

IMPERIAL COLLEGE LONDON

**BSc and MSci DEGREES – JANUARY 2011, 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

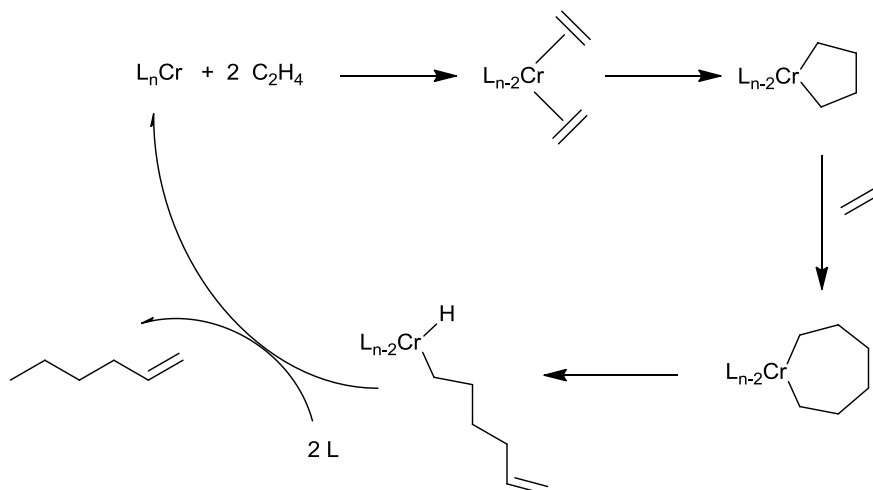
Thursday 13th January 2011, 14:00-17:00

**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) of this question.

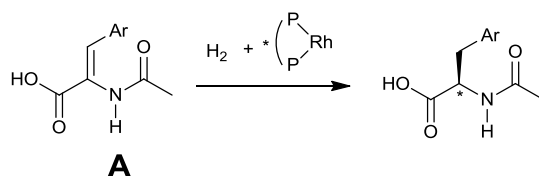
- a) Explain briefly the following terms: TOF, catalyst resting state, chemoselectivity (4 marks)
- b) In recent years, several chromium-based complexes $[L_nCr]$ have been found to catalyse the oligomerisation of ethylene selectively to 1-hexene. The unusual selectivity is believed to be due to a metallacyclic mechanism, which is shown below. Explain each step in the catalytic cycle. Provide an explanation why the formation of 1-hexene is preferred over the formation of other alkenes such as 1-butene or 1-octene. (12 marks)



- c) Answer **ALL** parts of this question.
- i) The 2001 Chemistry Nobel Prize was awarded to Sharpless, Noyori and Knowles for their contributions to the field of asymmetric catalysis. Give the structures of two examples of chiral diphosphine ligands used in asymmetric catalysis. (2 marks)

QUESTION CONTINUED OVERLEAF

- ii) One of the first commercial applications of asymmetric catalysis was an asymmetric hydrogenation of **A** to produce the chiral amino acid L-dopa (see reaction given below). The catalyst used in this process was a rhodium complex containing a chiral diphosphine ligand. Studies on the mechanism of this reaction have shown that of the two diastereomeric intermediates, the minor diastereomer gives the major product. Draw the two diastereomers and explain how they originate. Draw a Gibbs free energy diagram to illustrate your discussion.



(7 marks)

- d) Devise a catalytic route for the synthesis of polysulfone, an alternating polymer made from ethylene and SO_2 in methanol as the solvent. Draw a catalytic cycle for this process and explain the individual steps. Which metal catalyst would you choose and what side-products might be expected?

(9 marks)

3.I2 – Advanced Main Group Chemistry

Answer **ANY TWO** parts from a), b), **AND** c) of this question.

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

- i) Give four reasons for the high thermal stability of West's N-heterocyclic silylene.
(4 marks)
- ii) With reference to the CGMT model and frontier orbitals, explain why N-heterocyclic silylenes, unlike most diarylsilylenes, do not dimerise to disilenes.
(4 marks)
- iii) Give a three-step synthesis of a stable N-heterocyclic silylene starting from the diimine $t\text{BuN}=\text{CH}-\text{CH}=\text{N}t\text{Bu}$ and using two of the following reagents: SiMe_4 , K, SiCl_4 , Cl_2 , BBr_3 , HCl . Comment on the choice of solvent for each step.
(4.5 marks)

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

- i) Give three reasons why alkyl- and aryl-calcium compounds are less common than the corresponding Grignard compounds.
(3 marks)
- ii) Give reaction schemes for two possible decomposition pathways of mesityl calcium iodide, MesCaI , in tetrahydrofuran (Mes = 2,4,6-trimethylphenyl). Suggest an experiment to prove that both products are formed through the same intermediate.
(4.5 marks)
- iii) Suggest a synthesis for a stable magnesium(I) compound using all of the following reagents: Mg, $t\text{Bu}-\text{N}=\text{C}=\text{N}-t\text{Bu}$, PhLi , I_2 , K.

