

2.1: Introduction to Transition Metals and Mechanistic Steps

Objectives

After completing this section, you should be able to:

1. Understand bonding, electron counting, and oxidation states for transition metal complexes
2. Draw and understand common transition metal mechanistic steps

Key Terms

Make certain that you can define, and use in context, the key terms below.

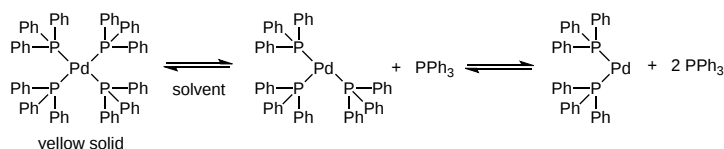
- Transition metal complex
- Ligands
- 18-electron rule
- Metal oxidation state
- Pi donor ligands
- Oxidative addition
- Transmetallation
- Reductive elimination
- Migratory insertion
- Beta hydrogen elimination

Study Notes

Transition metal catalyzed carbon-carbon bond forming reactions provide powerful methods to form key bonds in ways that are often impossible with traditional main group organometallic compounds (e.g., Grignard and organolithium reagents). This chapter provides an introduction to transition metal complexes including their bonding and common reactions. The following chapters will explore the most common transition metal catalyzed reactions including Pd catalyzed cross coupling reactions, olefin metathesis, and Co mediated ring forming reactions.

Content

Before learning about reactions catalyzed by transition metal complexes, we first need to understand a little about their structure and behavior. To begin, we need to update our vocabulary. You've already seen that we refer to molecules containing transition metals as **complexes**. Transition metal complexes contain the metal and other molecules bonded to the metal. These molecules bound to the metal are called **ligands**. Bonds between transition metals and their ligands are weaker than the covalent bonds you are used to from standard organic molecules. This is one reason why transition metals make such excellent catalysts, they are able to make and break bonds to ligands frequently throughout the course of a reaction. For example, tetrakis triphenylphosphine palladium is a yellow solid in which Pd has 4 triphenylphosphine ligands. As shown below, when dissolved in a solvent, this complex exists in equilibrium with complexes containing three and two triphenylphosphine ligands.



Electron Counting

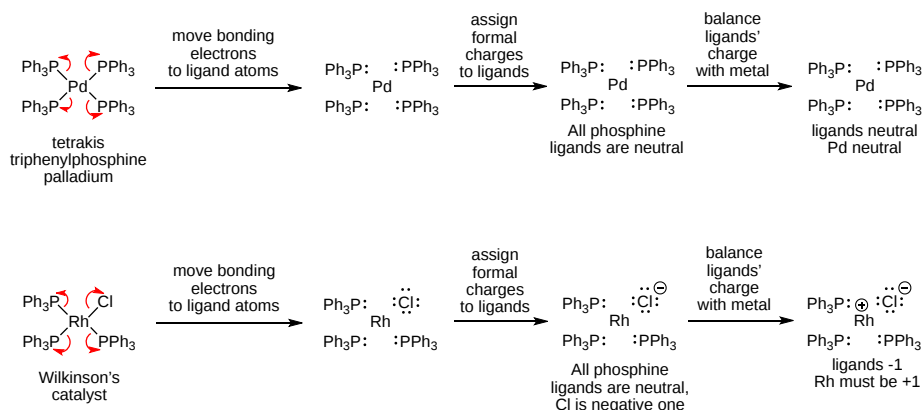
Much time in introductory organic chemistry is spent discussing the octet rule (based on filling s and p orbitals). Transition metals have ready access to d-orbitals, so the octet rule does not apply. Instead, we add 10 electrons (because of the 5 d orbitals) and come up with the **18-electron rule**. Transition metal complexes containing 18 electrons are generally stable and unreactive. For active catalysts, we must have metals that are surrounded by fewer than 18 electrons. Also, we need to learn how to determine the formal charge on the metal. This is called the metal's **oxidation state**. Metals with high oxidation states are electron poor and are much more reactive than low oxidation state or neutral metal complexes.

We will start by analyzing metal complexes where the ligands are bound to the metal via sigma bonds, like in tetrakis triphenylphosphine palladium above. First, we must determine the oxidation state (formal charge) of the metal. To do this, we will

- 1) Consider the sigma bond electrons between the metal and the ligand as belonging to the ligand.
- 2) Assign a formal charge to the

ligand atoms bound to the metal using standard organic chemistry formal charge rules. 3) Add up the charges on all of the ligands. 4) The metal oxidation state balances the ligands' summed formal charges so that the overall complex is neutral (or negative if it's an anionic complex/positive if it's a cationic complex).

