

Chemistry 652

Organometallic Chemistry

Final Examination, May 22, 2006

Please write your answers directly in the spaces provided.

Name: _____

1) _____

2) _____

3) _____

4) _____

5) _____

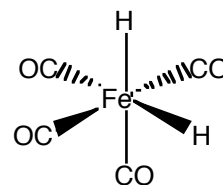
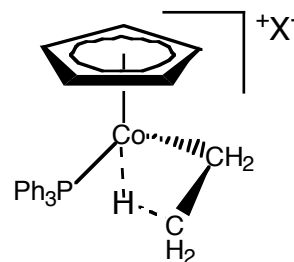
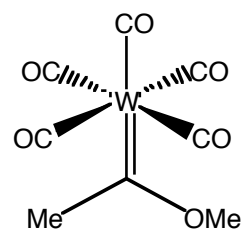
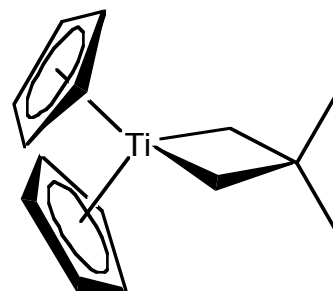
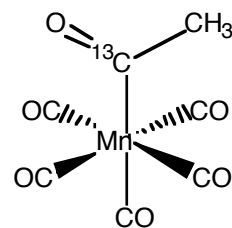
6) _____

7) _____

Total: _____

Enjoy a productive summer

- 1) (20 points) For the following organometallic molecules, give a) the valence electron count, b) the formal oxidation state of the metal, and c) provide a synthesis starting with readily available starting materials.



2) (15 points) Identify five different catalytic processes/reactions and use each one to provide an example of: a) an oxidative addition, b) a reductive elimination (the microscopic reverse of a) does not count!), c) a migratory insertion, d) a β -hydrogen elimination, and e) a nucleophilic attack at a ligand, as being one of the individual steps in the catalytic cycle. Draw structures of the intermediates being interconverted.

a)

b)

c)

d)

e)

3) (15 points) Draw the mechanistic cycle for the **Ring Opening Metathesis Polymerization (ROMP)** of norbornene, using $[\text{Ru}(=\text{CHPh})(\text{PCy}_3)_2\text{Cl}_2]$ as a catalysts. How would you determine whether this is a “living polymerization”?

4) (10 points) Reaction of excess PPh_3 with $\text{TpIr}(\text{C}_2\text{H}_4)_2$ ($\text{Tp} =$ hydrotris(pyrazolyl)borate) in methylene chloride solution under an argon purge yielded complex **1**. The characterization of **1** yielded the data shown below. Draw the structure of **1**.

(29 mg, 64%). Anal. Calcd for $\text{C}_{45}\text{H}_{40}\text{BIrN}_6\text{P}_2$: C, 58.14; H, 4.34; N, 9.04. Found: C, 57.66; H, 4.44; N, 8.86. ^1H NMR (500 MHz, CD_2Cl_2): 7.86 (d, 1H, H_e); 7.47 (m, 1H, H_h); 7.28 (m, 2H, Ph'_{para}); 7.25 (m, 4H, Ph_{meta}); 7.20 (m, 2H, Ph_{para}); 7.10 (dt, 4H, $J = 2$ Hz, 8 Hz, $\text{Ph}'_{\text{ortho}}$); 7.03 (dt, 4H, $J = 2$ Hz, 8 Hz, Ph_{ortho}); 6.89 (m, 4H, Ph'_{meta}); 6.78 (m, 1H, H_a); 6.80 (m, 1H, H_j); 6.54 (d, 1H, H_e); 5.83 (t, 1H, H_d); 5.43 (t, 1H, H_g); 4.76 (t, 1H, H_b); -18.95 (dd, $J_{\text{HP}} = 10$ Hz, 20 Hz, 1H, H-Ir). ^{31}P {aromatic ^1H }: 3.80 (dd, $J_{\text{PP}} = 10$ Hz, $J_{\text{PH}} = 10$ Hz); 1.02 (dd, $J_{\text{PP}} = 10$ Hz, $J_{\text{PH}} = 20$ Hz). ^{13}C { ^1H }: 144.9 (C_a); 143.6 (C_c); 138.6 (d $J_{\text{CP}} = 8.5$ Hz, C_j); 135.3 (C_e); 134.7 (d, $J_{\text{CP}} = 56$ Hz, Ph_{ipso}); 134.6 (d, $J_{\text{CP}} = 40$ Hz, Ph'_{ipso}); 133.9 (d, $J_{\text{CP}} = 9$ Hz, Ph'_{meta}); 133.8 (d, $J_{\text{CP}} = 9$ Hz, Ph_{meta}); 133.4 (d, $J_{\text{CP}} = 4$ Hz, C_h); 129.6 (Ph'_{para}); 129.5 (Ph_{para}); 127.9 (d, $J_{\text{CP}} = 11$ Hz, $\text{Ph}'_{\text{ortho}}$); 127.5 (d, $J_{\text{CP}} = 11$ Hz, Ph_{ortho}); 132.2 (dd, $J_{\text{CP}}(\text{cis}) = 12$ Hz, $J_{\text{CP}}(\text{trans}) = 98$ Hz, C-Ir); 114.4 (d, $J_{\text{CP}} = 8$ Hz, C_b); 105.5 (C_g); 105.4 (C_d). IR (Nujol, cm^{-1}): 2473 (ν_{BH}), 2179 (ν_{IrH}).

5) (10 points) A recent *Science* paper from the Grubbs laboratory cited in a Chem 652 lecture described a new single-component olefin polymerization catalyst.

- a) What is the metal on which the catalyst is based.
- b) What is the structure of the catalyst? Draw a molecular structure with as much detail as you can recall.
- c) What are the unusual and attractive attributes of this new catalyst?
- d) The Grubbs catalyst is related to a family of catalysts jointly developed by an academic laboratory (in North Carolina) and a major chemical company (headquartered in Delaware). Draw a structural formula representing this latter class of catalysts and identify a feature that makes them unique.

6) (15 points) List the techniques used to characterize metal complexes with “agostic interactions”. Give typical measured values and explain how they correlate with the nature of the electron deficient C \cdots H \cdots M interaction.

7) a) (10 pts) Construct the MO scheme for the bonding in metallocenes (Cp_2M). Fill in the appropriate number of electrons for ferrocene (Cp_2Fe).

b) (5 points)

I. Which compound is usually cited as the “first organometallic complex”?

II. When was ferrocene discovered?

III. What is the usual definition of an organometallic compound?

IV. Name the author of the textbook for this class, and where he teaches.

V. What aspect of organometallic chemistry do you find most interesting?