IMPERIAL COLLEGE LONDON

BSc and MSci DEGREES – JUNE 2012, 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

Monday 18th June 2012, 14:00-16:00

PLEASE NOTE THAT IT IS DEPARTMENTAL POLICY THAT THESE EXAM QUESTIONS MAY REQUIRE UNDERSTANDING OF ANY PRIOR CORE COURSE.
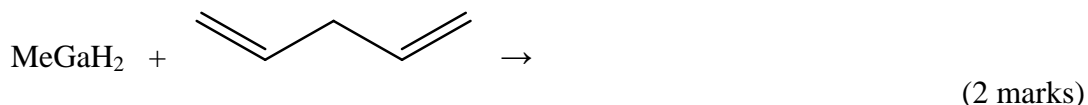
USE A SEPARATE ANSWER BOOK FOR EACH QUESTION. WRITE YOUR CANDIDATE NUMBER ON EACH ANSWER BOOK.

2.I2 – Main Group Chemistry

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

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

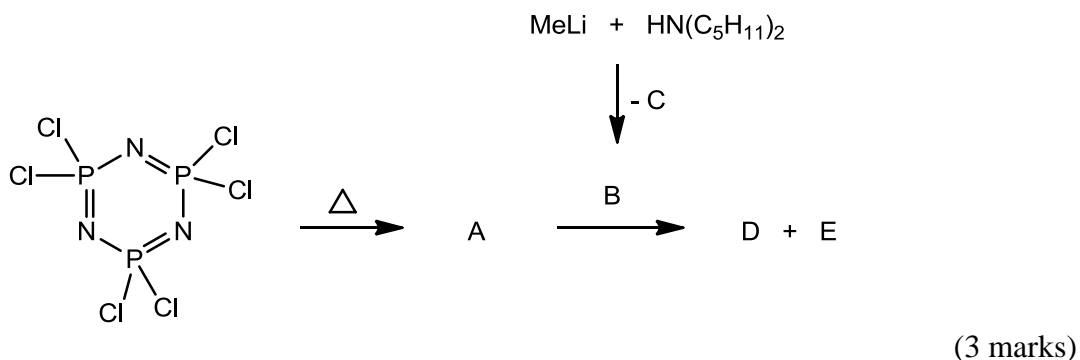i) Identify the product(s) of the following reaction and write a balanced equation. What type of reaction is this?

$MeGaH_2$ +

→

(2 marks)

ii) Write a balanced equation for the synthesis of $^nBu_3In$ by metathesis. What is the driving force for the reaction?

(2 marks)

iii) B_2H_6 reacts with Me_2SO to give a product which forms a 1:1 electrolyte in solution. The ^{11}B NMR spectrum of this solution shows two signals, one of which is a quintet.

Identify the product and write a balanced equation for the reaction. Explain why the product forms and account for the experimental evidence described above.

(4 marks)

iv) Identify compounds A - E in the following scheme:

$MeLi$ + $HN(C_5H_{11})_2$

(3 marks)

v) Identify the product of the following reaction and balance the equation. What conditions are required for the reaction to occur and why?

$3\ Et_4Ge$ + $GeBr_4$ →

(2 marks)

QUESTION CONTINUED OVERLEAF

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

   i) The structure of CB_4H_{10} is shown below. Account for this structure using Wade's rules of electron counting. What is the structural type?
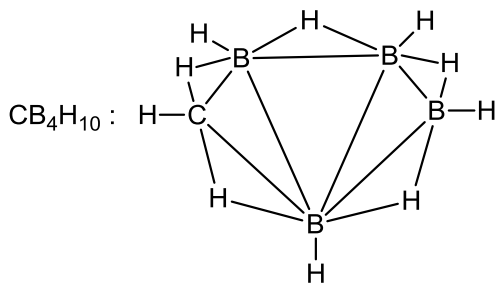
CB_4H_{10} :

   (3 marks)

   ii) Predict and draw the most stable isomer of $[CB_4H_5]^-$. Explain your reasoning and give the structural type.

   (2 marks)

   iii) Would you expect CB_4H_{10} or $[CB_4H_5]^-$ to be more reactive? Justify your answer.

   (1 mark)

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

   Describe the structure and composition of ^nBuMgI under the following conditions. What is the analytical evidence for these structures?

   i) In the solid state after recrystallisation from toluene containing one molar equivalent of dimethyl ether.
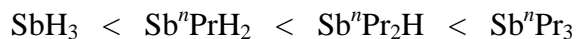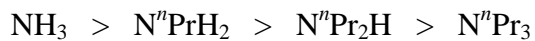
   (2.5 marks)
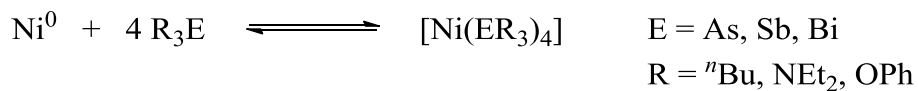
   ii) In diethyl ether solution.

