

STEREOCONTROLLED POLYMERIZATION

Asymmetric polymerization

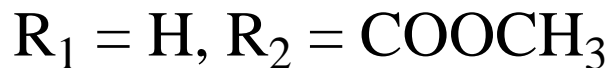
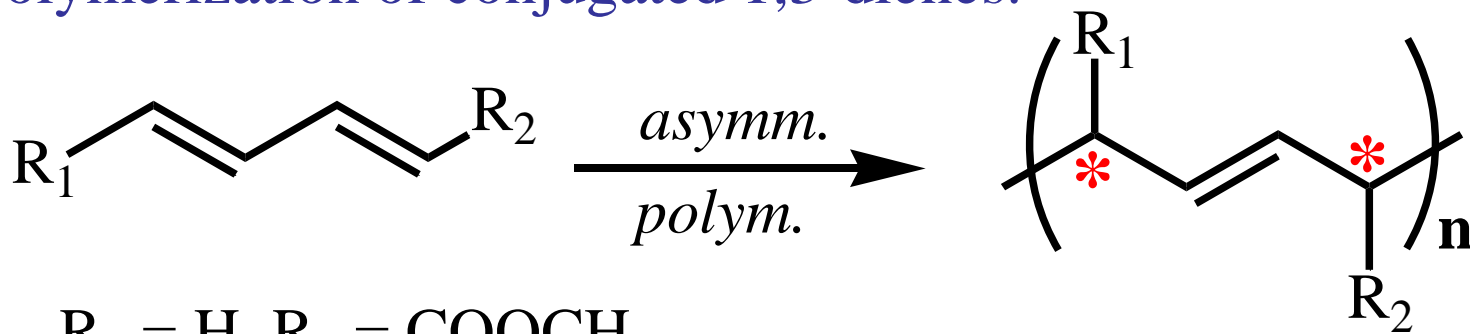
Polymerization via asymmetric synthesis

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.



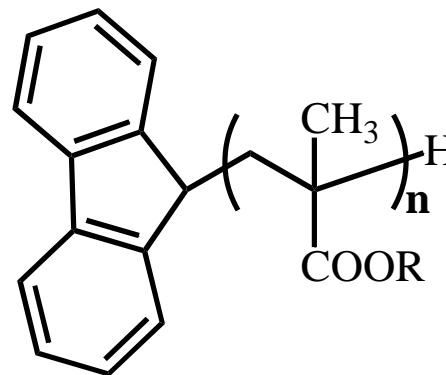
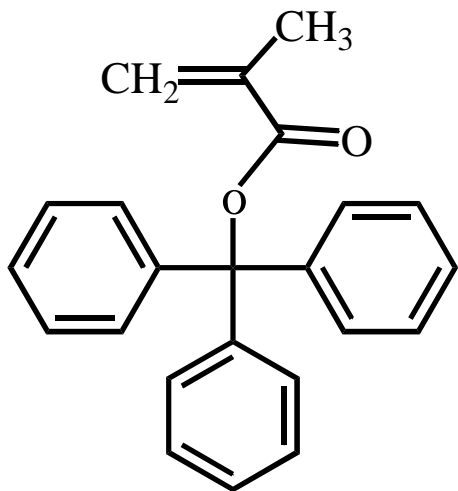
Asymmetric polymerization

*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:



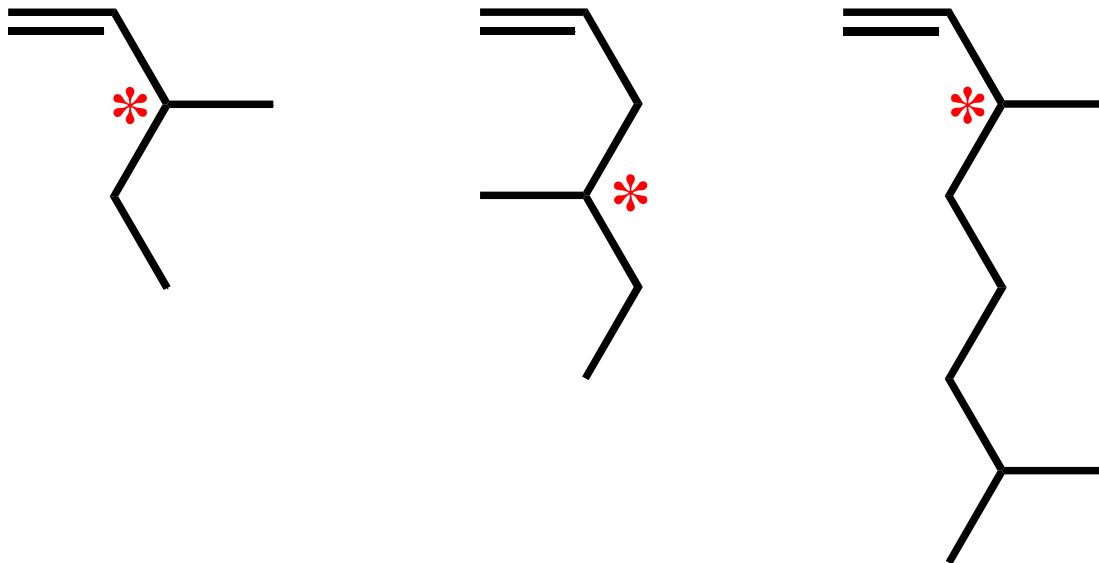
Asymmetric polymerization

*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

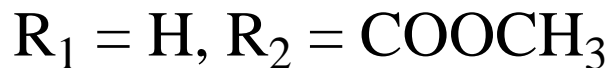
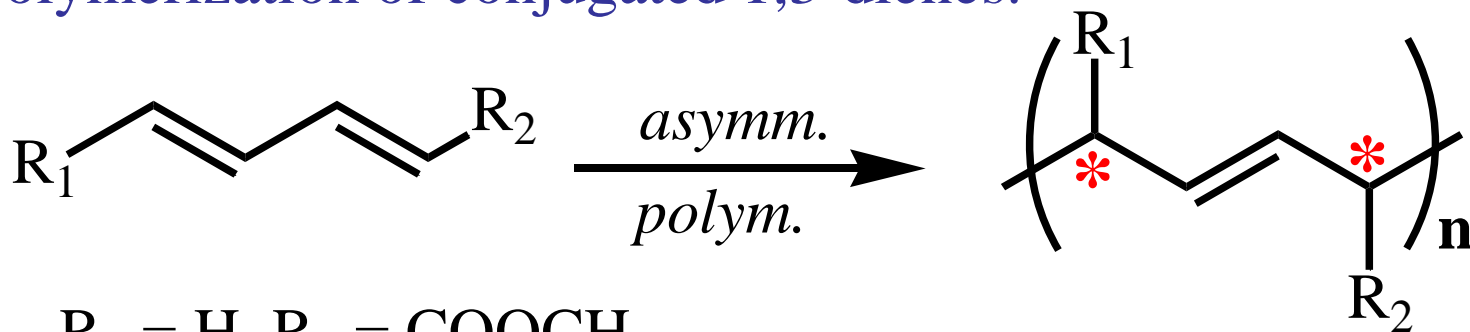
Polymerization via asymmetric synthesis

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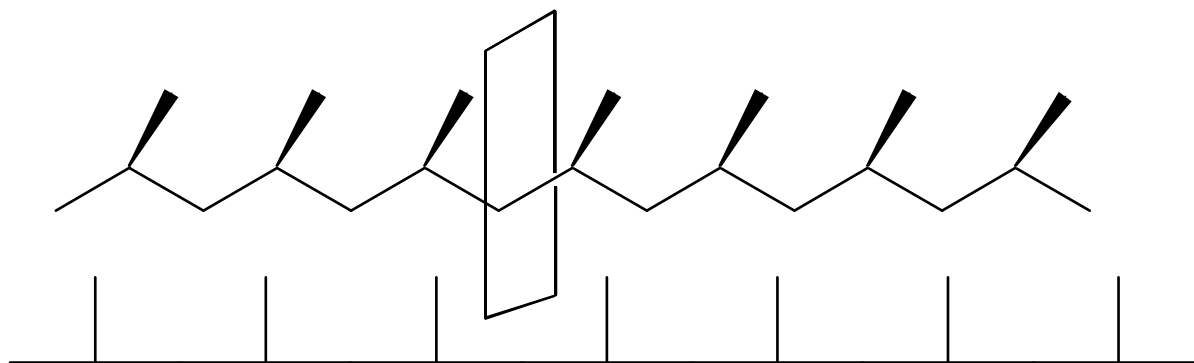
Examples:

Polymerization of vinylic monomers, such as propylene, styrene

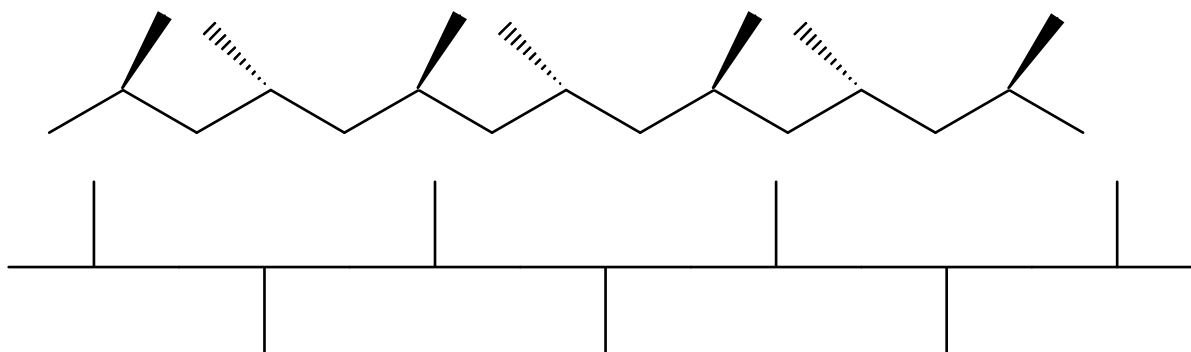
Polymerization of conjugated 1,3-dienes.



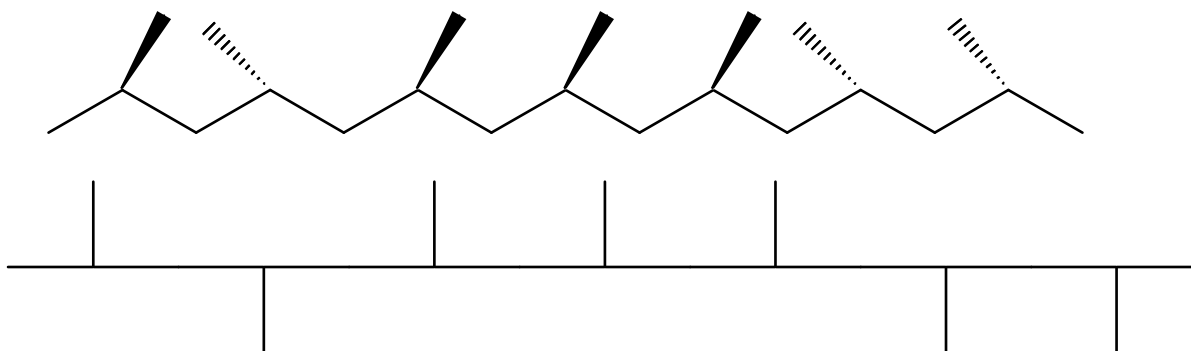
Polypropylene synthesis: The CRYPTOCHIRALITY phenomenon



isotactic



syndiotactic



atactic

Polypropylene synthesis

Stereocontrolled polymerization:

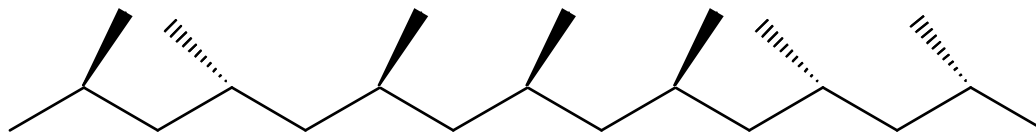
Control of stereochemistry via the nature of the ancillary ligands on the metal centre.



