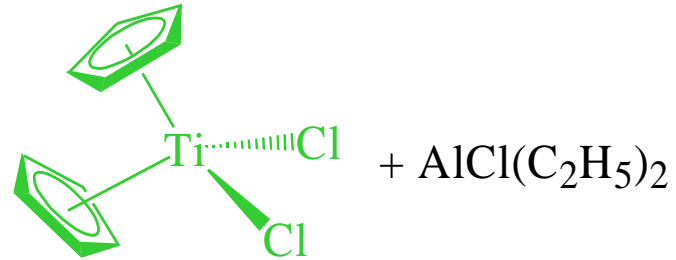


Catalizzatore **SOLUBILE**

1957



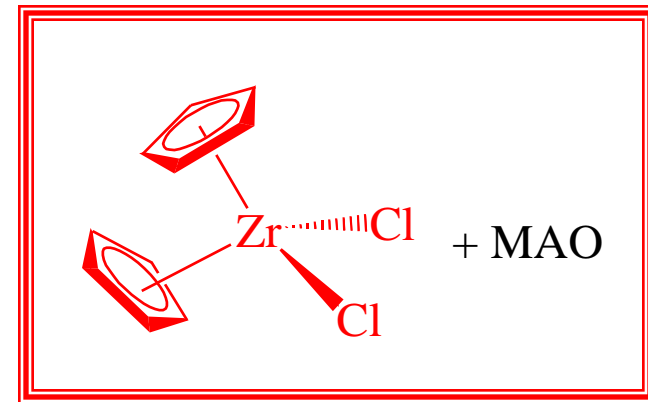
The “**Metallocene Revolution**”

1980

Catalizzatori **SOLUBILI**

Kaminsky e Sinn

STRUTTURA del catalizzatore



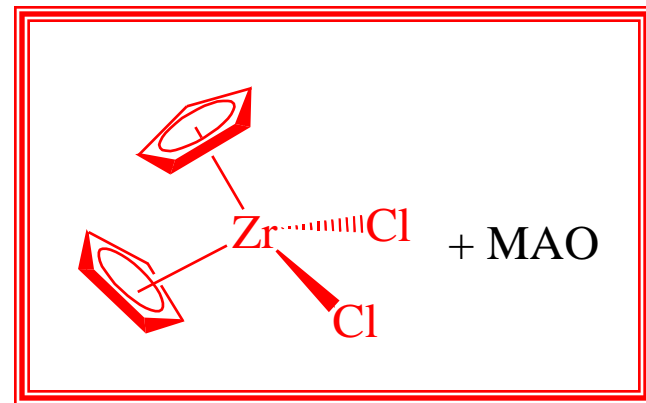
MECCANISMO della polimerizzazione

STRUTTURA e PROPRIETA' del polimero

The “Metallocene Revolution”¹

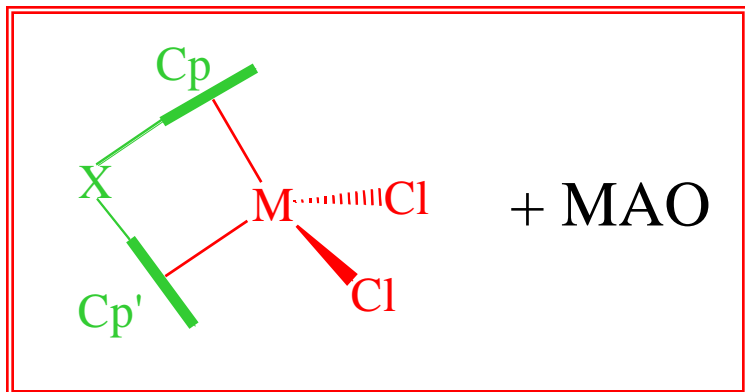
Caratteristiche:

- ❖ **catalizzatori omogenei**: 100 volte più attivi dei convenzionali Ziegler-Natta (300 t PE/g Zr h);
- ❖ promuovono la **polimerizzazione stereospecifica** di α -olefine prochirali;
- ❖ producono poliolefine con una stretta distribuzione dei pesi molecolari: **Single Site Catalysts**;
- ❖ si possono ottenere poliolefine con **ramificazioni** di diversa lunghezza regolarmente distribuite lungo la catena polimerica;
- ❖ possono venire **eterogeneizzati**.



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

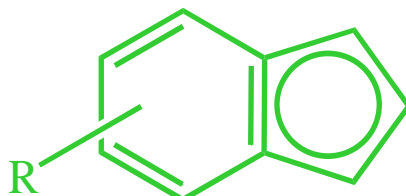
La Versatilità dei Catalizzatori metallocenici



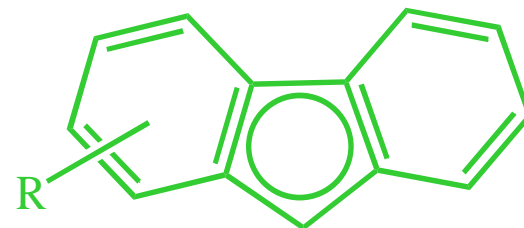
$M = Ti, Zr, Hf$

$Cp = Cp'$ o $Cp \neq Cp'$

Cp e $Cp' =$



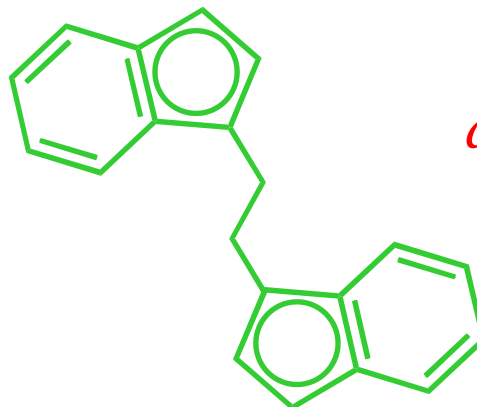
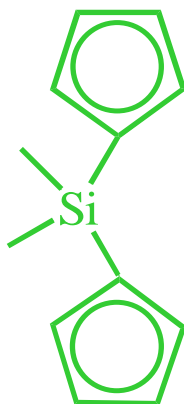
indenile



