Ziegler-Natta polymerization of olefins - stereoselectivity

CHEM 462: Inorganic/Organometallic Chemistry

Haomiao Xie & Xu Ye

Professor: Dr. Marcetta Y. Darensbourg

Outline

- 1. Introduction of polymerization and history of Ziegler-Natta Catalysts.
- 1.1 Overview of polymer and polymerization.
- 1.2 coordination polymerization and Ziegler-Natta Catalysts
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- 2. Mechanism of Ziegler-Natta polymerization.
- 2.1 The Cossee Mechanism
- 2.2 The Green-Rooney Mechanism
- 2.3 The evidence supporting the Cossee Mechanism
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- 3. Effect factor of Ziegler-Natta polymerization
- 3.1 Effect factors of 1,2-insertion
- 3.2 Effect factors of beta-elimination
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- 4. Stereoselectivity of Ziegler-Natta Catalysts
- 4.1 Categories of Stereoselective Ziegler-Natta Catalysts
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- 5. Conclusion

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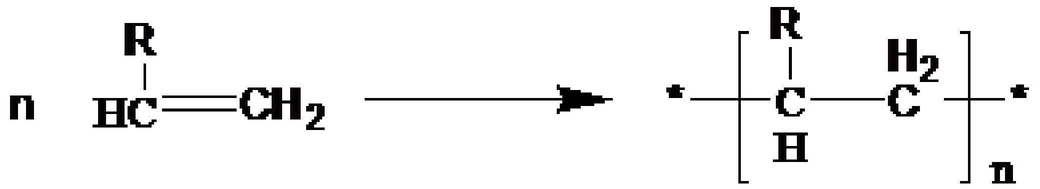
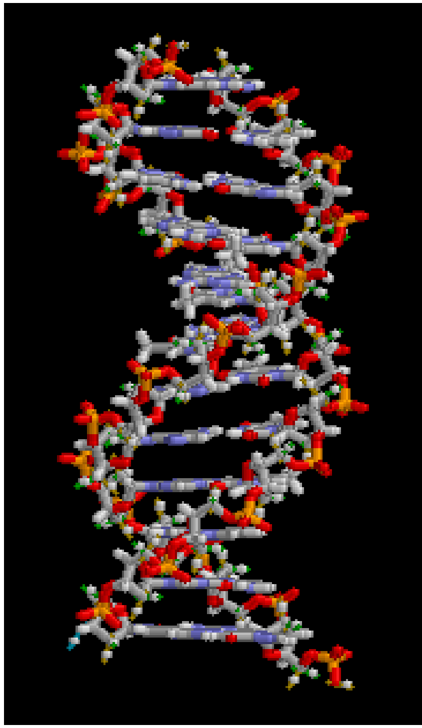
Overview

- Polymer: large molecule, composed with many repeated subunits.
- Use:
- Natural: DNA, protein
- Artificial: polystyrene,

  polyvinyl chloride (PVC)

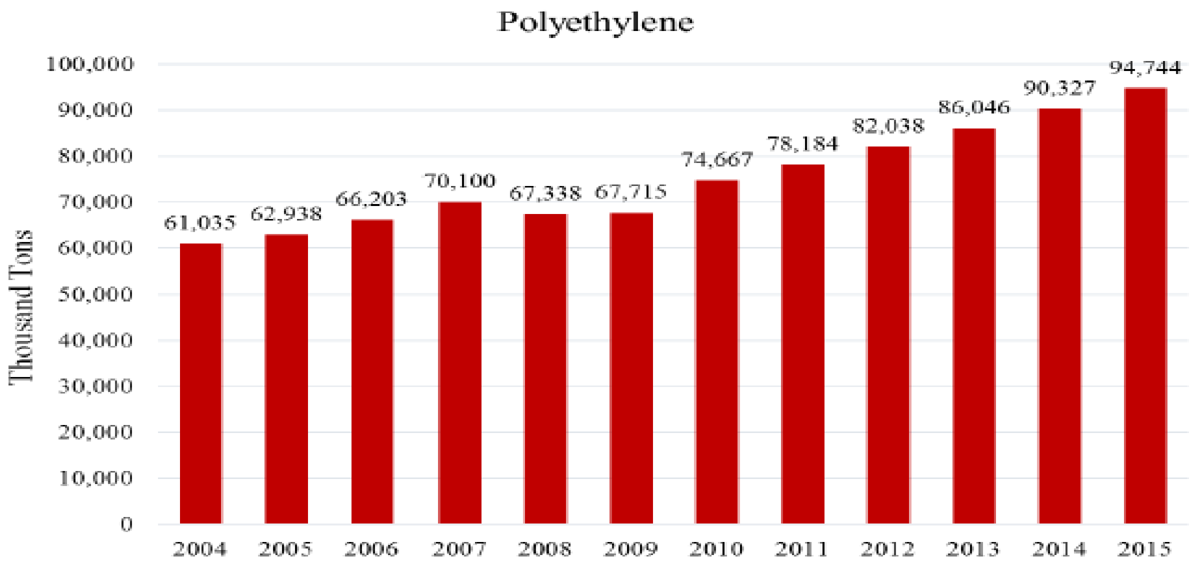


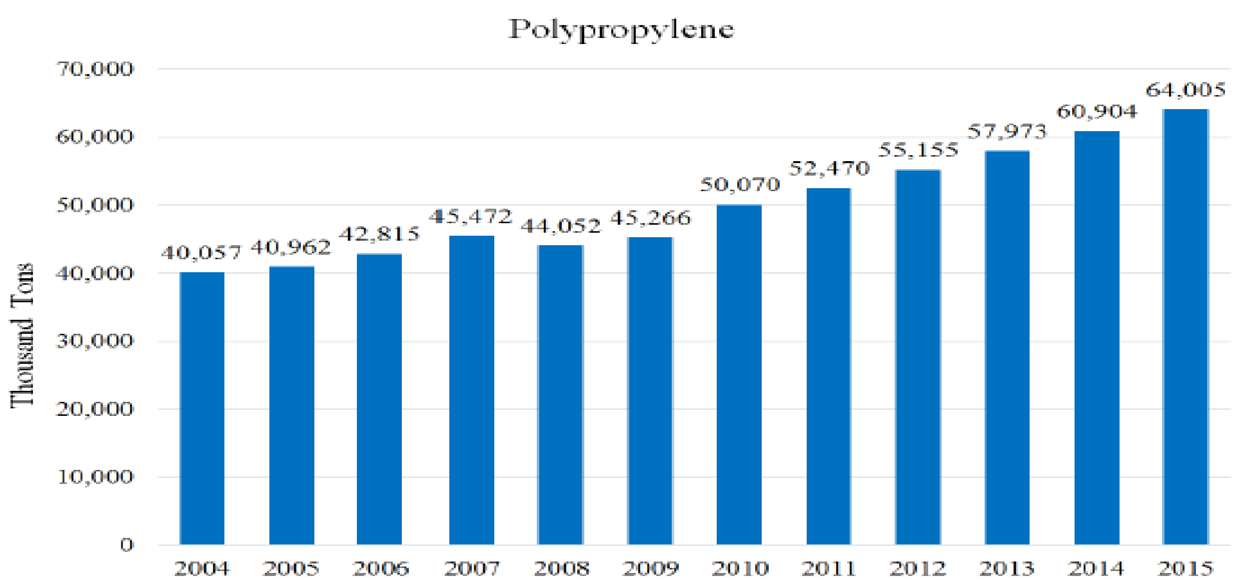


http://en.wikipedia.org/wiki/Polymer#mediaviewer/File:ADN_animation.gif

Artificial Polymer Products

- # World's demand for PE and PP

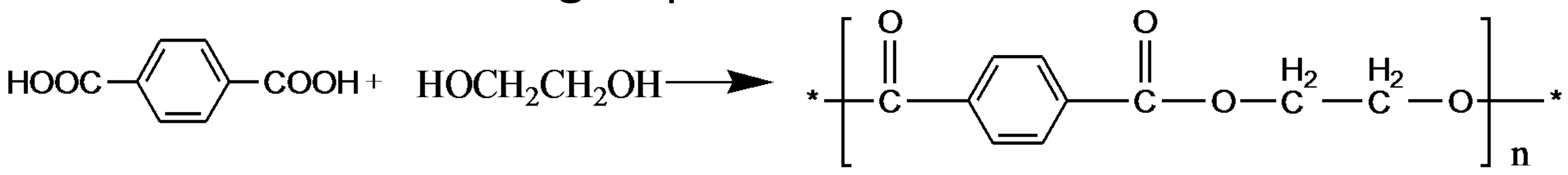




Callais, P. Outlook for PE and PP Resins. 16th Annual Canadian Plastics Resin Outlook Conference. Available online: http://www.canplastics.com/conference/2011Presentations/ 5._Peter_Callais.

Overview

- Polymerization reaction
- Step growth: polymers formed by the stepwise reaction between functional groups of monomers



PET

- Chain growth: linking together of molecules incorporating double or triple carbon-carbon bonds.
- radical addition polymerization
- cationic addition polymerization
- anionic addition polymerization
- Coordination polymerization (olefin binding/alkyl insertion)

Coordination Polymerization and Ziegler-Natta Catalysts

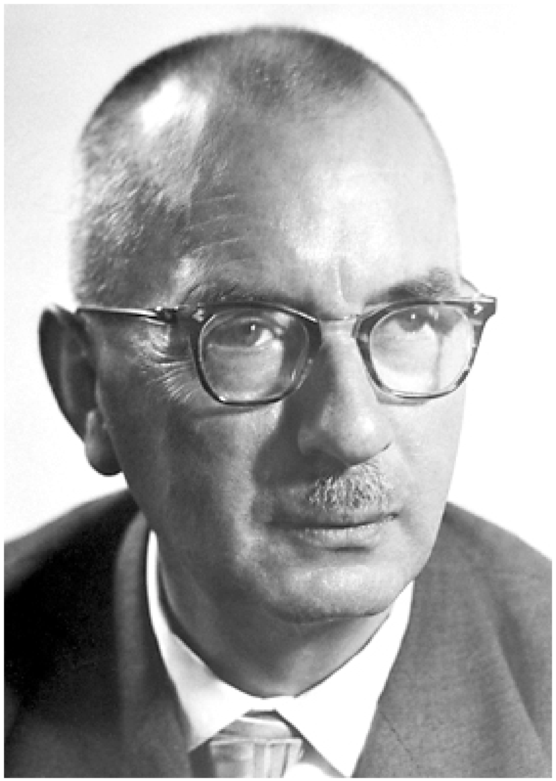
- Coordination polymerization: an addition polymerization in which successive monomers are added to the organometallic active center. Examples are:
  - ROMP (Ring open metathesis polymerization)
  - Polymerization catalyzed by Ziegler-Natta catalyst
  - Polymerization catalyzed by Late Transition Metal Complexes catalyst

Ziegler-Natta Catalyst: History

- *1953 Karl Ziegler polymerizes ethene into high MW-HDPE (high density polyethylene) with catalyst based on $TiCl_4$, and Et_2AlCl as co-catalyst.*
- Giulio Natta, utilizes Ziegler's catalyst to produce PP.
- *1963 Ziegler and Natta are awarded the Nobel Prize*
- 1973 2nd generation Ziegler-Natta catalysts introduced with $TiCl_3$ purple phases at lower temperatures.
- *1975-1978 3rd generation catalysts supported on $MgCl_2$ commercialized by many companies.*
- 1977-1980 Kaminsky and Sinn discover high activity metallocene single-site catalysts (SSCs) using methylaluminoxane (MAO) as co-catalyst.
- *1991 Fourth generation Ziegler-Natta catalysts based on aluminium-oxane activated metallocene complexes used.*
- 1997 Montel (or Lyondell Basell) commercialize PP based on 5th generation Ziegler-Natta catalyst that use 1.3-diethers, and succinate as donors.

