Encyclopediae: Dictionary of Organometallic Compounds, Comprehensive Organometallic Chemistry (I-III, IV in 2022)

Congresses: ICOMC, OMCOS, EUCOMC, ISHC,…CoGICO

Industrial manufacture of organometallic compounds: **Al**, **Sn**, Mg, Li…

Industrial synthetic processes involving organometallic reagents/catalysts: olefin hydroformylations, carbonylations, metathesis, (asymmetric) hydrogenations, alkane oxidations, cross-couplings…

Organometallic chemistry: quo vadis?

Synthesis and catalysis

Stabilization of organic fragments (carbanions, carbenes...)
Activation of inert substrates (CO, alkanes, arenes…)
Inversion of reactivity (Umpolung) (arenes, olefins…)
High activity, peculiar chemo-, regio- and stereoselectivity
Multistep synthesis: cascade, one-pot reactions

Organometallic photo/electrocatalysis («metallaphotoredox»)
Organometallic radical reactions (open-shell complexes)
Non-innocent ligands – cooperative catalysis
Surface organometallic chemistry
Single-atom catalysis
…..

Organometallic chemistry: quo vadis?

Bio-organometallic chemistry

«Natural» organometallic compounds

Bioactive organometallic compounds

Materials science

Polymer stabilizers (radical scavengers)

Precursors for metal deposition (MO-CVD)

Phosphors for photophysical applications

Organometallic frameworks (MOF), metallomesogens…

Course structure

Introduction (3h)

Historical evolution of organometallic chemistry. General properties of organometallic compounds.

Organometallic chemistry of the main group elements

Description of the organometallic compounds and of their properties and applications, according to their reactivity.

Organometallic chemistry of the transition elements

General features of the compounds and parameters for their description. Summary of reaction mechanisms. Description of the organometallic compounds, by type of coordinated organic fragment (nature of the interaction, properties, applications).