

**CHEM 361 — TEST 1**  
**Inorganic and Structural Chemistry**  
**Saturday 2 July 2005**

Time: 9:30 am to 11:10 am

Time allowed: 100 minutes

**Answer ALL eight questions.** There are 100 marks available.

Start each question on a new page.

A periodic table is attached.

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1. (10 Marks)

For each of the following compounds, give the electron count for the complex (as you would do for the 18-electron rule) and the d-electron count for the transition metal atom:

- (a)  $(\eta^5\text{-Cp})_2\text{Ni}$
- (b)  $(\eta^5\text{-Cp})\text{Fe}(\text{PPh}_3)_2\text{H}$
- (c)  $[\text{Pd}(\text{SnCl}_3)(\mu\text{-Cl})(\text{C}_2\text{H}_4)]_2$
- (d)  $\text{Co}(\text{NO})_3$
- (e)  $[\text{MeTi}(\mu\text{-S})\text{Cl}]_2$

2. (10 Marks)

Determine **n** for each of the following compounds:

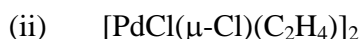
- (a)  $(\eta^5\text{-Cp})\text{Co}(\text{CO})_n$
- (b)  $(\eta^6\text{-C}_6\text{H}_6)\text{Cr}(\text{CO})_n$
- (c)  $[\text{Mo}(\text{CO})_n]^{4+}$
- (d)  $[(\eta^5\text{-Cp})\text{Fe}(\text{CO})_n]_2$
- (e)  $[\text{Fe}(\text{CO})_n]_2$

3. (10 Marks)

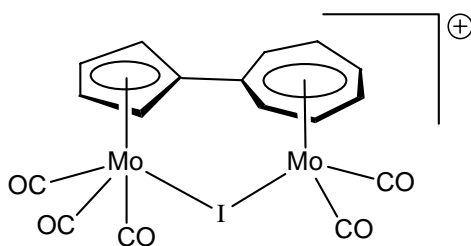
(a) Explain why ring-slippage is easier for indenyl ligands than it is for cyclopentadienyl ligands.

(b) Explain how NO and indenyl can promote associative substitution reactions.

(c) Explain why the following stable compounds do not obey the 18-electron rule:



(d) A dinuclear complex containing a cyclopentadienyl/cycloheptatrienyl ligand has the connectivity shown below. Determine the oxidation state of each metal (you will need to use the 18-electron rule and the  $4n + 2$  rule for aromatic compounds).



4. (20 Marks)

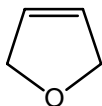
(a) Draw the molecular orbitals (MOs) for the four major bonding interactions between an alkyne and a transition metal and label each MO as one of the following bond types:  $\sigma$  donor,  $\pi$  donor,  $\pi$  acceptor,  $\delta$  acceptor.

(b) For the complexes  $(\eta^5-Cp)Mn(CO)_2(RCCR)$  and  $(\eta^5-Cp)V(CO)_2(RCCR)$ , which would you expect to display the shortest C–C bond distance, and why?

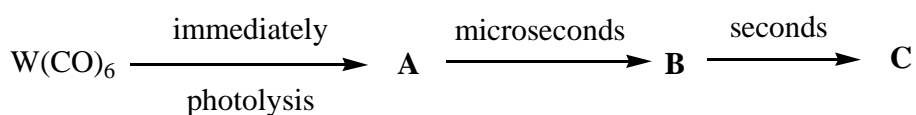
(c) Describe the factors which lead to the decomposition of alkyl and aryl transition metal complexes by  $\beta$ -elimination and give three examples of ligands that are not expected to undergo  $\beta$ -elimination.

5. (15 Marks)

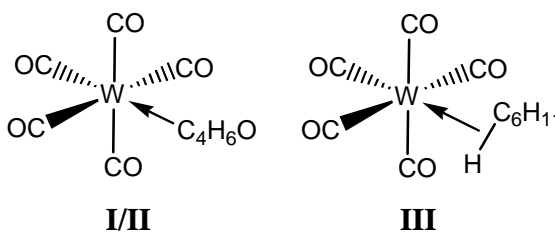
UV photolysis of a cyclohexane solution of  $W(CO)_6$  in the presence of 2,5-dihydrofuran (shown below) immediately gives product **A** with infrared CO stretching frequencies at 1954 and 1928  $cm^{-1}$ . Over several microseconds, these absorptions are replaced by new absorptions, due to product **B**, at 1934 and 1913  $cm^{-1}$ . Several minutes later, these peaks have all but disappeared, and new peaks, for product **C**, can be observed at 1963 and 1952  $cm^{-1}$ .



2,5-dihydrofuran



Two of the products are due to linkage isomers of 2,5-dihydrofuran, **I** and **II**, and the other is due to weakly coordinated cyclohexane (**III**).

