

FY2018 2<sup>nd</sup> CREST Workshop

**Theoretical analysis of the active site opening mechanism  
in olefin polymerization reaction by *ansa*-zirconocene catalyst**

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# Introduction: Polyolefins

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

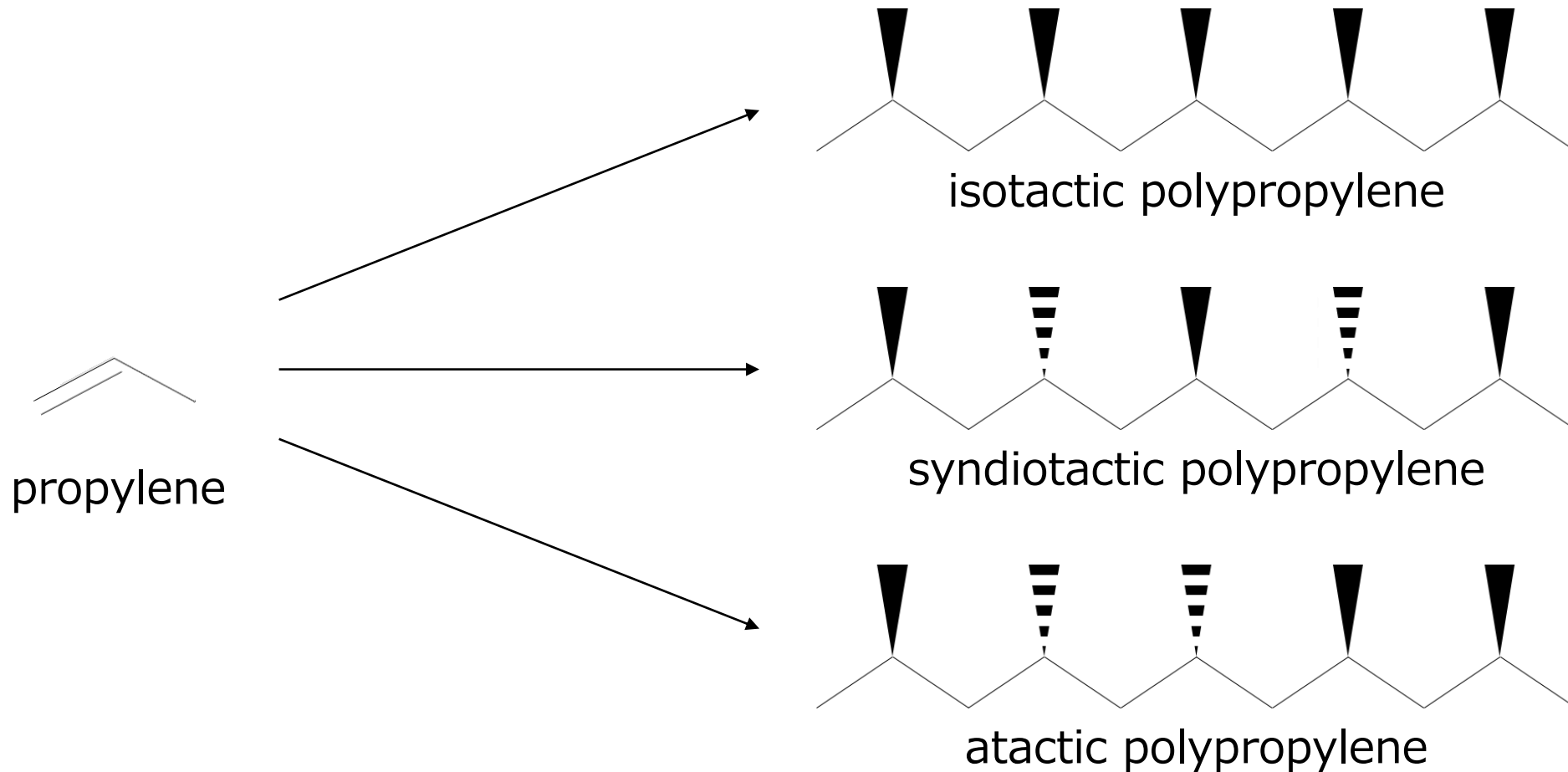


Global market for polypropylene  
 $\sim 5.5 \times 10^7$  t (in 2013)<sup>[1]</sup>



