

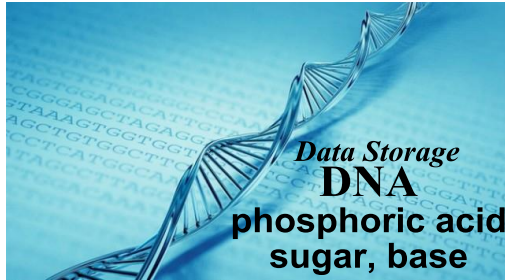
Controlled Coordination-Insertion Copolymerization

-For the Synthesis of Functional Polyolefins -

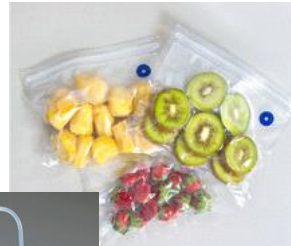
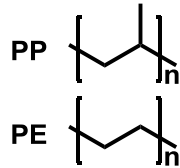
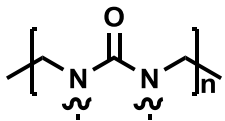
Literature Seminar 10/10/2015
Yamato Kanzaki (M1)

1. Introduction

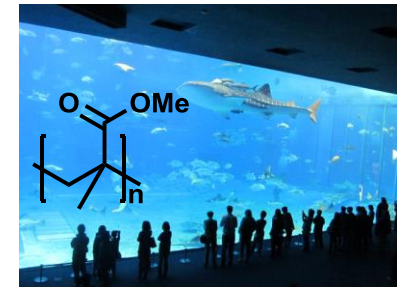
Examples of Polymers



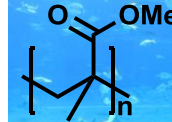
Urea-formaldehyde resin



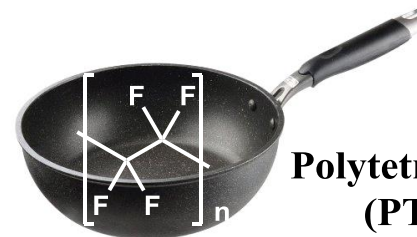
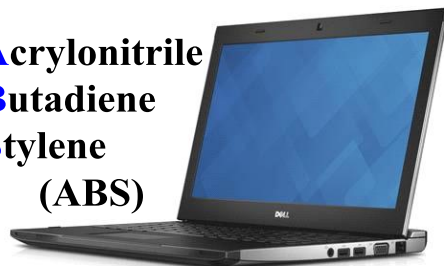
Polyolefins



Polymethyl methacrylate (PMMA)

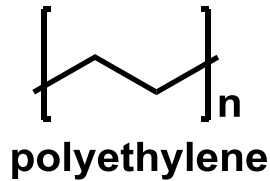


**Acrylonitrile
Butadiene
Styrene
(ABS)**



Polytetrafluoroethylene (PTFE, Teflon)

Characteristics of Polyethylene



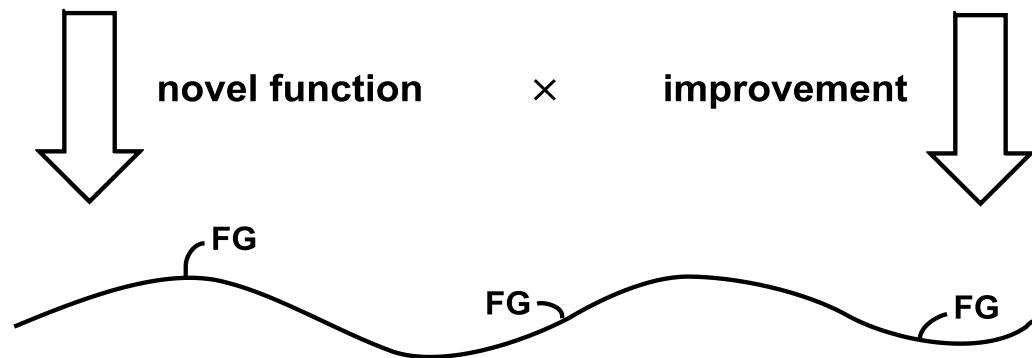
market share: 25% of all polymers in 2014¹⁾
(another quarter for polypropylene)

Advantages

water resistance (防水性)
electrical resistance (絶縁性)
impact resistance (衝撃耐性)
processibility (加工性)
lightweight (軽量性)
low temperature toughness (低温耐性)
low cost (安価)

Shortages

no dyeability (難染色性) → limited applications
no printability (難印刷性)
no compatibility (難混和性) → limited combination use
no adhesibility (難接着性) with other materials
gas permeability (ガス透過性) → unfavorable for food package

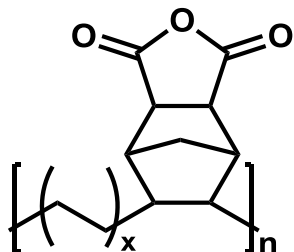


functional polyethylene for broader range of applications

1) http://www.vec.gr.jp/lib/lib2_4.html (原典: 日本プラスチック工業連盟)

Examples of Functionalization

Example 1

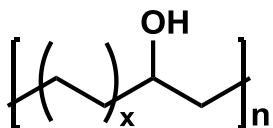


0.001 ~ 10% incorporation
and
 $M_n = 5.0 \times 10^3 \sim 5.0 \times 10^5$
are favored to keep PE's advantages.¹

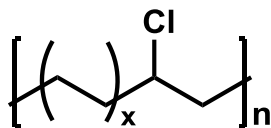
adhesibility (even to metals)

linear copolymer
synthesized by the catalyst
from today's topic (Drent-type)

Example 2



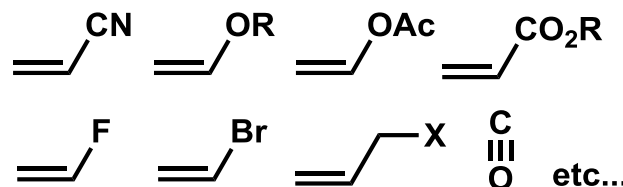
**gas impermeability
printability, etc.**



**gas impermeability
thermal stability
adhesibility, etc**

synthesized in radical manner: **branched structure**

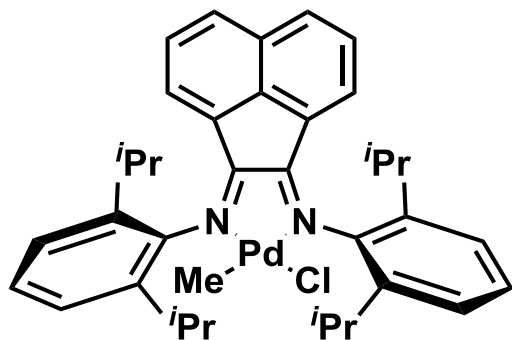
Example 3



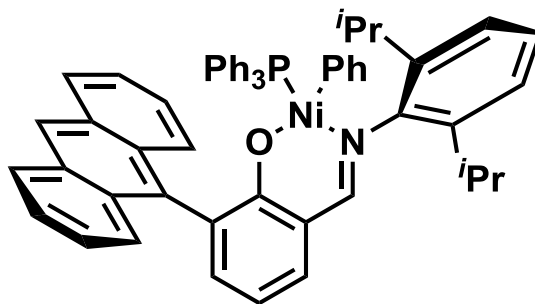
linear copolymer: not fully explored

**lack of general solution
for incorporation of polar monomer**

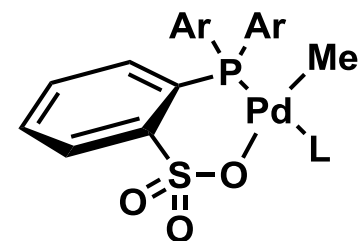
Today's Topic



Brookhart type



Grubbs type



Drent type
(main topic)

Introduction

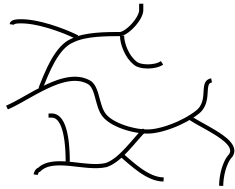
A. definition¹⁾

- Polymer: 1) relatively high molecular mass ($M_n > 10^4$, ca. 350 ethylene units)
2) **multiple repetition units** derived from molecules of small molecular mass

B. polyethylene (PE)

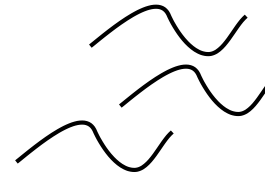
$M_n = 10^4$ - 10^5 scale: general PE in market

$M_n > 1.0 \times 10^6$: Ultra-High Molcubr Weight HDPE (**highest impact resistance** in all kind of polymers)



LDPE, branched
(Low Density PolyEthylene)

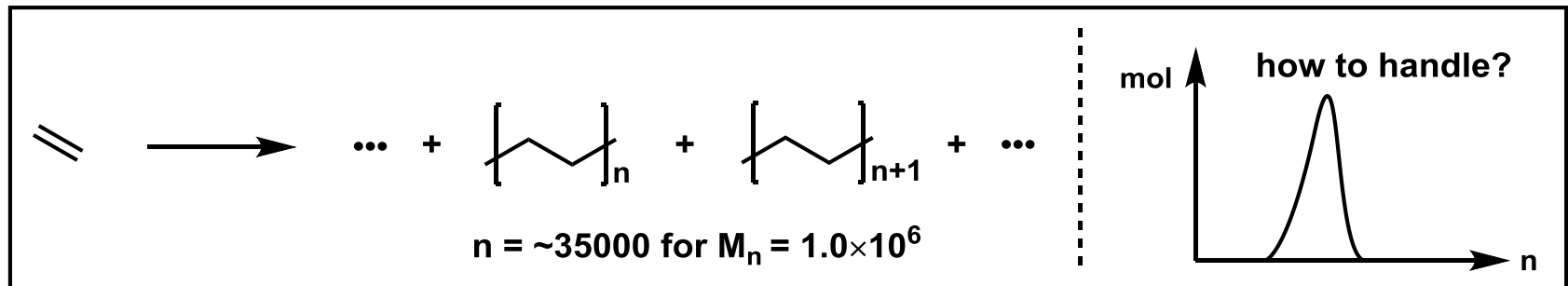
$T_m = 108 \sim 122 \text{ } ^\circ\text{C}^{2)}$
transparence
flexibility



HDPE, linear
(High Density PolyEthylene)

$T_m = 127 \sim 134 \text{ } ^\circ\text{C}^{2)}$
translucence
storength

C. distribution of polymers



1) Glossary of Basic Terms in Polymer Sciencech, IUPAC, *Pure & Appl. Chem.*, 1996, 12, 2287

2) Japan Polyethylene Cooperation: <http://www.pochem.co.jp/jpe/>

Introduction

1. M_n (number-average molecular mass)

→ used as an index of "the degree of polymerization"

$$M_n = \frac{\sum (M_i N_i)}{\sum N_i} \quad (\text{determined by } ^1\text{H-NMR, GPC})$$

2. M_w (weight-average molecular mass)

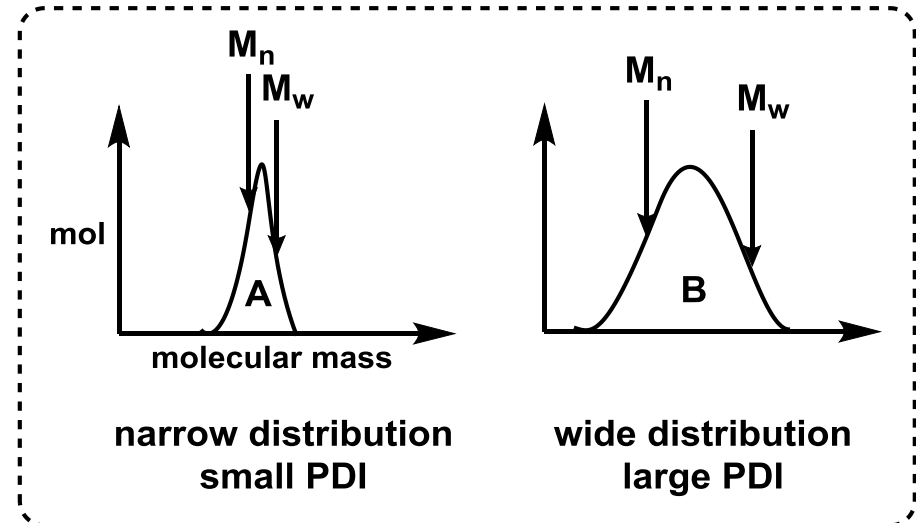
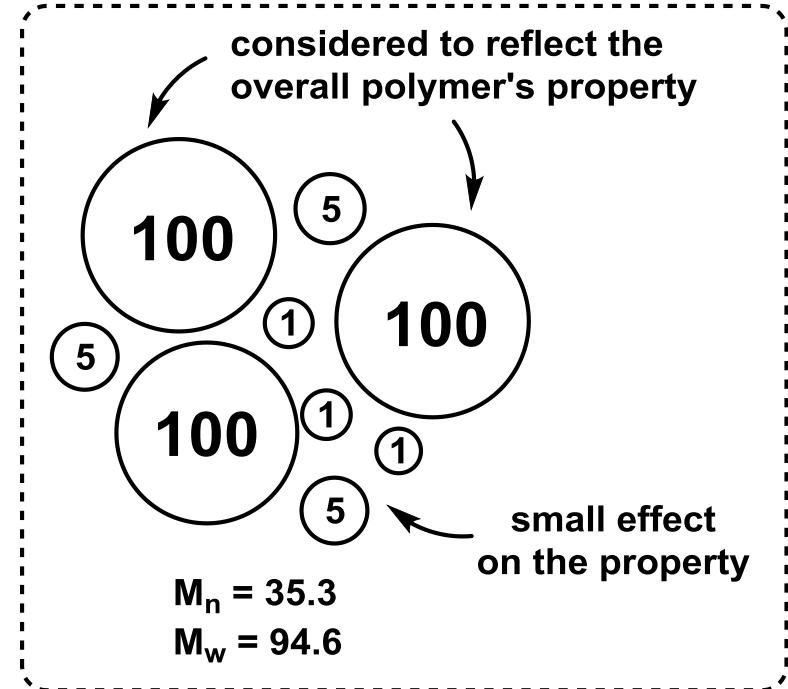
→ correlated with "the physical property" of polymer

$$M_w = \frac{\sum (M_i^2 N_i)}{\sum (M_i N_i)} \quad (\text{determined by GPC})$$

3. PDI (polydispersity index)

→ used for evaluation of "the distribution range"

$$\text{PDI} = M_w/M_n (\geq 1) \quad (\text{determined by GPC})$$



2. Copolymerization of ethylene with polar monomers

2-0. Difficulties in polar monomer incorporation

2-1. Brookhart-type catalyst (diimine ligand)

2-2. Grubbs-type catalyst (imine-phenoxy ligand)

2-3. Drent-type catalyst (phosphine-sulfonate ligand)

a. trans influence

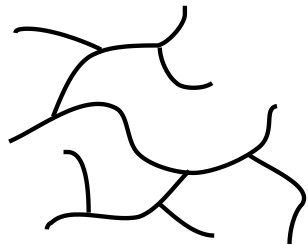
b. steric effect

c. regio/stereo control

Development of Polyolefin Synthesis

1930s

High pressure
(radical process)

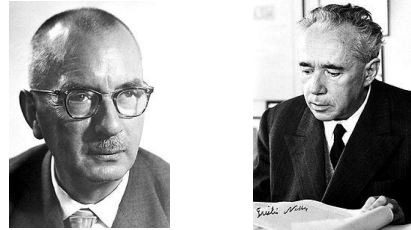


Low Density Poly-Ethylene
(LDPE, branched)

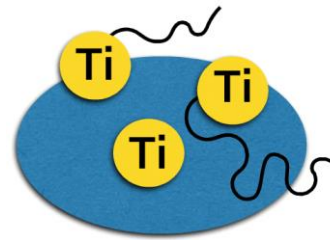
non-controllable

1950s

$TiCl_x/AlR_3$



Karl Ziegler Giulio Natta



Multi-site

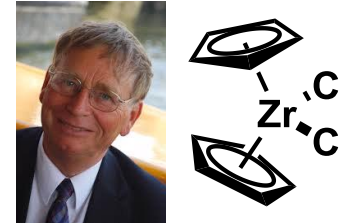
non-tunable active species



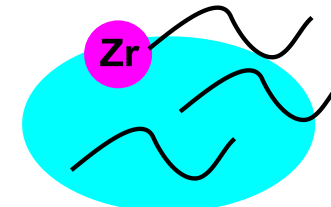
1. broad distribution
2. no control of microstructure

1980

metallocen catalyst



Walter Kaminsky



Single-site

designable reaction site



1. narrow distribution
2. tacticity control
3. copolymer with non-polar monomers, etc.

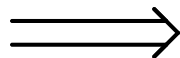
2015



Synthesis of Copolymer with Polar Monomers

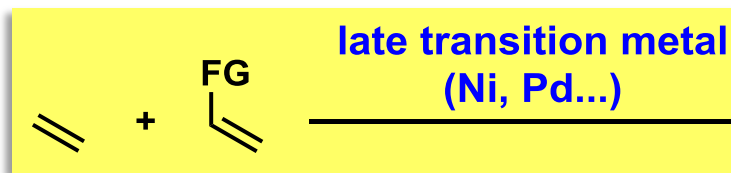
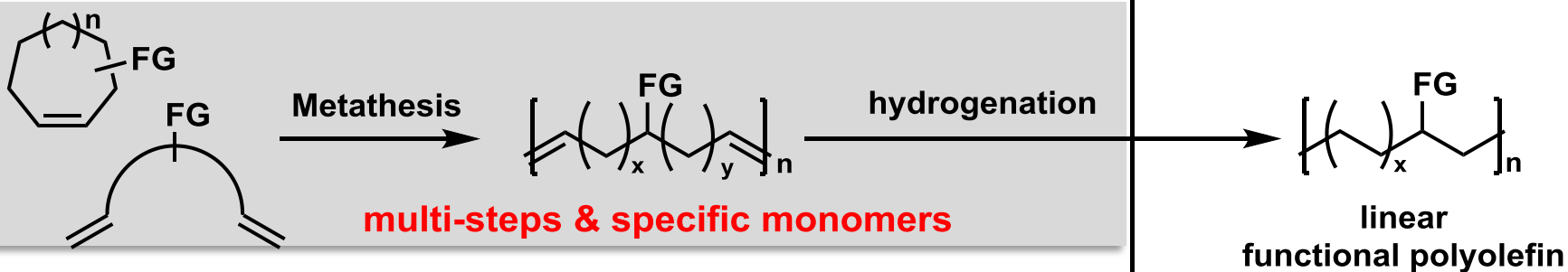
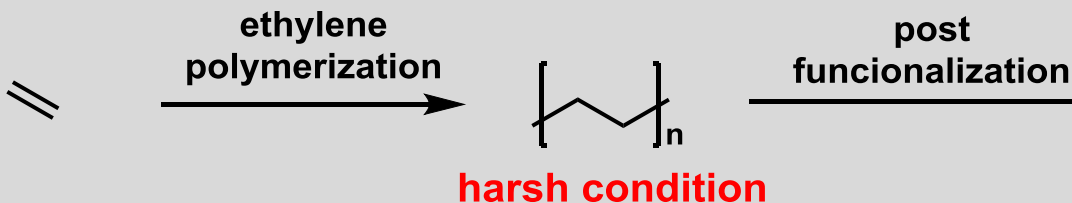
previous systems

Early transition metals
(Ti, Zr, etc)

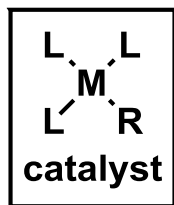


deactivated by
polar functional group

current methods

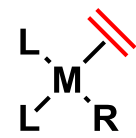


Coordination-Insertion Polymerization



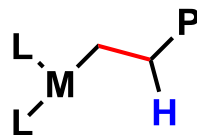
M = Ni, Pd

coordination



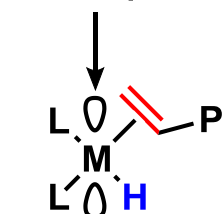
1. initiation

insertion

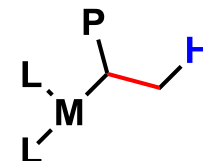


β -H elimination

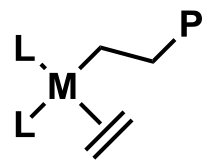
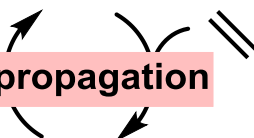
vacant axial p orbital



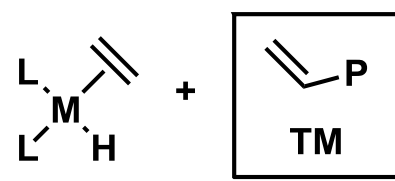
re-insertion
(chain walking)



