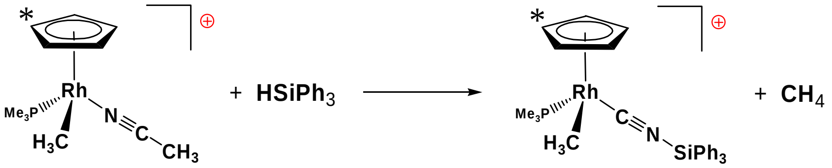
CHEM 4571 - *Organometallic Chemistry* **ANSWER KEY**

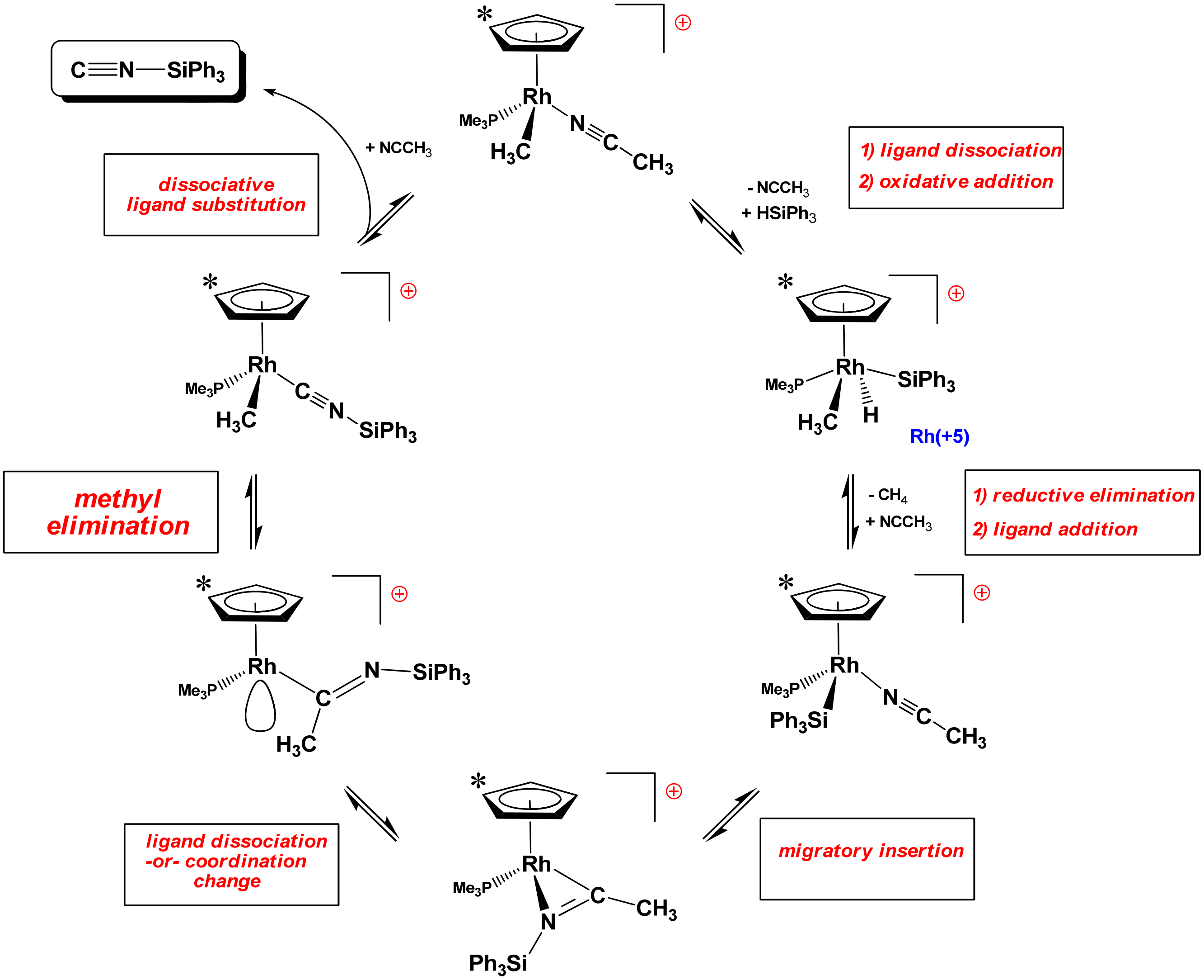
FINAL EXAM -- May 2008

Check this box if you want your graded test put out in the public boxes outside Prof. Stanley's office: ☐

