



# Frontier of Late-transition Metals Catalysts in Ethylene Polymerization

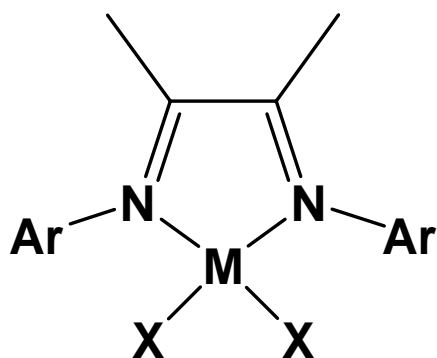
Wenjuan Zhang, Wenhong Yang, Jiangan Yu,  
Weizhen Zhao, Jingjuan Lai, Shengju Song, Liping  
Zhang, Peng Hao, Shu Zhang, Wen-Hua Sun

Key Laboratory of Engineering Plastics  
Institute of Chemistry, Chinese Academy of Sciences

Email: [whsun@iccas.ac.cn](mailto:whsun@iccas.ac.cn)  
<http://whsun.iccas.ac.cn>

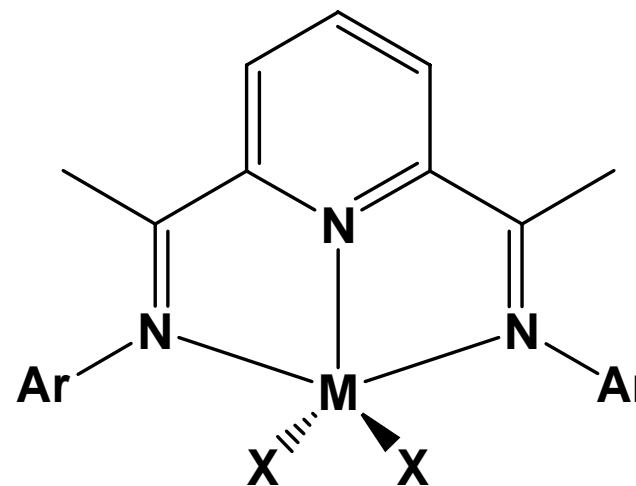


# Resurrection of Late-Transition Metal Catalysts for Ethylene Polymerization



M = Ni or Pd

M. Brookhart, et al, *J. Am. Chem. Soc.*  
1995, 117, 6414



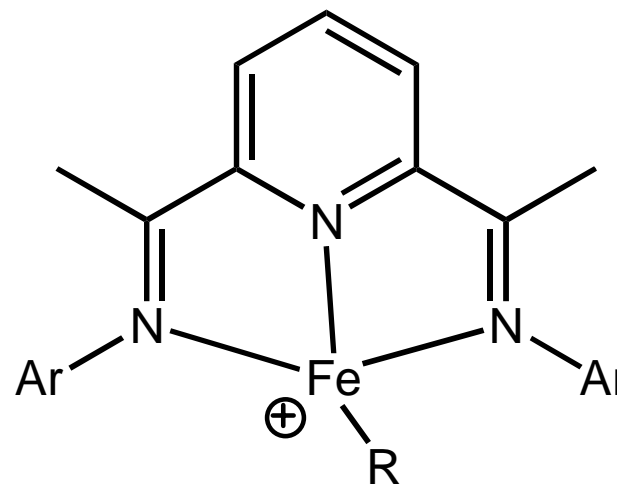
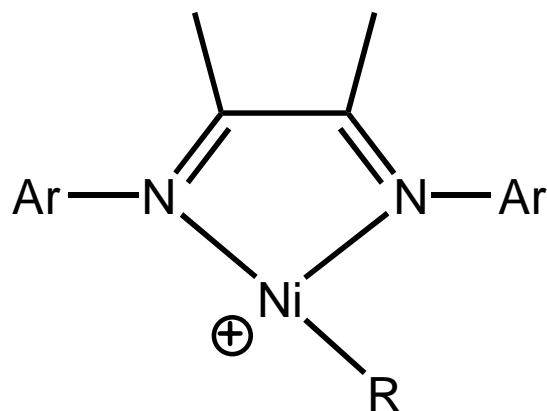
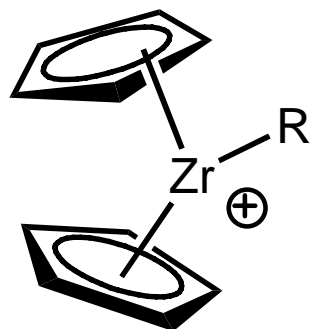
M = Fe or Co

