**IMPERIAL COLLEGE LONDON**

**BSc and MSci DEGREES – JUNE 2014, for Internal Students of the Imperial College of Science, Technology and Medicine**

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

# INORGANIC CHEMISTRY IIB

**Thursday 19th June 2013, 14:00-16:15**

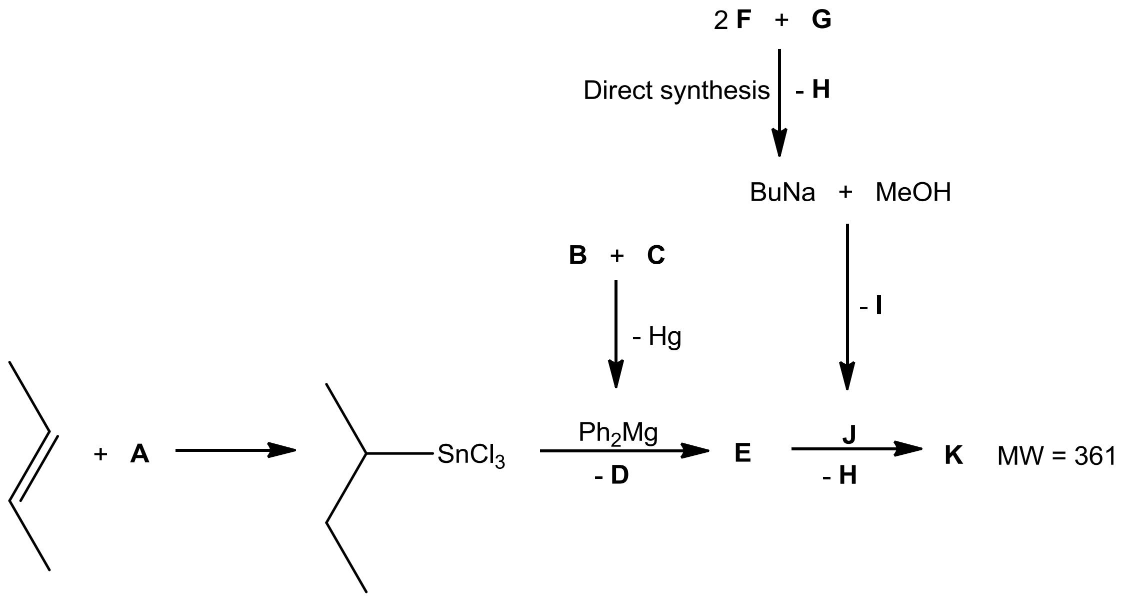
**PLEASE NOTE THAT IT IS DEPARTMENTAL POLICY THAT THESE EXAM QUESTIONS MAY REQUIRE UNDERSTANDING OF ANY PRIOR CORE COURSE.**

**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) Identify compounds **A** – **K** in the scheme below. All reactions are balanced.




(9 marks)

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

Solutions of $Me_3Al$ and $Me_3In$ were analysed by $^1H$ NMR spectroscopy at room temperature and at low temperature.

i) Sketch and explain the $^1H$ NMR spectra of $Me_3Al$ at high and low temperature.
(3 marks)

ii) Sketch and explain the $^1H$ NMR spectra of $Me_3In$ at high and low temperature. Account for any differences in the observed behaviour between $Me_3In$ and $Me_3Al$.

(2 marks)

iii) Using a balanced reaction, propose a synthesis of $Me_2InBr$ from $Me_3In$. What type of reaction is this?

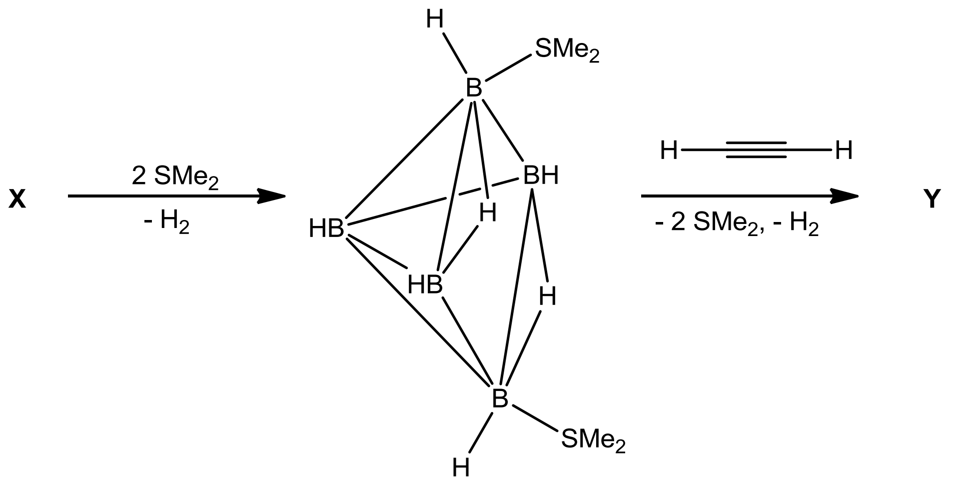
(1 mark)

iv) Draw the solid-state structure of $Me_2InBr$ and explain any difference from the structure of $Me_3In$.