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



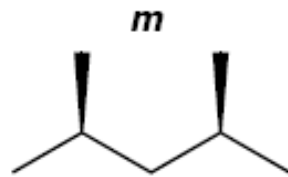
Multiple insertions of the **alternating enantiofaces:**
syndiotactic polymer



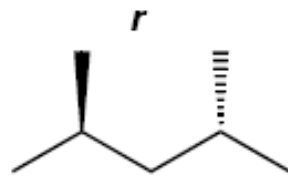
Random enantioface insertions:
atactic polymer

Tacticity

Dyad Tacticity

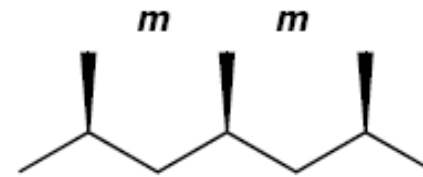


isotactic (*meso, m*)

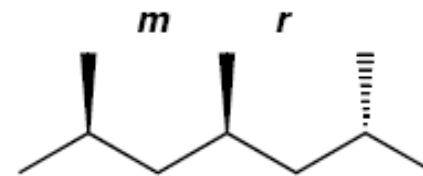


syndiotactic (*racemic, r*)

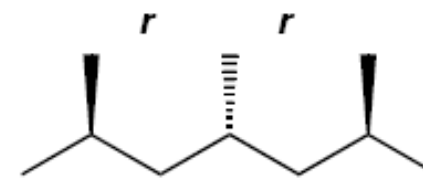
Triad Tacticity



isotactic (*mm*)



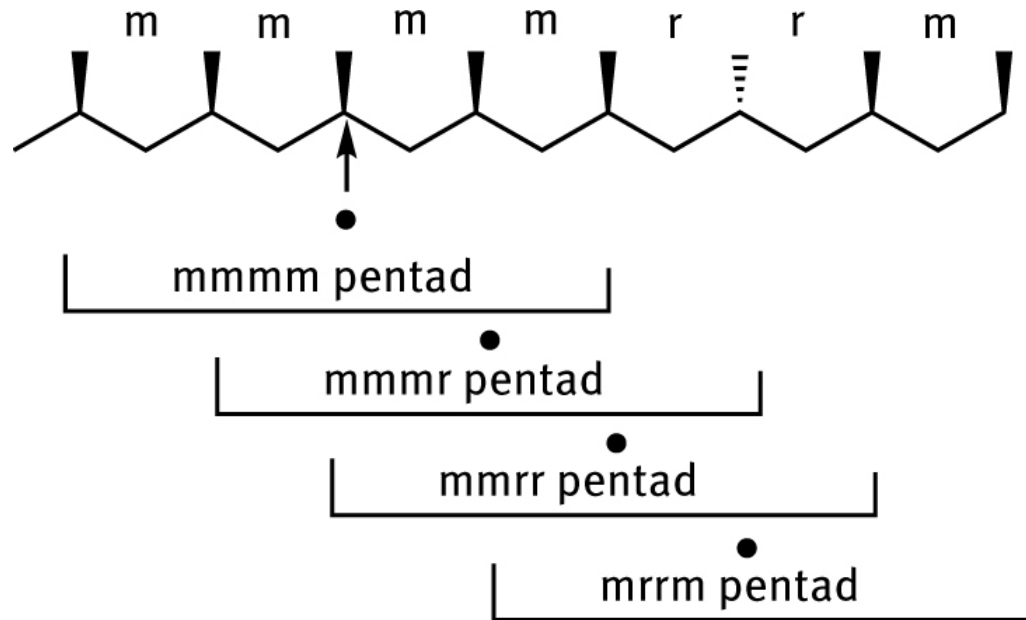
atactic (*mr*)



syndiotactic (*rr*)

Tacticity

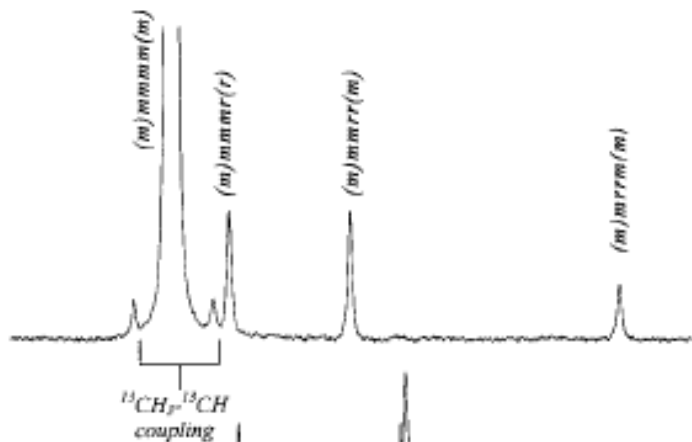
- **Isotactic and syndiotactic** polymers are **crystalline**, **atactic** is **amorphous**;
- **NMR spectroscopy** is a powerful tool for studying polymer **Stereochemistry**.
- Tacticity of polymer is determined by % *m* or *r* dyads
e.g. Perfectly isotactic polypropylene has 100% *m* dyads



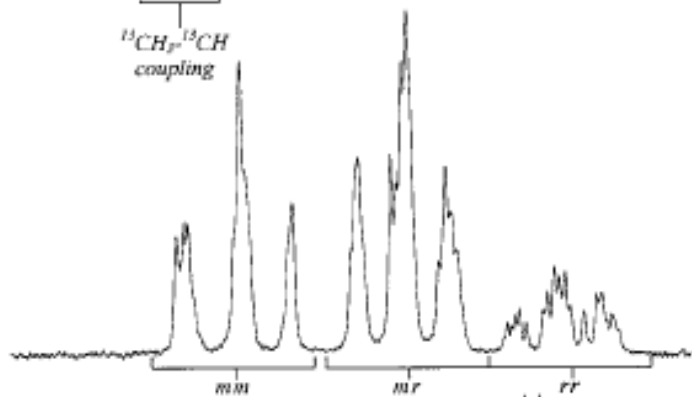
Microtacticity

^{13}C NMR Spectra of polypropylene: methyl pentad region

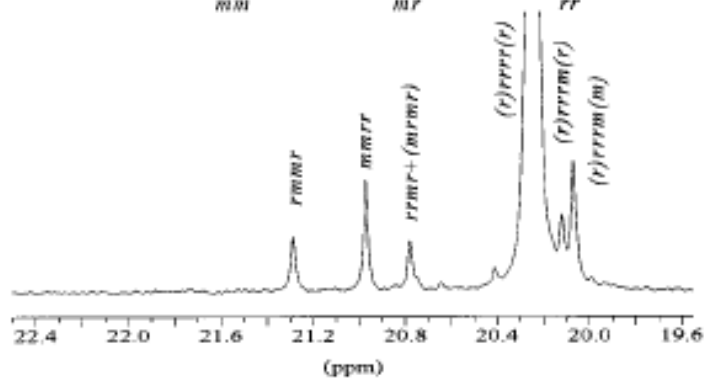
isotactic



atactic

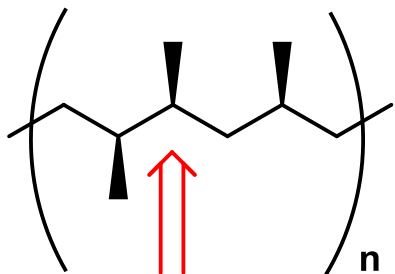


syndiotactic

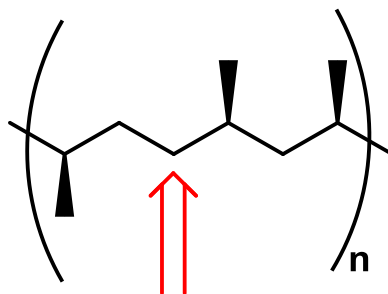


Regiochemistry

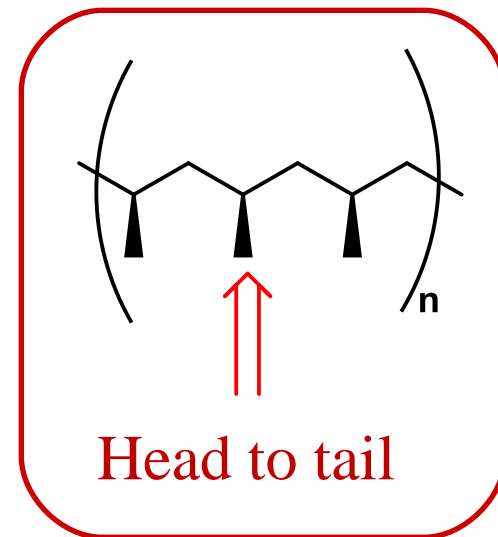
The possible regiosequences



Tail to tail

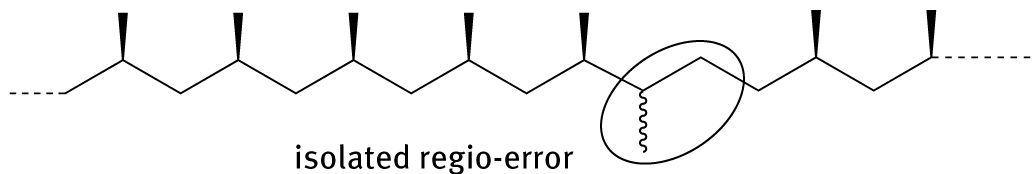


Head to head



Head to tail

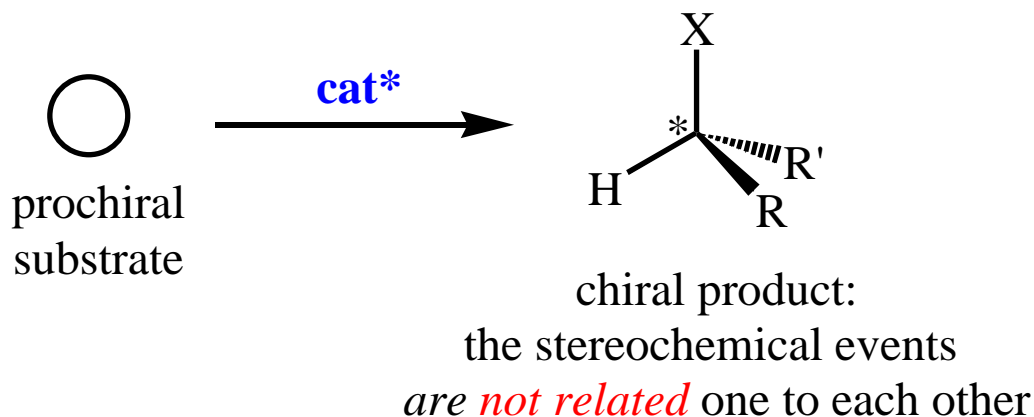
are originated by 1,2-Insertion or 2,1-Insertion



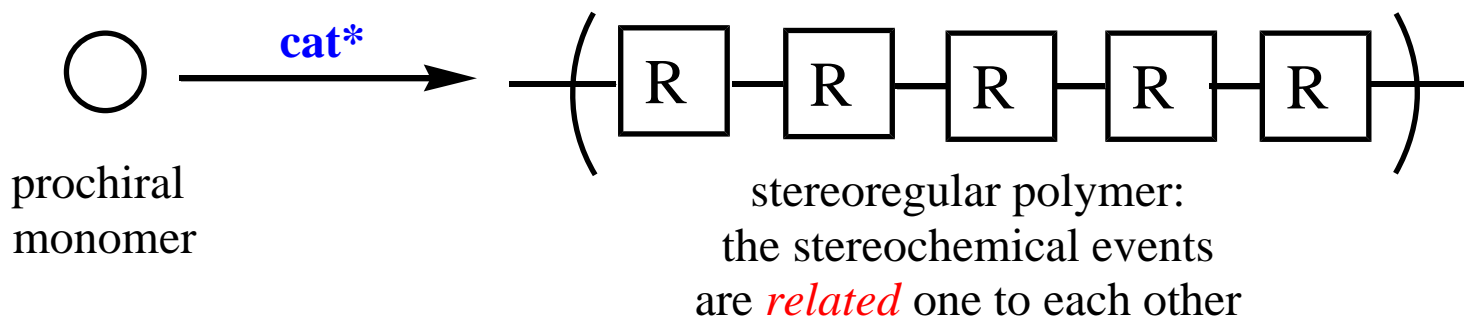
isolated regio-error

ENANTIOSELECTIVE CATALYSIS¹

Enantioselective synthesis of small molecules



Stereospecific polymerization

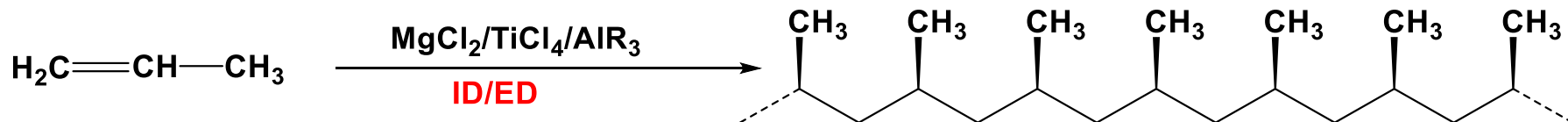


$\text{cat}^* = \text{chiral coordination compound}$

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

STEREOSPECIFIC Ziegler-Natta Catalysts

Sintesi di polipropilene *isotattico*

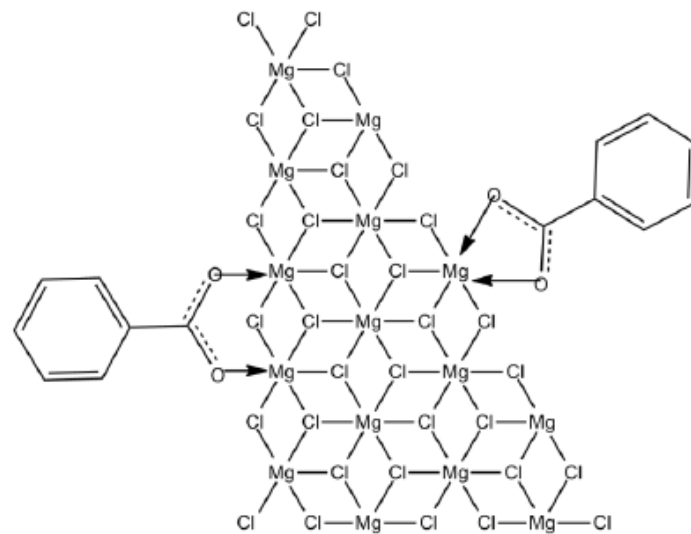
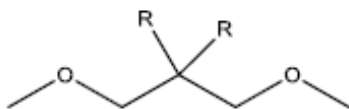
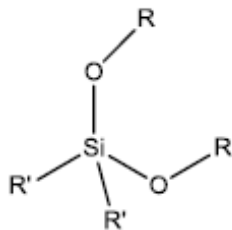
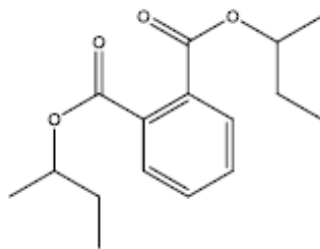
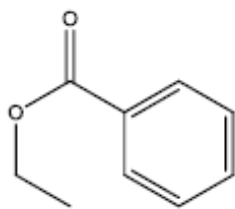


