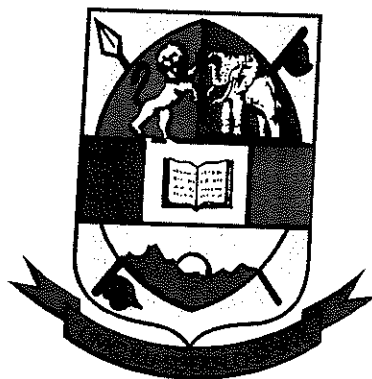


UNIVERSITY OF ESWATINI



MAIN EXAMINATION 2020/2021

TITLE OF PAPER: ORGANOMETALLIC CHEMISTRY

COURSE NUMBER: CHE422

TIME ALLOWED: THREE (3) HOURS

INSTRUCTIONS: THERE ARE TWO (2) SECTIONS:
SECTION A AND SECTION B.
ANSWER ALL THE QUESTIONS IN SECTION A AND ANY TWO (2) QUESTION FROM SECTIONS B

SECTION A IS WORTH 40 MARKS
AND EACH QUESTION IN SECTION B
IS WORTH 30 MARKS.

A PERIODIC TABLE AND OTHER USEFUL DATA HAVE BEEN PROVIDED WITH THIS EXAMINATION PAPER.

PLEASE DO NOT OPEN THIS PAPER UNTIL AUTHORISED TO DO SO BY THE CHIEF INVIGILATOR.

SECTION A (COMPULSORY)

QUESTION ONE [40 Marks]

- (a) (i) Classify the following reaction into either transmetallation or metathesis reaction.

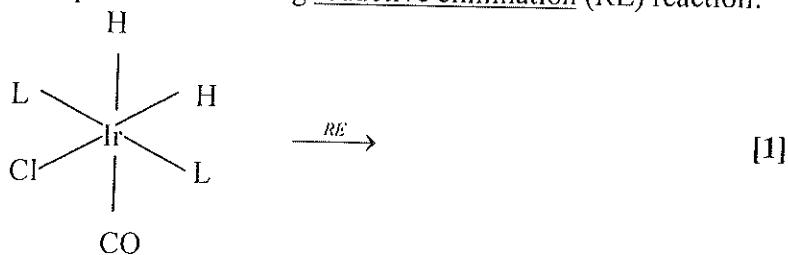
$$\text{Li}_4(\text{CH}_3)_4 + \text{SiCl}_4 \rightarrow 4\text{LiCl} + \text{Si}(\text{CH}_3)_4 \quad [1]$$
- (ii) For each of the following compounds, indicate which one may serve as a good carbanion nucleophile reagent or a mild Lewis acid at the central atom:
 (1) CH_3MgBr [1]
 (2) $\text{B}(\text{CH}_3)_3$ [1]
- (iii) Classify the compound $\text{SiH}(\text{CH}_3)_3$ as electron-precise or electron-deficient. [1]
- (iv) Sketch the structure of methyl lithium. [2]
- (b) (i) Compare formulas of the most stable hydrogen compounds of germanium, Ge and arsenic, As with those of their methyl compounds. Can the differences be explained in terms of the relative electronegativities of C and H? [4]
- (ii) The reaction of $[(\text{R}_3\text{C})_4\text{Ga}]$ (R = a bulky substituent) (I) with I_2 in boiling hexane results in the formation of $[(\text{R}_3\text{C})\text{GaI}]_2$ (II) and $[(\text{R}_3\text{C})\text{GaI}_2]_2$ (III). Draw the structures and state the oxidation states for (I) - (III). [6]
- (iii) State the oxidation state of the metal and the total valence electron count of the following species:
 (1) $(\eta^5\text{-C}_5\text{H}_5)\text{Mn}(\text{CO})_3$ [1]
 (2) $\text{Fe}_2(\text{CO})_8$ [1]
- (iv) Explain why the metal centre in cobalticene, $\text{Co}(\eta^5\text{-C}_5\text{H}_5)_2$ gets easily oxidized. [2]
- (c) (i) Write the product(s) of the following reaction:

$$\begin{array}{c} \text{Ph}_3\text{P} \\ \diagdown \\ \text{Pt} \\ \diagup \\ \text{Ph}_3\text{P} \end{array} \begin{array}{c} \text{CH}_2 \\ || \\ \text{CH}_2 \end{array} \xrightarrow{\text{CH}_3\text{I}}$$
 [2]
- (ii) (1) Despite O being more electronegative than C, the dipole moment of CO is almost zero. Explain. [2]
 (2) What are the two main modes of binding exhibited by CO ligand? [2]
- (iii) Specify whether the lengthening or shortening of the C-C bond distance in the metal bound olefin moiety is observed as a result of metal to ligand π - back donation? [1]
- (iv) (1) What are the hapticities displayed by an allyl moiety in binding to metals? [1]
 (2) Predict the product of the following reaction:

$$\text{Na}^+[\text{Mn}(\text{CO})_5]^- + \text{CH}_2=\text{CHCH}_2\text{Cl} \quad [2]$$

