IMPERIAL COLLEGE LONDON

BSc and MSci DEGREES – JUNE 2013, 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

Tuesday 18th 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.

Year 2/0613 **Turn Over**

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.

$$Ph_3Ga \;+\; \mathbf{X} \longrightarrow Ph_2GaBr$$

$$Me_4Ge \;+\; GeCl_4 \longrightarrow \mathbf{Y}$$

i) Identify **X** and **Y** in the reactions above and write balanced equations. What conditions are required for each reaction and why are they different?

(3 marks)

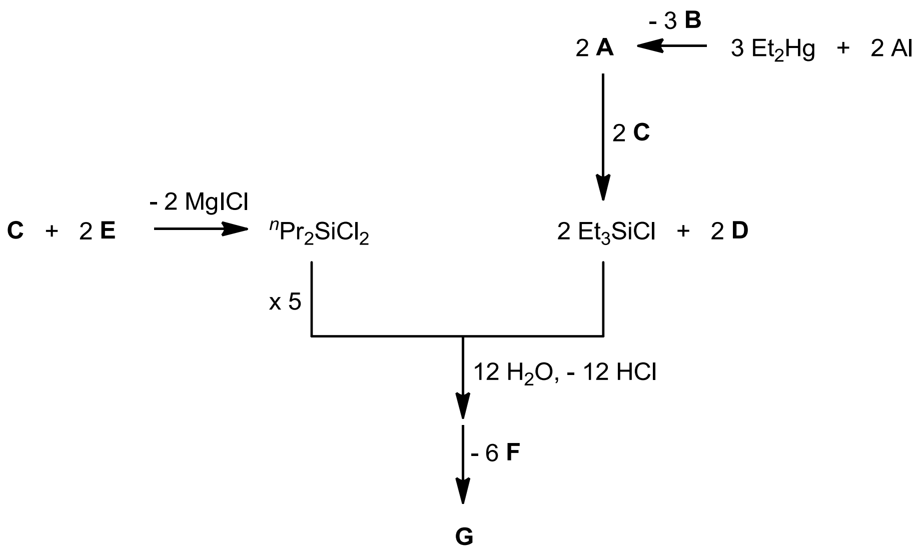
ii) Illustrate, using a scheme, the species formed in the reaction of magnesium turnings with bromobenzene in diethyl ether solution.

(2 marks)

iii) Write a balanced equation for the synthesis of $^{n}Bu_3As$ by metathesis. What is the driving force for the reaction?

(2 marks)

iv) Identify compounds **A** - **G** in the scheme below. All equations are balanced.



(4 marks)

QUESTION CONTINUED OVERLEAF

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

Polyhedral carborane $[B_3CH_8]^-$ shows two separate signals in its ^{11}B NMR spectrum, a doublet of doublets of doublets (ddd) and a doublet of triplets (dt).

i) Predict the structural type of $[B_3CH_8]^-$ and draw its structure.

(4 marks)

ii) Account for the observed NMR signals (Assume only $^1J_{BH}$ coupling is observed). [NMR-active nuclei: ^{11}B (I = 3/2, 80.42%)]

(3 marks)

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

i) ^{n}BuLi exists as a tetramer in diethyl ether solution. What could be added to the solution to promote formation of a dimer structure? Justify your answer.

(3 marks)

ii) Sketch the tetramer and dimer structures and describe the type of bonding present in each.

(4 marks)

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

The reaction of NH_4Cl with BCl_3 or with PCl_5 gives a six-membered ring in each case. The byproduct of both reactions is HCl.

i) Identify and draw the two different rings formed.

(3 marks)

ii) With diagrams, describe how multiple bonding occurs in each of the two rings. What are the structural effects of delocalised multiple bonding and how are these observed?

