Insertion and elimination reactions

Robert H. Crabree: The organometallic chemistry of the transition metals:
Pages: 183 -206 and 235 - 263

1

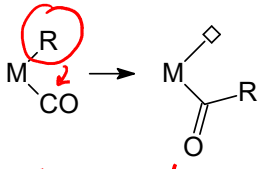
Insertion reactions

Metal center has

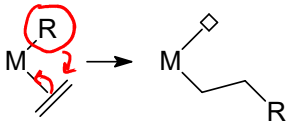
a) a σ-bound group (hydride, alkyl, aryl)

b) a ligand containing a π-system (olefin, alkyne, CO)

→ the σ-bound group can *migrate* to the π-system.



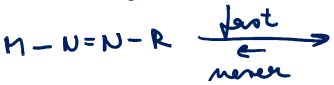
1,1 - insertion

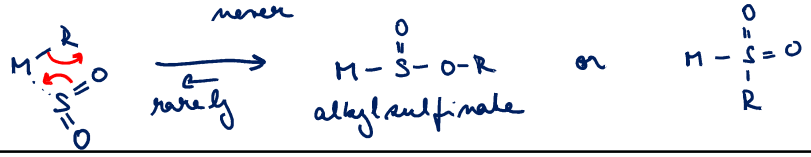


1,2 - insertion

- the ligands need to be in a **cis arrangement**
- 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 principle reversible – but often thermodynamically driven

one-way examples → thermodynamics

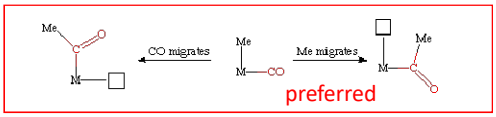


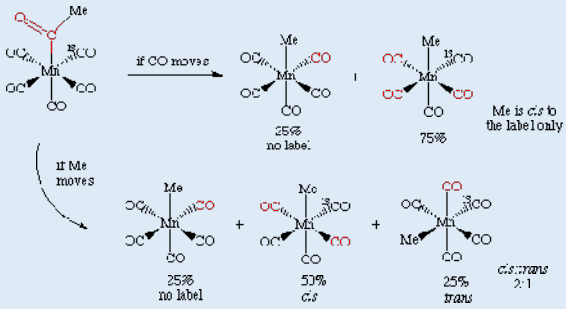


2

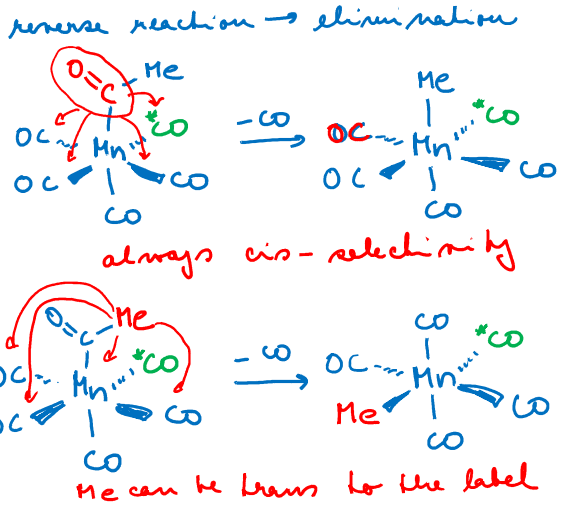
Insertion reactions

- 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 experimental result: cis/trans = 2/1
→ **the methyl group moves**



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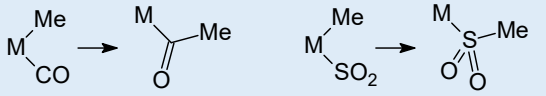
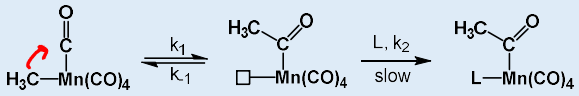
1,1 insertions

- In a 1,1-insertion, metal and X group "move" to the same atom of the inserting substrate
- X = alkyl → retains stereochemistry
- The metal-bound substrate atom increases its valence
- CO, isonitriles (RNC) and SO_2 often undergo 1,1-insertion

- CO insertion
  - 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.





$$Rate = \frac{-d[Reactant]}{dt} = \frac{k_1 k_2 [L][Reactant]}{k_{-1} + k_2 [L]}$$

