

# CHEMISTRY 423

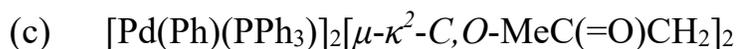
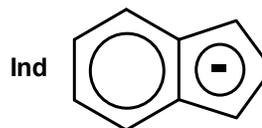
## MIDTERM EXAM 1

October 10, 2002

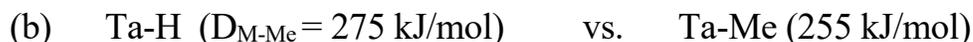
Answer all questions. There are 70 marks and 80 minutes so ration your time accordingly. A periodic table is included with this examination. To be answered in booklets. If you do not know an abbreviation used in this examination PLEASE ASK.

| <b>Question</b> | <b>Points</b> |
|-----------------|---------------|
| <b>1</b>        | <b>9</b>      |
| <b>2</b>        | <b>6</b>      |
| <b>3</b>        | <b>6</b>      |
| <b>4</b>        | <b>10</b>     |
| <b>5</b>        | <b>10</b>     |
| <b>6</b>        | <b>17</b>     |
| <b>7</b>        | <b>12</b>     |
| <b>Total</b>    | <b>70</b>     |

1(9) For each of the following compounds, draw a structure consistent with the formula given, give the oxidation state of the metal centres and deduce whether the complex contains a metal-metal bond. If you believe a metal-metal bond is present, indicate this in the structure you draw. (3 pts. each)



2 (6) Explain the following differences in M-C( $\sigma$ ) bond strengths ( $D_{\text{M-R}}$ ):

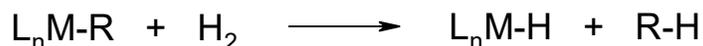


Assume the complexes have similar ligand sets and oxidation states.

3 (6) The geometry at the amido nitrogen in  $\text{Cp}_2\text{Re}(\text{NMe}_2)$  and  $\text{Cp}_2\text{Ta}(\text{NMe}_2)$  are different. Comment on the geometry in each case and explain why there is a difference in simple bonding terms.

4 (10) Explain the reason why square planar  $d^8$  complexes prefer 16  $e^-$  counts using a simple sketch of the orbital energy diagram.

5 (10) The NET reaction shown below occurs for both early (eg. Zr) and late (eg. Rh) metals but by dramatically different pathways.



(a) Discuss the two dominant pathways involved using Zr(IV) and Rh(I) as examples.

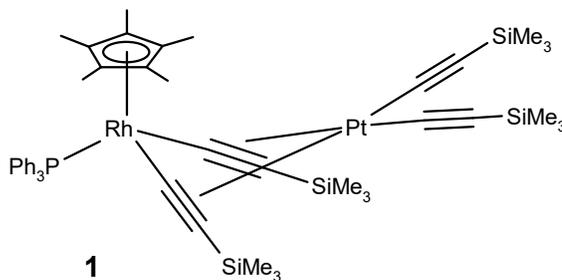
- (b) Is it possible for the Rh(I) mechanism to apply in the case of Zr(IV)? Explain.
- (c) Is it possible for the Zr(IV) mechanism to apply in the case of Rh(I)? Explain.

6 (17) The  $^{13}\text{C}\{^1\text{H}\}$  and  $^{31}\text{P}\{^1\text{H}\}$  NMR data for **1** is given below along with the IR data for the region between 1800 and 2300  $\text{cm}^{-1}$ . **NOTE:** Only the region of the  $^{13}\text{C}$  NMR spectrum between 80 and 120 ppm is listed. Answer the questions below with reference to this data and the structure shown.

**IR:** 2063, 2044, 1955, 1948  $\text{cm}^{-1}$  all very strong absorptions.

**NMR:**  $^{13}\text{C}\{^1\text{H}\}$  112.0 ppm (dd,  $^1J_{\text{Rh-C}} = 45$  Hz,  $^2J_{\text{P-C}} = 27$  Hz) Rh- $\text{C}_\alpha$   
 104.3 (d,  $J = 2.4$  Hz) Pt- $\text{C}_\alpha$   
 103.5 (dd,  $^1J_{\text{Rh-C}} = 4.2$  Hz,  $^2J_{\text{P-C}} = 2.5$  Hz) Cp\* ring C  
 102.8 (dd,  $^2J_{\text{Rh-C}} = 7.8$  Hz,  $^3J_{\text{P-C}} = 2.3$  Hz) Rh- $\text{C}_\beta$   
 101.7 (s) Pt- $\text{C}_\beta$

$^{31}\text{P}\{^1\text{H}\}$  41.9 (d,  $^1J_{\text{Rh-P}} = 139$  Hz).



- (a) Which IR stretches are most likely associated with the Rh-CCSiMe<sub>3</sub> units? (2 pts)
- (b) Explain why the Cp\* ring carbon shows much smaller  $^1J_{\text{Rh-C}}$  coupling than does the acetylide  $\alpha$ -C (4.2 vs. 45 Hz). (3 pts)
- (c) Suggest a reason why the Rh bound acetylide (RhCCSiMe<sub>3</sub>) units are farther downfield than the corresponding PtCCSiMe<sub>3</sub> units (assuming there is no significant difference in the Rh-C vs Pt-C sigma interaction). (3 pts)

- (d) How many electrons are donated by each  $\pi$ -bound acetylide unit to Pt? (2 pts)
- (e) The  $\alpha$ -C of the PtCCSiMe<sub>3</sub> sigma bonded unit shows a small coupling of 2.4 Hz. What nucleus could be responsible for this coupling? (2 pts)
- (f) What would the <sup>195</sup>Pt NMR spectrum for **1** look like? (3 pts)
- (g) What information can be derived from the <sup>31</sup>P{<sup>1</sup>H} NMR? (2 pts)

7 (12) Explain how you would synthesize the following six complexes from the starting material(s) listed and any other commonly accessible reagents. More than one step may be required. (2 pts each)

- (a) Ni(1,5-COD)<sub>2</sub> from NiCl<sub>2</sub>
- (b) MeMn(CO)<sub>5</sub> from HMn(CO)<sub>5</sub>
- (c) Cp<sub>2</sub>Ti(PhCCPh) from Cp<sub>2</sub>TiCl<sub>2</sub>
- (d) ( $\eta^6$ -C<sub>6</sub>H<sub>6</sub>)Cr(CO)<sub>3</sub> from Cr(CO)<sub>6</sub>
- (e) *trans*-Pt(PPh<sub>3</sub>)<sub>2</sub>(H)(Cl) from *trans*-Pt(PPh<sub>3</sub>)<sub>2</sub>(Me)(Cl)

**END**

(periodic table attached)