 (3) Specify the hapticities of the cyclopentadienyl ligands in $\text{Cp}_2\text{Mo}(\text{PPh}_3)_2$ [1]

- (d) (i) Complete the following sentences correctly:
- (1) Oxidative addition is frequently observed in coordinatively saturated/unsaturated metal complexes. [1]
 - (2) Oxidative addition is accompanied by increase/decrease in the oxidation state of the metal. [1]
 - (3) Reductive elimination is accompanied by increase/decrease in the coordination number of the metal. [1]
- (ii) (1) Give an example of a ligand that undergoes 1,2 - insertion. [1]
- (2) Complete the following reductive elimination (RE) reaction.



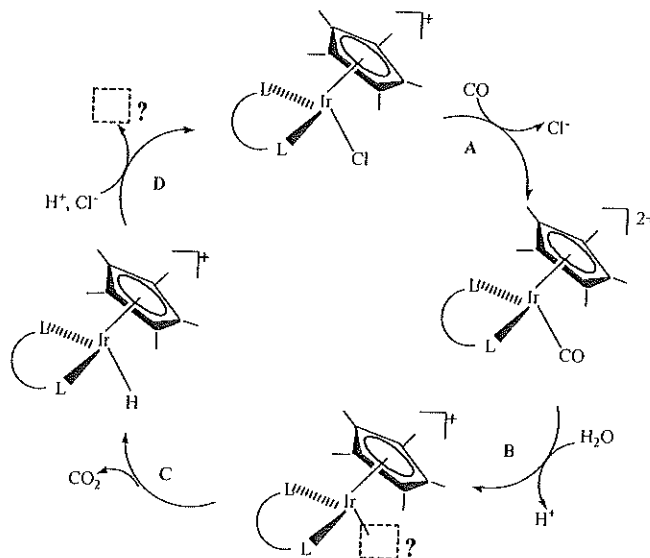
- (iii) What charge, z , would be necessary for $[(\eta^3\text{-C}_3\text{H}_5)\text{V}(\text{CNMe})_5]^z$ to obey the 18-electron rule? [1]
- (iv) Rationalise the observation that on going from $\text{Fe}(\text{CO})_5$ to $\text{Fe}(\text{CO})_5(\text{PPh}_3)_2$, absorptions in the IR spectrum at 2025 and 2000 cm^{-1} are replaced by bands at 1944, 1886 and 1881 cm^{-1} . [3]

SECTION B (ANSWER ANY TWO QUESTIONS)

QUESTION ONE [30 Marks]

- (a) (i) Alkynes readily bridge M–M bonds, in which case they act as 2-electron donors to each metal. Sketch the product, $(\mu_2\text{-PhCCPh})\text{Co}_2(\text{CO})_6$ of the reaction below, indicating the hybridization of the C atoms. [4]
 $\text{PhCCPh} + \text{Co}_2(\text{CO})_8 \rightarrow (\mu_2\text{-PhCCPh})\text{Co}_2(\text{CO})_6 + 2\text{CO}$
- (ii) The M–P distance in $(\eta^5\text{-C}_5\text{H}_5)\text{Co}(\text{PET}_3)_2$ is 221.8 pm and the P–C distance is 184.6 pm. The corresponding distances in $[(\eta^5\text{-C}_5\text{H}_5)\text{Co}(\text{PET}_3)_2]^+$ are 223 pm and 182.9 pm. Account for the changes in these distances as the former complex is oxidised. [4]

- (b) (i) Inspect the catalytic cycle below. Give the species in the two boxes (marked with “?”) and describe each of the steps A–D in as much detail as possible. [8]