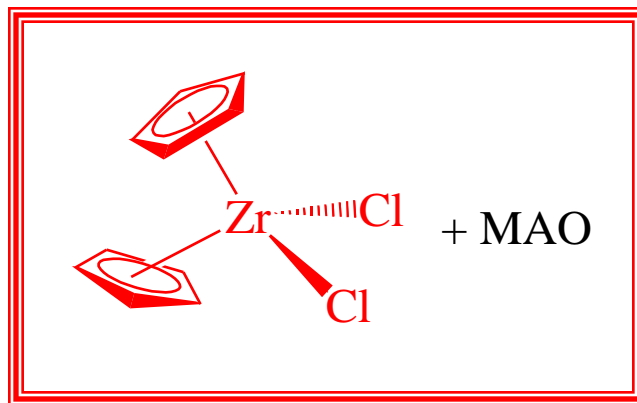
fluorene

$Cp-X-Cp' =$

$X = CH_2CH_2, R_2Si,$
 R_2C



ansa-metalloceni



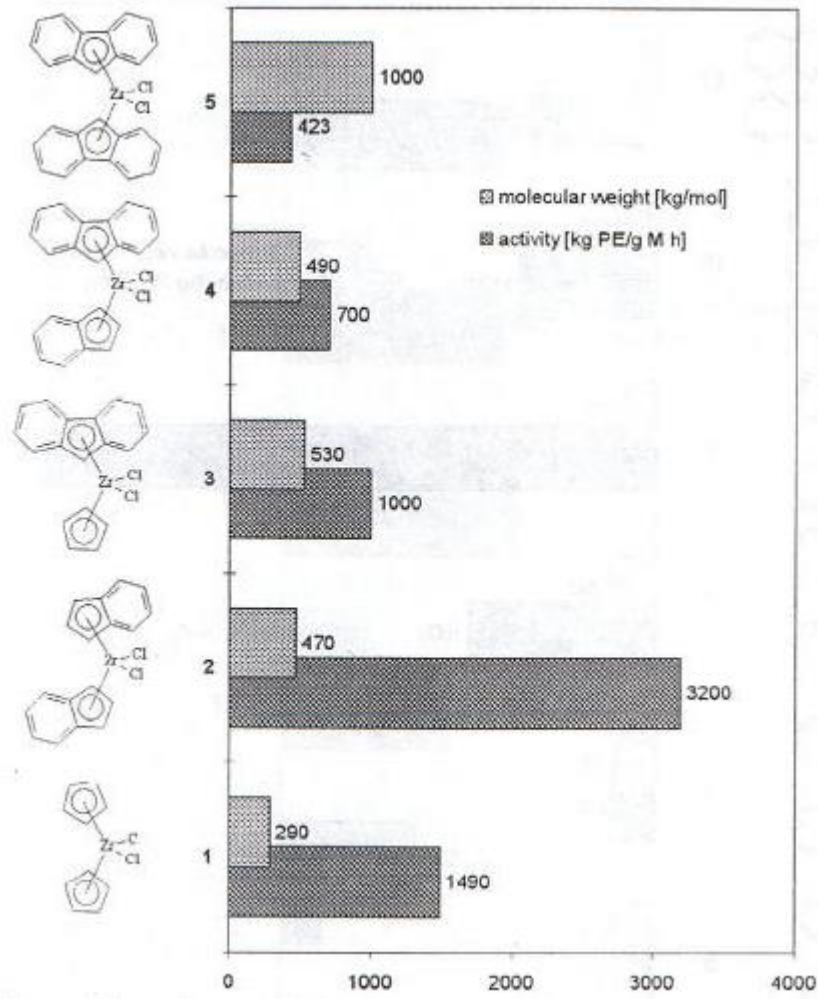
Condizioni di reazione: $T = 90^{\circ}\text{C}$, $P_{\text{etilene}} = 8 \text{ bar}$,
[Al]/[Zr] = 10 000,
solvente = toluene

Produttività: $5 \cdot 10^6 \text{ g PE/g Zr} \cdot \text{h} \cdot \text{bar}$
 $M_n = 122\,000$

