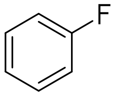
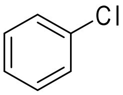
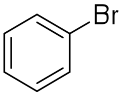
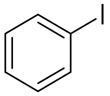
CHEM 344 Organometallic Chemistry Practice Problem Set (not for credit)

Summer 2013

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

1) The strength of the C-X bond of halobenzenes Ph-X was explored via computational chemistry in Chapter 5.

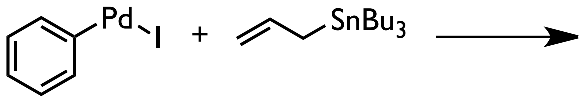
a) Explain the experimental bond dissociation enthalpy values shown below.

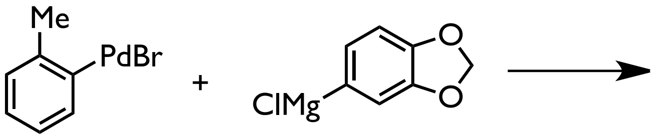
Ph-X	$\Delta H_{C\text{-}X}°$ (kcal/mol)
	127
	97
	84
	67

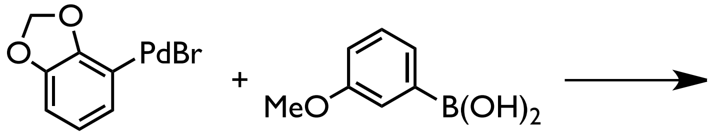
b) Briefly explain which of the above halobenzenes is the least reactive toward the oxidative addition of a metal such as Mg or Pd.

2) Show all products of the following transmetallation reactions. The electronegativity values for each element shown in the handout may be useful (think about the nature of the C-M bond in the product(s)).

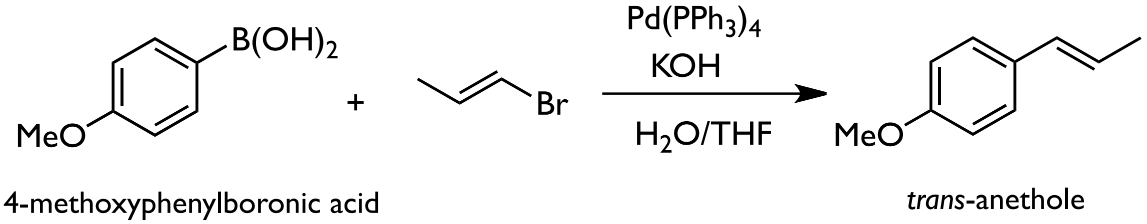
$2\,\mathrm{BuLi} + \mathrm{CuI} \longrightarrow$





