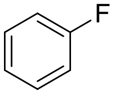
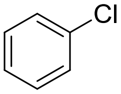
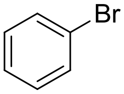
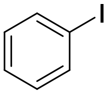
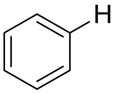
CHEM 344 Organometallic Chemistry Practice Problems (**not for credit**)

Summer 2014

Name (print): ________________________ TA name (print): ______________

1) The strength of the C–X bond of halobenzenes Ph–X was explored via computational chemistry in Chapter 4.

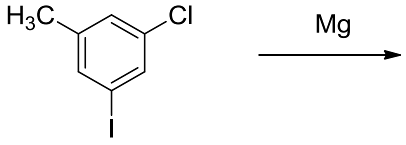
a) Explain the experimental bond dissociation enthalpy values shown below in terms of bond length and bond strength. (The benzene C–H bond enthalpy is provided for reference.)

Ph–X	ΔH°_{C-X} (kcal/mol)
	127
	97
	84
	67
	113

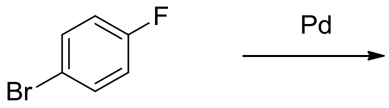
b) Briefly explain which of the above halobenzenes is the least reactive toward the oxidative addition of a metal such as Mg or Pd.

2) Show the product and justify the chemoselctivity of the following oxidative addition reactions.

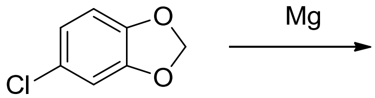
a)



b)



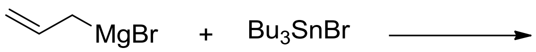
c)



3) Show all products of the following transmetallation reactions. (Think about the relative polarities of the C–M bond in the starting material and the main product. The periodic table of electronegativity values for each element attached to this problem set may be useful.)

a) $2\ \mathrm{BuLi} + \mathrm{CuI} \longrightarrow$

b)



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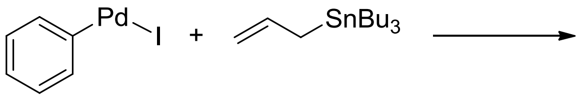
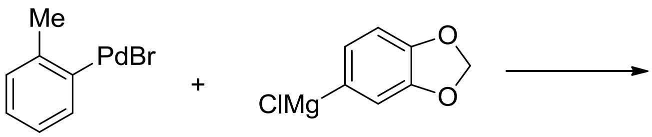
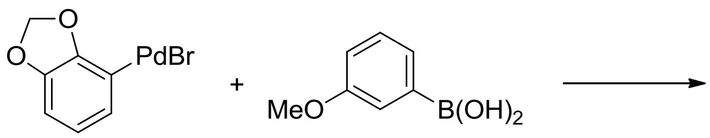


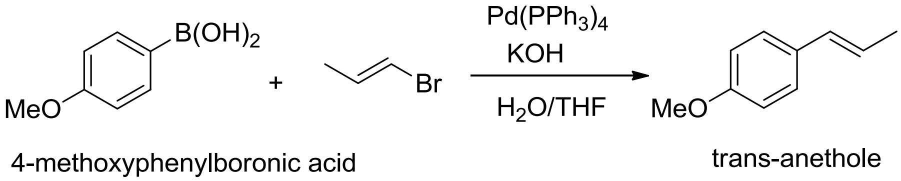
d)



e)