1. (50 pts) Bergman and coworkers reported the following transformation (*JACS*, **2002**, *124*, 4192-4193) that was also presented in your notes:



a) (35 pts) Shown below is a hypothetical catalytic cycle to transform acetonitrile (N≡CCH$_3$) and HSiPh$_3$ into the silyl-substituted isocyanide (C≡NSiPh$_3$) and CH$_4$. Label the forward steps (going clockwise) in the catalytic cycle using the boxes provided. There may be more than step per box – if the order is important label the steps 1) and 2), otherwise don't number the steps.

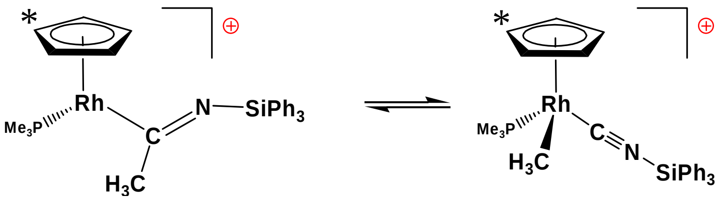


b) (5 pts) The last ligand substitution step in the cycle (perhaps the simplest step) is very unlikely to occur and keeps this from being a real catalytic reaction. Clearly discuss why this step is unlikely to happen.

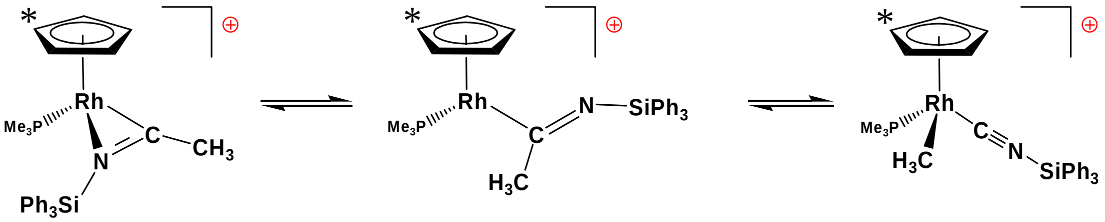
Isocyanides are more strongly bonding ligands relative to nitrile ligands like acetonitrile. They are not only stronger σ-donors, but also stronger π-acceptors. Both of these work in concert to make them relatively strongly bonding ligands. Thus, it will be difficult to replace a more strongly bonding ligand like isocyanide with a weaker bonding ligand like acetonitrile. If acetonitrile was the solvent, the large concentration present might drive the reaction for a while, but as more and more isocyanide is produced it would bind to the catalyst and inhibit it by tying up the empty coordination sites.

c) (5 pts) What other step in the catalytic cycle is rather unusual and difficult? Clearly discuss.

The elimination of the methyl group from the complex shown below is unusual and difficult. As discussed in your notes eliminating an alkyl group from a C-C bond is not easy due to the directed nature of the C-C sp^3 hybrid orbitals and the presence of C-H bonds that can short circuit the reaction via β-hydride elimination. Here, however, the β-hydride elimination would generate a relatively high energy ketene-imine and the CH_3 elimination turns out to be more favorable.

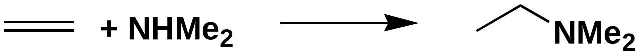


d) (5 pts) In the following sequence of steps, the dissociation of the N-atom from the Rh center is very important. Clearly discuss why this is important for the final reaction step.

