UNIVERSITY OF ESWATINI

MAIN EXAMINATION

ACADEMIC YEAR 2018/2019

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 two 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]**

Justify your answers. **[2]**

QUESTION THREE

(a) (i) Assign the oxidation state of M in $(\eta^4\text{-}C_8H_8)M(CO)_3]$. Assuming the 18-electron rule applies, identify the second row transition metal, M.

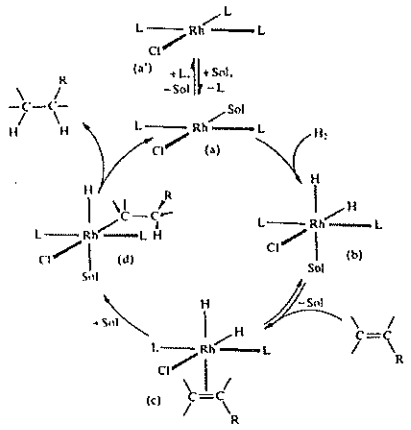
(ii) What charge, z, would be necessary for $[(\eta^5\text{-}C_6H_7)Fe(CO)_3]^z$ to obey the 18-electron rule? **[3]**

(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) What oxidation state do you think best describes $[Mn_2(CO)_{10}]$? **[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) Give the <u>electron count</u> for the metal centre in $Ir(CO)(NO)(PPh_3)_2$.

(ii) Draw the structures of <u>three</u> complexes (*cyclo*-C_5H_5)$Rd(CO)_n$ (n = 2, 3, 4) assuming that the complexes obey the 18-electron rule. **[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 (d)(i) above affect the total valence electron count?

(iii) Comment on the fact that $H_2Os_3(CO)_{10}$ also has a triangular Os_3-core. **[5]**

(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]**

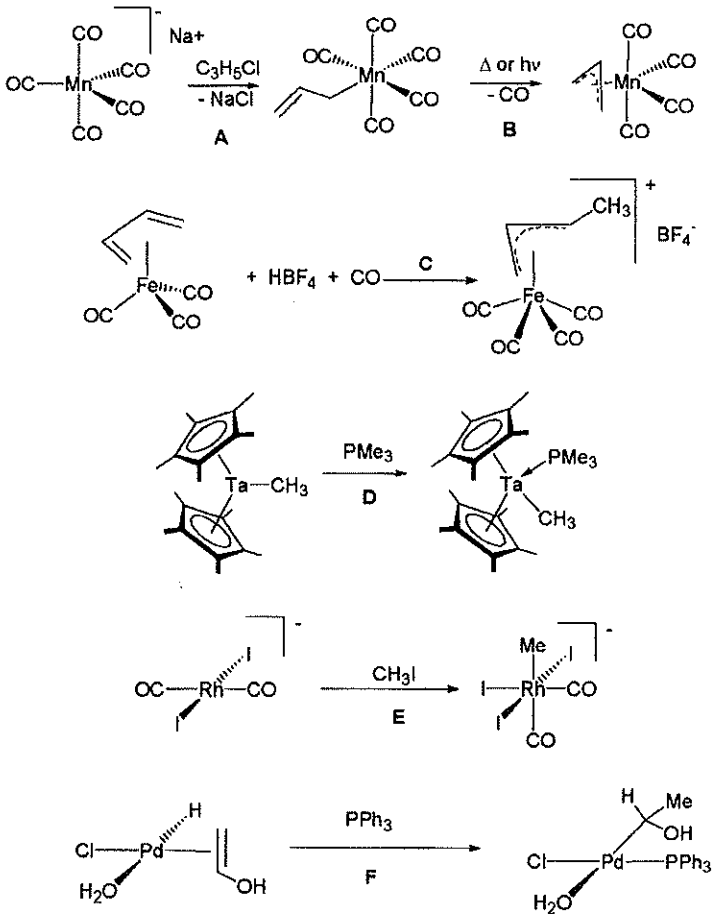
(c) Identify the starting isotopes **A** and **B** in each of the following syntheses of transactinoid elements:

(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 IA	2 IIA	3 IIIB	4 IVB	5 VB	6 VIB	7 VIIB	8	9	10 VIIIB	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.