Migratory Insertion and Elimination

\[ \text{Ln} M^{-c=0} \quad \xrightleftharpoons{\text{R}} \quad \text{Ln} M^{-c=0} \quad \xrightleftharpoons{\text{R}} \quad \text{Ln} M^{-c=0} \]

- These reactions play an important role in industrial catalysis:

**Ex: Hydroformylation**

\[ \text{CH}_3\text{CH} = \text{CH}_2 + \text{CO} + \text{H}_2 \xrightarrow{\text{Rh or Co}} \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}=\text{CH}_2 \]

- Monsanto Acetic Acid Synthesis (Also, Cativa Process \( \Rightarrow \) BP)

\[ \text{CH}_3\text{OH} + \text{CO} \xrightarrow{\text{Rh}^-} \text{CH}_3\text{COOH} \]
**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.
Insertion in MeMn(CO)$_5$

Insertion in MeMn(CO)$_5$
Insertion reactions

The $\sigma$-bound group migrates to the $\pi$-system.

But if you only see the result, it looks like the $\pi$-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.

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 some years ago:

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

This looks like it might involve double CO insertion.

But the actual mechanism is more complicated.
No double CO insertion! Generally not observed!!
Hydroformylation (Oxo) Catalysis

\[ \text{alkene isomerization} \quad \text{alkene hydrogenation} \]

* Largest homogeneous catalytic process
* > 15 billion pounds of aldehydes (alcohols) per year
* Commercial catalysts are complexes of Co or Rh
* Selectivity to linear (normal) or branched (iso) products is important
Credit: George Stanley

Monometallic

Bimetallic
proposed bimetallic pathway - NOT important in normal catalysis

3 atm CO = 1.6:1 L:B ratio
90 atm CO = 4.4:1 L:B ratio

increasing the CO pressure keeps the back reactions from occurring - this limits alkene isomerization and the corresponding opportunity for making branched alkyl
alkene isomerization

linear alkyl (leads to linear aldehyde)

branched acyl (leads to branched aldehyde)
The reaction is independent of CO pressure, and first order in both rhodium and MeI.

The rate determining step is the oxidative addition of MeI to the \([\text{Rh(CO)}_2\text{I}_2]\) catalyst. Thus, the production of MeI from methanol, catalyzed by HI, is critically important.

Iodide ligands are considered to be quite important in this reaction due to the HI catalyzed conversion of MeOH to MeI and their relatively good donor abilities on the Rh center.

The negative charge on the \([\text{Rh(CO)}_2\text{I}_2]\) catalyst is believed to be critical in assisting the oxidative addition of MeI to the rhodium center.

The alkyl species, \([\text{Rh(CO)}_2(\text{Me})\text{I}_3]\), is extremely reactive towards CO insertion to form the acyl complex.
Additional mechanistic details

- Mechanistic considerations

  \[(\text{CO})_5\text{Mn-c}_{43} \xrightarrow{^{13}\text{CO}} (\text{CO})_4(^{13}\text{CO})\text{Mn-}_{c_{43}}\]

  cis product only

  \(\Rightarrow\) implies a concerted mechanism. If CO were released, ~20% trans would be expected.

- But does the alkyl or CO migrate?
Product Distribution

The Me migrates!!!
Further stereochemical probes for alkyl migration: Retention in all cases.

\[ \text{Me}_3C \quad 3J_{\text{HHH}} = 9 \text{ Hz} \]

\[ \text{Cp}_2\text{Fe(\text{CO})}_2 \quad \text{w/ inversion} \quad S_n^2 \]

threeo "sym" \[ 3J_{\text{HHH}} = 4.5 \text{ Hz} \]

Whitesides J.A. (S., 1971, 93, 1529
1969, 91, 4313
1974, 96, 2814

\[ \text{Me}_3C \quad \text{TsoCHDCHDCMe}_3 \]

\[ \text{Cp(\text{CO})(\text{PPh}_3)}_2 \]

two doublets are observed \[ 3J_{\text{HHH}} = 4.5 \text{ Hz} \]

due to two diastereomers
Kinetic observables:

\[ \ln M \xrightarrow{c_0} \xrightarrow{k_1} \xrightarrow{k_{-1}} \frac{L'}{k_2} \xrightarrow{k_3} \ln M' \]

How do we discern?

If we assume no build-up of \( B \):

\[
\frac{d[B]}{dt} = 0 = k_1[A] - k_{-1}[B] - k_2[B][L']
\]

rate = \( k_2[B][L'] \) \( \Rightarrow \) \( \frac{k_1 k_2[A][L']}{k_{-1} + k_2[L']} \) since \( [B] = \frac{k_1[A]}{(k_{-1} + k_2[L'])} \)
At large $L'$, rate = $k_{\text{obs}}[A]$ 

At low $L'$, $B$ returns to $A$ many times

At high $L'$, $B$ is trapped every time

This type of plot is more consistent with step-wise.

