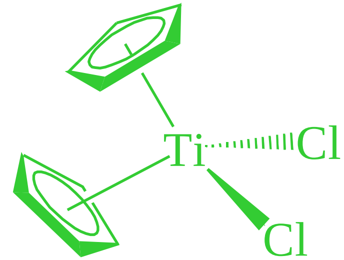
**SOLUBLE** Catalyst

1957




+ $AlCl(C_2H_5)_2$

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# The “Metallocene Revolution”

1980

Kaminsky e Sinn

**SOLUBLE** Catalysts

↓

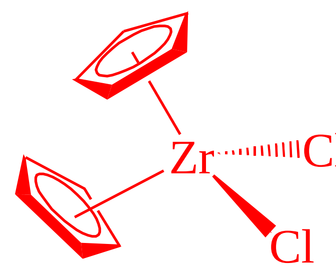
Catalyst **STRUCTURE**

↓

Polymerization **MECHANISM**

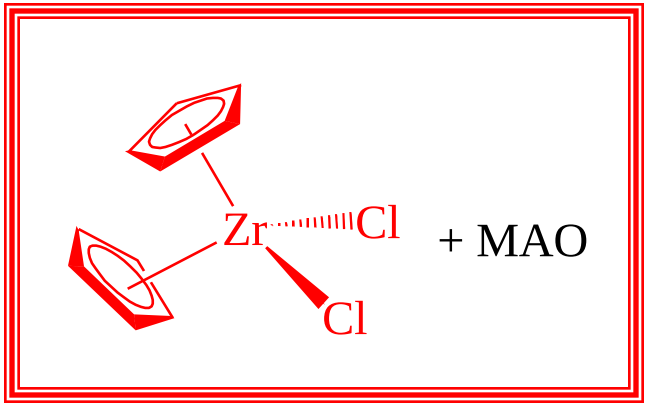
↓

Polymer **STRUCTURE and PROPERTIES**




+ MAO

# The "Metallocene Revolution"[1]

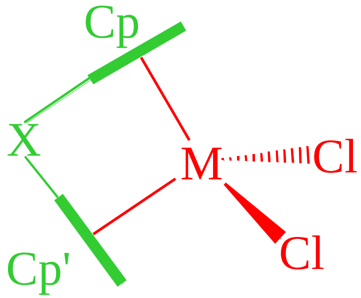



**Features:**

- homogeneous catalysts: 100 times more active than the conventional Ziegler-Natta (300 t PE/g Zr h);
- they catalyze the stereospecific polymerization of prochiral terminal alkenes;
- the synthesized polyolefins are featured by a narrow molecular weight distribution: Single Site Catalysts;
- branched poyolefins featured by branches of different length regularly distributed along the main chain are also obtained;
- these catalysts can be heterogenized.

[1]H. G. Halt et al., *Chem. Rev.* **2000**, *100*, 1205.

# Metallocene Catalysts are very versatile

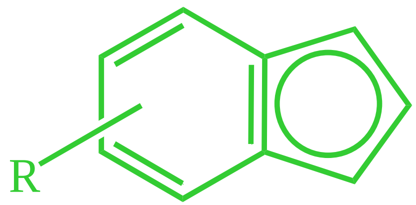



+ MAO

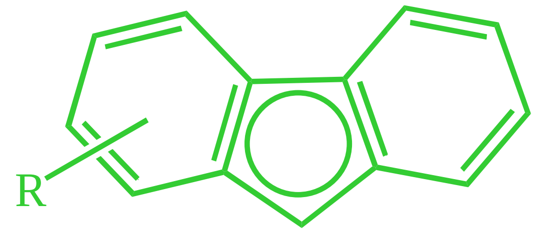
M = Ti, Zr, Hf

Cp = Cp' o Cp ≠ Cp'