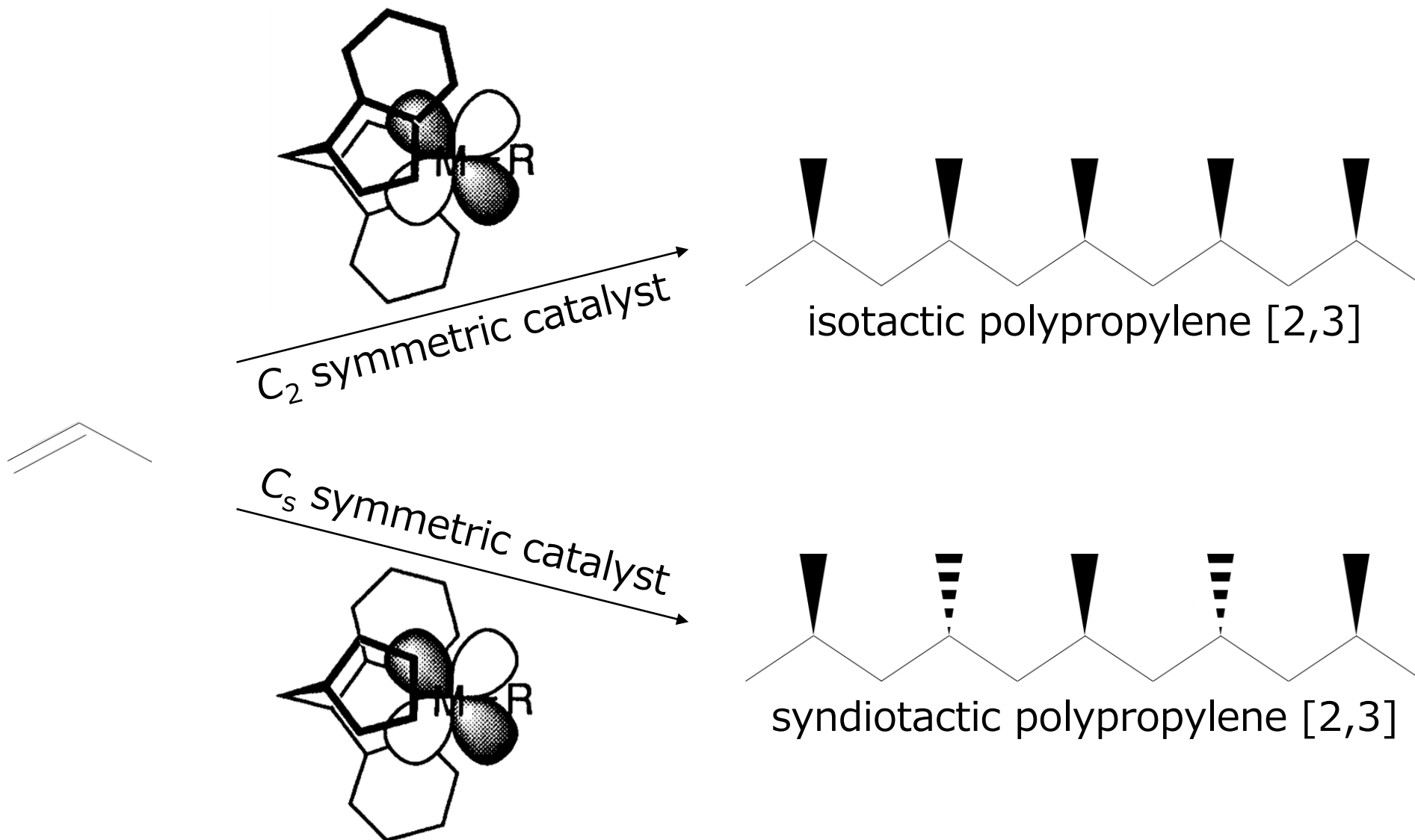
[1] <https://en.wikipedia.org/wiki/Polypropylene>

# Introduction: Stereochemistry of Polypropylene



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

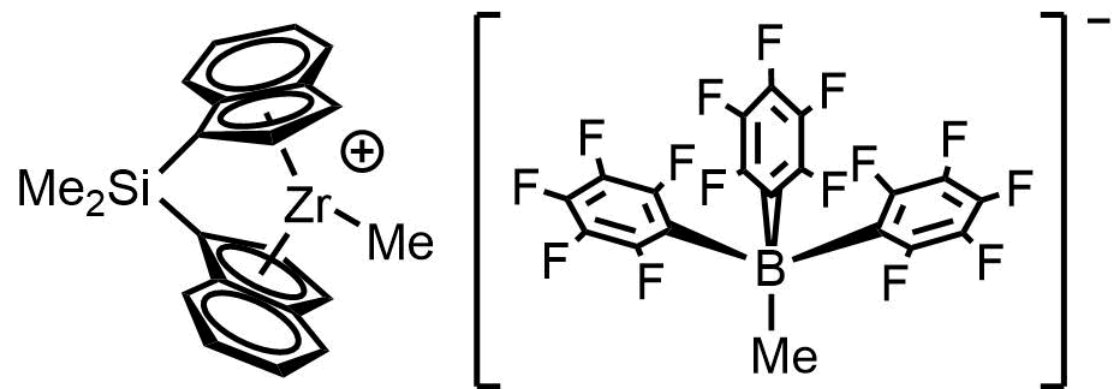
# Introduction: Stereochemistry of Polypropylene



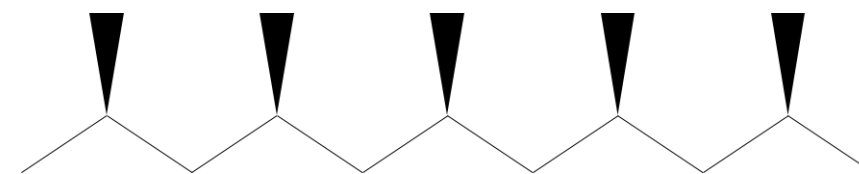
[2] Yoshida, T.; Koga, N.; Morokuma, K. *Organometallics* **1996**, *15*, 766.