M. Brookhart, et al, *J. Am. Chem. Soc.*  
1998, 120, 4049

V. C. Gibson, et al, *Chem. Commun.*  
1998, 849



# Hypothesis of Electronic Configuration of Model Catalysts

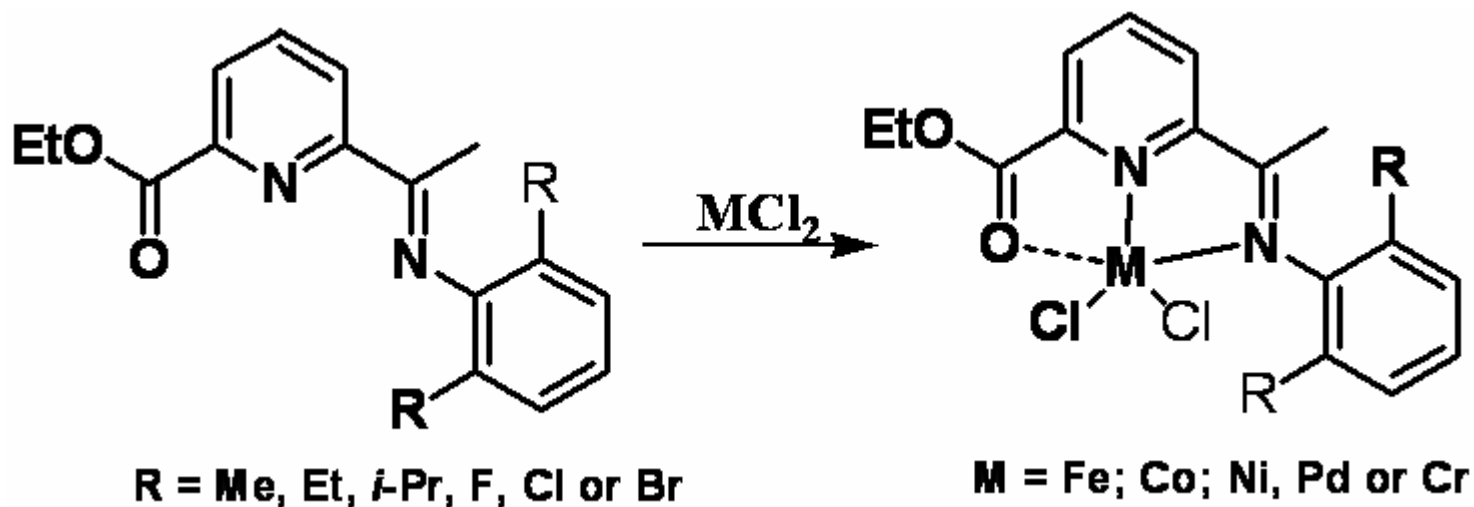


**Forming a 14e active species**

Feature article, C. R. Chim, 11 (2008) 307-316



## 6-Ester-2-iminopyridylmetal Pro-catalysts in Ethylene Reactivity



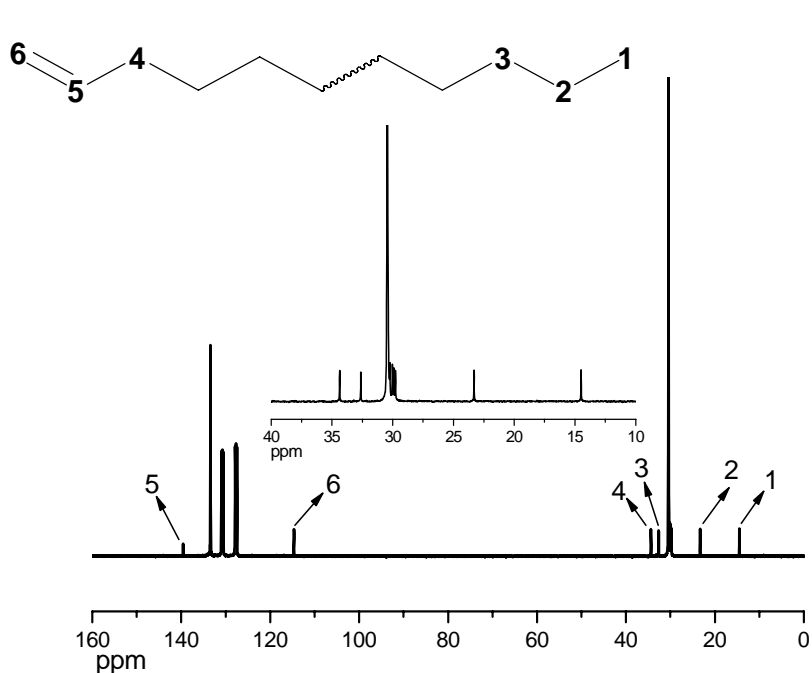
M=Fe:  $\sim 3.06 \times 10^5$  g Olig/(mol Fe·h)

M=Ni:  $\sim 10^5$  g PE/(mol Ni·h)

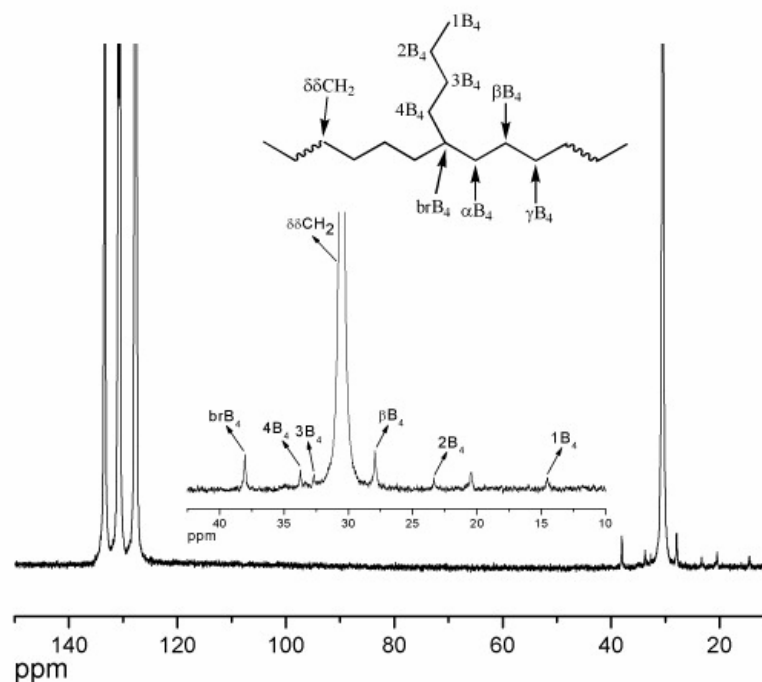
Organometallics, 2004, 23, 5037(Fe, Co); J. Organomet. Chem., 2005, 690, 1570 (Ni);  
J. Organomet. Chem., 2006, 691, 4759 (Pd); J. Mol. Catal. A: Chem., 2007, 265, 159 (Cr)



# NMR Evidences to Long-chain $\alpha$ -olefins by Fe-cat and Branched PE by Ni-cat



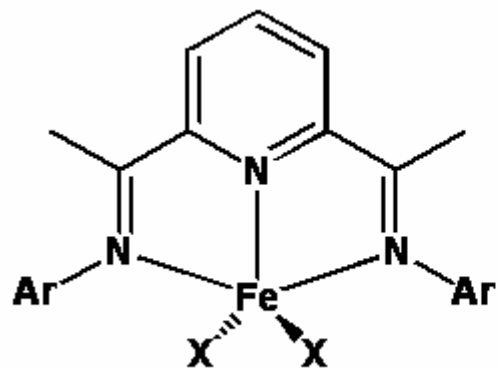
Organometallics, 2004, 23, 5037



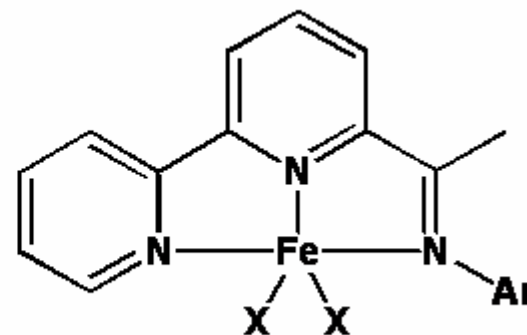
J. Organomet. Chem., 2005, 690, 1570



# Iron Pro-catalysts bearing NNN Ligands

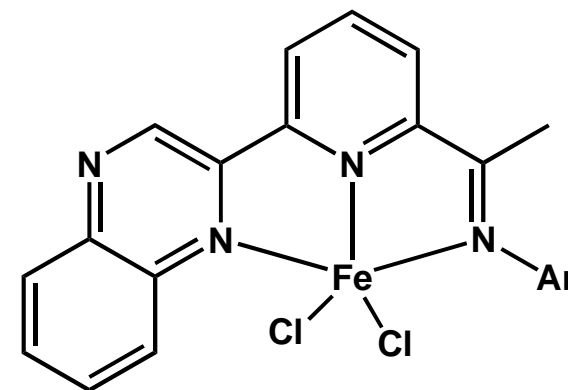
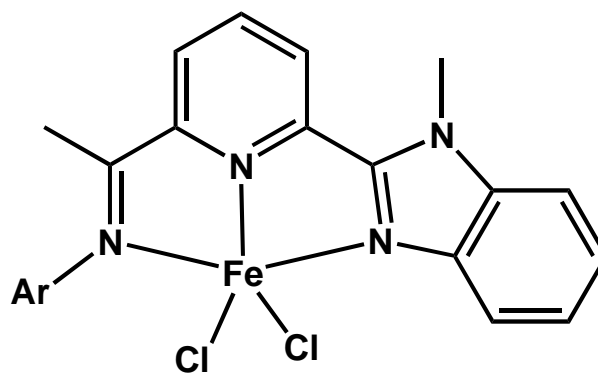
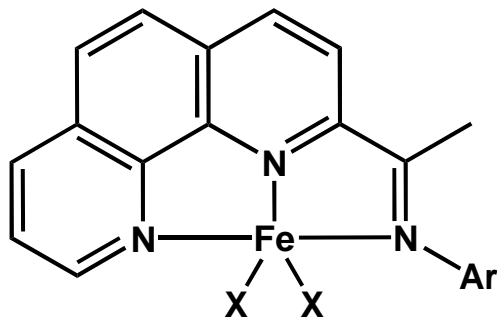


