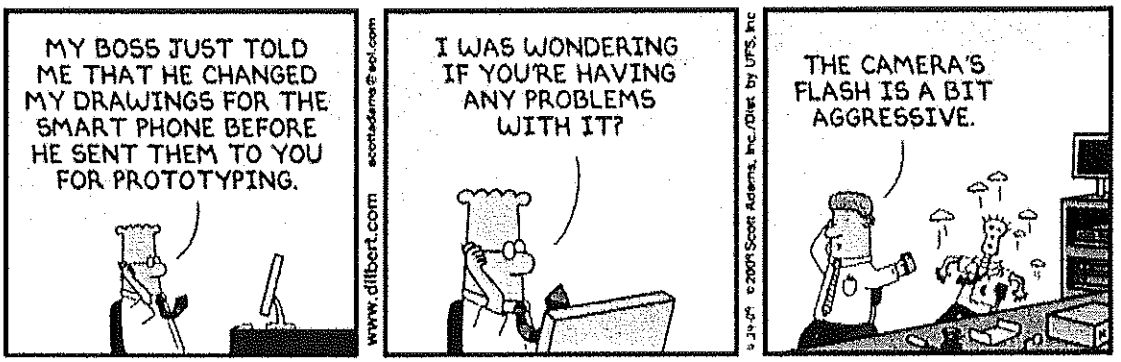


Chemistry 652

Organometallic Chemistry

Final Examination, May 25, 2009

Please write your answers directly in the spaces provided.

Name: Key

1) ____

2) ____

3) ____

4) ____

5) ____

6) ____

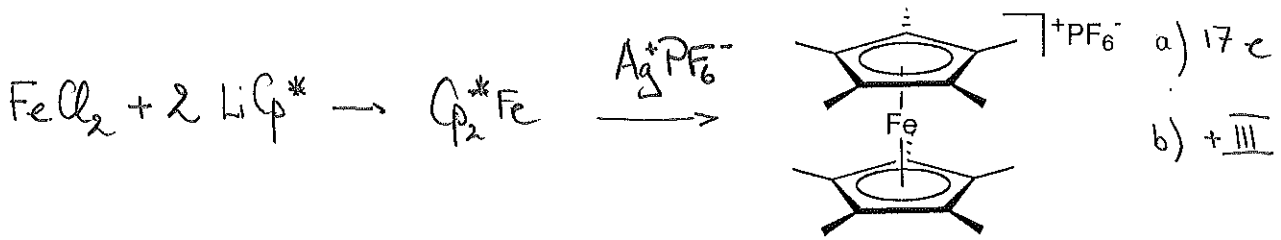
7) ____

8) ____

Total: _____ /100

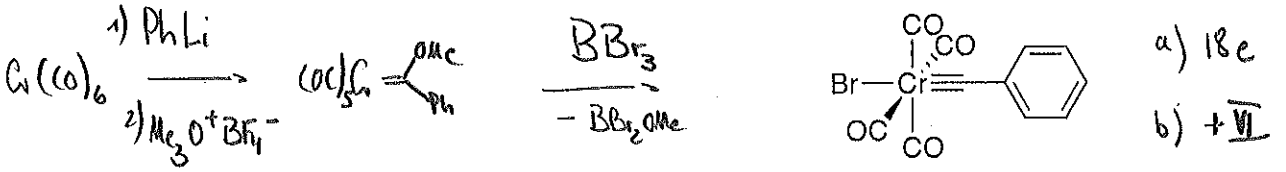
Enjoy a productive summer

1) (15 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.