[3] Resconi, L.; Cavallo, L.; Fait, A.; Piemontesi, F. *Chem. Rev.* **2000**, *100*, 1345.

# Introduction: Stereochemistry of Polypropylene



produces

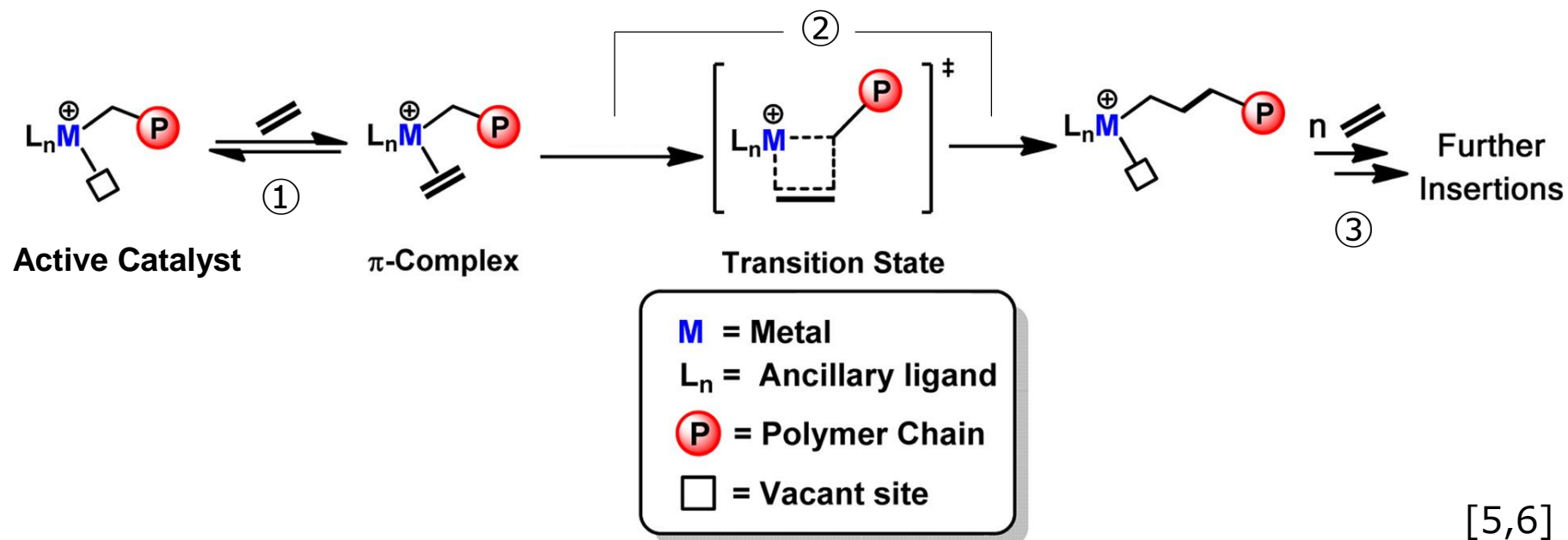


isotactic polypropylene.

$C_2$  symmetric *ansa*-zirconocene catalyst,  
 $[\text{SiMe}_2(\text{Ind})_2\text{ZrMe}]^+[\text{MeB}(\text{C}_6\text{F}_5)_3]^-$  (**1**) [4]

# Introduction:

## $\alpha$ -Olefin Polymerization Reaction by Catalyst



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

[5] Motta, A.; Fragalà, I. L.; Marks, T. J. *J. Chem. Theory Comput.* **2013**, *9*, 3491.

