
UNIVERSITI SAINS MALAYSIA

First Semester Examination
2009/2010 Academic Session

November 2009

KTT 313 – Inorganic Chemistry III
[Kimia Takorganik III]

Duration : 3 hours
[Masa : 3 jam]

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

Instructions:

Answer **FIVE** (5) questions.

The **FIRST QUESTION** is a compulsory question. Then answer **FOUR** (4) more questions by selecting **TWO** (2) questions from Section A and **TWO** (2) questions from Section B.

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

If a candidate answered more than five questions, only the first five questions in order of the arrangement in the received answer scripts will be marked.

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

...2/-

1. (a) Aluminium alkyls can be prepared by the transmetalation reaction or from Grignard reagents.
- Show by equations how you would prepare R_3Al from aluminium metal using the two methods described above.
 - Draw the structure of R_3Al .
- (10 marks)
- (b) Predict and sketch the structure of the main product in the following reactions:
- $Fe(CO)_5$ with butadiene, and
 - $Re_2(CO)_{10}$ with Na/Hg.

(10 marks)

SECTION A

2. (a) Organolithium compounds are useful as synthetic reagents in
- the conversion of boron trihalides to organoboron compounds, and
 - the regioselective metallation of alkylbenzene at the alkyl group.

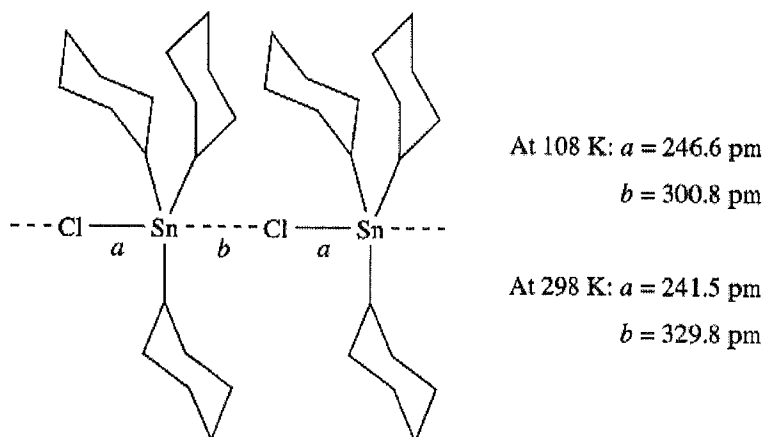
Give an example for each of the reactions described above.

(6 marks)

- (b) Describe the tendency towards association through methyl bridges for the trimethyl compounds of boron, aluminium and gallium. Give two reasons for the observed differences.

(7 marks)

- (c) The diagram below shows the structure of the polymeric triorganotin compound, $(cyclo-C_6H_{11})_3SnCl$. As the temperature is increased from 108 K to 298 K, the distance a is reduced and the distance b is increased. Explain.



(7 marks)

...3/-

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3. Describe the method used by biological systems for converting C–H bonds into C–OH bonds with the help of the metalloenzyme catalyst cytochrome P-450. Explain the role of the transition metal centre in this enzymatic reaction.

(20 marks)

4. (a) 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.

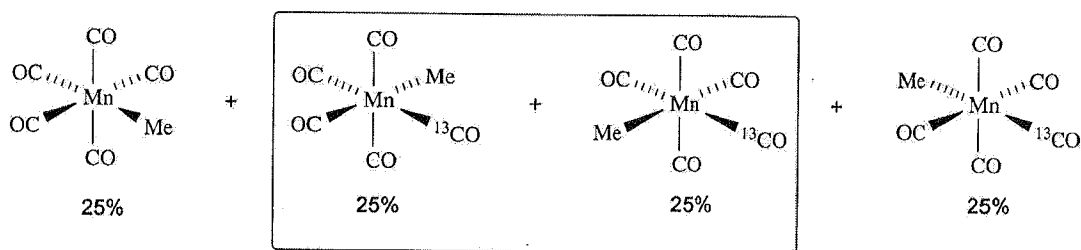
(10 marks)

- (b) How does the uptake and transport of iron in aerobic microorganism differ from that in mammals?

