

# STEREOCONTROLLED POLYMERIZATION

## Asymmetric polymerization

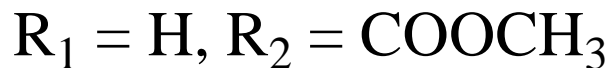
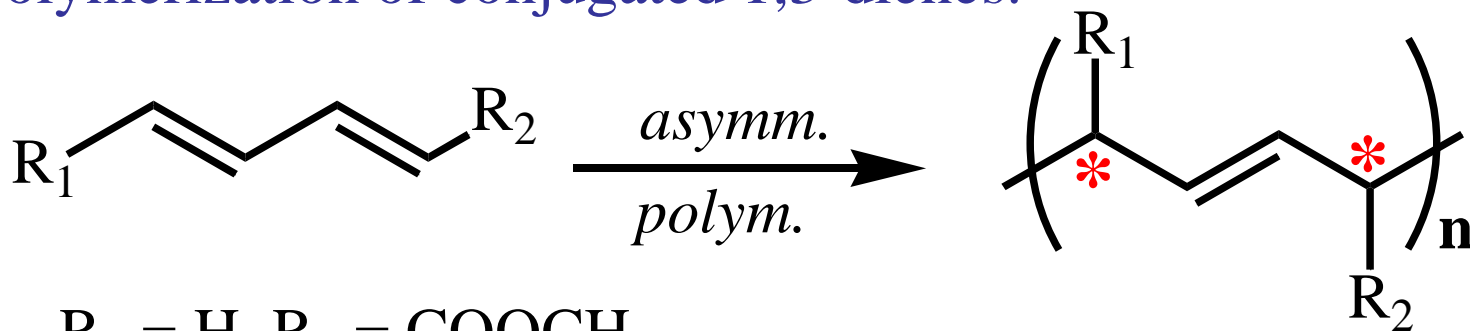
*Polymerization via asymmetric synthesis*

A *prochiral* monomer is polymerized to obtain a stereoregular polymer. During the polymerization process, the coordination of the incoming monomer on the catalyst takes place in a selective fashion through *only one enantiotopic face*.

*Examples:*

Polymerization of vinylic monomers, such as propylene, styrene.

Polymerization of conjugated 1,3-dienes.



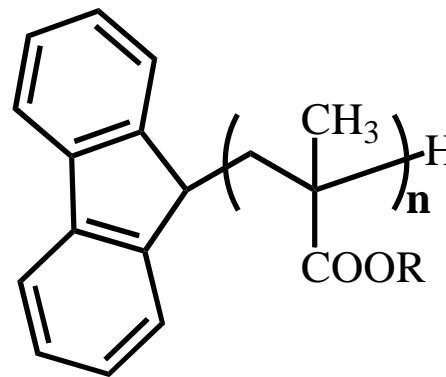
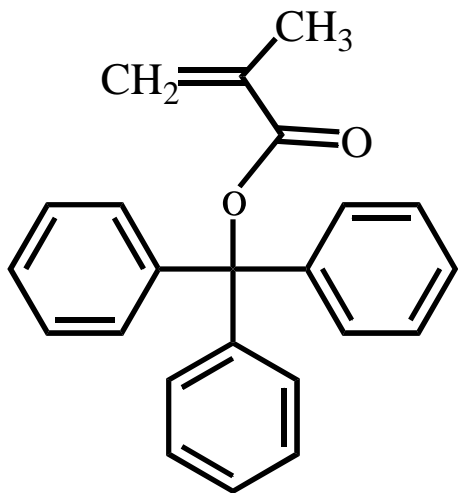
# Asymmetric polymerization

*Polymerization  
selective for the helical  
sense*

The chirality of the synthesized polymers is based on the *helical conformation*, that is right handed or left handed. The polymers are optically active.

Only one chain with a *preferential conformation* is synthesized.

*Examples:*



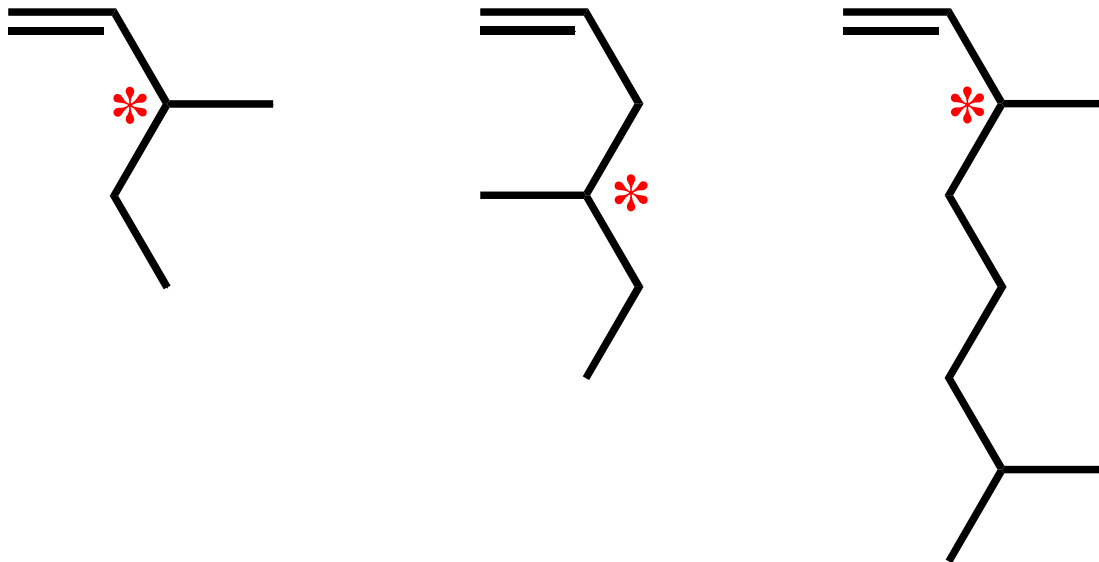
# Asymmetric polymerization

*Stereoselective  
polymerization*

A *chiral racemic monomer* is used. Only *one enantiomer* of the chiral racemic monomer is preferentially polymerized to yield an optically active polymer.

It is a *kinetic optical resolution* of a racemic monomer.

*Examples:*



# STEREOCONTROLLED POLYMERIZATION

## Asymmetric polymerization

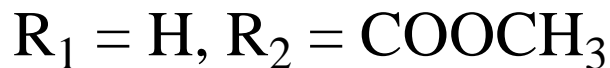
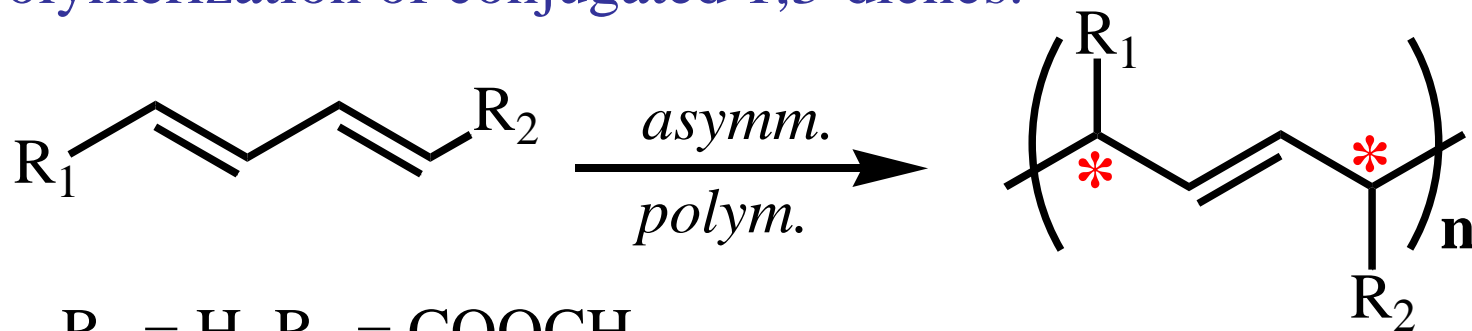
*Polymerization via asymmetric synthesis*

A *prochiral* monomer is polymerized to obtain a stereoregular polymer. During the polymerization process, the coordination of the incoming monomer on the catalyst takes place in a selective fashion through *only one enantiotopic face*.

*Examples:*

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Polymerization of conjugated 1,3-dienes.



# Polypropylene synthesis

***Stereocontrolled polymerization:***

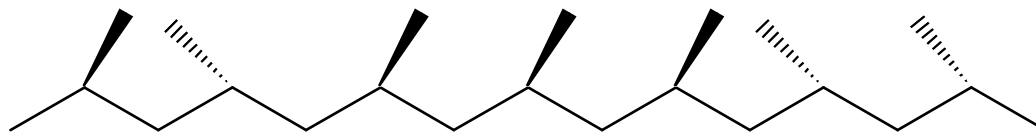
***Control of stereochemistry via the nature of the ancillary ligands on the metal centre.***



**Multiple insertions of the **same** enantioface:**  
***isotactic polymer***

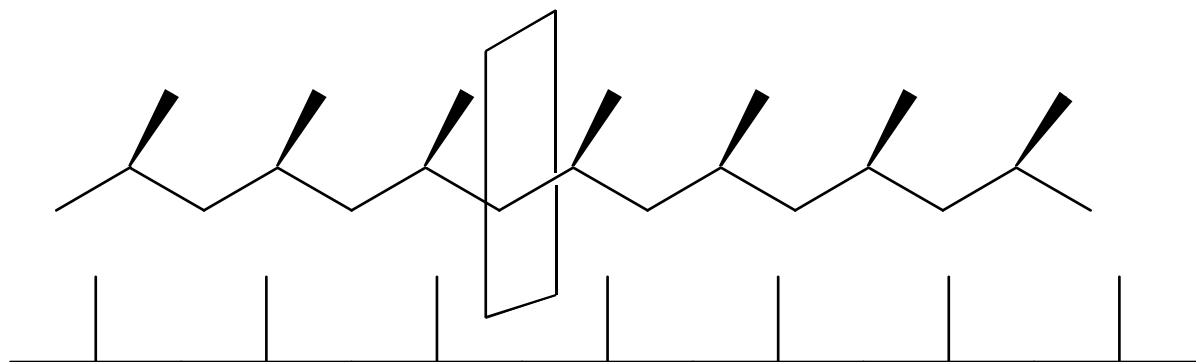


**Multiple insertions of the **alternating** enantiofaces:**  
***syndiotactic polymer***

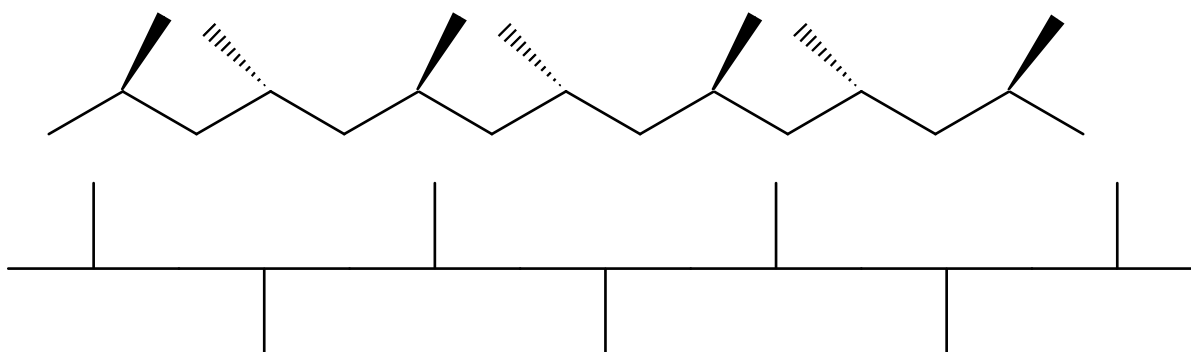


**Random enantioface insertions:**  
***atactic polymer***

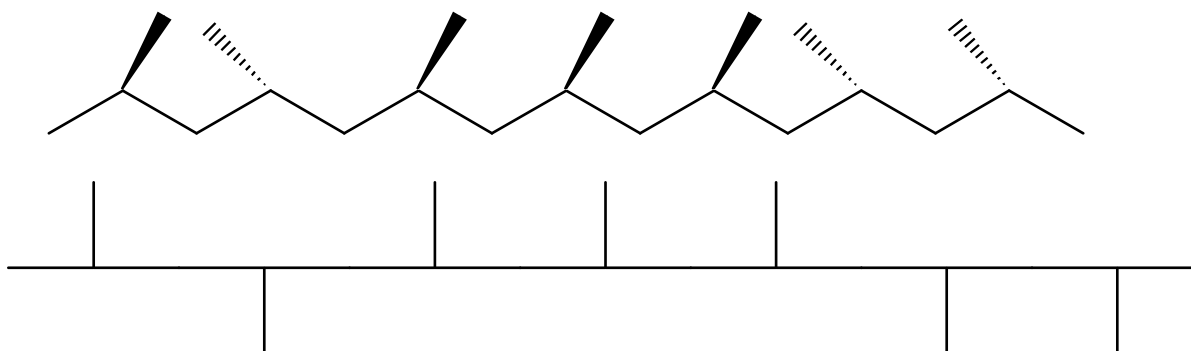
# Polypropylene synthesis: The CRYPTOCHIRALITY phenomenon



*isotactic*



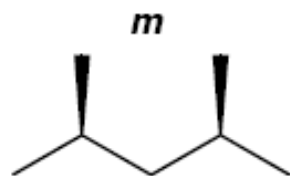
*syndiotactic*



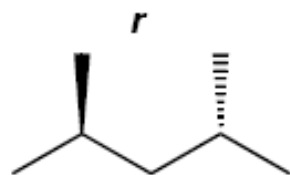
*atactic*

# Tacticity

## Dyad Tacticity

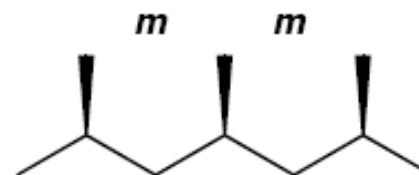


isotactic (*meso*, *m*)

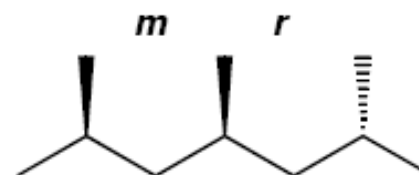


syndiotactic (*racemic*, *r*)