A. Shamiri, M. H. Chakrabarti, S. Jahan, M. A. Hussain, W. Kaminsky, P. V. Aravind and W. A. Yehye, *Materials* **2014**, *7*, 5069-5108.

Nobel Prize: 1963



Karl Ziegler, Germany

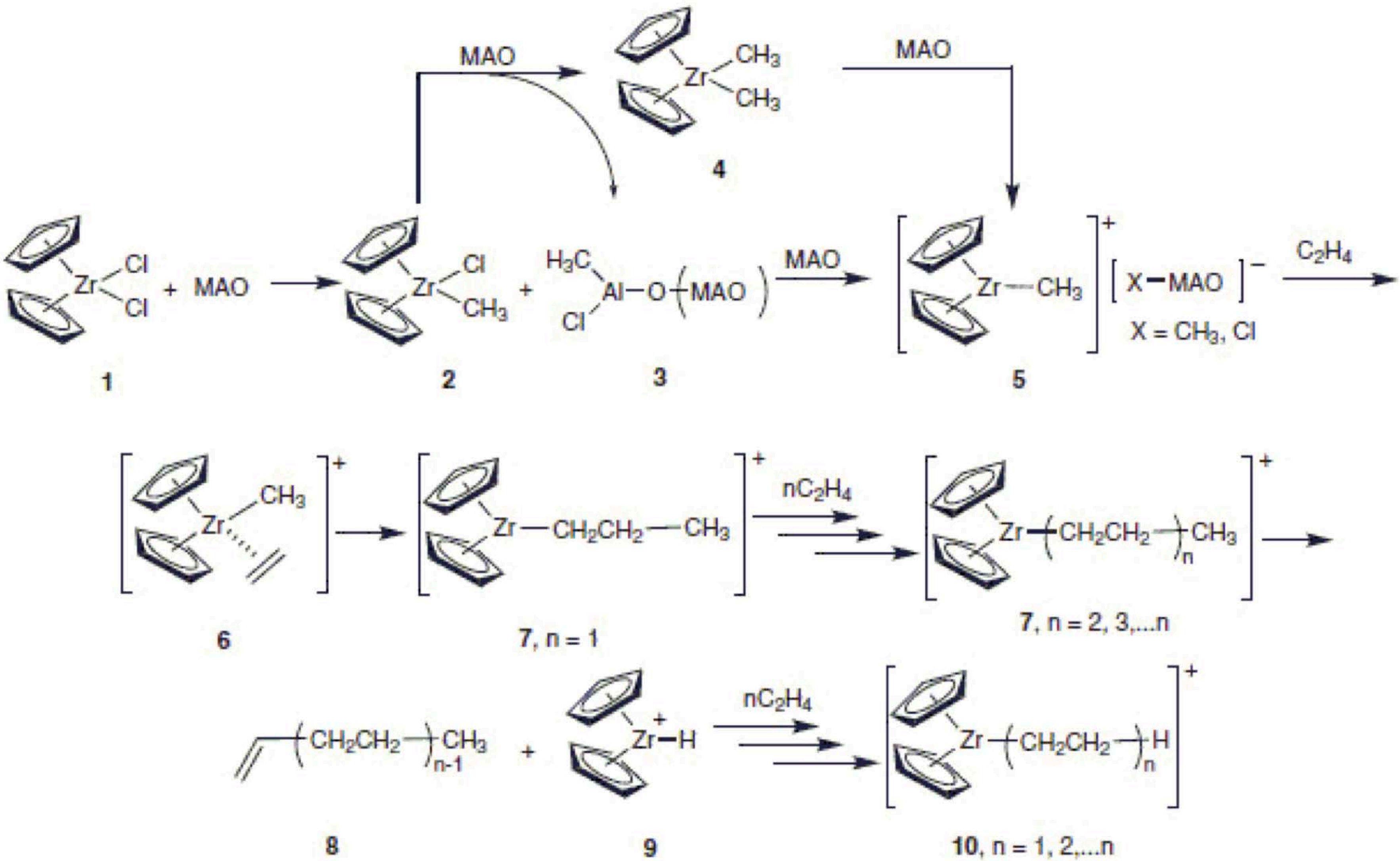
Giulio Natta, Italy

Prize motivation:

"for their discoveries in the field of the chemistry and technology of high polymers"

Giulio Natta - Facts". Nobelprize.org. Nobel Media AB 2014. Web. 17 Nov 2014. <http://www.nobelprize.org/nobel_prizes/chemistry/laureates/1963/natta-facts.html

Single Site Metallocene Catalysts: Living Polymerization



1. A. Shamiri, M. H. Chakrabarti, S. Jahan, M. A. Hussain, W. Kaminsky, P. V. Aravind and W. A. Yehye, *Materials* **2014**, *7*, 5069-5108.

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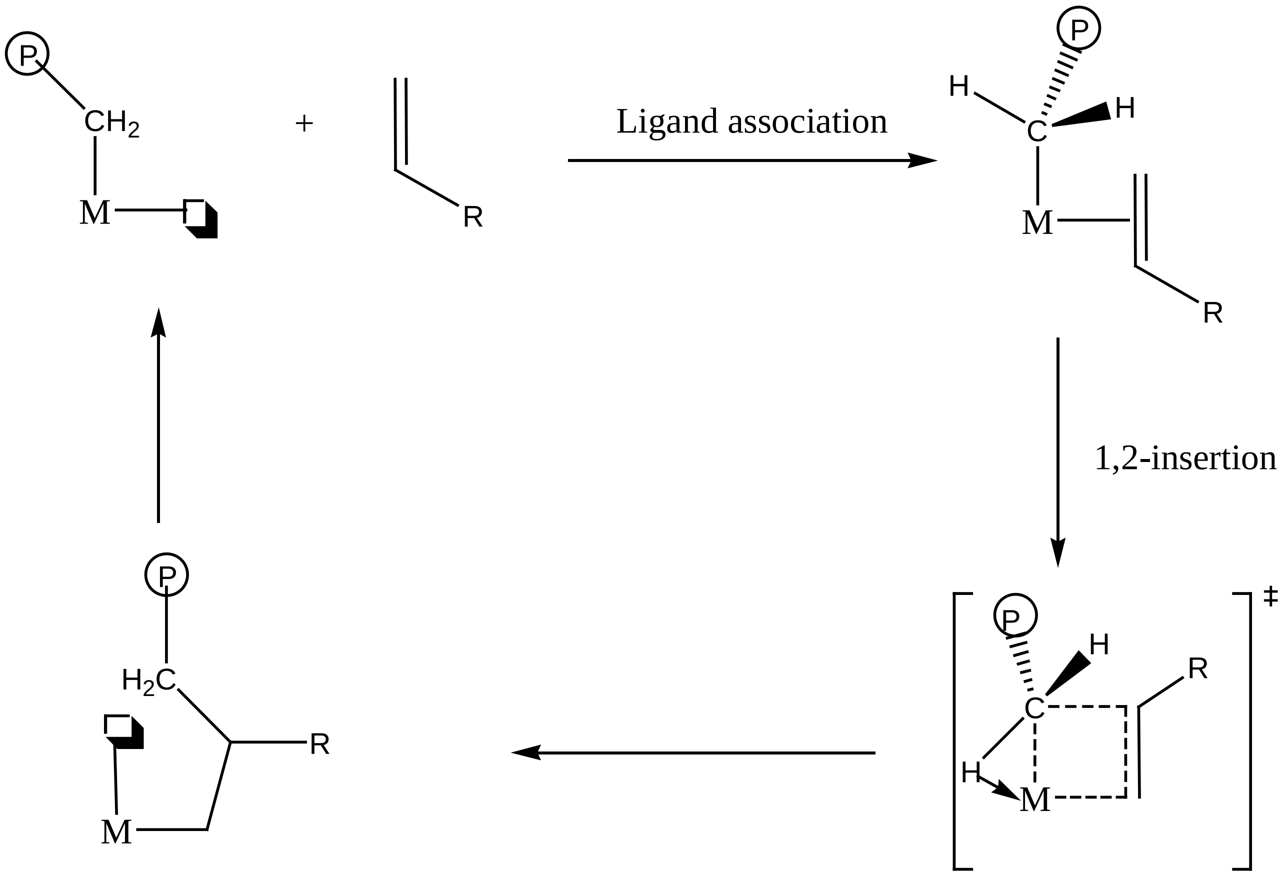
2.1 The Cossee Mechanism

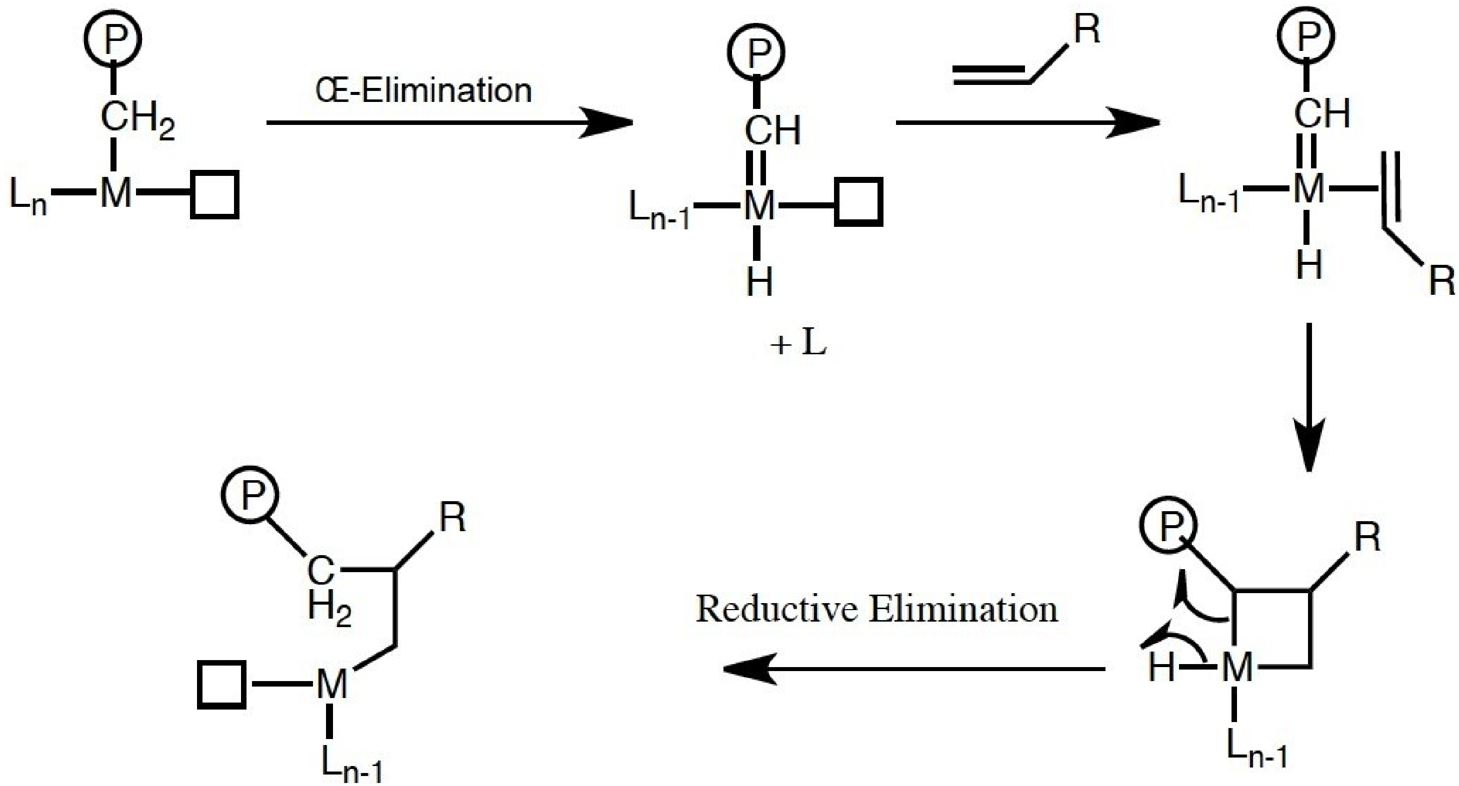


P.Cossee,*J.Catal*.,**1964**,3,80 and E.J.Arlman and P.Cossee,*J.Catal.*,**1964**,3,99

Brookhart, M.; Green, M.; Wong, L. L. *Prog. Inorg. Chem.* **1988**,36, 1-124.

