

UNIVERSITI SAINS MALAYSIA

Kursus Semasa Cuti Panjang  
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.

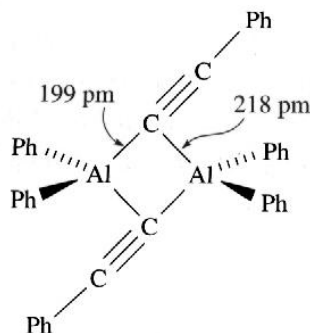
In the event of any discrepancies, the English version shall be used.

...2/-

- Describe the synthesis, structure and thermal stability of sodium cyclopentadienide, Na[Cp].  
(10 marks)
  - On going from  $\text{Fe}(\text{CO})_5$  to  $\text{Fe}(\text{CO})_3(\text{PPh}_3)_2$ , the C=O absorption bands in the IR spectrum at 2025 and 2000  $\text{cm}^{-1}$  are replaced by bands at 1944, 1886 and 1881  $\text{cm}^{-1}$ . Explain this observation.  
(10 marks)

### SECTION A

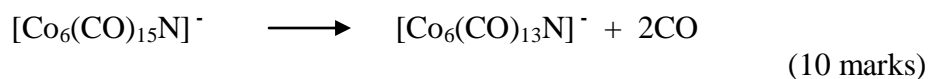
- The fungus *Amanita muscari* contains 400 times more vanadium than is typical of plants and the amount is independent of the vanadium content of the soil in which the fungus grows. Explain this observation on the basis of uptake of vanadium by the (S,S)-2,2'-(hydroxyimino)dipropionate anion, and its storage as the V(IV) complex, amavadin.  
(20 marks)
- Zinc plays an important role in enzymatic reactions in biological systems. Describe the enzymatic reaction mechanism of the metalloenzymes carbonic anhydrase II and carboxypeptidase A.  
(20 marks)
- The hydrolysis of the Si-Cl bond in  $(\text{CH}_3)_3\text{SiCl}$  leading to the formation of siloxane,  $(\text{CH}_3)_3\text{SiOSi}(\text{CH}_3)_3$  involves a two step reaction. Write an equation for each step of the reaction.  
(6 marks)
  - While  $\text{Cp}_2\text{Be}$  and  $\text{Cp}_2\text{Mg}$  are monomeric and are soluble in hydrocarbon solvents,  $\text{Cp}_2\text{Ca}$ ,  $\text{Cp}_2\text{Sr}$  and  $\text{Cp}_2\text{Ba}$  are polymeric and are insoluble in ethers and hydrocarbons. Explain this observation and draw the structure of the compounds.  
(7 marks)
  - The diagram below shows the structure of the alkynyl-bridged dimer of the organoaluminium compound,  $\text{Ph}_2\text{AlC}\equiv\text{CPh}_2$ . Explain why the alkynyl bridges tilt from the vertical position towards one of the aluminium centres.  
(7 marks)



(7 marks)

## SECTION B

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



- (b) Explain why the C=C absorption band appears at  $1652 \text{ cm}^{-1}$  in the infrared spectrum of free  $\text{MeCH}=\text{CH}_2$ , but the corresponding band is at  $1504 \text{ cm}^{-1}$  for the complex  $\text{K}[\text{PtCl}_3(\eta^2-\text{MeCH}=\text{CH}_2)]$ .

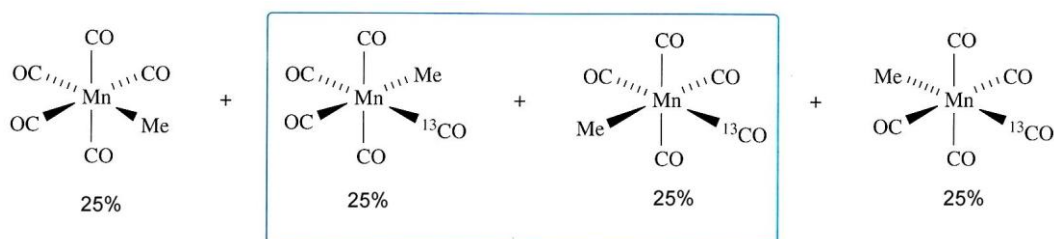
(10 marks)

6. The reaction of ferrocene with  $\text{MeC(O)Cl}$  and  $\text{AlCl}_3$  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) Explain how the products can be distinguished using  $^1\text{H}$  NMR spectroscopy.

(20 marks)

7. Rationalize why the reaction of  $\text{Mn}(\text{CO})_5(\text{Me})$  with  $^{13}\text{CO}$  produces the following products:



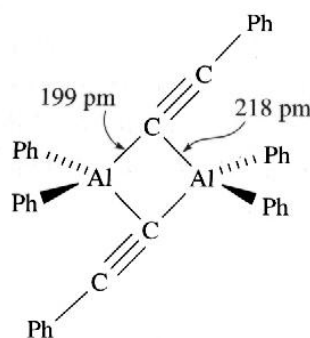
(20 marks)

1. (a) Huraikan sintesis, struktur dan kestabilan termal bagi natrium siklopentadienida, Na[Cp]. (10 markah)
- (b) Perubahan daripada  $\text{Fe}(\text{CO})_5$  kepada  $\text{Fe}(\text{CO})_3(\text{PPh}_3)_2$  memperlihatkan jalur serapan C=O dalam spektrum IR pada 2025 dan 2000  $\text{cm}^{-1}$  ditukarganti dengan jalur pada 1944, 1886 dan 1881  $\text{cm}^{-1}$ . Jelaskan pemerhatian ini.

