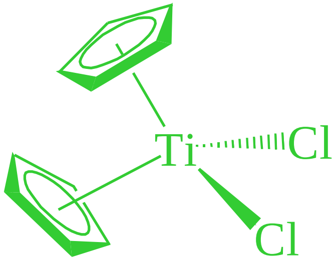
SOLUBLE Catalyst

1957

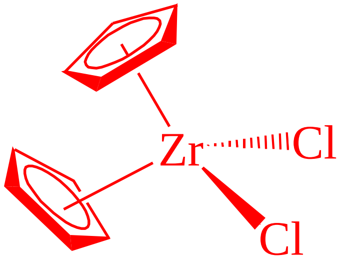


+ $AlCl(C_2H_5)_2$

The "Metallocene Revolution"

1980

Kaminsky e Sinn



+ MAO

SOLUBLE Catalysts

↓

Catalyst **STRUCTURE**

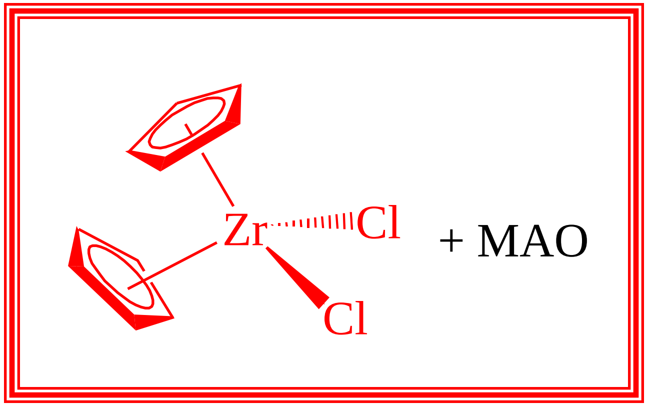
↓

Polymerization **MECHANISM**

↓

Polymer **STRUCTURE and PROPERTIES**

The “Metallocene Revolution”[1]

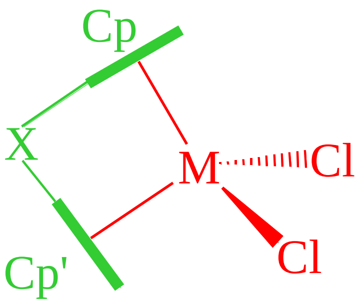


Features:

- 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

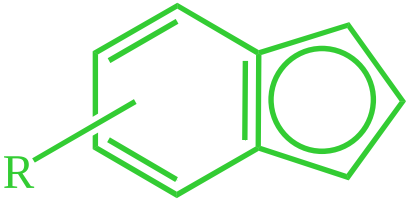


+ MAO

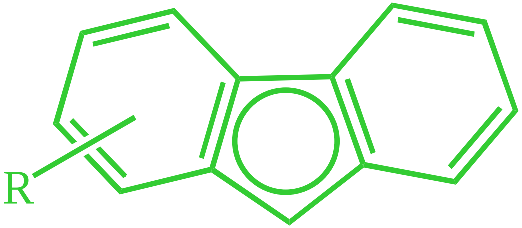
M = Ti, Zr, Hf

Cp = Cp’ o Cp ≠ Cp’