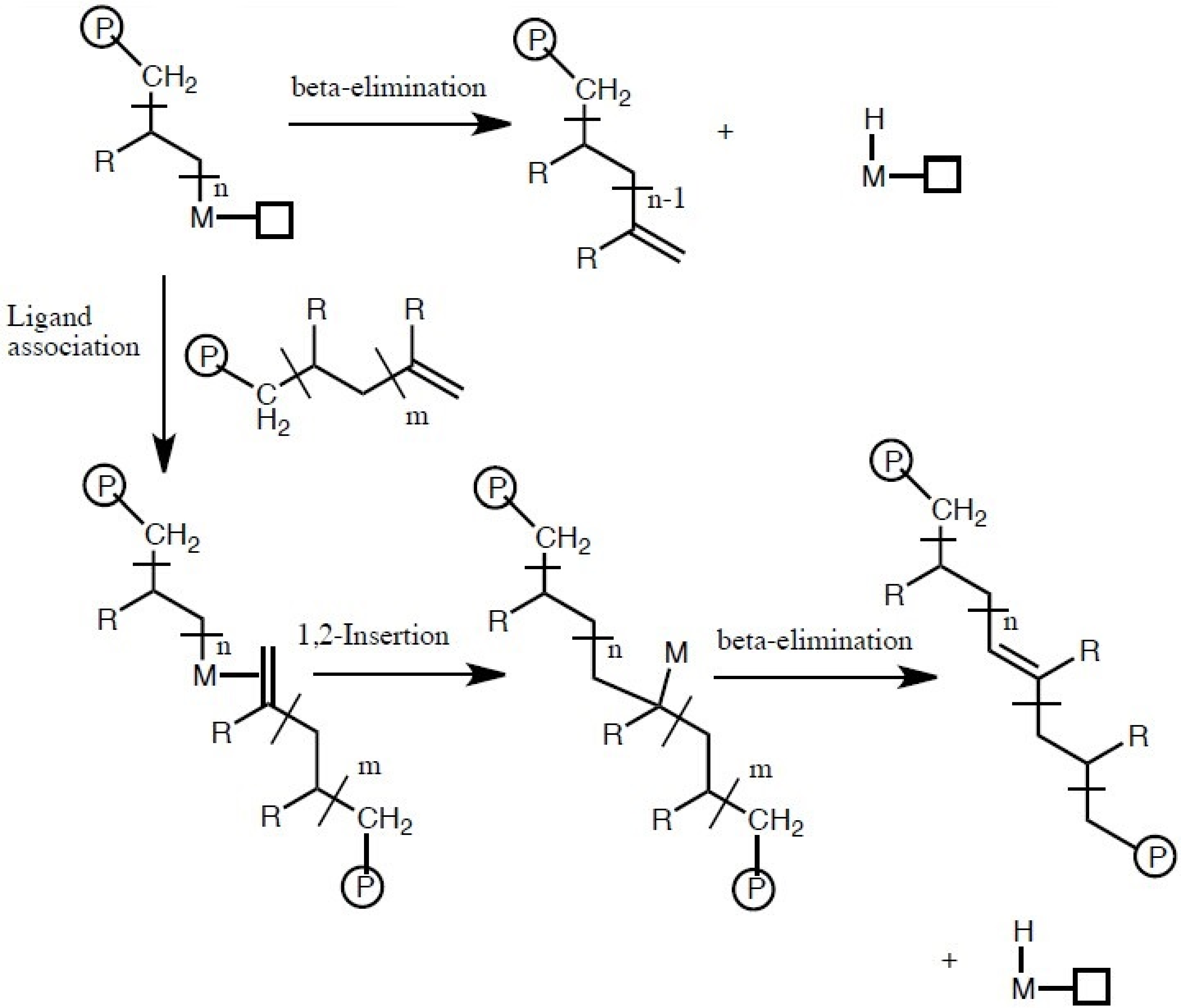
Brookhart, M.; Volpe, A. F., Jr.; Lincoln, D. M.; Horva´ th, I. T.;Millar, J. M. *J. Am. Chem. Soc.* **1990**, 112, 5634-

2.2 The Green-Rooney Mechanism

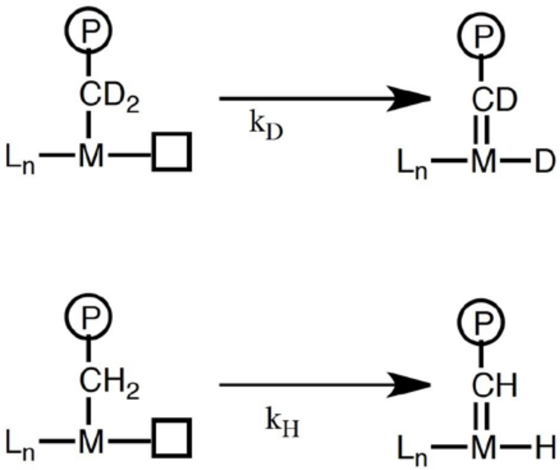


K.J.Ivin,J.J.Rooney,C.D.Stewart, M.L.H. Green, and J.R. Mahtab, *J. Chem. Soc, Chem. Commun*., **1978**, 604
M.L.H. Green, *Pure Appl. Chem.*, **1978**,100,2079

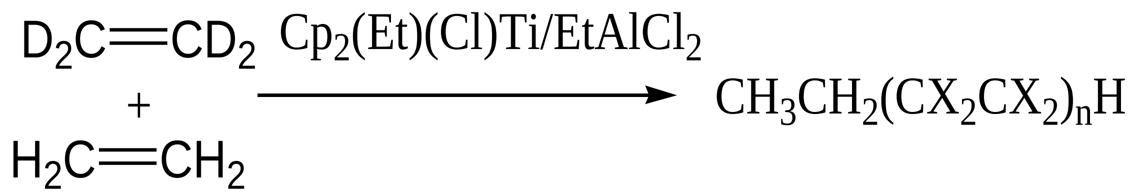
Chain Termination and Chain Transfer Steps



Kinetic Isotope Effect



$k_H > k_D$



X= H, D

1:1

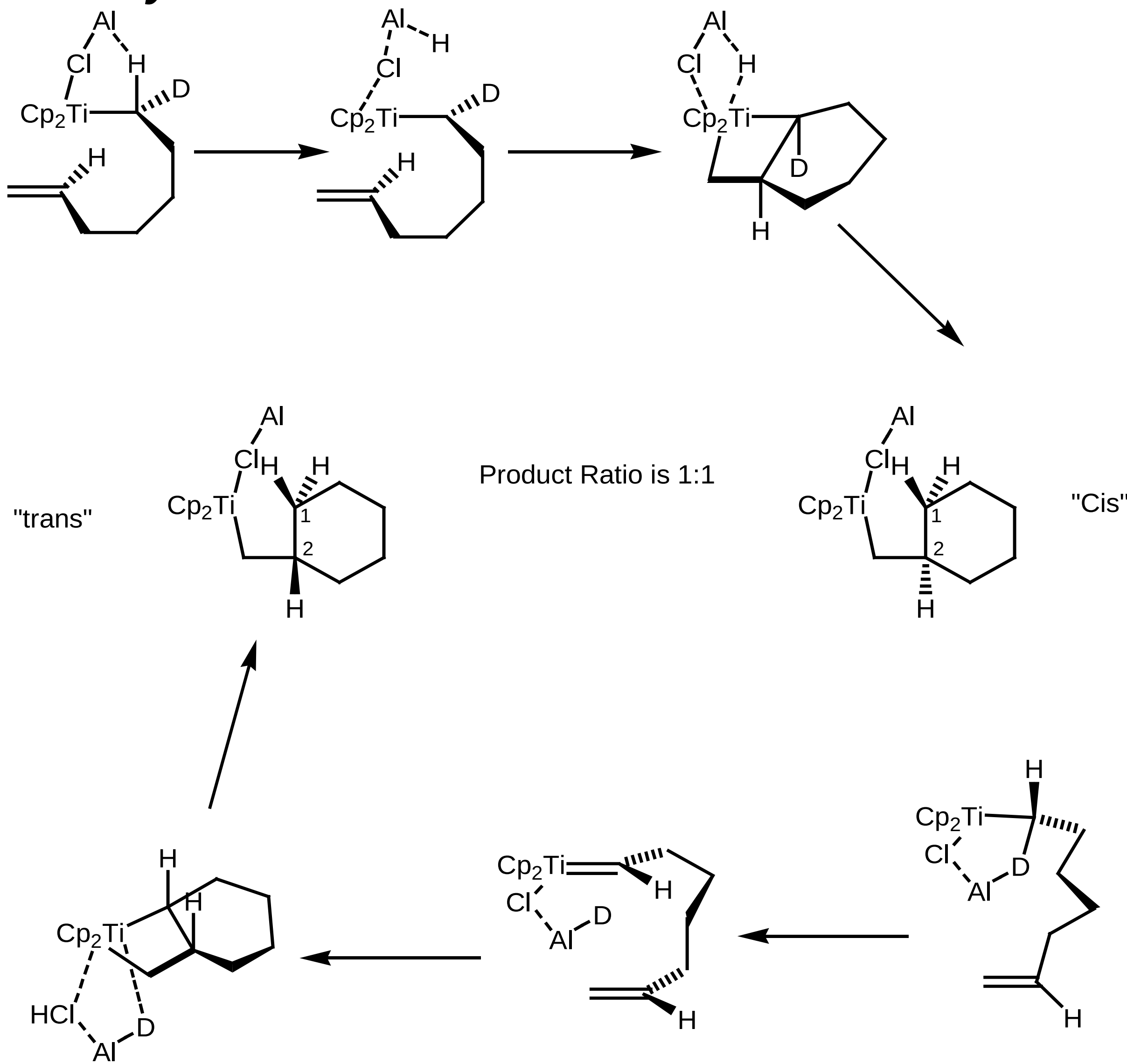
H:D = 1:1

Conclusion: Lack of KIE indicates no C-H bond breaking in RDS

J.Soto,M.Steigerwald, and R.H. Grubbs, *J. Am. Chem. Soc.* , **1982**,104,4479

Kinetic Isotope Effect, continued

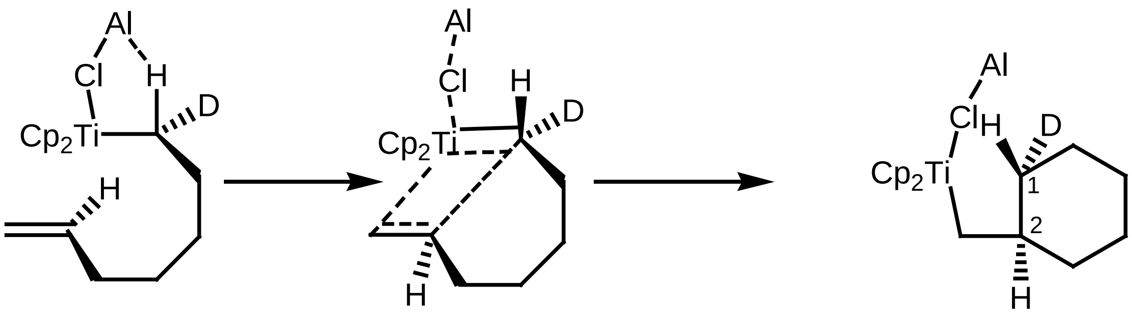
Green-Rooney Mechanism



L.Clawson,J.Soto,S.L.Buchwald,M.L.Steigerwald,and R.H.Grubbs, *J. Am. Chem. Soc*.,**1985**,107,3377

