FY2017 3rd CREST Workshop

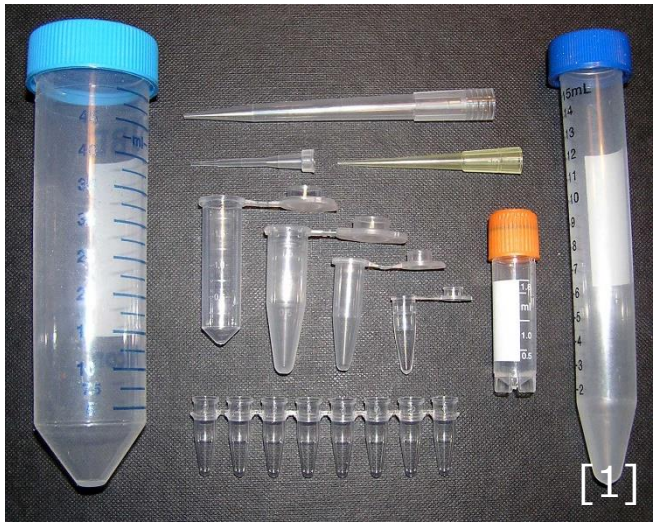
Development of Force Field Parameters for Molecular Dynamics Simulation of α-Olefin Polymerization Reaction by Zirconocene Catalyst

Dr. Yuichi Tanaka

2017/10/26

Introduction: Polyolefins

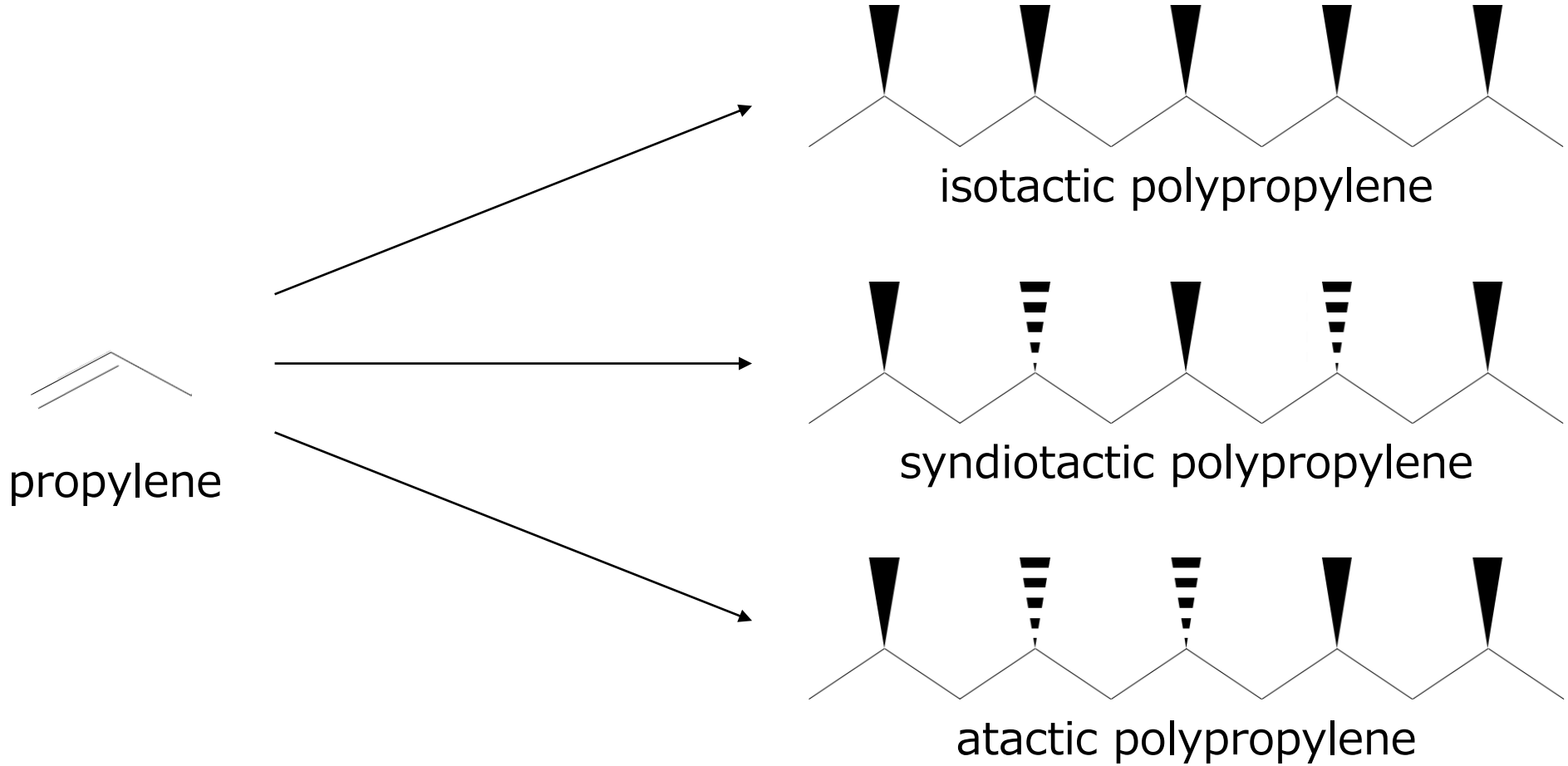
- Polyethylene
- **Polypropylene**
- Polystyrene
- Polyvinyl chloride



