STEREOCONTROLLED POLYMERIZATION

Asymmetric polymerization

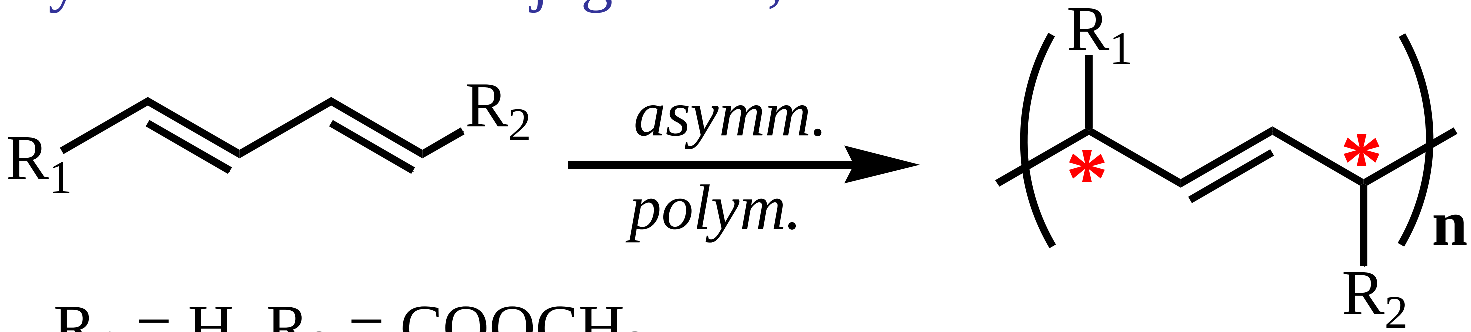
Polymerization via asymmetric synthesis

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.



R_1 = H, R_2 = $COOCH_3$

R_1 = H, R_2 = CH_3

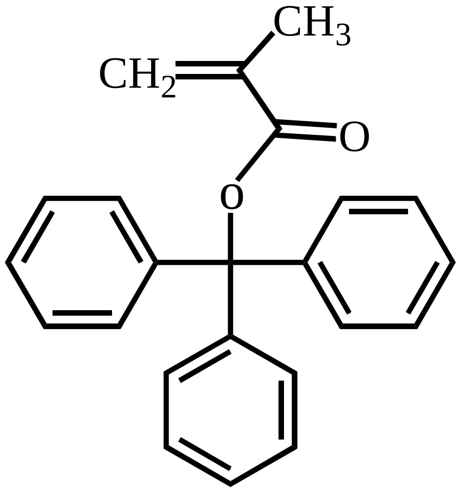
Asymmetric polymerization

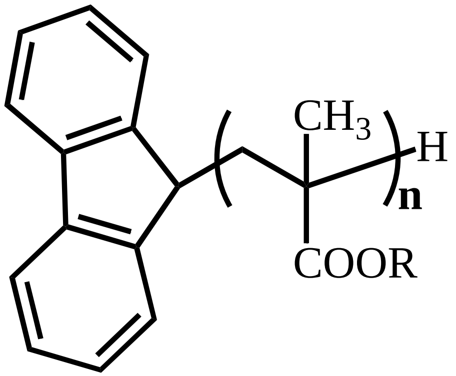
Polymerization selective for the helic sense

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

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

Examples:





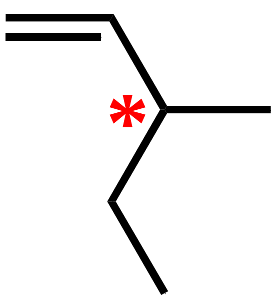
Asymmetric polymerization

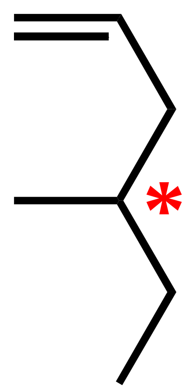
Stereoelective polymerization

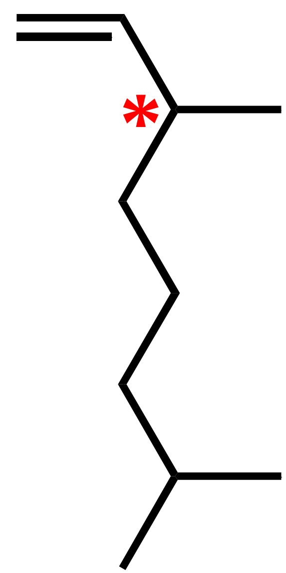
A ***chiral racemic monomer*** is used. Only ***one enantiomer*** of the chiral racemic monomer is preferentially polymerized to yield an optically active polymer.

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

Examples:







STEREOCONTROLLED POLYMERIZATION

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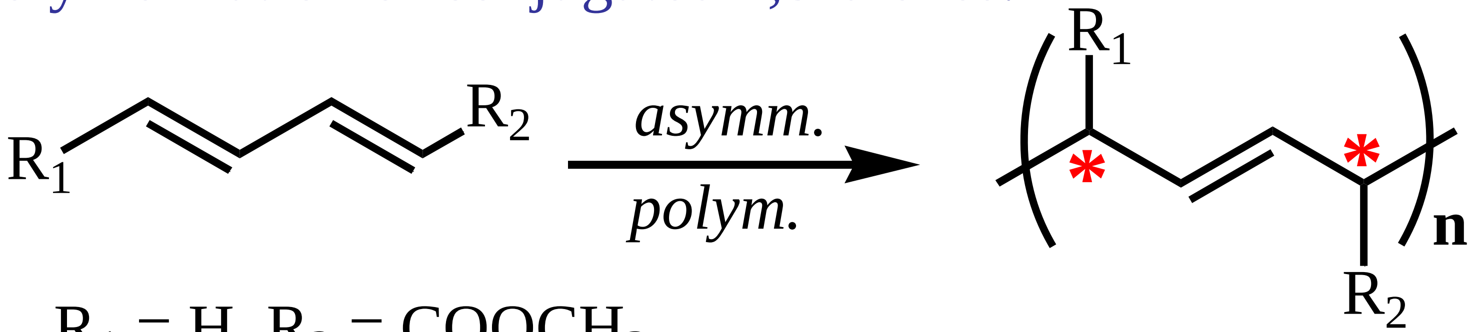
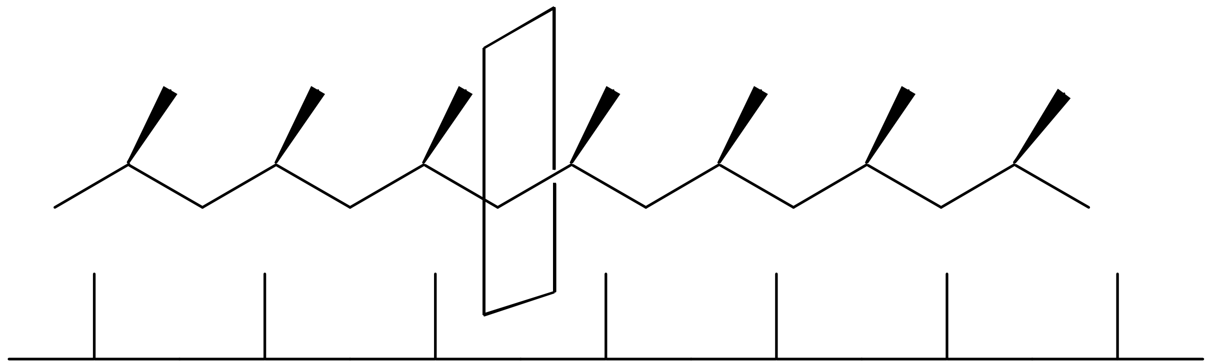


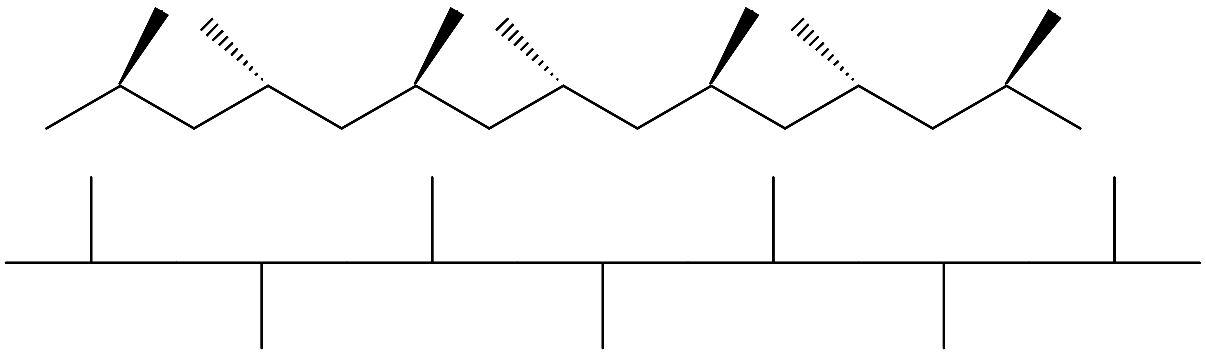
R_1 = H, R_2 = $COOCH_3$

R_1 = H, R_2 = CH_3

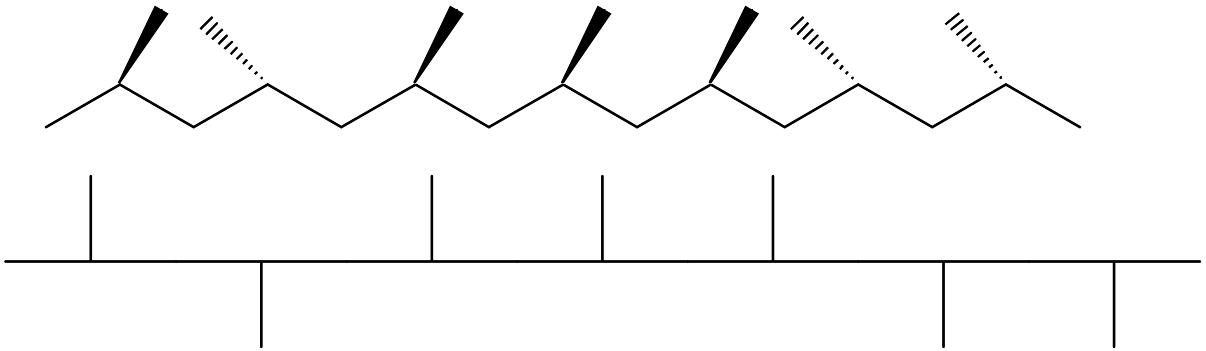
Polypropylene synthesis: The CRYPTOCHIRALITY phenomenon



isotactic



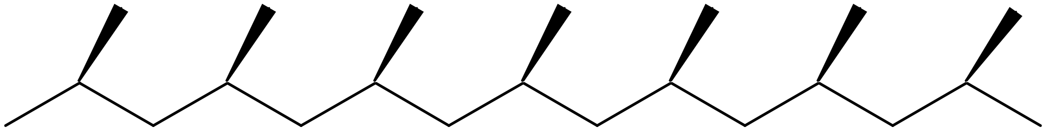
syndiotactic



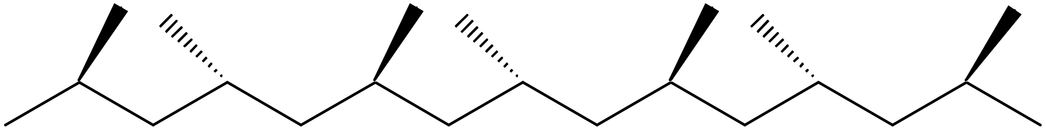
atactic

Polypropylene synthesis

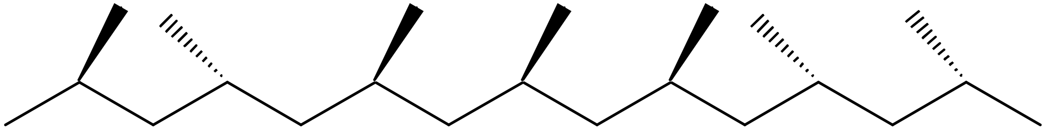
Stereocontrolled polymerization:
Control of stereochemistry via the nature of the ancillary ligands on the metal centre.



