

1. Complete the periodic table below: (10 pts.)

Group 3	4	5	6	7	8	9	10	11
Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu
Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag
La	Hf	Ta	W	Re	Os	Ir	Pt	Au

2. Predict the order of reactivity of MeTiCl_3 with the following ligands: NMe_3 , PMe_3 , CO . Briefly explain your reasoning. (10 pts.)

Order of reactivity: $\text{NMe}_3 > \text{PMe}_3 > \text{CO}$.

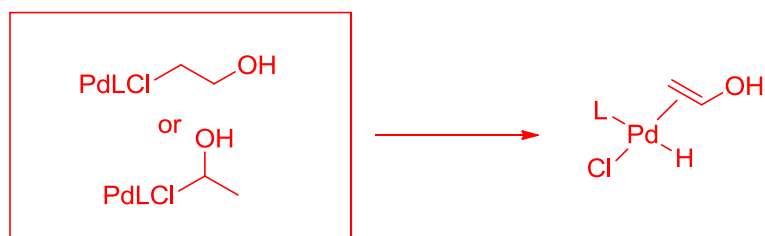
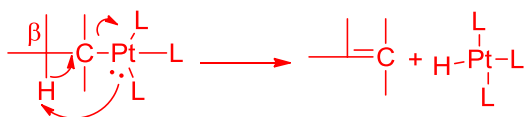
MeTiCl_3 is a Ti(IV), therefore a hard acid. NMe_3 is the hardest base while CO is the weakest or softest base.

(Crabtree, Ch. 1, question 5)

3. In class we described two important reactions that metal-alkyls can undergo. List these two reactions and give an example, generic or specific. (15 pts.)

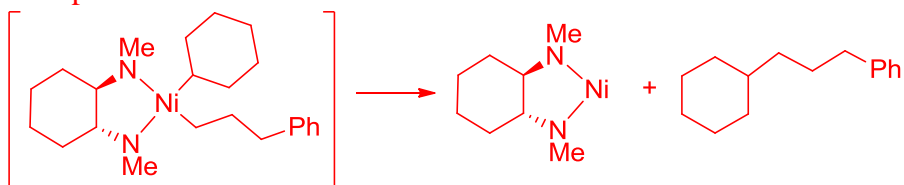
1. Beta-elimination (de-insertion)

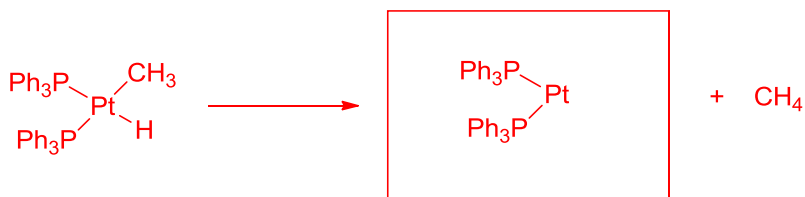
examples:



