

IMPERIAL COLLEGE LONDON

**BSc and MSci DEGREES – JUNE 2015, 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 IIB

Inorganic Chemistry

Monday 15th June 2015, 14:00-16:15

**PLEASE NOTE THAT IT IS DEPARTMENTAL POLICY THAT
THESE EXAM QUESTIONS MAY REQUIRE UNDERSTANDING OF
ANY PRIOR CORE COURSE.**

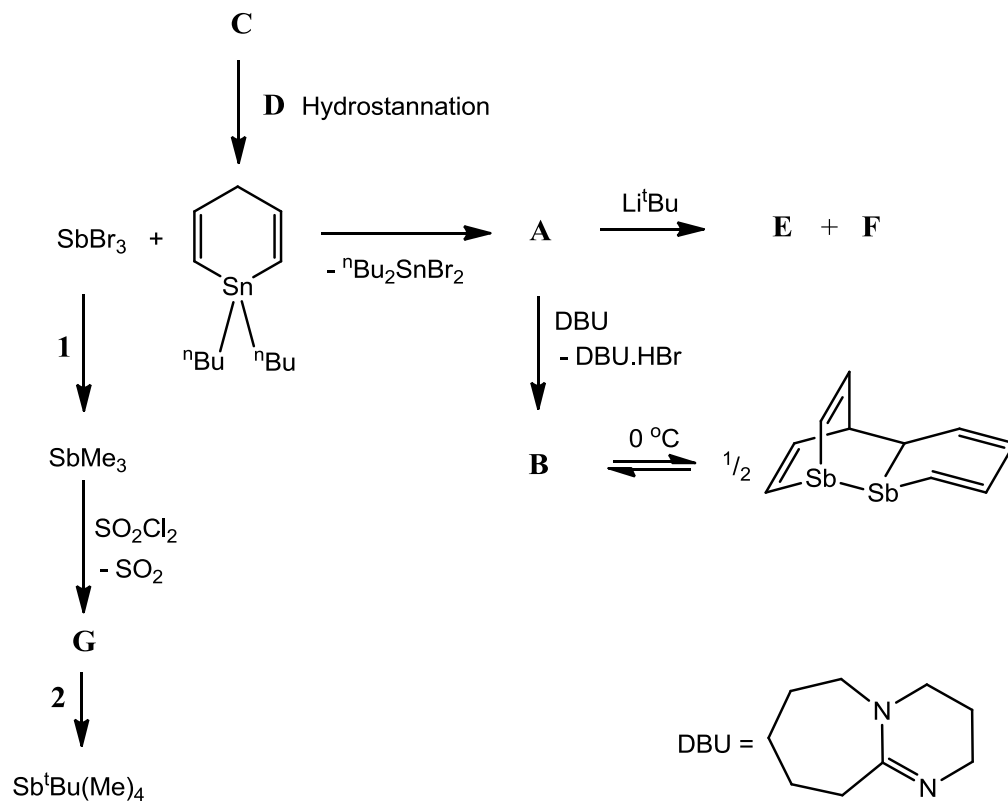
**USE A SEPARATE ANSWER BOOK FOR EACH
QUESTION. WRITE YOUR CANDIDATE NUMBER ON
EACH ANSWER BOOK.**

2.I2 – Main Group Chemistry

Answer part a) and any **TWO** of parts b), c) and d) of this question.

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

i) Identify compounds **A – G** in the scheme below. All reactions involving these species are balanced.



(5.5 marks)

ii) Explain why **B** exists in equilibrium with its dimer at 0°C whereas the phosphorous-containing equivalent of **B** is stable as a monomer.

(2 marks)

iii) Propose reagents and balanced equations for transformations **1** and **2**.

(1.5 marks)

iv) Draw the full structure of $\text{Sb}^t\text{Bu}(\text{Me})_4$. Compare and contrast the donor and acceptor properties of $\text{Sb}^t\text{Bu}(\text{Me})_4$, SbMe_3 and **E**.

(4 marks)

QUESTION CONTINUED OVERLEAF

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

- i) ^tButyllithium exists as tetramers in pentane solution. Explain why this aggregation occurs and describe, with illustrations of the orbitals involved, the bonding in (^tBuLi)₄. (3 marks)
- ii) The ⁷Li NMR spectrum of ^tBuLi in pentane shows a single signal. Upon adding 0.1 molar equivalents of diethyl ether a second signal is observed. Explain this observation. (3 marks)