Multiple insertions of the same enantioface:
isotactic polymer



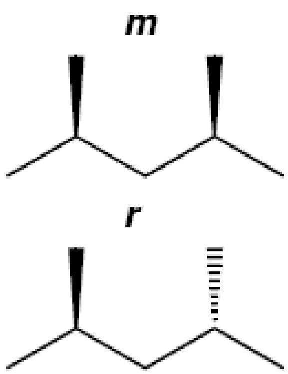
Multiple insertions of the alternating enantiofaces: *syndiotactic polymer*



Random enantioface insertions: *atactic polymer*

Tacticity

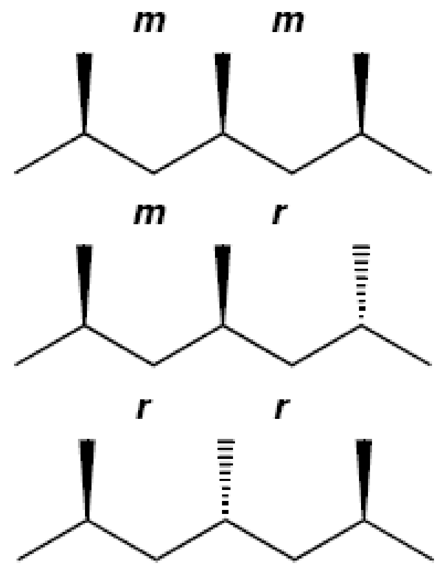
Dyad Tacticity



isotactic (*meso*, *m*)

syndiotactic (*racemic*, *r*)

Triad Tactícity



isotactic(*mm*)

atactic (*mr*)

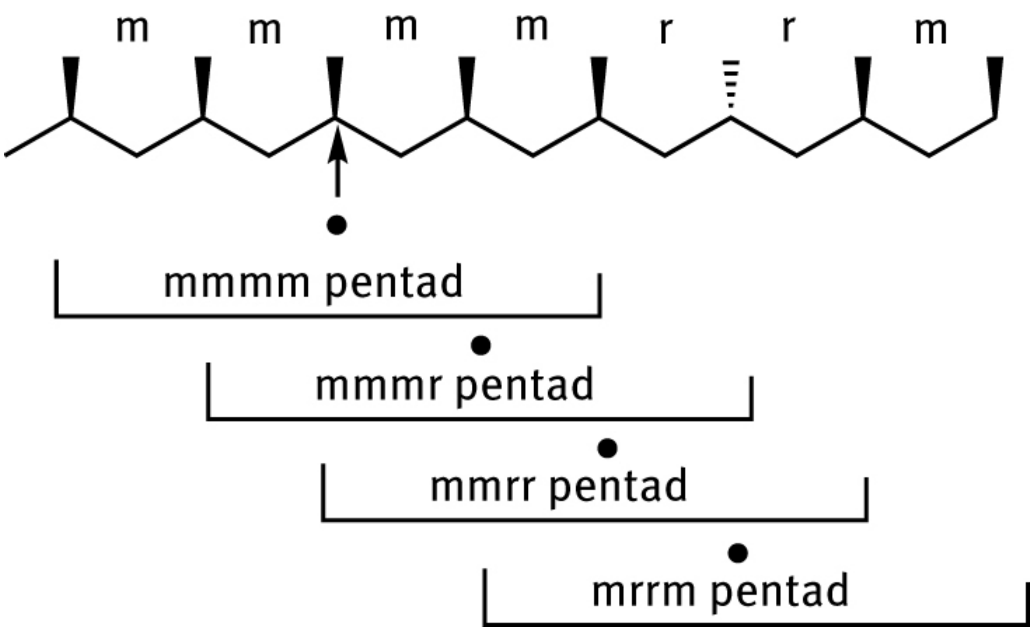
syndiotactic (*rr*)

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

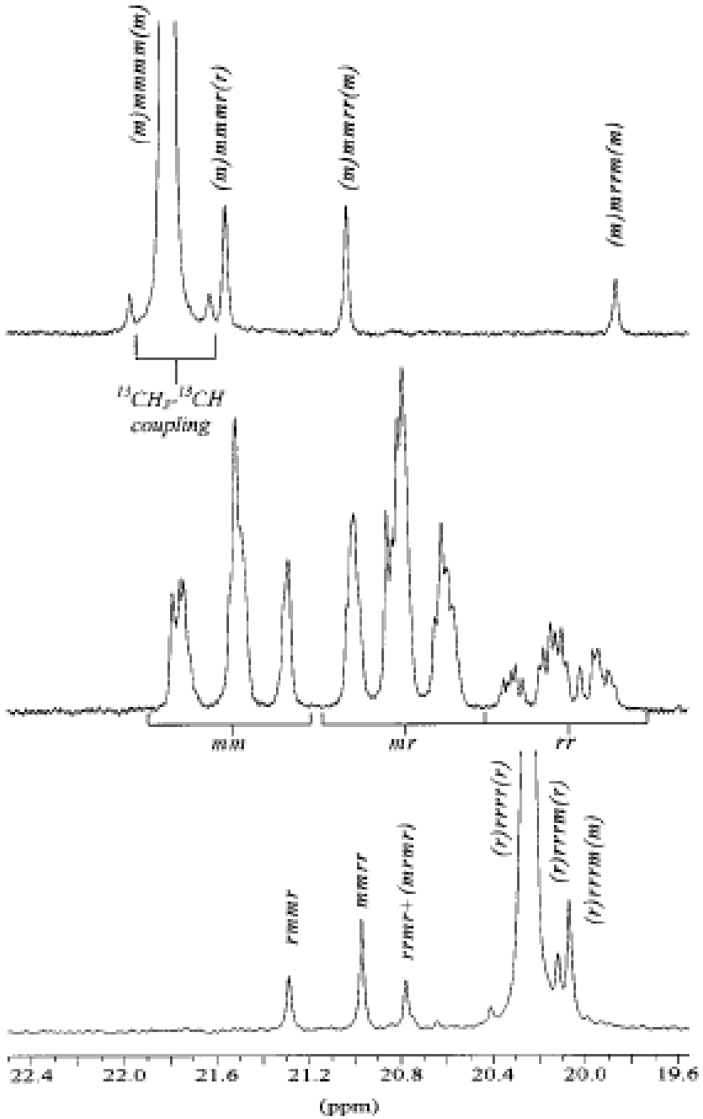


Microtacticity
^{13}C NMR Spectra of polypropylene: methyl pentad region

isotactic

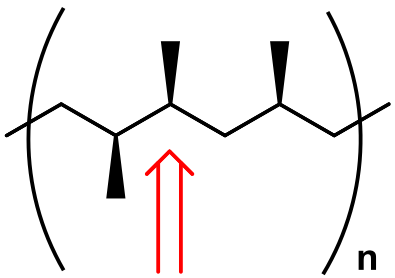
atactic

syndiotactic

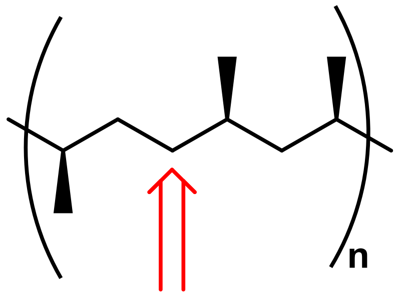


Regiochemistry

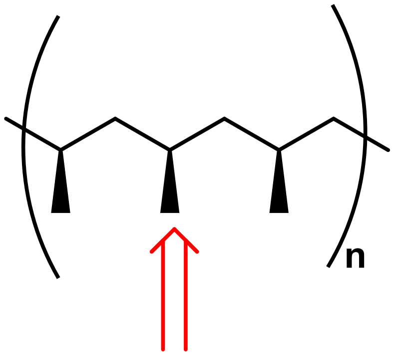
The possible regiosequences



Tail to tail

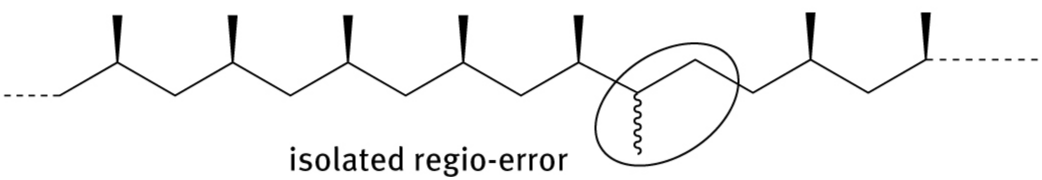


Head to head



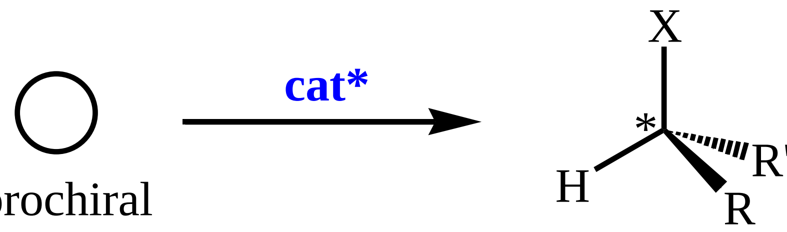
Head to tail

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



ENANTIOSELECTIVE CATALYSIS[1]

Enantioselective synthesis of small molecules

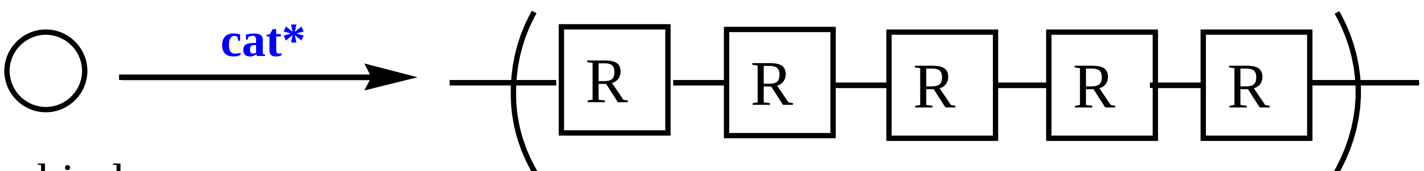


prochiral substrate

chiral product: the stereochemical events *are not related* one to each other

---

Stereospecific polymerization



prochiral monomer

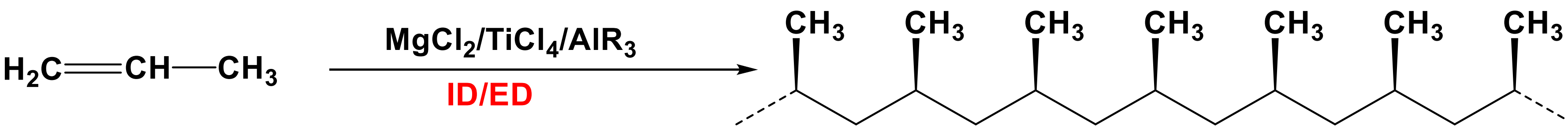
stereoregular polymer: the stereochemical events are *related* one to each other

