University of Canterbury

End-of-year Examinations 2009

Prescription Number(s):	CHEM 321
Paper Title:	Inorganic and Structural Chemistry

Time Allowed:	Three hours
Number of pages:	Seven plus periodic table plus answer sheet

Answer **FIVE** questions out of SIX.

All questions are of equal value.

There is a periodic table at the end of this paper.

1. (a) Using diagrams as appropriate, delineate as fully as possible how dissociative and associative reaction mechanisms may be differentiated experimentally.

   (b) For the following 3d transition metal cations, the dissociatively driven rate of water exchange occurs in the order:

   $$Cr^{3+} < Fe^{3+} < Ni^{2+} < Co^{2+} < Mn^{2+} < Cr^{2+}$$

   Outline what factors are responsible for this order.

   (c) For the alkali metal cations, the rate of water exchange is found to increase as the group is descended. Suggest possible reasons for this observation.

   (d) Discuss, using diagrams and examples as appropriate, the differences between *inner-sphere* and *outer-sphere* electron transfer mechanisms, and state what is meant by a self-exchange reaction.

2. (a) Indicate fully what is meant by each of the following terms, giving appropriate examples:

   (i) radioactive decay and half-life

   (ii) radiocarbon dating

   (iii) radio-pharmaceuticals.

   (b) A rock contains 0.257 mg of ^{206}Pb for every mg of ^{238}U. The half-life for the decay of ^{238}U to ^{206}Pb is 4.5×10^9 yr. Showing your full calculations, determine the age of the rock.

   (c) "Tl(I) is a soft toxic metal that is best treated with chelation therapy."

   Discuss this statement fully using appropriate examples to illustrate the concepts covered. Your answer should include discussion upon the nature and consequences of toxicity; the mode of interaction of Tl(I) with an affected individual; the basis of chelation therapy, and explain any potential problems associated with this treatment.

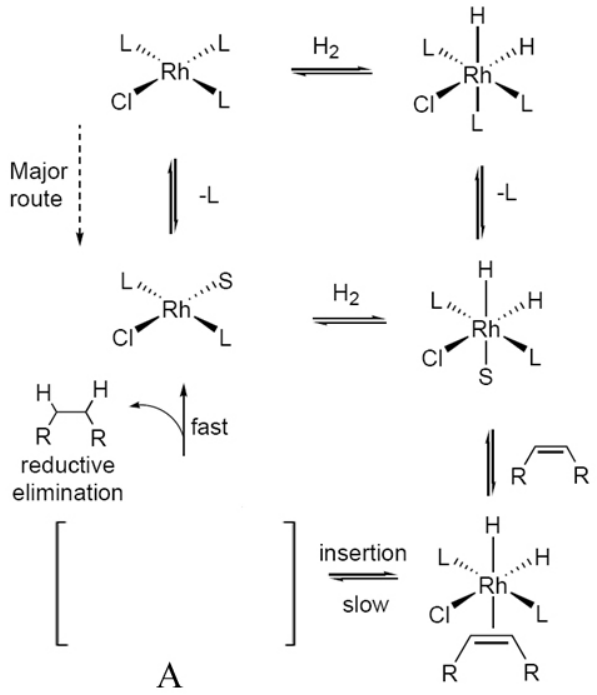
3. Answer **either** (a) **or** (b):

Either

(a) (i) Define the term asymmetric catalysis. Why are homogeneous catalysts particularly well suited for this "niche" type of catalysis (*cf.* heterogeneous catalysts)?

(ii) Name three major steps in the mechanism of olefin polymerization using Zirconocene-based Ziegler-Natta olefin polymerization catalysts.

(iii) Draw missing intermediate (A) in the scheme of catalytic hydrogenation of alkenes provided below. Assuming S (solvent) and L (phosphine) as being neutral 2-e donor ligands and Rh(0) as having 9e, perform an electron count for this intermediate.



Or

(b) (i) Give a definition of a catalyst AND provide an appropriate graphical illustration of the role of a catalyst in enabling a reaction to proceed.

