UNIVERSITY OF SWAZILAND

SUPPLEMENTARY EXAMINATION 2011/2012

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) Suggest products of the following reactions:
(i) $MeBr + 2Li \rightarrow$
(ii) $Na + C_5H_6 \rightarrow$
(iii) $MgCl_2 + LiR \rightarrow$
(iv) $Me_3SiCl + Na[C_5H_5] \rightarrow$ [4]

(b) Sketch interactions of 1,3-butadiene, (CH_2=CH-CH=CH_2) with a metal atom via
(i) η^2 (ii) η^4 [4]

(c) Suggest products in the following reactions, and give likely structures for the products:
(i) $Fe(CO)_5$ irradiated with C_2H_4
(ii) $Re_2(CO)_{10}$ with Na/Hg
(iii) $Na[Mn(CO)_5]$ with ONCl
(iv) $Ni(CO)_4$ with PPh_3 [8]

(d) (i) Using a suitable explanation determine which of the two isoelectronic compounds $Cr(CO)_6$ and $[V(CO)_6]^-$ will have
(1) the higher CO stretching frequency?
(2) the shorter M—C bond?
(ii) Comment on the observation that on going from $Fe(CO)_5$ to $Fe(CO)_3(PPh_3)_2$, absorptions in the IR spectrum at 2025 and 2000 cm^{-1} are replaced by bands at 1944, 1886 and 1881 cm^{-1}. [9]

QUESTION TWO

(a) Use Wade's rules to suggest likely structures for
(i) B_5H_9 (ii) $[B_8H_8]^{2-}$ (iii) $[Os_8(CO)_{22}]^{2-}$ [9]

(b) Pick out pairs of isoelectronic species from the following list:
HF, $[NO_2]^+$, NH_3, $[H_3O]^+$, $[OH]^-$, CO_2 [3]

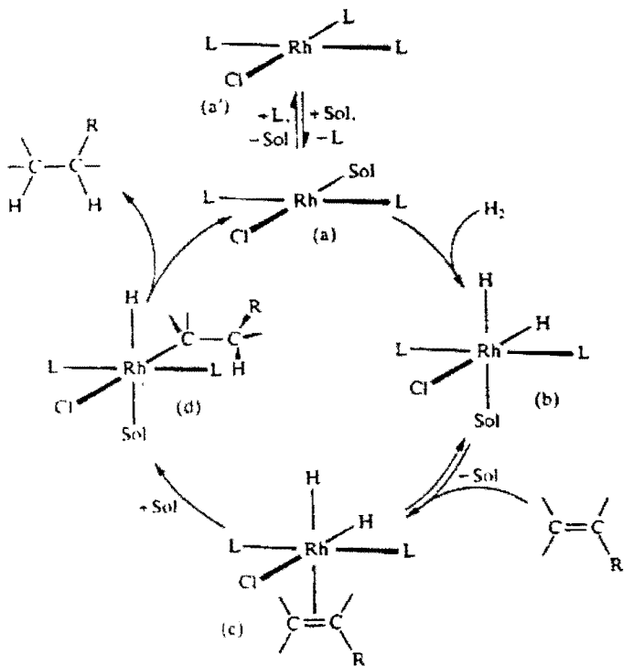
(c) Heating $[(\eta^5\text{-}C_5H_5)Fe(CO)_3]^+$ with NaH gives **A**, having formula $FeC_7H_6O_2$, plus colourless gas **B**. Molecule **A** reacts rapidly at room temperature to eliminate colourless gas **C**, forming solid **D**, which has empirical formula $FeC_7H_5O_2$. Compound **D** has two strong IR bands, one near 1850 cm^{-1}, the other near 2000 cm^{-1}. Treatment of **D** with iodine generates solid **E** of empirical formula $FeC_7H_5O_2I$. Reaction of NaC_5H_5 with **E** gives solid **F** of formula $FeC_{12}H_{10}O_2$. On heating **F** gives off **B**, leaving a sublimable, orange solid **G** of formula $FeC_{10}H_{10}$. Propose structures for **A** to **G**. [7]