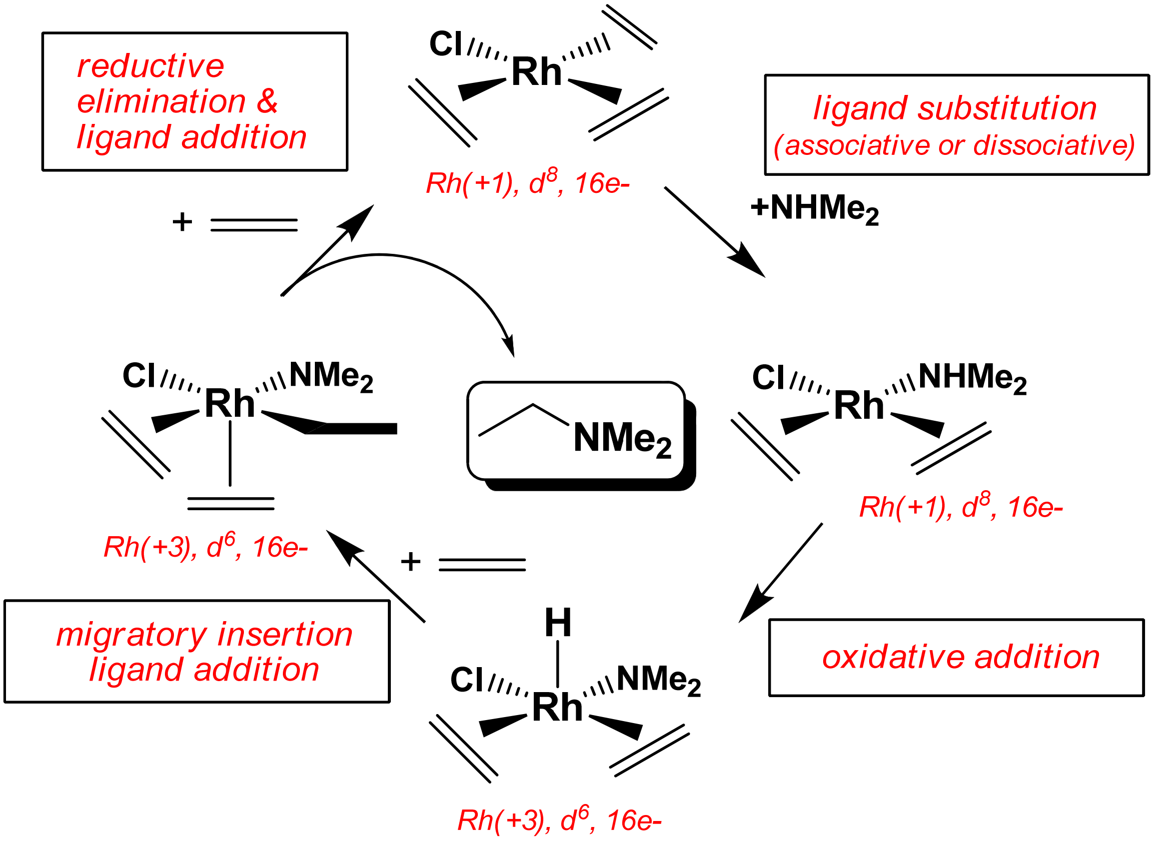


In order to do the methyl group elimination, you need to have an empty orbital on the Rh center and the first complex is 18e- saturated. The neutral nitrogen atom is the weakest donor and is the most likely to dissociate and allow the vinyl-like group to rotate the methyl group over to interact with the empty orbital on the Rh to enable the elimination reaction.