ID = internal donor

ED = external donor

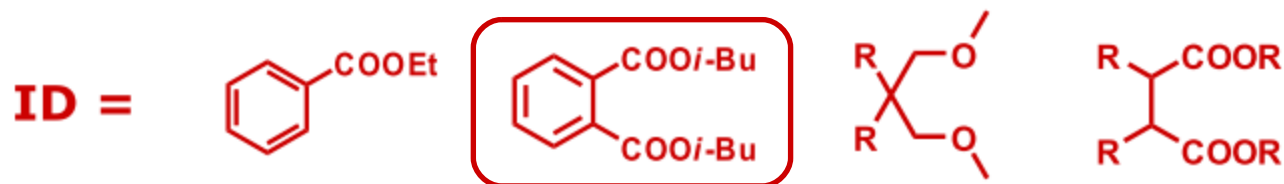
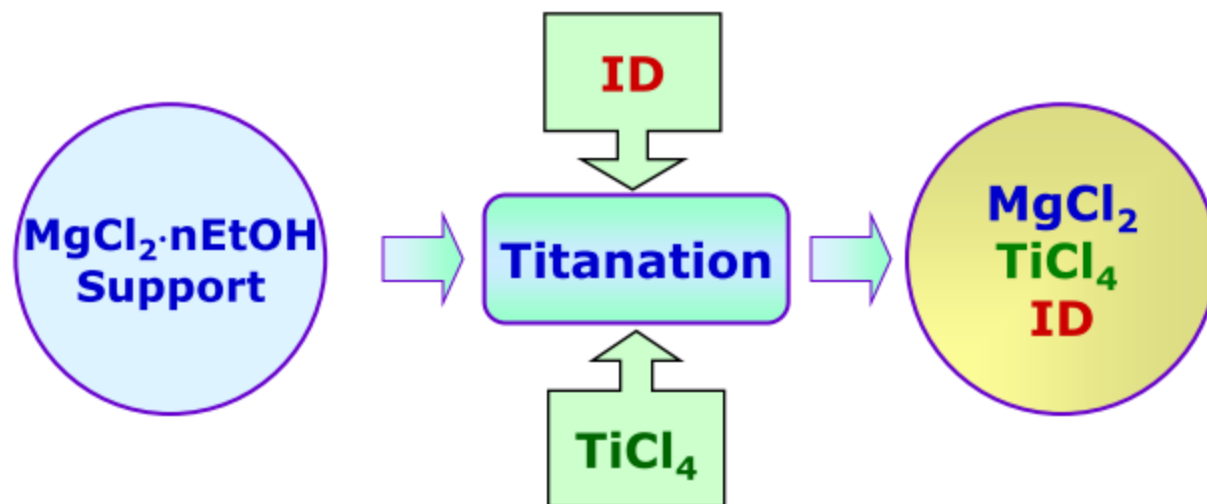
Catalyst nature: *heterogeneous*

The donors



Z-N Catalyst Preparation

The solid Catalyst Precursor

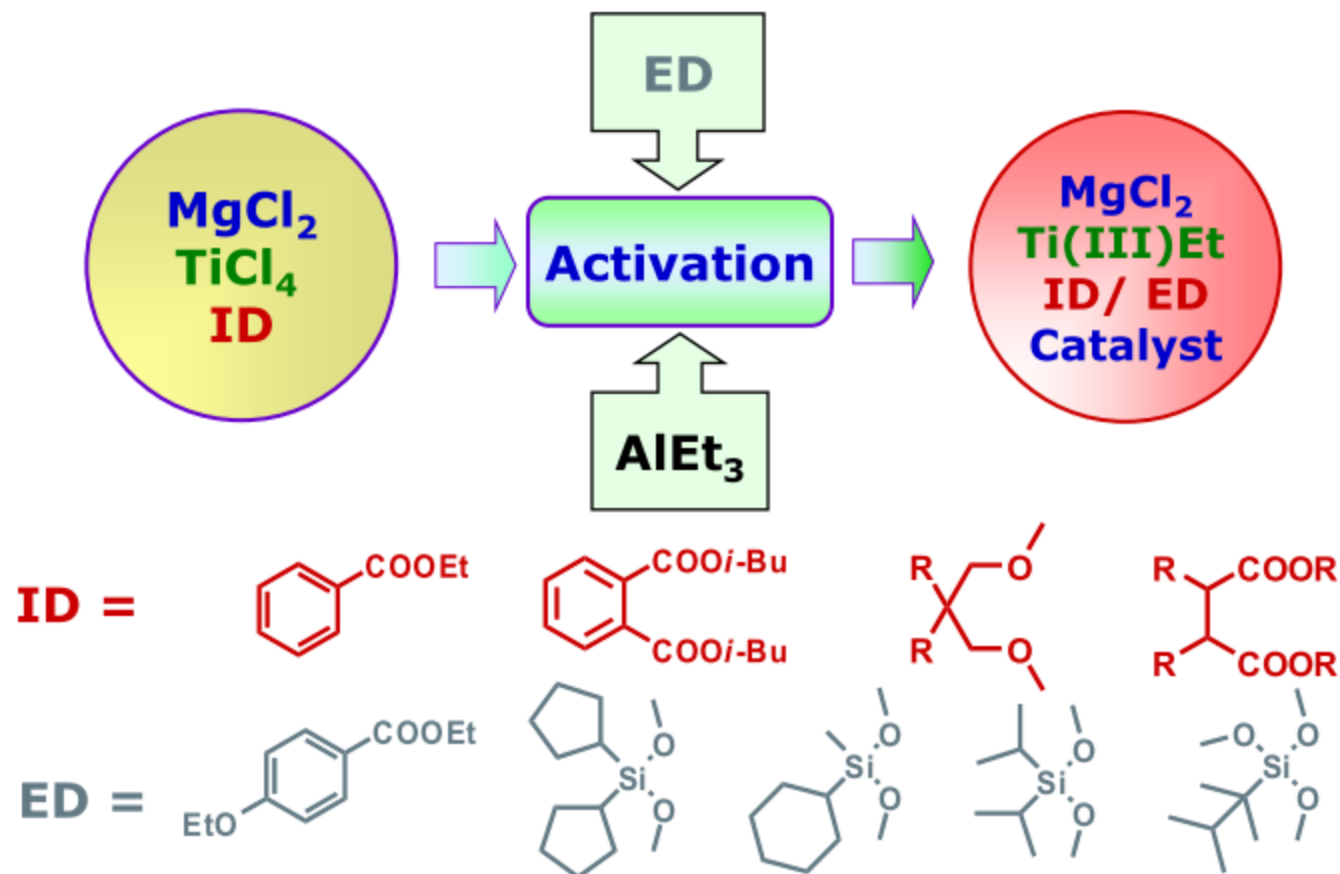


The Internal Donor is added (alone or in mixture) during the catalyst preparation, with the goal to:

- stabilize nascent MgCl₂ crystallites
- influence the crystallite dimensions and thus the "working surface" connected with the productivity of the resulting catalyst
- control of the distribution of TiCl₄ on the possible MgCl₂ cuts

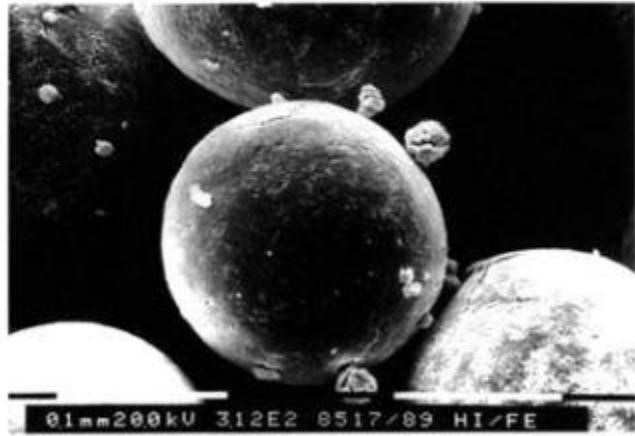
Z-N Catalyst Preparation

Activation of the catalyst: ED structures

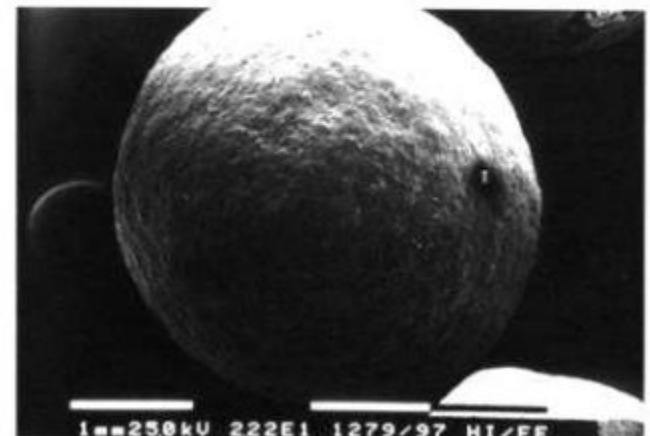


15000 kg PP/mol Ti MPa h di i-PP 97 -98 %

Morphology of supports and PP particle



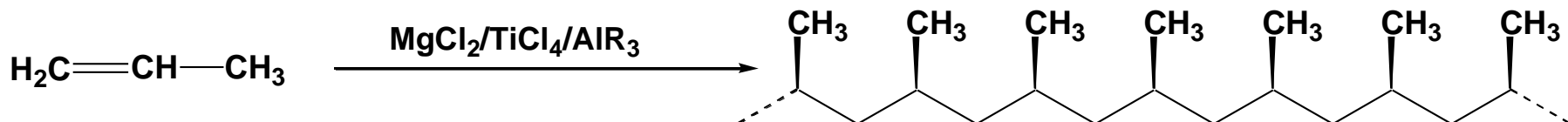
Morphology of catalyst support: spherical.



Morphology of catalyst of PP particles.

STEREOSPECIFIC Ziegler-Natta Catalysts

Synthesis of *isotactic* polypropylene



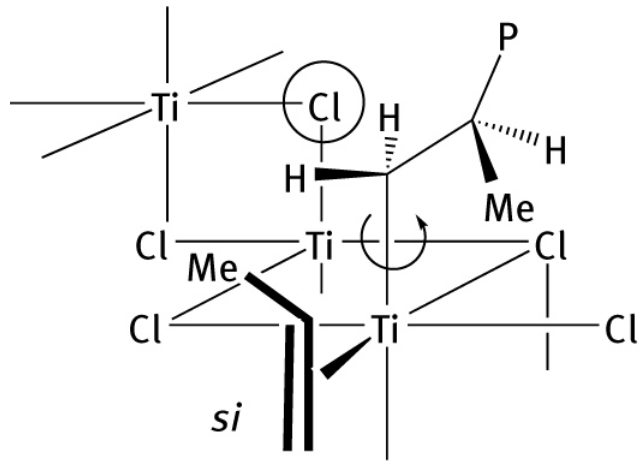
Heterogeneous catalyst.

Stereochemistry of the insertion step: nature of the errors:

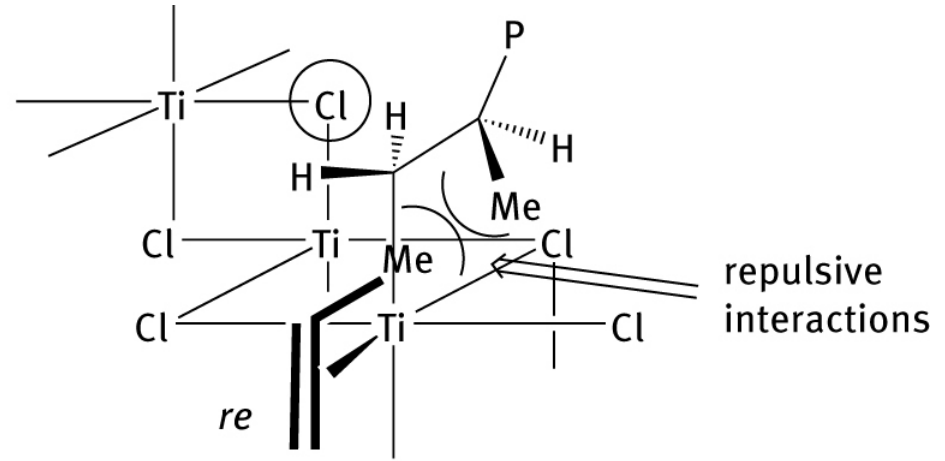


Errors of kind A are indicative for the chiral nature of the catalyst.

