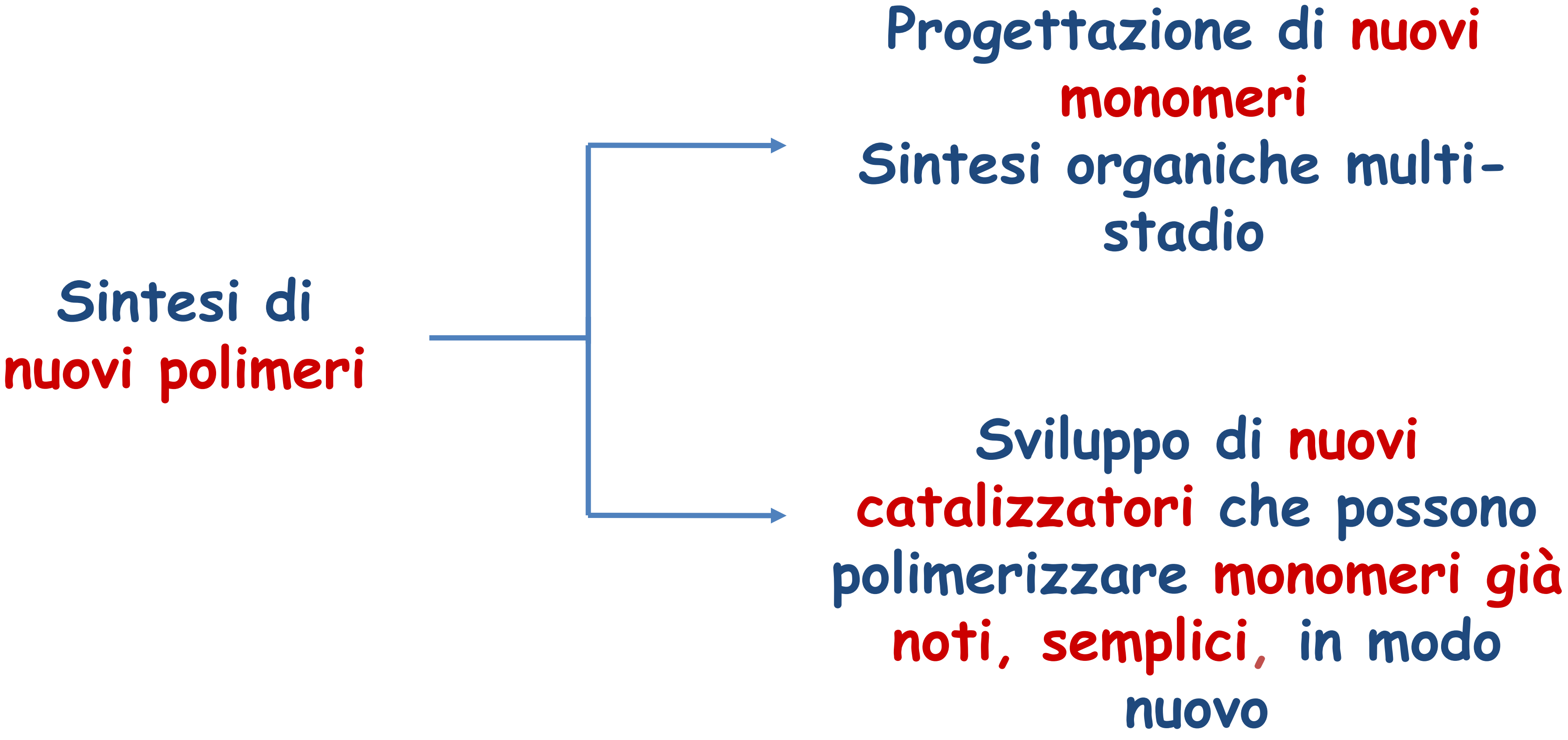
Catalisi di Polimerizzazione[1]



Sintesi di **nuovi polimeri**

Progettazione di **nuovi monomeri**
Sintesi organiche multi-stadio

Sviluppo di **nuovi catalizzatori** che possono polimerizzare **monomeri già noti, semplici**, in modo nuovo

Polimerizzazione di precisione

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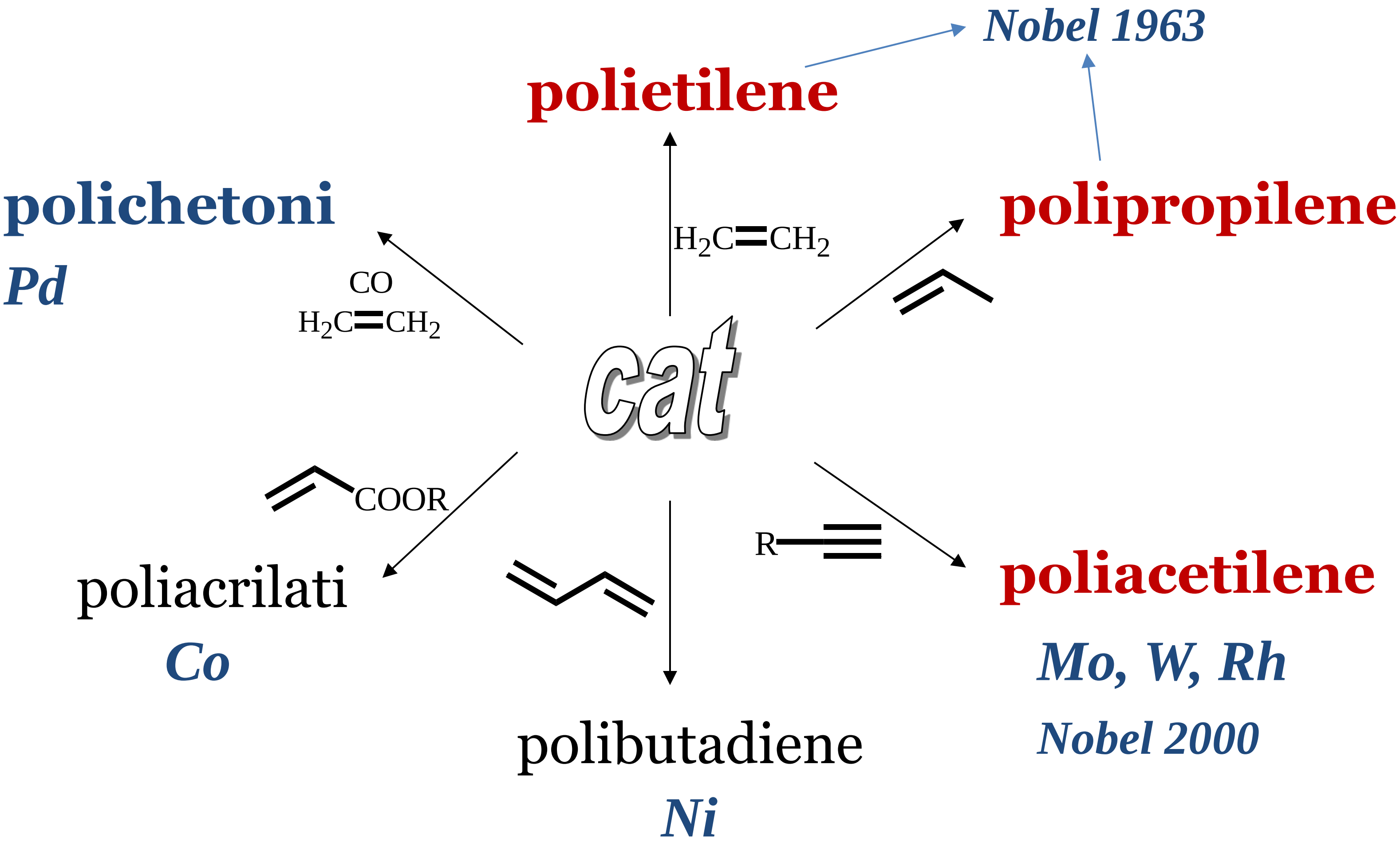
[1] G. Chen, X. S. Ma, Z. Guan *J. Am. Chem. Soc.* 2003, *125*, 6697.