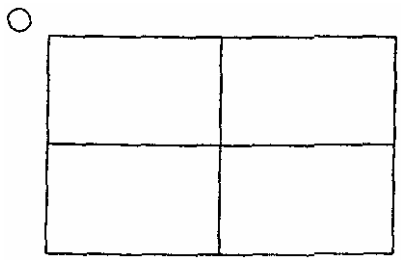
(ii) Name three major *advantages* of homogeneous catalysts. Name one major *disadvantage* of homogeneous catalysts.

(iii) Explain *in detail* how stereo-control is enforced in Zirconocene-based Ziegler-Natta polymerization catalysts. Why do syndiotactic and isotactic polypropylenes have higher melting points compared to atactic polypropylene?

4. (a) (10 marks)

Consider plane group *p2mg* shown below.

Rectangular *2mm* *No. 7 p2mg*

(I) 

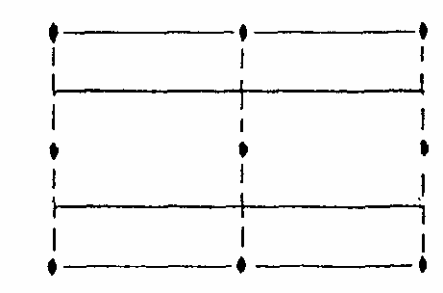
(II) 

Diagram (I) has been cleared of all information except a starting position.
Diagram (II) shows the symmetry elements of this plane group.

(i) Using the attached copy of (I), show all the equivalent positions generated by the symmetry elements in (II).

(ii) Explain each of the symmetry elements in (II) and describe how each position you have drawn was generated by one of these.

(b) (10 marks)

(i) Crystalline compounds can have symmetry elements not possible in isolated finite molecules. Describe these elements, using diagrams if necessary.

(ii) What are the advantages and disadvantages of using crystal structure analysis, rather than other spectroscopic techniques, to elucidate molecular structures.

5. (a) For each of the following compounds, suggest a one-step preparation from an appropriate **neutral metal carbonyl** complex (i.e. from a complex containing only a metal and carbonyl ligands):

   (i) $[Co(CO)_4]^-$

   (ii) $[CpFe(CO)_2]_2$

   (b) Give one example of each of the following:

   (i) A bent 18-electron sandwich complex

   (ii) An 18-electron piano stool complex

   (iii) A phosphine that can act as a strong π-acceptor ligand

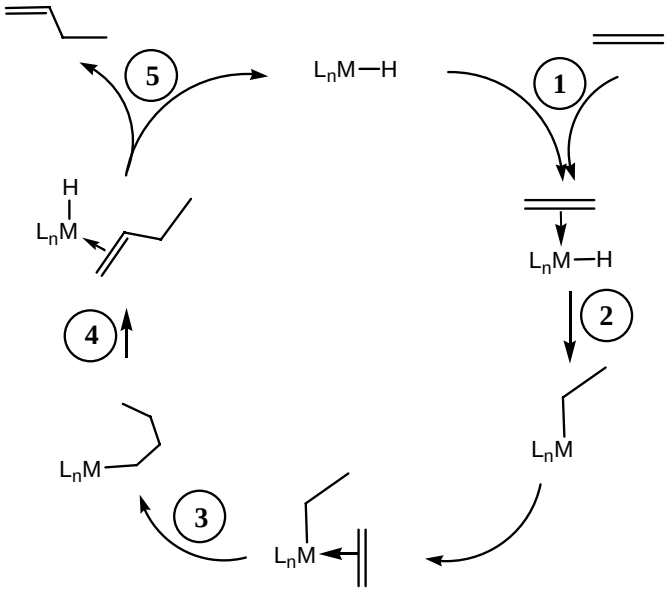
   (c) Explain why ring-slippage is easier for indenyl ligands than it is for cyclopentadienyl ligands.

   (d) Describe the factors which lead to the decomposition of alkyl and aryl transition metal complexes by β-elimination, and give three examples of ligands that are not expected to undergo β-elimination.

