CHEM 416 ORGANOMETALLIC CHEMISTRY EXAM APRIL 2023

CHUKA UNIVERISTY

UNIVERSITY EXAMINATIONS

FOURTH YEAR EXAMINATIONS FOR THE AWARD OF BACHELOR OF SCIENCE

CHEM 416: ORGANOMETALLC CHEMSTRY TIME 2 HOURS

STREAMS BSC(Y4S2)

INSTRUCTIONS: Question **ONE** and any other **TWO** questions

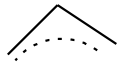
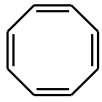
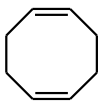
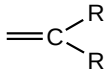
QUESTION ONE [30marks]

(a) (i). Define an organometallic compound and discuss briefly compounds that are regarded as organometallic compounds and those that are not **[3marks].**

(ii). Wilkinson's catalyst $Rh(PPh_3)_3Cl$ does not qualify in the definition of an organometallic compound though it is used as a hydrogenation catalyst for olefins? Comment **[1marks].**

b) (i). Based on the bond type, discuss the three broad classes of organometallic compounds. Give an example of each **[4marks]**

(ii) Give the names of the following ligands commonly used in organometallic chemistry **[2.5marks]**

I.  II.  III.  IV.  V. 

(iii) Give the formal names of the following compounds **[1.5marks]**

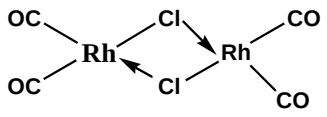
I. $(\eta^5\text{-}C_5H_5)_2Fe$ II. $[RhMe(PMe_3)_4]$ III. $(\eta^3\text{-}\ C_3H_5)Mn(CO)_4$

b).(i).State the 18 electron rule as applied to organotransition compounds

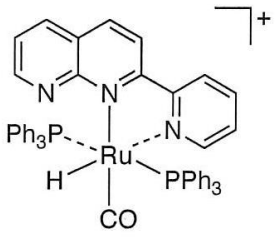
[2marks]

(ii). The following are recently prepared organometallic compounds. Determine the valence electron counts and the formal oxidation state of the metal for each compound. Show which of the compounds obey the 18e rule **[6marks]**

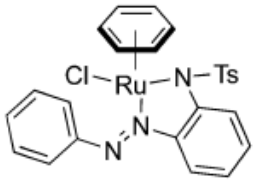
(i)



(ii)



(iii)



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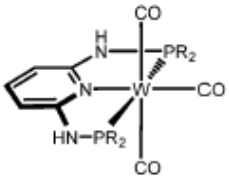
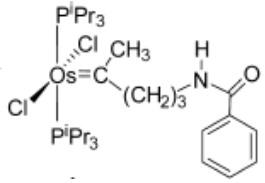


(v)



c).For **ANY TWO** of the following complexes, determine the total valence electrons(TVE), the total number of M-M bonds in the complex and the number of M-M bonds each metal makes with the other metal.**[6 marks]**

i. $Fe_3(CO)_{12}$ ii . $Co_4(CO)_{12}$

iii. $[(\eta^5\text{-}C_pMo(CO)_2]_2$ iv. $(\eta^4\text{-}C_4H_4)_2Fe_2(CO)$

(d) On the basis of 18 electron rule, determine the unknown quantity in the following stable complexes [**4 marks]**

(i). $[(\eta^5\text{-}C_5H_5)Fe(CO)_3]^z$ (ii). $[C_pMn(CO)_x]_2$ (Compound has Mn=Mn double bond])

(iii) [$Co(CO)_3]^z$ (iv) $[Ni(CO)_3(NO)]^z$ (assume linear NO)

QUESTION TWO [20marks]

a). (i). Define the term hapticity. Explain with a relevant example **[1.5marks]**

(ii). What hapticities are possible for interaction of each of the following

Ligands? **[2marks]**

I. $C_3H_5^+$ II. Butadiene III. Cyclopentadienyl IV. C_6H_6

b). Explain using a sketch what you understand by the following notations used in organometallic chemistry **[5marks]**

(i). μ–CO, (ii).μ_4–PR, (iii) η^5–C_5H_5, (iv) η^6 –C_6H_6 , (v) μ_3– H

c) In the complexes given below, M is either a first row or a second row transition metal. Identify M if the metal obeys 18e^- rule **[7.5marks]**

(i) $[M(CO)_3PPh_3]^-$ (ii).$HM(CO)_3$ (iii) $[M(CO)_3(NO)]^-$ (Compound contains linear NO) (iv) [η^4–$(C_4H_6)M(CO)_3$] (v). $[\eta^5$–$C_5H_5M(CO)_3]_2$ (Compound has 1 M–M bond)

d) Give explanation to the following observations

(i) Cyclopentadienyl (Cp) and carbon monoxide (CO) ligands are regarded as versatile in their bonding modes while triphenylphosphine ligand (PPR_3) is not.**[2marks]**