2. (50 pts) Hydroamination is the following catalytic process:

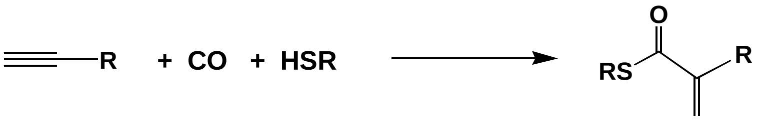


Sketch out a reasonable catalytic cycle for hydroamination using $RhCl(H_2C{=}CH_2)_3$ as the starting catalyst. Clearly show and label each step in the cycle.

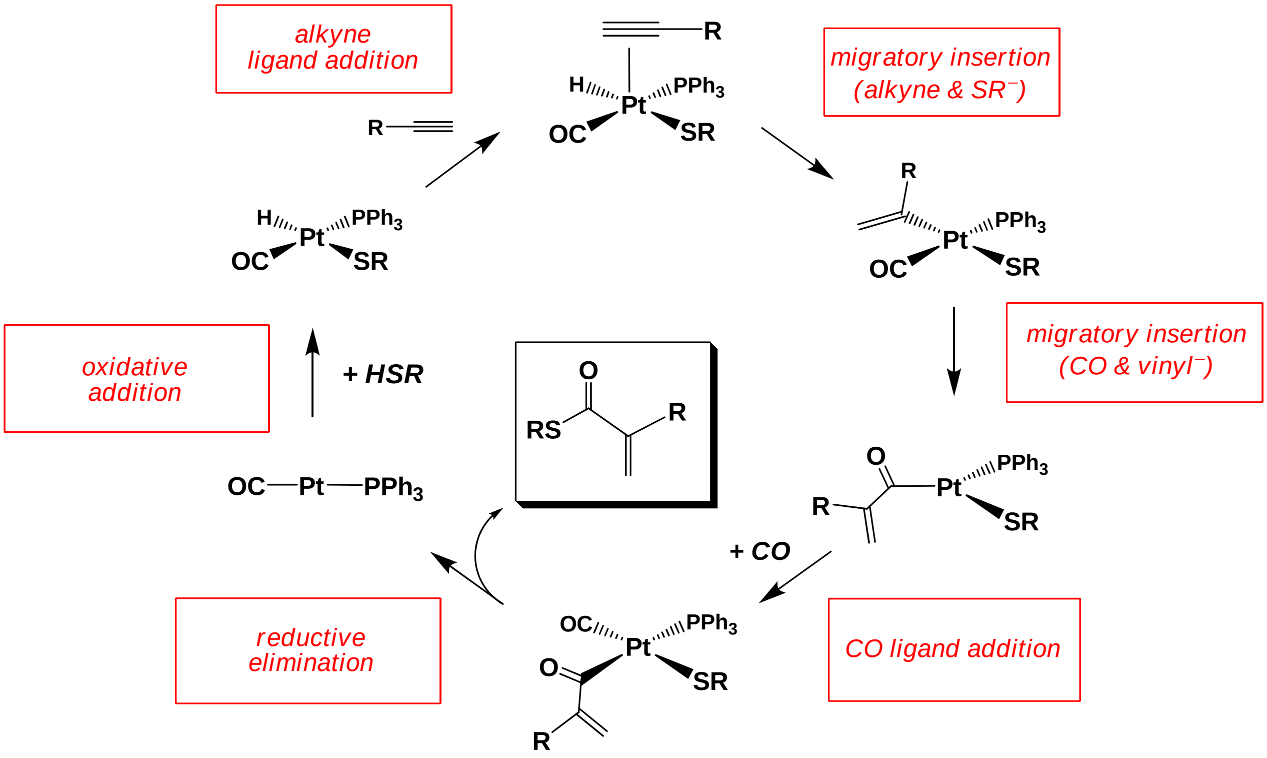


There are some variants in the order of the steps, exact # of ligands (16e- or 18e- Rh(III) complex shown at bottom) and the use of solvent or one of the other ligands present (ethylene, amine) to fill in coordination unsaturation generated by the migratory insertion step. The migratory insertion of the amide with the alkene is also OK (although hydride and alkene is somewhat more favorable).