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

Polimerizzazione dell'etilene

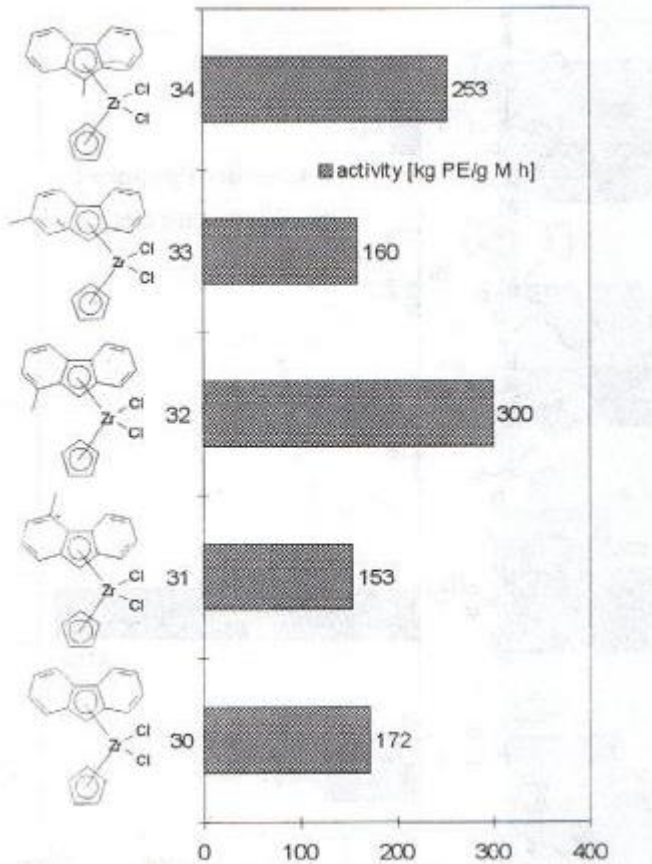
Effetto dell'**anello aromatico**



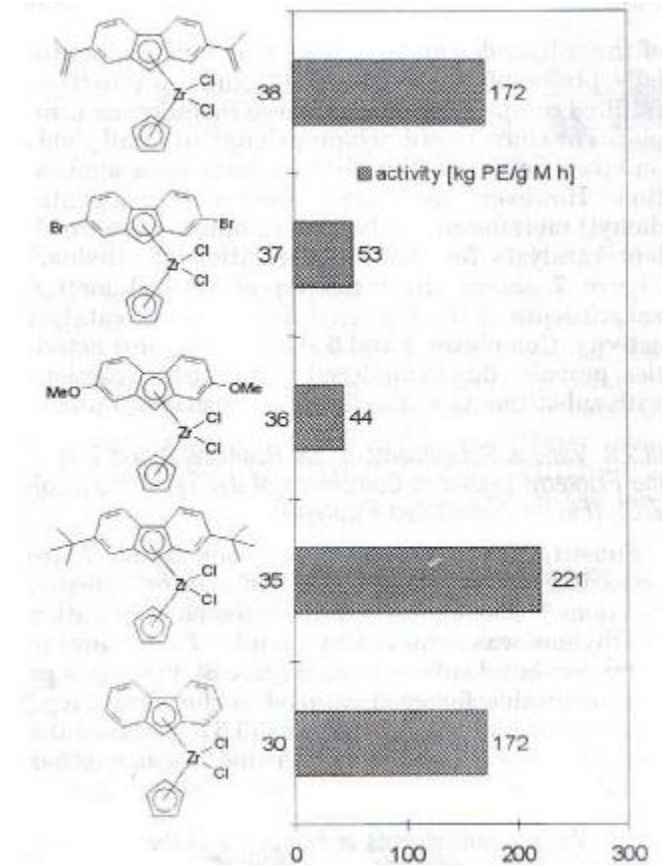
Condizioni di reazione: $T = 60^{\circ}\text{C}$; solvente: *n*-pentano; $P_{\text{etilene}} = 10.0 \text{ bar}$;
Cat. Prec. **1, 2, 4** $[\text{Al}]/[\text{Zr}] = 1000$; Cat. Prec. **3, 5** $[\text{Al}]/[\text{Zr}] = 2500$.

Polimerizzazione dell'etilene

Effetto della **posizione**



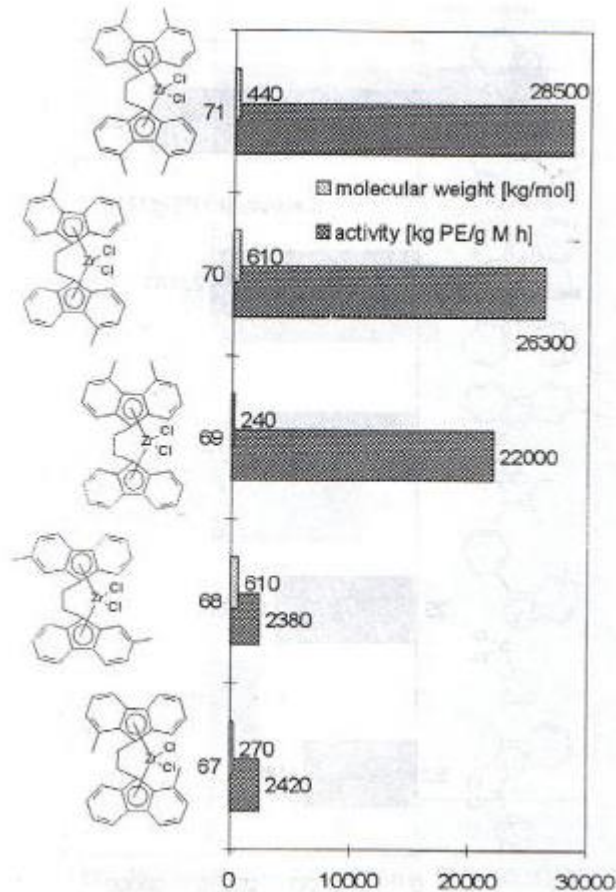
Effetto del **sostituente**



Condizioni di reazione: $T = 10^{\circ}\text{C}$; solvente: *n*-pentano; $P_{\text{etilene}} = 10.0 \text{ bar}$; $[\text{Al}]/[\text{Zr}] = 1000$.

