Theoretical Studies of Isomerism in Selected Ziegler-Natta Catalysts

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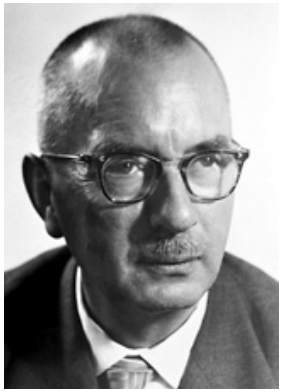
Outline

1. Milestones in Coordinative Olefin Polymerization
   - Classical, Metallocene and Post-Metallocene Systems
2. Molecular Modeling: Bailar Method and DFT Calculations
   - Bailar method
   - Classical Ziegler-Natta Catalysts
   - Bis(Phenoxyimine)-based Catalytical Systems
3. Conclusions and Prospect

Milestones in Coordinative Olefin Polymerization



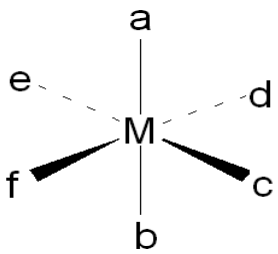
1953 - Karl Ziegler discovers titanium based coordinative olefin polymerization catalysts

1980 - Walter Kaminsky develops extremely active and stereoselective metallocene catalysts

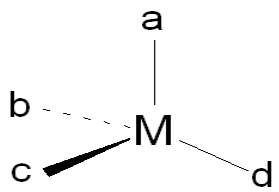
1999 - Terunori Fujita reports bis(phenoxyimine) catalysts of even higher activity

Classical, Metallocene and Post-Metallocene Systems

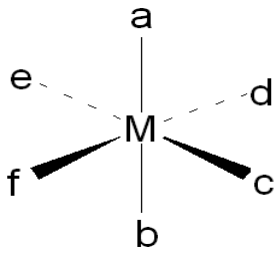
Octahedral coordination

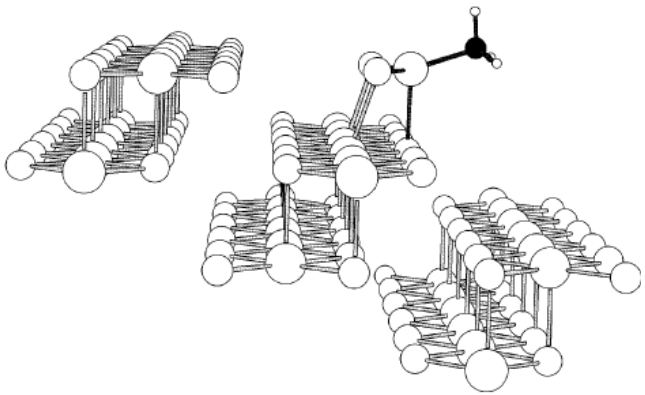


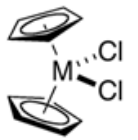
Tetrahedral coordination



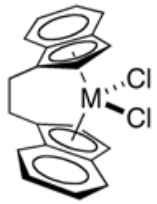
Octahedral coordination





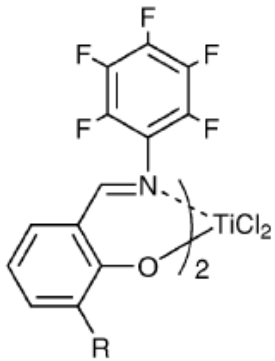


1, M = Zr, Hf



2, M = Zr, Hf

3, M = Zr, Hf



The Bailar Method

- Invented in 1957 to enumerate the isomers of octahedral complexes in an elegant way:
  J.C. Bailar, Jr. *J. Chem. Ed.* **1957**, 34, 334.

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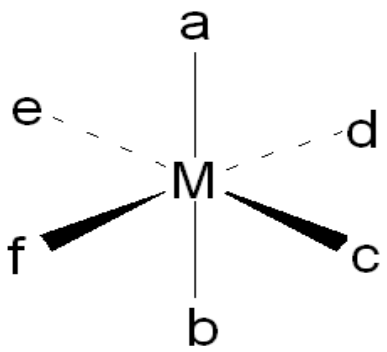
- Graphical interface was necessary...