3. (50 pts) Shown below is a proposed catalytic cycle for the hydrothiocarbonylation of an alkyne.



a) (35 pts) Label each step in the catalytic cycle. There may be more than one thing occurring per step – if the order is important, list them in the correct order.



b) (10 pts) The alkyne addition step as written above is probably NOT correct due to a property of the Pt center that makes this ligand addition unlikely. Discuss what I am referring to and a simple way to correct this reaction step.

Pt(+2) d^8 16e- square planar complexes do NOT like to add a fifth ligand due to the blocking effect of the extended $5d_{z^2}$ filled orbital. It is better to propose the loss of the PPh_3 ligand to make a 3-coordinate 14e- complex first, then bind the alkyne ligand. The dissociated PPh_3 ligand can then be re-coordinated after the migratory insertion of the CO and vinyl group.

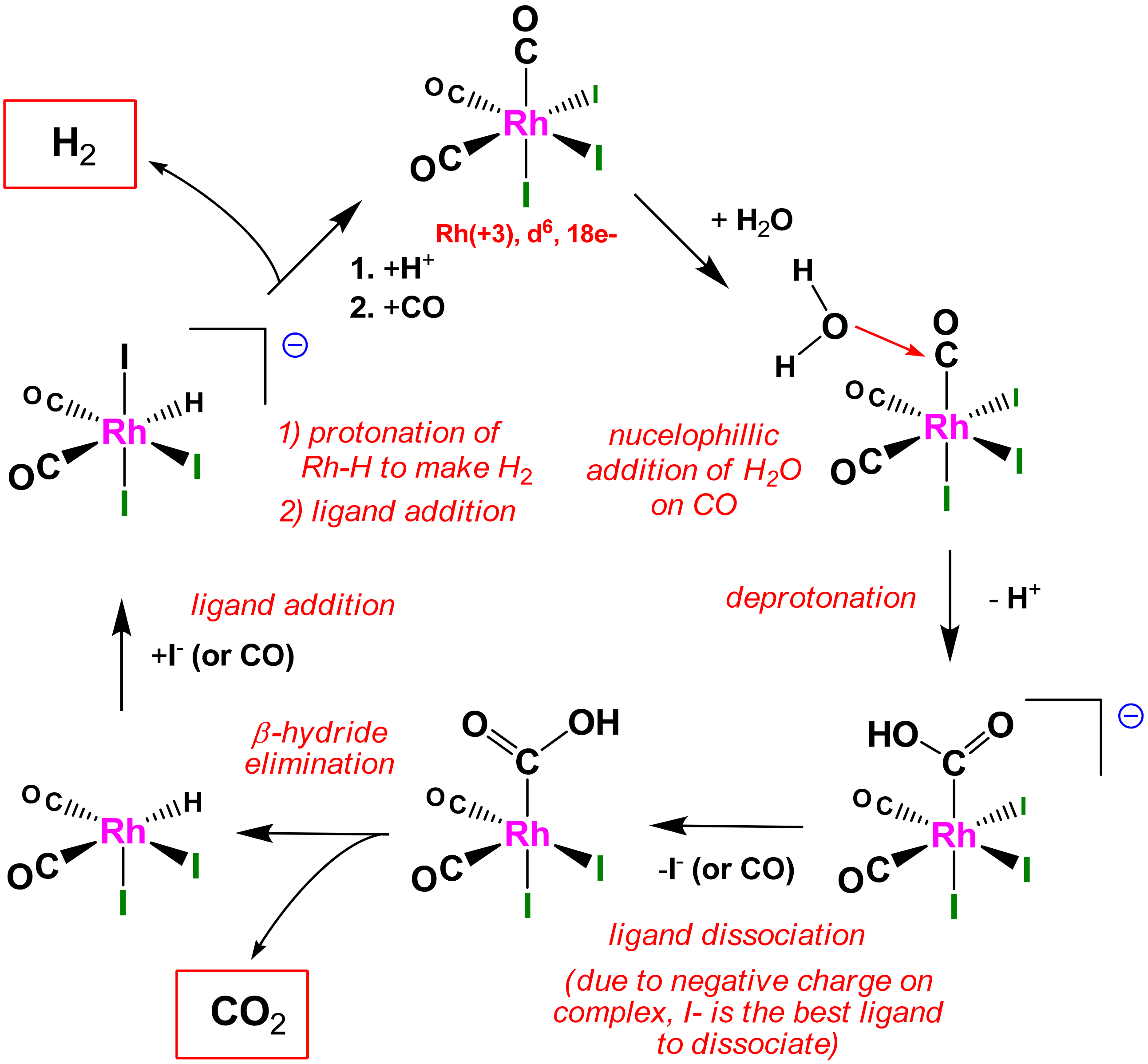
c) (5 pts) Assume that there is some excess PPh_3 present, along with excess CO and alkyne. In the bottom ligand addition step I used CO as the added ligand. Why is CO the best choice relative to PPh_3 or alkyne ligand?

