EASTERN UNIVERSITY, SRI LANKA

SPECIAL DEGREE EXAMINATION IN CHEMISTRY

(FEB/MARCH' 2014)

FOURTH YEAR FIRST SEMESTER-2009/2010

CHS 05 INORGANIC CHEMISTRY II

Answer all questions **Time allowed: 02 hours**

1. a) Using 18-electron rule indicate the probable numbers of carbonyl ligands in the following.
   i) $W(\eta^6\text{-}C_6H_6)(CO)_n$ ii) $Rh(\eta^5\text{-}C_5H_5)(CO)_n$ iii) $Ru_3(CO)_n$

   (30 marks)

   b) Give plausible equations to show the utility of metal carbonyl anions in the synthesis of M-C, M-H and M-M bonds.

   (30 marks)

   c) Give the probable structure of the product obtained from the treatment of $Mo(CO)_6$ with LiPh and followed by carbocation reagent, $CH_3OSO_2CF_3$.

   (20 marks)

   d) Propose a synthesis for $MnH(CO)_5$ starting with $Mn_2(CO)_{10}$ as the source of Mn and other reagents of your choice.

   (20 marks)

2. a) Ligand substitution reactions on metal clusters often occur by associative mechanism by M-M bond cleavage. If the mechanism is applicable, which of the following metal clusters would you expect to undergo faster exchange with added ^{13}CO. Explain.
   i) $Co_4(CO)_{12}$ ii) $Ir_4(CO)_{12}$

   (40 marks)

   b) Propose a set of reactions for the formation of $W(CO)_5(C(OCH_3)Ph)$ starting with hexacarbonyltungsten(0) and other reagents of your choice.

   (40 marks)

   c) Explain the difference in IR spectra of the following.
   $Mo(PF_3)_3(CO)_3$ *versus* $Mo(PMe_3)_3(CO)_3$

   (20 marks)

3. a) Predict the products of the following reactions and explain.

i) $[Pt(PR_3)_4]^{2+} + 2Cl^-$ ii) $[PtCl_4]^{2-} + 2\ PR_3$

(30 marks)

b) Write two step synthesis for *cis*- and *trans*-$[PtCl_2(NO_2)(NH_3)]^-$ starting from $PtCl_4^{2-}$.

(30 marks)

c) How does each of the following affect the rate of square-planar substitution reactions?

i) changing a *trans* ligand from H to Cl
ii) adding bulky substitution to a *cis* ligand
iii) increasing the positive charge of the complex
iv) changing the leaving group from Cl^- to I^-

(40 marks)

4. a) i) Explain the principle involved in catalysis with suitable diagram/s.

ii) Briefly discuss the differences between the homogeneous and heterogeneous catalyst.

(35 marks)

b) "The platinum-rhodium in the automobile catalytic converters is dispersed on the surface of a ceramic rather than is used in the form of thin foil". Briefly explain this statement.

(25 marks)

c) You are approached by an industrialist to develop catalysts for the following process at 80^0C with no input of electrical energy or electromagnetic radiation.

(i) The splitting of water into H_2 and O_2

(ii) The decomposition of CO_2 into C and O_2

(iii) The combination of N_2 with H_2 to produce NH_3

(iv) The hydrogenation of the double bonds in vegetable oil

The industrialist will build the plant to carry out the process and both will share the profits equally. Which of the above process/es would be worth to be investigated? Explain the decision with the basis of chemistry in each case.

(40 Marks)
