**Identifying Organometallic Reaction Classes in a Catalytic Cycle**

**Organometallic Reaction Classes and Mechanisms**

When organometallic chemist speak of “mechanisms” such as “oxidative addition”, they are very frequently speaking of reaction *classes* rather than of mechanisms *per se*. A reaction *class* is a reaction that converts one reactant type into one product type. There may be multiple possible reaction *mechanisms* for any given reaction class. To give an example from organic chemistry, a reaction *class* might be **nucleophilic substitution**, which we could define as any reaction:

**Nucleophilic Substitution:** R-LG + **:**Nuc → R-Nuc + **:**LG

where LG is a leaving group and Nuc is a nucleophile. The reaction *mechanism* might be **SN1** or **SN2**:

**SN­1:** R-LG + **:**Nuc → R + **:**LG + :Nuc → R-Nuc + **:**LG

(stepwise; leaving group leaves, then nucleophile enters)

**SN­2:** R-LG + **:**Nuc → LG**…**R**…**Nuc → R-Nuc + **:**LG

(concerted; leaving group leaves and nucleophile enters simultaneously)

Similarly, organometallic reaction classes such as oxidative addition, ligand substitution, and -elimination often can proceed by more than one possible mechanism. For purposes of this exercise, my goal is that you will be able to **identify reaction classes** **in a catalytic cycle**, and while I’ll mention a bit about the mechanisms, I don’t expect you to be able to predict those at this stage. While there is no perfect categorization scheme, I have broken the non-radical reactions of organometallics into one trivial class (ligand association/dissociation) and four non-trivial reaction classes.

1. **Ligand Association/Dissociation**
2. **Oxidative Addition/Reductive Elimination**
3. **Cycloaddition/Retrocycloaddition (used in -Bond Metathesis)**
4. **-Elimination/-Insertion (*e.g.* -hydride elimination/olefin insertion)**
5. **-Elimination/-Insertion (e.g. carbonyl migratory deinsertion/insertion)**

**0. Ligand Association/Dissociation**

As stated above, this is really a trivial class. It is simply the formation or separation of a Lewis acid-base complex:

M + **:**L → M-L (Association) M-L → M + **:**L (Dissociation)

These only proceed by a (rather obvious) mechanism. Because these reactions are simply the mechanistic reverse of one another (written from L->R or R-> L), and because such reactions must proceed by the *same* mechanism in each direction by the Principle of Microscopic Reversibility, we say that these reactions are the “microscopic reverse” of one another.

**Key Characteristics:**

* Removes/creates an “open site” at the metal.
* Increases/decreases the electron count by 2 in the “oxidation state method”.
* Doesn’t change the oxidation state.

**1. Oxidative Addition/Reductive Elimination**

Oxidative Addition is a general process by which a metal formally *adds* across an A-B bond (breaking it), and forming new M-A and M-B bonds, while *oxidizing* the metal from a formal +n oxidation state to a +(n+2) oxidation state.



The microscopic reverse of oxidative addition is Reductive Elimination. There are two primary mechanisms by which oxidative addition (and, by extension, reductive elimination) occurs: a stepwise pathway consisting of an SN­2 reaction followed by ligand association is favored for substrates capable of SN2 (e.g. CH3X, HX, X2) , and a concerted mechanism for rather non-polar bonds lacking a leaving group (H­2, C-H, Si-H).



**Key Characteristics:**

* Removes/creates two “open sites” at the metal.
* Increases/decreases the electron count by 2 in the “oxidation state method”.
* Changes the oxidation state by two.

**2. Cycloaddition/Retrocycloaddition (Particularly important in - (and -)Bond Metathesis)**

A general “catch-all” term for a large number of processes which feature a cyclic transition state or intermediate in which - (or bonds are made, destroyed, or both. The most important type today is olefin metathesis:



The most common mechanism for such transformations involves a 2+2 cycloaddition to a metal alkylidene via a 4-membered intermediate:



It should be noted that such reactions are well known for triple bonds as well as single bonds (which is, of course, a , rather than a -bond metathesis), and that mixing and matching is possible (double bond plus single bond, etc.).

