

**Chemistry 4000/5000**  
**Midterm Examination #2 (November 3, 2021)**

1. For each pair of complexes given below, predict which one will be more reactive towards oxidative addition of  $H_2$ . Give your reasoning in **two sentences or less**. (10 points)

a)  $[RhCl(CO)(P(C_6F_5)_3)_2]$  or  $[RhCl(CO)(PMe_3)_2]$  → both complexes are  $d^8$   $RhCl$  and square planar. Therefore the difference in reactivity is due to  $PMe_3$  ( $e^-$  donating) vs.  $P(C_6F_5)_3$  ( $e^-$  withdrawing). Thus  $[RhCl(CO)(PMe_3)_2]$  is more  $e^-$  rich and capable of oxidatively adding  $H_2$ .

Also:  $P(C_6F_5)_3$  is larger than  $PMe_3$ , making  $Rh$  less accessible sterically.

b)  $[Cp_2YBr]$  or  $[MoH(OMe)(PMe_3)_4]$ ; (Mes = mesityl = 2,4,6-trimethylphenyl)

→  $Y(III) d^0$ . No oxidative addition because the metal is electron deficient and cannot access an oxidation state two units higher. Sterics therefore are irrelevant in this case.  $[Mo(IV)(OMe)(PMe_3)_4]$  can oxidatively add  $H_2$ , as  $Mo(IV)$  is a reasonable oxidation state and the metal centre is not too sterically saturated.

2. Which complex in each of the following pairs of molecules would you expect to be more stable? Explain in **two sentences or less**. (10 points)

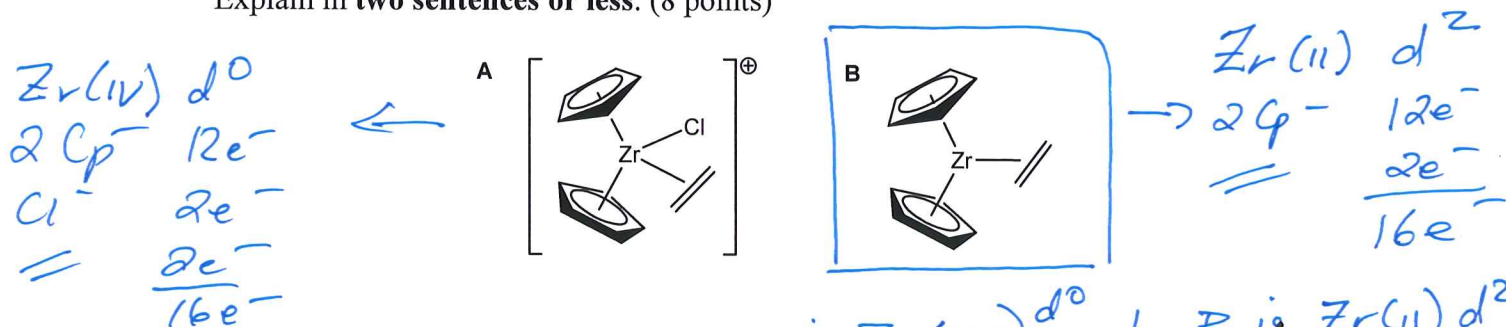
a)  $[YMe_3(THF)_2]$  vs  $[Y(CH_2Ph)_3(THF)_2]$  → both compounds are  $Y(III) d^0, 10e^-$ .  
→ Also possibility for interaction with Ph groups exist (e.g.  $\pi$   $CH_2Ph$ ). ∴ additional steric and electronic stabilization. →  $[Y(CH_2Ph)_3(THF)_2]$  is more sterically bulky ∴ more stable.

b)  $[Pt(H_2C=CH_2)_3]$  vs  $[TiCl_4(H_2C=CH_2)_2]$

→  $Pt(0) d^{10}, 16e^-$  → low oxidation state,  $e^-$  rich, lots of  $\pi$ -backbonding.

