

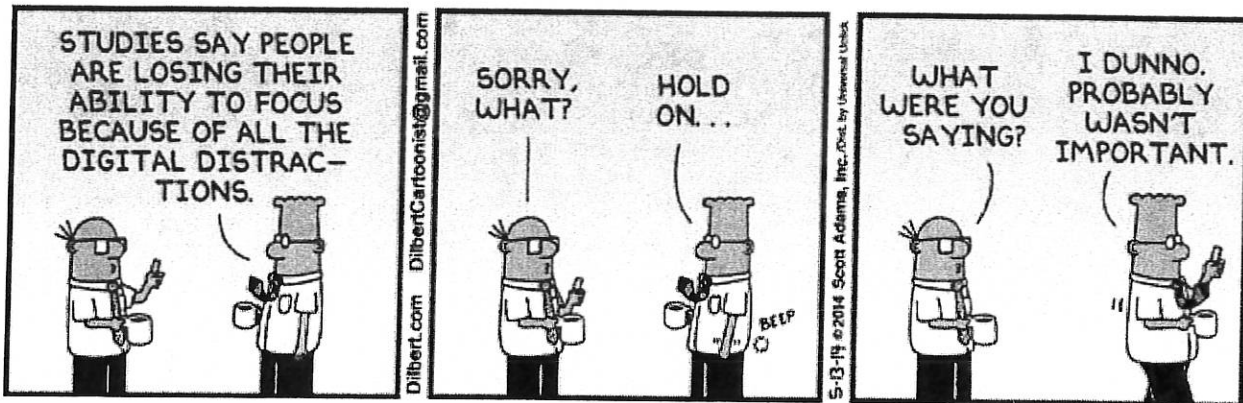
Chemistry 652

Organometallic Chemistry

Final Examination, May 22, 2014

Please write your answers directly in the spaces provided.