Let's practice this by looking at a Pd complex ($\text{Pd}(\text{PPh}_3)_4$) and a Rh complex ($(\text{Ph}_3\text{P})_3\text{RhCl}$). Phosphine ligands are common in transition metal complexes, and their charge is always neutral. (Just like N, which is in the same column in the periodic table, P is neutral with 3 bonds and a lone pair.) Halogens with eight electrons and no bonds have a negative one formal charge. So, in the Pd complex, the ligands have no formal charge, and Pd has a zero oxidation state: Pd(0). In the Rh complex, the net charge on the ligands is negative one. The metal must balance that charge so that the overall complex is neutral. This means Rh has a +1 oxidation state: Rh(I).



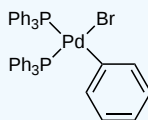
The next step is to determine the total electron count around the metal to see if it satisfies the 18-electron rule. To do this, we must determine 1) The total electrons donated to the metal from the ligands. 2) The valence electrons from the transition metal based on its oxidation state. 3) Add the ligand electrons plus the metal electrons.

Ligand electron counting is as simple as counting the bonds from the ligands to the metal and multiplying by 2. In both of the complexes above, there are four sigma bonds from the ligands to the metals, so there are 8 electrons from the ligands. To determine the metal's valence electrons, we must look at the periodic table and factor in its oxidation state. In the Pd complex above, we determined it is Pd(0) which means Pd has all of its valence electrons. It is in group 10 in the periodic table, so it has 10 valence electrons. In Wilkinson's catalyst above, we determined it is Rh(I) which means Rh has lost one valence electron. Rh is in group 9, so it has 8 valence electrons as a +1 metal.

Thus, we can complete our analysis of the example complexes above. Tetrakis triphenylphosphine palladium has 8 ligand electrons plus 10 metal electrons for a total of 18 electrons. It satisfies the 18 electron rule and is unreactive until it loses one or two ligands in solution. Wilkinson's catalyst has 8 ligand electrons plus 8 metal electrons for a total of 16 electrons. Thus, it can form one more bond and is reactive.

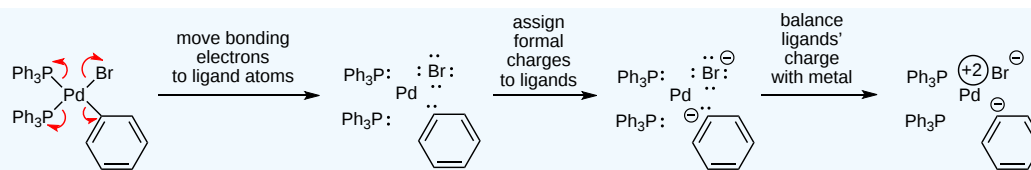
? Exercise 2.1.1

The following Pd complex is commonly formed in Pd catalyzed cross coupling reactions. Perform an electron counting analysis on the complex to determine the oxidation state of Pd and the total Pd electron count.

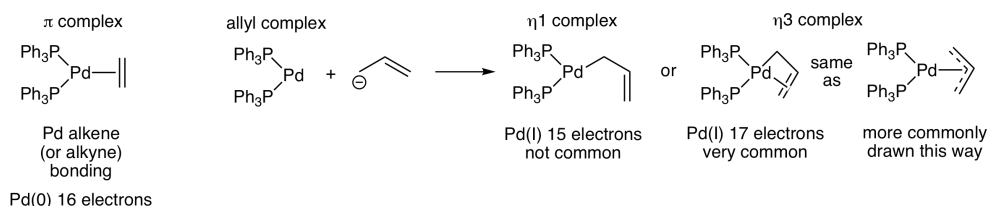


Answer

Following our strategy from above, we can determine that we have two negative one ligands, the Br and the Ph. This means that Pd must balance the net -2 charge by being in its +2 oxidation state: Pd(II). For the total electron count, we again have 8 ligand electrons. Metal ligands are 8 for a +2 Pd (two fewer than the 10 electrons for the neutral Pd). The means our total electron count is 16.

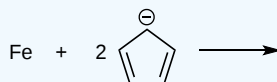


We have one more class of ligands to consider before moving on. These are pi donor ligands. This class of ligands can donate pi electrons via a pi bond. A common example is a pi complex formed when an alkene or alkyne bonds with a metal via its C-C pi bond (see below, left). This results in a neutral, 2 electron ligand. Another example that we will see frequently is an allyl ligand. There are two options for how an allyl anion can bond to a metal (see below, right). It can form a sigma bond which makes it a 2 electron, -1 ligand. However, it can also bond via its alkene pi bond, making it a 4 electron, -1 ligand. This latter option is much more common since it generally helps the metal get closer to an 18-electron complex. Here's another place to expand our transition metal vocabulary. We use the Greek letter eta to describe how many atoms in the ligand are bound to the metal. So, for the first allyl option (2 electrons, -1), we would say it is eta 1 (1 carbon sigma bonded to the metal). For the second allyl option (4 electrons, -1), we would say it is eta 3 (3 carbons bonded to the metal via one sigma and one pi bond).



