MURANG'A UNIVERSITY OF TECHNOLOGY

SCHOOL OF PURE AND APPLIED SCIENCES

DEPARTMENT OF PHYSICAL AND BIOLOGICAL SCIENCES

UNIVERSITY POSTGRADUATE EXAMINATION

2018/2019 ACADEMIC YEAR

FIRST YEAR **SECOND** SEMESTER EXAMINATION FOR MASTER OF SCIENCE IN CHEMISTRY

ACH 604 – ADVANCED CO-ORDINATION CHEMISTRY

DURATION: 3 HOURS

DATE: 23/04/2019

TIME: 9.00-12.00 PM

Instructions to candidates:

1. Answer **Any Four** questions.
2. Mobile phones are not allowed in the examination room.
3. You are not allowed to write on this examination question paper.
4. Plank's constant h = 6.626×10^{-34}J.s
5. Speed of Light = 3.0×10^{8} m/s

QUESTION ONE (25 MARKS)

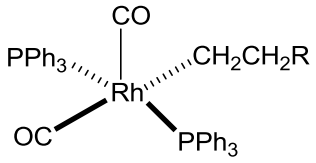
a) The total electron pairing energy (π_{total}) has two components, π_c and π_e. Determine the total pairing energy of the following complexes:

i. d^6 high spin (3 marks)

ii. d^7 low spin (3 marks)

iii. d^9 (3 marks)

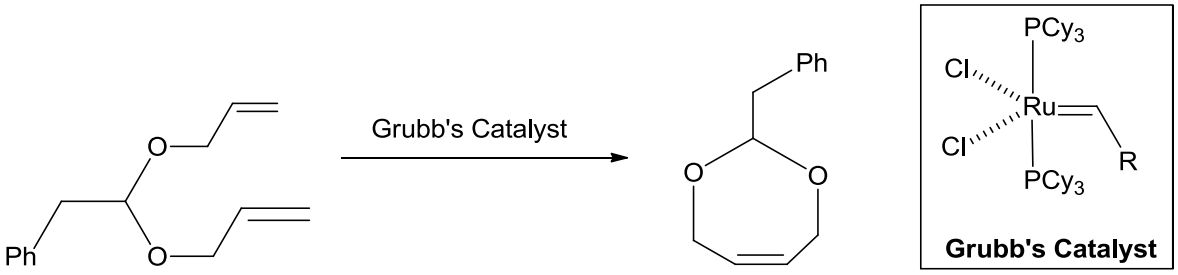
b) Using the Rhodium complex below, draw a mechanism to show:



i. 1, 1 – migratory insertion (4 marks)

ii. 1, 2 – migratory insertion (4 marks)

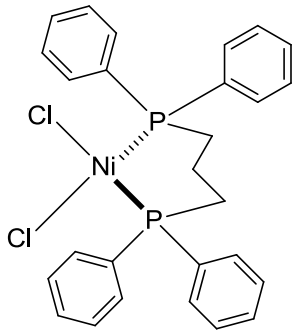
c.) Write detailed chemical mechanism for the following ring closing metathesis reaction (8 marks)



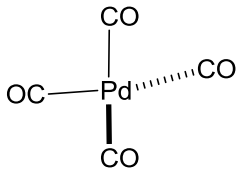
QUESTION TWO (25 MARKS)

a) While using Crystal Field Theory, write the d^n configuration of each of the transition metal ion in the following complexes (8 marks)

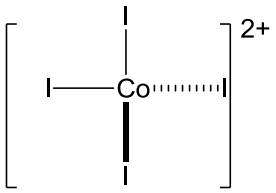
i.)



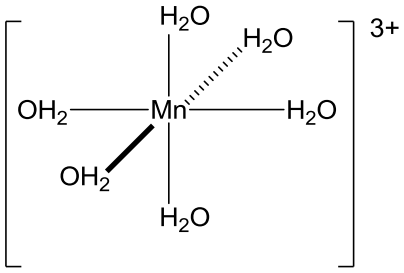
iii.)



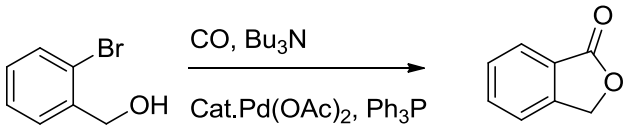
ii.)



iv.)