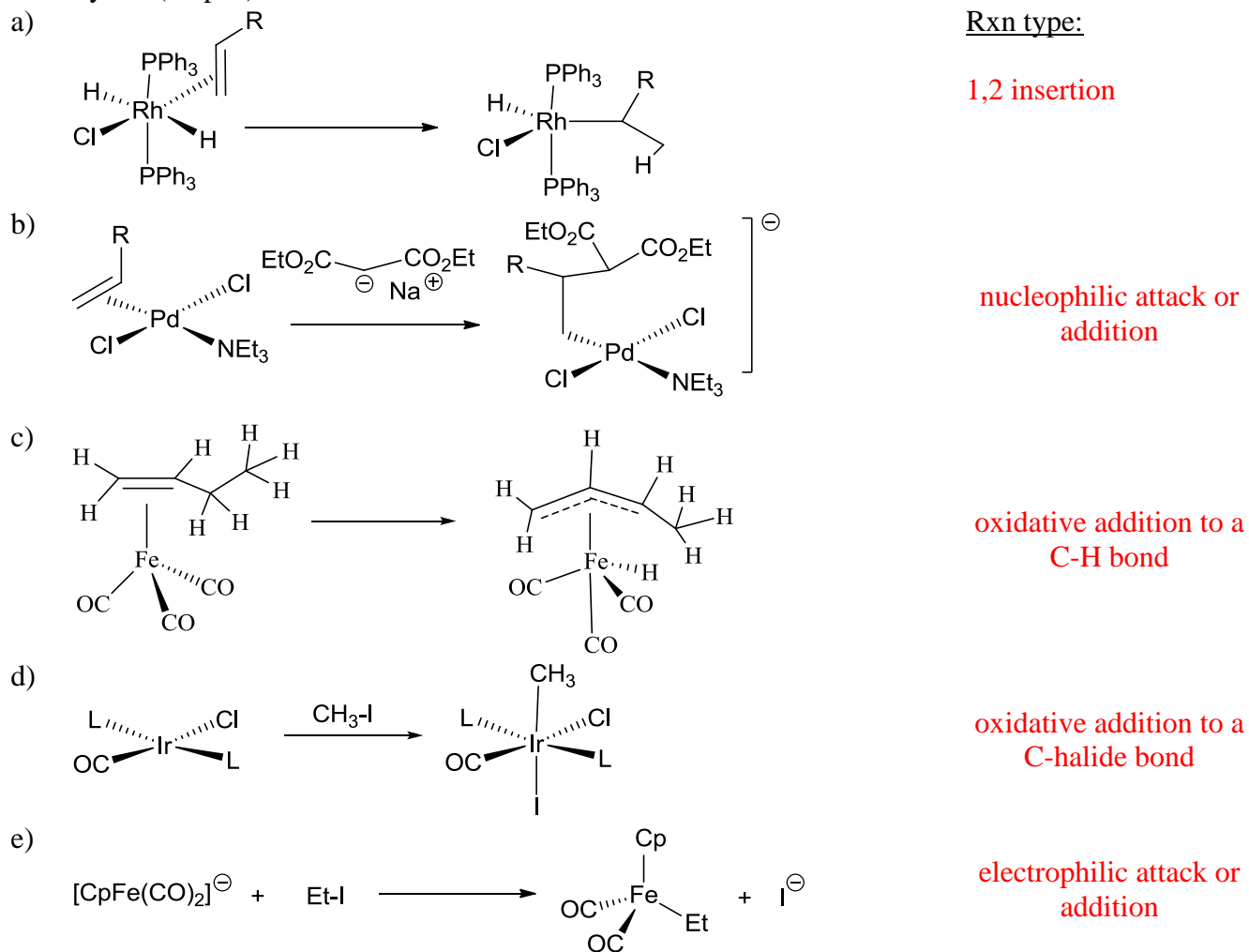
2. Reductive elimination

examples:





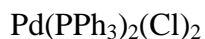
4. Identify the following reactions by the type of process occurring. *CHE-334* identify 4 of 5; *CHE-534* identify all. (15 pts.)



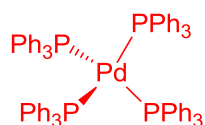
Questions 5 and 6: *CHE-334* answer one of two. *CHE-534* answer one completely and one part of the other question. (15 pts.)

5. Answer the following questions about two common forms of palladium.

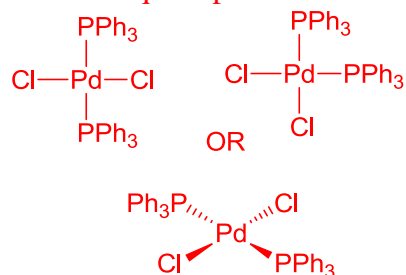
a) Predict the molecular geometry of the palladium complexes shown below. Draw their pseudo-three dimensional structures in the space below and label the geometry.



tetrahedral geometry

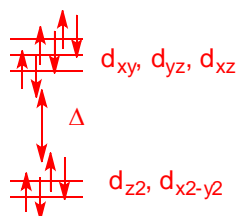


square planar



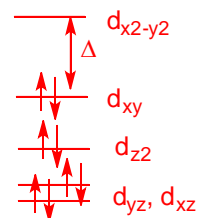
b) Draw the palladium d orbital electronic structure for both metal complexes. Place the correct number of palladium electrons in the orbital diagrams.