(10 marks)

SECTION B

5. Explain why the reaction of $\text{Mn}(\text{CO})_5(\text{Me})$ with $^{13}\text{C}\text{O}$ affords the following products:



(20 marks)

6. Rationalise the following observations:

- (a) Infrared spectra of $[\text{Mn}(\text{CO})_6]^+$ and $\text{Cr}(\text{CO})_6$ show ν_{CM} absorptions at 416 and 441 cm^{-1} , respectively.

(6 marks)

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

(6 marks)

- (c) Infrared spectrum of $\text{Mo}(\text{CO})_3(\text{PF}_3)_3$ shows ν_{CO} absorptions at 2090 and 2055 cm^{-1} whereas that of $\text{Mo}(\text{CO})_3(\text{PPh}_3)_3$ shows ν_{CO} absorptions at 1937 and 1841 cm^{-1} .

(8 marks)

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7. (a) Suggest and explain the change in cluster structure in the following reaction:



(8 marks)

- (b) The reaction of ferrocene with MeC(O)Cl and AlCl_3 affords two different products, $\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{C(O)Me})_2$ and $(\eta^5\text{-Cp})\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{C(O)Me})$.

- (i) Draw the structure of each product.
(ii) How would you distinguish the products by a method other than elemental analysis and X-ray crystallography?

(12 marks)

TERJEMAHAN

Arahan:

Jawab **LIMA** (5) soalan.

SOALAN PERTAMA adalah wajib. Kemudian jawab **EMPAT** (4) soalan lagi dengan memilih **DUA** (2) soalan dari Bahagian A dan **DUA** (2) soalan dari Bahagian B.

Anda dibenarkan menjawab soalan ini sama ada dalam Bahasa Malaysia atau Bahasa Inggeris.

Jika calon menjawab lebih daripada lima soalan, hanya lima soalan pertama mengikut susunan dalam skrip jawapan akan diberi markah.

Sekiranya terdapat sebarang percanggahan pada soalan peperiksaan, versi Bahasa Inggeris hendaklah diguna pakai.

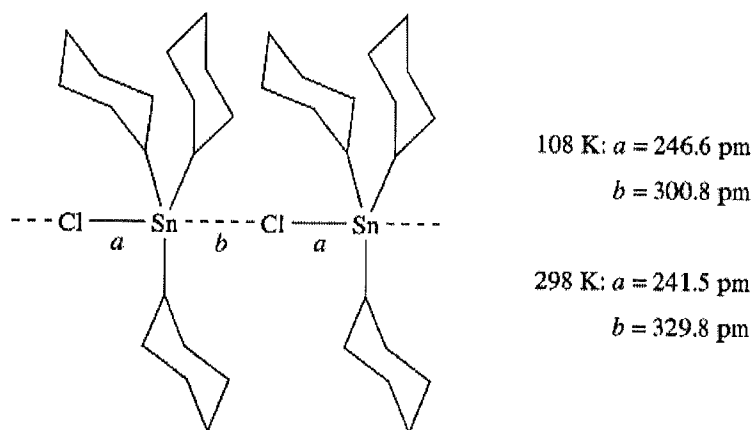
1. (a) Sebatian alkil aluminium boleh disediakan melalui tindak balas transpenglogaman atau dari reagen Grignard.
- (i) Tunjukkan melalui persamaan bagaimana anda akan menyediakan R_3Al dari logam aluminium dengan menggunakan kedua-dua kaedah di atas.
- (ii) Lukiskan struktur bagi R_3Al .
- (10 markah)
- (b) Ramal dan lakarkan struktur produk utama bagi tindak balas berikut:
- (i) $Fe(CO)_5$ dengan butadiena, dan
- (ii) $Re_2(CO)_{10}$ dengan Na/Hg.
- (10 markah)

BAHAGIAN A

2. (a) Sebatian organolitium berguna sebagai reagen sintetik di dalam
- (i) penukaran boron trihalida kepada sebatian organoboron, dan
- (ii) penglogaman regioselektif alkilbenzena pada kumpulan alkil.
- Beri satu contoh bagi setiap tindak balas di atas.
- (6 markah)
- (b) Huraikan kecenderungan terhadap pembentukan titian metil bagi sebatian trimetil boron, aluminium dan galium. Beri dua alasan untuk perbezaan yang diperhatikan.
- (7 markah)

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- (c) Gambarajah di bawah menunjukkan struktur bagi sebatian polimerik triorganostanum, (*siklo*-C₆H₁₁)₃SnCl. Apabila suhu dinaikkan dari 108 K ke 298 K, jarak *a* berkurangan dan jarak *b* bertambah. Beri penjelasan.