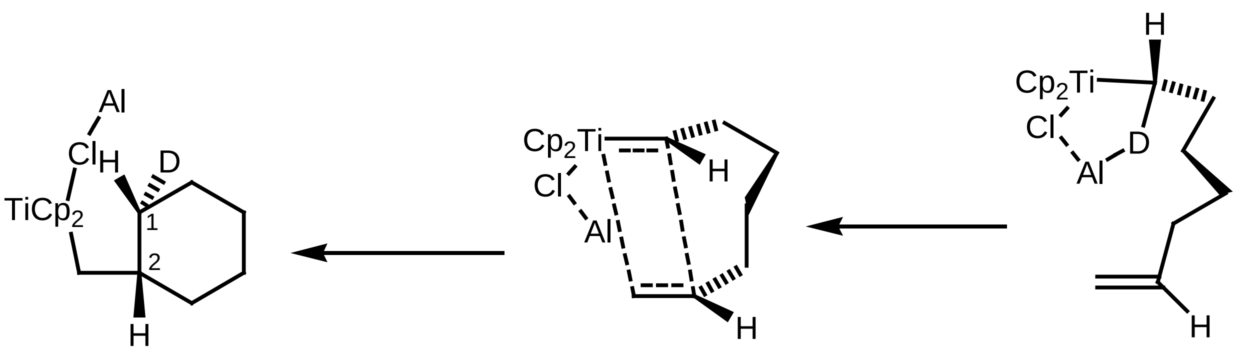
"Stereochemical" Isotope Effect

Cossee Mechanism



"Cis"

Product Ratio is 1:1



"trans"

L.Clawson,J.Soto,S.L.Buchwald,M.L.Steigerwald,and R.H.Grubbs, *J. Am. Chem. Soc*.,**1985**,107,3377

Conclusion: Cossee Mechanism

- Negative results of Kinetic Isotope Effect excludes Green-Rooney Mechanism
- "Stereochemical" Isotope Effect shows the Cossee Mechanism is reasonable

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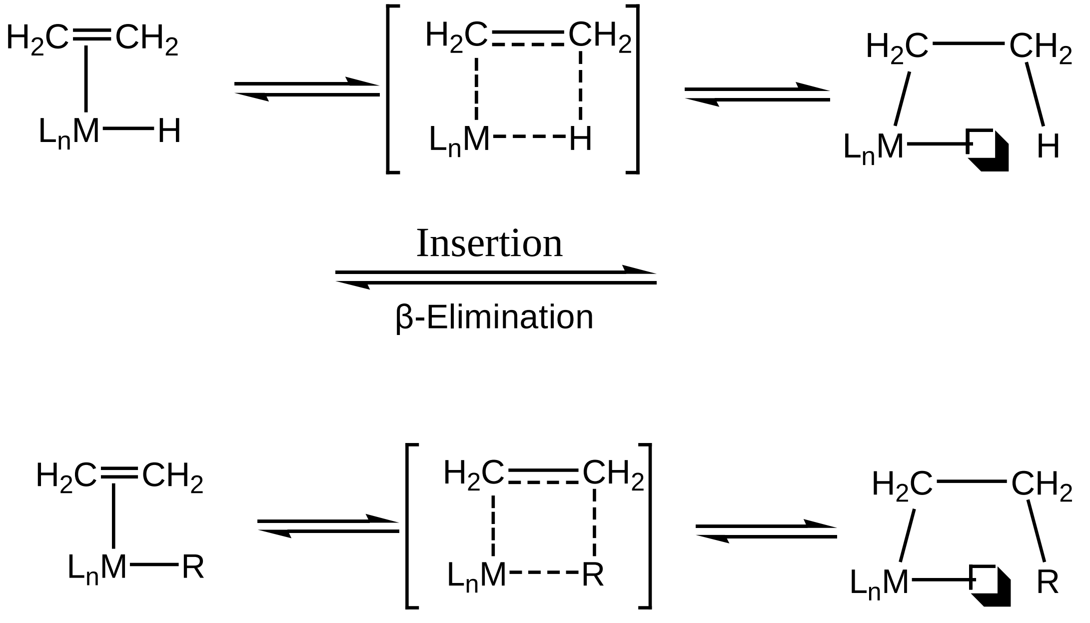
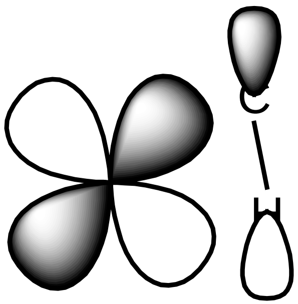
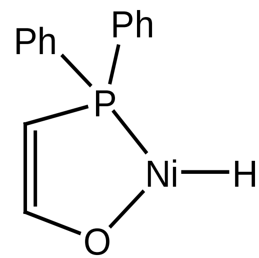
- 1,2-insertion and β-Elimination

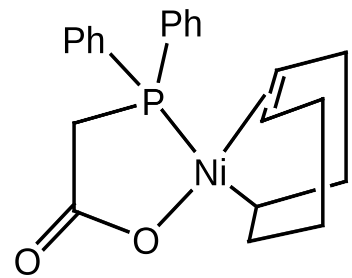


Electronic Characteristics of Early and Late Transition Metals in Olefin Polymerization/Oligomerization Catalysis

Catalysts for Polymerization	Catalysts for Oligomerization







d-σ* Interaction
Stabilizing factor

β-elimination favored for
Ni, yielding short chains

Late Transistion Metal: Ni(II) d^8

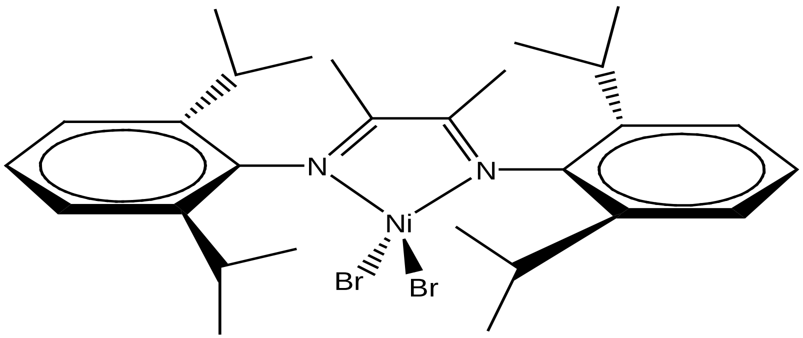
Ti(IV),Zr(IV),V(V): d^0

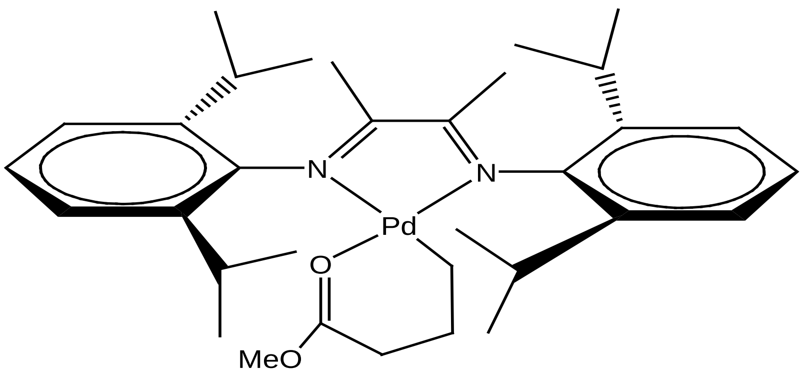
lower E_a for β-Elimination

Dynamically stable

Shell Higher Olefin Process(SHOP)

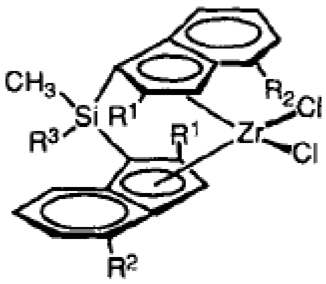
Bulky diimine groups impede the β-Elimination



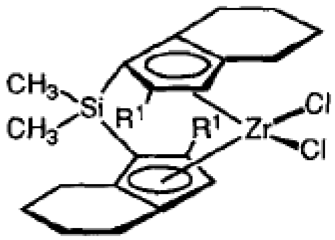


L.K.Johnson,C.M.Killian, and M. Brookhart,*J. Am. Chem. Soc.*,**1995**,117,6414

• Electronic Effect of β-Elimination



2a-e



3a,b

Catalyst (+ MAO)	R^1	R^2	R^3	Activity $\left[\frac{\text{kg PP}}{\text{mmol cat. h}}\right]$	M_w $[10^3\ \text{g mol}^{-1}]$
Indenyl type					
2a	H	H	CH_3	60	60
2a' [a]	H	H	H	2	350
2b	CH_3	H	CH_3	40	340
2c	C_2H_5	H	CH_3	30	370
2d	CH_3	*i*-C_3H_7	CH_3	105	460
2e	CH_3	H	C_6H_5	35	450
Tetrahydroindenyl type					
3a	H			35	32
3b	CH_3			10	65

[a] For comparison with **2a**, the hafnocene derivative with the same structural formula, **2a'**, has been listed.

Spaleck, W.; Antberg, M.; Rohrmann, J.; Winter, A.; Bachmann,B.; Kiprof, P.; Behm, J.; Herrmann, W. A. *Angew. Chem.*, Int.Ed. Engl. **1992**, 31, 1347-1350.

