ORGANOMETALLIC COMPOUNDS

1. Definition & General Characteristics

Concept	Description
Organometallic Compounds	Compounds containing at least one metal–carbon (M–C) bond where the carbon is part of an organic group.
Examples	Grignard reagents (RMgX), Organolithium (RLi), Ferrocene, Zeise's salt, Wilkinson's catalyst.
Bond Nature	Can be ionic (e.g., $NaCH_3$) or covalent (e.g., $Ni(CO)_4$).
Common Metals	Li, Mg, Zn, Fe, Co, Ni, Pd, Pt, Ti.

2. Synthesis of Organometallic Compounds

Method	Reaction Example
Direct combination	$2Li + R–X \rightarrow RLi + LiX$
Transmetallation	$2RLi + ZnCl_2 \rightarrow R_2Zn + 2LiCl$
Reduction of Metal Halide	$TiCl_4 + 4NaC_5H_5 \rightarrow Ti(C_5H_5)_4 + 4NaCl$
Carbonylation	$Ni + CO \rightarrow Ni(CO)_4$ (at 50°C, 1 atm)

3. Structure & Bonding

• σ (sigma) bond: Overlap of metal orbital with sp^3/sp^2 carbon orbital.

• π (pi) bond: Found in Zeise's salt due to π-back bonding between metal d-orbitals and alkene π* orbitals.

• Sandwich Compounds: e.g., Ferrocene ($Fe(\eta^5–C_5H_5)_2$) – aromatic π-electron interaction stabilizes Fe^{2+} center.

Type	Example	Nature of Bond
σ-bonded	R–Mg–X (Grignard)	σ M–C bond
π-complex	Zeise's salt	Metal–alkene π-backbonding
η^5-complex	Ferrocene	Delocalized π-bond

4. Important Reactions

Oxidative Addition : Metal oxidation state and coordination number increase by 2.
Example: Vaska's Complex $(IrCl(CO)(PPh_3)_2 + H_2 \rightarrow Ir(H)_2Cl(CO)(PPh_3)_2)$
Reductive Elimination: Reverse of oxidative addition, both decrease by 2.
Example: Pt(IV) → Pt(II) + R–R'

Process	Change in Oxidation State	Coordination Number	Example
Oxidative Addition	+2	+2	Ir(I) → Ir(III)
Reductive Elimination	−2	−2	Pt(IV) → Pt(II)

5. Catalysis by Organometallic Compounds

Process	Catalyst	Product
Hydrogenation	Wilkinson's (Rh)	Alkane
Hydroformylation	Co/Rh complexes	Aldehyde
Monsanto Process	$RhI_2(CO)_2^-$	Acetic acid
Wacker Process	$PdCl_2/CuCl_2$	Acetaldehyde
Ziegler–Natta Polymerization	$TiCl_4$ + $AlEt_3$	Polyethylene/Polypropylene

6. Quick Revision Points

- Organometallic bond: M–C σ or π type
- Ferrocene: Sandwich complex
- Zeise's salt: π-alkene complex
- Oxidative addition → Oxidation state ↑
- Reductive elimination → Oxidation state ↓
- Wilkinson's catalyst → Hydrogenation
- Monsanto → Acetic acid
- Wacker → Acetaldehyde
- Ziegler–Natta → Polyethylene, polypropylene
- Hydroformylation → Aldehydes

CAGES AND CLUSTERS

1. Introduction

Clusters are compounds containing metal–metal bonds and a definite number of atoms (metal and non-metal) arranged in a polyhedral structure. Classified by nuclearity: Binuclear (2 metals), Trinuclear (3 metals), Tetranuclear (4 metals), etc.

2. Metal Carbonyl Clusters

Type	Example	Structure / Features	Oxidation State
Binuclear	$[Mn_2(CO)_{10}]$	Two Mn atoms linked by Mn–Mn single bond; octahedral geometry	0
Trinuclear	$[Fe_3(CO)_{12}]$	Triangular Fe_3 core with	0

		terminal and bridging CO	
Tetranuclear	$[Co_4(CO)_{12}]$	Tetrahedral metal framework	0
Hexanuclear	$[Ru_6(CO)_{18}]$	Octahedral Ru_6 core; highly symmetric	0

Metal–metal bonds stabilize low oxidation states, while CO ligands provide π-back donation strengthening M–C bonds.

3. Classification (Structural)

Category	Example	Description
Carbonyl clusters	$[Fe_3(CO)_{12}]$, $[Co_4(CO)_{12}]$	Contain only CO as ligands
Halide clusters	$[Nb_6Cl_{12}]^{2-}$, $[Mo_6Cl_8]^{4+}$	Metal atoms bridged by halides
Carbido clusters	$[Fe_5C(CO)_{15}]$	Central C atom surrounded by metals
Mixed-ligand clusters	$[Mo_2Cl_4(CO)_2(PPh_3)_2]$	Contain different ligands (Cl, CO, PPh_3)

4. Wade–Mingos Rules

Type	Skeletal Electron Pairs	Structure
Closo	n + 1	Complete polyhedron ($B_6H_6^{2-}$ = octahedral)
Nido	n + 2	Missing one vertex (B_5H_9)
Arachno	n + 3	Missing two vertices (B_4H_{10})

5. Halide-Type Metal Clusters

Contain metal atoms linked via halogen bridges (Cl^-, Br^-, I^-). Example: $[Nb_6Cl_{12}]^{2-}$ with octahedral Nb_6 core, each edge bridged by Cl^-; each Nb is +2. Used as building blocks in solid-state and superconducting materials.

6. Borazines (Inorganic Benzene)

Feature	Details
Formula	$B_3N_3H_6$
Structure	Planar six-membered ring (B–N alternate)
Bonding	Delocalized π electrons; B–N bond = 1.44 Å
Preparation	$3NH_3 + 3BCl_3 \rightarrow B_3N_3H_6 + 9HCl$
Reactivity	Hydrolyzed by water to give boric acid and ammonia

Analogy	Aromatic like benzene but more reactive

7. Phosphazenes

Property	Details
General Formula	$(NPCl_2)_n$ (n = 3–15)
Common Example	$(NPCl_2)_3$ (hexachlorocyclotriphosphazene)
Structure	Alternating P–N single and partial double bonds, π-delocalization
Reactions	Chlorines replaced by alkoxy or amino groups → polymers
Applications	Flame-resistant plastics, elastomers, biomedical uses
Bonding	P: sp^3, N: sp^2; dπ–pπ bonding stabilizes ring

8. Metal Cluster Molecularity Overview

Cluster	Metal Centers	Key Feature
$[Mn_2(CO)_{10}]$	2	Single Mn–Mn bond
$[Fe_3(CO)_{12}]$	3	Triangular Fe_3 core
$[Co_4(CO)_{12}]$	4	Tetrahedral core
$[Ru_6(CO)_{18}]$	6	Octahedral core
$[Nb_6Cl_{12}]^{2-}$	6	Halide-bridged octahedron
$B_3N_3H_6$	3B + 3N	Inorganic benzene
$(NPCl_2)_3$	3P + 3N	Cyclic phosphazene

9. Quick Recall Summary

- Binuclear cluster: $[Mn_2(CO)_{10}]$ – single metal–metal bond
- Trinuclear cluster: $[Fe_3(CO)_{12}]$ – triangular framework
- Halide cluster: $[Nb_6Cl_{12}]^{2-}$ – edge-bridged halides
- Borazine: $B_3N_3H_6$ – inorganic benzene
- Phosphazene: $(NPCl_2)_3$ – cyclic P–N system
- Wade–Mingos rule: predicts cluster geometry