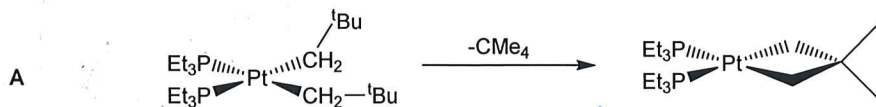
→  $Ti(IV) d^0, 12e^-$ . → No  $e^-$  available for crucial  $\pi$ -backdonation to  $\pi^* CH_2CH_2$  orbital. ∴  $[Pt(H_2C=CH_2)_3]$  is expected to be more stable.

3. Which of the following two zirconium complexes would have a longer alkene C=C bond? Explain in **two sentences or less**. (8 points)

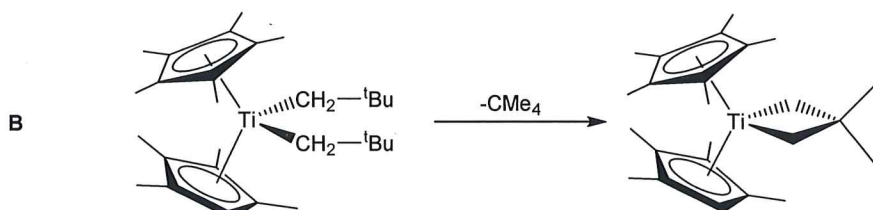
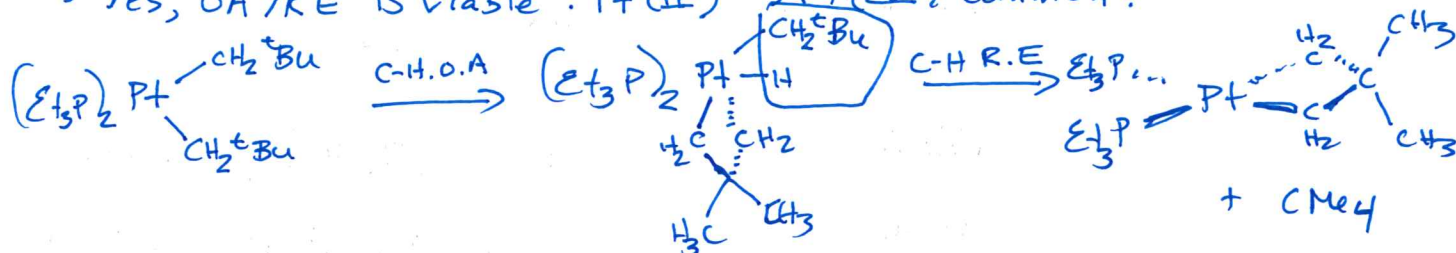


Both compounds are  $16e^-$ , but A is  $Zr(IV) d^0$  and B is  $Zr(II) d^2$ . Hence no backbonding in A, while there is in B. Correspondingly, that  $\pi$ -backbonding would populate an orbital that is antibonding with respect to  $C=C$ , rendering the  $C=C$  length longer (less double bond character) than that in A.

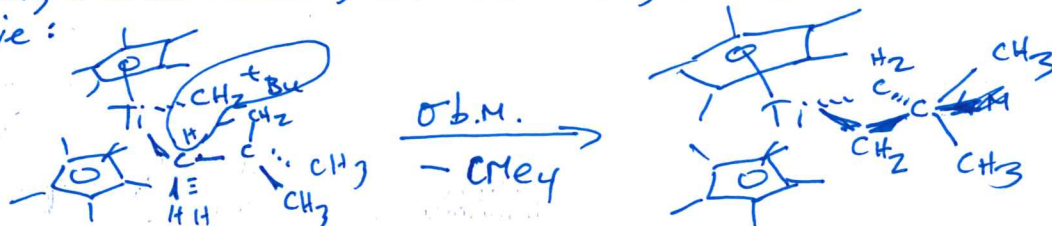
4. For the following two examples of intramolecular C-H bond activation (A and B), briefly explain why or why not oxidative addition followed by reductive elimination is a viable reaction pathway or whether some other mechanism must be operative. (14 points)



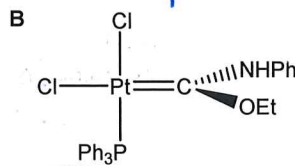
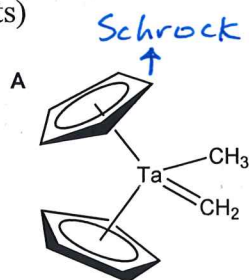
→ Yes, OA/RE is viable. Pt(II) → Pt(IV) common.