cat* = chiral coordination compound

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

STEREOSPECIFIC Ziegler-Natta Catalysts

Synthesis of ***isotactic*** polypropylene

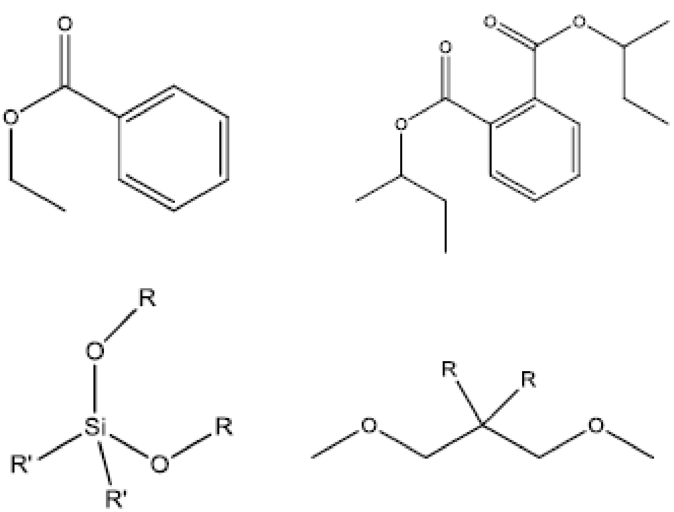


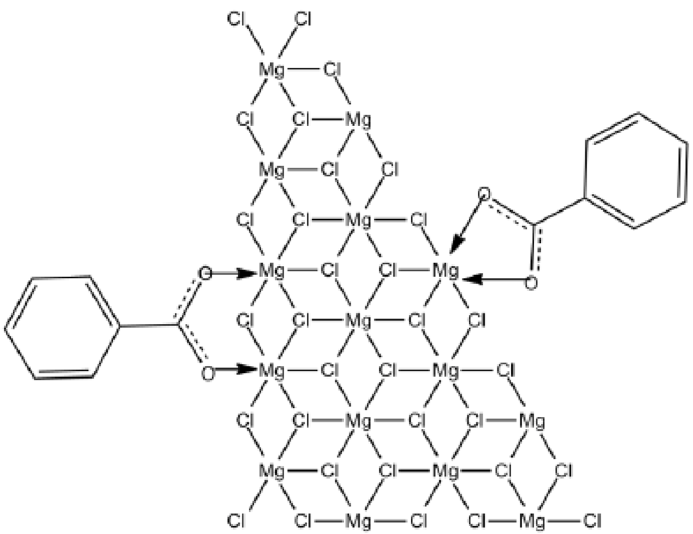
ID = internal donor

ED = external donor

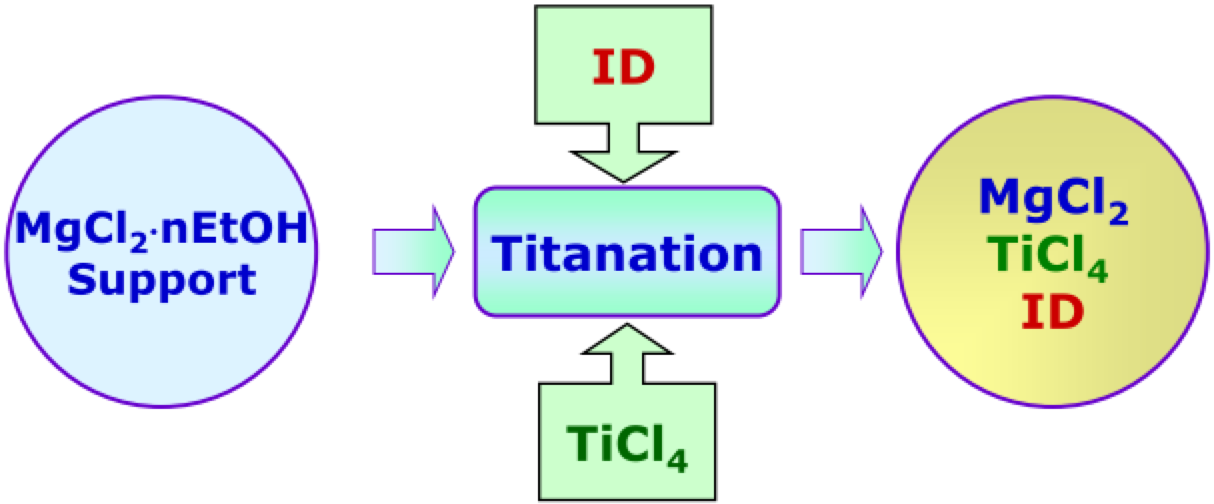
Catalyst nature: ***heterogeneous***

The donors

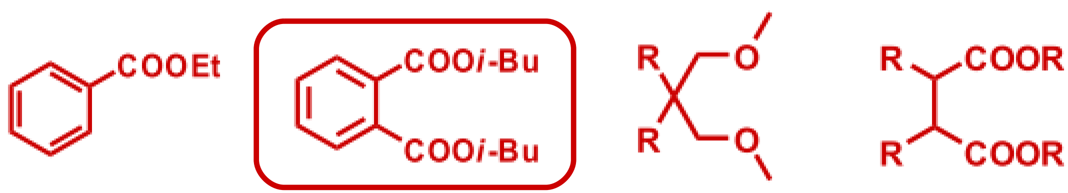




Z-N Catalyst Preparation
The solid Catalyst Precursor



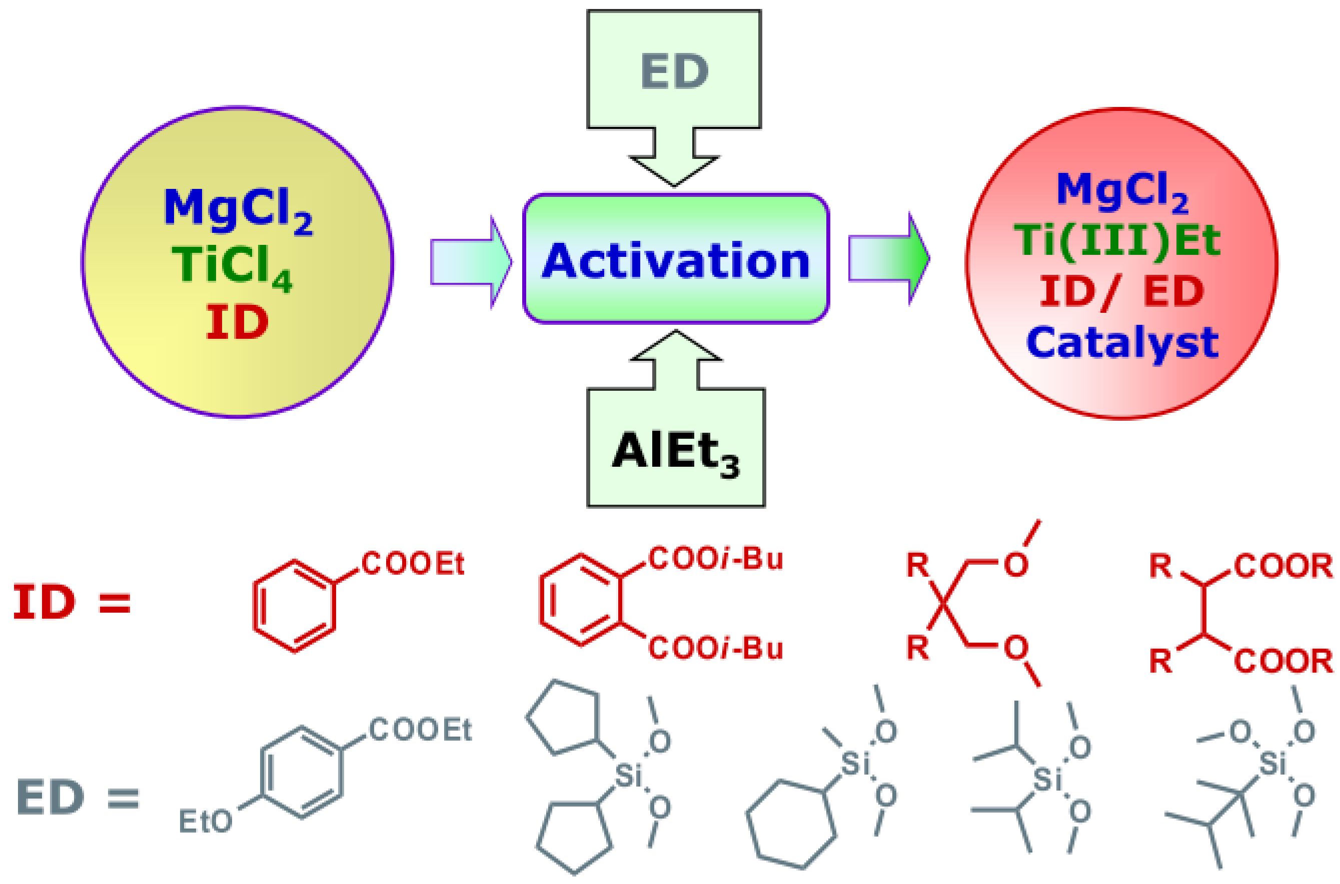
ID =



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

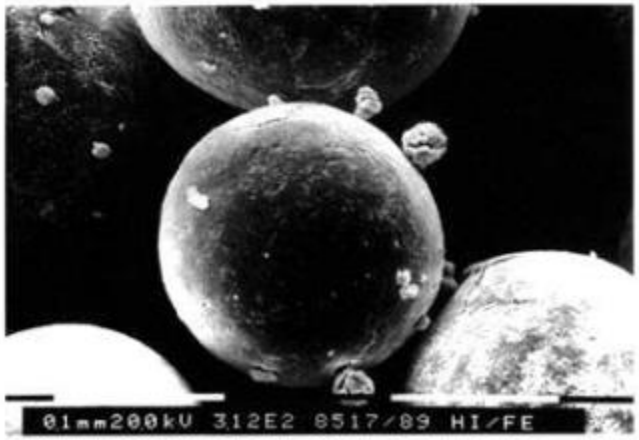
- stabilize nascent $MgCl_2$ crystallites
- influence the crystallite dimensions and thus the "*working surface*" connected with the productivity of the resulting catalyst
- control of the distribution of $TiCl_4$ on the possible $MgCl_2$ cuts

Z-N Catalyst Preparation
Activation of the catalyst: ED structures

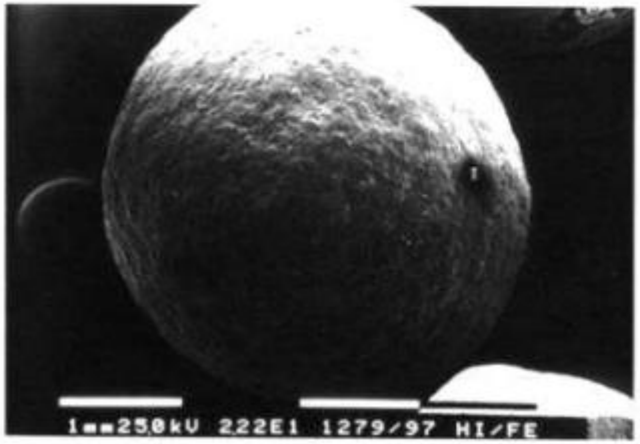


15000 kg PP/mol Ti MPa h di i-PP 97 -98 %

Morphology of supports and PP particle



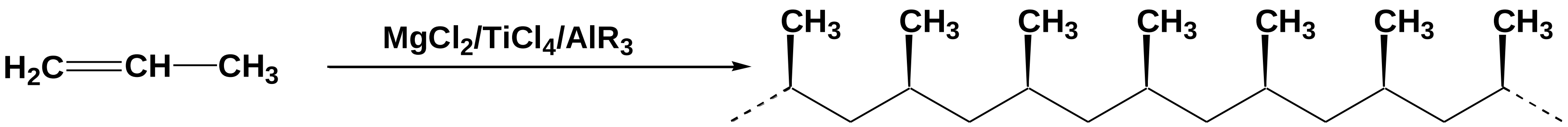
Morphology of catalyst support: spherical.



Morphology of catalyst of PP particles.

STEREOSPECIFIC Ziegler-Natta Catalysts

Synthesis of ***isotactic*** polypropylene

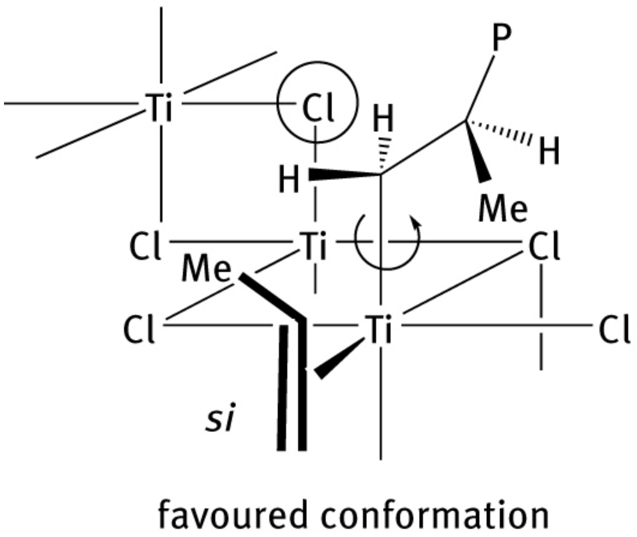


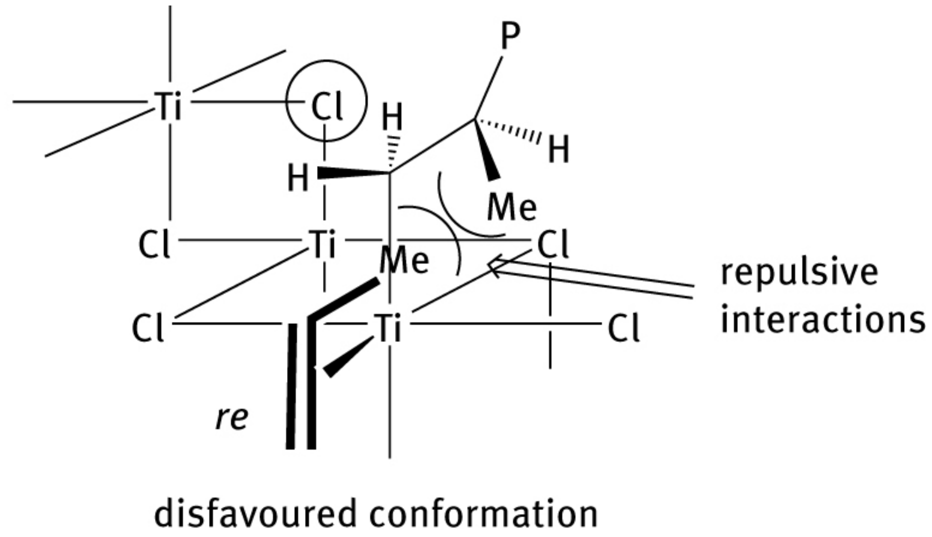
Heterogeneous catalyst.

Stereochemistry of the insertion step: nature of the errors:

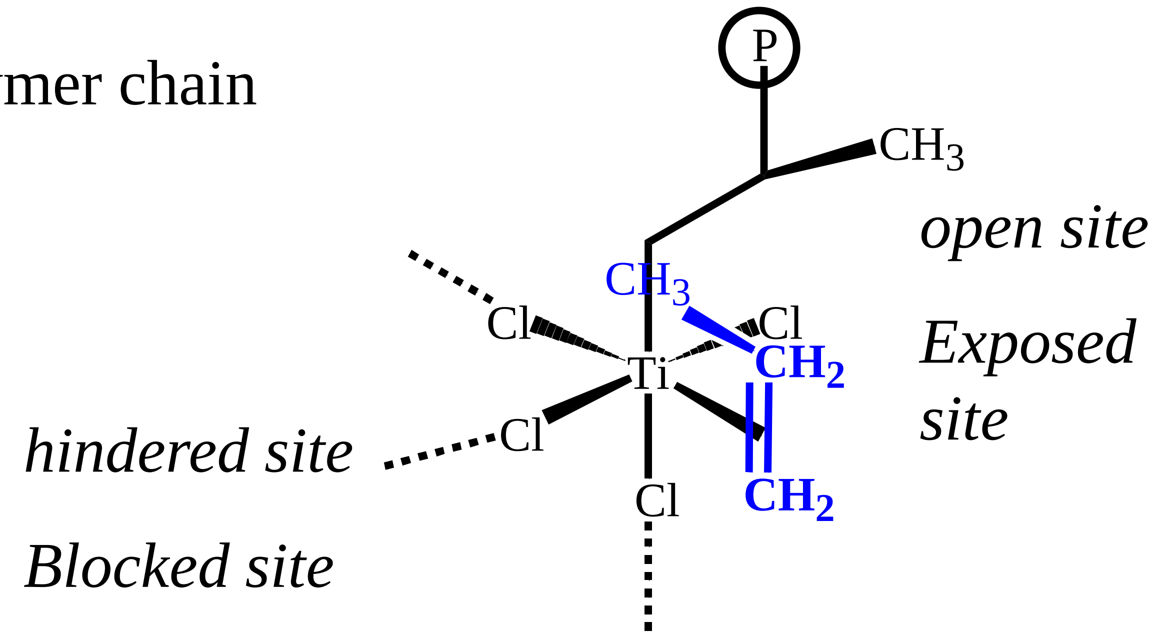
Errors of kind A are indicative for the chiral nature of the catalyst.

