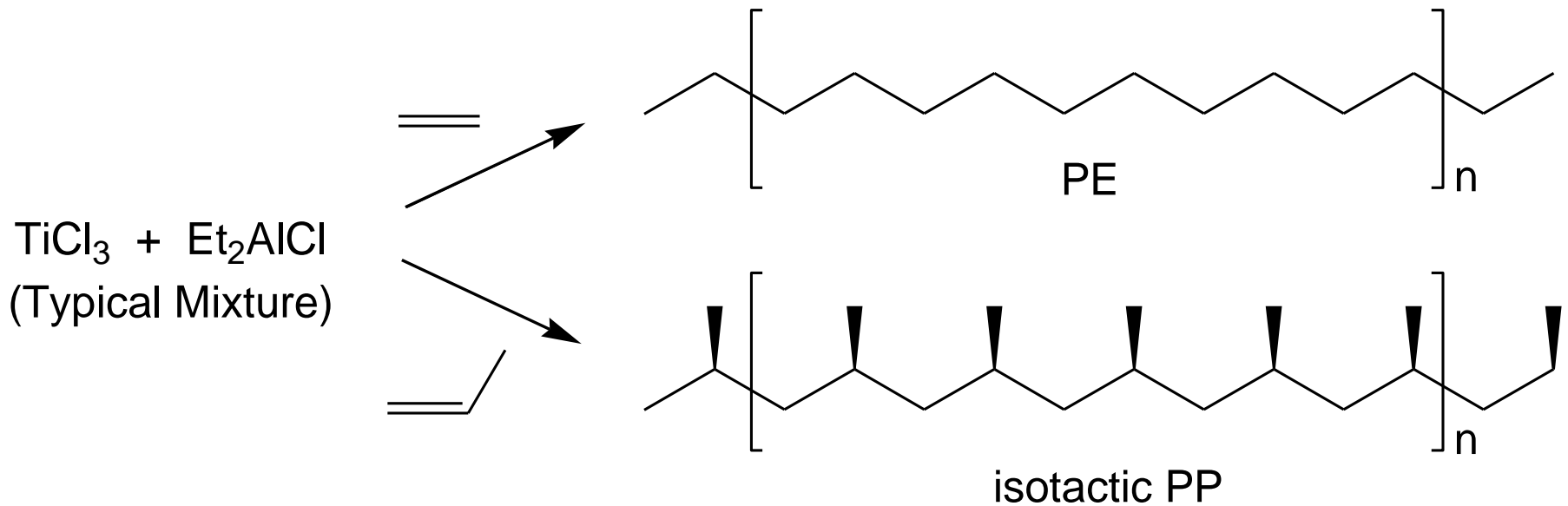


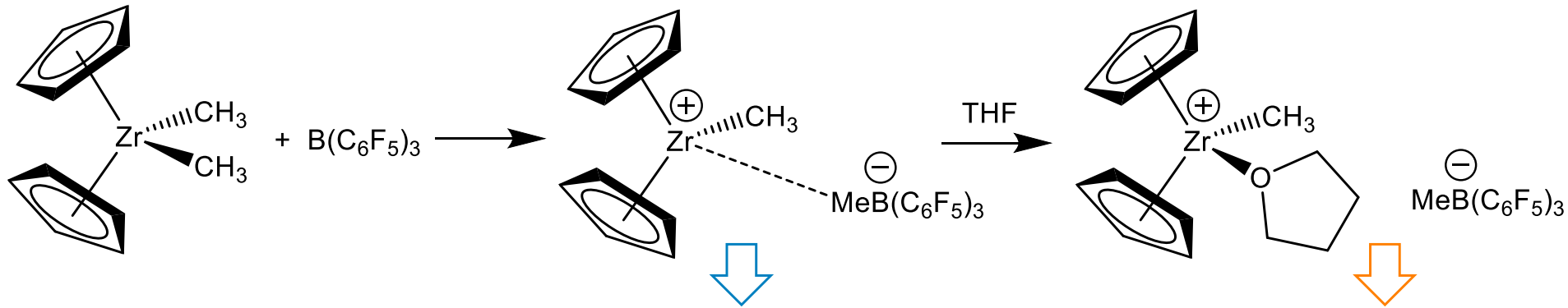
Alkene Polymerization – HETEROGENEOUS Ziegler-Natta

- Ziegler and Natta discovered Heterogeneous Ethylene Polymerization in 1955
- Nobel prize in 1963



- Used to make 15 million tonnes of PE and PP each year.
- Multisite Catalysts → broad molecular weight distribution
→ non-uniform polymer properties
- Complicated Chemistry → Active site still not understood
→ Catalyst tuning difficult

Alkene Polymerization – HOMOGENEOUS SYSTEMS



$M_w = 290 \text{ kg mol}^{-1}$ ($n \sim 10^4$)
Activity = $1500 \text{ kg PE g}^{-1} \text{ catalyst h}^{-1}$
(at 60°C , 10 atm C_2H_4 , pentane solvent)

Poor Catalyst -
Electrophilic 'vacant site' is
key in metallocene reactivity

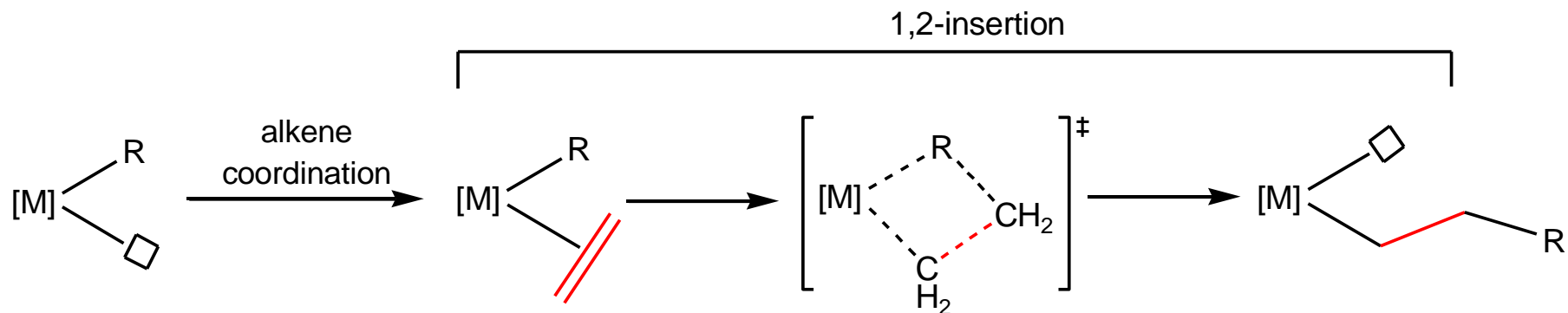
- Used to make several million tonnes of PE and PP each year
- Generally higher activities than with heterogeneous system
- Easier to probe mechanism → understand, improve
- For α -olefins, can control polymer microstructure by varying the ligands (this dictates polymer properties such as toughness, melting point, crystallinity, elastomeric, thermoplastic or optical properties, processability etc.)