→ No, OA/RE is not viable. Ti is  $d^0$  so no available  $e^-$  density for populating C-H antibonding orbitals. Hence, a  $\sigma$ -bond metathesis process is operative:



5. Explain whether the following complexes should be considered Fischer or Schrock carbene complexes. (12 points)



all suggest Schrock carbene

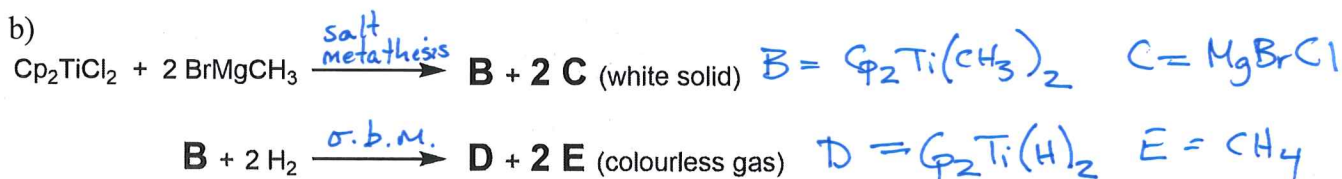
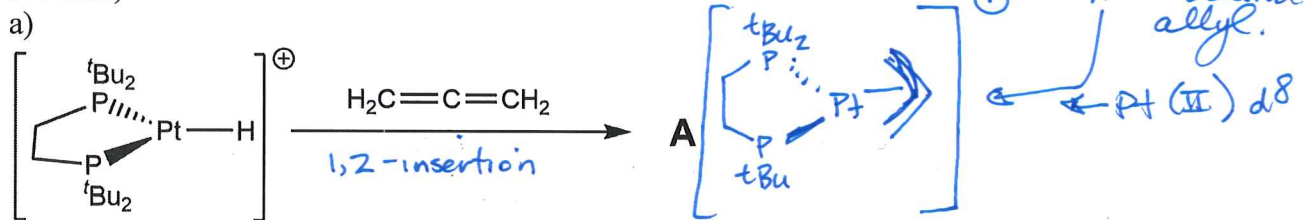
- H on carbon
- early TM,  $d^0$
- high oxidation state (Ta(V))
- Cp and  $CH_3$  co-ligands

Fischer

- $\pi$  donating groups on carbon.
- late TM, Pt(II)
- $PPh_3$  ( $\pi$  acceptor) co-ligand.

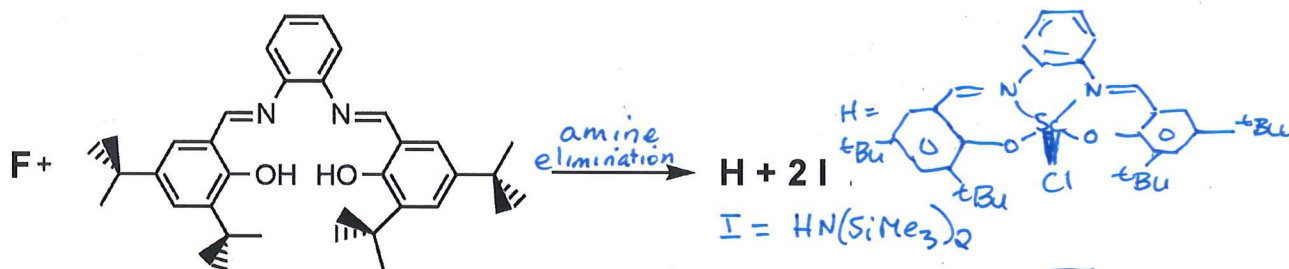
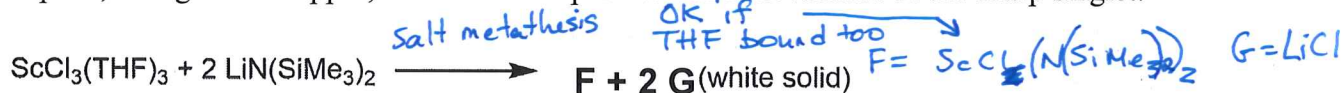
→ suggest Fischer carbene.