Octahedral M[abcdef] complex



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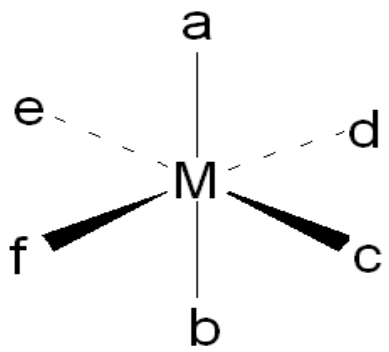
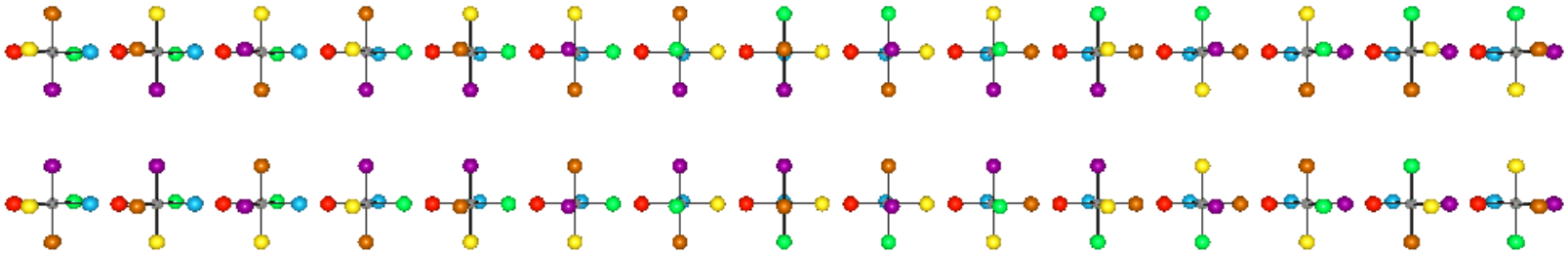
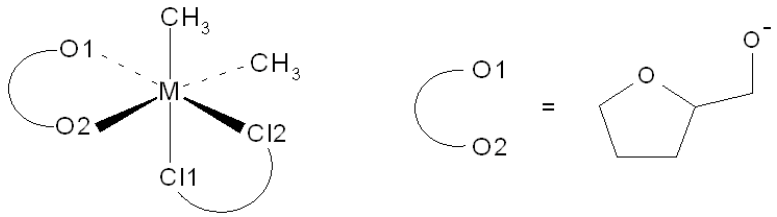




30 isomers: 15 pairs of enentiomers

Heterogeneous system, M[aa(BD)(CE)] complex



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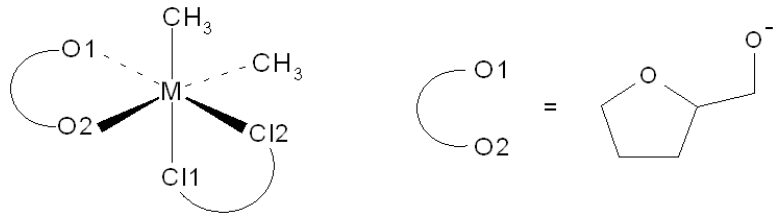
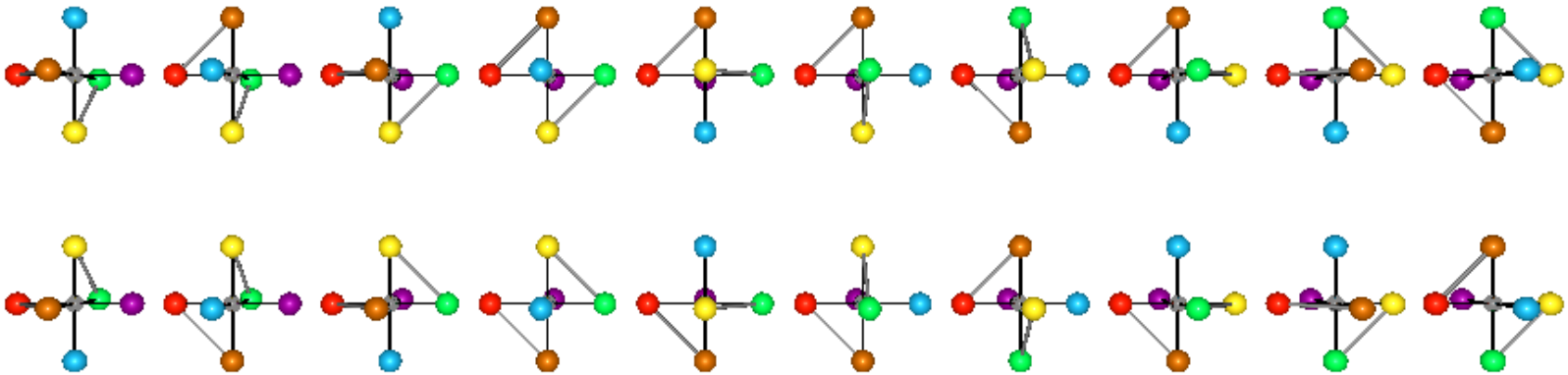