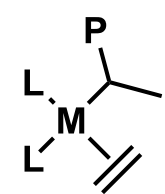
2. propagation



3. transfer



**2. propagation
(growth of branch)**

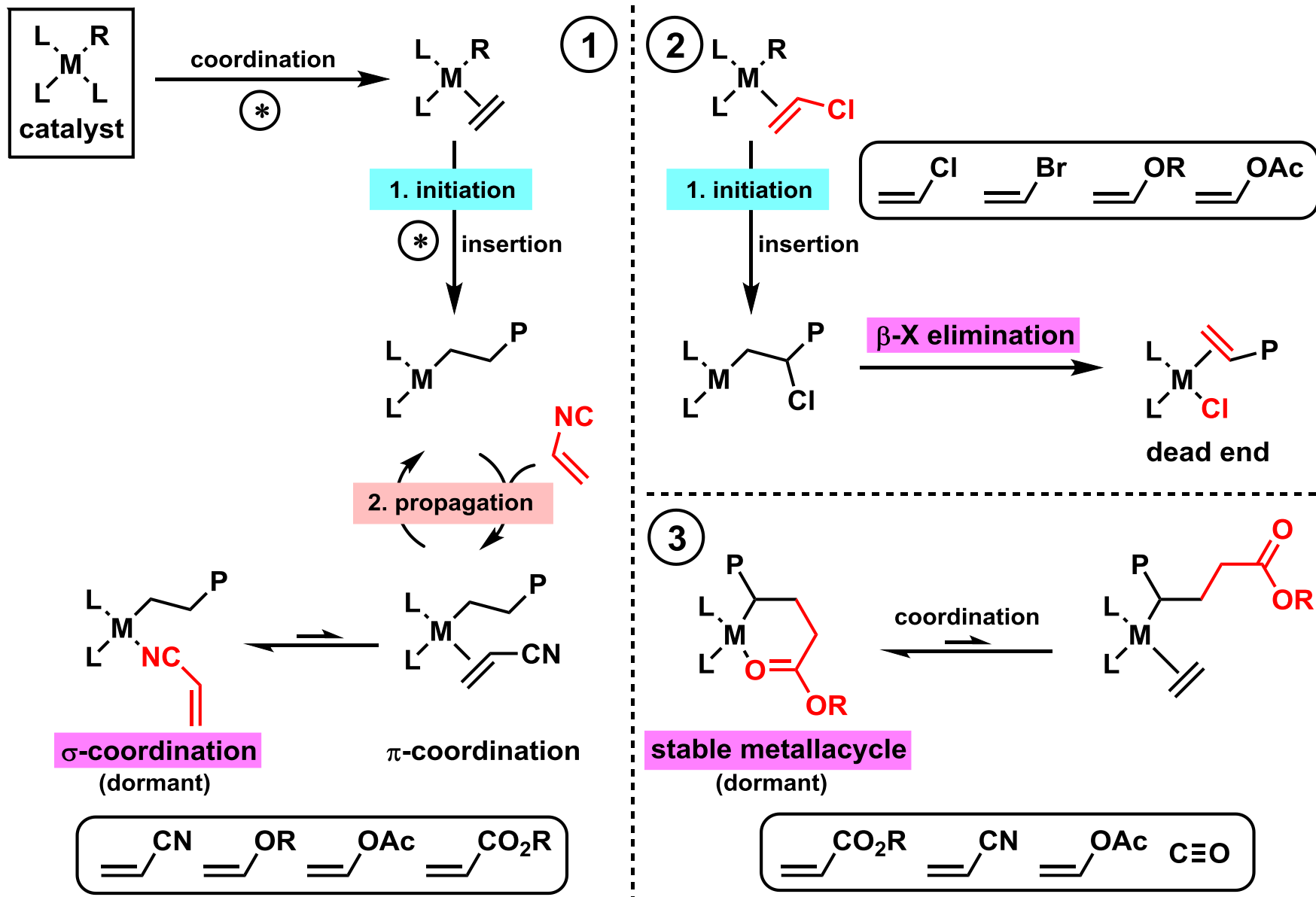


next catalytic cycle

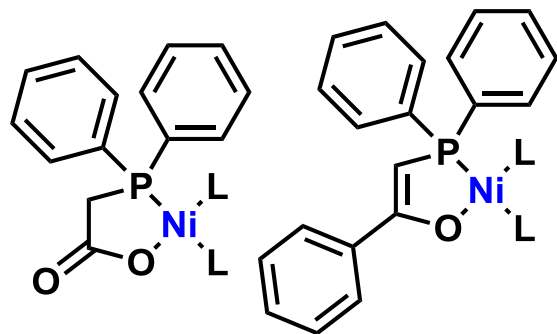
Key Points for Controlled Polymer Synthesis

1. control of β -H elimination
2. control of chain transfer (for high M_n)

Bottlenecks for Incorporating Polar Monomers



Shell Higher Olefin Process (SHOP) Catalyst



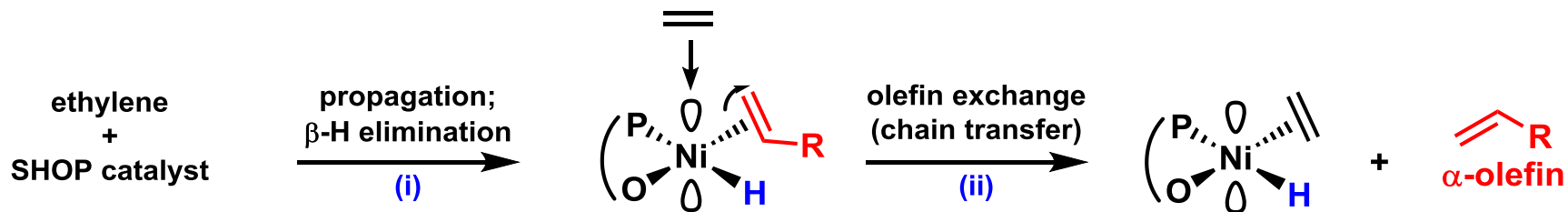
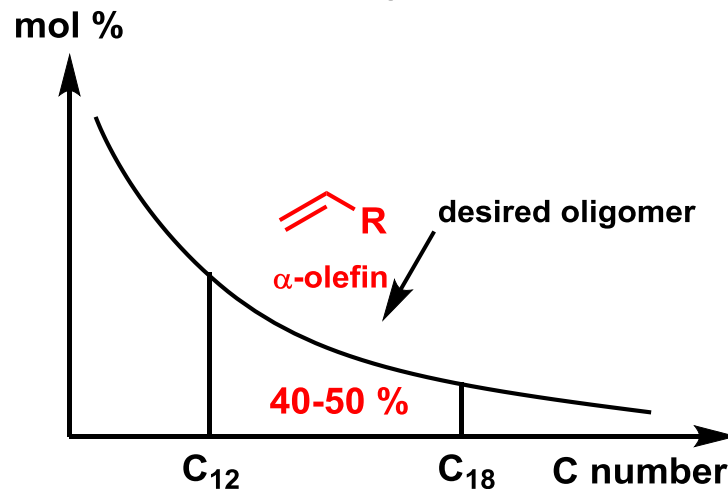
classical SHOP complexes (1968)
(prototype of the catalysts in this seminar)

Key Property of Catalyst

"oligomerization"
(i. fast β -H elimination)
(ii. axial vacant orbitals)



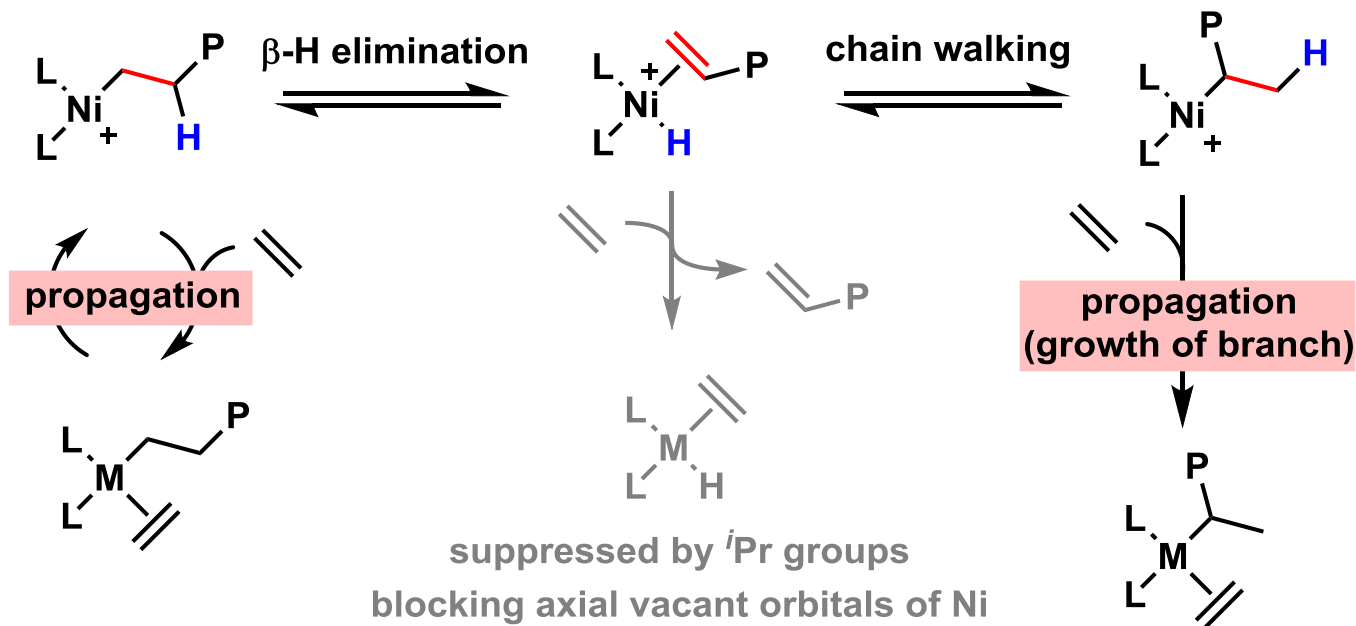
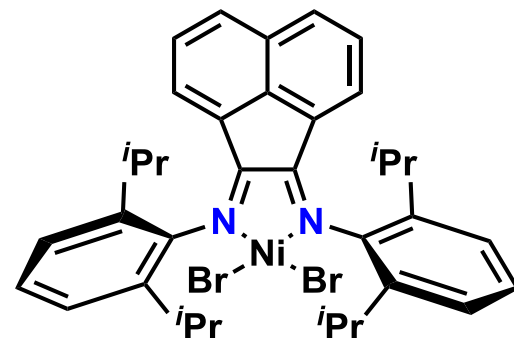
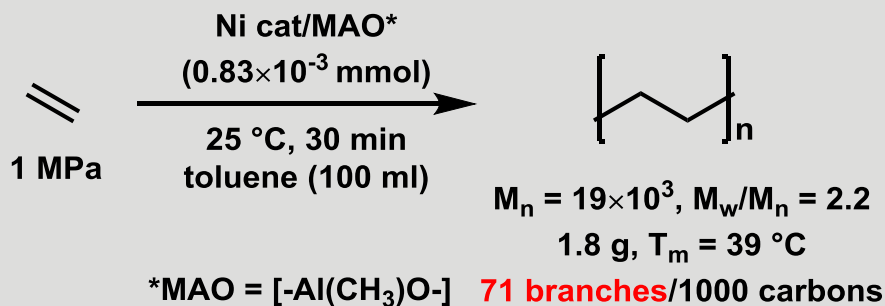
Schulz-Flory distribution



3-1. Diimine Catalysts (Brookhart-Type)



Maurice Brookhart

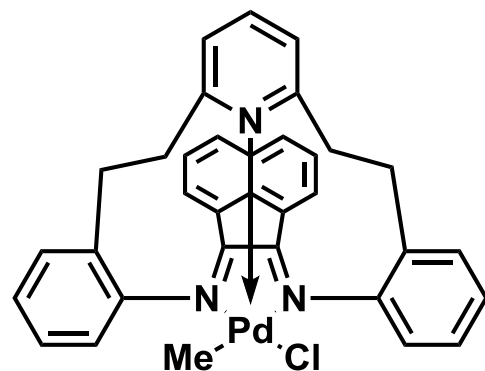


$\beta\text{-H elimination} \times$
 suppression of olefin exchange \longrightarrow highly branched chain \times
 high M_n

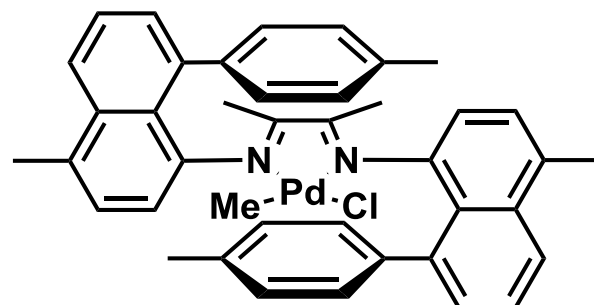
Diimine Catalysts (Brookhart-Type)

Shortages

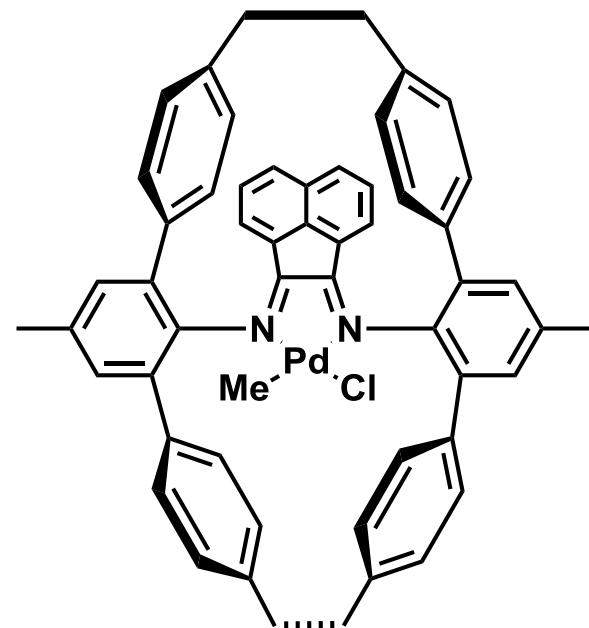
1. **instability** at high temperature (>50 °C)
2. **limited incorporation** of polar monomers (ex. acrylates)
3. **limited use** of produced highly branched polymer



coordination of pyridine to Pd
high activity
linear polymer



sandwich type
stable at 70 °C

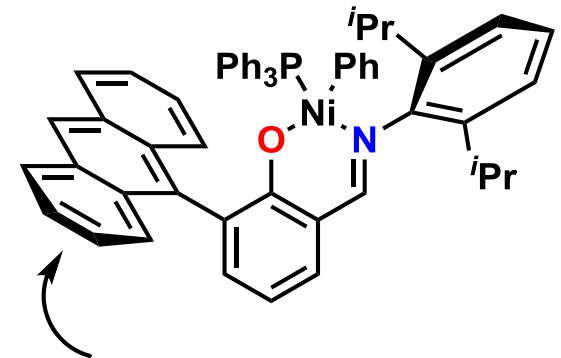
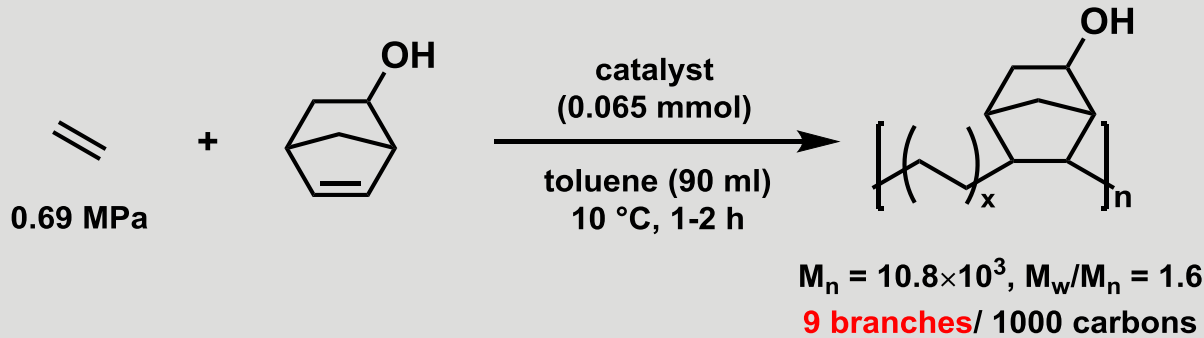
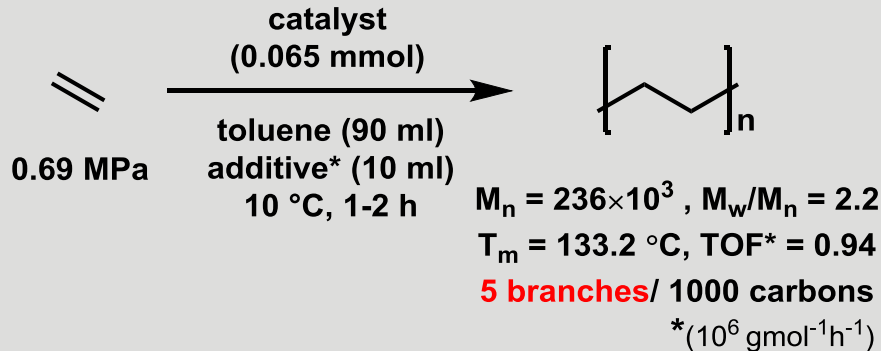


cyclophane type
highly active at 90 °C

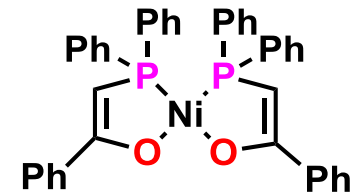
3-2. Imine-Phenoxy Catalysts (Grubbs-Type)



Robert Grubbs



designed to avoid the formation of $\text{Ni}[\text{N-O}]_2$, which is inactive



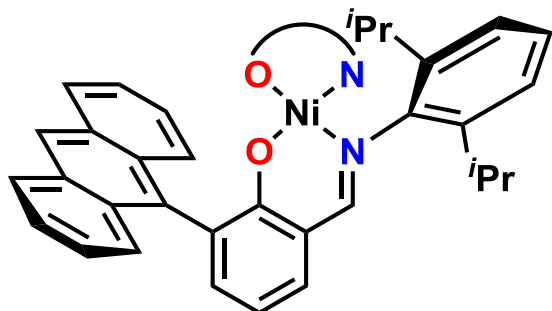
known as deactivated SHOP catalyst

Achievements

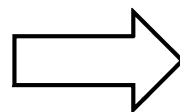
- i. **linear** polymer with **High M_n**
- ii. toleration of **polar monomer**

Drawbacks of Grubbs-Type Catalysts

A. thermal instability of catalyst

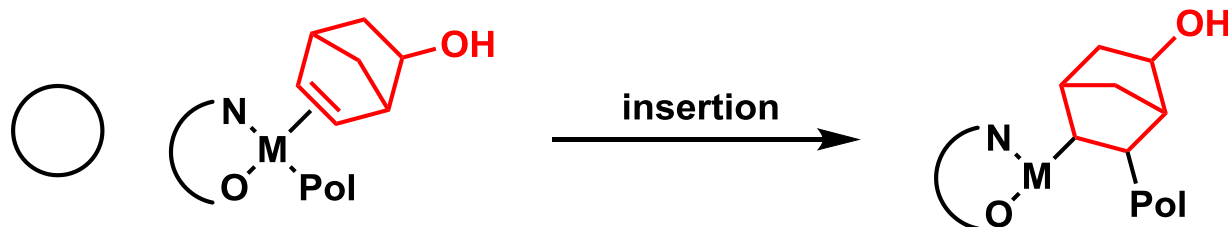


decomposition by biligation?



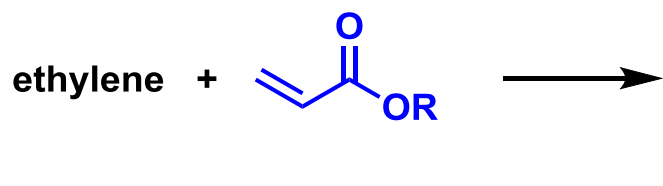
not observed
(will be discussed later)

B. Limited scope for incorporation of polar monomer



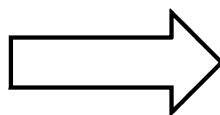
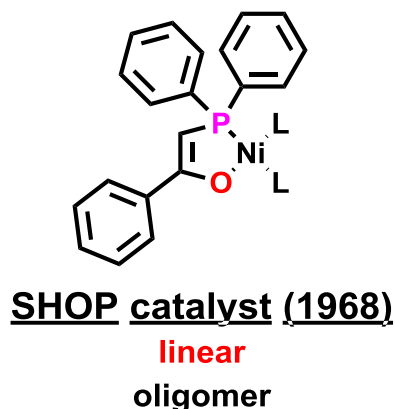
no interaction between metal and
spatially separated OH group

✗



metal - **polar FG** interaction
after migratory insertion
(will be discussed later)

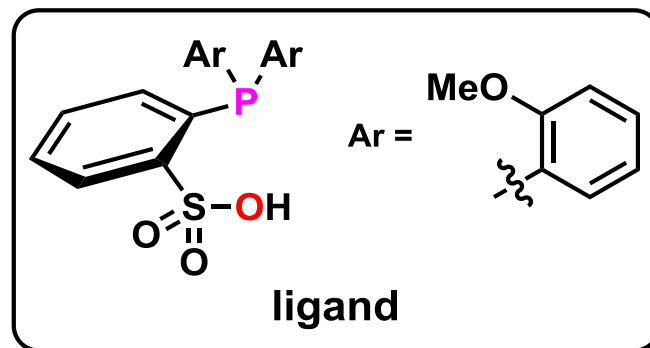
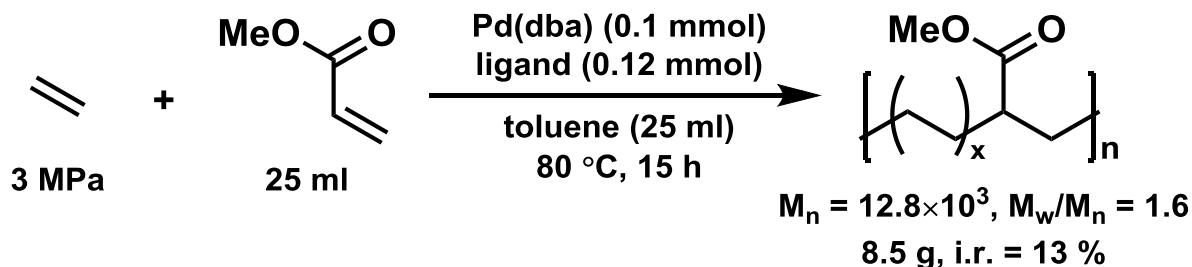
3-3. Phosphine-Sulfonate Catalyst (Drent-Type)



"Is **hetero bidentate** ligand crucial for **linear** polymerization?"