Enantiomorphous site control

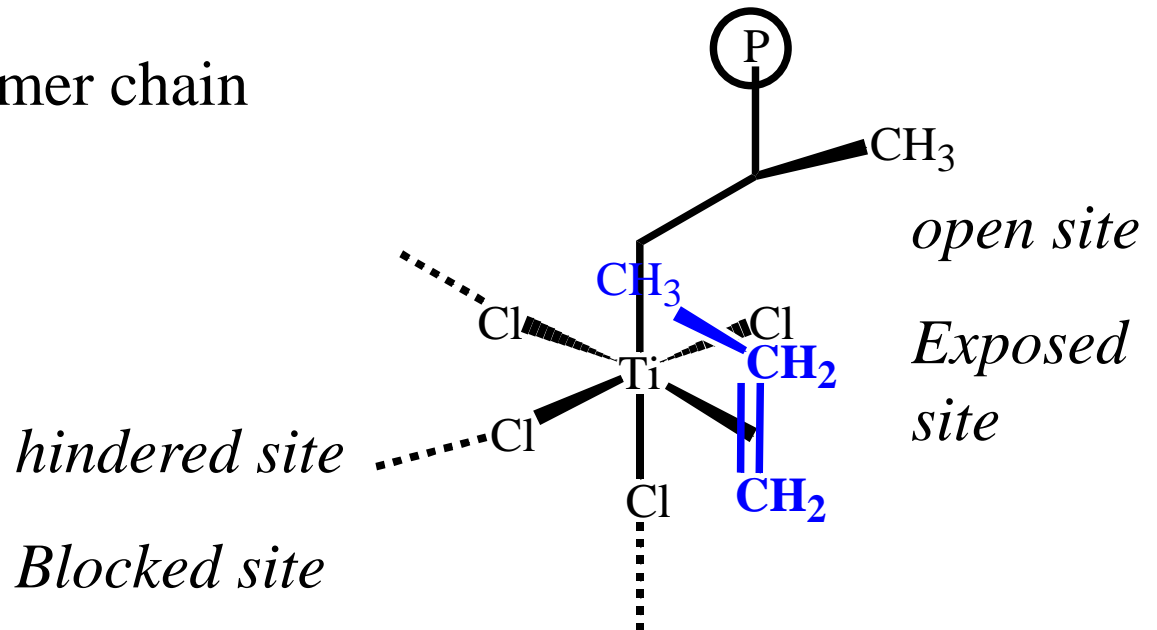


si
favoured conformation



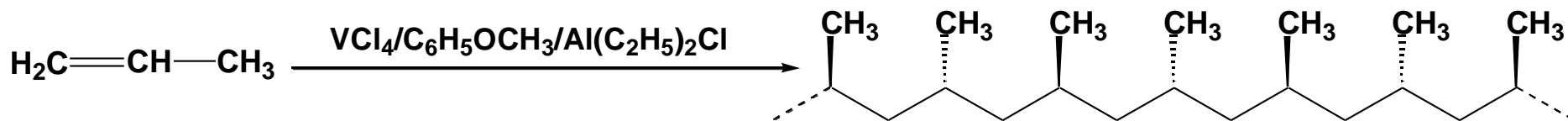
re
disfavoured conformation

P = growing polymer chain



STEREOSPECIFIC Ziegler-Natta Catalysts

Synthesis of *syndiotactic* polypropylene

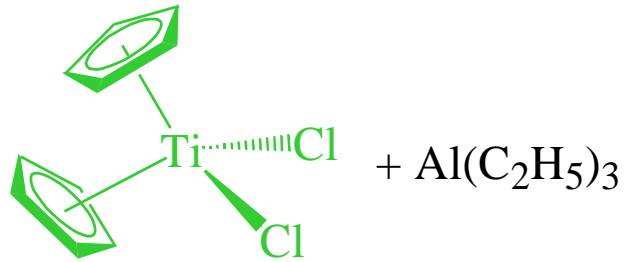


Catalyst nature: *homogeneous*

General aspects of **stereospecific** polymerization of propylene

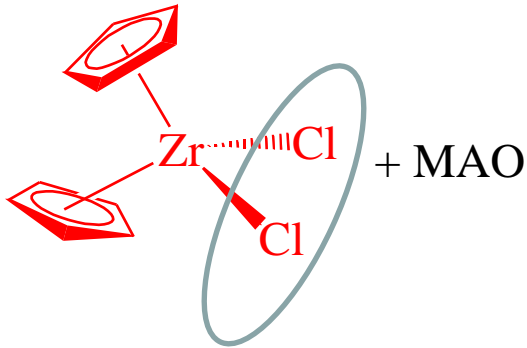
Catalyst	$\text{MgCl}_2/\text{TiCl}_4/\text{AlR}_3$	$\text{VCl}_4/\text{C}_6\text{H}_5\text{OCH}_3/\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}$
Stereoregularity	isotactic	syndiotactic
Regioselectivity	primary	secondary
Control of stereochemistry	enantiomeric site	chain end
	$\text{L}_n\text{M}-\text{CH}_2-\underset{\text{CH}_3}{\text{CH}}-\text{P}$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

Soluble catalysts



Low activity towards ethylene

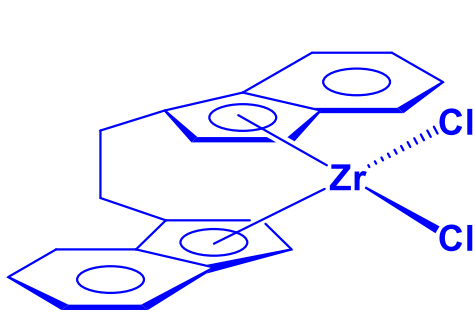
Inactivity towards propylene



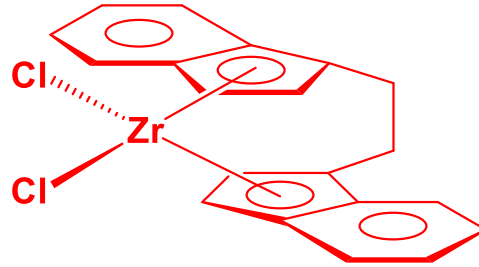
Very high activity towards ethylene

Good activity towards propylene

Metallocene catalysts

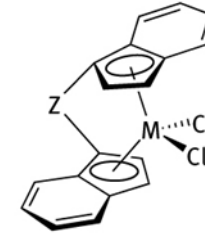


chiral A



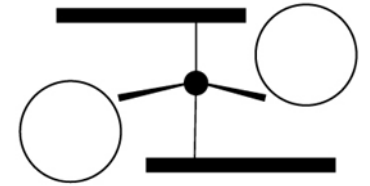
achiral B

C_2 -symmetric ligand framework:



M = Ti, Zr, Hf
Z = SiMe₂, CMe₂, CH₂CH₂, etc.

Schematic front view



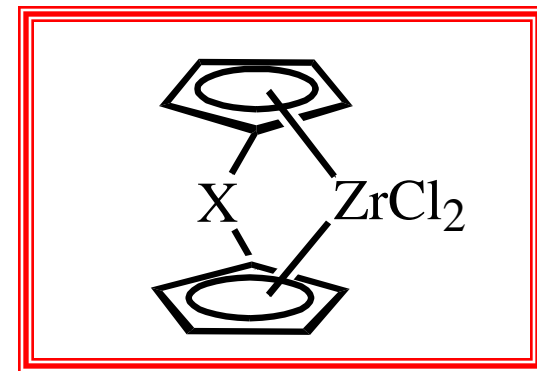
circles indicate more open quadrants of the ligand sphere

A + MAO leads to *isotactic* polypropylene

B + MAO leads to *atactic* polypropylene

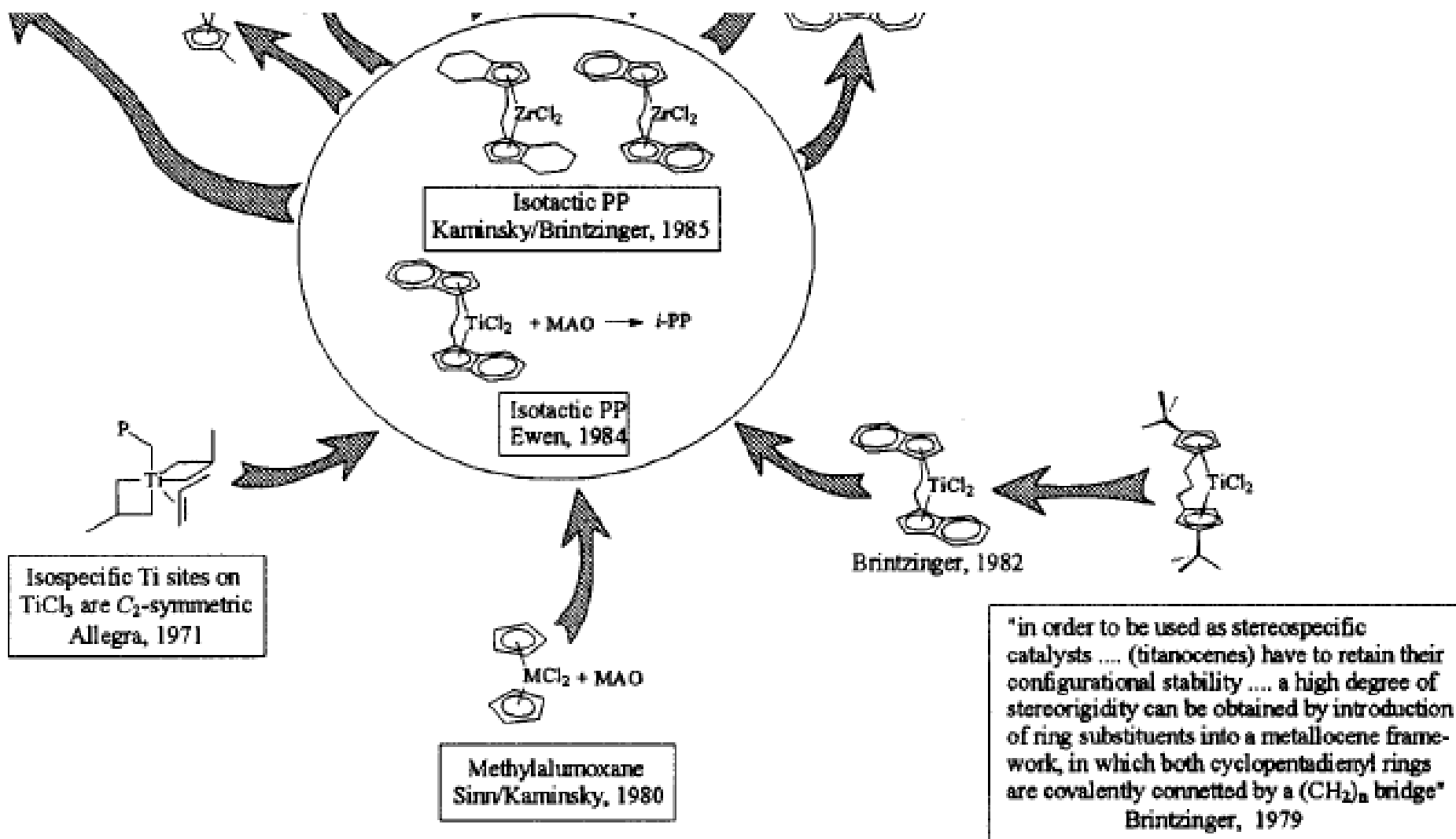
ansa-zirconocenes catalysts:
stereorigid of C_2 symmetry

