Course 201N
1st Semester 2006-2007
Inorganic Chemistry
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Contents

3. Organometallic Chemistry
   Oxidative Addition, Reductive Elimination, Migratory Insertion,
   Elimination
Survey of Reactions of Organometallic Compounds relevant to Catalysis

Oxidative Addition

An *oxidative addition* reaction is one in which (usually) a neutral ligand adds to a metal center and in doing so oxidizes the metal, typically by 2e-. The transferring of the two electrons from the metal to the incoming ligand breaks a bond in that ligand forming two new anionic ligands. At least one of these new anionic ligands ends up bonded to the metal center.

![Diagram of oxidative addition](image)

[The reverse of this reaction would be a *reductive elimination*. In the reverse reaction, the coordination number and the oxidation state of the metal decreases by the expulsion (elimination) of ligand(s)].

There are three main classes of molecules (substrates) that can perform oxidative additions to metal centers: *non-electrophillic*, *electrophillic*, and “intact.” Below are the examples.

**Non-electrophillic:** These molecules do NOT contain electronegative atoms and/or are not good oxidizing agents. Aside from H₂, they are often considered to be “non-reactive” substrates. These molecules generally require the presence of an *empty orbital* on the metal center in order for them to pre-coordinate prior to being activated for the oxidative addition rxn.

H₂, C-H bonds, S-H bonds, N-H bonds, S-S bonds, etc.

H₂ is by far the most important for catalytic applications. We will discuss the application part in the later class.

**Electrophillic:** these molecules *do* contain electronegative atoms and are good oxidizing agents. They are often considered to be “reactive” substrates. These molecules do **NOT** necessarily require the presence of an *empty orbital* (18e- is OK) on the metal center in order to perform the oxidative addition rxn.

X₂ (X = Cl, Br, I), R-X, Ar-X, H-X, etc.
The most common substrates used here are R-X (alkyl halides), Ar-X (aryl halides), and H-X. An example of the oxidative addition of CH$_3$Br to IrCl(CO)(PPh$_3$)$_2$ is shown below. Note that the starting metal complex in this case is 16e-:

Note that the H$_3$C-Br bond is broken on the oxidative addition reaction generating two new anionic ligands: CH$_3^-$ and Br$^-$. If the starting metal complex is 16e- (as shown above) both ligands will usually end up coordinated to the metal to make an 18e-complex.

In the case of a starting 18e-complex (shown below) only one of the two anionic ligands (usually the strongest binding) generated from the oxidative addition will end up coordinated to the metal unless a separate substitution reaction occurs.
In this case the alkyl anion is the best donor ligand compared to the more electronegative and poorly donating Cl\(^-\) anion. Note that the alkyl ligand (-CH\(_2\)CH=CH\(_2\)) initially coordinated to the Re after the oxidative addition is an \(\eta^1\)-allyl ligand and that it can convert to the generally more stable \(\eta^3\)-allyl on CO ligand dissociation.

"Intact": These molecules may or may not contain electronegative atoms, but they do need to have a **double** or **triple bond** present. Unlike most of the other substrate molecules that break a single bond and form two separate anionic ligands upon the oxidative addition, these ligands have double or triple bonds and only **one** of the \(\pi\)-bonds is broken leaving the \(\sigma\)-bond intact. The ligand does pick up **two electrons** from the metal and becomes a **dianionic** ligand.

One usually needs a metal center with an empty orbital (16e- or lower count) in order to pre-coordinate the ligand before the oxidative addition occurs. The one notable exception to this is \(O_2\), which can also act as an **electrophillic** substrate.

Typical “intact” ligands that can perform an oxidation addition without fragmenting apart are:

\[\text{alkenes, alkynes, and } O_2\]

One often needs to have electron withdrawing functional groups on the alkenes or alkynes in order to **enhance** their electron-withdrawing ability in order to help promote the transfer of electrons from the metal to the ligand.

In this case we have oxidized the Pt center from Pt(0) \(d^{10}\) to Pt(+2) \(d^8\) and generated a new **dianionic unsaturated alkenyl** ligand. Note that we have broken one of the alkyne \(\pi\)-bonds.

**General Features of Oxidative Additions**

Because oxidative addition involves oxidation (removal of electrons) of the metal center, the more **electron-rich** the metal is the easier the oxidative addition to the metal center will be. So in comparing two or more metal complexes to see which will be the most reactive towards a particular substrate for oxidative addition you would pick the metal center with the strongest donor ligands, fewest \(\pi\)-acceptor ligands, or most negative charge. Also remember that the non-electrophillic ligands and “intact” ligands usually require that there is an **empty orbital** (16e- or lower) on the metal center in order to react.
Reductive Elimination

A reductive elimination reaction is the reverse of an oxidative addition. It is a reaction in which two cisoidal anionic ligands on a metal center couple together. Each anionic ligand pushes one electron back onto the metal center (in the case of a monometallic complex) to reduce it by 2e-. The coupled anionic ligands then usually fall off the metal center as a neutral molecule.

Since electron-rich metal complexes favor oxidative addition, the reverse is true for reductive elimination. Since reductive elimination involves pushing electrons back onto the metal center from two anionic ligands that are usually more electronegative than the metal center, it is best if the metal center is electron deficient. This can be accomplished by having electron-withdrawing ligands (e.g., CO), cationic charge(s), and/or coordinative unsaturation (sub-18e- counts).