P-SO₃ bidentate
1987: ethylene oligomerization (patent)
(Murray, Union Carbide)¹

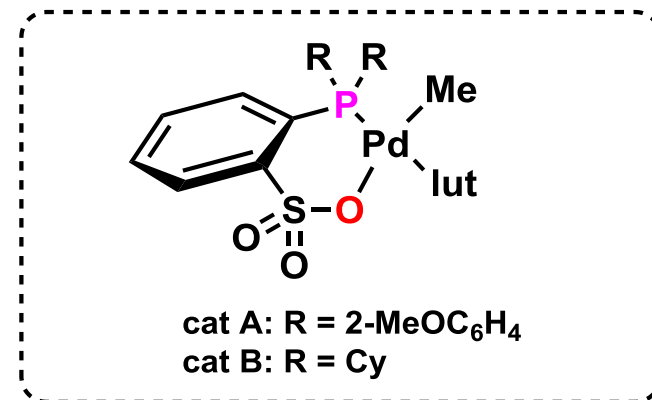
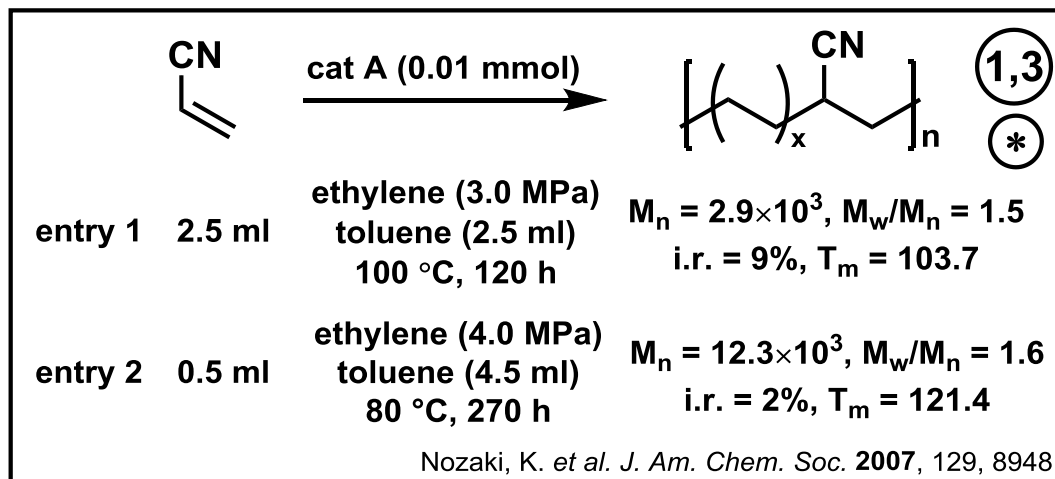
First report of P-SO₃ ligand for polymerization by Drent (Shell)²



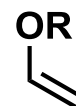
Advantages

- i. **linear** polymer
- ii. **thermal stability** of catalyst
- iii. incorporation of **methylacrylate**

Copolymerization with Other Polar Monomers



and...



(2)

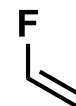
Jordan, R. F. *et al. J. Am. Chem. Soc.* **2007**, 129, 8946



(2)

Mecking, S. *et al. Angew. Chem. Int. Ed.* **2013**, 129, 8946

*



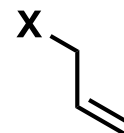
*

Jordan, R. F. *et al. Macromolecules.* **2010**, 43, 8706

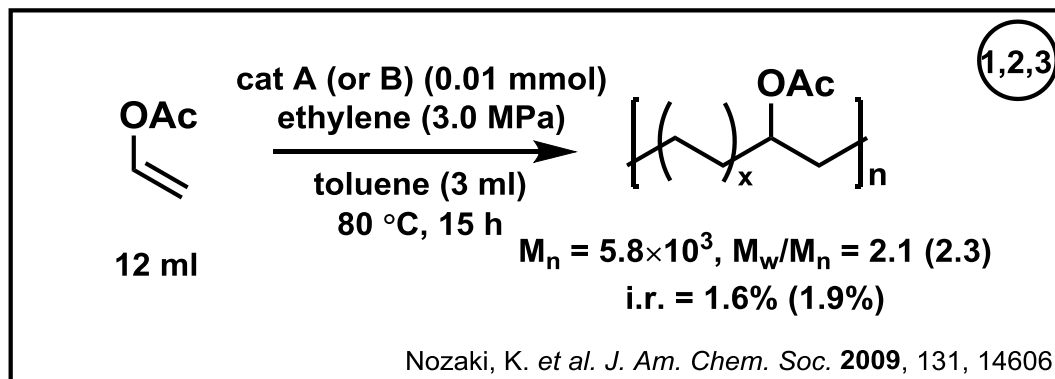


(3)

Rieger, B. *et al. Organometallics.* **2005**, 24, 2755



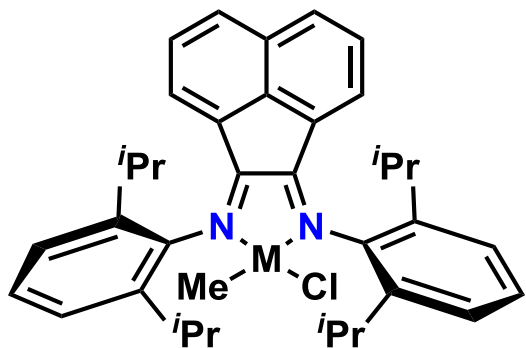
Nozaki, K. *et al. J. Am. Chem. Soc.* **2011**, 133, 1232



etc.

What is Special about Drent-Type Catalyst?

1. How does **hetero bidantate ligand** work for the reaction?
2. **Neutral metal center** seems to afford the tolerance for σ -coordination.
(anionic ligand)
3. What is the difference between [N-O] and [P-SO₃] ligands?

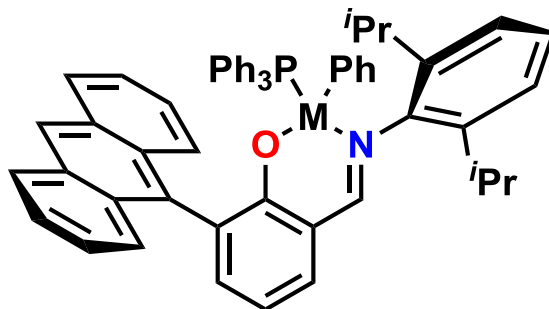


Brookhart type

diimine bidentate
cationic complex



branched polymer

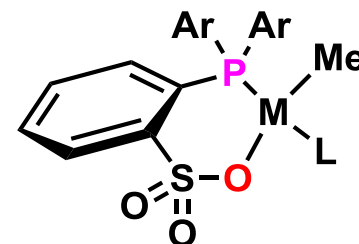


Grubbs type

hetero bidentate
neutral complex



linear polymer
instability
limited polar monomers



Drent type

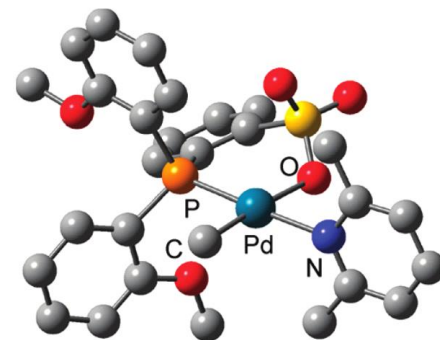
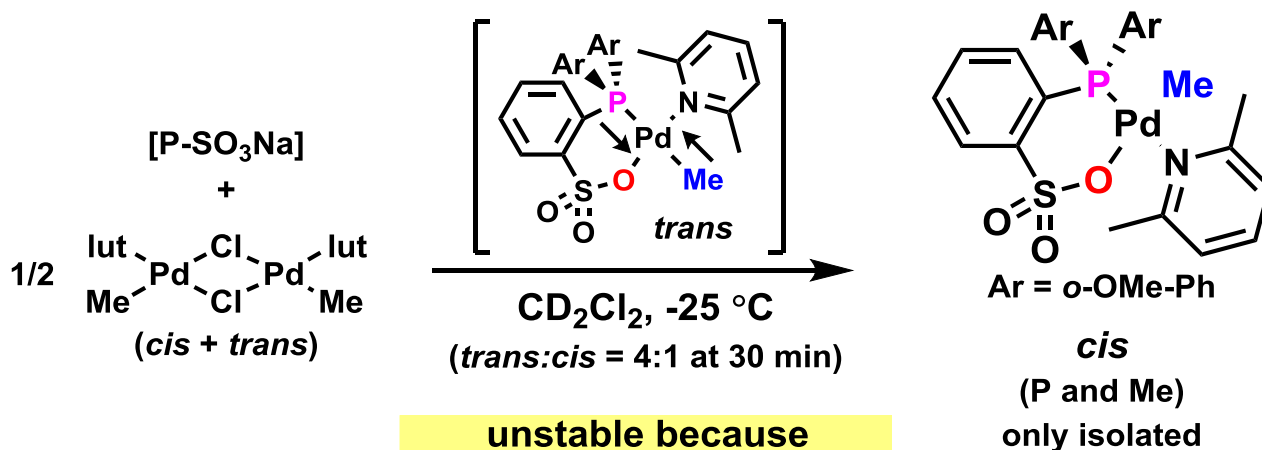
hetero bidentate
neutral complex



linear polymer
stability
various polar monomers

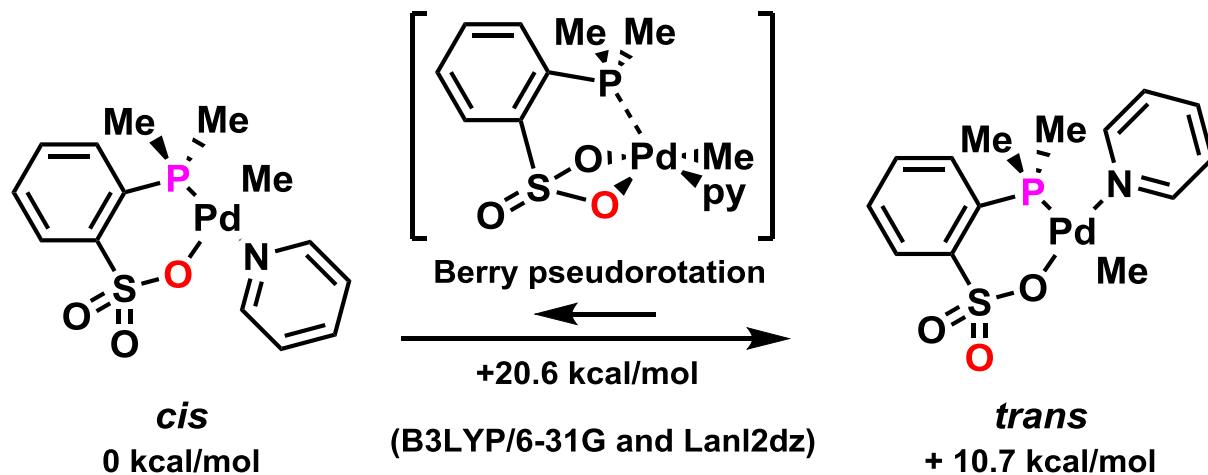
Trans Influence

A. isolation of more stable *cis*-isomer



unstable because
 P/Me are strong σ -donors

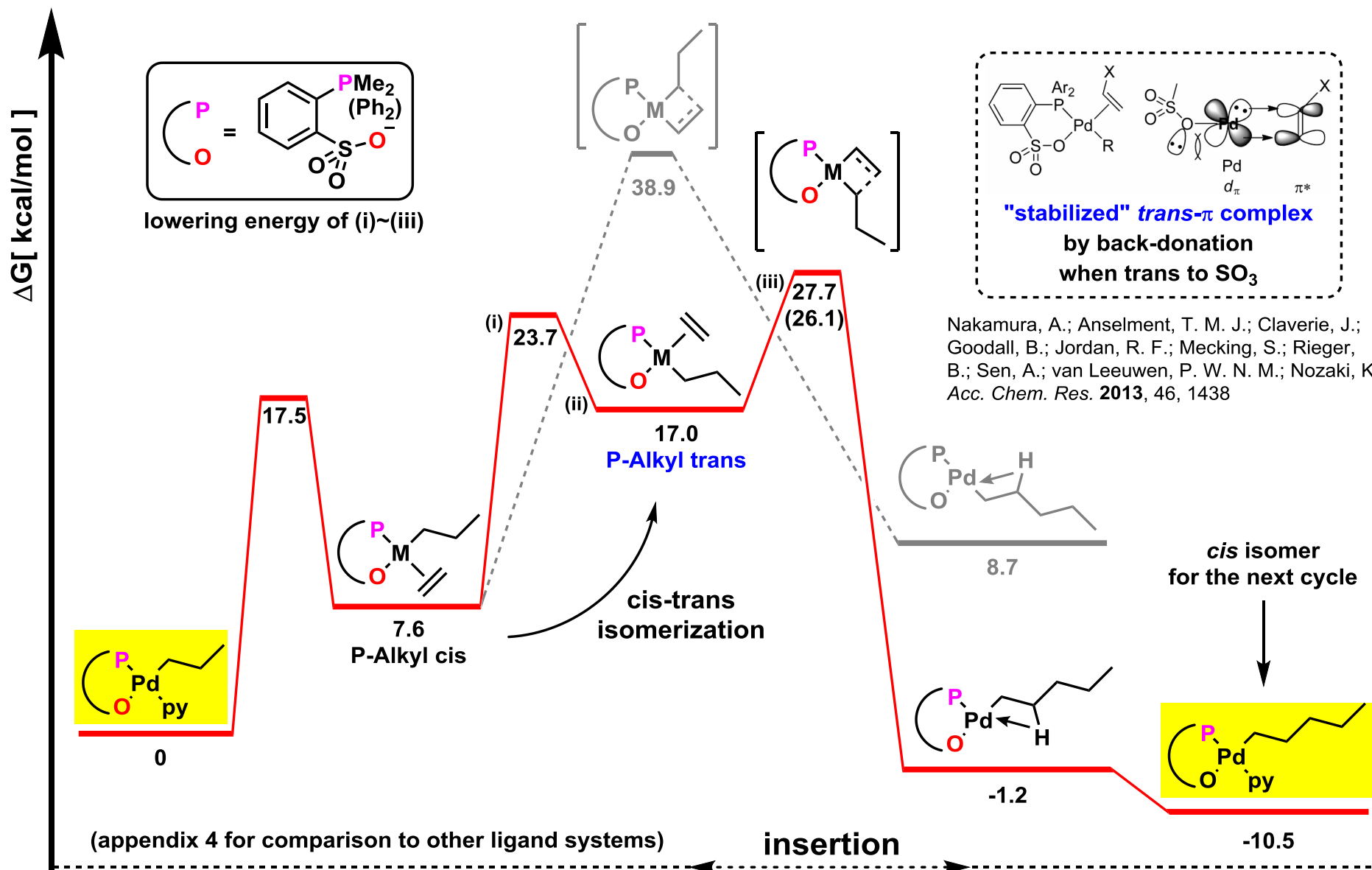
B. *cis*-*trans* isomerization via SO₃ assisted Berry pseudorotation



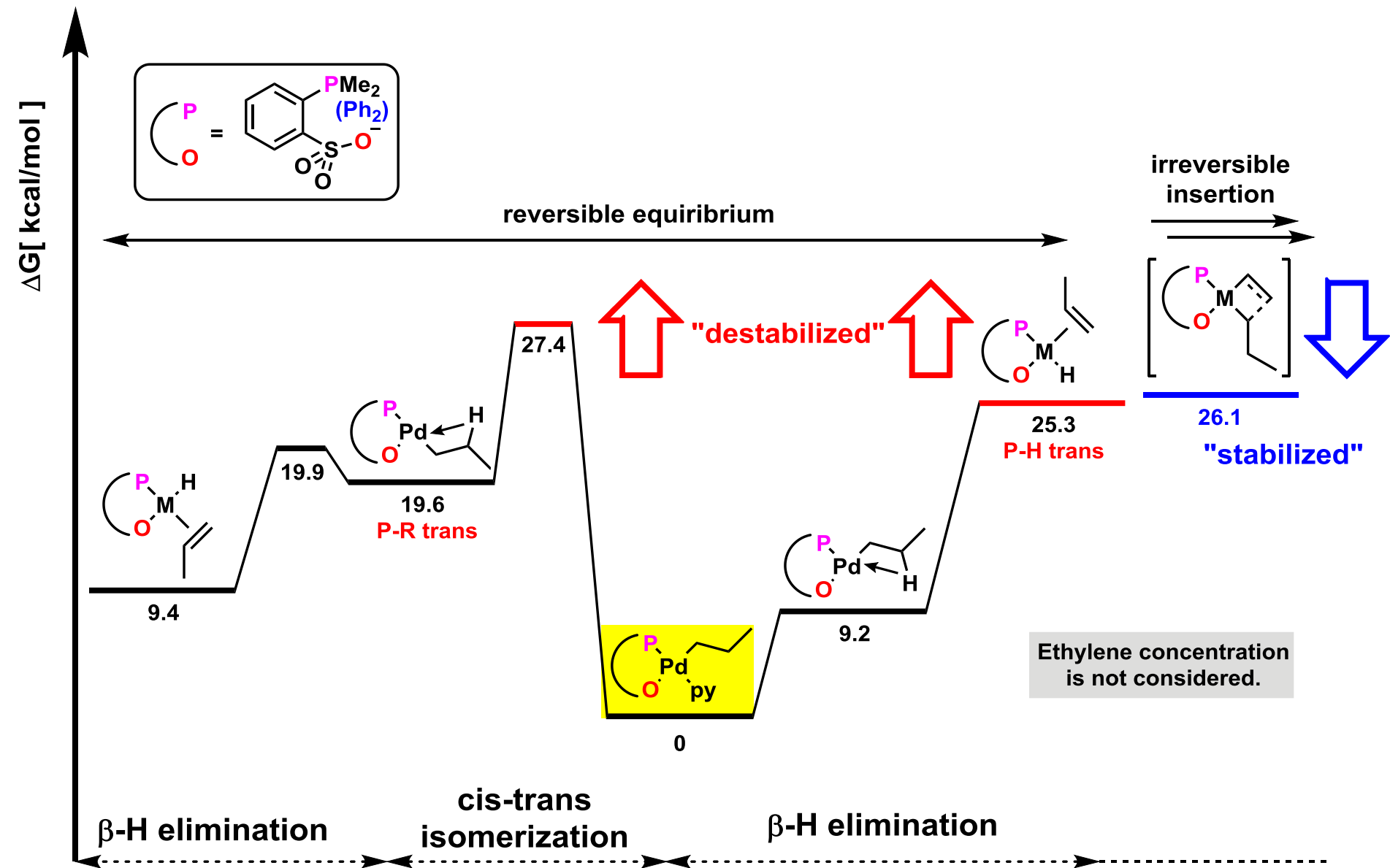
How does it work
 in the reaction?
 esp. in

1. insertion
2. β -H elimination

1. Ethylene Insertion from *Trans* Isomer



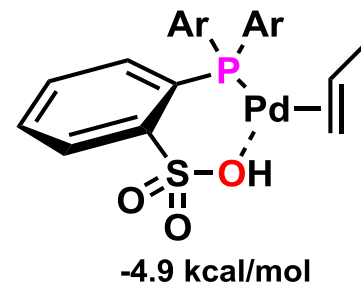
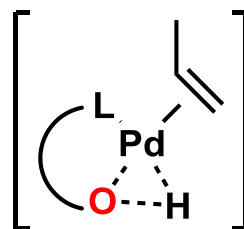
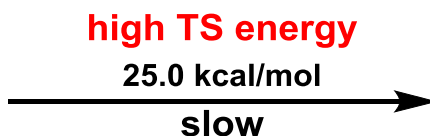
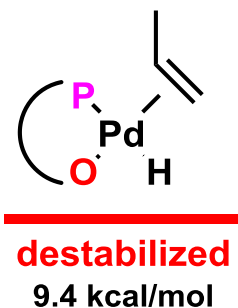
2. Inhibition of β -Hydride Elimination