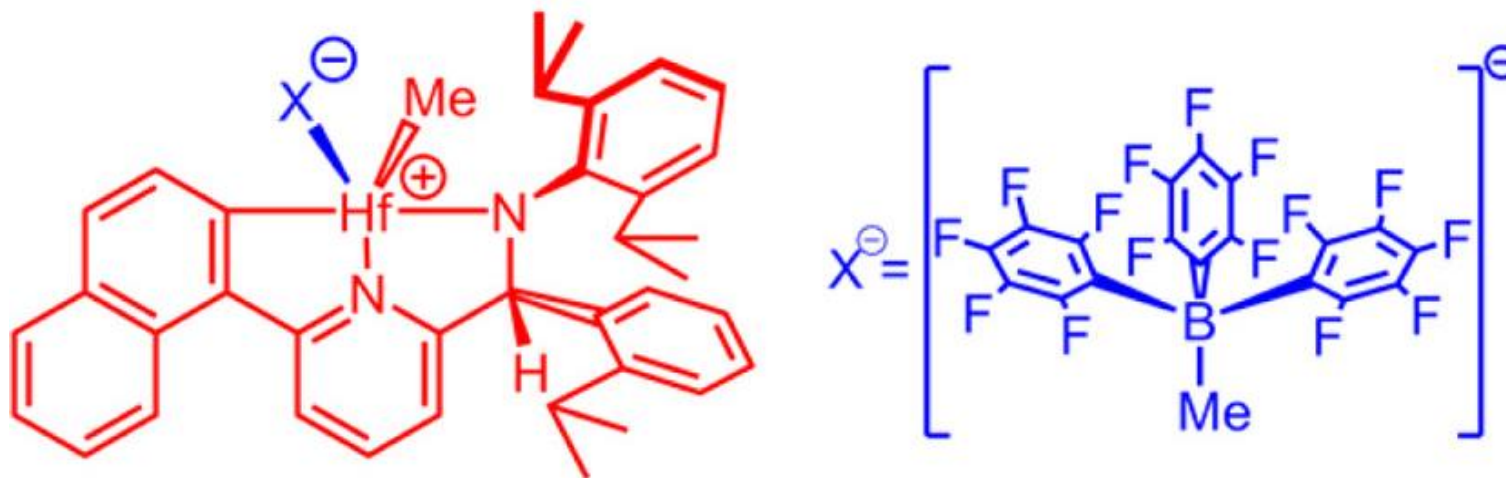
[6] Kaminsky, W. *J. Chem. Soc., Dalton Trans.* **1998**, 1413.

# Introduction:

## $\alpha$ -Olefin Polymerization Reaction by Catalyst

### Initiation Process of Polymerization Reaction

In (pyridylamide)Hf(IV) catalytic system [7–9], the active site opening (**ASO**) was observed when the polymerization reaction starts.



→ How about the catalyst (**1**)?

[7] Matsumoto, K.; Sandhya, K. S.; Takayanagi, M.; Koga, N.; Nagaoka, M. *Organometallics* **2016**, *35*, 4099.

[8] Matsumoto, K.; Takayanagi, M.; Sankaran, S. K.; Koga, N.; Nagaoka, M. *Organometallics* **2018**, *37*, 343.

[9] Matsumoto, K.; Takayanagi, M.; Suzuki, Y.; Koga, N.; Nagaoka, M. *J. Comput. Chem.* **2018**, accepted.