Polimerizzazione dell'etilene

Effetto della **posizione** del sostituito sugli *ansa-metalloceni*

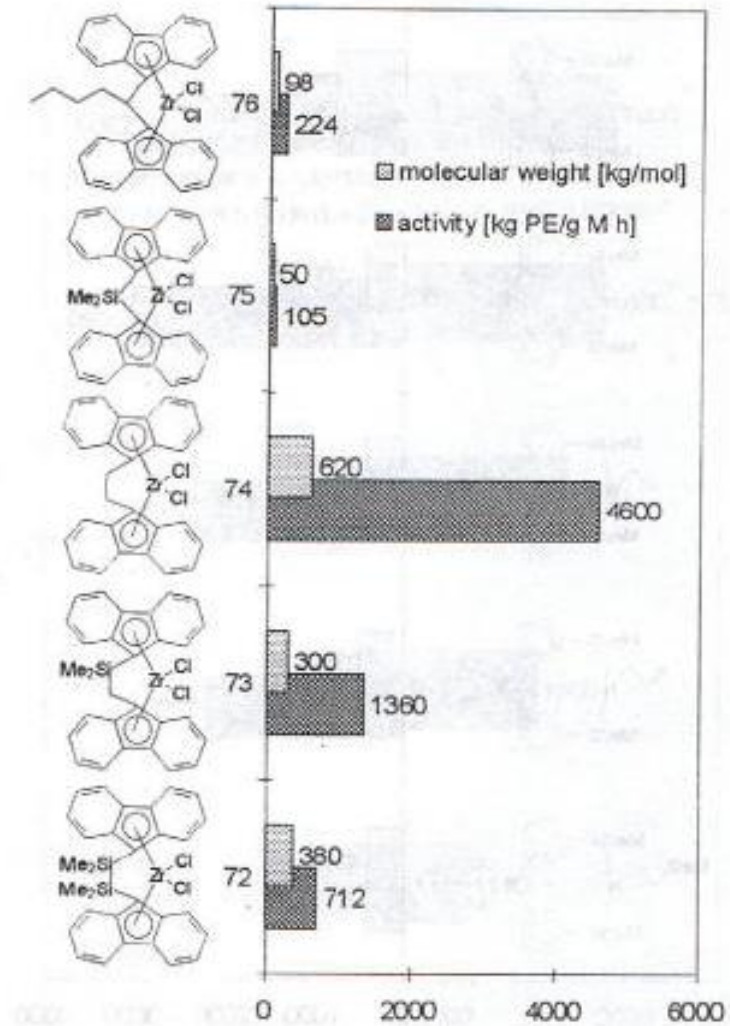
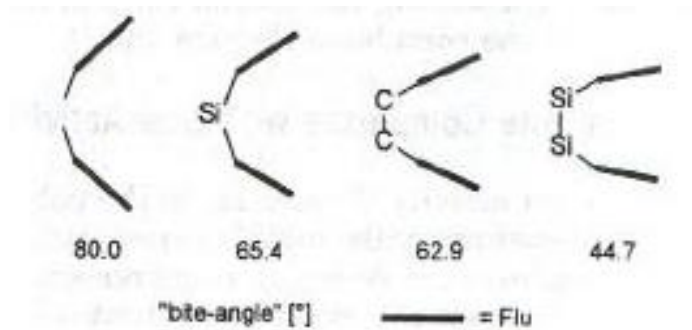


Condizioni di reazione: $T = 60^{\circ}\text{C}$; solvente: *n*-pentano; $P_{\text{etilene}} = 10.0 \text{ bar}$;

$[\text{Al}]/[\text{Zr}] = 20000$.

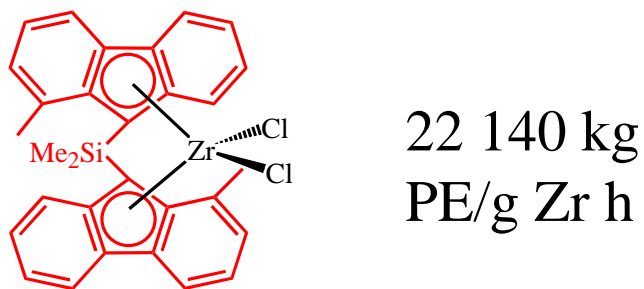
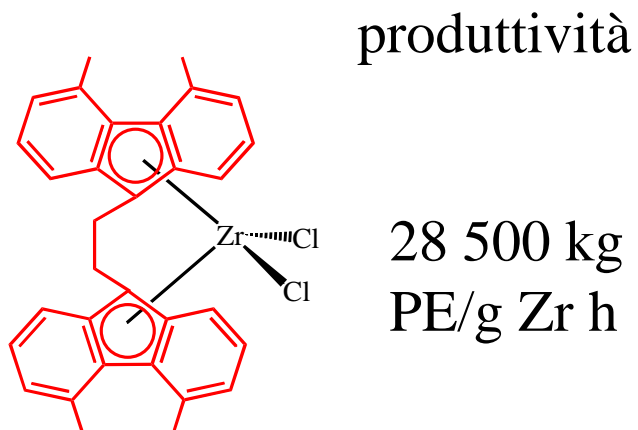
Polimerizzazione dell'etilene

Effetto del **bite angle**

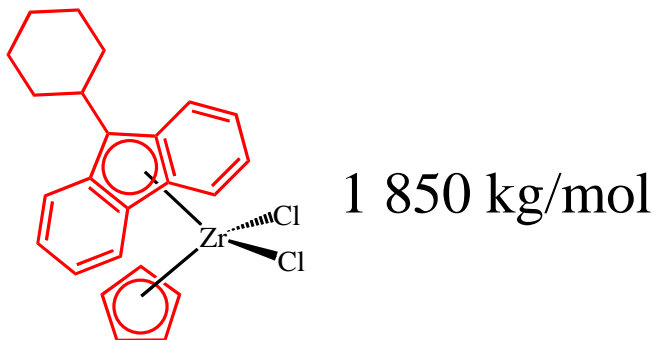
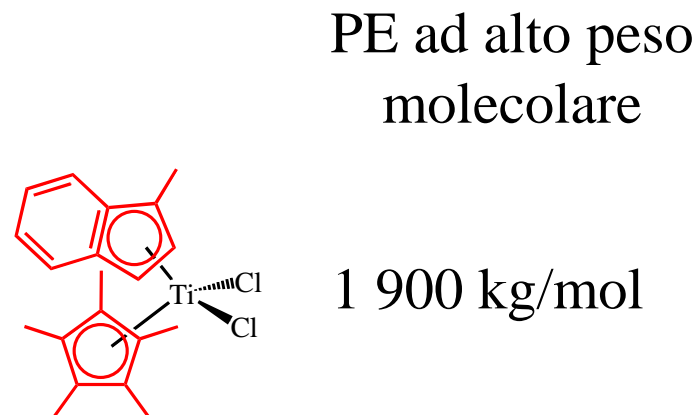


Condizioni di reazione: $T = 60^{\circ}\text{C}$; solvente: *n*-pentano; $P_{\text{etilene}} = 10.0 \text{ bar}$; $[\text{Al}]/[\text{Zr}] = 20000$.