$k_{-1} << k_2[L]$: $Rate = k_1 [Reactant]$

$k_{-1} >> k_2[L]$: $Rate = \frac{k_1 k_2}{k_{-1}} [L][Reactant]$

$k_{-1} \sim k_2[L]$

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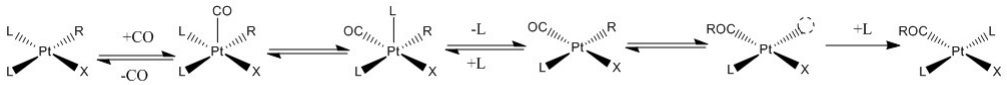
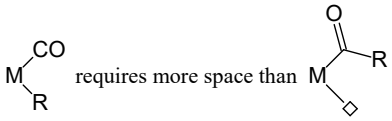
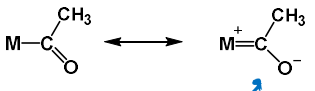
Insertion of CO



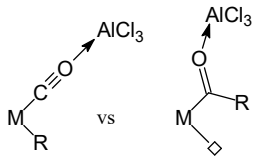
- Enhancing rate of insertion reactions:
  - Bulky ligands



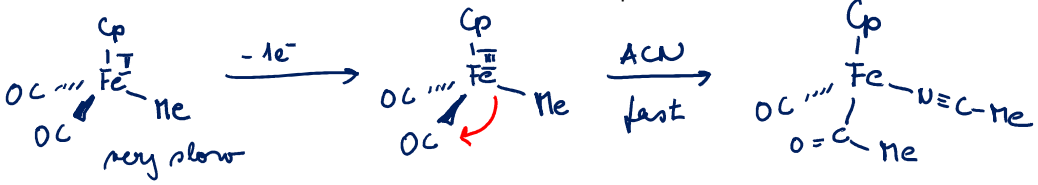
  - Lewis acids ($AlCl_3$, H^+) – can increase rate for reaction with small k_2



stabilization of TS
acceleration up to 10^8



  - Polar solvents → stabilization
  - 1e – oxidation of metal → less back-donation → more electrophilic carbon of CO



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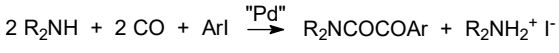
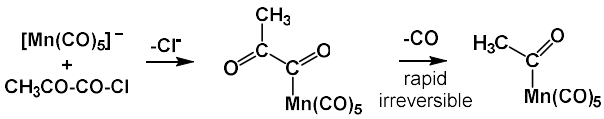
Double CO insertion ?

- Deriving a mechanism from a reaction stoichiometry is not always straightforward
- The following catalytic reaction was reported:

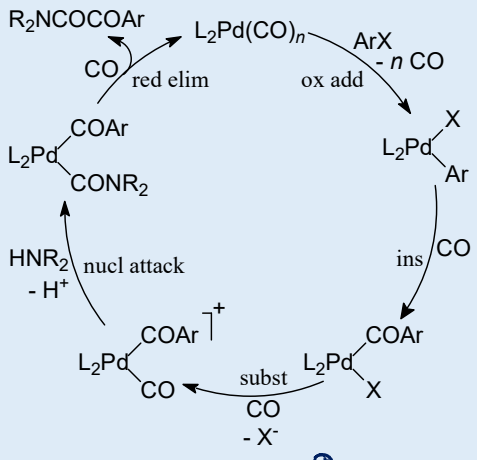


- This looks like it might involve double CO insertion, but:



- The actual mechanism of "double CO insertions" is more complicated
- **M-CO-H** and M-CO-CF_3 also eliminate CO irreversibly

M-H M-CF_3 strong bonds !