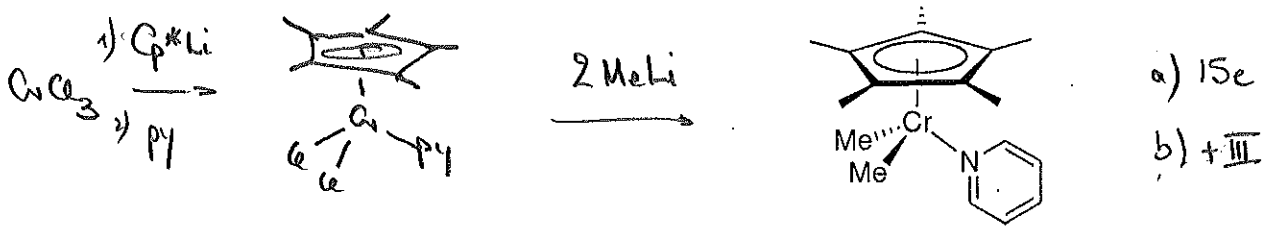
a) 17 e

b) +III



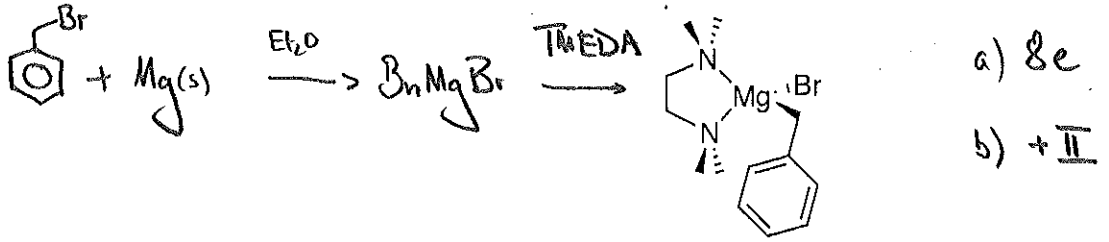
a) 18e

b) +VI



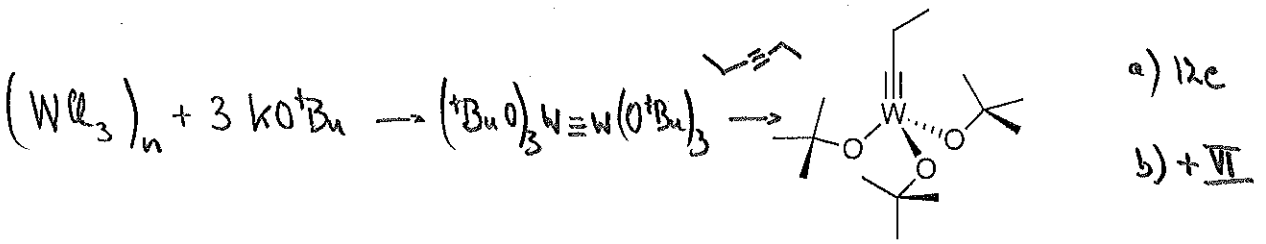
a) 15e

b) +III



a) 8e

b) +II

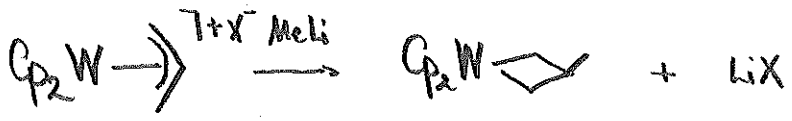


a) 12e

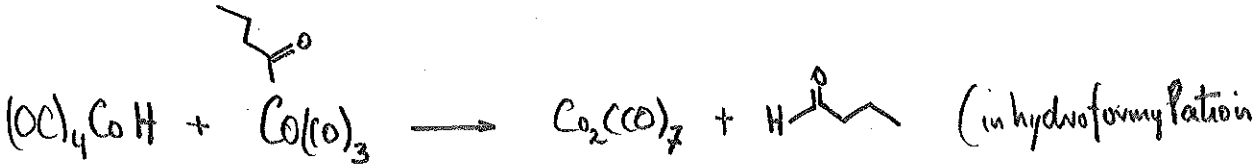
b) +VI

2) (15 points) Write <u>balanced</u> reaction equations showing actual examples of the following common organometallic reactions:

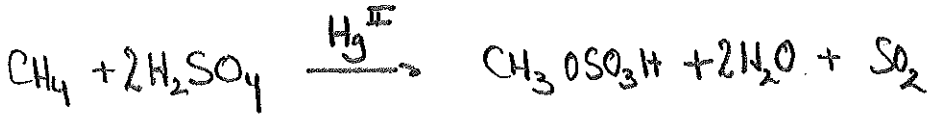
a) Nucleophilic addition to a coordinated ligand



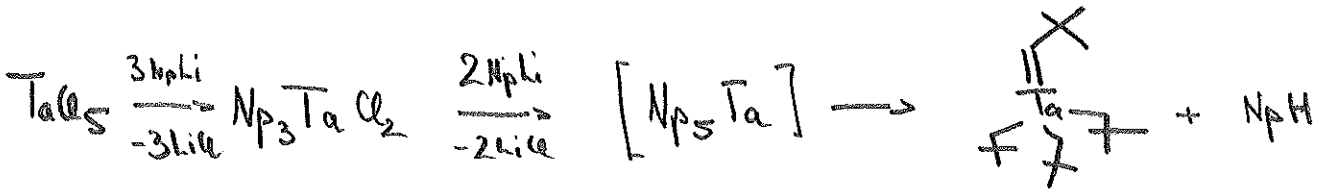
b) Binuclear reductive elimination



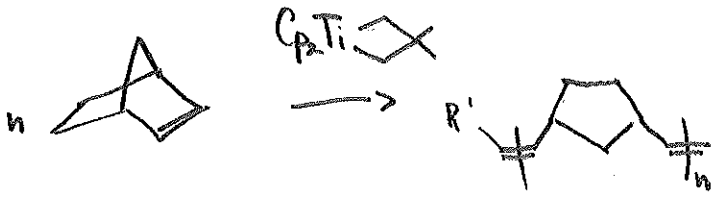
c) Electrophilic C-H activation



d) α-hydrogen elimination



e) Ring opening metathesis polymerization (ROMP)



3) (15 points) Coordinatively unsaturated electron deficient metal complexes often exhibit so called 'agostic interactions'.

a) Define what an agostic interaction is. You may use relevant examples of actual compounds and/or describe the interaction in your own words/diagrams.

An agostic interaction is a 3 center-2 electron-bond between a metal and a C–H bond, leading to close contact between the metal and the H, and weakening of the C–H bond

i.e.

b) What are the observable consequences of an agostic interaction; i.e., what experimental techniques are typically used to detect their presence.

Short M–H, M–C contacts, elongation of C–H bond : X-ray/neutron diffraction

Weakening of C–H bond : red-shift of ν_{C-H} in IR

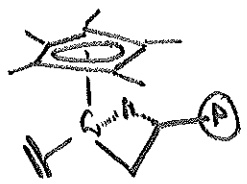
" : upfield shift in ^{1}H-NMR, decreased J_{C-H} coupling

Equilibrium isotope effect : isotopic perturbation of resonance

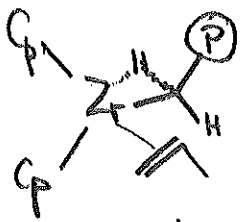
c) What role do agostic interactions play in the coordination polymerization of small olefins (e. g. propene to polypropylene, catalyzed by Ziegler Natta catalysts). How do you know?

Agostic interactions stabilize intermediates and transition states

e.g.



or



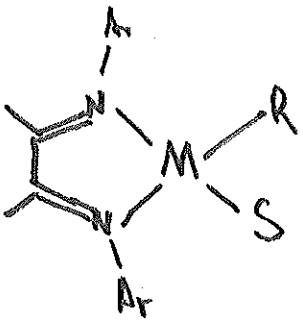
β-agostic

α-agostic

Isotopic Perturbation of stereochemistry expts. !

