Organometallic chemistry and catalysis

Nobel prize winning chemistry

Ref./Acknowl.:

CHM432/1204 Organometallic Chemistry & Catalysis

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- Lecture Time : Tuesday 11:10-12:00, Starting Sept. 10, 2019
- Thursday 11:10-12:00
- Location: Claude T. Bissell Building – BL 140 St. George Street Room 114
- Textbook: THE ORGANOMETALLIC CHEMISTRY OF THE TRANSITION METALS, 6th ed., Robert H. Crabtree, Wiley Interscience, 2014 (available on-line through the UoT library: http://onlinelibrary.wiley.com.myaccess.library.utoronto.ca/book/10.1002/9781118788301

 Ref./Acknowl.:

Topics Covered in This Course

- Phosphines, hydrides, dihydrogen, sigma complexes
- Sigma-bonded Hydrocarbon ligands
- Pi-bonded hydrocarbon ligands (Nobel prize)
- Key reactions
- Homogeneous catalysis
- Olefin isomerization
- Homogeneous hydrogenation
- Asymmetric hydrogenation (Nobel prize)
- Computational methods
- C-C Bond forming catalysis (Nobel prize)
- pi-Allyl palladium chemistry, Wacker process
- Catalytic oligomerization and polymerization using Ni
- Metallocenes and catalytic polymerization (Nobel prize)
- Carbenes and olefin metathesis (Nobel prize)
- Carbonyls and hydroformylation
- Summary

Ref./Acknowl.:

Other useful texts

- Housecroft and Sharpe, Inorganic Chemistry, Fourth edition, Chapters 24 and 25, 2012

Books on reserve in the Chemistry Department Bert Allen library:

- J. F. Hartwig. Organotransition Metal Chemistry. University Science Books 2010
- M. Bochmann, Organometallics 1 Complexes with Transition Metal-Carbon sigma Bonds (Oxford Chemistry Primers 1994)
- M. Bochmann, Organometallics 2 Complexes with Transition Metal-Carbon pi Bonds (Oxford Chemistry Primers 1994)

Evaluation

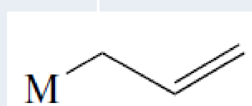
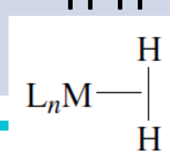
1. Problem Set #1: Due Oct 10	20 marks
2. Problem Set #2: Due Nov 14	20 marks
3. Computational project due Nov. 26	20 marks
4. Final Exam	40 marks

Organometallic Chemistry: An exciting field

- New types of unusual molecules, bonding and reactions
- A fast growing field with many Nobel prizes awarded
- Huge impact on synthetic organic and polymer and materials chemistry
- Industrially important organometallic processes for the synthesis of bulk chemicals and drugs
- Impact on medicine
- Opportunities for developing chemical processes with lower environmental impact (greener)

Ref./Acknowl.:

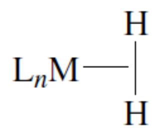
X and L ligands – useful classifications

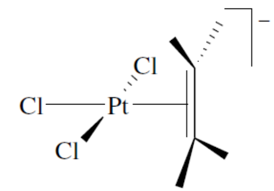
Maximum ionic bonding method: X and L are two electron donors				**Maximum covalent bonding method:** X is a one electron donor; L is two			
L→M-X =	L:	M^+	$:X^-$	L→M-X =	L:	M•	•X
	Ph_3P:		$:Cl^-$		Ph_3P:		•Cl
	MeCN:		$:H^-$		MeCN:		•H
	$CH_2{=}CH_2$		$:CH_2CH_3^-$		$CH_2{=}CH_2$		$•CH_2CH_3$
	OC:		$:Ph^-$		OC:		•Ph
	H_3N:		σ-allyl 		H_3N:		σ-allyl $•CH_2CH{=}CH_2$
	H-H 				H-H		

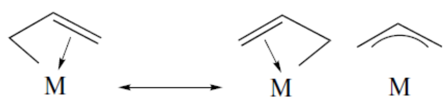
 Ref./Acknowl.:

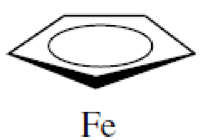
Common ligands and their electron count

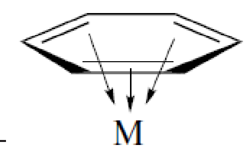
Ligand	Type	Covalent Model	Ionic Model
Me, Cl, Ph, H, η^1-allyl, NO (bent)[a]	X	1e	2e
Lone-pair donors: CO, NH_3, PPh_3	L	2e	2e
π-Bond donors: C_2H_4	L	2e	2e
σ-Bond donors: H_2	L	2e	2e
M–Cl (bridging)	L	2e	2e
η^3-Allyl, κ^2-acetate	LX	3e	4e
NO (linear)[a]		3e	2e[a]
η^4-Butadiene	L_2[b]	4e	4e
=O (oxo)	X_2[c]	2e	4e
η^5-Cp	L_2X	5e	6e
η^6-Benzene	L_3	6e	6e









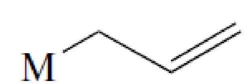


[a]Linear NO is considered as NO^+ and bent as NO^- on the ionic model; see Section 4.1.
[b]The alternative LX_2 structure sometimes adopted gives the same electron count.

Hapticity: η^n number of C or H atoms attached to metal.

Kappa: κ^n number of non-C atoms attached to metal

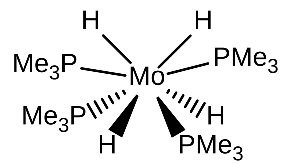
η^1-allyl, or σ-allyl



Electron Counting With Ionic and Covalent Models

Ionic Model	Compound	Covalent Model

MoX_4L_4



3	4	5	6	7	8	9	10	11	12
Sc	Ti	V	Cr	Mn	**Fe**	Co	Ni	Cu	Zn
Y	Zr	Nb	**Mo**	Tc	Ru	Rh	Pd	Ag	Cd

Ionic Model:

$4H^- + 4PR_3 + Mo^{4+}$

$8e + 8e + 2e = 18e$

X_4 L_4 (E)

$Mo(E_1)X_4L_4$

Note: 1+4+4=9 orbitals filled with 18 electrons

Compound:

$MoH_4(PR_3)_4$

2.8

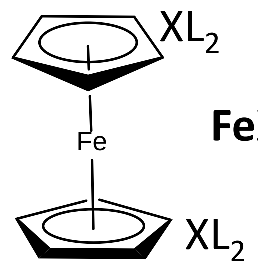
Covalent Model:

$4H\bullet + 4\ PR_3 + Mo(0)$

$4e + 8e + 6e = 18e$

X_4 L_4 (E) + 4Mo•

$Mo(E)X_4L_4$



FeX_2L_4

Ionic Model:

$2C_5H_5^- + Fe^{2+}$

$12e + 6e = 18e$

$(XL_2)_2$ $(E)_3$

$Fe(E_3)X_2L_4$

Compound:

Cp_2Fe

2.7

Covalent Model:

$2C_5H_5\bullet + Fe(0)$

$10e + 8e = 18e$

$(XL_2)_2$ $(E)_3$ + 2Fe•

$Fe(E_3)X_2L_4$

The 18-Electron Rule

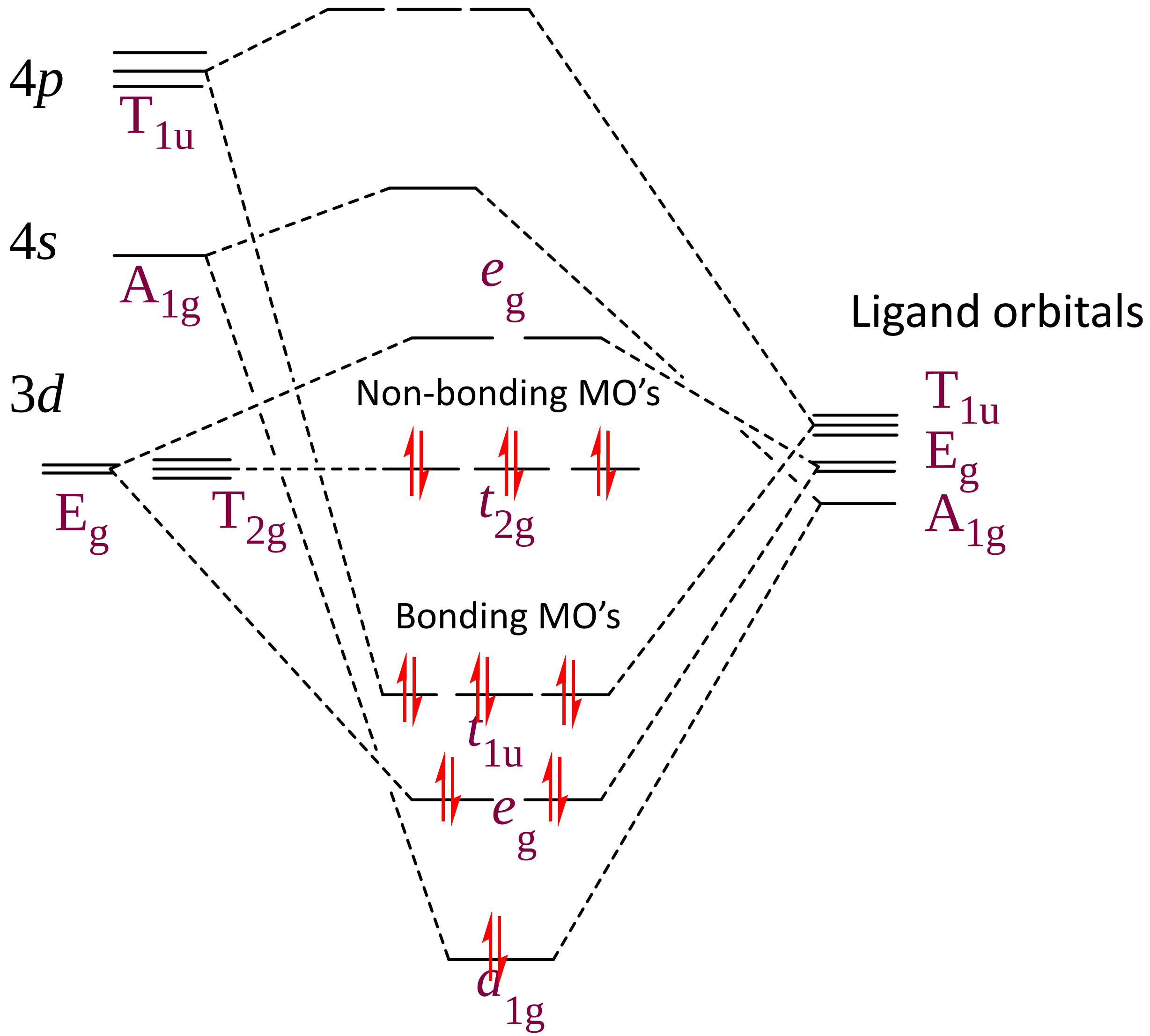
• organometallic complexes that are isolated often obey the 18 electron rule

• **9 valence orbitals:** upper limit of 9 bonds may be formed. In many cases a maximum of 6 σ bonds are formed and the remaining d orbitals are non-bonding often holding electron pairs (E). It's these non-bonding d orbitals and electrons that give TM complexes many of their unique properties.

• **18 electron rule:** upper limit of 18 e- can be accommodated without using antibonding molecular orbitals (MO).

Ref./Acknowl.: M. C. White web notes

Qualitative MO diagram for an 18-e d_6 octahedral complex



The 18-Electron Rule- Characteristic Metal Formulae

- applies to complexes with small, covalent ligands such as L = PMe_3 or CO and X= hydride or sometimes CH_3 in diamagnetic complexes

	3 Sc-La	4 Ti-Hf	5 V-Ta	6 Cr-W	7 Mn-Re	8 Fe-Os	9 Co-Ir	10 Ni-Pt
d^0	**MX_3L_4**	**MX_4L_4**	MX_5L_4	MX_6L_3	MX_7L_2			
d^2		MEX_2L_6	MEX_3L_5	MEX_4L_4	MEX_5L_3	MEX_6L_2		
d^4			ME_2XL_6	$ME_2X_2L_5$	$ME_2X_3L_4$	$ME_2X_4L_3$	$ME_2X_5L_2$	
d^6				ME_3L_6	ME_3XL_5	$ME_3X_2L_4$	$ME_3X_3L_3$	$ME_3X_4L_2$
d^8						ME_4L_5	ME_4XL_4	**$ME_4X_2L_2$**
d^{10}								ME_5L_4
Examples	**Cp_2ScMe**	**Cp_2TiMe_2**	TaH_5L_3	**WMe_6**	$ReH_7(PMe_3)_2$	OsH_6L_2	$IrH_5(PiPr_3)_2$	$PtMe_4L_2$
Examples		$Cp^*_2Zr(CO)_2$	$VH(CO)_6$	$Mo(CO)_6$	$MnMe(CO)_5$	$Fe(CO)_5$	$CoH(CO)_4$	$Ni(CO)_4$

Formulae in bold do not obey the rule

The lone pairs of d electrons on the metal (E_n) give these complexes their distinct reactivity

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