Catalisi di polimerizzazione[1]



Nobel 1963

polietilene

polichetoni

Pd

polipropilene

CO

$H_2C=CH_2$

$H_2C=CH_2$

cat

poliacrilati

Co

polibutadiene

Ni

poliacetilene

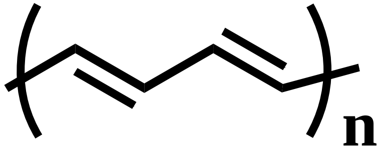
Mo, W, Rh

Nobel 2000

---

[1] S. Kobayashi, *Catalysis in Precision Polymerisation* **1997**, Ed. Wiley.

Polyacetylene and substituted polyacetylene

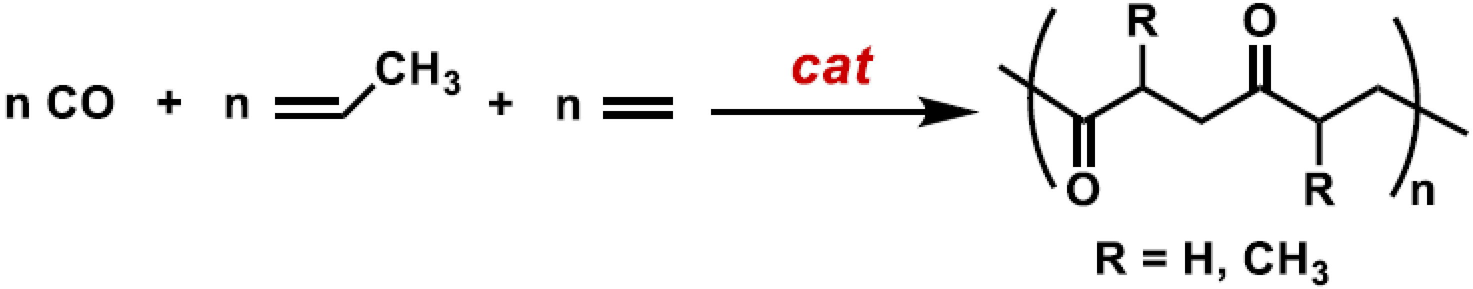


The polymers are featured by conjugated C-C double bonds. Thus, they show peculiar properties not found in polyolefins. The most important is the conductivity of electricity.

Polyacetylene is a black solid, unstable in air. It behaves like a semiconductor, but when properly dopped with AsF_5 or I_2 it shows the conductivity like a metal.

Substituted polyacetylenes have different colors depending on the number and the nature of the substituents; they are soluble in common organic solvents, they are stable in air for long time and they are insulators.

CO/terminal alkene copolymerization



Commercialized by Shell Chemicals

Drent, E. et al. *J. Organomet. Chem. Soc.* **1991**, *417*, 235; Drent, E. et al. *Chem. Rev.,* **1996**, *96*, 663; Alperwicz, N., *Chem. Week*. **1995**, 22.

Innovative engineering plastics we have dreamed of

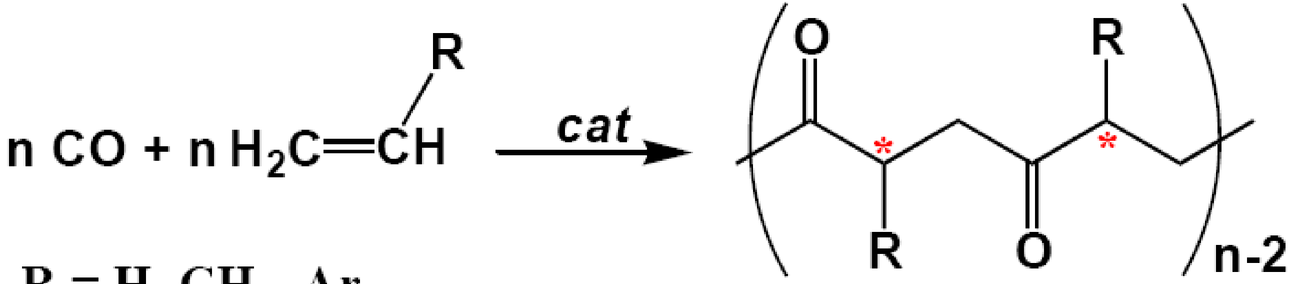
POKETONE is a new eco-friendly thermoplastic made of CO and olefins.
With its unique balance of excellent properties,
it will bring you various innovations for diverse applications.