1998



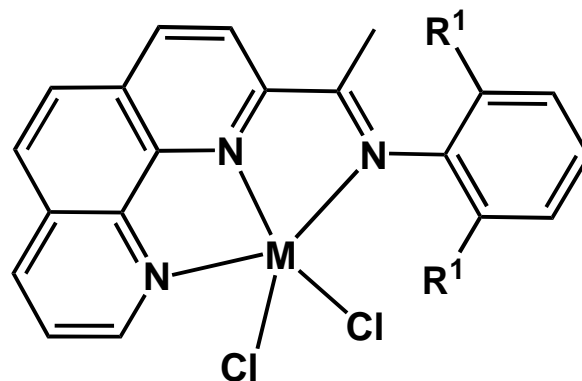
$10^5$  g Olig / (mol M·h)

Gibson, V.C. et al. *Inorg. Chem. Acta*, 2003, 345, 279





# Highly Active Procatalysts Bearing 2-Imino-1,10-phenanthrolines



M = Fe, Co, Ni, Cr

*Organometallics*, 2006, 25, 666-677. (Fe)  $\sim 10^7$  g Olig/(mol Fe·h)

——One of most-accessed and most-cited articles

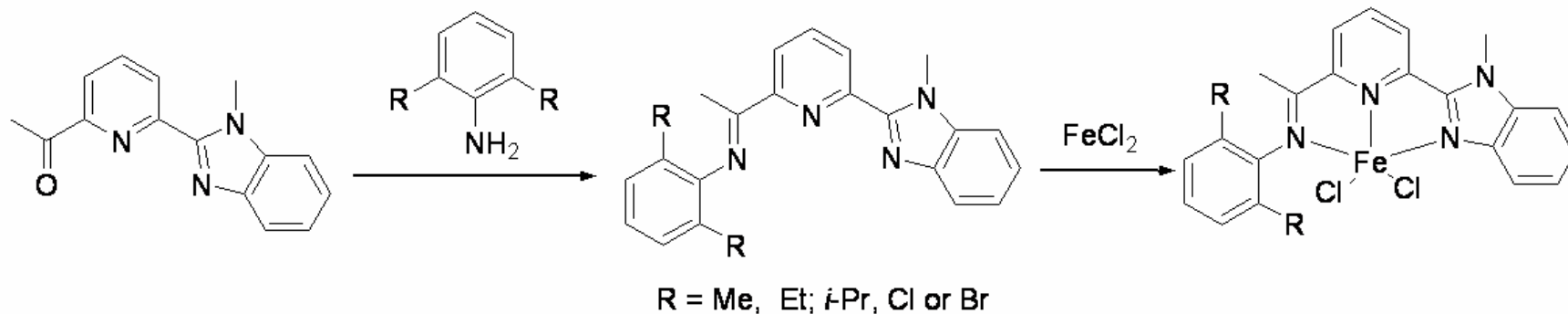
*J. Organomet. Chem.*, 2006, 691, 4196-4203. (Ni)

*J. Mol. Catal. A*, 2007, 269, 85—96 (Fe)

Ref: Solan, et al.; *J. Organomet. Chem.* 2006, 691, 4114 (Co)

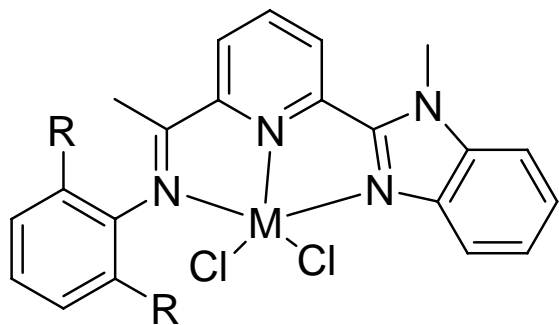


## 6-(2-Benzoimidazolyl)-2-iminopyridyliron Dichlorides



Organometallics, 2007, 26, 2720.

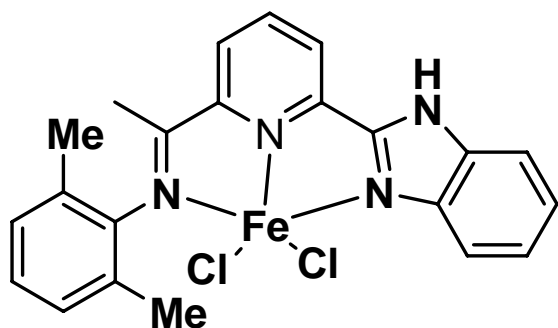
## 6-(2-Benzoimidazolyl)-2-iminopyridylmetal Pro-catalysts



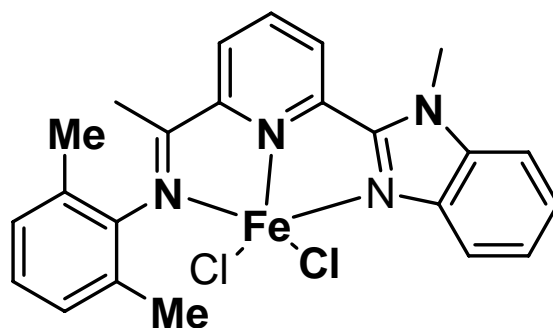
Organometallics, 2007, 26, 2720-2734. (Fe, Co)  
**one of most-accessed article and most-cited article**

Organometallics, 2007, 26, 2439-2446. (Ni)  
**one of most-accessed article and most-cited article**

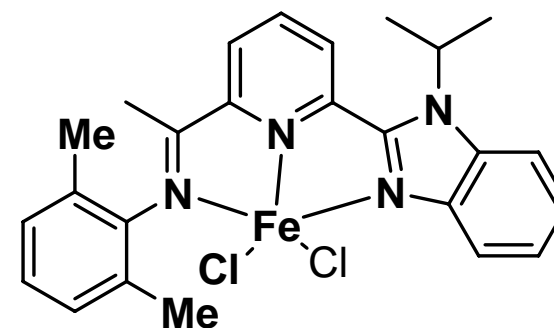
# Analogues of Iron Procatalysts

**13.2**

Organometallics,  
**2009**, 28, 2225-2233

**9.2**

Organometallics,  
**2007**, 26, 2720-2734

**5.96**

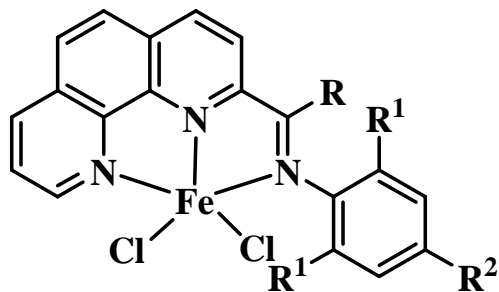
J. Organomet. Chem.  
**2008**, 693, 1829-1840

**Condition:** 5  $\mu$  mol Fe; 10 atm ethylene; 30 min; 20 °C;  
Al/Fe = 1000; 100 mL toluene;

**Activity unit:** 10<sup>6</sup>g/mol Fe·h.atm

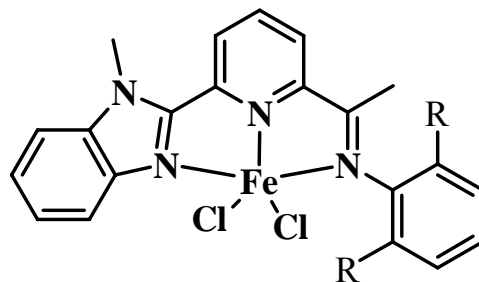


# Alternative Models of Iron Procatalysts



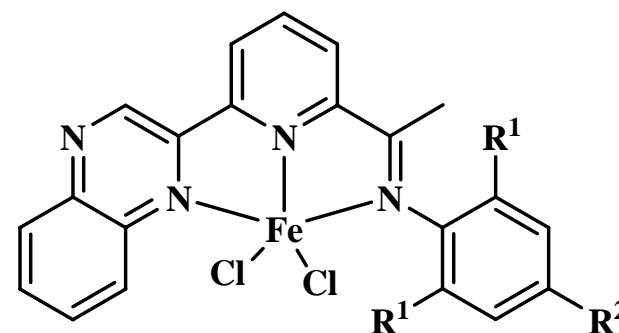
R = Me, R<sup>1</sup> = Cl, R<sup>2</sup> = H  
Olig:  $4.9 \times 10^7$  g mol<sup>-1</sup>(Fe) h<sup>-1</sup>  
Oligomer% > 99%