BUT : isonitriles $R-\overset{\oplus}{N}\equiv\overset{\ominus}{C}$

$L_nM-C\equiv\overset{\oplus}{N}-R$ → $L_nM-C(=N-R)-R'$

$L_nM\left(C(=NR)\right)_xR'$

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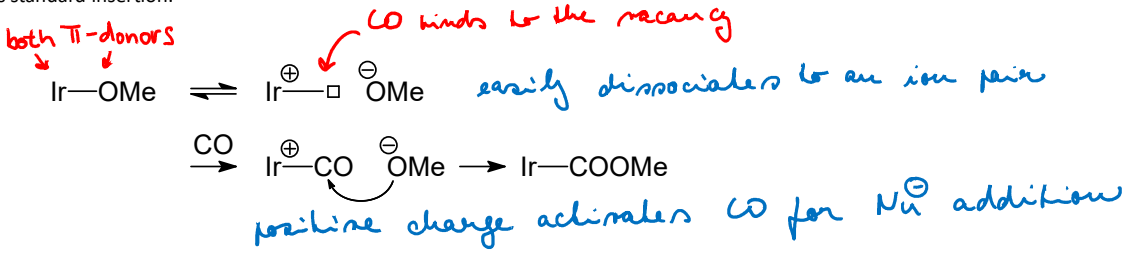
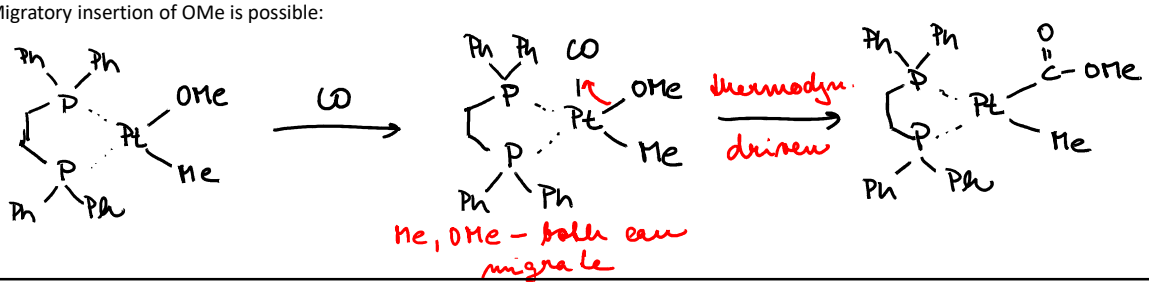
Sometimes it only looks like insertion

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

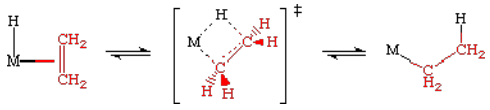


- Main difference: nucleophilic attack does not require an empty site
- Migratory insertion of OMe is possible:



1,2-insertion of olefins

- Insertion of an alkene in a metal-alkyl bond produces a new alkyl (polymerization).
- Opposite to β-elimination
  - Equilibrium – shifted by addition of a ligand, thermodynamics
  - TS – coplanar arrangement – catalyst design



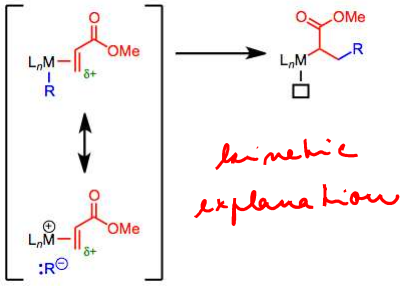
C_2H_4 prefers β-elimination

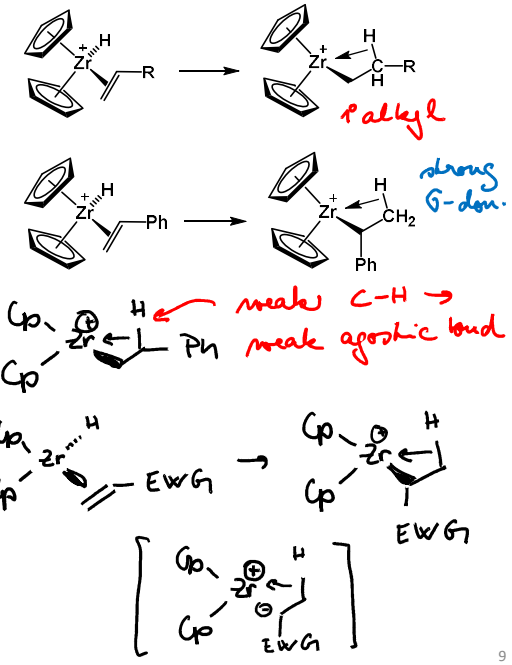
C_2F_4 → strong $M-CF_2$ bond $-CF_2H$

→ does not do β-elimination

Regioselectivity of insertion

- Insertion – reversible process → regioselectivity is driven by stability of the product (sterics)
- Terminal alkenes → 1° alkyls
- Internal alkenes → 2° alkyls – unstable – reverse β-elimination → towards terminal alkenes → 1° alkyls
- Arylalkenes → Metal bound to the benzylic position (in spite of sterics)
- EWG → after insertion - at the α carbon (-CN, -F, -CHO, COOMe)





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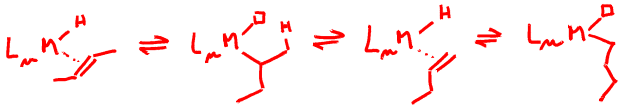
Insertion in M-H bonds

Insertion in M-H bonds is nearly always fast and reversible.