- ## Effect of Metal

Bond Energy of M-C and M-H

3rd row > 4th row> 5th row

1,2-insertion :

Ti < Zr < Hr   Ni< Pb < Pt

β-Elimination:

Ti > Zr > Hr   Ni > Pb > Pt

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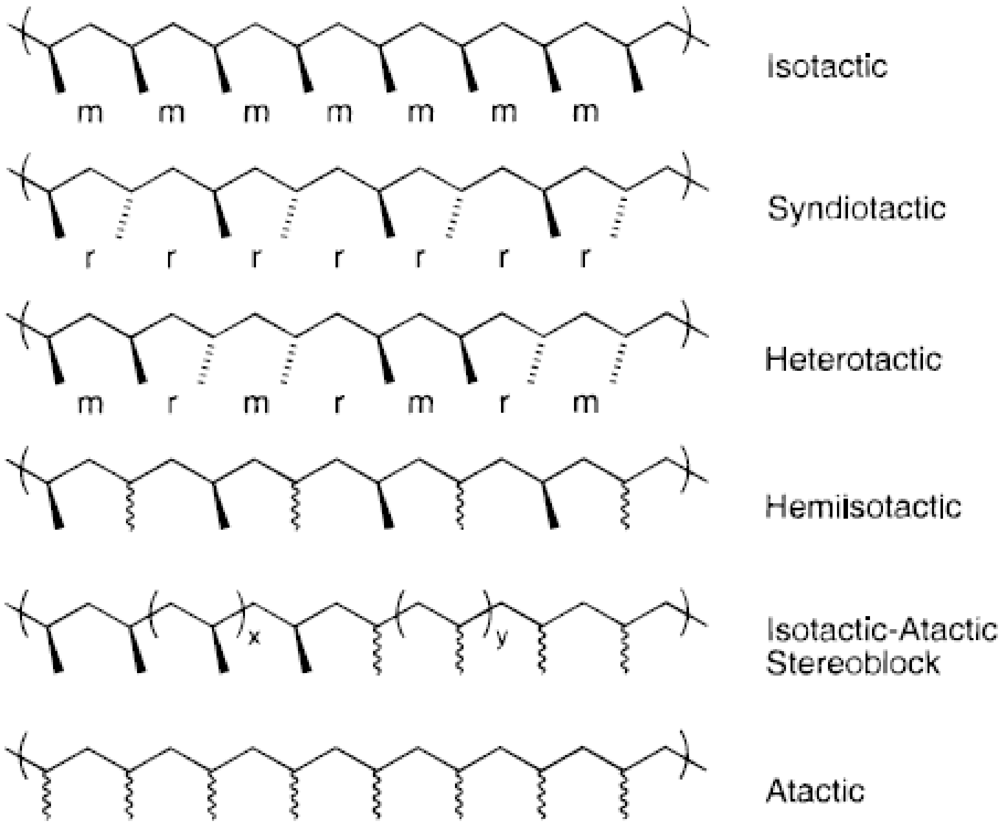
Designation of polymer stereotype



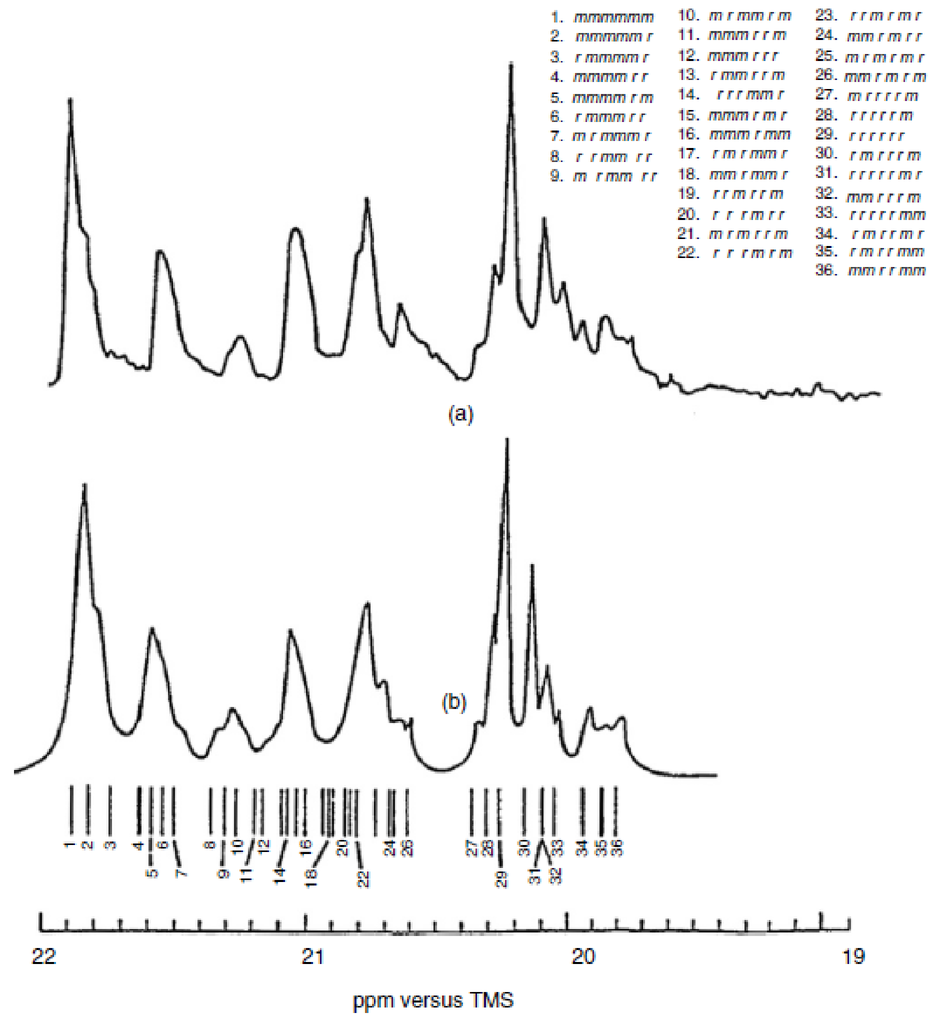
"m" for meso
"r" for racemic

Geoffrey W. Coates, *Chem. Rev.* **2000**, 100, 1223-1252 1223

• Characterization of tacticity

Method:

- solubility
- X-ray diffraction
- IR spectroscopy
- thermal properties
- <u>NMR (Most Important)</u>



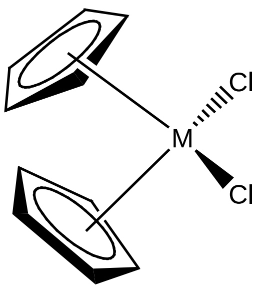
(a) methyl region of the ^{13}C NMR spectrum of atactic polypropylene
(b) Simulated 13C NMR spectrum by using γ-gauche effect

James E. Mark , *Physical properties of polymers handbook* , 2nd ed.Press. New York : Springer , **2007** ,page 359-384

Isotactic Polymerization

- C_{2v} : Cp_2MCl_2 only atactic polypropylene

  or End Control Cp_2TiPh_2 ; $(iPrCp)_2TiCl_2$



  isotactic or syndiotactic

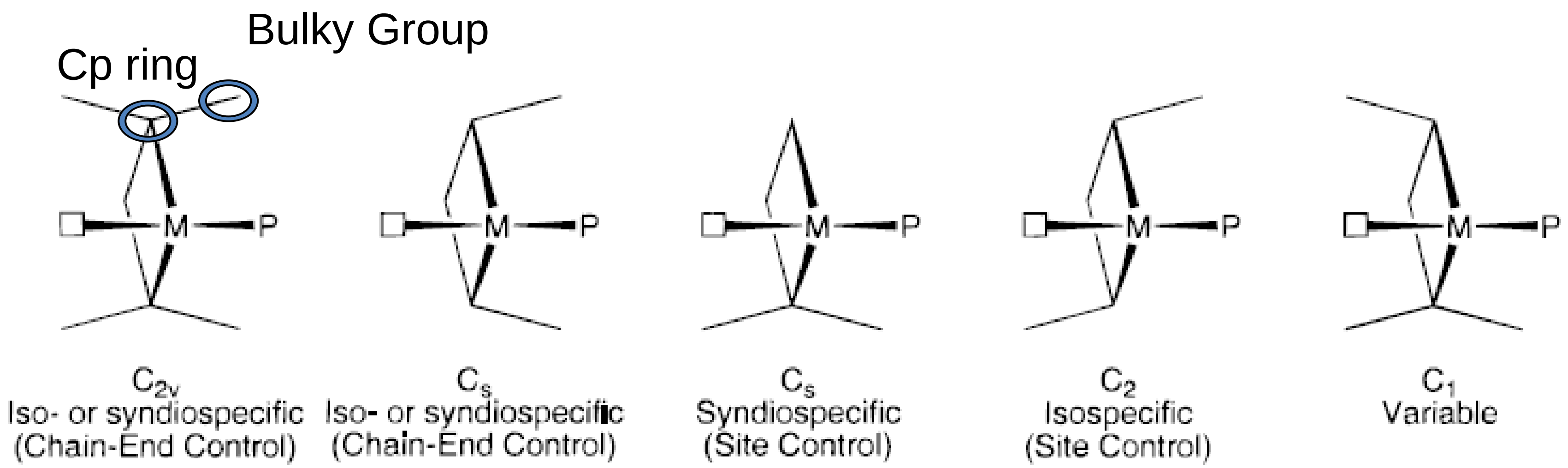
  (temperature dependent)

- C_2 Catalysts most successful :