CO is electron-withdrawing and will favor the following reductive elimination step. Remember that reductive elimination is favored by π-accepting ligands or electron-deficient metal centers. You do generate a rather unsaturated 14e- complex, but that isn't too bad for a Pt(0) d^{10} center that is right next to Au. Remember that Au(+1) d^{10} complexes strongly favor 14e- two-coordinate complexes.

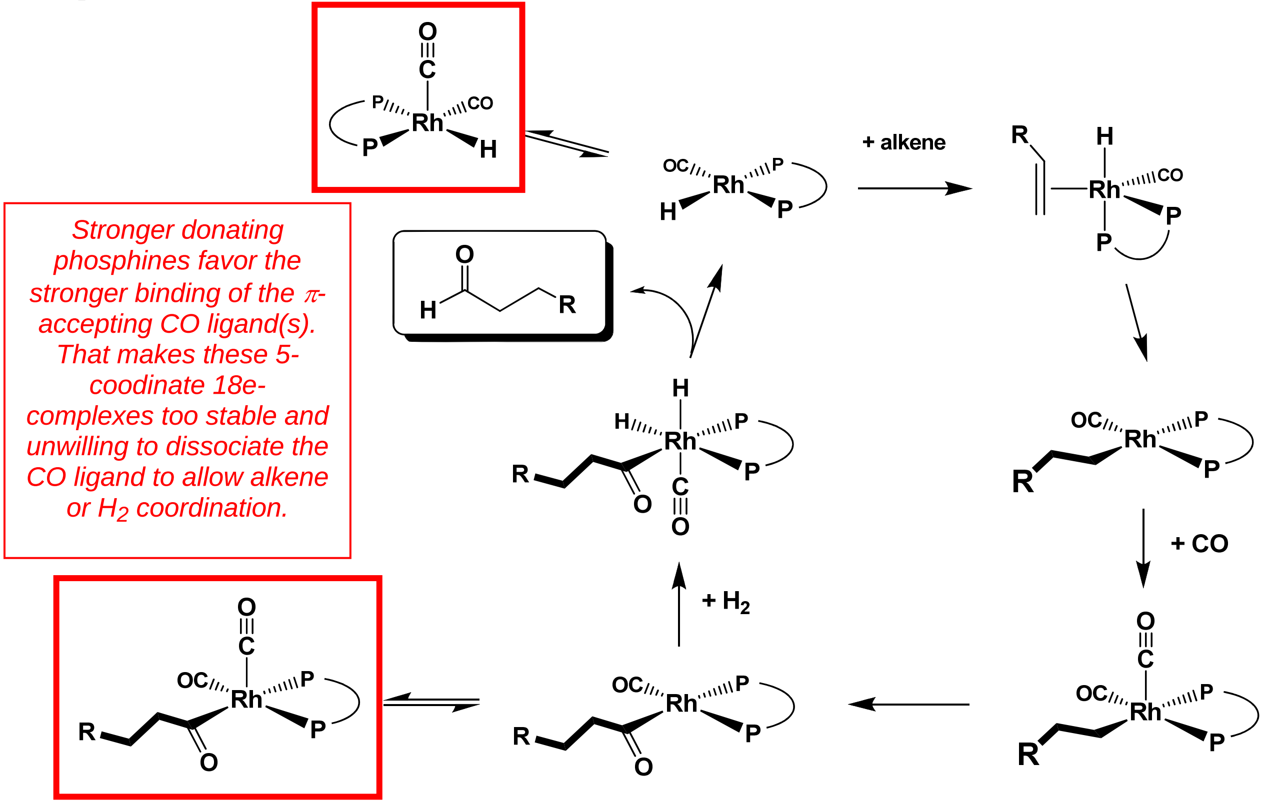
4. (50 pts) One of the side reactions in the Monsanto acetic acid process is the water-gas shift reaction:

$$H_2O + CO \rightleftharpoons H_2 + CO_2$$

Using $RhI_3(CO)_3$ as the starting catalyst, sketch out a catalytic cycle for this based on the following reaction steps: **1)** nucleophillic attack of water on a carbonyl ligand followed by loss of a proton (keep track of your charges on the complex!); **2)** ligand dissociation (pick best ligand, keep track of charges on your complex); **3)** β-hydride elimination and loss (dissociation) of CO_2; **4)** ligand addition (the one you dissociated); **5)** protonation of hydride to dissociate H_2 (proton from first reaction step, keep track of charges on your complex); **6)** ligand addition to regenerate starting catalyst.

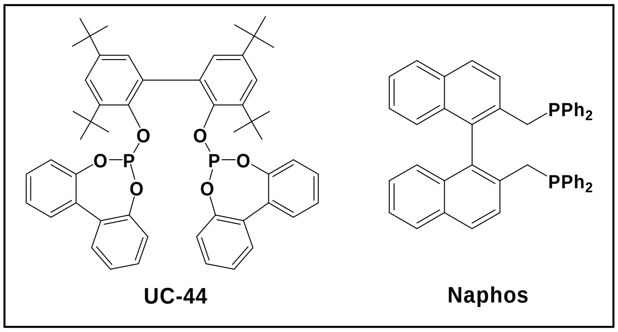


5. (50 pts) The two bisphosphine ligands shown in part **a)** are both excellent at generating very regioselective (high linear to branched aldehyde ratios) Rh-based hydroformylation catalysts (alkene + H_2 + CO → linear aldehyde). The proposed catalysis cycle is shown below with some side complexes:



Stronger donating phosphines favor the stronger binding of the π-accepting CO ligand(s). That makes these 5-coodinate 18e- complexes too stable and unwilling to dissociate the CO ligand to allow alkene or H_2 coordination.

a) (20 pts) Which bisphosphine ligand shown to the right generates a considerably more active Rh hydroformylation catalyst and why? Only consider electronic effects, both ligands have similar steric factors.



The bisphosphite ligand UC-44 will make the <u>most</u> active Rh hydroformylation catalyst since it is the poorest donor and a better π-acceptor relative to Naphos. The less electron-rich the metal center, the weaker the Rh-CO π-backbonding and the easier it is to get the alkene and H_2 ligands in to start and finish the hydroformylation catalytic cycle. Phosphite ligands make some of the most active Rh hydroformylation catalysts known, although they usually give poor regioselectivity due to their small size. UC-44 is sterically bulked up to compensate for this. One major problem with phosphite ligands (UC-44 included) is that they fragment via a number of pathways considerably more easily than ligands like PPh_3 or Naphos (which also have their own fragmentation problems).

b) (20 pts) Beller and coworkers have reported (*Angew. Chem.*, **2001**, *40*, 3408-3411) on hydroformylation catalysis using HRh(CO)(Naphos). The table of catalytic data from their paper is shown below. For experiment # 1, what is the theoretical maximum of turnovers that could have been done and how many turnovers did the authors actually do?