Enantiomorphic site control



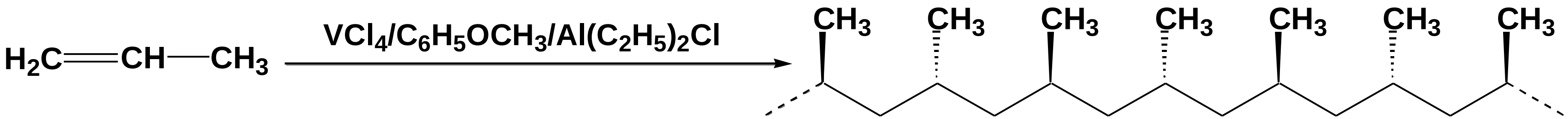


P = growing polymer chain



STEREOSPECIFIC Ziegler-Natta Catalysts

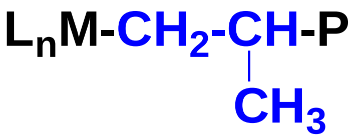
Synthesis of ***syndiotactic*** polypropylene

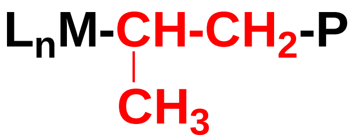


Catalyst nature: ***homogeneous***

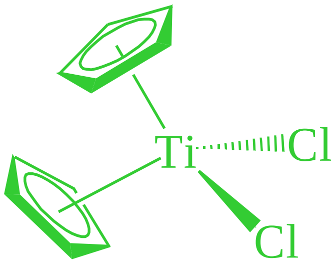
General aspects of stereospecific polymerization of propylene

Catalyst	$MgCl_2/TiCl_4/AlR_3$	$VCl_4/C_6H_5OCH_3/Al(C_2H_5)_2Cl$
Stereoregularity	isotactic	syndiotactic
Regioselectivity	primary	secondary
Control of stereochemistry	enantiomorfic site	chain end





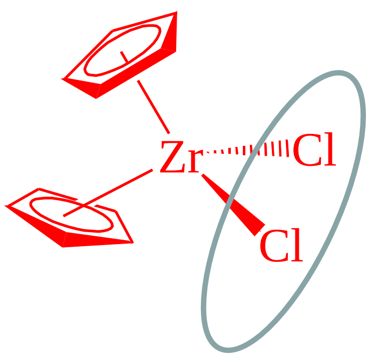
Soluble catalysts



+ $Al(C_2H_5)_3$

Low activity towards ethylene

Inactivity towards propylene

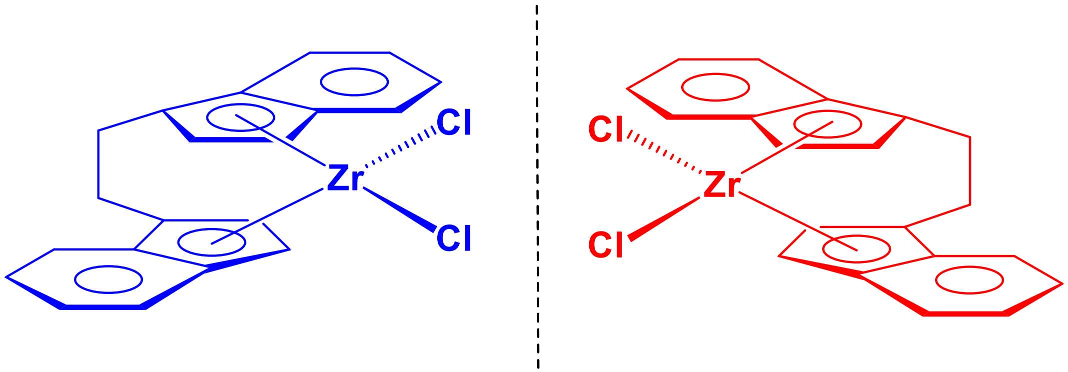


+ MAO

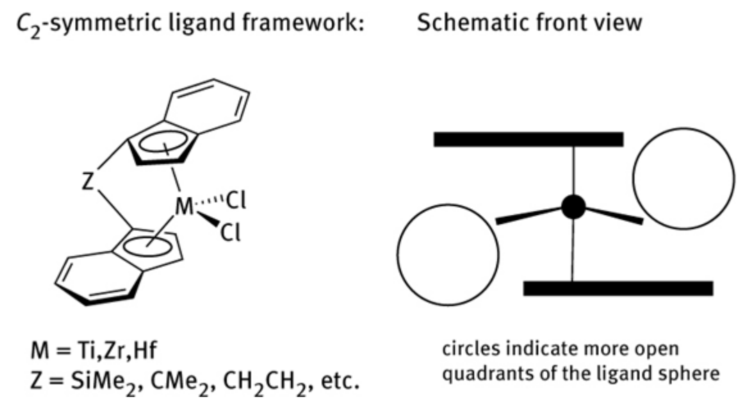
Very high activity towards ethylene

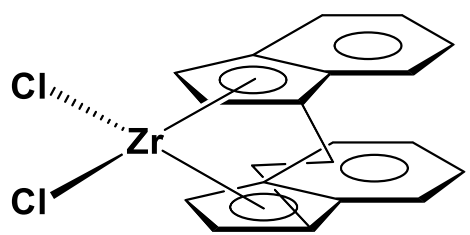
Good activity towards propylene

Metallocene catalysts



chiral A





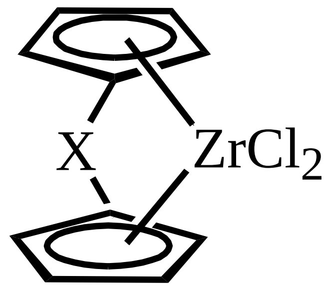
achiral

B

A + MAO leads to ***isotactic*** polypropylene

B + MAO leads to ***atactic*** polyproylene

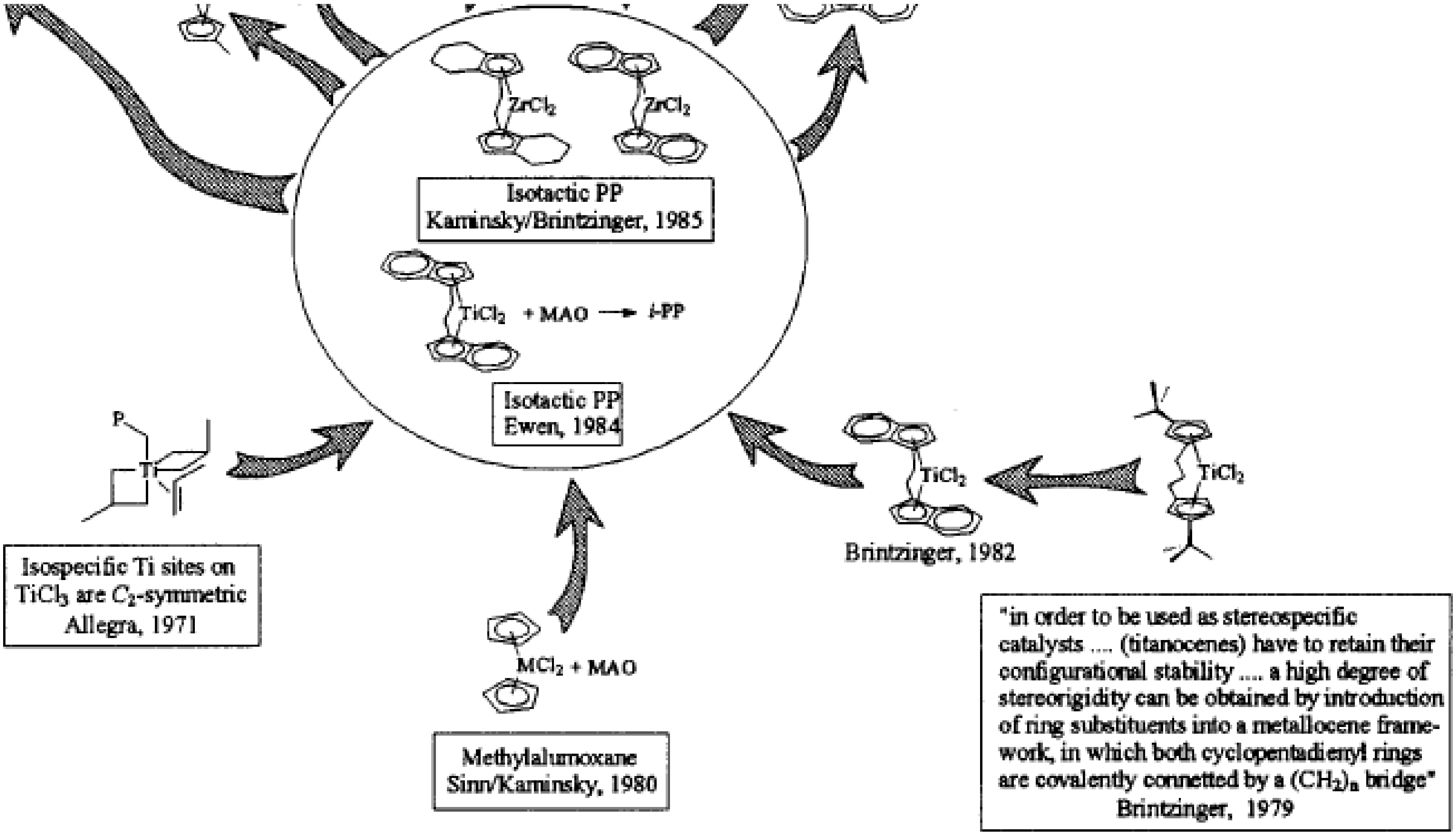
ansa-zirconocenes catalysts: stereorigid of C_2 symmetry



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

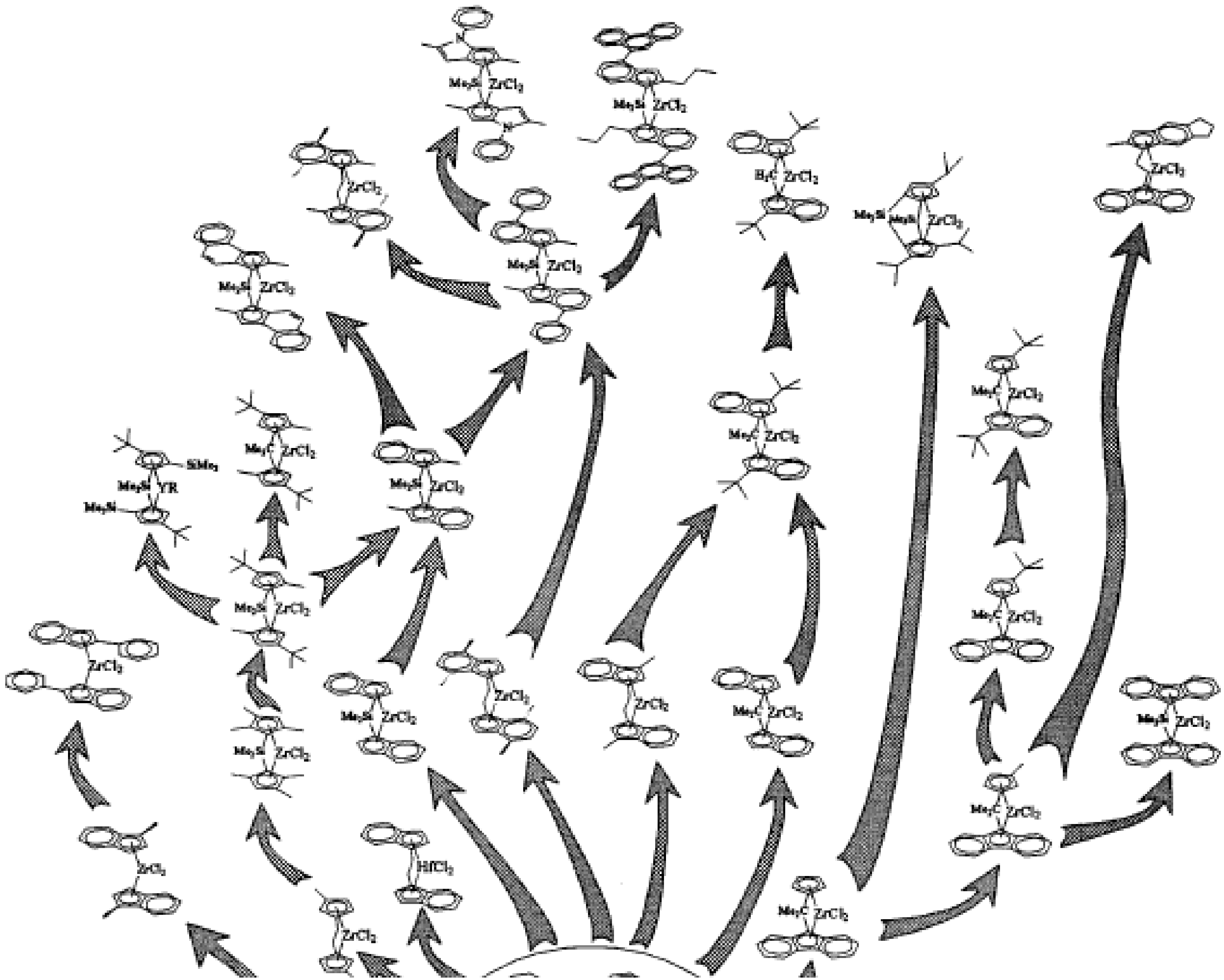
- lower molecular weight;
- narrower molecular weight distribution;
- the tacticity: from almost atactic to perfectly isotactic PP can be obtained;
- not fully regioregular: insertions with secondary regiochemistry are also observed;
- random distribution of stereo- and regio-errors.

