

## SEMESTER-V

### BSC. (HONS.) CHEMISTRY

#### DISCIPLINE SPECIFIC CORE COURSE -13 (DSC-13): Basics of Organometallic Chemistry

#### CREDIT DISTRIBUTION, ELIGIBILITY AND PRE-REQUISITES OF THE COURSE

Course title & Code	Credits	Credit distribution of the course			Eligibility criteria	Pre-requisite of the course (if any)
		Lecture	Tutorial	Practical/ Practice		
Basics of Organometallic Chemistry (DSC-13)-Inorganic Chemistry-V	04	03	--	01	Class 12 <sup>th</sup> with Physics, Chemistry, Mathematics	-

#### Learning Objectives

The Objectives of this course are as follows:

- To familiarize the students with the interactions of metal atom with organic molecules (or not so typical organic molecule), which is in an entirely different fashion as compared to coordination compounds.
- To familiarize the students with the structure and bonding in organometallic compounds
- To familiarize the student with how organometallic compounds can act as good catalysts for organic transformations and hence have industrial importance associated with medicines, bioorganic synthesis, and energy production.

#### Learning Outcomes

By studying this course, the students will be able to:

- Identify and classify organometallic compounds of different types.
- Explain the stability of organometallic compounds and hence the requirement of special experimental conditions for their synthesis.
- Explain the bonding modes through VBT and MOT in these compounds.
- Explain the chemical nature of these compounds through various reactions thus acquiring skills to understand their applications.
- Explain the mechanism of catalysis by these compounds. This may prepare the student to predict the catalytic pathways for new reactions

#### SYLLABUS OF DSC-13

Unit-1: Introduction to Organometallic Chemistry

(Hours: 6)

Definition, brief history, classification of organometallic compounds on the basis of bond type. Common notation used in organometallic chemistry, concept of hapticity of organic ligands, importance of organometallic chemistry, organometallic compounds as reagents, additives, and catalysts. Introduction to the 18-electron rule or effective atomic number rule, electron count of mononuclear, polynuclear and substituted metal carbonyls of 3d series and finding metal-metal bonds.

**Unit-2: Structure and Bonding in Organometallic Compounds (Hours : 12)**

Structures of mononuclear and binuclear carbonyls of Cr, Mn, Fe, Co and Ni using VBT.

Molecular orbital theory applied to organometallic compounds, description of bonding of two electron ligands to transition metals.  $\pi$ -acceptor behavior of CO (MO diagram of CO to be discussed),  $\pi$ -bonding of CO with metal (synergic effect) and use of IR data to explain extent of back bonding, bonding modes of CO, symmetry of metal carbonyls.

Bonding between metal atoms and organic  $\pi$ - systems: linear (ethylene, allyl, butadiene) and cyclic (cyclopentadiene, benzene), Zeise's salt and comparison of synergic effect with that in carbonyls.

Metal alkyls and Metal-carbene complexes

**Unit-3: Synthesis, Reactions and Applications of Organometallic Compounds (Hours: 16)**

General methods of synthesis of metal carbonyls: direct carbonylation, reductive carbonylation, thermal and photochemical decomposition, of mono and binuclear carbonyls of 3d series.

Reaction of metal carbonyls: reduction, oxidation, photochemical substitution, migratory insertion of carbonyls, and nucleophilic addition of CO.

Synthesis of metal-alkene complexes through ligand addition, reduction and substitution and reaction of metal bound alkenes, Zeise's salt

Metal-sandwich compounds: Ferrocene: synthesis, physical properties and reactions: acylation, sulfonation, alkylation metallation, acetylation, chloromercuration, Mannich reaction, comparison of aromaticity and reactivity of ferrocene with that of benzene.

Synthesis and reactions of Metal alkyls and Metal-carbenes

**Unit-4: Catalysis by Organometallic Compounds (Hours: 11)**

General principles of catalysis, properties of catalysts, homogeneous and heterogeneous catalysis. (Catalytic steps, examples and industrial applications), deactivation and regeneration of catalysts, (catalytic poisons and promoter).

Organometallic catalysis of the following reactions of commercial importance and their mechanism:

1. Alkene hydrogenation (using Wilkinson's Catalyst)
2. Synthetic gasoline preparation (Fischer Tropsch reaction)
3. Polymerisation of ethene using Ziegler-Natta catalyst
4. Wacker oxidation process (Smid process)
5. Hydroformylation reaction (Oxo-process)
6. Monsanto Acetic Acid process

**Theoretical aspects of enlisted practicals are also to be included in the theory paper.**

**Practical component**

**Practical:**

**Credits: 01**

**(Laboratory periods: 15 classes of 2 hours each)**

1. To study and compare the UV-Vis spectrum of ferrocene (in methanol or acetonitrile) and potassium ferrocyanide (in water).
2. To study the cyclic voltammogram of ferrocene.
3. Preparation of Bis(acetylacetonato)copper(II) complex and characterisation through UV-Visible spectrum of its aqueous solution..
4. Preparation of tris(acetylacetonato)manganese(III) complex.
5. Preparation of Potassium tris(oxalato)ferrate(III) complex.
6. Preparation of Tetraamminecopper(II) sulphate monohydrate complex.
7. Preparation of Pentaamminechloridocobalt(III) chloride.
8. Preparation of Hexaamminecobalt(III) chloride
9. Determination of number of chloride ions in ionisation sphere to confirm the formula of complexes prepared in (6) and (7) through potentiometric titration or conductance measurements. (See reference 5 & 6 of Practicals)
10. Compare and interpret the visible spectrum of complexes prepared in (6) and (7) for shifts in wavelength maxima.

**Any other organometallic compounds synthesised from time to time may also be included.**

#### **Essential/recommended readings**

##### **Theory:**

1. Gary L Miesler, Paul J Fiesher, and Donald A Tarr, **Inorganic Chemistry** 5<sup>th</sup> Edition, Pearson.
2. Shriver & Atkins **Inorganic Chemistry**, Edn V, W.H. Freeman and Company.
3. F.A. Cotton & G. Wilkinson, **Advanced Inorganic Chemistry**, 5th Edition.
4. William W. Porterfield, **Inorganic Chemistry**, 1<sup>st</sup> Edition.
5. Huheey, J.E.; Keiter, E.A., Keiter; R. L.; Medhi, O.K. (2009), **Inorganic Chemistry- Principles of Structure and Reactivity**, Pearson Education.
6. Principles of Organometallic Chemistry by M.L.H Green, Coward, G.E Coates and K.Wade 3<sup>rd</sup> Edition.
7. Cotton, F.A.; Wilkinson, G.; Gaus, P.L. **Basic Inorganic Chemistry**, 3<sup>rd</sup> Edition, Wiley India.
8. Greenwood, N.N.; Earnshaw, A. (1997), **Chemistry of the Elements**, 2<sup>nd</sup> Edition, Elsevier.
9. Gupta, B. D., Elias, A. J., (2013) **Basic Organometallic Chemistry: Concepts, Syntheses and Applications**, 2<sup>nd</sup> Edition, Universities Press.

##### **Practicals:**

1. ChemTexts (2020) 6:22, <https://doi.org/10.1007/s40828-020-00119-6>
2. J. Chem Education: 1971, Volume 48(2), 133
3. Front. Chem. Sci. Eng. 2013, 7(3): 329–337, DOI 10.1007/s11705-013-1339-0
4. Orbital: Electron. J. Chem. 2019, 11 (6): 348-354

6. Vogel's text book of quantitative chemical analysis. Edn V

**Note:** Examination scheme and mode shall be as prescribed by the Examination Branch,  
University of Delhi, from time to time.