(ii) Carbon atoms in CO and CN^- ligands are the preferred bonding sites in metal carbonyls and cyanide complexes respectively **[2marks]**

QUESTION THREE [20 marks]

a).(i) Explain what is meant by the term π– acid ligands and discuss how they stabilize transition metals in low oxidation state **[4 marks]**

(ii) Give two examples of π– acid ligands **[2marks]**

b) (i) What is synergic effect? Using a clear orbitals interaction diagram explain how synergic bonding in metal carbonyls occur. **[2.5marks]**

(ii) What is the difference between synergic bonding in transition metal carbonyls and synergic bonding in transition metal alkene compounds? **[2 marks]**

c).(i) Explain how you can distinguish experimentally between a terminally bonded CO and a bridged (CO) in metal carbonyls **[1.5marks]**

(ii). The stretching frequencies of Carbon monoxide in $Ni(CO)_4$, $Co(CO)_4$ and $Fe(CO)_4]^-$ compounds are in order, 2128, 1918 and 1788 cm^{-1} respectively. Explain this observation [**4 marks**]

d). Select the best choice in each of the following complexes and briefly justify the reasons for your choice

(i) Complex with the shortest C-O bond: $Ni(CO)_4$, $[Co(CO)_4]^-$, $[Fe(CO)_4]^{2-}$ **[2marks]**

(ii) Complex with the lowest C-O stretching frequency $Cr(CO)_6$, $[V(CO)_6]^-$, $[Fe(CO)_4]^{2-}$ **[2marks]**

QUESTION FOUR [20 marks]

(a).(i). Although not an organic ligand, the nitrosyl(NO) ligand has similarities to CO. List similarities and differences between these twos ligands in their bonding modes **[2.5marks]**

(ii). Why is a neutral NO ligand never a two electron donor**?.[1 mark]**

(iii). Explain the two different bonding modes in metal nitrosyls **[2marks]**

(b) (i). What are spectator ligands? Give one example of a spectator ligand that you know. What is the importance of these ligands in the study of organometallic chemistry? **[1.5marks]**

(ii). Define Tolman cone angle **[1.5marks]**

(iii) The Tolman cone angles of PPh_3 and $P(4\text{-}MeC_6H_4)_3$ ligands are both 145^0, but that of $P(2\text{-}MeC_6H_4)_3$ is 194^0. Draw the three ligands and comment on their Tolman cone angle **[2.5marks]**

(d). (i). Distinguish between a singlet and tripet carbene **[2marks]**

(ii). Discuss the difference between Schrock carbenes and Fischer carbenes in their bonding properties **[2.5 marks]**

(iii). Discuss briefly the Dewar – Chatt– Duncanson bonding model in metal alkenes **[5 marks]**.

QUESTION FIVE [20 marks]

a).(i) Arrange the following ligands in order of decreasing π– acidity

$P(CH)_3$, PCl_3, PF_3, $P(OCH_3)_3$, $P(OC_6H_5)_3$.Explain your answer**[3marks]**

(ii).The stretching frequencies(vCO) of $[Cr(CO)_3(NH_3)_3]$ and$[Cr(CO)_6]$.appear at 2100cm^{-1} and 1900 cm^{-1} respectively. Comment **[2marks]**

b).How would the metal– carbon (M–C) and carbonyl stretching (CO) frequencies in IR of the complex $M(CO)_6$ vary if

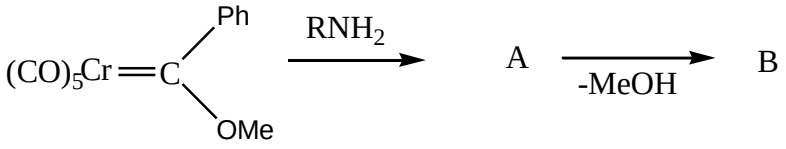
(i) One CO group of the complex is replaced by PR_3

(ii) a positive charge is introduced on the metal atom

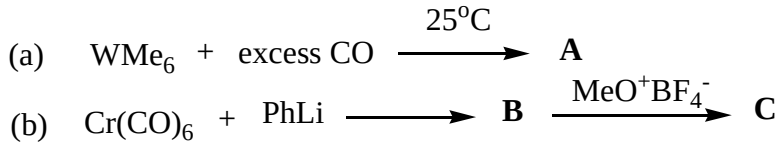
(iii) A negative charge is introduced on the metal atom

Explain your answer **[4.5marks]**

c). (i). Name Product A and B in the following reaction **[2marks]**



(ii). What are the major products **A, B** and **C** of the reactions shown below? **[3 marks]**



d) (i). Using Wilkinson's catalyst **$Rh(PPh_3)_3Cl$** as an example explain the meaning of the term "coordinative unsaturation" **[1.5marks]**

(ii) Outline six fundamental steps which show the function of Wilkinson's catalyst in the hydrogenation of alkenes to alkanes. Give an appropriate designation for each type of reaction step (such as oxidative addition, reductive elimination etc) **[5marks]**