Nucleophilic attack on ligand

Nucleophile "substitutes" metal
⇒ hapticity usually decreases
Oxidation state mostly unchanged

Competition: nucleophilic attack on metal
usually leads to ligand substitution
Nucleophilic abstraction

Mostly ligand deprotonation

\[ \text{Cp}_2\text{WH}_2 \xrightarrow{\text{BuLi}} \text{Cp}_2\text{WH}^- \text{Li}^+ \]

\[ \text{NaH} \]

\[ \text{Na}^+ \]
Nucleophilic addition

Key reaction of the Wacker process:

\[
\text{C}_2\text{H}_4 + \frac{1}{2} \text{O}_2 \xrightarrow{\text{PdCl}_2, \text{H}_2\text{O}} \text{CuCl}_2 \rightarrow \text{CH}_3\text{CHO}
\]
The Wacker process

\[ \text{Cl-Pd-Cl}^{2-} \xrightarrow{\beta-\text{H elim}} \text{C}_2\text{H}_4 \xrightarrow{\beta-\text{H elim}} \text{Cl-Pd-Cl} \xrightarrow{\text{H}_2\text{O}} \text{H}_2\text{O-Pd-Cl} \]

- \( \text{Pd}^{(0)} + \text{H}^+ + \text{H}_2\text{O} + 2 \text{Cl}^- \rightarrow -2 \text{e} (\text{CuCl}_2 \rightarrow \text{CuCl}) \)

- \( \text{CH}_3\text{CHO} \rightarrow \beta-\text{H elim} \)

- \( \text{H}_2\text{O-Pd-Cl} \xrightarrow{\text{ins}} \text{H}_2\text{O-Pd-Cl} \)

- \( \text{H}_2\text{O-Pd-Cl} \xrightarrow{\beta-\text{H elim}} \text{H}_2\text{O-Pd-Cl} \)

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The Wacker process

Characteristics of the Wacker process:

• The oxygen in the product derives from water, not directly from the oxygen used as oxidant
• higher olefins yield ketones, not aldehydes
• large amounts of halides required: corrosive
• side products resulting from nucleophilic attack of halide on olefin

No longer important for acetic acid synthesis
Several variations (with more complicated nucleophiles) used in organic synthesis
Nucleophilic attack on the ligand

How can you distinguish between *internal* and *external* attack of OH$^-$?

Use *trans*-CHD=CHD and trap the intermediate Pd-C-C-OH with CO:
Using isotopic labelling to study mechanisms
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Could acetaldehyde be formed directly as vinyl alcohol?

Perform reaction in D\textsubscript{2}O:

- \( \text{Pd} - \text{OH} \xrightarrow{\text{diss}} \text{OH} \xrightarrow{\text{H}_2\text{O}} \text{CH}_3\text{O} \)

- \( \text{Pd} - \text{OH} \xrightarrow{\text{"β-H elim"}} \text{Pd} - \text{O} \xrightarrow{\text{diss}} \text{CH}_3\text{O} \)

- \( \text{Pd} - \text{OD} \xrightarrow{\text{diss}} \text{OD} \xrightarrow{\text{D}_2\text{O}} \text{CH}_2\text{D} \)

- \( \text{Pd} - \text{OD} \xrightarrow{\text{"β-H elim"}} \text{Pd} - \text{O} \xrightarrow{\text{diss}} \text{CH}_3\text{O} \)

H\textsubscript{2}O
Insertion and elimination
Insertion reactions

If at a metal centre you have
a) a $\sigma$-bound group (hydride, alkyl, aryl)
b) a ligand containing a $\pi$-system (olefin, alkyne, CO)
the $\sigma$-bound group can *migrate* to the $\pi$-system.

\[
\begin{align*}
M & \underset{CO}{\arrow} M \underset{R}{\arrow} \underset{\text{O}}{\text{R}} \\
M & \underset{\text{C=C}}{\arrow} M \underset{\text{R}}{\arrow} \underset{\text{R}}{\text{R}}
\end{align*}
\]
Insertion in MeMn(CO)$_5$

CO adduct

HOMO

insertion

TS

agostic

LUMO

η$^2$-acyl
Insertion reactions

The σ-bound group migrates to the π-system.

But if you only see the result, it looks like the π-system has inserted into the M-X bond, hence the name insertion. To emphasize that it is actually (mostly) the X group that moves, we use the term migratory insertion.

The reverse of insertion is called elimination.