⇒ Hydrides catalyze olefin *isomerization*



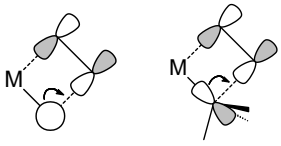
To **shift the equilibrium** to the insertion product:

- 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

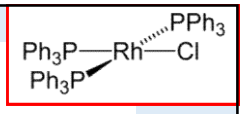
Insertion in M-H bonds is faster than in M-C

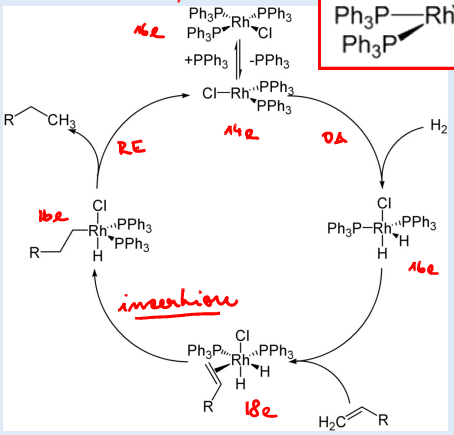
Barrier usually 5-10 kcal/mol lower → Factor 10^5-10^{10} in rate!

Reason: shape of orbitals (*s* vs. sp^3)

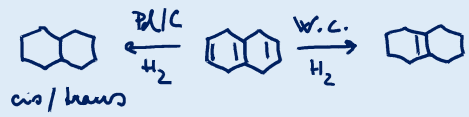


Wilkinson's catalyst:





Rate of hydrogenation:
Monosubstituted > disubst. > trisubst. > tetrasubst. = 0



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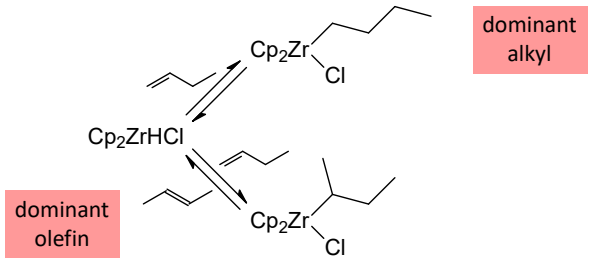
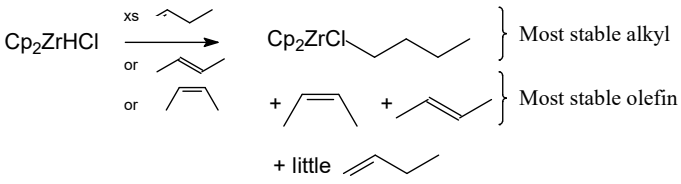
Catalyzed olefin isomerization

- Metals have a preference for primary alkyls.

  But substituted olefins are more stable!

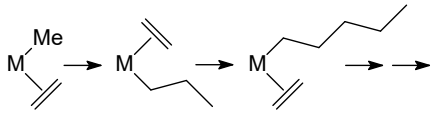


- In isomerization catalysis, the dominant products and the dominant catalytic species often do not correspond to each other

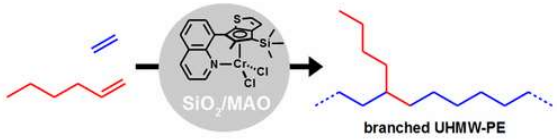


Polymerization

- Insertion of an olefin in a metal-alkyl bond produces a new alkyl
- Thus, the reaction leads to oligomers or polymers of the olefin
- Polyolefins are among the largest-scale chemical products made:
- polyethene (polythene) } 50 millions tons per year
- polypropene
- In addition, there are many specialty polyolefins