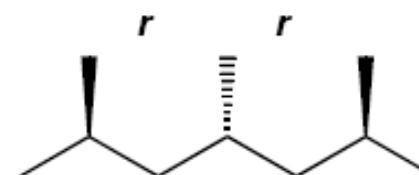
## Triad Tacticity



isotactic (*mm*)



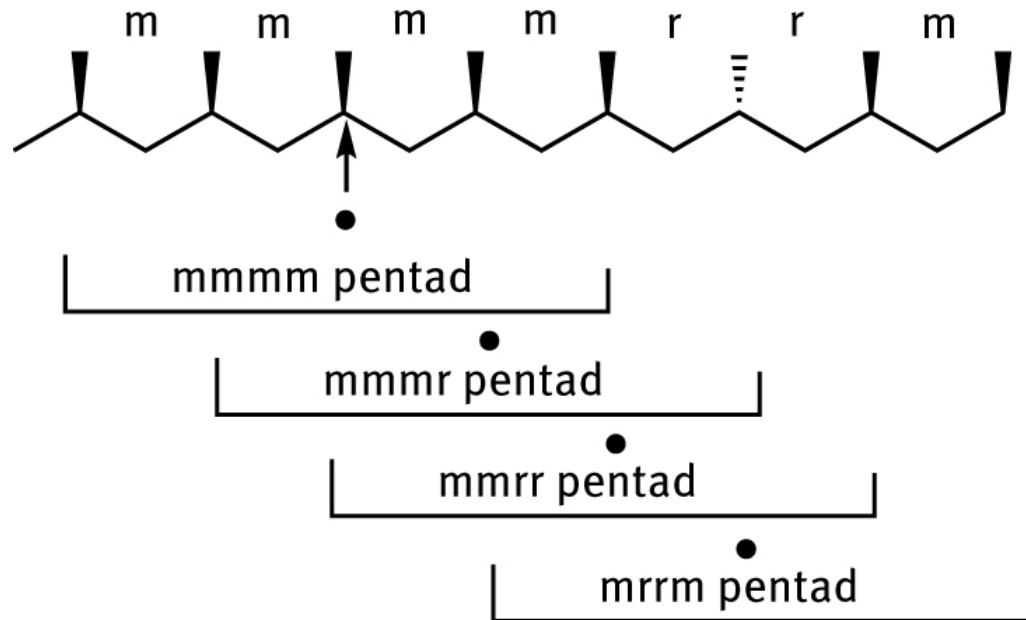
atactic (*mr*)



syndiotactic (*rr*)

# Tacticity

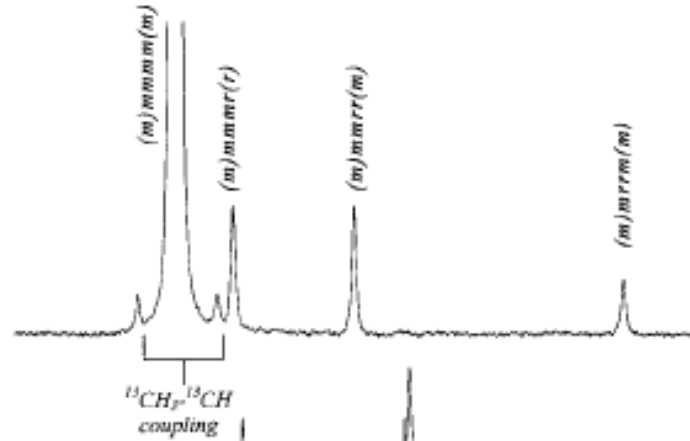
- **Isotactic and syndiotactic** polymers are **crystalline**, **atactic** is **amorphous**;
- **NMR spectroscopy** is a powerful tool for studying polymer **Stereochemistry**.
- Tacticity of polymer is determined by % *m* or *r* dyads  
e.g. Perfectly isotactic polypropylene has 100% *m* dyads



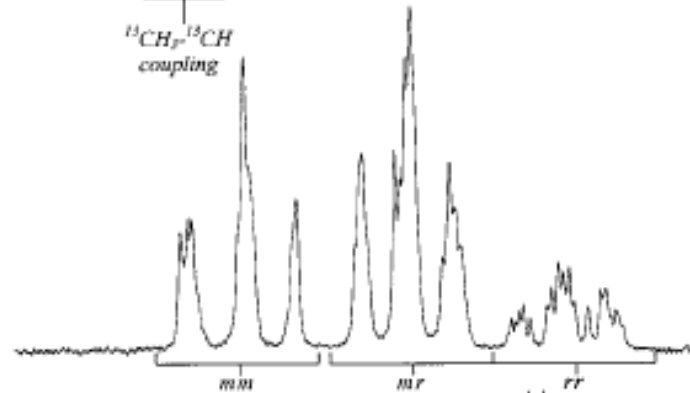
# Microtacticity

## $^{13}\text{C}$ NMR Spectra of polypropylene: methyl pentad region

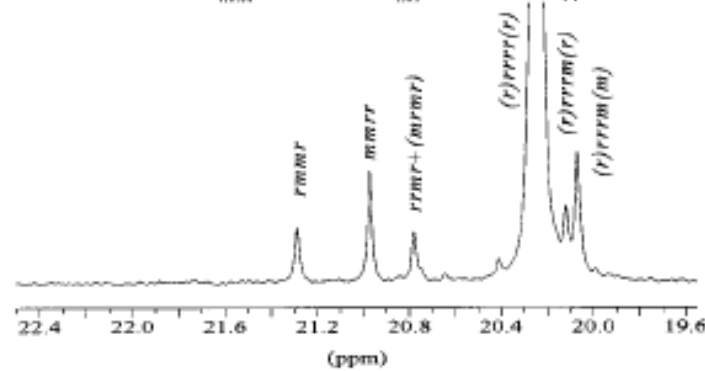
*isotactic*



*atactic*

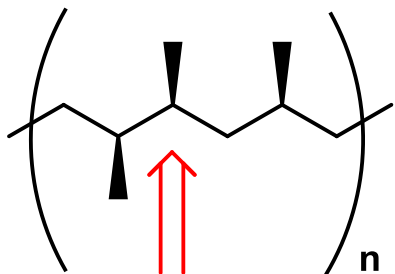


*syndiotactic*

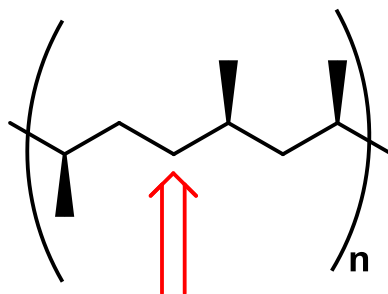


# Regiochemistry

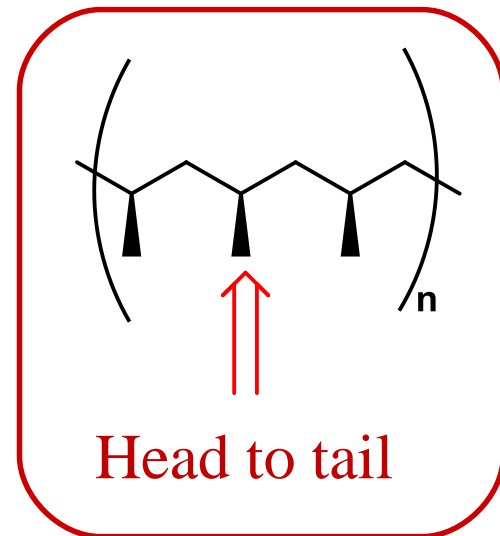
The possible regiosequences



Tail to tail

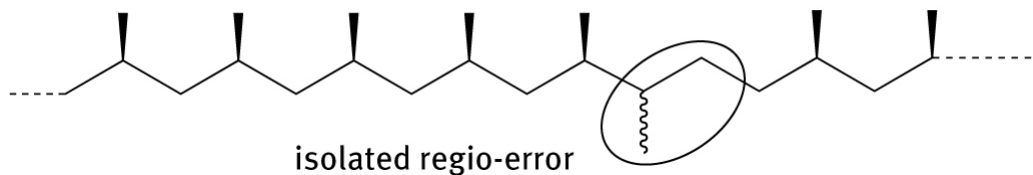


Head to head



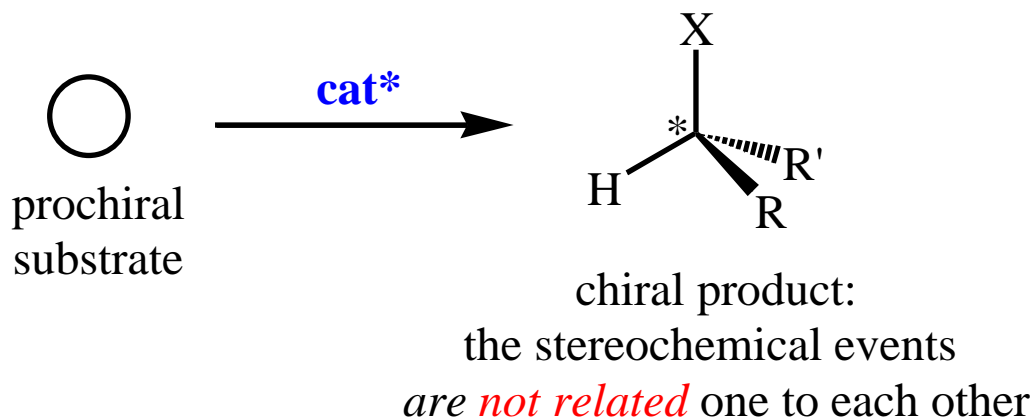
Head to tail

are originated by 1,2-Insertion or 2,1-Insertion

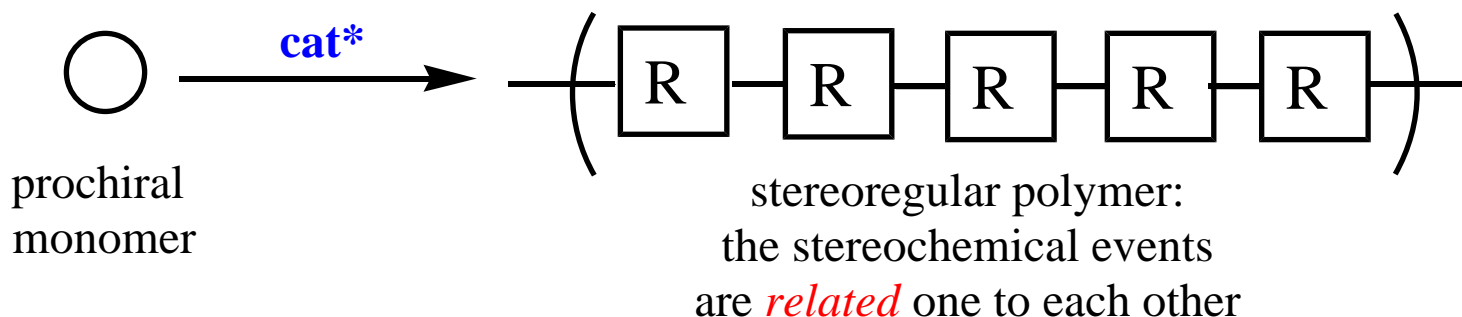


# ENANTIOSELECTIVE CATALYSIS<sup>1</sup>

Enantioselective synthesis of small molecules



Stereospecific polymerization

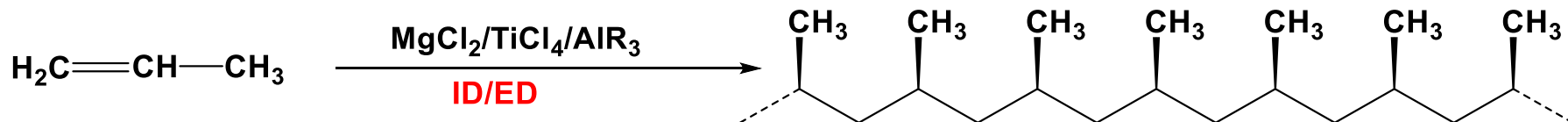


$\text{cat}^* = \text{chiral coordination compound}$

<sup>1</sup>G. W. Coates et al., *Angew. Chem. Int. Ed.* **2000**, 39, 3626.

