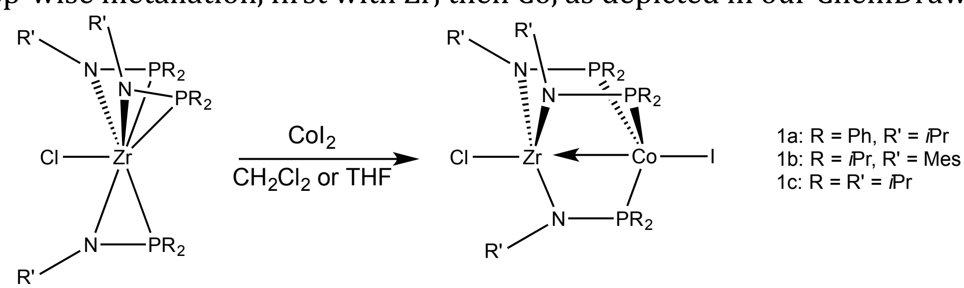
Reactivity and Bonding of Complexes with Metal-Metal Bonds

Goals:

- Determine electron counts and oxidation states of complexes with M-M bonds using CBC method of electron counting
- Draw molecular orbital diagrams for M-M bonds
- Determine M-M bond order
- Propose mechanisms for reactions at M-M centers
- Apply fundamental inorganic chemistry to reports in the literature

Much of the original work in synthesizing and characterizing metal-metal bonding was guided by an interest in understanding and quantifying the nature of chemical bonding. More recently, complexes containing metal-metal multiple bonds have also been found to harness unique reactivity.

1. Christine Thomas and coworkers synthesized a series of complexes with metal-metal bonds between a early and late transition metal in *Inorg. Chem.* **2009**, *48*, 6251-6260. The synthesis includes a step-wise metallation, first with Zr, then Co, as depicted in our ChemDraw rendition.



   a. Why do the amides coordinate to Zr and the phosphines to Co?

   b. What is the total electron count of the reactants and the products, as drawn? Treat the Zr-Co bond as a Z-type Zr ligand bound to Co (signified by the arrow).

   c. What is the formal oxidation state of each metal center in the reactants and the products?

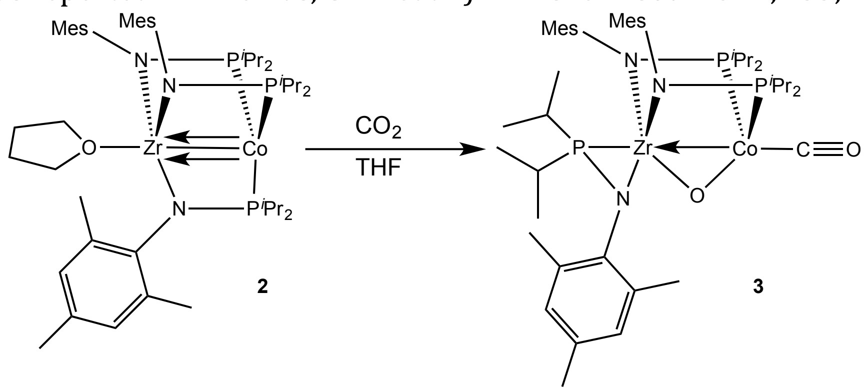
d. The solution magnetic moments of complexes 1a, 1b, 1c are 2.92, 2.87, 3.10 Bohr magnetons, respectively. What spin state does this correspond to?

e. What oxidation state does this suggest for Co?

f. Draw a general MO diagram for the Zr-Co interaction in complexes 1a/b/c.

g. What is the metal-metal bond order in complex 2?

2. CO_2 activation is of particular interest for generating new products from CO_2 feedstock. The Zr-Co complex in the following ChemDraw rendition was shown to activate CO_2 to generate a bridging oxo ligand and was reported in: Thomas, C. M. et al. *J. Am. Chem. Soc.* **2011**, *133*, 14582.



   a. What is the total electron count of complexes 2 and 3, as drawn?

   b. What is the formal oxidation state of each metal center in complexes 2 and 3?