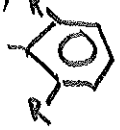
4) (10 points) Based on collaborative research with researchers as UNC Chapel Hill, DuPont has developed a family of late transition detal ethylene polymerization catalysts under the trade name of Versipol™.

a) Draw a prototypical structure of a catalyst belonging to this family. Specify the metal, the structure of the ligand, the charge, etc. Name the chemists at UNC, who was involved.



$T^+ X^-$ M. Brookhart

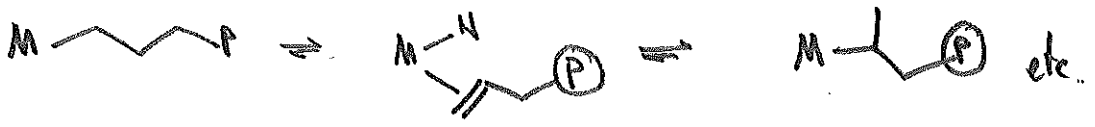
M = Ni, Pd

Ar = 

S = Et_2O, //, etc.

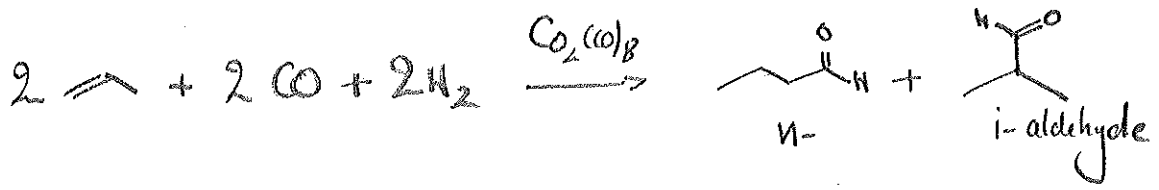
b) Ultimately, these catalysts did not become a commercial success, because the polymers exhibited inferior physical properties. What is the typical microstructure of the polymers produced by Versipol™ catalysts, and what is the mechanism by which it arises.

- Versipol™ polymers are often amorphous materials due to their 'hyperbranched' microstructures – i.e. containing branches and branches on branches.
- This structure is the result of facile 'chain-walking' by reversible β-H-elimination and olefin insertion.

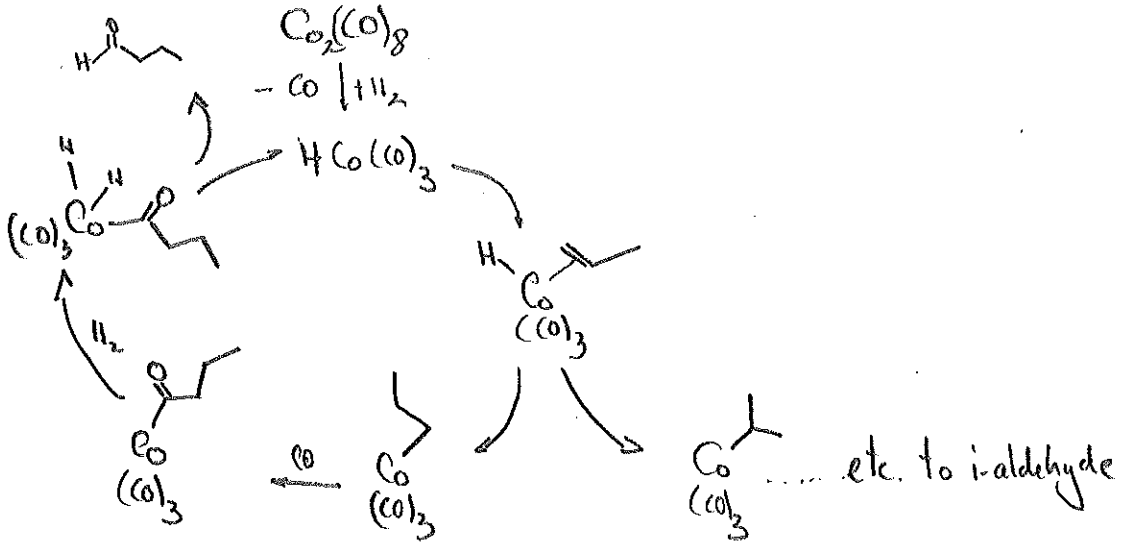


5) (15 points) The hydroformylation of α-olefins is one of the largest homogeneously catalyzed processes practiced by the chemical industry

a) Write a balanced reaction equation for the hydroformylation of propene, showing both possible products and indicate the catalysts used.