# STEREOSPECIFIC Ziegler-Natta Catalysts

Synthesis of *isotactic* polypropylene

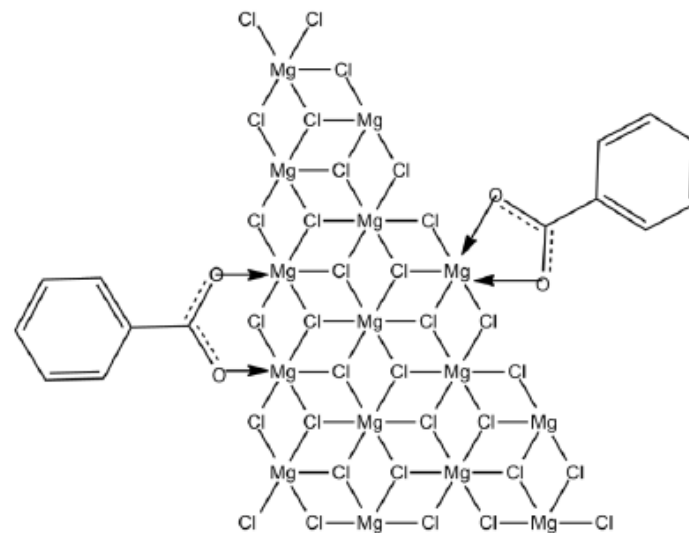
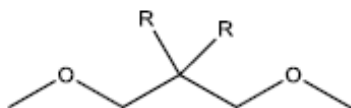
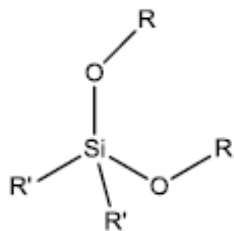
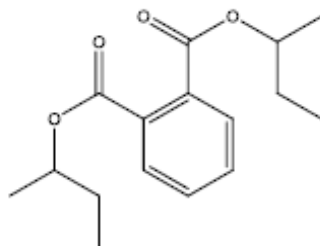
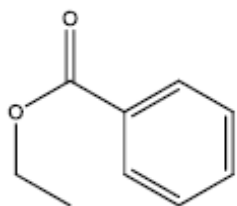


ID = internal donor

ED = external donor

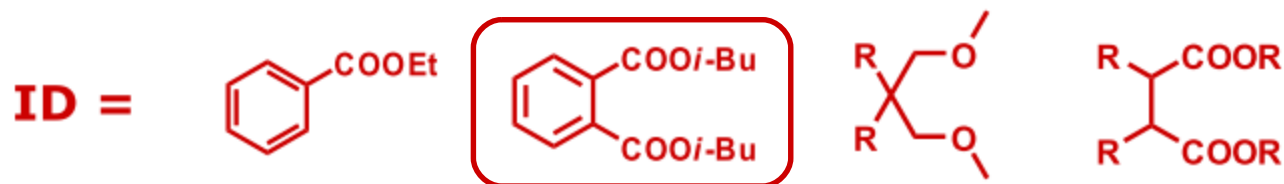
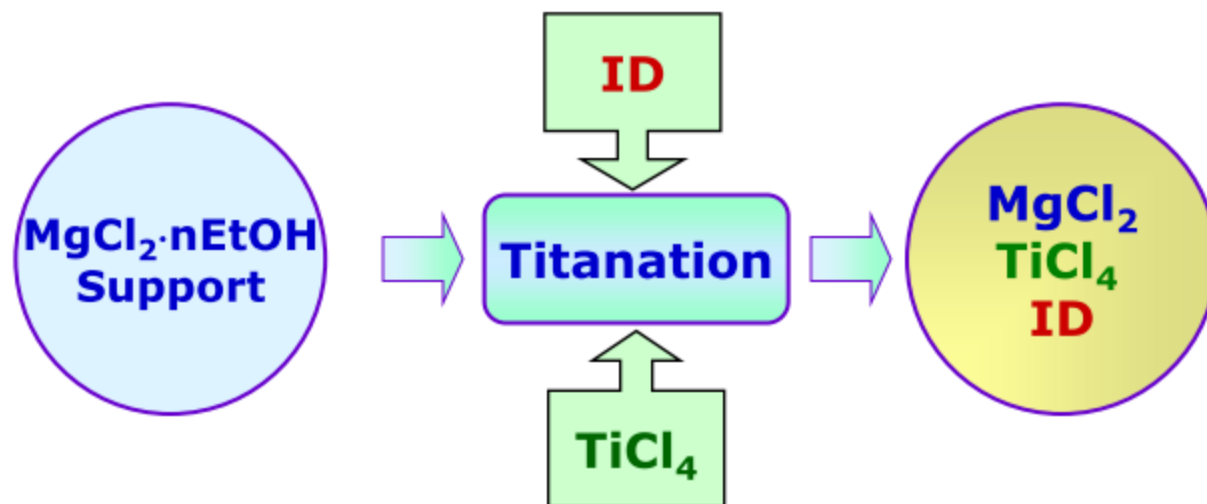
Catalyst nature: *heterogeneous*

The donors



# Z-N Catalyst Preparation

## The solid Catalyst Precursor



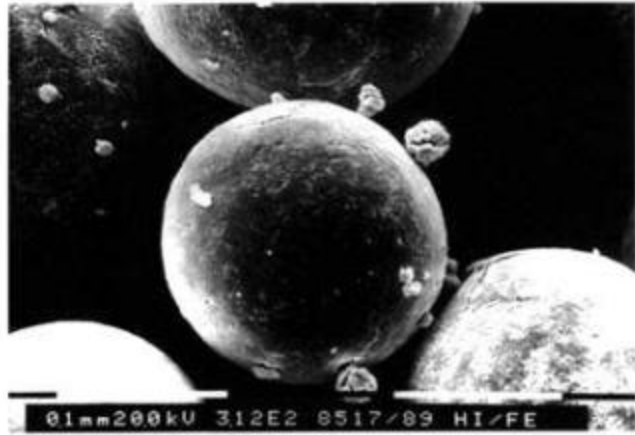
The Internal Donor is added (alone or in mixture) during the catalyst preparation, with the goal to:

- stabilize nascent MgCl<sub>2</sub> crystallites
- influence the crystallite dimensions and thus the "working surface" connected with the productivity of the resulting catalyst
- control of the distribution of TiCl<sub>4</sub> on the possible MgCl<sub>2</sub> cuts

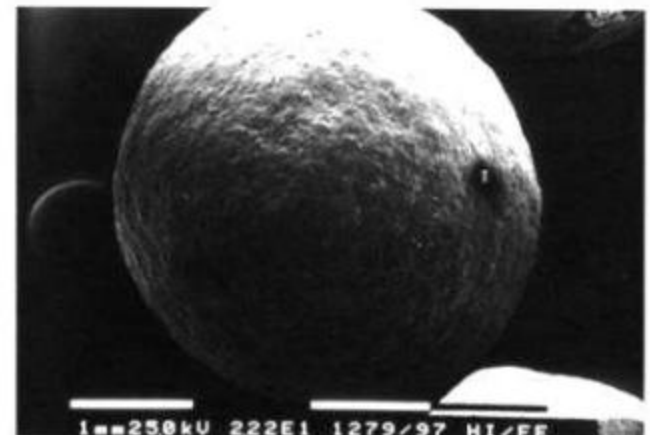


## Morphology of supports and PP particle

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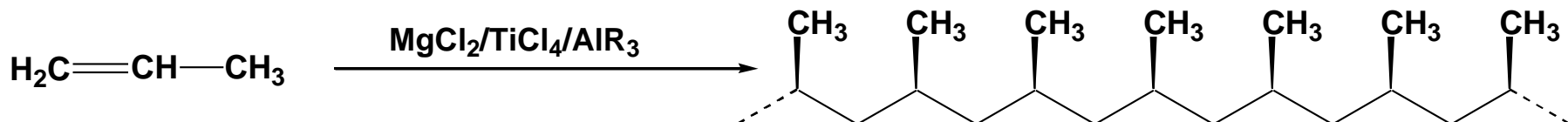
Morphology of catalyst support: spherical.



Morphology of catalyst of PP particles.

# STEREOSPECIFIC Ziegler-Natta Catalysts

Synthesis of *isotactic* polypropylene



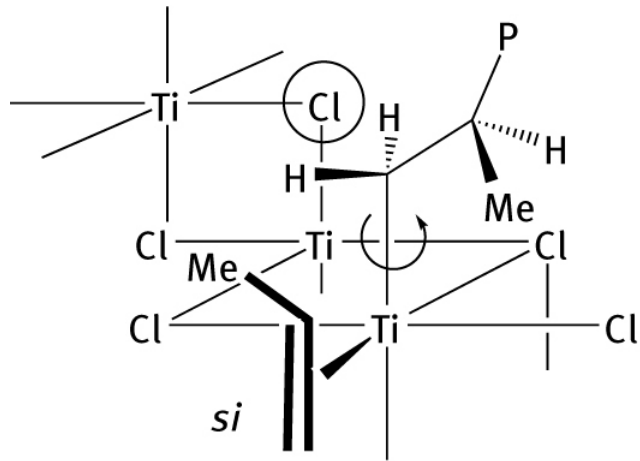
*Heterogeneous* catalyst.

Stereochemistry of the insertion step: nature of the errors:

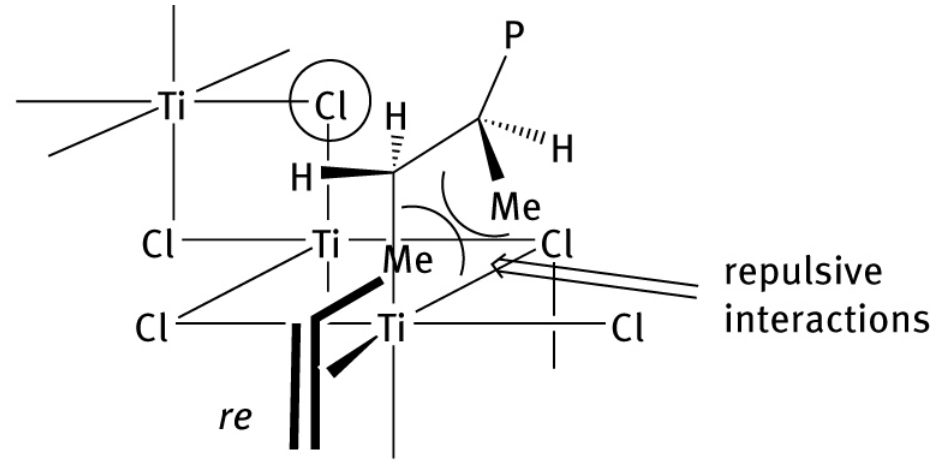


*Errors of kind A are indicative for the chiral nature of the catalyst.*

# Enantiomorphous site control

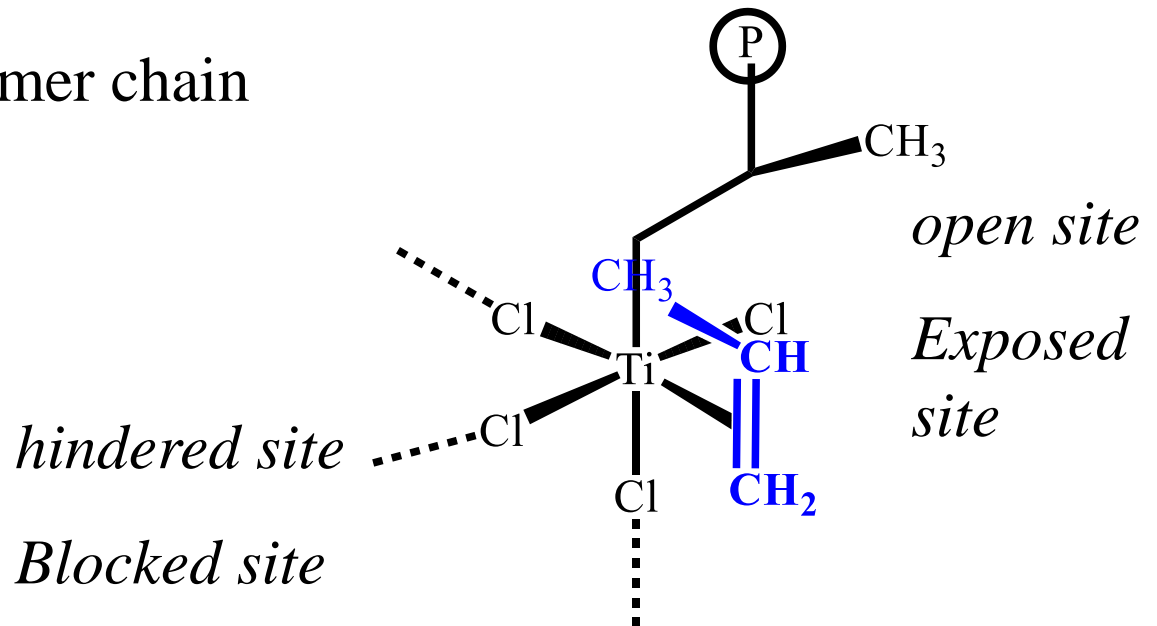


favoured conformation



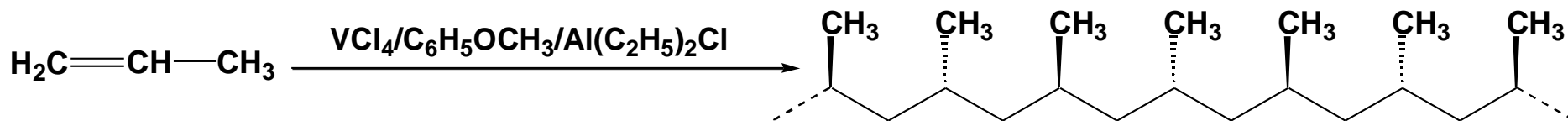
disfavoured conformation

P = growing polymer chain



# STEREOSPECIFIC Ziegler-Natta Catalysts

Synthesis of *syndiotactic* polypropylene



Catalyst nature: *homogeneous*

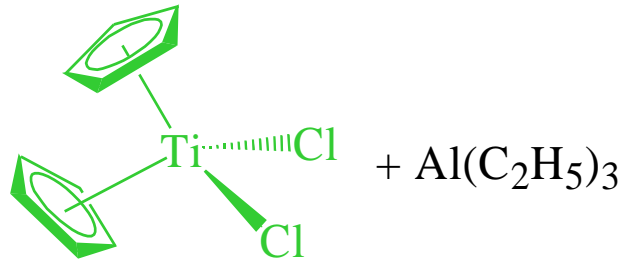
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General aspects of **stereospecific** polymerization of propylene

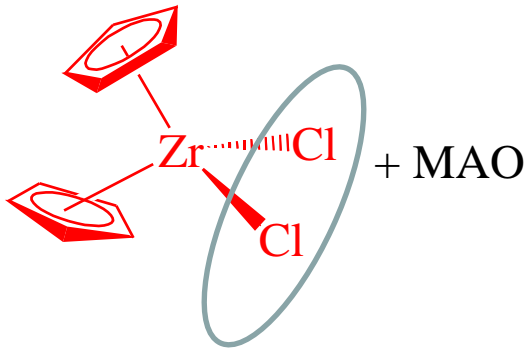
Catalyst	$\text{MgCl}_2/\text{TiCl}_4/\text{AlR}_3$	$\text{VCl}_4/\text{C}_6\text{H}_5\text{OCH}_3/\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}$
Stereoregularity	isotactic	syndiotactic
Regioselectivity	primary	secondary
Control of stereochemistry	enantiomeric site	chain end
	$\text{L}_n\text{M}-\text{CH}_2-\underset{\text{CH}_3}{\text{CH}}-\text{P}$	$\text{L}_n\text{M}-\underset{\text{CH}_3}{\text{CH}}-\text{CH}_2-\text{P}$