Cp e Cp’ =



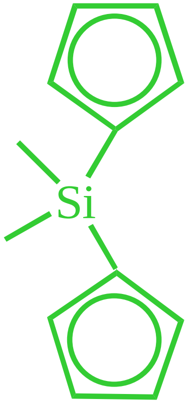
indenyl

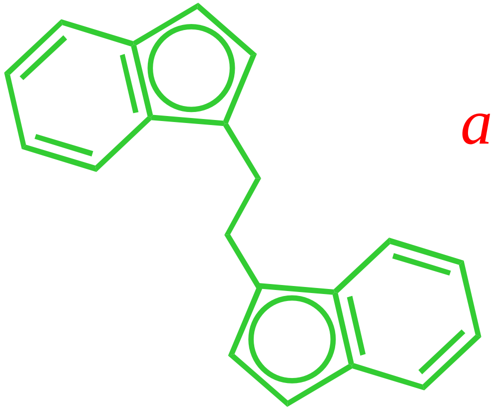


fluorenyl

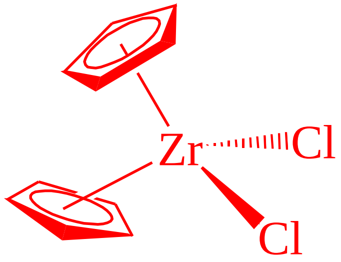
Cp-X-Cp’ =

X = CH_2CH_2, R_2Si, R_2C





ansa-metallocenes



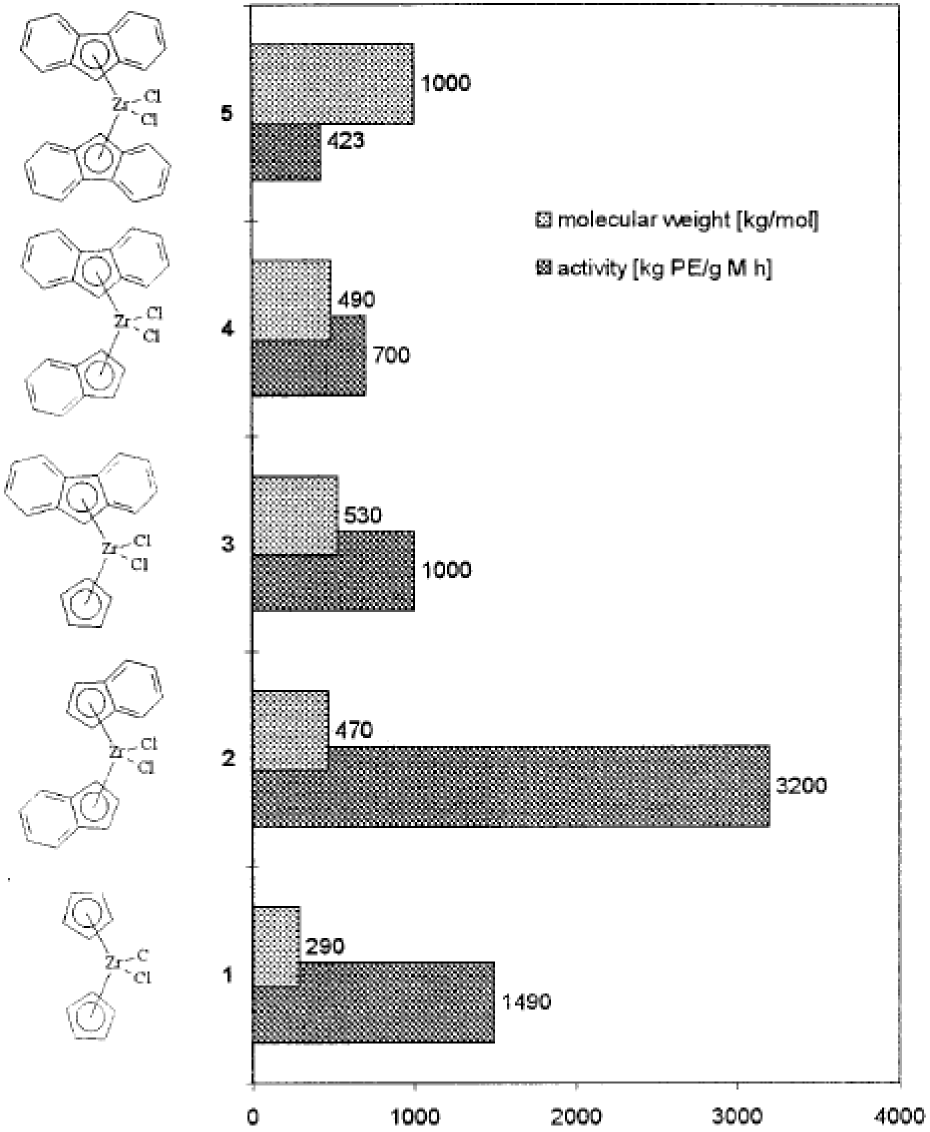
+ MAO

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

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

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

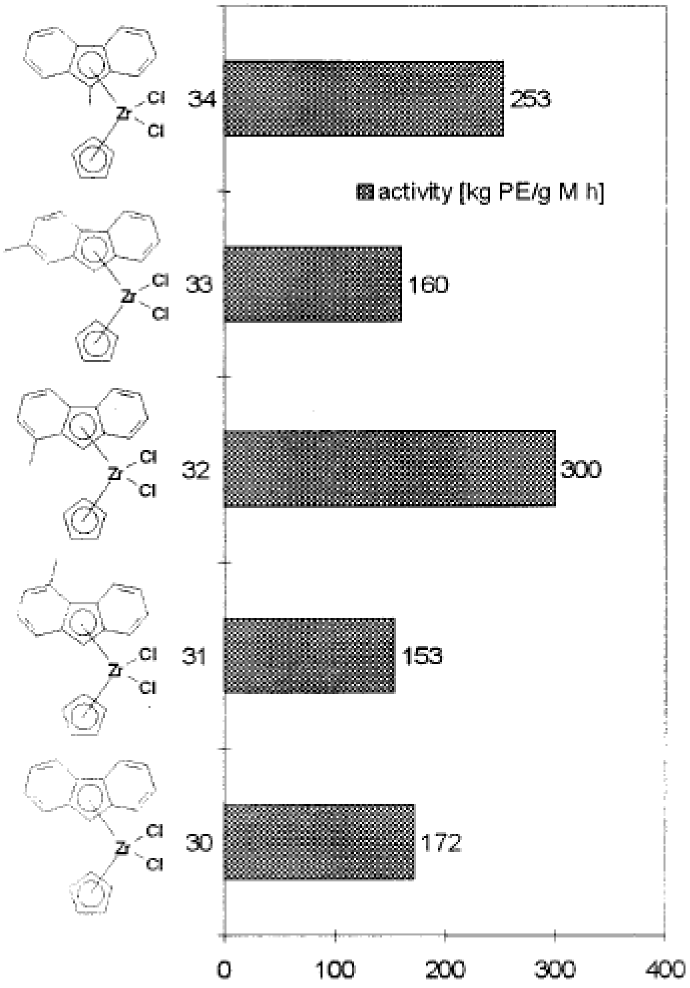
Ethylene polymerization: **Effect of the aromatic ring**



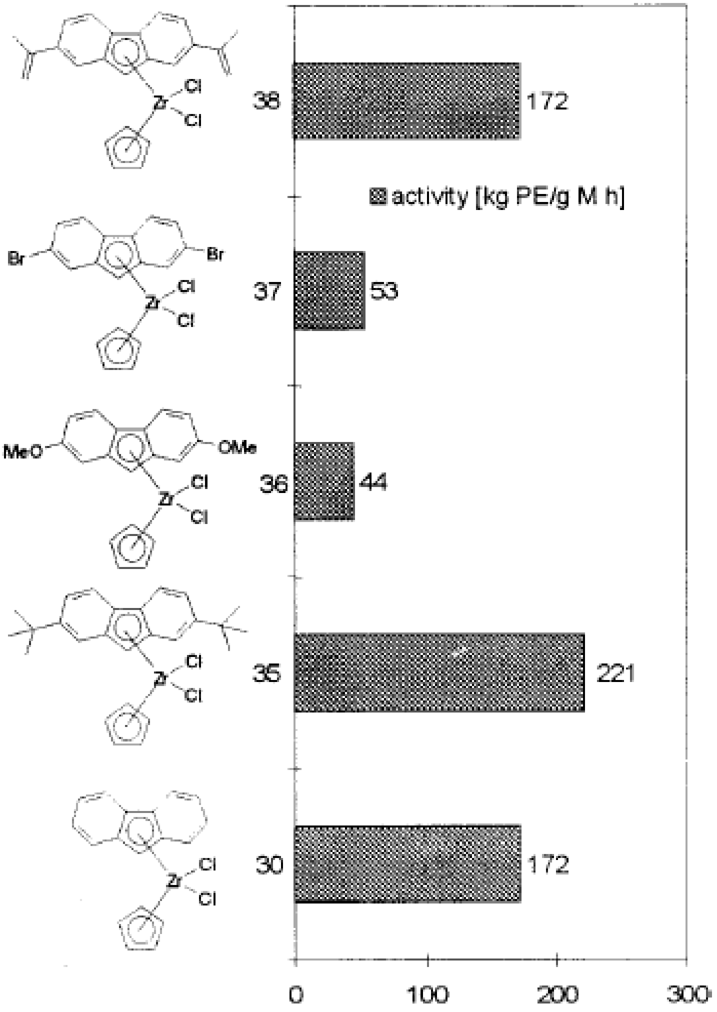
Reaction conditions: T = 60 °C; solvent: *n*-pentane; $P_{ethylene}$ = 10.0 bar; Cat. Prec. **1, 2, 4** [Al]/[Zr] = 1000; Cat. Prec. **3, 5** [Al]/[Zr] = 2500.