Mechanism for Olefin Polymerization

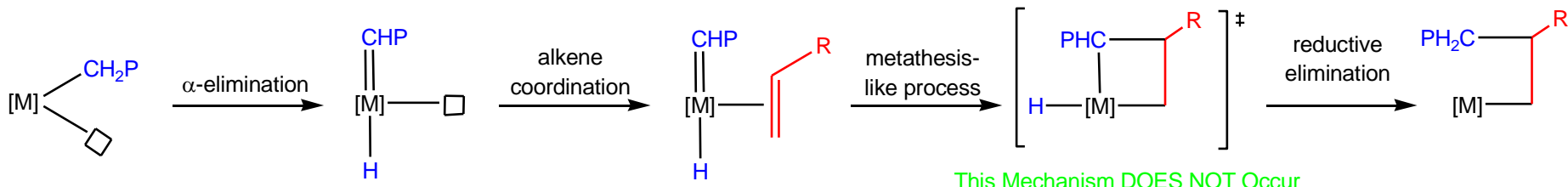
Chain Propagation

Cossee-Arlman Mechanism = good basic mechanism.

Cossee *et al.*, *J. Catal.*, **1964**, 3, 80 and 99.



Green-Rooney Mechanism involving metathesis-like step = totally wrong !

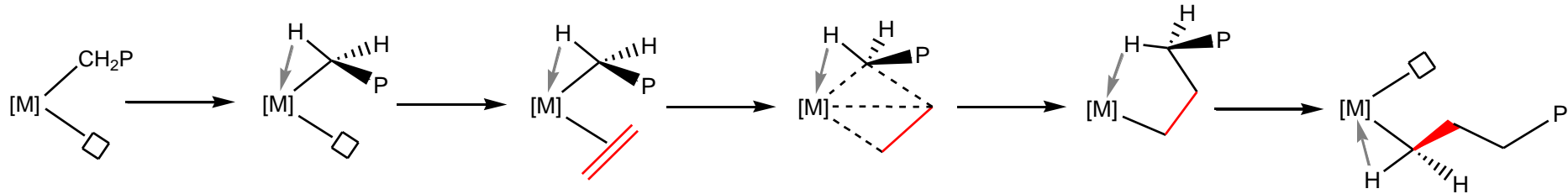


- Proposed by Green, Rooney *et al.*, *J. Chem. Soc., Chem. Commun.*, **1978**, 604. Refuted convincingly by Grubbs *et al.*, *J. Am. Chem. Soc.*, **1985**, 3377.

Mechanism for Olefin Polymerization

Brookhart-Green Mechanism = an improvement on the Cossee-Arlman mechanism → it includes an α -agostic interaction which helps to facilitate 1,2-insertion.

Brookhart *et al.*, *J. Organomet. Chem.*, **1983**, 250, 395.

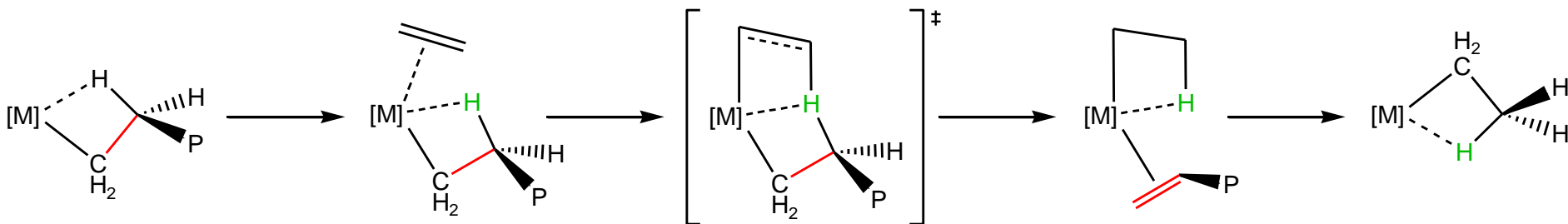


- Supporting calculations: Ziegler *et al.*, *Organometallics*, **2004**, 104.
- Supporting experiments: Brintzinger *et al.*, *Angew. Chem., Int. Ed.*, **1990**, 1412 (Zr), Piers and Bercaw, *J. Am. Chem. Soc.*, **1990**, 9406.

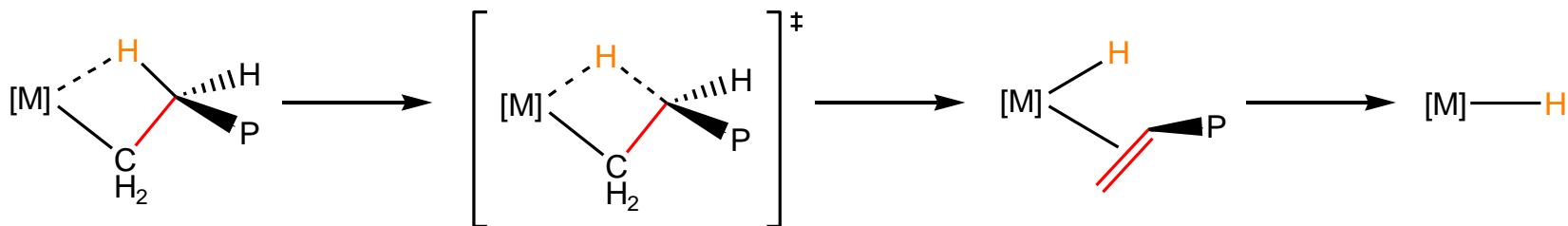
Mechanism for Olefin Polymerization

Chain Termination

β -Hydrogen Transfer: H⁻ transferred from the growing polymer chain to an incoming olefin. This is the dominant chain termination mechanism under the usual experimental conditions. Ziegler *et al.*, *J. Am. Chem. Soc.*, **1999**, 154.



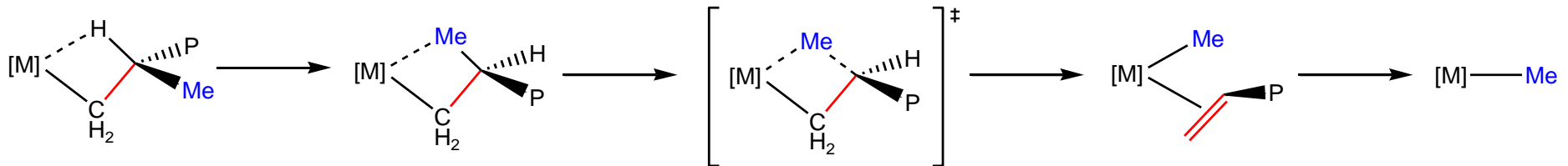
β -Hydrogen Elimination - β -hydrogen transferred to the metal. *ibid.*



Mechanism for Olefin Polymerization

β -Methyl Elimination - only occurs in special cases.

