

IMPERIAL COLLEGE LONDON

**BSc and MSci DEGREES – JANUARY 2010, for Internal Students of
the Imperial College of Science, Technology and Medicine**

**This paper is also taken for the relevant examination for the
Associateship**

ADVANCED CHEMISTRY THEORY IIIA

Inorganic Chemistry

Wednesday 13th January 2010, 09:30-12:30

Answer ONE question from each attended course

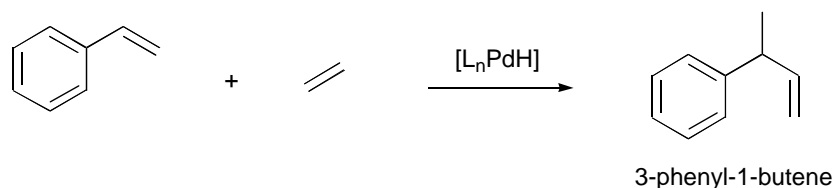
**USE A SEPARATE ANSWER BOOK FOR EACH
QUESTION. WRITE YOUR CANDIDATE NUMBER ON
EACH ANSWER BOOK.**

3.I1 – Inorganic Mechanisms and Catalysis

Answer parts a) **AND** b) and **EITHER** part c) **OR** part d)

a) Answer **ALL** parts of this question.

- i) The hydrovinylation of styrene (also referred to as the co-dimerisation of styrene and ethene) yields 3-phenyl-1-butene and is catalysed by the palladium hydride species $[L_nPdH]$. Draw a catalytic cycle for this reaction and explain each step. Which types of selectivity have to be considered?



(5 marks)

- ii) A side-reaction can sometimes occur, whereby the same palladium hydride species isomerises the product to internal alkenes. Identify the products and describe the mechanism.

(3 marks)

b) Describe the mechanism for the palladium-catalysed oxidation of ethene with oxygen (Wacker process).

(8 marks)

c) Give the mechanism for the iridium-catalysed carbonylation of methanol to acetic acid (Cativa Process). Discuss the role of promoters that are able to bind iodide.

(9 marks)

d) Discuss three different mechanisms for the oxidative addition reactions at a transition metal centre. Illustrate each mechanism with an example.

(9 marks)

3.I2 – Advanced Main Group Chemistry

Answer any **TWO** of the three parts a), b), and c).

a) Answer **ALL** parts of this question.

- i) Explain how the ground state multiplicity of silylenes (:SiR_2) is influenced by the steric and electronic properties of the R substituents. (3.5 marks)
- ii) Discuss the structural parameters that characterise a silicon-silicon double bond, using diagrams where necessary. (3 marks)
- iii) Predict the ground state structures of the following three hypothetical disilenes $\text{R}_2\text{Si}=\text{SiR}_2$ ($\text{R} = \text{Li}$, $\text{R} = \text{F}$, $\text{R} = \text{Si}^t\text{Bu}_3$) and explain your prediction. Illustrate the consequences of varying the R substituent on the HOMO and LUMO using a schematic diagram. Comment on the UV/vis spectra of each disilene. (6 marks)

b) Answer **ALL** parts of this question.

- i) Define the term *metalloid clusters* and comment briefly on their significance with reference to the grey area between metals and molecules. (3.5 marks)
- ii) Give balanced equations for the reaction of aluminium vapour (Al) and hydrogen chloride (HCl) at 1000°C and 10^{-5} mbar. Which of the products predominates under these conditions and why? What happens upon cooling to room temperature? (4 marks)
- iii) Discuss the factors which influence the outcome of the reactions of aluminium(I) halides (AlX) with a nucleophile RLi . Briefly describe how the choice of experimental conditions is influenced by these factors. (5 marks)