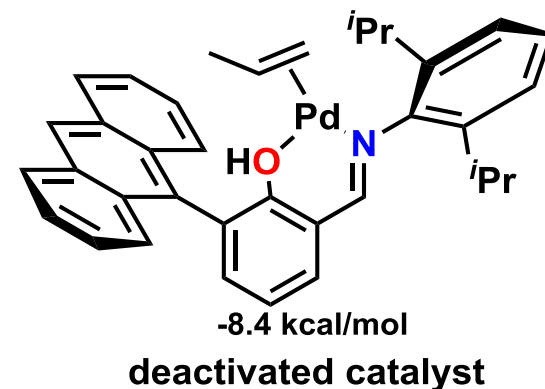
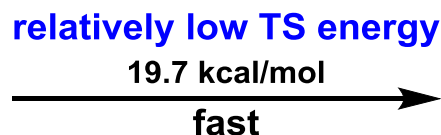
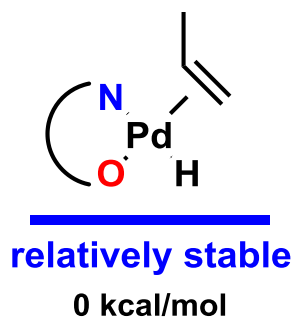
P-SO₃ vs N-O: What is the Critical Difference?

deactivation of catalyst via reductive elimination

P
stronger
trans influence

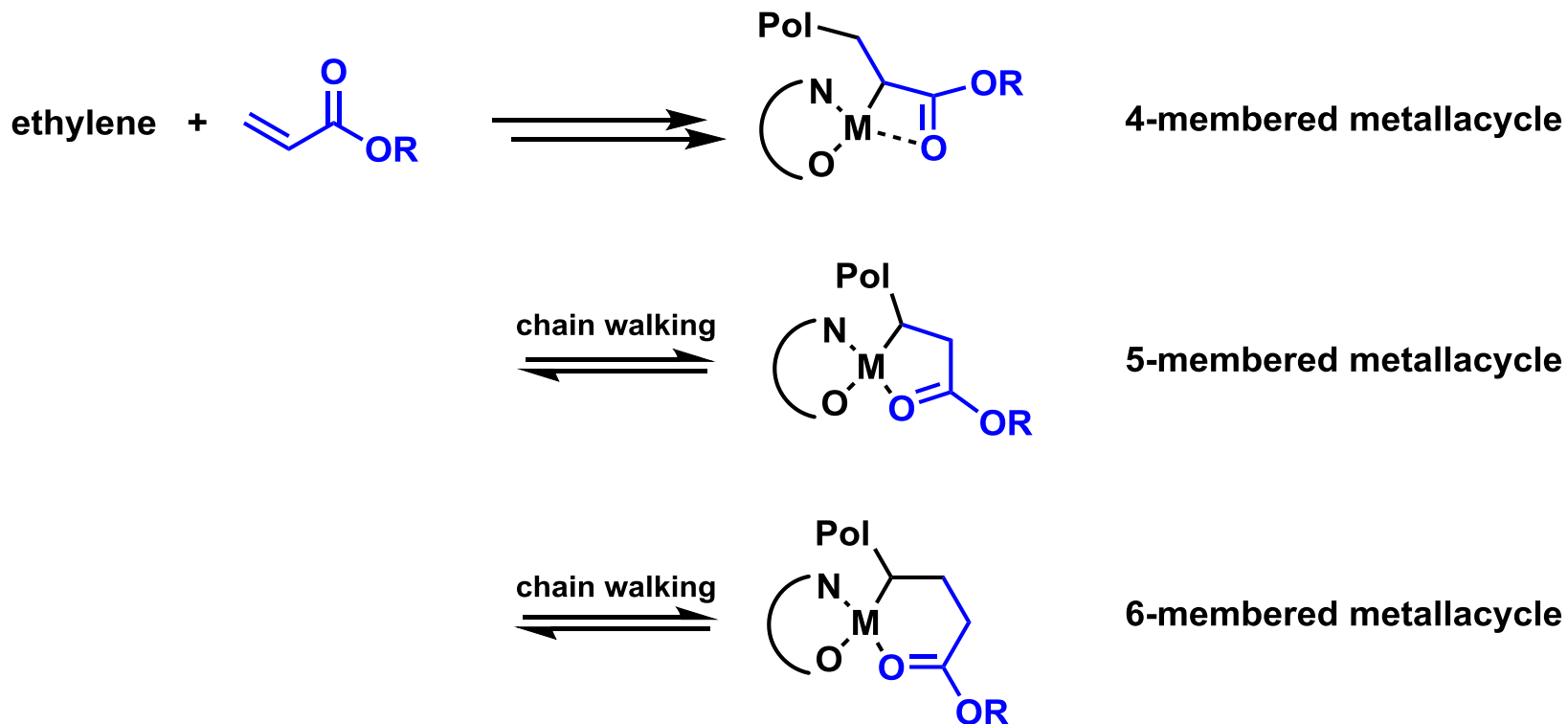


N
weaker
trans influence



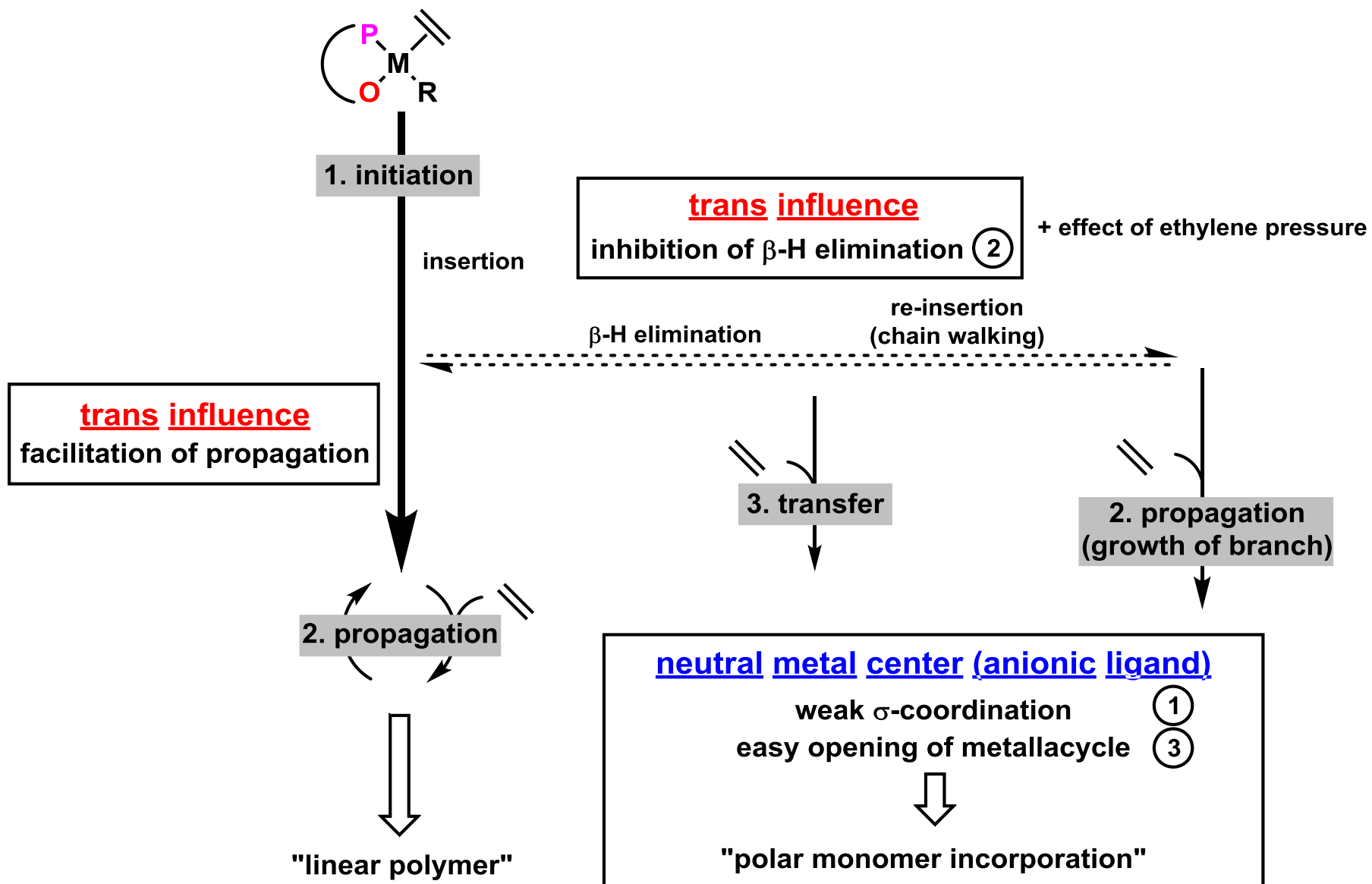
appendix 5 for detailed energy profiles

P-SO₃ vs N-O : What is the Critical Difference?

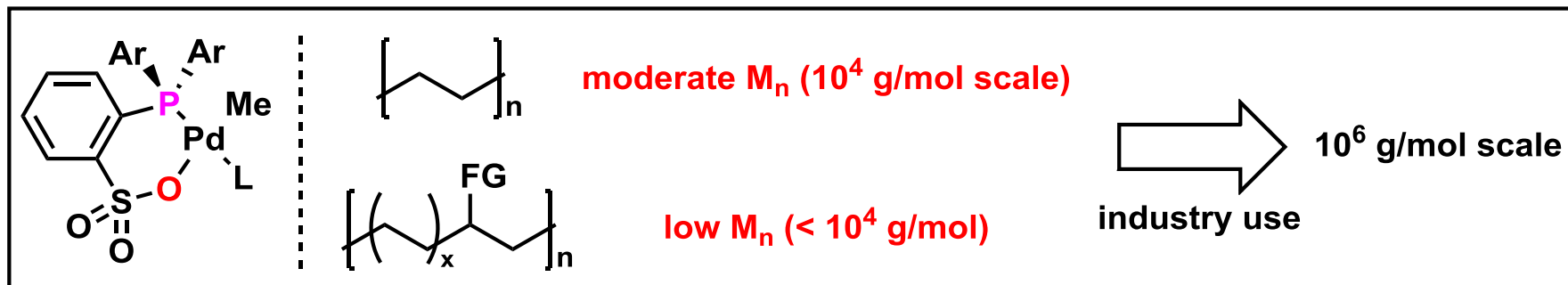


Formation of relatively stable hydride complex ends up decomposition of catalyst via reductive elimination.

Short Summary for Drent-Type



What is the Problem?



Finding parameter which correlates with M_n
is important for ligand design.

→screening ligand structure & mechanistic study



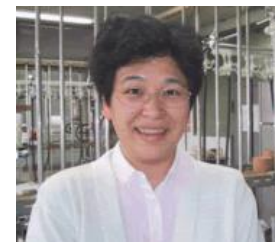
Stefan Mecking
(Universität Konstanz)



Richard Jordan
(The University of Chicago)

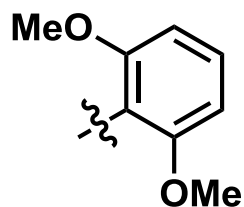
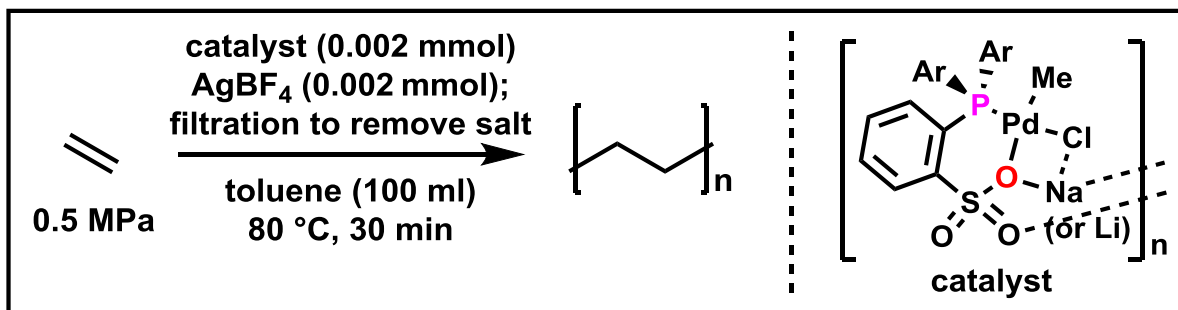


Bernhard Rieger
(Technische Universität Munchen)

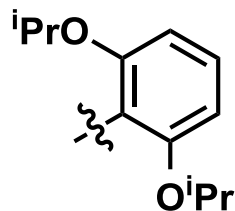


Kyoko Nozaki
(University of Tokyo)

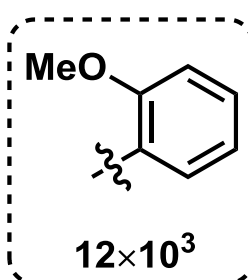
Exploring Steric Effect on Phosphine



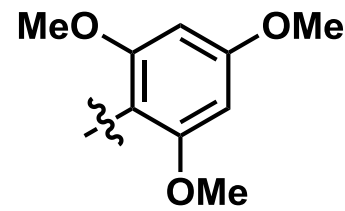
OR groups 1.6×10^3



10×10^3



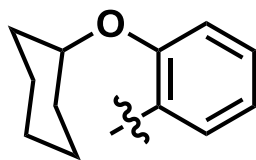
12×10^3



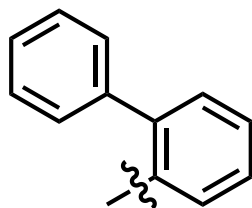
14×10^3

OR groups

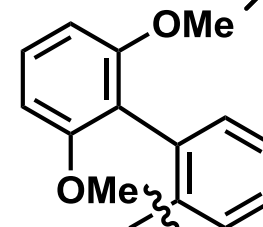
bulky groups



6×10^3



9.5×10^3



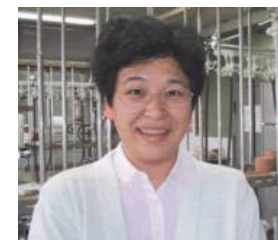
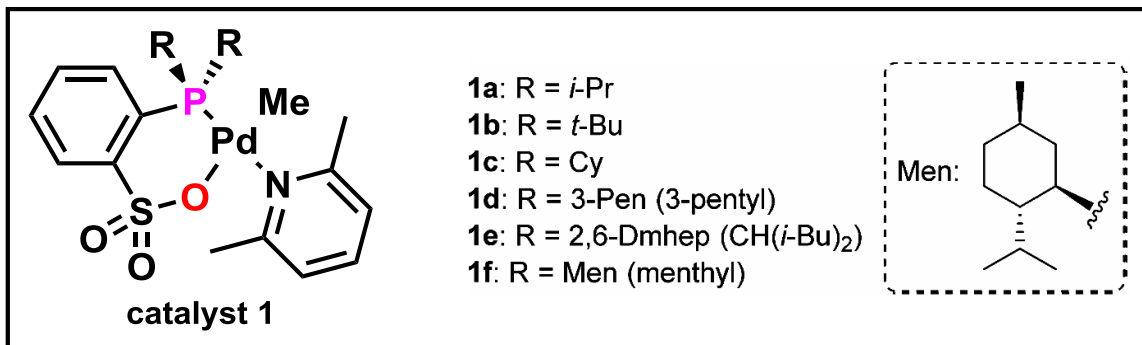
29×10^3

M_n (g/mol)

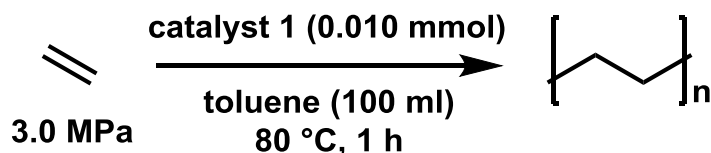
No clear trend to increase M_n

appendix 6 for electronic effect
appendix 7,8 for steric effect of other ligands

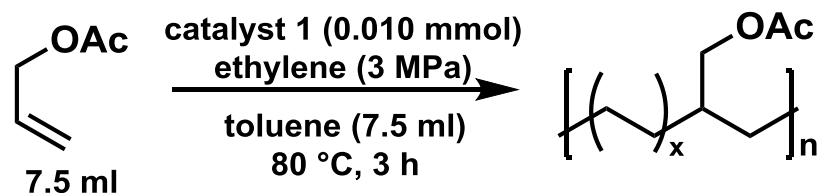
Screening of Alkyl Groups on Phosphine



Kyoko Nozaki



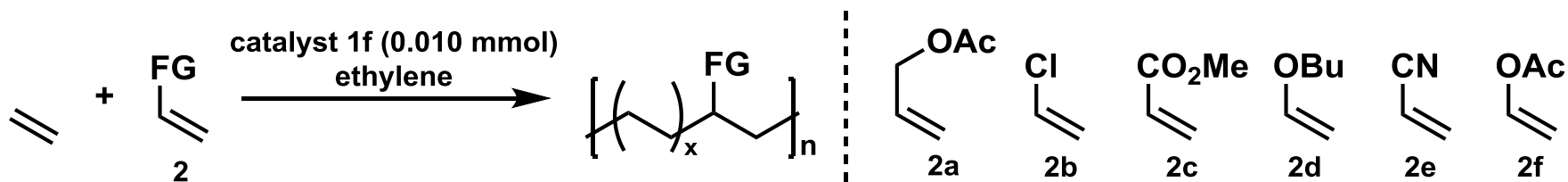
entry	catalyst	B5	yield ^b (g)	activity (g/mmol·h)	M_n^c ($\times 10^3$ g/mol)	M_w/M_n^c
1	1a (<i>i</i> -Pr)	3.07	6.41	641	6.7	2.7
2	1b (<i>t</i> -Bu)	3.09	18.6	1860	6.2	4.1
3	1c (Cy)	3.38	11.5	1150	9.9	2.4
4	1d (3-Pen)	4.28	1.25	125	33	2.4
5	1e (2,6-Dmhep)	5.22	1.97	200	72	2.4
6	1f (Men)	5.64	2.05	205	169	1.5



entry	catalyst	yield ^b (g)	activity (g/mmol·h)	M_n^c ($\times 10^3$ g/mol)	M_w/M_n^c	i.r. ^d (%)
1	1a (<i>i</i> -Pr)	0.35	12	5.2	2.4	1.9
2	1b (<i>t</i> -Bu)	0.31	10	10.3	5.1	0.6
3	1c (Cy)	0.30	10	7.8	2.0	1.8
4	1d (3-Pen)	0.36	12	17	2.4	1.5
5	1e (2,6-Dmhep)	0.35	12	29	2.8	1.1
6	1f (Men)	1.65	55	177	2.0	0.6

^bIsolated yields after precipitation with methanol. ^cMolecular weights determined by SEC using polystyrene standards and corrected by universal calibration. ^dMolar incorporation ratios of allyl acetate determined by ¹H NMR analysis.

Copolymerization with Other Polar Monomers



entry	comonomer	ethylene (MPa)	monomer (mL)	solvent (mL)	T (°C)	t (h)	yield ^b (g)	activity (g/mmol·h)	M _n ^c (×10 ³ g/mol)	M _w /M _n ^c	i.r. ^d (%)
◆ 1	2a (CH ₂ OAc)	3.0	7.5	7.5	80	3	1.65	55	177	2.0	0.6
2	2a	3.0	7.5	7.5	100	3	1.05	35	47	2.2	2.5
3	2a	2.1	7.5	7.5	80	3	1.10	37	86	2.1	2.2
4	2a	1.0	7.5	7.5	100	3	0.48	16	36	1.7	5.1
5	2a	1.0	12	3	100	13	0.30	2.3	17	2.0	7.8
◆ 6	2b (CH ₂ Cl)	3.0	3	12	80	16	0.35	2.2	33	2.3	0.6
◇ 7	2c (CO ₂ Me)	3.0	7.5	7.5	80	3	2.02	67	72	2.5	1.4
◇ 8	2c	2.0	7.5	7.5	80	3	0.88	29	40	2.0	3.0
◇ 9	2c	1.0	7.5	7.5	100	3	0.44	15	8.5	2.0	8.3
◇ 10	2c	1.0	12	3	100	15	0.24	1.6	6.1	1.8	11
◆ 11	2d (OBu)	3.0	7.5	7.5	80	3	1.61	54	15	4.1	1.1
12	2d	1.0	12	3	100	15	1.30	8.6	11	2.4	7.7
◆ 13	2e (CN)	3.0	7.5	7.5	80	15	0.30	2.0	14	1.9	0.7
14	2f (OAc)	3.0	12	3	80	15	0.34	2.3	4.8	2.7	1.3

^aA mixture of catalyst 1f (0.010 mmol) and monomers 2a–f in toluene was stirred under ethylene atmosphere in a 50 mL autoclave. ^bIsolated yields after precipitation with methanol. ^cMolecular weights determined by SEC using polystyrene standards and corrected by universal calibration. ^dMolar incorporation ratios of polar monomers determined by ¹H NMR analysis.