Commercialized by Hyosung

http://www.poly-ketone.com/utl/web/mediadownload.do?subpath=/download/catalogEn/poketone_catalogue2017_en.pdf.

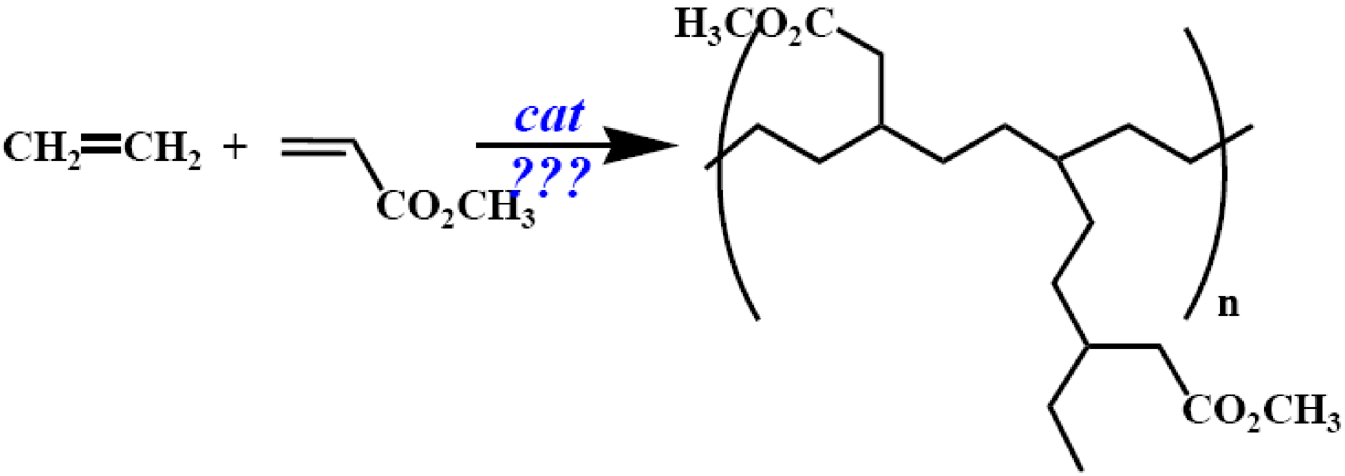
Sintesi di copolimeri

Copolimeri CO/olefina



R = H, CH_3, Ar

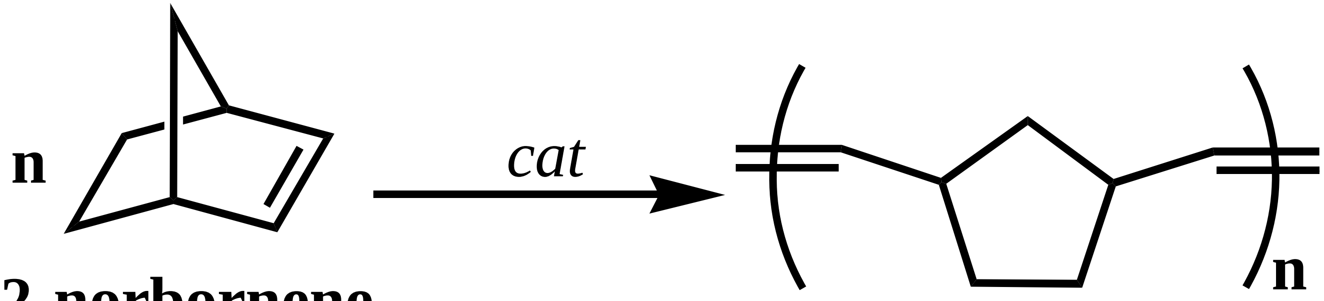
Copolimeri etilene/monomeri polari



Ring-opening metathesis polymerization

ROMP

A true success story



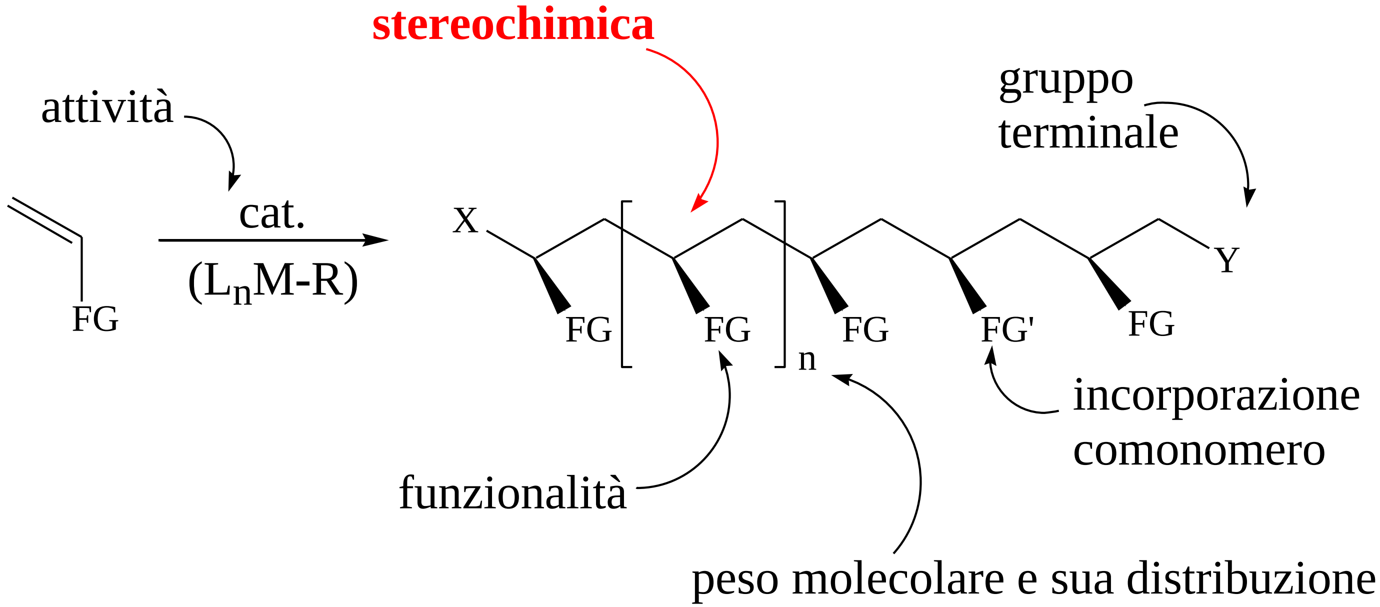
2-norbornene

Polymerization with retaining of the functional groups.

