



Master course in Chemistry

“Principles and Applications of Organometallic Chemistry”

Academic year 2023-2024

Prof. Andrea Biffis

Introduction

Practical Information

Credits: 6 CFU

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

Oral examination (upon arrangement)

Reference textbooks :

- Course slides, with audio comment (available on Moodle)

<https://stem.elearning.unipd.it>

Moodle pwd: metallorganica2023

- 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 Organometallic 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?*)

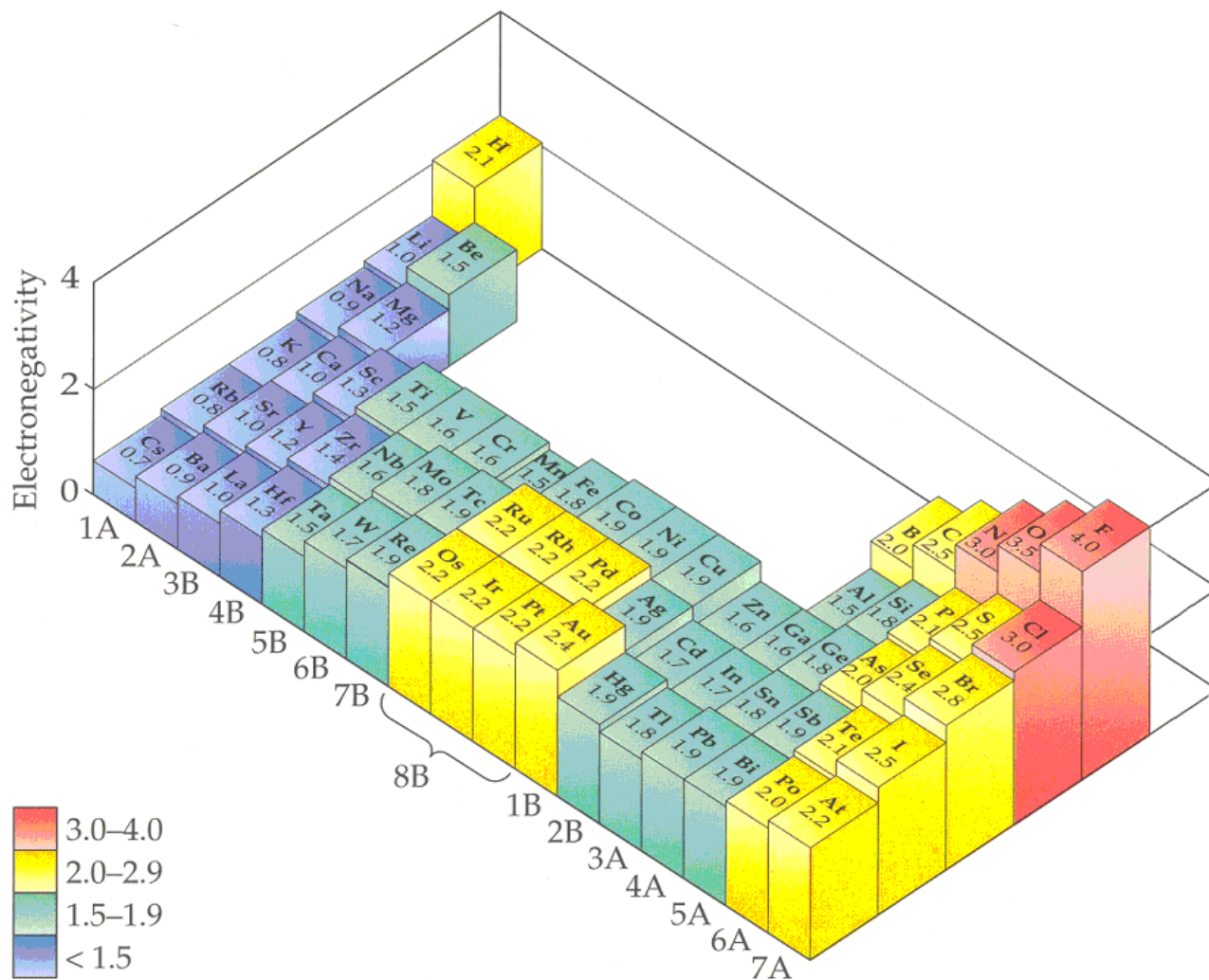
Organoelement compounds: those containing at least 1-bond between C and a less electronegative element (apart H: metals, but also B, Si, P, As, Sb, Se...)