The evolution of metallocene catalysts[1]: the root

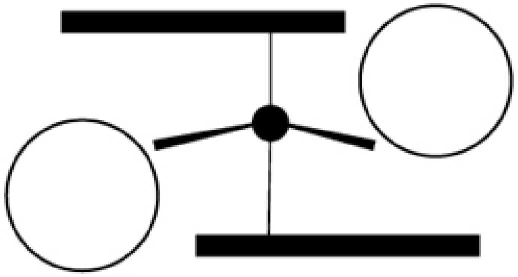


[1]L. Resconi et al., *Chem. Rev.* **2000**, *100*, 1253.

The evolution of metallocene catalysts: the tree

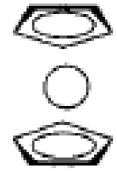
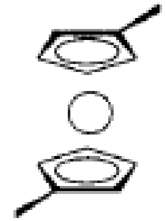
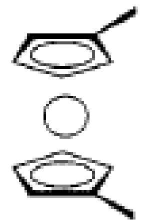
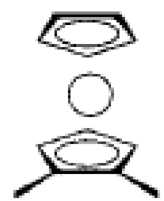
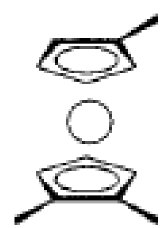


Ewen's Symmetry Rules



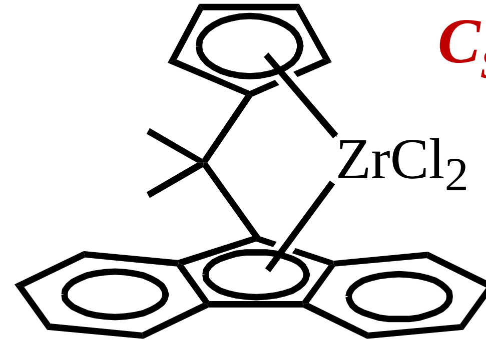
circles indicate more open quadrants of the ligand sphere

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

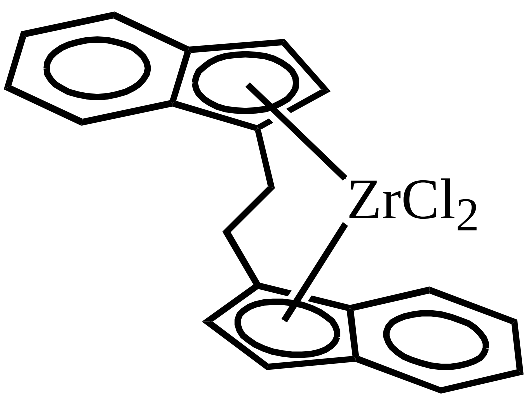
SYNDIOSPECIFIC Catalyst[1]

C_s

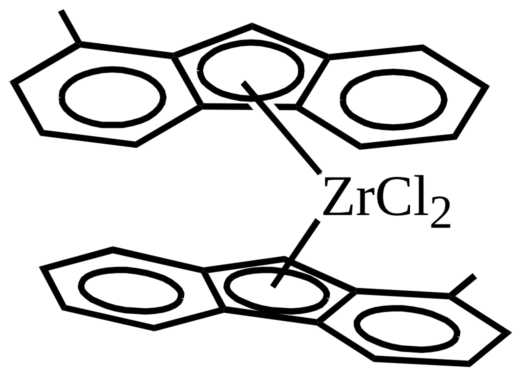


ISOSPECIFIC Catalysts[1]

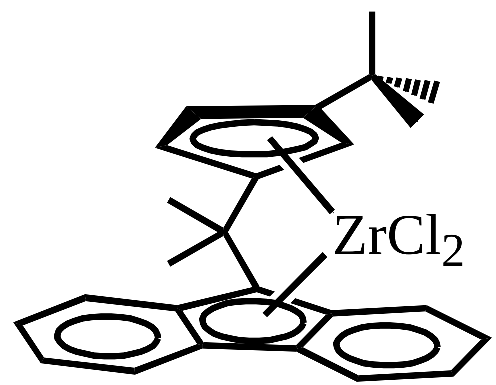
C_2



pseudo-*C_2*

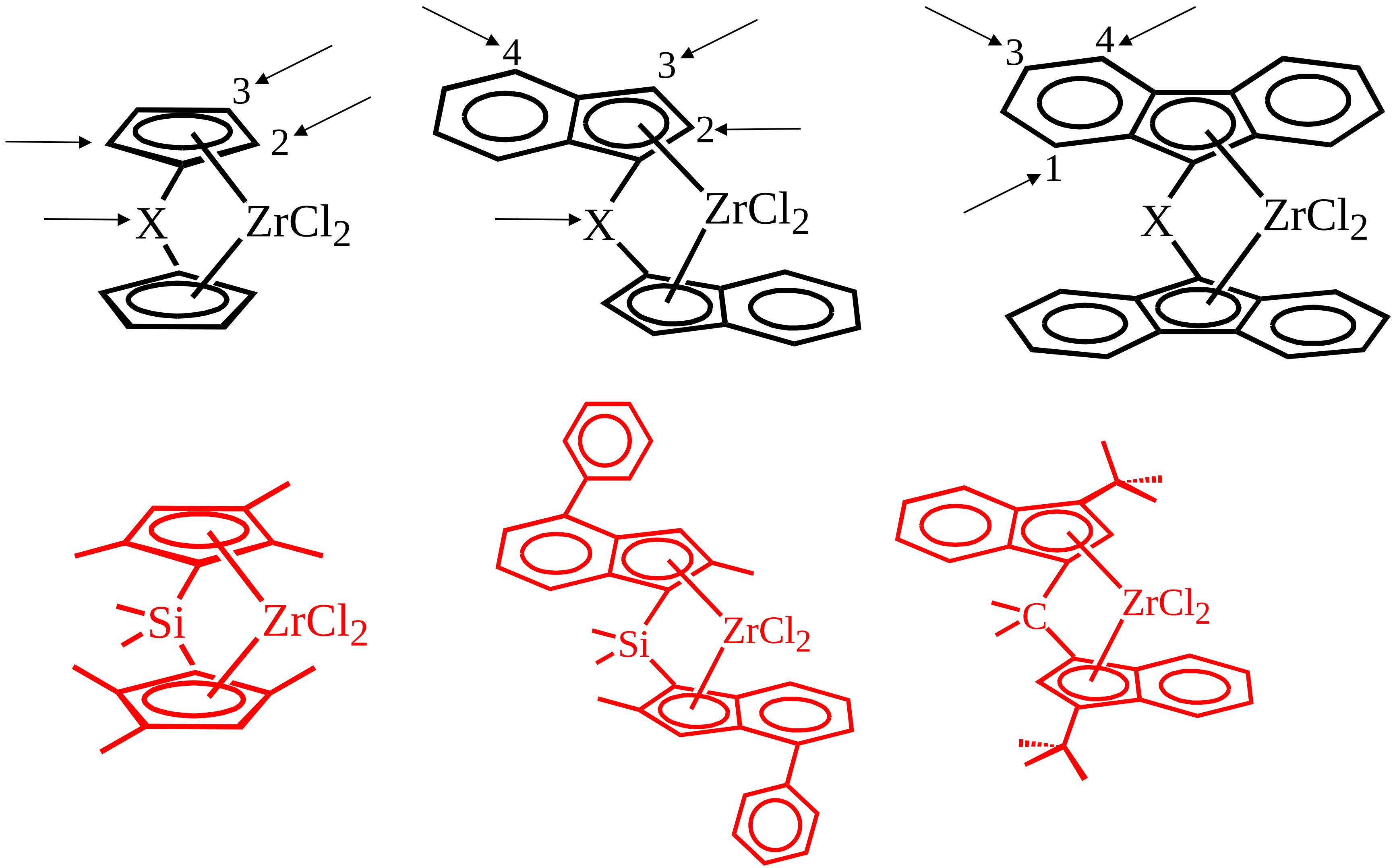


C_1



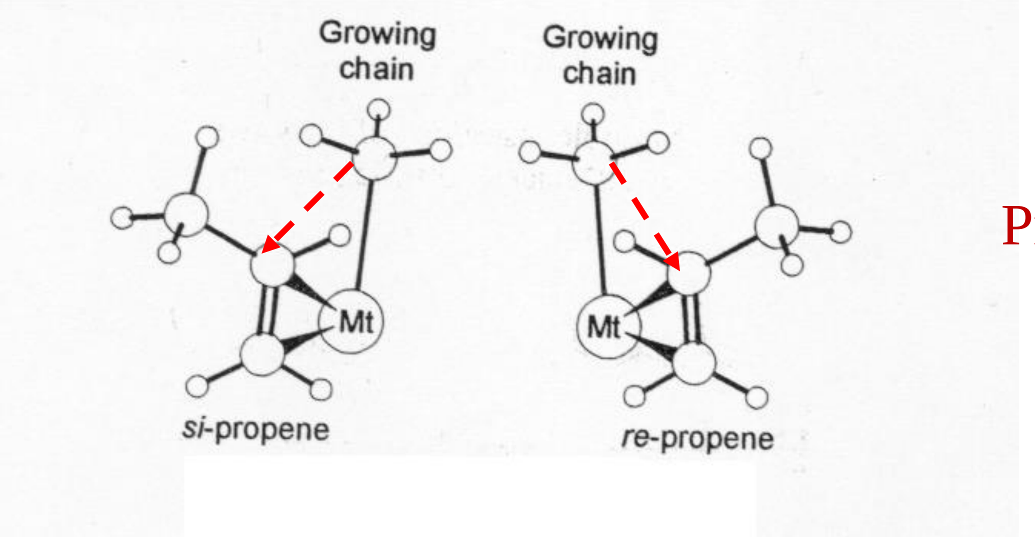
[1]L. Resconi et al., *Chem. Rev.* **2000**, *100*, 1253.

ansa-zirconocenes catalysts of C_2 symmetry



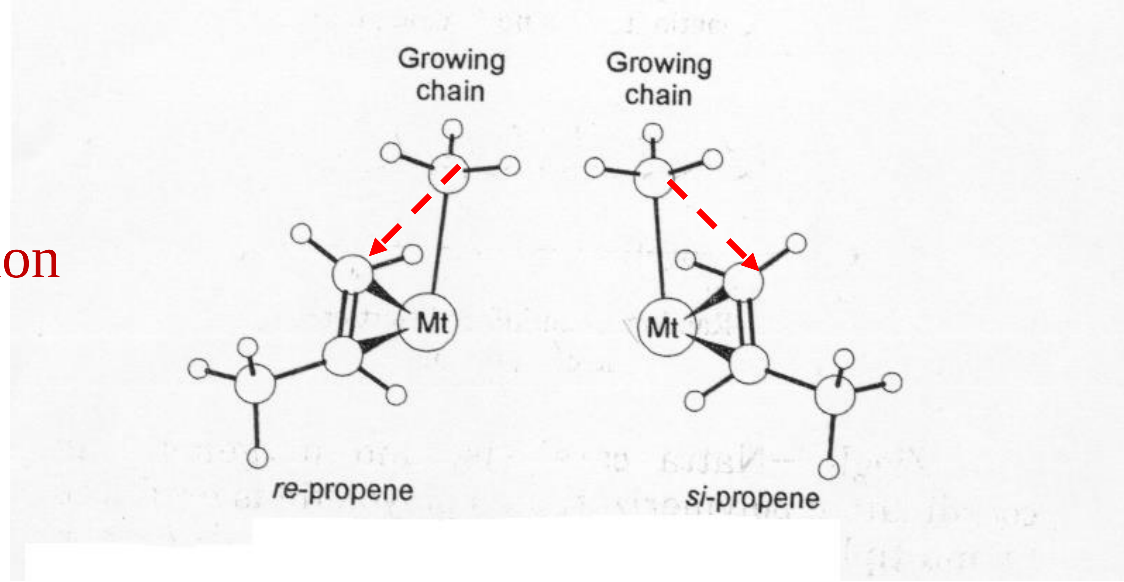
[1]L. Resconi et al., *Chem. Rev.* **2000**, *100*, 1253.