# Purpose

**I investigated the microscopic behavior of the catalyst (1) using the replica-exchange MD (REMD) and MD simulations.**

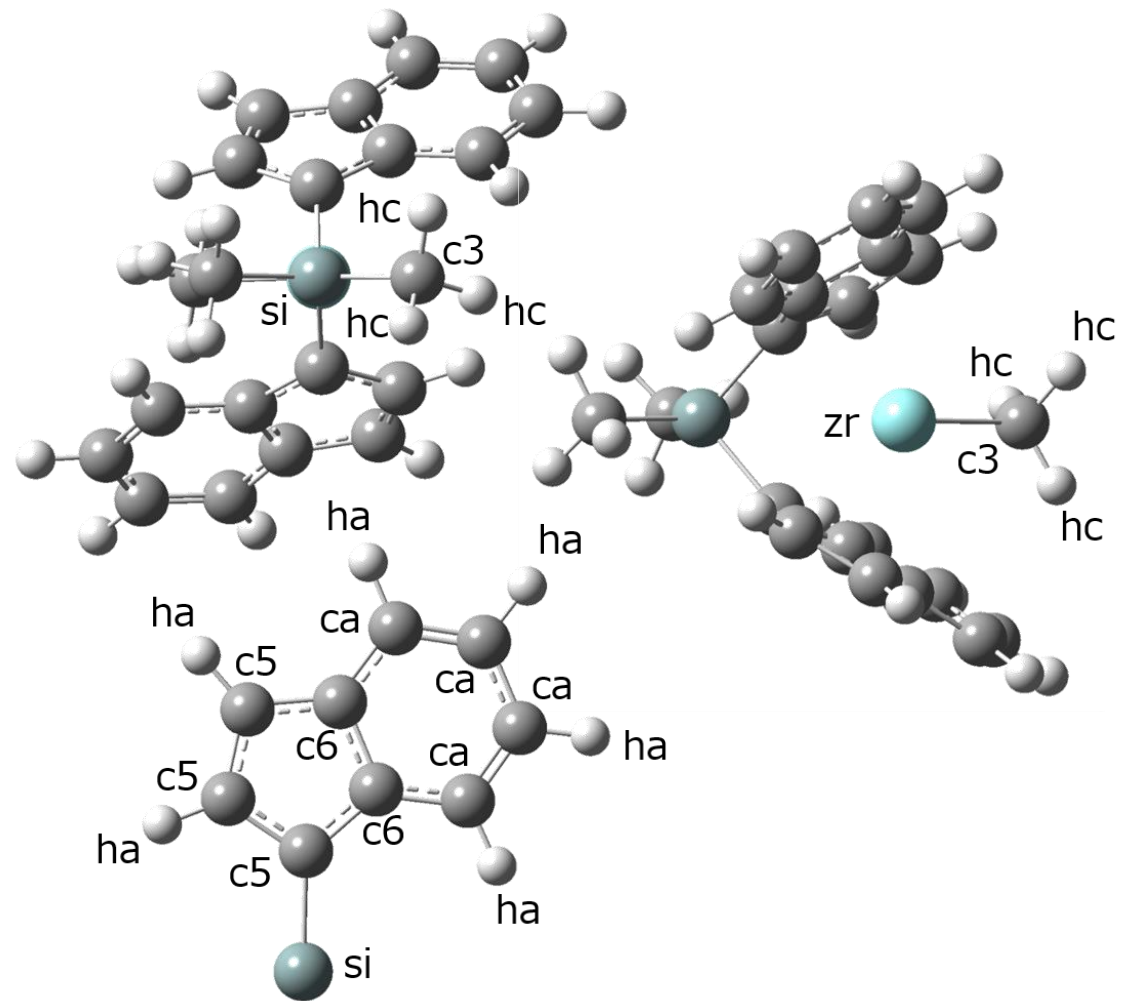


# Needed Force Field Parameters

- Intramolecular force field parameters of the *ansa*-zirconocene cation
- Intermolecular force field parameters (Lennard-Jones (LJ) parameters) for the cation–anion interaction
- Intermolecular force field parameters (LJ parameters) for the cation–propylene interaction

# Intramolecular Force Field Parameters

	$k_r$ [kcal mol <sup>-1</sup> Å <sup>-2</sup> ]	$r_0$ [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
	$k_\theta$ [kcal mol <sup>-1</sup> rad <sup>-2</sup> ]	$\theta_0$ [°]
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
	$k_\theta$ [kcal mol <sup>-1</sup> rad <sup>-2</sup> ]	$\theta_0$ [°]
c5-c5-ha	48.5	126.00
c6-c5-ha	48.5	126.00



Modified from 120.01° (GAFF)

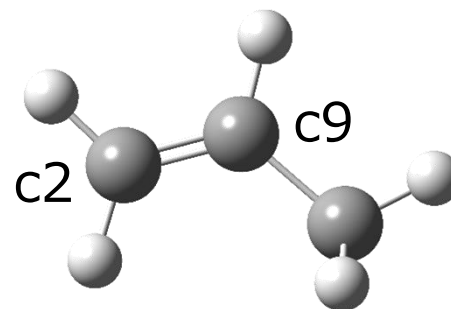
# Intermolecular Force Field Parameters

## LJ Parameters for the Cation–Anion Interaction

	$\epsilon$ [kcal mol <sup>-1</sup> ]	$r^e$ [Å]
Zr–H(CH <sub>3</sub> )	0.300	2.600
Zr–F	0.500	2.980

## LJ Parameters for the Cation–Propylene Interaction

	$\epsilon$ [kcal mol <sup>-1</sup> ]	$r^e$ [Å]
Zr–C(c2)	1.842	2.304
Zr–C(c9)	2.276	2.848



# Computational Details

## System

(1)with propylene

1 ion pair

63 propylene monomers

135 solvent pentanes

(2)without propylene

1 ion pair

135 solvent pentanes

# Computational Details

## REMD Simulation

- 36 replicas with temperatures ranging from 300 to 800 K
- Replica exchange: every 1 ps
- Each REMD simulation was run for 30000 attempts (in total, 30 ns of MD trajectory).
- The trajectory at 300 K was analyzed.