Cp e Cp' =

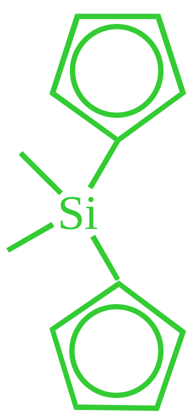

indenyl

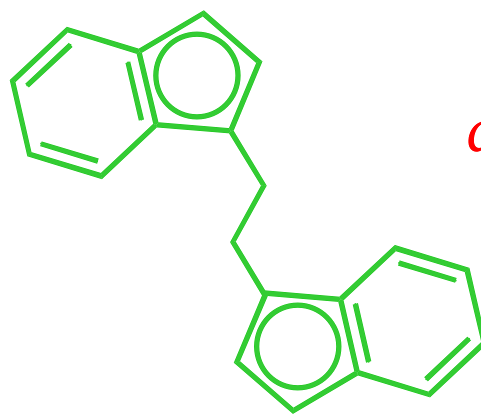



fluorenyl

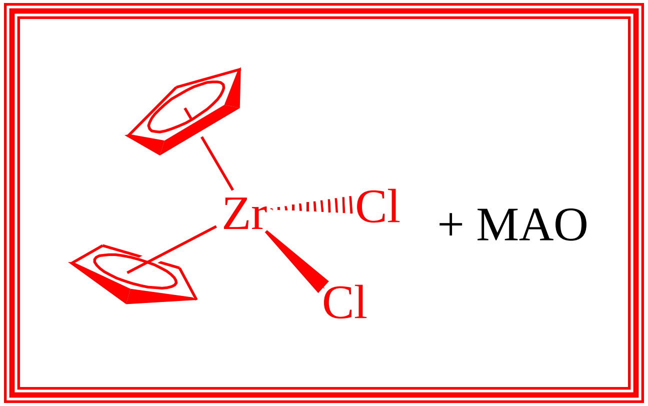
Cp-X-Cp' =

X = $CH_2CH_2$, $R_2Si$, $R_2C$



*ansa*-metallocenes

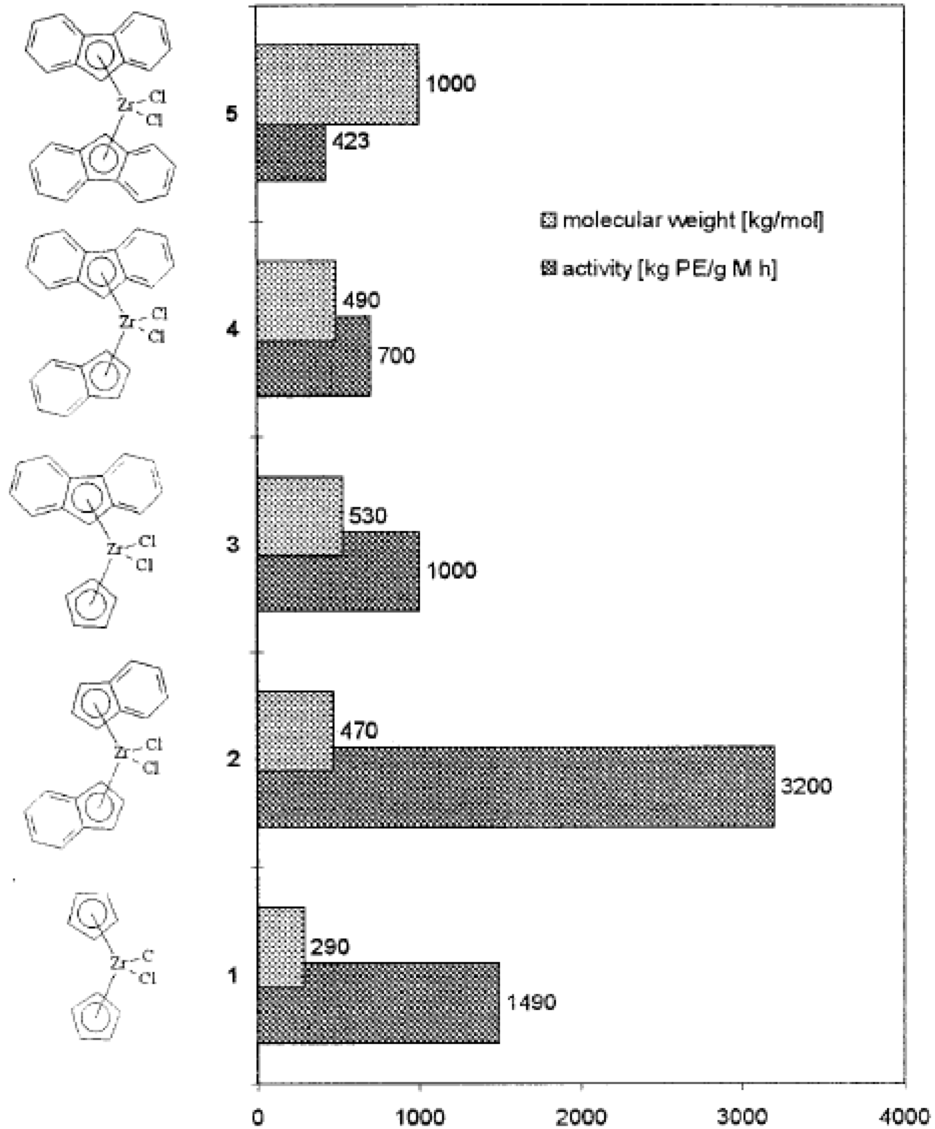



Reaction conditions: T = 90 °C, $P_{ethylene}$ = 8 bar,
[Al]/[Zr] = 10 000,
solvent = toluene

Productivity: 5 • $10^6$ g PE/g Zr • h • bar
$M_n$ = 122 000

T. Masuda, *Catalysis in Precision Polymerisation* **1997**, Ed. Wiley, pg. 18.

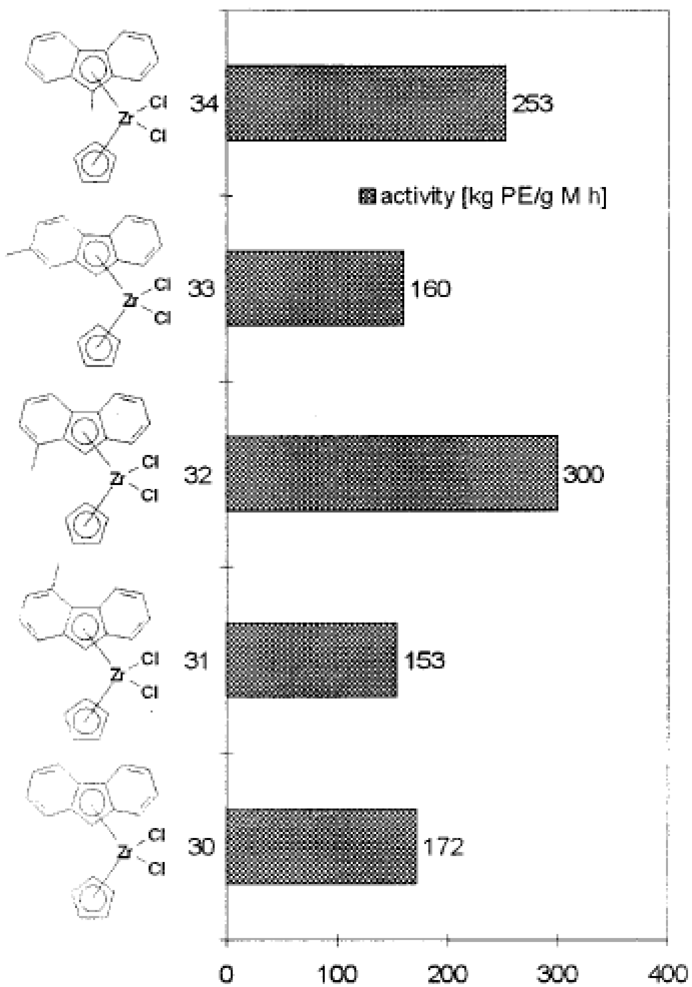
# Ethylene polymerization: **Effect of the aromatic ring**



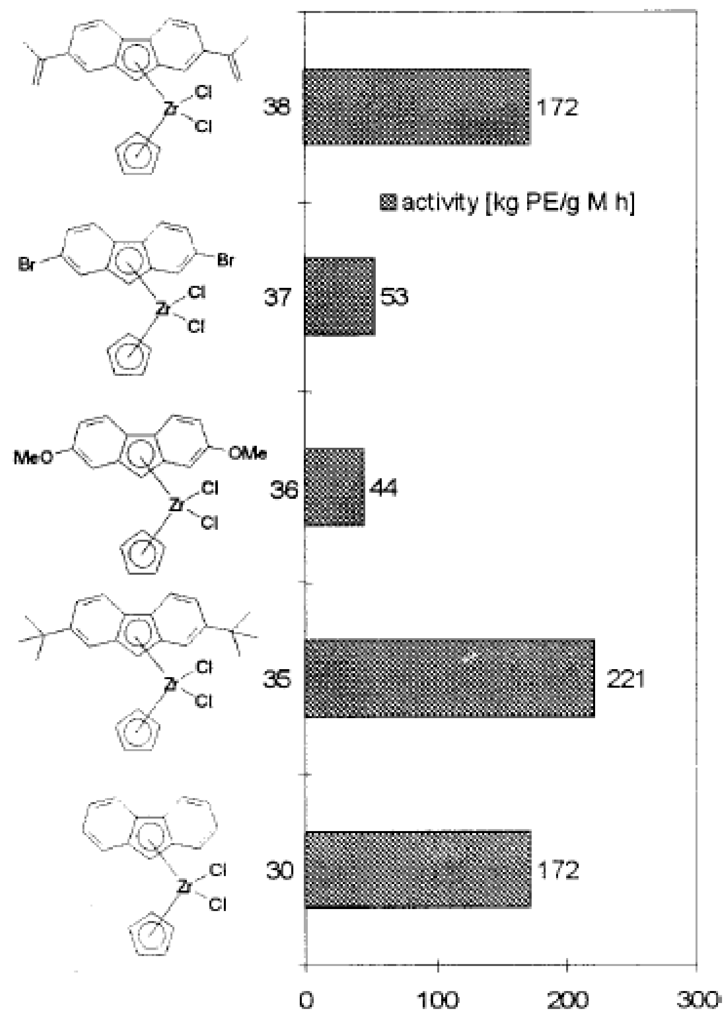

Reaction conditions: T = 60 °C; solvent: *n*-pentane; $P_{ethylene}$ = 10.0 bar; Cat. Prec. **1, 2, 4** [Al]/[Zr] = 1000; Cat. Prec. **3, 5** [Al]/[Zr] = 2500.