(2 marks)

QUESTION CONTINUED OVERLEAF

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




i) Identify higher borane **X** in the scheme above. Predict and draw the structure of **X**. What type of structure is it?

(3 marks)

ii) **Y** shows only a single signal in its $^{13}C\{^{1}H\}$ NMR spectrum. Predict and draw the structure of **Y**. What type of structure is it?

(3 marks)

iii) Heating **Y** gives an isomer which also shows only a single signal in its $^{13}C\{^{1}H\}$ NMR spectrum. What is the structure of this isomer and why is this the preferred product of thermal isomerisation?

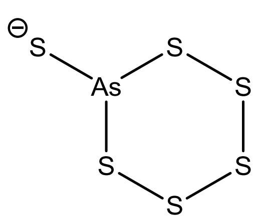
(2 marks)

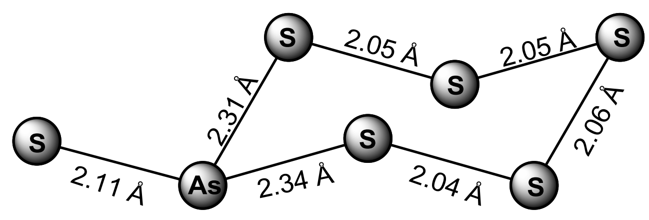
d) Answer **BOTH** parts of this question.

i) Describe, with orbital diagrams, the bonding present in $S_2N_2$ and demonstrate that the molecule is aromatic.

(3.5 marks)

ii) The Lewis structure of the polythioarsenate anion $[SAsS_5]^-$ could be drawn as shown below (left). Do the crystallographically observed bond lengths (below right) support this structure? Justify your answer.




[Covalent radii: S 1.05 Å, As 1.19 Å]

(4.5 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.

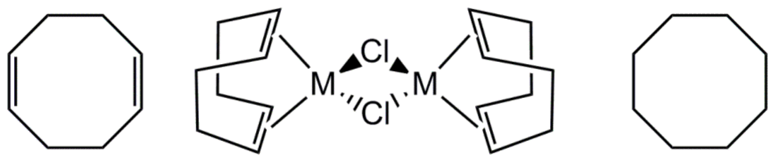
i) Describe, using an appropriate diagram, the Dewar-Chatt-Duncanson (DCD) model of bonding in a transition metal alkene complex.

(5 marks)

ii) When ethylene ($CH_2=CH_2$) coordinates to a transition metal centre, what are the expected effects upon the C–C bond length and H–C–H bond angle?

(1 mark)

iii) Rationalise the variation in $^{13}C$ NMR shifts for the alkene carbon atoms in the Rh and Ir organometallic species below. Use the $^{13}C$ NMR data reported for 1,5-COD (COD = cyclooctadiene; alkene carbon atoms only) and cyclooctane to explain your answer.




| | **1,5-COD** | **[MCl($\eta^4$-1,5–COD)]$_2$** | **Cyclooctane** |
|---|---|---|---|
| **$^{13}C$ NMR ($\delta$, ppm)** | 128.6 | M = Rh 78.0<br>M = Ir 62.1 | 26.9 |

(3 marks)

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

i) Define the 'Jahn-Teller' distortion and explain whether the geometries of the following complexes will be affected: $[Fe(CN)_6]^{4-}$ and $[Cu(H_2O)_6]^{2+}$.

(4 marks)

ii) Sketch the change in d-orbital splitting of an octahedral complex when four equatorial ligands are removed to give a linear structure.

(4 marks)

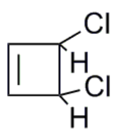
QUESTION CONTINUED OVERLEAF

c) Explain the origins of colour in the transition metal complexes listed below and comment on their relative intensity.