# Soluble catalysts



Low activity towards ethylene

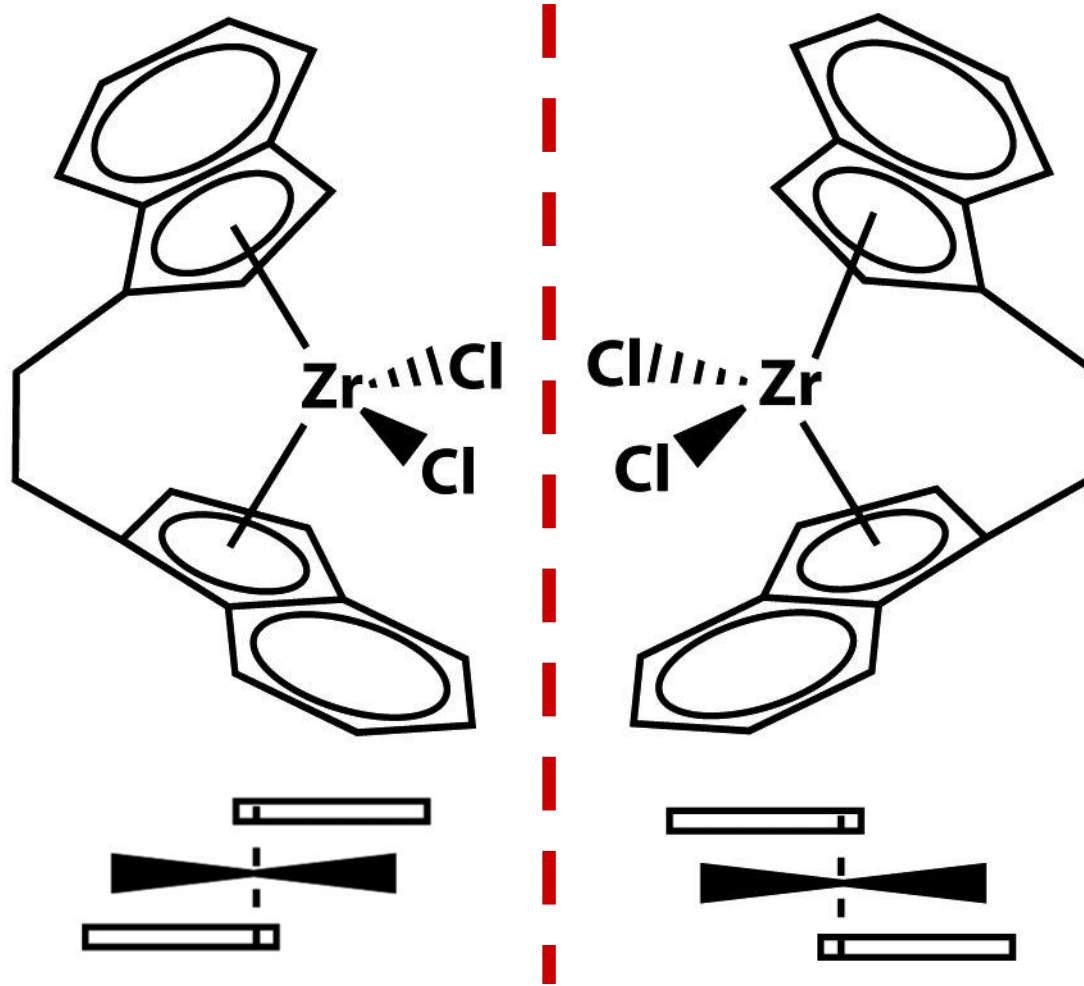
Inactivity towards propylene



Very high activity towards ethylene

Good activity towards propylene

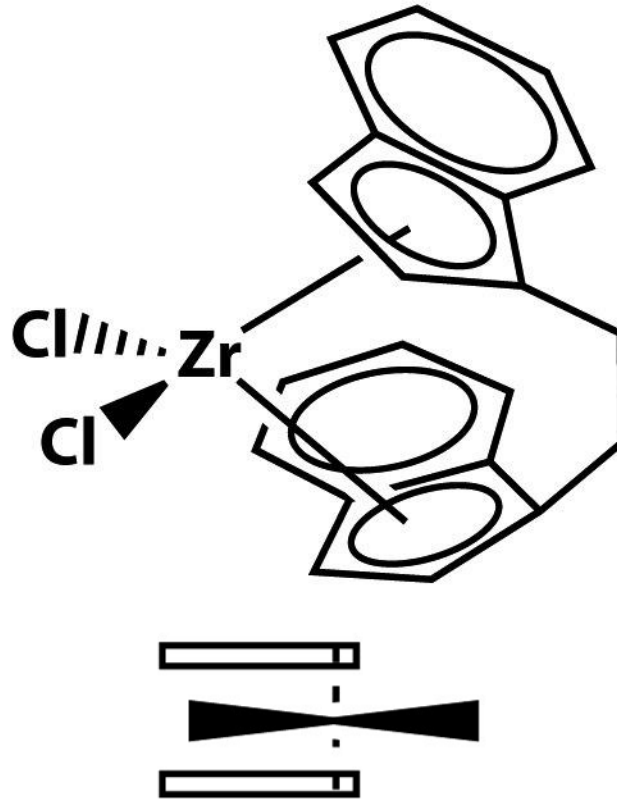
# Metallocene catalysts



**Chiral molecules**  
**C<sub>2</sub> symmetry**

+ MAO leads to *isotactic* polypropylene

# Metallocene catalysts

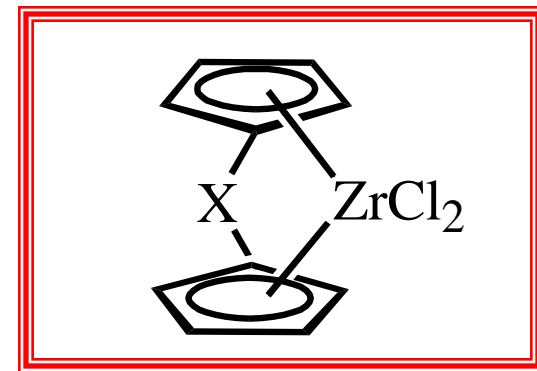


**meso form of the molecule**  
 **$C_s$  symmetry**

+ MAO leads to *atactic* polypropylene

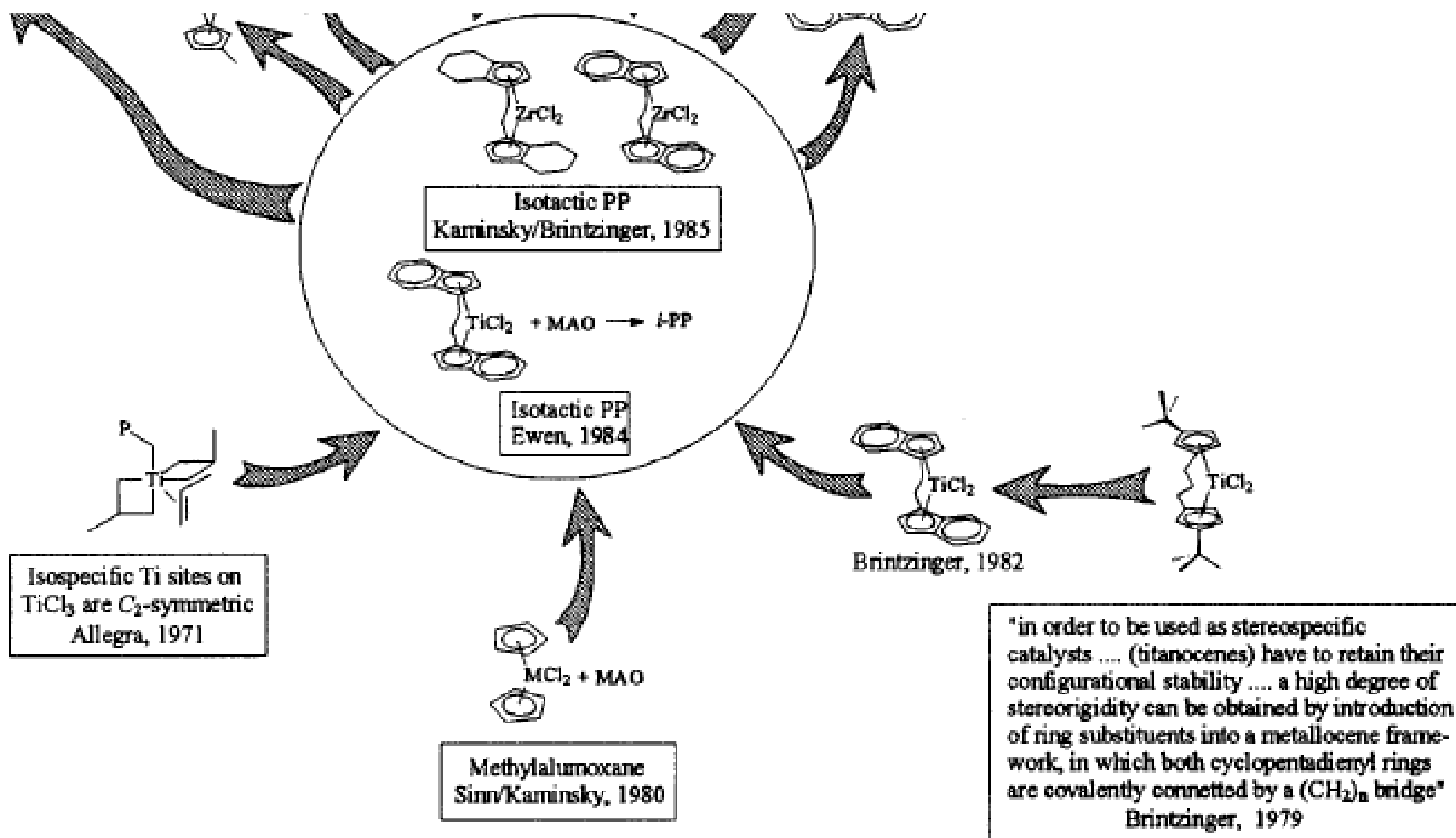
*ansa*-zirconocenes catalysts:  
stereorigid of  $C_2$  symmetry

The **isotactic PP** synthesized with metallocene catalysts differs from that obtained with catalysts based on Ti for:



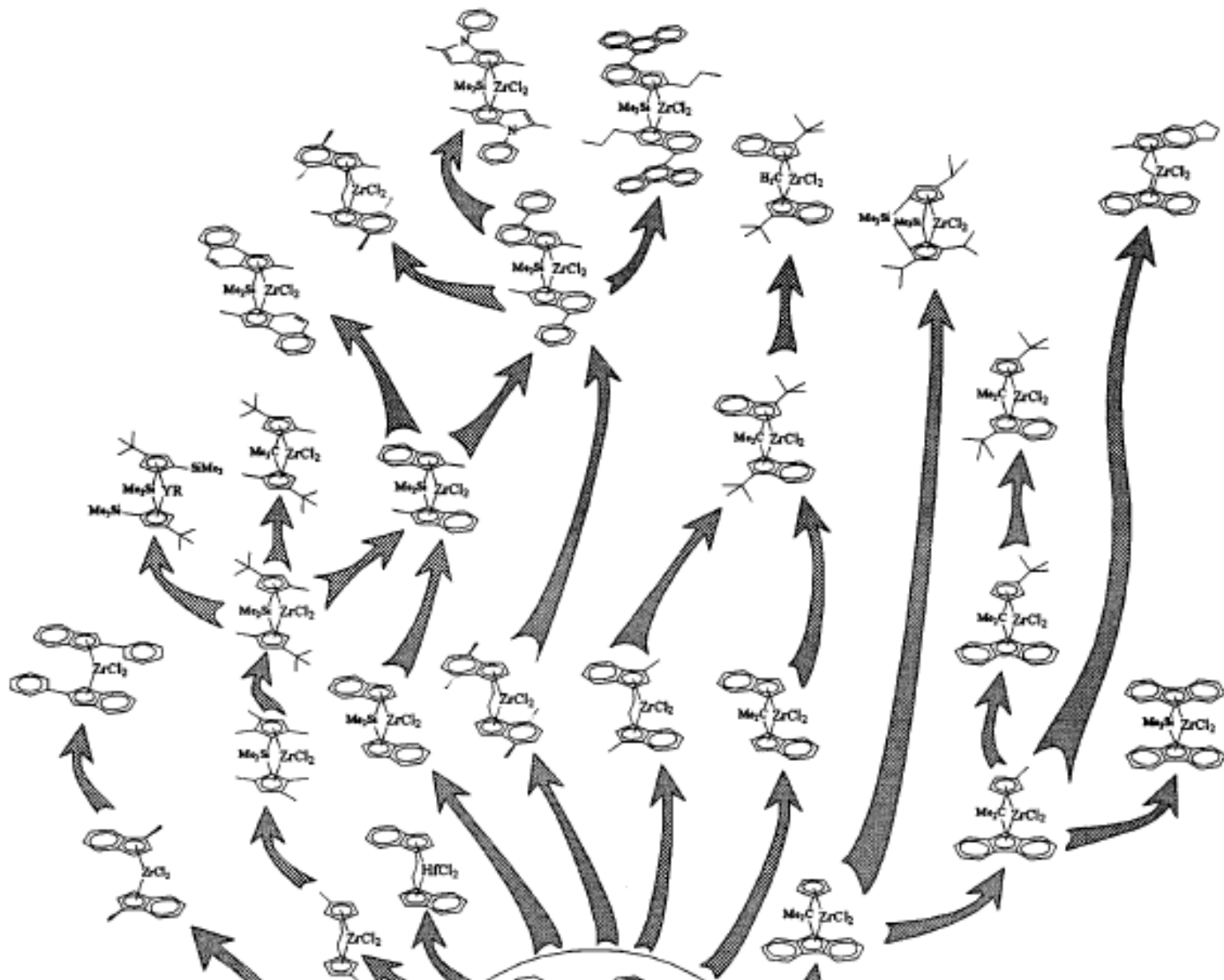
- ❖ lower **molecular weight**;
- ❖ narrower **molecular weight distribution**;
- ❖ the **tacticity**: from **almost atactic** to **perfectly isotactic** PP can be obtained;
- ❖ not **fully regioregular**: insertions with secondary regiochemistry are also observed;
- ❖ random distribution of **stereo- and regio-errors**.

# The evolution of metallocene catalysts<sup>1</sup>: the root

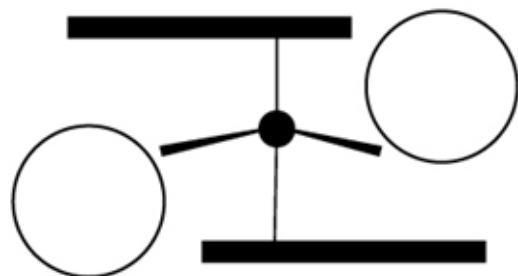


<sup>1</sup>L. Resconi et al., *Chem. Rev.* **2000**, *100*, 1253.

