

THE OPEN UNIVERSITY OF SRI LANKA

B.Sc./B.Ed. DEGREE /STAND ALONE COURSES IN SCIENCE- LEVEL 5

FINAL EXAMINATION-2008/2009

CHU3127/CHE5127 - ORGANOMETALLIC CHEMISTRY

Date: 20th January 2009 (Tuesday)

Time 1.00 – 3.30 p.m.

Answer any **FOUR** (04) questions. If more than four questions are answered, **only the first four answers will be marked.**

1. (a) Give IUPAC name for each of the following complexes.
- $[\text{RuBr}(\eta^6\text{-C}_6\text{H}_6)(\eta^3\text{-C}_3\text{H}_5)]$
 - $[\text{CoCl}(\eta^2\text{-C}_2\text{H}_4)(\text{CO})(\eta^4\text{-C}_4\text{H}_4)]$ (20 marks)
- (b) Draw the **structures** of the following complexes,
- Bromo(η^5 -cyclopentadienyl)di(η^2 -ethene)chromium.
 - (η^3 -Allyl)carbonylbis(triphenylphosphine)(vinyl)ruthenium.
 - Bromocarbonyl(η^6 -cycloheptatriene)(methyl)iron (30 marks)
- (c) (i) Determine the valence electron count (VEC) of the complex $[\text{CoBrH}(\eta^3\text{-C}_3\text{H}_5)(\text{CO})(\eta^2\text{-C}_2\text{H}_4)]$ using the **ionic model**. (Indicate in your work out, the electron contribution made by each ligand, Co is a Group 9 metal).
- (ii) Determine the valence electron count (VEC) of the complex $[\text{NiCl}(\text{Me})(\text{PPh}_3)(\eta^4\text{-C}_4\text{H}_4)]$ using the **covalent model**. (Indicate in your work out, the electron contribution made by each ligand, Ni is a Group 10 metal). (22 marks)
- (d) The iron complex $[\text{FeCl}(\text{Br})(\text{PPh}_2)_2]$ shows **three** isomers with the **trigonal-pyramidal** geometry. Draw the **structures** of them. (18 marks)
- (e) Arrange CS, N₂ and NO in the order of increasing π -acceptability. (10 marks)

2. (a) Draw the orbital diagrams showing (i) σ -orbital overlap and (ii) π -orbital overlap between Ru and N_2 in the cation $[Ru(NH_3)_5(N_2)]^{2+}$. (20 marks)

(b) The complex $[RhH(CO)(PPh_3)_3]$ reversibly loses two PPh_3 ligands to give two intermediates (A) and (B) containing 16 and 14 electrons, respectively. Write the reaction sequence for this dissociation process. (20 marks)

(c) How would you account for the variation in the CO stretching frequency in the following compounds?

Compound	$\nu(CO)$ in cm^{-1}	
free CO	2143	
$[Cr(CO)_6]$	2000	
$[V(CO)_6]^-$	1860	(20 marks)

(d) The tetrahedral d^{10} -complex $[Pt(PEt_3)_4]$ undergoes a 2e-oxidative addition reaction with PhI to give a four coordinated neutral complex (C). Draw and identify the two possible structures for (C). (20 marks)

(e) What is an β -agostic interaction? $[W(CO)_3(PCy_3)_2]$ has an octahedral arrangement with one agostic type interaction. Draw structure of the complex and identify the type of agostic interaction associated with it. (Cy = cyclohexyl) (20 marks)

3. (a) Reaction of pinacolone oxime, $(Me)_2CC(=NOH)Me$, with $Na_2[PdCl_4]$ and $NaOAc$ gives the cyclometallated chloride-bridged palladium(II) dimer which contains a 5-membered chelate ring. Draw the structure of this dimeric complex (20 marks)