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



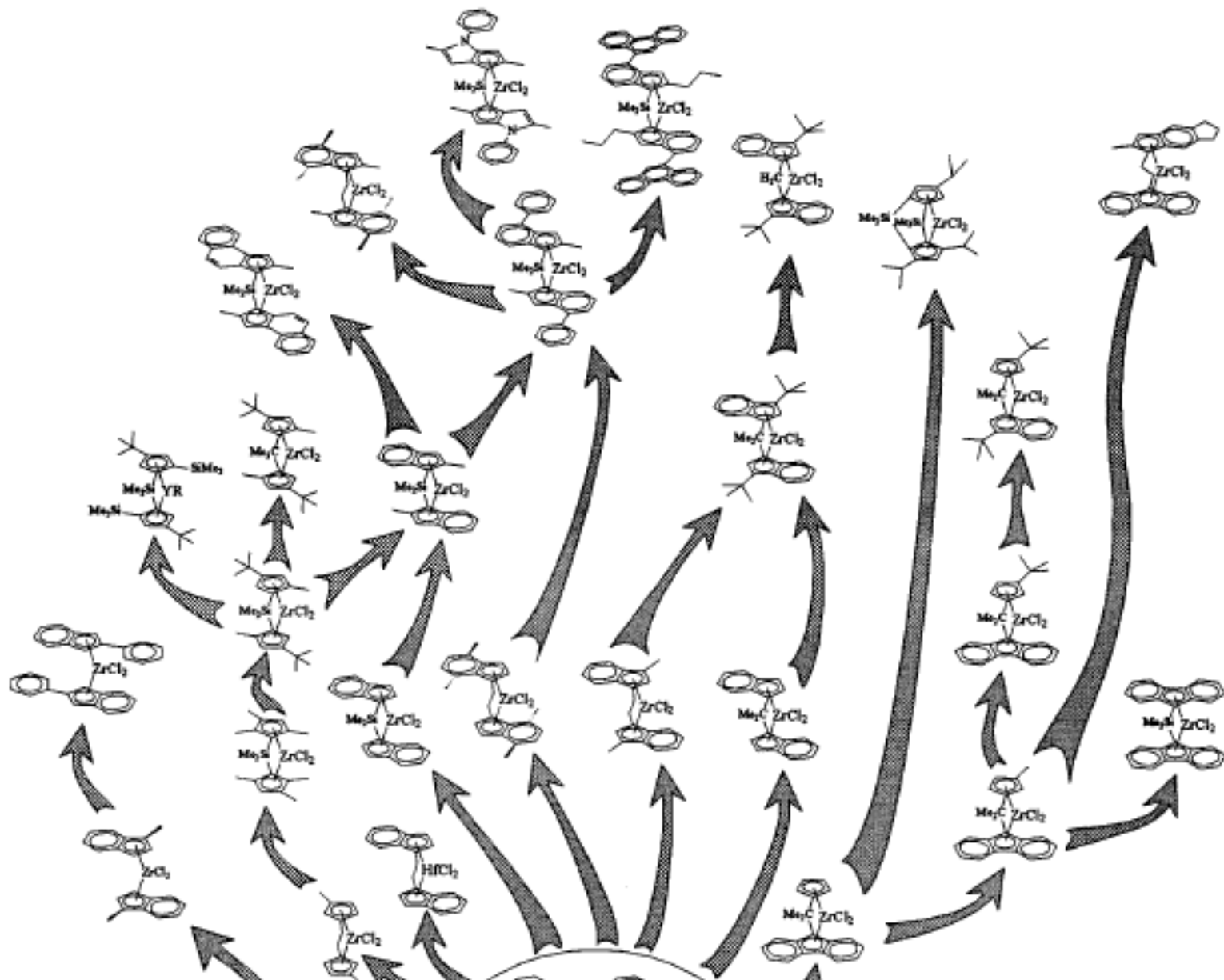
- ❖ lower **molecular weight**;
- ❖ narrower **molecular weight distribution**;
- ❖ the **tacticity**: from **almost atactic** to **perfectly isotactic** PP can be obtained;
- ❖ not **fully regioregular**: insertions with secondary regiochemistry are also observed;
- ❖ random distribution of **stereo-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

The evolution of metallocene catalysts¹: the root

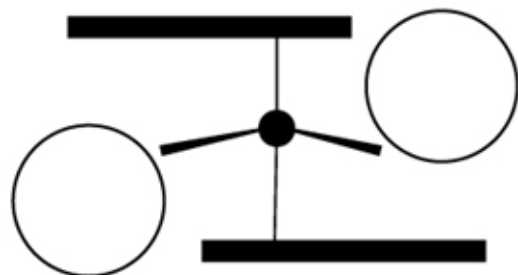


¹L. Resconi et al., *Chem. Rev.* **2000**, *100*, 1253.

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



Ewen's Symmetry Rules

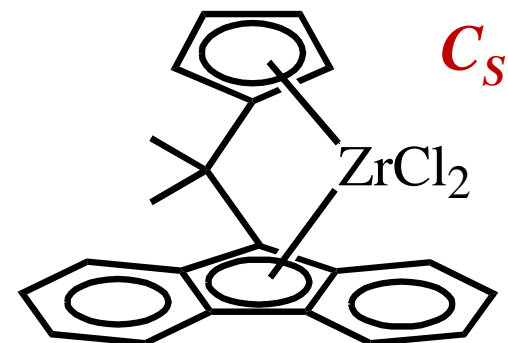


circles indicate more open quadrants of the ligand sphere

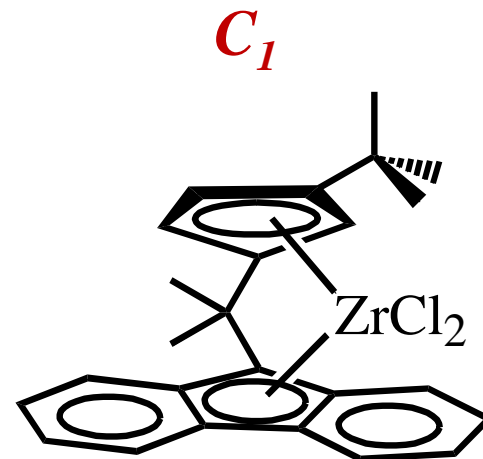
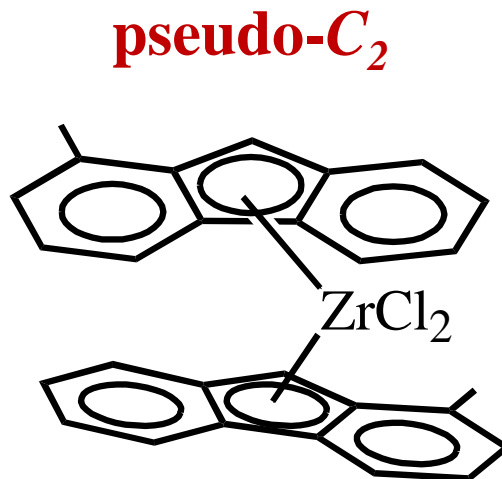
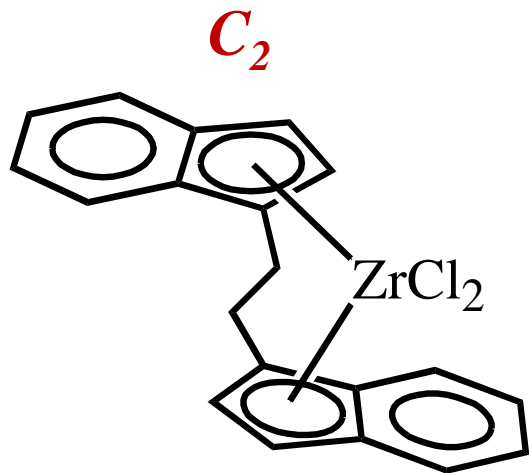
E = enantioselective site; A = nonselective site.

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 Catalyst¹

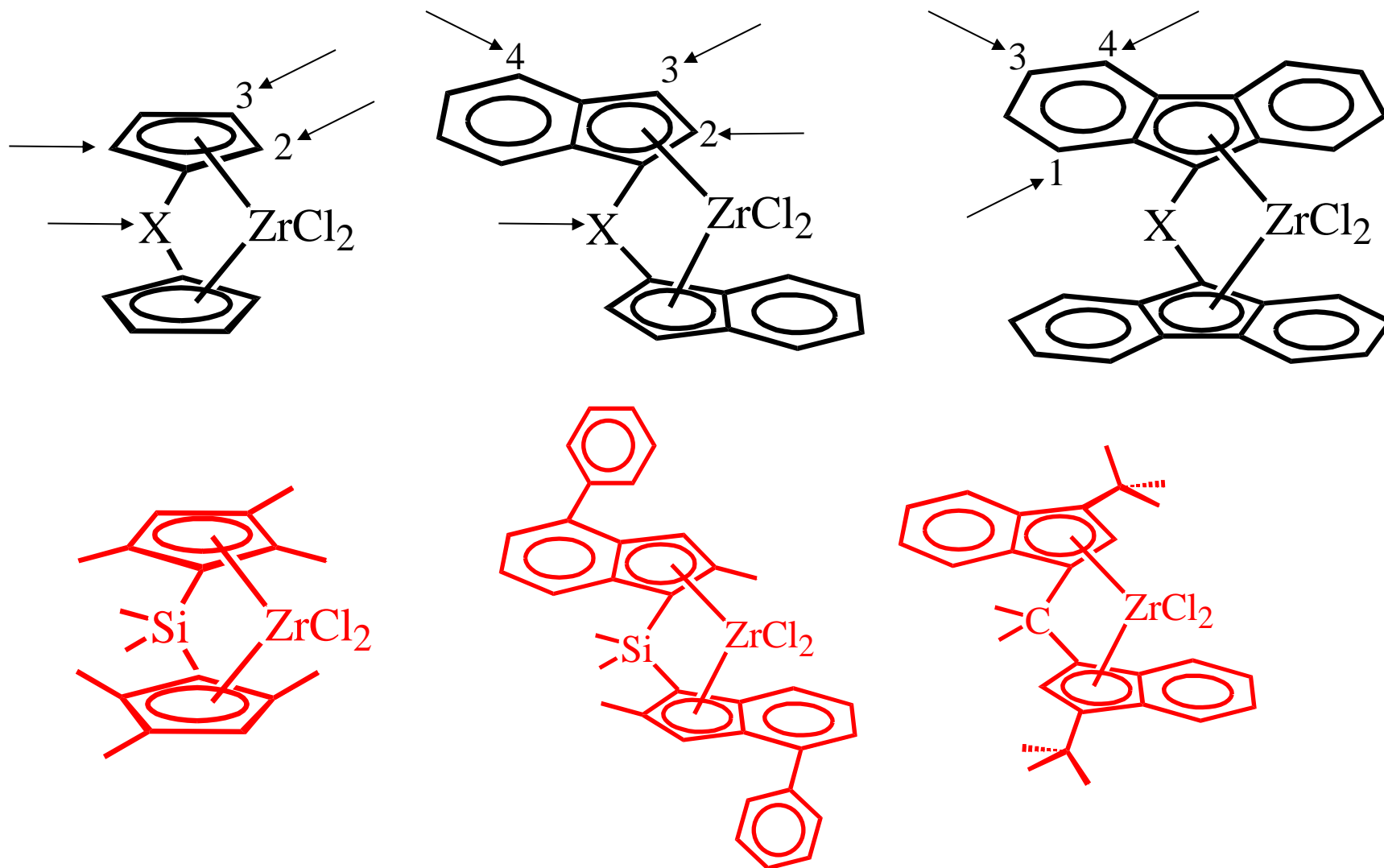


ISOSPECIFIC Catalysts¹



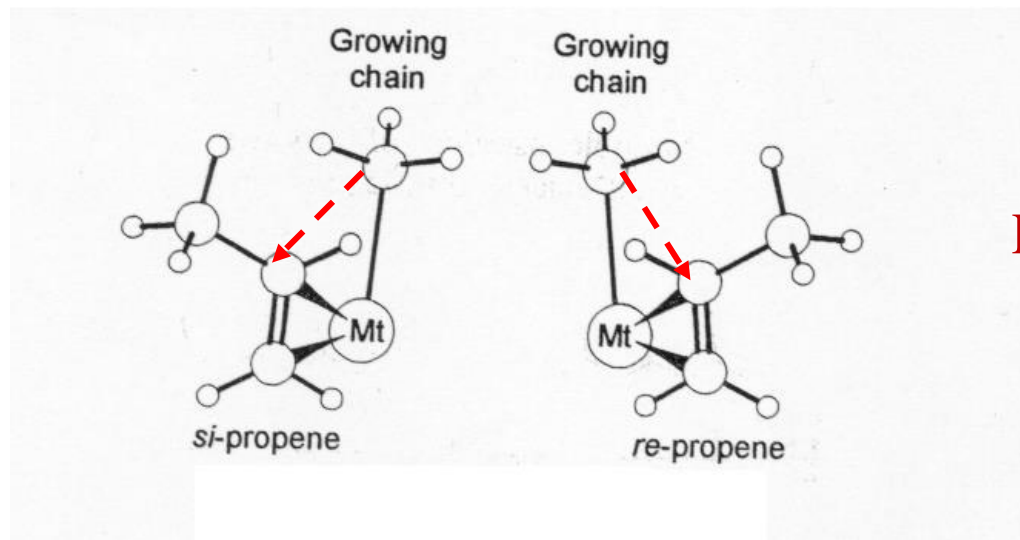
¹L. Resconi et al., *Chem. Rev.* **2000**, *100*, 1253.

ansa-zirconocenes catalysts of C_2 symmetry



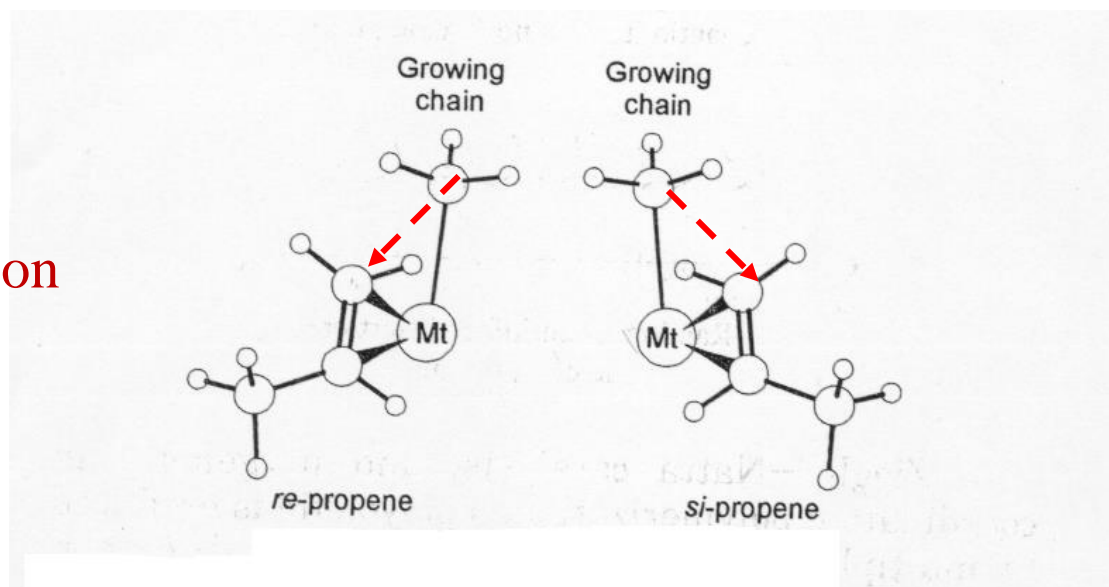
¹L. Resconi et al., *Chem. Rev.* **2000**, *100*, 1253.

