

UNIVERSITY OF SWAZILAND

SUPPLEMENTARY EXAMINATION 2012

TITLE OF PAPER: **ADVANCED INORGANIC
CHEMISTRY**

COURSE NUMBER: **C401**

TIME ALLOWED: **THREE (3) HOURS**

INSTRUCTIONS: **THERE ARE SIX (6) QUESTIONS.
ANSWER ANY FOUR (4) QUESTIONS.
EACH QUESTION IS WORTH 25
MARKS.**

**A PERIODIC TABLE HAS BEEN PROVIDED WITH THIS
EXAMINATION PAPER.**

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QUESTION ONE

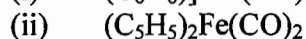
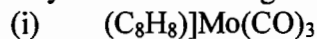
- (a) (i) Assuming that the 18-electron rule applies, identify the third-row transition metal:
- (1) $[(\eta^3\text{-C}_3\text{Ph}_3)(\eta^4\text{-C}_4\text{H}_4)\text{M}(\text{NH}_3)_2]^+$
 - (2) $[(\eta^5\text{-C}_5\text{H}_5)\text{M}(\text{CO})_3]_2$ (assume single M–M bond)
 - (3) $\text{M}(\text{CO})_4\text{Br}(\equiv\text{CPh})$
- (ii) What charge, z , would be necessary for $[(\eta^6\text{-C}_6\text{H}_6)_2\text{Os}]^z$ to obey the 18-electron rule? [4]
- (b) If CO is a two electron donor and NO is a three electron donor, what are the possible formulae of the stable 18 electron Mo^0 and Ru^0 compounds containing just NO and/or CO? [5]
- (c) Identify the Lewis acids and bases in the following reactions
- (i) $\text{BrF}_3 + \text{F}^- \rightarrow \text{BrF}_4^-$
 - (ii) $\text{KH} + \text{H}_2\text{O} \rightarrow \text{KOH} + \text{H}_2$ [4]
- (d) (i) Complex A, $\text{Ir}(\text{PPh}_3)_2(\text{Cl})_2(\text{COCH}_2\text{Ph})$ [$\nu(\text{CO}) = 1670 \text{ cm}^{-1}$] rearranges cleanly to the isomeric compound B [$\nu(\text{CO}) = 2040 \text{ cm}^{-1}$] at 30°C in benzene. Draw a possible structure for B.
- $$\text{Ir}(\text{PPh}_3)_2(\text{Cl})_2(\text{COCH}_2\text{Ph}) \xrightarrow{\text{C}_6\text{H}_6/30^\circ\text{C}} \text{B} \quad [4]$$
- (ii) Suggest products in the following reactions:
- (1) excess FeCl_3 with $(\eta^5\text{-C}_5\text{H}_5)_2\text{Fe}$
 - (2) $(\eta^5\text{-C}_5\text{H}_5)_2\text{Fe}$ with $\text{PhC}(\text{O})\text{Cl}$ in the presence of AlCl_3
 - (3) $(\eta^5\text{-C}_5\text{H}_5)_2\text{Fe}$ with toluene in the presence of Al and AlCl_3
 - (4) $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{Cl}$ with $\text{Na}[\text{Co}(\text{CO})_4]$ [8]

QUESTION TWO

- (a) Explain the following:
- (i) $[\text{Ti}(\text{CH}_2\text{Ph})_4]$ does not undergo β -H elimination.
 - (ii) The separation of lanthanides and actinides is very difficult.
 - (iii) During ion-exchange chromatography lutetium (Lu) is separated first and lanthanum (La) the last. [6]
- (b) Of the metals Cd, Rb, Cr, Pb, Sr and Pd, which might be expected to be found in aluminosilicate minerals (silicate oxo anions) and which in sulphides? Justify your answer. [3]
- (c) The reaction of the tetrahedral cluster $\{(\text{Me}_3\text{Si})_3\text{C}\}_4\text{Ga}_4$ with I_2 in boiling hexane results in the formation of $\{(\text{Me}_3\text{Si})_3\text{CGaI}\}_2$ and $\{(\text{Me}_3\text{Si})_3\text{CGaI}_2\}_2$. In each compound there is only one Ga environment. Suggest structures for these compounds and state the oxidation state of Ga in the starting material and products. [5]
- (d) Predict the structures of
- (i) $[\text{IF}_6]^+$
 - (ii) BrF_5 [6]
- (e)
- (i) Determine the ground state term symbol for Tm^{3+} .
 - (ii) Calculate the g -value expected for Tm^{3+} .
 - (iii) Hence, calculate the effective magnetic moment, μ_{eff} , of Tm^{3+} . [5]