Name: Key



1) _____

2) _____

3) _____

4) _____

5) _____

6) _____

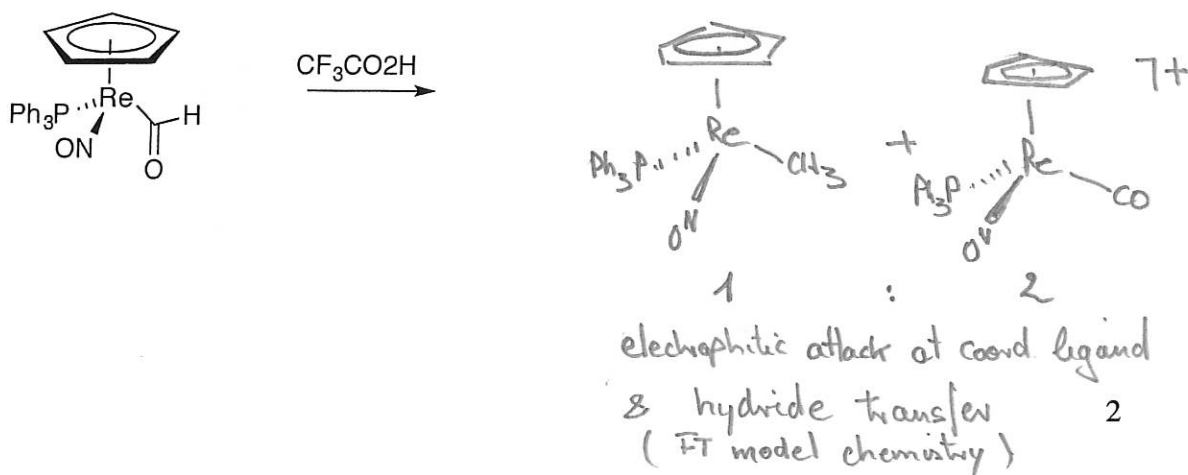
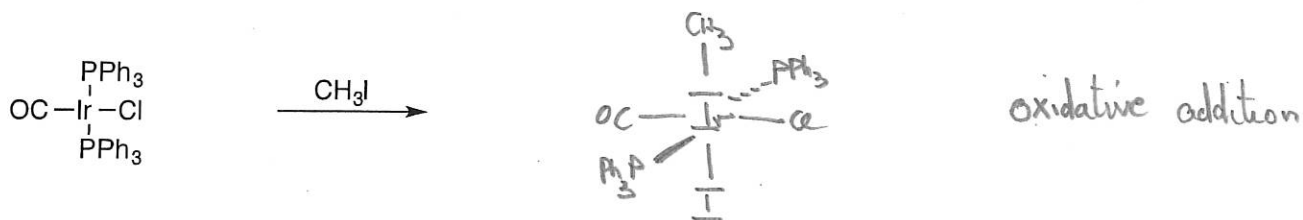
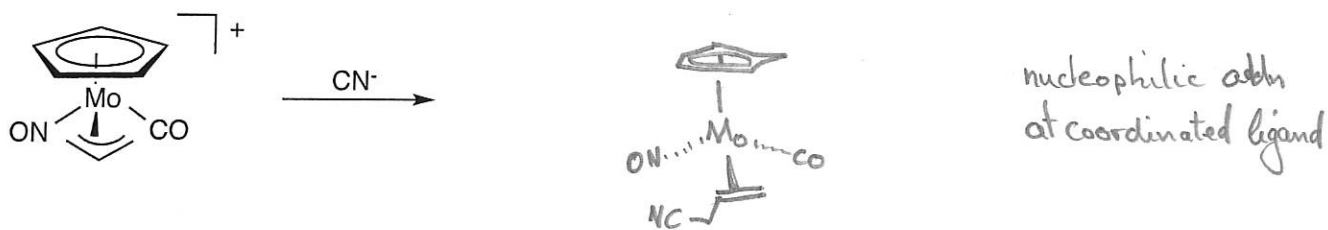
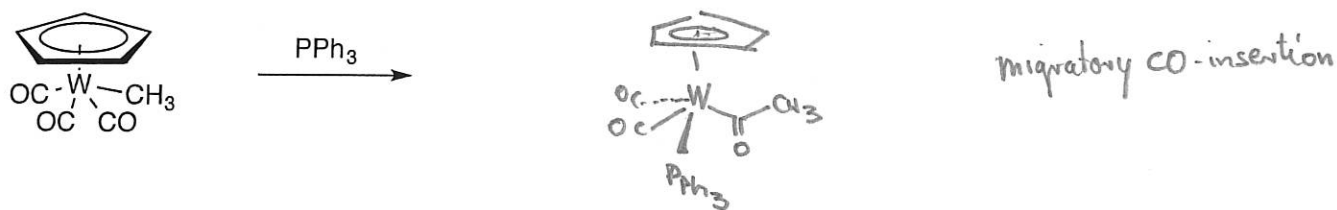
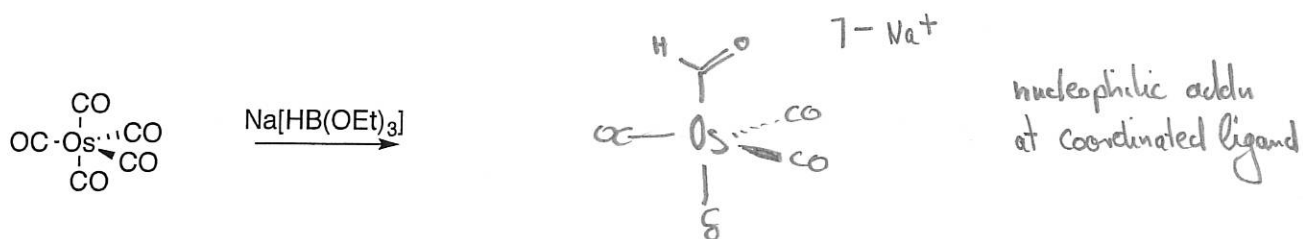
7) _____

8) _____

Total: _____

Have a productive summer!

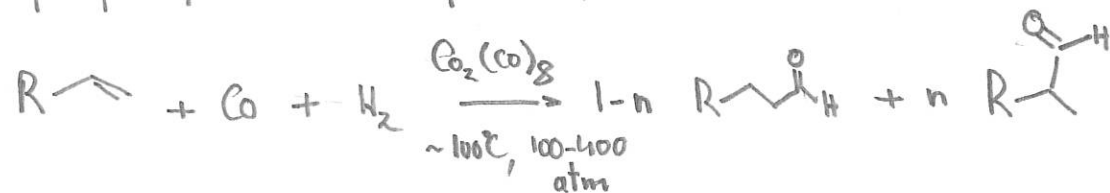
- 1) (15 points) Predict the products of the following organometallic transformations. Draw structures indicating stereochemistry and identify the type of reaction (e. g. "reductive elimination" etc.)