The "TOP FOUR" Catalysts¹

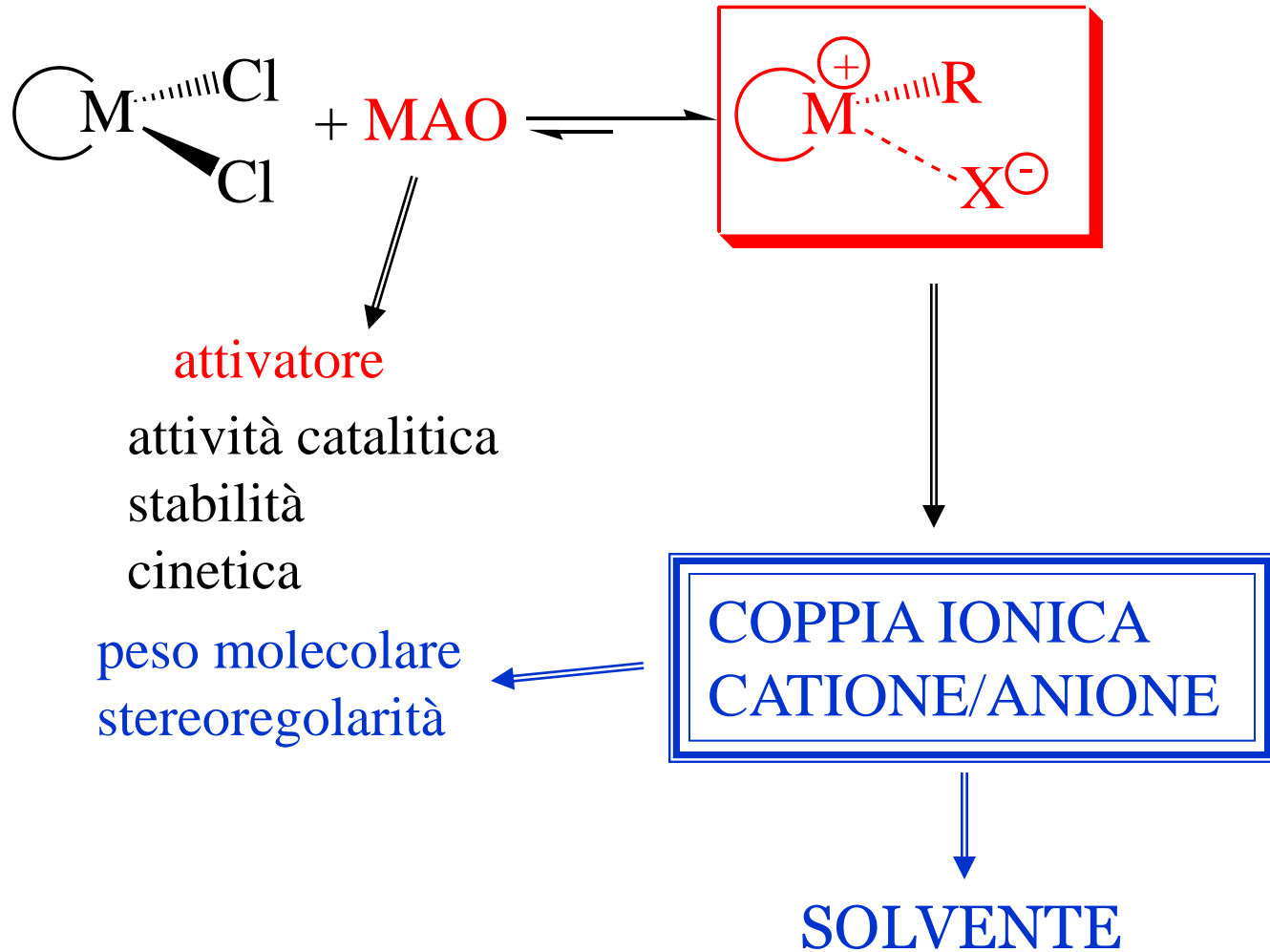


[Al]/[Zr] = 20 000



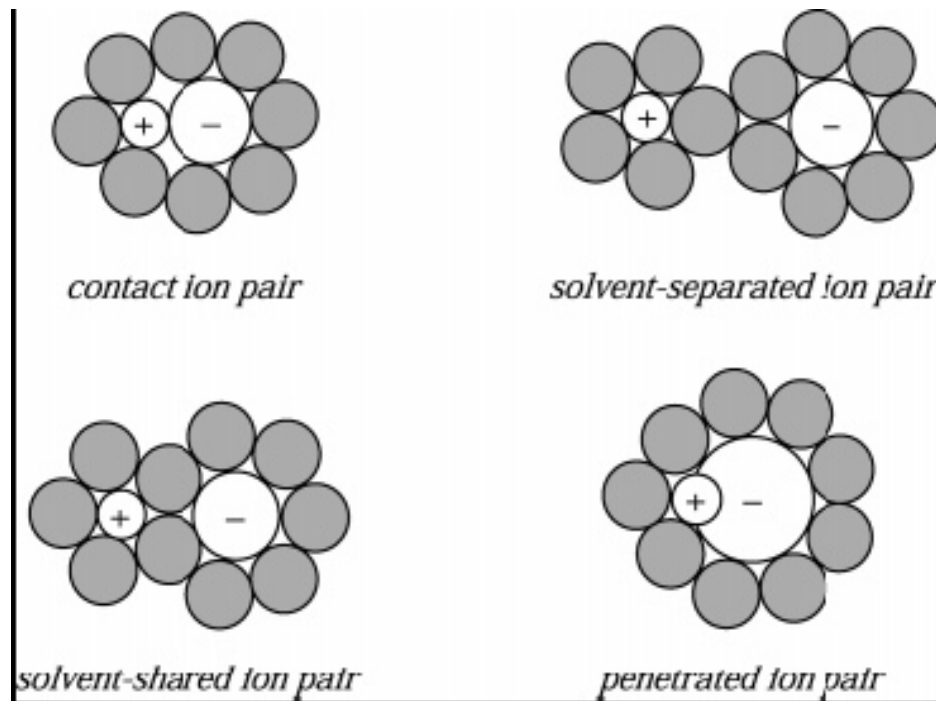
¹H. G. Alt et al., *Chem. Rev.* **2000**, *100*, 1205.