? Exercise 2.1.2

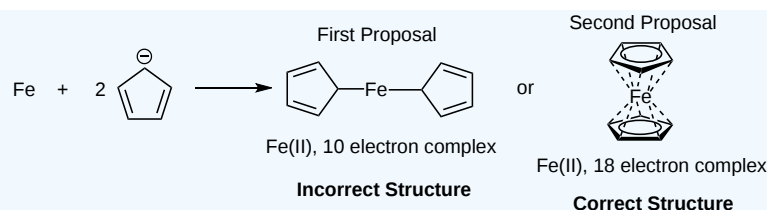
Propose a structure for the iron complex that is formed in the following reaction. Hint: This molecule is very stable.



Answer

This deceptively simple reaction was the start of a new field of chemistry. Originally published as the sigma bond structure in 1951, an alternate "sandwich" complex was published in 1952. An X-ray crystal structure proved the novel sandwich structure and a new subdiscipline of organometallic chemistry was born. For their work in this area, Geoffrey Wilkinson and Ernst Fisher were awarded the Nobel Prize in 1973. This 2001 [article](#) in Chemical and Engineering News provides an overview of the discovery. An entertaining examination of this discovery and the subsequent scientific credit appeared in Angewandte Chemie in 2000. This [article](#) was co-authored by Roald Hoffmann and examines the role of R.B. Woodward in the ferrocene story. (These are Woodward and Hoffmann from pericyclic reaction fame appearing again!)

The initial proposal is likely the first structure that you drew. This complex has the two cyclopentadienyl ligands (abbreviated Cp) sigma bonded to Fe. This yields a 10 electron Fe(II) complex that would not be very stable. Thinking about the two Cp ligands participating in bonding to the Fe via their pi electrons yields a completely different structure. (Don't forget that the cyclopentadienyl anion is an aromatic anion.) This is the correct structure with each Cp ligand contributing 6 electrons to the complex (still a -1 donor) via eta 5 bonding. This results in a stable 18 electron Fe(II) complex. This fascinating molecule is aromatic, participating like benzene in Friedel-Crafts reactions, and is known as ferrocene. Cp ligands are ubiquitous in organometallic chemistry, so be aware of this unique bonding when reading the literature and you see metal-Cp complexes.



Common Mechanistic Steps

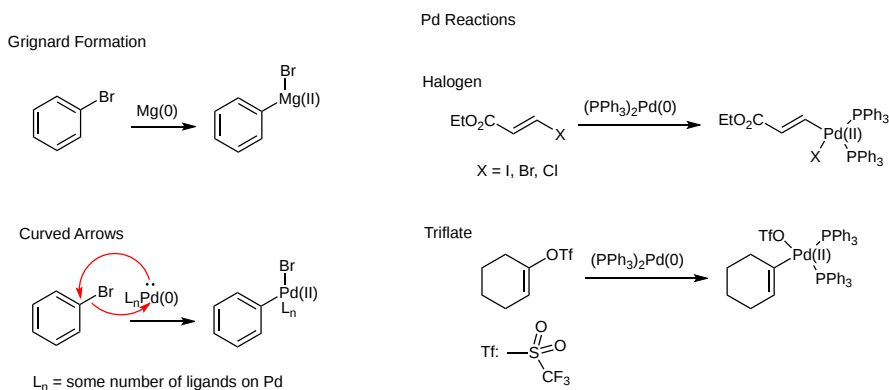
Many transition metal catalyzed reactions share common mechanistic steps that include oxidative addition, reductive elimination, transmetallation, migratory insertion, and beta hydrogen elimination. We will explore each of these individually and then see in the next chapter how that are combined in specific Pd catalyzed cross coupling reactions.

One note about organometallic mechanisms is that chemists often don't use curved arrows to show electron flow. Why? It is often because electron flow isn't always clear. For example, some of these mechanisms might actually be radical reactions. In this chapter, we will shown how electrons could flow if they were polar reactions since this often helps students understand what is happening. However, in keeping with the conventions of transition metal mechanisms, we won't always do this.

