Master course in Chemistry

“Principles and Applications of Organometallic Chemistry”

Academic year 2021-2022

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General Properties of Organometallic Compounds

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 (**new!**)

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).

Organometallic compounds of the main groups (and of group 12)

MR_n or MR_nX_m

R= “organic” anionic ligand, X= “inorganic” anionic ligand

n or n+m = maximum valence of the element

-The compounds contain **M-C σ bonds**, sometimes with notable ionic character (with less electronegative metal centers) and/or multicentric (with the most polarising metal centers);

- The **polarity** of the bond increases from right to left and from top to bottom in the periodic table;

$M\text{-}R \rightarrow M^+ + R^-$ heterolytic scission

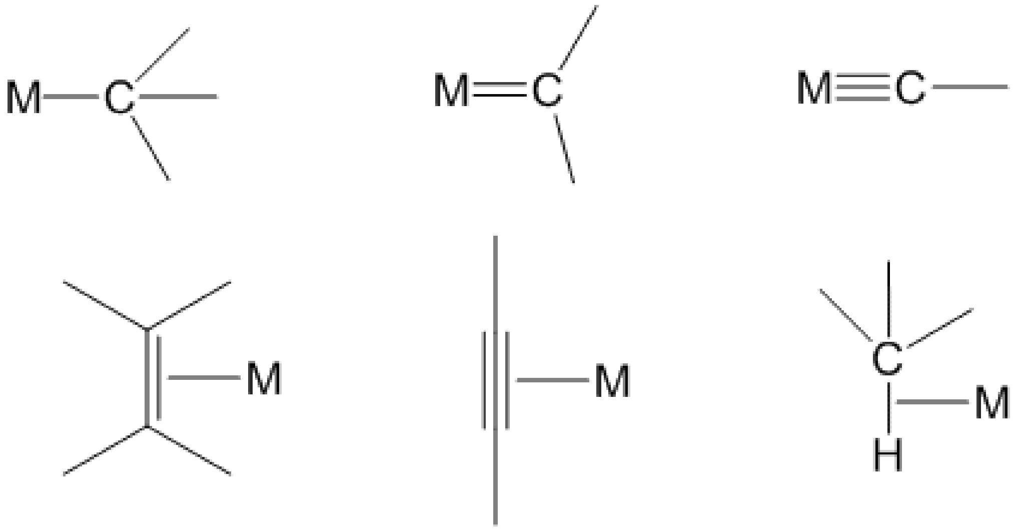
- The **strength** of the bond decreases from top to bottom in the periodic table;

$M\text{-}R \rightarrow M\bullet + R\bullet$ homolytic scission

A group treatment is possible

Organometallic compounds of the transition metals (organotransition metal chemistry)

- The compounds contain **different kinds of M-C bonds**: σ M-C, multiple M-C, π M-C, agostic interactions…



- The polarity of the (single) bond generally increases from right to left in the periodic table; the bond polarity, strength and reactivity are however extremely dependent on the nature of the bond, of the metal, of the other ligands present….

Treatment by type of ligand is preferable

General properties of organometallic compounds

- Physical properties often more <u>close to those of organic compounds</u> rather than coordination compounds: molecular compounds with low melting points, liquid or even gaseous, soluble in organic solvents;

- <u>Extremely variable stability</u> in dependence of the different nature and strength of the M-C bond, of the nature of M and of the existence of low-energy decomposition pathways.

- <u>Extremely variable sensitivity to air and moisture</u>, dependent on the same factors listed above.

Let us consider very simple M-C single bonds and R groups…

Behaviour of $M(CH_3)_n$ compounds

$Ti(CH_3)_4$	decomposes above -40 °C
$Zn(CH_3)_2$	pyrophoric, hydrolysed by water
$Hg(CH_3)_2$	stable to aqueous acids in boiling water and to air
$B(CH_3)_3$	pyrophoric, but stable to water
$Al(CH_3)_3$	pyrophoric, hydrolysed by water
$In(CH_3)_3$	pyrophoric, hydrolysed by water
$Sn(CH_3)_4$	stable to air and water
$Pb(CH_3)_4$	boils without decomposition at 110 °C
$Sb(CH_3)_3$	pyrophoric, but stable to water