Insertion reduces the electron count, elimination increases it. Neither insertion nor elimination causes a change in oxidation state.
In a 1,1-insertion, metal and X group "move" to the same atom of the inserting substrate. The metal-bound substrate atom increases its valence. CO, isonitriles (RNC) and SO\textsubscript{2} often undergo 1,1-insertion.
Insertion of CO and isonitriles

• CO insertion is hardly exothermic.

• An additional ligand may be needed to trap the acyl and so drive the reaction to completion.

• In the absence of added ligands often fast equilibrium.

• CO insertion in M-H, M-CF$_3$, M-COR endothermic.
  – no CO polymerization.
  – but isonitriles do polymerize!
Double CO insertion?

Deriving a mechanism from a reaction stoichiometry is not always straightforward.

The following catalytic reaction was reported a few years ago:

\[
2 \text{R}_2\text{NH} + 2 \text{CO} + \text{ArI} \xrightarrow{"Pd"} \text{R}_2\text{NCOCOAr} + \text{R}_2\text{NH}_2^+ \text{I}^-
\]

This looks like it might involve double CO insertion.

But the actual mechanism is more complicated.
No double CO insertion!
Promoting CO insertion

- "Bulky" ligands
  \[ M \text{CO}_\text{R} \text{ requires more space than } M \text{O}_\text{R} \]

- Lewis acids
  Coordinate to O, stabilize product
  \[ M \text{C}_\text{O} \text{Cl}_\text{3} \text{ vs } M \text{O}_\text{C}_\text{R} \text{Cl}_\text{3} \]

Drawback: usually stoichiometric
Sometimes it only looks like insertion

Nucleophilic attack at coordinated CO can lead to the same products as standard insertion:

\[
\text{Ir} \equiv \text{OMe} \quad \Leftrightarrow \quad \text{Ir}^+ \equiv \Box \equiv \text{OMe}
\]

\[
\text{CO} \quad \text{Ir}^+ \equiv \text{CO} \equiv \text{OMe} \quad \rightarrow \quad \text{Ir} \equiv \text{COOMe}
\]

Main difference: nucleophilic attack does not require an empty site.
1,2-insertion of olefins

Insertion of an olefin in a metal-alkyl bond produces a new alkyl. Thus, the reaction leads to *oligomers* or *polymers* of the olefin.
1,2-insertion of olefins

Insertion of an olefin in a metal-alkyl bond produces a new alkyl. Thus, the reaction leads to **oligomers** or **polymers** of the olefin. Best known polyolefins:
- polyethene (polythene)
- polypropene

In addition, there are many specialty polyolefins.

Polyolefins are among the largest-scale chemical products made. They are chemically inert. Their properties can be tuned by the choice of catalyst and comonomer.
Why do olefins polymerize?

Driving force: conversion of a $\pi$-bond into a $\sigma$-bond
- One C=C bond: 150 kcal/mol
- Two C-C bonds: $2 \times 85 = 170$ kcal/mol
- Energy release: about 20 kcal per mole of monomer (independent of mechanism!)

Many polymerization mechanisms
- Radical (ethene, dienes, styrene, acrylates)
- Cationic (styrene, isobutene)
- Anionic (styrene, dienes, acrylates)
- Transition-metal catalyzed ($\alpha$-olefins, dienes, styrene)

Transition-metal catalysis provides the best opportunities for tuning of reactivity and selectivity
Mechanism of olefin insertion

Standard Cossee mechanism

Green-Rooney variation (\(\alpha\)-agostic assistance):

Interaction with an \(\alpha\) C-H bond could facilitate tilting of the migrating alkyl group

The "fixed" orientation suggested by this picture is probably incorrect
Insertion in M-H bonds

Insertion in M-H bonds is nearly always fast and reversible. ⇒ Hydrides catalyze olefin isomerization

Regiochemistry corresponds to Markovnikov rule (with $M^{\delta^+}-H^{\delta^-}$)

To shift the equilibrium to the insertion product:
- Electron-withdrawing groups at metal
  alkyl more electron-donating than H
- Early transition metals
  M-C stronger (relative to M-H)
- Alkynes instead of olefins
  more energy gain per monomer, both for M-H and M-C insertion
Catalyzed olefin isomerization

Metals have a preference for primary alkyls. But substituted olefins are more stable!

In isomerization catalysis, the dominant products and the dominant catalytic species often do not correspond to each other. For each separately, concentrations at equilibrium reflect thermodynamic stabilities via the Boltzmann distribution.
Catalyzed olefin isomerization

Cp₂ZrHCl → Cp₂ZrCl + \text{alkyl} + \text{olefin}