Oxidative Addition

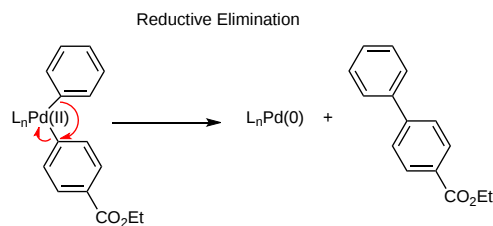
Many transition metal catalyzed reactions begin with a step called oxidative addition where the metal adds to a carbon-halogen bond. You have already seen this reaction type though it may not have been called an oxidative addition. Forming a Grignard reagent from Mg and an organohalogen compound is an oxidative addition. This step is oxidative with respect to the metal because it formally loses electrons when adding carbon and halogen ligands. In the examples below, a neutral metal adds two -1 ligands, meaning the metal becomes +2. We will see many examples of oxidative addition of Pd(0). Two are shown below highlighting the reactivity of halogens and triflates (OTf). (If you haven't met a triflate before, it is a more reactive version of a tosylate that can easily be made from an alcohol or a carbonyl. We will see examples of this in later sections.) A third Pd(0) example is shown to illustrate how you can think about electron flow and curved arrows for oxidative addition. As mentioned above, we generally won't draw curved arrows for this step, and the arrows likely don't depict what is actually happening in the mechanism. The most common and synthetically useful oxidative additions occur between Csp²-X/OTf and metals like Pd. So, we will encountered oxidative additions with vinyl, phenyl/aryl, and alkynyl substrates.

Oxidative Addition Examples



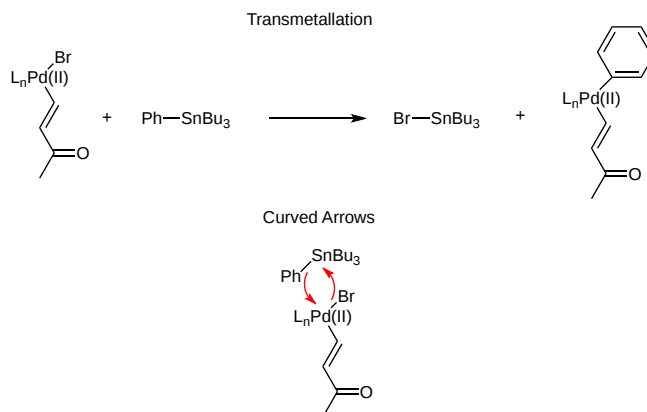
Reductive Elimination

The opposite mechanistic step to oxidative addition is reductive elimination. In this step, two groups bound to the metal, often two carbon ligands, form a new bond while formally giving electrons back to the metal. Thus, this step reduces the metal. It is often the last step in the cycle, regenerating the transition metal catalyst and forming the key carbon-carbon bond in the product. Curved arrows are show below, but this is another step where we will normally resist drawing curved arrows.



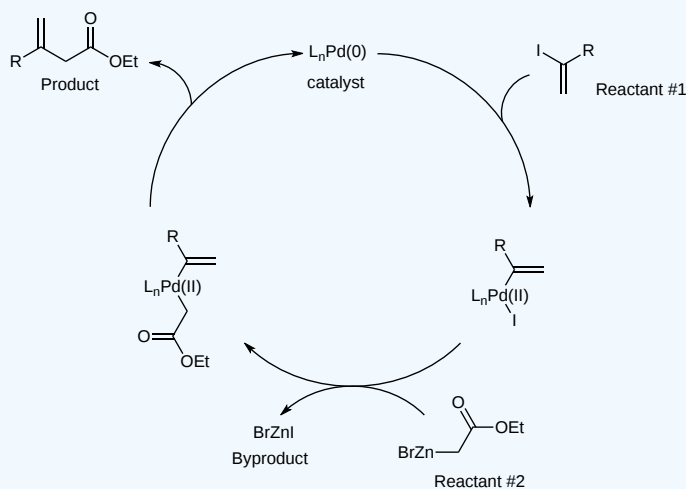
Transmetalation

A common strategy to form a new carbon bond to the transition metal catalyst is to start with a carbon group on a different metal. The stoichiometric metal reagent then transfers the carbon group to the catalytic metal during the catalytic cycle. We will see in the next section that Pd participates in transmetalation with metals like B, Sn, Cu, and Ni. As shown below, the net result is that the halogen group on the catalytic metal (Pd) switches places with the carbon group on the stoichiometric metal (Sn). Also, note that the oxidation state of Pd doesn't change, so this is neither an oxidation nor a reduction.