Organometallics  
2006, 25, 666-677



R = *i*-Pr  
Olig.:  $1.43 \times 10^7$  g mol<sup>-1</sup>(Fe) h<sup>-1</sup>  
Polym.:  $3.1 \times 10^5$  g mol<sup>-1</sup>(Fe) h<sup>-1</sup>  
Oligomer% = 97.9%

Organometallics,  
2007, 26, 2720-2734

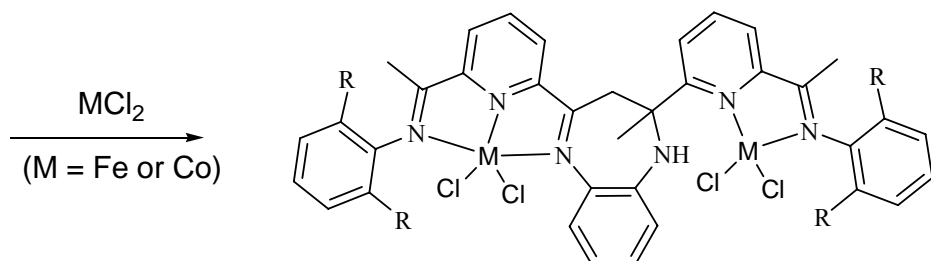
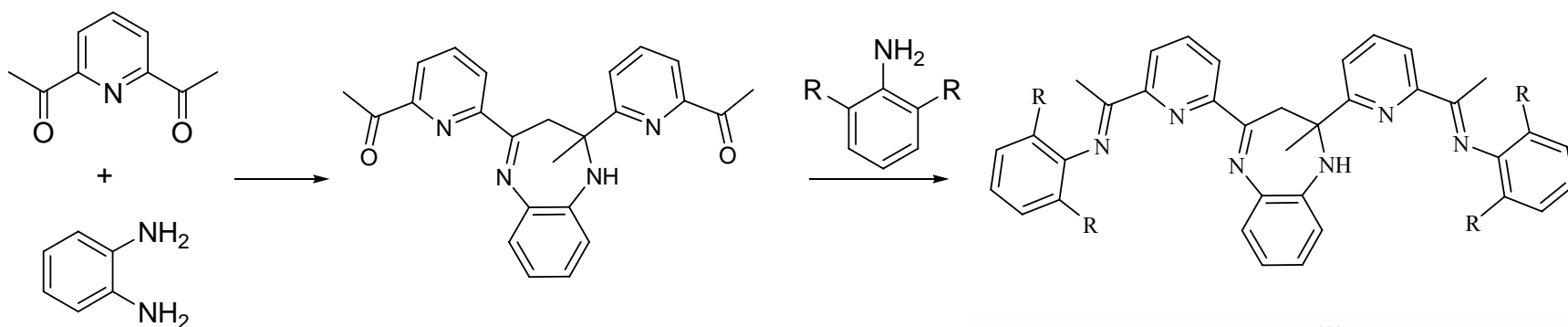


$2.24 \times 10^6$  g Oligomers/mol Fe·h  
C<sub>4</sub>-C<sub>6</sub> as major products

J. Organomet. Chem.,  
2007, 692, 4506-4518

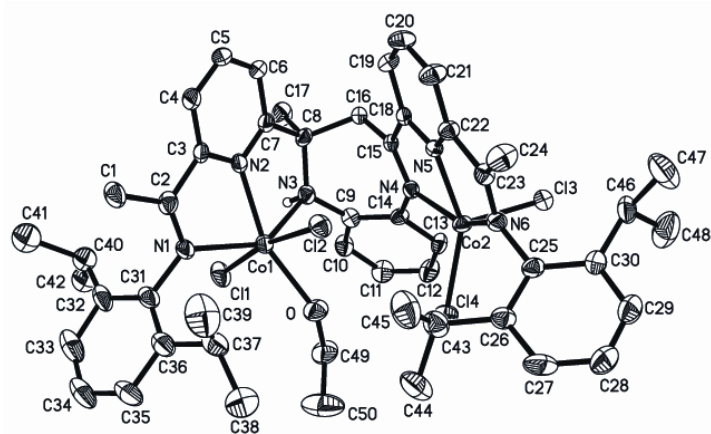


# Bimetallic Complex Catalyst



**Fn** (iron complex) or **Cn** (cobalt complex)

$n = 1$ : R = Me;  $n = 2$ : R = *i*-Pr



M = Fe:  $10^7 \text{ g mol}^{-1}(\text{cat.})\text{h}^{-1}$

M = Ni:  $10^5 \text{ g mol}^{-1}(\text{cat.})\text{h}^{-1}$

Organometallics, 2007, 26, 2456-2460.

J. Organomet. Chem., 2008, 692, 5307-5316



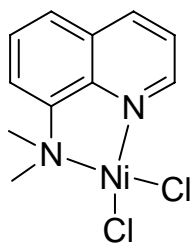
# 500t Pilot Process for $\alpha$ -Olefins



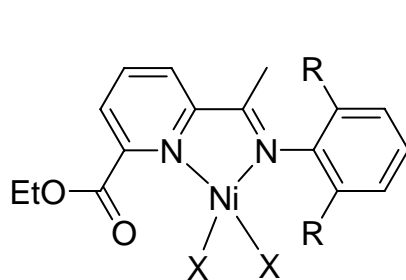


# Alternative Models of Nickel Procatalysts

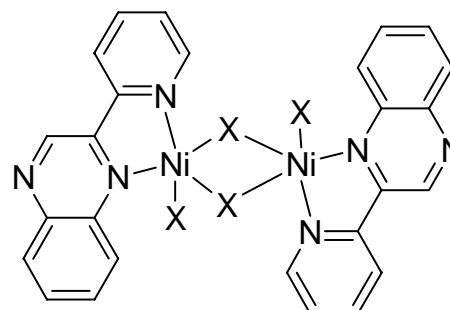
## Ethylene oligomerization



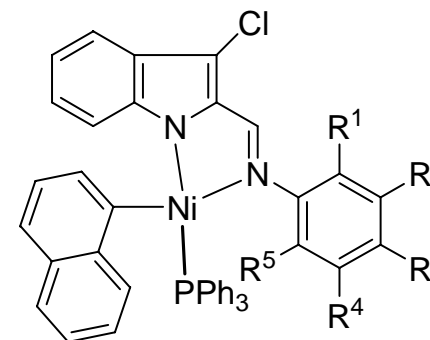
Chin. Chem. Let.  
2001, 12, 691



J. Organomet. Chem.  
2005, 690, 1570

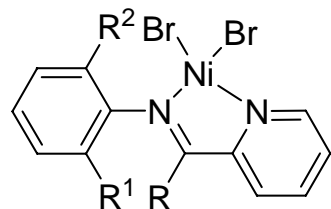


Cat. Commun.  
2002, 3, 405



Inorg. Chem. Commun.,  
2003, 6, 1372.

