UNIVERSITY OF SWAZILAND

FINAL EXAMINATION

ACADEMIC YEAR 2008/2009

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 valence electron count and oxidation number for the metal in each of the following complexes:
(i) $[Fe(\eta^5\text{-}C_5H_5)_2][BF_4]$
(ii) $[Fe(CO)_4]^{2-}$
(iii) $Co_2(CO)_8$ [6]

(b) Provide the products (draw the structure) for the reaction of $Ir(CO)Cl(PPh_3)_2$ with the following:
(i) H_2
(ii) MeI
(iii) CO [6]

(c) If CO is a two electron donor and NO is a three electron donor, what are the possible formulae of the stable 18 electron Cr^0 and Fe^0 compounds containing just NO and/or CO? [5]

(d) Identify the Lewis acids and bases in the following reactions
(i) $BrF_3 + F^- \rightarrow BrF_4^-$
(ii) $KH + H_2O \rightarrow KOH + H_2$ [4]

(e) Identify the compounds **A** to **D**:

$$Si \xrightarrow{Cl_2} \mathbf{A} \xrightarrow{RLi} \mathbf{B} \xrightarrow{H_2O} \mathbf{C} \xrightarrow{\Delta} \mathbf{D}$$ [4]

QUESTION TWO

(a) Explain the following:

(i) Transition metal ions are coloured due to *d-d* electronic transitions. Although *f*-block elements do not have unpaired electrons in *d* orbitals, yet their ions are coloured.
(ii) The separation of lanthanides and actinides is very difficult.
(iii) The filling of *5f* orbital in actinides is not as regular as it is for *4f* orbital in case of lanthanides.
(iv) Oxidation states of more than +3, in case of thorium (Th), protactinium (Pa) and uranium (U), are more stable.
(v) During ion-exchange chromatography lutetium (Lu) is separated first and lanthanum (La) the last. [10]

(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. [6]

(c) Using the reactor irradiation method, write down a sequence of nuclear reactions that will produce $^{237}_{93}Np$ from $^{235}_{92}U$. [3]

(d) Predict the structures of
(i) $[IF_6]^+$
(ii) BrF_5 [6]

QUESTION THREE

(a) Draw the structures of
(i) $Ru_3(CO)_{12}$
(ii) $Rh_4(CO)_{12}$ [4]

(b) How are the following compounds made?
(i) $Fe(CO)_5$
(ii) $Co_2(CO)_8$
(iii) $Mn_2(CO)_{10}$ [6]

(c) Describe the <u>three</u> classes of aprotic solvents, citing examples of each. [6]

(d) Give organic fragments isolobal with each of the following:
(i) $(\eta^5\text{-}C_5H_5)Ni$
(ii) $(\eta^6\text{-}C_6H_6)Cr(CO)_2$
(iii) $[Fe(CO)_2(PPh_3)]^-$ [3]

(e) Show how cyclohepta-1,3,5-triene is coordinated to the
(i) $Mo(CO)_3$ fragment
(ii) $Ru(CO)_3$ fragment [6]

QUESTION FOUR

(a) (i) Using diagrams describe the orbital overlaps responsible for the two main bonding interactions between carbon monoxide (CO) and a transition metal.
(ii) Describe and account for the effect each of the bonding interactions above has upon
(1) the C-O bond length
(2) the energy of the C-O stretching vibration observed in the infra-red spectrum. [10]

(b) Explain why the spin-only formula cannot be used to describe the magnetic properties of lanthanide (Ln) ions? [2]

(c) Write balanced Brønsted acid-base equations for the dissolution of the following compounds in liquid hydrogen fluoride (HF):
(i) CH_3CH_2OH
(ii) NH_3
(iii) C_6H_5COOH [6]

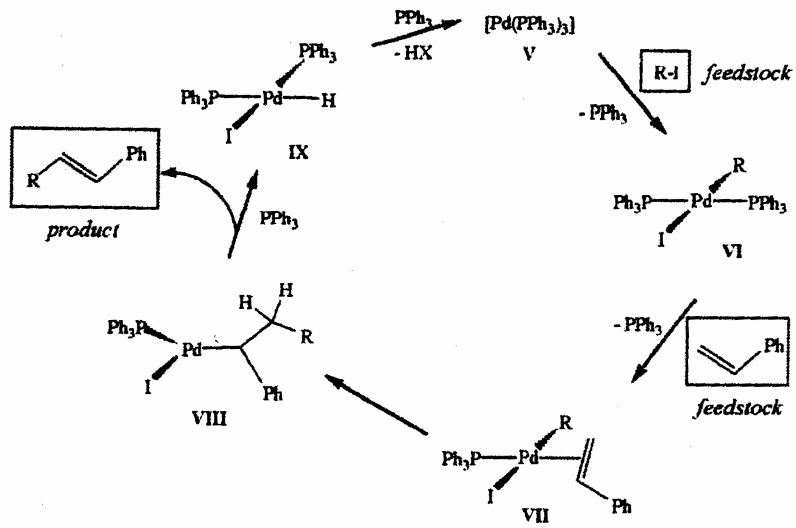
(d) Suggest synthesis of $[IrCl_2(COMe)(CO)(PPH_3)_2]$ from $[IrCl(CO)(PPh_3)_2]$. [4]

