UNIVERSITY OF ESWATINI

RE-SIT 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.

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SECTION A (COMPULSORY)

QUESTION ONE [40 Marks]

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

$$2Ga + 3CH_3\text{-}Hg\text{-}CH_3 \rightarrow 3Hg + 2Ga(CH_3)_3$$ [1]

(ii) For each of the following compounds, indicate which one may serve as a good carbanion nucleophile reagent or a mild Lewis base at the central atom:

(1) CH_3MgCl [1]

(2) $As(CH_3)_3$ [1]

(iii) Classify the compound $BCl(C_6F_5)_2$ as electron-precise or electron-deficient. [1]

(iv) (1) Sketch the structure of hexamethyldialuminum [1]

(2) Propose a structure for $Al_2(Me)_4Cl_2$ [1]

(b) (i) The I_2 oxidation of $[(^tBu)_4In_4]$ leads to the formation of the In^{II} compound $[(^tBu)_4In_4I_4]$ in which each indium atom retains a tetrahedral environment. Draw the correct structure. [2]

(ii) Do you think that the following reaction proceeds? If so, explain why and how? [5]

$$ZnCl_2 + Al_2Me_6 \rightarrow ZnMe_2 + Al_2Cl_2Me_4$$

(iii) State the oxidation state of the metal and the total valence electron count of the following species:

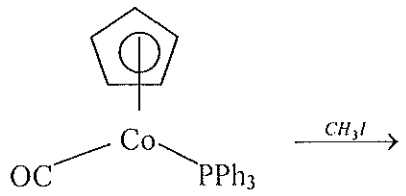
(1) $[Cu(NH_3)_6]^{2+}$ [1]

(2) $CH_3Co(CO)_4$ [1]

(iv) (1) What different hapticities are exhibited by cyclopentadienyl (C_5H_5) ligand? [1½]

(2) Specify the hapticity of the cyclopentadienyl ligand in $CpRh(CO)_2(PMe_3)$ [½]

(c) (i) Write the product(s) of the following reaction:



[2]

(ii) (1) Upon binding to a metal centre does the C–O stretching frequency increase or decrease with regard to that of the free CO? [1]

(2) Explain why low - valent metal centres stabilize CO binding in metal carbonyl complexes? [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 ligand to metal σ - donation? **[1]**

(iv) Complete the following sentences correctly:

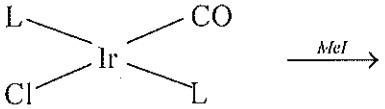
(1) Reductive elimination is frequently observed in coordinatively saturated/unsaturated metal complexes. **[1]**

(2) Reductive elimination is accompanied by increase/decrease in the oxidation state of the metal. **[1]**

(3) Oxidative addition is accompanied by increase/decrease in the coordination number of the metal. **[1]**

(d) (i) (1) Give an example of a ligand that undergoes 1,1 - insertion. **[1]**

(2) Complete the following oxidative addition (OA) reaction:



[1]

(ii) Rationalise the observation that a single ν(CO) band is observed for the ion $[Co(CO)_3(PPh_3)_2]^+$ **[4]**

(iii) What charge, z, would be necessary for the following to obey the 18-electron rule?

(1) $[Ru(CO)_4(SiMe_3)]^z$ **[1]**

(2) $[(\eta^6\text{–}C_6H_6)_2Ru]^z$ **[1]**

(3) $[W(CO)_5(SnPh_3)]^z$ **[1]**

(iv) The reaction of $[(\eta^6\text{–}C_6H_6)RuCl]_2$ (**A**) with C_6H_6 in the presence of $AgBF_4$ gives $[(\eta^6\text{–}C_6H_6)_2Ru][BF_4]$ containing cation **B**. Treatment of this compound with Na in liquid NH_3 yields a neutral Ru(0) complex, **C**. Suggest structures for **A**, **B** and **C**. **[6]**

SECTION B (ANSWER ANY TWO QUESTIONS)

QUESTION ONE [30 Marks]

(a) (i) Rationalise the observation that on forming $IrBr(CO)\{\eta^2\text{-}C_2(CN)_4\}(PPh_3)_2$, the unique C–C bond in $C_2(CN)_4$ lengthens from 135 to 151 pm. **[4]**

(ii) Explain the difference between *homogeneous* and *heterogeneous* catalysts and detail the advantages and disadvantages of both. **[8]**

(b) Draw a catalytic cycle for phosphine-cobalt catalysed hydroformylation. The catalyst precursor is $H(CO)Co(PPh_3)_3$. **[10]**

(c) (i) For the pair of complexes given below, predict which one will be more reactive towards *oxidative addition* of H_2. Justify your choice. **[4]**

$IrCl(CO)(PPh_3)_2$ or $[PtCl(CO)(PPh_3)_2]^+$

(ii) In the substitution of $V(CO)_6$, the rate of reaction changes with respect to phosphine nucleophile according to the order

$PMe_3 > PBu_3 > P(OMe)_3 > PPh_3$

What does this suggest about the mechanism? **[4]**

QUESTION TWO [30 Marks]

(a) Provide a mechanism for the reaction:

$L_nZr\text{–}H + 2\text{-butene} \rightarrow L_nZr\text{–}CH_2CH_2CH_2CH_3$ **[10]**