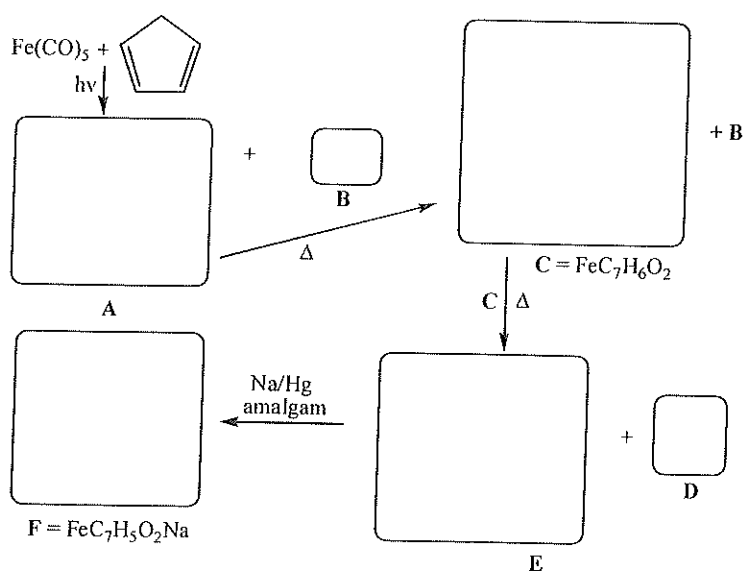


- (ii) Which of the following constitute genuine examples of catalysis and which do not? Justify your answers.
- (1) The addition of H_2 to C_2H_4 when the mixture is brought into contact with finely divided platinum. [2]
 - (2) The reaction of a H_2/O_2 gas mixture when an electrical arc is struck. [2]
 - (3) The combination of N_2 gas with lithium metal to produce Li_3N , which then reacts with H_2O to produce NH_3 and LiOH . [2]
- (c) (i) Suggest products in the following reactions:
- (1) $[(\text{C}_6\text{H}_5)_3\text{PCH}_3]^+\text{Br}^-$ with $\text{C}_4\text{H}_9\text{Li}$ (${}^n\text{BuLi}$) [2]
 - (2) $(\eta^5\text{-C}_5\text{H}_5)_2\text{Fe}$ with $\text{C}_4\text{H}_9\text{Li}$ (${}^n\text{BuLi}$) [2]

- (ii) For the pair of complexes given below, predict which one will be more reactive towards *oxidative addition* of H_2 . Justify your choice. [4]
 $RhCl(PPh_3)_3$ or $RhCl(CO)(PPh_3)_2$

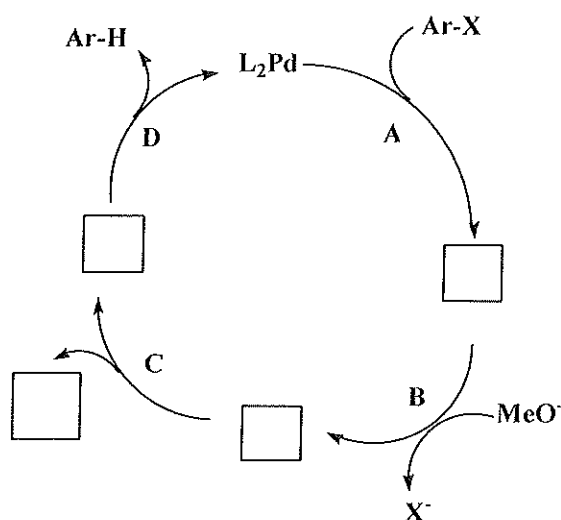
QUESTION TWO [30 Marks]

- (a) (i) $Mo(CO)_6$ undergoes substitution reactions with phosphine ligands, but the reaction never proceeds further than the $Mo(CO)_3(PR_3)_3$ stage. If the phosphines are very bulky, the phosphines are arranged *mer*, but otherwise are always *fac*. Explain these two observations. [5]
- (ii) The product of reaction between $PtCl_2$ and CO at high pressure and $200^\circ C$ has a molecular weight of 322. Determine the formula and suggest possible isomers. [5]
- (b) (i) NO^+ is isoelectronic with CO and often replaces CO in substitution reactions, so it might seem the reaction below is favourable. Comment on whether the process is likely. [4]
 $Mo(CO)_6 + NOBF_4 \rightarrow [Mo(NO)_6][BF_4]_6 + 6CO$
- (ii) Write balanced equations for the following reaction types: [2]
 (1) $(CH_3CH_2)_3Ga + CH_3OH \rightarrow$ [2]
 (2) $Al_2(CH_3)_6 + N(C_2H_5)_3 \rightarrow$ [2]
- (c) Irradiating $Fe(CO)_5$ with UV light in the presence of cyclopentadiene results in the formation of A and colourless gas B. A has four different 1H NMR environments in a 2:2:1:1 ratio. Heating A further results in the release of more B to make C, having the formula $FeC_7H_6O_2$. Molecule C reacts rapidly with itself at room temperature to eliminate colourless gas D, forming solid E. Compound E has two strong IR bands, one near 1850 cm^{-1} , the other near 2000 cm^{-1} . Treatment of E with Na metal generates solid F of empirical formula $FeC_7H_5O_2Na$. Draw structures of A to F indicated by the boxes in scheme below. [12]