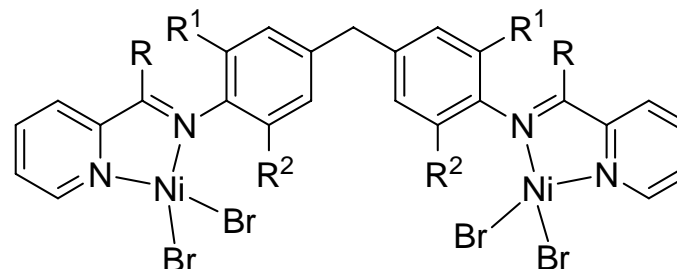
## Ethylene polymerization



Laine, T.V et al:

Macromol. Rapid Commun., 1999, 20, 487

J. Organomet. Chem., 2000, 606, 112



also producing oligomers

J. Organomet. Chem.

2005, 690, 1739



# Problems and Prospects of Late-transition Metal Procatalysts

- **Too many late-transition metal pro-catalysts for ethylene oligomerization!**

*That is true. Some of them, especially iron pro-catalysts, are promising and practical for industrial consideration in ethylene oligomerization.*

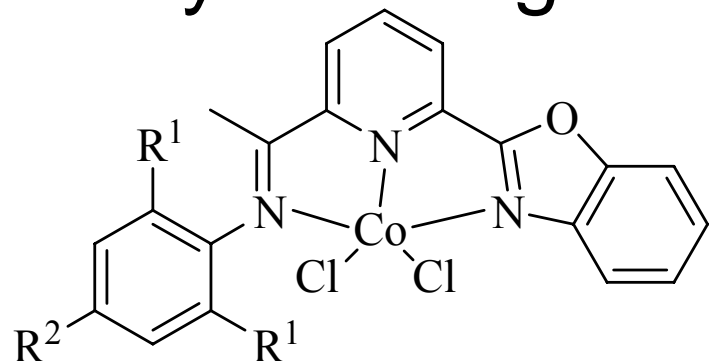
- **What is the critical problem for polymerization by iron procatalysts?**

*At elevated reaction temperature, deactivation was commonly happened and more oligomers or PE waxes were formed.*

*The highly exothermal reaction of ethylene oligomerization or polymerization.*



# Temperature Switch: Ethylene Oligomerization and Polymerization



|                |    |    |              |    |    |    |    |
|----------------|----|----|--------------|----|----|----|----|
|                | 1  | 2  | 3            | 4  | 5  | 6  | 7  |
| R <sup>1</sup> | Me | Et | <i>i</i> -Pr | Me | Me | Cl | Br |
| R <sup>2</sup> | H  | H  | H            | Me | Br | H  | H  |

|       | 1        | 2        | 3        | 4        | 5        | 6                   | 7                  |
|-------|----------|----------|----------|----------|----------|---------------------|--------------------|
| 20 °C | 3.70 (O) | 0.91 (O) | 0.68 (O) | 0.50 (O) | 1.12 (O) | 7.24 (O)            | 7.52 (O)           |
| 40 °C | 5.63(P)  | 3.70(P)  | 2.21(P)  | 1.04(P)  | 1.91(P)  | 0.05 (O)<br>0.61(P) | 0.14(O)<br>0.72(P) |

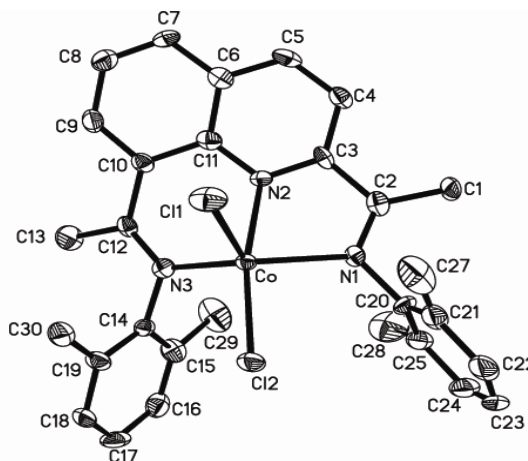
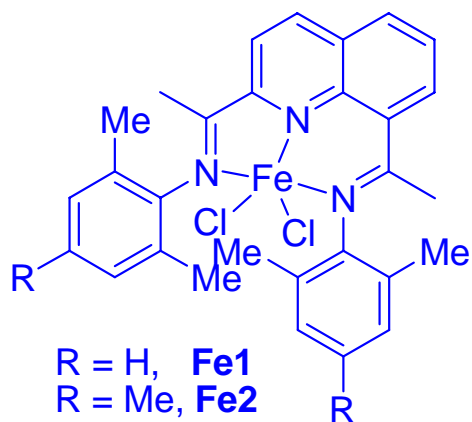
**Condition:** 5  $\mu$  mol Co; 1000 equiv. MAO; 10 atm ethylene;  
30 min; 100 mL toluene.  $10^5 \text{ g (mol Co)}^{-1} \text{ h}^{-1}$

J. Mol. Catal. A: Chem. 309 (2009) 166-171  
Cooperated with Prof. M. Bochmann



# Highly Active Procatalyst at 100°C

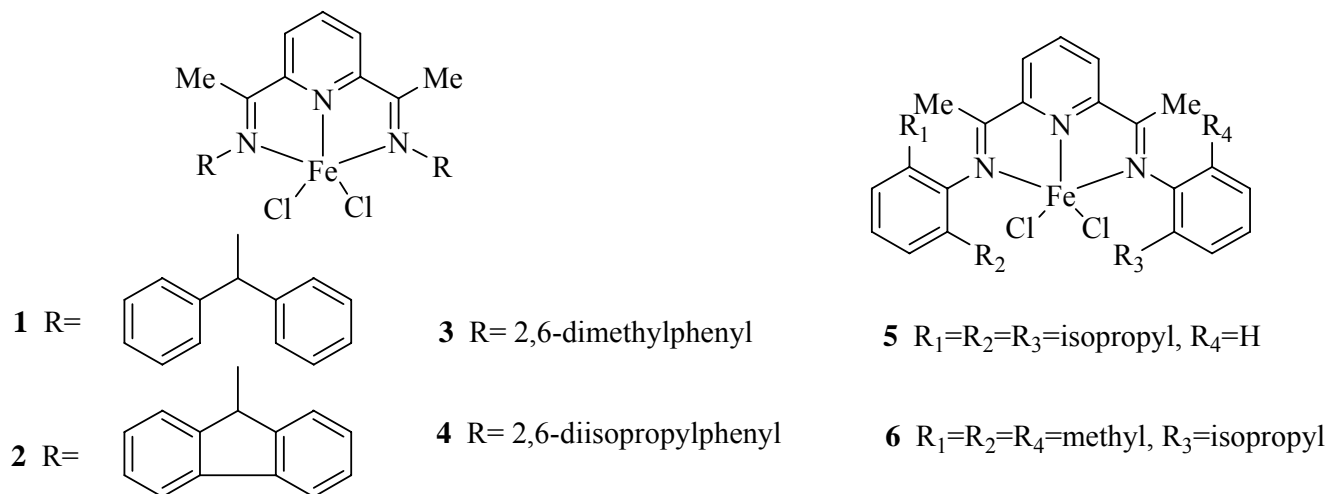
| Cat | Al/Fe | Atm | T/°C | $10^5\text{g/mol}^{-1}\cdot\text{h}^{-1}$ | $M_w/\times 10^{-4}$ | $M_w/M_n^b$ |
|-----|-------|-----|------|---|----------------------|-------------|
| Fe1 | 3000  | 10  | 100  | 4.14                                      | 11.3                 | 2.9         |
| Fe1 | 3500  | 10  | 100  | 3.76                                      | 15.7                 | 3.1         |
| Fe1 | 3000  | 10  | 80   | 2.00                                      | 22.1                 | 3.2         |
| Fe1 | 3000  | 10  | 60   | 1.35                                      | 24.1                 | 4.3         |
| Fe1 | 3000  | 10  | 40   | trace                                     | nd                   | Nd          |
| Fe1 | 3000  | 20  | 100  | 26.3                                      | 10.2                 | 2.3         |
| Fe1 | 3000  | 30  | 100  | 76.1                                      | 9.9                  | 2.8         |
| Fe2 | 3000  | 30  | 100  | 65.1                                      | 12.5                 | 3.3         |