(d) (i) Which Ln^{3+} ion would you expect to show the same colour as
(1) Eu^{3+}. (2) Pr^{3+} (3) Dy^{3+}
Explain. [6]
(ii) Verify that the equation below is an oxidative addition reaction.
$[(CO)_3Ir(PMePh_2)_2]^+ + H_2 \leftrightarrows [(CO)_2Ir(PMePh_2)_2(H)_2]^+ + CO$

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 °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 to produce the complex **C** which has the molecular formula $C_4H_{14}NA$. Identify **A**, **B**, and **C**. [6]

(b) There is one oxidative addition reaction and one reductive elimination reaction in the figure below. Give balanced chemical equations for them both and assign oxidation numbers to all the rhodium complexes in the equations. [6]



The main catalytic cycle in the homogeneous hydrogenation of alkene by rhodium-phosphine complexes, L = PPh_3.

(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:

$$RCH_2CH{=}CH_2 \rightarrow \textit{E}\text{-}RCH{=}CHMe + \textit{Z}\text{-}RCH{=}CHMe$$

By determining the cluster valence electron count for $H_2Os_3(CO)_{10}$ deduce what makes this cluster an effective catalyst. [5]

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) Propose <u>two</u> syntheses for $MeMn(CO)_5$ both starting with $Mn_2(CO)_{10}$, with one using Na and one using Br_2. You may use other reagents of your choice. [8]

(c) The complex $[(\eta^5\text{-}C_5H_5)Mo(CO)_3]_2$ 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 organic fragments isolobal with the following:
(1) $[Re(CO)_4]$
(2) $Tc(CO)_4(PPh_3)$
(3) $(\eta^5\text{-}C_5H_5)Ir(CO)$
(ii) Propose an organometallic fragment isolobal with:
(1) CH_3^+
(2) CH_2
(3) CH_2^- [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) $CdI_2 + CaF_2 \leftrightarrows CdF_2 + CaI_2$
(ii) $[CuI_4]^{2-} + [CuCl_4]^{3-} \leftrightarrows [CuCl_4]^{2-} + [CuI_4]^{3-}$ [4]

QUESTION FIVE

(a) (i) Reaction of $Fe(CO)_5$ with $Na_2[Fe(CO)_4]$ in THF gives a salt Na_2[**A**] and CO. The Raman spectrum of $[Et_4N]_2$[A] shows absorption at 160 cm^{-1} assigned to an unbridged Fe–Fe bond. Suggest an identity and structure for $[A]^{2-}$
(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) Metal-Metal bonding in multinuclear species is not always clear-cut. *Solely on the basis of the 18-electron rule,* suggest whether $(\eta^5\text{-}C_5H_5)Ni(\mu\text{-}PPh_2)_2Ni(\eta^5\text{-}C_5H_5)$ might be expected to contain a metal-metal bond. [3]

(c) Suggest what change in cluster structure might accompany the reaction:
$[Co_6(CO)_{15}N]^- \rightarrow [Co_6(CO)_{13}N]^- + 2CO$ [5]

(d) (i) Confirm that $H_2Os_3(CO)_{11}$ 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 $H_2Os_3(CO)_{10}$ 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) $ClF + BF_3 \rightarrow$

(ii) $CsF + IF_5 \rightarrow$

(iii) $SbF_5 + ClF_5 \rightarrow$

(iv) $Me_4NF + IF_7 \rightarrow$ [4]

(b) Predict the structures of

(i) $[ICl_4]^-$ (ii) $[BrF_2]^+$ [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) $\mathbf{A} + {}^{4}_{2}He \rightarrow {}^{256}_{101}Md + {}^{1}_{0}n$

(ii) $\mathbf{B} + {}^{16}_{8}O \rightarrow {}^{255}_{102}No + 5({}^{1}_{0}n)$ [2]

(e) The hydrogenation of propene is catalysed by $RhCl(PPh_3)_3$ or $HRh(CO)(PPh_3)_3$. Outline the mechanism by which this reaction occurs using $RhCl(PPh_3)_3$, indicating clearly what the active catalyst is and explaining what is happening in each step. [8]

PERIODIC TABLE OF ELEMENTS

GROUPS

PERIODS	1 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								

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.