Pd(PPh₃)₄



Tetrahedral

Pd(PPh₃)₂(Cl)₂



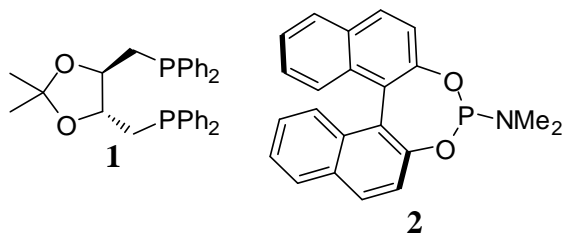
Square planar

c) Briefly explain why these two palladium transition metal complexes have different geometries.

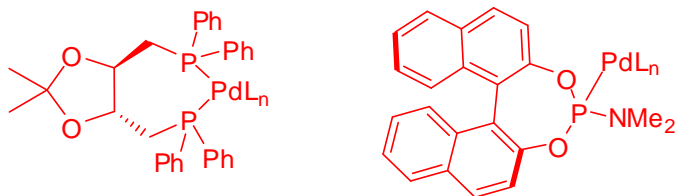
Pd(PPh₃)₄ is a d¹⁰ Pd(0) which prefers to have a tetrahedral geometry to limit, as best as possible, ligand electron-electron repulsion with the 10 d electrons of the Pd. The tetrahedral geometry has the smallest Δ (field) difference between the highest and lowest E orbitals, therefore with 10 electrons all orbitals are filled and the tetrahedral geometry offers the lowest E arrangement possible.

Pd(PPh₃)₂(Cl)₂ is a d⁸ Pd(II) which will prefer a square planar geometry since it has no d electrons in one d orbital. This one d orbital without electrons (conventionally designated the d_{x²-y²}) offers a path (along the x and y axes) which can be used by four ligands to approach the metal and avoid electron-electron repulsions.

6. In their effort to further optimize organometallic reactions and related catalytic processes, chemists have created many complex phosphorus ligands. Two examples are shown below. Compare and contrast these two ligands in the questions below.



a) Draw a hypothetical complex with each of these ligands and a palladium atom (PdL_n).



b) Compare and contrast the steric and electronic effects of both ligands in a complex with a palladium atom.

Pd-1 complex

- bidentate, therefore occupies two coordination sites
- cone angle medium, but should be sterically congested with four phenyl rings closely arranged around Pd
- relatively stronger σ donor: alkyl group on P is a strong σ donor, phenyl groups on P are medium σ donors
- weak π acceptor/acid: alkyl group on P makes a weak π acid, while phenyl groups are medium π acids

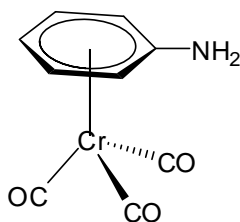
Pd-2 complex

- monodentate, therefore occupies only one coordination site
- cone angle medium
- relatively weaker σ donor: O-aryl (aryloxy) groups on P are weak σ donors, amino group on P is a good σ donor according to Tolman table on exam front page (Note: some studies indicate amino groups are weaker)
- strong π acceptor/acid: O-aryl groups on P makes a strong π acid, while amino group should be a weak π acid

c) Overall, which complex will occupy more space around the palladium metal? **(1)** or **2** (circle one)

Overall, which complex will have a more electron rich palladium metal? **(1)** or **2** (circle one)

7. Answer the questions about the metal-arene complex shown below. *CHE-334* answer 3 of 5 parts; *CHE-534* answer 4 of 5 parts. (15 pts.)



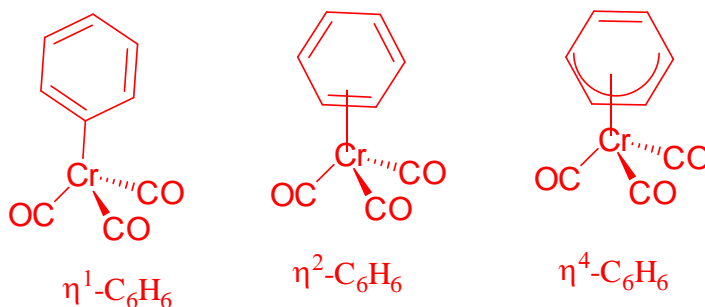
a) Provide the oxidation state of the metal, the d^n count, the total electron count and the coordination number (CN) for the complex.