6. For each reaction below, provide the correct products (both inorganic and organic). None of the reactants or products are present in excess of the amount shown in the equations. No explanation is required. (20 points for undergraduate students, 22 points for graduate students)



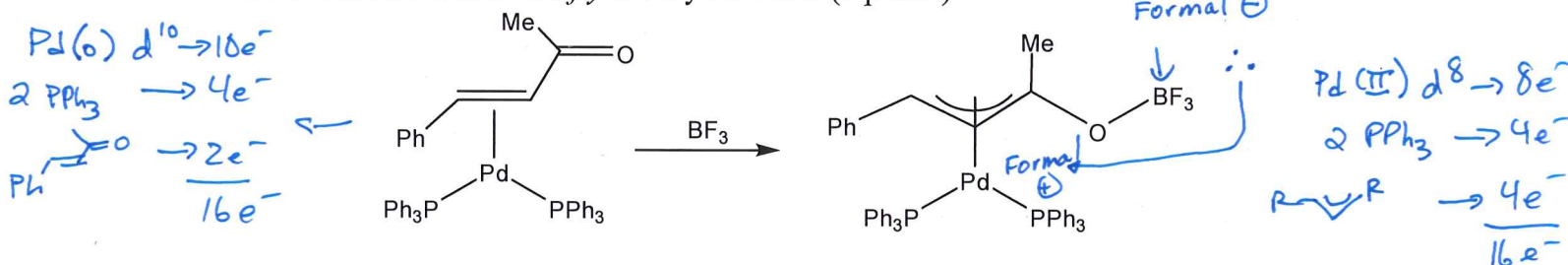
c) **Graduate Students Only** (bonus for undergraduate students)

**Hint:** The IR spectrum of compound I, which is an organic compound, exhibits a broad signal at  $3215 \text{ cm}^{-1}$ . The  $^1\text{H}$  NMR spectrum (in  $\text{CDCl}_3$  solvent) of I contains one sharp peak, a singlet at 0.1 ppm, and one broad peak which is downfield of the sharp singlet.



7. **Undergraduate Students Only**

For the following reaction, indicate whether the metal is oxidized, reduced or retains the same oxidation state. Briefly show your work. (8 points)

