

UNIVERSITI SAINS MALAYSIA

First Semester Examination
Academic Session 2011/2012

January 2012

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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COMPULSORY questions

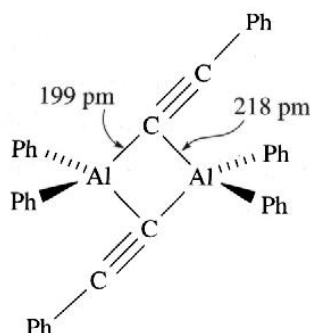
1. (a) (i) Describe the regioselective reaction for the metallation of alkylbenzene using ${}^n\text{BuLi} \cdot \text{TMEDA}$ in hexane at 303 K for 2 hours.
- (ii) How do you reverse the regioselectivity in favour of the *meta* position of the benzene moiety by the use of heterometallic reagent prepared from ${}^n\text{BuNa}$, ${}^n\text{Bu}_2\text{Mg}$, 2,2,6,6-tetramethylpiperidine and TMEDA?
- (10 marks)
- (b) The C=O absorption bands in the infrared spectrum of $\text{Fe}(\text{CO})_5$ appeared at 2025 and 2000 cm^{-1} whereas that of $\text{Fe}(\text{CO})_3(\text{PPh}_3)_2$ are observed at 1944, 1886 and 1881 cm^{-1} . Explain why there are three C=O absorption bands for $\text{Fe}(\text{CO})_3(\text{PPh}_3)_2$ and why the bands appeared at lower frequencies.
- (10 marks)

Section A

Answer any **TWO** (2) questions

2. 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)
3. (a) Differentiate between Type 1, Type 2 and Type 3 copper centres in blue copper proteins, giving both structural and experimental observations.
- (10 marks)
- (b) How does the blue copper protein *ascorbate oxidase* catalyse the reduction of O_2 to H_2O ?
- (10 marks)
4. (a) Discuss the thermal stability of alkali metal (Group 1) organometallic compounds.
- (6 marks)
- (b) While Cp_2Be and Cp_2Mg are monomeric and are soluble in hydrocarbon solvents, Cp_2Ca , Cp_2Sr and Cp_2Ba are polymeric and are insoluble in ethers and hydrocarbons. Explain these observations and draw the structures of the compounds.
- (7 marks)

- (c) 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)

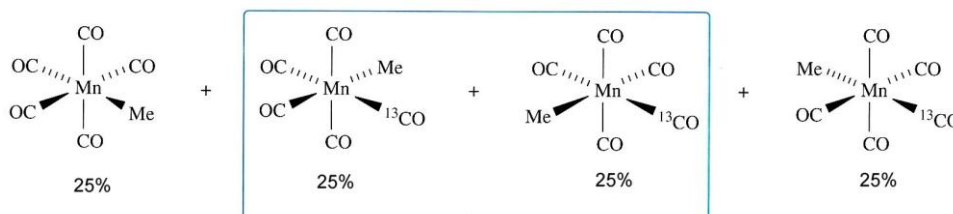
Section B

Answer any **TWO** (2) question.

5. Explain the following observations:

- (a) The C=C absorption band in an infrared spectrum of free $\text{MeCH}=\text{CH}_2$ appeared at 1652 cm^{-1} whereas that of complex $\text{K}[\text{PtCl}_3(\eta^2\text{-MeCH}=\text{CH}_2)]$ appeared at 1504 cm^{-1} . (7 marks)
- (b) Only two proton resonances (singlets) are observed in the ^1H NMR spectrum of $(\eta^5\text{-Cp})(\eta^1\text{-Cp})\text{Fe}(\text{CO})_2$ which was recorded at 303 K. (7 marks)
- (c) An infrared spectrum of $\text{Mo}(\text{CO})_3(\text{PF}_3)_3$ shows C=O absorption bands at 2090 and 2055 cm^{-1} but that of $\text{Mo}(\text{CO})_3(\text{PPh}_3)_3$ shows C=O absorption bands at 1937 and 1841 cm^{-1} . (6 marks)

6. The reaction of $\text{Mn}(\text{CO})_5(\text{Me})$ with ^{13}C that was conducted without solvent or in tetrahydrofuran afforded the same products:



Explain by providing a likely transition state for the reaction in each condition.

(20 marks)

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7. (a) Determine whether the total valence electron count for $\text{Co}_3(\text{CO})_9\text{Ni}(\eta^5\text{-Cp})$ and $[\text{Ru}_6(\text{CO})_{18}]^{2-}$ 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, $\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{C(O)Me})_2$ 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) Can the products be distinguished using ^1H NMR spectroscopy? Explain. (12 marks)