# Ethylene polymerization: **Effect of**

## substituent position



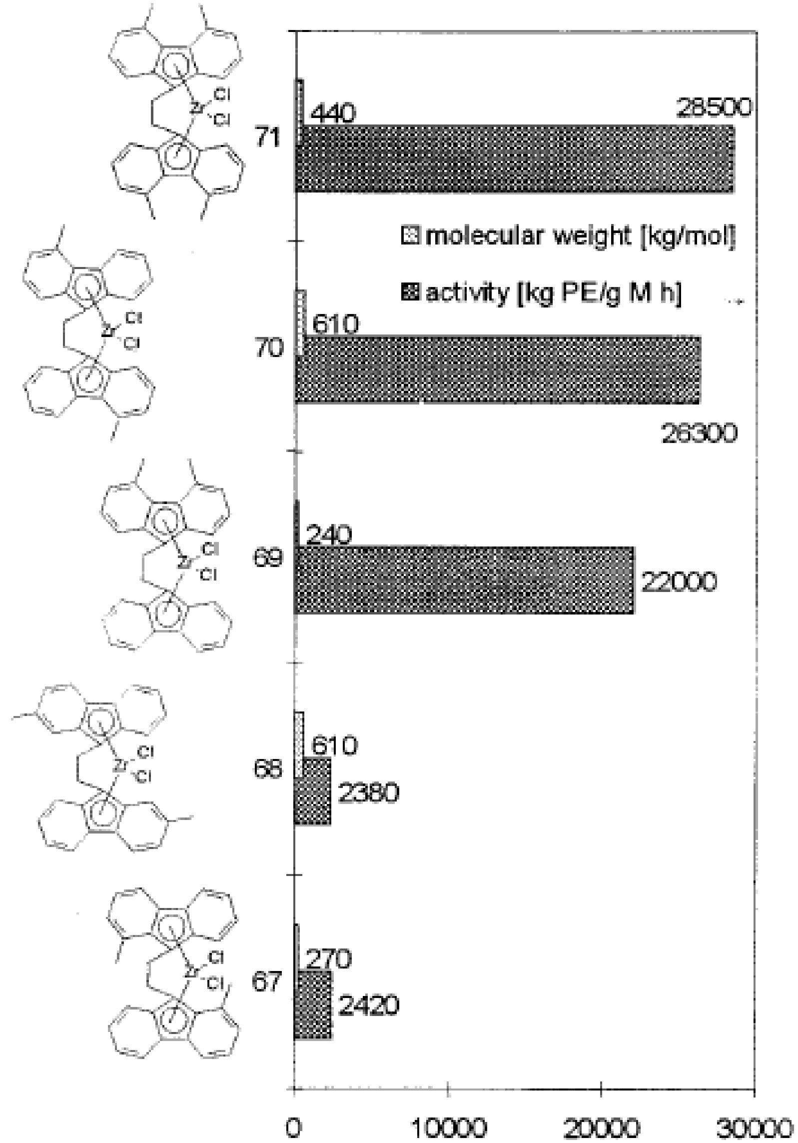

## substituent nature



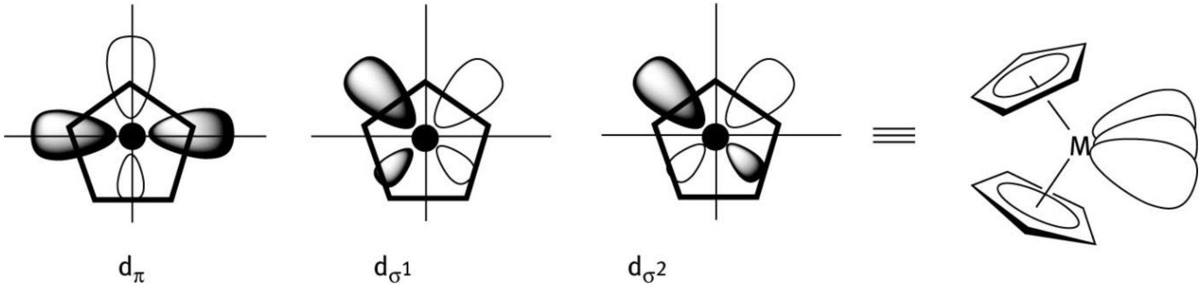

Reaction conditions: T = 10 °C; solvent: *n*-pentane; $P_{ethylene}$ = 10.0 bar; [Al]/[Zr] = 1000.

# Ethylene polymerization: **Effect of substituent position in *ansa-metallocenes***

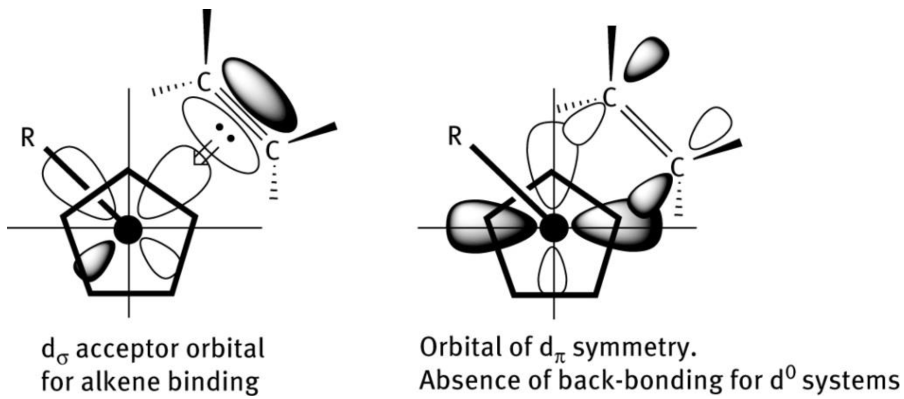
Reaction conditions:
T = 60°C;
solvent: *n*-pentane;
$P_{ethylene}$ = 10.0 bar;
[Al]/[Zr] = 20000.