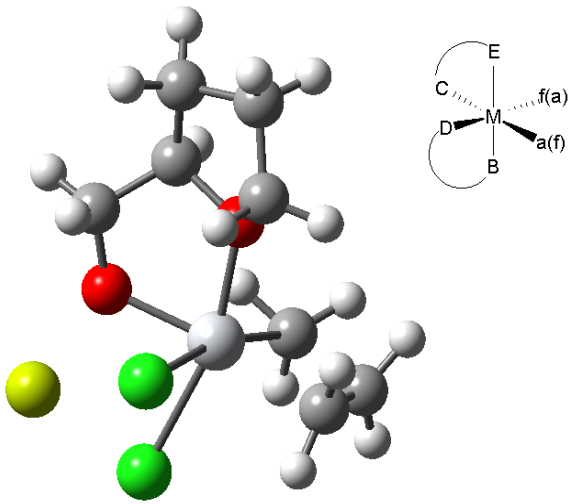
20 isomers: 10 pairs of enantiomers

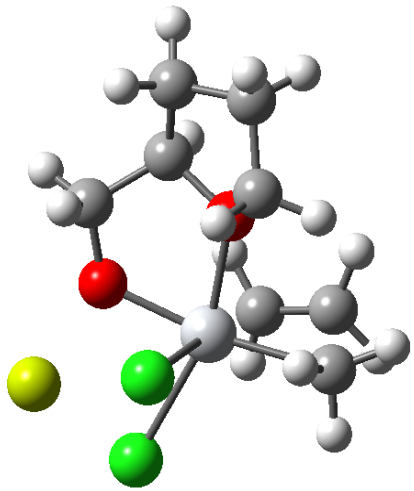
Heterogeneous system - chemistry of the system

Additional restrictions due to chemistry of the system:

- Methyl groups must be in the *cis* position with respect to each other,
- Bidentate ligand must not sterically interfere with the support surface.

There are only two pairs of diastereomers to be considered.





M2 M3

Insertion barriers calculated with DFT

	THF	THFFO (M2)	THFFO (M3)
	Initiation		
$\Delta E^{\#}_{ins}$, ethylene	6.9	15.7	11.7
$\Delta E^{\#}_{ins}$, propylene max	7.9	17.8	12.4
$\Delta E^{\#}_{ins}$, propylene min	5.8	14.4	11.3
	Propagation		
$\Delta E^{\#}_{ins}$, ethylene	5.1	13.9	9.8
$\Delta E^{\#}_{ins}$, propylene max	7.6	15.3	9.1
$\Delta E^{\#}_{ins}$, propylene min	2.0	12.6	7.8

Z. Flisak, *Macromolecules* 2008, **41**, 6920.

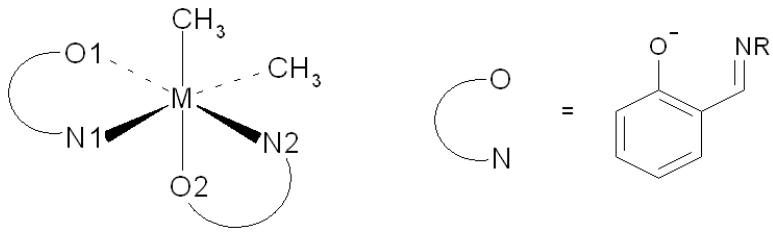
Selectivity calculated with DFT

- Regio- and stereoselectivity

	THF	THFFO (M2)	THFFO (M3)
	Initiation		
$\Delta\Delta E_{regio}$	3.6	1.8	3.8
$\Delta\Delta E_{stereo}$	0.6	0.6	0.4
	Propagation		
$\Delta\Delta E_{regio}$	2.3	2.2	3.4
$\Delta\Delta E_{stereo}$	3.2	4.3	2.3