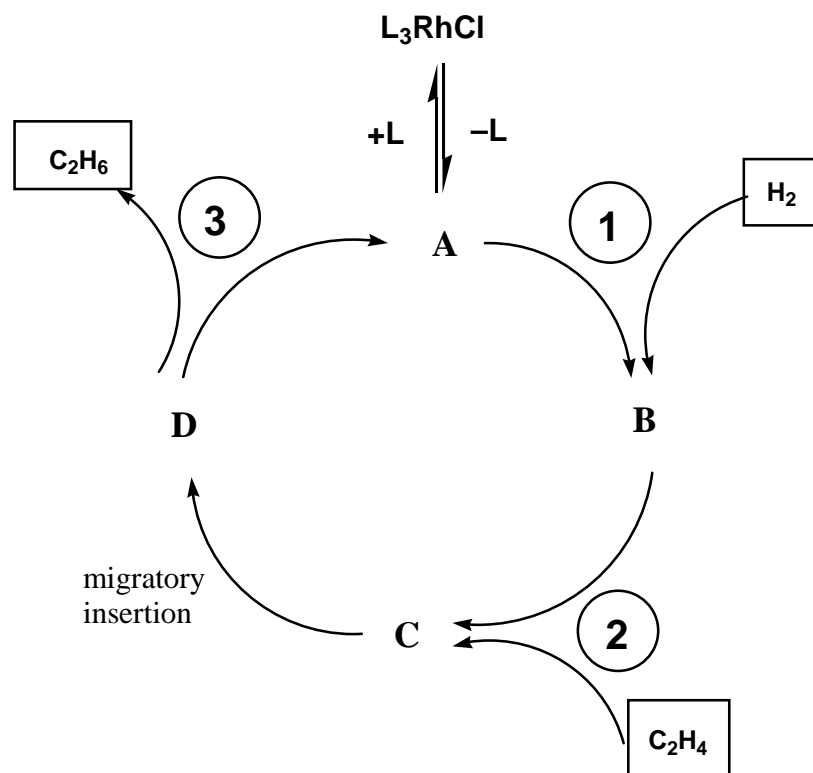


- (i) Sketch the linkage isomers **I** and **II**.
- (ii) Assign compounds **A**, **B** and **C** to structures **I**, **II** and **III**, and **justify** your assignments.
- (iii) Based on the IR spectra, compare the  $\sigma$ -donor and  $\pi$ -acceptor properties of the cyclohexane ligand to the two coordination modes of 2,5-dihydrofuran.
- (iv) Rationalise the stability of isomer **C** over isomer **B**.
- (v) Suggest why **B** is the kinetic product, rather than **C**.

6. (15 Marks)

Shown below is a catalytic cycle for the hydrogenation of ethylene.

- (a) Draw intermediates **A**, **B**, **C** and **D**.  
(b) Describe steps **1**, **2** and **3**.



- (c) Sketch a mechanism for the hydrosilation of  $CH_2=CHPh$  with  $Me_3SiD$  using a Pt catalyst (there is no need to describe the Pt catalyst).

7. (10 Marks)

For each of the following compounds, suggest a preparation from an appropriate metal carbonyl complex:

- (a)  $[Mn(CO)_5]^-$   
(b)  $[CpMo(CO)_3]^-$   
(c)  $CoBr(CO)_4$   
(d)  $Cr(CO)_5(=CPh(OMe))$   
(e)  $Fe(CO)_3(1,5\text{-cyclooctadiene})$

8. (10 Marks)

Draw the structure of each of the following compounds:

- $[\text{Mn}_3(\text{CO})_{14}]^-$
- $\text{W}(\text{Cp})(\text{In})(\text{CO})_2$  (In = indenyl)
- $\text{CpCo}(\text{SiMe}_3)(\text{NO})$
- $\text{CpFe}(\text{CO})(\text{CH}_2\text{CHCH}_2)$
- $[\text{CpMo}(\text{CO})_2]_2$

### Periodic Table

1 H 1.008																	2 He 4.00
3 Li 6.94	4 Be 9.01											5 B 10.8	6 C 12.01	7 N 14.01	8 O 16.00	9 F 19.0	10 Ne 20.2
11 Na 23.0	12 Mg 24.3											13 Al 27.0	14 Si 28.1	15 P 31.0	16 S 32.1	17 Cl 35.5	18 Ar 39.9
19 K 39.1	20 Ca 40.1	21 Sc 45.0	22 Ti 47.9	23 V 50.9	24 Cr 52.0	25 Mn 54.9	26 Fe 55.9	27 Co 58.9	28 Ni 58.7	29 Cu 63.5	30 Zn 65.4	31 Ga 69.7	32 Ge 72.6	33 As 74.9	34 Se 79.0	35 Br 79.9	36 Kr 83.8
37 Rb 85.5	38 Sr 87.6	39 Y 88.9	40 Zr 91.2	41 Nb 92.9	42 Mo 95.9	43 Tc (99)	44 Ru 101.1	45 Rh 102.9	46 Pd 106.4	47 Ag 107.9	48 Cd 112.4	49 In 114.8	50 Sn 118.7	51 Sb 121.8	52 Te 127.6	53 I 126.9	54 Xe 131.3
55 Cs 132.9	56 Ba 137.3	57-71 see below	72 Hf 178.5	73 Ta 181.0	74 W 183.9	75 Re 186.2	76 Os 190.2	77 Ir 192.2	78 Pt 195.1	79 Au 197.0	80 Hg 200.6	81 Tl 204.4	82 Pb 207.2	83 Bi 209.0	84 Po (210)	85 At (210)	86 Rn (222)
87 Fr (223)	88 Ra (226)	89-103 see below	104 Rf (257)	105 Db (260)	106 Sg (263)	107 Bh (262)	108 Hs (265)	109 Mt (266)	110	111	112						

57 La 138.9	58 Ce 140.1	59 Pr 140.9	60 Nd 144.2	61 Pm (147)	62 Sm 150.4	63 Eu 152.0	64 Gd 157.3	65 Tb 158.9	66 Dy 162.5	67 Ho 164.9	68 Er 167.3	69 Tm 168.9	70 Yb 173.0	71 Lu 175.0
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89 Ac (227)	90 Th 232.0	91 Pa (231)	92 U 238.1	93 Np (237)	94 Pu (242)	95 Am (243)	96 Cm (247)	97 Bk (245)	98 Cf (251)	99 Es (254)	100 Fm (253)	101 Md (256)	102 No (254)	103 Lr (257)
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