UNIVERSITY OF ESWATINI

MAIN 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.

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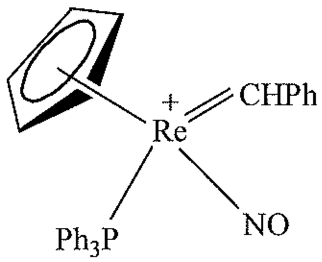
QUESTION ONE (COMPULSORY) [40 Marks]

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

(1) $Ir(CO)(NO)(PPh_3)_2$

(2) $[PtCl_3(\eta^2\text{-}H_2C{=}CH_2)]^-$

(3)



[3]

(ii) Assign the <u>oxidation state</u> of each metal, M. Assuming the 18-electron rule applies, <u>identify</u> the <u>second row</u> transition metal.

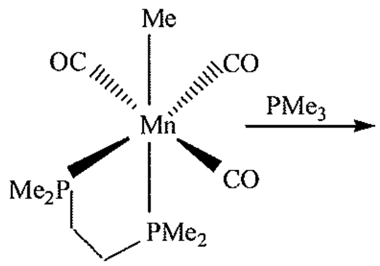
(1) $[(\eta^5\text{-}C_5H_5)(\eta^4\text{-}C_5H_6)M]^+$

(2) $[M(CO)_3(PMe_3)]^-$

(3) $(\eta^5\text{-}C_5H_5)(\eta^1\text{-}C_3H_5)(\eta^3\text{-}C_3H_5)_2M$ (16-electron complex) **[6]**

(iii) What charge, z, would be necessary for $[(\eta^3\text{–}C_3H_5)V(CNMe)_5]^z$ to obey the 18-electron rule? **[1]**

(b) (i) Predict the product of the following reaction and show 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]**

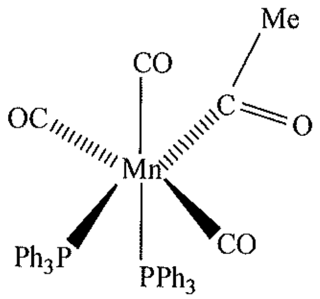


(ii) Rationalise the observation that on going from $Fe(CO)_5$ to $Fe(CO)_5(PPh_3)_2$, absorptions in the IR spectrum at 2025 and 2000 cm^{-1} are replaced by bands at 1944, 1886 and 1881 cm^{-1}. **[4]**

(c) (i) Sketch the products of the reaction when the following complex loses

(1) one PPh_3

(2) one CO **[4]**



(ii) Draw the structures of the <u>three</u> complexes (cyclo-C_7H_7)$Co(CO)_n$ (n = 1, 2 and 3) assuming that the complexes obey the 18-electron rule. **[6]**

(d) (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 (d)(i) above. **[3]**

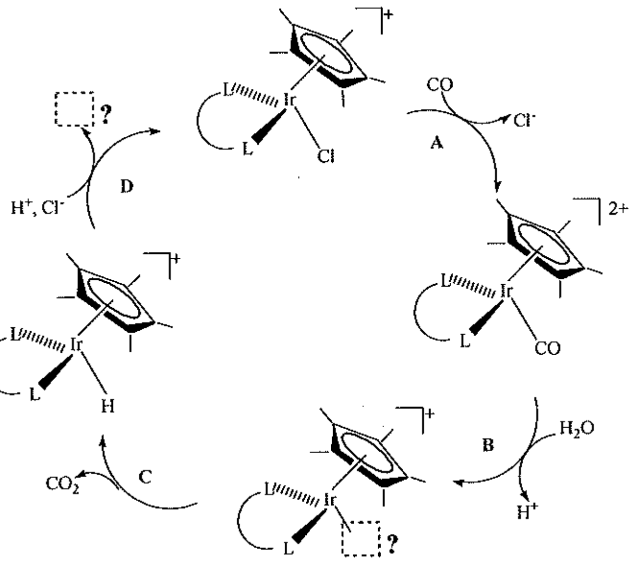
QUESTION TWO [30 Marks]

(a) (i) Alkynes readily bridge M–M bonds, in which case they act as 2-electron donors to each metal. Sketch the product of the reaction below, indicating the hybridization of the C atoms. **[4]**

$$PhCCPh + Co_2(CO)_8 \rightarrow (\mu_2\text{-}PhCCPh)Co_2(CO)_6 + 2CO$$

(ii) The M–P distance in $(\eta^5\text{-}C_5H_5)Co(PEt_3)_2$ is 221.8 pm and the P–C distance is 184.6 pm. The corresponding distances in $[(\eta^5\text{-}C_5H_5)Co(PEt_3)_2]^+$ 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) The reaction of a H_2/O_2 gas mixture when an electrical arc is struck.

