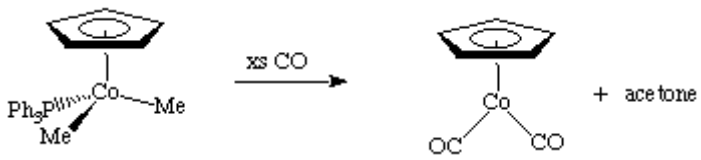
Problem set (exercise) 1

1. Which of the following mechanisms is **most** plausible for the following reaction? Why



a) loss of phosphine, b) addition of CO, c) insertion of CO, d) addition of excess CO with reductive elimination of acetone.

a) addition of CO, b) loss of phosphine, c) insertion of CO, d) addition of CO with reductive elimination of acetone.

a) addition of CO, b) insertion of CO, c) reductive elimination of acetone, d) addition of CO, e) loss of phosphine.

a) loss of phosphine, b) addition of CO, c) addition of CO, d) reductive elimination of acetone, d) addition of CO.

Number a. Reason: 6 coordinate – Cp counts as 3 dentate. Saturated. So addition of CO is not likely first step. For the same reason the c step is not CO addition.

2. Which **one** of the following can **NOT** undergo oxidative addition of MeI? Why

$Ir(PPh_3)_2(CO)Cl$ $[RhI_2(CO)_2]^-$ $Cp^*_2Zr(Me)Cl$ $Na_2[Fe(CO)_4]$

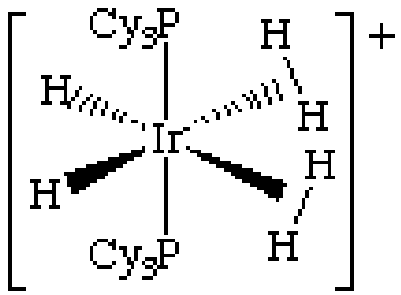
The Zr complex because it is Zr(4+), no d electron so cannot be oxidized.

3. Which of the following will be **more** reactive towards oxidative addition of dihydrogen? Why?

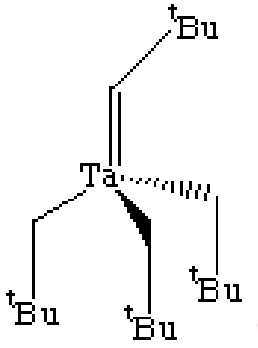
$Rh(PPh_3)_3Cl$ $Rh(PPh_3)_2(CO)Cl$

$Rh(PPh_3)_3Cl$; because PPh3 is more electron rich than CO, so Rh is more electron rich in the first complex. Better for oxidative addition.

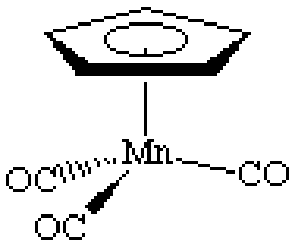
4. Name the oxidation states, d electron count, and valence electrons of the following complexes.



Ir (3+), d6, 18



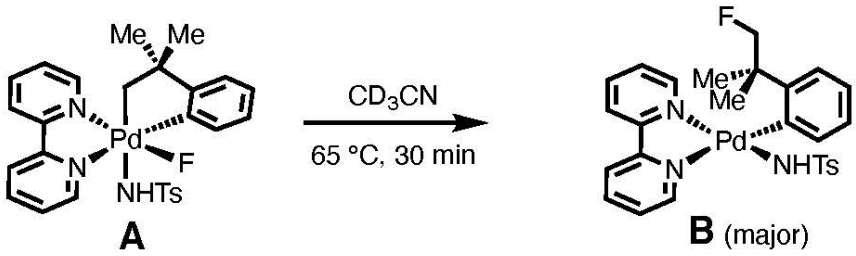
Ta (5+), d0, 10



Mn(+), d6, 18

5.

Cyclometallated palladium species **A** rapidly undergoes reductive elimination to give **B**.



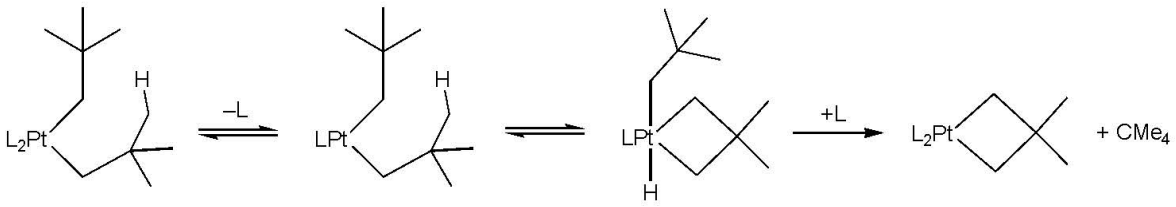
A. For both complexes, **provide the (a) coordination number, (b) d-electron count, (c) geometry, (d) metal oxidation state, and (e) total electron count.**

A: 6, d6, octahedral, Pd(4+), 18.

B: 4, d8, square planar, Pd(2+), 16.

6. Metal alkoxides, like metal alkyls, can also β-eliminate. With this in mind:
(a) explain why –O$_t$Bu is a common ligand in metal alkoxide chemistry.
No β-hydrogens.
(b) what are the products of decomposition of primary and secondary alkoxide ligands?
Aldehydes and ketones.
(c) why are alcohols, in the presence of a base, used as reducing agents in combination with metal complexes?
The base converts the alcohol to an alkoxide, which after coordinating can β-eliminate an aldehyde (or ketone) to give M-H. M-H is a reducing reagent.

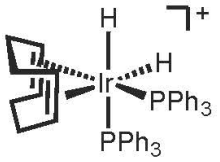
7. In the following reaction scheme, name the reaction(s) occurring at each step.



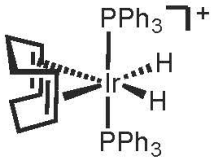
Ligand dissociation; oxidative addition; reductive elimination.

8.

Complex **A** underdoes 1,2-migratory insertion with a rate that is ~40x faster than that of complex **B.** **explain this observation.**



A



B

In A, H is three times cis to olefins; in B, H is two times cis to olefins. Migratory insertion is best for cis.