

QUESTION ONE

- (a) (i) Assuming that the 18-electron rule applies, identify the second-row transition metal:
- (1) $[(\eta^3\text{-C}_3\text{Ph}_3)(\eta^4\text{-C}_4\text{H}_4)\text{M}(\text{NH}_3)_2]^+$
 - (2) $[(\eta^5\text{-C}_5\text{H}_5)\text{M}(\text{CO})_3]_2$ (assume single M–M bond)
 - (3) $\text{M}(\text{CO})_4\text{Br}(\equiv\text{CPh})$
- (ii) What charge, z , would be necessary for $[(\eta^6\text{-C}_6\text{H}_6)_2\text{Ru}]^z$ to obey the 18-electron rule? [4]
- (b) 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]
- (c) Identify the Lewis acids and bases in the following reactions
- (i) $\text{BrF}_3 + \text{F}^- \rightarrow \text{BrF}_4^-$
 - (ii) $\text{KH} + \text{H}_2\text{O} \rightarrow \text{KOH} + \text{H}_2$ [4]
- (d) (i) Complex A, $\text{Ir}(\text{PPh}_3)_2(\text{Cl})_2(\text{COCH}_2\text{Ph})$ [$\nu(\text{CO}) = 1670 \text{ cm}^{-1}$] rearranges cleanly to the isomeric compound B [$\nu(\text{CO}) = 2040 \text{ cm}^{-1}$] at 30°C in benzene. Draw a possible structure for B.
- $$\text{Ir}(\text{PPh}_3)_2(\text{Cl})_2(\text{COCH}_2\text{Ph}) \xrightarrow{\text{C}_6\text{H}_6/30^\circ\text{C}} \text{B} \quad [4]$$
- (ii) Suggest products in the following reactions:
- (1) excess FeCl_3 with $(\eta^5\text{-C}_5\text{H}_5)_2\text{Fe}$
 - (2) $(\eta^5\text{-C}_5\text{H}_5)_2\text{Fe}$ with $\text{PhC}(\text{O})\text{Cl}$ in the presence of AlCl_3
 - (3) $(\eta^5\text{-C}_5\text{H}_5)_2\text{Fe}$ with toluene in the presence of Al and AlCl_3
 - (4) $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{Cl}$ with $\text{Na}[\text{Co}(\text{CO})_4]$ [8]

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) During ion-exchange chromatography lutetium (Lu) is separated first and lanthanum (La) the last. [6]
- (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. [3]

- (c) The reaction of the tetrahedral cluster $\{(\text{Me}_3\text{Si})_3\text{C}\}_4\text{Ga}_4$ with I_2 in boiling hexane results in the formation of $\{(\text{Me}_3\text{Si})_3\text{CGaI}\}_2$ and $\{(\text{Me}_3\text{Si})_3\text{CGaI}_2\}_2$. In each compound there is only one Ga environment. Suggest structures for these compounds and state the oxidation state of Ga in the starting material and products. [5]
- (d) Predict the structures of
 (i) $[\text{IF}_6]^+$
 (ii) BrF_5 [6]
- (e) (i) Determine the ground state term symbol for Tm^{3+} .
 (ii) Calculate the g -value expected for Tm^{3+} .
 (iii) Hence, calculate the effective magnetic moment, μ_{eff} , of Tm^{3+} . [5]

QUESTION THREE

- (a) Sketch the structures of each of the following molecules, clearly indicating the ways in which the ligands are attached to the metal.
 (i) $(\text{C}_8\text{H}_8)\text{Mo}(\text{CO})_3$
 (ii) $(\text{C}_5\text{H}_5)_2\text{Fe}(\text{CO})_2$ [4]
- (b) How are the following compounds made?
 (i) $\text{Fe}(\text{CO})_5$
 (ii) $\text{Co}_2(\text{CO})_8$
 (iii) $\text{Mn}_2(\text{CO})_{10}$ [6]
- (c) (i) Describe the three classes of aprotic solvents, citing examples of each.
 (ii) Hydrosilation is a useful reaction that converts an alkene into a silylalkane. Predict the product of the following general hydrosilation reaction:

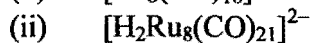
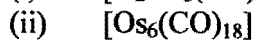
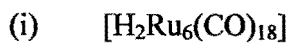
$$\text{R}'\text{-CH}=\text{CH}_2 + \text{H-SiR}_3 \rightarrow$$
 where $\text{R} = \text{H, alkyl, aryl}$
- (iii) SbCl_3 may be used as a non-aqueous solvent above its melting point. Suggest a possible self-ionization process for this solvent. [9]
- (d) (i) For the following, propose examples of isolobal organometallic fragments:
 (1) A fragment isolobal with CH_2^+
 (2) A fragment isolobal with CH^-
 (3) A fragment isolobal with CH_3
 (ii) Give organic fragments isolobal with each of the following:
 (1) $(\eta^5\text{-C}_5\text{H}_5)\text{Ni}$
 (2) $(\eta^6\text{-C}_6\text{H}_6)\text{Cr}(\text{CO})_2$
 (3) $[\text{Fe}(\text{CO})_2(\text{PPh}_3)]^-$ [6]

QUESTION FOUR

- (a) (i) Give a description of the bonding in $[\text{Ir}(\text{CO})_6]^{3+}$ and compare it with that in the isoelectronic compound $\text{W}(\text{CO})_6$.
(ii) How would you expect the IR spectra of these species to differ in the carbonyl stretching region? [6]
- (b) Suggest reasons for the following observations:
(i) Although Pd(II) complexes with monodentate *O*-donor ligands are not as plentiful as those with *P*-, *S*- and *As*-donor ligands, Pd(II) forms many stable complexes with bidentate *O,O'*-donor ligands.
(ii) EDTA⁴⁻ forms very stable complexes with first-row *d*-block metal ions M^{2+} (e.g. $\log K = 18.62$ for the complex with Ni^{2+}); where the M^{3+} ion is accessible, complexes between M^{3+} and EDTA⁴⁻ are more stable than between the corresponding M^{2+} and EDTA⁴⁻ (e.g. $\log K$ for the complex Cr^{2+} is 13.6, and for Cr^{3+} is 23.4). [4]
- (c) (i) Explain why the spin-only formula cannot be used to describe the magnetic properties of lanthanide (Ln) ions?
(ii) Suggest (giving equations) how the following species behave in H_2SO_4 :
(1) H_2O
(2) NH_3
(3) HCO_2H (given that it decomposes) [8]
- (d) What type of reaction is the following, and by what mechanism does it occur?
 $\text{Mn}(\text{CO})_5\text{CH}_3 + \text{CO} \rightarrow \text{Mn}(\text{CO})_5(\text{COCH}_3)$ [4]
- (e) Using the cluster valence electron count (C_{VE}) suggest the metal cage framework adopted by each of the following clusters:
(i) $\text{Os}_5(\text{CO})_{16}$
(ii) $\text{HRu}_6(\text{CO})_{17}\text{B}$
(iii) $\text{Co}_3(\text{CO})_9\text{Ni}(\eta^5\text{-C}_5\text{H}_5)$ [3]

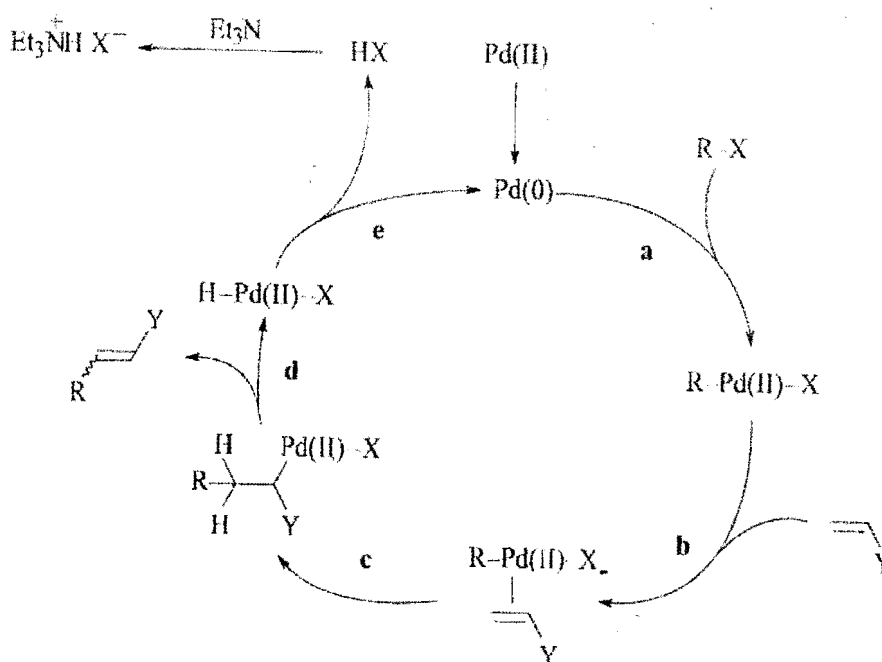
QUESTION FIVE

(a) Using Polyhedral Skeletal Electron Pair Theory (PSEPT) predict the metal core structures of the following clusters:



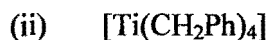
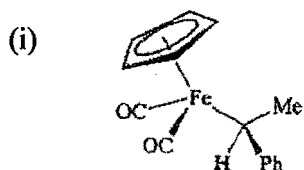
[9]

(b) Below is the catalytic cycle associated with the Heck olefination reaction. For each step marked with a letter, attach the name of one of the fundamental types of organometallic reactions (e.g., nucleophilic abstraction or ligand substitution).



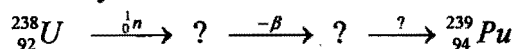
[5]

(c) Explain why the following compounds do not undergo β -elimination:



[6]

(d) (i) Complete the following scheme, inserting the missing nuclides and mode of decay:



(ii) Explain what is meant by the term 'coordinatively unsaturated'.

(iii) What features of $[\text{Rh}(\text{CO})_2\text{I}_2]^-$ allow it to act as an active catalyst? [5]

QUESTION SIX

- (a) When dichlorodimethylsilane, $(\text{CH}_3)_2\text{SiCl}_2$, is treated with alkali metals in tetrahydrofuran, THF, the main product **X** is a crystalline solid of composition, C, 41.4%; H, 10.3%; Si, 48.3%, and molecular weight 290. The proton NMR spectrum of **X** measured in benzene consists of a single band. Suggest structure for **X**. [4]
- (b) **M** is a First Transition Series element. It forms a carbonyl **F** of empirical formula $\text{M}(\text{CO})_5$ which reacts with sodium amalgam, Na/Hg in tetrahydrofuran, THF to give a solution **G**. Treatment of **G** with 3-chloro-1-propene, $\text{CH}_2=\text{CHCH}_2\text{Cl}$ gives a compound **H** of molecular formula $\text{C}_8\text{H}_5\text{H}_5\text{M}$. The infrared spectrum of **H** shows carbonyl stretching bands between 2110 and 2004 cm^{-1} , the ^1H NMR spectrum of **H** indicates protons in *four* chemically distinct environments. On heating **H** to 100 °C one mole of carbon monoxide, CO is eliminated to give **I**, $\text{C}_7\text{H}_5\text{O}_4\text{M}$ [ν_{CO} between 2110 and 1950 cm^{-1}]. The ^1H NMR spectrum of **I** indicates protons in *three* chemically distinct environments.
- Identify the metal **M**.
 - Propose and draw structures for the compounds **F**, **H** and **I** and for the species present in solution **G**.
 - Interpret the ^1H NMR features of **H** and **I**.
 - Discuss the bonding of the organic ligand to **M** in compound **I**. [8]
- (c) It is believed that the catalytic role of organometallic complexes in effecting organic reactions may be understood in terms of successive steps generating 16- and 18-electron complexes from 18- and 16-electron molecules, respectively. Thus, the "hydroformylation" of olefins below is catalysed by $\text{HCo}(\text{CO})_4$ derived from $\text{Co}_2(\text{CO})_8$.
- $$\text{CH}_2=\text{CHR} + \text{H}_2 + \text{CO} \rightarrow \text{RCH}_2\text{CH}_2\text{CHO}$$
- Outline the steps of the catalytic cycle.
 - Identify each cobalt-containing species as a 16- or 18-electron molecule
 - Kinetic studies indicate that the hydroformylation reaction is enhanced by an increase in H_2 pressure and inhibited by an increase in CO pressure. How is the mechanism in your cycle above consistent with these observations? [10]
- (d) The iron atom in $\text{Fe}(\text{CO})_5$ is a weak Lewis base. However, replacement of a CO ligand with a phosphine to give, for example, $\text{Fe}(\text{CO})_4(\text{PPh}_3)$ causes the metal basicity to be enhanced. Why should this be the case? [3]

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	VIIIB	VIII			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	TRANSITION ELEMENTS										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								

*Lanthanide Series

**Actinide 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

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