Metodi di polimerizzazione[1]

Radicalica Anionica

Cationica **Coordinativa**



stereochimica

attività

gruppo terminale

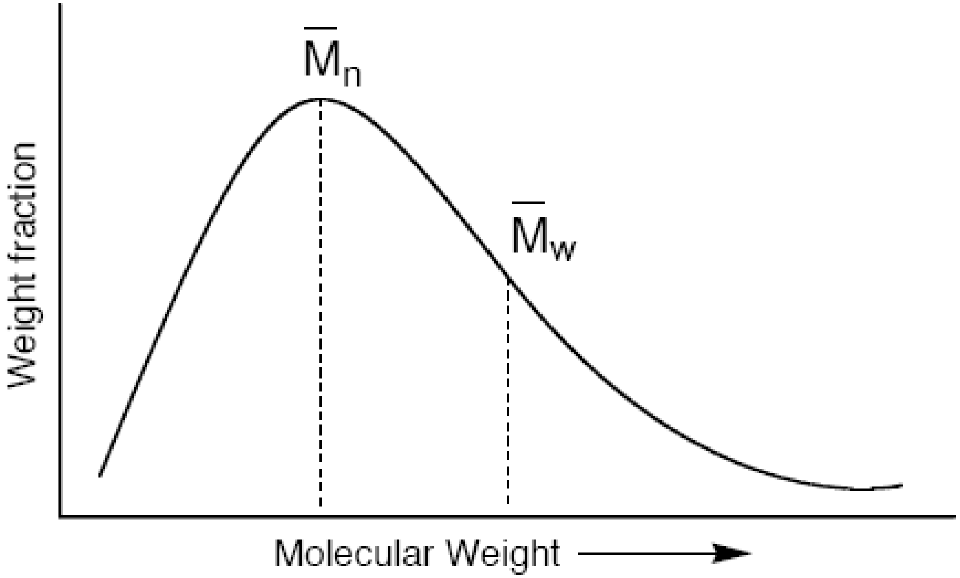
funzionalità

incorporazione comonomero

peso molecolare e sua distribuzione

[1] **G. W. Coates et al. *Angew. Chem. Int. Ed.* 2002, *41*, 2236.**

Molecular weight distribution

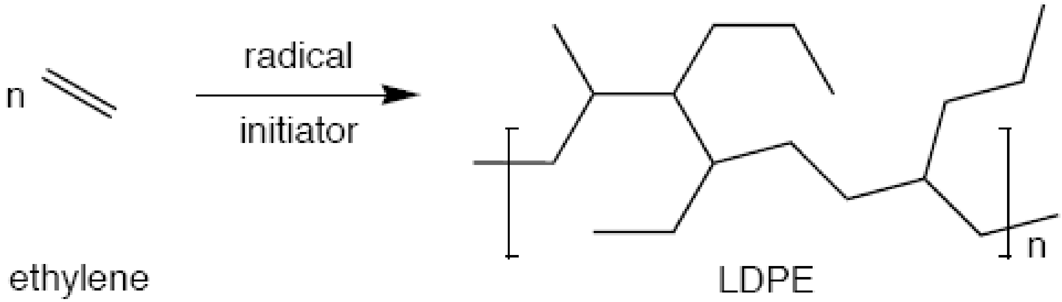


- In a polydisperse polymer, Mw ≥ Mn
- The polydispersity and breadth of plot, has bearing on the
mechanism of polymerization and the properties of the resulting
polymer

Kind of polyolefins

	LLDPE	LDPE	HDPE	UHMWPE	iPP
Density (g cm^{-3})	0.90-0.94	0.91-0.94	0.94	0.930-0.935	0.88-0.92
Melting point (°C)	100-125	98-115	125-132	130-136	160-166
Cristallinity (%)	22-55	30-54	55-77	39-75	30-60

LDPE



- LDPE: Low density polyethylene
- Highly branched material
- Properties and usage:

Stretchable before tearing
Used for flexible plastic bags
Recycled material: trash bags, grocery sacks

