Basic Organometallic Reactions

There are several additional fundamental types of reactions in organometallic chemistry.

The more complex reactions are normally some combination of these fundamental ones.

1) Lewis Acid Dissociation

- many transition metal compounds, especially hydrides, can lose as Lewis acid (i.e., deprotonate)

\[ \text{H} - \text{Co(CO)}_4 \rightleftharpoons \text{H}^+ + \text{Co(CO)}_4^- \]

change in number of metal valence e\textsuperscript{-}s \hspace{1cm} 0
change in formal metal oxidation state \hspace{1cm} -2
change in coordination number at the metal \hspace{1cm} -1

This may be a surprise, but many transition metal hydrides are quite acidic
- notice that making the metal more electron rich decreases acidity

\[
\begin{align*}
\text{HCo(CO)}_4 & \quad (pK_a = 8.3, \text{CH}_3\text{CN}) \quad \text{H}_2\text{Fe(CO)}_4 & \quad (11.4) \quad \text{HCo(CO)}_3\text{PPh}_3 & \quad (15.4) \\
\text{H}_2\text{O} & \quad (pK_a = 10.3, \text{CH}_3\text{S(O)CH}_3) & \quad \text{H}_2\text{O} & \quad (32.0) \quad \text{H}_3\text{C} & \quad \text{CH}_3 & \quad (24.4)
\end{align*}
\]

2) Lewis Base Dissociation

Very, very, very........common process

\[
\begin{align*}
18e & \quad \text{Fe(CO)}_5 & \rightleftharpoons & \quad \text{Fe(CO)}_4 + \text{CO} \\
16e & \quad \text{Pd(PPh}_3)_4 & \rightleftharpoons & \quad \text{Pd(PPh}_3)_3 + \text{PPh}_3
\end{align*}
\]

- change in number of metal valence e-'s: -2
- change in formal metal oxidation state: 0
- change in coordination number at the metal: -1

-Reverse reaction: Lewis base Association

Obvious application are in ligand substitution processes, which may be dissociative ('S\textsubscript{N}1 like')

\[
\begin{align*}
\text{Ni(CO)}_4 & \quad \text{slow} & \quad \text{Ni(CO)}_3 + \text{CO} & \quad \text{L} & \quad \text{fast} & \quad \text{LNi(CO)}_3 \\
\end{align*}
\]

\[v = k \ [\text{Ni(CO)}_4]\quad \text{1st order}\]

Most common for 18 e\textsuperscript{-} systems
- Alternatively, this can be associative, i.e., "S_N2 like"
- more common for 16 e⁻, d⁸ square planar complexes (i.e., Ni^{II}, Pd^{II}, Pt^{II}, Rh^{I}, Ir^{I})

\[
\begin{align*}
\text{rate } v &= 2^{nd} \text{ order} \\
\text{square pyramidal} &\iff \text{trig. bipy} \\
\text{square planar} &\iff \text{square pyramidal}
\end{align*}
\]
3) Oxidative Addition

- represented by

\[ \text{LnM}^n + \text{A-B} \rightleftharpoons \text{LnM}^{n+2} \]

- change in number of metal valence e\textsc{-}'s: \( +2 \) (14 - 16 e)

- change in formal metal oxidation state: \( -+2 \) (0 - +2)

- change in coordination number at the metal: \( +2 \)

for more details, see: R Yamamoto pp. 222-239
   R Collman & Hegedus pp. 279-321

- Overall reaction is cleavage of the A-B bond with bonding to the metal

- Most common A-B is \( \text{R}_3\text{C-X} \) \( \text{X} = \text{halogen or pseudohalogen} \)

- Classic 'organic' example is Grignard reagent formation

\[ \text{Br} + \text{Mg}^0 \rightarrow \text{MgBr} \]
- Most common example in this course will be of the following type:

\[
Pd(PPh_3)_4 \rightleftharpoons 2 \text{PPh}_3 + \text{Pd}(PPh_3)_2 + \text{Ph}_3\text{P} \text{PPh}_3
\]

- the 2\textsuperscript{nd} step is the oxidative addition

Therefore, system needs:  
- a) 2 available oxidation states i.e., Pd\textsuperscript{0}/Pd\textsuperscript{II}, Fe\textsuperscript{0}/Fe\textsuperscript{II}, Ir\textsuperscript{I}/Ir\textsuperscript{III}
- b) open coordination site

Note: v. hindered ligands (Pt-Bu\textsubscript{3}) may encourage monocoordination, which then adds rapidly.

- Reverse reaction: Reductive Elimination

**Mechanism**

- Most is known about late transition metals (such as Ir, Ni groups)

A) If the R of R-X is alkyl (especially 1° or 2°), the reaction is believed to (often) occur via an \textit{S\textsubscript{N}2} substitution

\[
\text{Cl} \cdot \text{Ir} \cdot \text{PPh}_3 \text{Ph}_3\text{P} \text{CO} \text{CH}_3-I \xrightarrow{\text{rds}} \text{Cl} \cdot \text{Ir} \cdot \text{PPh}_3 \text{Ph}_3\text{P} \text{CO} \text{CH}_3 \xrightarrow{\text{fast}} \text{Cl} \cdot \text{Ir} \cdot \text{PPh}_3 \text{Ph}_3\text{P} \text{CO}
\]

- \textit{Inversion} at alkyl carbon has been observed

- Kinetics are overall 2\textsuperscript{nd} order \( v = k [Ir^I] [CH_3I] \)
B) Vinyl (and perhaps aryl) halides go via π - complex formation, with ultimate direct insertion

- Goes with retention of configuration of C=C configuration
- Also believed to be mechanism for addition of H₂