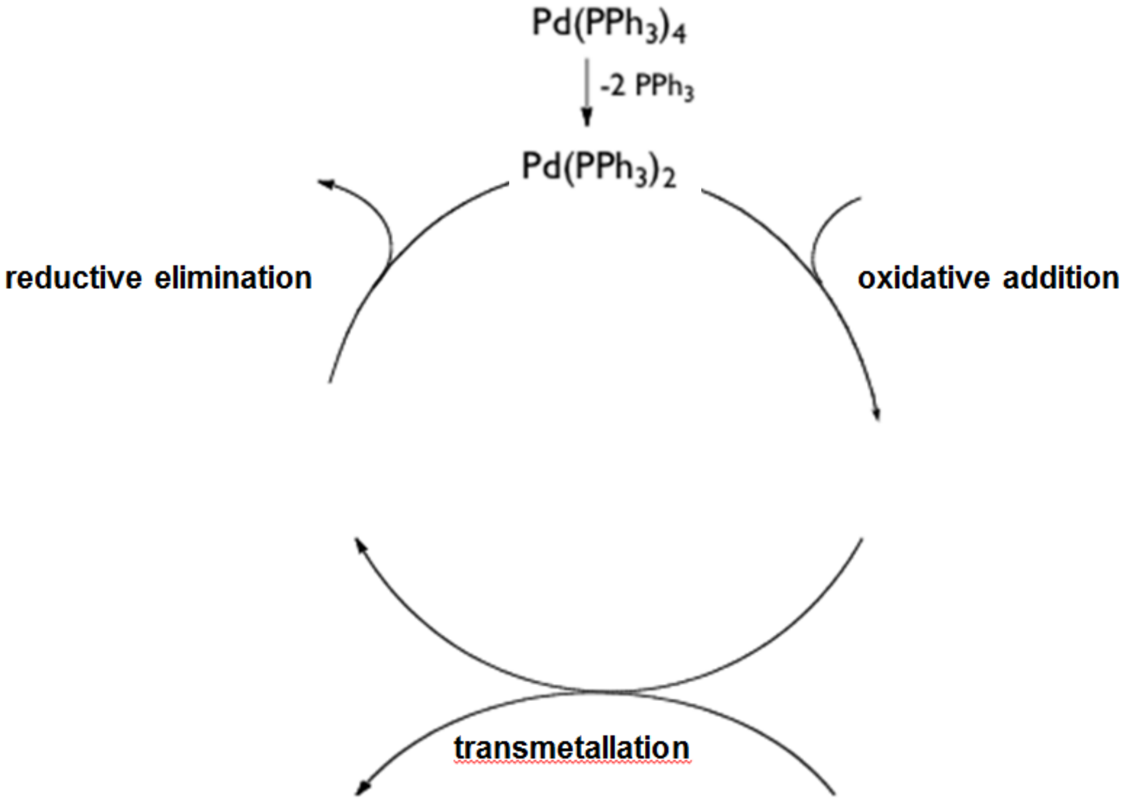


3) Suzuki-Miyaura coupling reactions typically occur between aryl or alkenyl halides and an arylboronic acid. An example of such a reaction is shown below for the synthesis of the food flavoring compound *trans*-anethole (*trans*-1-methoxy-4-(1-propenyl)benzene).

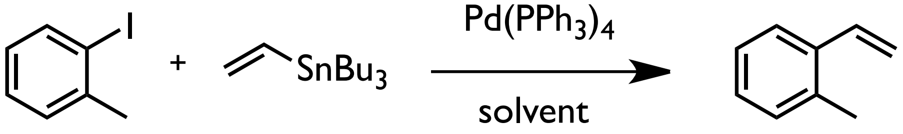


a) Propose a synthesis of 4-methoxyphenylboronic acid starting from phenol. Recall that trimethylborate, $B(OMe)_3$, reacts as an electrophile toward Grignard reagents. Show all isolated intermediates/products formed. You do not need to give a mechanism for the individual steps.

b) Complete the catalytic cycle for the Suzuki-Miyaura coupling reaction shown above, 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.



4) Draw the balanced reaction for the formation of isopropylmagnesium bromide in diethyl ether and show the charge distribution along the carbon-metal bond. Explain why diethyl ether is a common solvent for the generation of Grignard reagents.

5) Draw the electron-pushing mechanism and show the product(s) of the following reactions (assume 1:1 stoichiometry, appropriate solvents, and aq. HCl workup of the reaction mixture).