If it's $L'$ promoted:

$k_{\text{obs}} = k_3[L']$

Here perhaps more ambiguous
For a good study on this topic: Bergman & Wex, JACS, 1981, 7028

\[ \text{CpMo(CO)_3 Me + PMe}_2\text{Ph} \xrightarrow{\text{Solv}} \text{Cp(CO)_2(PhMe}_2\text{P)Mo=O}^{\text{CH}_3} \]

\[ \text{Solv} = \text{[similar dielectric but variable donicity]} \]

This study provided first compelling evidence that solvent effects on rates can reflect direct attack of donor solv. on migration is occurring.
The plot indicates super-imposed saturation & 2\textsuperscript{nd} order kinetics.

\[ k_{obs} = \frac{k_1 k_2 [P]}{k_1 + k_2 [P]} + k_3 [P] \]

\( P = \text{PMc}_2\text{Ph} \)

To establish that the rate of the solvent-assisted pathway is first order in solvent:

* Varying THF/Me\textsubscript{2}THF ratio over entire mole fraction.
Other factors can also influence rates of migr. ins.

LA promoters: Collman, JACS, 1978, 4766

\[
\left[ (\text{CO})_4 \text{Fe}-R \right] M^+ + L \longrightarrow \left[ (\text{CO})_3 L \text{Fe-L}_R \right] M^+
\]

The rxn rate is \(~400\times\) faster in NMP vs THF

Rate decreases from \(L^+ > Na^+ > \text{Ph}_3P = N = \text{PP}_{\text{N}} \text{Ph}_3\)

Suggests:
Also: McClain, JACS, 1983, 105, 6355

Also,

\[
\text{MoMn(CO)₅ + AlX₃} \rightarrow \text{(CO)₄MnX} \rightarrow \text{alkaline earth salts promote insertion}
\]

Shriver, JACS, 1980, 102, 5093
Inorg. Chem., 1987, 26, 1272

Presence of a catalytic oxidant can also affect the rate: Magnuson, OM, 1983, 960

\[
\text{Complete in minutes!} \quad \frac{\text{CO}}{5\%} \quad \text{CpFe(PPh₃)(CO)} \rightarrow \text{CpFe(PPh₃)(CO)} \quad \text{large kinetic barrier}
\]

\[
\begin{align*}
\text{A} & \xrightarrow{A^+} \text{B}^+ \\
\text{A} + \text{CO} & \rightarrow \text{B}^+ \\
\text{B}^+ + \text{A} & \rightarrow \text{B} + \text{A}^+ + \text{CO} \quad \text{etc...}
\end{align*}
\]
Do migratory insertions occur similarly in a late metal/hetero-atom system?

Bryndza (DuPont), OM, 1985, 4, 1686

While modeling Pd-catalyzed carbylolation of alcohols:

\[
\begin{align*}
\begin{array}{ccc}
\text{P} & \text{Pt} & \text{CH}_3 \\
\text{P} & \text{Pt} & \text{OCH}_3 \\
\end{array}
\end{align*}
\begin{align*}
\text{CO} & \rightarrow \\
\end{align*}
\begin{align*}
\begin{array}{ccc}
\text{P} & \text{Pt} & \text{CH}_3 \\
\text{P} & \text{Pt} & \text{OCH}_3 \\
\end{array}
\end{align*}
\]

- Mechanistic possibilities:

1. Pre-dissoc. of OCH\(_3\): \[
\begin{align*}
\begin{array}{ccc}
\text{P} & \text{Pt} & \text{CH}_3 \\
\text{P} & \text{Pt} & \text{OCH}_3 \\
\end{array}
\end{align*}
\begin{align*}
\text{CO} & \rightarrow \\
\end{align*}
\begin{align*}
\begin{array}{ccc}
\text{P} & \text{Pt} & \text{CH}_3 \\
\text{P} & \text{Pt} & \text{OCH}_3 \\
\end{array}
\end{align*}
\]

- Was known that: \[
\begin{align*}
\begin{array}{ccc}
\text{L}_2 \text{Pt} & \text{Cl} & \text{H} \\
\text{L}_2 \text{Pt} & \text{Cl} & \text{OCH}_3 \\
\end{array}
\end{align*}
\begin{align*}
\text{CO} & \rightarrow \\
\end{align*}
\begin{align*}
\begin{array}{ccc}
\text{P} & \text{Pt} & \text{CH}_3 \\
\text{P} & \text{Pt} & \text{OCH}_3 \\
\end{array}
\end{align*}
\]