(b) (i) A metal **A** reacts with dimethylmercury, $(CH_3)_2Hg$, to give metallic mercury and mercury free compound **B**, **B** contains 50.0% carbon and has the empirical formula C_3H_9A. The mass spectrum of **B** gives a molecular ion peak at m/z = 144, and the ^1H NMR spectrum at 20 °C consists of a sharp singlet at $\delta = -0.31$ which at –65 °C becomes two sharp singlets at $\delta = +0.07$ and $\delta = -0.50$, with relative intensities 1:2. **B** reacts with methylamine, NH_2CH_3, to produce the complex **C** which has the molecular formula $C_4H_{14}NA$. Identify **A**, **B**, and **C**. **[6]**

(ii) Draw <u>four</u> bonding modes for the *cyclooctatetraene*. **[4]**

(c) (i) Predict the hapticity (i.e. what is *n* in η^n) of each Cp ring in $Cp_2W(CO)_2$. **[2]**

(ii) How is an *alkylidenetriphenylphosphorane* (Wittig reagent) synthesised? **[2]**

(iii) Give chemical equations to show what *alkylidenetriphenylphosphorane* is used for. **[2]**

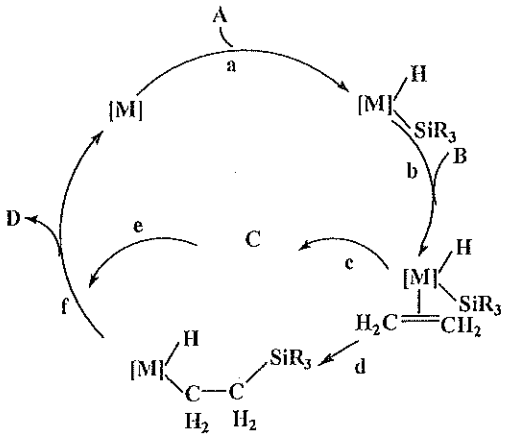
(iv) Comment on the observation that the ν(CO) peak in $[Fe(CO)_6]^{2+}$ appears at 2203 cm^{-1} compared with free CO which occurs at 2143 cm^{-1}. **[4]**

QUESTION THREE [30 Marks]

(a) (i) Using silicon (Si) and chloromethane (CH_3Cl) as primary starting materials, state reactions and give equations for the synthesis of hexamethyldisiloxane. **[6]**

(ii) Explain with necessary diagrams the bonding of ethylene, C_2H_4 to transition metal atoms with emphasis on the σ-donation and π*-acceptance functions of the ligand. **[6]**

(b) Examine the scheme below. Draw structures for **A**, **B**, **C** and **D**. Describe steps **a**, **b**, **c**, **d**, **e** and **f**. Given that [M] is IrL_2X (L = phosphine i.e. PR_3, X = halide), give oxidation states and electron counts for all metal complexes. **[10]**



(c) Suggest a sequence of reactions (give equations and reaction types) for the preparation of the following compounds:

(i) $Mo(\eta^6\text{-}C_6H_6)(CO)_3$ given $MoCl_3$, Al, CO and C_6H_6 **[4]**

(ii) $H_3C\text{-}Re(CO)_5$ using Re_2O_7, CO, CH_3I and Na as the primary starting materials **[4]**

PERIODIC TABLE OF ELEMENTS

GROUPS

PERIODS	1 IA	2 IIA	3 IIIB	4 IVB	5 VB	6 VIB	7 VIIB	8	9 VIIIB	10	11 IB	12 IIB	13 IIIA	14 IVA	15 VA	16 VIA	17 VIIA	18 VIIIA
1	1.008 H 1																	4.003 He 2
2	6.941 Li 3	9.012 Be 4											10.811 B 5	12.011 C 6	14.007 N 7	15.999 O 8	18.998 F 9	20.180 Ne 10
3	22.990 Na 11	24.305 Mg 12											26.982 Al 13	28.086 Si 14	30.974 P 15	32.06 S 16	35.453 Cl 17	39.948 Ar 18
4	39.098 K 19	40.078 Ca 20	44.956 Sc 21	47.88 Ti 22	50.942 V 23	51.996 Cr 24	54.938 Mn 25	55.847 Fe 26	58.933 Co 27	58.69 Ni 28	63.546 Cu 29	65.39 Zn 30	69.723 Ga 31	72.61 Ge 32	74.922 As 33	78.96 Se 34	79.904 Br 35	83.80 Kr 36
5	85.468 Rb 37	87.62 Sr 38	88.906 Y 39	91.224 Zr 40	92.906 Nb 41	95.94 Mo 42	98.907 Tc 43	101.07 Ru 44	102.91 Rh 45	106.42 Pd 46	107.87 Ag 47	112.41 Cd 48	114.82 In 49	118.71 Sn 50	121.75 Sb 51	127.60 Te 52	126.90 I 53	131.29 Xe 54
6	132.91 Cs 55	137.33 Ba 56	138.91 *La 57	178.49 Hf 72	180.95 Ta 73	183.85 W 74	186.21 Re 75	190.2 Os 76	192.22 Ir 77	195.08 Pt 78	196.97 Au 79	200.59 Hg 80	204.38 Tl 81	207.2 Pb 82	208.98 Bi 83	(209) Po 84	(210) At 85	(222) Rn 86
7	223 Fr 87	226.03 Ra 88	(227) **Ac 89	(261) Rf 104	(262) Ha 105	(263) Unh 106	(262) Uns 107	(265) Uno 108	(266) Une 109	(267) Uun 110								

TRANSITION ELEMENTS

Atomic mass →
Symbol →
Atomic No. →

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

*Lanthanide Series

**Actinide Series

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