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

Problem 2: electronegativity 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 covalent bond between a metal and an “organic” carbon atom
(no CN^- , $\text{CO}_2\ldots$)

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

1												18																							
1 H 1,007 94(7)												2 He 4,002 602(2)																							
3 Li 6,941(2)		4 Be 9,012 182(3)		numero atomico simbolo peso atomico										13 B 10,811(7)		14 C 12,0107(8)		15 N 14,0067(2)		16 O 15,9994(3)		17 F 18,998 4032(5)		10 Ne 20,1797(6)											
11 Na 22,989 769 28(2)		12 Mg 24,3050(6)												13 Al 26,981 538 6(8)		14 Si 28,0855(3)		15 P 30,973 762(2)		16 S 32,065(5)		17 Cl 35,453(2)		18 Ar 39,948(1)											
19 K 39,0983(1)		20 Ca 40,078(4)		21 Sc 44,955 912(6)		22 Ti 47,867(1)		23 V 50,9415(1)		24 Cr 51,9961(6)		25 Mn 54,938 045(5)		26 Fe 55,845(2)		27 Co 58,933 195(5)		28 Ni 58,6934(2)		29 Cu 63,546(3)		30 Zn 65,409(4)		31 Ga 69,723(1)		32 Ge 72,64(1)		33 As 74,921 60(2)		34 Se 78,96(3)		35 Br 79,904(1)		36 Kr 83,798(2)	
37 Rb 85,4678(3)		38 Sr 87,62(1)		39 Y 89,905 85(2)		40 Zr 91,224(2)		41 Nb 92,906 38(2)		42 Mo 95,94(2)		43 Tc [98]		44 Ru 101,07(2)		45 Rh 102,905 50(2)		46 Pd 106,42(1)		47 Ag 107,8682(2)		48 Cd 112,411(8)		49 In 114,818(3)		50 Sn 118,710(7)		51 Sb 121,760(1)		52 Te 127,60(3)		53 I 126,904 47(3)		54 Xe 131,293(6)	
55 Cs 132,905 451 9(2)		56 Ba 137,327(7)		57-71 lantanoidi		72 Hf 178,49(2)		73 Ta 180,9488(2)		74 W 183,84(1)		75 Re 186,207(1)		76 Os 190,23(3)		77 Ir 192,217(3)		78 Pt 195,084(9)		79 Au 196,966 569(4)		80 Hg 200,59(2)		81 Tl 204,3833(2)		82 Pb 207,2(1)		83 Bi 208,980 40(1)		84 Po [209]		85 At [210]		86 Rn [222]	
87 Fr [223]		88 Ra [226]		89-103 attinoidi		104 Rf [261]		105 Db [262]		106 Sg [266]		107 Bh [264]		108 Hs [277]		109 Mt [268]		110 Ds [271]		111 Rg [272]		112 Cn [285]													
				57 La 138,905 47(7)		58 Ce 140,116(1)		59 Pr 140,907 65(2)		60 Nd 144,242(3)		61 Pm [145]		62 Sm 150,36(2)		63 Eu 151,964(1)		64 Gd 157,25(3)		65 Tb 158,925 35(2)		66 Dy 162,500(1)		67 Ho 164,930 32(2)		68 Er 167,259(3)		69 Tm 168,934 21(2)		70 Yb 173,04(3)		71 Lu 174,967(1)			
				89 Ac [227]		90 Th 232,038 06(2)		91 Pa 231,035 88(2)		92 U 238,028 91(3)		93 Np [237]		94 Pu [244]		95 Am [243]		96 Cm [247]		97 Bk [247]		98 Cf [251]		99 Es [252]		100 Fm [257]		101 Md [258]		102 No [259]		103 Lr [262]			

Historical development: the beginnings...

1827 Zeise: $\text{Na}_2\text{PtCl}_4 + \text{EtOH} \rightarrow \text{Na}[\text{PtCl}_3(\text{C}_2\text{H}_4)] \cdot \text{H}_2\text{O} + \text{NaCl}$

1849 Frankland: $\text{Et-I} + \text{Zn} \rightarrow \text{Et-Zn-I}$ e R_2Zn (and afterwards compounds of Pb, Al, Hg...)

1868 Schützenberger: $[\text{Pt}(\text{CO})\text{Cl}_2]$

1890 Mond: $\text{Ni}(\text{CO})_4$

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 $\rightarrow$ 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 XXIst 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

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).