Global market for polypropylene
~ 5.5×10^7 t (in 2013)[1]

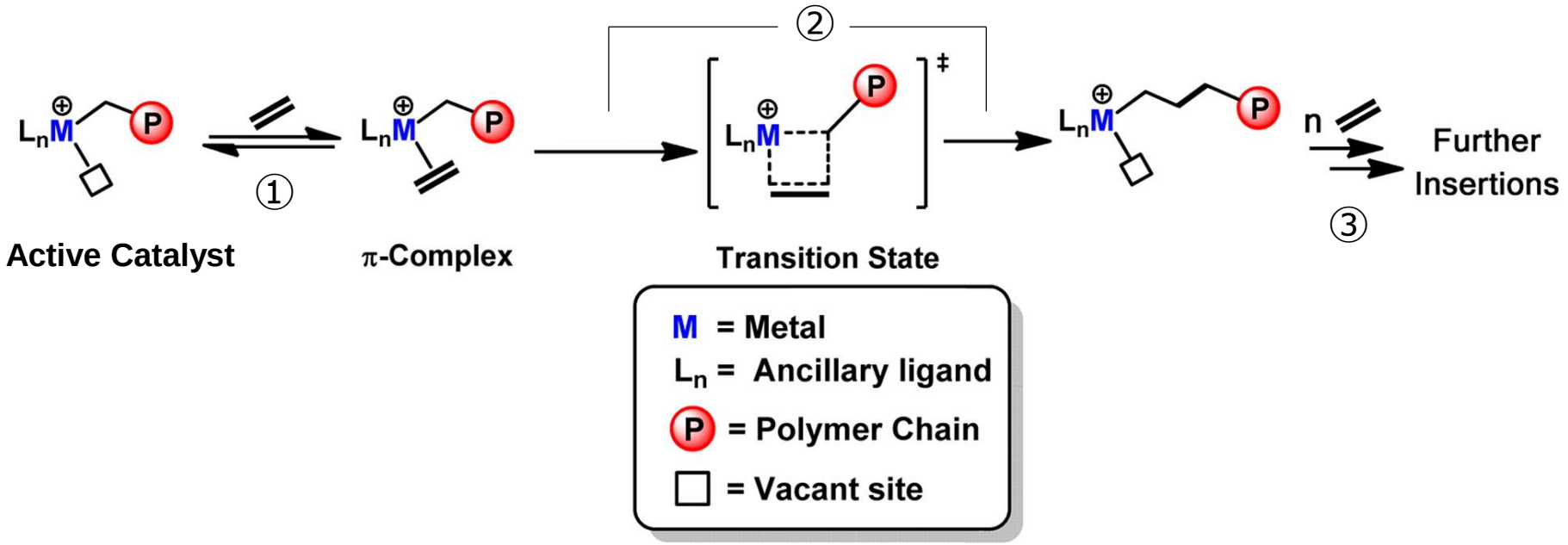
[1] https://en.wikipedia.org/wiki/Polypropylene

Introduction: Microstructures of Polypropylene



Tacticity affects the properties of polymer.
→ The control of the tacticity is important.

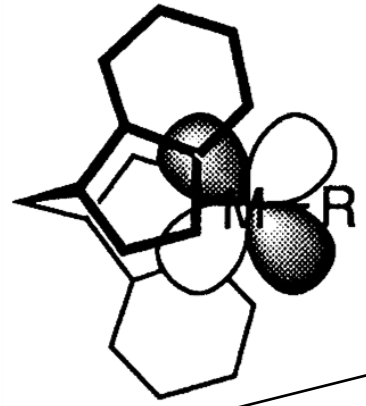
Introduction:
α-Olefin Polymerization Reaction by Catalyst[2,3]



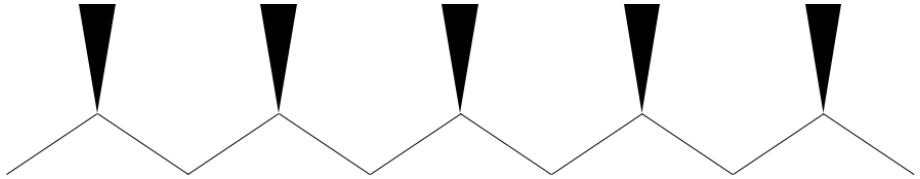
① coordination of the monomer (olefin) to the catalyst
② insertion of the olefin into the metal–alkyl bond
③ repetition of step ②

[2] A. Motta, I. L. Fragalà, T. J. Marks *J. Chem. Theory Comput.* **2013**, *9*, 3491.
[3] W. Kaminsky *J. Chem. Soc., Dalton Trans.* **1998**, 1413.

