

University of Canterbury

End of Year Examinations 2007

Prescription Number(s): CHEM 321

Paper Title: Inorganic & Structural Chemistry

Time Allowed: THREE HOURS

Number of pages: EIGHT

Answer **FIVE** questions out of **SIX**.

All questions are of equal value.

TURN OVER

1. (a) Rationalise the following observations:
 - (i) On going from $\text{Fe}(\text{CO})_5$ to $\text{Fe}(\text{CO})_3(\text{PPh}_3)_2$, absorption bands in the infrared spectrum at 2025 and 2000 cm^{-1} are replaced by bands at 1944, 1886 and 1881 cm^{-1} .
 - (ii) For anions of the type $[\text{M}(\text{CO})_4]^{n-}$, $n = 1$ for $\text{M} = \text{Co}$, but $n = 2$ for $\text{M} = \text{Fe}$.

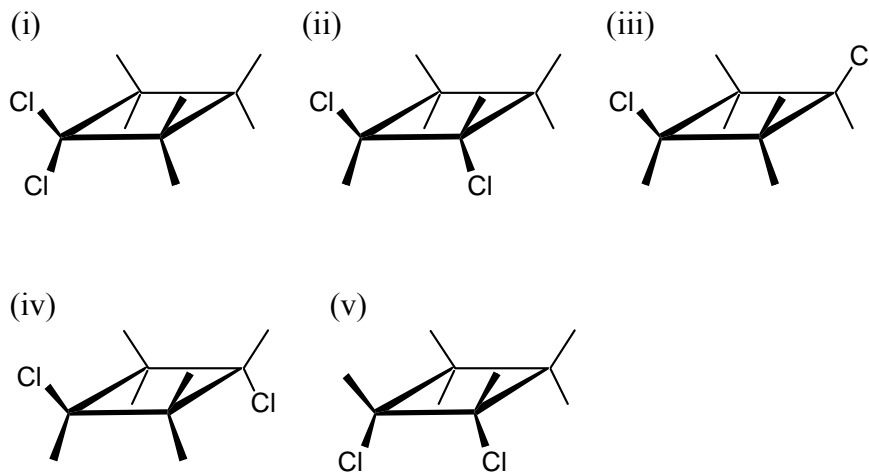
- (b) For each of the following compounds, suggest a one-step preparation from an appropriate **neutral metal carbonyl** complex (i.e. from a complex containing only a metal and carbonyl ligands):
 - (i) $[\text{Co}(\text{CO})_4]^-$
 - (ii) $[\text{CpFe}(\text{CO})_2]_2$

- (c) Draw the expected transition metal product from each of the following reactions:
 - (i) $\text{VCl}_3 + \text{Na} + \text{CO}$ (200 atm) at $160\text{ }^\circ\text{C}$;
 - (ii) $\text{Cr}(\text{CO})_6 + h\nu$ in tetrahydrofuran ($\text{C}_4\text{H}_8\text{O}$).

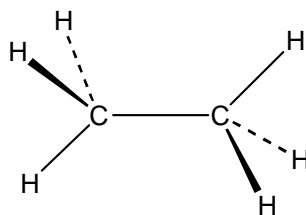
- (d) Explain what is meant by the term “oxidative addition”. Give at least one example.

- (e) Explain what is meant by the term “migratory insertion”. Give at least one example.