DIFFERENT INSERTION WAYS FOR PROPYLENE¹



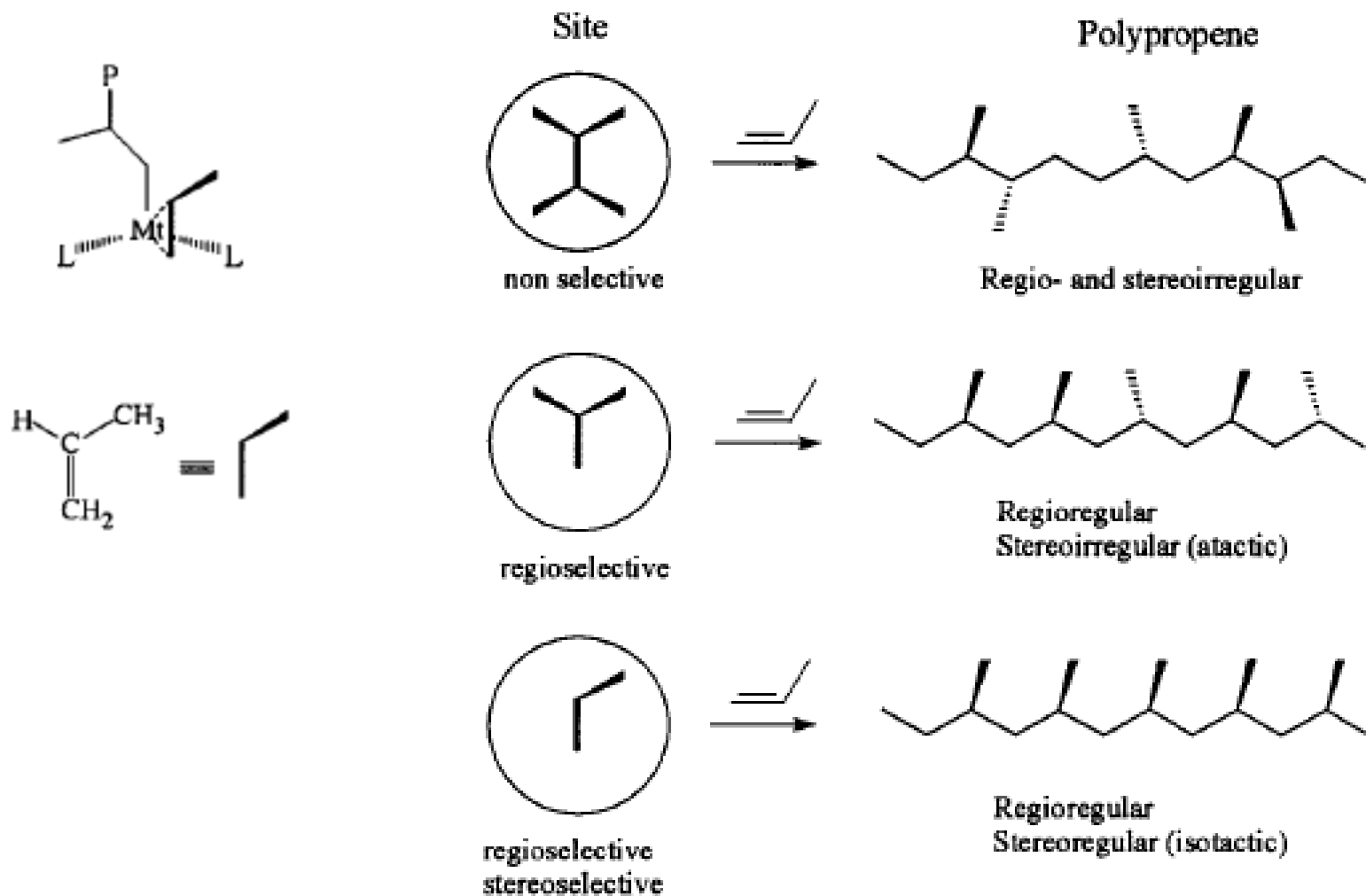
Primary insertion

Secondary insertion

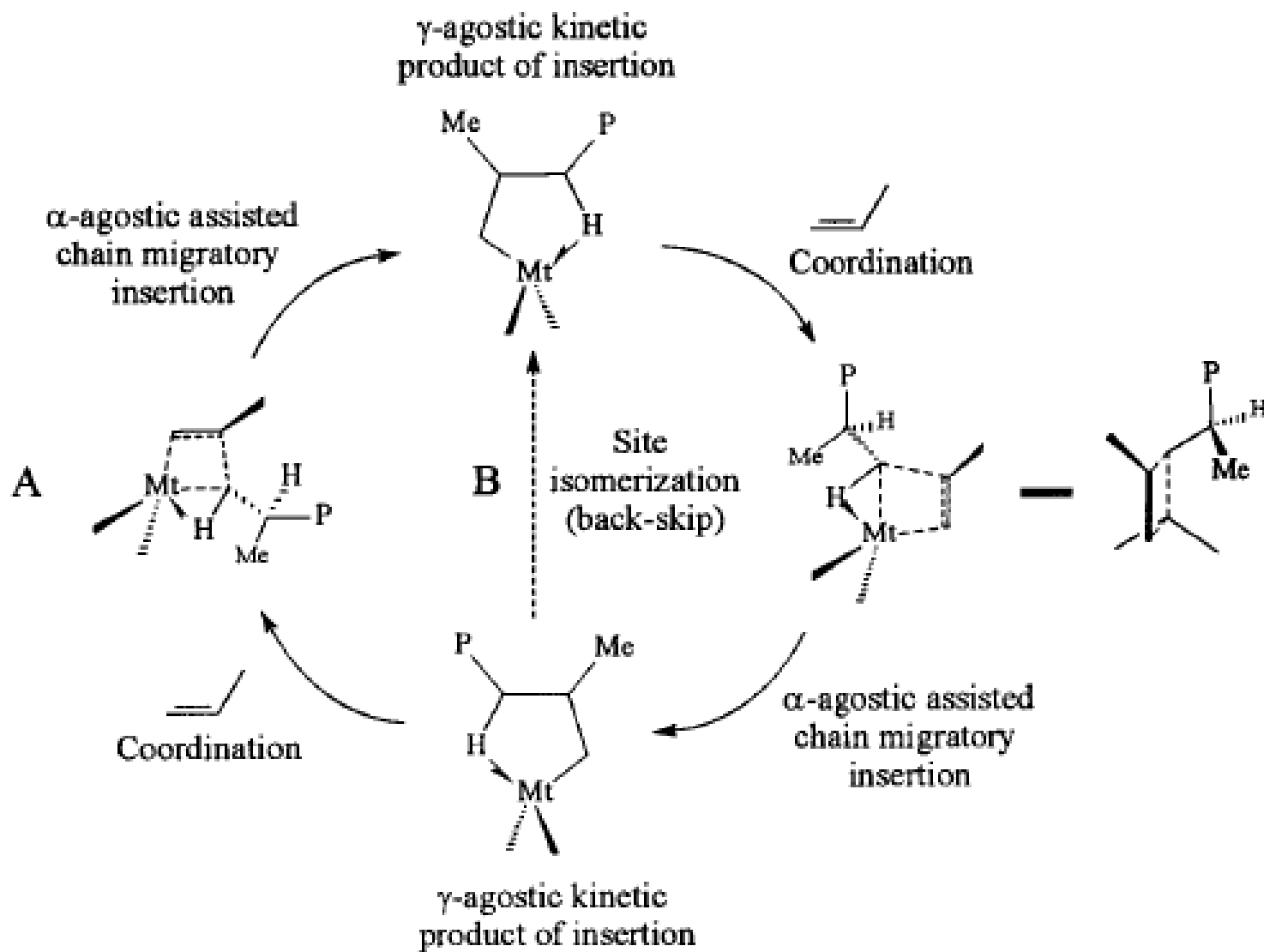


¹L. Resconi et al., *Chem. Rev.* **2000**, *100*, 1253.

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

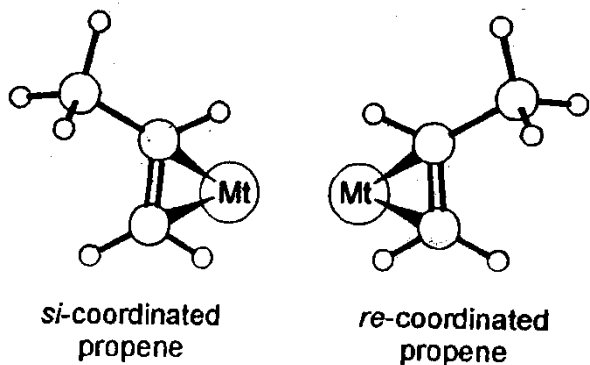


The key-in-the-lock model: **two locks, one key**

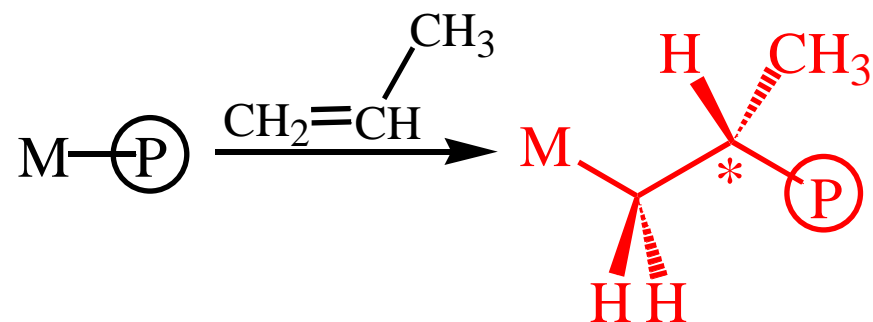


THE ELEMENTS OF CHIRALITY¹

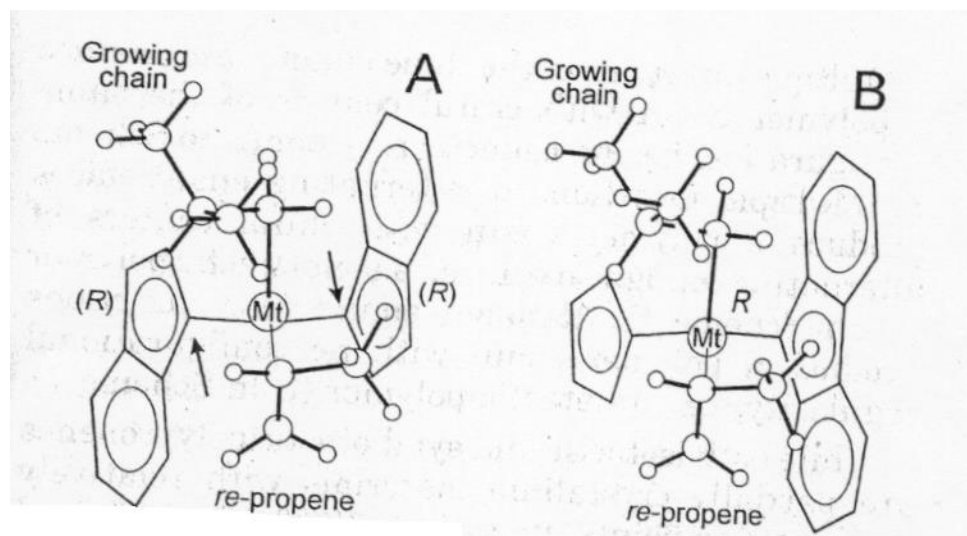
propylene enantioface



growing chain

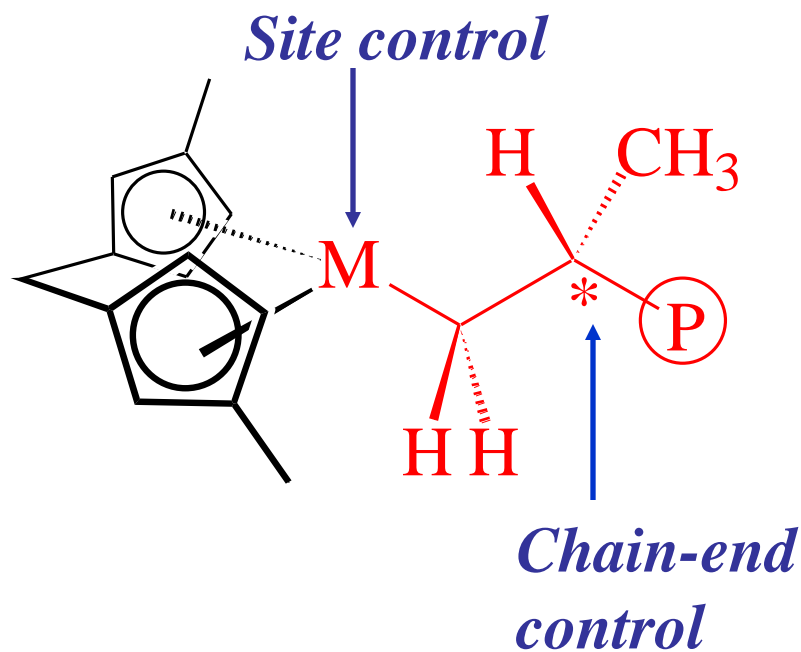


enantiomeric site



¹L. Resconi et al., *Chem. Rev.* **2000**, *100*, 1253.