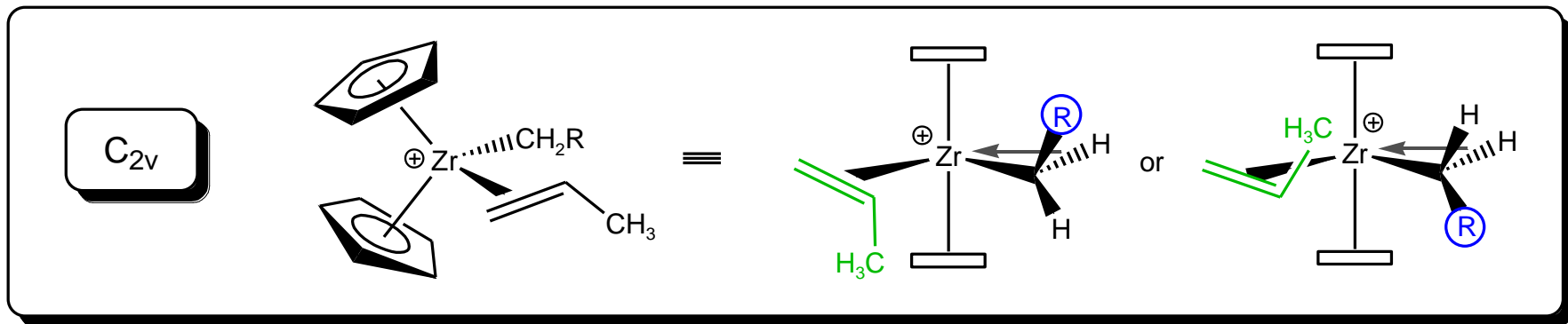
Bercaw *et al.*, *Organometallics*, **1994**, 1147 (Sc), Jordan *et al.*, *Organometallics*, **1994**, 1424 (Hf), Resconi *et al.*, *Organometallics*, **1996**, 5046 (Zr), Resconi *et al.*, *Organometallics*, **1992**, 1025 (Zr, Hf).



Chain transfer to aluminium - MAO usually contains leftover AlR_3 - chain transfer to Al is more common at lower alkene monomer concentration.

Resconi *et al.*, *Macromolecules*, **1990**, 4489, Naga *et al.*, *Polymer*, **1998**, 5059.

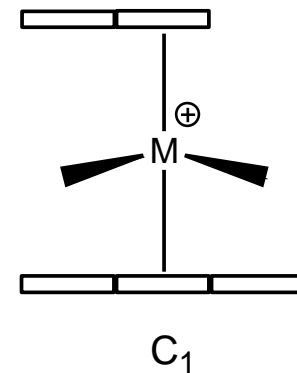
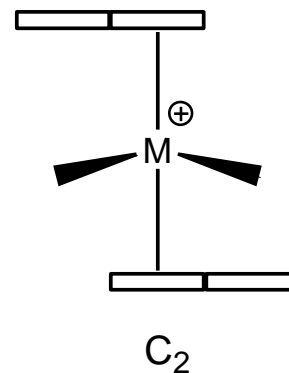
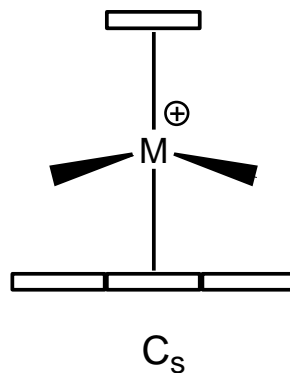
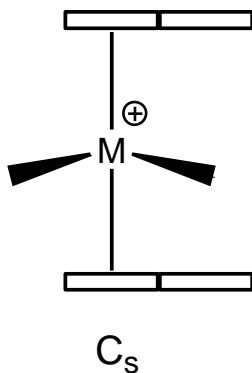
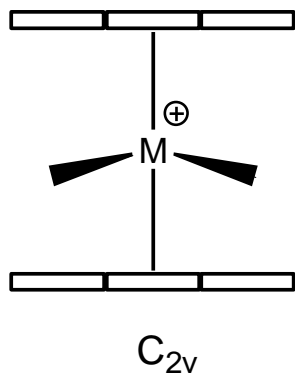
Atactic Polymerization of Propene



Background:

1) Assigning the symmetry of olefin polymerization catalysts

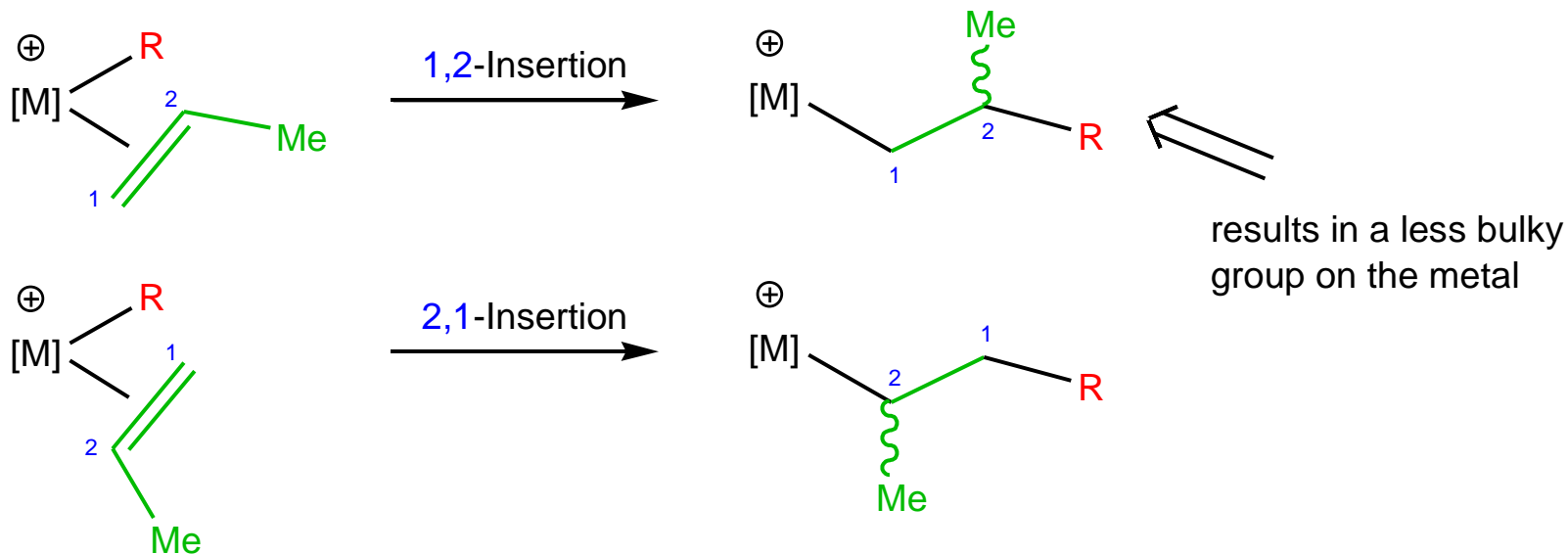
- Assign the symmetry just by considering the metal and the cyclopentadienyl ligand (C_{2v} , C_2 , C_s , C_1 are the most common – see below). Don't worry about the other groups since we are only concerned with the symmetry that the complex presents to the alkyl and alkene group, and these groups swap sides after each insertion.