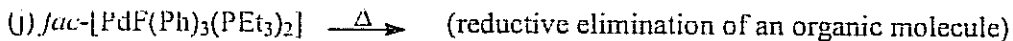
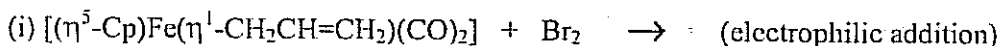
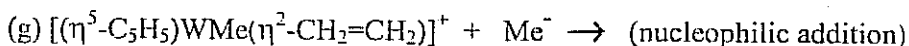
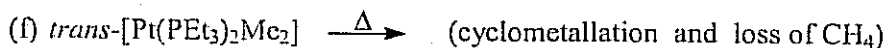
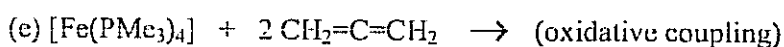
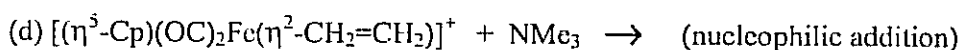
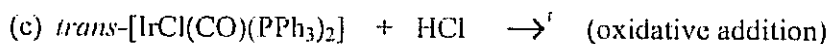
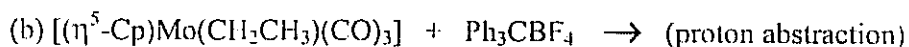
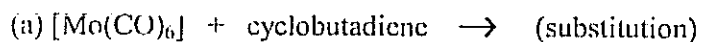
(b) $Na[Re(CO)_5]$ reacts with $CH_2=CHCH_2I$ to give (P) and NaI . On heating, (P) gives (Q) and CO . Identify (P) and (Q). (20 marks)

(c) What is a carbene ligand? Explain the bonding between a carbene ligand and a metal centre using orbital diagrams. (20 marks)

(d) Reduction of $[Re_2(CO)_{10}]$ with Na gives the salt (X), which reacts with PhI to give the complex (Y) and NaI . (Y) in the presence of CO gives (Z). Identify (X), (Y) and (Z). (30 marks)

(e) What is the major product formed due to cross-coupling of $PhMgBr$ with 2-bromopyridine in the presence of the catalyst $[Pd(PPh_3)_4]$. (10 marks)

4 Predict the major product(s) of each of the following reactions, using the hint given in the brackets).

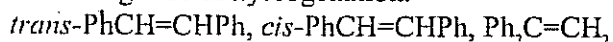


(10 x 10 marks)

5. (a) How would you prepare the acyl complex $[(\eta^5\text{-Cp})(\text{OC})_2\text{FeC}(=\text{O})\text{Et}]$ from $[(\eta^5\text{-Cp})\text{FeH}(\text{CO})_3]$?

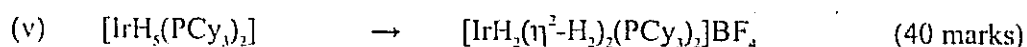
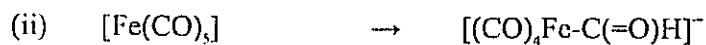
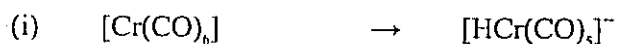
(20 marks)

(b) Hydrogenation of olefins gives alkanes. Arrange the following olefins in the order of increasing ease of hydrogenation.

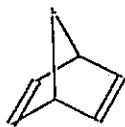


(15 marks)

(c) Suggest reagent(s), which can be used to carry out the following conversions.



- (d) $[\text{Mo}(\text{CO})_n]$ reacts with **three** moles of PPh_3 to give a coordinatively saturated mononuclear tricarbonyl $\text{Mo}(0)$ complex $\bar{\text{R}}$, which shows **two** infra-red bands in the carbonyl region. Deduce the structure of $\bar{\text{R}}$. (15 marks)
6. (a) $[\text{RhCl}(\text{PPh}_3)_3]$ catalyses the hydrogenation of $\text{RCH}=\text{CH}_2$ to RCH_2CH_3 . Draw the **catalytic cycle** for this process. (40 marks)
- (b) In the presence of $[\text{PdL}_4]$ ($\text{L} = \text{PPh}_3$), $\text{ArCH}=\text{CH}_2$ reacts with PhBr to give *trans*- $\text{ArCH}=\text{CHPh}$ and HBr . Draw the **catalytic cycle** for this process. (30 marks)
- (c) Give the **active catalyst(s)** for the following processes. (20 marks)
- Wacker process
 - Original Roelen Process.
 - Monsanto acetic acid process
 - Hydrocyanation of ethene by NiL_4 , $\text{L} = \text{P}(\text{OPh})_3$.
- (d) Draw the **structure** of the polymer formed due to ring opening metathesis polymerization of norbornadiene. (10 marks)



(norbornadiene)