Organometallics,  
2010, 29, 1168



# (Un)Symmetrical Diiminopyridinyliron Pro-catalysts



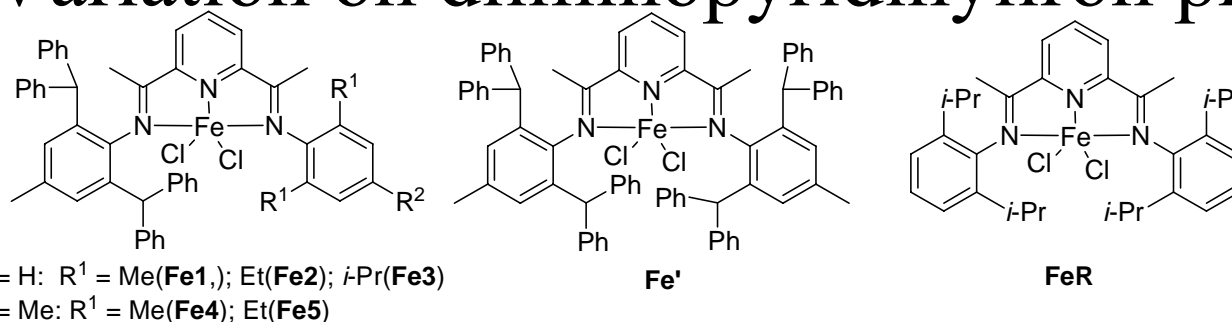
| Complex | Loading (μmol) | Al/Fe ratio (mol/mol) | T (°C) | Activity (10 <sup>6</sup> gPE·mol <sup>-1</sup> Fe·h <sup>-1</sup> ·atm <sup>-1</sup> ) |
|---------|----------------|-----------------------|--------|---|
| 1       | 2              | 2000                  | 40     | 0   |
| 2       | 4              | 2000                  | 40     | 0.66( oligomn.)   |
| 3       | 2              | 2000                  | 40     | 5.10  |
| 4       | 2              | 2000                  | 40     | 4.56  |
| 5       | 2              | 2000                  | 40     | 4.34  |
| 6       | 2              | 2000                  | 40     | 4.46  |

**Condition:** 1 atm ethylene, 30min and 50 mL toluene, MAO as cocatalyst.

*Polym. Int.* **2002**, 51 994-997



# Our Variation on diiminopyridinyliron procatalysts



## Ethylene polymerization using MAO

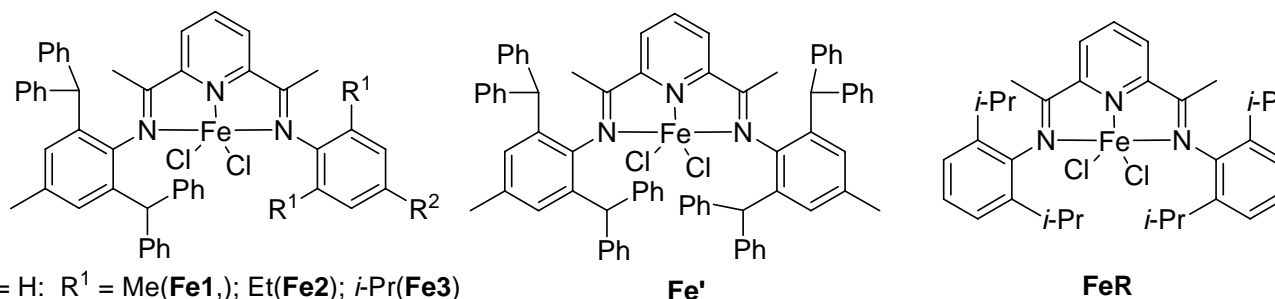
| procat.    | Activity<br>10 <sup>6</sup> g·mol <sup>-1</sup> (Fe)·h <sup>-1</sup> | $M_w^b$<br>kg/mol | $M_w/M_n^b$ | $T_m^c$<br>°C |
|------------|--|-------------------|-------------|---------------|
| <b>Fe1</b> | 13.1   | 313.7             | 16.4        | 134.0         |
| <b>Fe2</b> | 12.4   | 260.0             | 8.8         | 132.3         |
| <b>Fe3</b> | 9.95   | 166.5             | 10.9        | 136.7         |
| <b>Fe4</b> | 4.89   | 443.1             | 23.4        | 133.7         |
| <b>Fe5</b> | 22.3   | 99.8              | 8.3         | 132.7         |
| <b>Fe'</b> | 0.76   | 285.2             | 7.2         | 134.4         |
| <b>FeR</b> | 5.71   | 101.6             | 14.1        | 133.3         |

Condition: 1.5  $\mu$ mol Fe; Al/Fe: 1500; 100 mL Toluene; 30 min; 60 °C

Chem. Commun., 2011, 14, 235



# Our Variation on diiminopyridinyliron procatalysts



## Ethylene polymerization using MMAO

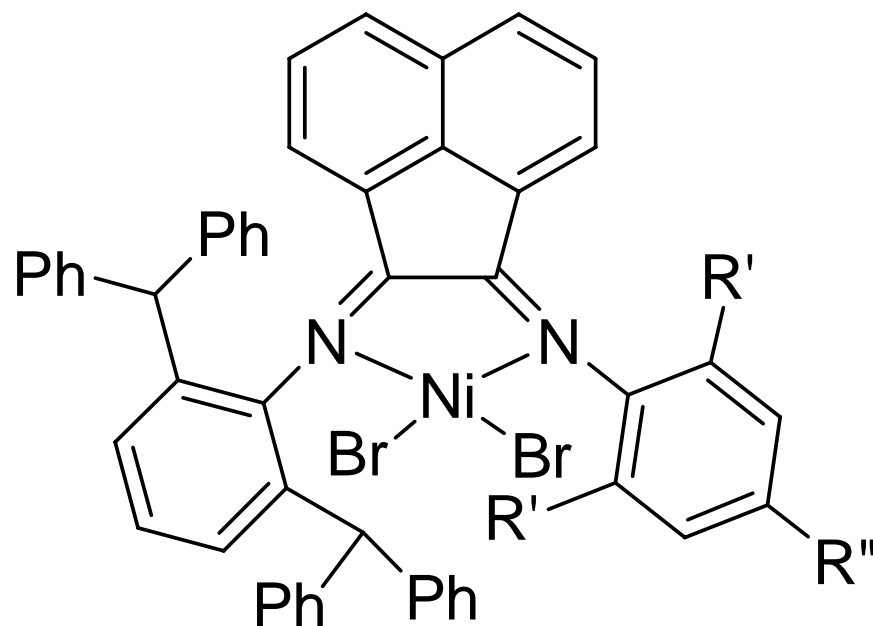
| procat.    | Activity<br>$10^6\text{g}\cdot\text{mol}^{-1}(\text{Fe})\cdot\text{h}^{-1}$ | $M_w^b$<br>kg/mol | $M_w/M_n^b$ | $T_m^c$<br>$^{\circ}\text{C}$ |
|------------|---|-------------------|-------------|-------------------------------|
| <b>Fe1</b> | 21.5  | 7.6               | 1.6         | 129.3                         |
| <b>Fe2</b> | 19.4  | 6.5               | 1.5         | 131.0                         |
| <b>Fe3</b> | 11.9  | 17.7              | 4.3         | 129.3                         |
| <b>Fe4</b> | 22.4  | 25.5              | 5.1         | 129.7                         |
| <b>Fe5</b> | 5.10  | 294.9             | 12.2        | 133.7                         |
| <b>Fe'</b> | trace   | -                 | -           | -                             |
| <b>FeR</b> | 4.80  | 178.5             | 22.7        | 130.0                         |