   (3.5 marks)

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

   i) Variation in σ donor ability for two sets of ligands is shown below. Account for the trend within each set of compounds. Why are the trends different for nitrogen- and antimony-based donors?

     $NH_3 \; > \; N^nPrH_2 \; > \; N^nPr_2H \; > \; N^nPr_3$

     $SbH_3 \; < \; Sb^nPrH_2 \; < \; Sb^nPr_2H \; < \; Sb^nPr_3$

                                                                 (3 marks)

   ii) For the reaction shown below, select E and R for which the position of equilibrium will lie furthest to the right. Justify your answer.

     $Ni^0 \; + \; 4 \, R_3E \; \rightleftharpoons \; [Ni(ER_3)_4]$ $E = As, \, Sb, \, Bi$

                                                                 $R = {}^nBu, \, NEt_2, \, OPh$

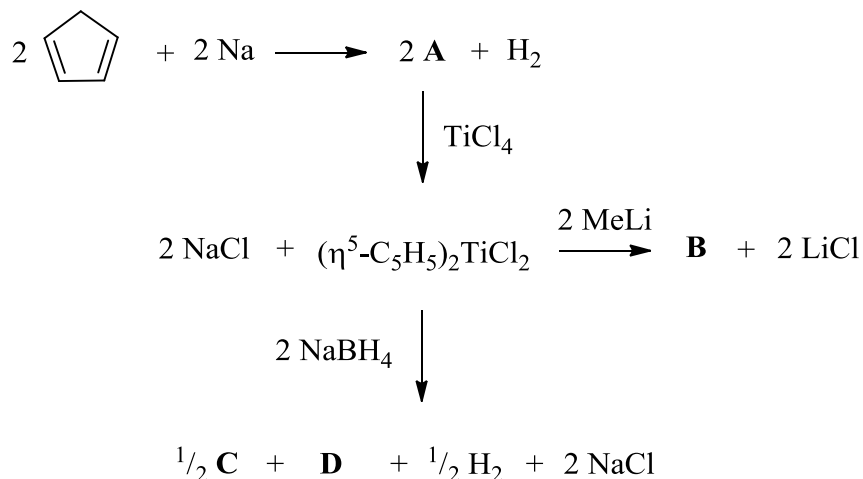   (3 marks)

2.I3 – 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.

$$2 \text{ (cyclopentadiene)} + 2 \text{ Na} \longrightarrow 2 \textbf{ A } + \text{H}_2$$

$$\downarrow \text{TiCl}_4$$

$$2 \text{ NaCl} + (\eta^5\text{-C}_5\text{H}_5)_2\text{TiCl}_2 \xrightarrow{\ 2 \text{ MeLi}\ } \textbf{B} + 2 \text{ LiCl}$$

$$2 \text{ NaBH}_4 \downarrow$$

$$\tfrac{1}{2}\,\textbf{C} + \textbf{D} + \tfrac{1}{2}\,\text{H}_2 + 2 \text{ NaCl}$$

A is a white air-sensitive solid and dissolves in THF as a 1:1 electrolyte. The ^{1}H NMR and ^{13}C{^{1}H} NMR spectra of **A** in this solvent both consist solely of a sharp singlet ($\delta = 5.60$ ppm and $\delta = 103.3$ ppm respectively).

B is a very air-sensitive compound which displays two singlets in its ^{1}H NMR spectrum at $\delta = 6.09$ ppm and $\delta = -0.11$ ppm (intensity ratio 5:3).

C is a gas which is spontaneously flammable when exposed to air. It is a non-metallic dimer (D_{2h} symmetry) and behaves as a Lewis acid, reacting with two equivalents of PMe_3 to form a 1:1 adduct.

D is an extremely air-sensitive paramagnetic purple solid, containing 62.27 % C, 7.32 % H and 5.60 % B, by weight. It adopts C_{2v} molecular symmetry in solution and its ESR spectrum shows very strong coupling to ^{47}Ti ($I = 5/2$, 7.4 %), ^{49}Ti ($I = 7/2$, 5.4 %), and two magnetically equivalent H atoms.

[NMR nuclei: ^{1}H ($I = 1/2$, 100 %), ^{13}C = ($I = 1/2$, 1.1 %)]
[Atomic masses: C 12.01; H 1.00; B 10.81; Ti 47.87]
Group theory tables are provided.

i) Identify **A** and draw a structure for the non-metal component, consistent with the solution-phase NMR spectra.

(1 mark)

ii) Draw a structure for **B** and give the formal oxidation state and electron count for the metal centre.

(2 marks)

iii) Draw a structure consistent with the description of **C**, and write a balanced equation for its reaction with PMe_3.

