

UNIVERSITY OF SWAZILAND

FINAL 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) Identify the following reactions by their type (oxidative addition, reductive elimination, associative substitution, dissociative substitution, β -hydride elimination, ligand addition, ligand dissociation, etc). In some cases a reaction may have several steps. In that case list each step in the correct order.
- (i) $\text{Re}(\text{SiMe}_3)(\text{CO})_5 + \text{PMe}_3 \rightarrow \text{Re}(\text{SiMe}_3)(\text{CO})_4(\text{PMe}_3) + \text{CO}$
(ii) $\text{CpRu}(\text{Et})(\text{N}\equiv\text{CCH}_3)_2 \rightarrow \text{CpRu}(\text{H})(\text{CH}_2=\text{CH}_2)(\text{N}\equiv\text{CCH}_3) + \text{N}\equiv\text{CCH}_3$
(iii) $\text{PtCl}(\text{CH}_3)_3(\text{PMe}_3)(\text{N}\equiv\text{CCH}_3) \rightarrow \text{PtCl}(\text{CH}_3)(\text{PMe}_3)(\text{N}\equiv\text{CCH}_3) + \text{CH}_3\text{CH}_3$
(iv) $\text{CpRh}(\text{PMe}_3)_2 + \text{C}_6\text{H}_6 \rightarrow \text{CpRh}(\text{H})(\text{Ph})(\text{PMe}_3) + \text{PMe}_3$ [9]
(where $\text{Cp} = \eta^5\text{-C}_5\text{H}_5$)
- (b) Sketch interactions of benzene (C_6H_6), with a metal atom via
(i) η^2 (ii) η^4 (iii) η^6 [3]
- (c) Suggest products in the following reactions, and give likely structures for the products:
- (i) $\text{Fe}(\text{CO})_5$ irradiated with C_2H_4 (ii) $\text{Re}_2(\text{CO})_{10}$ with Na/Hg
(iii) $\text{Na}[\text{Mn}(\text{CO})_5]$ with ONCl (iv) $\text{Ni}(\text{CO})_4$ with PPh_3 [4]
- (d) (i) Select the best choice in each of the following isoelectronic compounds, and briefly justify the reason for the selection:
(1) Shortest C–O bond: $\text{Ni}(\text{CO})_4$; $[\text{Co}(\text{CO})_4]^-$; $[\text{Fe}(\text{CO})_4]^{2-}$
(2) Higher C–O stretching frequency: $\text{Ni}(\text{CO})_3(\text{PF}_3)$; $\text{Ni}(\text{CO})_3(\text{PMe}_3)$
(ii) Comment on the observation that the vanadium–carbon distance in $\text{V}(\text{CO})_6$ is 200 pm, but only 193 pm in $[\text{V}(\text{CO})_6]^-$. [9]

QUESTION TWO

- (a) Using the cluster valence electron (CVE) count suggest the metal cage framework adopted by each of the following clusters:
(i) $\text{Ru}_6\text{C}(\text{CO})_{17}$ (ii) $[\text{Rh}_2\text{Fe}_2(\text{CO})_{13}]$ (iii) $[\text{Fe}_4\text{N}(\text{CO})_{12}]^-$ [3]
- (b) Use Wade's rules to suggest likely structures for
(i) B_5H_{11} (ii) $[\text{Os}_6(\text{CO})_{19}]$ (iii) $[\text{Ru}_8(\text{CO})_{22}]^{2-}$ [9]
- (c) Pick out pairs of isoelectronic species from the following list:
 $\text{Cr}(\text{CO})_3$, $\text{Co}(\text{CO})_3$, $\text{Mn}(\text{CO})_5$, $\text{Re}(\text{CO})_5$, $\eta^5\text{-C}_5\text{H}_5\text{Mn}$, $[\text{Fe}(\text{CO})_3]^-$ [3]
- (d) Heating $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_3]^+$ with NaH gives **A**, having formula $\text{FeC}_7\text{H}_6\text{O}_2$, plus colourless gas **B**. Molecule **A** reacts rapidly at room temperature to eliminate colourless gas **C**, forming solid **D**, which has empirical formula $\text{FeC}_7\text{H}_5\text{O}_2$. Compound **D** has two strong IR bands, one near 1850 cm^{-1} , the other near 2000 cm^{-1} . Treatment of **D** with iodine generates solid **E** of empirical formula $\text{FeC}_7\text{H}_5\text{O}_2\text{I}$. Reaction of NaC_5H_5 with **E** gives solid **F** of formula $\text{FeC}_{12}\text{H}_{10}\text{O}_2$. On heating **F** gives off **B**, leaving a sublimable, orange solid **G** of formula $\text{FeC}_{10}\text{H}_{10}$. Propose structures for **A** to **G**. [7]
- (e) Which Ln^{3+} ion would you expect to show the same colour as
(i) Tb^{3+} . (ii) Tm^{3+} (iii) Sm^{3+} [3]