Ethylene polymerization: **Effect of**

substituent position



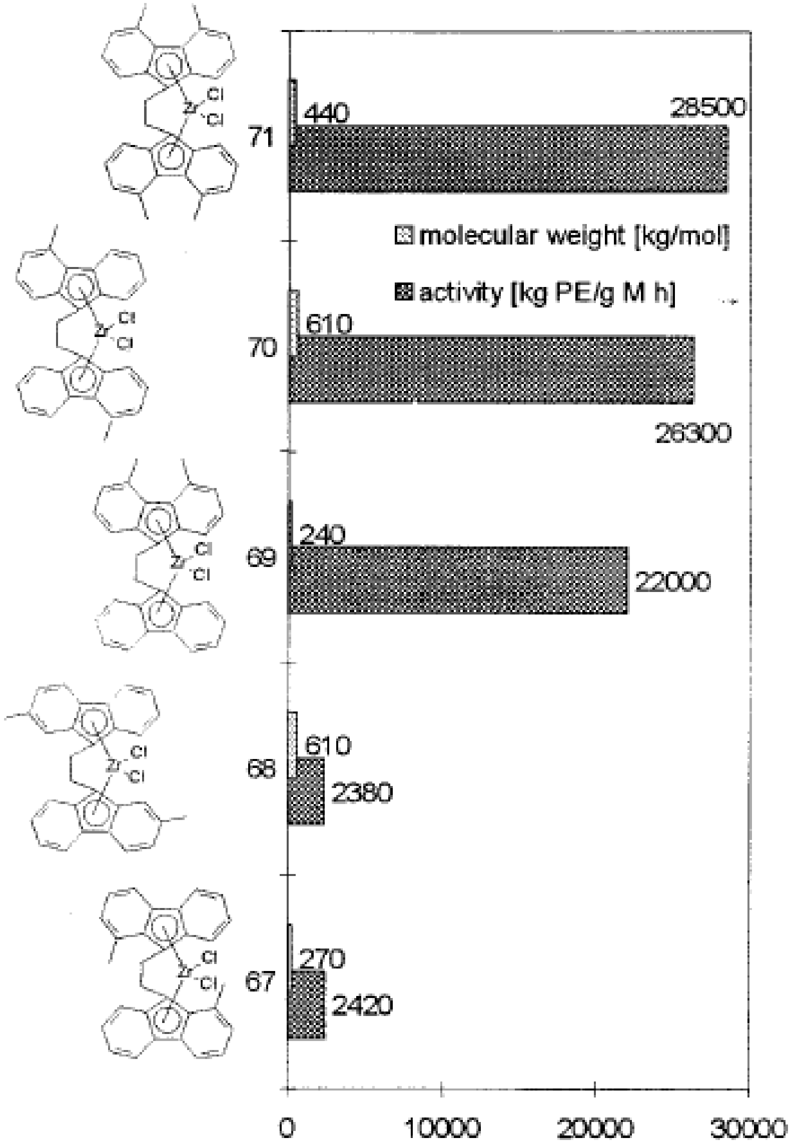
substituent nature



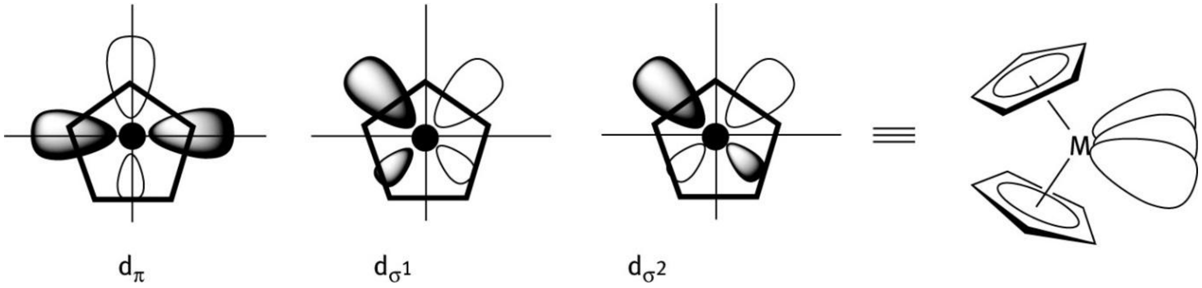
Reaction conditions: T = 10 °C; solvent: *n*-pentane; $P_{ethylene}$ = 10.0 bar; [Al]/[Zr] = 1000.

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

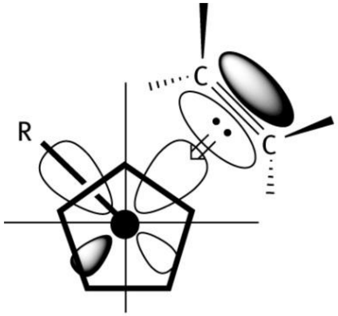
Reaction conditions:
T = 60°C;
solvent: *n*-pentane;
$P_{ethylene}$ = 10.0 bar;
[Al]/[Zr] = 20000.



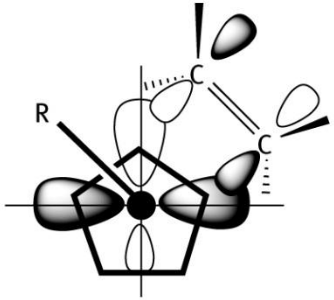
Frontier orbitals in $[Zr(Cp)_2]^{2+}$



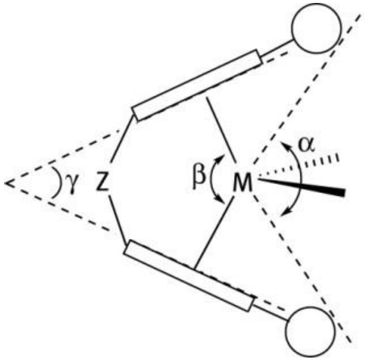
Frontier orbitals in $[Zr(Cp)_2R]^+$



d_σ acceptor orbital
for alkene binding

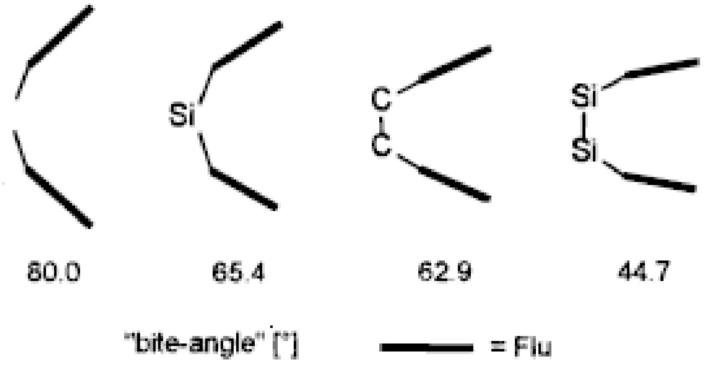


Orbital of d_π symmetry.
Absence of back-bonding for d^0 systems

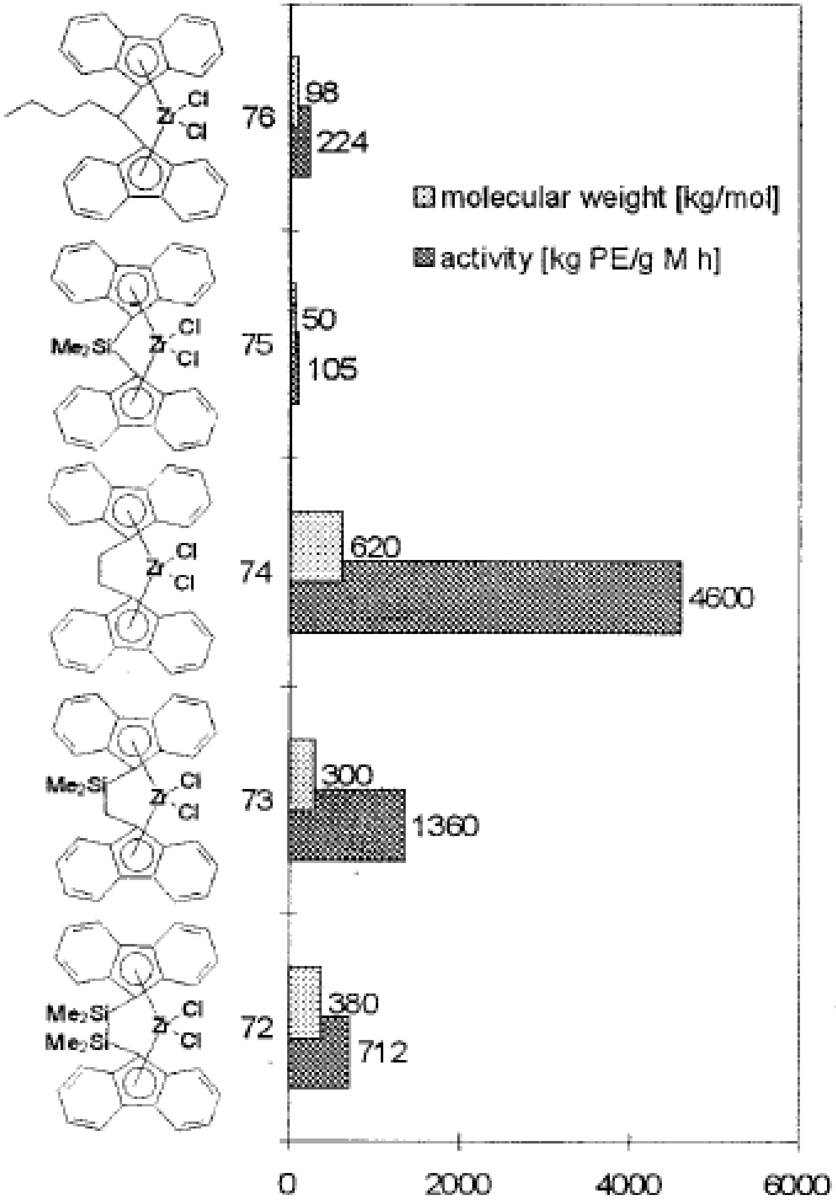


coordination gap aperture, α,
and characteristic angles
in *ansa*-metallocenes

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

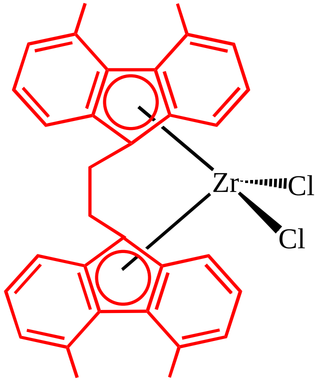


Reaction conditions: T = 60 °C; solvent: *n*-pentane; $P_{ethylene}$ = 10.0 bar; [Al]/[Zr] = 20000.

