UNIVERSITY OF EMBU

2017/2018 ACADEMIC YEAR

SECOND SEMESTER EXAMINATIONS

FOURTH YEAR EXAMINATION FOR THE DEGREE OF BACHELOR OF SCIENCE AND BACHELOR OF EDUCATION (SCIENCE)

SCH 404: ORGANOMETALLIC CHEMISTRY

DATE: APRIL 12, 2018 **TIME: 2:00-4:00PM**

INSTRUCTIONS:

Answer question ONE and any other TWO questions

QUESTION ONE (30 MARKS)

a) Define the following terms: (6 marks)
   i) Organometallic compound.
   ii) Hapticity
   iii) Transmetalation

b) What are the three broad classes of organometallic compounds? Give an example of each. (6 marks)

c) Organometallic reagents are useful synthetically because they react as if they were free carbanions. Explain. (3 marks)

d) Using an equation, briefly explain how Grignard reagents prepared? (3 marks)

e) Determine the formal oxidation number and electron count of the metal atom in: (6 marks)
   i) $[Fe(\eta^5\text{-}C_5H_5)_2]$
   ii) $[Cr(\eta^5\text{-}C_5H_5)(\eta^6\text{-}C_6H_6)]$
   iii) $[Mn(CO)_5]^-$.

f) List three factors that influence the degree of association of organolithium compounds. (3 marks)

g) Give the formal names for the following compounds: (3 marks)
   i) Ferrocene, $[Fe(\eta^5\text{-}C_5H_5)_2]$
   ii) $[RhMe(PMe_3)_4]$

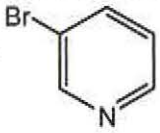
iii) $[Mo(\eta^6\text{-}C_6H_6)(CO)_3]$

QUESTION TWO (20 MARKS)

a) Which of the two isoelectronic compounds Cr(CO)6 and [V(CO)6]- will have the higher CO stretching frequency? Explain. (3 marks)

b) Describe any two important general methods of preparing organometallic compounds. (4 marks)

c) Draw the products of the following organometallic reactions. (4 marks)

i. C_4H_9Li + 

⟶

ii.  + $Hg(OCOCH_3)_2$ ⟶

d) Write equations for a two-step preparation of $(\eta^5\text{-}C_5H_5)_2Ni$ from C_5H_6, Na and $NiCl_2$. (4 marks)

e) Predict the products from the hydroboration of: (2 marks)

i. $3\ (CH_3)_2C{=}CH_2 + BH_3$ ⟶

ii. $CH{\equiv}CH + BH_3$ ⟶

f) Explain the difference between a Fischer-type carbine and a Schrock-type carbine. (3 marks)

QUESTION THREE (20 MARKS)

a) Write a balanced equation showing the overall net reaction in the hydroformylation process. (2 marks)

b) The hydroformylation of pent-2-ene using $Co_2(CO)_8$ as the catalyst was found to give rise to three aldehydes in the ratio 35:12:5. Suggest which of the three products was formed the most and which in the least amount. (4 marks)

c) Draw out a catalytic cycle for the conversion of pent-1-ene to hexanal using $HRh(CO)_4$ as the catalyst precursor. (14 marks)

QUESTION FOUR (20 MARKS)

a)

i) Explain what is meant by 'oxidative addition' and discuss the conditions that must be met for such a reaction to occur. What is the reverse of this reaction called? (6 marks)

ii) Write an equation for the oxidative addition of H_2 to $Os(CO)_5$. (2 marks)

b) How can one account for the low activation energy for oxidative addition of H_2 with its very strong H-H bond? (3 marks)

c) $Fe_2(\eta^5\text{-}C_5H_5)_2(CO)_4$ exhibits CO stretches in both the 2000 cm^{-1} and 1800 cm^{-1} regions.