   (e) Shown below is a catalytic cycle for the dimerisation of ethylene.

   (i) Describe briefly what is happening in each of steps 2–4.

   (ii) Ignoring *cis*/*trans* isomers, draw the possible products for a dimerisation of styrene ($PhCH{=}CH_2$).



6. (a) Explain which spectroscopic techniques you would use, and how you would employ them, in order to determine the following parameters:

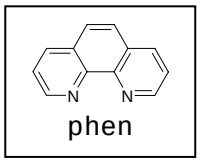
(i) Extinction coefficient

(ii) Excited state lifetimes

(iii) Fluorescence quantum yields

(b) Discuss, using diagrams and giving examples as appropriate, the changes commonly observed in the absorption and emission spectra of d-metal complexes possessing MLCT transitions following the absorption of a photon of light.

(c) Draw and discuss a Jablonsky diagram for 1,10-phenanthroline (phen) and then modify the diagram to account for the use of this chromophore as a ligand in $[Ru(phen)_3]^{2+}$ complexes.



phen

You should also discuss how O_2 can affect the photophysical properties of such complexes, using the Jablonsky diagram to support your answer.

END OF PAPER

Periodic Table on following page

Periodic Table

1 H 1.008																	2 He 4.00
3 Li 6.94	4 Be 9.01											5 B 10.8	6 C 12.01	7 N 14.01	8 O 16.00	9 F 19.0	10 Ne 20.2
11 Na 23.0	12 Mg 24.3											13 Al 27.0	14 Si 28.1	15 P 31.0	16 S 32.1	17 Cl 35.5	18 Ar 39.9
19 K 39.1	20 Ca 40.1	21 Sc 45.0	22 Ti 47.9	23 V 50.9	24 Cr 52.0	25 Mn 54.9	26 Fe 55.9	27 Co 58.9	28 Ni 58.7	29 Cu 63.5	30 Zn 65.4	31 Ga 69.7	32 Ge 72.6	33 As 74.9	34 Se 79.0	35 Br 79.9	36 Kr 83.8
37 Rb 85.5	38 Sr 87.6	39 Y 88.9	40 Zr 91.2	41 Nb 92.9	42 Mo 95.9	43 Tc (99)	44 Ru 101.1	45 Rh 102.9	46 Pd 106.4	47 Ag 107.9	48 Cd 112.4	49 In 114.8	50 Sn 118.7	51 Sb 121.8	52 Te 127.6	53 I 126.9	54 Xe 131.3
55 Cs 132.9	56 Ba 137.3	57-71 see below	72 Hf 178.5	73 Ta 181.0	74 W 183.9	75 Re 186.2	76 Os 190.2	77 Ir 192.2	78 Pt 195.1	79 Au 197.0	80 Hg 200.6	81 Tl 204.4	82 Pb 207.2	83 Bi 209.0	84 Po (210)	85 At (210)	86 Rn (222)
87 Fr (223)	88 Ra (226)	89-103 see below	104 Rf (257)	105 Db (260)	106 Sg (263)	107 Bh (262)	108 Hs (265)	109 Mt (266)	110	111	112						

57 La 138.9	58 Ce 140.1	59 Pr 140.9	60 Nd 144.2	61 Pm (147)	62 Sm 150.4	63 Eu 152.0	64 Gd 157.3	65 Tb 158.9	66 Dy 162.5	67 Ho 164.9	68 Er 167.3	69 Tm 168.9	70 Yb 173.0	71 Lu 175.0

89 Ac (227)	90 Th 232.0	91 Pa (231)	92 U 238.1	93 Np (237)	94 Pu (242)	95 Am (243)	96 Cm (247)	97 Bk (245)	98 Cf (251)	99 Es (254)	100 Fm (253)	101 Md (256)	102 No (254)	103 Lr (257)

Answer sheet for Question 4(a) Name: .....

Student #: .....

Please answer Question 4 (a) using the following diagram and the information given in the question. Make sure you fully explain how you generated each equivalent position.

Diagram (I)