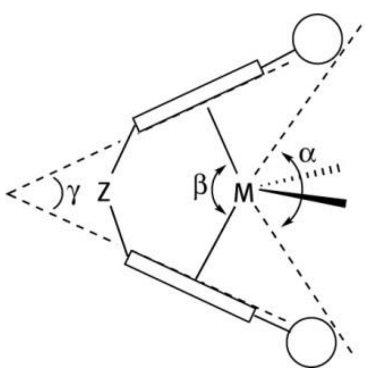


# Frontier orbitals in $[Zr(Cp)_2]^{2+}$



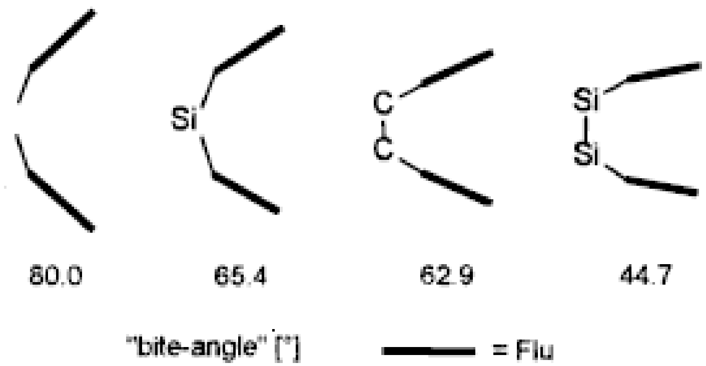

# Frontier orbitals in $[Zr(Cp)_2R]^+$

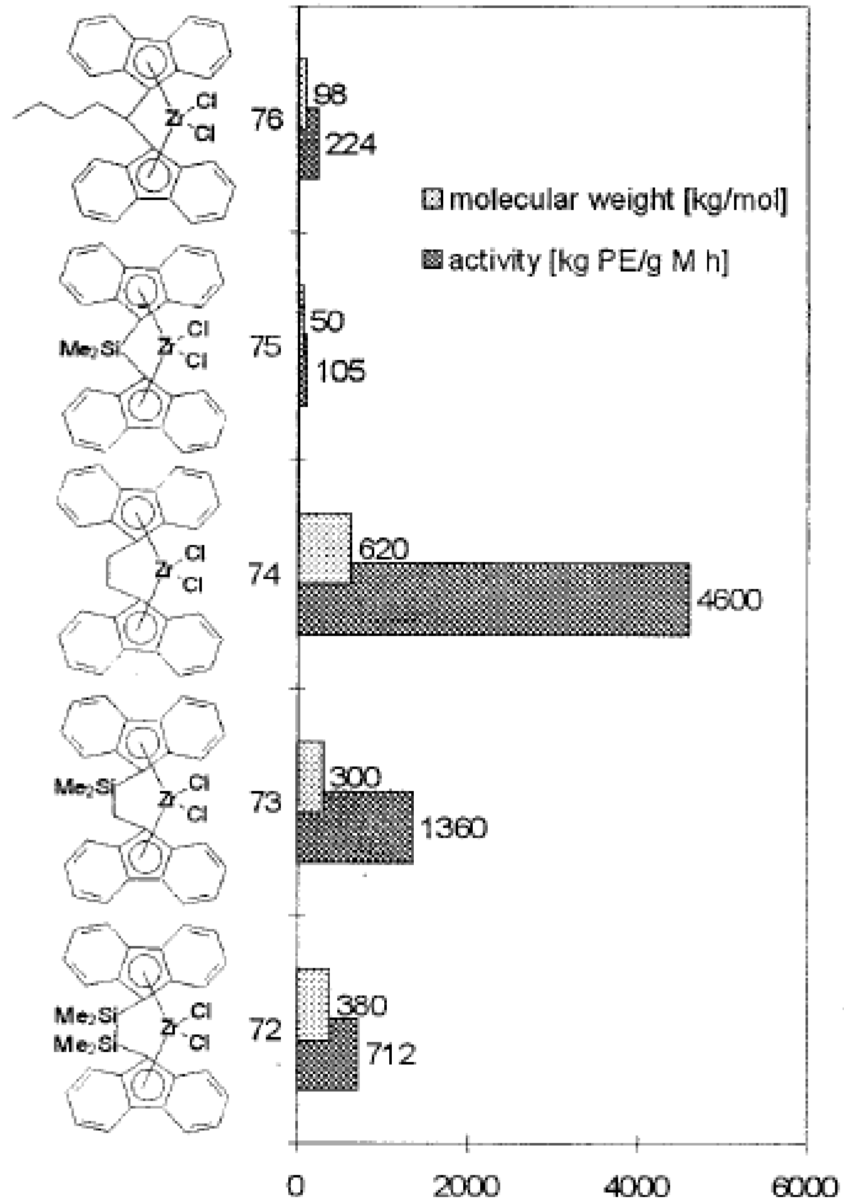



coordination gap aperture, $\alpha$,
and characteristic angles
in *ansa*-metallocenes

# Ethylene polymerization: **Effect of ligand bite angle**

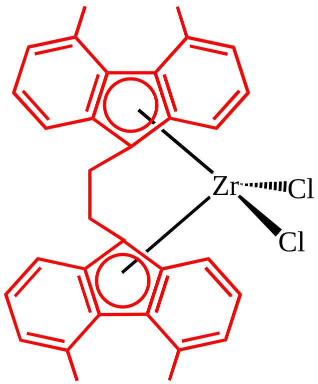


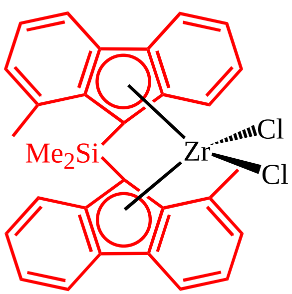

Reaction conditions: T = 60 °C; solvent: *n*-pentane; $P_{ethylene}$ = 10.0 bar; [Al]/[Zr] = 20000.

# The "TOP FOUR" Catalysts[1]

## productivity



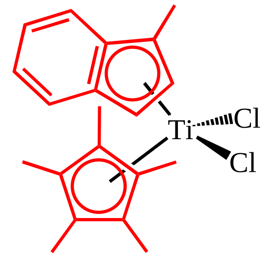

28 500 kg
PE/g Zr h



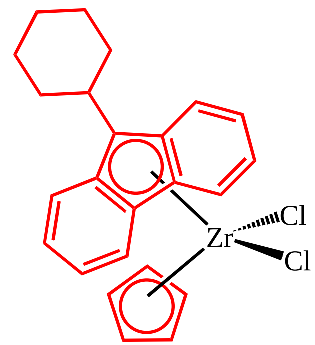

22 140 kg
PE/g Zr h

[Al]/[Zr] = 20 000

## High molecular weight polyethylene



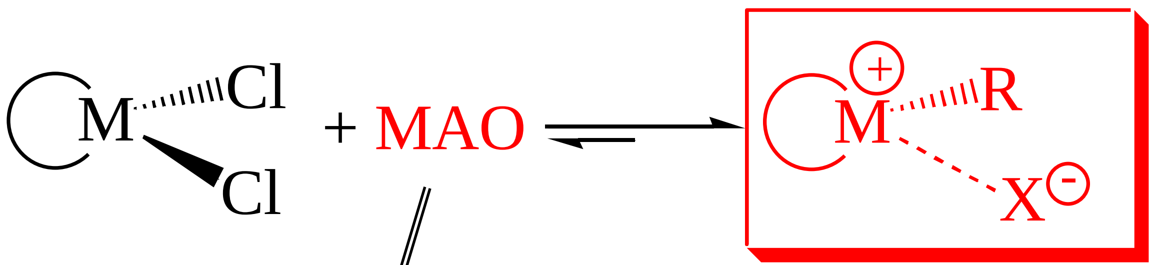

1 900 kg/mol




1 850 kg/mol

[1]H. G. Alt et al., *Chem. Rev.* **2000**, *100*, 1205.

# Methylalumoxane: MAO[1]




Catalyst activator

catalytic activity
stability
kinetic

Molecular weight
stereoregularity

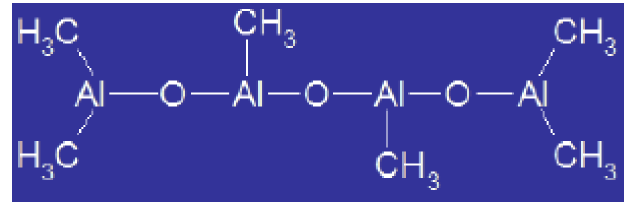
ION PAIR
CATION/ANION

SOLVENT

[1]T. J. Marks et al., *Chem. Rev.* **2000**, *100*, 1391.

# MAO[1]: structural features

$[-Al(Me)-O-]_n$    n = 5 - 20

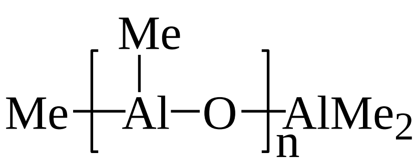



Multiple equilibria:

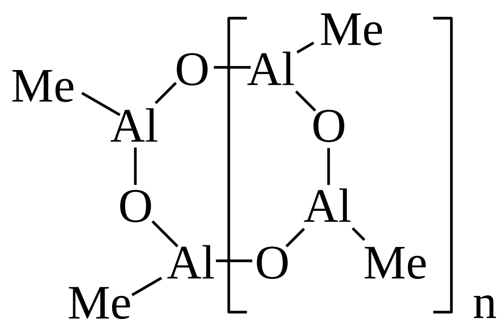
$$[Al(Me)O]_n \cdot x\,AlMe_3 \rightleftharpoons [Al(Me)O]_n \cdot (x\text{-}y)\,AlMe_3 + y\,AlMe_3$$

"associated"    "free"

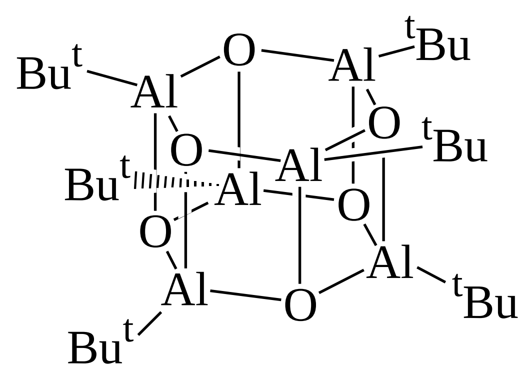
Main proposed structures :




*One-dimensional linear*




*Cyclic rings*




*Cage structure*

[1]T. J. Marks et al., *Chem. Rev.* **2000**, *100*, 1391.