QUESTION THREE [30 Marks]

- (a) (i) Explain the following: The *cis* isomer of $(PPh_3)_2Pd(CH_2CH_3)_2$ decomposes immediately to give butane, but the *trans* isomer produces a 1:1 mixture of ethene and ethane. [4]
- (ii) $Ru(CO)_3L_2$, where $L = PPh_3$ reacts with CH_3I as shown:
 $Ru(CO)_3L_2 + CH_3I \rightarrow cis-Ru(CO)_2(L)_2(CH_3)(I) + CO$
 The product features CH_3I oxidatively added *cis* (C and I have very similar electronegativities). The reaction mechanism involves two steps.
- (1) After counting the electrons in $Ru(CO)_3L_2$, what is the first step in the mechanism? [2]
- (2) What is the second step? [2]
- (3) Sketch the transition state in the second step. [2]
- (b) Examine the scheme below ($L =$ phosphine i.e. PR_3). Give appropriate structures and give electron counts and oxidation states for all palladium complexes. Name reactions A, B, C and D. [10]



- (c) (i) Propose the main steps in the catalytic cycle for the conversion of pent-1-ene to hexanal using $HCo(CO)_4$ as the catalyst precursor. [7]
- (ii) Predict giving reason(s) the influence of an increase in the CO partial pressure above a certain threshold on the rate of the reaction (c)(i) above. [3]

PERIODIC TABLE OF ELEMENTS

PERIODS	GROUPS																	
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
	IA	IIA	IIIB	IVB	VB	VIB	VII B	VIII B	VIII B	X	IB	IIB	IIIA	IVA	VA	VIA	VIIA	VIIIA
1	H 1.008																	
2	Li 6.941	Be 9.012																
3	Na 22.990	Mg 24.305																
4	K 39.098	Ca 40.078	Sc 44.956	Ti 47.88	V 50.942	Cr 51.996	Mn 54.938	Fe 55.847	Co 58.933	Ni 58.69	Cu 63.546	Zn 65.39	Ga 69.723	Ge 72.61	As 74.922	Se 78.96	Br 79.904	Kr 83.80
5	Rb 85.468	Sr 87.62	Y 88.906	Zr 91.224	Nb 92.906	Mo 95.94	Tc 98.907	Ru 101.07	Rh 102.91	Pd 106.42	Ag 107.87	Cd 112.41	In 114.82	Sn 118.71	Sb 121.75	Te 127.60	I 126.90	Xe 131.29
6	Cs 132.91	Ba 137.33	*La 138.91	Hf 178.49	Ta 180.95	W 183.85	Re 186.21	Os 190.2	Ir 192.22	Pt 195.08	Au 196.97	Hg 200.59	Tl 204.38	Pb 207.2	Bi 208.98	(209)	Po (210)	At (210)
7	Rf 223	Ra 226.03	**Ac (227)	Rf (261)	Ha (262)	Unh (263)	Uns (262)	Uno (265)	Une (266)	Uun (267)								

TRANSITION ELEMENTS

Atomic mass —
Symbol —
Atomic No.

140.12	Ce	140.91	Pr	144.24	Nd	(145)	Pm	150.36	Sm	151.96	Eu	157.25	Gd	158.93	Tb	162.50	Dy	164.93	Ho	167.26	Er	168.93	Tm	173.04	Yb	174.97	Lu
58		59		60		61		62		63		64		65		66		67		68		69		70		71	
232.04	Th	231.04	Pa	238.03	U	237.05	Np	(244)	Pu	(243)	Am	(247)	Cm	(247)	Bk	(251)	Cf	(252)	Es	(257)	Fm	(258)	Md	(259)	No	(260)	Lr
90		91		92		93		94		95		96		97		98		99		100		101		102		103	

*Lanthanide Series

**Actinide Series

() indicates the mass number of the isotope with the longest half-life.