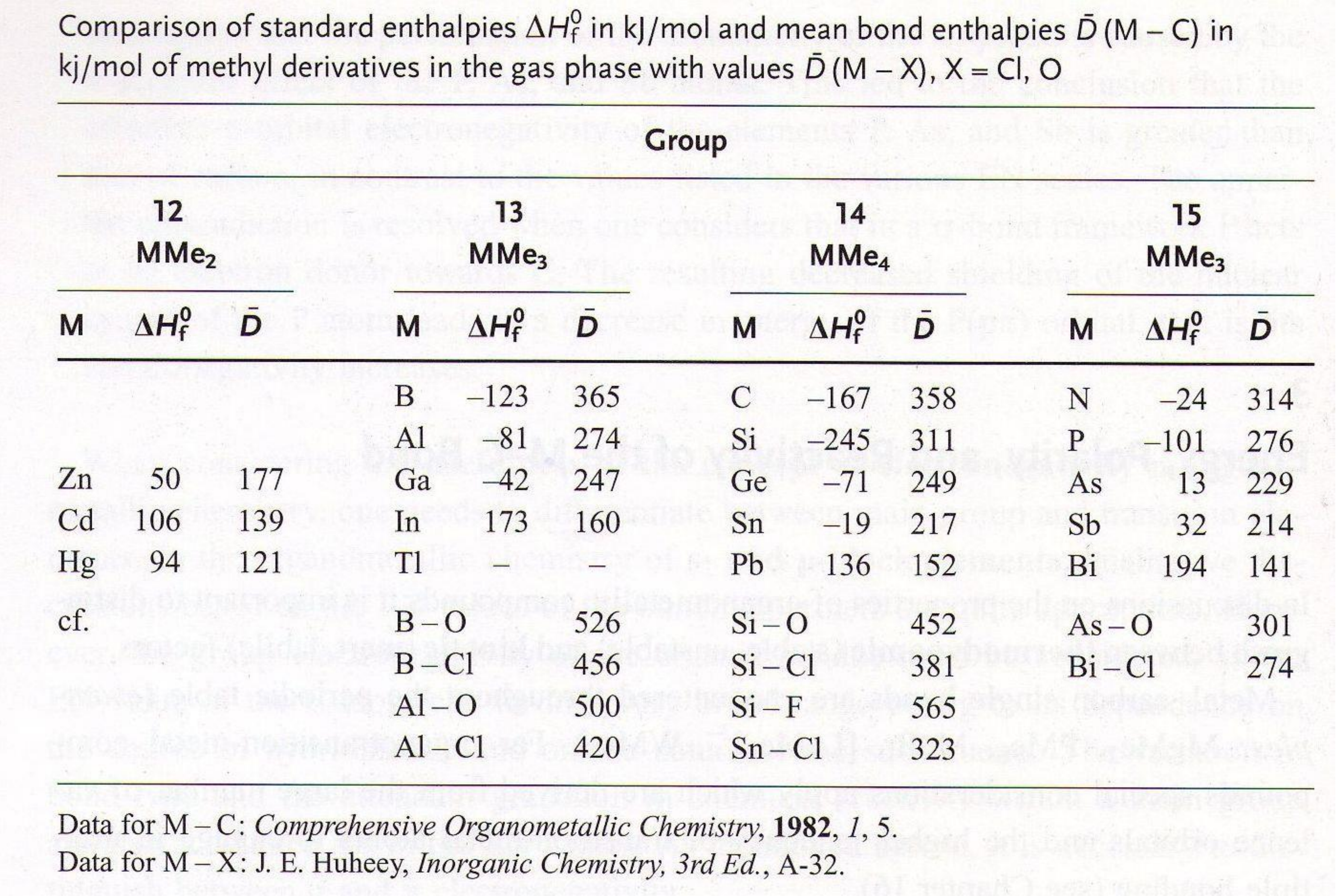
General properties of organometallic compounds

Concerning main group & group 12 organometallics, it is possible to evaluate the **thermodynamic** stability (with respect to the constituting elements) of the methyl derivatives $M(CH_3)_n$ on the basis of:

- enthalpy of formation;
- mean bond enthalpy D (enthalpy change related to the homolytic scission of the M-C bond in the gas phase, <u>mediated among the various bonds present</u>)

D(MeHg-Me)=214 kJ/mol, but D(•Hg-Me)= 29 kJ/mol!

General properties of organometallic compounds



Comparison of standard enthalpies ΔH_f^0 in kJ/mol and mean bond enthalpies $\bar{D}$ (M – C) in kj/mol of methyl derivatives in the gas phase with values $\bar{D}$ (M – X), X = Cl, O

Group											
12			13			14			15		
MMe_2			MMe_3			MMe_4			MMe_3		
M	ΔH_f^0	$\bar{D}$	M	ΔH_f^0	$\bar{D}$	M	ΔH_f^0	$\bar{D}$	M	ΔH_f^0	$\bar{D}$
			B	–123	365	C	–167	358	N	–24	314
			Al	–81	274	Si	–245	311	P	–101	276
Zn	50	177	Ga	–42	247	Ge	–71	249	As	13	229
Cd	106	139	In	173	160	Sn	–19	217	Sb	32	214
Hg	94	121	Tl	–	–	Pb	136	152	Bi	194	141
cf.			B – O		526	Si – O		452	As – O		301
			B – Cl		456	Si – Cl		381	Bi – Cl		274
			Al – O		500	Si – F		565			
			Al – Cl		420	Sn – Cl		323			

Data for M – C: *Comprehensive Organometallic Chemistry*, **1982**, *1*, 5.
Data for M – X: J. E. Huheey, *Inorganic Chemistry, 3rd Ed.*, A-32.

«Stability» of organometallic compounds

The average bond enthalpy M-C decreases down the groups: consequently, the thermodynamic stability (with respect to the elements) decreases. These compounds are often endothermic!

The average bond enthalpy M-C is generally **lower** than the M-X ed **M-O** bond enthalpy: consequently, organometallic compounds, like organic compounds, are e.g. unstable towards oxidation, or towards hydrolysis.

However, many organometallic compounds are **kinetically inert** towards oxidation and hydrolysis, and also towards thermodynamically favoured decomposition reactions, which is the consequence of the unavailability of reaction mechanisms with low activation energy.

«Stability» of organometallic compounds

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Conditions for kinetic inertness: absence of low energy, free coordination sites at M; absence of free electron pairs at M; low polarity of the M-C bond.