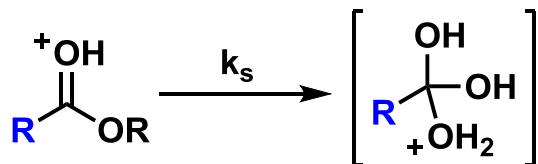
◆ : higher M_n than reported data

◇ : higher M_n/i.r. ratio than reported data

What is the point of steric effect?

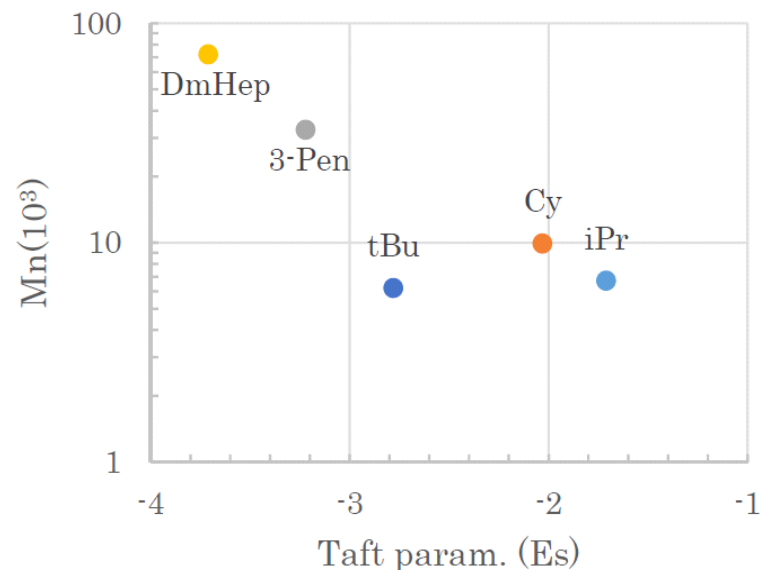
Evaluation of Steric Effect of Ligands

A: Taft Parameter¹⁾



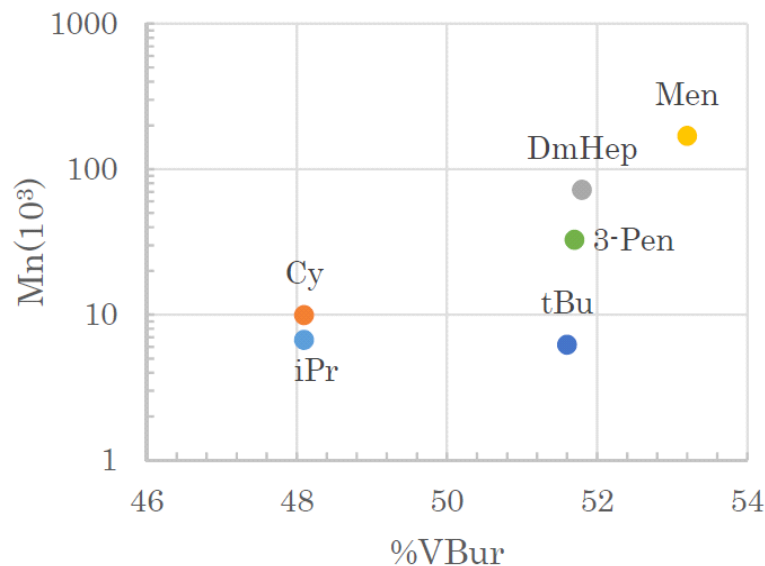
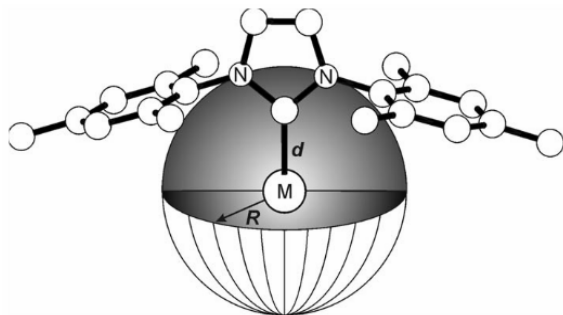
Steric Substituent Constant: $E_s = \frac{1}{\delta} \log \left(\frac{k_s}{k_{\text{CH}_3}} \right)$

$\delta = 1$ for the definition reaction above



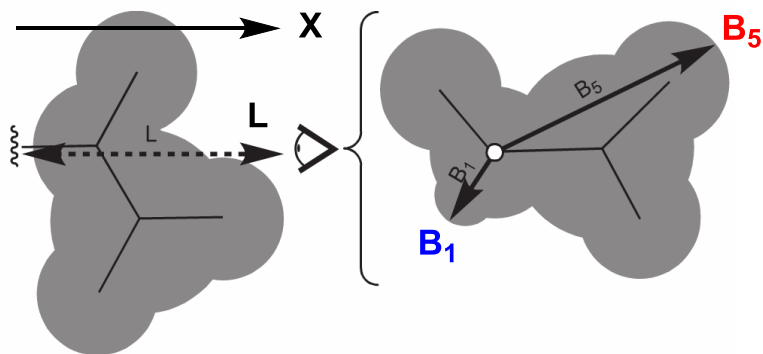
B: Percent Buried Volume (%Vbur) Parameter²⁾

"The space occupied by the ligand in the first coordination sphere of the metal center"

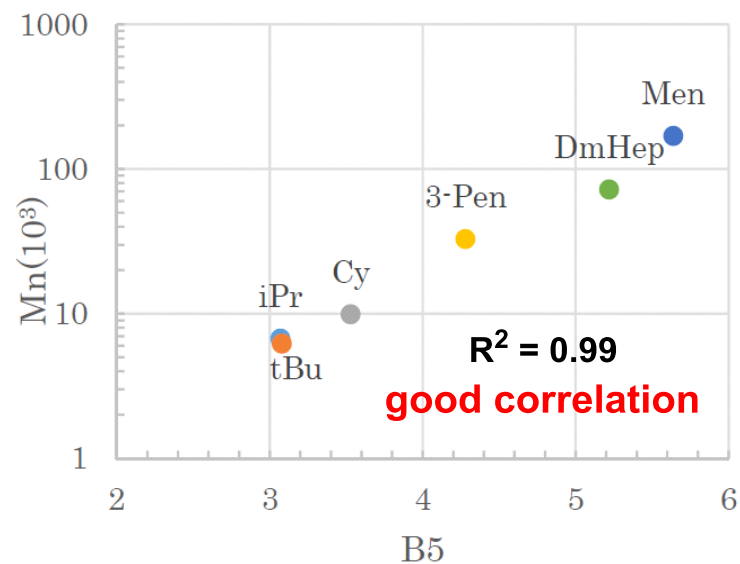
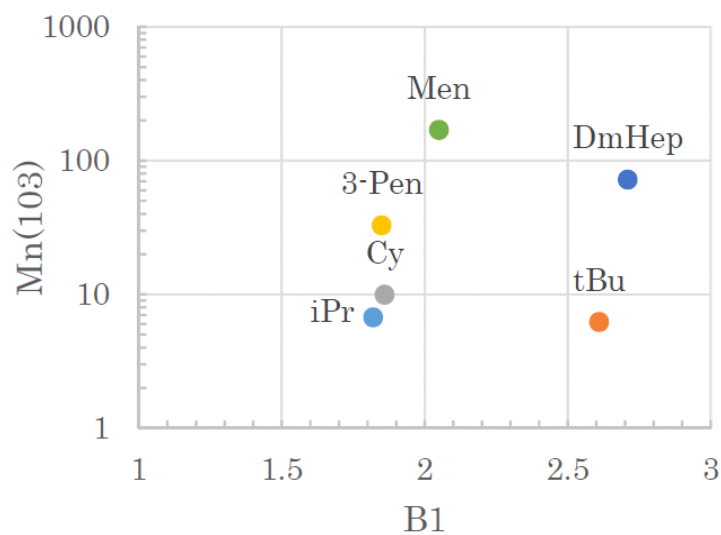


Evaluation of Steric Effect of Ligands

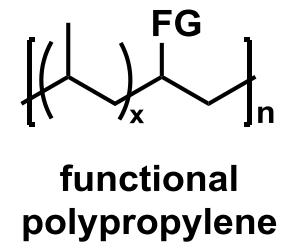
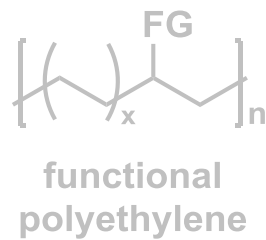
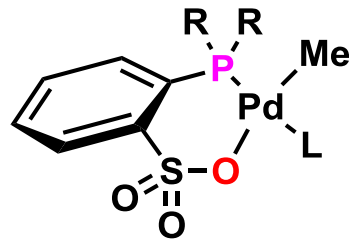
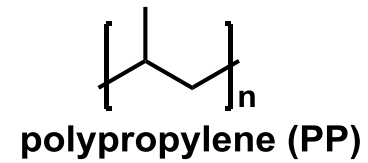
C: Sterimol B1/B5 Parameter



L: maximum width along the bonding axis, X
B₁: **minimum** width when viewed down from X
B₅: **maximum** width when viewed down from X

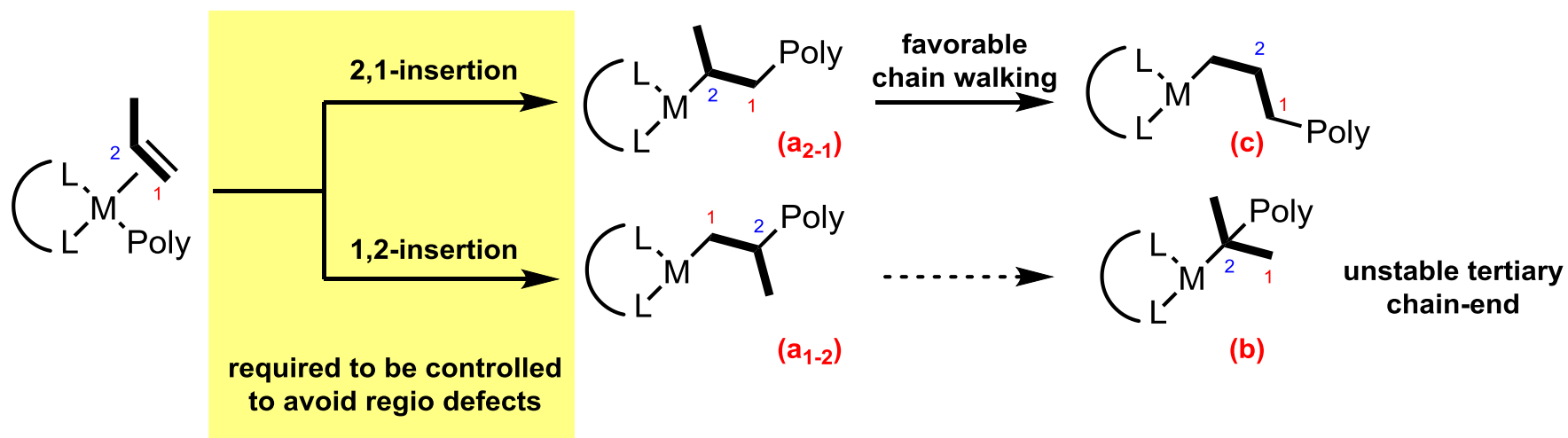
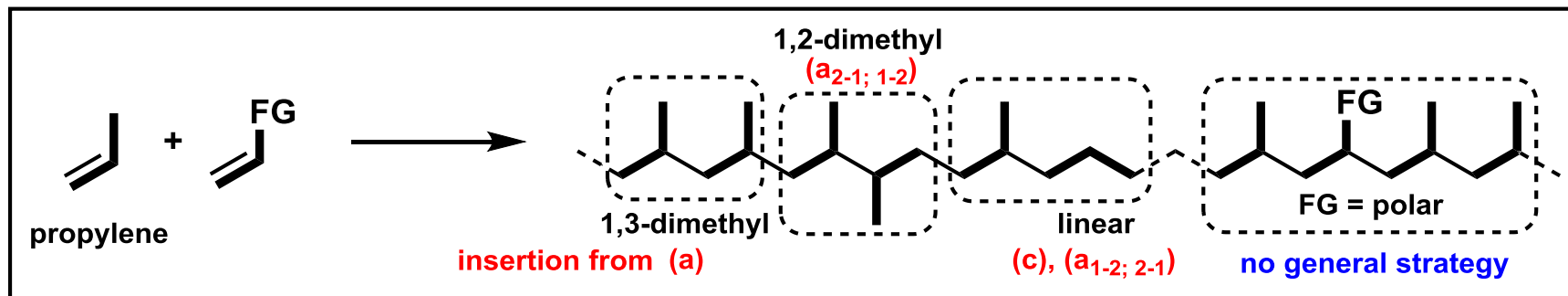


Polypropylene

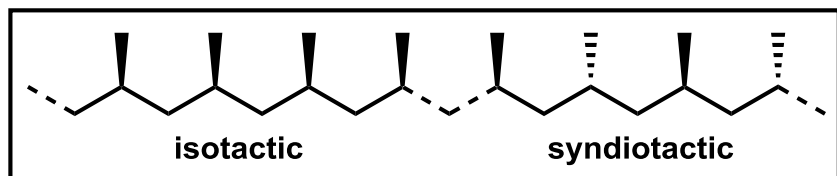


Polypropylene: Regio/Stereo-Control

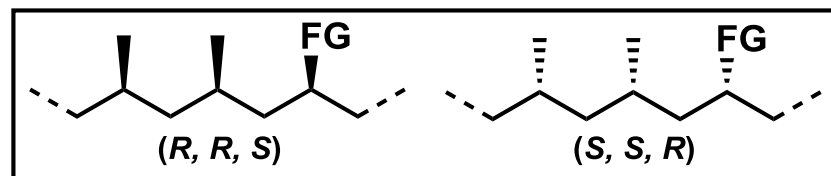
A. regio-control



B. tacticity control



C. enantio-control

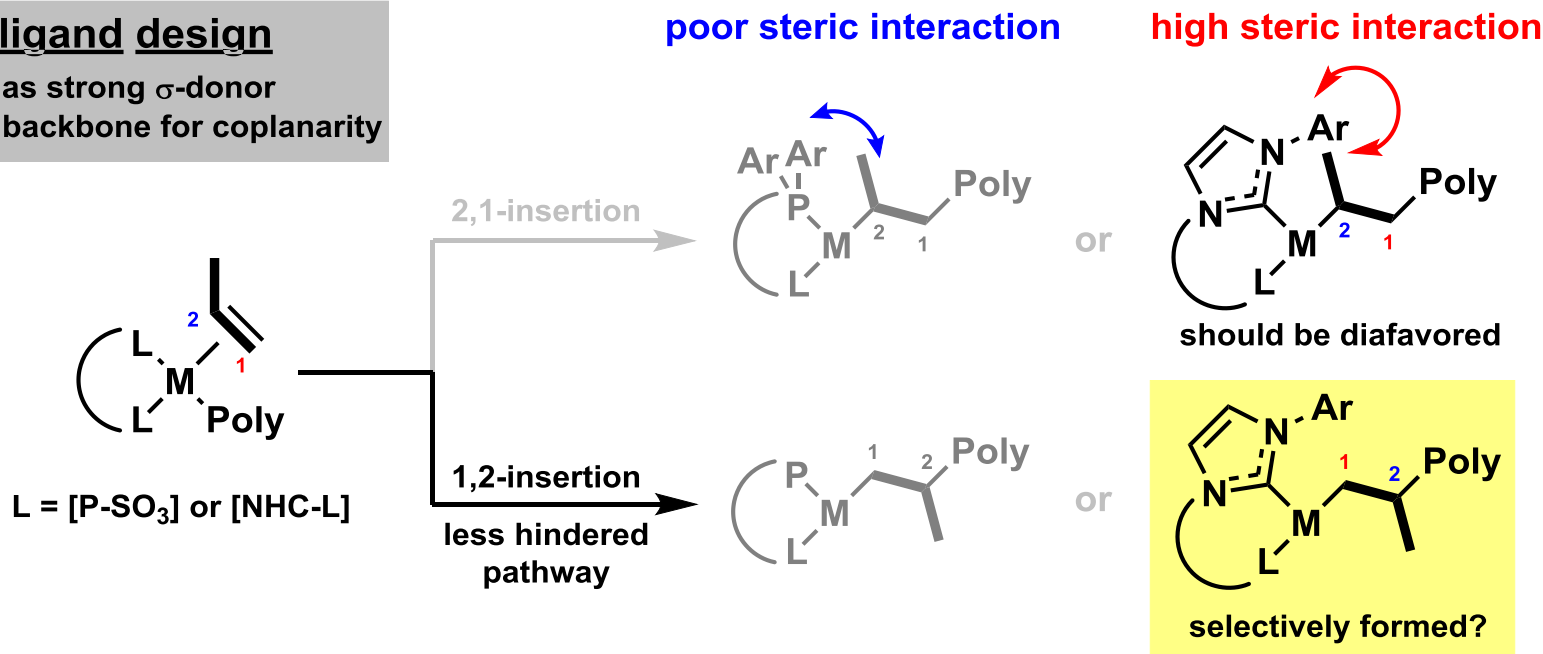


Steric Control & Rigid Backbone for Coplanarity

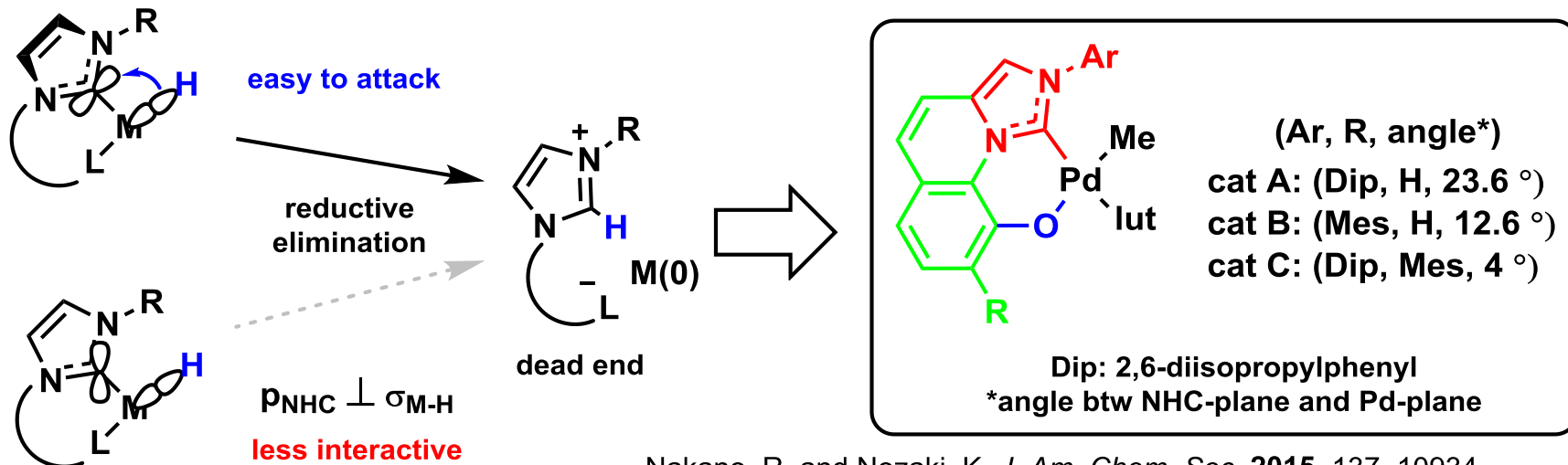
ligand design

1. NHC as strong σ -donor
2. rigid backbone for coplanarity

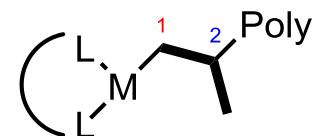
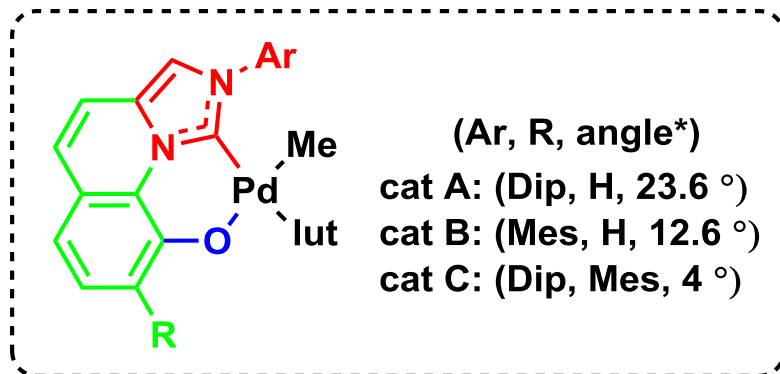
1