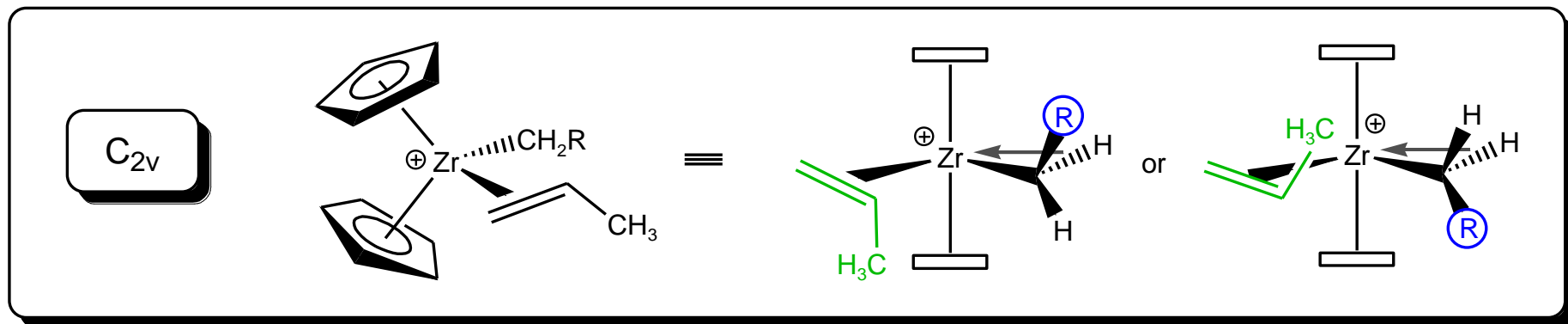
Atactic Polymerization of Propene

2) 1,2-Insertion versus 2,1-Insertion

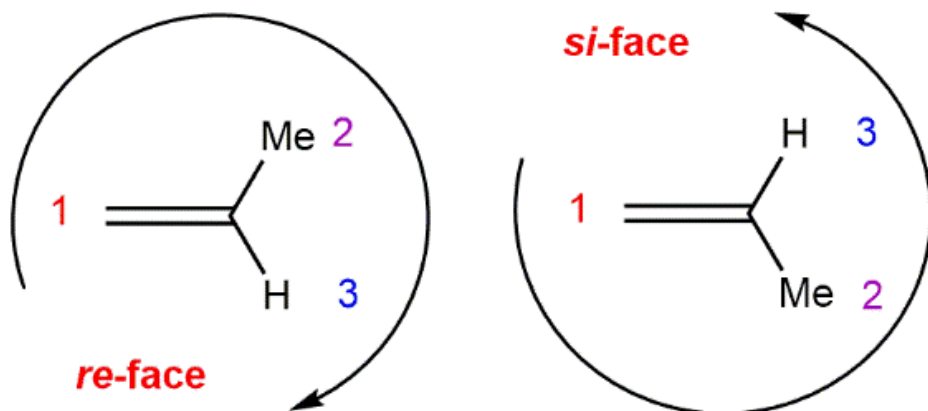
With early transition metal complexes, insertion generally occurs in a 1,2-fashion. Catalysts that produce regular poly(α -alkenes) are designed in order to maximize 1,2-insertion relative to 2,1-insertion (generally reaches approximately 100%):



Atactic Polymerization of Propene



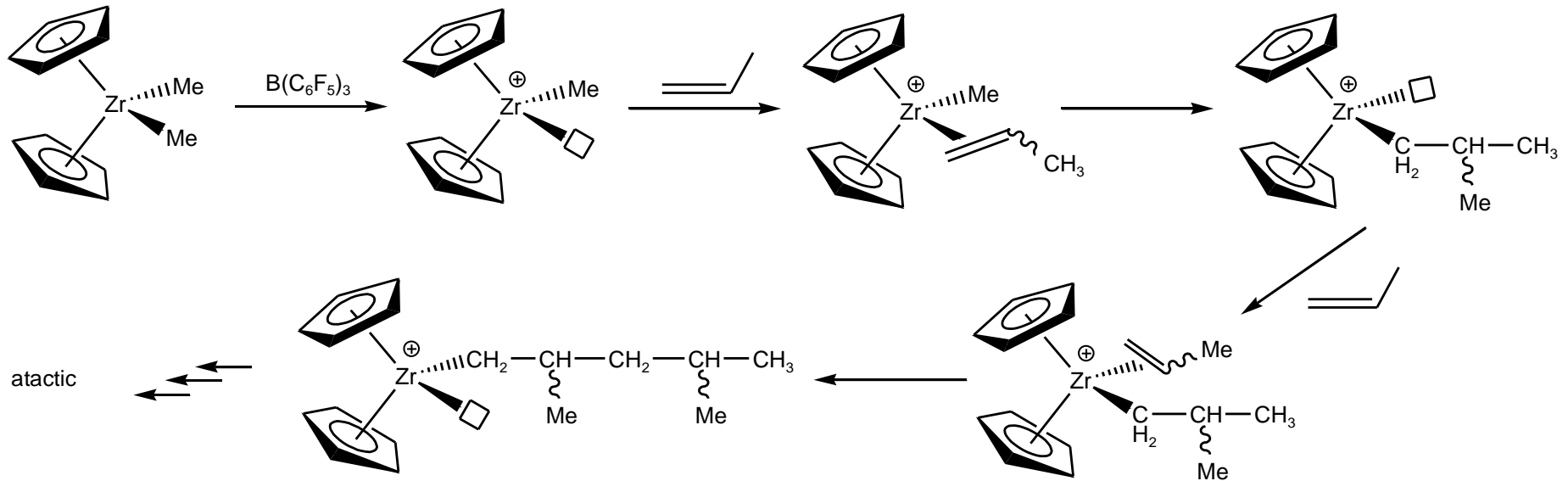
- agostic interaction locks the growing polymer chain in position.
- however, the polymer chain (R) doesn't care if it is up or down, and more importantly, neither does the methyl group of propene: it binds *via* either the *re*- or *si*-face.