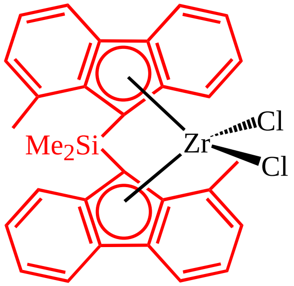


The “TOP FOUR” Catalysts[1]

productivity



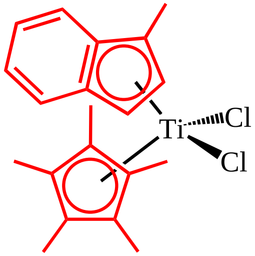
28 500 kg
PE/g Zr h



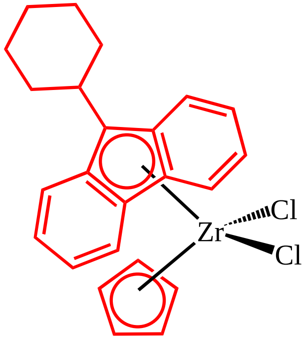
22 140 kg
PE/g Zr h

$[Al]/[Zr] = 20\,000$

High molecular weight polyethylene



1 900 kg/mol



1 850 kg/mol

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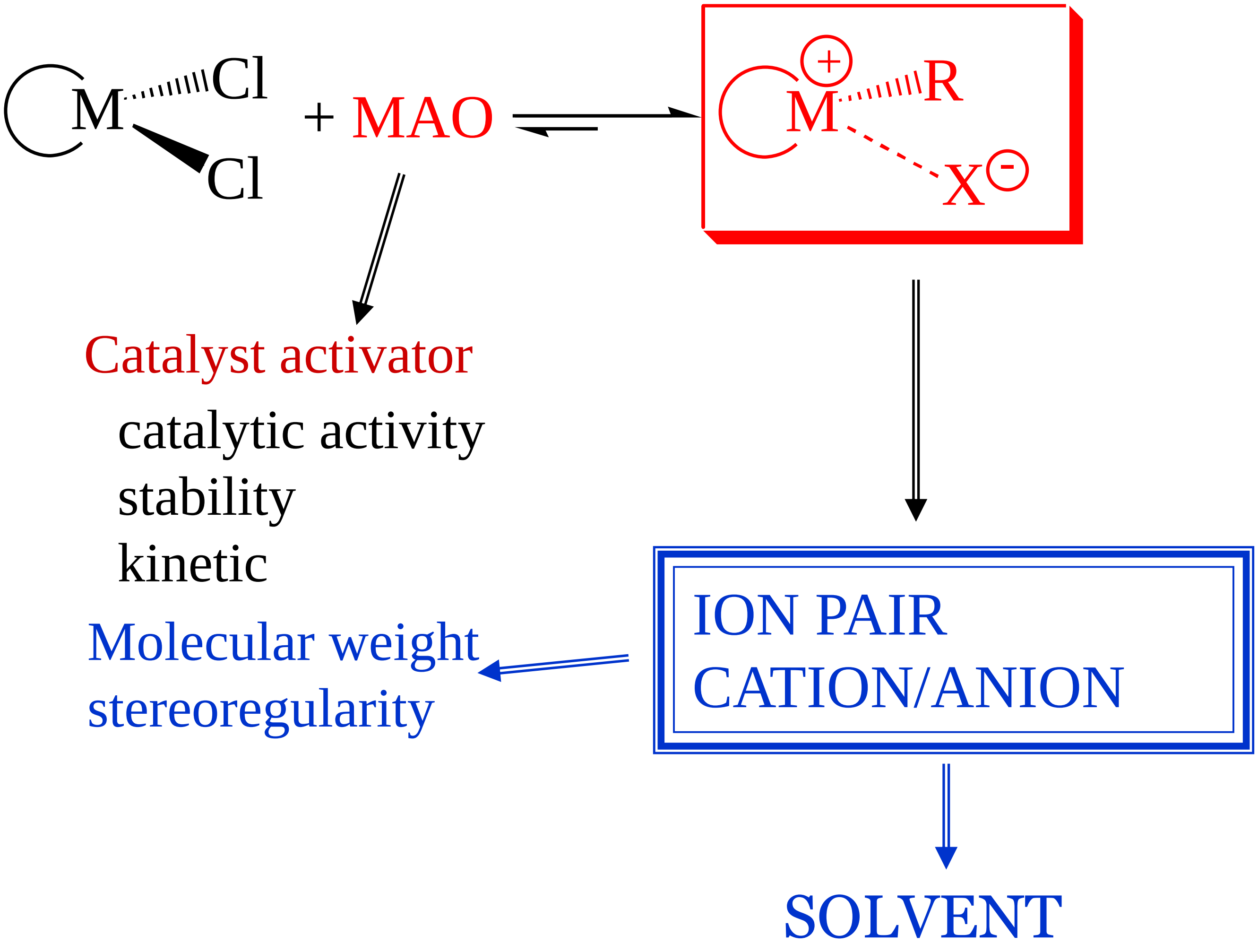
[1] H. G. Alt et al., *Chem. Rev.* **2000**, *100*, 1205.

Methylalumoxane: MAO[1]



Catalyst activator

catalytic activity
stability
kinetic

Molecular weight
stereoregularity

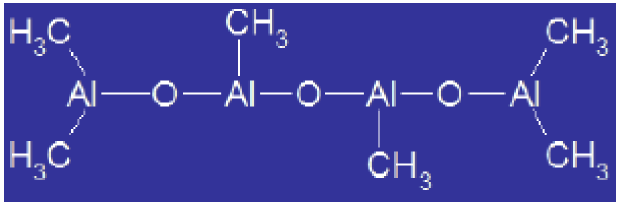
ION PAIR
CATION/ANION

SOLVENT

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

MAO[1]: structural features

$[\!-\mathrm{Al(Me)}-\mathrm{O}-]_n$ n = 5 - 20

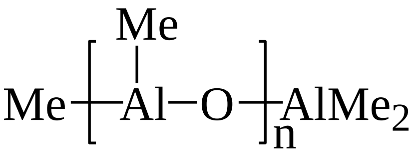


Multiple equilibria:

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

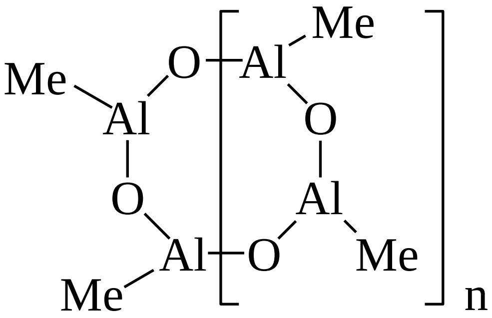
"associated"   "free"

