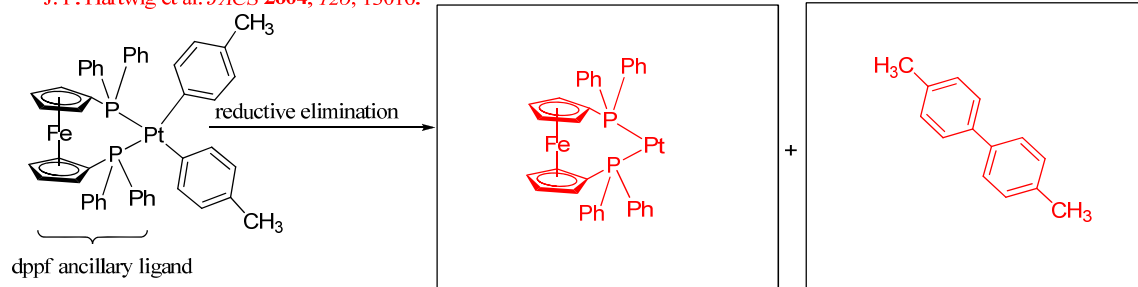


Answers to the portion of the exam given by Prof. Malachowski

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

J. F. Hartwig et al. *JACS* **2004**, *126*, 13016.



a) Draw the two products of the reductive elimination in the boxes to the right.

b) What's the oxidation state of the Pt before the elimination? +2

c) What's the oxidation state of the Pt after the elimination? 0

d) 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 dppf ligand is a bidentate ligand that forces the aryl groups into a cis position, which is necessary for a 3-center concerted reductive elimination to occur.

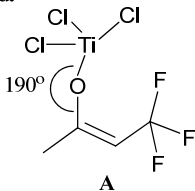
e) The authors report that the reaction was first order. Write a reasonable rate equation for the reaction based on this information.

$$\text{rate} = k[(\text{dppf})\text{Pt}(\text{Ar})_2]$$

f) The authors added excess PPh_3 , but saw no change in the rate of the reaction. Why did the authors do this?

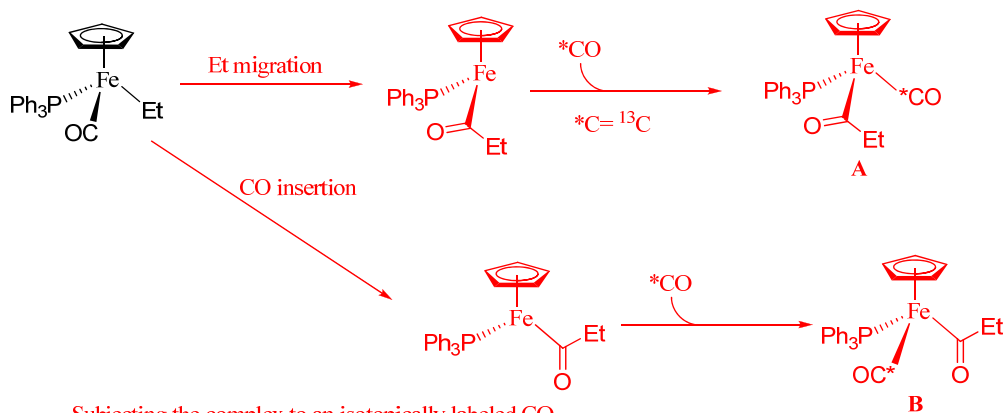
It's possible that the reductive elimination might occur after another ligand, such as PPh_3 , adds to the complex. An additional ligand on the Pt complex would make an 18 e- complex which would be more prone to reductive elimination.

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.



The Ti-O-C bond has multiple bond nature due to electron density being donated from the lone pairs of oxygen to the electron deficient Ti(IV). Therefore, in addition to the sigma bond between oxygen and Ti, the oxygen is acting as a π base, donating electron density to an empty d-orbital of Ti(IV). This second bond causes the Ti-O-C bond angle to be nearly linear. (see K. Mikami et al. *JACS* **2004**, *126*, 13174)

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?



Subjecting the complex to an isotopically labeled CO environment would predict **A** as the product of alkyl migration. Whereas CO insertion would result in **B**. **A** and **B** are enantiomers.

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?

Oxidative addition requires the donation of electron density from a metal to cleave a covalent bond. Metals with more electron density should be able to undergo this process more readily. Iron with a -2 formal oxidation state are very electron rich.