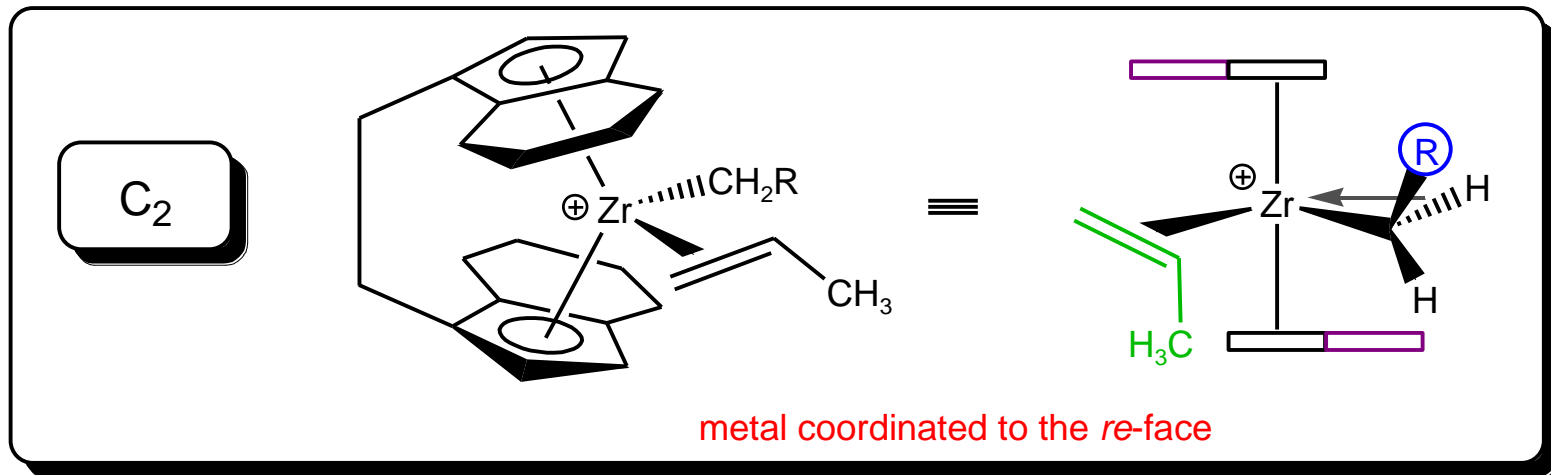
IMPORTANT: When establishing if increasing priority flows clockwise (*re*) or counterclockwise (*si*), remember it is from the metal's perspective. In other words, pretend you are the metal looking at the bound propylene.

Atactic Polymerization of Propene

- The only real preference is for the growing chain and the methyl group to be as far away from each other as possible (they prefer to occupy opposite quadrants).
- This indifference of the alkene to bind *via* either the *re*- or the *si*-face (irrespective of which side of the complex the alkene is bonded) leads to atactic polypropylene.

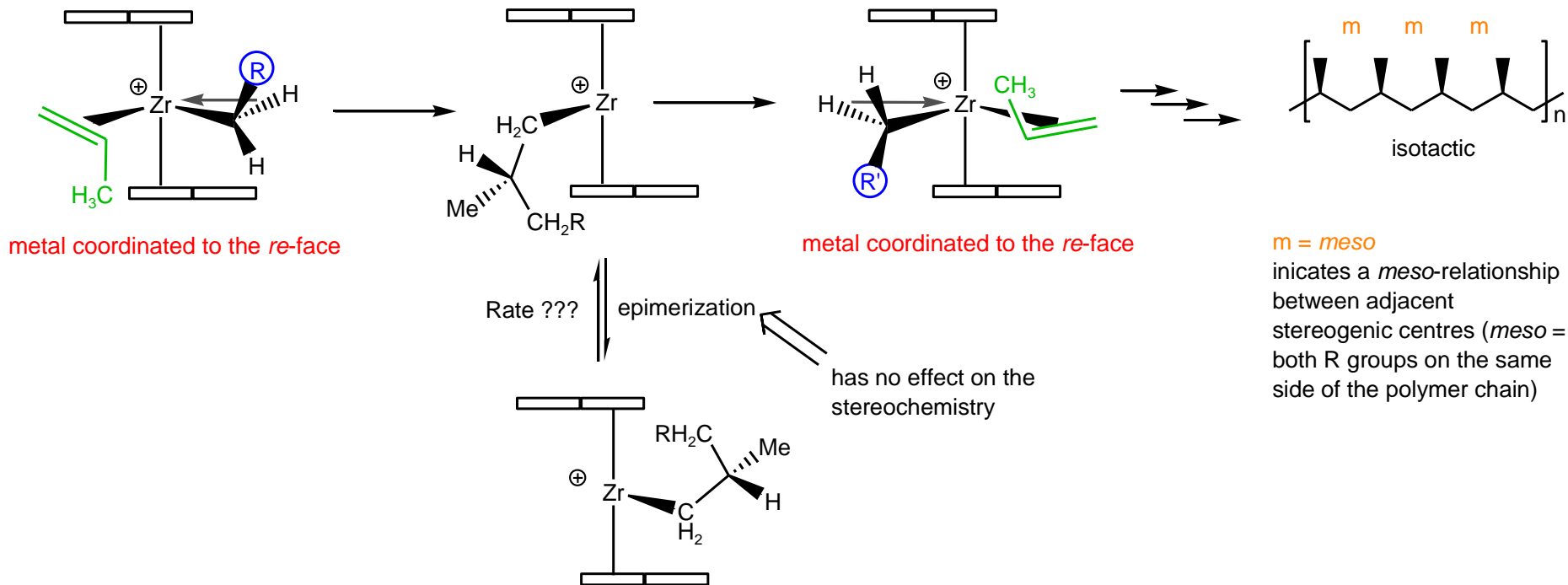


Isotactic Polymerization of Propene

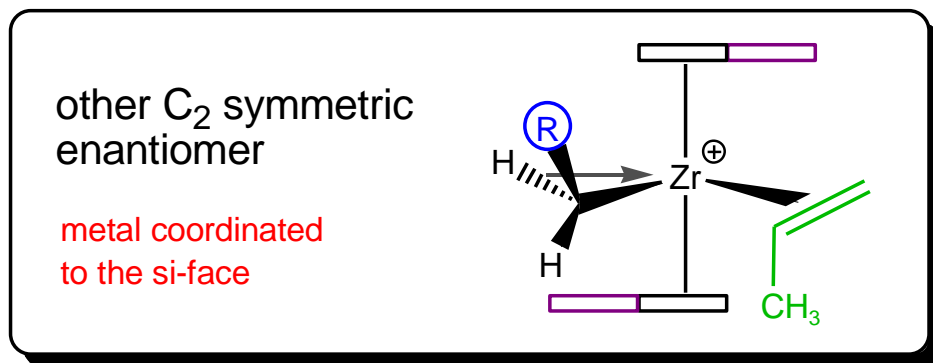


- Agostic interaction locks the growing polymer chain in position (growing chain oriented in order to minimize unfavourable steric interactions with the ligand).
- In the drawing above, the polymer chain wants to occupy the top right quadrant, and the methyl group of propene wants to occupy the bottom left quadrant.
- In this arrangement, the growing polymer chain and the methyl group of propene are also as far apart as possible. Very important → only decently isotactic once $R \neq H$.
- Irrespective of which side of the metallocene propene is bound, it binds *via* the *re*-face. This results in isotactic polypropylene.