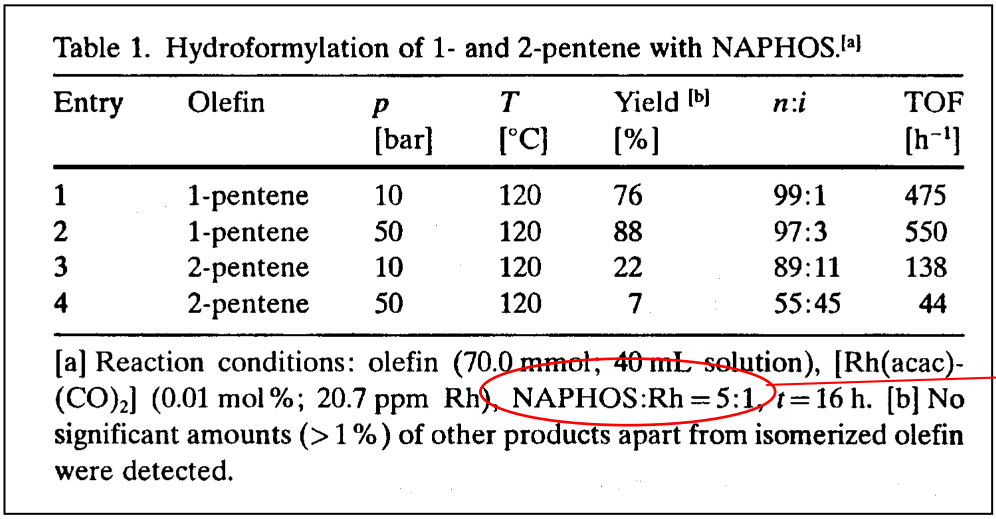


Table 1. Hydroformylation of 1- and 2-pentene with NAPHOS.[a]

Entry	Olefin	p [bar]	T [°C]	Yield [b] [%]	n:i	TOF [h^{-1}]
1	1-pentene	10	120	76	99:1	475
2	1-pentene	50	120	88	97:3	550
3	2-pentene	10	120	22	89:11	138
4	2-pentene	50	120	7	55:45	44

[a] Reaction conditions: olefin (70.0 mmol, 40 mL solution), [Rh(acac)(CO)$_2$] (0.01 mol%; 20.7 ppm Rh), NAPHOS:Rh = 5:1, t = 16 h. [b] No significant amounts (> 1%) of other products apart from isomerized olefin were detected.

Excess Naphos is not relevant to the TON calculation, but is needed to make sure all the Rh is complexed with Naphos to generate active catalyst

a) Theoretical Turnover # = 10,000 (0.01 mol % of catalyst)

b) Actual turnover # for experiment # 1:

There are <u>two</u> ways to calculate the TON:

(1.0 equivalent alkene/0.0001 equivalent of Rh)*(0.76 yield) = **7,600 TO**

or: (475 hr $^{-1}$)(16 hr) = **7,600 TO** (average TOF multiplied by time of run)

c) (10 pts) Why is the hydroformylation of 2-pentene (cis and trans isomers are about the same) slower than 1-pentene (Table 1 above, experiments #1 and #3)? Why is experiment # 4 especially slow? Clearly explain and discuss.

2-pentene is a more sterically hindered alkene and has a harder time fitting into the empty binding site on the HRh(CO)(bisphosphine) catalyst. 1-alkenes are the least sterically hindered and typically hydroformylate the fastest.

Experiment # 4 is especially slow because the CO pressure has been increased to 50 bar. CO is a considerably better ligand than 2-pentene (no steric hindrance) and the more that is present in solution, the less 2-pentene that can coordinate to the Rh and be hydroformylated. Note that the smaller 1-pentene can compete more effectively with the CO and the average TOF actually increases for experiment # 2 relative to # 1.