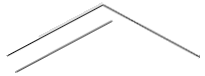
Introduction:
α-Olefin Polymerization Reaction by Catalyst[4]



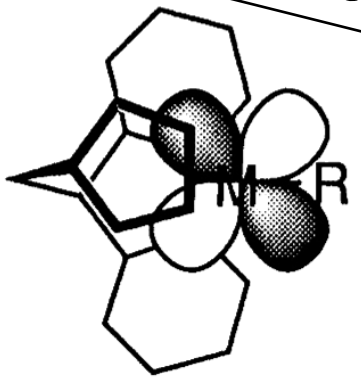
C_2 symmetric catalyst

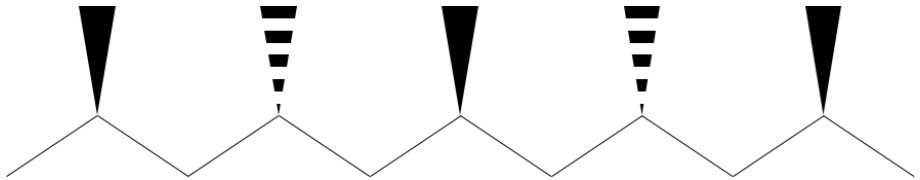


isotactic polypropylene



C_s symmetric catalyst

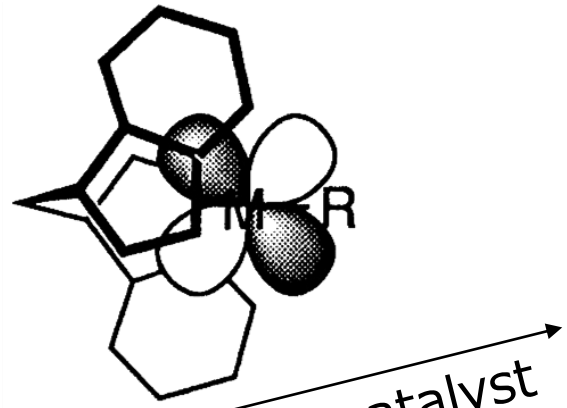




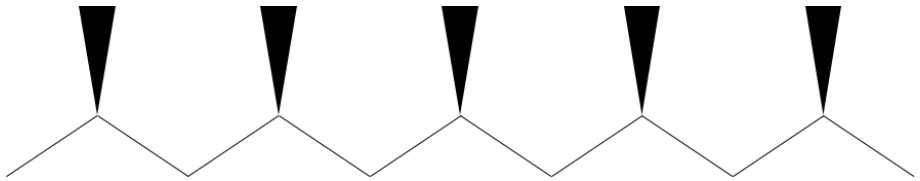
syndiotactic polypropylene

[4] T. Yoshida, N. Koga, K. Morokuma *Organometallics* **1996**, *15*, 766.

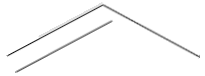
Introduction:
α-Olefin Polymerization Reaction by Catalyst[4]