4
LDPE

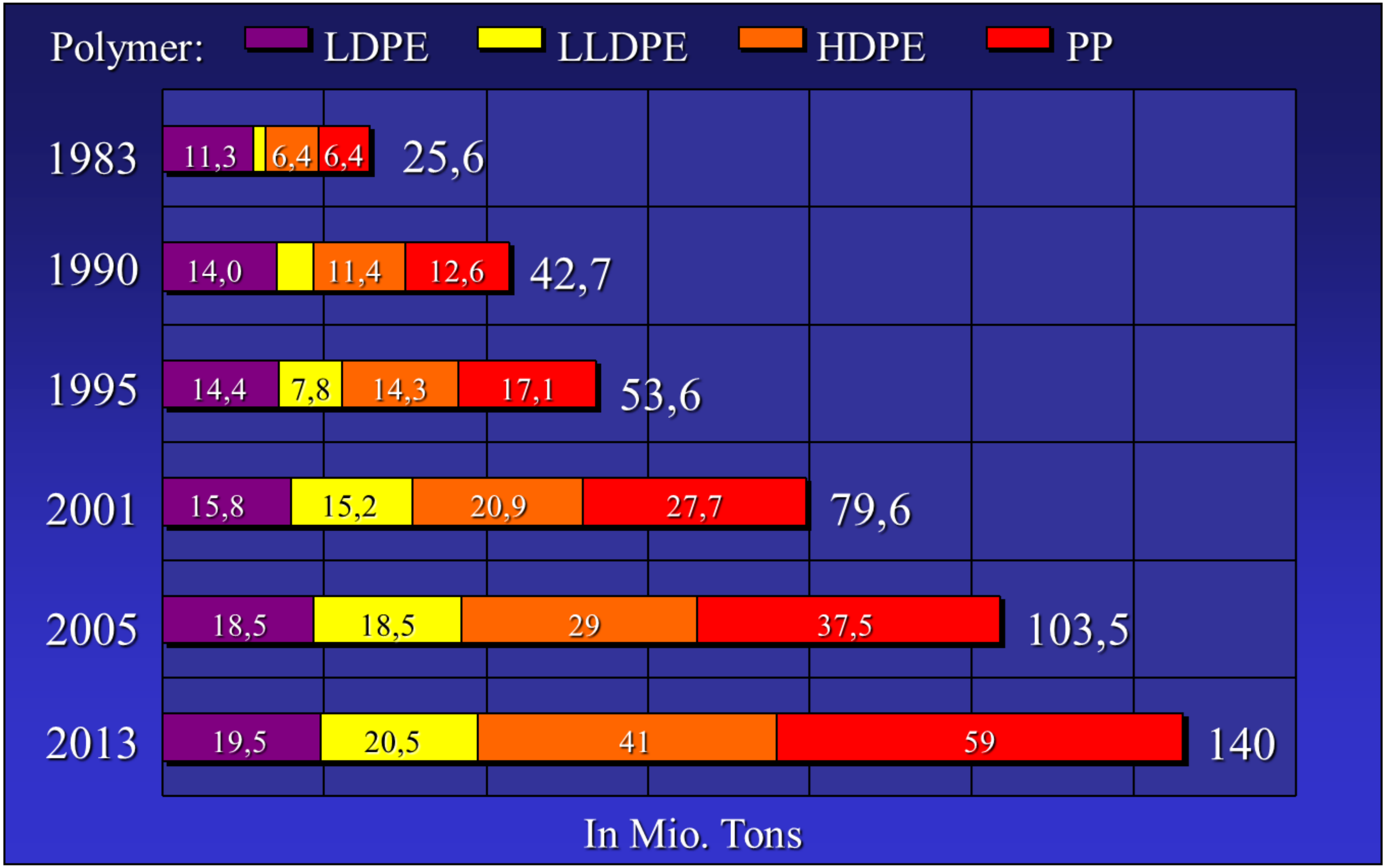
Worldwide production of polyolefins in 2005 (10^6 ton/year)

Total production in 2010: 120 10^6 ton.*

W. Kaminsky *Macromol. Chem. Phys.* **2008**, *209*, 459.

* Barzan, C.; Gianolio, D.; Groppo, E.; Lamberti, C.; Monteil, V.; Quadrelli, E. A.; Bordiga, S. *Chem.-Eur. J.* **2013**, *19*, 17277.

Produzione mondiale di poliolefine[1] (10^6 ton)



[1] W. Kaminsky, *comunicazione personale*.

Polimerizzazione Coordinativa:
tre date importanti.

1953. Prima sintesi del POLIETILENE per via catalitica con catalizzatori attivi in condizioni blande. Ziegler.

1954. Prima sintesi del POLIPROPILENE STEREOREGOLARE. Viene definito il principio di POLIMERIZZAZIONE STEREOSPECIFICA. Natta.

1963. Premio Nobel per la Chimica
a Ziegler e Natta

Sintesi di poliolefine

Catalizzatori di **Ziegler Natta**	Catalizzatori **metallocenici**	Catalizzatori di **Brookhart**
1950	**1980**	**1995**
Catalizzatori **eterogenei**	Catalizzatori **omogenei**	Catalizzatori **omogenei**
Catalizzatori a base di **Ti o V**	Catalizzatori a base di **Ti o Zr**	Catalizzatori a base di **Fe o Co o Ni o Pd**

***early** transition metals*

***late** transition metals*

Il sistema catalitico di Ziegler – Natta[1]

Catalizzatori eterogenei:

$TiCl_4$-AlR_3 $TiCl_3$-AlR_3

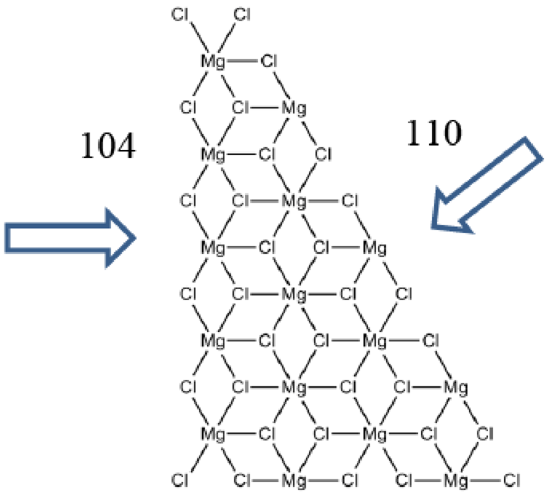
$MgCl_2$/ $TiCl_4$-AlR_3 $\longrightarrow$ 1 000 kg PE/g Ti

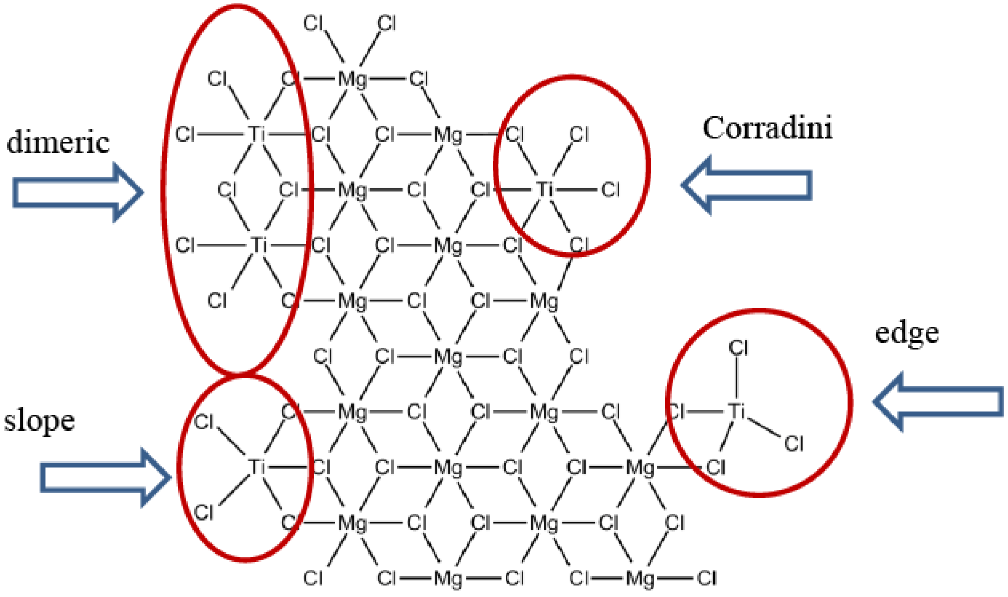
R = Et, *i*-But

$P_{etilene} \approx 1$ atm;

$T \leq 0°C$

Processo molto esotermico:
93.6 kJ/mol.