  Ligand with a bridging group

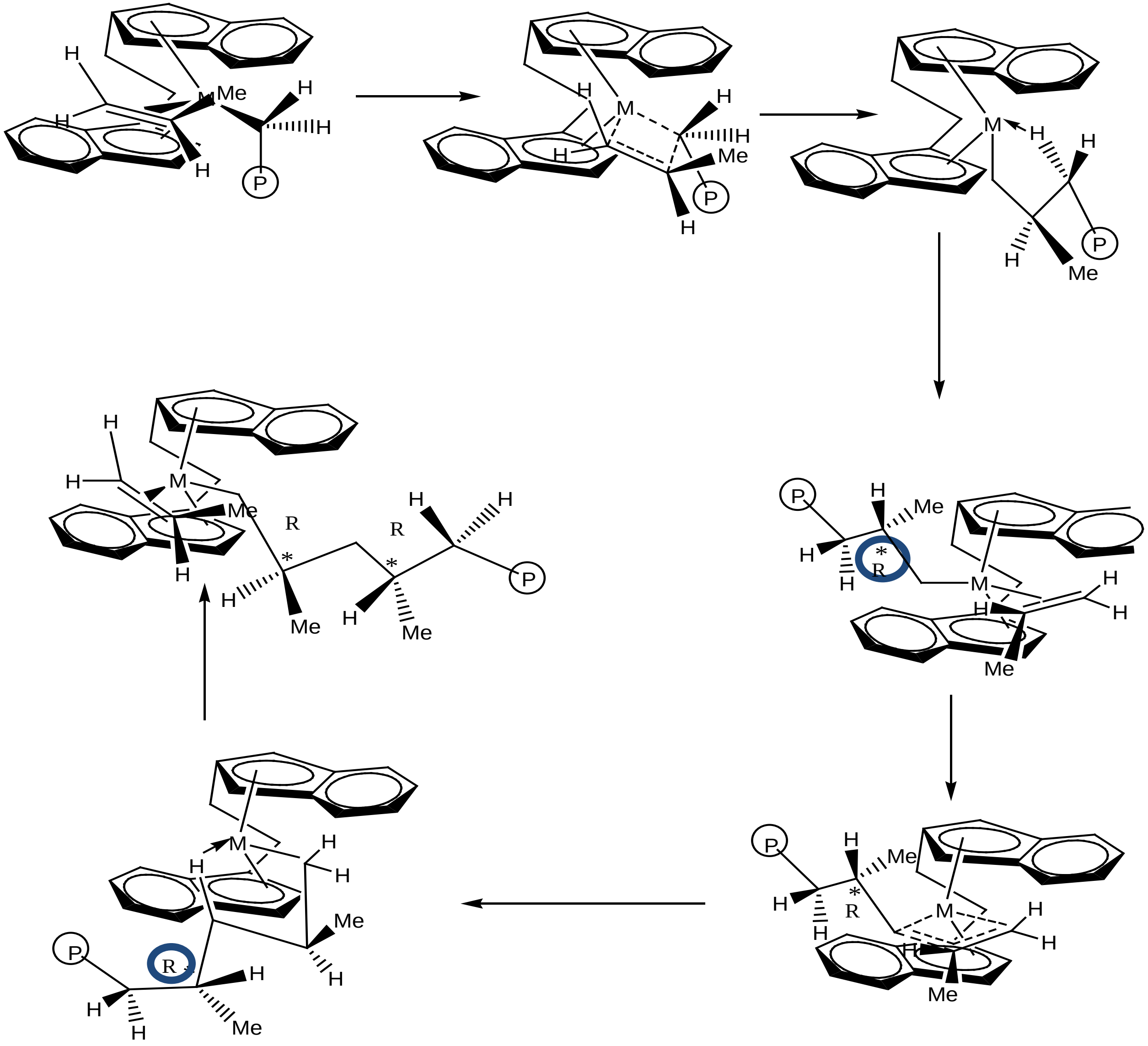
  --rigid structure

Five Main Symmetry Catagories of Single-site Polymerization Catalysts

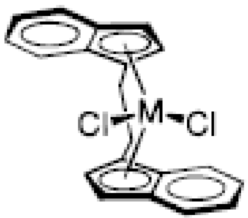


Geoffrey W. Coates, *Chem. Rev.* **2000**, 100, 1223-1252 1225

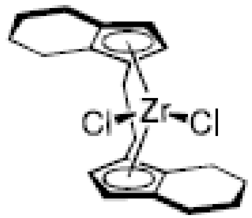
Mechanism of C_2 Catalysts



R.H. Grubbs and G.W.Coates,*Acc.Chem.Res.***1996**.29.85



5; M = Ti
6; M = Zr
7; M = Hf



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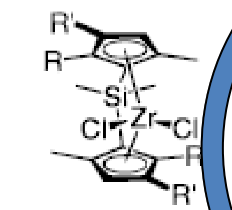
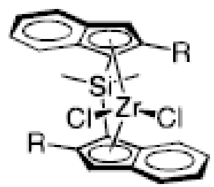
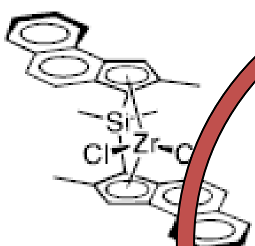


9; R = H, R' = ^{t}Bu
10; R, R' = Me



11; R = H
12; R = Me



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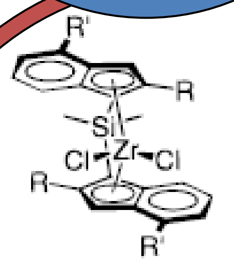


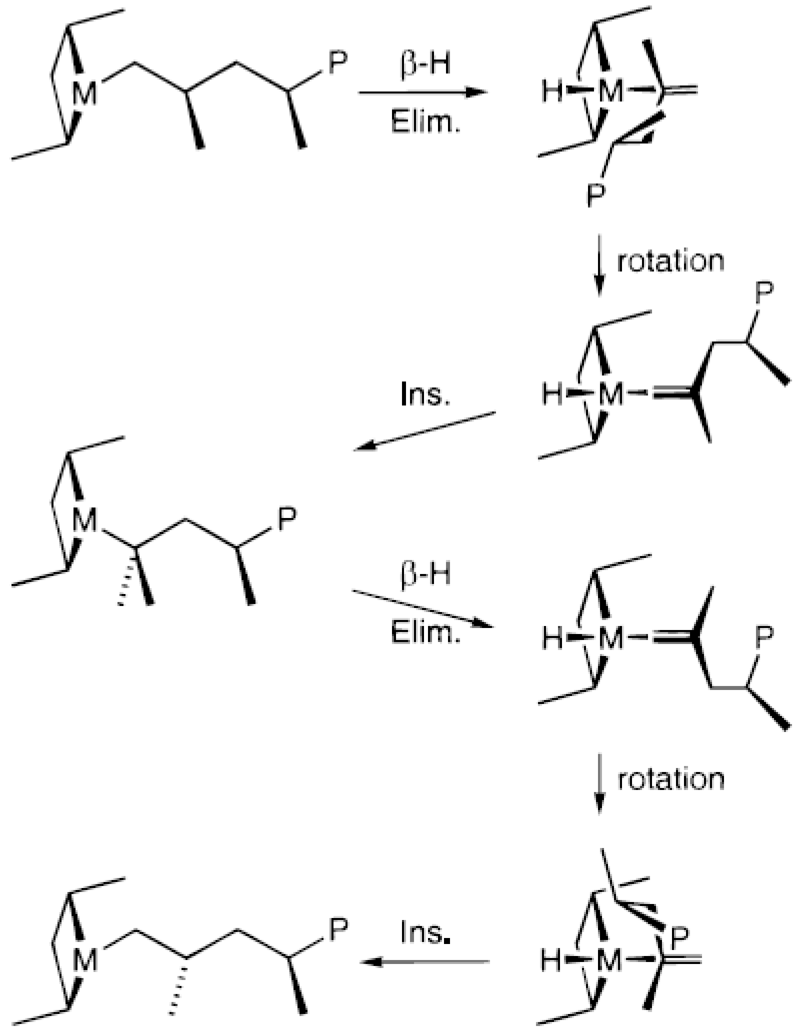
14; R = Me, R' = ^{i}Pr
15; R = Me, R' = 1-Naphthyl
16; R = ^{n}Pr, R' = 9-Phenanthryl

Table 1. Polymerization of Propylene with Bridged, C_2-Symmetric Zirconocene Catalysts[a]

metallocene	productivity[b]	T_m (°C)	M_w	[*mmmm*]
6	188	132	24 000	0.78
9	5[c]	149	4 000	0.97
10	1.6[d]	162	134 000	0.977
11	190	137	36 000	0.82
12	99	145	195 000	0.88
13	403	146	330 000	0.89
14	245	150	213 000	0.89
15	875	161	920 000	0.991
16	47	160	400 000	0.992

Geoffrey W. Coates, *Chem. Rev.* **2000**, 100, 1223-1252 1226,1227

- Stereoerror:



Geoffrey W. Coates, *Chem. Rev.* **2000**, 100, 1223-1252 1226,1227

Busico, V.; Brita, D.; Caporaso, L.; Cipullo, R.; Vacatello, *M.Macromolecules* **1997**, 30, 3971-3977.

Strategies for modifying bridged metallocene structure:

- Modification of bridge:

Si , P , B Bridged catalysts

- Modification of metalloncene ligands

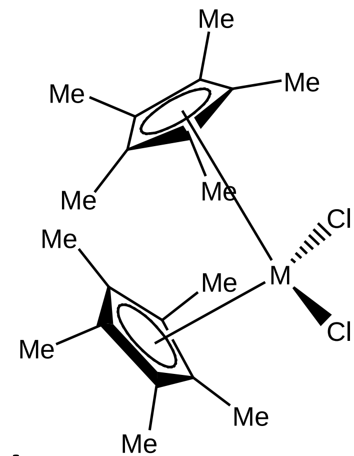
Substitution and derivatives of Cp rings

- Variation of the activator

Bu_3Al with $[PhNHMe_2][B(C_6F_5)_4]$

Syndiotactic Polymerization

- C_{2v} : $Cp^*{}_2MCl_2$ (M=Zr, Hf)



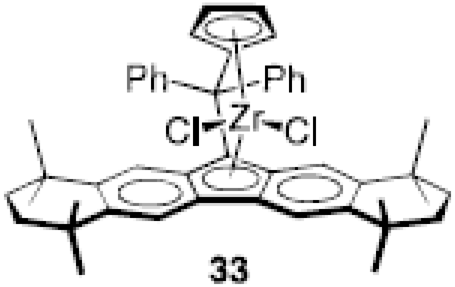
  Syndiotactic polymer

  2 kcal/mol preference for syndiotactic versus isotactic

- C_s Catalysts : Regularly alternating insertion of olefins at the enantiotopic sites

Resconi, L.; Abis, L.; Franciscono, G. *Macromolecules* **1992**, 25,6814-6817.

Examples of C_s Catalysts



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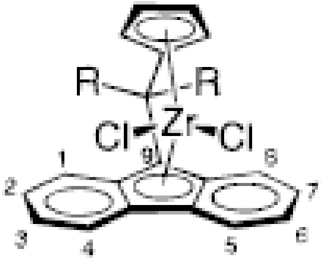
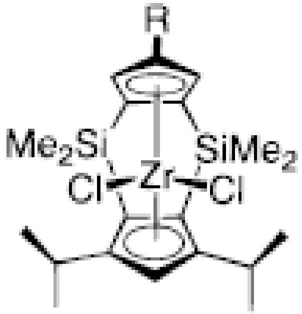
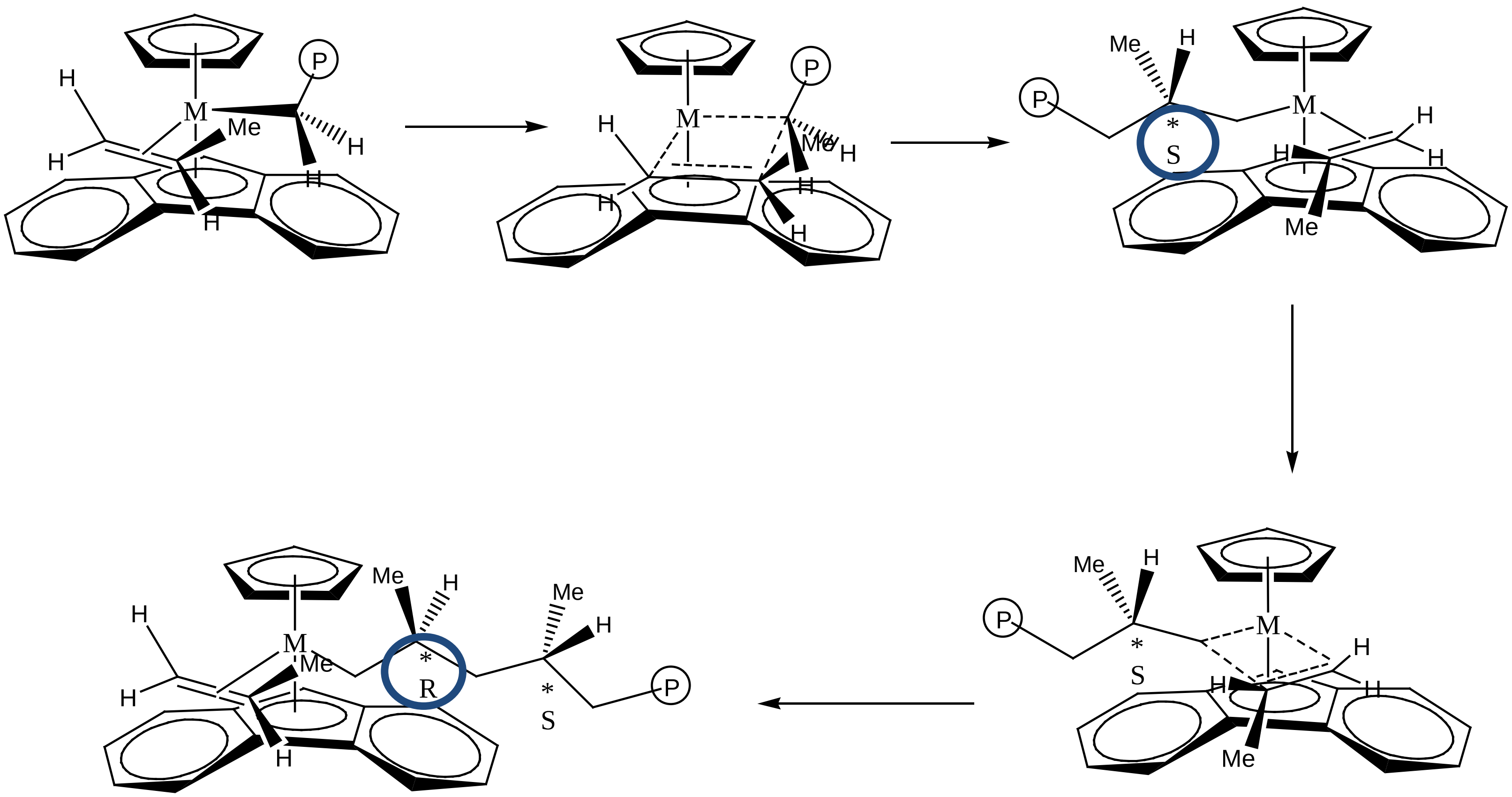