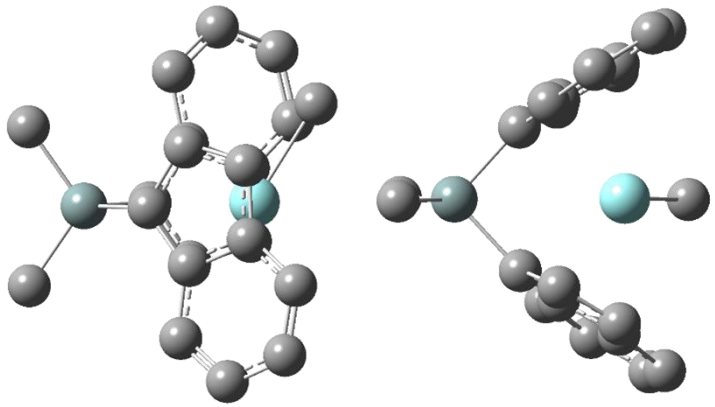


C_2 symmetric catalyst



isotactic polypropylene



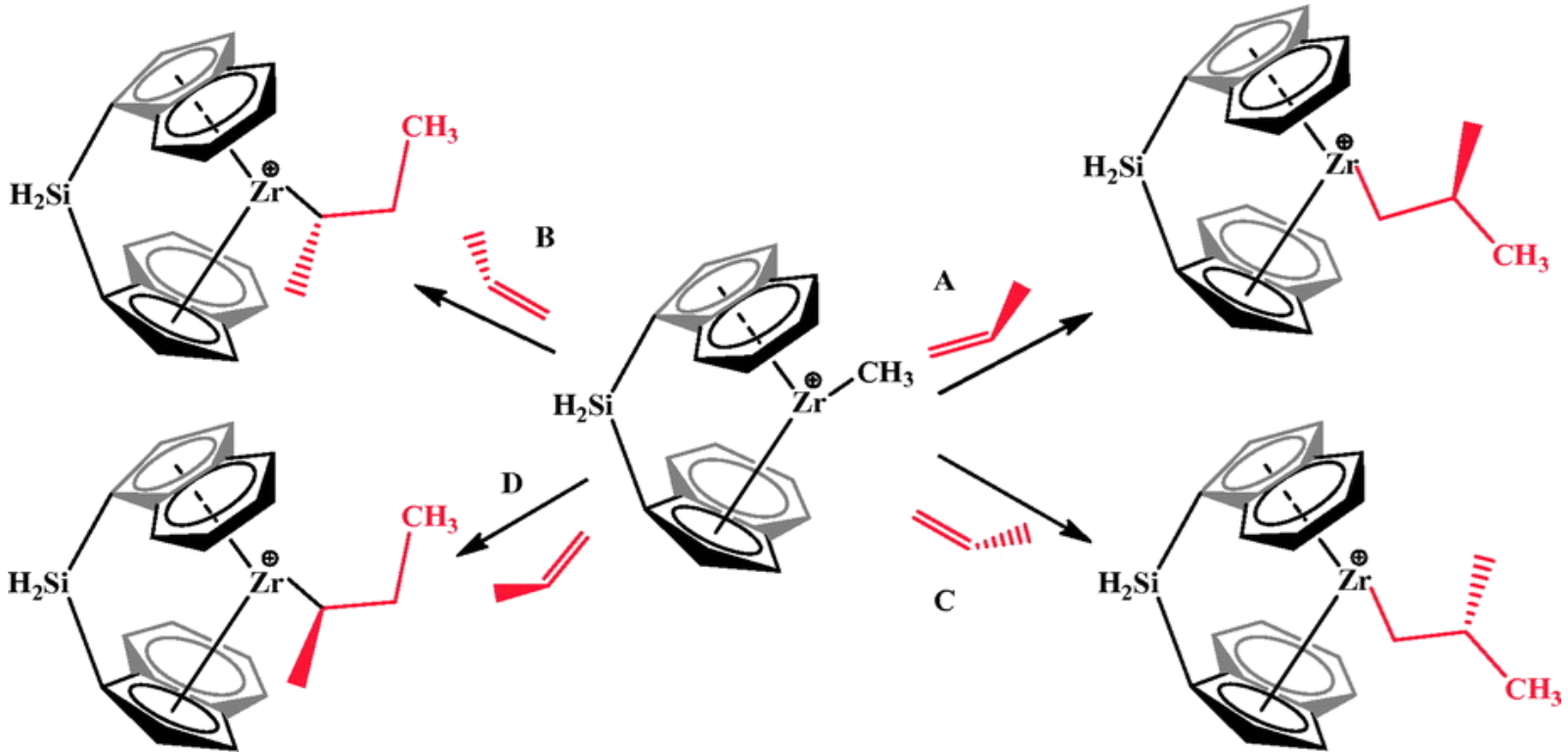


top side

C_2 symmetric ansa-zirconocene
($[Si(CH_3)_2(Ind)_2ZrCH_3]^+$) catalyst

[4] T. Yoshida, N. Koga, K. Morokuma *Organometallics* **1996**, *15*, 766.

Introduction: Quantum Chemical Calculation Study[5]

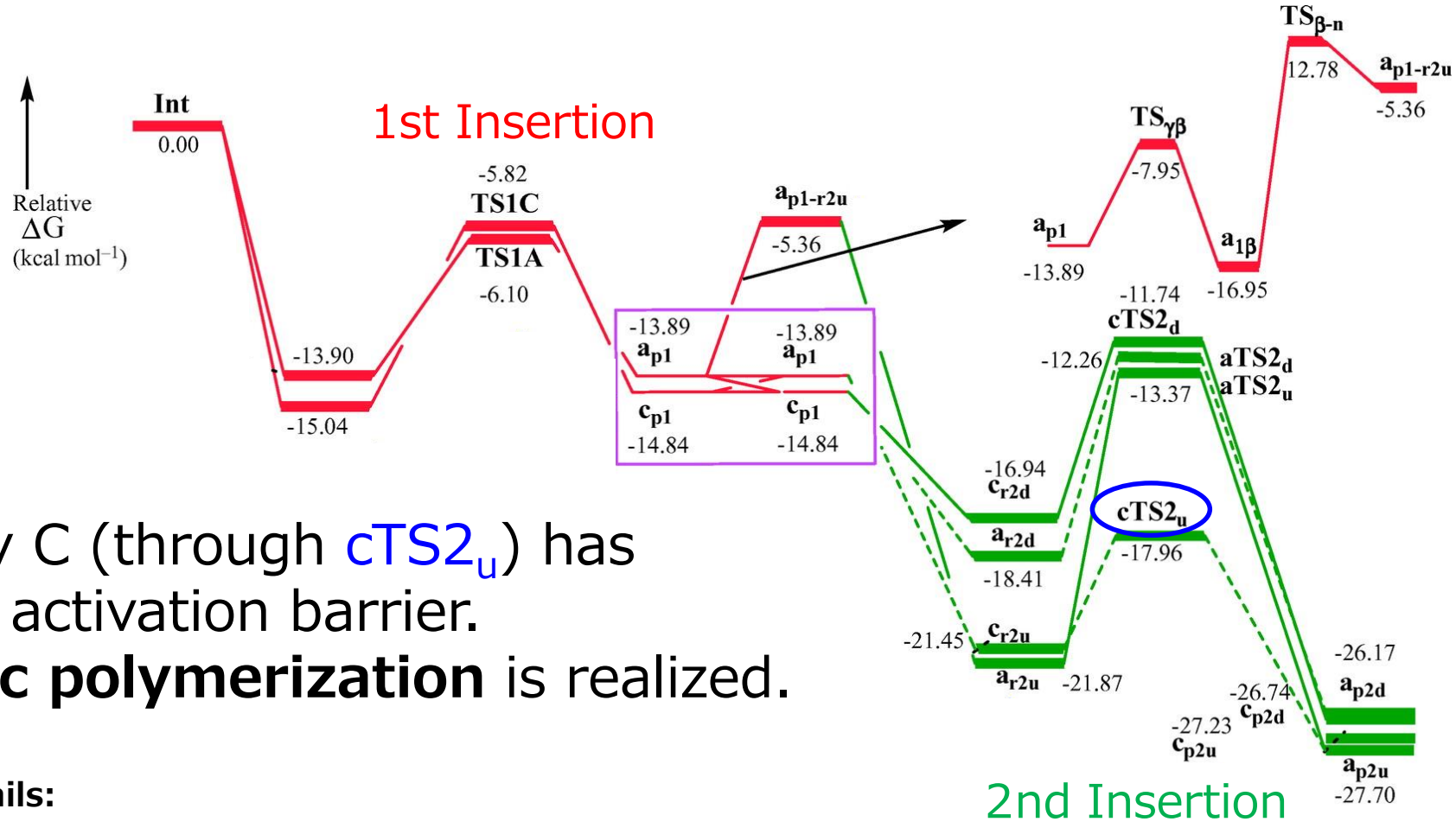


Four possible modes in the first insertion of propylene

The products in the A and C approaches are stereochemically the same, but the conformations are different.