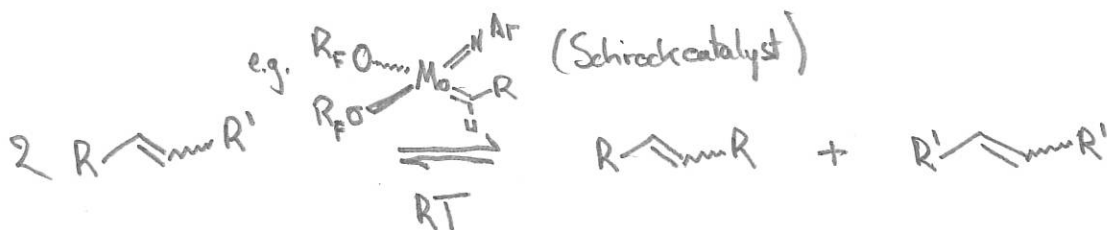
- 2) (15 points) Pick three different homogeneous catalytic reactions. Write **balanced reaction equations** for these reactions and give as much detail as you can remember about the catalyst and the reaction conditions required (Note: the Wacker process does not count – see question 3).

Some examples – others possible

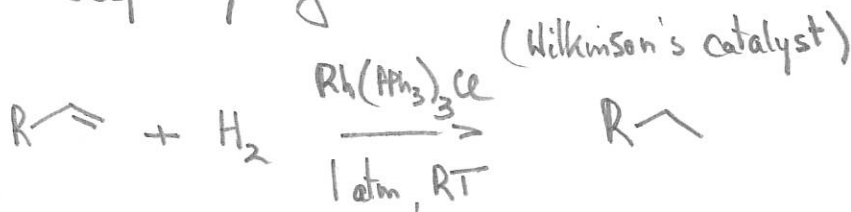
- a) hydroformylation ("oxo-process")