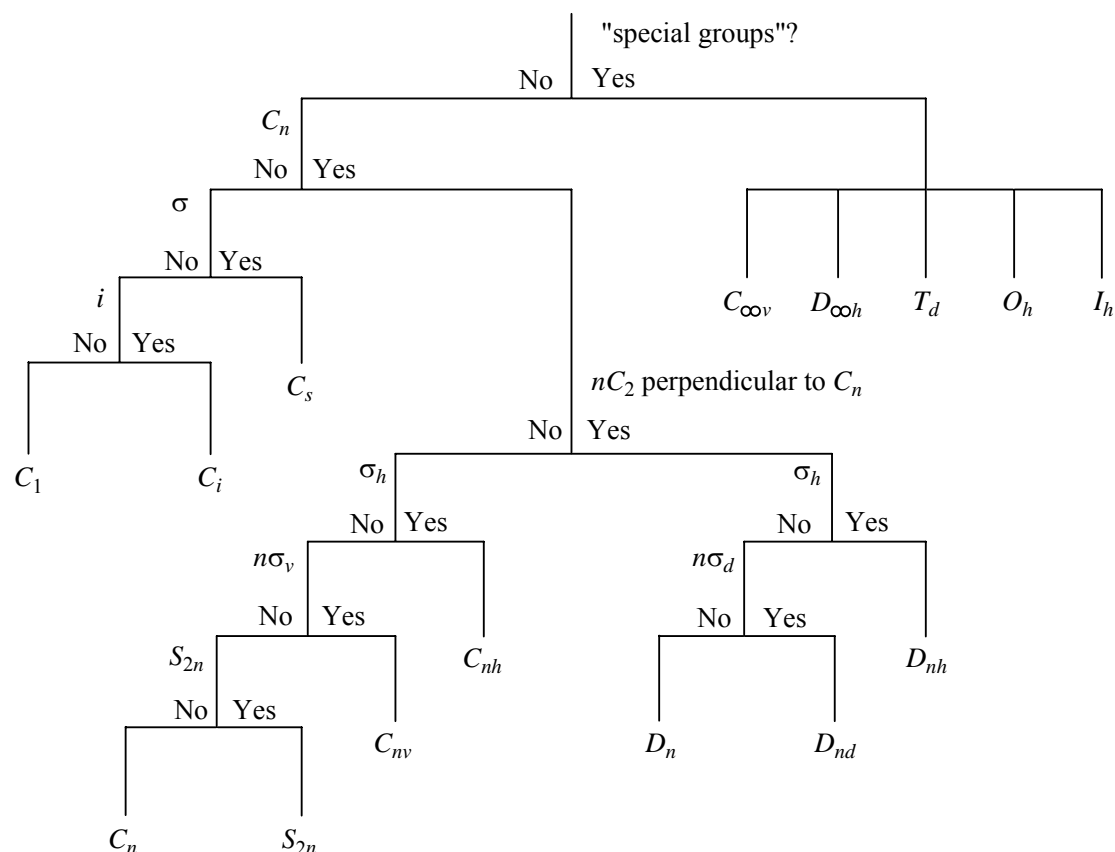
2. (a) Shown below are five isomers of dichlorocyclobutane. For each isomer, determine its point group (note your workings through the chart on the following page) and list all of the symmetry operations for that point group.



- (b) Which of the molecules in part (a) is/are polar?
- (c) Which of the molecules in part (a) is/are dissymmetric?
- (d) Which of the molecules in part (a) is/are centrosymmetric?
- (e) List all of the symmetry operations for staggered ethane, shown below.



