UNIVERSITI SAINS MALAYSIA

First Semester Examination
Academic Session 2010/2011

KTT 313 – Inorganic Chemistry III
[Kimia Takorganik III]

Duration : 3 hours
[Masa : 3 jam]

Please check that this examination paper consists of EIGHT pages of printed material before you begin the examination.

Instructions:

Answer **FIVE** (5) questions. The first question is a **COMPULSORY**. Answer **FOUR** (4) questions by selecting **TWO** (2) questions from **Section A** and **TWO** (2) questions from **Section B**. If a candidate answers more than five questions only the first five questions in the answer sheet will be graded.

Answers each question on a new page.

You may answer the questions either in Bahasa Malaysia or in English.

In the event of any discrepancies, the English version shall be used.

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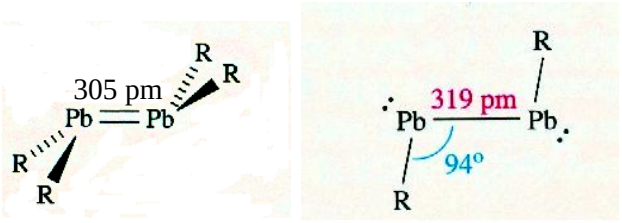
1. (a) The structures of $R_2Pb=PbR_2$ and RPb-PbR are shown below.

i. Show by equation how you would prepare RPb-PbR from RPbBr.

ii. Describe the bonding in $R_2Pb=PbR_2$ and RPb-PbR.



(10 marks)

(b) Predict and sketch the structure of the products in the following reactions:

i. $(\eta^5\text{-Cp})_2Fe$ with toluene in the presence of Al and $AlCl_3$, and

ii. $Ni(CO)_4$ with PPh_3.

(10 marks)

SECTION A

2. (a) Organolithium compounds are useful as synthetic reagents in

i. the conversion of silicon tetrahalides to organosilicon compounds, and

ii the regioselective metallation of alkylbenzene at the alkyl group.

Give an example for each of the reactions described above.

(6 marks)

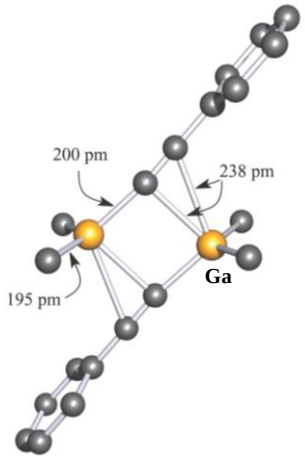
(b) The following reaction,

$$2\ Na[Cp] + BeCl_2 \longrightarrow Cp_2Be + 2NaCl$$

leads to the formation of $(\eta^1Cp)(\eta^5Cp)Be$ in which the Be atom is disordered over two equivalent sites. Draw structures of the disordered compound to illustrate what is meant by disordering.

(7 marks)

(c) The diagram below shows the structure of the alkynyl-bridged dimer of the organogallium compound, $Me_2GaC{\equiv}CPh$. Explain why the alkynyl bridges tilt from the vertical position towards one of the gallium centres.



(7 marks)

3. The enzyme cytochrome c oxidase is the last enzyme in the respiratory electron transport chain of the mitochondria. Draw the structure of the enzyme and show how the structure is related to its function.

(20 marks)

4. Draw a model compound to show the biomineralization of Fe^{3+} in ferritin. Discuss the features in the structure that make ferritin an efficient storage system for iron in mammals. How does the uptake and transport of iron in aerobic microorganism differ from that in mammals?

(20 marks)

SECTION B

5. Explain the following observations:

(a) In the infrared spectrum of free $MeCH{=}CH_2$, the C=C absorption band appears at 1652 cm^{-1}, but in the complex $K[PtCl_3(\eta^2\text{- }MeCH{=}CH_2)]$ the corresponding absorption is at 1504 cm^{-1}.

(7 marks)

(b) $V(CO)_6$ and $[V(CO)_6]^-$ are octahedral complexes. However, the length of the V-C and C-O bonds of $V(CO)_6$ are different from that of $[V(CO)_6]^-$.

(7 marks)

(c) At 303 K, the ^1H NMR spectrum of $(\eta^5\text{-Cp})(\eta^1\text{-Cp})Fe(CO)_2$ shows two singlets.

(6 marks)

6. Predict and explain the formation in percentage amount of all possible products from an equimolar reaction of $Mn(CO)_5(Me)$ with ^{13}CO.

(20 marks)

7. (a) Determine whether the total valence electron count for $Co_3(CO)_9Ni(\eta^5\text{-Cp})$ and $[Ru_6(CO)_{18}]^{2-}$ is consistent with metal cage framework of a tetrahedron and an octahedron, respectively.

(8 marks)

(b) The reaction of ferrocene with MeC(O)Cl and $AlCl_3$ affords two different products, $Fe(\eta^5\text{-}C_5H_4C(O)Me)_2$ and $(\eta^5\text{-Cp})Fe(\eta^5\text{-}C_5H_4C(O)Me)$.

i. Draw the structure of each product.