## MD Simulation

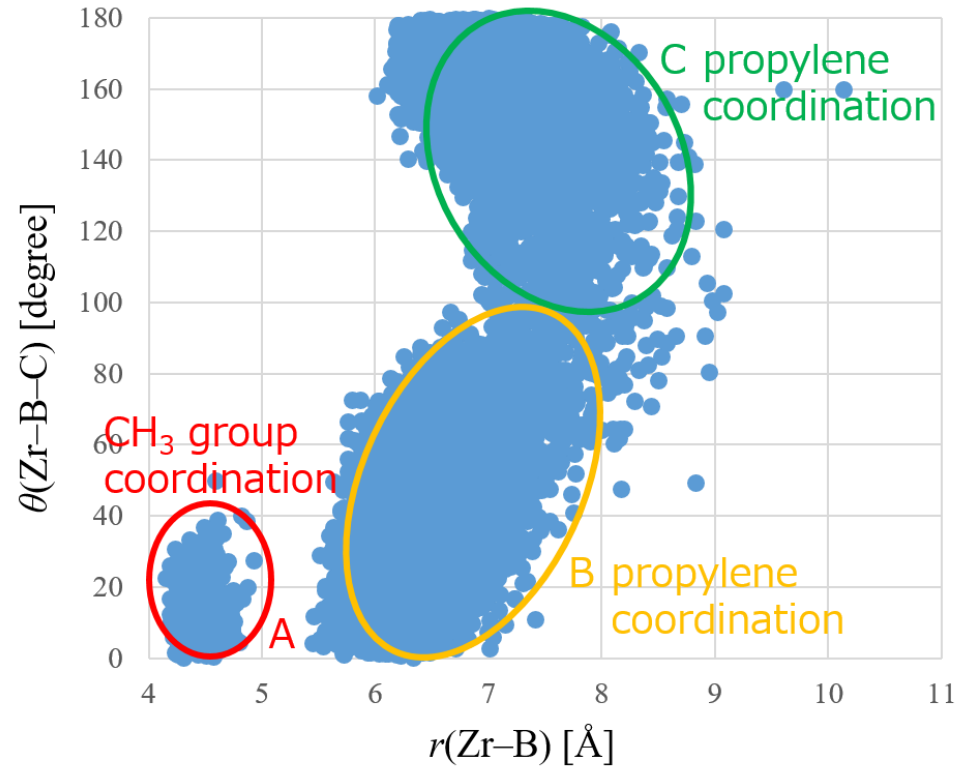
Equilibration MD  
*NPT*, 300 K, 1 ns



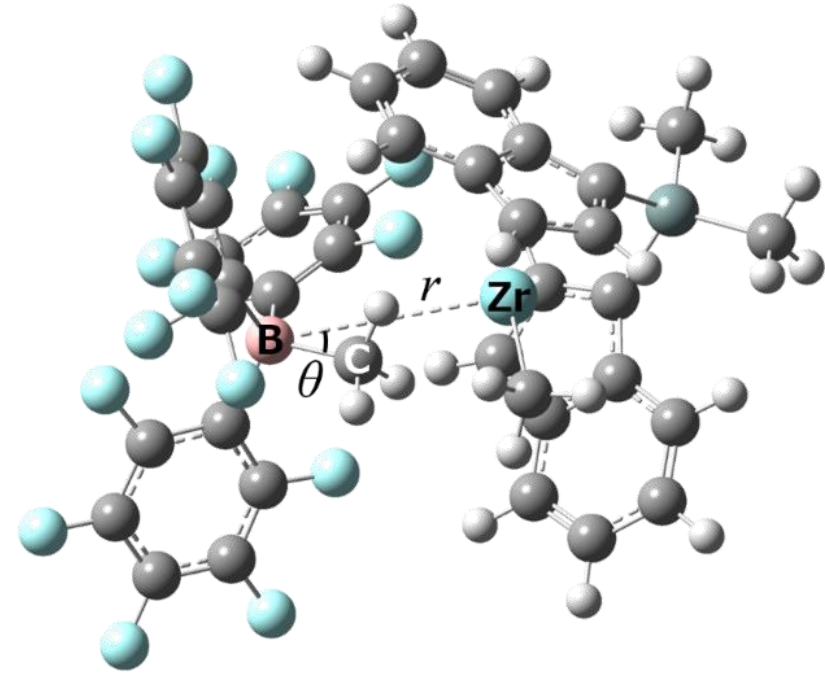
Production MD  
*NPT*, 300 K, 1.4  $\mu$ s