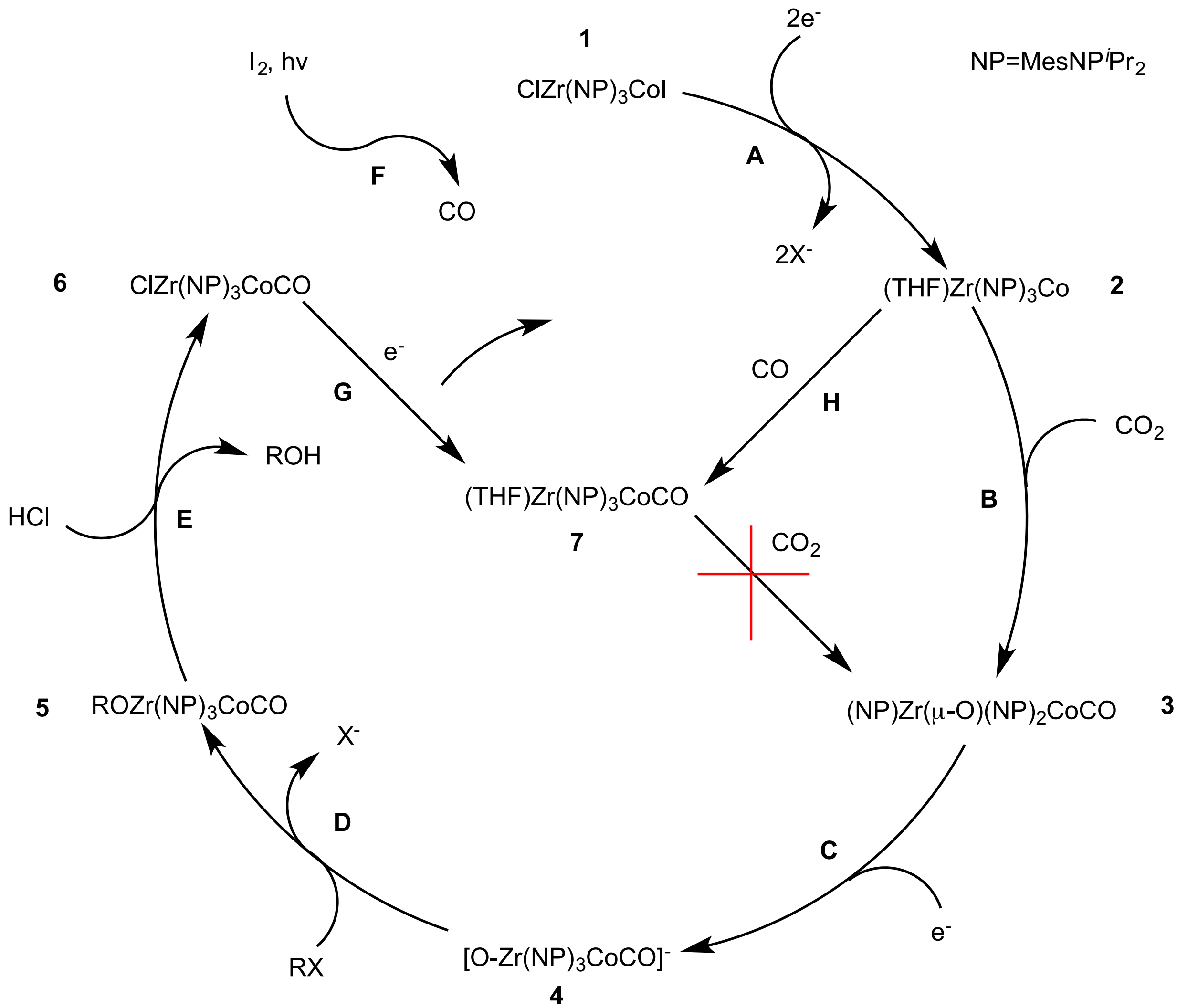
   c. What net fundamental reaction is taking place?

   d. Propose an alternative mechanistic pathway for getting to the same product?