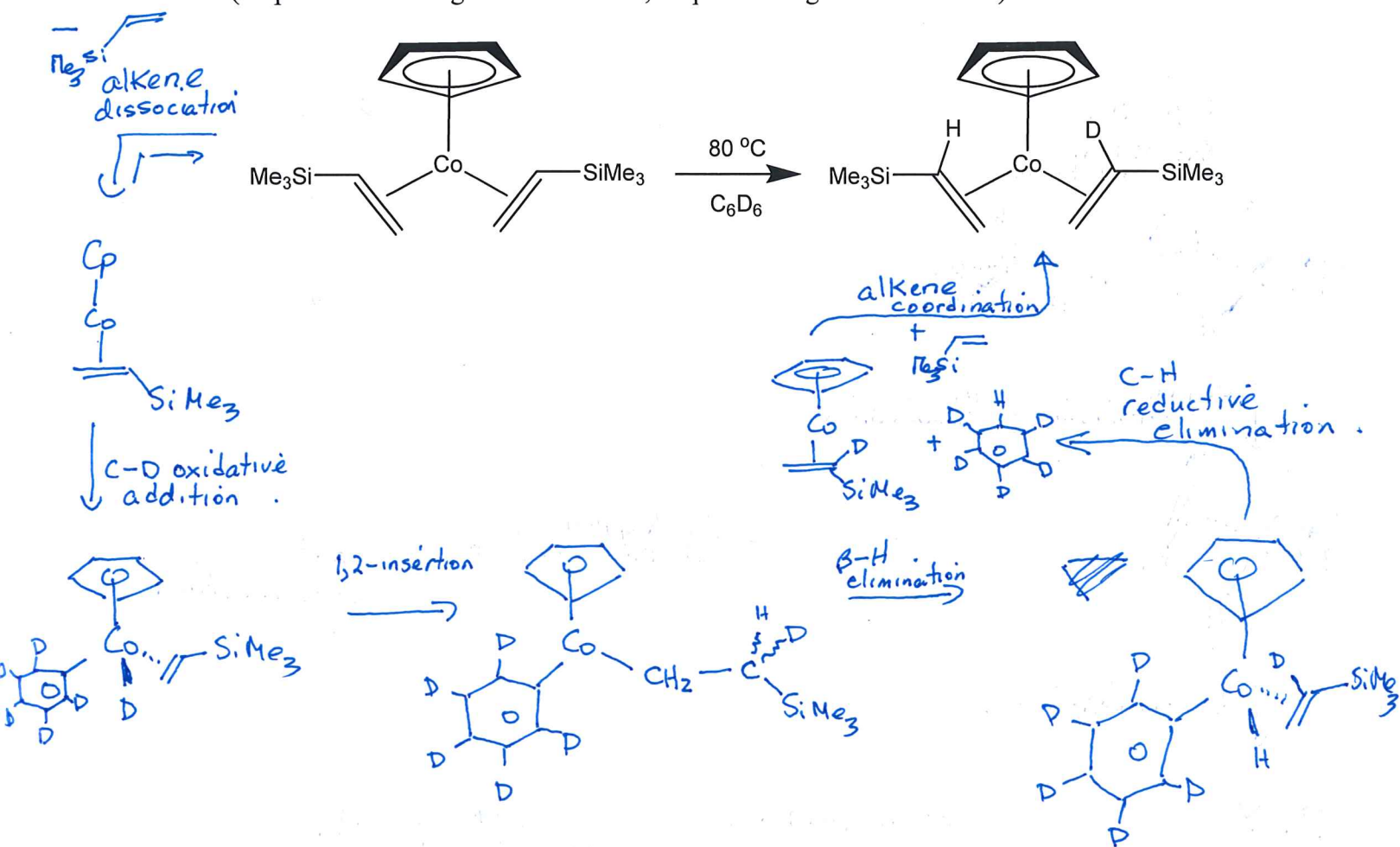


$\rightarrow \text{Pd is oxidized from Pd(0) to Pd(II)}$

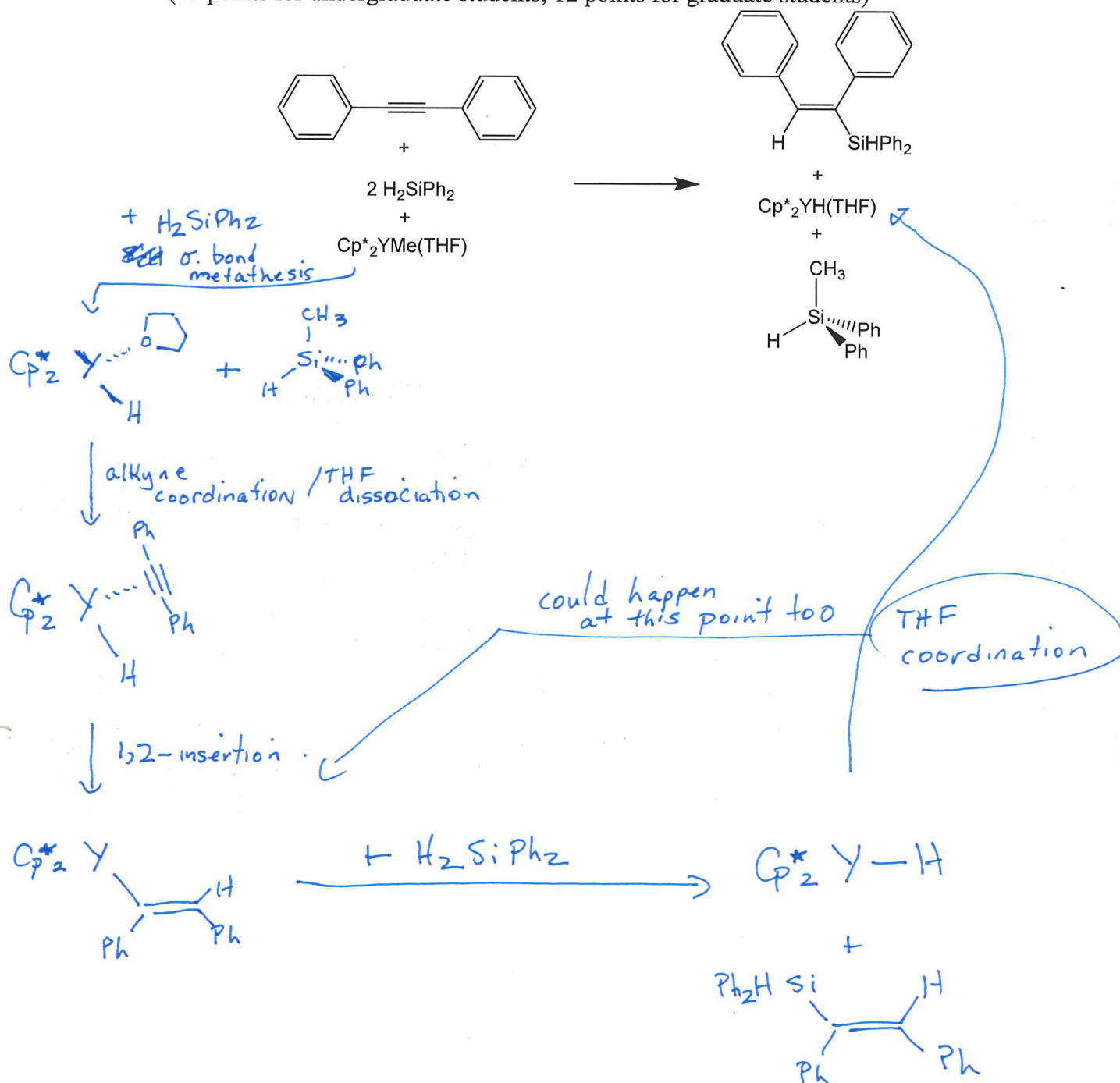
**Undergraduate Students: Answer ONE of the following TWO questions (8 and 9).**

**Graduate Students: Answer BOTH of the following two questions (8 and 9).**

8. Provide a mechanism (based on the fundamental reactions that you have learned) to explain the following. Note that it is not necessary to indicate electron movement, but the structure of every intermediate is required. Indicate in words (5 or less/step) what kind of fundamental organometallic reaction(s) are taking place in each step of the mechanism. (18 points for undergraduate students; 12 points for graduate students)



9. Provide a mechanism (based on the fundamental reactions that you have learned) to explain the following. Note that it is not necessary to indicate electron movement, but the structure of every intermediate is required. Indicate in words (5 or less/step) what kind of fundamental organometallic reaction(s) are taking place in each step of the mechanism. (18 points for undergraduate students; 12 points for graduate students)



**BONUS:**

The periodic table provided on the last page of this exam paper has 5 missing elements. Add in the symbol and name of the missing elements. (5 points)