CHIRAL INDUCTION FOR THE PRIMARY INSERTION¹



¹L. Resconi et al., *Chem. Rev.* **2000**, *100*, 1253.

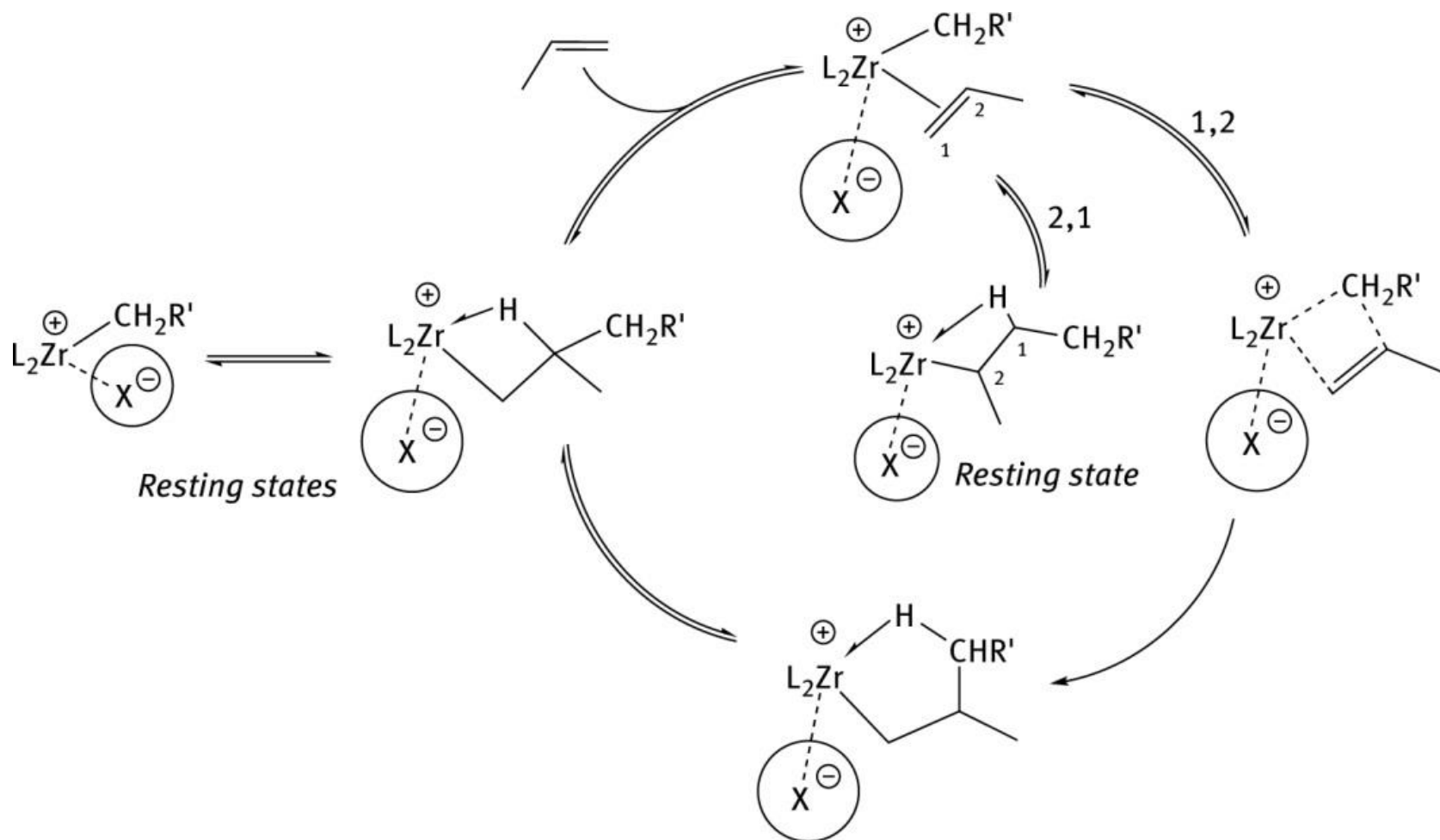
INDUZIONE CHIRALE NELL'INSERZIONE PRIMARIA¹

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

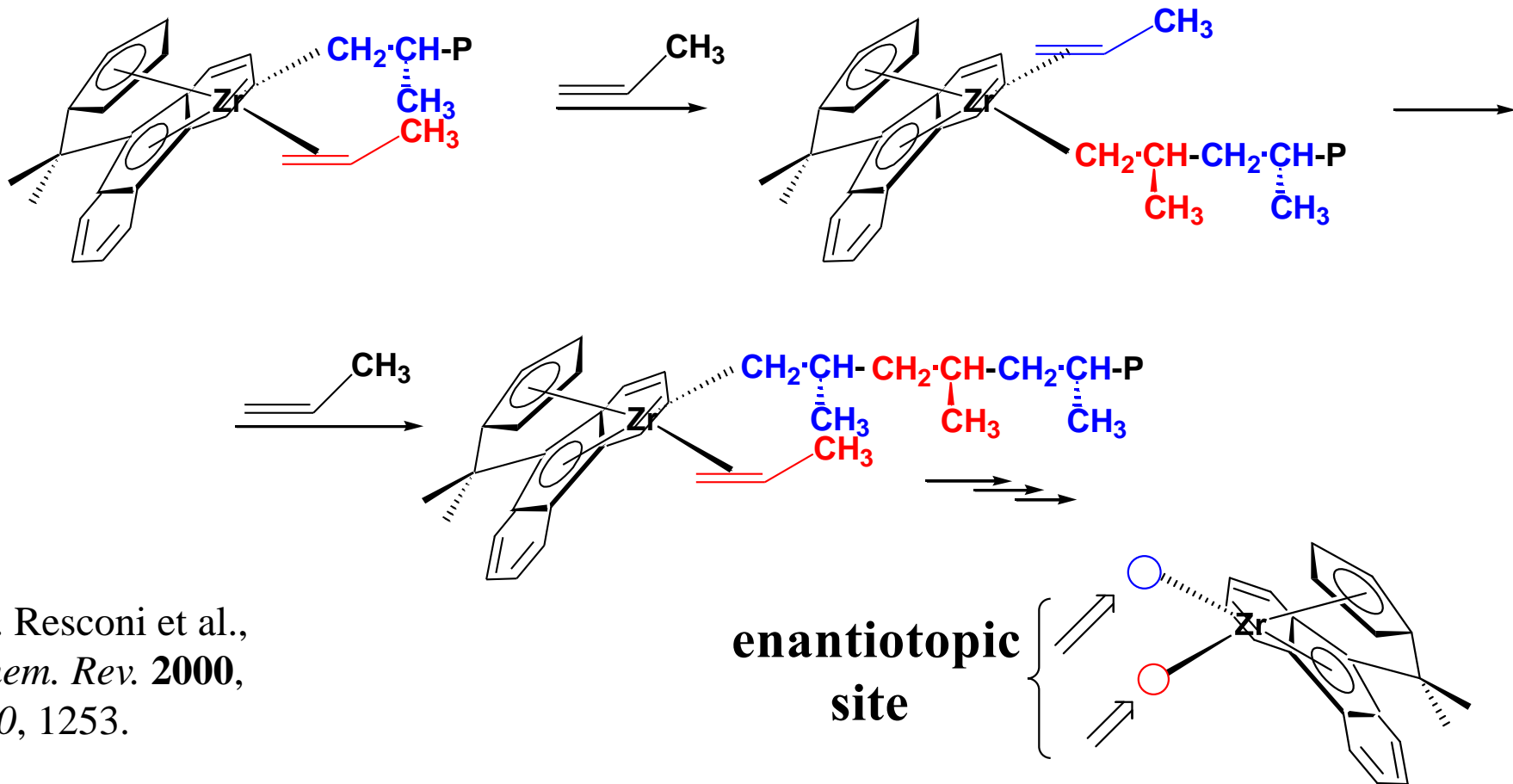
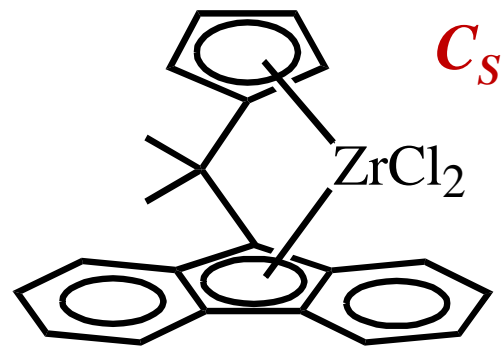
stereoerrors

¹L. Resconi et al., *Chem. Rev.* **2000**, *100*, 1253.