[5] K. S. Sandhya, N. Koga, M. Nagaoka *Bull. Chem. Soc. Jpn.* **2016**, *89*, 1093.

Introduction: Quantum Chemical Calculation Study[5]



The pathway C (through $cTS2_u$) has the smallest activation barrier.

→ **Isotactic polymerization** is realized.

Computational Details:

Optimization:

M06/LANL2DZ + f polarization functions (for Zr), 6-31++G(d,p) (for other atoms)

Single Point Calculation:

M06/def2-TZVPP with SMD method (toluene)

[5] K. S. Sandhya, N. Koga, M. Nagaoka *Bull. Chem. Soc. Jpn.* **2016**, *89*, 1093.

Introduction: Remaining Problems

- The dynamic behavior of this catalyst in solution and the formation mechanism of the coordination space for propylene monomer are unknown.

- The reaction system is very fluxional and has many possibilities in conformations, coordination modes, and so on.

- Solvent effects were included implicitly and it is assumed that the entropic effect by solvent molecules is also important for studying stereochemistry of polymerization reaction.

→ To take care of these problems using the QM method is almost impossible.

MD simulation is necessary in order to solve these problems.

Introduction: Remaining Problems

MD simulation is necessary in order to solve these problems.

However, there are not the force field parameters
for this zirconocene catalyst.

We need to develop the force field parameters.

Needed Force Field Parameters

- Intramolecular force field parameters of the zirconocene cation
- Intermolecular force field parameters
  for the cation–anion interaction
- Intermolecular force field parameters
  for the cation–propylene interaction

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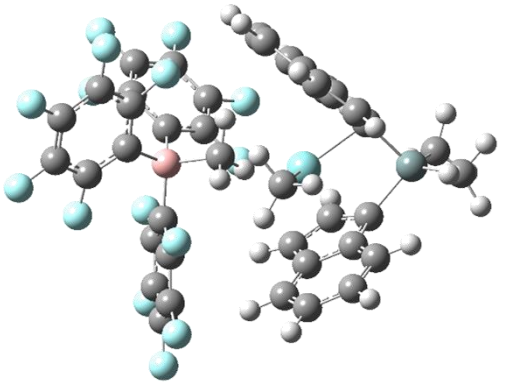
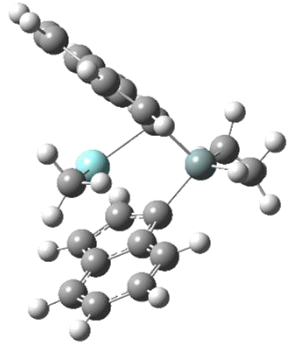
Making Intramolecular Force Field Parameters

Partial optimizations of zirconocene cation with counter anion



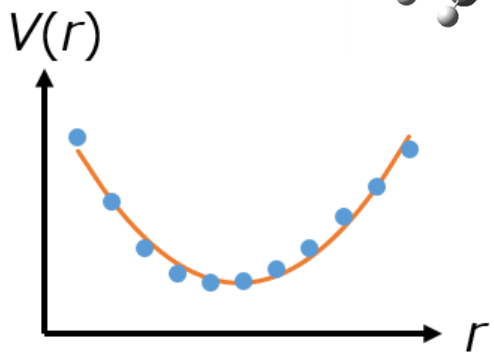
Single-point quantum chemical calculations of
the partial-optimized zirconocene cation without counter anion