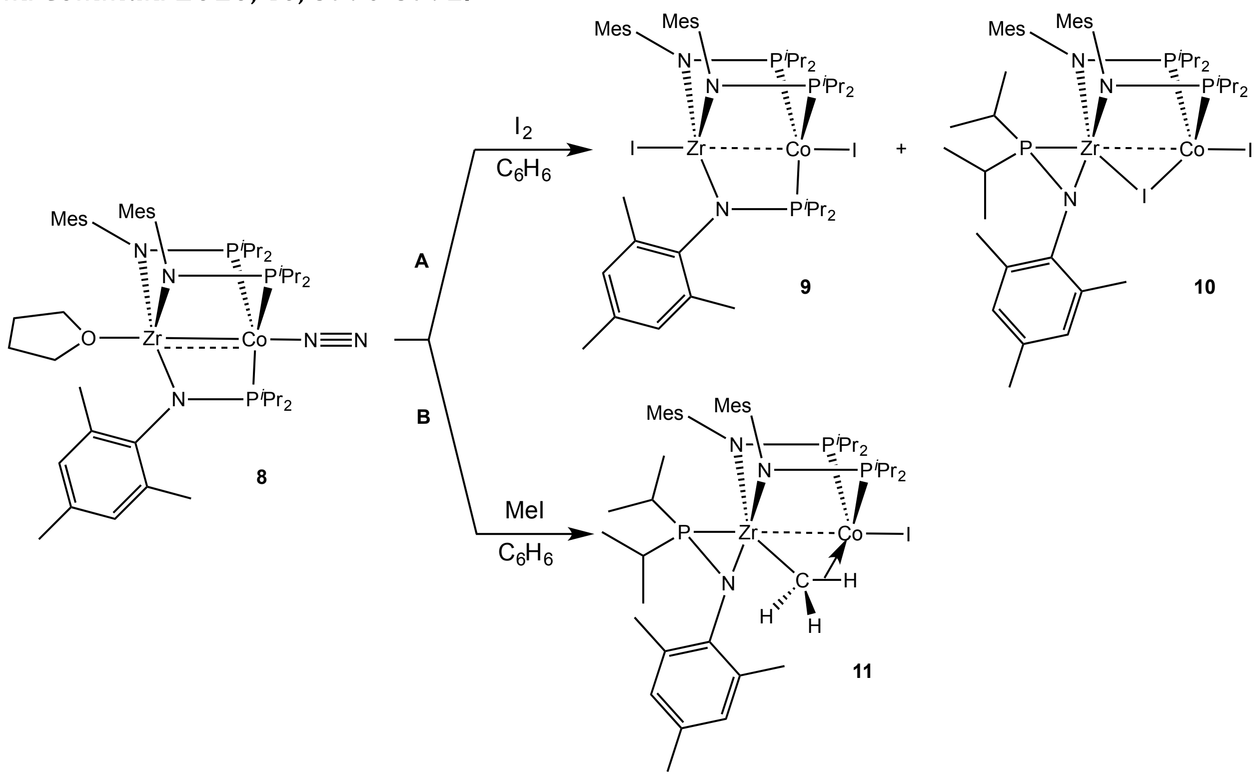
e. Draw an MO diagram for the Zr-Co interaction in complex 2.

f. What would be necessary to turn this reaction into a catalytic cycle? What could be next possible steps?

g. A potential full reaction cycle for CO_2 activation was proposed through the demonstration of individual fundamental reaction steps in: Thomas, C. M. et al. *Inorg. Chem.* **2013**, *52*, 3022-3031. What fundamental reactions are taking place during each step of the following cycle? It may be helpful to look up the paper (note that the numbers are different).



3. Given the following ChemDraw rendition of a reaction scheme reported in: Thomas, C. M. et al. *Chem. Commun.* **2010**, *46*, 5790-5792.



a. What fundamental reaction is taking place in steps A and B?

b. Why does step A produce two products? What experiments might you propose to determine the origins of these products?