Describe the bonding of the nitrogen atoms to the magnesium centre in the product.

(5 marks)

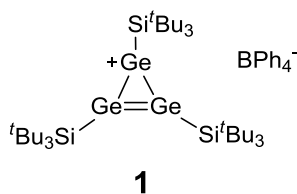
QUESTION CONTINUED OVERLEAF

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

i) Explain the concept of homoaromaticity with the use of appropriate drawings, and give an example of a strongly homoaromatic compound. (4 marks)

ii) Explain the endocyclic bond orders of both pentaphenylborole (PhBC_4Ph_4) and its dianion. Comment on the strongly differing ^7Li NMR shifts of a Li^+ cation when η^5 -coordinated to the BC_4 -ring of these compounds. (3.5 marks)

iii) The reaction of **1** with LiCl yields a product with one ^{29}Si NMR signal at 25°C , which splits into two signals in the ratio 2:1 at -80°C . Conversely, the product of the reaction of **1** with MesLi ($\text{Mes} = 2,4,6\text{-trimethylphenyl}$) shows two ^{29}Si NMR signals in the ratio 2:1 at all temperatures. Explain these observations.



(5 marks)

3.I3 – Advanced Transition Metal Chemistry

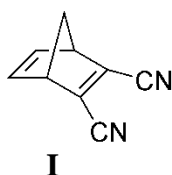
Answer part a) **AND** part b) and **EITHER** part c) **OR** part d) of this question.

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

- i) Describe the orbital overlap between the metal centre and the carbon atom in a Fischer carbene complex and in a Schrock alkylidene complex, and outline the factors that determine which type of complex is formed between a metal centre and benzyldiene (CHPh).

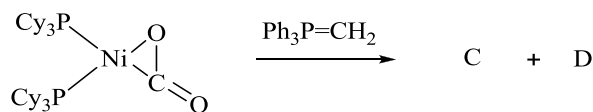
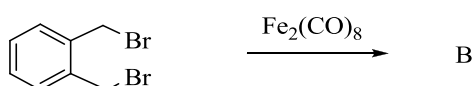
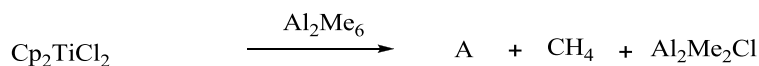
(5 marks)

- ii) Draw a mechanism for the ring-opening metathesis polymerization (ROMP) of compound **I** (include the structure of a suitable initiator in your answer). Briefly outline why norbornenes and norbornadienes are popular monomers for ROMP.



(4 marks)

b) Suggest structures for compounds **A – D** in the following reactions:



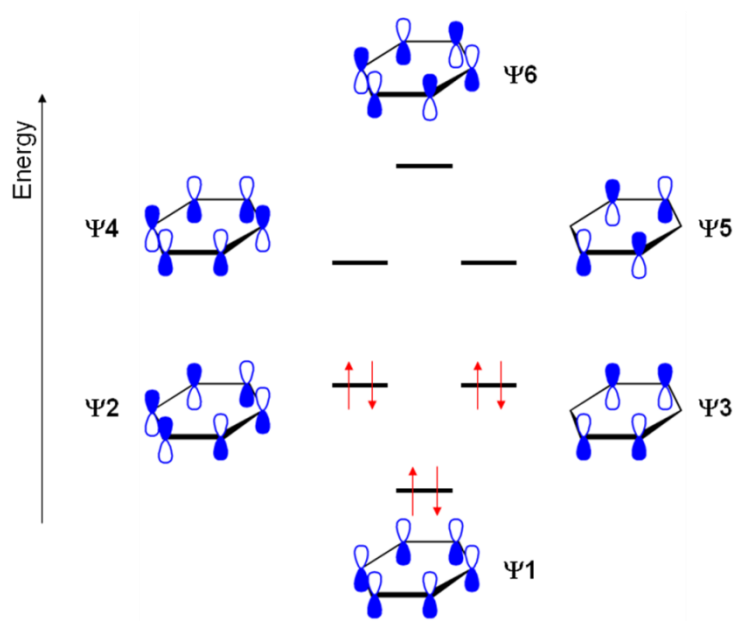
(8 marks)

- c) Discuss and sketch the 'averaged' and 'static' ^1H NMR spectra for $\text{Fe}_2(\text{CO})_4(\eta^5\text{-C}_5\text{H}_5)_2$ and $\text{Fe}(\text{CO})_3(\eta^4\text{-C}_8\text{H}_8)$. Give details of the fluxional process(es) involved and state whether the spectra are taken at low ($< -50^\circ\text{C}$) or room (25°C) temperatures.

(8 marks)

QUESTION CONTINUED OVERLEAF

- d) The molecular orbitals for the π -cloud of benzene are shown below. With the aid of diagrams, explain how these might interact with the valence orbitals of a first row transition metal.



(8 marks)