

## 5.2: Reaction Overview

Oxidative addition is a general term for the insertion of a metal between two atoms that were previously bonded together.



Figure 5.2.1: Our general scheme for an oxidative addition of hydrogen to a metal.

Oxidative addition is a reaction type rather than mechanism. Several different mechanisms are possible, including polar reactions, non-polar / concerted reactions and radical reactions. For example the formation of Grignard nucleophiles by treatment of alkyl halides with magnesium could be described as an oxidative addition.



Figure 5.2.2: Formation of a Grignard reagent could be described as an oxidative addition, although the mechanism does not resemble the ones that we will look at here.

However, Grignard formation is believed to occur via a radical reaction, and has very little relationship to the addition of hydrogen to Vaska's complex, for instance. In this section, we will look at polar oxidative additions and concerted oxidative additions. Radical oxidative additions will be left for a later chapter on radical chemistry.

Where do the terms "oxidative addition" and "reductive elimination" come from? Think back to how we learned to count valence electrons in transition metal complexes. One of the first things we did was remove the ligands from the complex to see whether there would be a charge on the metal without the ligands.

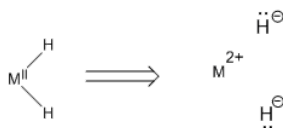


Figure 5.2.3: Deconstruction of a metal complex to discern the charge on the metal.

If each H ligand in Figure OA2.2 is a hydride (reasonable because H is more electronegative than the metal), then removing them would leave the metal with a 2+ charge. That means the metal is in the (II) oxidation state, even if it doesn't formally have a charge on it in the complex. Addition of  $\text{H}_2$  to a metal atom, M, is accompanied by increase in formal oxidation state at the metal (by +2).

Reductive Elimination is microscopic reverse of oxidative addition.

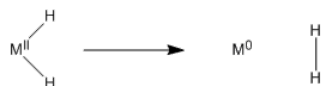


Figure 5.2.4: Deconstruction of a metal complex to discern the charge on the metal.

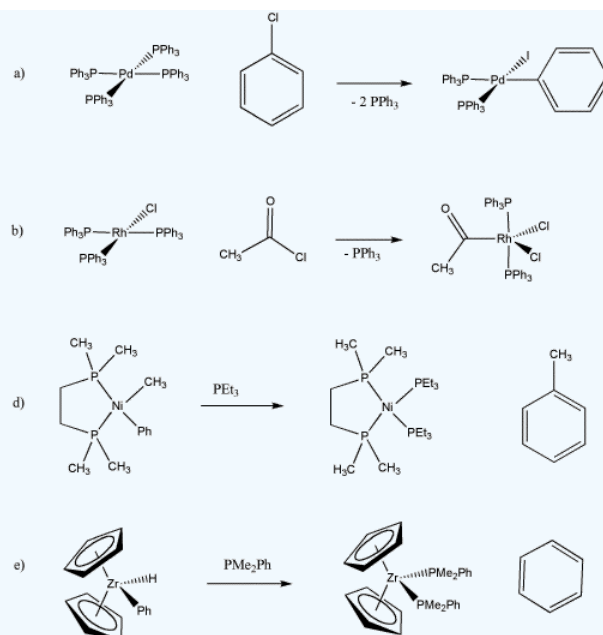
Two atoms that were bonded to one metal atom become bonded to each other, instead. Keep in mind the formal oxidation state of the metal. This elimination is accompanied by decrease in formal oxidation state at the metal (by -2).

Remember, oxidation state can often be determined by giving each ligand the pair of electrons it shares with the metal. Sort out the formal charge on the donor atom in the ligand, and you will know the charge or oxidation state of the metal.

For example, in the example of  $\text{MH}_2$  in Figure OA2.3., assume each bond between M and H is a pair of electrons that belongs with the hydrogen. A hydrogen with two electrons is an anion. As a result, the metal must have an oxidation state of +2 (usually written with Roman numeral II).

### ? Exercise 5.2.1

Determine the oxidation state on the metal before and after each of the following reactions.



**Answer a**

Pd(0) to Pd(II) (I and Ph are negative)

**Answer b**

Rh(I) to Rh(III) (Cl and acyl are negative)

**Answer d**

Ni(II) to Ni(0) (Methyl and phenyl are negative)

**Answer e**

Zr(IV) to Zr(II) (Cp, H and Ph are negative)

**? Exercise 5.2.2**

Propose a reason why the addition of a ligand such as a phosphine can sometimes result in reductive elimination from a coordination complex.

**Answer**

Increased steric crowding in the coordination sphere may force two groups to reductively eliminate together.

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