DIFFERENT INSERTION WAYS FOR PROPYLENE[1]



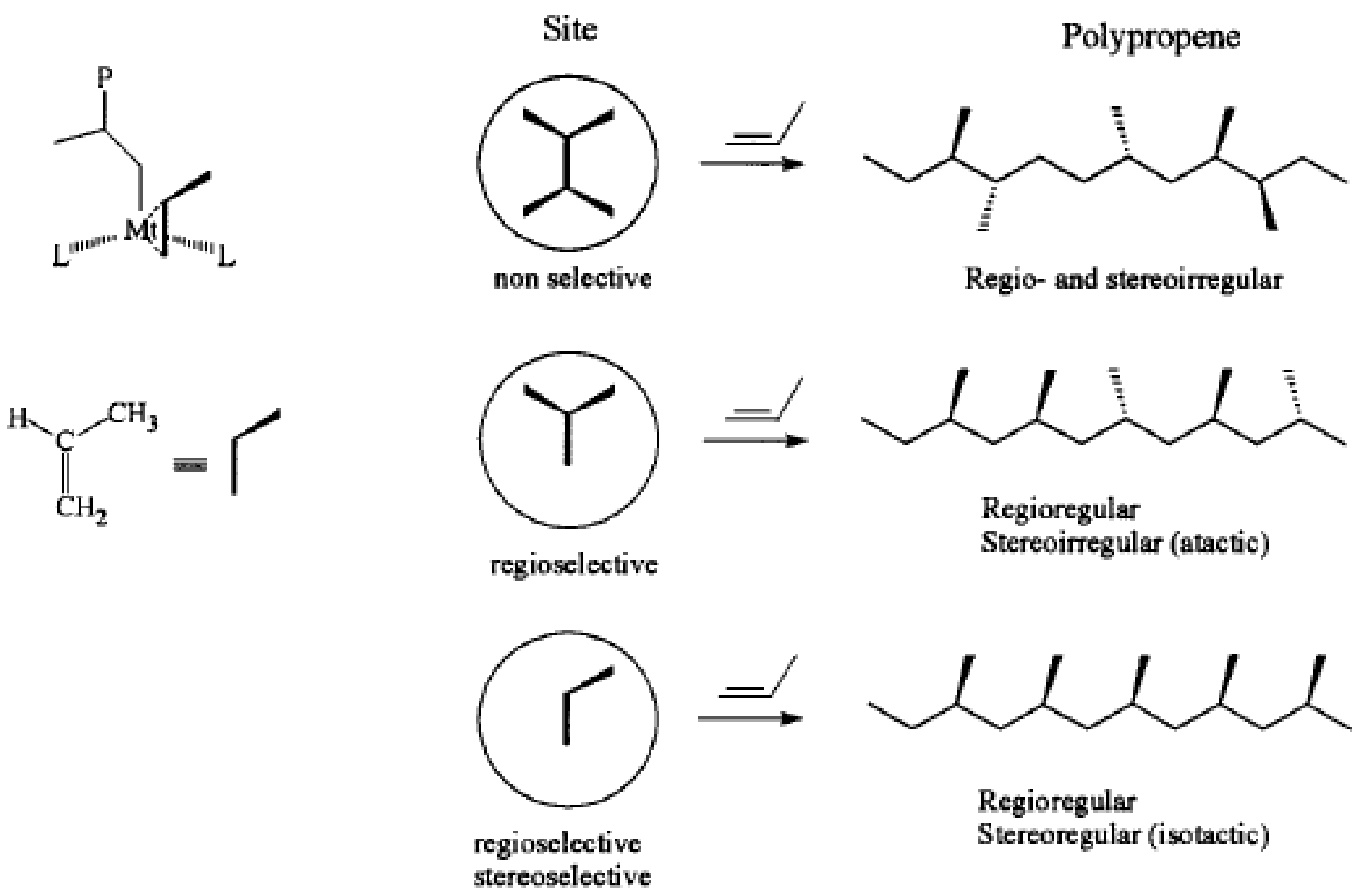
Primary insertion

Secondary insertion

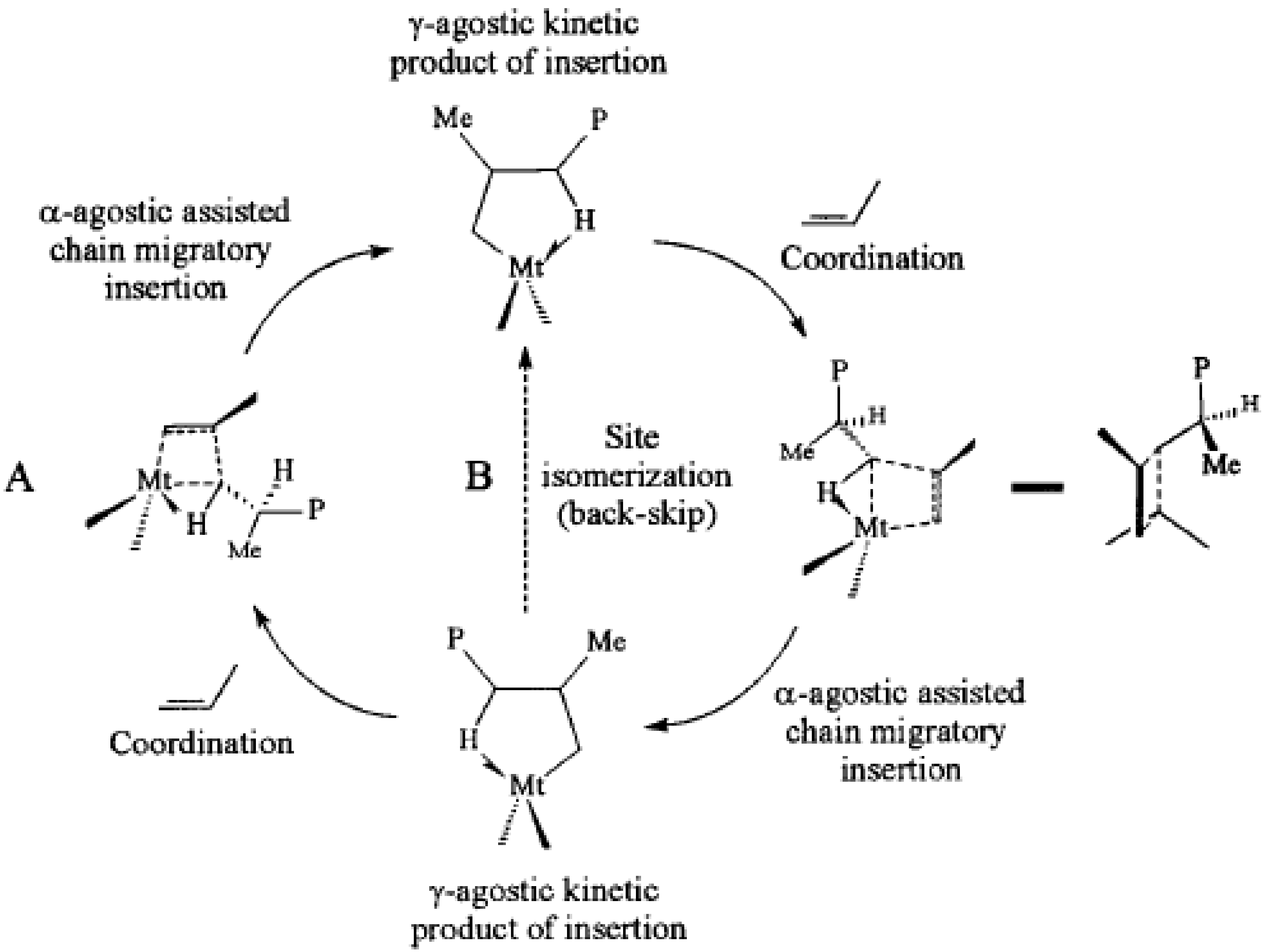


[1]L. Resconi et al., *Chem. Rev.* **2000**, *100*, 1253.

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

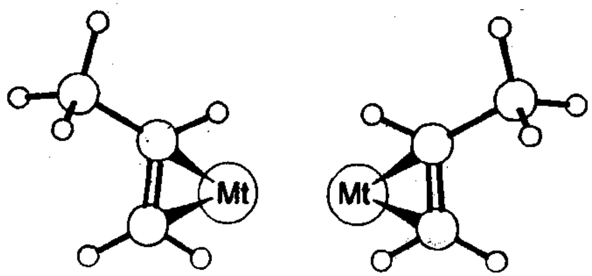


The key-in-the-lock model: two locks, one key



THE ELEMENTS OF CHIRALITY[1]