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

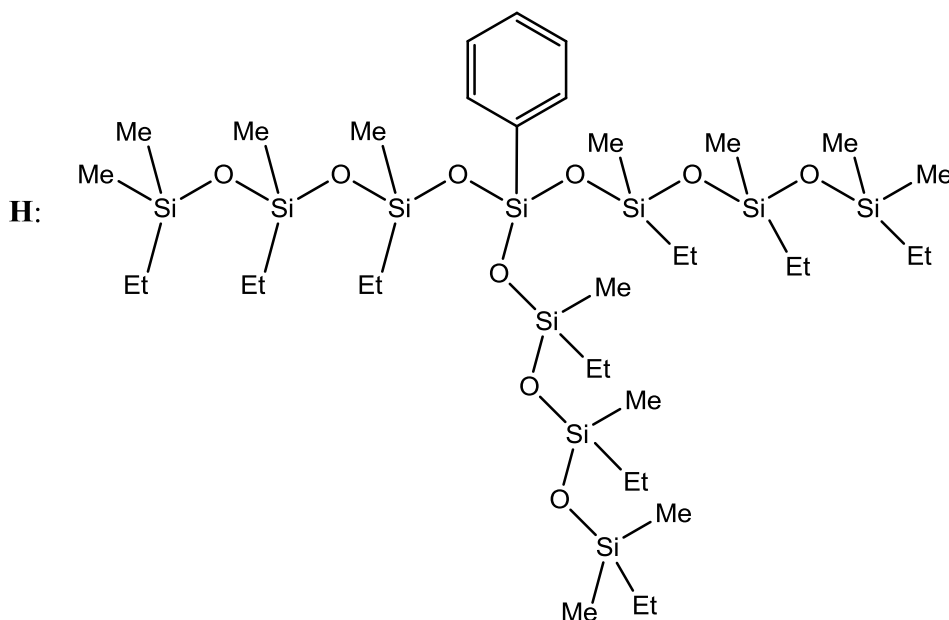
UV irradiation of B₅H₉ causes B-H bond cleavage and formation of B-B coupled *conjuncto*-borane B₁₀H₁₆.

- i) Write a balanced equation for the formation of B₁₀H₁₆ and give the structural type(s) of the cages which comprise it. (2 marks)
- ii) Sketch the skeletal structures (omit the hydrogen atoms) of the three isomers of B₁₀H₁₆. (2 marks)
- iii) One isomer of *conjuncto*-B₁₀H₁₆ has D_{4h} symmetry and shows two signals in its ¹H NMR spectrum. For this isomer draw a full structure, justifying your answer, and account for the NMR spectrum. (2 marks)

QUESTION CONTINUED OVERLEAF

d) Answer **ALL** parts of this question

i) Compound **H** (below) could be prepared via the following reaction:



Identify **J**, **K** and **L** and give balanced reactions for their synthesis from tetrachlorosilane.

(3.5 marks)

ii) Is it a reasonable assumption that **H** will be the only product of this reaction? What spectroscopic analysis could you perform to test this assumption?

(1 mark)

iii) Explain, with diagrams if appropriate, **ONE** macroscopic property **H** is likely to exhibit.

(1.5 marks)

2.I3 – Transition Metal, Coordination and Organometallic Chemistry

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

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

WCl_6 reacts with Et_3Al under CO atmosphere to provide a colourless volatile compound **A** (FW = 352) which shows no signals in its ^1H NMR spectrum, whereas a single signal is observed in the ^{13}C NMR spectrum at *ca.* $\delta = 210$ ppm. **A** reacts with NaC_5H_5 in refluxing THF to yield three equivalents of gas and an organometallic salt, **B**, the ^1H NMR spectrum of which consists only of a singlet at $\delta = 5.5$ ppm. Reaction of **B** with MeCO_2H gives **C**, which gives rise to two singlets in its ^1H NMR spectrum, one at $\delta = 5.9$ ppm and the other at $\delta = -7.5$ ppm (relative integration 5:1 respectively).

Treatment of **C** with excess $\text{CF}_3\text{SO}_3\text{H}$ ($\text{pK}_a \sim -12$) at -80°C in CH_2Cl_2 forms the new thermally unstable complex **D**; at room temperature this compound decomposes by elimination of one equivalent of gas. The ^1H NMR spectrum of **D** exhibits two resonances at $\delta = 5.5$ and -2.1 ppm (relative integration 5:2 respectively). If $\text{CF}_3\text{SO}_3\text{D}$ was used in the synthesis of **D**, the latter resonance splits into a broad 1:1:1 triplet and halves in intensity.

- i) Identify organometallic compounds **A** to **D** by drawing a full structure, and account for the spectroscopic observations.
(5 marks)
- ii) Compound **B** displays two carbonyl stretches in its IR spectrum with an approximate relative intensity ratio of 2:1. Using group theory, account for this observation.
(3 marks)

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

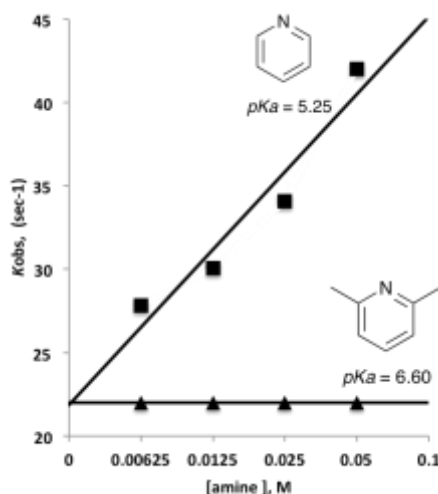
Answer **ALL** parts of this question.