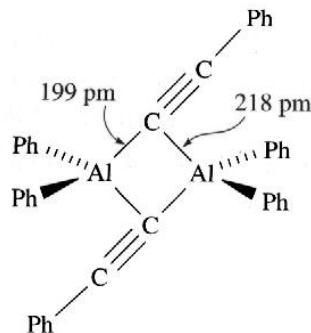
Soalan **WAJIB**

1. (a) (i) Huraikan tindakbalas regioselektif bagi penglogaman alkilbenzena dengan menggunakan ${}^n\text{BuLi} \cdot \text{TMEDA}$ dalam heksana pada 303 K selama 2 jam.
- (ii) Bagaimanakah keregioselektifan dapat dibalikkan supaya memihak pada posisi *meta* moiety benzena dengan menggunakan reagen heterometalik disediakan daripada ${}^n\text{BuNa}$, ${}^n\text{Bu}_2\text{Mg}$, 2,2,6,6-tetrametilpiperidina and TMEDA? (10 markah)
- (b) Jalur serapan C=O dalam spektrum infra merah bagi $\text{Fe}(\text{CO})_5$ muncul pada 2025 dan 2000 cm^{-1} manakala jalur serapan tersebut bagi $\text{Fe}(\text{CO})_3(\text{PPh}_3)_2$ diperhatikan pada 1944, 1886 dan 1881 cm^{-1} . Jelaskan kenapa ada tiga jalur serapan C=O bagi $\text{Fe}(\text{CO})_3(\text{PPh}_3)_2$ dan kenapa jalur-jalur tersebut muncul pada frekuensi yang lebih rendah. (10 markah)

Bahagian AJawab **DUA** (2) soalan

2. Kulat *Amanita muscari* mengandungi 400 kali lebih vanadium dibandingkan dengan paras yang biasa bagi tumbuhan lain 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'-(hydroxyimino)dipropionat, dan penyimpanannya sebagai kompleks V(IV), amavadin. (20 markah)
3. (a) Bezakan antara pusat kuprum Jenis 1, Jenis 2 and Jenis 3 di dalam protein kuprum biru, dengan memberi kedua-dua pemerhatian struktur dan eksperimental. (10 markah)
- (b) Bagaimanakah protein kuprum biru *ascorbate oxidase* memangkinkan penurunan O_2 ke H_2O ? (10 markah)
4. (a) Bincangkan kestabilan termal bagi sebatian organologam logam alkali (Kumpulan 1). (6 markah)
- (b) Walaupun Cp_2Be and Cp_2Mg merupakan monomerik dan terlarut di dalam pelarut hidrokarbon, Cp_2Ca , Cp_2Sr dan Cp_2Ba 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 bertitan 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

Jawab **DUA** (2) soalan

5. Terangkan pemerhatian berikut:

- (a) Jalur serapan C=C dalam spektrum infra merah bagi $\text{MeCH}=\text{CH}_2$ bebas muncul pada 1652 cm^{-1} manakala jalur serapan tersebut bagi kompleks $\text{K}[\text{PtCl}_3(\eta^2\text{-MeCH}=\text{CH}_2)]$ muncul pada 1504 cm^{-1} .

(7 markah)

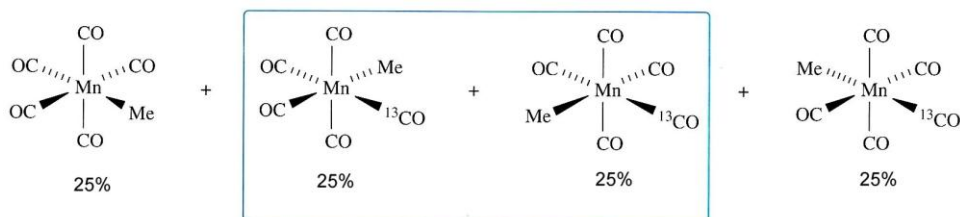
- (b) Hanya dua resonan proton (singlet) diperhatikan dalam spektrum ^1H NMR bagi $(\eta^5\text{-Cp})(\eta^1\text{-Cp})\text{Fe}(\text{CO})_2$ yang dirakamkan pada 303 K.

(7 markah)

- (d) Spektrum infra merah bagi $\text{Mo}(\text{CO})_3(\text{PF}_3)_3$ menunjukkan jalur serapan C=O pada 2090 dan 2055 cm^{-1} tetapi spektrum infra merah bagi $\text{Mo}(\text{CO})_3(\text{PPh}_3)_3$ menunjukkan jalur serapan C=O pada 1937 dan 1841 cm^{-1} .

(6 markah)

6. Tindak balas $\text{Mn}(\text{CO})_5(\text{Me})$ dengan ^{13}CO yang dilakukan tanpa pelarut atau dalam tetrahidrofuran menghasilkan produk yang sama:



Terangkan dengan memberi bahan perantaraan yang berkemungkinan bagi tindak balas tersebut dalam setiap keadaan.

(20 markah)

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7. (a) Tentukan sama ada jumlah bilangan elektron bagi for $\text{Co}_3(\text{CO})_9\text{Ni}(\eta^5\text{-Cp})$ dan $\text{Ru}_6(\text{CO})_{18}]^{2-}$ 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, $\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{C(O)Me})_2$ 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) Bolehkah kedua-dua produk itu dibezakan dengan menggunakan spektroskopi ^1H NMR? Jelaskan. (12 markah)