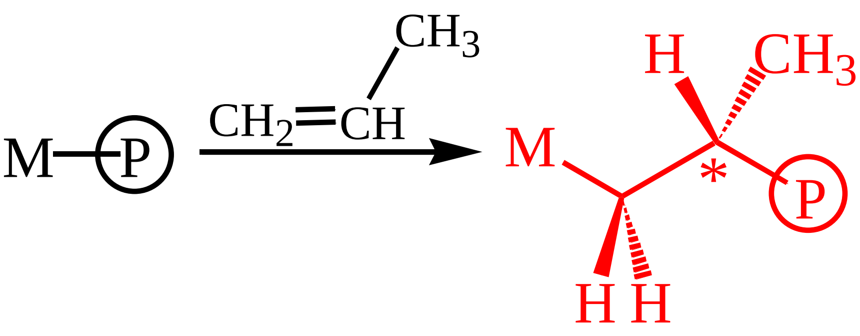
propylene enantioface



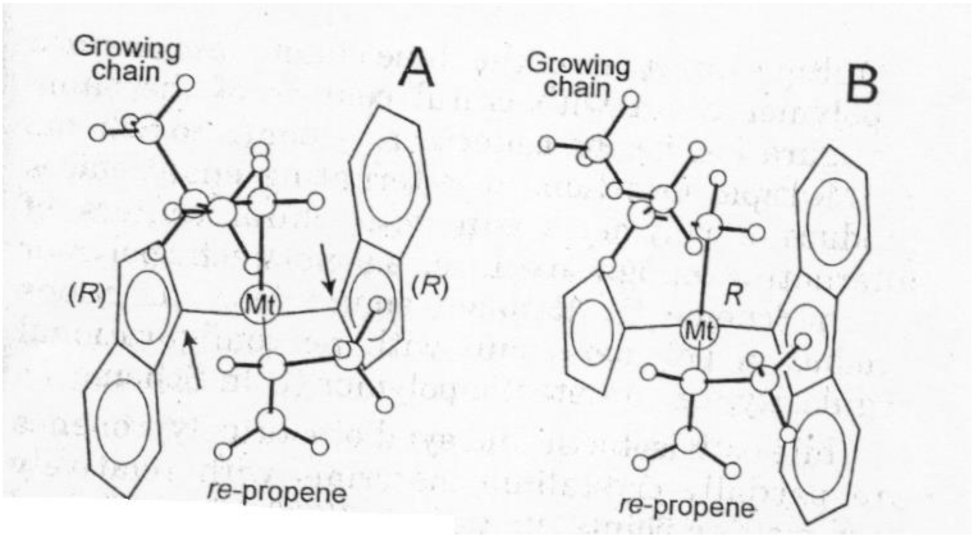
si-coordinated propene

re-coordinated propene

growing chain

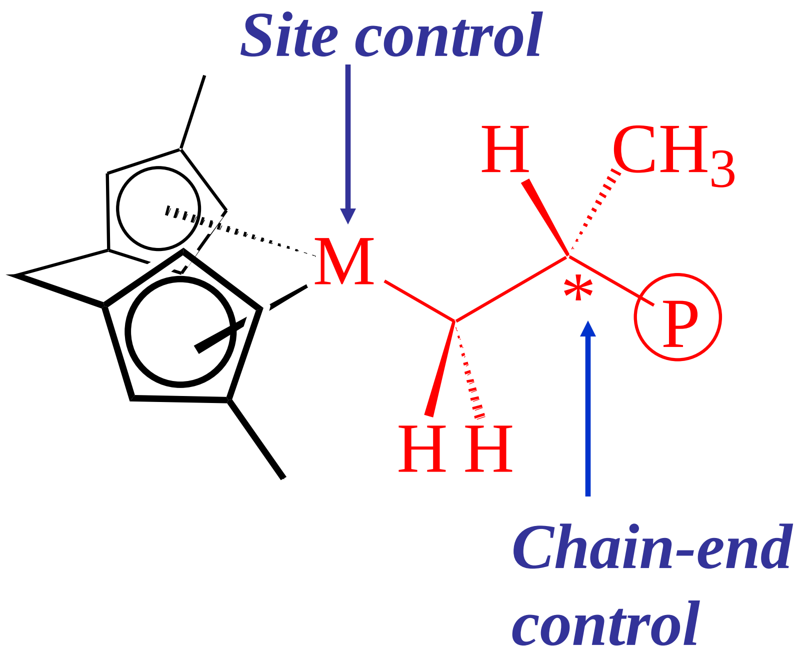


enantiomorphic site



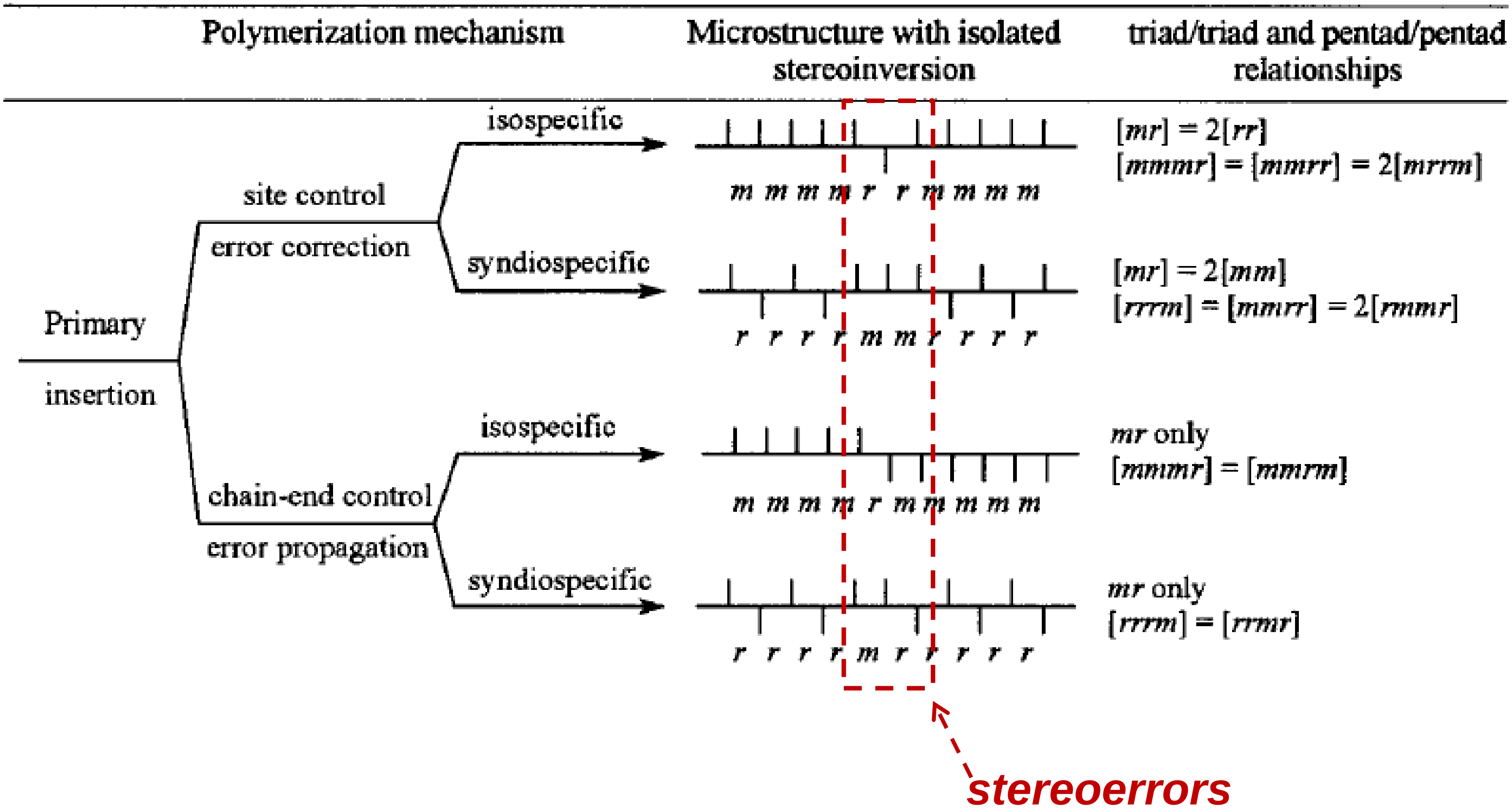
[1]L. Resconi et al., *Chem. Rev.* **2000**, *100*, 1253.

CHIRAL INDUCTION FOR THE PRIMARY INSERTION[1]



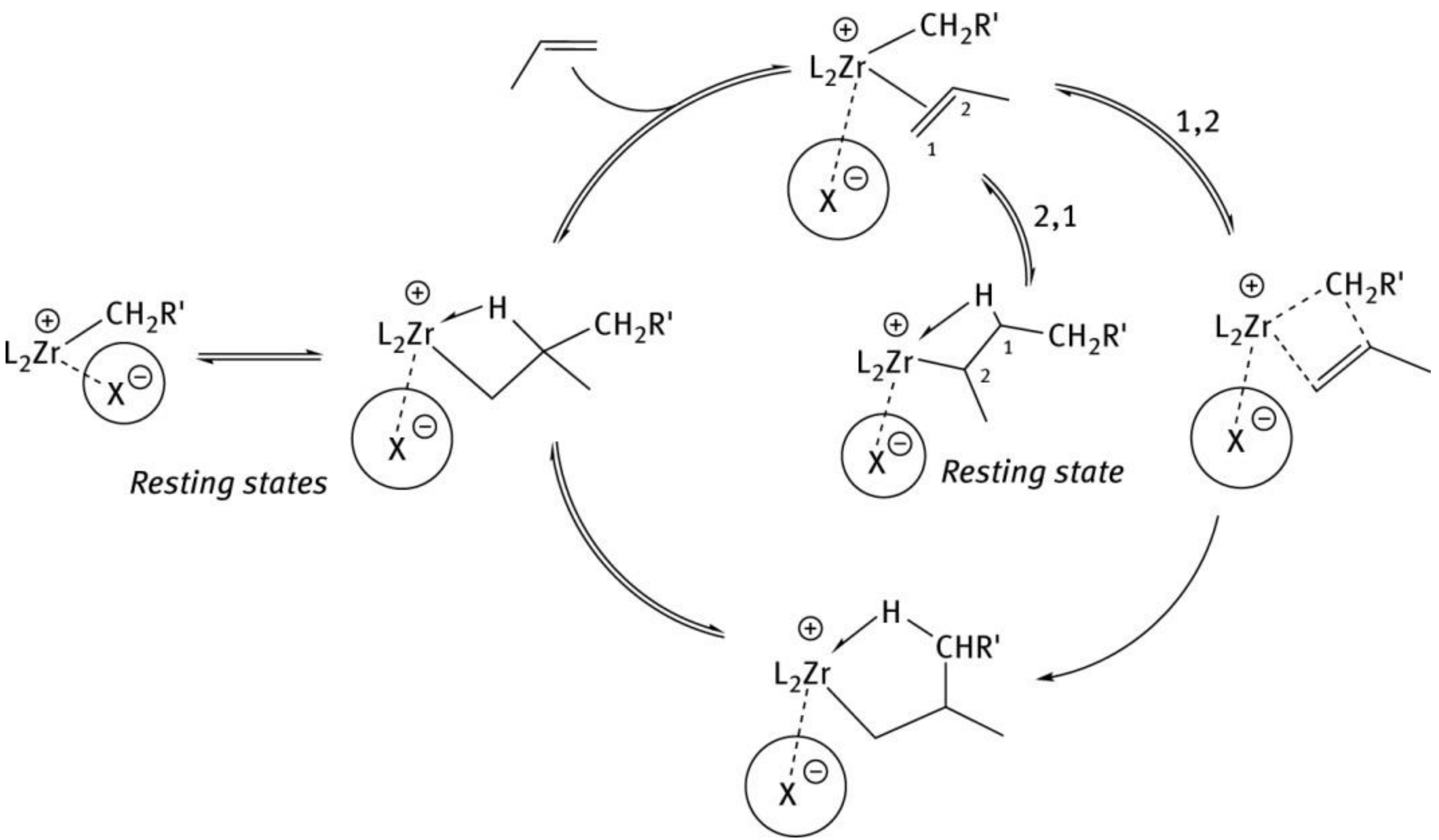
[1]L. Resconi et al., *Chem. Rev.* **2000**, *100*, 1253.

CHIRAL INDUCTION FOR THE PRIMARY INSERTION[1]

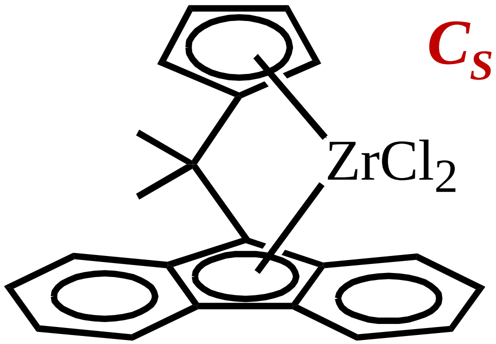


[1]L. Resconi et al., *Chem. Rev.* **2000**, *100*, 1253.

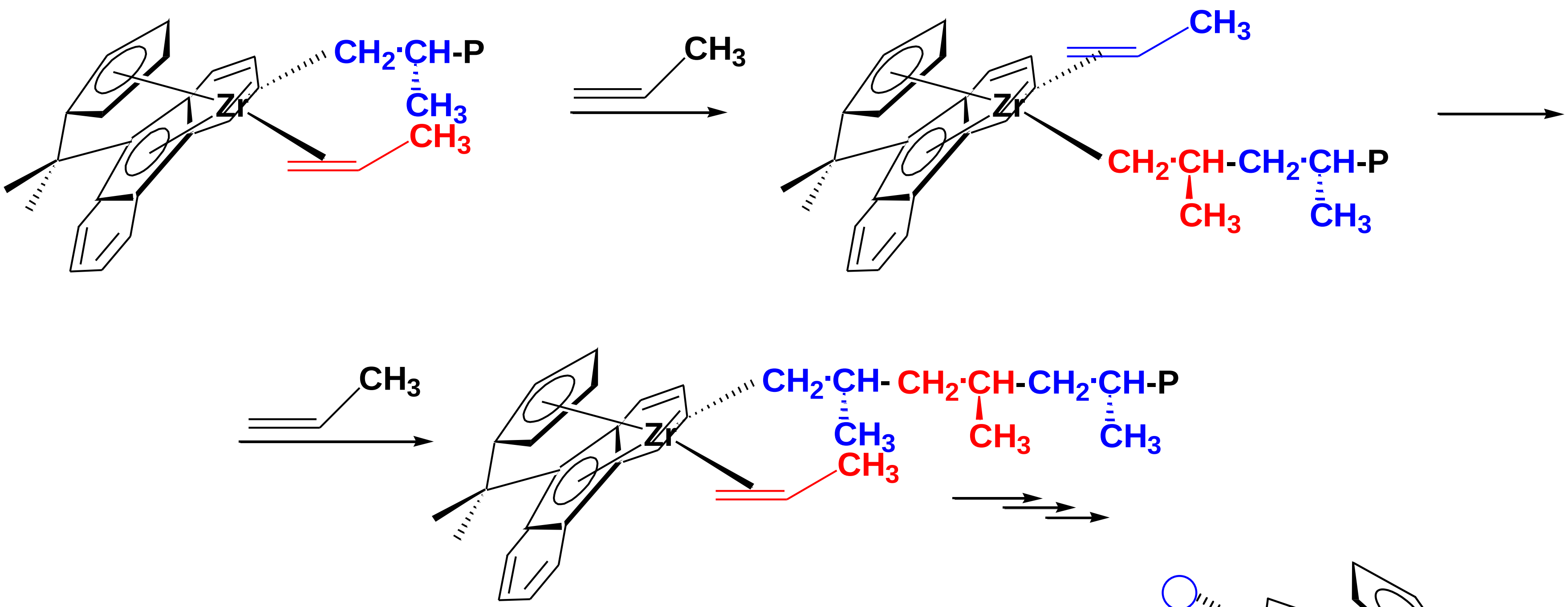
THE CATALYTIC CYCLE



SYNDIOSPECIFIC Catalyst [1]