B') Aryl halides go via direct insertion into C-X bond (clearly related to B)

i.e.,

Could result in retention of configuration in some cases

C) - Now defrocked - Nucleophilic Aromatic Substitution - was an old proposal for aryl cases, to rationalized that cases with electron withdrawing groups "always" go faster
C)' - much more likely and often detected in calculations is initial formation of an $\eta^2$-benzene complex

\[ \text{transition state} \]


- comment - I think oxidative additions to aryl halides/pseudo halides 'always' go this was

D) - Electron transfer, radical mechanisms of competitive for alkyl-X cases (Ni, Mg)

\[ \text{i.e.} \quad L_nM + RX \quad \text{rds} \quad [L_nM^+ RX^-] \]

\[ [L_nM^+ RX^-] \quad \text{rds} \quad [L_nM-X + R^+] \quad \text{rds} \quad L_nM^\text{R} \]

-this is likely the Grignard oxidative addition mechanism
-means racemization during the process for alkyl R
Note: C-H Activation - one of the major mechanisms is an oxidative addition

\[
\begin{align*}
\text{Me}_3\text{P}^+\text{Rh}^+ & \quad + \quad \text{C}_6\text{H}_5\text{H} & \quad \rightarrow \quad \text{Me}_3\text{P}^+\text{Rh}^+\text{C}_6\text{H}_5^-
\end{align*}
\]


\[
\begin{align*}
[Rh(R_2\text{PCH}_2\text{CH}_2\text{PR}_2)]\text{BF}_4^- & \quad + \quad \text{RC}=\text{H} & \quad \rightarrow \quad \text{R}_2\text{P}^+\text{Rh}^+\text{C}=\text{H}\text{R}_2
\end{align*}
\]


Aside: One electron oxidative additions also exist

\[
2 \text{L}_n\text{M}^0 + \text{A}-\text{B} \quad \rightarrow \quad \text{L}_n\text{M}-\text{A} + \text{L}_n\text{M}-\text{B}
\]

Conventional organic example - Lithium-Halogen exchange

\[
\begin{align*}
\text{C}_6\text{H}_5\text{Br} & \quad + \quad 2\text{Li} & \quad \rightarrow \quad \text{LiBr} + \text{C}_6\text{H}_5\text{Li}
\end{align*}
\]

Many new opinions on these matters:

Alcazar-Roman, L. M.; Luis, M.; Hartwig, J.F.; Rheingold, A. L.; Liable-Sands, L. M.; Guzei, I. A.
4) Reductive Elimination - reverse of oxidative addition

\[
\text{LnM} \underset{\text{B}}{\overset{\text{A}}{\rightleftharpoons}} \text{L}_n\text{M}^0 + \text{A-B}
\]

- change in number of metal valence e\(^{-}\)'s: -2 (16e - 14e)
- change in formal metal oxidation state: -2 (+2 - 0) (or +3 - +1)
- change in coordination number at the metal: -2

In 'normal' cases, the reaction goes by a concerted mechanism.
-and, importantly for organic chemists…….

Other notes on reductive elimination:

- Again, need two accessible oxidation states
- Non 18 e\(^{-}\) situations must be accessible
- Ni group (Ni, Pd, Pt) are the usual synthetic choices; Co group (Rh, Ir) are also common

Since metal becomes more electron rich during the reaction, the reaction is sometimes accelerated by addition of a ligand which is electron withdrawing

Note: Whether the precursor is square planar or trigonal bipyramidal, it's the \(c/s\) groups which reductively eliminate


More details in general:

Yamamoto, pp. 240-5
Collman, Hegedus pp 322-33
5) Insertion (Migration)
- There is more than one type possible

\[
\begin{align*}
A & \equiv B \\
M & \rightarrow R \\
M & \rightarrow A \\
B & \rightarrow R
\end{align*}
\]

Best examples - Heck reaction carbopalladation
- β- hydride elimination (reverse)
- [2+2] step of alkene metathesis

or

\[
\begin{align*}
M & \rightarrow R^* \\
A & \rightarrow B \\
M & \rightarrow A \\
R^* & \rightarrow B
\end{align*}
\]

Best example - carbonylation of metal carbonyl complexes

Most common : A-B is CO
-The reaction is a concerted migration of R*, with retention of configuration at R* and the metal, if they are chiral

Change in # of valence electron at the metal \(-2\) (18 to 16e)

Change in metal oxidation state \(0\) (+1 to +1)

Change in coordination number \(-1\) (6 to 5)
Note: Reverse reaction is deinsertion

Most common A=B in this case are alkenes or alkynes
- for example, the intermediate step in hydrogenation

- The reverse reaction in this case (β-elimination) is one of the most common reactions of alkylmetals - main mode of decomposition

- again, if inserting group is alkyl, generally there is retention of configuration at R*

see R Cross, R. J., in "Chemistry of the Metal-Carbon Bond", Hartley and Patai, 1982, V.2

R Yamamoto, p. 246-272
Oxidative Coupling
(sometimes being called reductive coupling, since the alkene/alkyne is reduced)

Oxidative coupling occurs when two 'π-bound' ligands on the metal react with each other to form (usually) a C-C σ bond

\[
\text{L-M} \quad \rightarrow \quad \text{L-M}
\]

One of the best known examples is....

- This has become increasingly important with a variety of metals and transformations
  - The 2+2 cycloadditions of metal carbene/alkylidenes could be considered this process, or it could be considered an insertion

| Change in number of valence electrons at metal | -2 (18 to 16e) |
| Change in metal oxidation state | +2 (+1 to +3) |
| Change in metal coordination number | 0 ('3' to '3') |

Note: There are several other fundamental mechanisms, but they have a close 'organic' analogy