(7 markah)

3. Huraikan kaedah yang digunakan oleh sistem biologi untuk mengubah ikatan C–H kepada ikatan C–OH dibantu oleh mangkin metaloenzim sitokrom P-450. Jelaskan peranan pusat logam peralihan di dalam tindak balas berenzim tersebut.

(20 markah)

4. (a) Lukiskan sebatian model untuk menunjukkan pengbiomineralisasi bagi Fe³⁺ di dalam ferritin. Huraikan ciri-ciri di dalam struktur ferritin yang menjadikannya sebagai suatu sistem penyimpanan berkesan bagi ferum di dalam mamalia.

(10 markah)

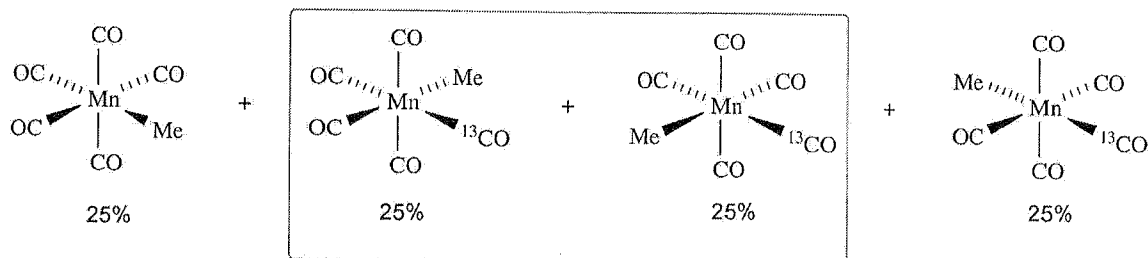
- (b) Bagaimanakah proses pengambilan dan pengangkutan ferum di dalam mikroorganisme aerobik berbeza daripada proses tersebut di dalam mamalia?

(10 markah)

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BAHAGIAN B

5. Jelaskan kenapa tindakbalas $\text{Mn}(\text{CO})_5(\text{Me})$ dengan ^{13}CO menghasilkan produk berikut:



(20 markah)

6. Terangkan pemerhatian berikut:

(a) Spektrum infra merah $[\text{Mn}(\text{CO})_6]^+$ dan $\text{Cr}(\text{CO})_6$ memperlihatkan serapan ν_{CM} masing-masing pada 416 dan 441 cm^{-1} .

(6 markah)

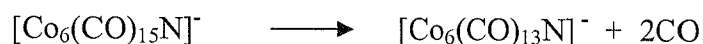
(b) Pada 303 K, spektrum ^1H NMR $(\eta^5\text{-Cp})(\eta^1\text{-Cp})\text{Fe}(\text{CO})_2$ memperlihatkan dua singlet.

(6 markah)

(c) Spektrum infra merah $\text{Mo}(\text{CO})_3(\text{PF}_3)_3$ memperlihatkan serapan ν_{CO} pada 2090 dan 2055 cm^{-1} manakala $\text{Mo}(\text{CO})_3(\text{PPh}_3)_3$ memperlihatkan serapan ν_{CO} pada 1937 dan 1841 cm^{-1} .

(8 markah)

7. Cadang dan jelaskan perubahan struktur kluster yang berlaku dalam tindak balas berikut:



(8 markah)

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- (b) Tindakbalas ferrosena dengan MeC(O)Cl dan AlCl_3 menghasilkan dua produk yang berbeza, $\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{C(O)Me})_2$ dan $(\eta^5\text{-Cp})\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{C(O)Me})$.
- (i) Lukiskan struktur bagi setiap produk.
 - (ii) Bagaimanakah anda dapat membezakan produk-produk tersebut dengan satu kaedah selain dari analisis unsur dan kristalografi sinar-X?

(12 markah)