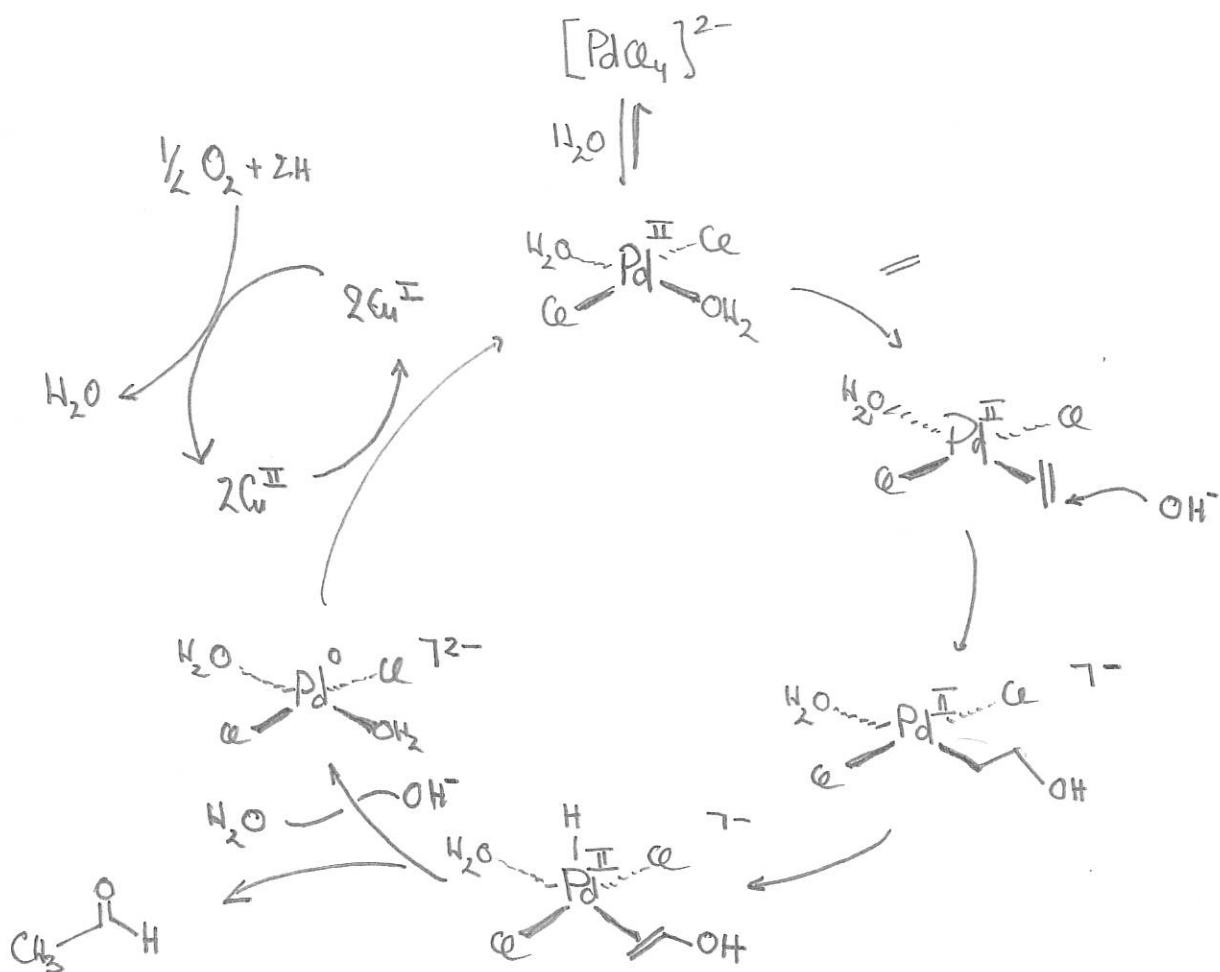
- b) olefin metathesis



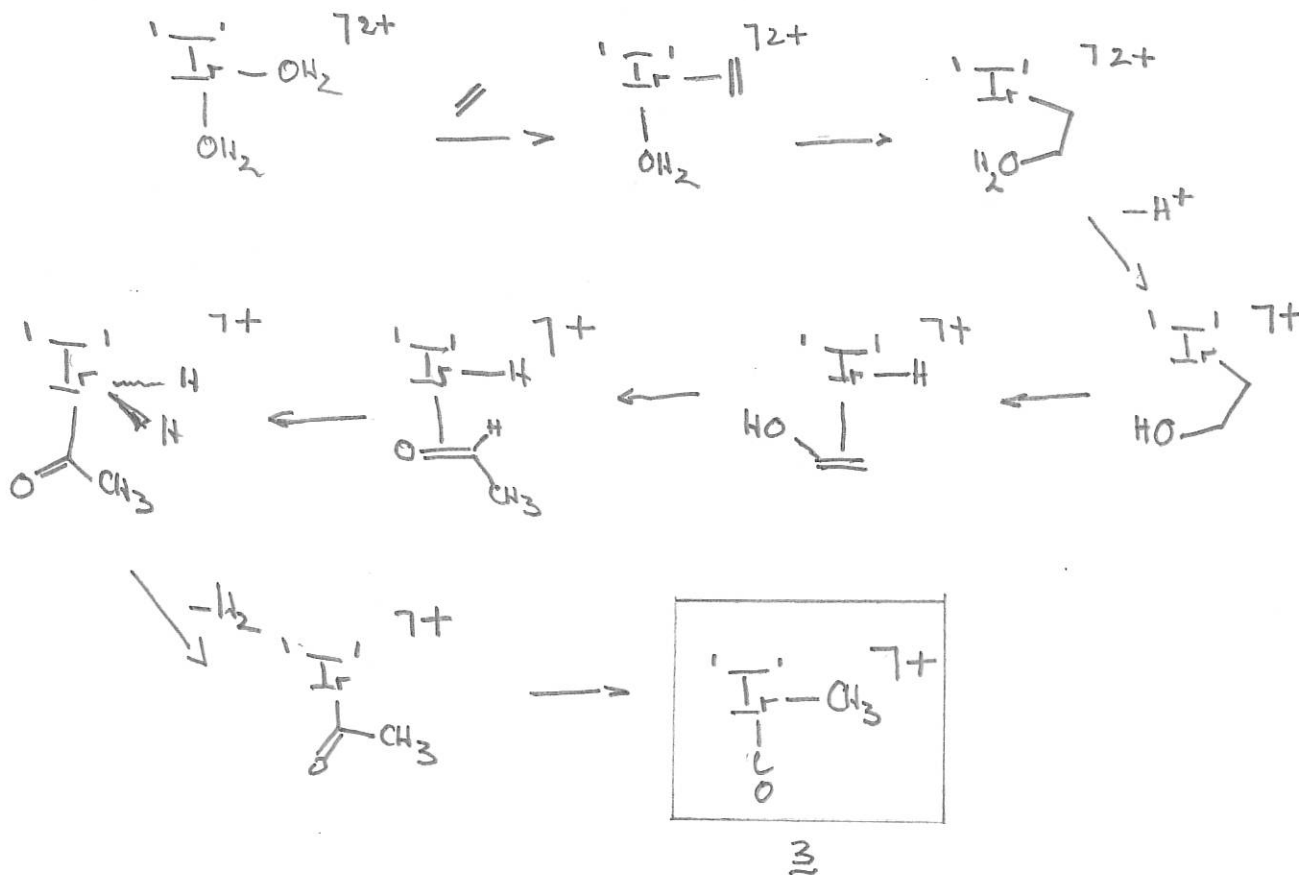
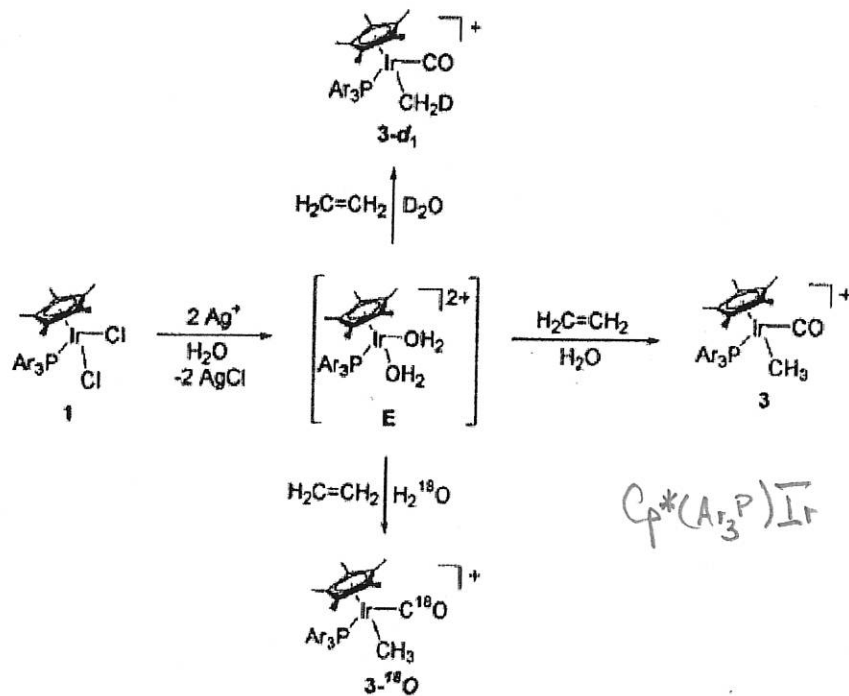
- c) olefin hydrogenation



3) (10 points) Draw the mechanistic cycle for the **Wacker process**, using both palladium and copper as a catalyst. Begin by writing a **balanced reaction equation** identifying the reagents and products. Then draw the catalytic cycle with its individual steps.