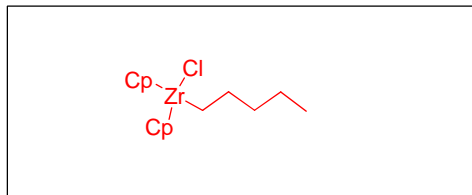
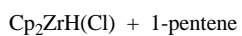
b) Another iron complex, $\text{Na}_2\text{Fe}(\text{CO})_4$, with a -2 formal oxidation state did not react with aryl chlorides. Suggest a reason for the inability of $\text{Na}_2\text{Fe}(\text{CO})_4$ to undergo similar oxidative additions.

$\text{Na}_2\text{Fe}(\text{CO})_4$, although formally placing a -2 charge on the metal, has strongly electron withdrawing CO ligands. The CO ligands are strong π acceptors and therefore would be involved in considerable backbonding with the electron rich Fe. Since the CO ligands are withdrawing electron density from the Fe, the metal would be less electron rich and therefore less capable of oxidative addition reactions.

ref.: A. Furstner et al. *Angew. Chem. Int. Ed.* **2002**, *41*, 609. and *JACS* **2002**, *124*, 13856.

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?

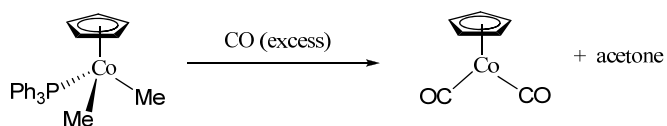
Since alkyl-zirconium complexes, such as shown in part a, are with Zr(IV), they have no d orbital electrons. Without any d orbital electrons, the metal can not add electron density to the β C-H σ^* orbital, which is the first step in β -elimination or 1,2-deinsertion reactions.

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.

Since the Zr of alkyl-zirconium complexes is at the +4 oxidation state, it can not be oxidized any more, therefore the oxidation of alkyl-zirconium complexes probably goes by another mechanism.

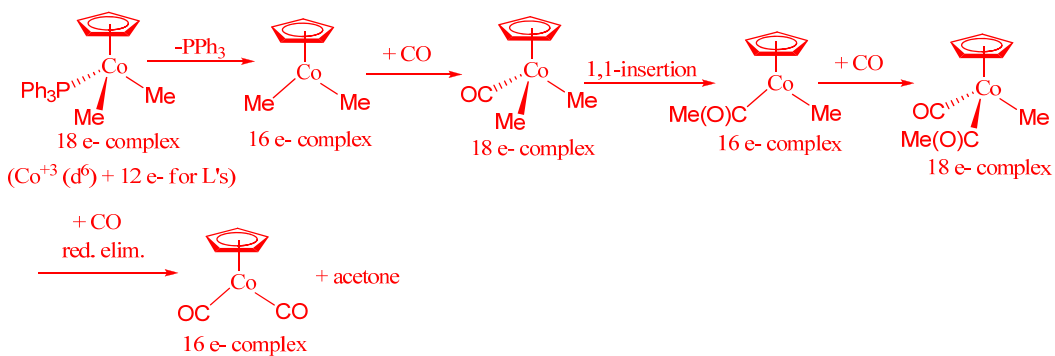
ref. J. Schwartz et al. *JACS* **1975**, 97, 3851.

14. Identify the most plausible mechanism for the following reaction and explain your reasoning.

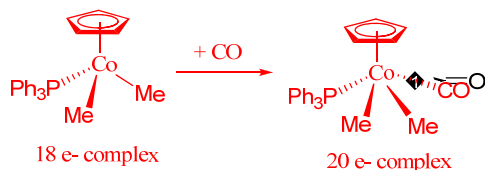


- a) (1) loss of phosphine; (2) addition of CO; (3) insertion of CO; (4) addition of excess CO with reductive elimination of acetone.
 b) (1) addition of CO; (2) loss of phosphine; (3) insertion of CO; (4) addition of CO with reductive elimination of acetone.
 c) (1) addition of CO; (2) insertion of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

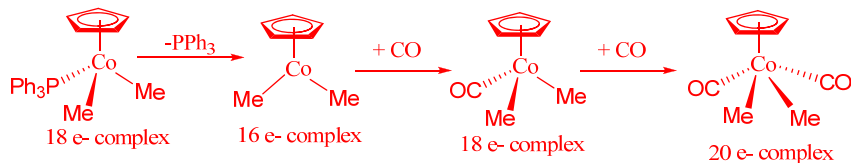
a) is the most likely mechanism:



b) and c) are less likely due to formation of a 20 e⁻ complex in the first step.



d) would also involve a 20 e⁻ complex in the third step.



ref. R. G. Bergman *Acct. Chem. Res.* **1980**, *13*, 113.