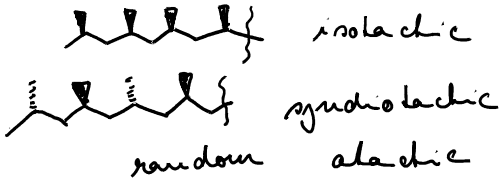
- They are chemically inert
- Their properties can be tuned by the choice of catalyst and co-monomer



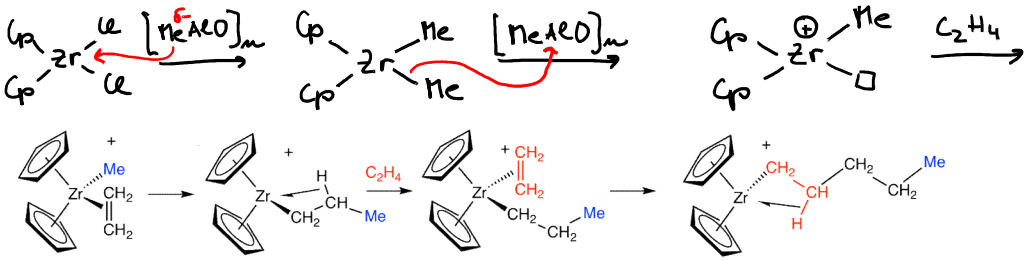
- Applications:
  - Oligomers: surfactants, comonomers
    - High added value, but limited market
  - Polymers: plastics, construction materials, foils and films
    - Very large market, bulk products

Macromolecules 2017, 50, 1, 35-43

Polymerization



- Thermally ~ 200°C, 1000 atm.
- Ziegler-Natta – titanium based catalysis ($TiCl_3$ + Et_2AlCl) → 25°C, 1 atm.
  Less branching
- Better defined catalysts: [LL'MCl_2] (M = Ti, Zr, Hf),
  L – initially Cp → metallocene catalysts Cp_2MCl_2
  → isotactic, syndiotactic polymers
  → softer, tougher, more transparent
  only possible after introduction of metallocene complexes
- Catalysts have to be activated by methylalumoxane (MAO) $[MeAlO]_n$
- Variation of L/L' → control of structure, distribution of chain lengths, physical properties



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Polymerization

Why do olefins polymerize ?

Driving force: conversion of a π-bond into a σ-bond

- One C=C bond: 150 kcal/mol
- Two C-C bonds: 2×85 = 170 kcal/mol
- Energy release: about 20 kcal per mole of monomer (independent of mechanism!)

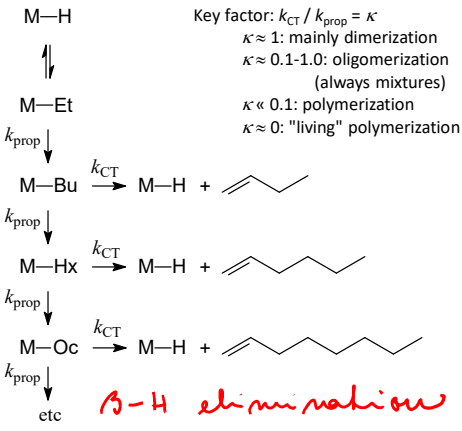
Many polymerization mechanisms

- Radical (ethene, dienes, styrene, acrylates)
- Cationic (styrene, isobutene)
- Anionic (styrene, dienes, acrylates)
- Transition-metal catalyzed (α-olefins, dienes, styrene)

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

Multiple insertion leads to ***di***merization, ***oligo***merization or ***poly***merization

chain termination / propagation



Key factor: $k_{CT} / k_{prop} = \kappa$
$\kappa \approx 1$: mainly dimerization
$\kappa \approx 0.1$-1.0: oligomerization (always mixtures)
$\kappa \ll 0.1$: polymerization
$\kappa \approx 0$: "living" polymerization

β-H elimination

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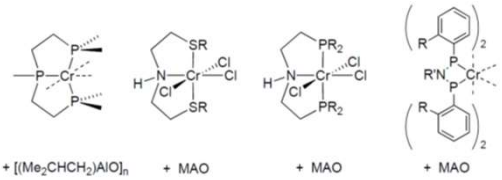
Selective synthesis of trimers etc. ?