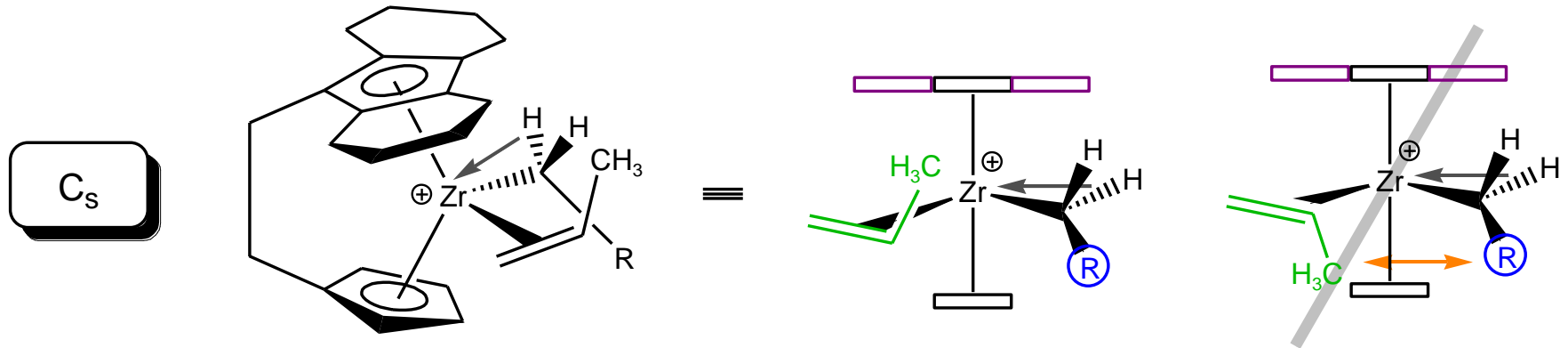
Isotactic Polymerization of Propene



- For the other C_2 -symmetric enantiomer, the alkene will bind only *via* the *si*-face, also resulting in isotactic polypropylene. Therefore, the two enantiomers of the C_2 -symmetric catalyst do not have to be resolved.

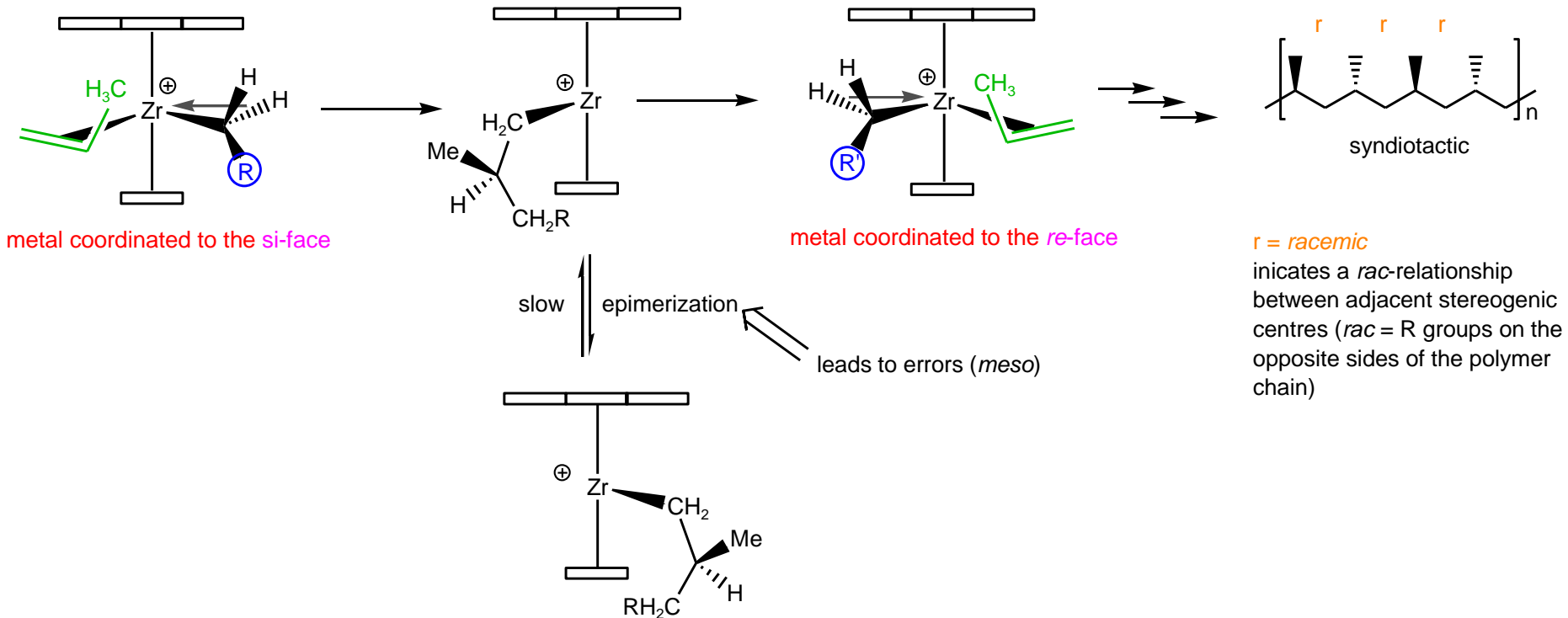


Syndiotactic Polymerization of Propene



- In the drawing above, the polymer chain occupies the bottom right quadrant.
- The methyl group of propene occupies top left quadrant – two competing influences:
 - (1) desire to avoid the growing polymer chain
 - (2) desire to avoid the more bulky fluorenyl group. The first influence is more powerful.

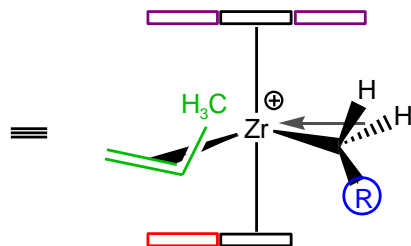
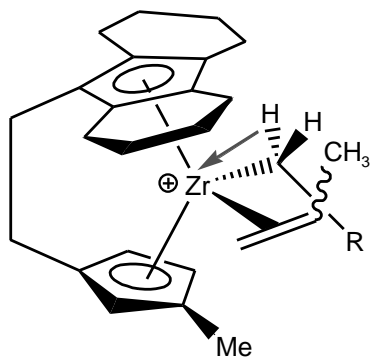
Syndiotactic Polymerization of Propene



▪ In the preparation of atactic or isotactic polypropylene, chain epimerization (the chain alkyl group moving from one side of the complex to the other without insertion occurring) does not result in errors. For the atactic case, the polymer is random anyway. For isotactic polypropylene formation, the alkene binds *via* the same face irrespective of which side of the complex it is bonded to.

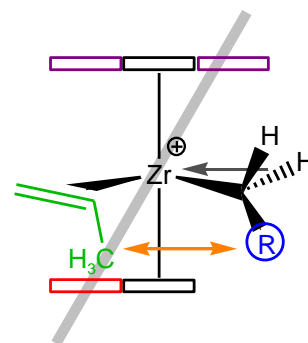
▪ By contrast, in the formation of syndiotactic PP, chain epimerization results in stereoerrors. Instead of strict alternation between binding to the *re*- and *si*-face, the alkene bonds to the same face twice, resulting in a *meso* placement, rather than *rac*.

