

10.2.2: Oxidative Addition

Overview

In the next few sections we will introduce reactions that are unique to organometallic complexes and play important roles in organometallic catalysis. The first reaction type is oxidative addition. As the name implies, the oxidative addition reaction involves increasing the coordination number of the metal complex by two and oxidizing the metal center by two electrons as shown in Figure 10.2.2.1. The metal donates two electrons to break the A-B bond and form two new bonds, M-A and M-B.

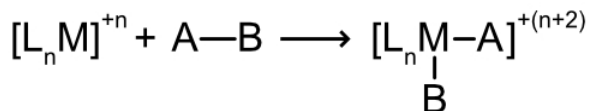


Figure 10.2.2.1: General scheme for oxidative addition. (CC BY-NC-SA; Catherine McCusker)

How important are oxidative additions? Very. The addition of dihydrogen (H_2) is an important step in catalytic hydrogenation reactions. Organometallic C-H activations depend on oxidative additions of C-H bonds. In a fundamental sense, oxidative additions of organic compounds are commonly used to establish critical metal-carbon bonds. Non-polar oxidative additions get the ball rolling in all kinds of catalytic organometallic reactions. Here the mechanisms and important trends associated with oxidative additions are discussed.

Oxidative Additions of H_2

Electron-rich metal centers with open coordination sites (or the ability to form them) undergo oxidative additions with dihydrogen gas. The actual addition step is concerted, but before the addition step, some interesting gymnastics are going on. The status of the σ complex that forms prior to H-H insertion is an open question—for some reactions it is a [transition state](#), others a discrete [intermediate](#). In either case, the two new hydride ligands end up cis to one another. Subsequent isomerization may occur to give a trans dihydride.

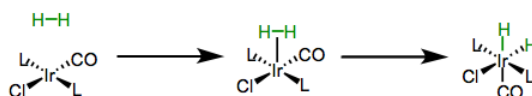


Figure 10.2.2.2: Oxidative addition of dihydrogen to Vaska's complex. Note the cis arrangement of the hydride ligands.

Oxidative Additions of Silanes (H-Si)

Silanes bearing Si-H bonds may react with organometallic complexes in oxidative addition reactions. [Spectroscopic experiments](#) support the intermediacy of a silyl σ complex before insertion. Since the mechanism is concerted, oxidative addition occurs with retention of configuration at Si. The usual pair of forward bonding ($\sigma Si-H \rightarrow d\sigma$) and backbonding ($d\pi \rightarrow \sigma^* Si-H$) orbital interactions are at play here. File this reaction away as a great method for the synthesis of silyl complexes.

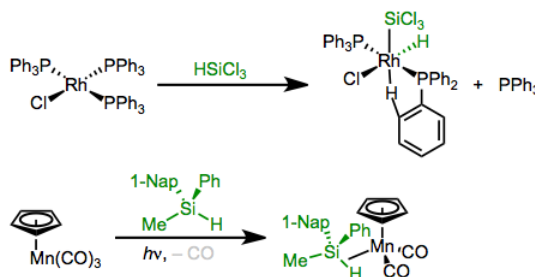


Figure 10.2.2.3: Si-H bonds undergo oxidative addition to electron-rich metal complexes. Electron-poor complexes may stop at the σ complex stage

Oxidative Additions of C-H Bonds

Needless to say, oxidative addition reactions of C-H bonds are highly prized among organometallic chemists. As simple as it is to make silyl complexes through oxidative addition, analogous reactions of C-H bonds that yield alkyl hydride complexes are harder

to come by. The thermodynamics of C–H oxidative addition tell us whether it's favorable, and depend heavily on the nature of the organometallic complex. The sum of the bond energies of the new M–C and M–H bonds must exceed the sum of the energies of the C–H bond and any M–L bonds broken during the reaction. For many complexes, the balance is not in favor of oxidative addition. For example, the square planar [Vaska's complex](#) ($\text{L}_2(\text{CO})\text{IrCl}$; $\text{L} = \text{PPh}_3$) seems like a great candidate for oxidative addition of methane—at least to the extent that the product will be six-coordinate and octahedral. However, thermodynamics is a problem:

$$104 (\text{C–H}) - [60 (\text{Ir–H}) + 35 (\text{Ir–Me})] + 9 \text{ kcal/mol (entropy)} = 18 \text{ kcal/mol}$$

18 kcal/mol is prohibitively high in energy, and playing with the temperature to adjust the entropy factor can't "save" the reaction. More electron-rich complexes exhibit favorable thermodynamics for insertions of C–H bonds. The example below is so favorable ($104 - [75 + 55] + 9 = -17 \text{ kcal/mol}$) that the product is a rock.

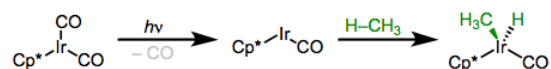


Figure 10.2.2.4: This thermodynamically favorable C–H oxidative addition is helped by the electron-donating Cp^* ligand.

Arenes undergo C–H oxidative addition faster (and more favorably) than alkanes for several reasons. It [seems likely](#) that an intermediate arene π complex and/or C–H σ complex precede insertion, and these complexes ought to be more stable than alkyl σ complexes. In addition, metal-aryl bonds tend to be stronger than metal-alkyl bonds.

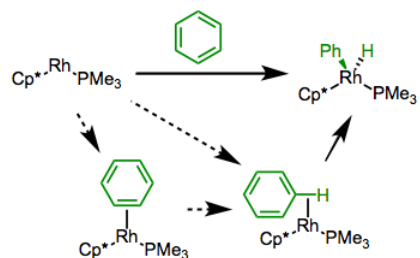


Figure 10.2.2.5: Mechanistic possibilities for the oxidative addition of arene C–H bonds.

Contributors and Attributions

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