# MAO[1]: the activation process

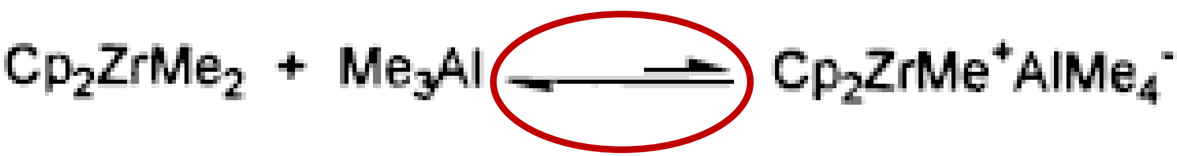
$$Cp_2ZrCl_2 + MAO \rightleftharpoons Cp_2ZrCl_2 \cdot MAO$$ *Complexation*

$$Cp_2ZrCl_2 \cdot MAO \rightleftharpoons Cp_2Zr(CH_3)Cl + (H_3C)(Cl)Al\text{—}O\text{—}$$ *Alkylation*

$$Cp_2Zr(CH_3)Cl + MAO \rightleftharpoons Cp_2Zr(CH_3)Cl \cdot MAO$$ *Abstraction*

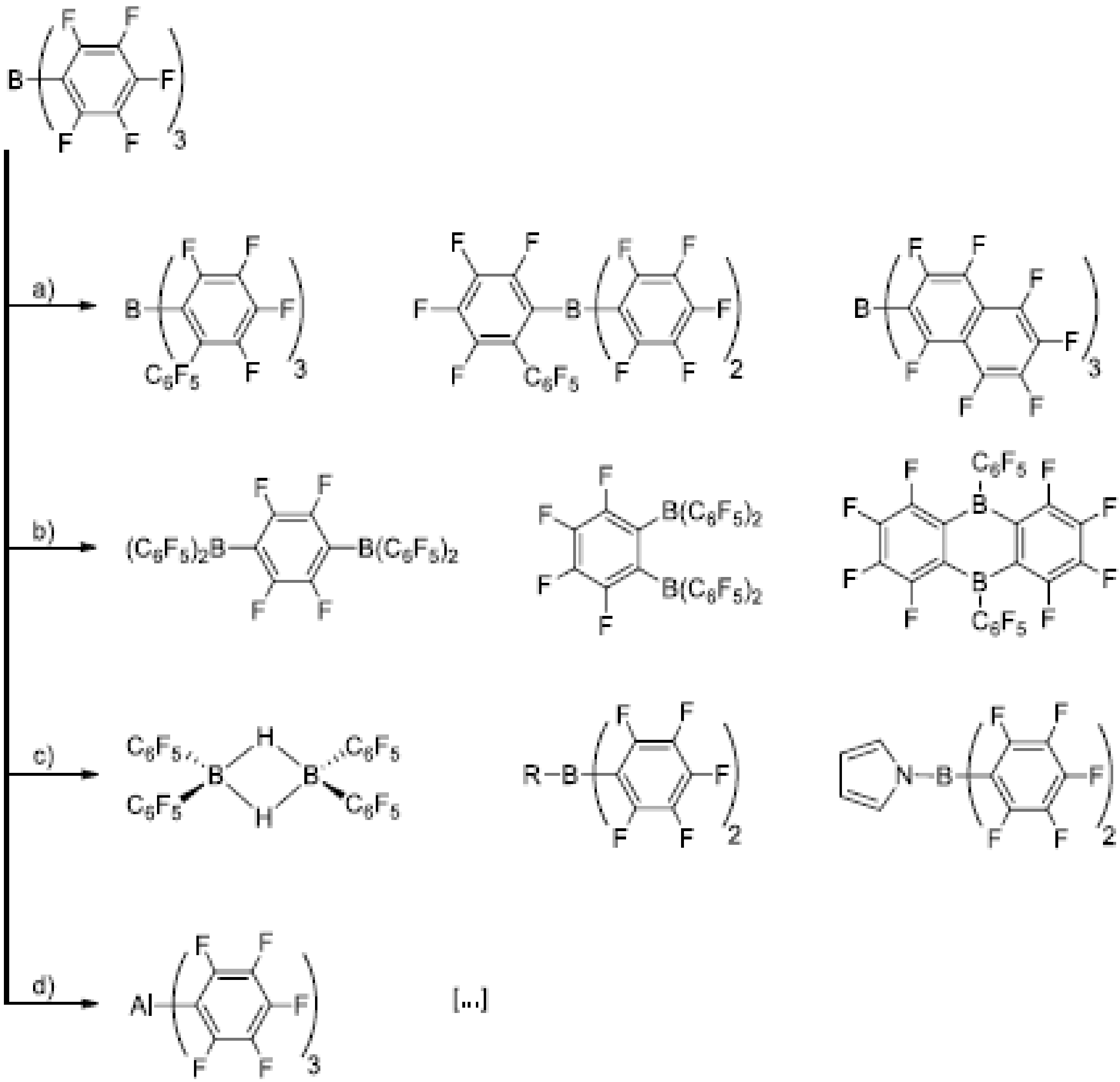
$$Cp_2Zr(CH_3)Cl \cdot MAO \rightleftharpoons \left[Cp_2Zr(CH_3)\right]^{+}\left[Cl\text{-}MAO\right]^{-}$$

| [Al]/[Zr] ≥ 1000 |
|---|

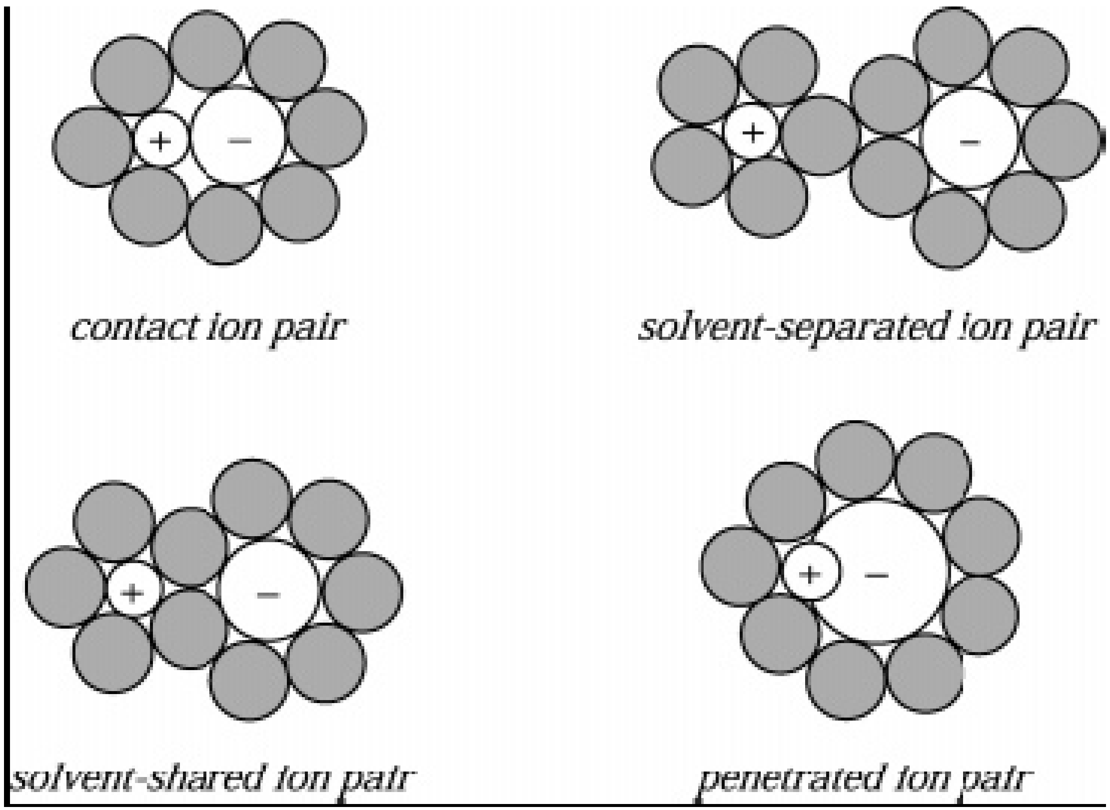



[1]T. J. Marks et al., *Chem. Rev.* **2000**, *100*, 1391.