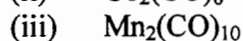
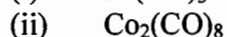
QUESTION THREE

- (a) Sketch the structures of each of the following molecules, clearly indicating the ways in which the ligands are attached to the metal.



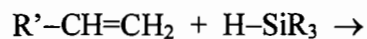
[4]

- (b) How are the following compounds made?



[6]

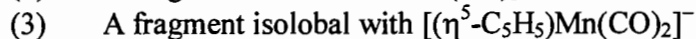
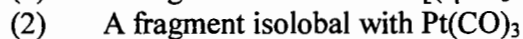
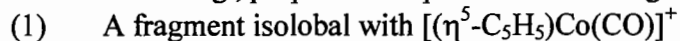
- (c) (i) Describe the three classes of aprotic solvents, citing examples of each.
(ii) Hydrosilation is a useful reaction that converts an alkene into a silylalkane. Predict the product of the following general hydrosilation reaction:



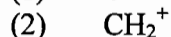
where R = H, alkyl, aryl

- (iii) $SbCl_3$ may be used as a non-aqueous solvent above its melting point. Suggest a possible self-ionization process for this solvent. [9]

- (d) (i) For the following, propose examples of isolobal organic fragments:



- (ii) Give organometallic fragments isolobal with each of the following:



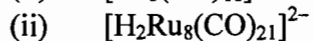
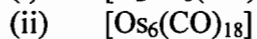
[6]

QUESTION FOUR

- (a) (i) Give a description of the bonding in $[\text{Ir}(\text{CO})_6]^{3+}$ and compare it with that in the isoelectronic compound $\text{W}(\text{CO})_6$.
(ii) How would you expect the IR spectra of these species to differ in the carbonyl stretching region? [6]
- (b) Suggest reasons for the following observations:
(i) Although Pd(II) complexes with monodentate *O*-donor ligands are not as plentiful as those with *P*-, *S*- and *As*-donor ligands, Pd(II) forms many stable complexes with bidentate *O,O'*-donor ligands.
(ii) EDTA⁴⁻ forms very stable complexes with first-row *d*-block metal ions M^{2+} (e.g. $\log K = 18.62$ for the complex with Ni^{2+}); where the M^{3+} ion is accessible, complexes between M^{3+} and EDTA⁴⁻ are more stable than between the corresponding M^{2+} and EDTA⁴⁻ (e.g. $\log K$ for the complex Cr^{2+} is 13.6, and for Cr^{3+} is 23.4). [4]
- (c) (i) Explain why the spin-only formula cannot be used to describe the magnetic properties of lanthanide (Ln) ions?
(ii) Suggest (giving equations) how the following species behave in H_2SO_4 :
(1) H_2O
(2) NH_3
(3) HCO_2H (given that it decomposes) [8]
- (d) What type of reaction is the following, and by what mechanism does it occur?
 $\text{Mn}(\text{CO})_5\text{CH}_3 + \text{CO} \rightarrow \text{Mn}(\text{CO})_5(\text{COCH}_3)$ [4]
- (e) Using the cluster valence electron (CVE) count suggest the metal cage framework adopted by each of the following clusters:
(i) $\text{Os}_5(\text{CO})_{16}$
(ii) $\text{HRu}_6(\text{CO})_{17}\text{B}$
(iii) $\text{Co}_3(\text{CO})_9\text{Ni}(\eta^5\text{-C}_5\text{H}_5)$ [3]

QUESTION FIVE

(a) Using Polyhedral Skeletal Electron Pair Theory (PSEPT) predict the metal core structures of the following clusters:



[9]

(b) The following is a list of reaction classes which encompasses the majority of the transformations of organometallic compounds:

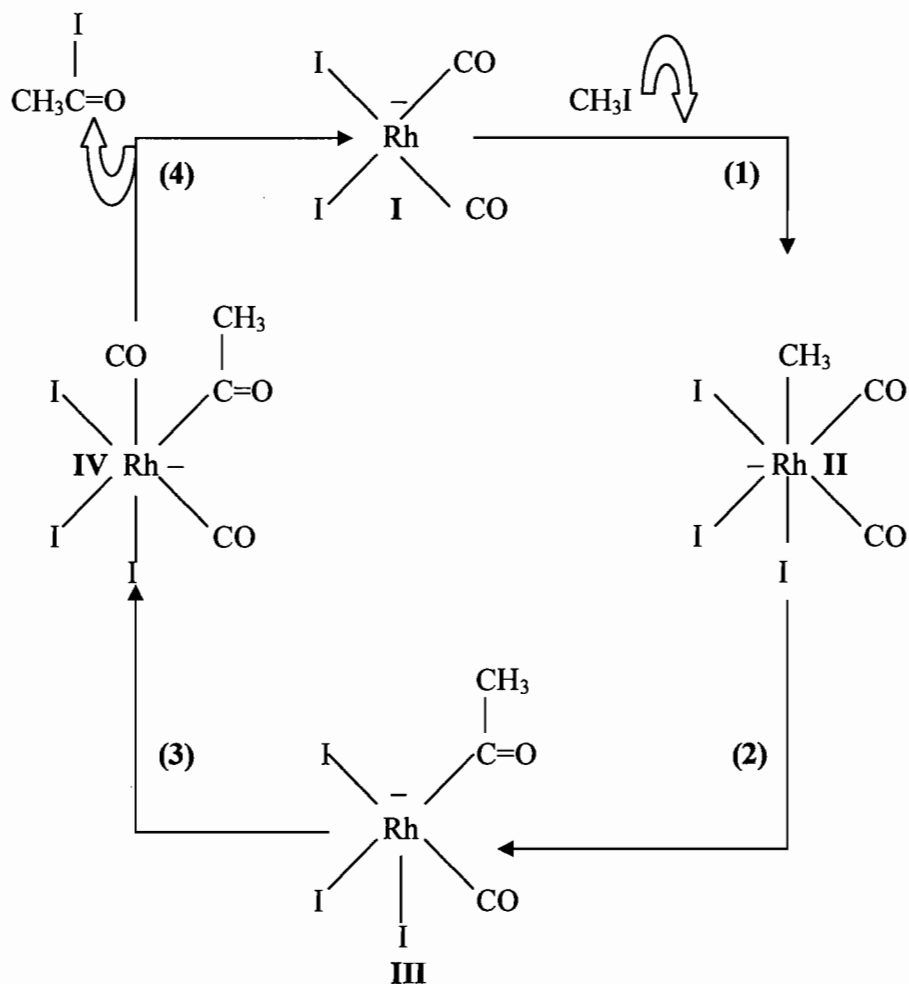
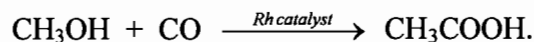
A: Ligand substitution or dissociation

B: Oxidative addition

C: Reductive elimination

D: Migratory insertion

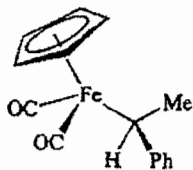
Now consider the catalytic cycle of reactions which are known to occur in the Monsanto acetic acid process in which methanol combines with CO to form acetic acid:



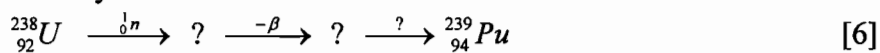
The steps in this cycle are labelled (1), (2), (3), and (4); the intermediate complexes are labelled I, II, III, and IV.