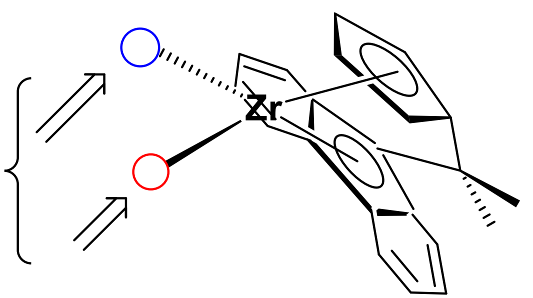


Cs

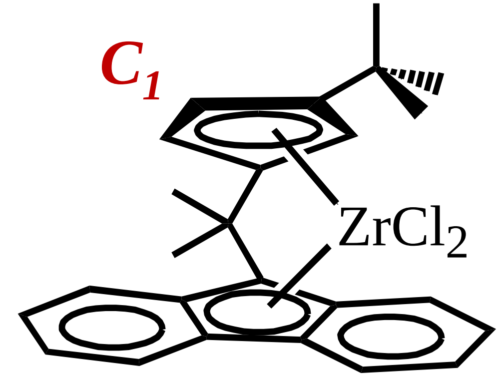


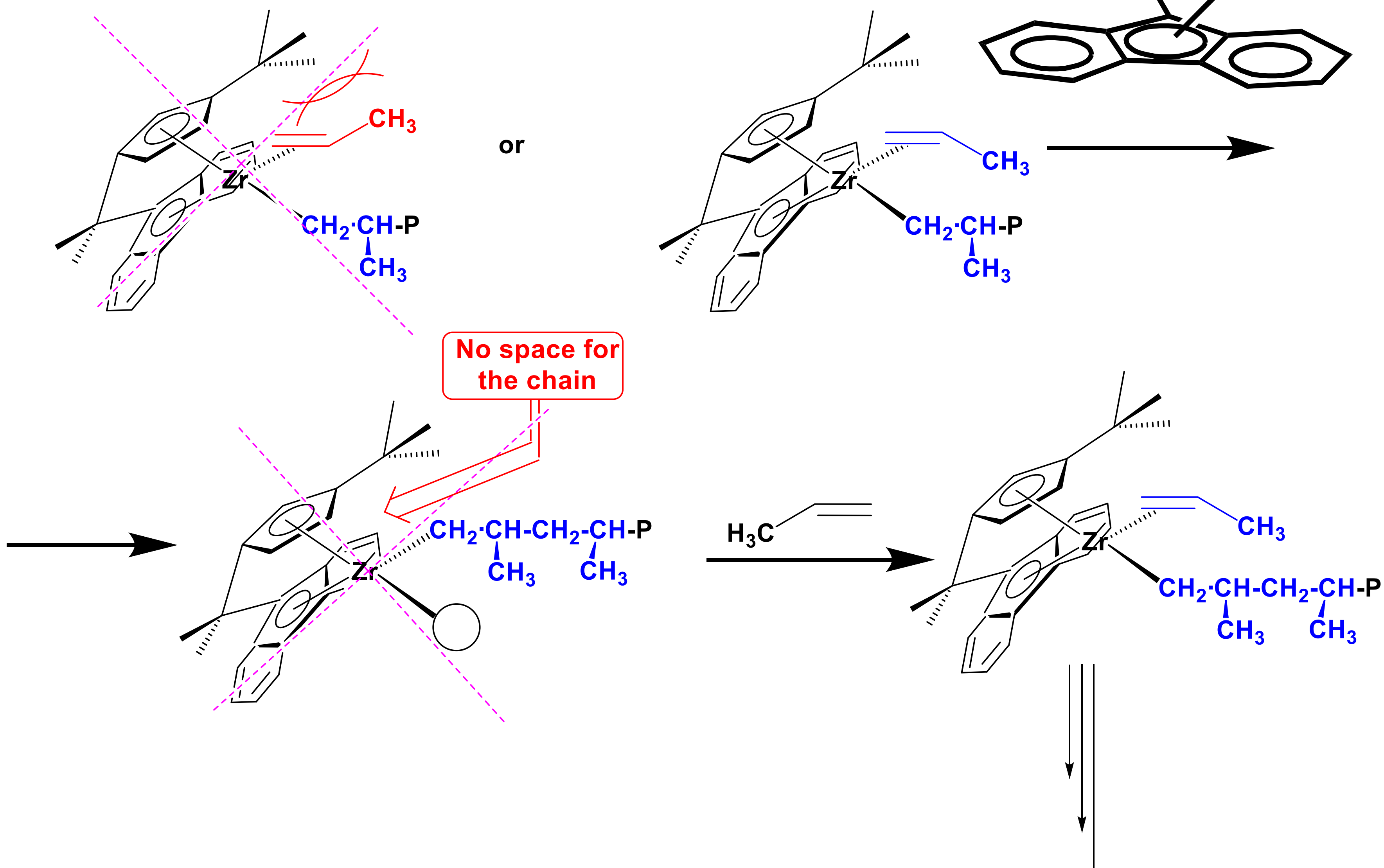
[1]L. Resconi et al., *Chem. Rev.* **2000**, *100*, 1253.

enantiotopic site



ISOSPECIFIC Catalyst[1]

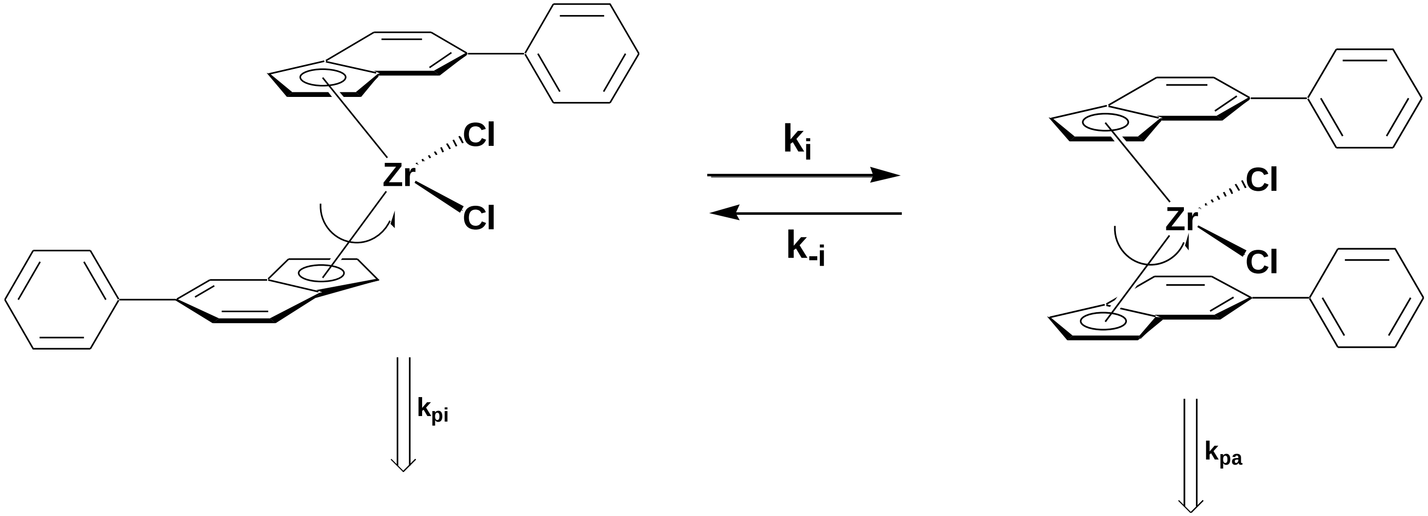




Catalyst for the synthesis of ***polypropylene with stereoblocks***

Catalyst in chiral conformation

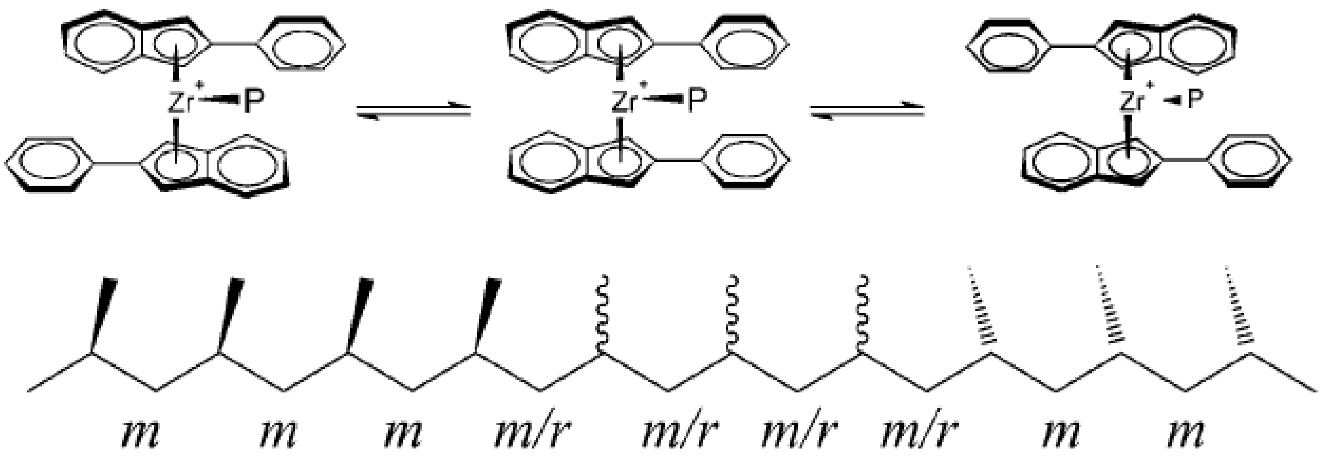
Catalyst in meso conformation



Isotactic block

Atactic block

Catalyst for the synthesis of
polypropylene with stereoblocks

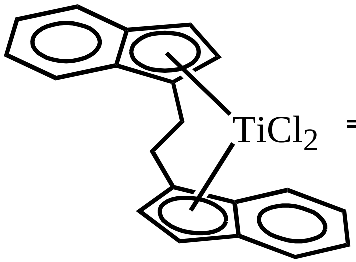


Trend of productivity:

$MeB(C_6F_5)_3^{-} << B(C_6F_5)_4^{-} \backsimeq MAO$

STEREOSPECIFIC Catalysts [1]: a summary

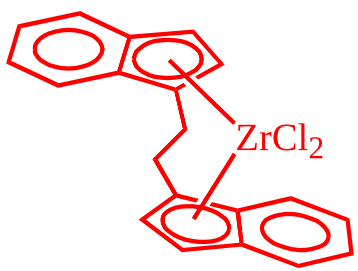
$TiCl_3$ ⟹ The Ti isospecific sites are featured by C_2 symmetry (Allegra, 1971)



⟹ Brintzinger, 1982 ⟹ Isotactic PP (Ewen, 1984)

racemic complex ⟹ *isotactic PP*

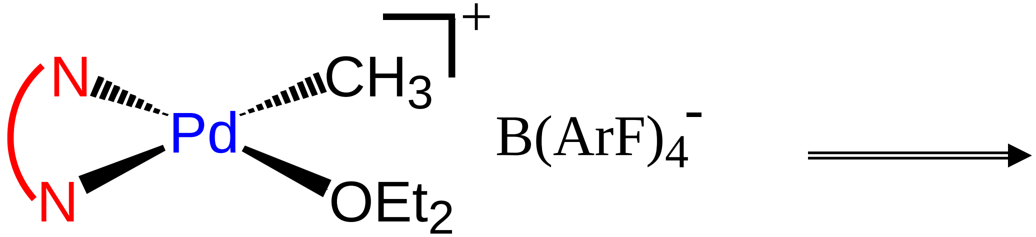
meso complex ⟹ *atactic PP*



⟹ Kaminsky and Brintzinger, 1985

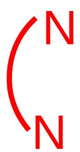
[1]L. Resconi et al., *Chem. Rev.* **2000**, *100*, 1253.

Propylene polymerization catalyzed by NON metallocene complexes

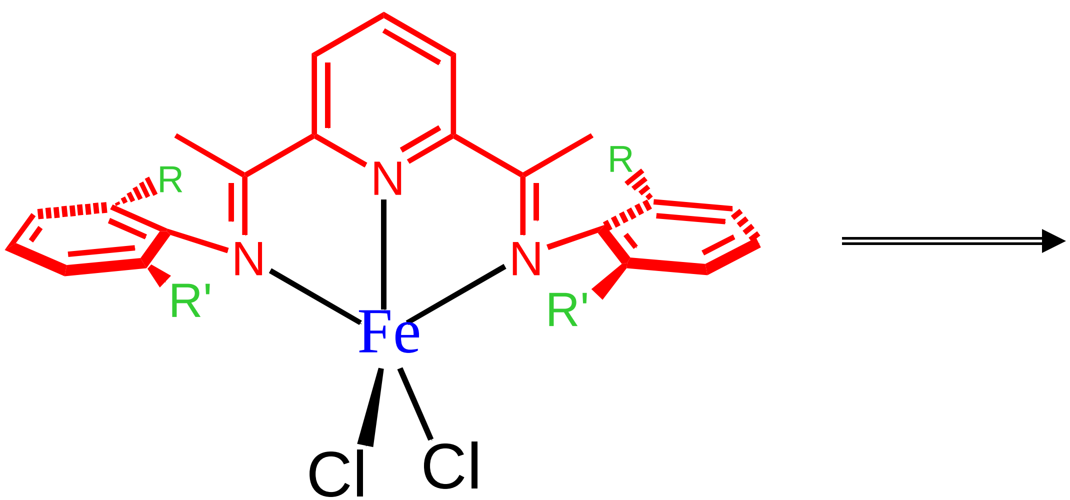


amorfous PP

M_w = 15 000



= (2,6-*i*-PrPh)$_2$DABH$_2$

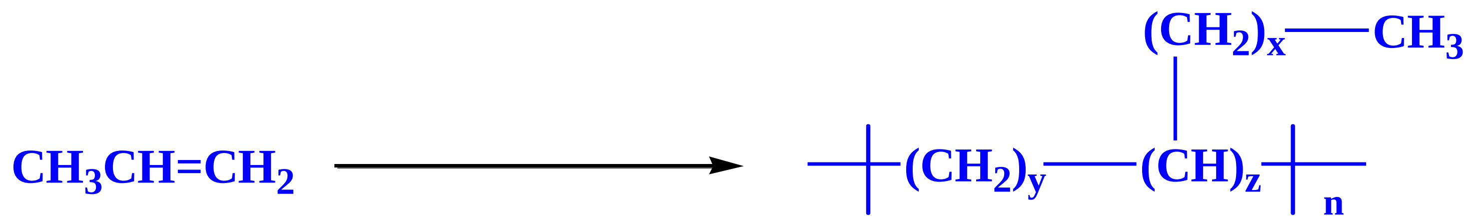


isotactic PP

(insertion with secondary regiochemistry)

[1]S. D. Ittel et al., *Chem. Rev.* **2000**, *100*, 1169.

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.