CHUKA  **UNIVERSITY**

UNIVERSITY EXAMINATIONS

FOURTH YEAR EXAMINATION FOR THE AWARD OF DEGREE OF BACHELOR OF SCIENCE

CHEM 416: ORGANOMETALLIC CHEMISTRY

STREAMS: **TIME: 2 HOURS**

DAY/DATE: MONDAY 20/09/2021 **11.30 A.M – 11.30 A.M**

INSTRUCTIONS

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

QUESTION ONE [30MARKS]

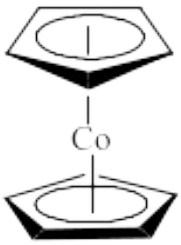
(a).(i).Explain briefly what is organometallic chemistry [2marks]

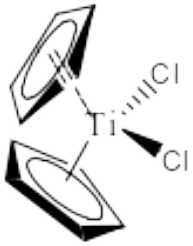
(ii) Discuss briefly the importance of studying organometallic chemistry as a sub discipline of chemical sciences. [2marks]

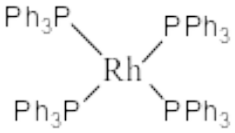
(b). Explain by giving examples the basis on which organometallic compounds may conveniently be classified [3marks]

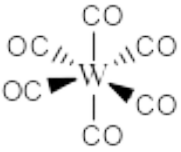
(c). (i). State the 18 electron rule as applied to organotransition compounds [2marks]

(ii). Determine the valence electron counts for the following complexes and show the ones that obey the 18 electron rule [9marks]

(i) 

(ii) 

(iii) 

(iv) 

(v) η^5-$C_5H_5Ni(NO)$ [NO is linearly bonded]

(d) For 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. Also draw the most appropriate structure in each case. [12marks]

i. $Fe_3(CO)_{12}$ ii $Co_4(CO)_4$

iii $[(\eta^5\text{-}C_pMo(CO)_2]_2$ iv $(\eta^4\text{-}C_4H_4)_2Fe_2(CO)_3$

QUESTION TWO [20MARKS]

(a) 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^4-C_6H_6 , (v) μ_3- H.

(b) Why can Cp and CO ligands be regarded as being versatile in their bonding modes while PPh_3 is not. [2marks]

(c). For each of the following pairs of organometallic compounds, identify the species that has a greater thermal stability and justify your choice .[4marks]

(i). $CH_3Mn(CO)_5$ versus $CF_3Mn(CO)_5$

(ii) $[Co(CO)_4]^-$ versus $[Cu(CO)_4]^-$

(d). On the basis of the 18-e rule identify the first –row transition metal for each of the following .

[4.5marks]

(i). $[M(CO)_7]^+$ (ii)[$M(CO)_3PPh_3$]$^-$ (iii) $[\eta^5\text{-}C_5H_5M(CO)_3]_2$ [Compound has 1 M-M bond]

(e).On the basis of the 18-e rule, determine the expected charge on the following organometallic complexes. [4.5marks]

(i). [$Co(CO)_3]^z$ (ii) $[Ni(CO)_3(NO)]^z$ (assume linear NO) (iii). $[(\eta^5 C_5H_5)Fe(CO)_3]^z$

QUESTION THREE [20 MARKS]

(a)(i). Draw the molecular energy level diagram for carbon monoxide (CO)[show clearly the HOMO and LUMO and their characteristics] [3marks]

(ii) Explain precisely what is meant by the term π- acid ligands and discuss how they stabilize transition metals in low oxidation state [2 marks]

(iii) 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? [1.5marks]

c).(i) Explain how you can distinguish experimentally between a terminally bonded CO and a bridged (CO) in metal carbonyls [2marks]

(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. Discuss this observation [3marks]

(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. Discuss in details similarities and differences between these twos ligands in their bonding modes. [3marks]

(ii).The cyanide ion (CN^-) as a ligand is isoelectronic with CO and as such exhibits structural and chemical properties parallels with CO yet, its compounds are often studied in the context of classical coordination chemistry rather than organometallic chemistry. Discuss this assertion [2marks]

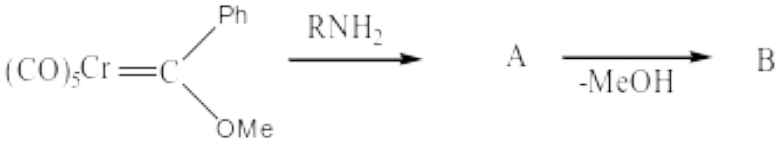
(b).) (i). Define Tolman cone angle [2marks]

(ii) 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]

(c). (i). Distinguish between a singlet and tripet carbene [3marks]

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

(d). (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]