QUESTION CONTINUED OVERLEAF

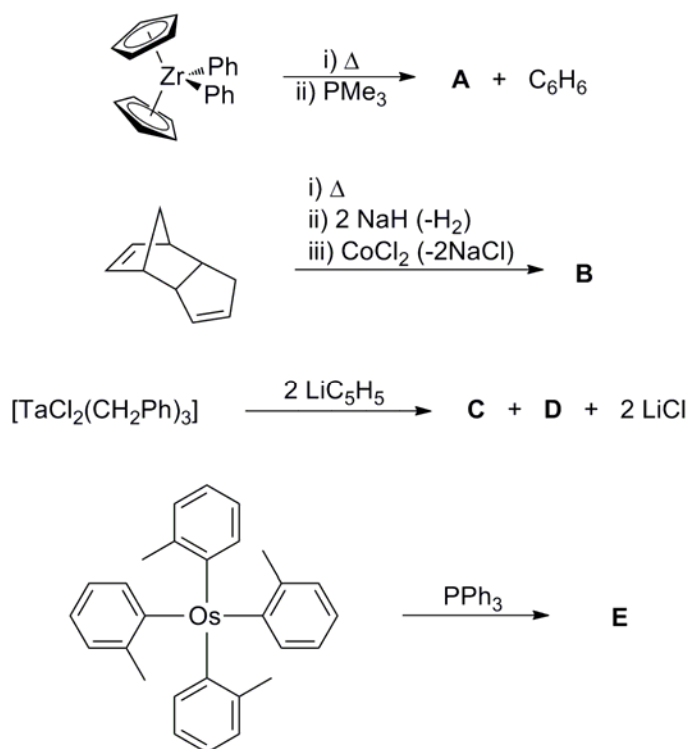
c) Answer **ALL** parts of this question.

- i) Discuss which parameters determine the degree of “frustration” in *Frustrated Lewis Pairs* (FLPs). Illustrate your answer with examples.
(4.5 marks)
- ii) List the advantages and disadvantages of N-heterocyclic carbenes versus phosphanes as Lewis bases in FLPs. Use Lewis structures where necessary to illustrate your answer.
(3 marks)
- iii) Draw the catalytic cycle for the hydrogenation of imines with an FLP as the catalyst. Explain why the hydrogenation of ketones is not catalysed by FLPs.
(5 marks)

3.I3 – Advanced Transition Metal Chemistry

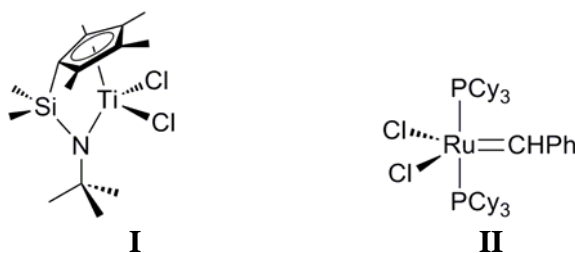
Answer part a) and **EITHER** part b) **OR** part c).

a) Predict the products **A-E** of the following reactions, drawing key intermediates where possible:



(15 marks)

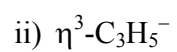
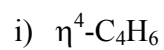
b) Describe the mechanisms by which **I** and **II** may be used to polymerise alkenes.



(10 marks)

QUESTION CONTINUED OVERLEAF

- c) Outline a simple frontier orbital bonding diagram for the following ligand fragments when coordinated to a first row transition metal. Give an example of a complex containing each ligand type:



(10 marks)

3.I4 – Solid State Chemistry

Answer both part (a) **AND** part (b)

- a) Sketch and explain what is meant by *hysteresis* for a ferromagnetic material; define the terms *remanence* and *coercivity*. Hence, explain what is meant by *hard* and *soft* magnetic materials.

(11 marks)

b) Answer any **TWO** of the following **THREE** parts:

- i) Vanadium monoxide, with approximate composition VO, has the sodium chloride structure [Cubic F, V at (0,0,0); O at ($\frac{1}{2}, \frac{1}{2}, 0$)]. Experimental measurements on a particular sample indicate a unit cell parameter, $a = 4.137 \text{ \AA}$, a V:O ratio of 1:1.30, and a density of 5220 kgm^{-3} . Suggest two possible types of defect that might account for the non-stoichiometry, and calculate which is present. Hence, write down the formula in an appropriate style.
- ii) A range of fast ion conductors are based on the fluorite structure [CaF_2 , Cubic F, Ca at (0,0,0); F at $\pm(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$]. Using an appropriate sketch, suggest which type of intrinsic defect is likely to dominate, and how it might lead to ionic conduction in the solid. Explain whether oxides or fluorides (based on the fluorite structure) are more likely to have the higher ionic conductivity at a given temperature.
- iii) Low concentrations of both beryllium and aluminium can dissolve in iron to form substitutional solid solutions. Explain why these alloys are mechanically stronger than the pure iron. Suggest which element will produce the greater strengthening effect at a given atomic concentration.

(7 marks for each part)