Fitting the intramolecular force field parameters

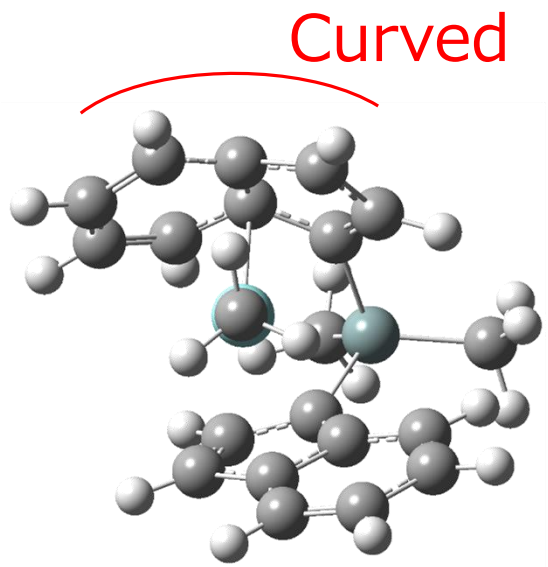
Bond: $V(r) = k_r(r - r_0)^2 + V_r$

Angle: $V(\theta) = k_\theta(\theta - \theta_0)^2 + V_\theta$

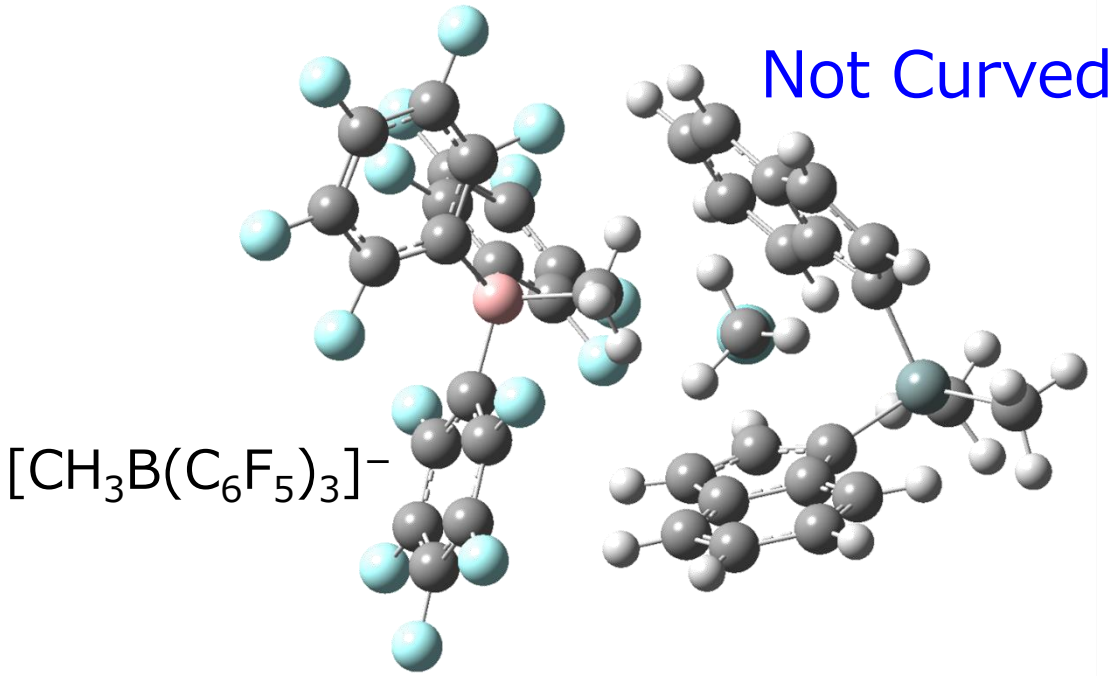


Making Intramolecular Force Field Parameters

Without Counter Anion



With Counter Anion



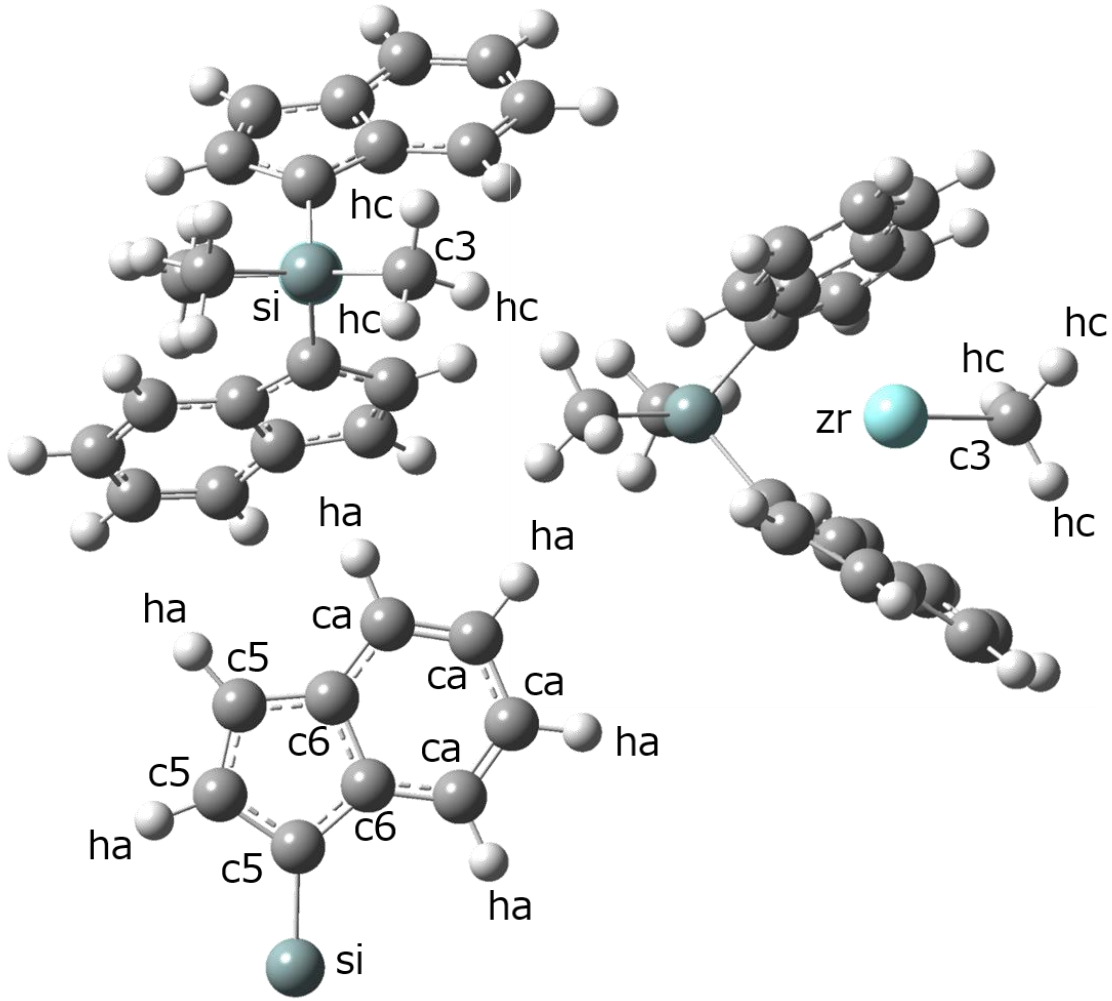
Method: M06/LANL2DZ + f (on Zr), 6-31G(d,p) (on all other atoms)