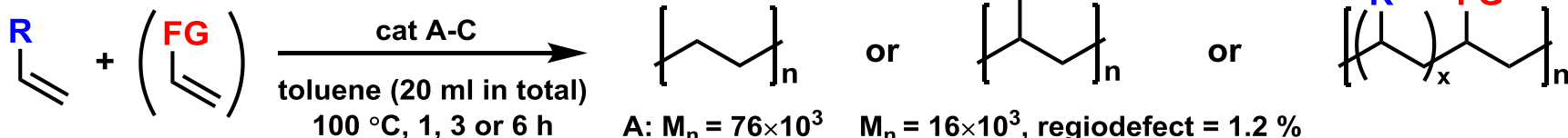
2



Propylene × Polar Monomers



desired
1,2-insertion



A: $M_n = 76 \times 10^3$
 B: $M_n = 19 \times 10^3$
 C: $M_n = 51 \times 10^3$

$M_n = 16 \times 10^3$, regiodeflect = 1.2 %
 $M_n = 2.1 \times 10^3$, regiodeflect = 2.1 %
 $M_n = 18 \times 10^3$, regiodeflect = 1.4 %

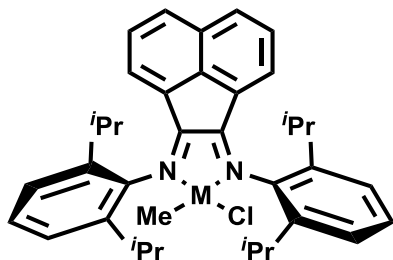
see below

R = Me (propylene)

	 0.01 ml (A) 0.005 ml (C)	 0.1 ml	 0.1 ml
cat A	$M_n = 3.0 \times 10^3$, $M_w/M_n = 2.2$ i.r. = 1.5 %, regiodeflect = 0.9 %	$M_n = 3.9 \times 10^3$, $M_w/M_n = 2.2$ i.r. = 2.0 %, regiodeflect = 1.6 %	$M_n = 7.7 \times 10^3$, $M_w/M_n = 2.4$ i.r. = 1.2 %, regiodeflect = 1.3 %
cat C	$M_n = 3.0 \times 10^3$, $M_w/M_n = 3.0$ i.r. = 1.1 % regiodeflect = not mentioned	$M_n = 11 \times 10^3$, $M_w/M_n = 2.3$ i.r. = 0.9 %, regiodeflect = 1.3 %	$M_n = 13 \times 10^3$, $M_w/M_n = 2.5$ i.r. = 0.5 %, regiodeflect = 1.6 %

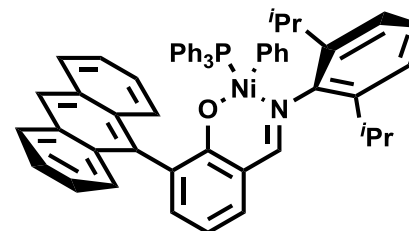
no stereo control here (appendix 8 for stereo controlled copolymer)

Summary



Brookhart type

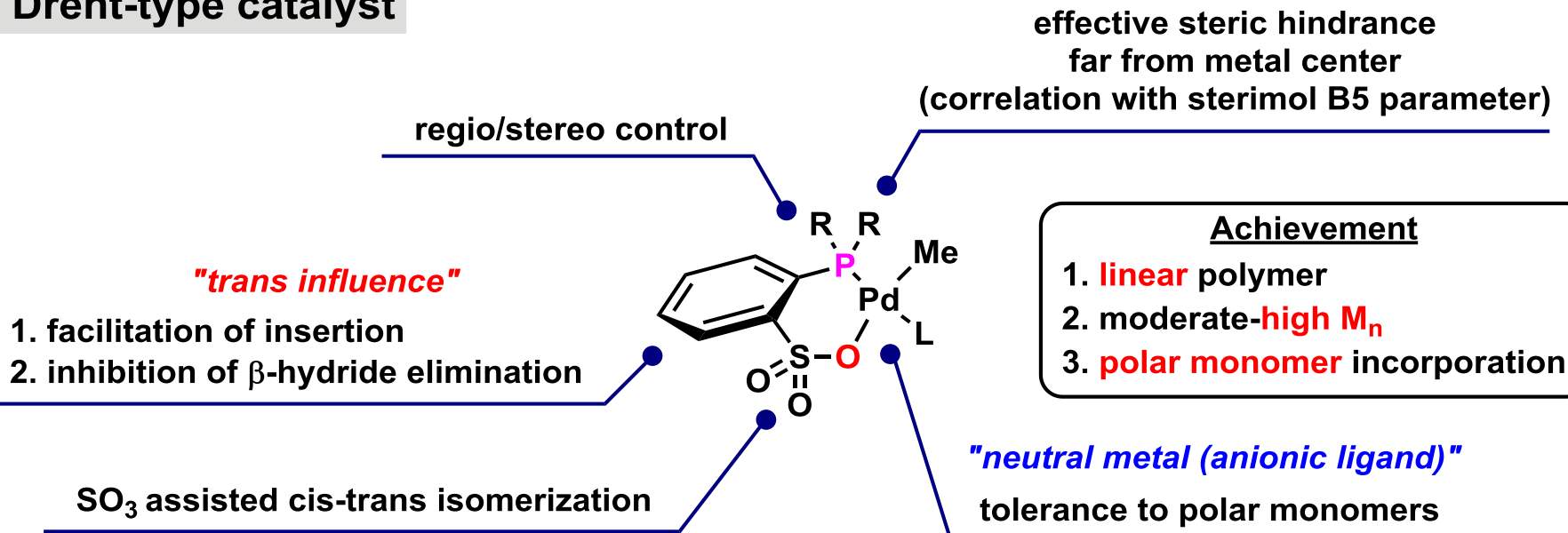
1. branched polymer with high M_n
2. unstability at high temperature
3. low polar monomer tolerance



Grubbs type

1. linear polymer with high M_n
2. unstability due to reductive elimination
3. low polar monomer tolerance

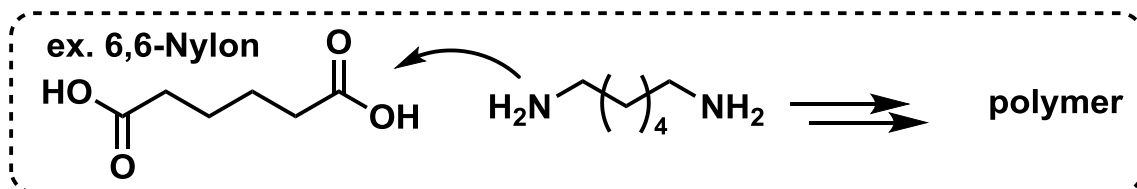
Drent-type catalyst



Appendix

1. Classification by Carothers: Reaction Mechanism

1) Condensation Polymerization

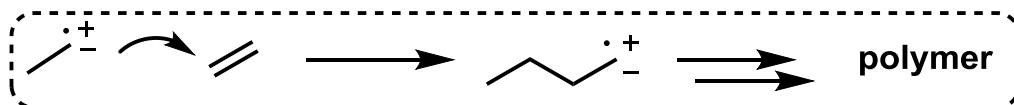


2) Addition Polymerization

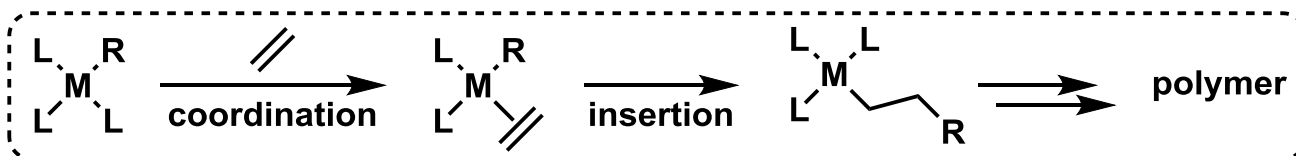
2-1) radical (ex. RAFT/ATRP/NMP)

2-2) cationic

2-3) anionic



* Coordination-Insertion Polymerization



* Metathesis Polymerization

1) Ring Opening Metathesis Polymerization (ROMP)

2) Acyclic Diene Metathesis Polymerization (ADMET)



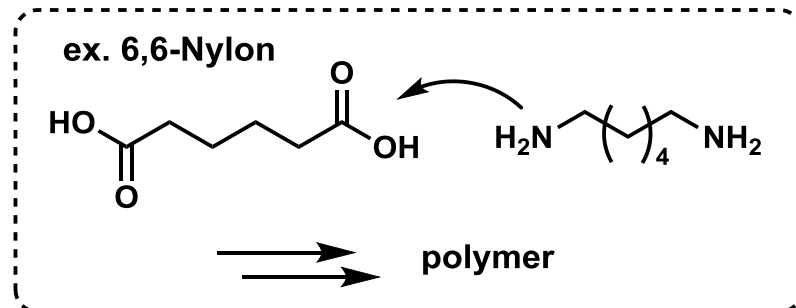
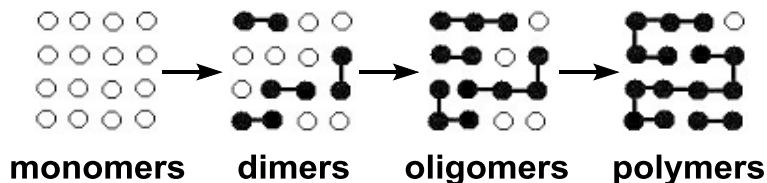
Wallace Hume Carothers
(1896-1937, Du Pont)

2. Classification by Flory: Active Reaction Site

1) Step Growth Polymerization

"reactions everywhere in a system"

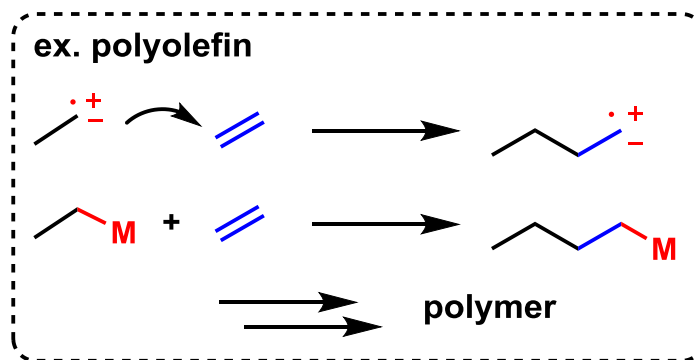
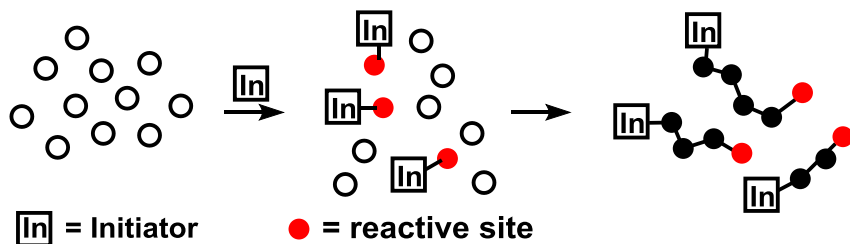
(two FGs at the both ends of monomer to react with)



2) Chain Growth Polymerization

"propagation of reactive site"

(radicals, ions, metal complexes, etc)



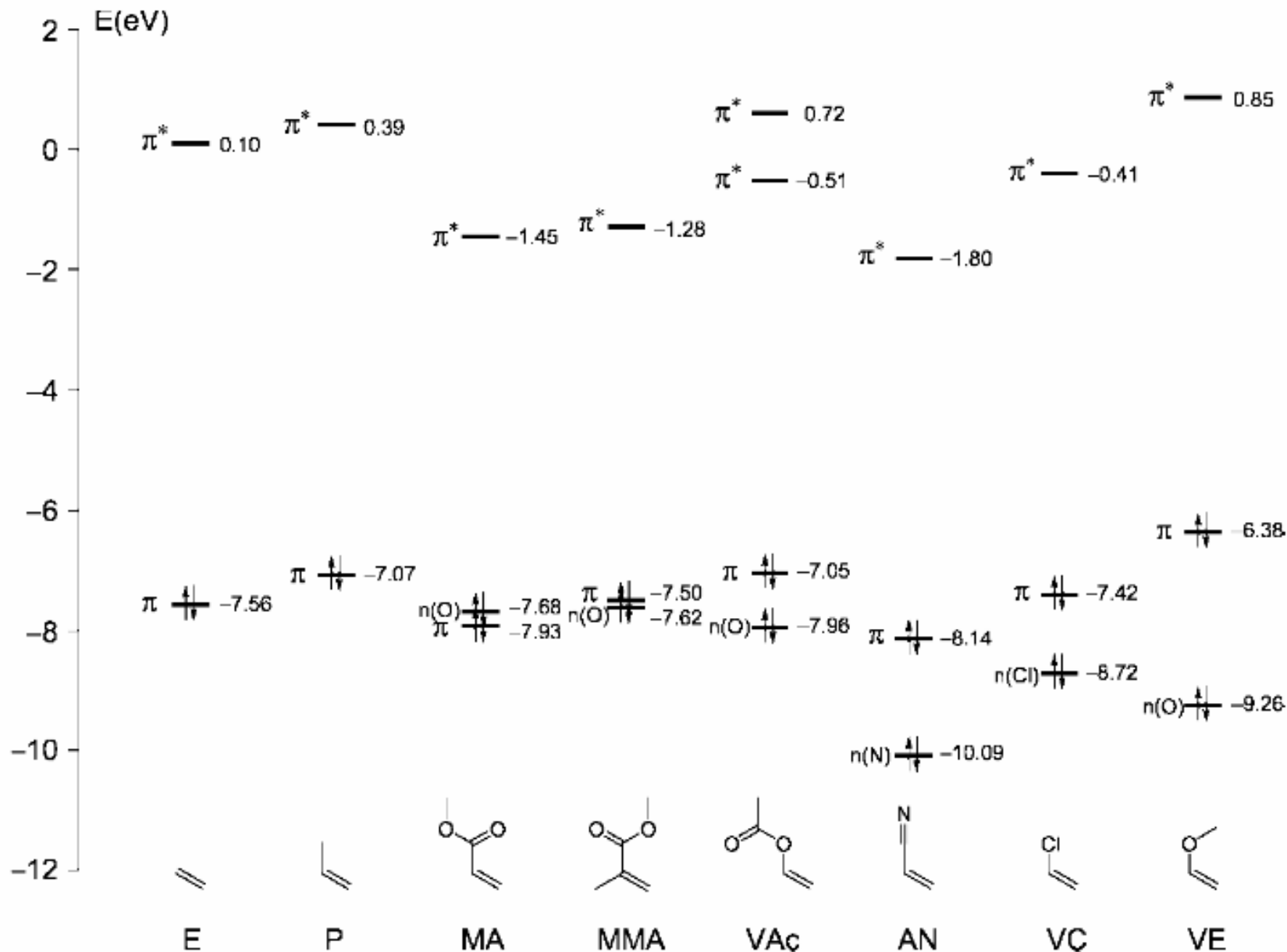
* Living Polymerization

- 1) chain polymerization without 3 & 4
- 2) Initiation rate > propagation rate

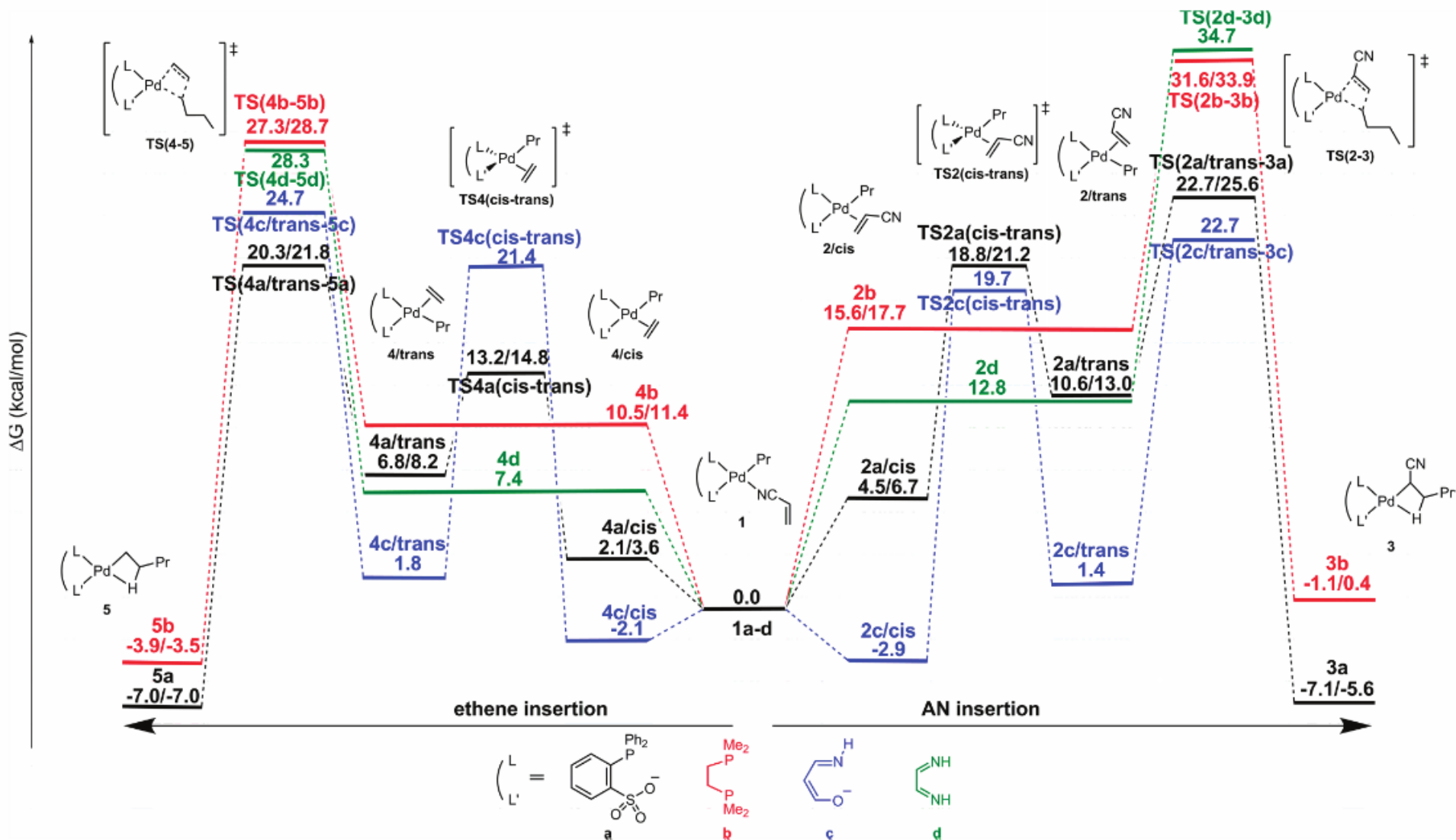


Paul John Flory
(1910-1985)
Nobel Prize in chemistry (1974)