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

Meccanismo di polimerizzazione

Stadio di iniziazione

$\mathbf{k_i}$

- formazione della specie attiva;
- reazione con le prime unità monomeriche;

Stadio di propagazione

$\mathbf{k_p}$

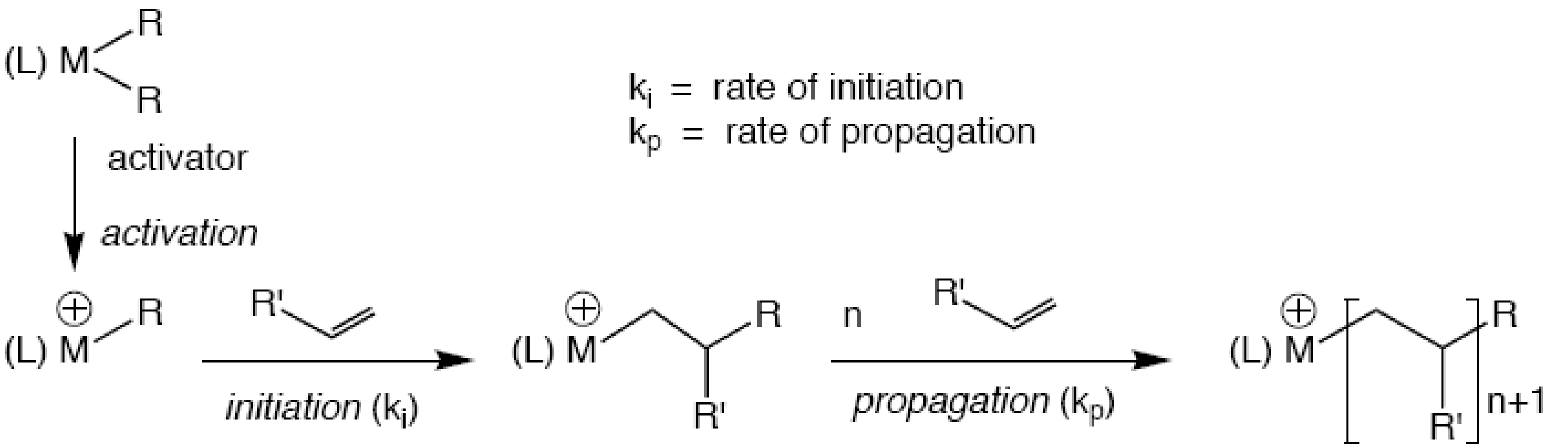
- crescita della catena polimerica sul centro metallico;

Stadio di terminazione

$\mathbf{k_t}$

- interruzione della crescita della catena polimerica;
- riformazione della specie attiva.

Living polymerization: A special case



k_i = rate of initiation
k_p = rate of propagation

- Initiator and intermediates are stable under reaction conditions
- There is no chain termination
- ki ≥ kp,

This means that the rate of initiation is greater than rate of propagation and that all the metal centers are initiated before propagation takes place

- Polymers with narrow molecular weight distributions are obtained

Meccanismo di polimerizzazione

Stadio di iniziazione

$TiCl_4 + Al(C_2H_5)_3 \longrightarrow (C_2H_5)TiCl_3 + (C_2H_5)_2AlCl$ *Alchil.*