Main proposed structures :

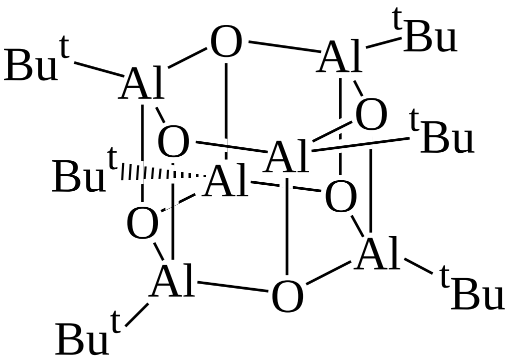


$\mathrm{Me}\!\left[\overset{\mathrm{Me}}{\overset{|}{\mathrm{Al}}}-\mathrm{O}\right]_n\!\mathrm{AlMe_2}$

One-dimensional linear



Cyclic rings



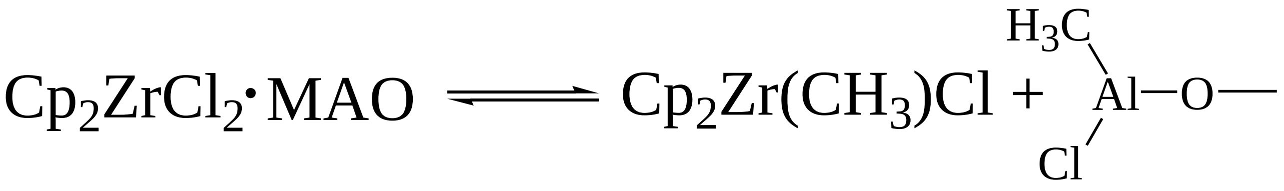
Cage structure

---

[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*



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

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

$$\Updownarrow$$

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

$$\boxed{[Al]/[Zr] \geq 1000}$$

$$Cp_2ZrMe_2 + Me_3Al \rightleftharpoons Cp_2ZrMe^+AlMe_4^-$$

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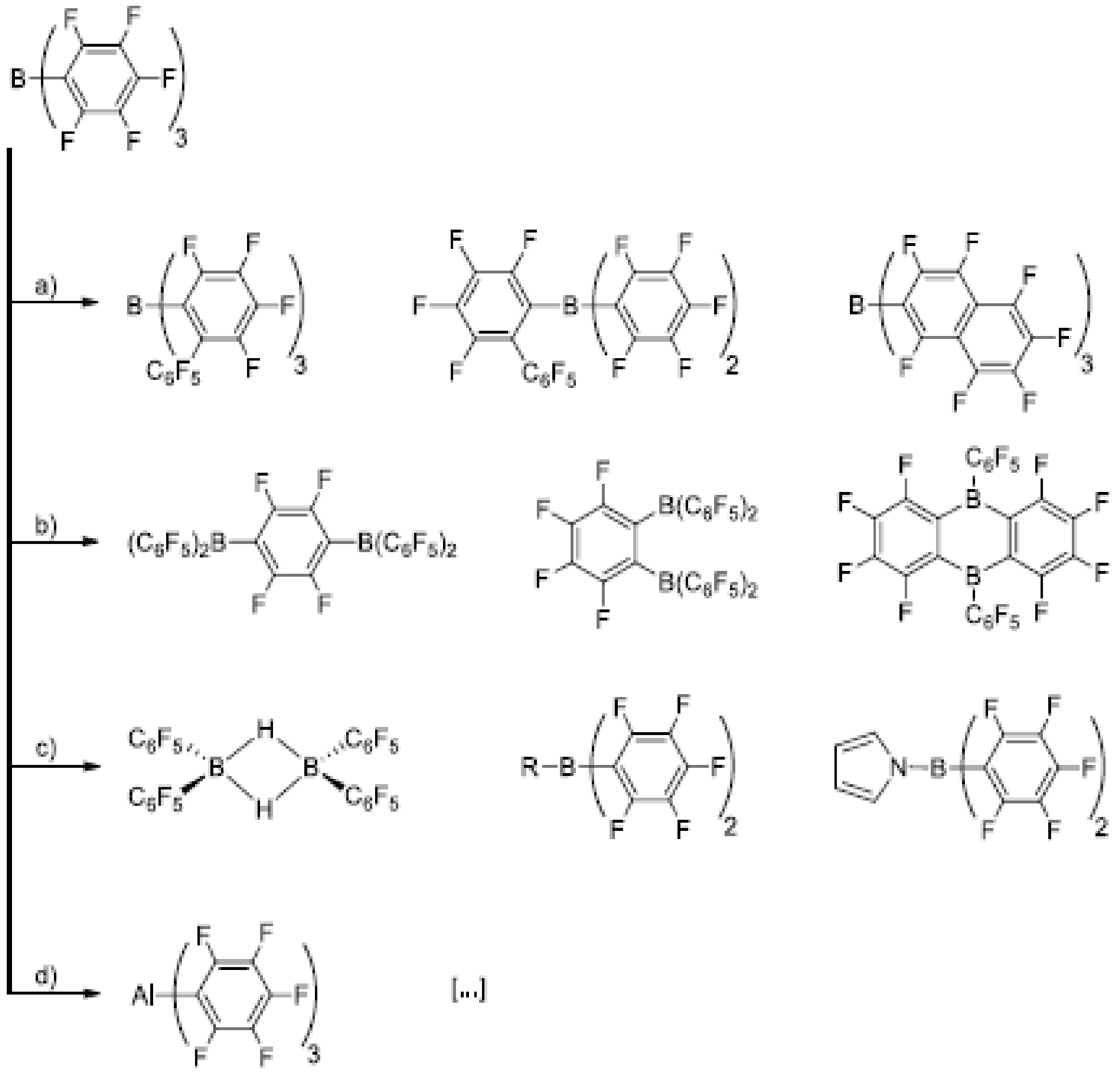
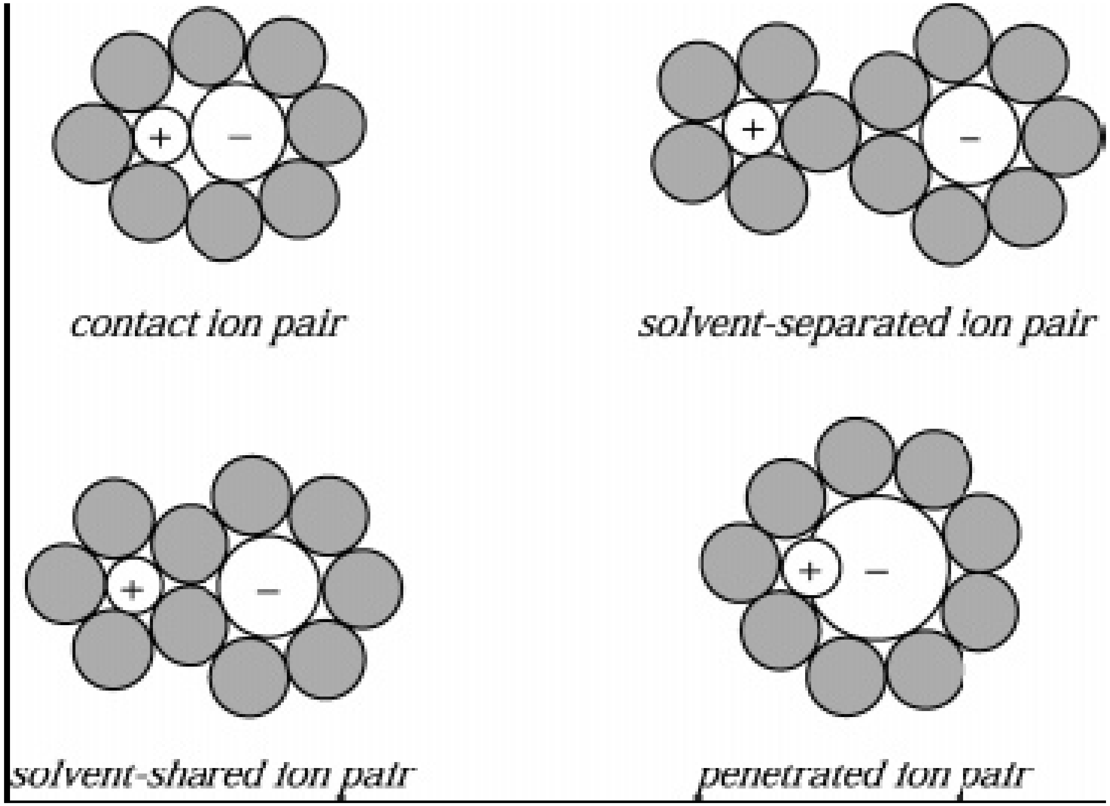
[1] T. J. Marks et al., *Chem. Rev.* **2000**, *100*, 1391.