Cr(0); d^6 ; 18 total e-'s; CN=6

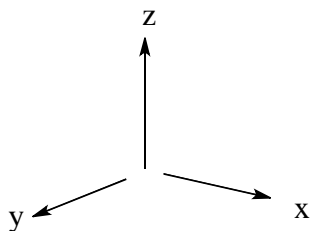
b) What is the likely hapticity of the benzene ring in binding to the Cr? Briefly explain your answer.

The benzene ring is likely to have a hapticity, η , of 6 because that provides the Cr with a total electron count of 18, which is a stable form of most transition metals.

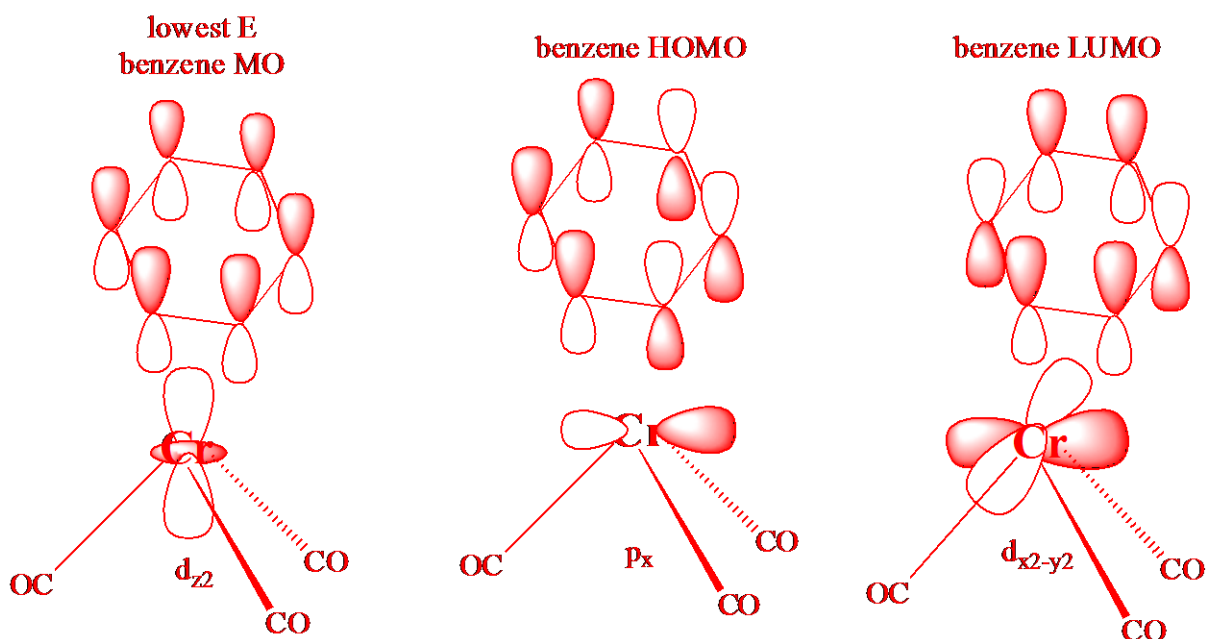
c) Show one example of a benzene interaction with the Cr that has a different hapticity.



d) Draw one example of a molecular orbital interaction between a Cr d orbital and a benzene MO.