- 1-Hexene and 1-octene are valuable co-monomers.
- Selective synthesis of 1-hexene from ethene is not possible using the standard insertion/elimination mechanism.
- There are a few catalysts that selectively trimerize ethene via a different mechanism ("metallacycle" mechanism).
  - Redox-active metals (Ti, V, Cr, Ta) required
  - Cr systems are used commercially



- There are also one or two catalysts that preferentially produce 1-octene. The mechanism has not been firmly established.

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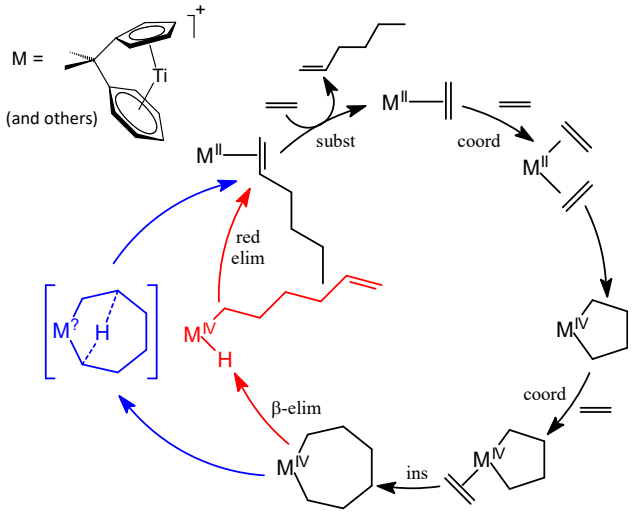
Trimerization via metallacycles



Key issues:

- Geometrical constraints prevent β-elimination in metallacyclopentane.
- Formation of 9-membered rings unfavourable.
- Ligand helps balance (*n*) and (*n*+2) oxidation states.

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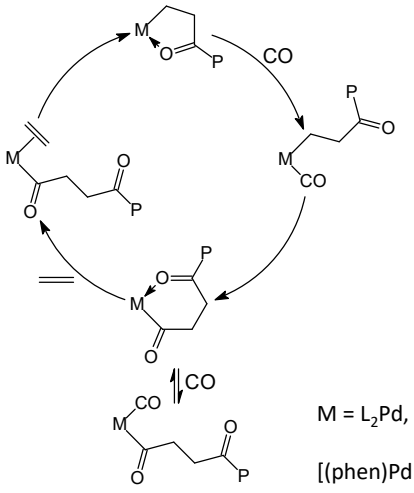
CO/olefin copolymerization

- CO cheaper than ethene
- Copolymer more polar than polyethene
  - ***much*** higher melting point
- Chemically less inert

- No double CO insertion (uphill)
- No double olefin insertion
  CO binds more strongly, inserts more quickly
- Slow β-elimination from alkyl
  5-membered ring hinders elimination



M = L_2Pd, L_2Ni

$[(phen)PdMe(CO)]^+$

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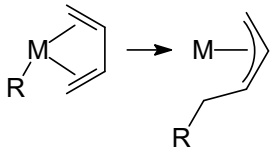
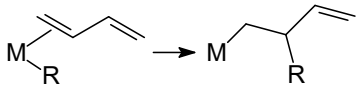
Insertion of longer conjugated systems

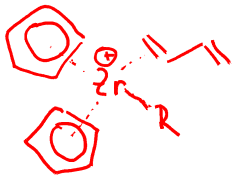
Attack on an η^4-polyene is always at a terminal carbon
⇒ Usually α,ω-insertion



A diene can be η^2 bound
⇒ 1,2-insertion



Metallocenes often do not have enough space for η^4 coordination:



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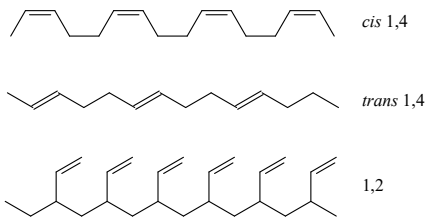
Diene rubbers

- Butadiene could form three different "ideal" polymers:



- In practice one obtains an imperfect polymer containing all possible insertion modes
- Product composition can be tuned by catalyst variation
- Polymer either used as such or (often) after cross-linking and hydrogenation

