UNIVERSITY OF ESWATINI

RE-SIT EXAMINATION 2018/2019

TITLE OF PAPER:	**ORGANOMETALLIC CHEMISTRY**
COURSE NUMBER:	**CHE422**
TIME ALLOWED:	**THREE (3) HOURS**
INSTRUCTIONS:	**ANSWER QUESTION ONE (TOTAL 40 MARKS) AND ANY TWO OTHER QUESTIONS (EACH QUESTION IS 30 MARKS)**

A PERIODIC TABLE HAS BEEN PROVIDED WITH THIS EXAMINATION PAPER.

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

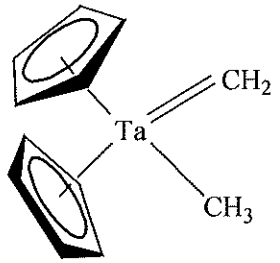
QUESTION ONE (COMPULSORY) [40 Marks]

(a) (i) Give the electron count for each metal centre of the following species:

(1) $[Mn(SnPh_3)_2(CO)_4]^-$

(2) $[Re(CO)_6]^+$

(3)



[3]

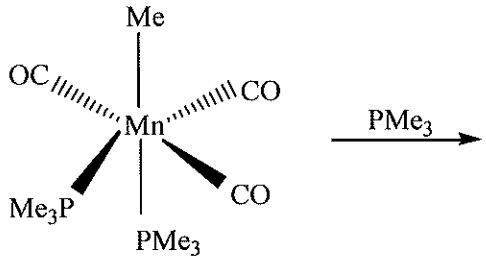
(ii) Assign the oxidation state of each metal, M. Assuming the 18-electron rule applies, identify the first row transition metal.

(1) $M(CO)(CS)(PPh_3)_2Br$

(2) $[M(CO)_7]^+$

(3) $[(\eta^3\text{–}C_3H_5)M(CN)_4]^{2-}$ **[6]**

(b) (i) Predict the product of the addition of PMe_3 to the complex shown below, showing the structure. Note that the product includes all the atoms of the original complex and of the PMe_3. Describe in as much detail as you can its ν(CO) IR spectrum. **[6]**



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

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

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

(2) $[(\eta^6\text{–}C_6H_6)_2Ru]^z$

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

(ii) A complex has the empirical formula $Re(CO)_3Cl$. How could it attain the 18-electron configuration without requiring any different additional ligands? **[2]**

(iii) Draw the structure of the three complexes (cyclo-C_5H_5)$Co(CO)_n$ (n =2, 3 and 4) assuming that the complexes obey the 18-electron rule. **[6]**

(d) (i) 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]**

(ii) For each of the following metal and ligand combinations, formulate the simplest neutral compound that conforms to the 18-electron rule and draw a reasonable structure for each compound.

(1) Ir, $\eta^5\text{–}C_5H_5$, CO

(2) Pt, $\eta^5\text{–}C_5H_5$, NO **[4]**

QUESTION TWO [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 THREE [30 Marks]

(a) Provide a mechanism for the reaction:

$L_nZr–H + 2\text{-butene} \rightarrow L_nZr–CH_2CH_2CH_2CH_3$ **[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_9**A**. 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}N**A**. 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]**

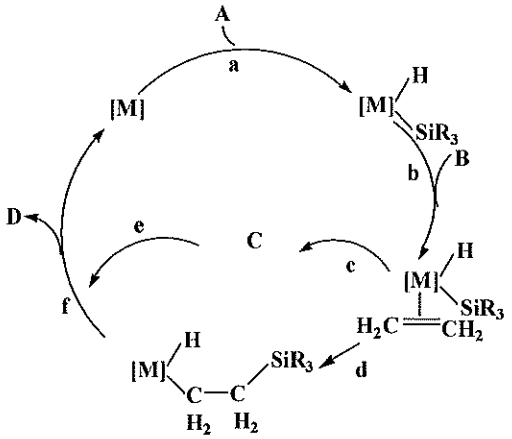
(iv) Comment on the observation that the ν(CO) peak in $[Fe(CO)_6]^{2+}$ appears at 2203 cm^{-1} compared with free CO which occurs at 2143 cm^{-1}. **[4]**

QUESTION FOUR [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

PERIODS	GROUPS 1 IA	2 IIA	3 IIIB	4 IVB	5 VB	6 VIB	7 VIIB	8 VIIIB	9 VIIIB	10 VIIIB	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								

Atomic mass → 10.811
Symbol → **B**
Atomic No. → 5

TRANSITION ELEMENTS

***Lanthanide Series**	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
****Actinide Series**	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

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