# Results and Discussion

## ① REMD Simulation



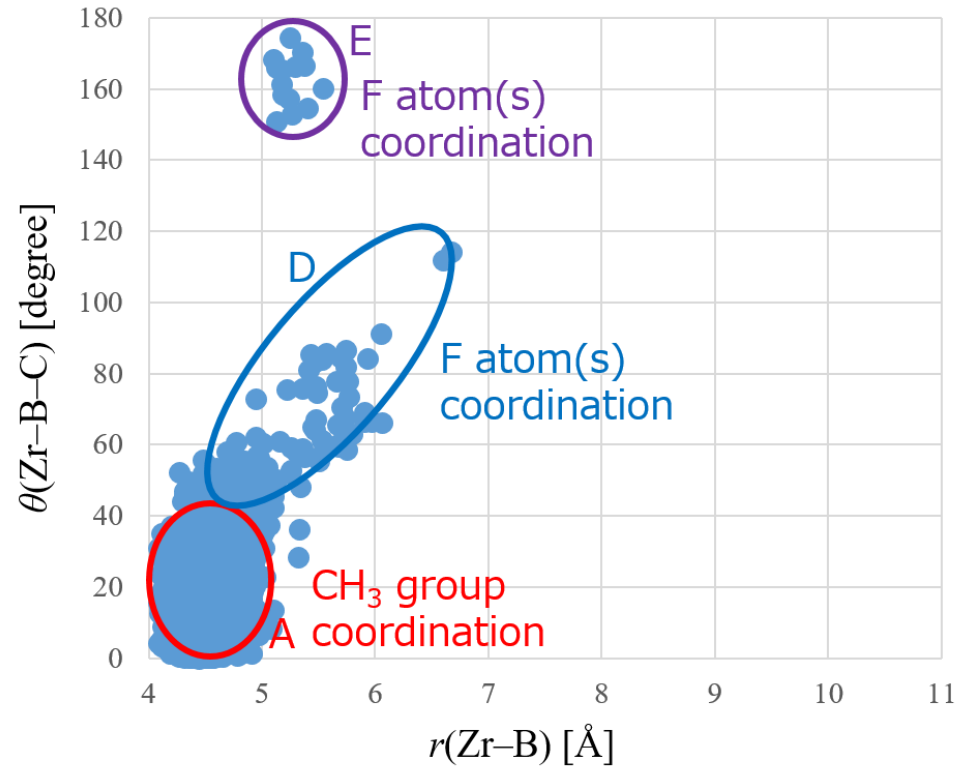
with propylene



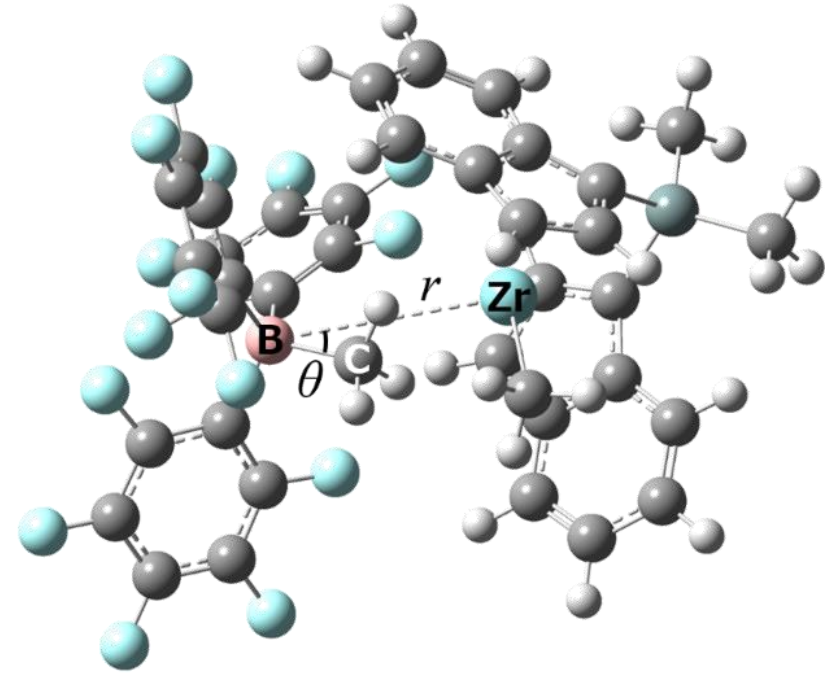
- In the system with propylene, the dissociated structure of the ion pair (regions **B** and **C**) was observed.
- Transition from region **A** to **B** or **C** indicates that the ASO occurs.

# Results and Discussion

## ① REMD Simulation



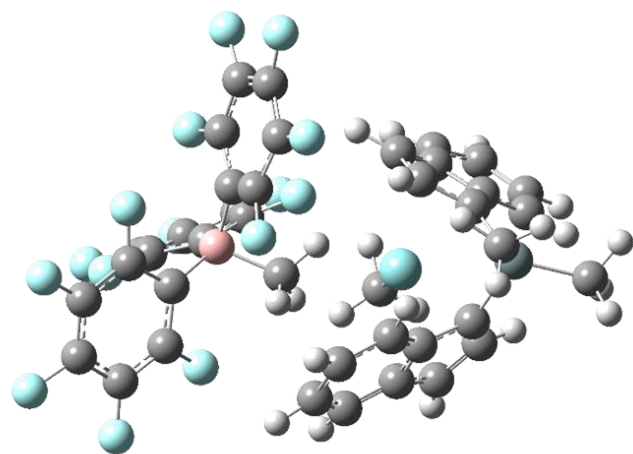
without propylene



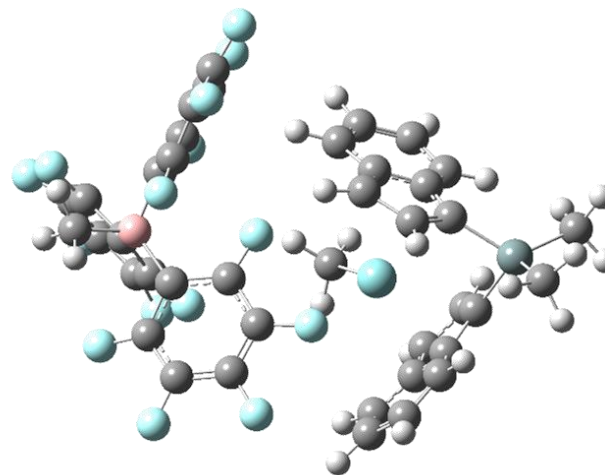
- On the other hand, in the system without propylene, the dissociated structure was not observed.