(10 markah)

**BAHAGIAN A**

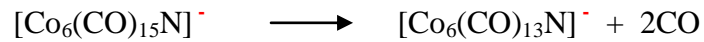
2. Kulat *Amanita muscari* mengandungi 400 kali lebih vanadium dibandingkan dengan paras yang biasa bagi tumbuhan dan kuantiti itu bebas daripada kandungan vanadium di dalam tanah di mana kulat itu tumbuh. Jelaskan pemerhatian ini berdasarkan perolehan vanadium oleh anion (S,S)-2,2'-(hidroksimino)dipropionat, dan penyimpanannya sebagai kompleks V(IV), amavadin. (20 markah)
3. Zink memainkan peranan penting dalam tindak balas enzim di dalam sistem biologi. Huraikan mekanisme tindak balas enzim bagi metaloenzim karbonik anhidrasa II dan karboksipeptidasa A. (20 markah)
4. (a) Hidrolisis ikatan Si-Cl dalam  $(\text{CH}_3)_3\text{SiCl}$  yang membawa kepada pembentukan siloksana,  $(\text{CH}_3)_3\text{SiOSi}(\text{CH}_3)_3$  melibatkan suatu tindak balas dua langkah. Tulis persamaan bagi setiap langkah bagi tindak balas tersebut. (6 markah)
- (b) Walaupun  $\text{Cp}_2\text{Be}$  dan  $\text{Cp}_2\text{Mg}$  merupakan monomerik dan terlarut di dalam pelarut hidrokarbon,  $\text{Cp}_2\text{Ca}$ ,  $\text{Cp}_2\text{Sr}$  dan  $\text{Cp}_2\text{Ba}$  merupakan polimerik dan tidak terlarut di dalam eter dan hidrokarbon. Jelaskan pemerhatian ini dan lukiskan struktur sebatian tersebut. (7 markah)
- (c) Gambarajah berikut menunjukkan struktur dimer bertitian alkinil bagi sebatian organoaluminium,  $\text{Ph}_2\text{AlC}\equiv\text{CPh}_2$ . Jelaskan mengapa titian alkinil condong dari posisi tegak terhadap salah satu pusat aluminium.



(7 markah)

**BAHAGIAN B**

5. (a) Cadang dan jelaskan perubahan struktur kluster yang berlaku dalam tindak balas berikut:



(10 markah)

- (b) Jelaskan kenapa jalur serapan C=C dalam spektrum infra merah MeCH=CH<sub>2</sub> bebas muncul pada 1652 cm<sup>-1</sup>, tetapi jalur tersebut didapati pada 1504 cm<sup>-1</sup> bagi kompleks K[PtCl<sub>3</sub>(η<sup>2</sup>-MeCH=CH<sub>2</sub>)].

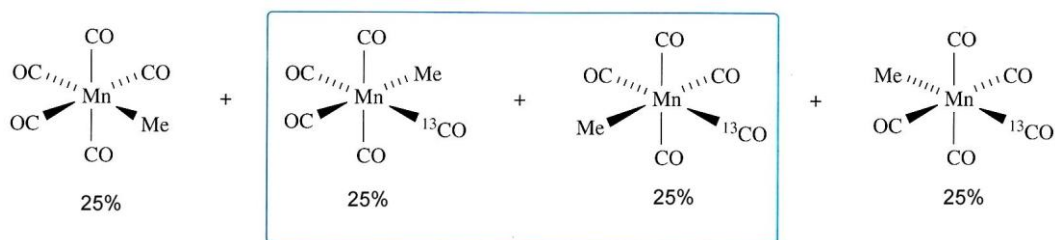
(10 markah)

6. Tindak balas ferosena dengan MeC(O)Cl dan AlCl<sub>3</sub> menghasilkan dua produk yang berbeza, Fe(η<sup>5</sup>-C<sub>5</sub>H<sub>4</sub>C(O)Me)<sub>2</sub> dan (η<sup>5</sup>-Cp)Fe(η<sup>5</sup>-C<sub>5</sub>H<sub>4</sub>C(O)Me).

- (i) Lukiskan struktur bagi setiap produk.  
 (ii) Terangkan bagaimana kedua-dua produk itu boleh dibezakan dengan menggunakan spektroskopi <sup>1</sup>H NMR.

(20 markah)

7. Jelaskan kenapa tindak balas Mn(CO)<sub>5</sub>(Me) dengan <sup>13</sup>CO menghasilkan produk berikut:



(20 markah)