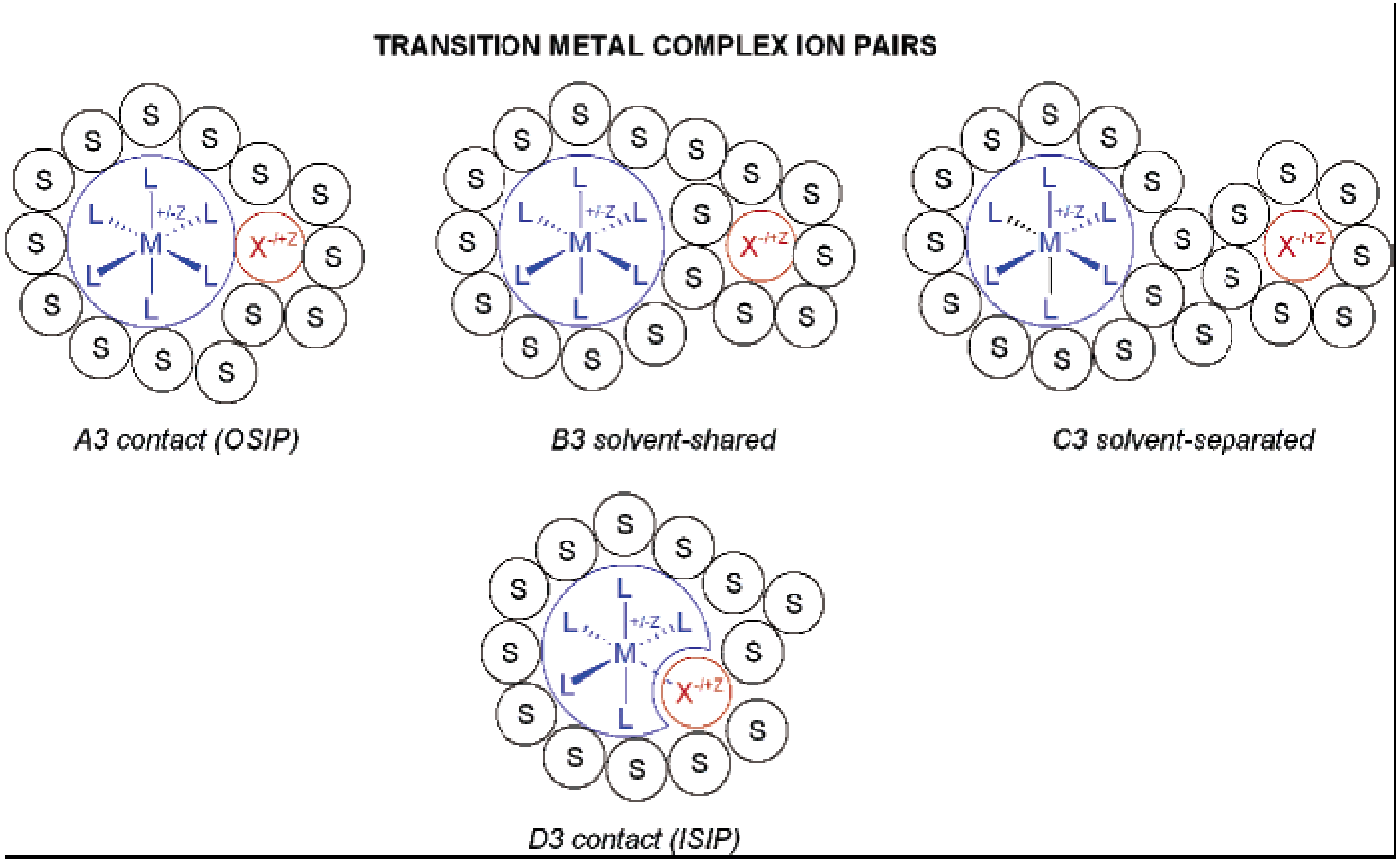
# Lewis acids as activators: Perfluoroaryl boranes



# THE ION PAIR[1]



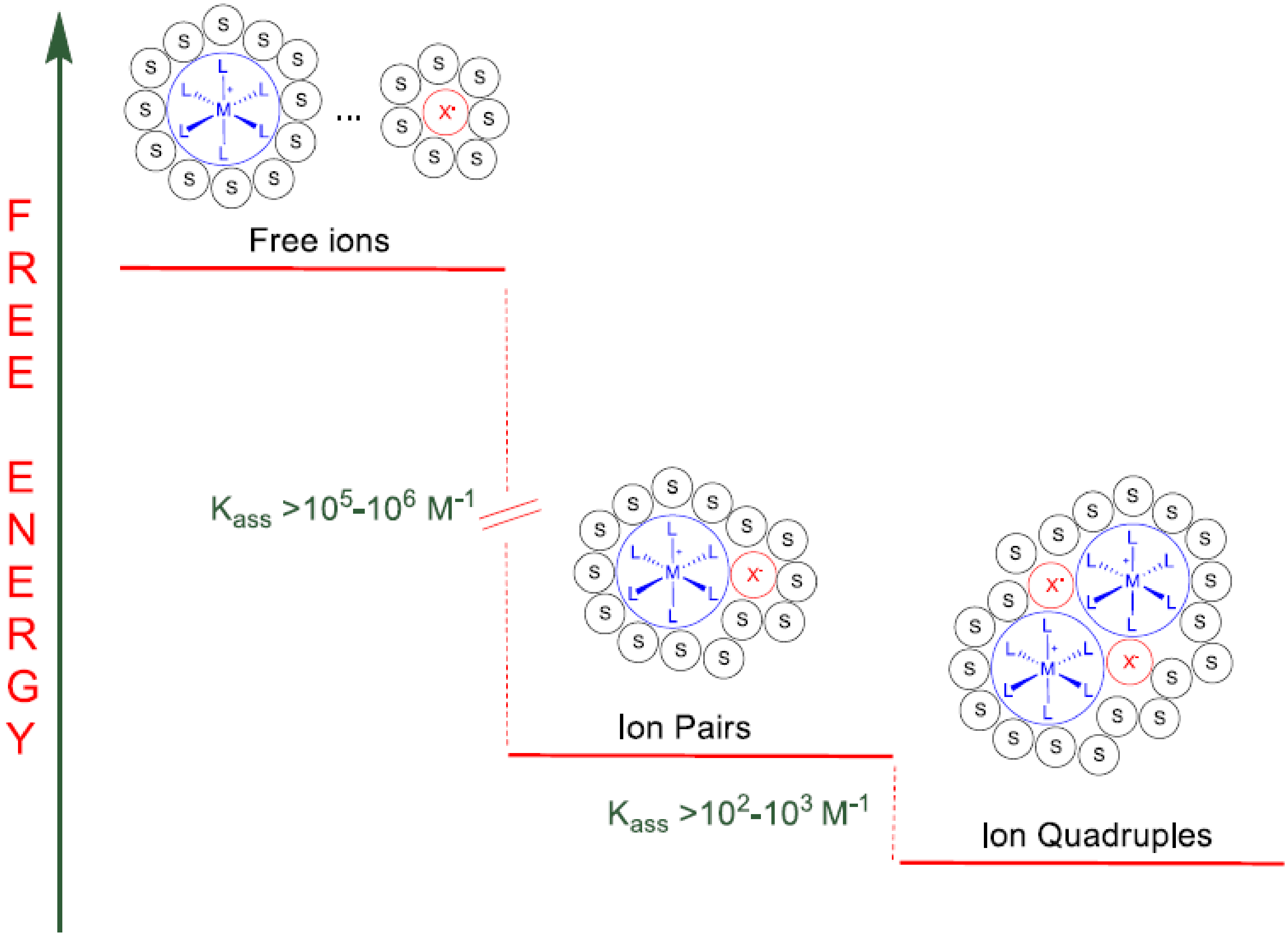

[1]A. Macchioni *Chem. Rev.* **2006**, *105*, 2039.