Three possible answers:

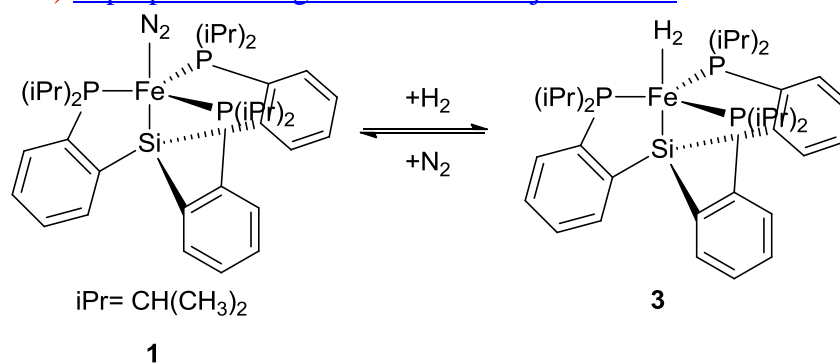


e) What effect do you think the $\text{Cr}(\text{CO})_3$ binding to the benzene ring will have on the amine group basicity?

Since the $\text{Cr}(\text{CO})_3$ complex will be electron withdrawing, it will likely remove electron density from the arene ring. With less electron density in the ring and due to resonance with the benzene ring, the amine nitrogen will have less electron density as well. The net effect of this withdrawn electron density is an amine that is less electron rich and therefore less capable of donating electron density and acting as a base.

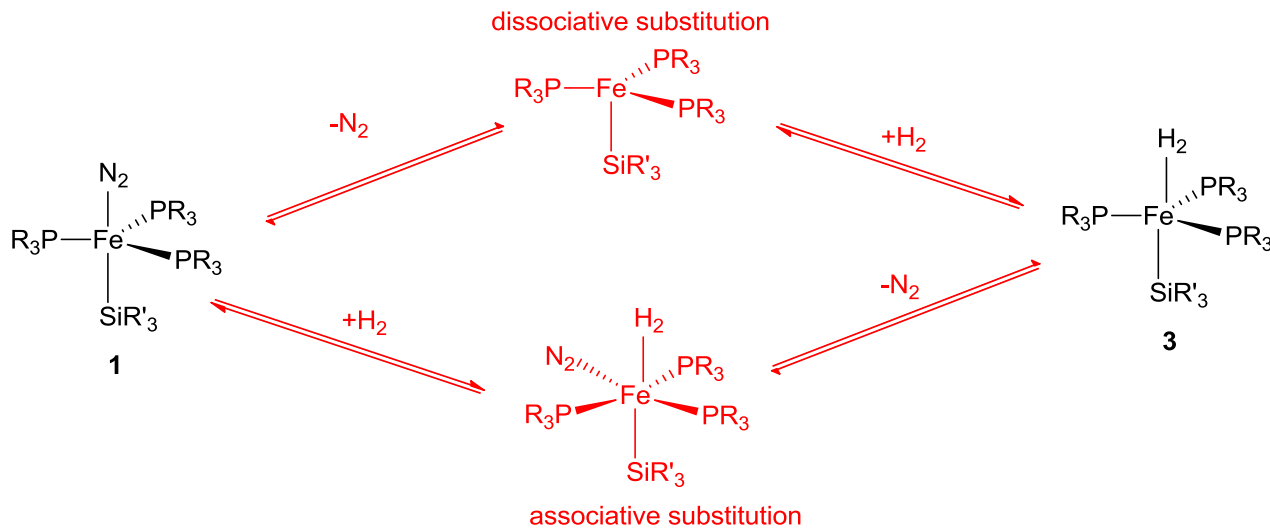
8. A recent article in the literature entitled “A Nonclassical Dihydrogen Adduct of $S = 1/2 \text{Fe}(\text{I})$ ” reported on the equilibrium shown below. (Hint: Si is located immediately below C on the periodic table.) CHE-334 answer 5 of 7 parts; CHE-534 answer 6 of 7 parts. (20 pts.)

Yunho Lee, R. Adam Kinney, Brian M. Hoffman, and Jonas C. Peters *J. Am. Chem. Soc.*, Article ASAP (Sept. 28, 2011) <http://pubs.acs.org/doi/abs/10.1021/ja207003m>



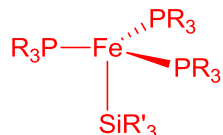
a) The equilibrium between **1** and **3** is a ligand substitution reaction. Show the possible paths, including intermediates, for this ligand substitution. Be sure to label each possible path by the type of

ligand substitution process. You may use the abbreviated forms of the complex shown below to limit your drawing.