QUESTION THREE

- (a) A metal **A** reacts with dimethylmercury 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 $20\text{ }^\circ C$ consists of a sharp singlet at $\delta = -0.31$ which at $-65\text{ }^\circ C$ becomes two sharp singlets at $\delta = +0.07$ and $\delta = -0.50$, with relative intensities 1:2.
B reacts with methylamine to produce the complex **C** which has the molecular formula $C_4H_{14}NA$. Identify **A**, **B**, and **C**. [6]
- (b) Following are classifications of organometallic reactions. Next to each type of reaction put letters which correspond to the nature of this reaction.
A: This reaction is also known for d^0 complexes.
B: A change in d^0 occurs.
C: A change in coordination number is involved.
(i) Migratory insertion.
(ii) Oxidative addition. [4]
- (c) Propose the main steps in the catalytic cycle for the conversion of 1-pentene to hexanal using $HRh(CO)_4$ as the catalyst precursor. [8]
- (d) $H_2Os_3(CO)_{10}$ catalyses the isomerization of alkenes:
 $RCH_2CH=CH_2 \rightarrow E-RCH=CHMe + Z-RCH=CHMe$
By determining the cluster valence electron (CVE) count for $H_2Os_3(CO)_{10}$ deduce what makes this cluster an effective catalyst. [4]
- (e) For each of the following compounds:
 $(Bu_3P)_2Pt(CH_3)_2$; $(\eta^5-C_5H_5)_2Ni$; $Re(CO)_5$
(i) Which compound could dimerise?
(ii) Which compound is not coordinatively saturated?
(iii) Which compound has more than 18 electrons? [3]

QUESTION FOUR

- (a) (i) Which of the following compounds behave as acids in liquid HF: ClF_3 , BF_3 , SbF_5 , SiF_4 ?
(ii) Write equations to explain this behaviour. [3]
- (b) (i) Propose two syntheses for $\text{MeMn}(\text{CO})_5$ both starting with $\text{Mn}_2(\text{CO})_{10}$, with one using Na and one using Br_2 . You may use other reagents of your choice.
(ii) Some chemistry of sodium cyclopentadienyltricarbonyl tungstate is shown below:
$$\text{Na}[(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{CO})_3] + \text{CH}_2=\text{CHCH}_2\text{Cl} \rightarrow \text{A} \xrightarrow{\nu\nu} \text{B}$$

(1) Propose structures for A and B.
(2) Describe the bonding of the acyclic hydrocarbon ligand to the metal in B. [8]
- (c) The complex $[(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})_3]_2$ reacts with I_2 to give a product A having three infrared bands near 2000 cm^{-1} . This product reacts with triphenylphosphine, PPh_3 to give B, which has two bands near 2000 cm^{-1} . Identify A and B. [4]
- (d) (i) Propose organometallic fragments isolobal with the following:
(1) CH (2) CH_3 (3) CH_2
(ii) Propose an organic fragment isolobal with:
(1) $\text{Cr}(\text{CO})_5$ (2) $[\text{Co}(\text{CO})_4]^+$ (3) $[\text{Fe}(\text{CO})_4]^-$ [6]
- (e) Predict whether the equilibrium constants for the following reactions should be greater than 1 (reaction lies to the right) or less than 1 (reaction lies to the left):
(i) $\text{CdI}_2 + \text{CaF}_2 \rightleftharpoons \text{CdF}_2 + \text{CaI}_2$
(ii) $[\text{CuI}_4]^{2-} + [\text{CuCl}_4]^{3-} \rightleftharpoons [\text{CuCl}_4]^{2-} + [\text{CuI}_4]^{3-}$ [4]