OSIP = OUTER-SPHERE ION PAIR

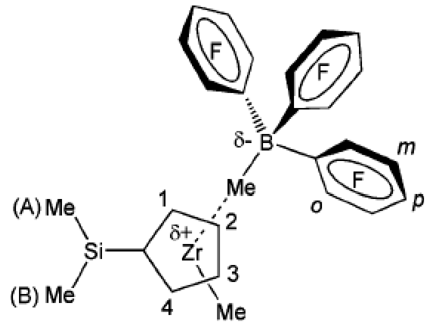
ISIP = INNER-SPHERE ION PAIR

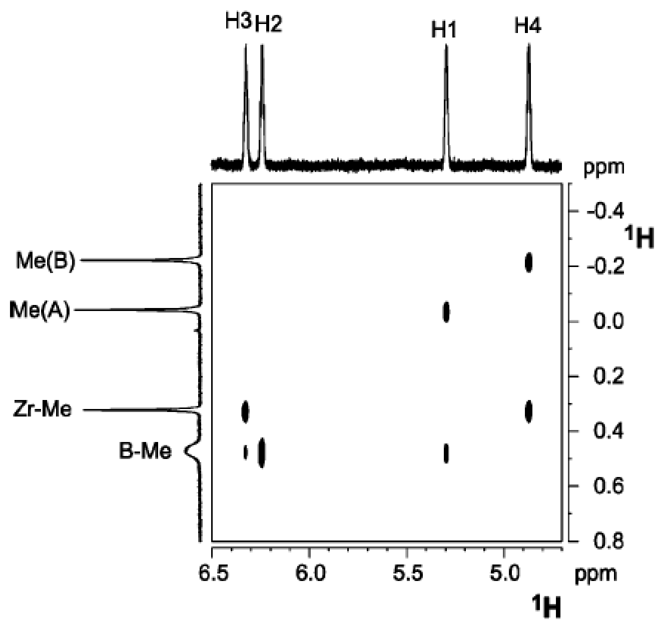
# Possible ion pairs in polymerization reactions



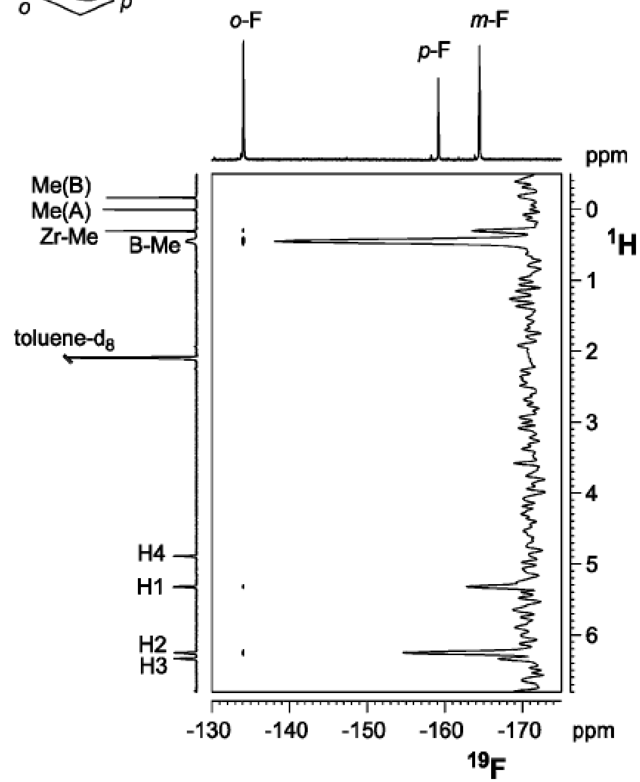
# Experimental evidences for the ione pair formation