# The evolution of metallocene catalysts: **the tree**



# Ewen's Symmetry Rules

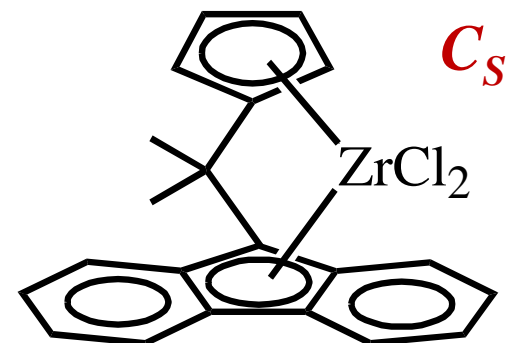


circles indicate more open quadrants of the ligand sphere

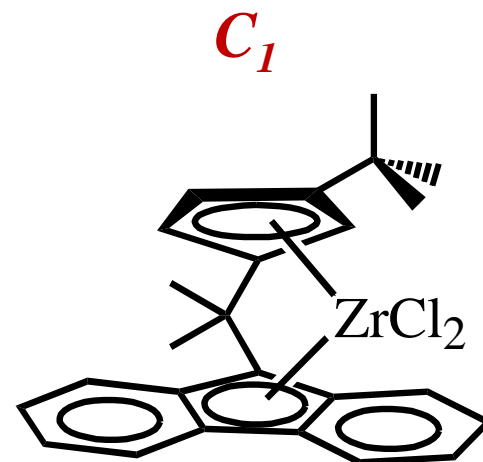
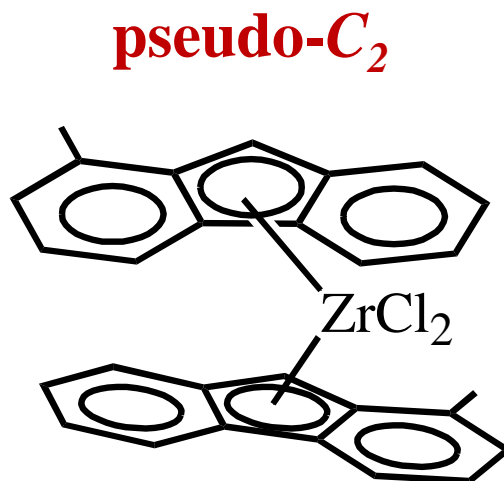
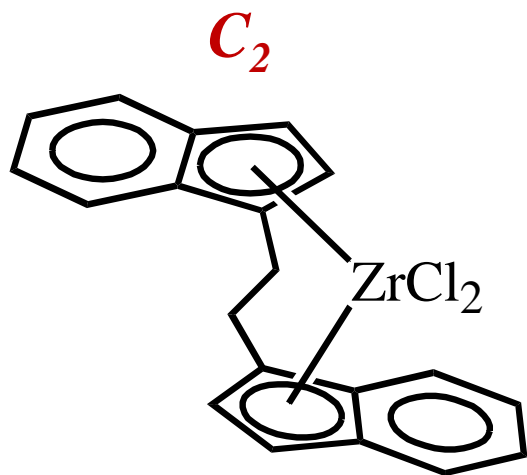
E = enantioselective site; A = nonselective site.

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

## SYNDIOSPECIFIC Catalyst<sup>1</sup>

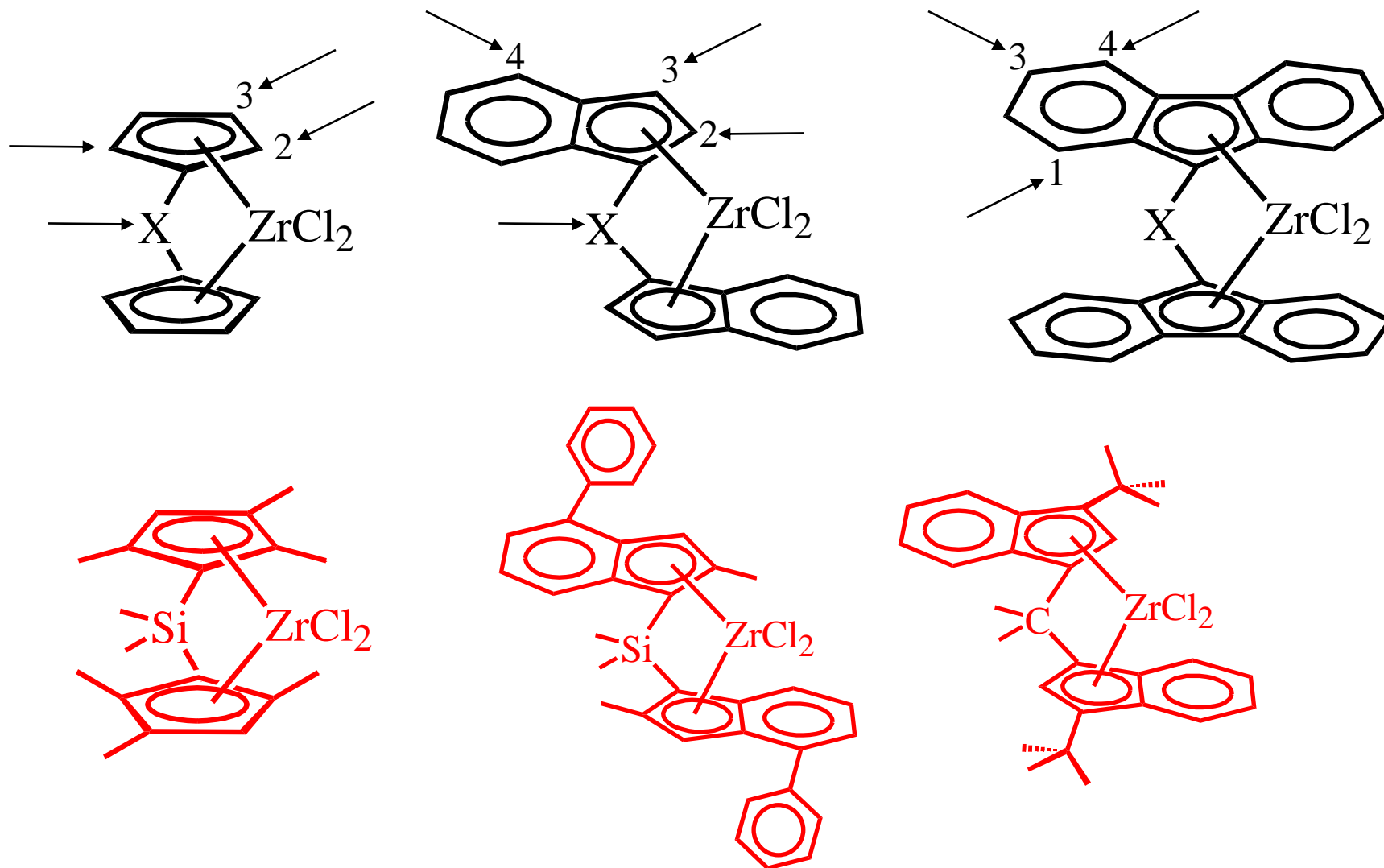


## ISOSPECIFIC Catalysts<sup>1</sup>



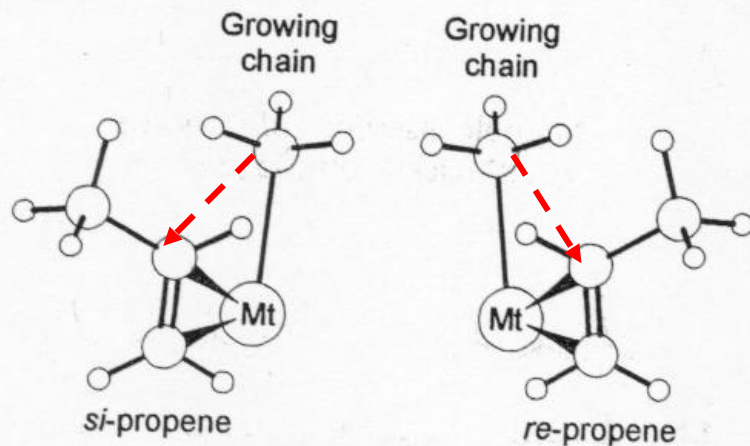
<sup>1</sup>L. Resconi et al., *Chem. Rev.* **2000**, *100*, 1253.

# ansa-zirconocenes catalysts of $C_2$ symmetry



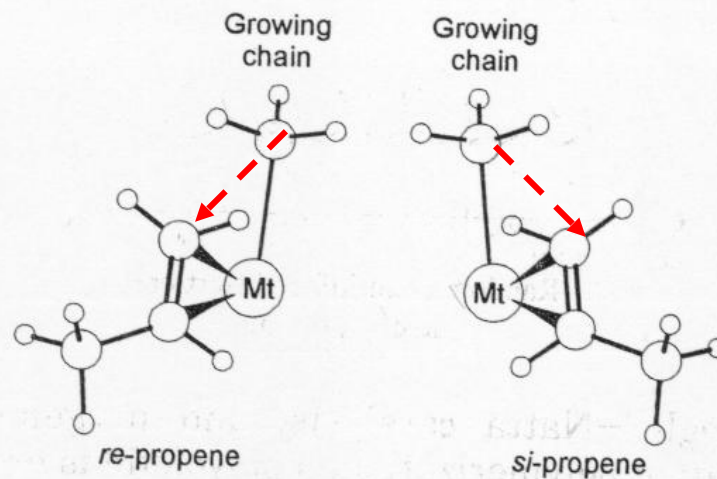
<sup>1</sup>L. Resconi et al., *Chem. Rev.* **2000**, *100*, 1253.

# DIFFERENT INSERTION WAYS FOR PROPYLENE<sup>1</sup>



Primary insertion

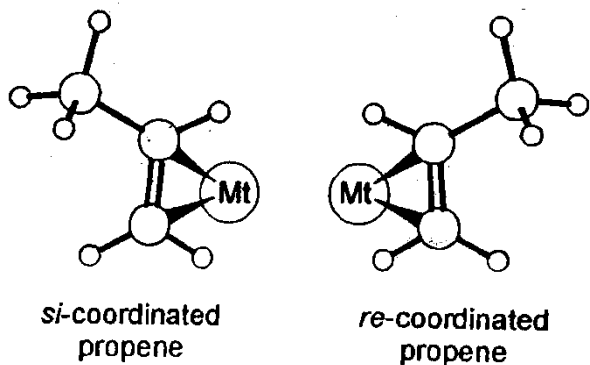
Secondary insertion



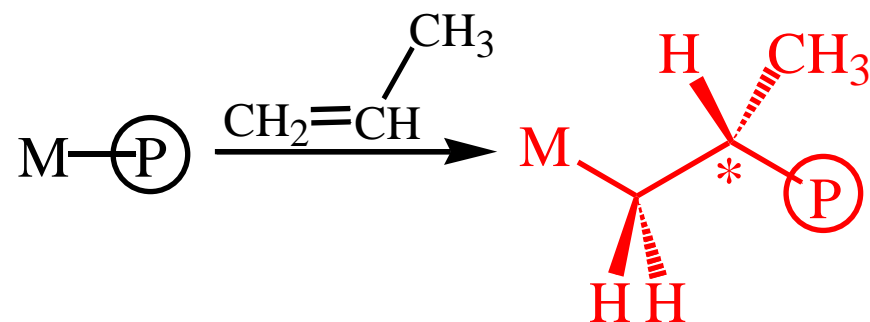
<sup>1</sup>L. Resconi et al., *Chem. Rev.* **2000**, *100*, 1253.

# THE ELEMENTS OF CHIRALITY<sup>1</sup>

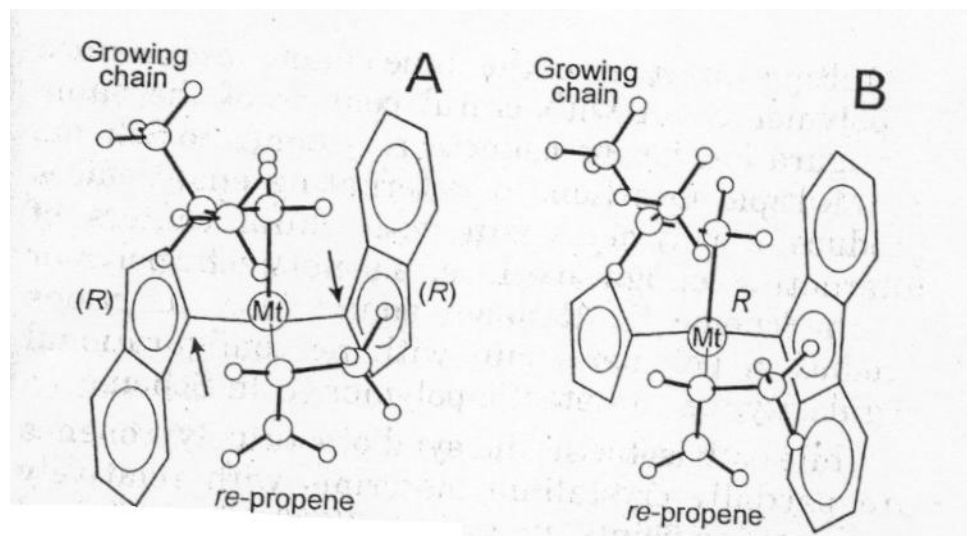
propylene enantioface



growing chain

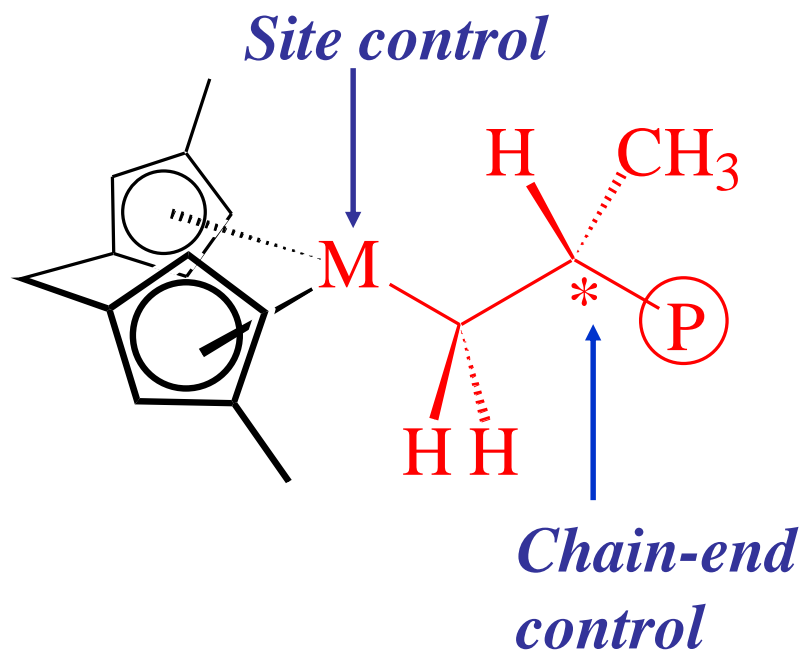


enantiomorphous site



<sup>1</sup>L. Resconi et al., *Chem. Rev.* **2000**, *100*, 1253.