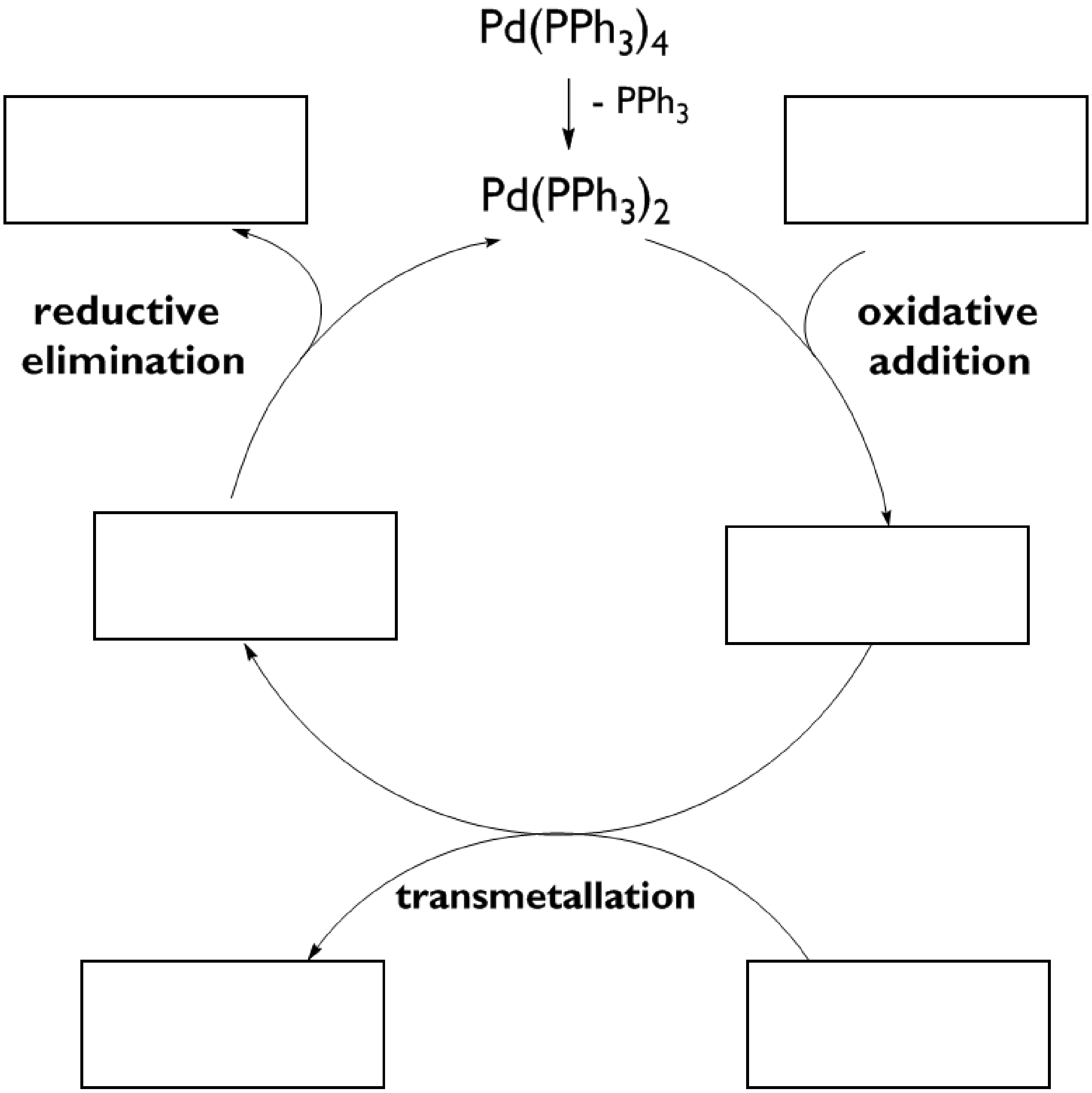


4) Suzuki-Miyaura coupling reactions typically occur between aryl or alkenyl halides and an arylboronic acid. An example of such a reaction is shown below for the synthesis of the food flavoring compound *trans*-anethole (*trans*-1-methoxy-4-(1-propenyl)benzene).