IL MAO¹



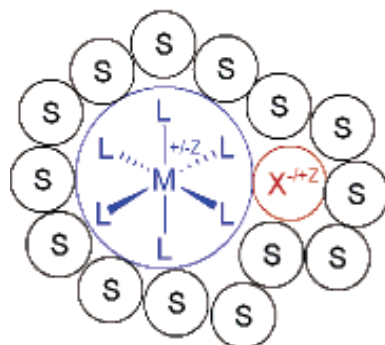
¹T. J. Marks et al., *Chem. Rev.* **2000**, *100*, 1391.

LA COPPIA IONICA¹

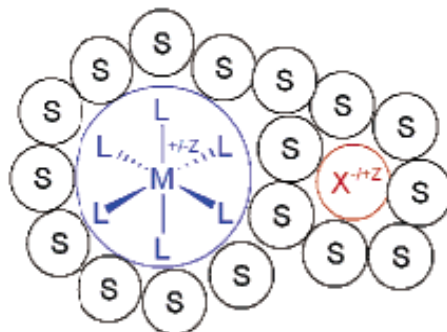


¹A. Macchioni *Chem. Rev.* **2006**, *105*, 2039.

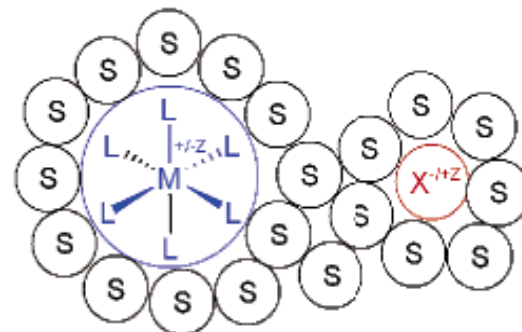
TRANSITION METAL COMPLEX ION PAIRS



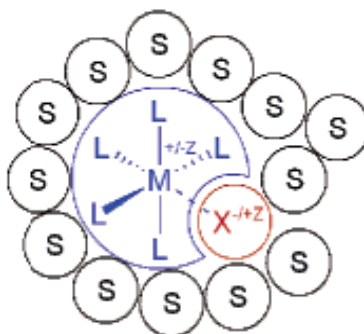
A3 contact (OSIP)



B3 solvent-shared



C3 solvent-separated



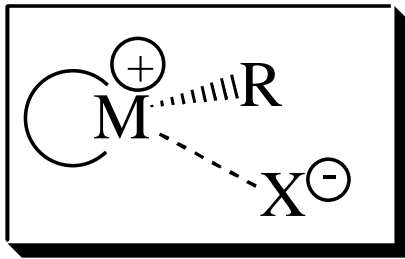
D3 contact (ISIP)

OSIP = OUTER-SPHERE ION PAIR

ISIP = INNER-SPHERE ION PAIR

Effetto della **coppia ionica** nelle reazioni di polimerizzazione

- ❖ il sistema catalitico è a **due componenti**: il **precatalizzatore** che è il **composto organometallico metallocenico** e l'**attivatore** che è il **composto organometallico di Al o di B**;
- ❖ i due componenti reagiscono originando la **coppia ionica**:

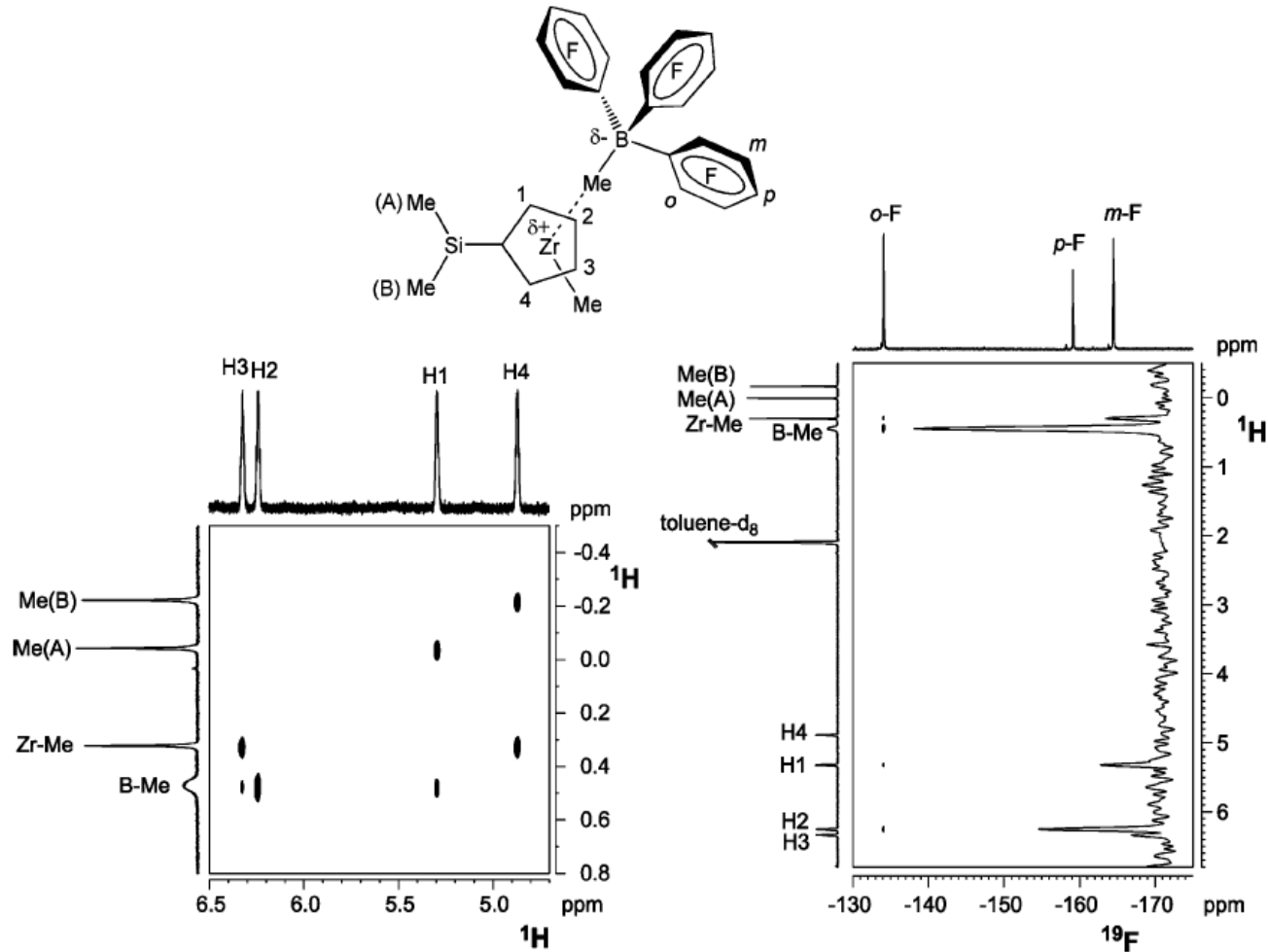


ISIP

è il *resting state* del ciclo catalitico

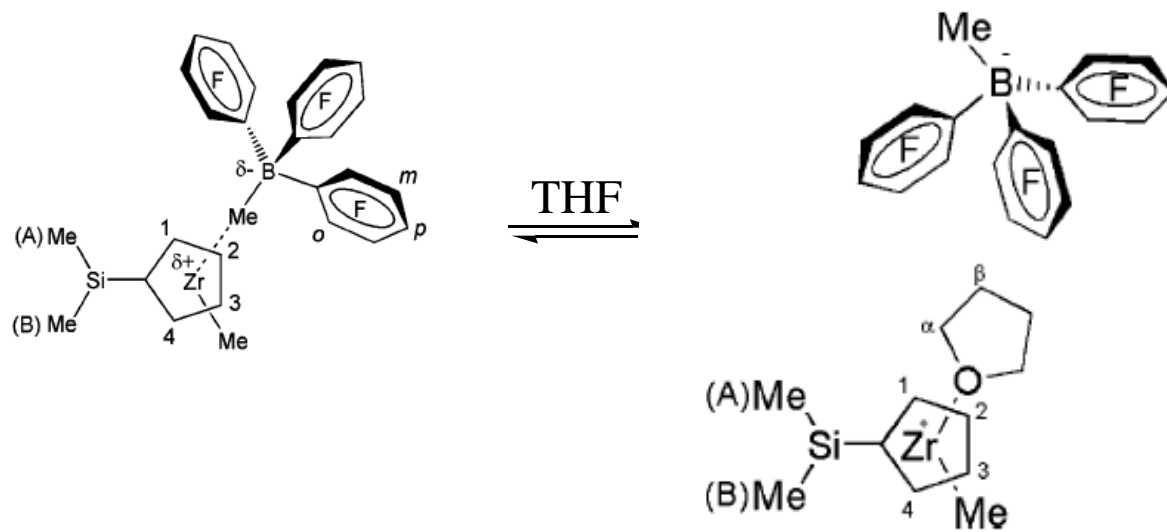
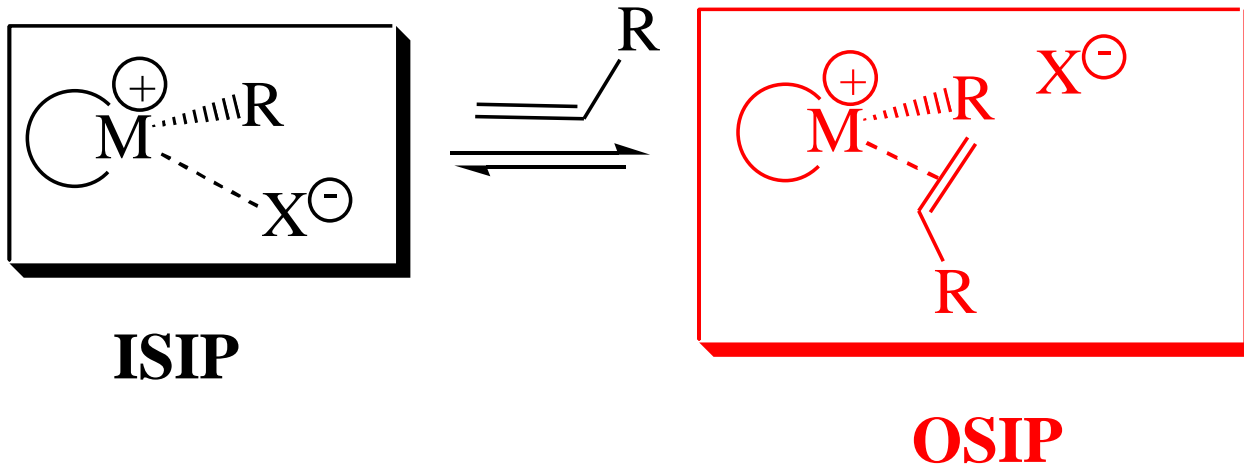
Evidenze sperimentali dell'esistenza della **coppia ionica**

Spettroscopia NMR in soluzione



^1H -NOESY

^{19}F , ^1H -HOESY



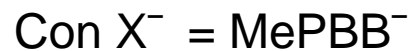
Effetto dell'**anione** nelle reazioni di polimerizzazione

L'attività catalitica aumenta al diminuire del potere coordinante dell'anione.