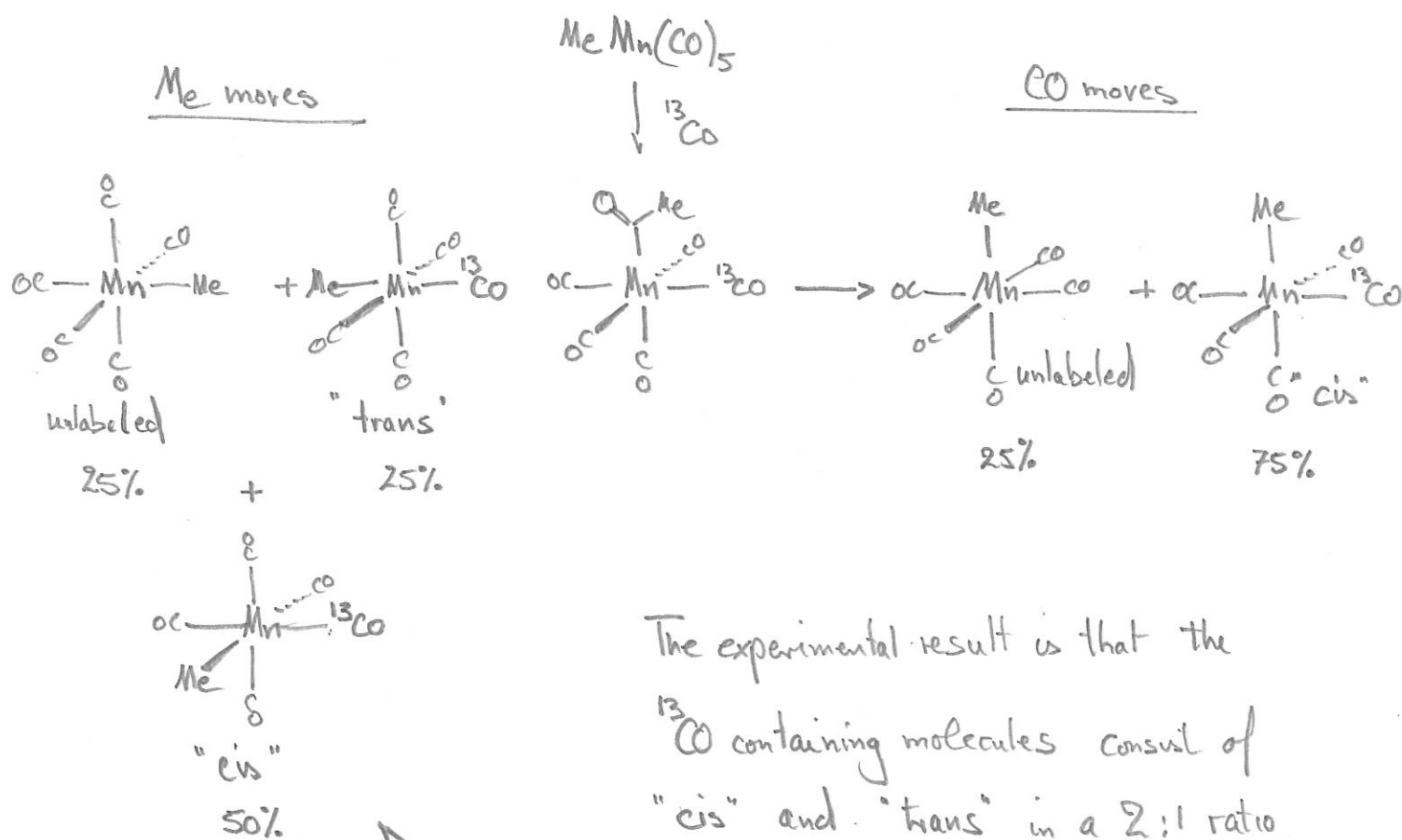


4) (10 points) Reaction of $\text{Cp}^*\text{Ir}(\text{PAr}_3)_2\text{Cl}_2$ with silver triflate (AgOTf) and ethylene in water yields the isotopologs shown in the scheme below. Write a mechanism for this transformation that is consistent with the labeling results shown in the scheme.



5) (15 points) In the CO induced migratory insertion of $\text{MeMn}(\text{CO})_5$, there arises the mechanistic question whether the CO inserts into a 'stationary' Mn-Me bond or the Me-group migrates to a CO (in other words: "which moves – the Me or the CO?"). Prof. F. Calderazzo has performed an ingenious experiment to address this subtle question. Describe the experiment, its outcome, and its interpretation, including the answer to the question posed above.

An example of the mechanistic use of the 'Principle of microscopic reversibility'.



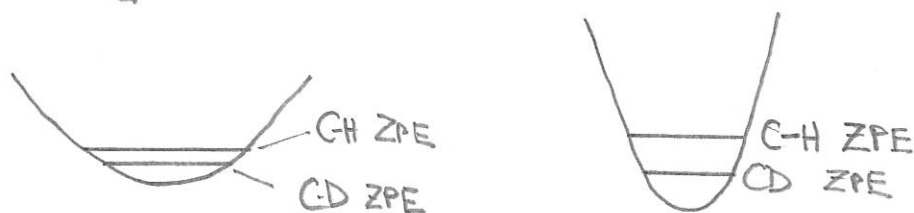
Me - moves !