(3 marks)

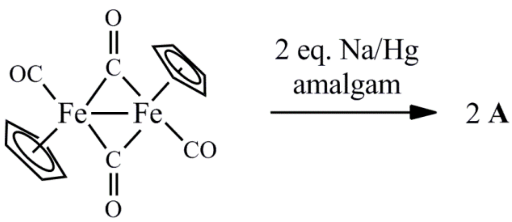
iii) The phosphorus-nitrogen ring can form a polymer when heated. Draw the product formed by the reaction of this polymer with EtOLi.

(1 mark)

2.13 – Transition Metal, Coordination and Organometallic Chemistry

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

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



$[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$

$$\mathbf{C} \xleftarrow{P(C_6H_5)_3} \mathbf{B} \xleftarrow[\text{- NaI}]{\text{MeI}} \mathbf{A} \xrightarrow[\text{(ii) }[Ph_3C]^+[PF_6]^-,\ \text{- }Ph_3CH]{\text{(i) EtI, - NaI}} \mathbf{D}$$

A is a highly air-sensitive salt which dissolves in THF as a 1:1 electrolyte. It displays two ν(CO) bands in its infrared spectrum at 2015 cm^{-1} and 1910 cm^{-1}.

B shows *only* two singlets in its ^1H NMR spectrum at 4.6 ppm and 0.1 ppm (5:3 ratio respectively) and two ν(CO) bands in its infrared spectrum at *ca.* 2000 cm^{-1}.

C is a monometallic species which shows three resonances in its ^1H NMR spectrum at 7.1 ppm (multiplet), 5.1 ppm (singlet) and 2.1 ppm (singlet) with relative integration 15:5:3, respectively. The infrared spectrum displays two ν(CO) bands at 2000 cm^{-1} and 1680 cm^{-1}.

D is a salt containing an inorganic anion. The mass spectrum of the cation shows a main peak at m/z = 204.8 and further peaks at m/z = 176.8, 148.8, and 120.8.

i) Identify the organometallic products **A** to **D** in the reaction sequence above and draw their structures, paying particular attention to the 18-electron rule. In each case give justification to your answer using the characterisation data provided for the compounds. All equations in the scheme are balanced.

(8 marks)

ii) Name the type of reaction represented by transformations

$[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2 \rightarrow$ **A**, and **B** $\rightarrow$ **C**.

[NMR-active nuclei: ^1H (I = 1/2, 100 %)]
[Atomic masses: Fe = 55.8; C = 12.0; H = 1.0; O = 16.0]

(1 mark)

QUESTION CONTINUED OVERLEAF

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

i) Define the ‘lanthanide contraction’ and explain how it affects the sizes of the metallic radii in the third row d-block elements relative to the second row.

(4 marks)

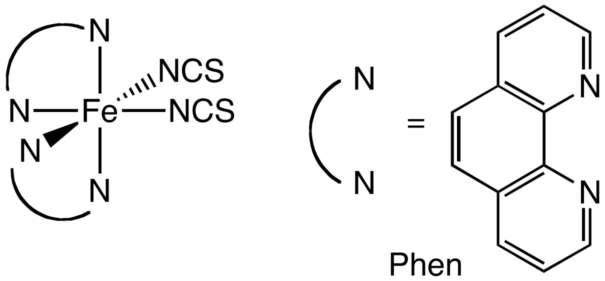
ii) Sketch the change in d-orbital splitting when an octahedral complex rearranges to a trigonal prismatic structure.

(4 marks)

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

i) Describe the features of spin crossover complexes that could make them useful as molecular switches.

(4 marks)



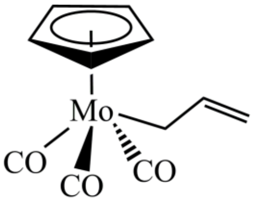
ii) [Fe(Phen)$_2$(<u>N</u>CS)$_2$] shown above displays an abrupt spin crossover at 175 K. Sketch the spin transition curve for this complex and calculate its spin-only magnetic moment μ_{so} at 200 K. Comment on any difference you might expect between the spin-only magnetic moment and the experimentally determined μ_{eff} value at this temperature.