Partial optimizations of cation with counter anion were performed.

Making Intramolecular Force Field Parameters

	k_r [kcal mol^{-1} Å^{-2}]	r_0 [Å]
zr-c3	175.89	2.25
zr-c5	74.43	2.56
zr-c6	72.89	2.59
si-c3	255.20	1.91
si-c5	266.80	1.93
	k_θ [kcal mol^{-1} rad^{-2}]	θ_0 [°]
zr-c3-hc	19.45	114.91
c5-c6-ca	131.56	132.75
c3-si-c3	56.49	112.99
si-c3-hc	31.09	111.83

	k_θ [kcal mol^{-1} rad^{-2}]	θ_0 [°]
c5-c5-ha	48.5	126.00
c6-c5-ha	48.5	126.00



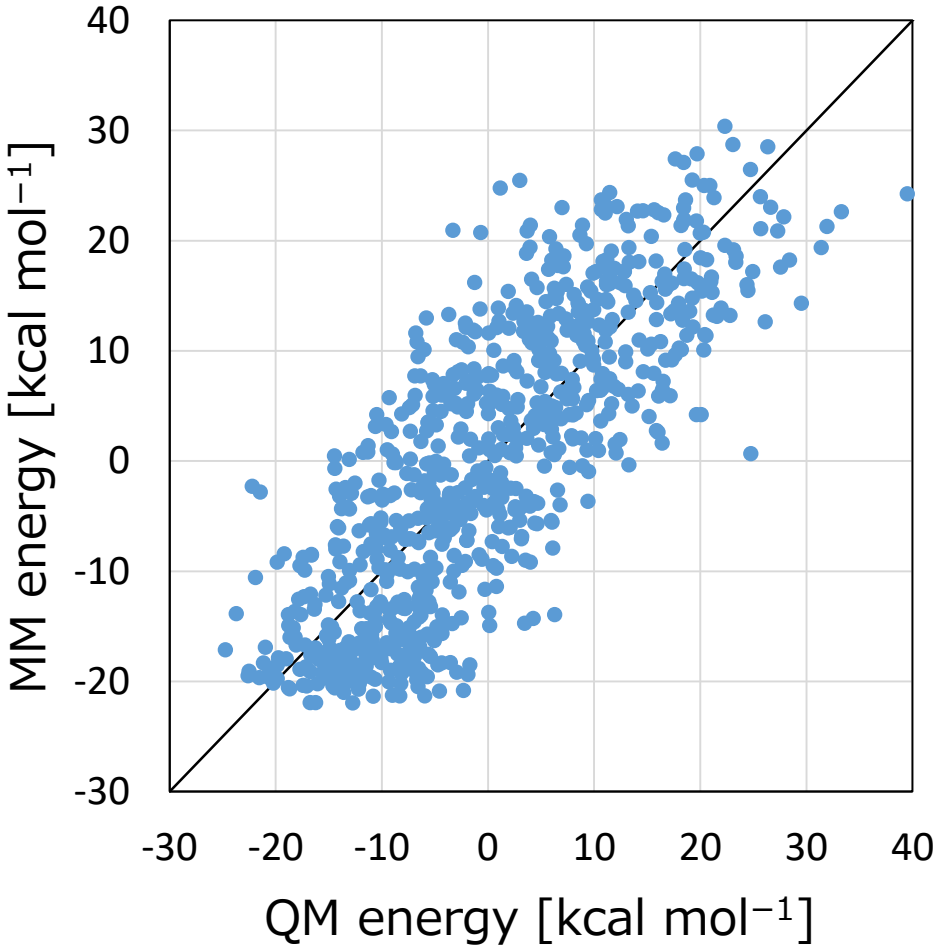
Modified from 120.01° (GAFF)

Making Intramolecular Force Field Parameters

Correlation Coefficient

- 8 MD calculations of the zirconocene cation in a vacuum for 10 ns by using the developed intramolecular force field parameters at different temperatures (100, 200, ⋯, 800K) were performed.
- Structures were sampled every 100 ps from each trajectory; 800 samples were obtained in total.
- The QM and MM energy calculations at each structure were performed and the calculated energies were compared.

Making Intramolecular Force Field Parameters



Correlation coefficient = 0.805

I modified other parameters and calculated the correlation coefficient,
however the correlation did not improve.
→ I use this parameter set.