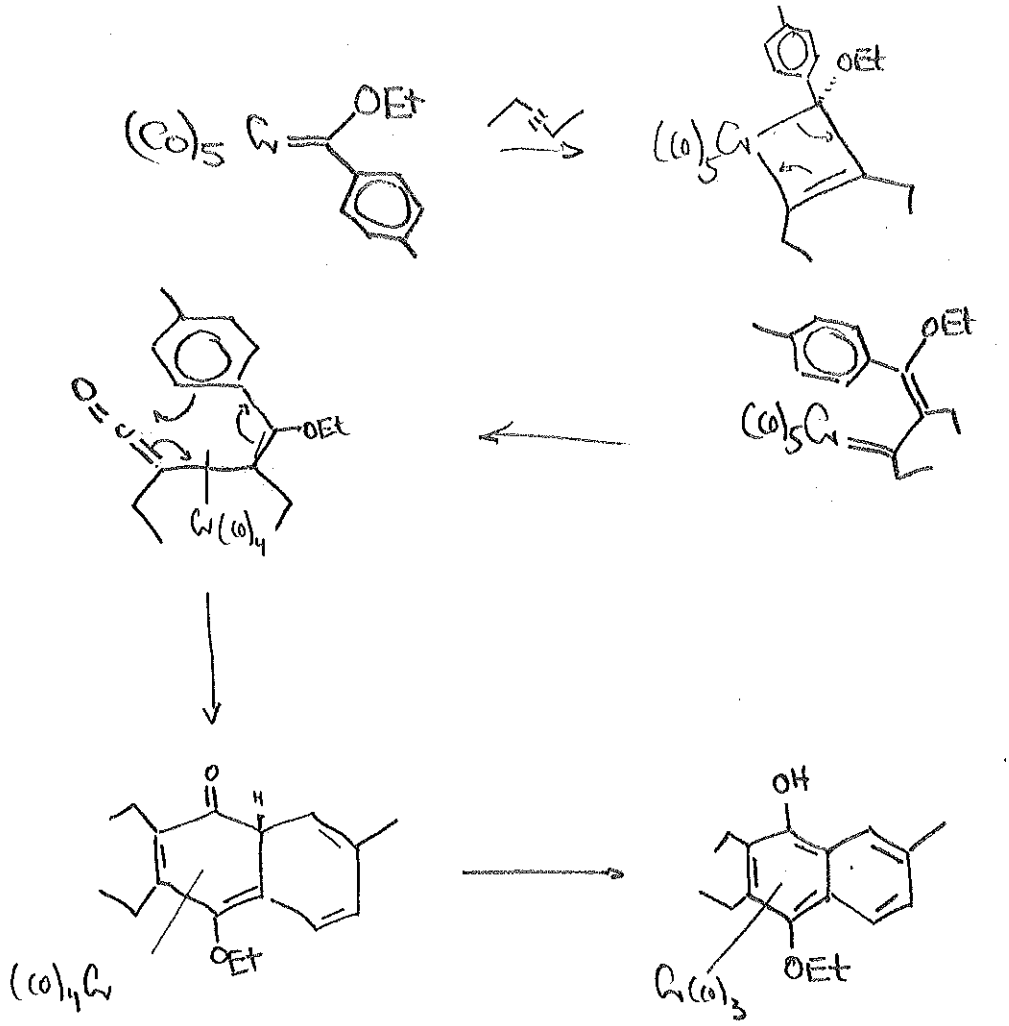
b) Draw a catalytic cycle showing the mechanism of this reaction



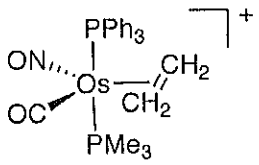
c) One of the two products is the more valuable one. What determines the selectivity between the two, and how might it be influenced to increase the yield of the more valuable product?