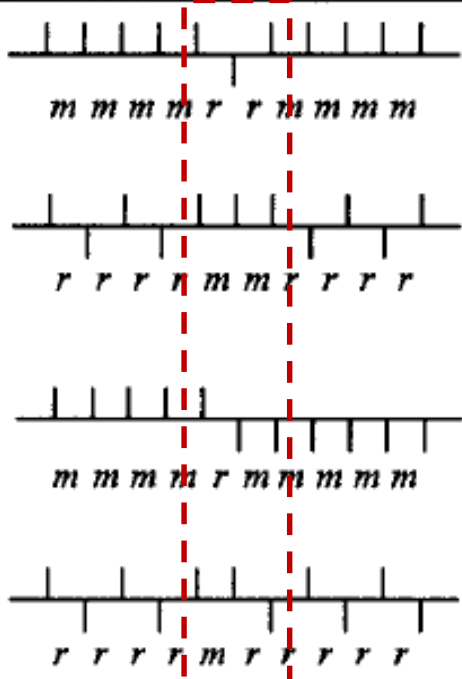
# CHIRAL INDUCTION FOR THE PRIMARY INSERTION<sup>1</sup>



<sup>1</sup>L. Resconi et al., *Chem. Rev.* **2000**, *100*, 1253.

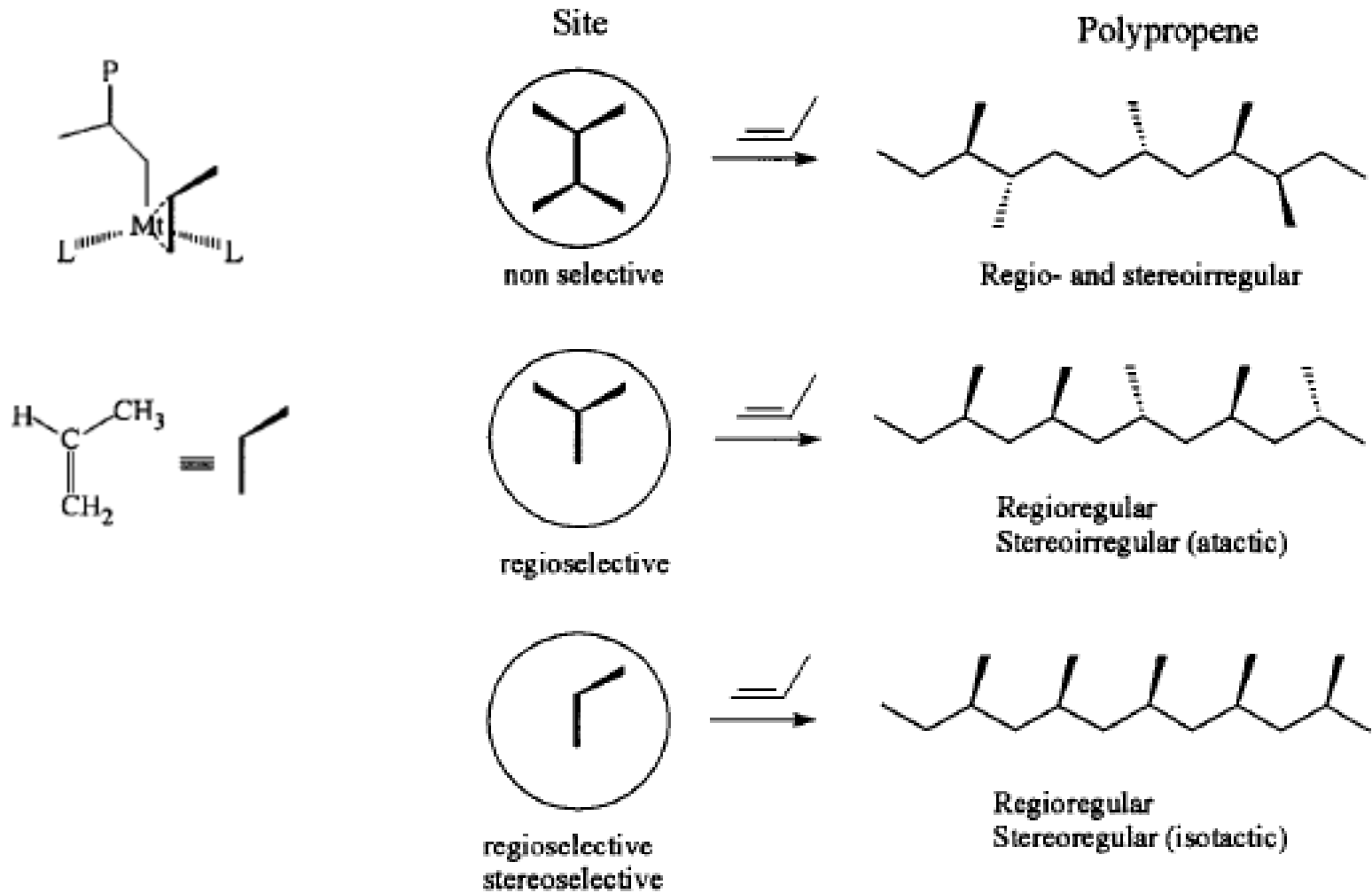
# CHIRAL INDUCTION FOR THE PRIMARY INSERTION<sup>1</sup>

Polymerization mechanism		Microstructure with isolated stereoinversion	triad/triad and pentad/pentad relationships
Primary insertion	site control	isospecific	$[mr] = 2[rr]$ $[mmmr] = [mmrr] = 2[mrrm]$
	error correction	syndiospecific	$[mr] = 2[mm]$ $[rrrm] = [mmrr] = 2[rmmr]$
		isospecific	$mr$ only $[mmmr] = [mrrm]$
	chain-end control error propagation	syndiospecific	$mr$ only $[rrrm] = [rmmr]$

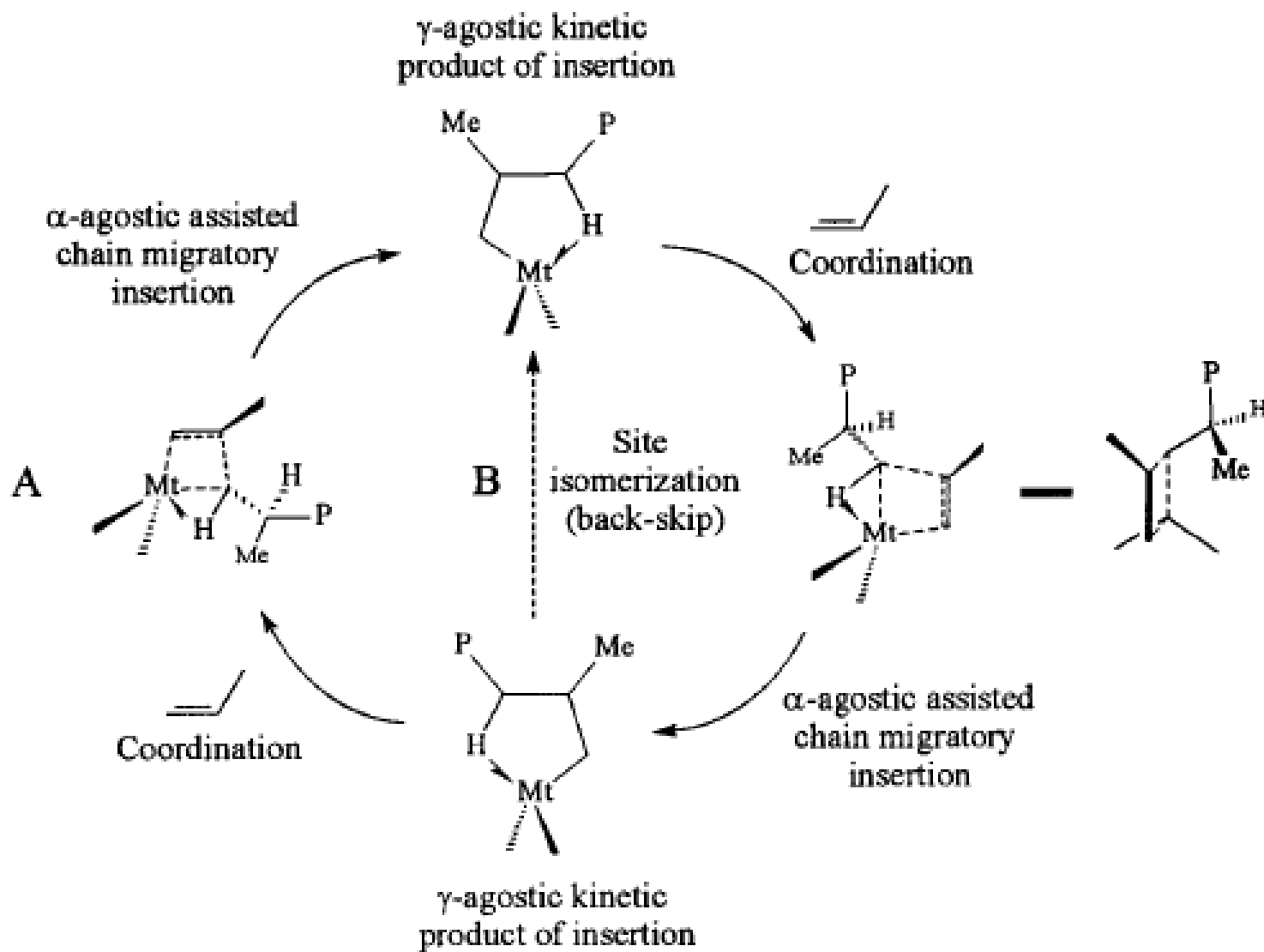

  
 stereoerrors

<sup>1</sup>L. Resconi et al., *Chem. Rev.* **2000**, *100*, 1253.

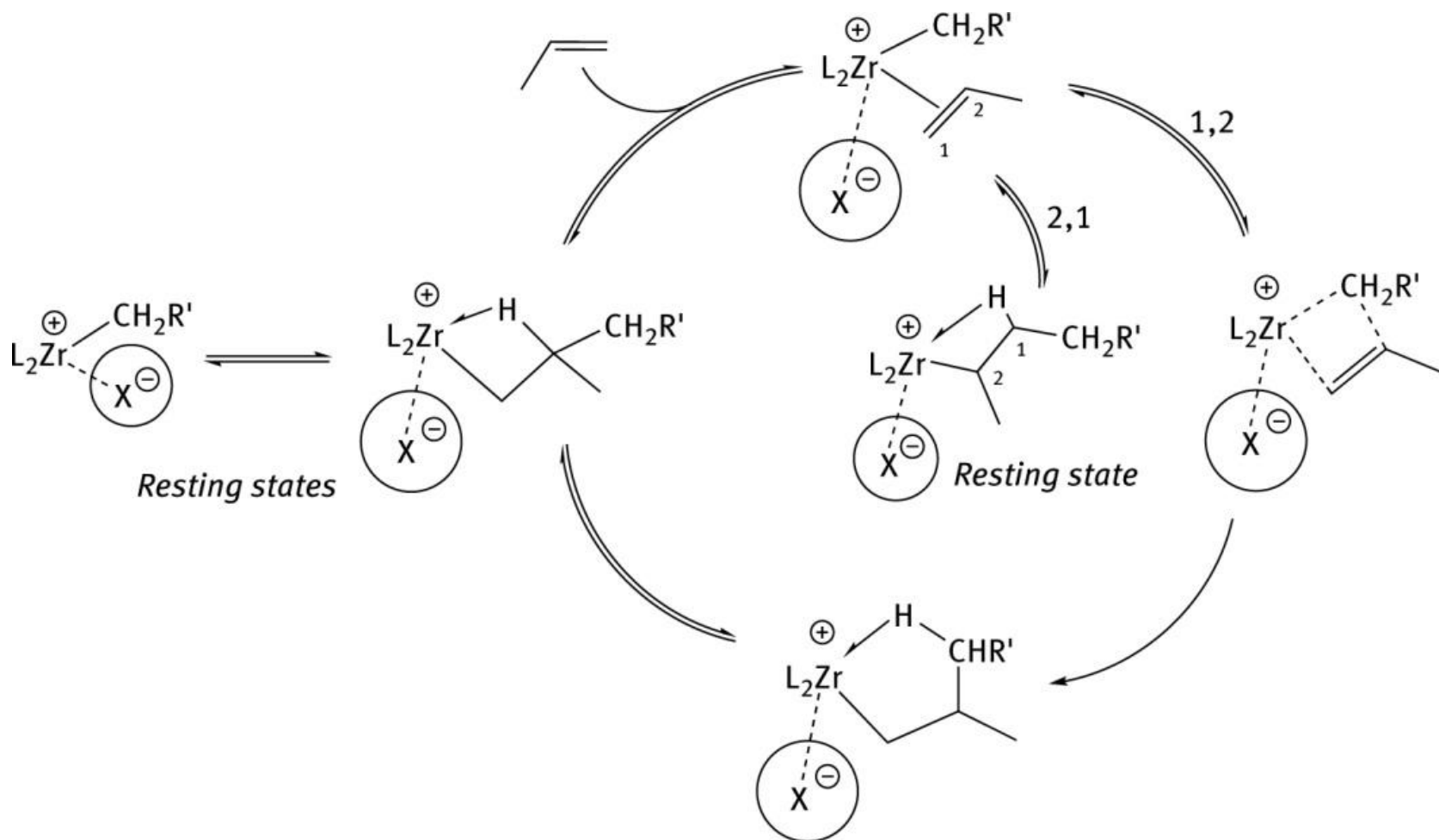
# The key-in-the-lock model: **one lock, one key**