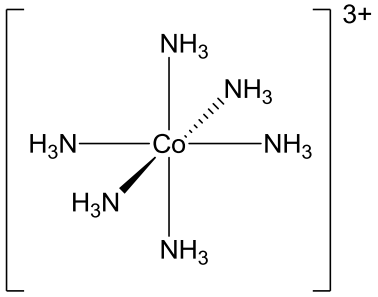


b) Write a detailed chemical mechanism for the following chemical transformation



(6 marks)

c) Consider the following complex



If the complex splitting energy (Δ_o) was found to be 12,456 cm^{-1} while the coulombic term (π_c) of 21,800 cm^{-1} and exchange term (π_e) of -3,750 cm^{-1}. Determine the energy for:

i. High spin complex (4 marks)

ii. Low spin complex (4 marks)

iii. Explain which complex is most stable (3 marks)

QUESTION THREE (25 MARKS)

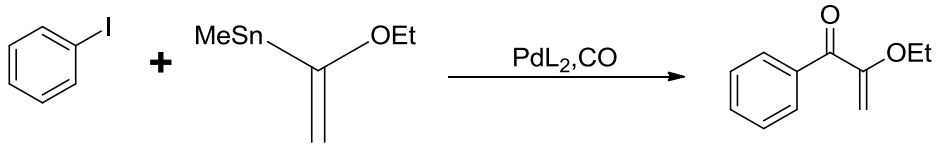
a) Using Ligand field theory approach, draw splitting energy diagram for δ-only Metal-Ligard orbitals in:

i. Tetrahedral complex (6 marks)

ii. Octahedral complex (6 marks)

iii. Explain how angular overlap method (AOM) is used to estimate energy of d-orbitals in transition metal complexes (3 marks)

b) Write a detail mechanism showing the following transformation (6 marks)



c) The octahedral crystal field energy (Δ_o) of a cobalt complex was found to be $3.64\times10\text{-}^{23}$J/ion. Determine:

i. The absorption wavelength of the complex (2 marks)

ii. Predict the colour of the solution (2 marks)

QUESTION FOUR (25 MARKS)

a) Explain and classify the following reactions as oxidative addition, reductive elimination or migratory insertion

i.) $Ir(PPh_3Me)_2(CO)Cl + CF_3I \longrightarrow Ir(I)(CF_3)(PPh_3Me)_2(CO)Cl$ (3 marks)

ii.) $TiCl_4 + 2Et_3N \longrightarrow TiCl_4(NEt_3)_2$ (3 marks)

iii.) $HCo(CO)_3(CH2{=}CHCH3) + CO \longrightarrow CH_3CH_2CH_2Co(CO)$ (3 marks)

b) Calculate the Ligand field stabilization energies (LFSE) of the octahedral complexes formed by Co^{2+} and:

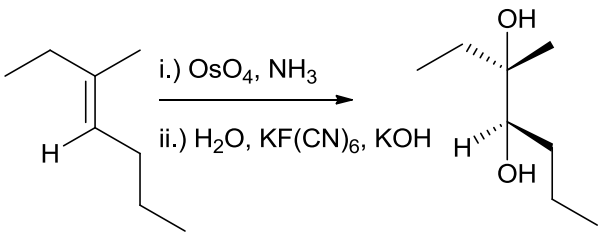
i. Cl^- (weak field) (3 marks)

ii. CN^- (strong field) (3 marks)

iii. NH_3 (intermediate) (3 marks)

iv. Arrange the complexes in order of increasing stability (2 marks)

c) Give a detail chemical mechanism to show the following transformation (5 marks)



QUESTION FIVE (25 MARKS)

a) Using ethane as an example, write a β-hydride elimination mechanism (4 marks)

b) Calculate the crystal field stabilization energies for a d^8 system in:

i. Octahedral complex (3 marks)

ii. Tetrahedral complex (3 marks)

c) State two factors that determine the value of Δ_o (splitting energy of a complex) (2 marks)

d) The absorptions for the complex ion $[Co(NH_3)_6]^{3+}$ occurs at 596nM

i. Predict the colour for the complex (4 marks)

ii. Calculate the crystal field stabilization energy in KJ/mol (3 marks)

e) Write a detailed chemical mechanism for the following Stille reaction (6 marks)