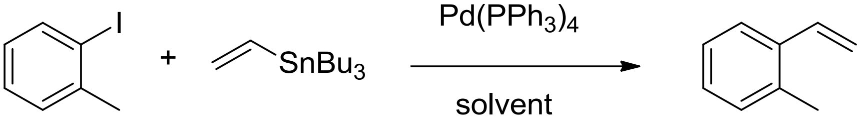


a) Propose a synthesis of 4-methoxyphenylboronic acid starting from phenol (it involves more than one step). Recall that trimethylborate, B(OMe)$_3$, reacts as an electrophile toward Grignard reagents. Show all isolated intermediates/products formed. You do not need to give a mechanism for the individual steps.

b) Complete the catalytic cycle for the Suzuki-Miyaura coupling reaction shown previously on page 4, drawing the appropriate reagents and products of each of the three labeled steps. The role of KOH in the reaction will be discussed in the Suzuki pre-lab session next week.



c) Draw and label the full catalytic cycle for the Stille coupling of 2-iodotoluene and tributyl(vinyl)stannane shown below.

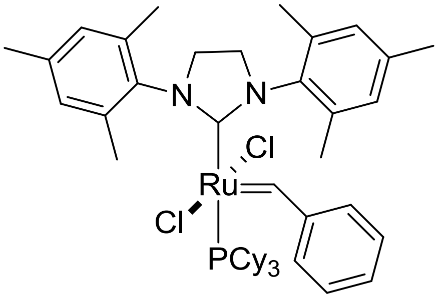


5) Draw the balanced reaction for the formation of isopropylmagnesium bromide from isopropyl bromide in diethyl ether and show the charge distribution along the carbon-metal bond.

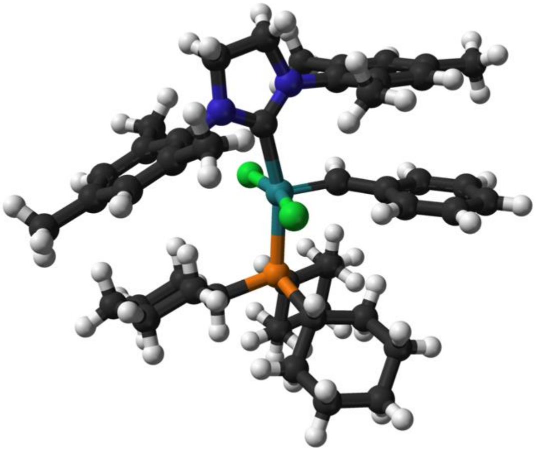
6) The solvent chosen for Grignard reactions is critical.
   a. Explain why diethyl ether and THF are common solvents for the generation of Grignard reagents.

   b. Explain why water, ethanol, and acetone are all incompatible with a Grignard reagent. Provide a chemical reaction in each case.

7) Ruthenium- and molybdenum-based complexes are used as catalysts for alkene metathesis reactions. One such Ru-based complex, the Grubbs 2nd generation catalyst (G2), is shown below. The complex features both an *N*-heterocyclic carbene ligand and a tertiary phosphine ligand (Cy = cyclohexyl group).

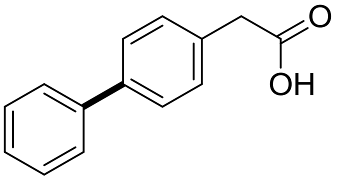


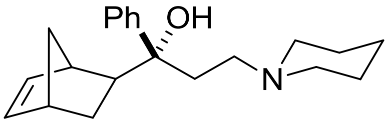
Grubbs 2nd generation catalyst (G2)



Ruthenium metal alone does not catalyze alkene metathesis reactions. Give 3 reasons why metal-ligand coordination complexes such as G2 are more useful than elemental metals for organometallic catalysis.

8) Each of the compounds a) through d) can be synthesized by either a Grignard reaction or by a Pd-catalyzed coupling reaction. The C-C bond generated by the organometallic reaction is shown in **bold**. Draw starting materials, reagents, catalysts, etc. that could be used to form the **bold** C-C bond in each compound and name each reaction used to form each **bold** bond.

a) 

b) 

c)