(4 marks)

QUESTION CONTINUED OVERLEAF

d) For **FOUR** of the following reactions i)-v)

Identify the unknown compound by drawing a full structural formula. For the **underlined** compound give the formal oxidation state **and** valence electron count of the metal centre. All equations are balanced.

(i)  $\xrightarrow{h\nu}$ $\underline{\mathbf{A}}$ + CO

(ii) $Cr(CO)_6$ $\xrightarrow[\text{(ii) } [Et_3O]^+[BF_4]^-]{\text{(i) MeLi}}$ $\underline{\mathbf{B}}$ + $Li[BF_4]$

(iii) $\underline{\textit{trans}\text{-}[IrCl(CO)(PPh_3)_2]}$ $\xrightarrow{H_2}$ **C**

(iv) $W(CO)_6$ $\xrightarrow{Na[C_5H_5]}$ $[Na]^+ \underline{\mathbf{[D]}}^-$ + 3 CO

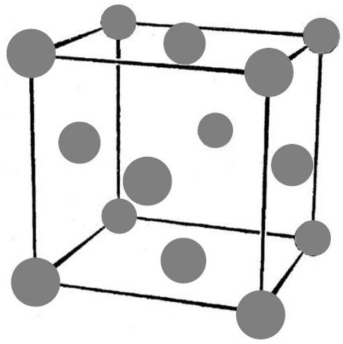
(v) $\underline{Co(\eta^5\text{-}C_5H_5)_2}$ $\xrightarrow{Ag[BF_4]}$ $[\mathbf{E}]^+[BF_4]^-$ + $Ag_{(s)}$

(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.



i) Identify the generic structure above, giving the lattice type it adopts. Draw a fully labelled plan view of the structure, assuming only one atom type. Indicate which atoms are on lattice points.

(4 marks)

ii) What is the stacking sequence of the close packed layers? What is the coordination number of the metal atoms in this structure? Give an example of a metal which adopts this structure (apart from silver).

(3 marks)

iii) Show the location of one octahedral hole and one tetrahedral hole on your plan view.

(2 marks)

iv) Metallic silver adopts the structure shown above and has a lattice constant (a) of 4.07 Å. Calculate the volume occupied by a silver atom in the structure.

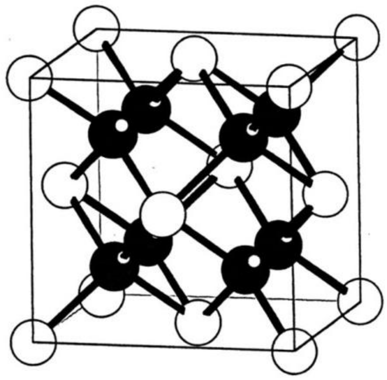
(3 marks)

v) Calculate the density of silver in g cm^{-3}. Atomic mass of silver is 107.9.

(3 marks)

QUESTION CONTINUED OVERLEAF

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



i) Draw a fully labelled plan view of the structure of CeO_2 shown above and state the type of structure.

(3 marks)

ii) Determine how many formula units are in the unit cell and the coordination numbers of the cerium and oxide ions.

(2 marks)

iii) Calculate the shortest separation between the centres of the cations and anions in Å. The lattice constant (a) is 5.41 Å.

(2 marks)

iv) Draw a fully labelled plan view of the alternative unit cell which has oxide ions at the corners.

(3 marks)

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

i) Describe the two types of solid solution.

(2 marks)

ii) Draw the *Halite* structure in plan view. X-ray diffraction shows that the edge of the unit cell of NiO (which has the *Halite* structure) is 4.17 Å. Experimental density determination gives a value of 6.67 g cm^{-3}. Based on these data, rationalise the presence or absence of any defects.
Atomic masses: Ni = 58.7, O = 16.0.

(5 marks)

iii) Doping NiO with Li_2O in air results in one lithium ion per unit cell. Indicate on your plan view from part ii) any changes that have occurred, other than addition of a lithium ion.

(3 marks)