- (i) Name the reaction steps corresponding to (1), (2), (3), and (4).
- (ii) Determine the formal oxidation state and *d* electron configuration of the central metal (i.e. Mo(II) d^4) for each intermediate complexes I, II, III, and IV.
- (iii) Identify coordinatively unsaturated ("16-electron") complexes. [10]

- (c) (i) Explain why the following compound does not undergo β -H elimination:



- (ii) Complete the following scheme, inserting the missing nuclides and mode of decay:



QUESTION SIX

- (a) When dichlorodimethylsilane, $(\text{CH}_3)_2\text{SiCl}_2$, is treated with alkali metals in tetrahydrofuran, THF, the main product **X** is a crystalline solid of composition, C, 41.4%; H, 10.3%; Si, 48.3%, and molecular weight 290. The proton NMR spectrum of **X** measured in benzene consists of a single band. Suggest structure for **X**. [4]
- (b) **M** is a First Transition Series element. It forms a carbonyl **F** of empirical formula $\text{M}(\text{CO})_5$ which reacts with sodium amalgam, Na/Hg in tetrahydrofuran, THF to give a solution **G**. Treatment of **G** with 3-chloro-1-propene, $\text{CH}_2=\text{CHCH}_2\text{Cl}$ gives a compound **H** of molecular formula $\text{C}_8\text{H}_5\text{H}_5\text{M}$. The infrared spectrum of **H** shows carbonyl stretching bands between 2110 and 2004 cm^{-1} , the ^1H NMR spectrum of **H** indicates protons in *four* chemically distinct environments. On heating **H** to 100 °C one mole of carbon monoxide, CO is eliminated to give **I**, $\text{C}_7\text{H}_5\text{O}_4\text{M}$ [ν_{CO} between 2110 and 1950 cm^{-1}]. The ^1H NMR spectrum of **I** indicates protons in *three* chemically distinct environments.
- Identify the metal **M**.
 - Propose and draw structures for the compounds **F**, **H** and **I** and for the species present in solution **G**.
 - Interpret the ^1H NMR features of **H** and **I**.
 - Discuss the bonding of the organic ligand to **M** in compound **I**. [8]
- (c) It is believed that the catalytic role of organometallic complexes in effecting organic reactions may be understood in terms of successive steps generating 16- and 18-electron complexes from 18- and 16-electron molecules, respectively. Thus, the "hydroformylation" of olefins below is catalysed by $\text{HCo}(\text{CO})_4$ derived from $\text{Co}_2(\text{CO})_8$.
- $$\text{CH}_2=\text{CHR} + \text{H}_2 + \text{CO} \rightarrow \text{RCH}_2\text{CH}_2\text{CHO}$$
- Outline the steps of the catalytic cycle.
 - Identify each cobalt-containing species as a 16- or 18-electron molecule
 - Kinetic studies indicate that the hydroformylation reaction is enhanced by an increase in H_2 pressure and inhibited by an increase in CO pressure. How is the mechanism in your cycle above consistent with these observations? [10]
- (d) The iron atom in $\text{Fe}(\text{CO})_5$ is a weak Lewis base. However, replacement of a CO ligand with a phosphine to give, for example, $\text{Fe}(\text{CO})_4(\text{PPh}_3)$ causes the metal basicity to be enhanced. Why should this be the case? [3]

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	VIIA	VIIIB	VIIIB	IB	IIIB	IIIB	IIIA	IVA	VA	VIA	VIA	VIA	VIA	VIA	VA	VA	VA	VA	VA	VA	VA	VA	VA	VA	VA	VA	VA	VA	VIIIA	
1	H 1																																		He 2	
2	Li 3	Be 4																																	Ne 10	
3	Na 11	Mg 12																																	Ar 18	
TRANSITION ELEMENTS																																				
4	K 19	Ca 20	Sc 21	Ti 22	V 23	Cr 24	Mn 25	Fe 26	Co 27	Ni 28	Cu 29	Zn 30	Ga 31	Ge 32	As 33	Se 34	Br 35	Kr 36																		
5	Rb 37	Sr 38	Y 39	Zr 40	Nb 41	Mo 42	Tc 43	Ru 44	Rh 45	Pd 46	Ag 47	Cd 48	In 49	Sn 50	Sb 51	Te 52	I 53	Xe 54																		
6	Cs 55	Ba 56	*La 57	Hf 72	Ta 73	W 74	Re 75	Os 76	Ir 77	Pt 78	Au 79	Hg 80	Tl 81	Pb 82	Bi 83	Po 84	At 85	Rn 86																		
7	Fr 87	Ra 88	**Ac 89	Rf 104	Ha 105	Unh 106	Uns 107	Uno 108	Unk 109	Uun 110																										

Atomic mass
Symbol
Atomic No.

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

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

*Lanthanide Series
**Actinide Series