1,2-insertion / de-insertion

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)

a) alkene and alkyne insertion into M-H bonds
insertion is slightly exothermic:

\[
\text{M-H} + \text{C=C} \rightarrow \text{M-C-C-H}
\]

<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>
<tr>
<td>124</td>
<td>133</td>
</tr>
</tbody>
</table>

therefore \(\Delta H^o\) is ca. \(-9\) kcal/mol but \(\Delta S^o\) is negative
Factors favouring insertion (disfavouring β-H elimination):

- no β-H available
- unstable alkene product (e.g., C=Si, Bredt’s rule)
- coordinatively saturated (18 e-): 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

So, what is the mechanism? Generally agreed that migratory insertion is operative
insertion (and elimination) go by a planar 4-centre transition state:

thus, alkyls that cannot easily achieve coplanarity of the M-C and β C-H bond, do not eliminate rapidly:
The coplanar, 4-centre transition state implies syn elimination and insertion. This requirement therefore dictates the stereochemistry of the alkene product obtained.
Schwartz's reagent allows easy (but stoichiometric) functionalization of alkenes and alkynes by single insertion. Note that this is a $d^0$ metal centre and $\beta$-H elimination is not favourable.
b) alkene insertion into M-C bonds

Mechanism not established with certainly but most evidence suggests the Cossee-Arlman option:

From Hartwig: Organotransition Metal Chemistry
Ziegler-Natta polymerization of alkenes (*a heterogeneous reaction*) is the classic example of this reaction:
• *Homogeneous* versions of the Z-N reaction using \( \text{Cp}_2\text{ZrR}^+ \) as the catalysts are used industrially.

• *Stereochemical* control is possible by careful design of the catalyst structure.
Isotactic polypropylene

Scheme 10.17
A Mechanism for Isotactic Polymerization

From Spessard and Meissler
Syndiotactic polypropylene

Scheme 10.18
Mechanism for Syndiotactic Polymerization
c) alkene insertion into Metal-E bonds (E = O, N, Si)

Insertions into M-O bonds are rare, but known:

WHY?
Hydroamination: insertion into amido M-N bonds
Hydroamination at a late TM centre: competing $\beta$-H elimination and reductive elimination
Insertion of alkene into a M-Si bond is a key step in hydrosilation (aka hydrosilylation)
d) Insertion of other multiple bonds into the M-C bond

Most common examples:

• **Aldehydes** (ketones less so)

• **Imines**
CO₂ insertion: virtually all metal alkyls will do this