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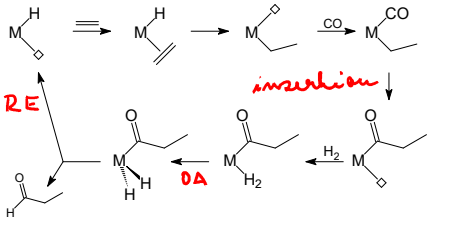
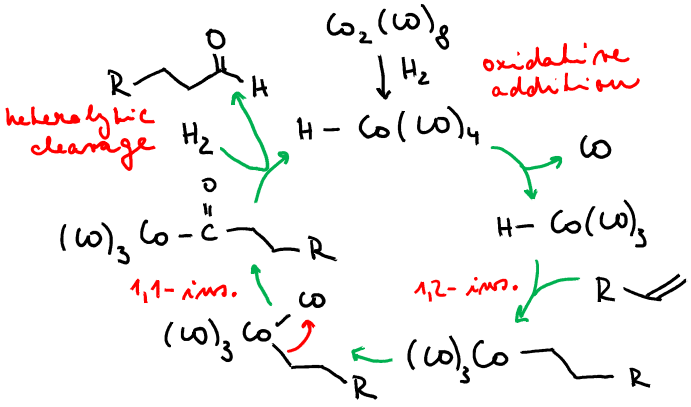
Hydroformylation

- Used to make long-chain alcohols and acids from 1-alkenes
  - Often in situ reduction of aldehydes to alcohols
  - Unwanted side reaction: hydrogenation of olefin to alkane
- Main issue: linear vs branched aldehyde formation

  It is possible to make linear aldehydes from internal olefins !

→ use bulky ligands
→ larger selectivity for 1° aldehydes
→ much more reactive
eg. $[(PPh_3)RhH(CO)]$
even better $P(n\text{-}Bu)_3$





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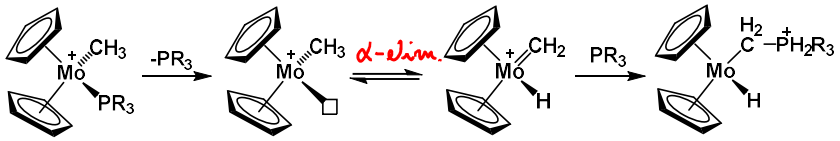
Elimination reactions

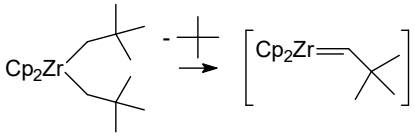
β-elimination:

Previous lectures

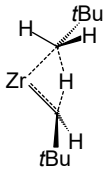
α-elimination

- Lack of β-hydrogens
- α-elimination can by up to 10^6 faster than β-elimination
- Methylene hydride complexes rarely seen, because methyl complexes are thermodynamically preferred
- Methylene intermediate can be trapped by nucleophilic addition or by removing hydride by reductive elimination with a second alkyl





Reductive elimination
(probably via σ-bond metathesis):



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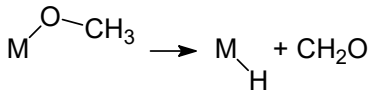
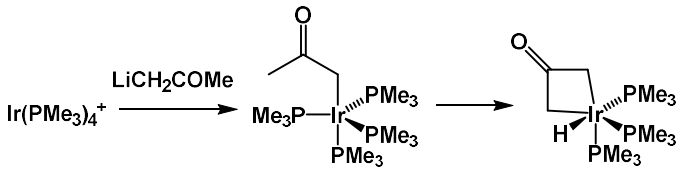
Less common elimination reactions

- β-elimination from alkoxides of ***late*** transition metals is easy:

  The hydride often decomposes to H^+ and reduced metal: alcohols easily ***reduce*** late transition metals



- γ, δ - eliminations (if no β-hydrogen)



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What did you learn today?

- Insertion reactions are usually reversible
- The X ligand migrates to the π ligand (migratory insertion)
- 1,1-Insertion reactions occur for η^1 ligands such as CO (details on CO insertion)
- 1,2-Insertion reactions occur for η^2 ligands such as ethylene (details such as regioselectivity, olefin isomerizations, hydrogenation)
- Insertions are kinetically favored for X = H over X = alkyl

  Exception: CO insertion into M-H bond is thermodynamically disfavored
- Polymerization, trimerization, hydroformylation
- Elimination reactions – α, β, γ, δ
  - end the polymerization and similar reactions,
  - preparation of metal hydrides, metal carbenes

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