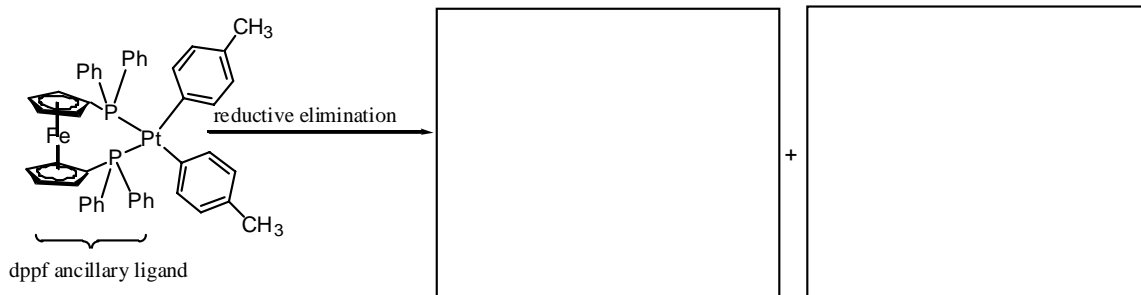
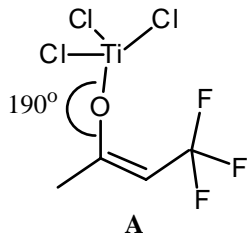


9. A recent report analyzed the reductive elimination of the complex shown below.

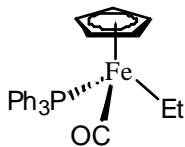


- Draw the two products of the reductive elimination in the boxes to the right.
- What's the oxidation state of the Pt before the elimination? _____
- What's the oxidation state of the Pt after the elimination? _____
- The authors surveyed a variety of ancillary ligands before settling on the dppf ligand. Suggest one reason the dppf ligand might promote reductive elimination.
- The authors report that the reaction was first order. Write a reasonable rate equation for the reaction based on this information.
- The authors added excess PPh_3 , but saw no change in the rate of the reaction. Why did the authors do this?

10. The Ti-enolate complex **A** has a Ti-O-C bond that is almost linear (170°). Suggest a reason for the linear nature of the Ti-O-C bond.



11. In class we talked about the classic experiments of Calderazzo with $\text{MeMn}(\text{CO})_5$ in which the mechanism of 1,1-insertion was studied. Another approach that could be used is to start with a metal complex that is chiral at the metal and perform the insertion reaction. Using the complex shown below, describe an experiment and predict the products in the event of alkyl migration versus CO insertion. What is the stereochemical relationship of the two products?



12. "Inorganic Grignard reagents" like $\text{Fe}(\text{MgBr})_2$ have recently been found to undergo oxidative addition to aryl chlorides. The formal oxidation state of iron in these complexes is -2.

a) Why would this oxidation state of iron be expected to rapidly undergo oxidative addition?

b) Another iron complex, $\text{Na}_2\text{Fe}(\text{CO})_4$, with a -2 formal oxidation state did not react with aryl chlorides. Suggest a reason for the inability of $\text{Na}_2\text{Fe}(\text{CO})_4$ to undergo similar oxidative additions.

13. Schwartz's reagent, $\text{Cp}_2\text{ZrH}(\text{Cl})$, has found considerable use in synthetic chemistry, primarily due to several unique and useful properties of the zirconium reagent and organometallic complexes that it forms.

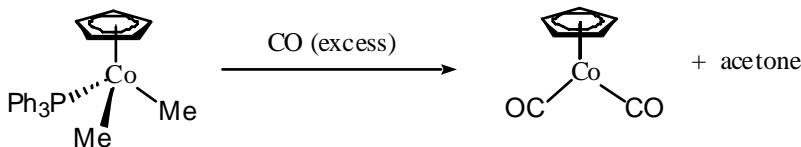
a) One of the useful reactions of Schwartz's reagent is 1,2-insertion across alkenes. Show the 1,2-insertion product of Schwartz's reagent with 1-pentene.



b) One characteristic of alkyl-zirconium complexes, such as the product in part a, is their unusual stability. Why do you think alkyl-zirconium complexes are more stable than other alkyl-metal complexes?

c) The alkyl-zirconium complexes can undergo a range of oxidation reactions, e.g. reaction with I_2 . Many alkyl-metal oxidation reactions occur via oxidative addition to the metal. Is this the likely path for the alkyl-zirconium oxidation reactions or is another mechanism likely? Explain.

14. Identify the most plausible mechanism (a, b, c or d) for the following reaction and explain your reasoning.



- a) (1) loss of phosphine; (2) addition of CO; (3) insertion of CO; (4) addition of excess CO with reductive elimination of acetone.
- b) (1) addition of CO; (2) loss of phosphine; (3) insertion of CO; (4) addition of CO with reductive elimination of acetone.
- c) (1) addition of CO; (2) insertion of CO; (3) reductive elimination of acetone; (4) addition of CO; (5) loss of phosphine.
- d) (1) loss of phosphine; (2) addition of CO; (3) addition of CO; (4) reductive elimination of acetone; (5) addition of CO.