$(C_2H_5)TiCl_3 \longrightarrow TiCl_3 + C_2H_5^{\bullet}$ *Riduz.*

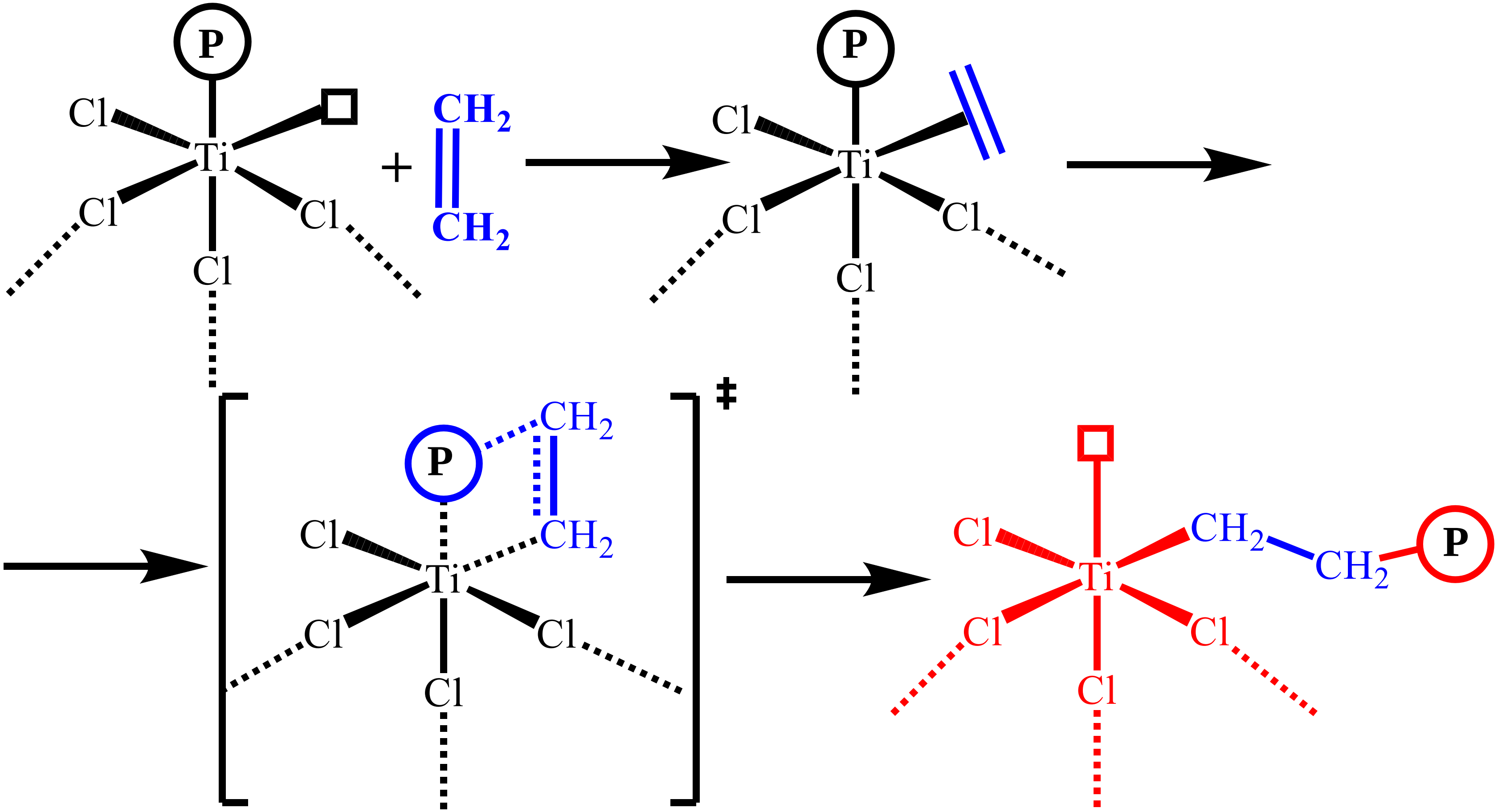
$TiCl_3 + Al(C_2H_5)_3 \longrightarrow (C_2H_5)TiCl_2 + (C_2H_5)_2AlCl$ *Alchil.*

$(C_2H_5)TiCl_2 \longrightarrow TiCl_2 + C_2H_5^{\bullet}$ *Riduz.*

$(C_2H_5)TiCl_n \xrightarrow{C_2H_4} Cl_nTi\text{-}CH_2CH_2\text{-}C_2H_5$ *Inserz.*

Meccanismo di polimerizzazione:
(Cossee-Arlman)