But several observations seemingly inconsistent with above scenario:

Ex: Run is 1st order in \([L_2 \text{Pt} - \text{CH}_3] \) and \([\text{CO}] \) from 0 to 150 psi;
seems to exclude pre-dissoc. of OCH\(_3\).
- Three other scenarios:

\[
\begin{align*}
\text{CO} & \rightarrow L_2 Pt \xrightarrow{\text{CH}_3} \text{stepwise} \\
L_2 Pt \xrightarrow{\text{CO}} \text{conc.} & \rightarrow L_2 Pt \xrightarrow{\text{CH}_3} \\
\text{CO} & \rightarrow L_2 Pt \xrightarrow{\text{CH}_3} \text{charged intermediate} \\
L_2 Pt & \xrightarrow{\text{CO}} \text{Assoc. Displacement}
\end{align*}
\]

- Data was most consistent with 2.
  
  (i) $SM + ^{13}CO$ at -20 to 100°C shows a broad resonance at $S=184$ ppm.
  
  $\Rightarrow$ No loss of $^{195}$Pt coupling to either $OCH_3$ or DPPE evident.

(ii) Crossover exp:

$SM + 15 CD_3OD + 10 \text{ atm CO} \rightarrow \text{NMR shows <5\% OCD}_3$ incorporation

and this is consistent with exchange of CD$_3$OD w/ SM.

$\Rightarrow OCH_3^-$ does not dissociate!
Migratory Insertions into M-H bonds? Rarely observed

\[
\text{LnM-CEO} \xrightleftharpoons{} \text{LnM-}^{\text{H}}_0
\]

Ex:

\[
\text{Fe}^{2+} + \text{H} + \text{OAc}^- \rightarrow \text{Fe}^{2+} \text{H} + \text{OAc}^- \rightarrow \text{Fe}^{2+} \text{H} \rightarrow \text{Fe}^{2+} \text{H} \quad \text{not stable}
\]

Ex:

\[
\text{ReO} + \text{NO} \rightarrow \text{ReO} + \text{NO} \rightarrow \text{ReO} + \text{NO} \rightarrow \text{ReO} + \text{NO} \rightarrow \text{ReO} + \text{NO} \quad 25^\circ C
\]

appears to be generally true
Does this derive from M-H vs M-C bond strength? Likely contributor

\[
\text{H} - \text{Mn(CO)}_5 + \text{CO} \rightleftharpoons \text{H} \cdot \text{Mn(CO)}_5 \quad \Rightarrow \Delta H^o \approx 0 \text{ kcal}
\]

\[
\text{H} \cdot + \cdot \text{Mn(CO)}_5 + \text{CO} \rightleftharpoons \text{H} \cdot \text{C} \cdot + \cdot \text{Mn(CO)}_5
\]

+59 kcal

\[-39\]

\[-20\]

\[
\text{In general, M-H bonds are 5-15 kcal/mol stronger than M-CH}_3 \text{ bonds.}
\]

One can shift the thermodynamics to observe M-H insertion:

T. Marks, JACS, 1981, 69, 59

\[
\text{Cp}_2^* \text{Th} \cdot \text{OR} + \text{CO} \underbrace{\rightarrow}_{-40^\circ C} \text{Cp}_2^* \text{Th} \cdot \text{OR} \cdot \text{H} \quad R = \text{X} \cdot \text{Y}
\]
Another, less easily explained M-H insertion:

\[ \text{H-Rh(OEP)} + \text{CO} \rightarrow \text{H-Rh(OEP)} \]

Wayland, JCS Chem Comm, 1981, 700
Halpern, JACS, 1985, 107, 4333
- argues for radical chain mechanism instead of concerted migratory insertion.

Linear NO complexes rarely undergo migratory insertions:

Ex:

\[ \text{Cp} \quad \text{Cp} \quad \text{Cp} \]
\[ \text{NO} \quad \text{ON} \quad \text{ON} \]
\[ \text{Me} \quad \text{Me} \quad \text{L} = \text{PPh}_3 \]

\[ 1780 \text{ cm}^{-1} \]

\[ \text{k}_1 \quad \text{k}_2 \quad \text{k}_3 \]

\[ \text{1310 cm}^{-1} \]

\[ \text{Bent NO unreactive towards insertion.} \]

\[ \text{Cp} \quad \text{L} = \text{PET}_{3} \text{ (more nucleophilic)} \]
\[ \text{L} = \text{PET}_{3} \]
\[ \text{Me} \quad \text{Me} \]

\[ 1530 \text{ cm}^{-1} \]

Bergman, JACS, 1983, 105, 3922