UNIVERSITY OF SWAZILAND

SUPPLEMENTARY EXAMINATION 2014/2015

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) Determine the oxidation state of the metal, its d^n total electron count, and the total number of electrons in each of the following compounds. Which of these compounds will be stable?

(i) $Ir(H)(CO)(dppe)_2$ (comment: dppe is bidentate)

(ii) $[Mo(H)(CO)_2(dppe)_2]^+$ (comment: dppe is bidentate)

(iii) Cp_3NbMe_2 (comment: one Cp is η^1)

(iv) $Rh(O_2CCH_3)_2$ (comment: dimer with Rh-Rh bond) [8]

(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) $H_2Os_3(CO)_{10}$ catalyses the isomerization of alkenes:

$RCH_2CH=CH_2 \rightarrow$ *E*-RCH=CHMe + *Z*-RCH=CHMe

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

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) 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]

(d) Which Ln^{3+} ion would you expect to show the same colour as

(i) Tb^{3+}. (ii) Tm^{3+} (iii) Sm^{3+} [3]

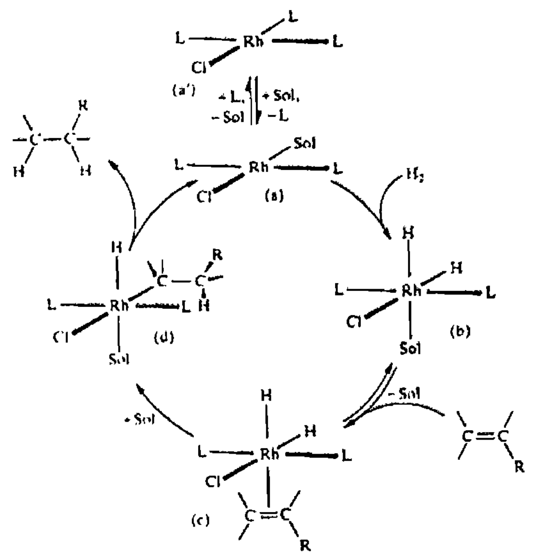
Explain. [2]

QUESTION THREE

(a) The reaction of chloroform with $Co_2(CO)_8$ yields a compound of formula $Co_3(CH)(CO)_9$. NMR and IR data indicate the presence of only terminal CO ligands and the presence of a CH group. Propose a structure consisitent with the spectra and the correlation of cluster valence electron (CVE) count with structure. [3]

(b) (i) Give a definition of a metal cluster.
(ii) What are the two broad classes of metal carbonyl clusters?
(iii) $M_3(CO)_{12}$ clusters (M = Ru and Os) are unreactive. Give three ways by which they can be converted into more reactive derivatives. [8]

(c) 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.

(d) Propose the main steps in the catalytic cycle for the conversion of pent-1-ene to hexanal using $HRh(CO)_4$ as the catalyst precursor. [8]

QUESTION FOUR

(a) Using the concept of isolobality, give

(i) the hydrogen-nitrogen molecule or molecular fragment that is isolobal with CH_3^-.

(ii) the hydrogen-boron molecule or molecular fragment that is isolobal with the O atom.

(iii) a nitrogen-containing species that is isolobal with $[Mn(CO)_5]^-$. [3]

(b) $[Mn_2(CO)_{10}]$ contains a metal-metal bond. Its "formal oxidation state" is zero because M-M bonds "do not count" in the calculation of oxidation state.

(i) What is the formal oxidation state of octahedral $[Mn(CO)_5Me]$?

(ii) Which do you think best describes $[Mn_2(CO)_{10}]$, an oxidation state of zero or 1? [4]

(c) (i) 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):

(1) $CdI_2 + CaF_2 \leftrightarrows CdF_2 + CaI_2$

(2) $[CuI_4]^{2-} + [CuCl_4]^{3-} \leftrightarrows [CuCl_4]^{2-} + [CuI_4]^{3-}$

(ii) Account for the trend in acidity:
$[Fe(OH_2)_6]^{2+} < [Fe(OH_2)_6]^{3+}$ [7]

(d) (i) An empty, a half-filled and a completely-filled 4f electronic level is often said to confer stability on the oxidation state of a lanthanide ion. Cite examples which bear out this statement.

(ii) Use Hund's rules to derive the ground state term of Nd^{3+}.