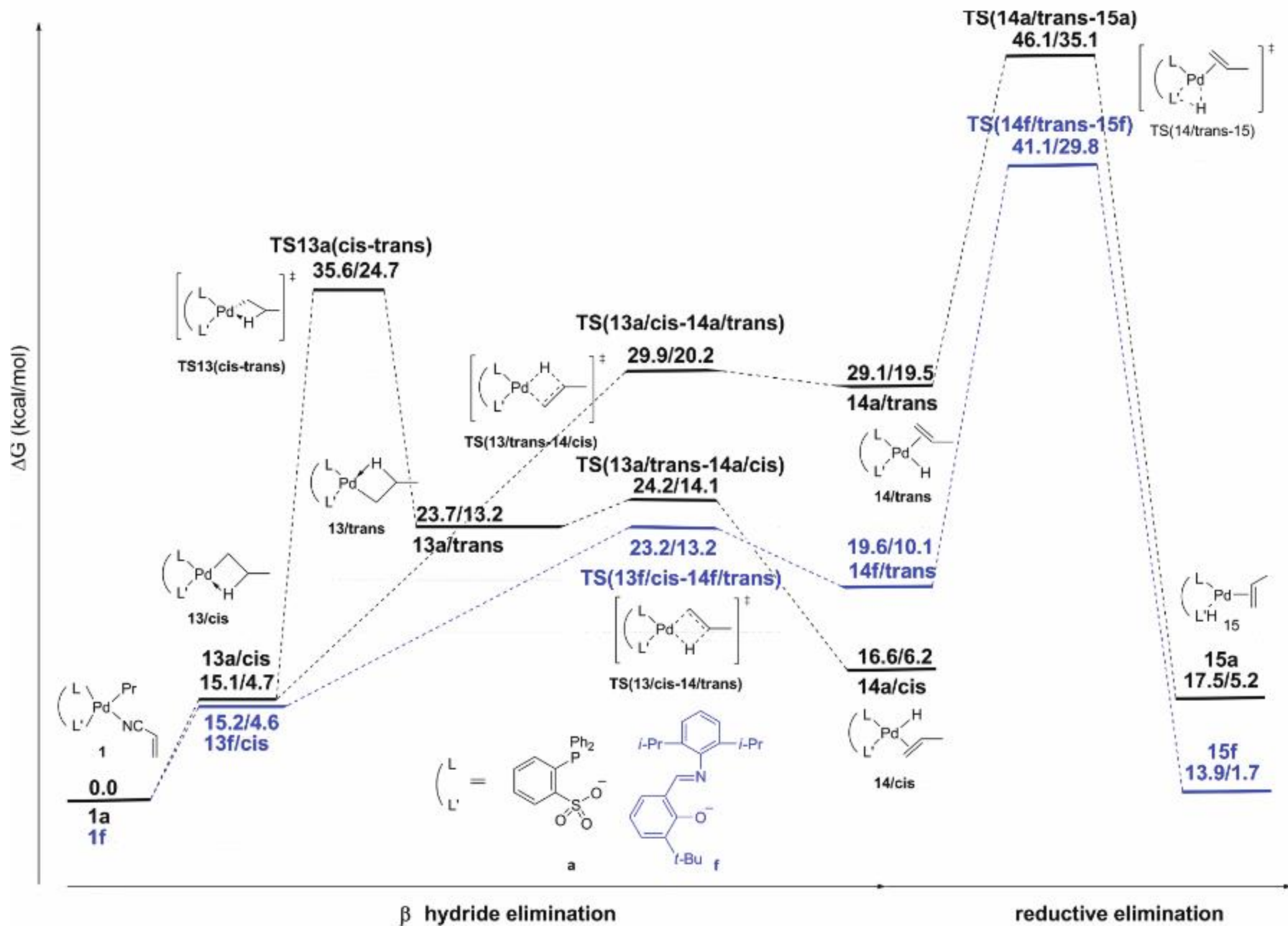
3. Key MO of Polar Monomers



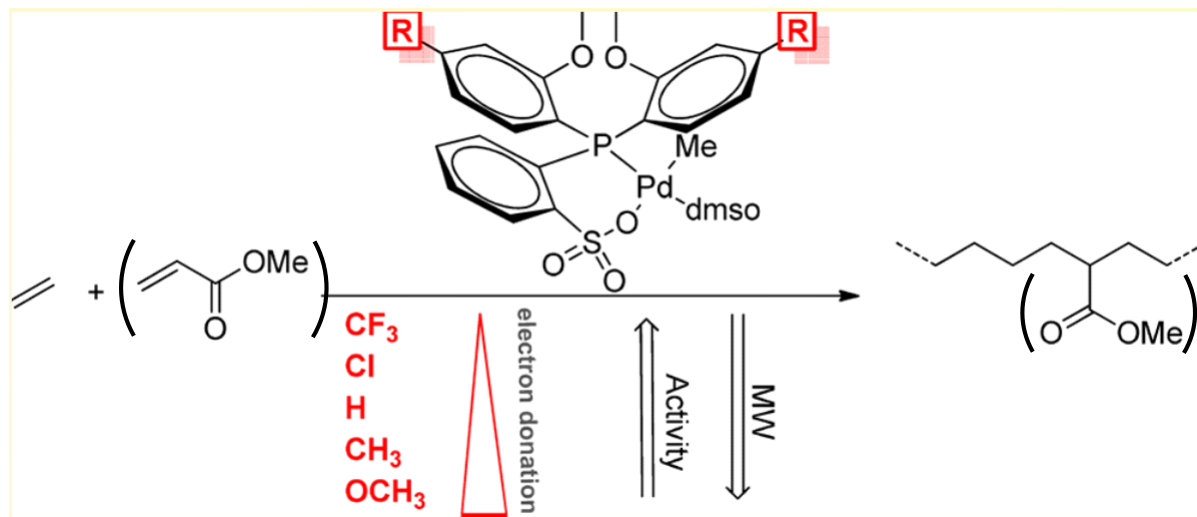
4. Ethylene and AN Insertion



5. Reductive Elimination



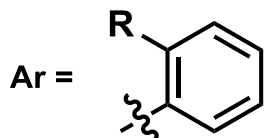
6. Electronic Effect



Mecking, S. *et al. Organometallics*. 2013, 32, 4516.

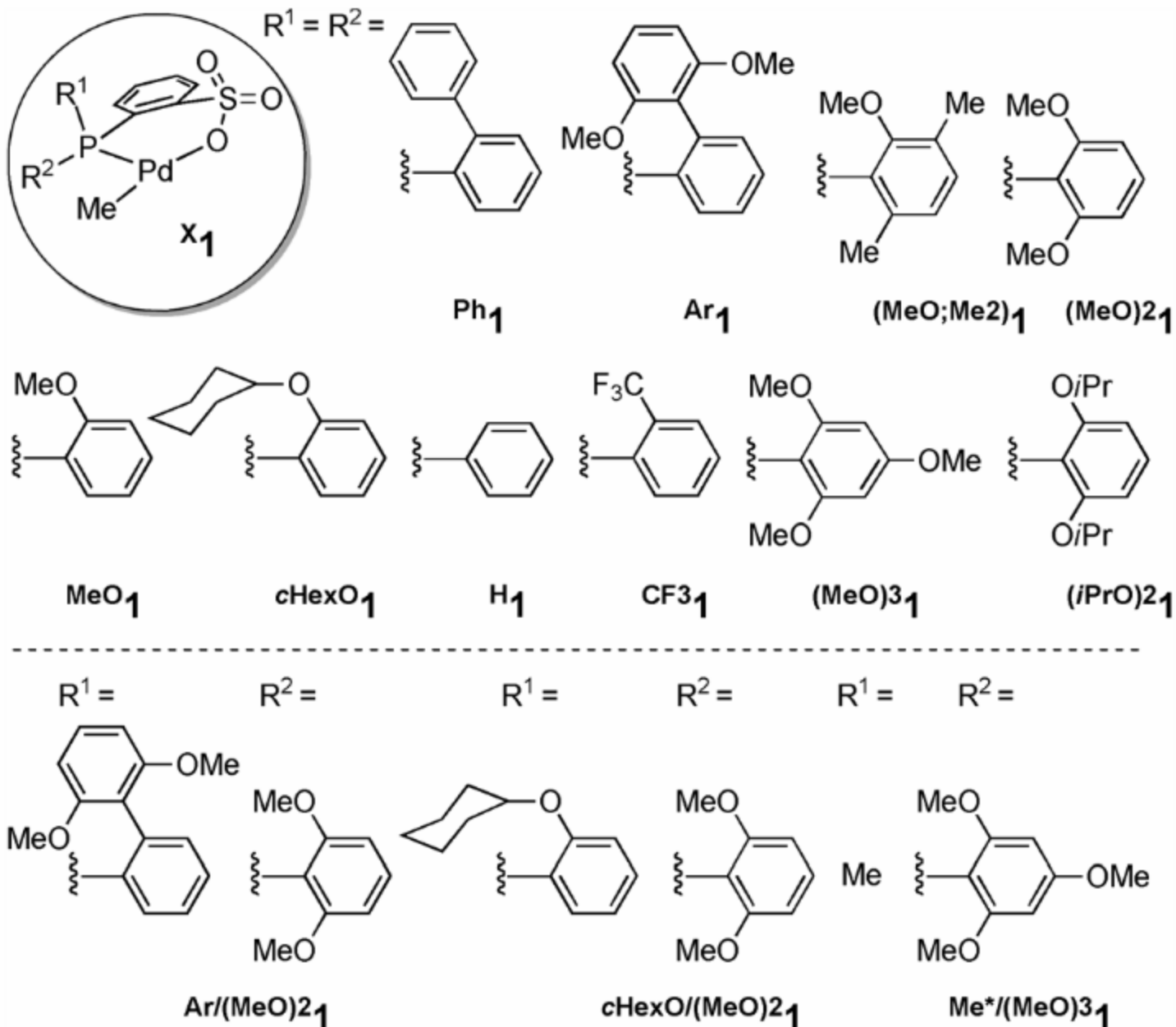
clear tendency of electronic effect,
but it has only small effect on M_n (ex. M_n -OCH₃/ M_n -CF₃ = ca. 2)

Ethylene Polymerization



R = OMe	($M_n = 19.1 \times 10^3$, $M_w/M_n = 2.1$, 3.0 MPa, 80 °C)	Jordan, R. F. <i>et al.</i>
Et	($M_n = 18.8 \times 10^3$, $M_w/M_n = 2.1$, 3.0 MPa, 80 °C)	<i>Organometallics</i> . 2007, 26, 6624.
OMe	($M_w = 33 \times 10^3$, $M_w/M_n = 1.7$, 2.0 MPa, 50 °C)	Rieger B. <i>et al.</i>
SMe	($M_w = 500 \times 10^3$, $M_w/M_n = 6.3$, 2.0 MPa, 50 °C)	<i>Organometallics</i> . 2011, 30, 6602.

7. Steric Effect



8. Steric Effect

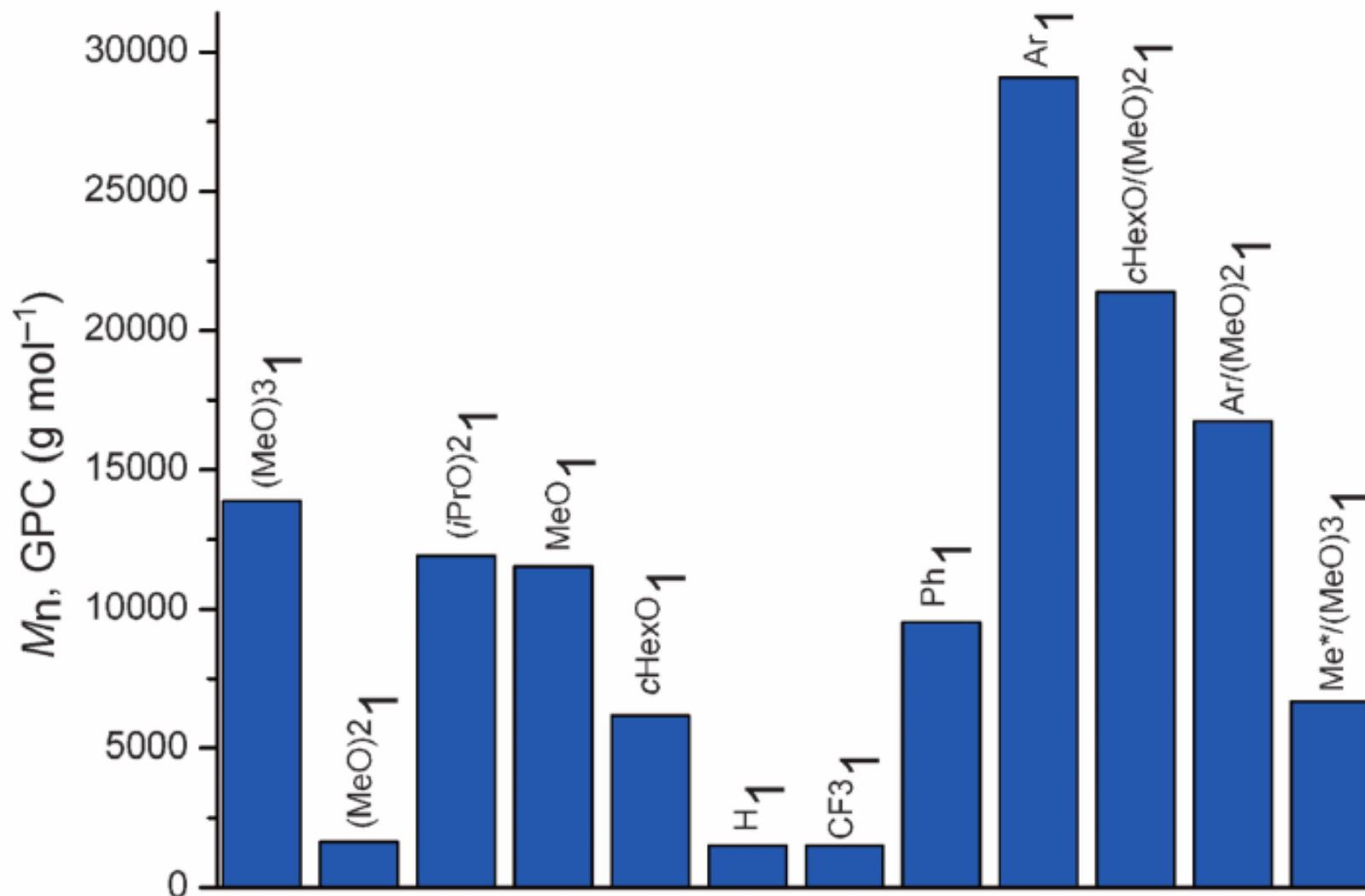
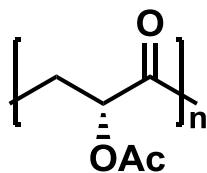
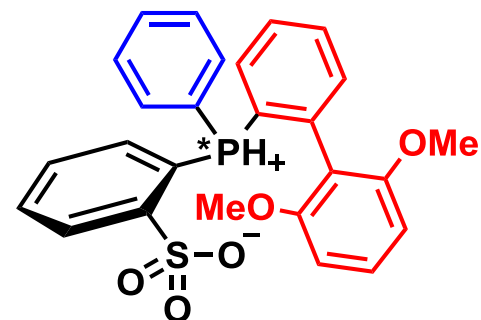
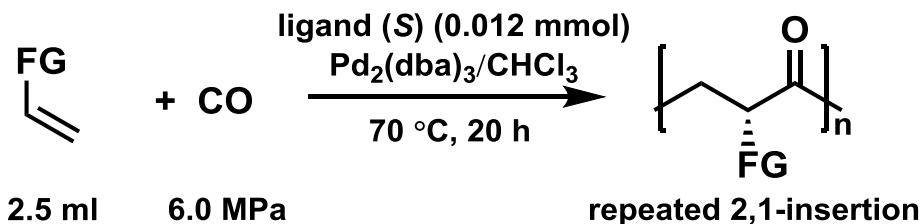


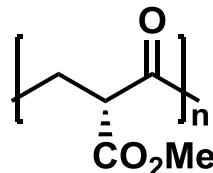
Figure 9. Molecular weights (M_n) of polyethylene obtained with different catalysts ($p_{\text{C}_2\text{H}_4} = 5 \text{ bar}$, 80°C).

9. Optically-Active Isotactic Polyketone (Stereo Control)

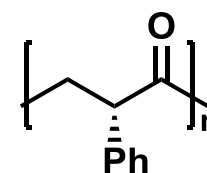
B/C. tacticity/enantioselectivity control



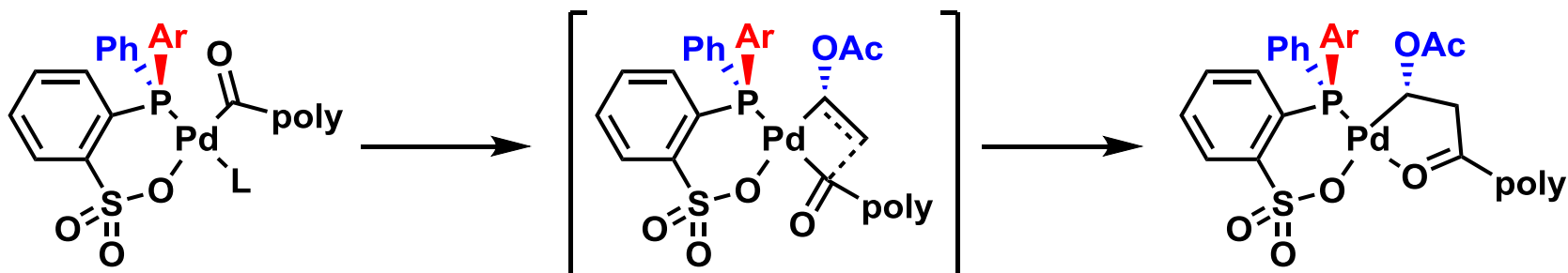
$M_n = 20 \times 10^3$, $M_w/M_n = 1.8$
 regio defect = 10%
 $[\Phi]_D^{22} = -8.5$ (c = 0.32, CHCl₃)



$M_n = 10 \times 10^3$, $M_w/M_n = 1.2$
 regio defect < 1%
 $[\Phi]_D^{22} = +4.4$ (c = 0.32, CHCl₃)



$M_n = 12 \times 10^3$, $M_w/M_n = 1.1$
 regio defect < 1%
 $[\Phi]_D^{22} = +463$ (c = 0.053, CHCl₃)



Nozaki, K. *et al.* *J. Am. Chem. Soc.* **2012**, 134, 12366

10. Selected Topics Uncoverd in This Seminar

1. Cationic Bisphosphine Monoxide Palladium Catalyst for Polar Monomer Incorporation

Nozaki, K. *et al. J. Am. Chem. Soc.* **2012**. 134. 8802

2. Polymerization of Non-Polar Monomers Using Rare-Earth Metal Dialkyl Complexes

Hou, Z. *et al. Nat. Chem.* **2010**. 2. 257

3. Modern Polymerization Techniques (Review in Japanese: RAFT/NMP/ATRP)

https://www.sigmaaldrich.com/content/dam/sigma-aldrich/docs/SAJ/Brochure/1/saj1227_mm5-1.pdf

4. Metal-Catalyzed Living Radical Polymerization (Review)

Kamigaito, M. *et al. Chem. Rec.* **2004**. 4. 159

Kamigaito, M. *Polym. J.* **2011**. 43. 105

5. "Controlled Radical Polymerization: Industrial Stakes, Obstacles and Achievements" (Review)

Destarac, M. *Macromole. React. Eng.* **2010**. 4. 165

6. "Post-Metallocenes in the Industrial Production of Polyolefins" (Review)

Mecking, S. *et al. Angew. Chem. Ed. Int.* **2014**. 53. 9722

7. Polymer Blend Enabled by Porous Coordination Polymers (PCPs)

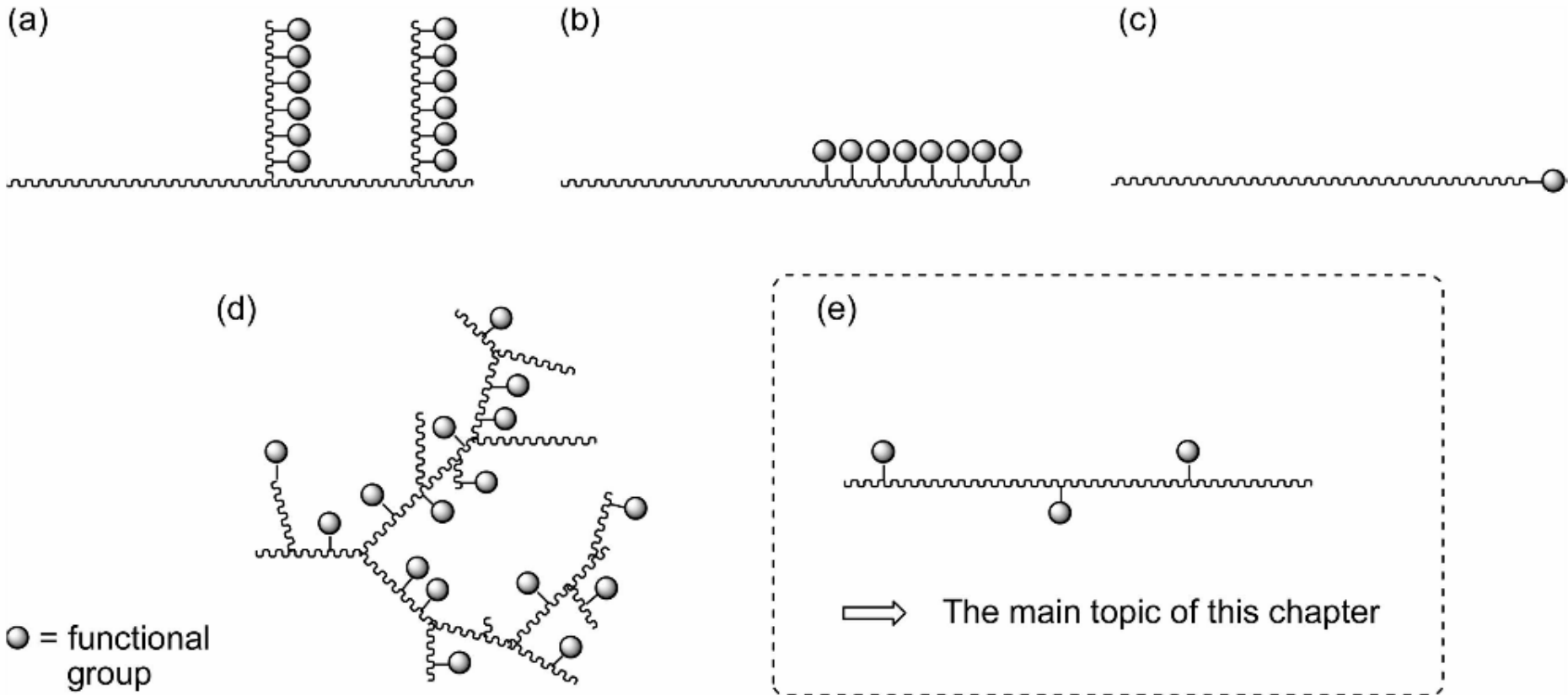
Kitagawa, S. *et al. Nat Commun.* **2015**. 6. 7473

8. Data Storage Using Sequence-Controlled Polymers

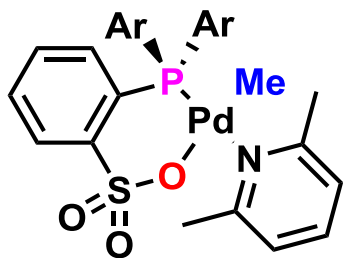
Lutz, J. F. *et al. Nat Commun.* **2015**. 6. 7237