- $[Cr_2O_7]^{2-}$
- $[Mn(H_2O)_6]^{2+}$
- $[NiCl_4]^{2-}$
- $[Fe(\underline{N}CS)(H_2O)_5]^{2+}$

(8 marks)

d) Identify the unknown compounds A-F in the following reactions, using the information provided. For all organometallic products DRAW a full structural formula and give the formal oxidation state of the metal in these compounds; each of these are 18-electron. Give the valence electron count for the metal centre in the UNDERLINED compounds ONLY.



$$+ \; Fe_2(CO)_9 \xrightarrow[\text{- 6CO}]{} \textbf{A} + \textbf{B}$$

$$\underline{(\eta^5\text{-}C_5H_5)_2ZrCl_2} + Mg \xrightarrow[\text{atmosphere}]{\text{CO}} \textbf{C} + MgCl_2$$

$$Mn(CO)_5Cl + AlCl_3 \xrightarrow[\text{- 2CO}]{C_6H_6} \mathbf{[D]^+[E]^-}$$

$$\underline{(\eta^5\text{-}C_5H_5)_2Ni} + Ni(CO)_4 \xrightarrow[\text{- 2CO}]{\text{heat}} \textbf{F}$$

Compound **A** exhibits only a singlet in its $^1H$ NMR spectrum. **B** is a water-soluble inorganic salt.

**C** displays two stretches in its IR spectrum at 1975 and 1885 $cm^{-1}$.

Cation **D** shows only a singlet in its $^1H$ NMR spectrum, whilst **E** is a highly symmetric inorganic anion.

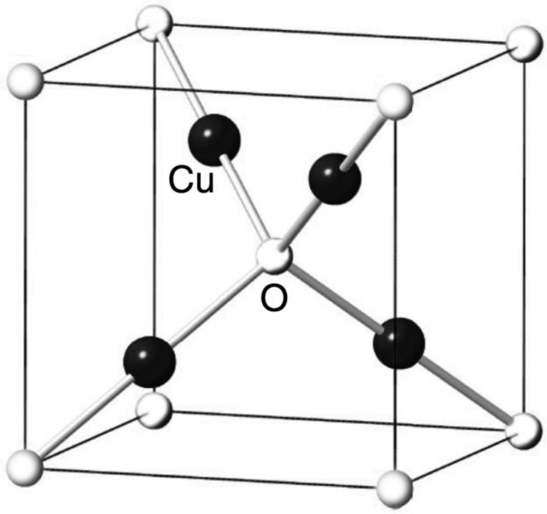
Compound **F** shows only two singlets in its $^{13}C\ \{^1H\}$ NMR spectrum, a strong band in its IR spectrum at 1833 $cm^{-1}$, and contains Ni centres 239 pm apart (the corresponding distance in Ni metal is 250 pm).

(8 marks)

## 2.I4 – Crystal and Molecular Architecture

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

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




i) The structure shown above is adopted by an oxide of copper. What is the formula of this compound and how many formula units are there in the unit cell shown?

(2 marks)

ii) What are the coordination numbers and geometries of the copper and oxide ions? What Bravais lattice does the structure adopt? Indicate the atoms which lie on lattice points.

(4 marks)

iii) Draw the structure in plan view.

(2 marks)

iv) The density of the copper oxide is 6.0 g $cm^{-3}$. Cu = 63.5 a.m.u., O = 16 a.m.u. Calculate the lattice constant ($a$) in Å.

(3 marks)

v) Calculate the Cu-O distance in Å.

(2 marks)

vi) This oxide of copper is bright red. Suggest the origin of the observed colour.

(2 marks)

QUESTION CONTINUED OVERLEAF

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

i) Graphite is commonly found as a hexagonal primitive (*P*) lattice with a motif of carbon atoms at the following positions (0,0,0); (0,0,½); (⅔,⅓,0); (⅓,⅔,½) with lattice parameters $a = b = 2.46$ Å and $c = 6.70$ Å. Draw the unit cell in plan view along the *c*-axis and state how many atoms are contained within it.

(4 marks)

ii) Calculate the density of graphite in g $cm^{-3}$.

(3 marks)

iii) Describe how graphite plays a role in the design of lithium ion batteries.

(3 marks)

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

i) In one of its forms, zirconia ($ZrO_2$) adopts the fluorite structure. Draw the plan view for this form indicating the identity of the ions.

(3 marks)

ii) $ZrO_2$ can be used to prepare zircon ($ZrSiO_4$). Show the equation for this and describe the factors which must be taken into account in the direct synthesis of such materials. How can the progress of the process be monitored?

(4 marks)

iii) Briefly describe the sol-gel process for preparing solids, including the role of heating.

(3 marks)