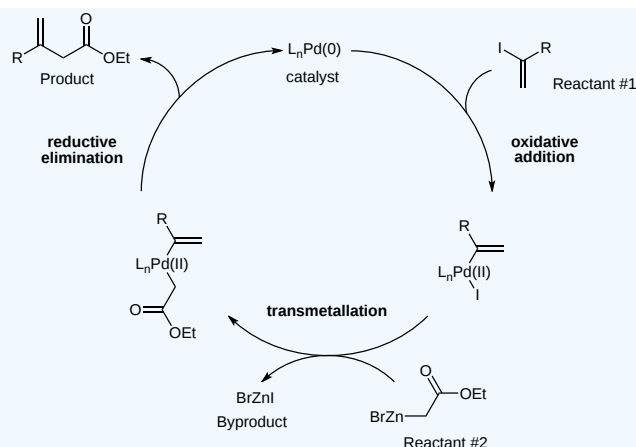
? Exercise 2.1.3

Shown below is the catalytic cycle for a Negishi reaction. Label each mechanistic step as oxidative addition, reductive elimination, or transmetalation.



Answer

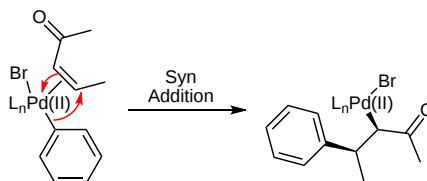
As with many Pd catalyzed reactions, the steps proceed in this order: oxidative addition (making one Pd-C bond), transmetalation (making a second Pd-C bond), and reductive elimination (making the key C-C bond).



Migratory Insertion

Some transition metal catalyzed reactions involve addition of a metal-carbon bond across a pi bond, like an alkene or alkyne, that is also bound to the metal. This is a powerful way to build up complexity in a molecule, especially when it is an intramolecular reaction, and we will see numerous examples of this step when we explore the Heck reaction in the next chapter. As shown below, an alkene (or alkyne) that is complexed to the metal via its pi bond can insert into an adjacent metal-carbon sigma bond. This is a syn addition to the alkene and is similar to the alkene hydrogenation mechanism that you learned in intro organic. The new carbon-carbon bond generally forms at the least hindered/most electron poor carbon of the alkene.

Migratory Insertion

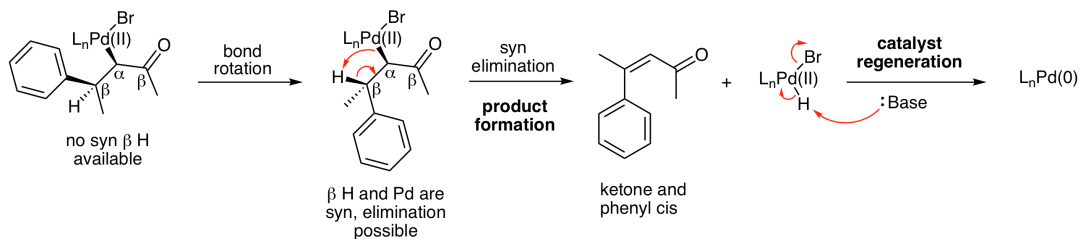


Beta Hydrogen Elimination

For many transition metal complexes bound to an sp^3 hybridized carbon, beta hydrogen elimination is a common mechanistic step. This is a product yielding step and demonstrates the ability of transition metal reactions to form alkene products. Unlike E2 reactions that you learned in intro organic that proceed via an anti elimination, beta hydrogen eliminations are syn eliminations. This has important implications for product alkene geometry and must be carefully considered when proposing this type of mechanistic step. In some complicated substrates, a syn arrangement of the metal and beta hydrogen are not possible. In these cases, the base included in the reaction mixture that usually regenerates the active catalyst instead does a traditional anti E2 reaction to yield an alkene product. We will see examples of this in the following chapter.

Beta hydrogen elimination reactions occur most often after migratory insertion steps. We can explore this mechanism beginning with the product of our migratory insertion step shown above. The migratory insertion product has two beta carbons; however, only the beta carbon on the left has a hydrogen. In the initial conformation, this beta hydrogen is anti to the Pd, so intramolecular elimination is not possible. Thus, our next step is a bond rotation to orient the Pd and beta H syn. Our syn beta hydrogen elimination is now possible, and the reaction occurs. This generates our alkene product with the ketone and phenyl positioned cis, due to their orientation in the reactive conformation. Note that this reaction does not regenerate our Pd(0) catalyst. Instead, we form a Pd(II) complex containing a Pd-H bond. Standard reaction conditions include a base so that deprotonation and loss of bromide regenerates the active catalyst.

Beta Hydrogen Elimination



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