## NMR Spectroscopy in solution



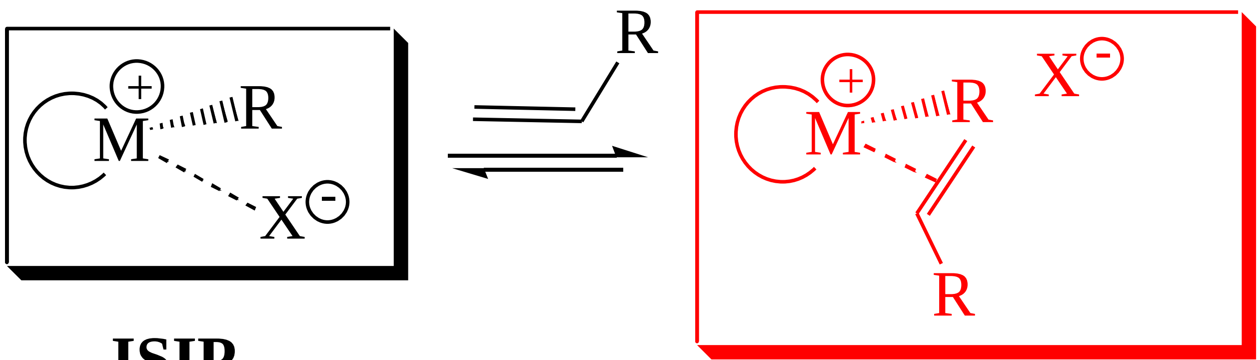




$^{1}$H-NOESY



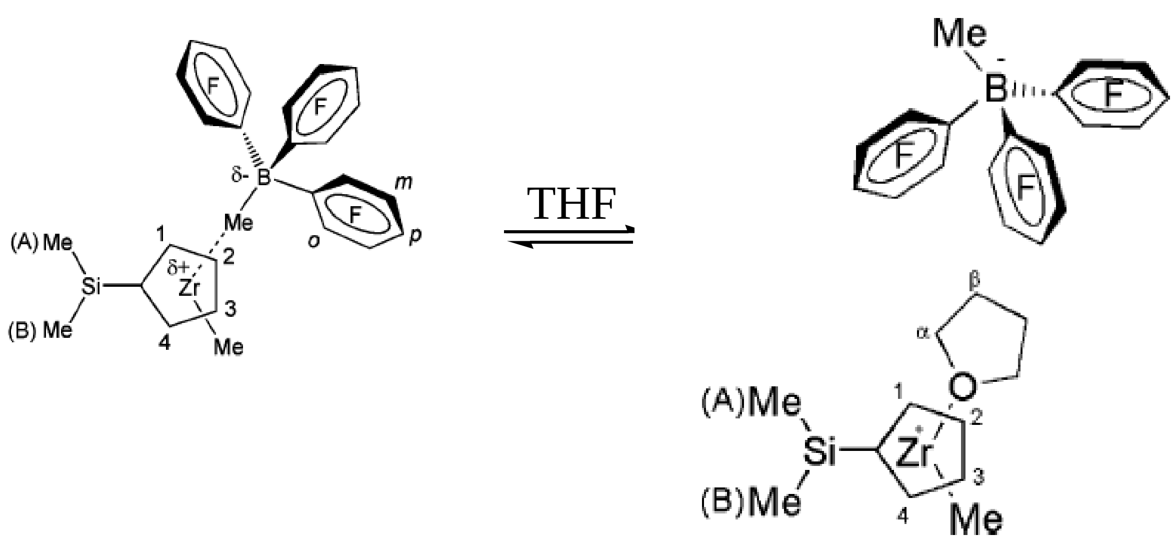

$^{19}$F ,$^{1}$H-HOESY

# Accepted mechanism for the growth of polymer chain

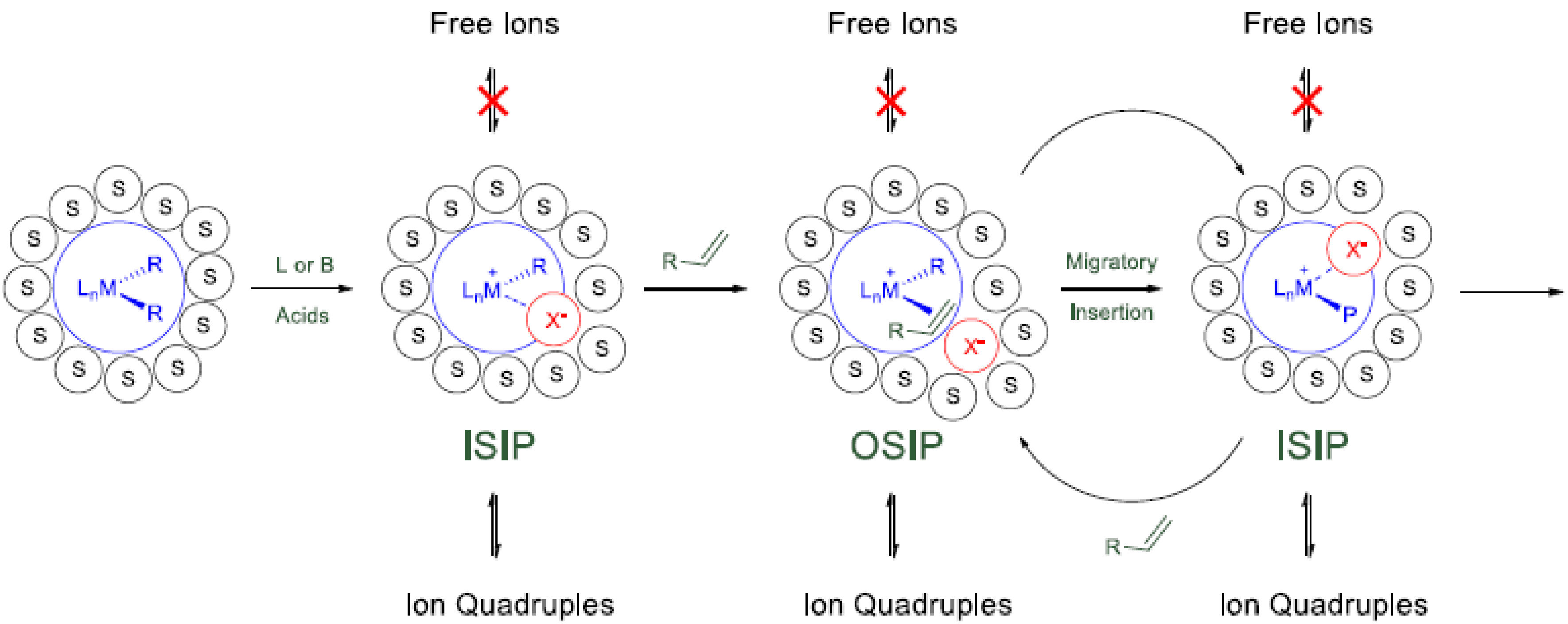



**ISIP**

**OSIP**

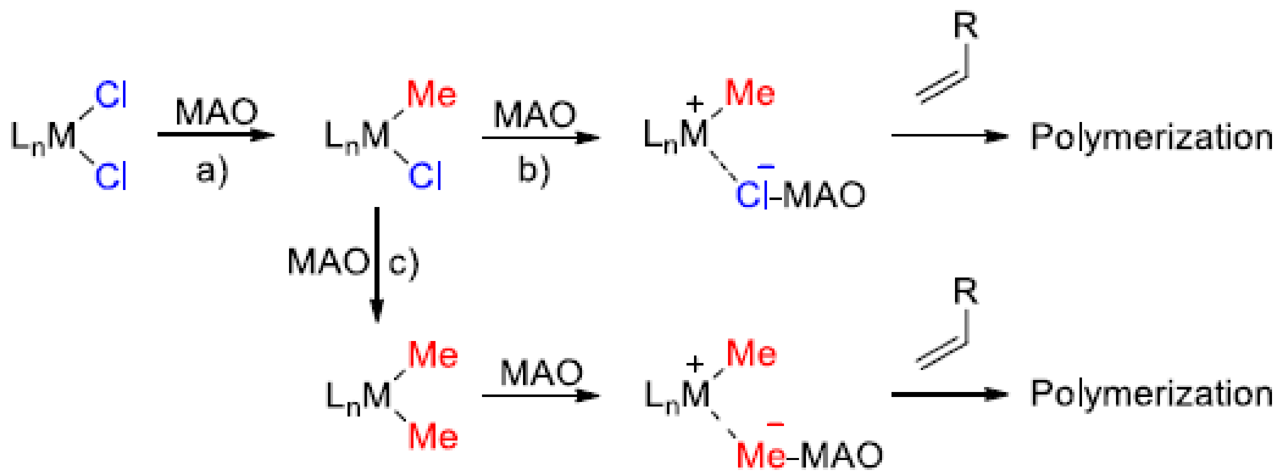


# Overall mechanism for catalyst activation and growth of polymer chain

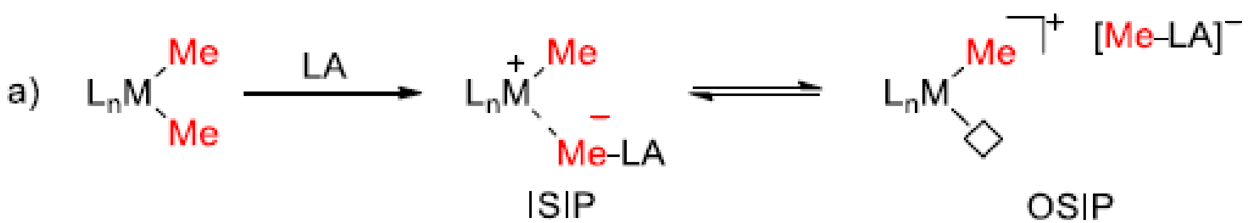


# Activation process: a comparison

## MAO as activation agent



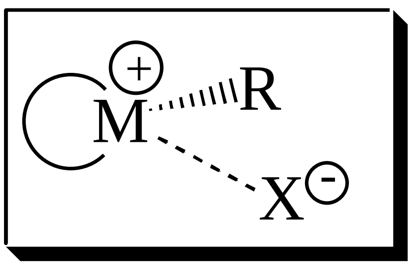

## Boranes as activation agents



# Ion pair effect in polymerization reactions

- the catalytic system is a two component system: the precatalyst that is a metallocene organometallic species and the catalyst activator that is an organometallic compound based on Al or on B;

- the two components react each other leading to the ion pair:




It is the catalyst ***resting state.***

**ISIP**

# Effect of the anion in polymerization reactions

Catalytic activity increases on decreasing the coordination capability of the anion.

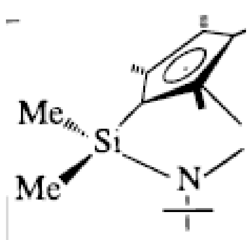
[(CGC)M(Me)][X]

When $X^{-} = MeB(C_6F_5)_3{}^{-}$ — when M = Zr: inactive system

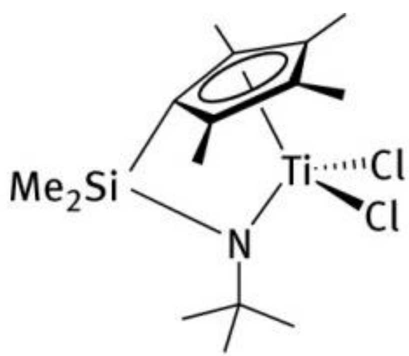
when M = Ti: slightly active system

When $X^{-} = MePBB^{-}$ — when M = Zr: active system: $v = 10^5$

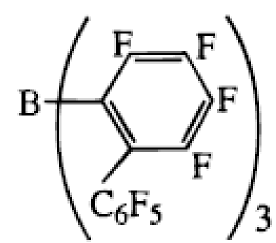
when M = Ti: the system is 70 times more active than the previous one




CGC




Cp-amido "constrained geometry" complex




PBB

# Drawbacks of metallocene catalysts[1]

- They are easily poisoned by compounds containing heteroatoms;

- they are very expensive and are synthesized according to a multistep process;

- the use of MAO:

i. in large excess with respect to the metal;

ii. it has a relatively high cost, due to the high cost of $AlMe_3$;

iii. high residual content of alumina in the final product;

iv. intrinsic danger due to the use of extrimely pyrophoric $AlMe_3$.

[1]P. Chen et al., *Helv. Chim. Acta* **2002**, *85*, 4337.