Lewis acids as activators: Perfluoroaryl boranes

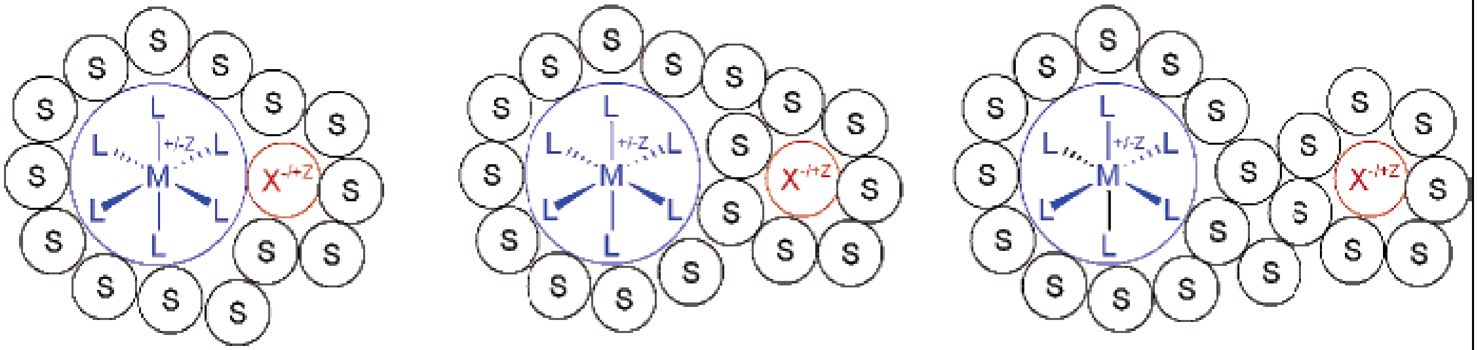


THE ION PAIR[1]

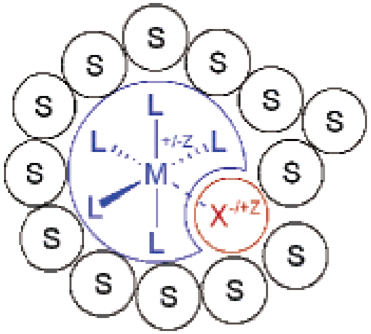


[1] A. Macchioni *Chem. Rev.* **2006**, *105*, 2039.

TRANSITION METAL COMPLEX ION PAIRS



A3 contact (OSIP)   *B3 solvent-shared*   *C3 solvent-separated*

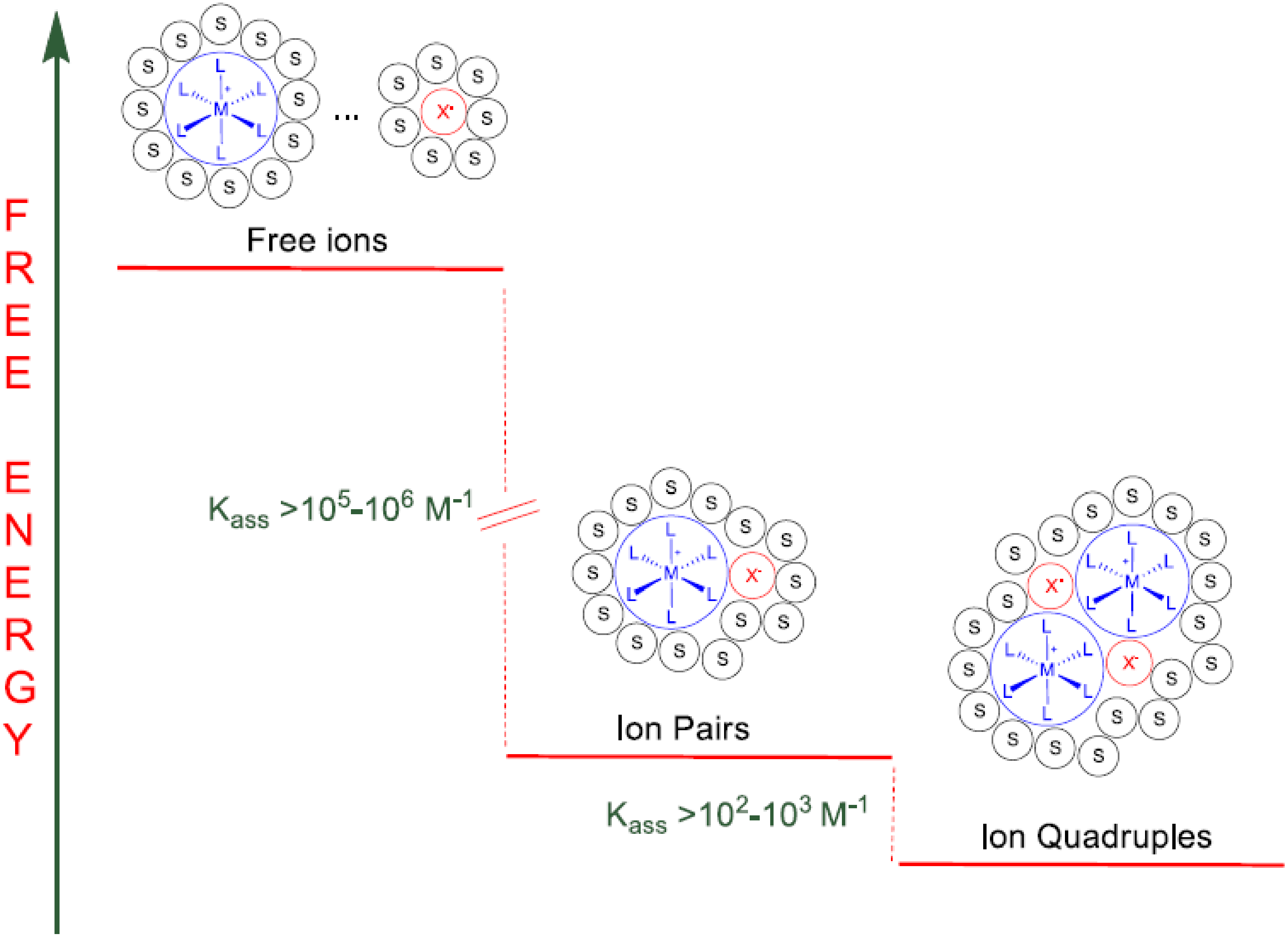


D3 contact (ISIP)