6) (15 points) The so-called 'isotopic perturbation of resonance' is sometimes used as evidence for the presence of an agostic interaction in the ground state of a molecule, whereas the 'isotopic perturbation of stereochemistry' has been used to detect agostic interactions in the transition state for the insertion of olefins into metal alkyls. What causes these effects (i.e. what chemical or physical principle is responsible), and how do they manifest themselves (i.e. what are the observable results)?

i) Both phenomena result from an 'equilibrium isotope effect', which favors the positioning of a C-H bond in a $3c/2e$ agostic interaction, which makes for a weaker C-H (C-D) bond.



The agostic bond is weaker, and therefore its difference in zero point energy (ZPE) are smaller



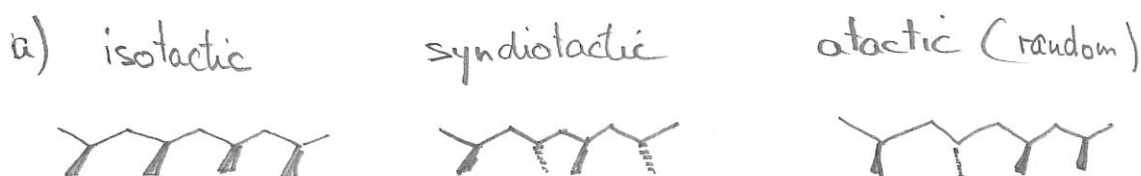
ii) For the 'isotopic perturbation of resonance', increasing D-substitution pushes the remaining H into the agostic interaction, thus engendering more and more upfield (hydride-like) chemical shifts.
(see p. 281 in Crabtree)

iii) For the 'isotopic perturbation of stereochemistry' the preferred C-H agostic interaction favors a particular stereochemistry of subsequent insertion of labeled olefins of the type

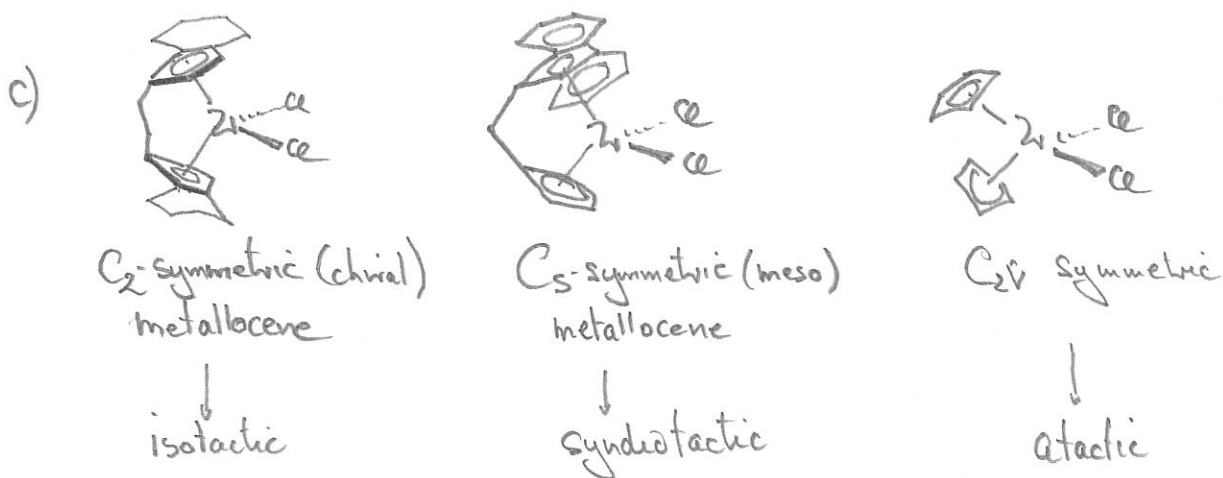
(see p. 339 in Crabtree)

7) (10 points) The catalytic polymerization of α -olefins like propene gives rise to different materials, depending on the catalyst used. The difference lies in the microstructure of the polymer.