QUESTION FIVE

- (a) (i) Reaction of $\text{Fe}(\text{CO})_5$ with $\text{Na}_2[\text{Fe}(\text{CO})_4]$ in THF gives a salt $\text{Na}_2[\text{A}]$ and CO. The Raman spectrum of $[\text{Et}_4\text{N}]_2[\text{A}]$ shows absorption at 160 cm^{-1} assigned to an unbridged Fe–Fe bond. Suggest an identity and structure for $[\text{A}]^{2-}$
- (ii) Explain why the metallic radii of Ru and Os are similar, whereas the value of r_{metal} for Fe is smaller than r_{metal} for Ru. [7]
- (b) Draw a reasonable structure for $[\eta^5\text{-C}_5\text{H}_5]_3\text{Nb}_3(\mu_3\text{-CO})(\text{CO})_6$. [3]
- (c) Suggest what change in cluster structure might accompany the reaction:
 $[\text{Co}_6(\text{CO})_{15}\text{N}]^- \rightarrow [\text{Co}_6(\text{CO})_{13}\text{N}]^- + 2\text{CO}$ [5]
- (d) (i) Confirm that $\text{H}_2\text{Os}_3(\text{CO})_{11}$ has sufficient valence electrons to adopt a triangular metal framework..
- (ii) Do the modes of bonding of the CO and H ligands in (i) above affect the total valence electron count? [5]
- (iii) Comment on the fact that $\text{H}_2\text{Os}_3(\text{CO})_{10}$ also has a triangular Os_3 -core.
- (e) (i) Why are the colours of Ln^{3+} ions less intense than those of the first-row transition metal ions?
- (ii) Why are Eu^{2+} and Yb^{2+} somewhat more stable with respect to oxidation than other Ln^{2+} cations? [5]

QUESTION SIX

- (a) Suggest products for the following reactions:
- (i) $\text{ClF} + \text{BF}_3 \rightarrow$
- (ii) $\text{CsF} + \text{IF}_5 \rightarrow$
- (iii) $\text{SbF}_5 + \text{ClF}_5 \rightarrow$
- (iv) $\text{Me}_4\text{NF} + \text{IF}_7 \rightarrow$ [4]
- (b) Predict the structures of
- (i) $[\text{BrF}_4]^-$ (ii) $[\text{ICl}_2]^+$ [6]
- (c) (i) Determine the ground state term symbol for Yb^{3+} .
- (ii) Calculate the g -value expected for Yb^{3+} .
- (iii) Hence, calculate the effective magnetic moment, μ_{eff} , of Yb^{3+} . [5]
- (d) Identify the starting isotopes A and B in each of the following syntheses of transactinoid elements:
- (i) $\text{A} + {}^4_2\text{He} \rightarrow {}^{256}_{101}\text{Md} + {}^1_0\text{n}$
- (ii) $\text{B} + {}^{16}_8\text{O} \rightarrow {}^{255}_{102}\text{No} + 5({}^1_0\text{n})$ [2]
- (e) The hydrogenation of propene is catalysed by $\text{RhCl}(\text{PPh}_3)_3$ or $\text{HRh}(\text{CO})(\text{PPh}_3)_3$. Outline the mechanism by which this reaction occurs using $\text{RhCl}(\text{PPh}_3)_3$, indicating clearly what the active catalyst is and explaining what is happening in each step. [8]

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	VII B	VIII B			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 → 10.811 Symbol → B Atomic No. → 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
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

****Actinide Series**

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