i) Based on your understanding of carbonyl complexes and the information above, draw the structure for the diamagnetic species. (3 marks)

ii) Why does this complex display CO-stretches in two distinct regions? (2 marks)

iii) Place the following phosphines in order of highest to lowest V_{CO} for $Ir(CO)_2ClL$. (4 marks)

L= PPh_3, PPh_2Me, PMe_3, PF_3, PPh_2OMe

QUESTION FIVE (20 MARKS)

a) Consider each pair of carbonyl complexes. In each case decide which one would have the lower infrared CO stretching frequency. Explain your choice. (6 marks)

i) $[Fe(CO)_5]$ and $[Fe(CO)_4Cl]$

ii) $[Mo(CO)_6]$ and $[Mo(CO)_4(PPh_3)_2]$

iii) $[Mo(CO)_4(PPh_3)_2]$ and $[Mo(CO)_4(PMe_3)_2]$

b) $V(CO)_6$ is not stable by the EAN rule (demonstrate this) while the predicted stable structure is $V_2(CO)_{12}$ (demonstrate this, too). Experimentally, the observed compound is $V(CO)_6$. Propose an explanation why the divanadium compound is not observed. (6 marks)

c) Explain the difference between homogeneous and heterogeneous catalysts and discuss the advantages and disadvantages of both. (8 marks)

PERIODIC TABLE

1																	18
1 H 1.008	2											13	14	15	16	17	2 He 4.003
3 Li 6.941	4 Be 9.012											5 B 10.81	6 C 12.01	7 N 14.01	8 O 16.00	9 F 19.00	10 Ne 20.18
11 Na 22.99	12 Mg 24.31	3	4	5	6	7	8	9	10	11	12	13 Al 26.98	14 Si 28.09	15 P 30.97	16 S 32.07	17 Cl 35.45	18 Ar 39.95
19 K 39.10	20 Ca 40.08	21 Sc 44.96	22 Ti 47.88	23 V 50.94	24 Cr 52.00	25 Mn 54.94	26 Fe 55.85	27 Co 58.93	28 Ni 58.69	29 Cu 63.55	30 Zn 65.39	31 Ga 69.72	32 Ge 72.61	33 As 74.92	34 Se 78.96	35 Br 79.90	36 Kr 83.80
37 Rb 85.47	38 Sr 87.62	39 Y 88.91	40 Zr 91.22	41 Nb 92.91	42 Mo 95.94	43 Tc 98.91	44 Ru 101.1	45 Rh 102.9	46 Pd 106.4	47 Ag 107.9	48 Cd 112.4	49 In 114.8	50 Sn 118.7	51 Sb 121.8	52 Te 127.6	53 I 126.9	54 Xe 131.3
55 Cs 132.9	56 Ba 137.3	57* La 138.9	72 Hf 178.5	73 Ta 180.9	74 W 183.8	75 Re 186.2	76 Os 190.2	77 Ir 192.2	78 Pt 195.1	79 Au 197.0	80 Hg 200.6	81 Tl 204.4	82 Pb 207.2	83 Bi 209.0	84 Po (209)	85 At (210)	86 Rn (222)
87 Fr (223)	88 Ra (226)	89** Ac (227)	104 Db (261)	105 Jl (262)	106 Rf (263)	107 Bh (262)	108 Hn (?)	109 Mt (?)									

* Lanthanides	58 Ce 140.1	59 Pr 140.9	60 Nd 144.2	61 Pm (147)	62 Sm 150.4	63 Eu 152.0	64 Gd 157.2	65 Tb 158.9	66 Dy 162.5	67 Ho 164.9	68 Er 167.3	69 Tm 168.9	70 Yb 173.0	71 Lu 175.0
** Actinides	90 Th (232)	91 Pa (231)	92 U (238)	93 Np (237)	94 Pu (239)	95 Am (243)	96 Cm (247)	97 Bk (247)	98 Cf (252)	99 Es (252)	100 Fm (257)	101 Md (256)	102 No (259)	103 Lr (260)

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