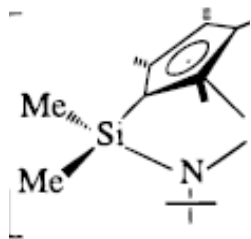
se $M = \text{Zr}$: sistema inattivo

se $M = \text{Ti}$: sistema leggermente attivo

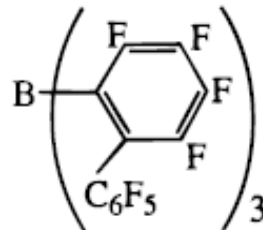


se $M = \text{Zr}$: sistema attivo: $v = 10^5$

se $M = \text{Ti}$: sistema 70 volte più attivo



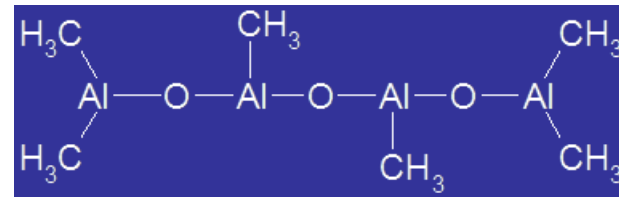
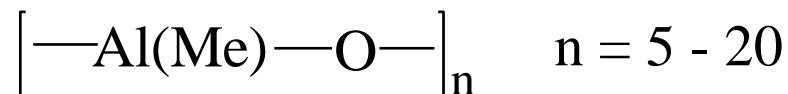
CGC



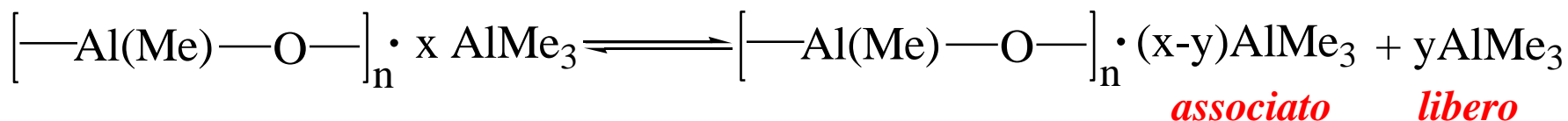
PBB

IL MAO¹

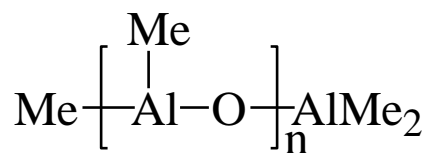
Caratteristiche strutturali



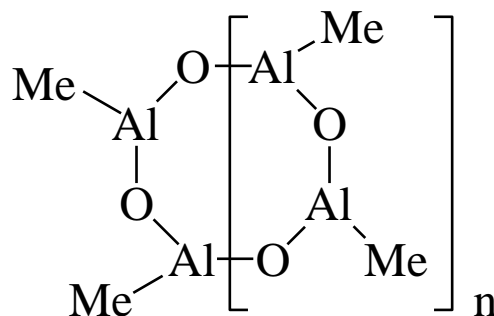
Equilibri multipli:



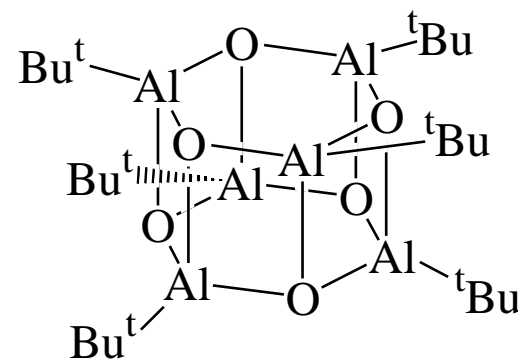
Principali strutture proposte:



lineare



ciclica

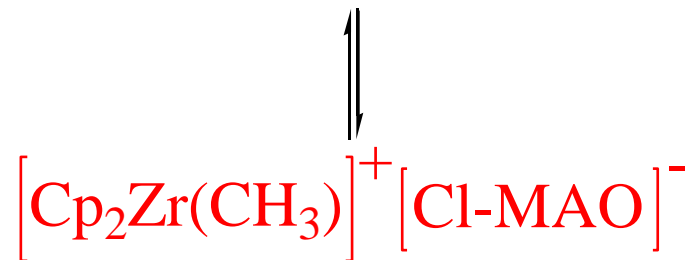
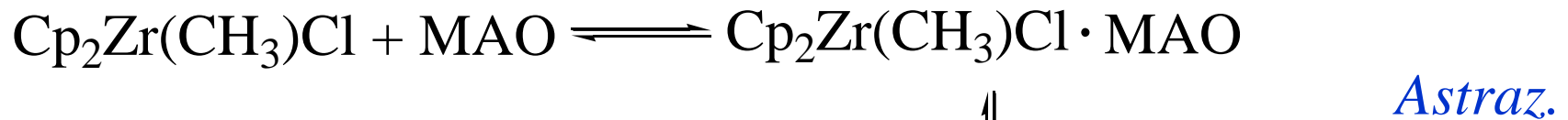
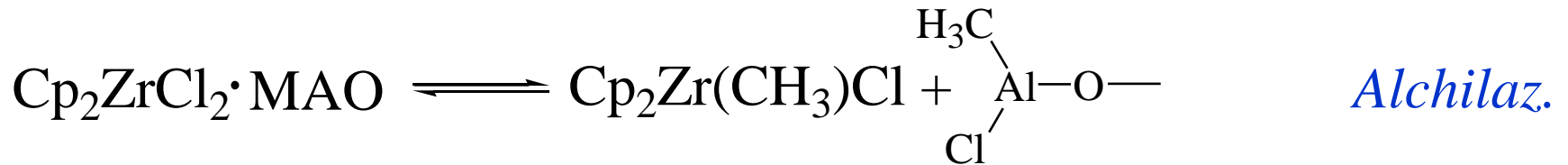


gabbia

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

IL MAO¹

Il processo di attivazione



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

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

Limiti dei catalizzatori metallocenici¹

- ❖ Vengono facilmente **avvelenati** da composti contenenti eteroatomi;
- ❖ sono **molto costosi** e vengono preparati in un processo a più stadi;
- ❖ il **MAO** viene usato in grande eccesso rispetto al metallo, pertanto è un componente importante nella definizione del costo finale del prodotto.

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