

ORGANOMETALLIC COMPOUNDS

Organometallic compounds are compounds which contain bonds between carbon and a metal. To differentiate the compounds of these type, we use the nomenclature **E-C** (**E** binds to carbon where **E** is a **P-block metalloid**), and **M-C** (**M** binds to carbon where **M** is an **electropositive metal**). When the properties of these compounds are considered the oxidation number has also to be considered because the physical properties change according to the oxidation number.

Stability: E.g. For the methyl compounds in case of light elements (groups 13/III to 15/V) the Gibbs energies of formation are exothermic in relation to the elements → decreases down the groups → compounds of heavy elements have endothermic Gibbs energies of formation.

Ferrocene: $\text{Fe}(\text{C}_5\text{H}_5)_2$: cyclopentadienyl rings at opposite sides of the metal (Sandwich compounds).

Physical properties: Insoluble in water, soluble in most organic solvents.

Synthesis: Way 1: Educts: Grignard reagent (cyclopentadienyl magnesium bromide), diethyl ether, iron chloride. Process: Iron chloride is added to diethyl ether and then Grignard reagent is added. Ferrocene is formed along with MgBr_2

Way 2: Dehydrogenation: Educts: cyclopentadiene (gas phase), iron, Temp: 350 °C. Products: Ferrocene, H_2 (gas).

Applications: Used in the fuel for petrol engines; Ferrocenium salts has anticancer activity, the drug name is TAMOXIFEN. Mechanism → Tamoxifen binds to the Estrogen binding sites, results in cytotoxicity effect.

Bis(Benzenechromium): $\text{Cr}(\text{C}_6\text{H}_6)_2$: Two benzene rings at opposite sides of the central chromium atom. Physical Properties: This is a brown-black, crystalline solid, soluble in benzene, poorly soluble in diethyl ether.

Synthesis: Friedel-Crafts reaction. Educts: chromium trichloride, aluminium, benzene, aluminium chloride, sodium sulphate. Process: chromium trichloride reacts with aluminium and benzene with aluminium chloride as catalyst. The buildet complex then reacts with sodium sulphate and forms $\text{Cr}(\text{C}_6\text{H}_6)_2$.

Electron Counting in organometallic compounds: 18-electron rule (N.V. Sigwick Rule): by applying this rule one can make predictions about the stability of complexes, which is high in case of 18 electrons (noble gas configuration)

To count the electrons one has to add all valence electrons of the metal and the ligands as if they were neutral. If there is a charged complex the respective electrons has to be added or subtracted

e.g. $\text{Cr}(\text{CO})_6$: $6 * 2 e^-$ for the six carbonyl ligands and $6 e^-$ for the chromium = $18 e^-$ = stabile complex

Types of compounds: First group: Weak ligand fields, low Δ values, no strong back bonding. Ex: TiF_6^{2-} , $\text{Mn}(\text{CN})_6^{3-}$. Second group: Weak ligand fields compared to third group, higher Δ values than first group, no strong back bonding. Ex: ZrF_6^{2-} , PtF_6^{2-} . Third group: high Δ values and strongly back bond. Ex: $\text{Fe}(\text{CO})_5$, $\text{Co}(\text{CO})_4^-$.

Metal Organic Frameworks: Crystalline compounds consisting of metal ions and organic ligands. Common ligands in MOFs: oxalic acid, malonic acid, succinic acid, trimesic acid, pyrrodiazole, squaric acid.....etc;

Synthesis: mostly by hydrothermal or solvothermal techniques, where crystals are slowly grown from a hot solution of metal such as metal nitrates and bridging ligands.

Types of MOFs: carboxylate based MOFs, heterocyclic based MOFs, metal cyanide and covalent organic MOFs. Often used are the carboxylate MOFs because they are commercially available and they can be easily synthesized. Ex: $\text{Zn}_4\text{O}(\text{BTB})_2$: BTB – 1,3,5-benzenetribenzoate; $\text{Zn}_4\text{O}(\text{BDC})_3$: BDC – 1,4-benzenedicarboxylate

Physical properties: they more surface area the more hydrogen can be stored, sensitive to air.
Applications: gas separation, gas purification, storage and heterogeneous catalysis.

TASKS:

1. Discuss the Organo Metallic Compounds Ferrocene and Bis(Benzenechromium) according their properties.
2. Count the electrons using the 18-electron rule for the examples: $\text{Ni}(\text{CO})_4$; $\text{Fe}(\text{CO})_5$; $\text{Mn}_2(\text{CO})_{10}$; $\text{Co}_2(\text{CO})_8$