THE CATALYTIC CYCLE

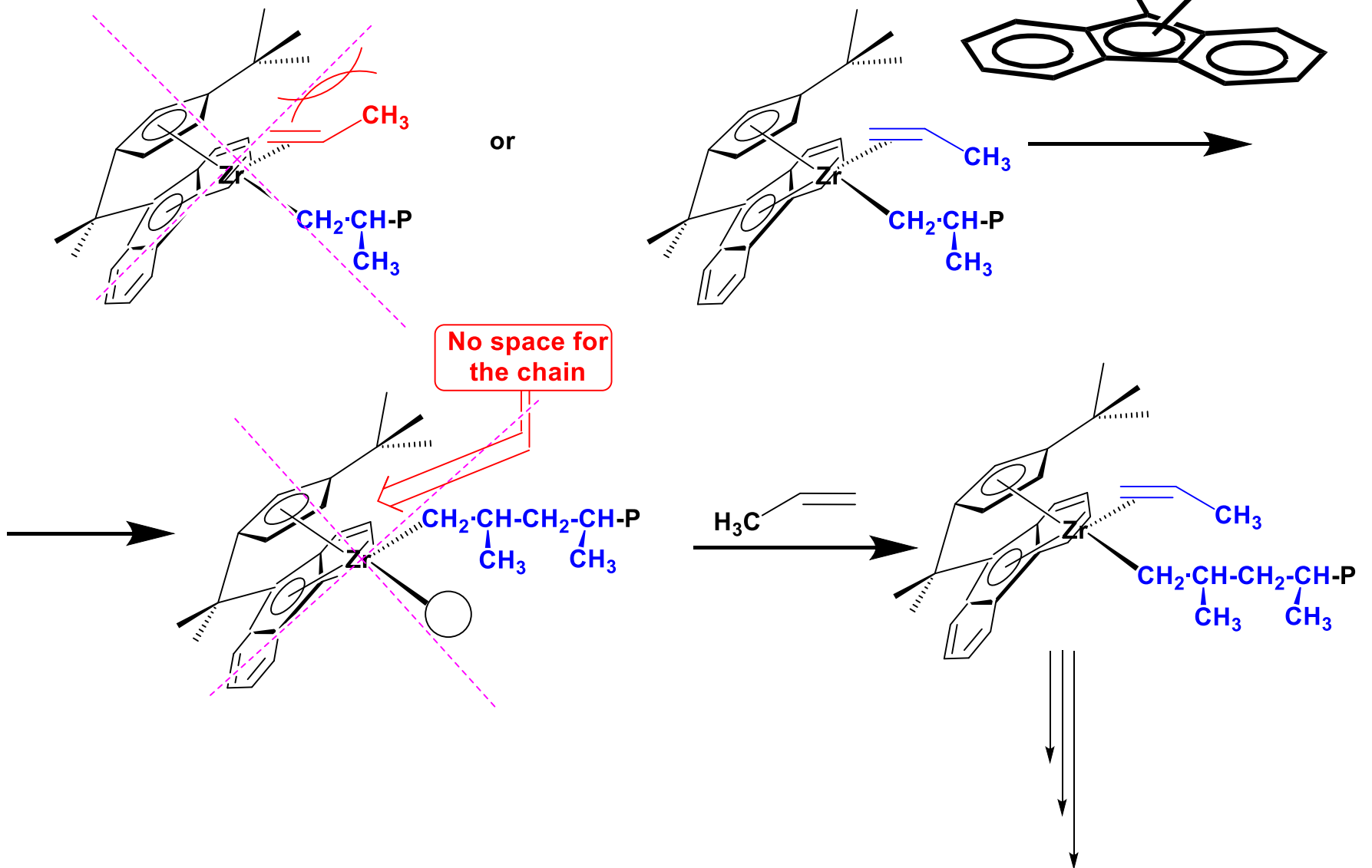


SYNDIOSPECIFIC Catalyst ¹



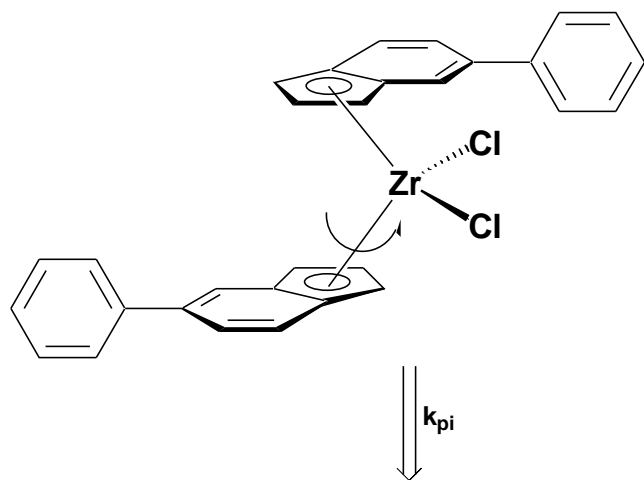
¹L. Resconi et al.,
Chem. Rev. **2000**,
100, 1253.

ISOSPECIFIC Catalyst¹



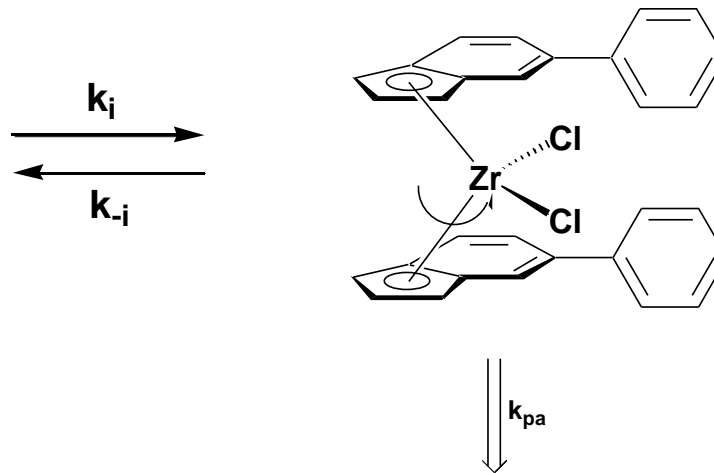
Catalyst for the synthesis of *polypropylene with stereoblocks*

Catalyst in
chiral conformation

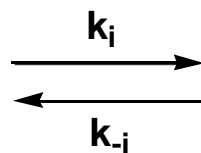


Isotactic block

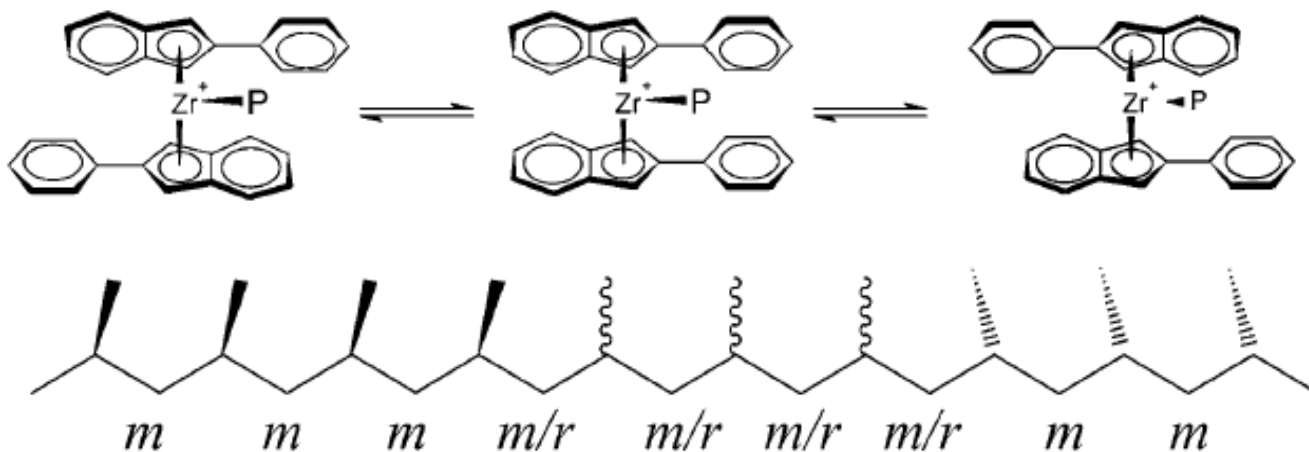
Catalyst in
meso conformation



Atactic block



Catalyst for the synthesis of *polypropylene with stereoblocks*



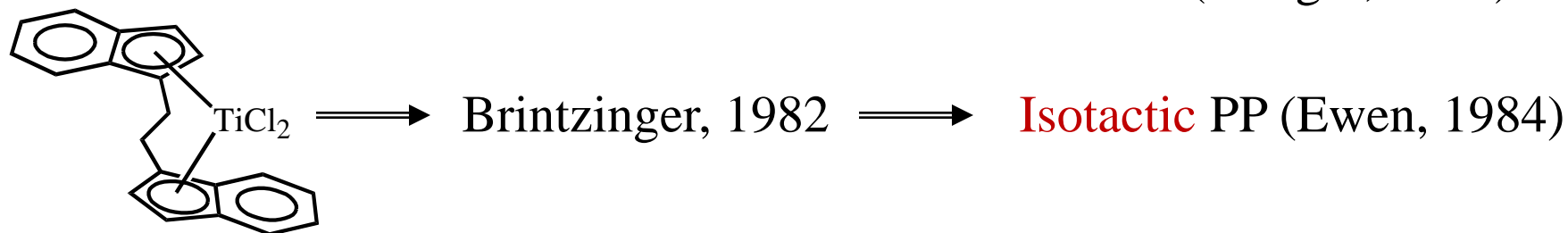
Trend of productivity:



STEREOSPECIFIC Catalysts ¹:

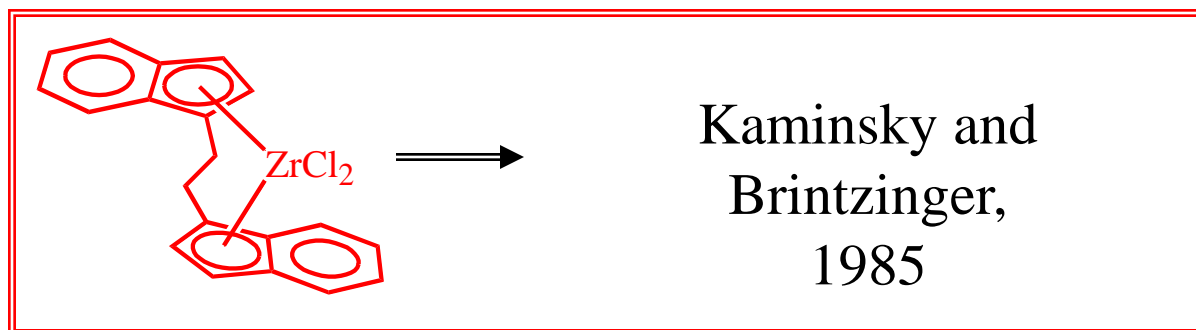
a summary

$\text{TiCl}_3 \implies$ The Ti **isospecific** sites are featured by **C_2 symmetry**
(Allegra, 1971)



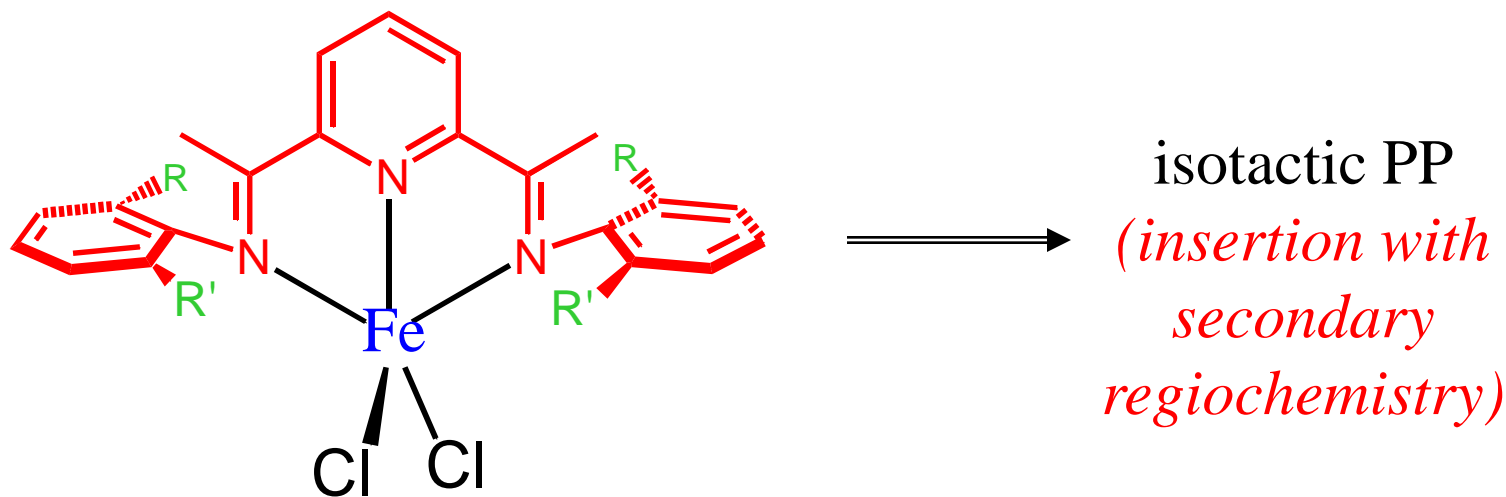
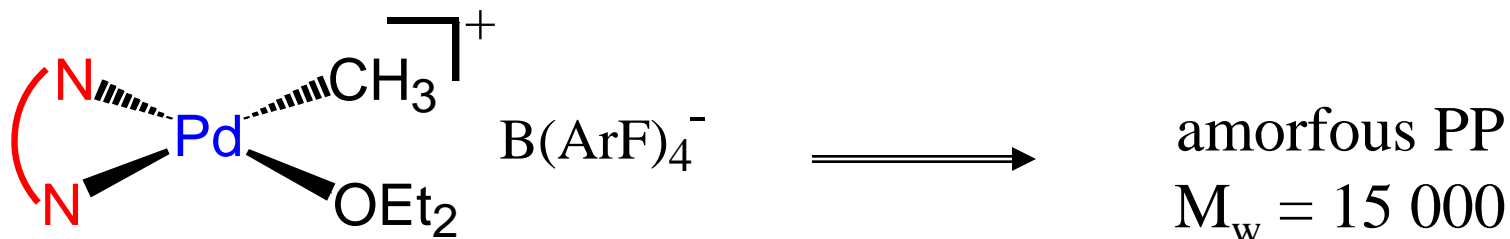
racemic complex \implies *isotactic PP*

meso complex \implies *atactic PP*

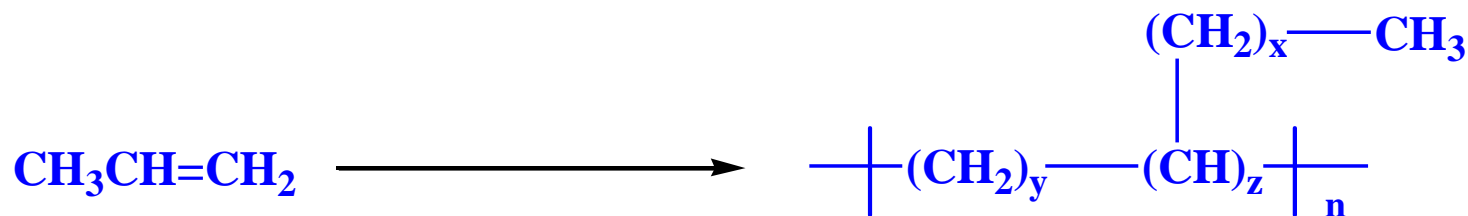


¹L. Resconi et al., *Chem. Rev.* **2000**, *100*, 1253.

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.