**Key Characteristics:**

* Does not change the number of “open sites” at the metal (though usually requires one open site to form the intermediate).
* Doesn’t change the electron count (though this may change in the intermediate).
* Doesn’t change the oxidation state (though this may change in the intermediate).

**3. -Elimination/Addition**

Another general reaction class of which the most famous member is -hydride elimination/olefin insertion.



The most famous type of catalytic reaction to follow this sort of pathway is olefin polymerization, which typically is a series of -insertions of an alkene into the M-P bond, in which P is a growing polymer chain.

While the most common X-group is a hydride, alkyls, halides, and many other groups are known to undergo these reactions. Most frequently the A and B groups are carbons, but cases of oxygen and nitrogen are very common. The astute observer will note that, technically, these reactions are mixed metathesis reactions between a -bond and a -bond.

**Key Characteristics:**

* Decreases/Increases the number of “open sites” at the metal (though exceptions are known).
* Increases/decreases the electron count by 2 in the “oxidation state method” (though exceptions are known).
* Doesn’t change the oxidation state.

**4. -Elimination/Insertion (Carbonyl Deinsertion/Migratory Insertion)**

While there are other examples of this reaction type, the most common type is carbonyl migratory insertion/deinsertion, shown below.



In the general case, a group migrates to (from) the metal from (to) the -atom, increasing (decreasing) the - bond order by one. Typically, for carbonyls, this requires (generates) an open site *cis* to the carbonyl.

**Key Characteristics:**

* Decreases/Increases the number of “open sites” at the metal.
* Increases/decreases the electron count by 2 in the “oxidation state method”.
* Doesn’t change the oxidation state.

**The Recap**

Int = in the intermediate var = varies (depending on the groups involved)

|  |  |  |  |
| --- | --- | --- | --- |
| **Reaction Class** | **Open Site Change** | **e- Count Change** | **Ox State Change** |
| Ligand Dissociation/Association | +/- 1 | -2/+2 | 0 |
| Reductive Elimination/Oxidative Addition | +/-1 | -2/+2 | -2/+2 |
| Cycloaddition/Retrocycloaddition | 0 (-1 int) | 0 (+2 int) | 0 (var) |
| -Insertion/Elimination | +/-1 | -2/+2 | 0 |
| -Insertion/Elimination (Carbonyl) | +/-1 | -2/+2 | 0 |

**Your Mission (Should You Choose to Accept It…)**

On the next several pages are some examples of catalytic cycles. The first is the Monsanto Acetic Acid Process, by which most of the world’s acetic acid is made.

**In the Square Boxes, please give:**

1. The electron count for each metal complex. Note that these will often *not* be 18! Two of the reasons transition metals are amazing catalysts are the variable electron counts and coordination numbers they can support.
2. The FORMAL oxidation state. Malcolm Green and others (most notably Ged Parkin) have proposed replacing the use of oxidation state with “valence”. I’m still learning their new Covalent Bond Convention, but it looks like it may be a better way to think about this. For now, stick with oxidation state.
3. The dn electron count

**In the Ovals, please give:**

The reaction class for the transformation in question. Note that the square boxes are associated with compounds, and that the ovals are associated with arrows.

Also please not that all arrows drawn should be reversible “equilibrium arrows”. The fact that the arrows point in one direction is a reflection of my poor Chemdraw ™ skills, not chemical reality.

**Stop when you get there, and help any groups that aren’t done!**

**So what’s on the following pages?**

Another similar exercise. This system is the Brookhart & Goldman alkane metathesis system. It is a great example of *tandem* catalysis, in which two catalytic cycles are operating. On top, you have a “Schrock-Type” molybdenum catalytic system (I won’t spoil the game by telling you what reactions it does), and on the bottom, you have an “iridium pincer” catalytic system. **Fill in the boxes and ovals like you did the first page**. Continue onto the last page, where the cycle completes itself by running in reverse.