

IV SEMESTER

CH H 561: ORGANOMETALLIC CHEMISTRY

Course Outcome

- The students will learn historical development of organometallic compounds and classification.
- Understand the chemistry of transition metal-carbon multiple bonded compounds and transition metal-carbon pi complexes.
- Application of catalysis by organometallic compounds, homogeneous catalysis by organometallics and hydrocarbonylation of olefins.
- Acquire knowledge on Ziegler-Natta catalyst, Fischer-Tropsch and Water Gas Shift reactions.

UNIT-I

[12 Hours]

Historical development-Classification and nomenclature, bond energies and stability. 16- and 18-electron rules. **Transition metal alkyls and aryls-types**, routes of synthesis, stability and decomposition pathways, Nucleophilic and electrophilic cleavage of metal-carbon sigma bonded compounds. Alkane activation.

Transition metal-carbon multiple-bonded compounds-Carbenes, carbynes, synthesis, nature of bond, agostic interactions, structural characteristics and reactivity. Transition metal hydrides-Synthetic routes, properties, structure and reactivity, synthetic applications.

UNIT-II

[12 hours]

Transition metal-carbon, pi-complexes-Preparative methods, nature of bonding, structural features of olefinic, acetylenic, allylic, butadiene, cyclobutadiene, η^5 -cyclopentadienyl, η^6 -benzene and other arenes, cycloheptatriene and cyclooctatetraene complexes. Important reactions relating to nucleophilic and electrophilic attack on ligands. Fluxional isomerism in olefin, allyl, dienyl and cyclopentadienyl complexes. Carbene complexes and metallacycles, arene complexes. Isolobal concept.

UNIT-III

[12 hours]

Catalysis by organometallic compounds: oxidative addition, insertion, deinsertion and reductive elimination reactions.

Homogeneous catalysis by organometallics: Hydrogenation, hydrosilation, hydrocyanation and isomerization of olefins, immobilisation of homogeneous hydrogenation catalysts, Hydrocarbonylation of olefins (oxo reaction-cobalt and rhodium oxo catalysts), Wacker process. Carbonylation of alcohols-Monsanto acetic acid process.

Polymerization of olefins and acetylenes: Ziegler-Natta catalyst systems. Fischer-Tropsch reaction, Water Gas Shift reactions.

Unit-IV

[12 Hours]

Metal complexes as drugs and therapeutic agents: Antibacterial agents, antiviral agents, metal complexes in cancer therapy, metal complexes for the treatment of rheumatoid arthritis–Gold based therapeutic agents, vanadium in diabetes, metal complexes as radio diagnostic agents.

Treatment of toxicity due to inorganics: General aspects of mechanism of metal ion toxicity- i) Mechanism of antidote complex with poison, rendering it inert: arsenic, lead, mercury, iron, copper; ii) Antidote accelerated metabolic conversion of poison to non-toxic product: cyanide and carbon monoxide.

References

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3. Organometallic Chemistry of Transition Metals, R. H. Crabtree, Wiley (1999).
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7. Basic Organometallic Chemistry, B. D. Gupta and A. J. Elias, Universities Press (2013).
8. Medicinal Applications of Coordination Chemistry, C. Jones and J. Thornback, RSC Publishing (2007).
9. Transition Metal Complexes as Drugs and Chemotherapeutic Agents, N. Farrell, Kluwer, Academic Publishers (1989).
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