Migratory Insertion

A migratory insertion reaction is when a cisoidal anionic and neutral ligand on a metal complex couple together to generate a new coordinated anionic ligand. This new anionic ligand is composed of the original neutral and anionic ligands now bonded to one another. There is no change in the oxidation state of d-electron count of the metal center. But the overall electron-count on the metal decreases by 2e-. The empty orbital generated by the migratory insertion reaction can enable the reverse of a migratory insertion reaction, which is known as ‘elimination’ reaction. To stop the reverse elimination reaction from occurring after a migratory insertion, one often adds a neutral ligand to coordinate to this empty orbital thus stopping the elimination reaction from occurring. This is sometimes called the trapping ligand.

General Features:

1) No change in formal oxidation state
2) The two groups that react must be cisoidal to one another
3) A vacant coordination site is generated by the migratory insertion. Therefore, a vacant site is required for the back elimination reaction (e.g., β-hydride elimination). A trapping ligand is often needed to coordinate to the empty site formed from a migratory insertion in order to stop the back elimination reaction.

4) Migratory insertions are usually favored on more electron-deficient metal centers.

The following are common anionic and neutral ligands that can do migratory insertion reactions with one another:

**Anionic:** $H^-$, $R^-$ (alkyl), $Ar^-$ (aryl), acyl$, O^2-$ (oxo)

**Neutral:** CO, alkenes, alkynes, carbenes

- CO and alkyl migratory insertions (as shown above) are extremely important and are often generically referred to as carbonylation reactions. Hydride and CO migratory insertions to produce formyl groups are not common due to the thermodynamic instability of the formyl-metal interaction.

- Note that the acyl ligand formed is not as good a donor compared to the starting alkyl. But the metal has gained (replaced) an electron withdrawing CO ligand with a better donating phosphine. Thus, the overall reaction with a trapping ligand is usually towards the migratory insertion.

- The reason that more electron-deficient metals favor CO-alkyl migratory insertions is that makes the carbon atom of the CO more electrophillic and susceptible to nucleophillic attack from the more electron-rich alkyl group.
Migration vs. Insertion

There are two different “directions” that a migratory insertion can occur. A migration is when the anionic ligand moves and performs a nucleophillic-like intramolecular attack on the electrophillic neutral ligand. An insertion is when the neutral ligand moves and “inserts” into the bond between the metal and anionic ligand. Both of these pathways are illustrated below:

**Migration**

Mn
\[\begin{array}{c}
\text{OC} \\
\text{OC} \\
\text{CO} \\
\text{CH}_3
\end{array}\]

\[\text{Mn}^{(+1)} \quad 18e^-\]

\[\text{OC} \\
\text{OC} \\
\text{CO} \\
\text{CH}_3
\]

\[\text{Mn}^{(+1)} \quad 16e^-\]

a MIGRATION rxn involves the anionic ligand doing a nucleophillic-like attack on the neutral ligand. This involves the anionic ligand moving to the site where the neutral ligand is coordinated. An empty coordination site is left behind.

**Insertion**

Mn
\[\begin{array}{c}
\text{OC} \\
\text{OC} \\
\text{CO} \\
\text{CH}_3
\end{array}\]

\[\text{Mn}^{(+1)} \quad 18e^-\]

\[\text{OC} \\
\text{OC} \\
\text{CO} \\
\text{CH}_3
\]

\[\text{Mn}^{(+1)} \quad 16e^-\]

an INSERTION rxn involves the neutral ligand moving over to where the anionic ligand is coordinated and “inserting” into the anionic ligand-metal bond to generate the new anionic ligand. An empty coordination site is left behind from where the neutral ligand originally was located.

We will not care in this course exactly how the reaction is proceeding. The redundant term “migratory insertion” is used to indicate that either directional pathway is fine. Many organometallic chemists short-cut this and just say insertion reaction. It does not necessarily mean that the mechanism is indeed insertion.

**Alkene Migratory Insertions**

An alkene and a hydride usually react via a migration of the hydride to the coordinated alkene ligand:
The backwards reaction, of course, is a $\beta$-hydride elimination and is usually quite favorable if there is an empty orbital cis to the alkyl ligand. Thus, the general importance of having a trapping ligand to coordinate to the empty orbital generated from the migratory insertion.

Alkene/alkyl migratory insertions are also extremely important and an example is shown below:

This is the basis for almost all transition metal-based polymerization catalysts. A polymerization $\text{rxn}$ is just many, many migratory insertions of an alkene and alkyl (the growing polymer chain) interspaced with alkene ligand addition reactions.
Eliminations

Elimination reactions are just the reverse of migratory insertion reactions. The various common elimination reactions are as follows:

\[ 	ext{M} - 	ext{H} \rightarrow \text{H} \quad \text{β-hydride elimination} \]

\[ 	ext{M} - \text{H} \quad \text{R} \rightarrow \text{H} \quad \text{M} = \text{R} \quad \text{α-hydride elimination} \]

\[ 	ext{M} \quad \text{O} \quad \text{R} \rightarrow \text{R} \quad \text{M} = \text{CO} \quad \text{carbonyl elimination or decarbonylation} \]

The key points to remember are:

1) No change in formal oxidation state (exception: alkylidenes)

2) You must have an empty orbital that is cisoidal to the group that you are doing an elimination reaction on. Alternatively, a cisoidal labile ligand that can easily dissociate to open up an empty orbital.

One of the hardest elimination reactions is the breaking of a C-C bond. For example, the following migratory insertion is quite common and plays a critical role in polymerization catalysis:

\[ \text{migratory insertion} \]

But the reverse methyl elimination rxn is very difficult:

\[ \text{rotation of C-C bond to move CH}_3 \quad \text{group away from metal to avoid steric effects} \]

\[ \text{β-hydride elimination} \]