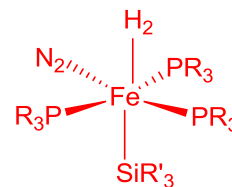


b) For all intermediates, determine the metal oxidation state, total electron count and coordination number.

dissociative substitution



Fe(I)
d⁷, so 15 e- complex
CN=4



associative substitution
Fe(I)
d⁷, so 19 e- complex
CN=6

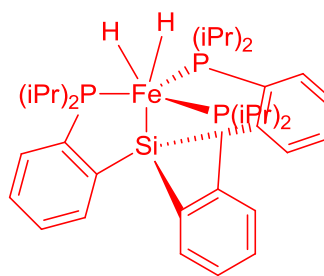
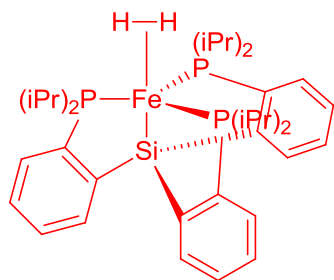
c) Which path do you think is more likely and why?

The dissociative substitution seems more likely since a 19 e- complex will be less stable as it exceeds the 18e-'s that most transition metals prefer. With a coordination number of 6 and a bulky tetradentate ligand, it would also have a steric barrier to the associative substitution.

d) The hydrogen complex **3** with the iron can exist in two possible forms. Draw both possible forms and label them as described in class.

non-classical sigma hydrogen complex

classical dihydride complex



e) Which factors will determine whether one complex occurs over the other?

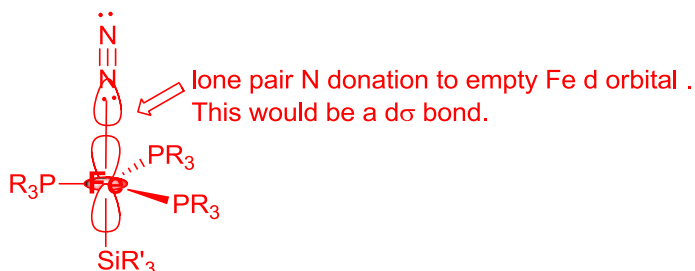
π basic (late) transition metals with lower coordination number will favor the classical dihydride complex.

Metals without d electrons (early transition metals) and with little space for multiple ligands (high coordination number) will be more inclined to exist as the non-classical sigma hydrogen complex.

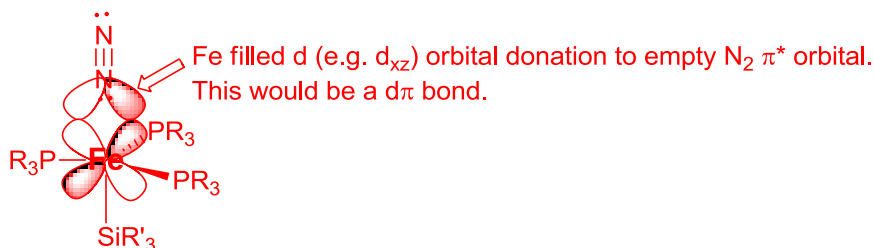
f) The nitrogen (N_2) ligand usually binds like a carbon monoxide (CO) ligand. Show how this would look in the space below. Highlight the interactions with Fe that would be expected with N_2 if it were acting just like a CO ligand. Again, you can use the abbreviated drawing of the complex to save time.

Two possible interactions:

(1) d_σ between N_2 lone pair and empty Fe d orbital (such as d_{z^2})



(2) d_π between filled Fe d orbital (such as d_{xz}) and $N_2 \pi^*$ antibonding orbital.



g) Compare the N_2 ligand bonds with the same CO bonds. Would you expect them to be stronger or weaker? Briefly explain.

Nitrogen is more electronegative than carbon and therefore the lone pair of nitrogen would be less basic, so the N_2 would be a weaker σ donor to the Fe. Likewise the N_2 π^* antibonding orbital would be lower in energy and smaller in size due to the greater electronegativity of the N versus C. These factors would make the backbonding a weaker interaction for the N_2 than the CO. For both these reasons, metal- N_2 bonding is typically very weak.