1 Insertion / Deinsertion

- 1,1-insertion / deinsertion

1,1-insertion because both M and Y end up bound to the atom in position 1 (X)

Specific examples:

1. O
   - O
   - C
   - R
   - M
   \[ \text{acyl} \]

2. R'N
   - R'N
   - C
   - R
   - M
   \[ \text{iminoacyl} \]

3. S
   - S
   - O
   - R
   - M
   \[ \text{S-sulphinate} \]
Migratory insertion of CO

- general reaction of M-C bonds
- important in the ‘Oxo’ hydroformylation process and the Monsanto acetic acid process (next section)

The classic example:

Suggests that direct CO insertion from the gas phase is NOT involved
• 1,2-insertion / deinsertion

1,2-insertion because M ends up bound to the atom in position 1 (X) while Y ends up bound to the atom in position 2 (Z)

Alkene and alkyne insertion into M-H (or M-C) bonds

18 e⁻, 18 e⁻ agostic, 16 e⁻, a vinyl complex
insertion is slightly exothermic for M-H bonds:

\[
\begin{array}{c}
\text{M-H} + \quad \rightarrow \quad \text{M-C-C-H}
\end{array}
\]

<table>
<thead>
<tr>
<th>bonds broken</th>
<th>bonds formed</th>
</tr>
</thead>
<tbody>
<tr>
<td>M-H</td>
<td>M-C</td>
</tr>
<tr>
<td>60 kcal/mol</td>
<td>35 kcal/mol</td>
</tr>
<tr>
<td>(\pi)-C=C</td>
<td>C-H</td>
</tr>
<tr>
<td>64</td>
<td>98</td>
</tr>
</tbody>
</table>

\[
\text{124} \quad \text{133}
\]

therefore \(\Delta H^\circ\) is ca. –9 kcal/mol but \(\Delta S^\circ\) is negative

Factors favouring insertion (disfavouring \(\beta\)-H elimination):

- no \(\beta\)-H available
- unstable alkene product (egs. C=Si, Bredt’s rule)
- coordinatively saturated (18 e\textsuperscript{-}): no vacant site for agostic H
- \(d^0\) metal centre: no electron density to donate into C-H \(\sigma^*\)
- inability to achieve a coplanar transition state (see next page)
insertion (and elimination) goes by a **planar 4-centre transition state**:

$$\begin{array}{c}
\text{C} \\
\text{M} \\
\text{H}
\end{array}$$

thus, alkyls that cannot easily achieve coplanarity of the M-C and $\beta$ C-H bond, do not eliminate rapidly:

$$\begin{array}{c}
\text{(Ph}_3\text{P)}_2\text{Pt} \\
\text{Cyclic alkyl}
\end{array} \quad \begin{array}{c}
\text{(Ph}_3\text{P)}_2\text{Pt} \\
\text{Linear alkyl}
\end{array}$$

| rel. elimination rate | 1 | 10,000 |
Ziegler-Natta polymerization of alkenes (a heterogeneous reaction) is the classic example of this reaction:

\[ R' \overset{\text{RCH=CH}_2}{\longrightarrow} R \overset{\text{RCH=CH}_2}{\longrightarrow} \text{high polymer} \]
2. σ-Bond Metathesis

Recognized as a major class of reaction for metal-alkyls in cases where the metal is *incapable* of doing oxidative-addition/reductive elimination sequences:

*for example:*

\[ \text{Cp}_2\text{Zr} - \text{H} \quad \text{M} - \text{R} + \text{H} - \text{H} \quad \text{concerted 4-centre transition state} \quad \text{M} + \text{R} \quad \text{H} - \text{H} \]

Common for *d*⁰ *metals* (Sc³⁺, Ti⁴⁺, Zr⁴⁺, Hf⁴⁺), *f-elements* and some p-block metals, especially Al³⁺ but not believed to be very important with late transition metals that can do redox chemistry (empty orbitals on the metal facilitate σ-bond metathesis)