# The key-in-the-lock model: **two locks, one key**

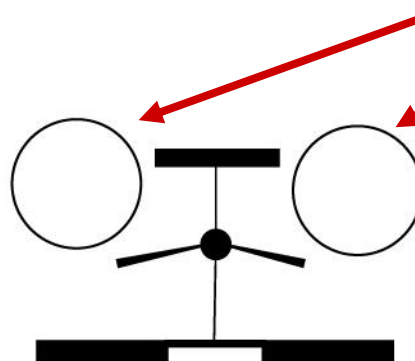
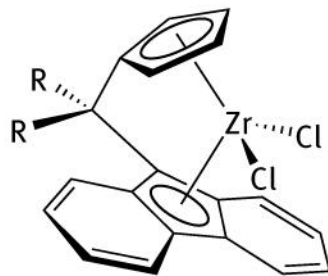


# THE CATALYTIC CYCLE



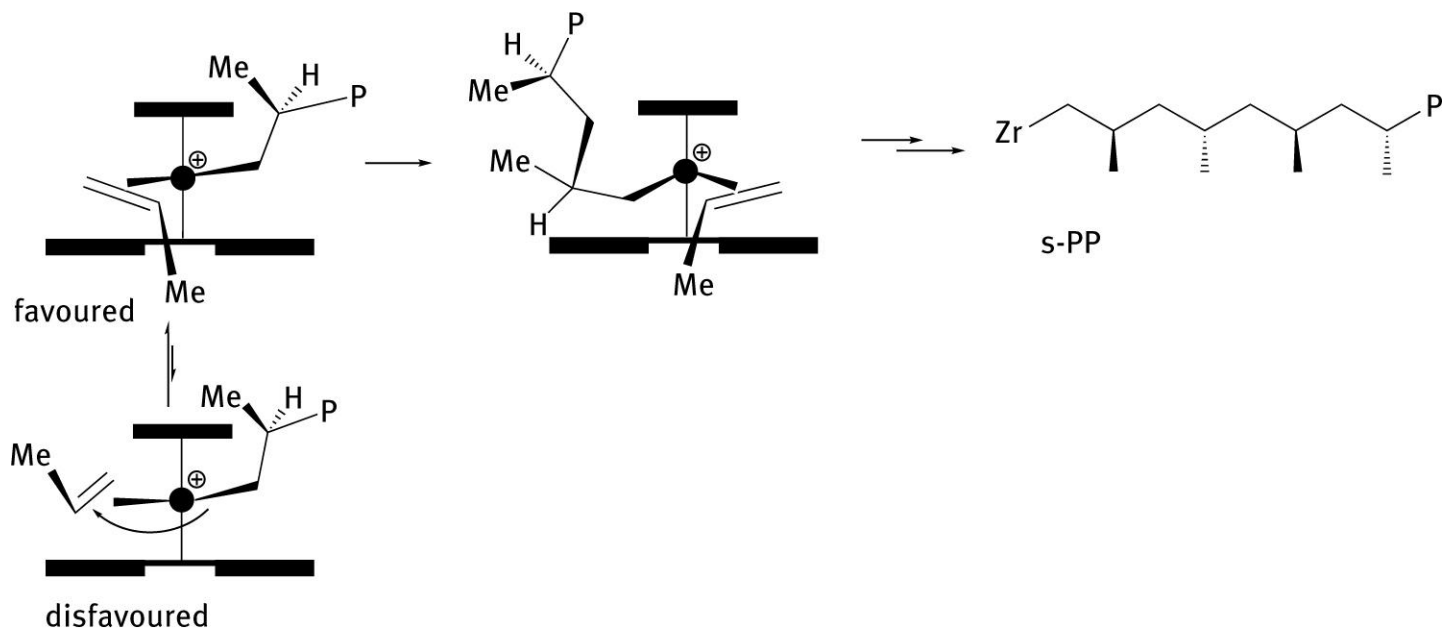
# SYNDIOSPECIFIC Catalyst

$C_5$ -symmetric ligand framework:

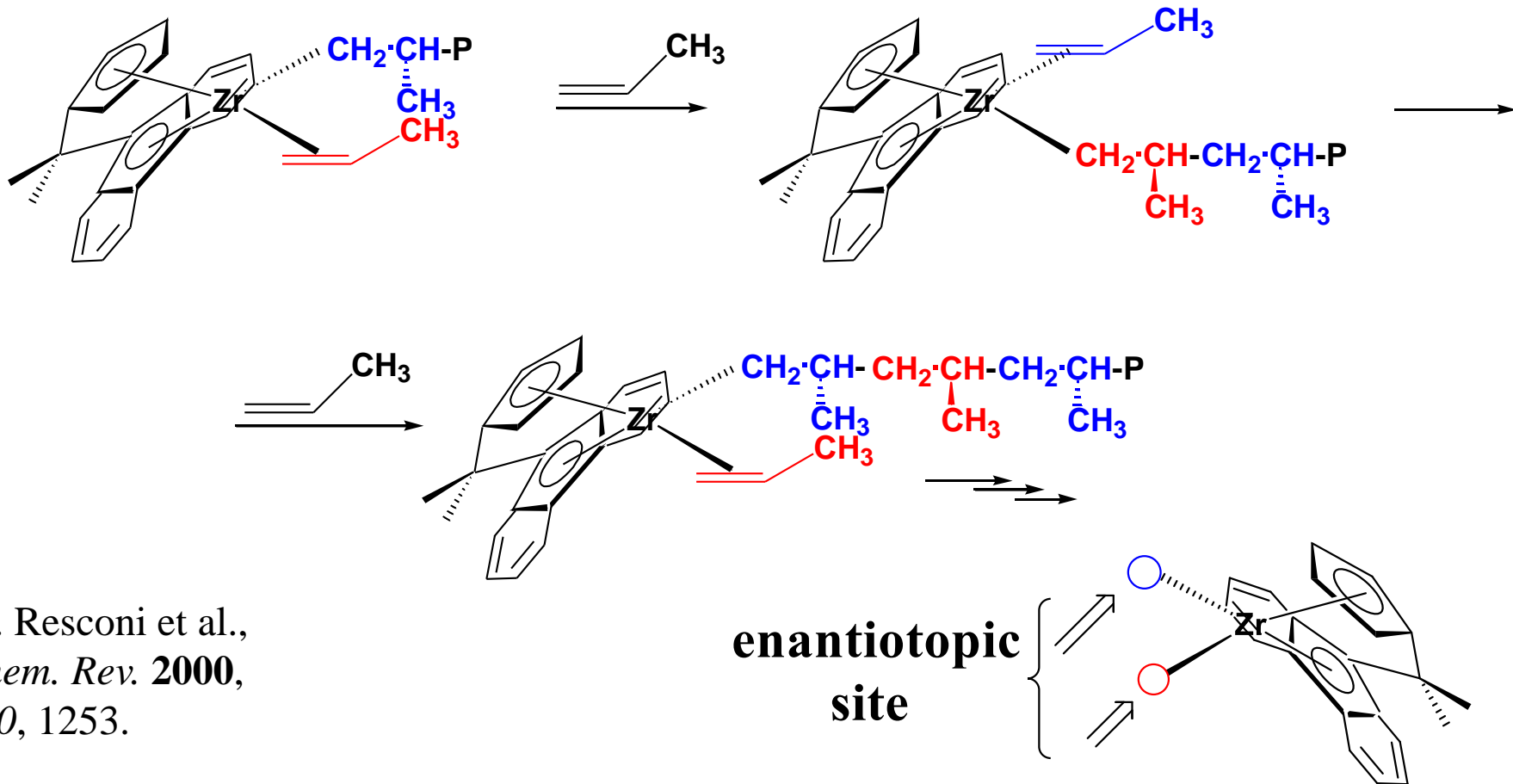
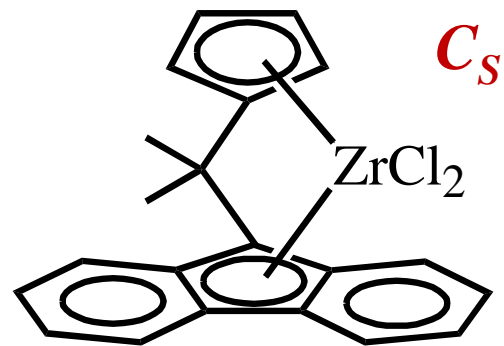


**Enantiotopic sites**

circles indicate more open quadrants of the ligand sphere



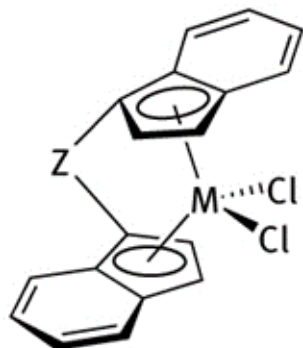
# SYNDIOSPECIFIC Catalyst <sup>1</sup>



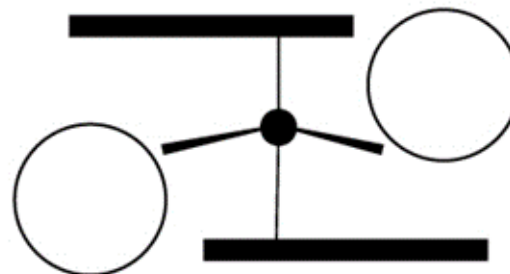
<sup>1</sup>L. Resconi et al.,  
*Chem. Rev.* **2000**,  
*100*, 1253.

# ISOSPECIFIC Catalyst

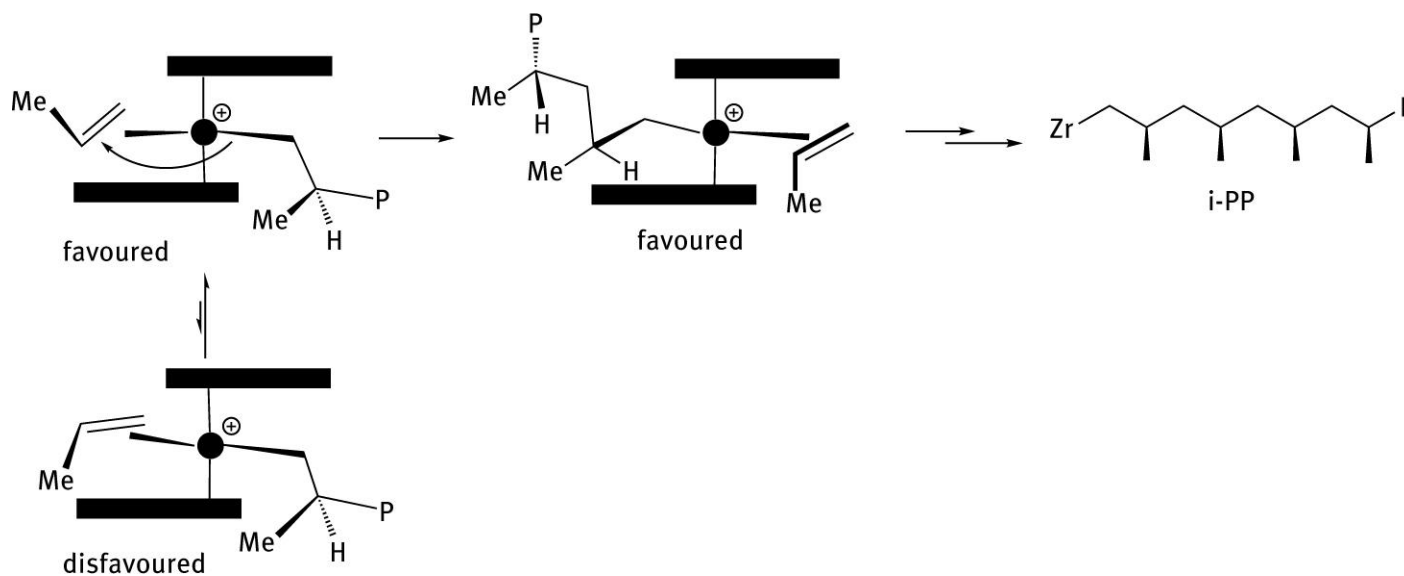
$C_2$ -symmetric ligand framework: Schematic front view



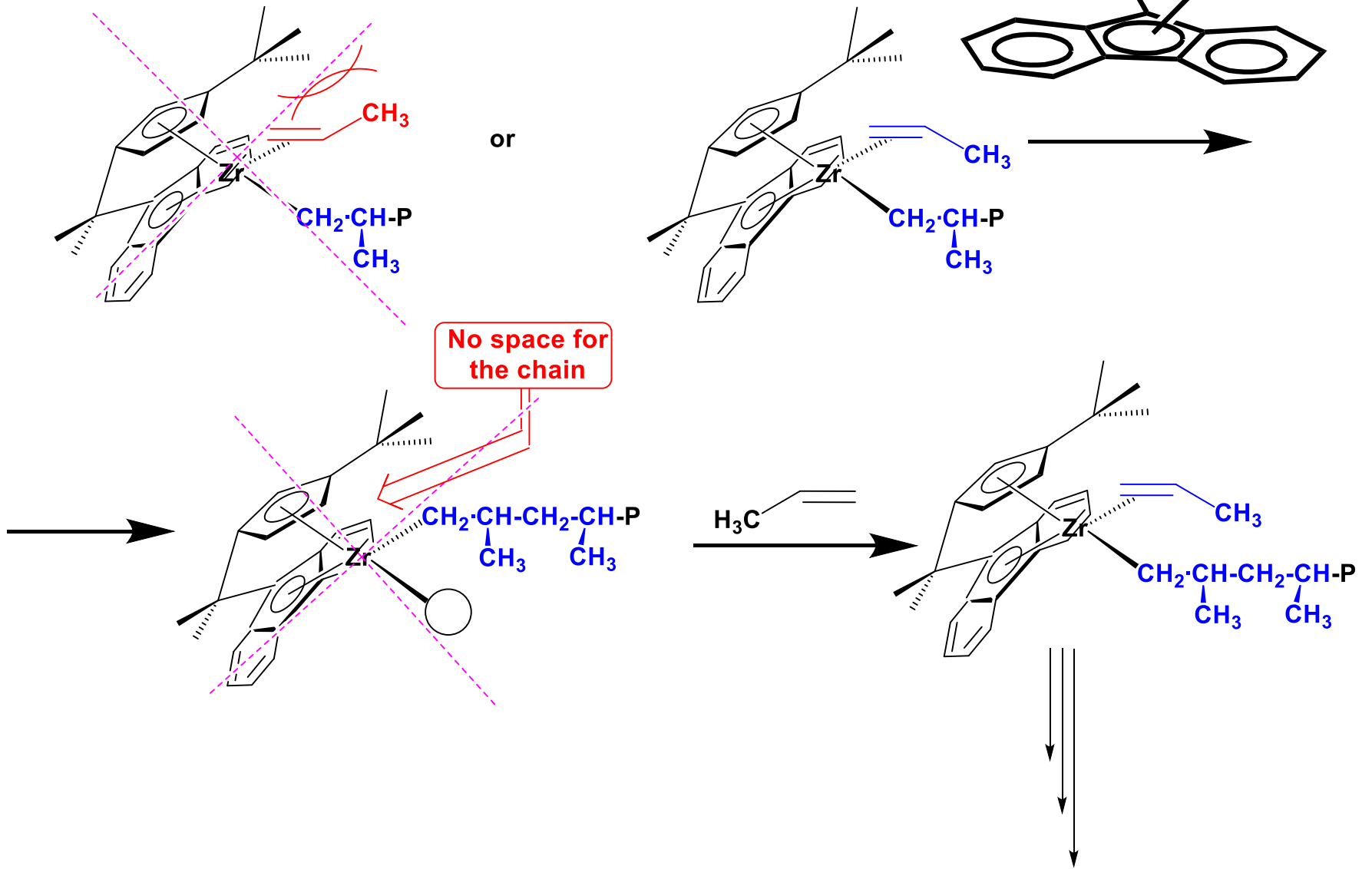
M = Ti, Zr, Hf  
Z = SiMe<sub>2</sub>, CMe<sub>2</sub>, CH<sub>2</sub>CH<sub>2</sub>, etc.