Hemioisotactic Polymerization of Propene



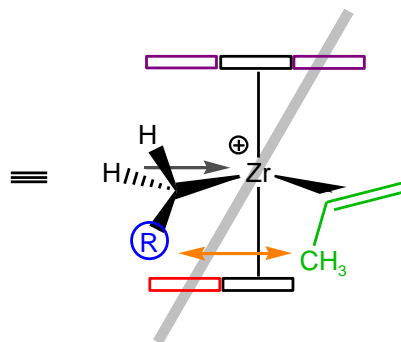
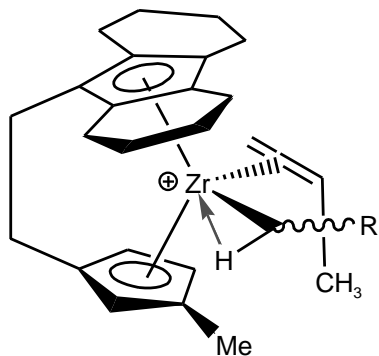
alkene binds exclusively through the *si*-face

or



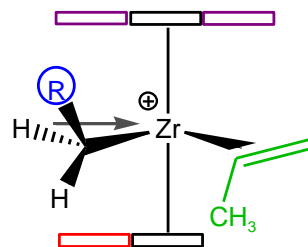
isospecific

C₁

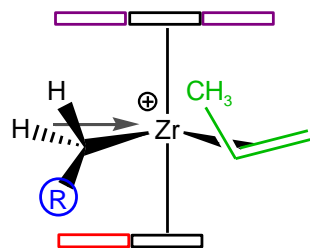


alkene binds through the *si*-face

or

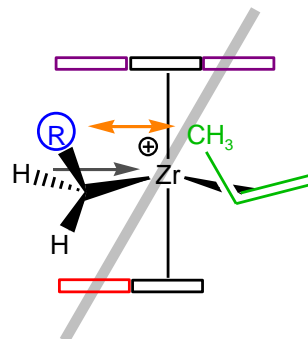


aspecific



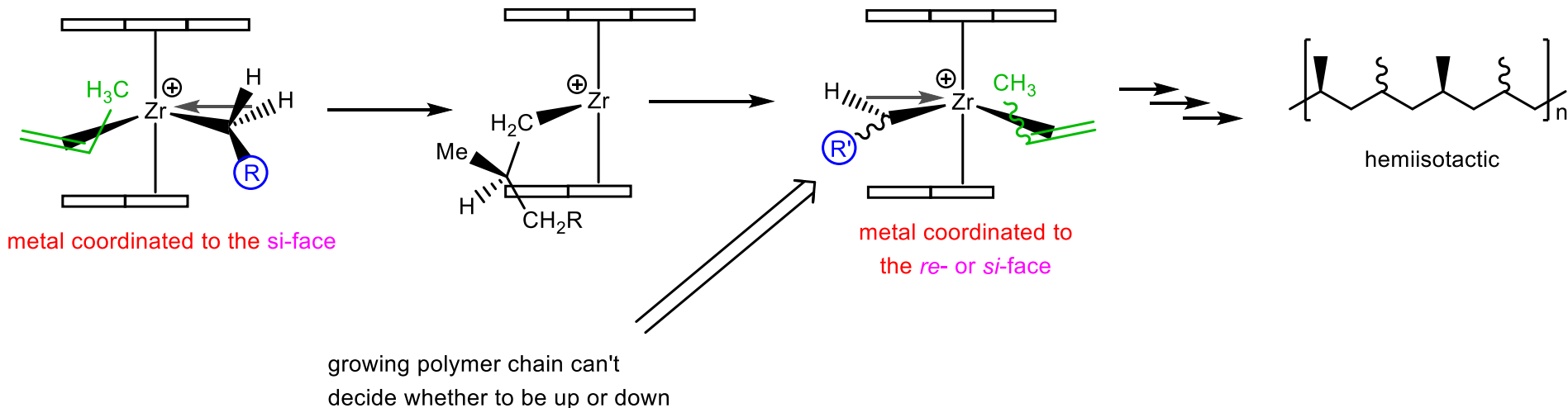
alkene binds through the *re*-face

or



Hemioisotactic Polymerization of Propene

- For the C_1 -symmetric catalyst drawn above, both sides of the complex are different:
 - When bonded to the right hand side of the complex, the polymer chain occupies the bottom right quadrant. In order to minimize unfavourable steric interactions with the growing polymer chain, the alkene bonds to the left hand side of the complex by its *si*-face \rightarrow isospecific monomer placement.
 - When bonded to the left hand side of the complex, the polymer chain can't decide whether to point up or down. As a result, the alkene bonds to the right hand side by either the *si*- or the *re*-face \rightarrow aspecific monomer placement.
 - The overall result is isospecific monomer placements separated by units of random stereochemistry.