Lutz, J. F., Sawamoto, M. *et al. Science.* **2013**. 341. 1238149

Classification of Copolymers

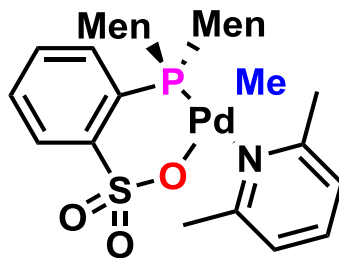


X-ray

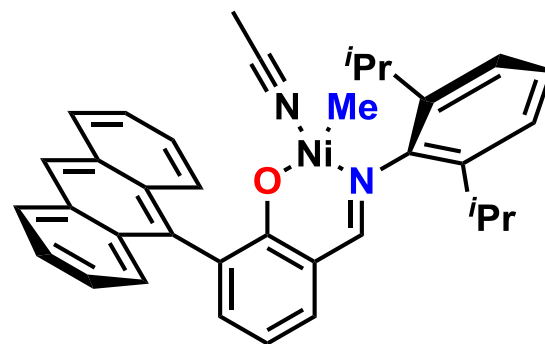


Ar = 2-OMe-Ph

bond	X-ray (calculation)
Pd-C	2.134 (2.056)
Pd-N	2.134 (2.181)
Pd-O	2.159 (2.190)
Pd-P	2.234 (2.311)



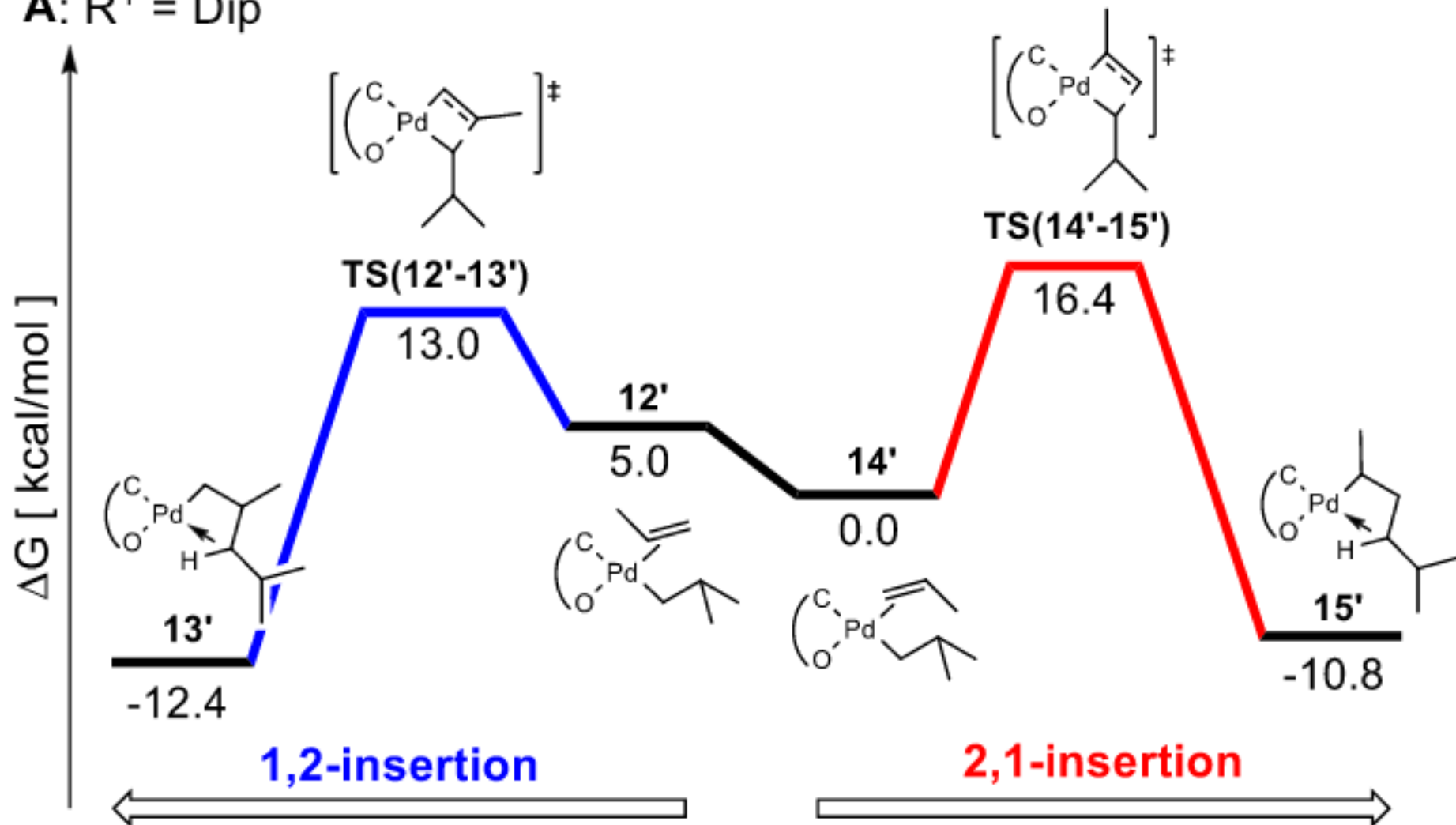
Pd-C	2.062
Pd-N	2.150
Pd-O	2.140
Pd-P	2.247



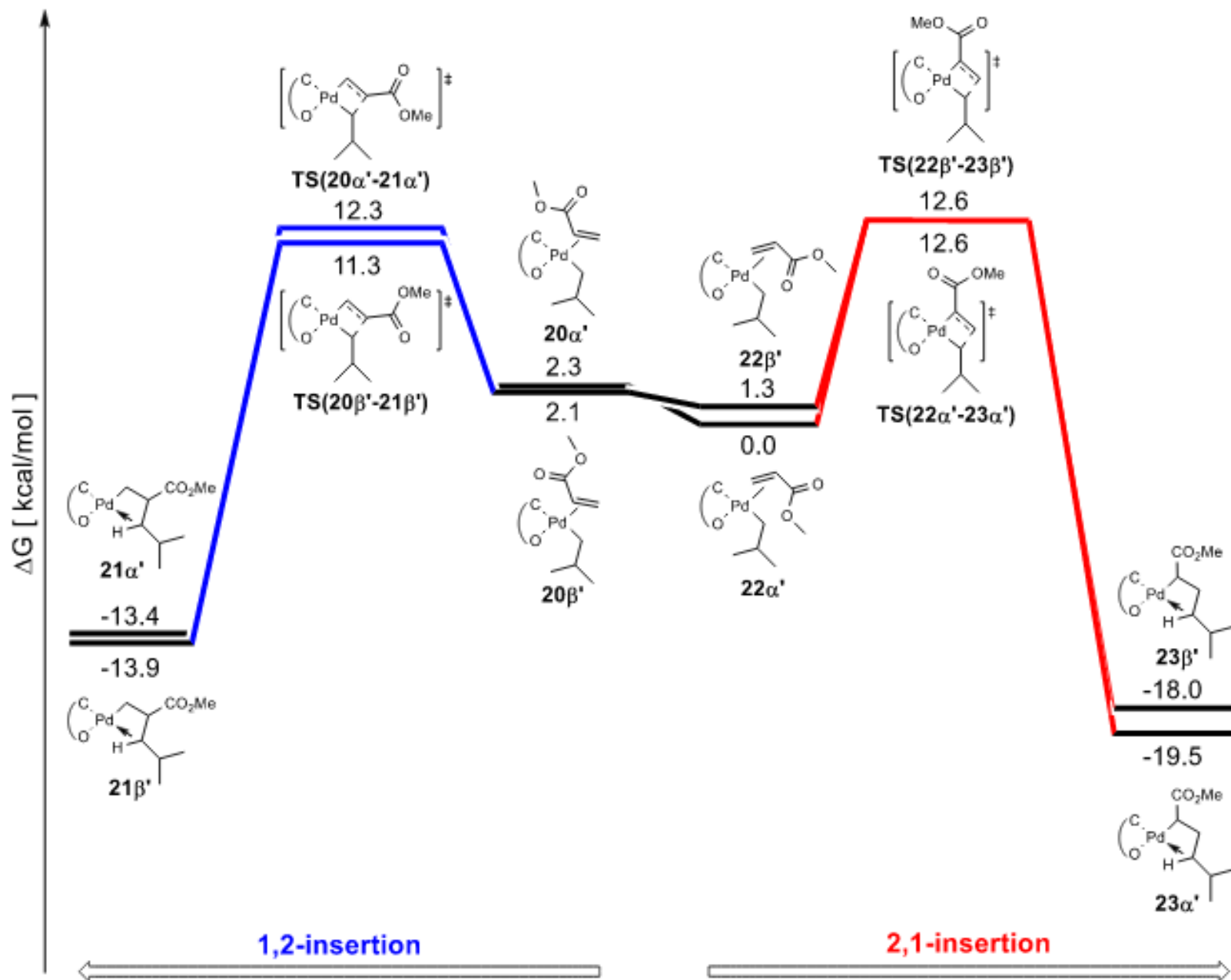
Ni-C	1.931
Ni-N	1.859
Ni-O	1.911
Ni-N	1.887

DFT calculation for Catalyst A

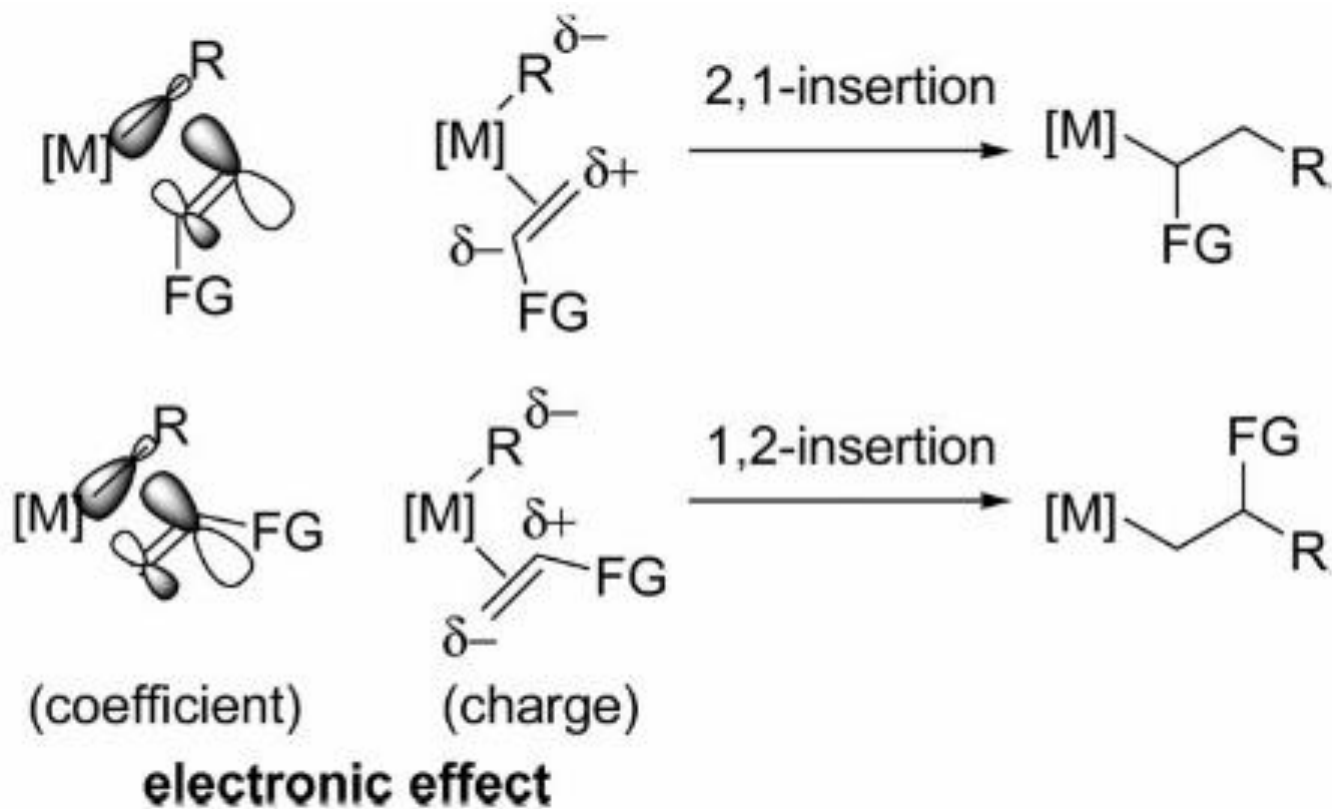
A: $R^1 = \text{Dip}$



DFT calculation for Catalyst A



Regioselectivity



Other Catalysts Trials

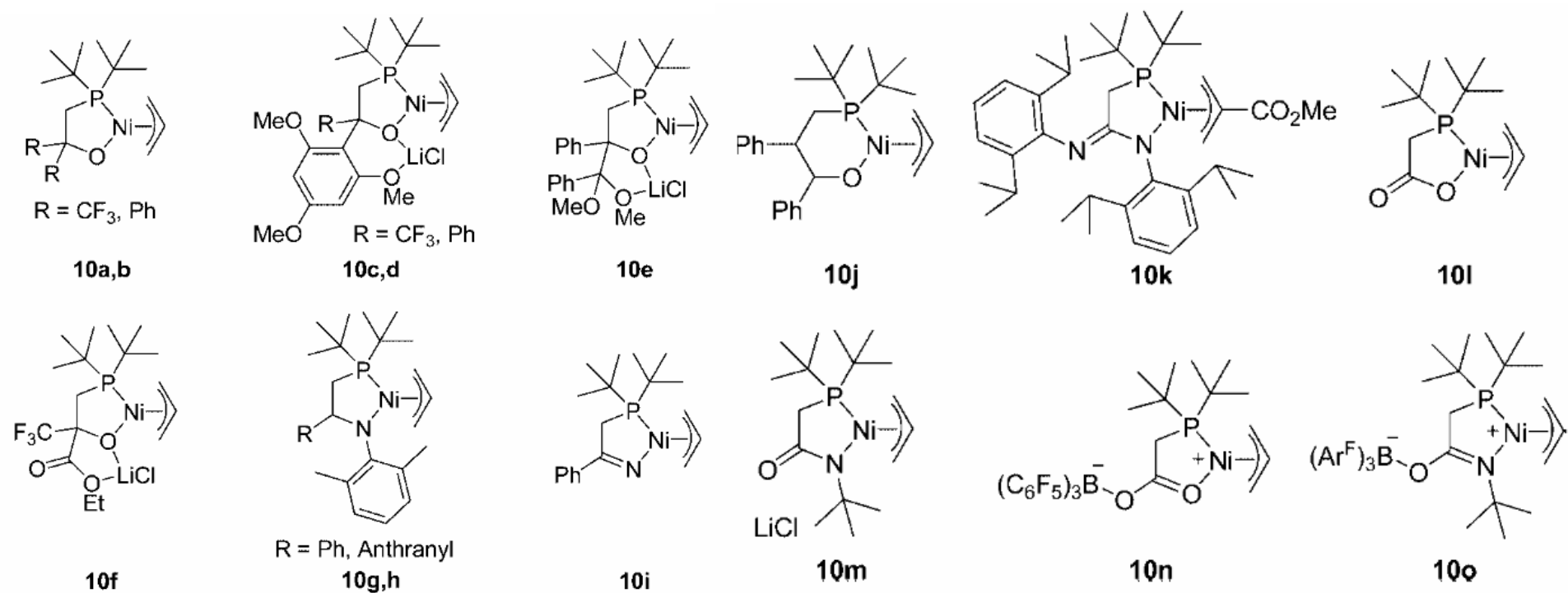
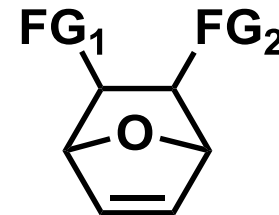
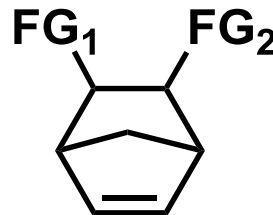
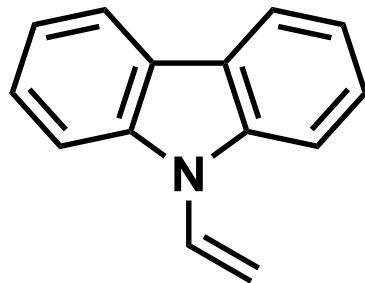
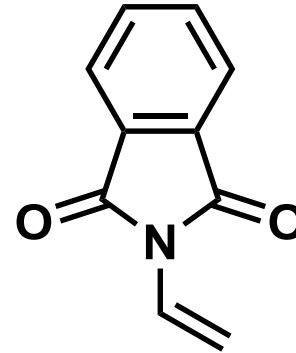
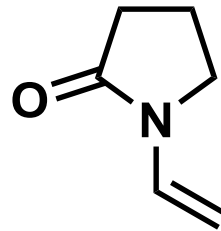
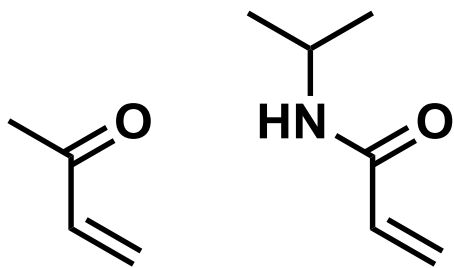
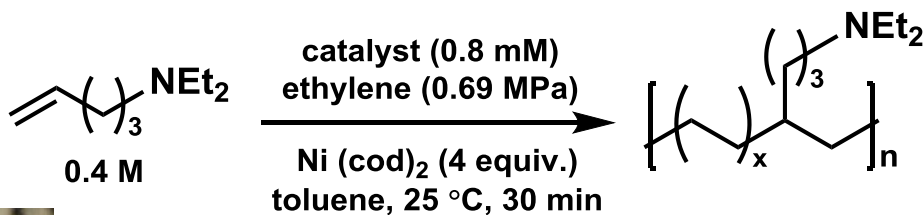


Figure 10. Phosphine-based neutral Ni catalysts reported by Johnson et al.^{60,134,135}

Other Polar Monomers

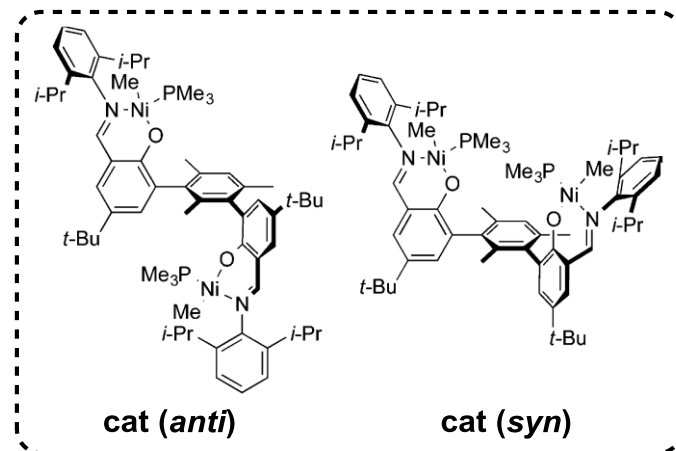


Bimetallic system (Grubbs-Type)

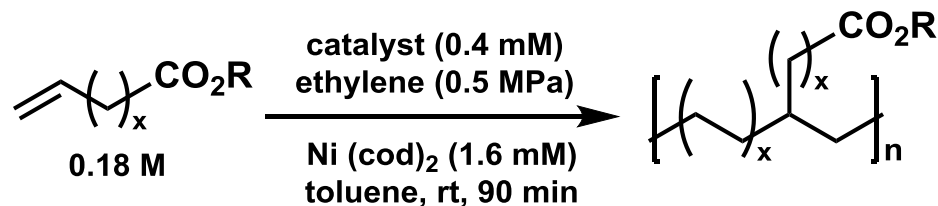


Agapie (Caltech)

	activity catalyst (kg mol ⁻¹ h ⁻¹) (mol %)	i.r. (mol %)
<i>anti</i>	8	0.7
<i>syn</i>	45	0.3



Agapie, T. *et al.* *J. Am. Chem. Soc.* **2013**, 135, 3874.

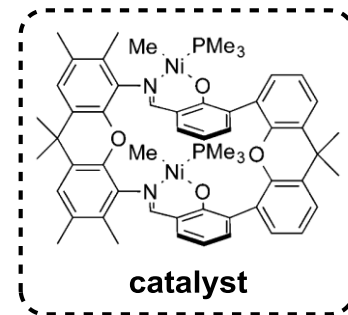


<i>x</i>	R	av activity ^b	Me branches per 1000 C	<i>M_n</i>	<i>M_w</i> / <i>M_n</i>	incorp (mol %)
0	Me					
1	<i>t</i> -Bu	0.10	35	nd ^c	nd ^c	1.4
2	Et	0.25	32	2700 ^d	6.5 ^d	0.4



Osakada

^acod = 1,5-cyclooctadiene. ^bIn kg (mol Ni)⁻¹ h⁻¹. ^cNot determined. ^dBimodal molecular weight distribution.



- i. **longer life time** than mononuclear catalyst
- ii. **improvement of incorporation of polar monomer**

Takeuchi, D.; Osakada, K. *et al.* *Angew. Chem. Int. Ed.* **2013**, 52, 12536.