OSIP = OUTER-SPHERE ION PAIR

ISIP = INNER-SPHERE ION PAIR

Possible ion pairs in polymerization reactions



FREE ENERGY

Free ions

$K_{ass} > 10^5\text{-}10^6\ M^{-1}$

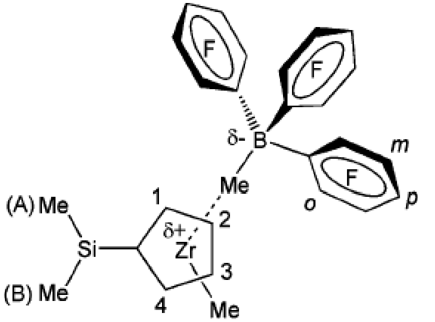
Ion Pairs

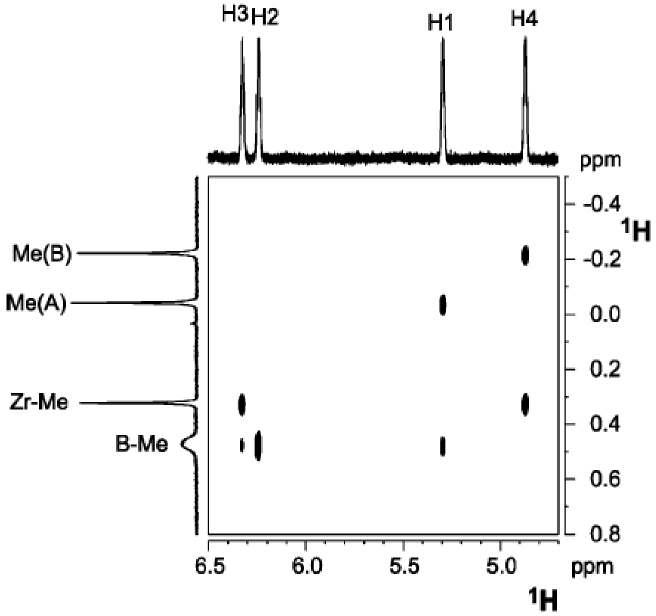
$K_{ass} > 10^2\text{-}10^3\ M^{-1}$

Ion Quadruples

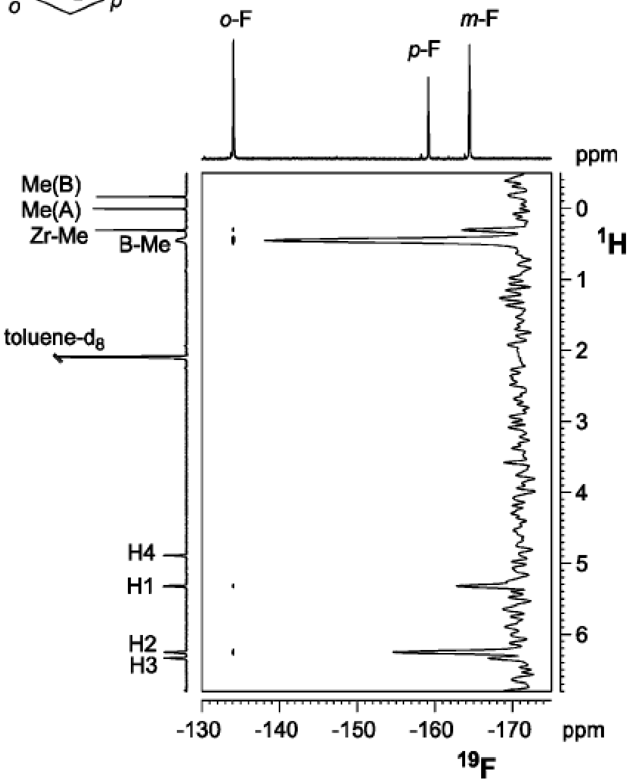
Experimental evidences for the ione pair formation