The n-aldehyde is typically the desired product – high n/i ratios being sought.
The selectivity is determined at the olefin insertion step, giving either a primary or secondary alkyl. Destabilization of the secondary alkyl, e.g. by steric crowding, can influence the n/i ratio advantageously.

6) (10 points) Stoichiometric reactions of certain organometallic compounds with organic molecules represent useful synthetic organic transformations. For example: what is the product of a 'Dötz reaction' of $(OC)_5Cr{=}C(OEt)(p\text{-tolyl})$ with 3-hexyne? Draw structures of likely intermediates to arrive at the final structure.



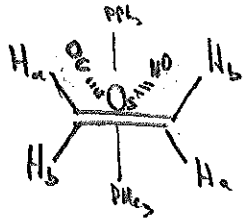
7) (10 points) Consider this pseudo-octahedral ethylene complex of osmium. At +80 °C, the ^{31}P-decoupled ^{1}H NMR spectrum of this complex in solution with an equimolar amount of added ethylene shows a single sharp line at 6.0 ppm (ignoring the PMe_3 and PPh_3 resonances).



a) Cooling this solution to 0 °C results in the splitting of this resonance into a single line at 4.9 ppm (about where free ethylene is observed) and two doublets at 7.5 (J = 2 Hz) and 6.7 (J = 2 Hz) ppm.
b) Upon cooling to -80 oC, the two doublets split further into a complex multiplet.

Explain these observations. Label the hydrogens and use structural drawings indicating what is happening.

- At +80°C there is only a single line for all ethylene protons
  ⇒ exchange between free ethylene and bound ethylene is fast on the NMR time scale, leading to one average (coalesced) resonance
- At 0°C one sees 1 single line at 4.9 ppm and two doublets w/ J = 2
  ⇒ ligand exchange has been 'frozen out', i.e. free ethylene has a single resonance
  The two doublets represent protons H_a and H_b. Rotation of the ethylene is still fast on NMR time scale, but because of the dissymmetry of the Os does not equilibrate H_a & H_b.



- At −80°C the 2 doublets split into several (4!) multiplets.
  ⇒ Rotation of the ethylene is now slow on NMR time scale, and all 4 ethylene protons are inequivalent and coupled to each other.

7) (10 points) Random organometallic chemistry facts:

a) The first organometallic compound – Zeise's salt was discovered in:
i) 1932 ii) 1827 iii) 1492

b) Coordination of dihydrogen to a metal makes it i) more acidic, ii) enriched in deuterium, or iii) paramagnetic

c) Estimate the C-O bond distance in a typical metal carbonyl in units of Å.

~ 1.15 Å

d) What does the acronym NHC stand for? Draw a structure of an example.

N-heterocyclic carbene 

e) The cyclopentadienyl ligand (Cp) is **NOT** a good π-acceptor, a strong σ-donor, a good π-donor?

f) The 18-electron rule applies most rigorously to i) metal oxides, ii) actinide metal aquo ions, or iii) homoleptic metal carbonyls?

g) The α-carbon of Schrock type alkylidenes is i) electrophilic, ii) nucleophilic, or iii) Lewis-acidic?

h) Catalytic olefin isomerization produces i) pure a-olefins, ii) pure trans-olefins, or iii) a mixture of all possible isomers.

i) Metal-alkyl bond strength i) vary randomly, ii) increase or iii) decrease upon going down in a goup. (e. g., Co -> Rh -> Ir)?

j) Which of the following is not a stable (isolable) compound/ion:
i) WMe_6 ii) $[VH_6]^-$ iii) $[ReH_9]^{2-}$ iv) $[ZrMe_6]^{2-}$