Needed Force Field Parameters

- Intramolecular force field parameters of the zirconocene cation
- Intermolecular force field parameters
  for the cation–anion interaction
- Intermolecular force field parameters
  for the cation–propylene interaction

Making Intermolecular Parameters for the Cation–Anion Interaction

MD calculation

- MD calculation of the ion pair in a vacuum for 1 ns at 800 K by using the developed intramolecular force field for the zirconocene cation and intramolecular force field for the borate anion [6] was performed.

- Harmonic constraint on the angle Si-Zr-B was imposed. (Constraint angle = 139.30°, Force constant = 15 kcal mol^{-1})

Sampling the configurations

- The configurations every 1 ps from the trajectory were sampled; 1000 configurations were obtained.

[6] C. N. Rowley, T. K. Woo *Organometallics* **2011**, *30*, 2071.

Making Intermolecular Parameters for the Cation–Anion Interaction

K-means clustering

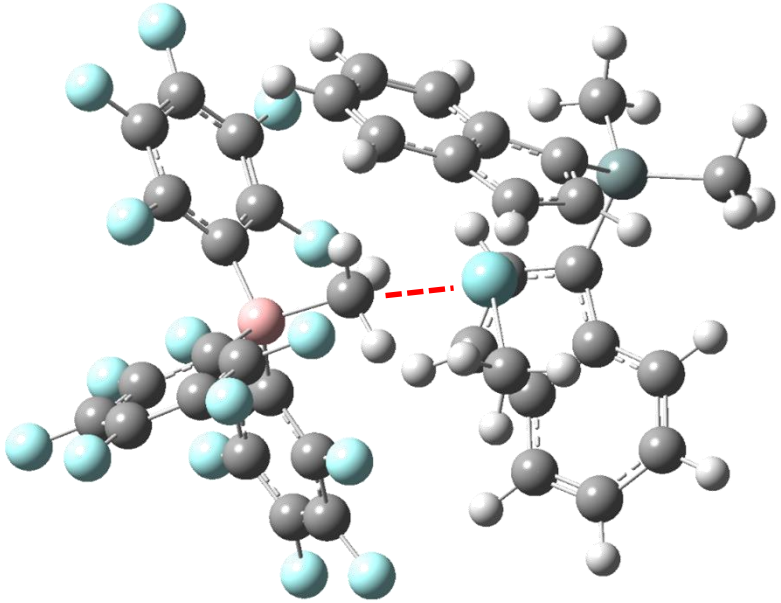
- 1000 configurations were classified into 40 clusters by K-means clustering.

QM optimization ← I’m doing now.

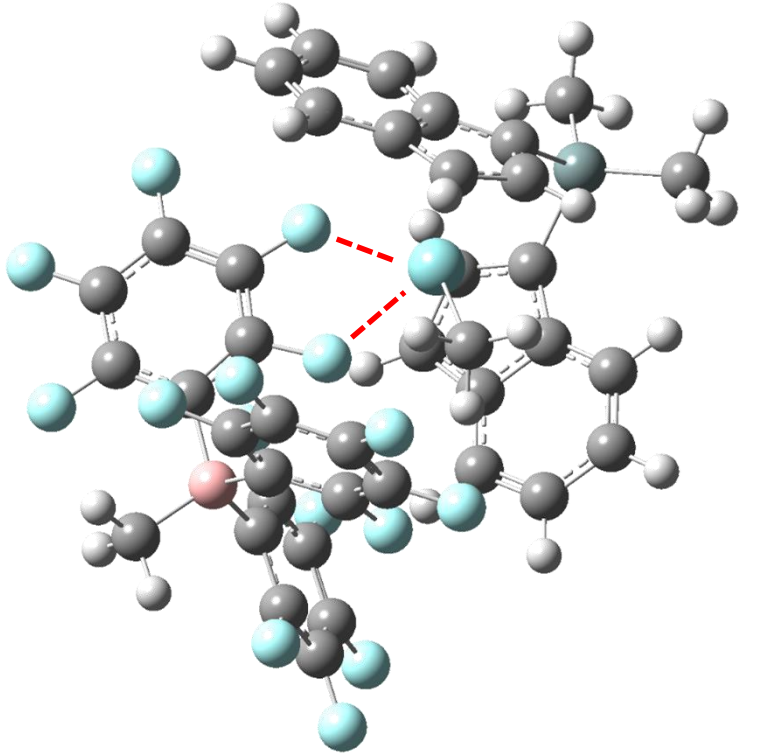
- QM optimizations starting from the obtained 40 configurations are being performed;
  → Reference configurations and the QM energies will be obtained.

Making Intermolecular Parameters for the Cation–Anion Interaction

QM optimized structures



Interaction between
Zr atom and CH_3 group



Interaction between
Zr atom and F atoms

Making Intermolecular Parameters for the Cation–Anion Interaction

MM optimization

- MM optimizations starting from reference configurations will be performed.
  → The MM energies will be obtained.

Fitting the Lennard-Jones parameters

- The Lennard-Jones parameters for Zr-(H in CH_3 of the anion) and Zr-(F of the anion) will be fitted to reproduce the QM energy.

Needed Force Field Parameters

- Intramolecular force field parameters of the zirconocene cation
- Intermolecular force field parameters for the cation–anion interaction
- Intermolecular force field parameters for the cation–propylene interaction

Summary

- The developed intramolecular force field parameters of the C_2 symmetric zirconocene cation have an accuracy.
- The development of the intermolecular force field parameters for the cation–anion and cation–propylene interactions is now in progress.