- name the three most important forms of polypropylene and indicate their structures.
- What analytical technique is used to determine the structure of polypropylene? How are the results of the analysis expressed?
- Draw structures of homogeneous catalysts that produce the three different types of polypropylene.
- What material/molecule is commonly used (in large excess) as co-catalyst in propene polymerizations?



b) distinguished by $^{13}\text{C-NMR}$ at the dyad level: vs or nowadays, the pentad level: 'mmmm' vs 'rrrr' ^m

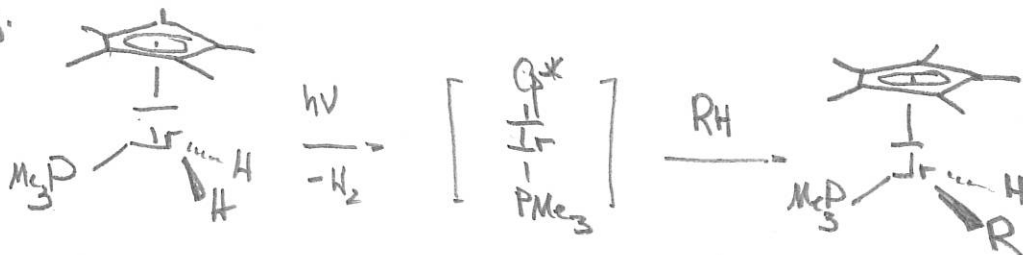


d) Methylaluminoxane (MAO) - i.e. a product of partial hydrolysis of AlMe_3 , is often used in huge excess (≥ 1000 equiv).

8) (10 pts) There are different types of metal-mediated C-H activation reactions. Using example reactions (draw structures and show reactants and products in balanced reactions), identify as many of them as possible

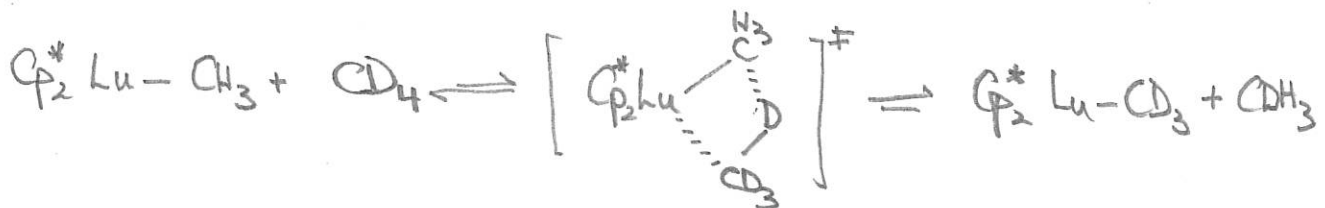
1) Oxidative addition of C-H to electron rich (low-valent) metals

e.g.



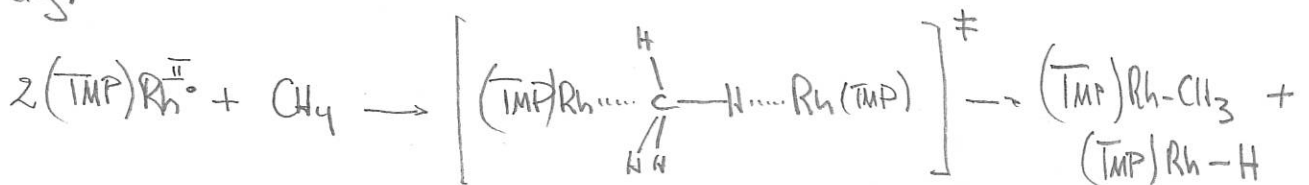
2) σ -bond metathesis - C-H exchange w/out oxidative addition

e.g.

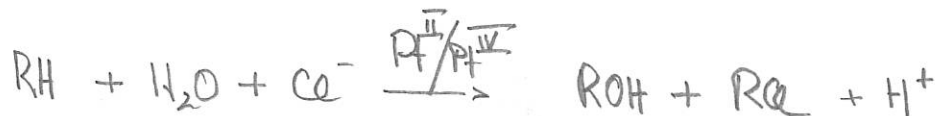


3) metallaradicals

e.g.



4) electrophilic C-H activation (aka Shilov chemistry)



or