31; R = Me
32; R = Ph

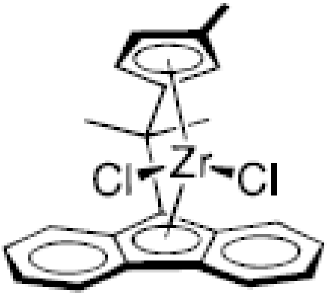


Mechanism of C_s Catalysts



Hemiisotactic Polymerization

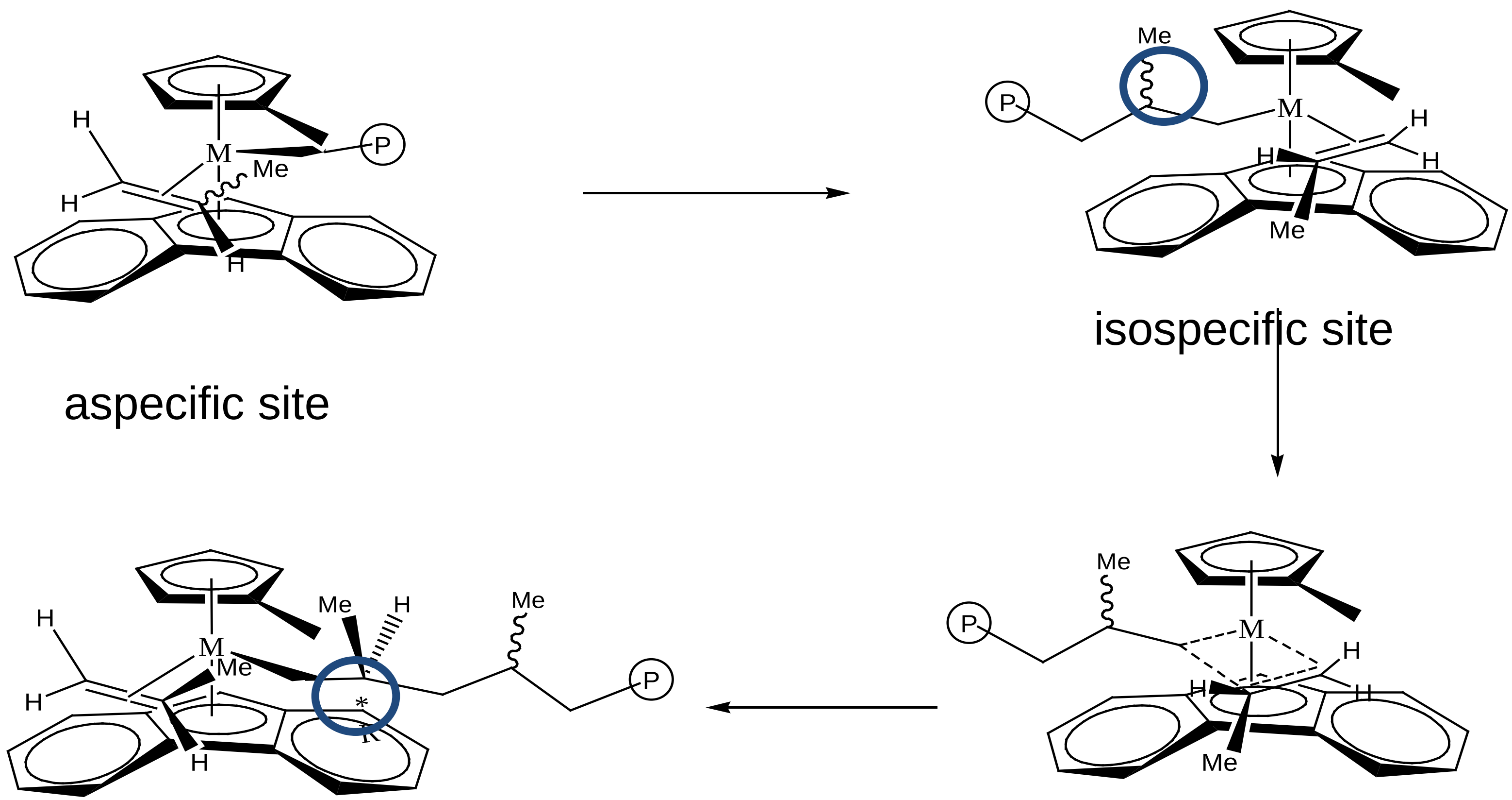
- C_1 Catalysts :



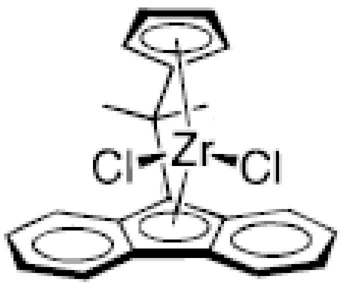
Two Different Coordination Sites

One isospecific site, One aspecific site

Mechanism of C_1 Catalysts for Hemiisotactic Polymer

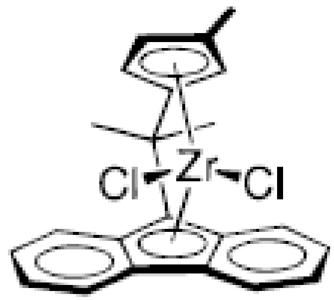


Influence of substituent



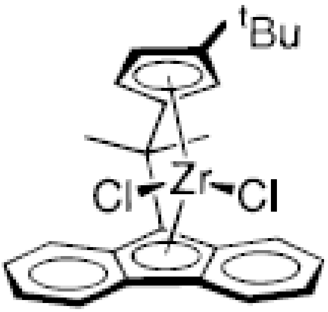
C_s

Syndiatactic



C_1

Hemiisotactic



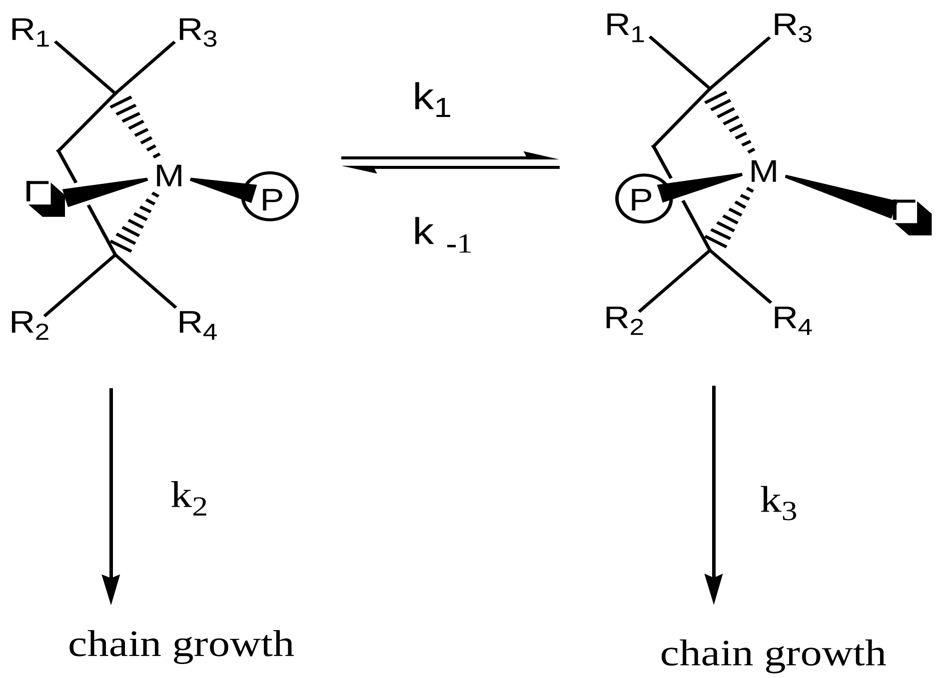
C_1

Isotactic

Ewen, J. A.; Jones, R. L.; Razavi, A.; Ferrara, J. D. *J. Am. Chem.Soc.* **1988**, 110, 6255-6256.

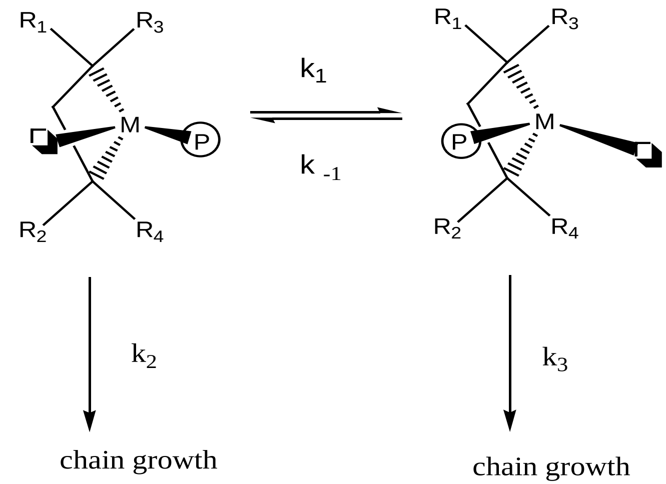
Ewen, J. A.; Elder, M. J.; Jones, R. L.; Haspeslagh, L.; Atwood,J. L.; Bott, S. G.; Robinson, K. *Makromol. Chem., Macromol.Symp.* **1991**, 48-9, 253-295.

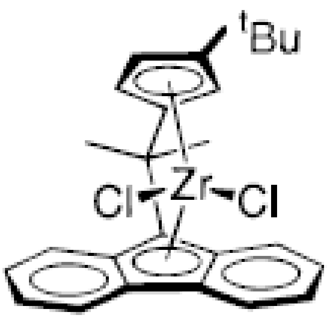
Site Epimerization



Site Epimerization Induced Isotactic polymerization

One site has very bulky groups (for example R3,R4), $k_1 << k_{-1}$ the other is stereospecific.