Z. Flisak, *Macromolecules* 2008, **41**, 6920.

Bis(phenoxyimine) system, M[aa(BC)(BC)] complex



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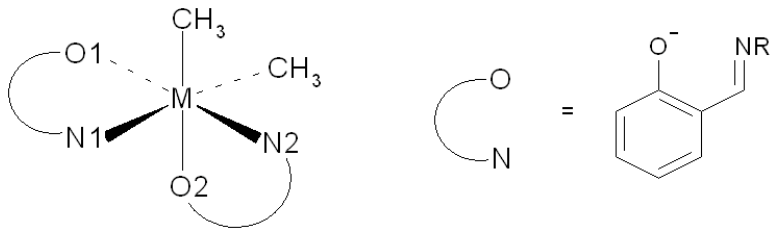

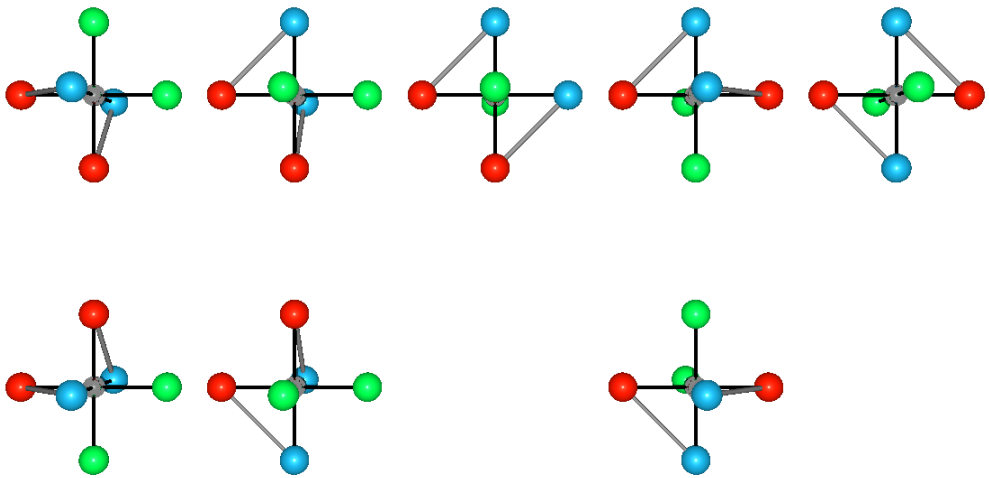

N-trans-O-cis N-cis-O-cis N-cis-O-trans

8 isomers, including 3 pairs of enantiomers

Stability of Isomers and Corresponding Transition States

- What are the relative energies of the isomers? $\rightarrow$ Talk by Patrycja Suchorska today at 13:30

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- Insertion barriers, kcal/mol

Isomer	Ti imine	V imine	Ti amine	V amine
N-trans-O-cis	21.1	23.3	23.1	-
N-cis-O-cis	20.4	22.6	20.7	26.5
	17.1	16.7	19.9	21.1
N-cis-O-trans	13.4	16.6	13.2	20.6

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- A few termination barriers wrt insertion, kcal/mol

Isomer	Ti imine	V imine
N-trans-O-cis	15.8	19.0
N-cis-O-trans	8.6	10.2

Conclusions and Prospect

- The existence of isomeric octahedral complexes must be considered in the theoretical study of:
  - Classical Ziegler-Natta catalysts supported on $MgCl_2$,
  - Post-metallocene phenoxyimine catalysts,
  - Other organometallic systems of similar geometry.

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  - Classical Ziegler-Natta catalysts supported on $MgCl_2$,
  - Post-metallocene phenoxyimine catalysts,
  - Other organometallic systems of similar geometry.
- To get an insight into the action of the Fujita catalyst, this study will be supplemented by:
  - NMR spectra,
  - Laboratory polymerization tests,
  - Analyses of the resulting polymer.

This is not the equipment we utilize...

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Thank you for your kind attention