Condition: 1.5  $\mu\text{mol}$  Fe; Al/Fe: 2000; 100 mL Toluene; 30 min; 80  $^{\circ}\text{C}$

Chem. Commun., 2011, 14, 235



# The bulky aniline Shared for nickel pro-catalysts



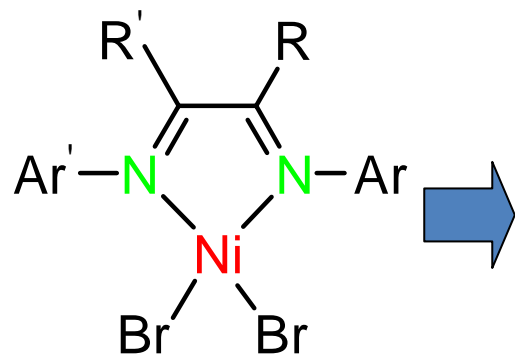
Act:  $\sim 10^7 \text{g(PE)} \cdot \text{mol}^{-1}(\text{Ni}) \cdot \text{h}^{-1}$

PE:  $M_w 5\sim 9 \times 10^5 \text{g} \cdot \text{mol}^{-1}$ , PDI: 2.2~2.7

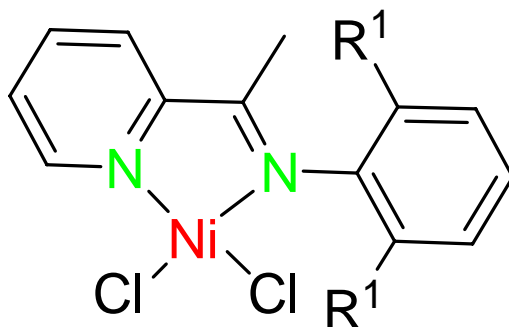
**Organometallics, 2011, 30, 2418**



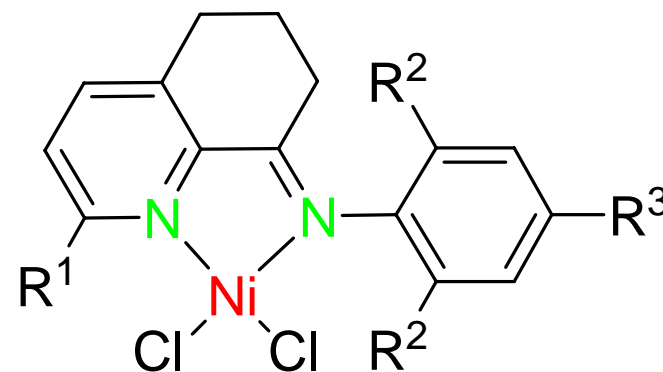
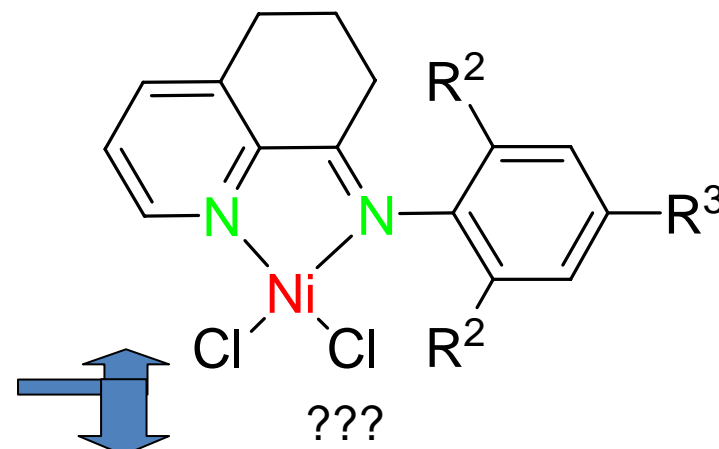
# Altering bidentate nickel pro-catalysts



Brookhart, et al.  
J. Am. Chem. Soc.,  
1995, 117, 6414.



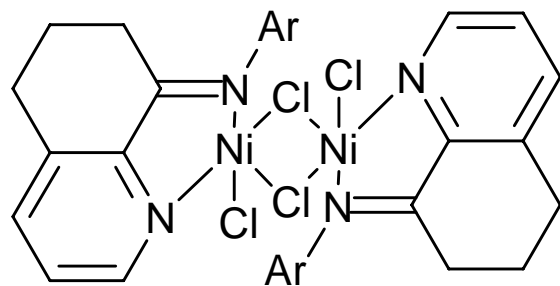
Laine, et al.  
J. Organomet. Chem.  
2000, 606, 112.



