**CHEM 321 — 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) $(\eta^5\text{-Cp})\text{Fe(CO)}_2\text{H}$

(c) $[\text{PdCl}(\mu\text{-Cl})(\text{C}_2\text{H}_4)]_2$

(d) $\text{Co(NO)}_3$

(e) $\text{MeTiCl}_3$

2. (10 Marks)

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

(a) $(\eta^5\text{-Cp})\text{Co(CO)}_{\mathbf{n}}$

(b) $(\eta^6\text{-C}_6\text{H}_6)\text{Cr(CO)}_{\mathbf{n}}$

(c) $[\text{Cr(CO)}_{\mathbf{n}}]^{2-}$

(d) $[(\eta^5\text{-Cp})\text{Fe(CO)}_{\mathbf{n}}]_2$

(e) $[\text{Mn(CO)}_{\mathbf{n}}]_2$

3. (8 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:

(i) $V(CO)_6$

(ii) $[PdCl(\mu\text{-}Cl)(C_2H_4)]_2$

(iii) $Cp_2ZrCl_2$

4. (10 Marks)

Draw the expected transition metal product from each of the following reactions:

(a) $Mn_2(CO)_{10}$ + Na(Hg)

(b) $Mo(CO)_6$ + $Cp^-$

(c) $Co_2(CO)_8$ + $Br_2$

(d) $Cr(CO)_6$ + PhLi

(e) $Fe(CO)_5$ + 1,5-$C_8H_{12}$ (1,5-cyclooctadiene)

5. (10 Marks)

Draw the structure of each of the following compounds:

(a) $Fe_3(CO)_{12}$

(b) $Cp_2W(CO)_2$

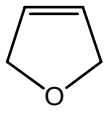
(c) $(\eta^5\text{-}Cp)CoCl(NO)$

(d) $(\eta^5\text{-}Cp)Fe(CO)(CH_2CHCH_2)$

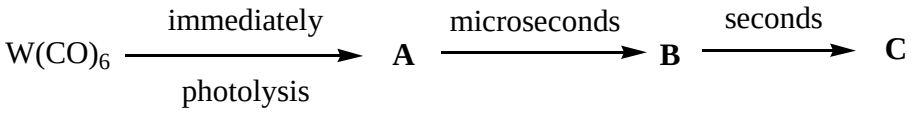
(e) $[(\eta^5\text{-}Cp)Mo(CO)_2]_2$

6. (15 Marks)

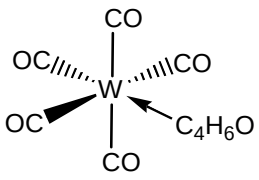
UV photolysis of a cyclohexane solution of $W(CO)_6$ in the presence of 2,5-dihydrofuran (shown below) immediately gives product **A** with infrared CO stretching frequencies at 1954 and 1928 $cm^{-1}$. Over the course of tens of microseconds, these absorptions are replaced by new absorptions, due to 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 $cm^{-1}$.



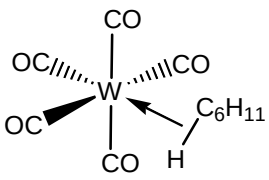

2,5-dihydrofuran




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/II**




**III**

(i) Sketch the 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 σ-donor and π-acceptor properties of the cyclohexane ligand to the two coordination modes of 2,5-dihydrofuran.

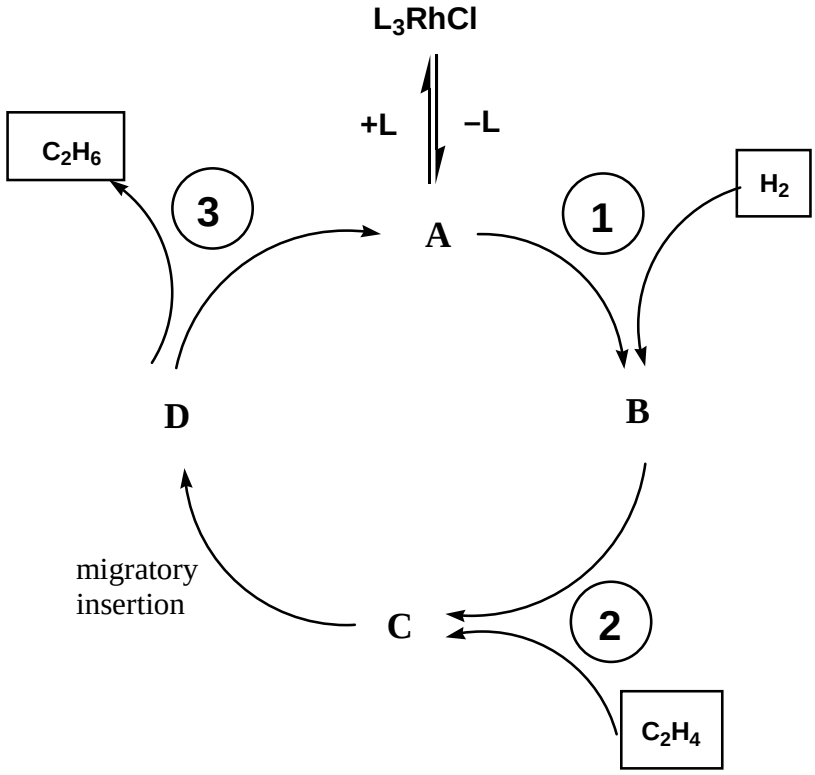
(iv) Rationalise the stability of isomer **C** over isomer **B**.

7. (12 Marks)

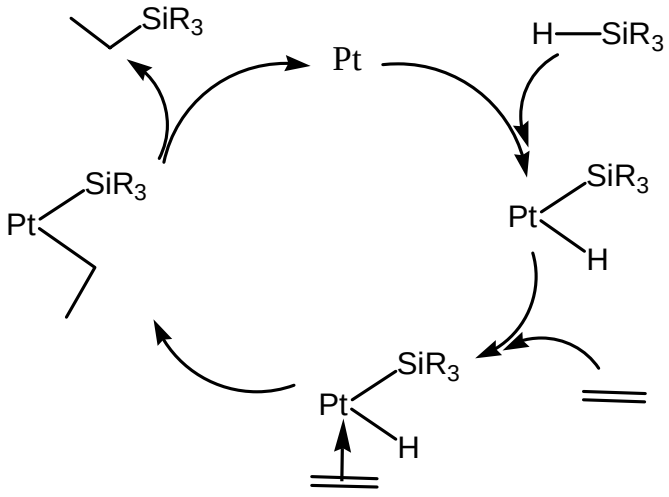
Shown below is a catalytic cycle for the hydrogenation of ethylene.

(a) Draw intermediates **A**, **B**, **C** and **D**.

(b) Describe steps **1**, **2** and **3**.




(c) Shown below is a mechanism for the hydrosilation of ethylene. Draw the product for the reaction of $PhCH{=}CH_2$ with $Me_3SiD$.



8. (25 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: σ donor, π donor, π acceptor, δ acceptor.

(b) For the complexes $(\eta^5\text{-Cp})Mn(CO)_2(RCCR)$ and $(\eta^5\text{-Cp})V(CO)_2(RCCR)$, which of the bonding interactions in part (a) are primarily involved in bond formation?

(c) Describe the factors which lead to the decomposition of alkyl and aryl transition metal complexes by β-elimination and approaches that have been taken to prepare stable alkyl and aryl transition metal complexes.

**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 | | | | | | |

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|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 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 |

| | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 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) |