i) *trans*-4-tert-butyl-cyclohexanol + isopropylmagnesium bromide

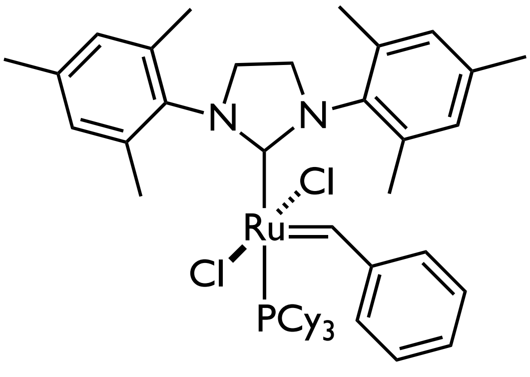
iii) 1-propyne + n-butyllithium

iii) acetone + phenylmagnesium bromide

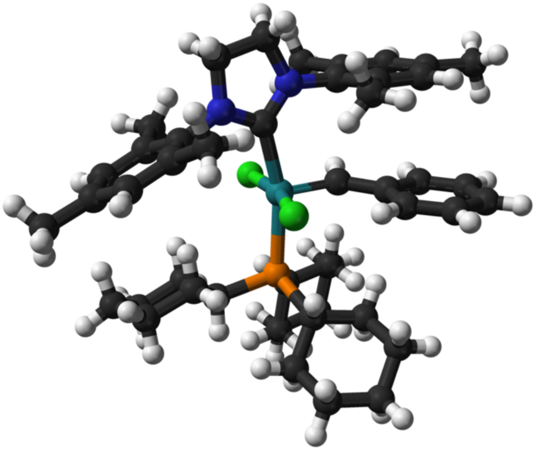
iv) diisopropylamine + n-butyllithium

v) ethyl acetate + phenylmagnesium bromide

6) Ruthenium- and molybdenum-based complexes are used as catalysts for alkene metathesis reactions. One such Ru-based complex, the Grubbs 2^{nd} generation catalyst, is shown below. The complex features both a N-heterocyclic carbene ligand and a tertiary phosphine ligand (Cy = cyclohexane).



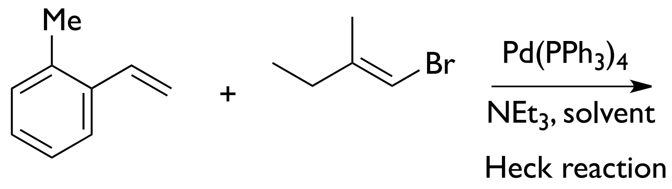
Grubbs 2nd generation catalyst



Ruthenium metal by itself 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.

7) Draw the products of the following organometallic reactions.

a)



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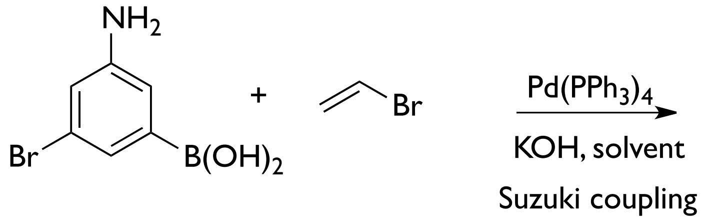

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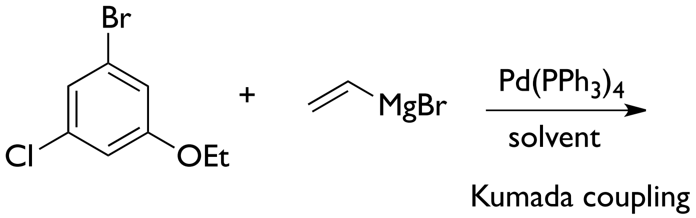

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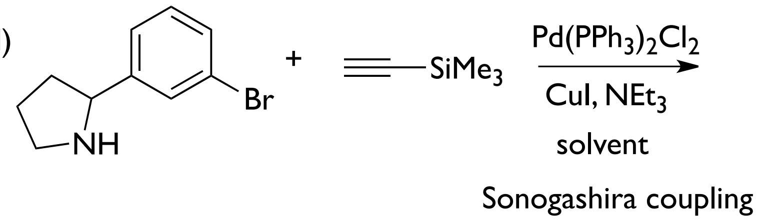
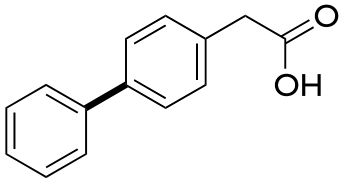


8) Each of the following compounds can be synthesized by either a Grignard reaction or by a Pd-catalyzed coupling reaction. The bond generated by the organometallic reaction is in **bold**. Draw starting materials that could be used for each target compound and name each reaction used to form each **bold** bond.

a)



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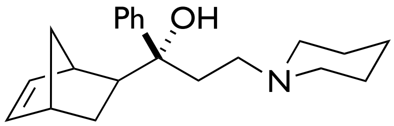
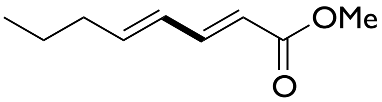


c)



d)