# Results and Discussion

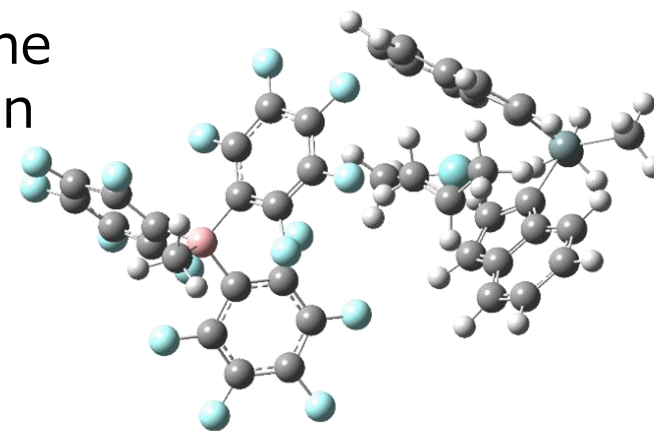
## ② MD Simulation



CH<sub>3</sub> group coordination



F atom(s) coordination



propylene coordination

propylene  
insertion

**ASO**

- The ASO and propylene insertion occurs at the same time.  
→ The associative ASO (**AASO**) occurs.  
(It was observed in (pyridylamide)Hf(IV) catalytic system [7–9].)
- F atom(s) coordination was not observed in the REMD simulation.  
→ It is indicated that propylene coordination is more stable than F atom(s) coordination.

[7] Matsumoto, K.; Sandhya, K. S.; Takayanagi, M.; Koga, N.; Nagaoka, M. *Organometallics* **2016**, *35*, 4099.

[8] Matsumoto, K.; Takayanagi, M.; Sankaran, S. K.; Koga, N.; Nagaoka, M. *Organometallics* **2018**, *37*, 343.

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# Summary and Conclusions

- REMD simulation indicates that  $C_2$  symmetric *ansa*-zirconocene catalyst,  $[\text{SiMe}_2(\text{Ind})_2\text{ZrMe}]^+[\text{MeB}(\text{C}_6\text{F}_5)_3]^-$  shows the ASO in the system with propylene as well as (pyridylamide)Hf(IV) catalytic system [7–9].
- MD simulation indicates that the AASO occurs in this catalytic system.

[7] Matsumoto, K.; Sandhya, K. S.; Takayanagi, M.; Koga, N.; Nagaoka, M. *Organometallics* **2016**, *35*, 4099.

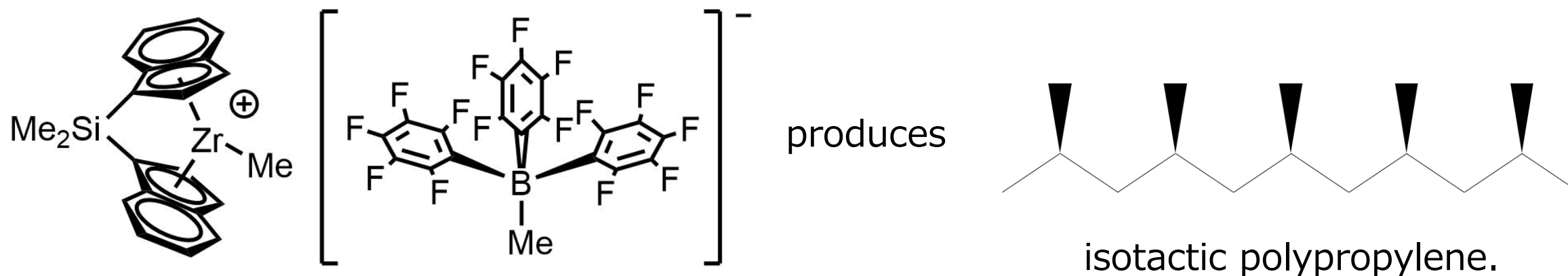
[8] Matsumoto, K.; Takayanagi, M.; Sankaran, S. K.; Koga, N.; Nagaoka, M. *Organometallics* **2018**, *37*, 343.

[9] Matsumoto, K.; Takayanagi, M.; Suzuki, Y.; Koga, N.; Nagaoka, M. *J. Comput. Chem.* **2018**, accepted.

# Perspective

One of the goals of my research is to reproduce the stereochemistry of polymerization reaction theoretically.

→ I'm proceeding with the investigation using the Red Moon (RM) simulation.



$C_2$  symmetric *ansa*-zirconocene catalyst,  
 $[\text{SiMe}_2(\text{Ind})_2\text{ZrMe}]^+[\text{MeB}(\text{C}_6\text{F}_5)_3]^-$  (**1**) [4]