- i) 1,5-cyclooctadiene (cod) reacts with $\text{RhCl}_3 \cdot \text{H}_2\text{O}$ in ethanol to form the dimeric organometallic complex $[\text{RhCl}(\text{cod})]_2$. Draw the structure of this complex and indicate the geometry of the Rh centre.
(1 mark)
- ii) The IR stretching frequency of the C=C bonds in the cod ligand changes from 1665 cm^{-1} to 1465 cm^{-1} upon coordination to Rh. Draw a suitable bonding picture and explain this observation.
(4 marks)

QUESTION CONTINUED OVERLEAF

- iii) The plots of variation of k_{obs} against concentration of pyridyl ligand for the reactions of $[\text{Rh}(\text{cod})(\text{PPh}_3)_2]^+$ in acetone solvent with pyridine and 2,6-dimethylpyridine, along with their pK_a , are shown below. Assuming that the pyridyl ligands are in vast excess, what do these plots tell you about the reaction pathways and the nature of the Rh centre.

(4 marks)



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

- i) Determine the metal-metal bond order and comment on the expected magnetic properties of $[\text{Rh}_2(\mu\text{-O}_2\text{CCH}_3)_4(\text{H}_2\text{O})_2]$.

(2 marks)

- ii) With reference to the Curie temperature (T_c), explain how temperature affects ferromagnetic substances.

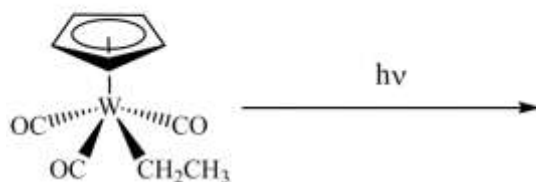
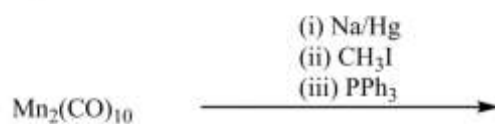
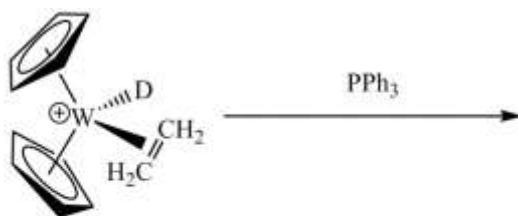
(2 marks)

- iii) The complex $[\text{NiCl}_2(\text{Ph}_2\text{PCH}_2\text{PPh}_2)]$ changes colour from a red diamagnetic solid to a light blue solid with a $\mu_{\text{eff}} = 2.9 \mu_B$ on heating to 110 °C for 3 hours. Explain these observations, draw structures for the complexes and comment on any possible applications.

(4 marks)

QUESTION CONTINUED OVERLEAF

- d) Predict the products of **TWO** of the following transformations, paying attention where appropriate to the stereochemistry of the products. Provide mechanistic reasoning for your answer.



(8 marks)

2.I4 – Crystal and Molecular Architecture

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

- a) Like pure carbon, boron nitride exhibits a number of different polymorphs with different properties. One common structure has a hexagonal lattice, $a = 2.504 \text{ \AA}$ and $c = 6.66 \text{ \AA}$, with a motif B: (0,0,0); (2/3, 1/3, 1/2); N (1/3, 2/3, 0); (0, 0, 1/2). Use this information to answer **ALL** the following questions:
- i) Draw at least 2x2 unit cells of this structure projected along [001]. Identify the nature of the stacking in the [001] direction.
(6 marks)
 - ii) Describe the coordination environment around each type of atom in this structure, and calculate the B-N bond length. Comment on any similarities to the equivalent pure carbon structure (in which the bond length is 1.42 \AA).
(5 marks)
 - iii) Calculate the density of this boron nitride polymorph, and compare it to that of the equivalent pure carbon structure (2.260 g/cm^3).
(4 marks)
- b) Considering the hexagonal boron nitride structure introduced in part (a), answer **ALL** the following questions.
- i) On separate three dimensional sketches of one unit cell, indicate the traces of the following Miller planes: (010); (002); (110); ($\bar{1}\bar{1}0$); (100).
(7 marks)
 - ii) Identify which of these planes are related by threefold rotational symmetry and indicate the location of the relevant triad(s).
(3 marks)
- c) Answer **ALL** the following questions about an alternative boron nitride polymorph which has a cubic F structure with lattice parameter $a = 3.616 \text{ \AA}$, and motif B (0, 0, 0); N (1/4, 1/4, 1/4)
- i) Draw a sketch of one unit cell of this structure projected along a principal axis; describe the coordination number and arrangement of the coordination polyhedra, and hence identify the conventional name for this class of binary structure. To which pure carbon allotrope is it analogous?
(5 marks)
 - ii) On a sketch, draw the traces of the {200} Miller planes. What spacing do these planes have? In an X-ray diffraction experiment, how would the appearance of the {200} peaks in this boron nitride structure compare to the analogous pure carbon structure?
(5 marks)