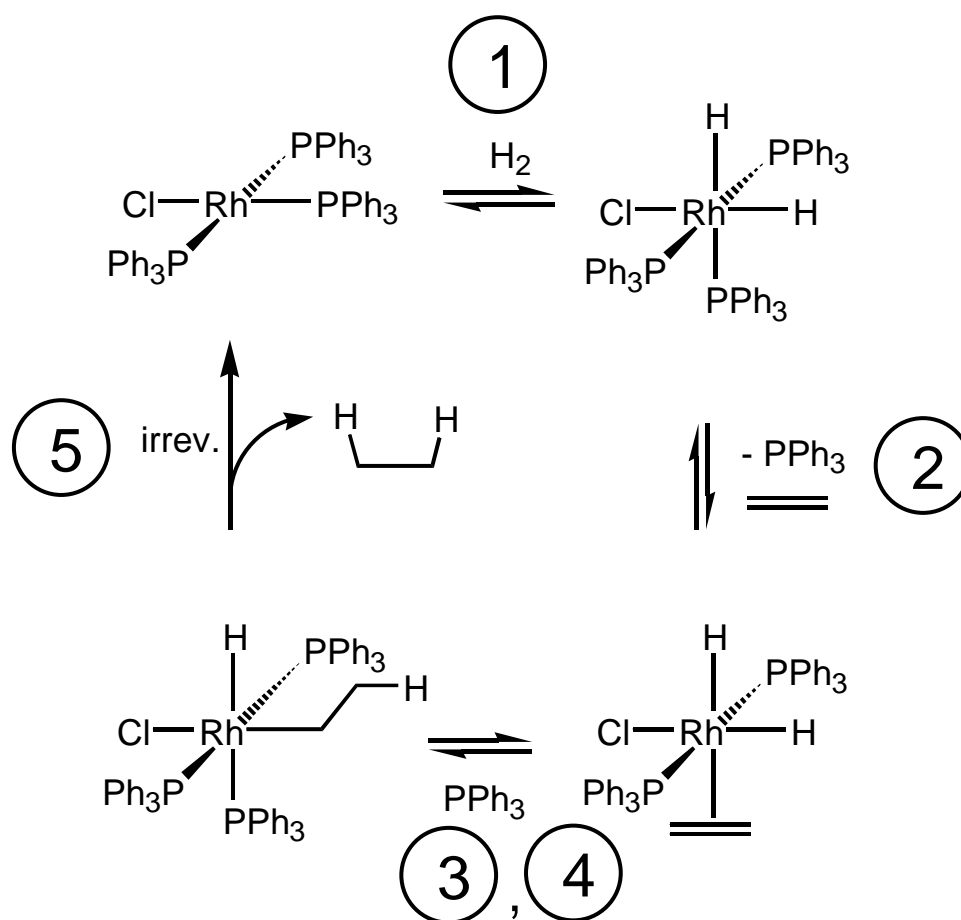
Question 2 continued on following page

Question 2 continued

3. (a) What is meant by the **lattice** of a structure and how does a **unit cell** relate to a lattice?
- (b) Crystal structures can have symmetry elements never found in single, finite molecules. Describe these elements, using diagrams if necessary.
- (c) What is meant by “**atomic scattering factor**”?
- (d) How is the **structure factor** related to:
- the intensity of a diffracted X-ray beam; and
 - the equation
$$F_c(hkl) = \sum_{\text{all atoms}} f_i \cos 2\pi(hx_i + ky_i + lz_i)$$
- (e) X-ray intensity data are often collected at $-110\text{ }^\circ\text{C}$ rather than at room temperature. Why?
- (f) Why are X-rays, rather than other forms of electromagnetic radiation, used for the determination of structures by diffraction methods?

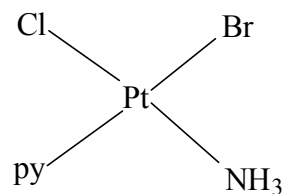
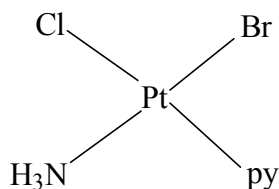
TURN OVER

4. (a) Shown below is a catalytic cycle for the hydrogenation process. For each step, labelled 1 – 5, name the type of reaction.

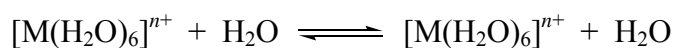


- (b) (i) Describe how phosphines bind to transition metals.
- (ii) What is the “Tolman angle” and how is it defined?
- (iii) What alterations would you need to make to convert the hydrogenation process shown in (a) into an enantioselective process? Name a suitable catalyst.
- (c) (i) Which products (main products and side products) can be formed in the metal-catalysed homogeneous reaction of 1-butene with H_2 and CO ?
- (ii) Name the process in part (i) and give a suitable catalyst for this reaction.

5. (a) Given the trans effect series $\text{Br}^- > \text{Cl}^- > \text{pyridine (py)} > \text{NH}_3$, specify the most direct ways of synthesising the following complexes from $[\text{PtCl}_4]^{2-}$, Br^- , NH_3 and pyridine.



- (b) The water exchange reaction below proceeds via an I_d mechanism at the rates tabulated, for the following cations.



M^{n+}	Rate (s^{-1})	M^{n+}	Rate (s^{-1})
Cr^{2+}	7×10^9	Co^{2+}	1×10^6
Mn^{2+}	3×10^7	Ni^{2+}	3×10^4
Fe^{2+}	3×10^6	Cu^{2+}	8×10^9
Cr^{3+}	3×10^{-6}	Rh^{3+}	4×10^{-8}

Comment fully upon the following:

- The variation in rate across the M^{2+} species on traversing the first row transition series.
- The difference in rate between Cr^{2+} and Cr^{3+} .
- At what rate might you expect $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ to undergo water exchange relative to the other tabulated metal complexes?

6. (a) Explain how zinc finger proteins bind to DNA. Include comments on the selectivity of binding and the mechanism by which binding can be switched on and off.
- (b) Discuss whether you think that the zinc ion(s) of a zinc finger protein could be replaced by another metal ion. Your answer should consider the properties of the metal ions and also possible changes to the protein.
- (c) Describe how footprinting experiments work and the nature of the information that can be gained from them. What are the key requirements of a footprinting agent in each kind of experiment?

END OF PAPER