(iii) Hence determine the magnetic moment, μ of Nd^{3+}. [7]

(e) For the metallocene complex $[(\eta^5\text{–}C_5H_5)_2TiCl_2]$:

(i) Calculate the number of valence electrons for the complex.

(ii) Calculate the formal oxidation state for the titanium (Ti) atom.

(iii) Show that the complex could be regarded as having a coordination number of 4 or 12. [4]

QUESTION FIVE

(a) (e) Identify isotopes **A – F** in the following sequence of nuclear reactions:

(i) $^{238}U \xrightarrow{(n,\gamma)} \mathbf{A} \xrightarrow{-\beta^-} \mathbf{B} \xrightarrow{-\beta^-} \mathbf{C}$

(ii) $\mathbf{D} \xrightarrow{-\beta^-} \mathbf{E} \xrightarrow{(n,\gamma)} {}^{242}Am \xrightarrow{-\beta^-} \mathbf{F}$ [6]

(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:

$[Co_6(CO)_{15}N]^- \rightarrow [Co_6(CO)_{13}N]^- + 2CO$ [6]

(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) Considering the bonding in metal carbonyls, what factors would affect the C-O stretching vibrations?

(ii) A carbonyl complex has linear OC-M-CO group. How will the CO stretching frequency change (increase, decrease or remain the same) when one CO is replaced by triethylamine, $(CH_3CH_2)_3N$? Justify your answer.

[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) $[BrF_2]^+$ (iii) $BrICl^-$ [9]

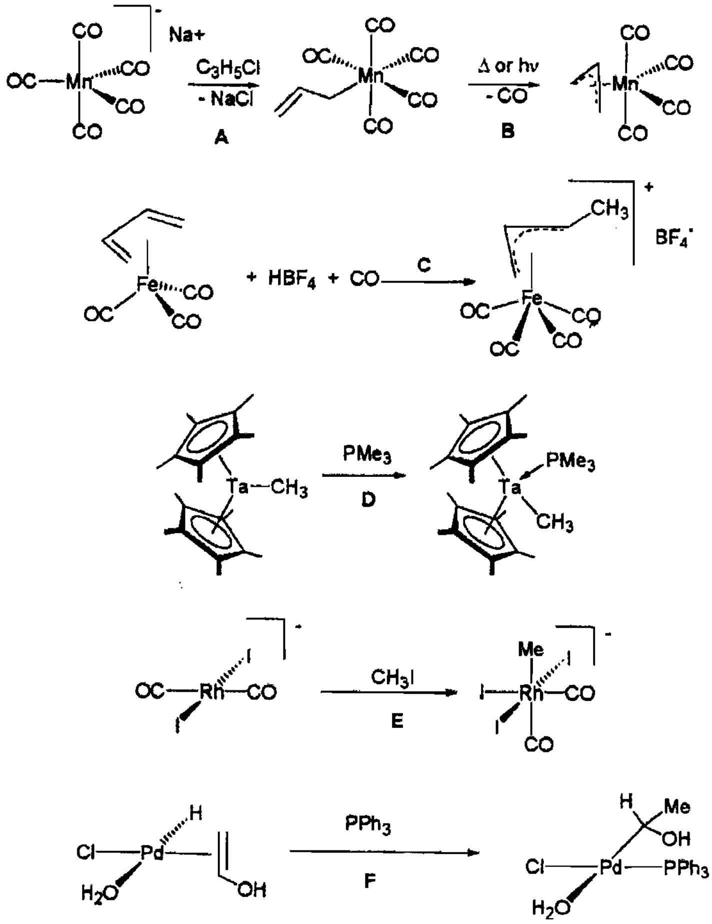
(c) Identify the starting isotopes **A** and **B** in each of the following syntheses of transactinoid elements:

(i) $\mathbf{A} + {}^4_2He \rightarrow {}^{256}_{101}Md + {}^1_0n$

(ii) $\mathbf{B} + {}^{16}_8O \rightarrow {}^{255}_{102}No + 5({}^1_0n)$ [2]

(d) The common ores of nickel and copper are sulphides. By contrast, aluminium is obtained from the oxide and calcium from the carbonate. Explain these observations in terms of hardness. [4]

(e) Which of the following reactions **A-F** are oxidative additions? Justify your answers. [6]



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.