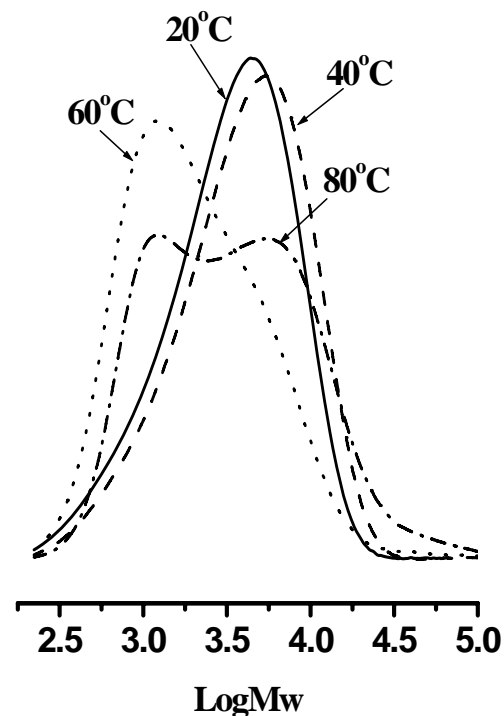
*New J. Chem.*  
2011, **35**, 178



# Single-site nickel pro-catalyst



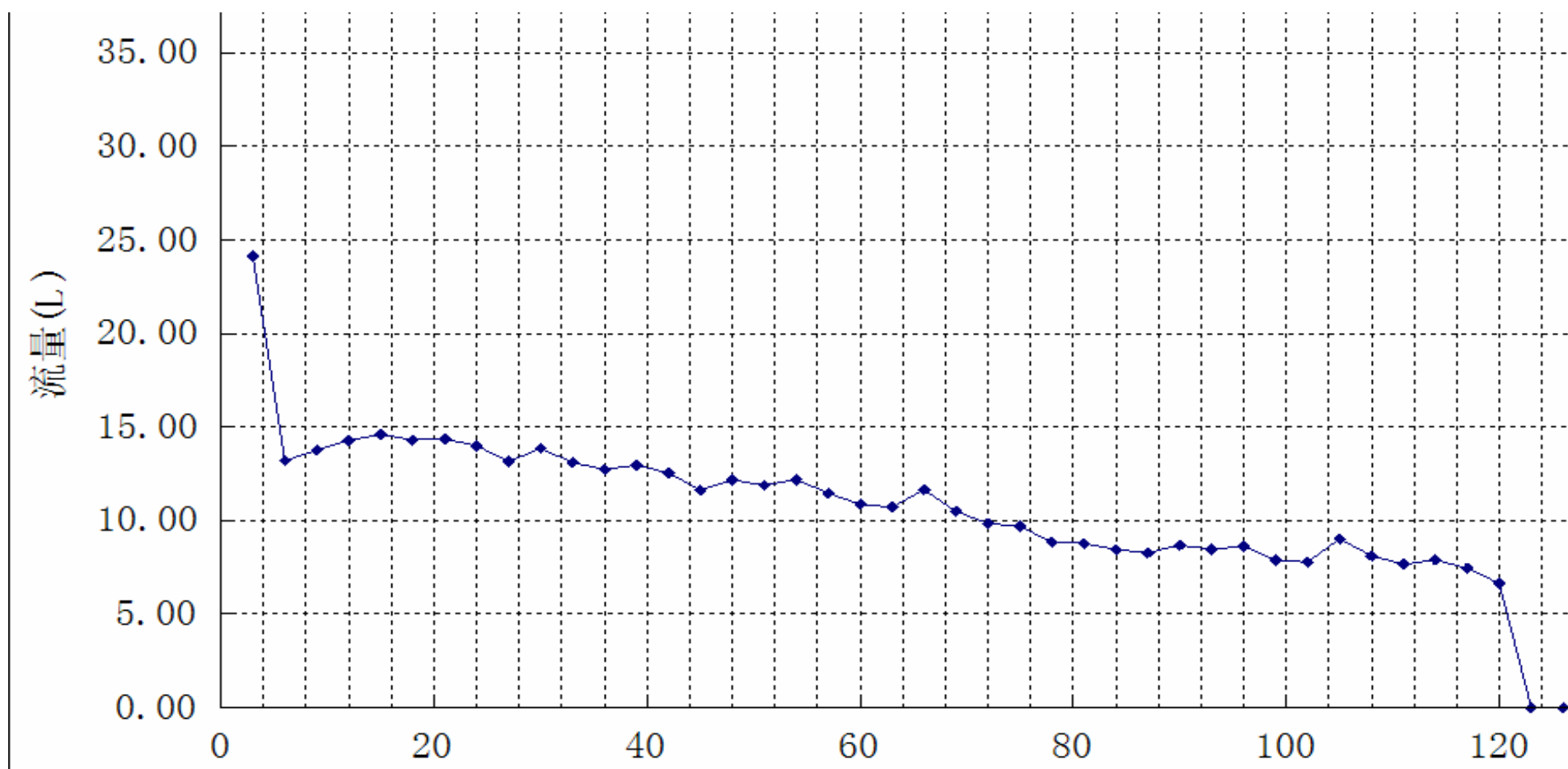
Act:  $10^6 \text{ g(PE)} \cdot \text{mol(Ni)}^{-1} \cdot \text{h}^{-1}$



Dalton Trans., 2011, 40 (33), 8436 – 8443  
ACS Catal., **2011**, 1, 1213

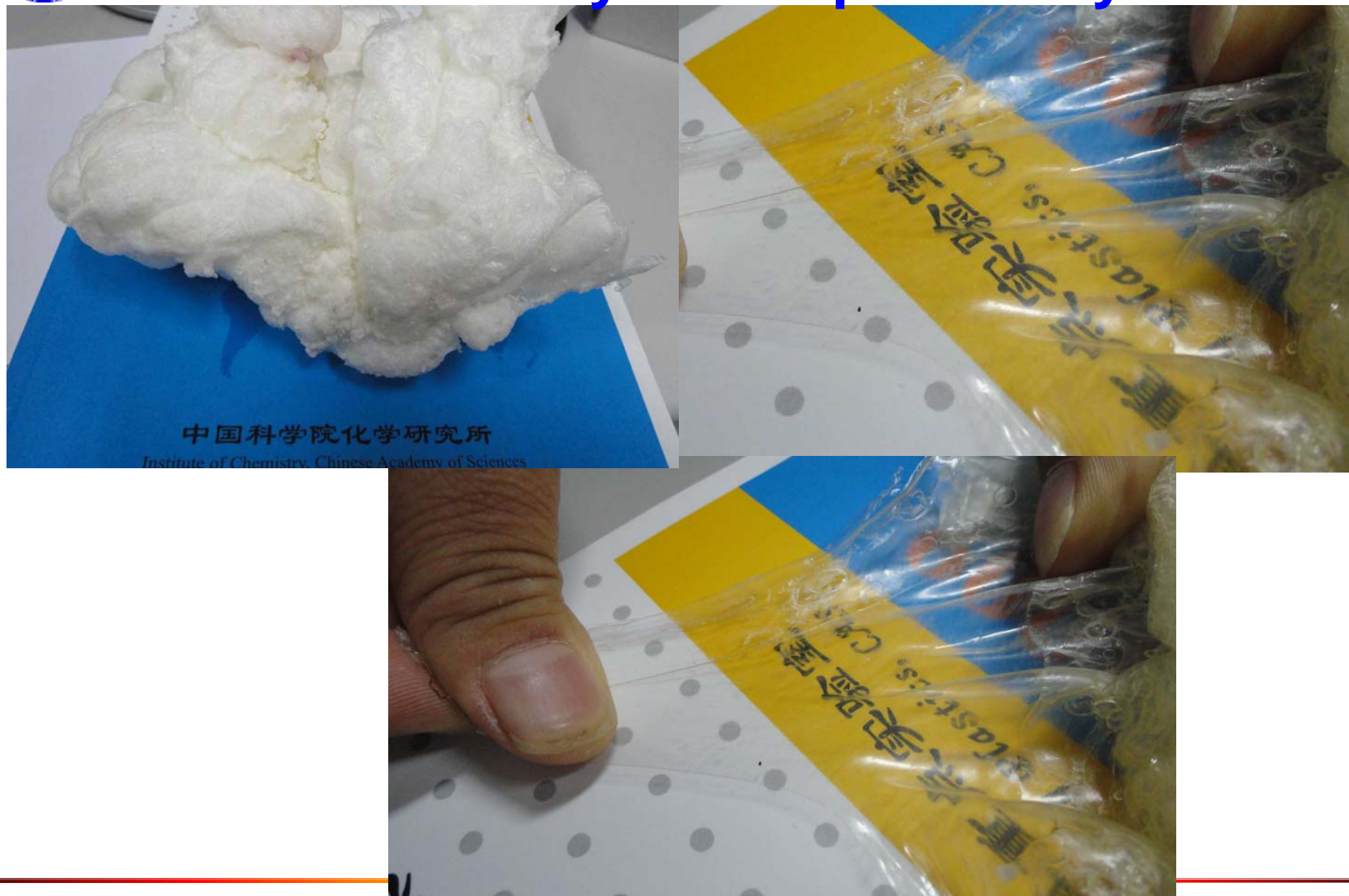


# Lifetime of late-transition pre-catalyst (within 120 min)





# PE obtained by nickel pro-catalyst





# Characteristic features: iron and nickel pro-catalysts

## Iron pro-catalysts

Highly activity

Adaptable active species

Highly linear PE:

HDPE or PE waxes

## Nickel pro-catalysts

Highly activity

Adaptable active species

Highly branched PE

Elastic PE or waxes



# Advantages of Late-transition metal Pre-catalysts

Highly efficiencies in ethylene reactivity

Solely catalytic processes achievable for  
Oligomerization or Polymerization

Good immobilization easily achieved

Drop-in processes



中国科学院化学研究所 工程塑料重点实验室

Fenghuang (Phoenix), Hunan



Key Laboratory of Engineering Plastics, Institute of Chemistry, Chinese Academy of Sciences



The Chinese Academy of Sciences  
The Ministry of Science and Technology, China  
National Science Foundation of China  
PetroChina SinoPec

Do not forget our enjoyment together under sunshine

Thank You for Your Kind Attention

Email: [whsun@iccas.ac.cn](mailto:whsun@iccas.ac.cn)

<http://whsun.iccas.ac.cn>

April 12, 2010