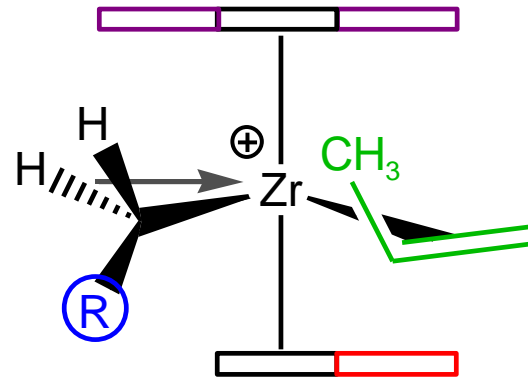


Hemiisotactic Polymerization of Propene

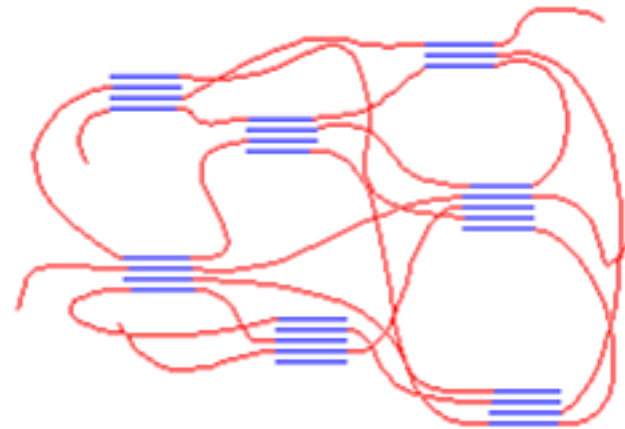
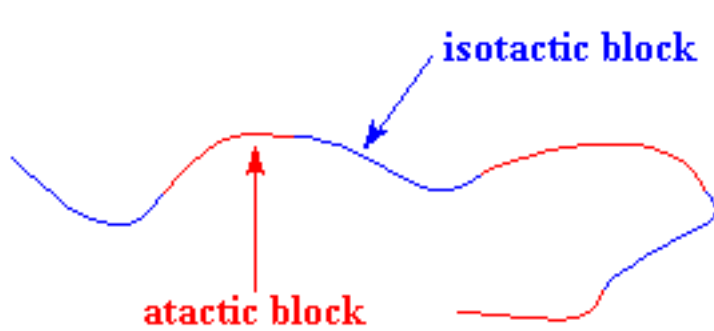
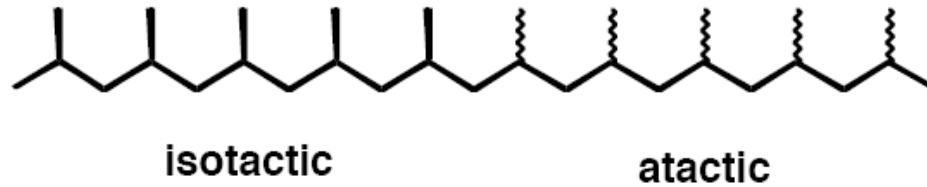
- For the other C_1 -symmetric enantiomer, the alkene will bind only *via* the *re*-face on one side of the catalyst, and by either the *re*- or *si*-face on the other. This also results in hemiisotactic polypropylene. Therefore, the two enantiomers of the C_1 -symmetric catalyst do not have to be resolved.

other C_1 symmetric enantiomer

metal coordinated to the *re*-face of the alkene (while the growing polymer chain is in the least sterically hindered position)

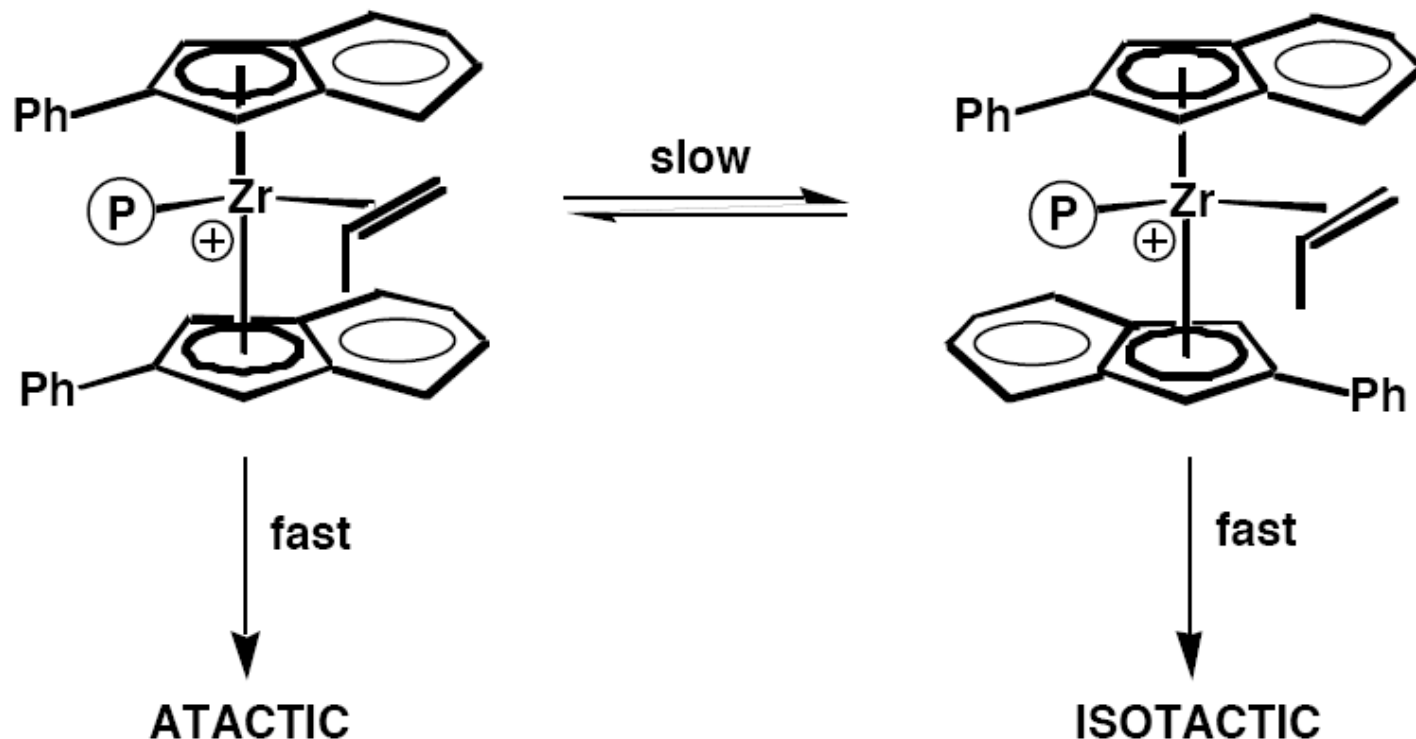


Atactic-Isotactic Block Polypropylene



Atactic-Isotactic Block Polypropylene

No tether:



- Initial papers : Coates, Waymouth *et al.*, *Science*, **1995**, 267, 217.
Coates, Waymouth *et al.*, *JACS*, **1995**, 11586.
- Alternative mechanism : Busico *et al.*, *JACS*, **2003**, 5451.

Polypropylene properties

- Also dependent on M_w , polydispersity, amount of errors *etc.*

General - PP generally has higher T_m , better stiffness and higher tensile strength than PE.

Atactic - elastomeric (rubbery)

Isotactic - highly crystalline, $T_m = 125-160$ °C

- Can be a wax if low M_w ($10-70$ kg mol⁻¹), or a very hard polymer if high M_w .

Syndiotactic - lower density and lower T_m than isotactic PP.

- higher clarity than isotactic PP due to smaller crystal size (better for optical applications)
- quite porous to gases (no good for food packaging)
- medical applications

Atactic-Isotactic Block - a thermoplastic elastomer (rubbery and strong, but recyclable since it can be melted)

Hemiisotactic - ???

Catalyst Structure/Polymer Microstructure Summary

Symmetry

Sites

Polymer

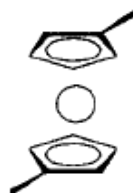
C_{2v}
Achiral



A, A
Homotopic

Atactic

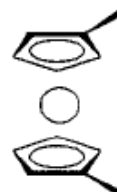
C_2
Chiral



E, E
Homotopic

Isotactic

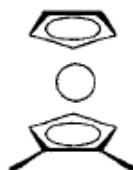
C_s
Achiral



A, A
Diastereotopic

Atactic

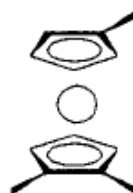
C_s
Prochiral



E, -E
Enantiotopic

Syndiotactic

C_1
Chiral



E, A
Diastereotopic

Hemi-isotactic

^a E = enantioselective site; A = nonselective site.