(e) The interhalogen compound, BrF_3, has been one of the most widely used non-aqueous solvent. Give three main reasons why it is such a useful solvent. [3]

QUESTION FIVE

(a) Using Polyhedral Skeletal Electron Pair Theory (PSEPT) predict the metal core structures of the following clusters:
(i) $[H_2Ru_6(CO)_{18}]$
(ii) $[Os_6(CO)_{18}]$
(ii) $[H_2Ru_8(CO)_{21}]^{2-}$ [9]

(b) The Heck olefination is immensely important to organic chemists (bless them!), and they always seem to ask questions about it in PhD *viva* exams. Just in case you are ever in this position, a possible catalytic cycle for this is given below. The feedstocks and products are indicated.

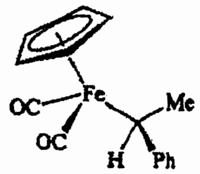


(i) Show that step V→VI is an example of oxidative addition.
(ii) Name the type of reaction VII→VIII and suggest why it might be that the substituent R transfers to the terminal position of the alkene.

(iii) What properties of **VIII** make it susceptible to the reaction **VIII→IX**?
(iv) Comment on the importance of the cis stereochemistry of intermediate **IX** and its conversion **IX→V**. [10]

(c) Explain why the following compounds <u>do not</u> undergo β-elimination:

(i)



(ii) $[Ti(CH_2Ph)_4]$ [6]

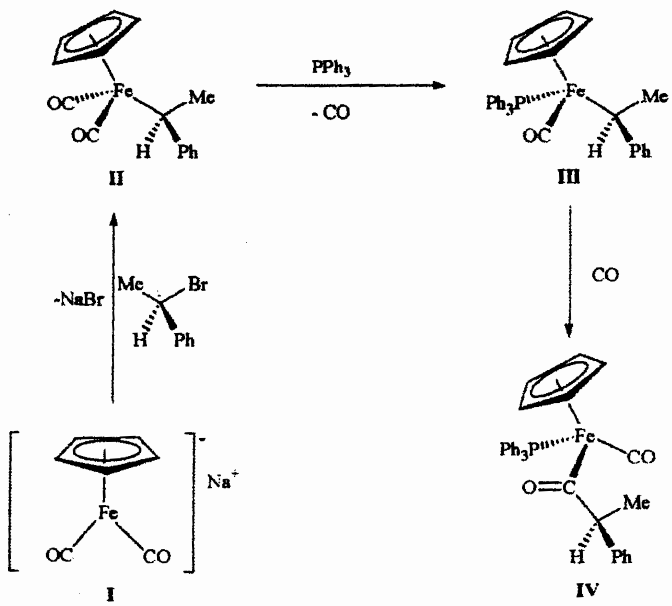
QUESTION SIX

(a) Determine the ground-state term symbol for a Tb^{3+} ion and calculate the expected magnetic moment (μ) value. [6]

(b) Explain why the complex $[Ce\{N(SiMe_3)_2\}_3]$ is colourless but $[Eu\{N(SiMe_3)_2\}_3]$ is an intense orange colour. [3]

(c) Use the HSAB theory to predict which of the following pairs of adducts should be more stable:
(i) $[Fe(NMe_3)_6]^{3+}$ or $[Fe(SbMe_3)_6]^{3+}$.
(ii) BeI_2 or BeF_2 [4]

(d) (i) Give the number of valence electrons, the formal oxidation states and the coordination numbers for each of the compounds **I** to **IV**.
(ii) On the basis of your answer to (i) above and the structures of **I** to **IV**, give the names for the reactions that interconvert them. [12]



PERIODIC TABLE OF ELEMENTS

GROUPS

PERIODS	1 IA	2 IIA	3 IIIB	4 IVB	5 VB	6 VIB	7 VIIB	8 VIIIB	9	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										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.