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Register Number:

DATE: **12** **-04-2018 (1 PM)**

**ST. JOSEPH’S COLLEGE (AUTONOMOUS), BENGALURU-27**

**End Semester Examination, April, 2018**

**IV Semester M.Sc. Chemistry**

**CH 0216 – Organometallic Chemistry & Inorganic Reaction Mechanisms**

Time: 2½ hours Max. Marks:70

***Note: This question paper has 2 pages and 3 sections***

**PART A**

**Answer any SIX of the following: 6 X 2 = 12**

1. The self- exchange rate constant of [Co(NH3)6]2+/[Co(NH3)6]3+ couple is 10-6mol-1s-1 while that of [Ru(NH3)6]2+/ [Ru(NH3)6]3+ couple is 8.2×102 mol-1s-1. Explain.
2. Represent any one racemization pathway of a tris-chelate complex that goes through bond rupture.
3. Mention any two conditions under which β-elimination does not occur in transition metal alkyls.
4. Explain how cyclobutadiene is stabilized on complexation with a metal.
5. State 18 - valence electron rule. Give any one of its limitations.
6. Compare alkali metal organyls with respect to their nucleophilic character and solubility in organic solvents across the group. Justify your order.
7. What is ‘Collman’s reagent’? Give anyone of its synthetic applications.
8. What is a fluxional structure? Explain with an example of a metallocene.

**PART B**

**Answer any FOUR of the following: 4 X 12 = 48**

1. a) Explain the SN1CB mechanism of base hydrolysis in octahedral complexes using a suitable example. Give any two evidences for this mechanism. Write and explain the rate law of this reaction.

b) Discuss the bonding in transition metal- alkene complexes. Bring out the essential difference beween the two extreme modes of binding in these complexes. (6+6)

1. a) Discuss the theories of trans effect .

b) Draw and explain the cycle for the photochemical reduction of water to hydrogen using [Ru(bpy)3]2+ as the photosensitizer and methyl viologen as the reductive quenching agent.

(6+6)

1. a) What are the main characteristics of Fischer carbene complexes? Explain these characteristics in terms of bonding in these complexes.

b) Using suitable MO diagrams explain why a 16- electron ML4 complex is considered to be isolobal with a CH2 fragment. If cyclopropane is considered as a trimer of CH2 fragments, draw the structure of the trimer of Os(CO)4. (6+6)

1. a) Outline the catalytic cycle of Monsanto acetic acid process.

b) Explain the following reactions with an example each:

(i) Hydrometallation (ii) Oxidative addition (8+4)

1. a) Write a note on ‘ Zeigler’s Growth reaction’. What are the limitations of this reaction?

b) Describe the structure of Be(CH3)2 in the gas phase and solid state.

c) Discuss any two applications of organoselinium compounds in organic synthesis. (4+4+4)

1. a) Discuss any three applications of trialkylsilyl derivatives of organic compounds.

b) Draw the catalytic cycle of Heck reaction. (6+6)

**PART C**

**Answer any TWO of the following: 2 X 5 = 10**

1. a) For [PtX4]2- complexes both ligand exchange rate and thermodynamic stability increase in the order X= Cl < Br < I < CN. Explain why these observations are **not** inconsistent.

b) Predict M if it is a first row transition element and [M(η3-C3H5)(CO)5]is a stable complex. (3+2)

1. Show the steps of the electron-transfer mechanism that accounts for the following reaction. Note that one of the reactant metal ion is labeled making its identification in the products possible.

[\*Co(NH3)5-NCS]2+ + 5 CN- + Co2+(aq) → [Co(CN)5-SCN]3- + 5 NH3 + \*Co2+(aq).

1. Identify A, B & C in the following reactions:



(2+2+1)

-----------End of questions-----------