(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. **[6]**

(c) (i) Suggest products in the following reactions:

(1) $[(C_6H_5)_3PCH_3]^+Br^-$ with C_4H_9Li (^nBuLi)

(2) $(\eta^5\text{-}C_5H_5)_2Fe$ with C_4H_9Li (^nBuLi) **[4]**

(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 THREE [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. **[4]**

(ii) The product of reaction between $PtCl_2$ and CO at high pressure and 200 °C has a molecular weight of 322. Find the formula and suggest possible isomers. **[6]**

(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]**

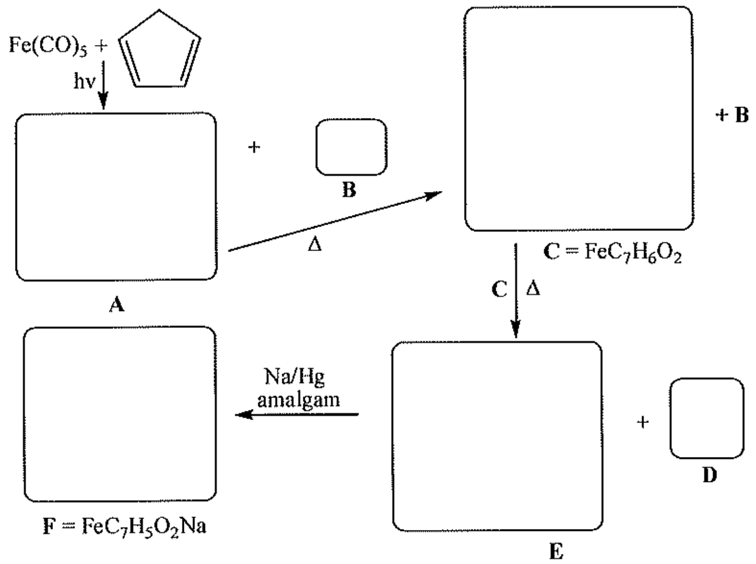
$$Mo(CO)_6 + NOBF_4 \rightarrow [Mo(NO)_6][BF_4]_6 + 6CO$$

(ii) Write balanced equations for the following reaction types:

(1) $(CH_3CH_2)_3Ga + CH_3OH \rightarrow$

(2) $Al_2(CH_3)_6 + N(C_2H_5)_3 \rightarrow$ **[4]**

(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 <u>four</u> different ^{1}H 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 FOUR [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:

$$Ru(CO)_3L_2 + CH_3I \rightarrow cis\text{-}Ru(CO)_2(L_2)(CH_3)(I) + CO$$

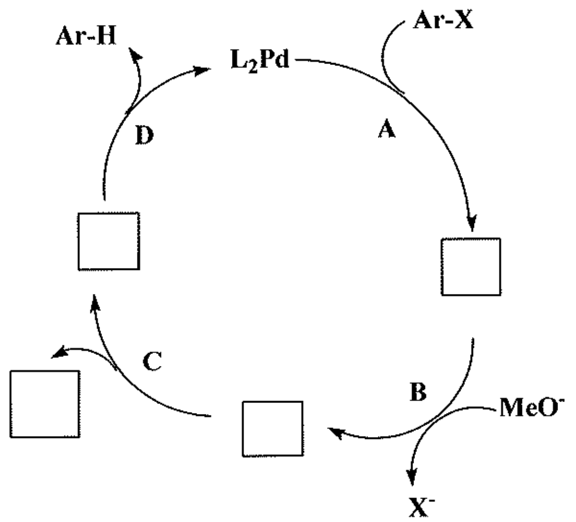
The product features CH_3I oxidatively added *cis* (C and I have very similar electronegativities). The reaction mechanism involves two steps.

(1) After counting the electrons in $Ru(CO)_3L_2$, what is the first step in the mechanism?

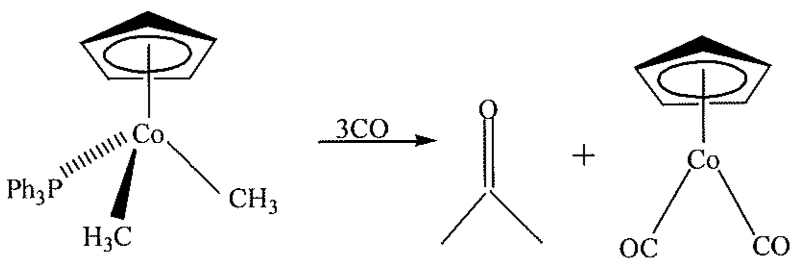
(2) What is the second step?

(3) Sketch the transition state in the second step. **[6]**

(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) Suggest a plausible mechanism for the following reaction: **[10]**



PERIODIC TABLE OF ELEMENTS

GROUPS

PERIODS	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
	IA	IIA	IIIB	IVB	VB	VIB	VIIB	VIIIB			IB	IIB	IIIA	IVA	VA	VIA	VIIA	VIIIA
1	1.008 **H** 1																	4.003 **He** 2
2	6.941 **Li** 3	9.012 **Be** 4										Atomic mass → **Symbol** → Atomic No. →	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				**TRANSITION ELEMENTS**							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								

***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.