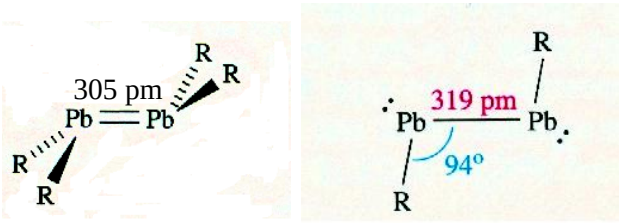
ii. Can the products be distinguished using ^1H NMR spectroscopy? Explain.

(12 marks)

1. (a) Struktur bagi $R_2Pb=PbR_2$ dan RPb-PbR ditunjukkan di bawah.

i. Tunjukkan melalui persamaan bagaimana anda akan menyediakan RPb-PbR daripada RPbBr.

ii. Huraikan pengikatan dalam $R_2Pb=PbR_2$ dan RPb-PbR.



(10 markah)

(b) Ramal dan lakarkan struktur produk bagi tindak balas berikut:

i. $(\eta^5\text{-Cp})_2Fe$ dengan toluena dalam kehadiran Al dan $AlCl_3$, dan

ii. $Ni(CO)_4$ dengan PPh_3.

(10 markah)

BAHAGIAN A

2. (a) Sebatian organolitium sangat berguna sebagai reagen sintetik dalam

i. pengubahan silikon tetrahalida kepada sebatian organosilikon, dan

ii. penglogaman regioselektif bagi alkilbenzena pada kumpulan alkil.

Beri satu contoh bagi setiap tindak balas yang dinyatakan di atas.

(6 markah)

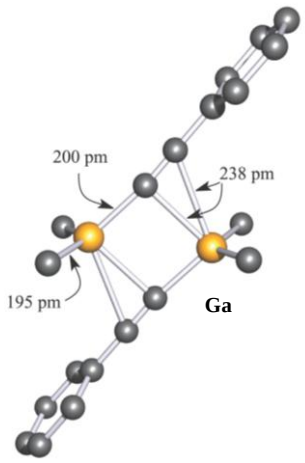
(b) Tindak balas berikut,

$$2\ Na[Cp] + BeCl_2 \longrightarrow Cp_2Be + 2NaCl$$

membawa kepada pembentukan $(\eta^1Cp)(\eta^5Cp)Be$ di mana atom Be adalah tak teratur terhadap dua kawasan ekuivalen. Lukiskan struktur bagi sebatian tak teratur itu untuk menunjukkan makna ketidakteraturan.

(7 markah)

(c) Gambarajah di bawah menunjukkan struktur dimer bertitian alkinil bagi sebatian organogalium, $Me_2GaC{\equiv}CPh$. Jelaskan mengapa titian alkinil condong dari posisi tegak terhadap salah suatu pusat galium.



(7 markah)

3. Enzim sitokrom c oksidasa adalah enzim terakhir di dalam rantai pengangkutan elektron respiratori bagi mitochondria. Lukiskan struktur enzim tersebut dan tunjukkan bagaimana struktur enzim itu berkaitan dengan fungsinya.

(20 markah)

4. Lukiskan sebatian model untuk menunjukkan pengbiomineralisasi bagi Fe^{3+} di dalam ferritin. Huraikan ciri-ciri di dalam struktur ferritin yang menjadikannya sebagai suatu sistem penstoran berkesan bagi ferum di dalam mamalia. Bagaimanakah proses pengambilan dan pengangkutan ferum di dalam mikroorganisma aerobik berbeza daripada proses tersebut di dalam mamalia?

(20 markah)

BAHAGIAN B

5. Terangkan pemerhatian berikut:

(a) Dalam spektrum infra merah $MeCH{=}CH_2$ bebas, jalur serapan C=C muncul pada 1652 cm^{-1}, tetapi bagi kompleks $K[PtCl_3(\eta^2\text{- }MeCH{=}CH_2)]$ serapan tersebut adalah pada 1504 cm^{-1}.

(7 markah)

(b) $V(CO)_6$ dan $[V(CO)_6]^-$ adalah kompleks oktahedral. Namun, jarak ikatan V-C dan C-O bagi $V(CO)_6$ adalah berbeza berbanding dengan jarak ikatan V-C dan C-O bagi $[V(CO)_6]^-$.

(7 markah)

(c) Pada 303 K, spektrum ^1H NMR $(\eta^5\text{-Cp})(\eta^1\text{-Cp})Fe(CO)_2$ memperlihatkan dua singlet.

(6 markah)

6. Ramal dan terangkan pembentukan peratusan semua produk yang mungkin daripada tindak balas ekuimolar $Mn(CO)_5(Me)$ dengan ^{13}CO.

(20 markah)

7. (a) Tentukan sama ada jumlah bilangan elektron bagi for $Co_3(CO)_9Ni(\eta^5\text{-Cp})$ dan $Ru_6(CO)_{18}]^{2-}$ adalah masing-masing konsisten dengan bentuk sangkar logam tetrahedron dan oktahedron.

(8 markah)

(b) Tindak balas ferosena dengan MeC(O)Cl dan $AlCl_3$ menghasilkan dua produk yang berbeza, $Fe(\eta^5\text{-}C_5H_4C(O)Me)_2$ dan $(\eta^5\text{-Cp})Fe(\eta^5\text{-}C_5H_4C(O)Me)$.

i. Lukiskan struktur bagi setiap produk.

ii. Bolehkah kedua-dua produk itu dibezakan dengan mengunakan spektroskopi ^1H NMR? Jelaskan.

(12 markah)

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