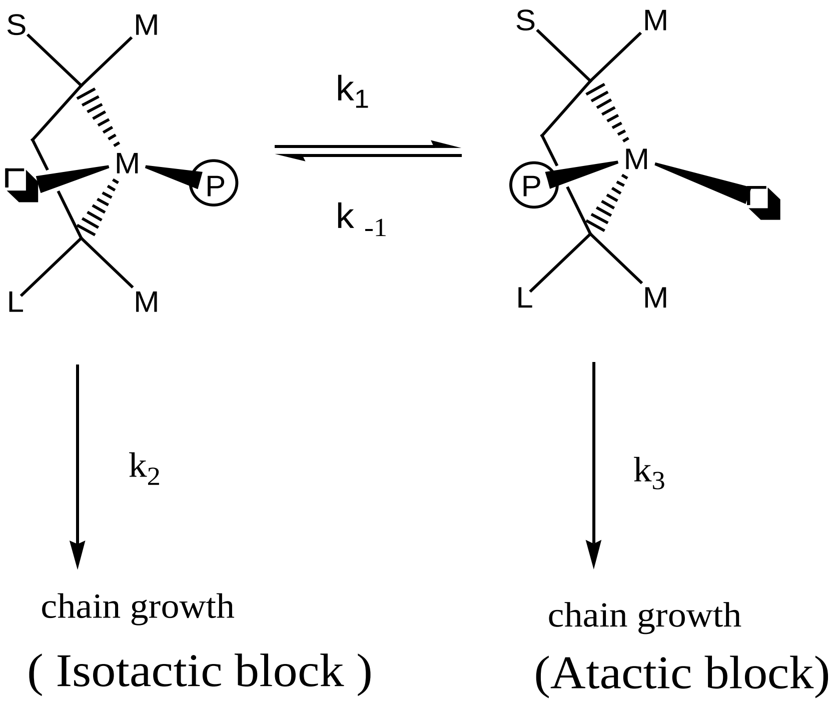


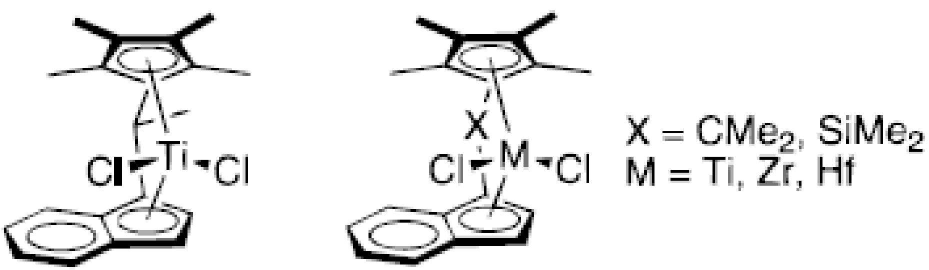
Ewen, J. A.; Elder, M. J.; Jones, R. L.; Haspeslagh, L.; Atwood,J. L.; Bott, S. G.; Robinson, K. *Makromol. Chem., Macromol.Symp.* **1991**, 48-9, 253-295.

Ewen, J. A.; Elder, M. J. *Makromol. Chem., Macromol. Symp.***1993**, 66, 179-190

Stereoblock Polymerization

- k_1 and k_{-1} are large; sites exchange rapidly
- $k_2, k_3 << k_1, k_{-1}$
- Sensitive to the reaction temperature

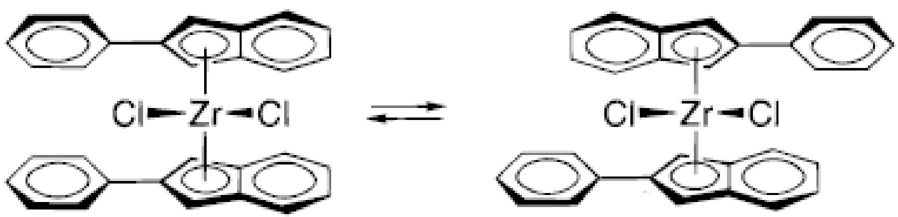




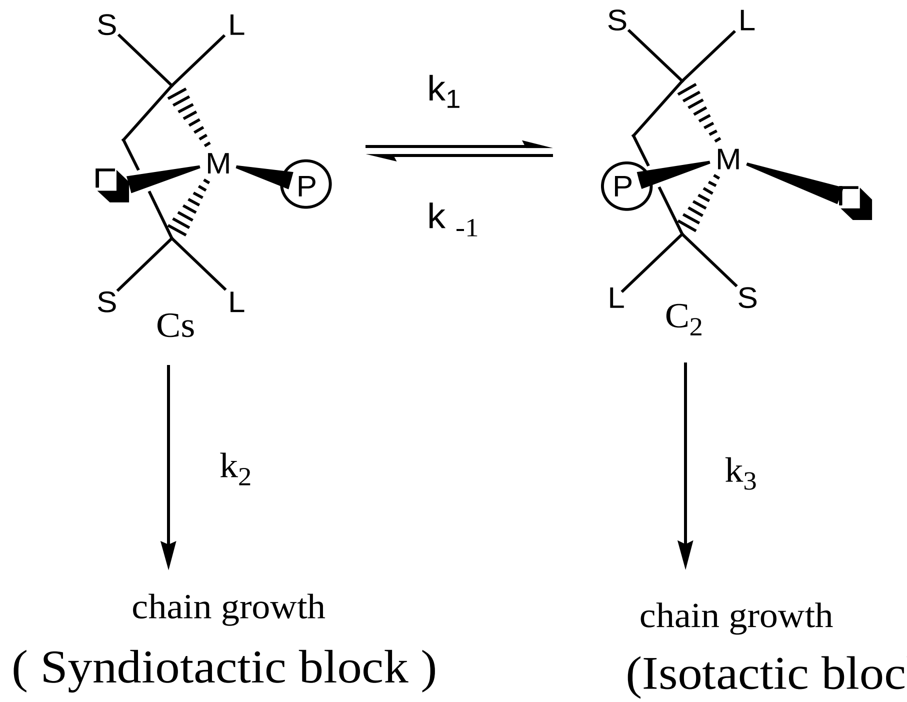
Gauthier, W. J.; Corrigan, J. F.; Taylor, N. J.; Collins, S.*Macromolecules* **1995**, 28, 3771-3778.

Mallin, D. T.; Rausch, M. D.; Lin, Y. G.; Dong, S.; Chien, J. C.W. *J. Am. Chem. Soc.* **1990**, 112, 2030-2031.

• Oscillating Catalysts

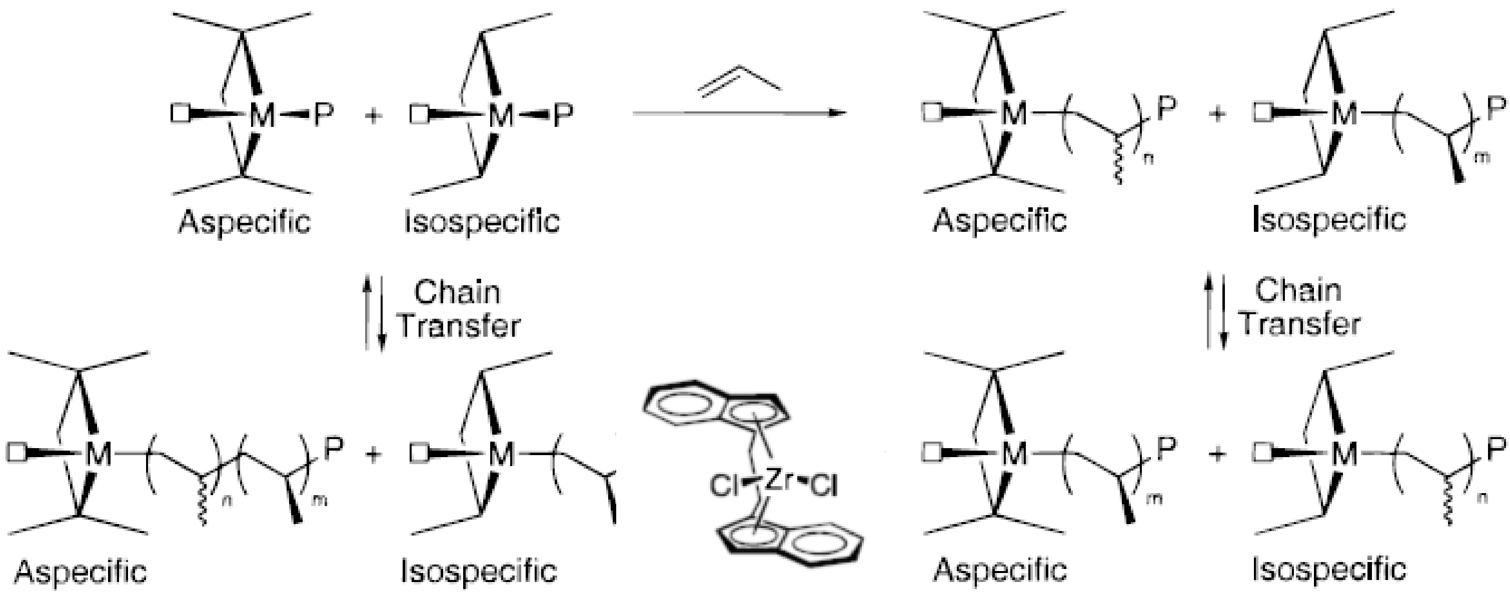


C_s C_2

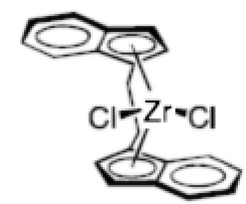


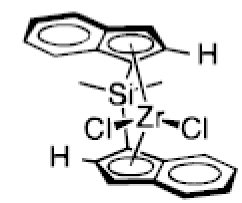
Coates, G. W.; Waymouth, R. M. *Science* **1995**, 267, 217-219.

- # Chain Transfer

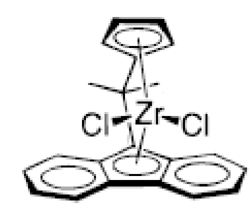


$Et(Ind)_2ZrCl_2$ & $Me_2Si(Ind)_2ZrCl_2$: atactic - isotactic





$Me_2Si(Ind)_2ZrCl_2$ & $Me_2C(Cp)(Fl)ZrCl_2$: isotactic - syndiotactic



Geoffrey W. Coates, *Chem. Rev.* **2000**, 100, 1223-1252 1226,1227

Chien, J. C. W.; Iwamoto, Y.; Rausch, M. D.; Wedler, W.; Winter,H. H. *Macromolecules* **1997**, 30, 3447-3458.

Chien, J. C. W.; Iwamoto, Y.; Rausch, M. D. J. *Polym. Sci. A* **1999**, 37, 2439-2445.

Przybyla, C.; Fink, G. *Acta Polym*. **1999,** 50, 77-83.

Conclusion

- Polymers play an important part in our daily lives. Various methodologies make it possible to synthesize polymers with different properties and functions. Coordination polymerization, especially Ziegler- Natta catalysis, dominates the olefin polymerization industry.
- Ziegler-Natta catalysts can be categorized into heterogenous and homogenous by their form in catalysis process. The heterogenous one is widely used in industry while the homogenous one, single site catalysts , are intensely investigated for the clarity of mechanism and development of strategies to modulate the properties of catalysts and polymers.
- Ziegler-Natta catalysts with different symmetry and ligands enrich the library of stereospecific polymers. Possibility of synthesizing different Ziegler-Natta Catalysts for mutifunctional polymers remains to be explored.

Thanks for your attention!

Questions?