NMR Spectroscopy in solution



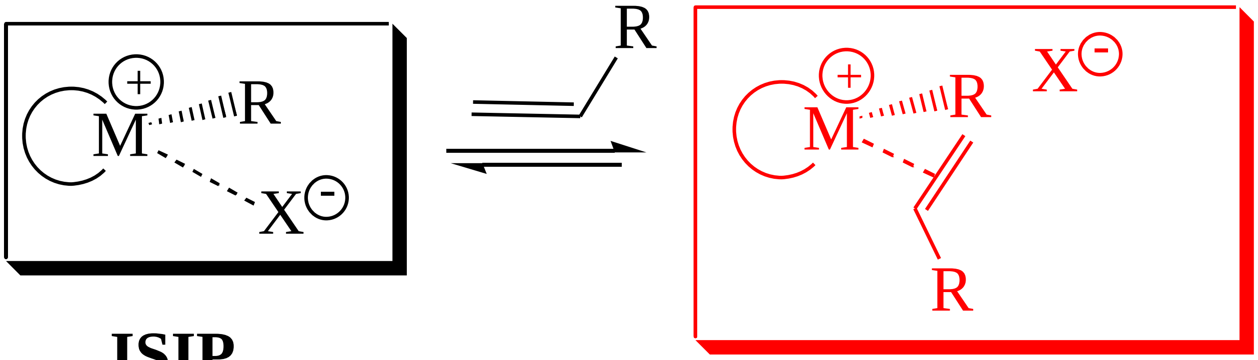


^{1}H-NOESY



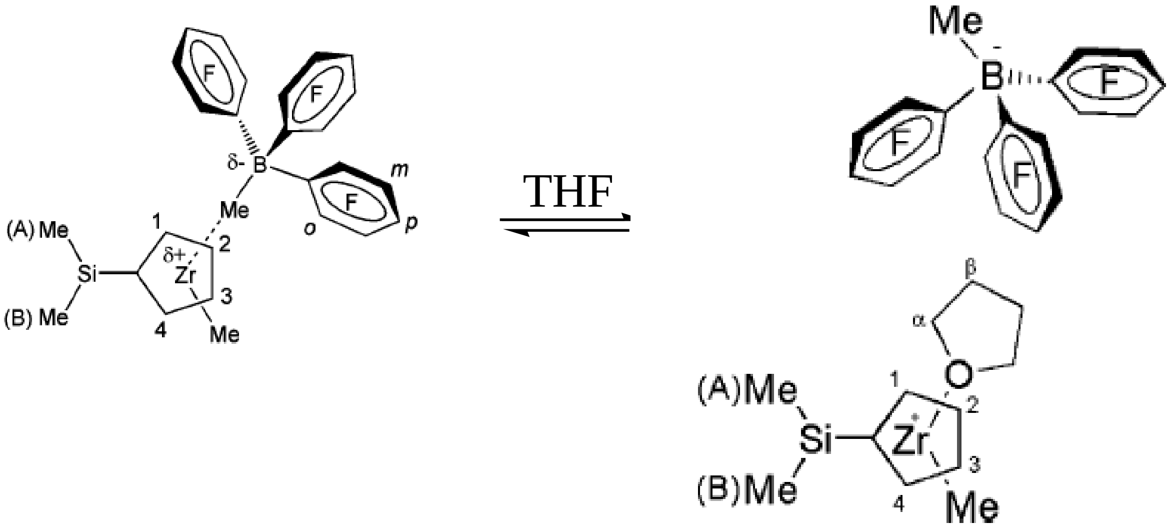
^{19}F ,^{1}H-HOESY

Accepted mechanism for the growth of polymer chain

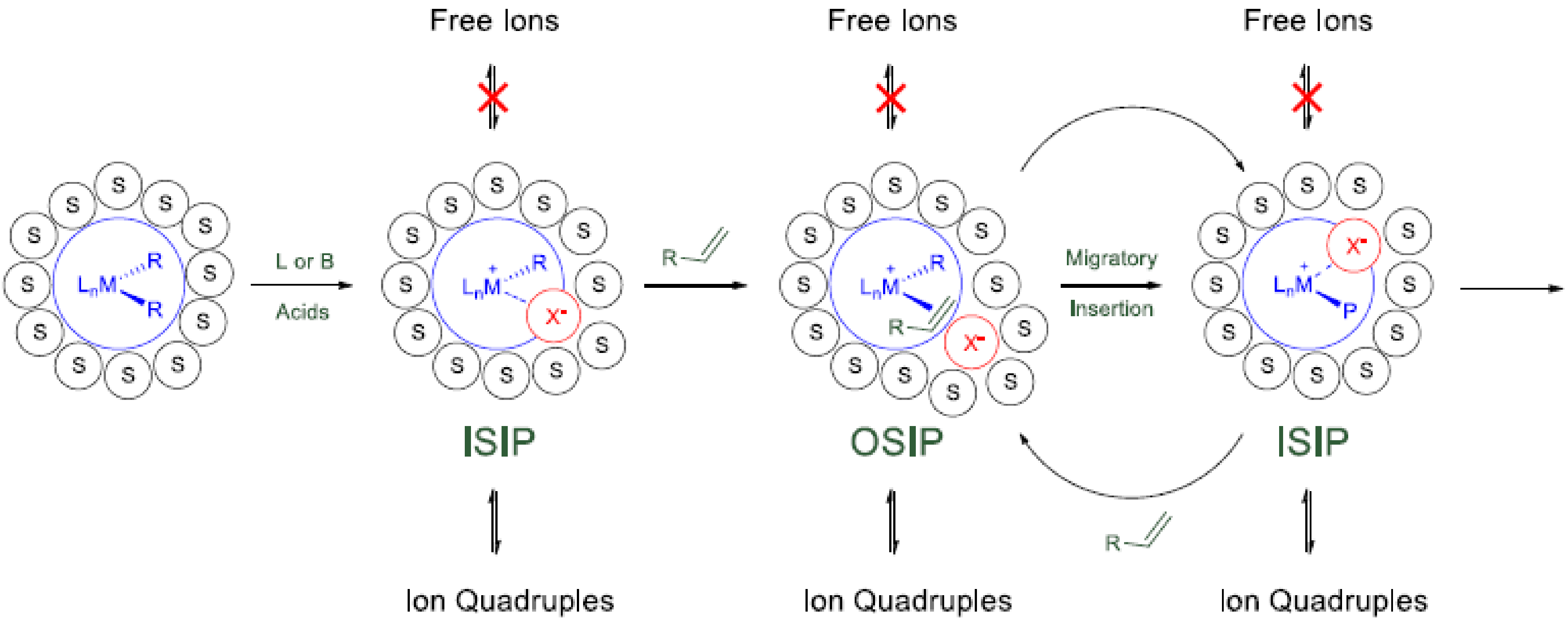


ISIP

OSIP

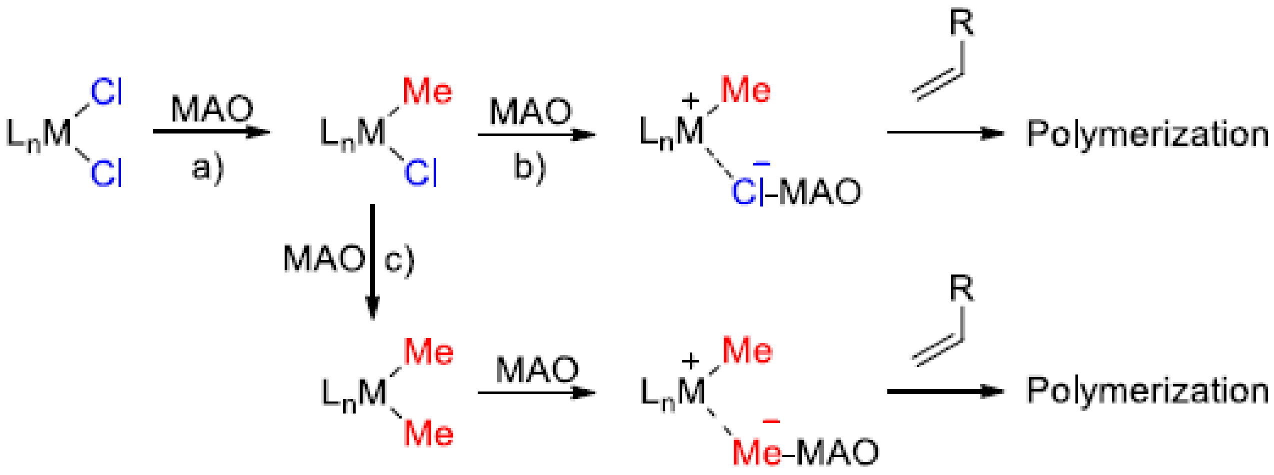


Overall mechanism for catalyst activation and growth of polymer chain

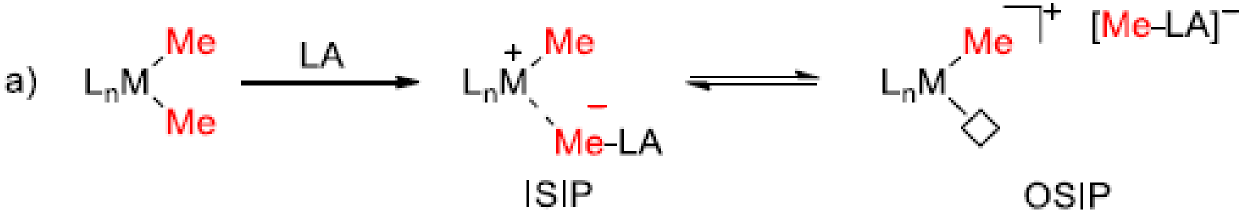


Activation process: a comparison

MAO as activation agent



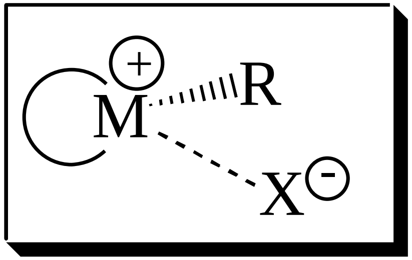
Boranes as activation agents



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:



ISIP

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

Effect of the anion in polymerization reactions

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

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

When $X^- = MeB(C_6F_5)_3^-$

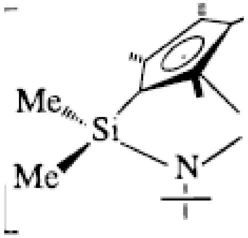
when M = Zr: inactive system

when M = Ti: slightly active system

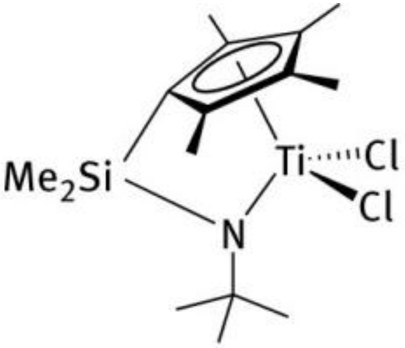
When $X^- = MePBB^-$

when M = Zr: active system: $v = 10^5$

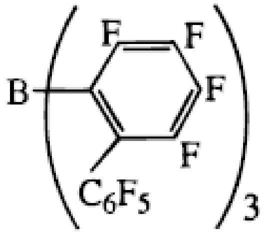
when M = Ti: the system is 70 times more active than the previous one



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.