(2 marks)

iv) For compound **D**, draw a structure consistent with the data. Give the formal oxidation state and number of *d*-electrons for the metal centre. Deduce the total electron count for the metal and boron centres, using MLXZ formalism, and show your working.

(4 marks)

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

i) Briefly explain the origins of the Jahn-Teller distortion and how it affects the geometry in octahedral metal complexes.

(3 marks)

ii) The complex $[Ti(H_2O)_6]^{3+}$ undergoes a Jahn-Teller distortion. Draw the two possible structures and the corresponding d-orbital splitting diagrams of the Jahn-Teller distortion for this complex. Explain, using CFSE arguments, which distortion is most likely.

(5 marks)

QUESTION CONTINUED OVERLEAF

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

   i) Explain briefly what is meant by the effective magnetic moment μ_{eff} for metal complexes.

(3 marks)

   ii) Find **x,y** and **z** in the following complexes by determining the oxidation state of the central metal from the experimental values of the effective magnetic moment μ_{eff} at 298K.

   $K_x[Fe(CN)_6]$ $\mu_{eff} = 2.3$ BM
   $K_y[Co(CN_6)]$ $\mu_{eff} = 0$ BM
   $Na_z[CoF_6]$ $\mu_{eff} = 5.3$ BM

   The effective magnetic moment for the last complex decreases to zero at lower temperatures. Explain this observation.

(5 marks)

d) Rationalise the following experimental data about metal-alkyl complexes. Use chemical illustrations for decomposition pathways to support your answer.

   Force constants k, derived from metal-carbon IR stretching frequencies, for $M(CH_3)_4$:

M	Ti	Pb
k (M–C) N cm^{-1}	2.28	1.90

   Decomposition temperatures ($T_{decomposition}$) for $M(alkyl)_4$ complexes:

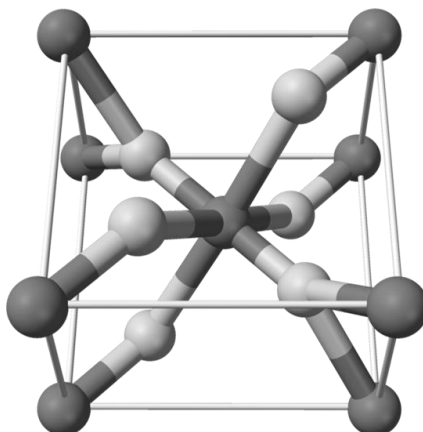| Compound	$T_{decomposition}$ (°C)
$PbEt_4$	> 200
$TiEt_4$	–80
$TiMe_4$	–40
$Ti(CH_2{}^tBu)_4$	> 60

(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.

The structure of nickel(II) fluoride is shown below ($a = b = 465$ pm, $c = 308$ pm; $\alpha = \beta = \gamma = 90°$; Ni = 58.7 a.m.u., F = 19.0 a.m.u.):

i) Draw a fully labelled plan view of the structure, indicating which ions are nickel and which are fluoride.

(3 marks)

ii) State the coordination number and geometry at the nickel and fluoride ions.

(2 marks)

iii) Calculate the number of formula units (Z) in the unit cell shown above.

(1 mark)

iv) Calculate the density of nickel(II) fluoride in g cm^{-3}.

(3 marks)

v) If the experimentally determined density is 4.12 g cm^{-3}, explain whether defects are likely to be present.

(1 mark)

vi) Explain whether you would expect nickel(II) fluoride to be diamagnetic or paramagnetic.

(2 marks)

vii) Nickel(II) fluoride adopts a structural type which takes its name from which compound? State which lattice type the anions in this structure adopt. Explain which sites, within this lattice, the cations occupy.

(3 marks)

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

   i) Name a compound which exists in both cubic close-packed (CCP) and hexagonal close-packed (HCP) structures. What are the names of the different forms?

(2 marks)

   ii) Draw a CCP structure and indicate the close-packed slip planes contained within the unit cell.

(3 marks)

   iii) Explain how these slip planes lead to the ductility of CCP metals being different to that of HCP metals.

(3 marks)

   iv) Using diagrams, describe how an edge dislocation works through a solid.

(2 marks)

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

   ZrO_2 adopts the fluorite (CaF_2) structure ($\alpha = \beta = \gamma = 90°$; Zr = 91.2 a.m.u, O = 16.0 a.m.u, Ca = 40.1 a.m.u).

   i) Draw a fully labelled plan view of the unit cell, indicating the position of the cations and anions.

(3 marks)

   ii) Describe the geometry and coordination number of the zirconium and oxide ions in the structure.

(2 marks)

   iii) State the lattice type on which the structure of ZrO_2 is based.

(1 mark)

   iv) The introduction of Ca^{2+} ions results in the replacement of a zirconium position in the unit cell and a fall in density of 4.55%. Explain the change in density and draw a fully labelled plan view of the calcium doped structure.

(4 marks)