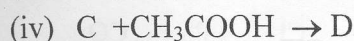
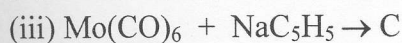
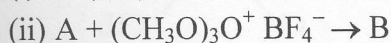
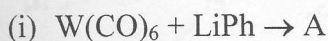


EASTERN UNIVERSITY, SRI LANKA
FOURTH EXAMINATIONS IN SCIENCE
FIRST SEMESTER 2011-2012 (Aug. 2016)
SPECIAL DEGREE IN CHEMISTRY
CHS 05: INORGANIC CHEMISTRY II

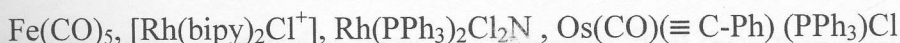
Answer all questions

Time allowed: 2 hrs

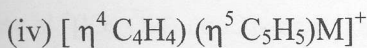
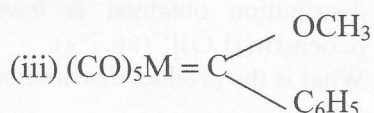
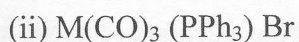
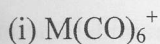
1. (a) Write down the structures of the major products in the following reactions.



(b) Among the complexes given below, deduce the complexes which exhibit the 18-electron rule.



(c) Following complexes obey the 18-electron rule. Identify the transition metal in each of these complexes.



2. (a) Given the following information:

An organometallic compound **A** reacts with sodium to give complex **B**. Treatment of **B** with methyl iodide yields a complex **C** which upon treatment with CO affords product **D**.

Complex A: Mass spectrum of parent ion at m/e of 490 and IR spectrum has a peak at 2070 cm^{-1} . 1H NMR exhibited a single peak due to a cyclopentadienyl ring. ^{13}C NMR gave two types of carbons in a 5:3 ratio.

Complex B: 1:1 electrolyte, IR spectrum showed terminal CO groups and cyclopentadienyl rings. ^{13}C NMR gave two types of carbons in a 5:3 ratio.

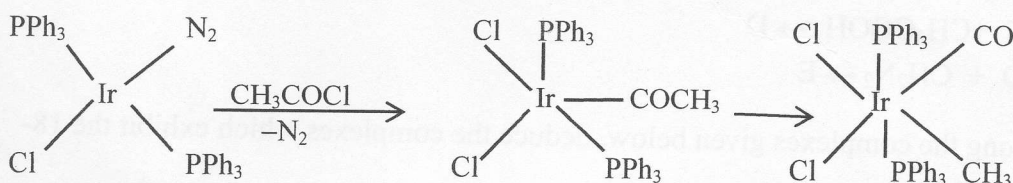
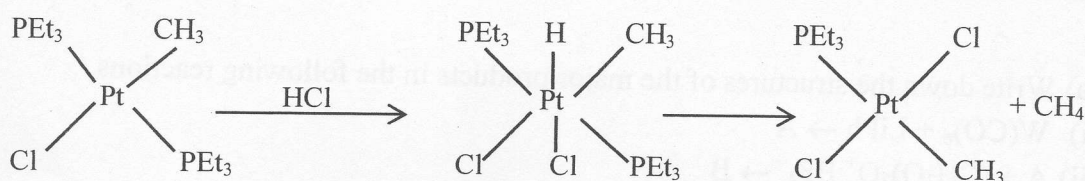
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Complex C: IR spectrum showed terminal CO groups and cyclopentadienyl rings. ^1H NMR exhibited a single peak due to a C-H of a cyclopentadienyl ring and CH_3 groups in a 5:3 ratio. ^{13}C NMR gave three types of carbons in a 5:3:1 ratio.

Complex D: IR spectrum showed terminal and ketonic CO groups and cyclopentadienyl rings. ^1H NMR exhibited a single peak due to a C-H of a cyclopentadienyl ring and CO groups in a 5:3 ratio. ^{13}C NMR gave four types of carbons in a 5:2:1:1 ratio.

Identify **A**, **B**, **C** and **D** explaining the reactions involved.

(b) Calculate the number of valence electrons and the formal oxidation state of the metal in each of the compounds in the following reaction sequence. Place the steps of these reactions into the different types of reactions encountered in homogeneous organometallic catalysis (e.g. oxidative addition, migratory insertion etc.).



3. (a) The complex $\text{trans}[\text{Co}(\text{en})_2\text{Br}_2]^{2+}$ undergoes acid catalysed hydrolysis where one of the coordinated Br^- ions undergoes substitution with a water molecule. Show that, if the substitution occurs via a trigonal bipyramidal intermediate and considering only statistical factors into account, the product distribution obtained is $\text{trans}[\text{Co}(\text{en})_2\text{Br}(\text{H}_2\text{O})]^{2+}$ (33%) and a racemic mixture of the $[\text{Co}(\text{en})_2\text{Br}(\text{H}_2\text{O})]^{2+}$ (66.7%).

What is the product distribution ratio if the reaction occurs via a square pyramidal intermediate?

- (b) The substitution reaction of Cl^- with NO_2^- in the complex, $\text{trans}[\text{Co}(\text{en})_2(\text{NO}_2)\text{Cl}]^+$ is very slow with a $t_{1/2}$ of over five hours while with the addition of a trace of NH_2^- , this reaction takes place in two minutes. However, the reaction of NO_2^- with the $\text{trans}[\text{Co}(\text{en})_2(\text{NO}_2)\text{OH}]^+$ is also very slow. Explain these observations giving a plausible explanation.

Contd.

Explain the following observations and answer **all** parts.

- (a) The rate constants for the acid hydrolysis for the complexes of the type $\text{Co}(\text{diamine})_2\text{Cl}_2^+$ for a series of diamines at 298 K are given below.

| Diamine | Rate constant/L mol ⁻¹ |
|--|-----------------------------------|
| $\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2$ | 3.2×10^{-5} |
| $\text{NH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2$ | 6.2×10^{-4} |
| $\text{NH}_2\text{C}(\text{CH}_3)_2\text{CH}_2\text{CH}_2\text{NH}_2$ | 4.2×10^{-3} |
| $\text{NH}_2\text{C}(\text{CH}_3)_2\text{C}(\text{CH}_3)_2\text{NH}_2$ | 3.2×10^{-2} |

Explain giving reasons whether the reaction is of the associative or the dissociative type. You may assume that there is little difference in the basicities of the ligand diamines in this series.

- (b) The rate of reduction of $[\text{Co}(\text{NH}_3)_5\text{NCS}]^{2+}$ by Ti^{3+} is very much slower than that of $[\text{Co}(\text{NH}_3)_5\text{N}_3]^{2+}$. Write down the steps in the electron transfer reaction for the reduction of $[\text{Co}(\text{NH}_3)_5\text{N}_3]^{2+}$.
- (c) Both V^{2+} and Cr^{2+} appear to reduce $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$ by an outer sphere mechanism. However, V^{2+} appears to react faster although the redox potential is more favourable with Cr^{2+} .

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