circles indicate more open quadrants of the ligand sphere

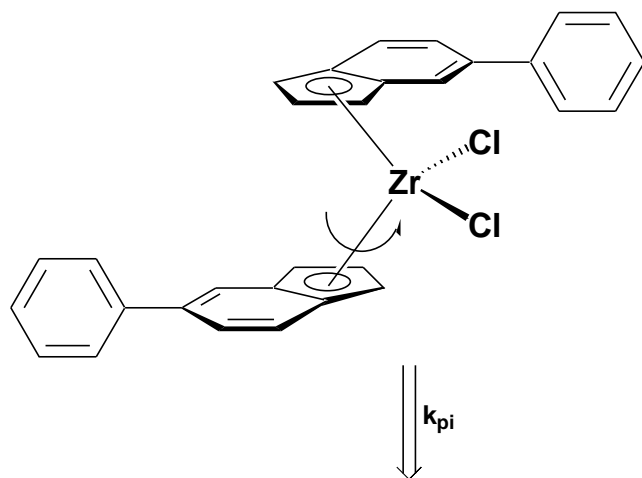


# ISOSPECIFIC Catalyst<sup>1</sup>



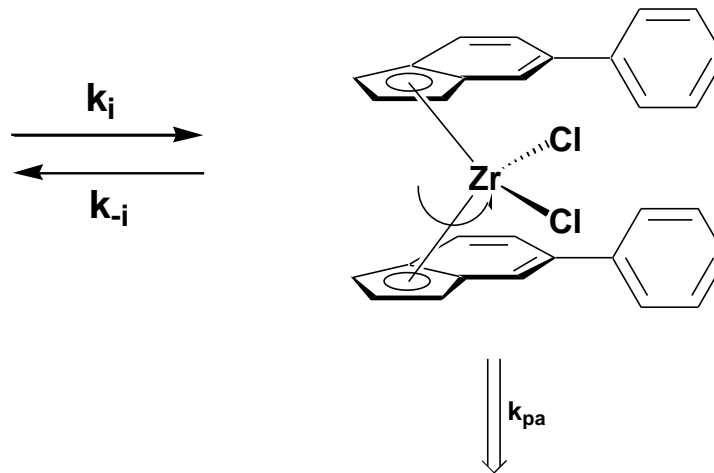
# Catalyst for the synthesis of *polypropylene with stereoblocks*

Catalyst in  
chiral conformation



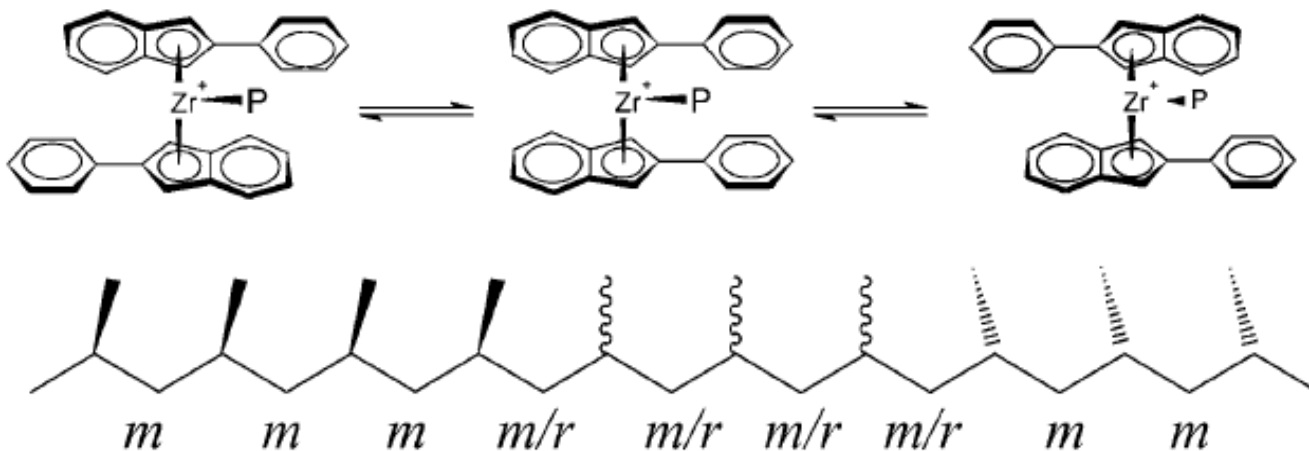
Isotactic block

Catalyst in  
meso conformation



Atactic block

# Catalyst for the synthesis of *polypropylene with stereoblocks*

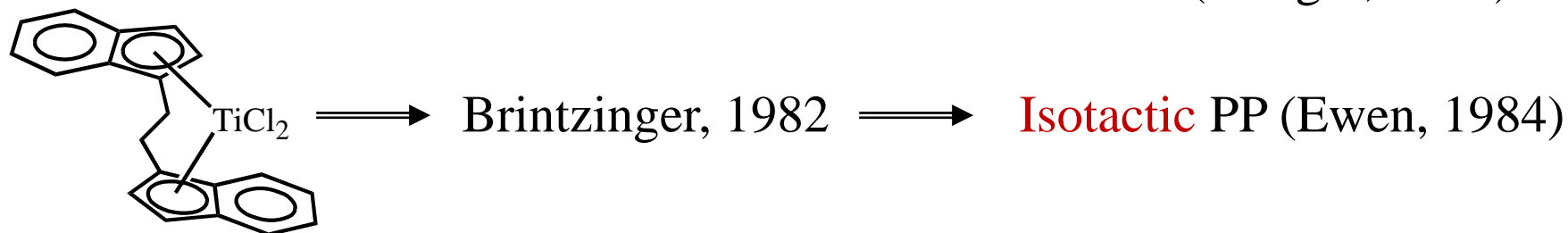


Trend of productivity:



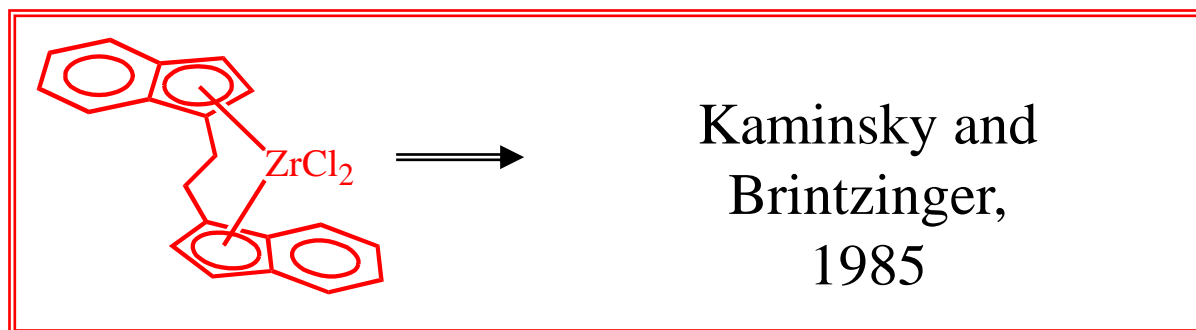
# STEREOSPECIFIC Catalysts <sup>1</sup>: a summary

$\text{TiCl}_3 \implies$  The Ti **isospecific** sites are featured by  **$\text{C}_2$  symmetry**  
(Allegra, 1971)



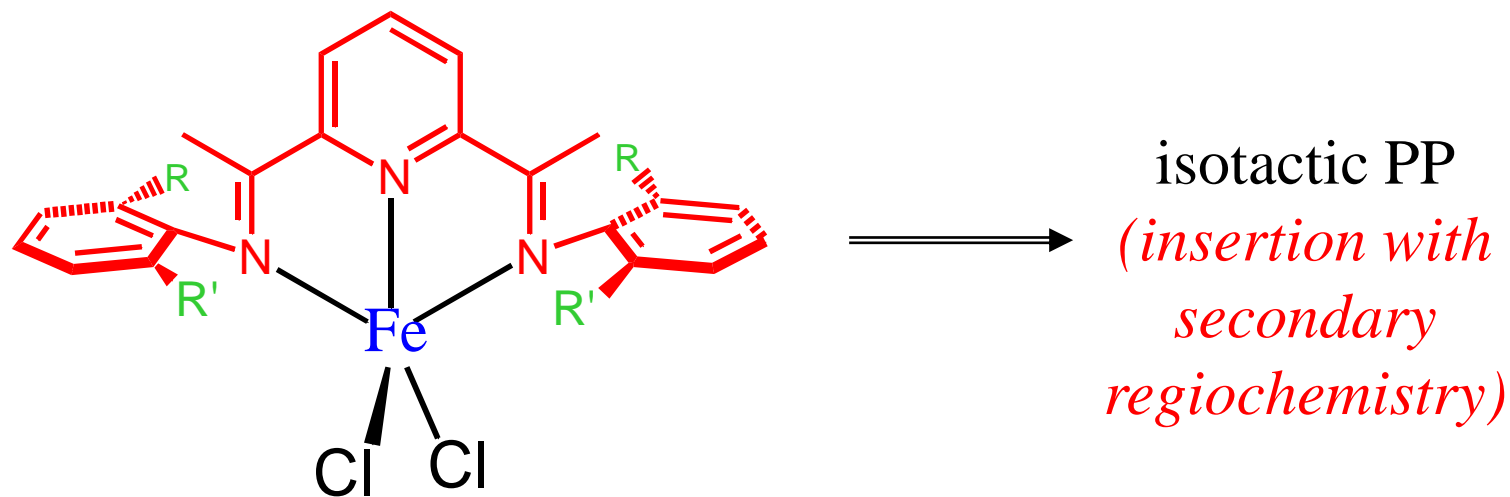
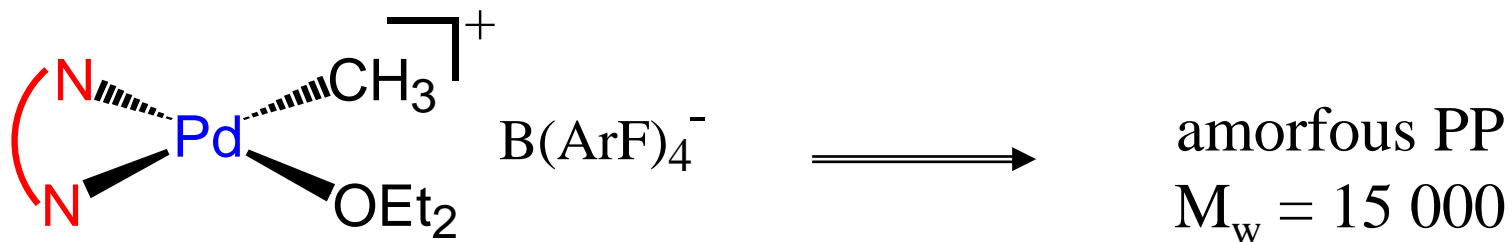
*racemic complex*  $\implies$  *isotactic PP*

*meso complex*  $\implies$  *atactic PP*

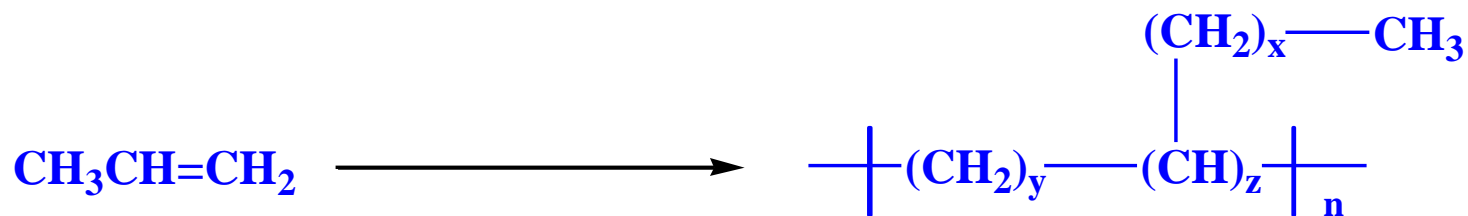


<sup>1</sup>L. Resconi et al., *Chem. Rev.* **2000**, *100*, 1253.

# Propylene polymerization catalyzed by **NON** metallocene complexes



Propylene polymerization with catalysts based  
 on Pd(II):  
*microstructure* of synthesized polypropylene



Polymer *microstructure* might be related to the following features of the catalyst:

- alkene insertion might occur with both primary and secondary regiochemistry;
- the catalyst can move along the polymer chain in both directions.