Stadio di propagazione

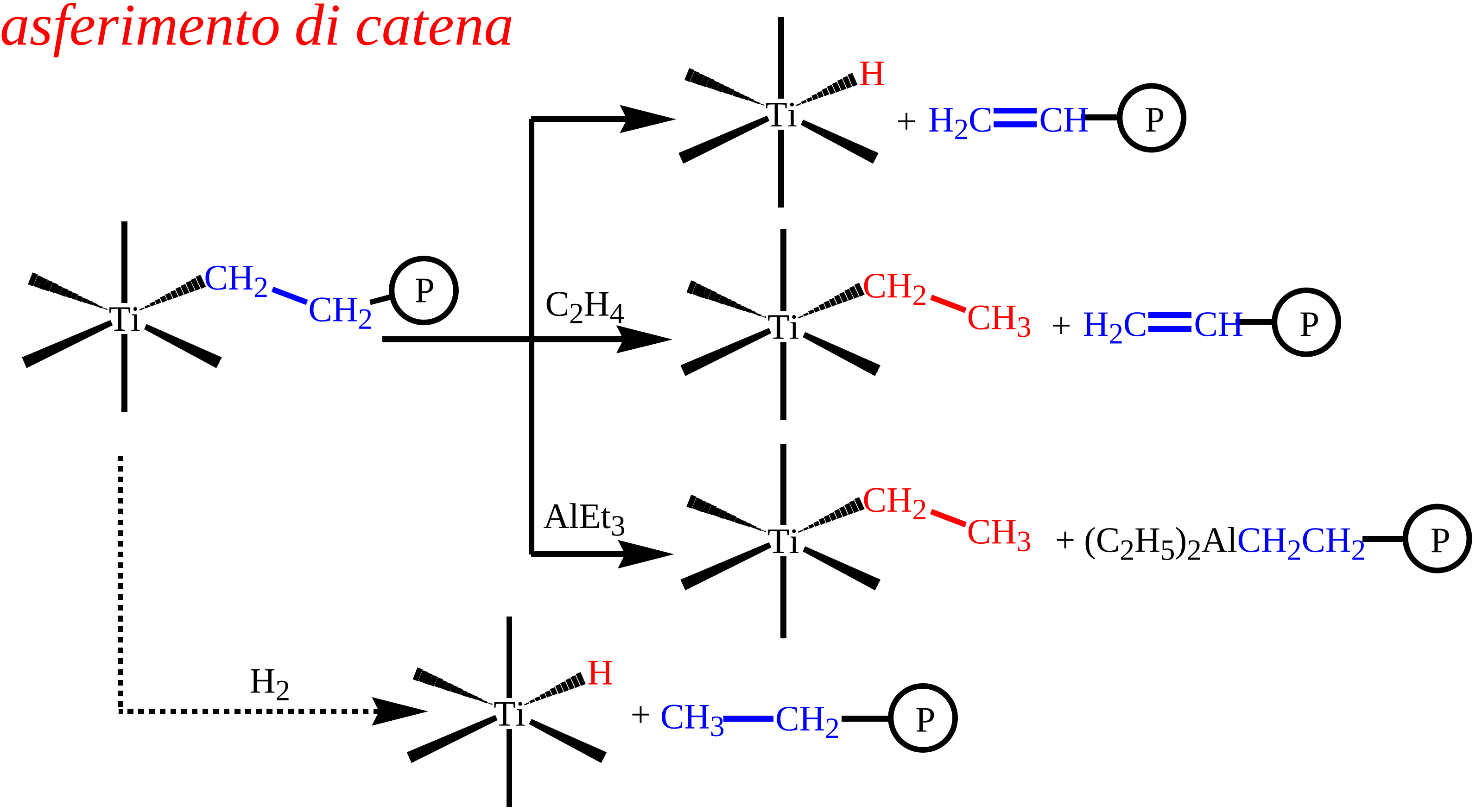


Ⓟ = catena polimerica in crescita

$$\boxed{v = k_p[C^*][M]}$$

Meccanismo di polimerizzazione

Stadio di terminazione: trasferimento di catena

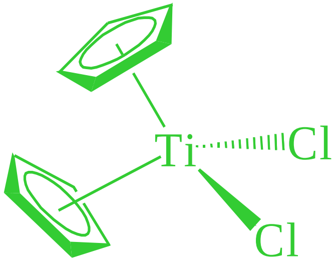


Limiti dei catalizzatori Ziegler Natta

- bassa percentuale di siti attivi: 1 – 20 % di Ti;
- 5 – 50 ppm di Cl_2 derivante dal supporto $MgCl_2$ rimangono nel polimero, con relativi fenomeni di corrosione nella lavorazione del polimero stesso;
- solo alcuni alcheni terminali vengono copolimerizzati con l'etilene, ma in modo non random;
- nel polimero rimane il 3 – 4 % di oligomeri, che a lungo andare vengono rilasciati;
- difficoltà di controllare la microstruttura delle macromolecole.

Catalizzatore **SOLUBILE**

1957



+ $AlCl(C_2H_5)_2$

The “Metallocene Revolution”

1980

Kaminsky e Sinn

Catalizzatori **SOLUBILI**

⇓

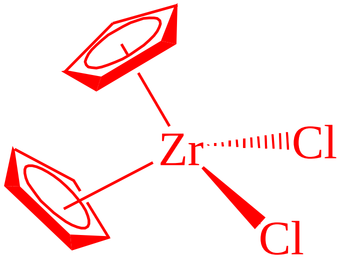
STRUTTURA del catalizzatore

⇓

MECCANISMO della polimerizzazione

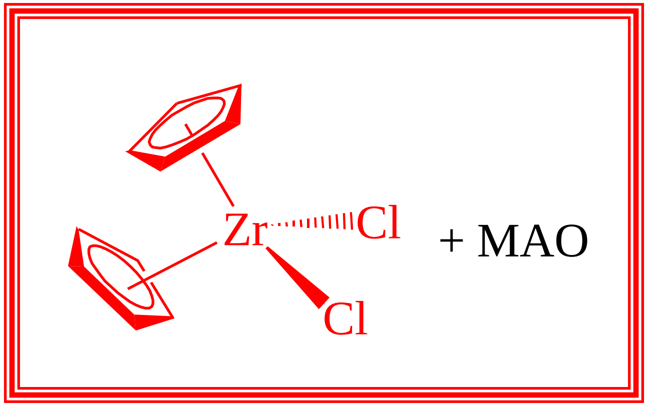
⇓

STRUTTURA e PROPRIETA’ del polimero



+ MAO

The “Metallocene Revolution”[1]

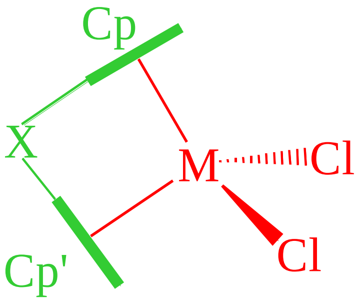


Caratteristiche:

- 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.

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

La Versatilità dei Catalizzatori metallocenici

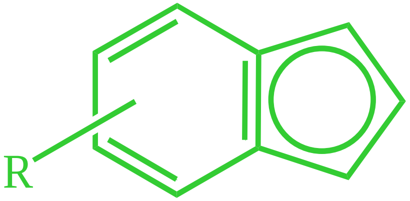


+ MAO

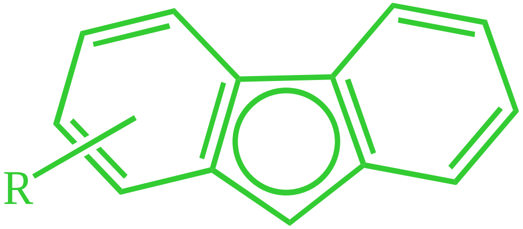
M = Ti, Zr, Hf

Cp = Cp’ o Cp ≠ Cp’

Cp e Cp’ =



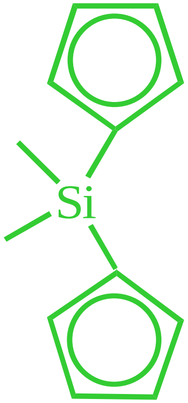
indenile

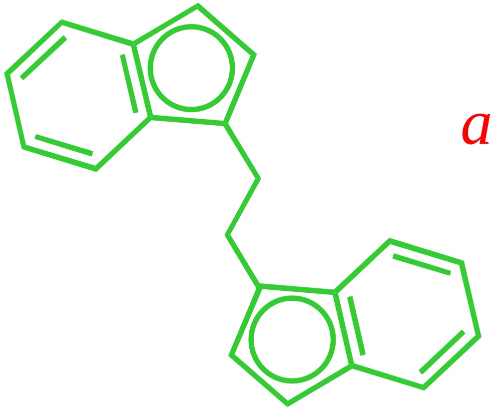


fluorenile

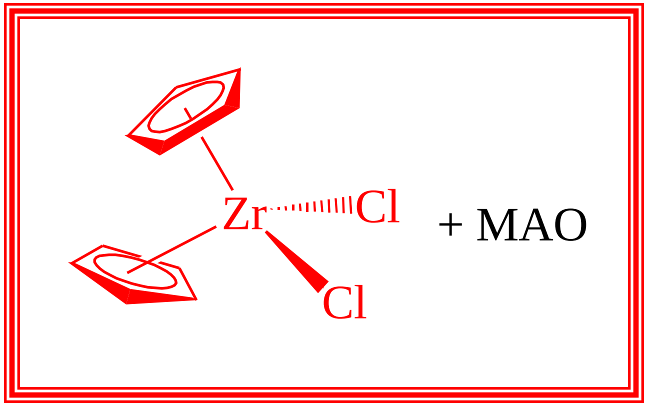
Cp-X-Cp’ =

X = CH$_2$CH$_2$, R$_2$Si, R$_2$C





ansa-metalloceni

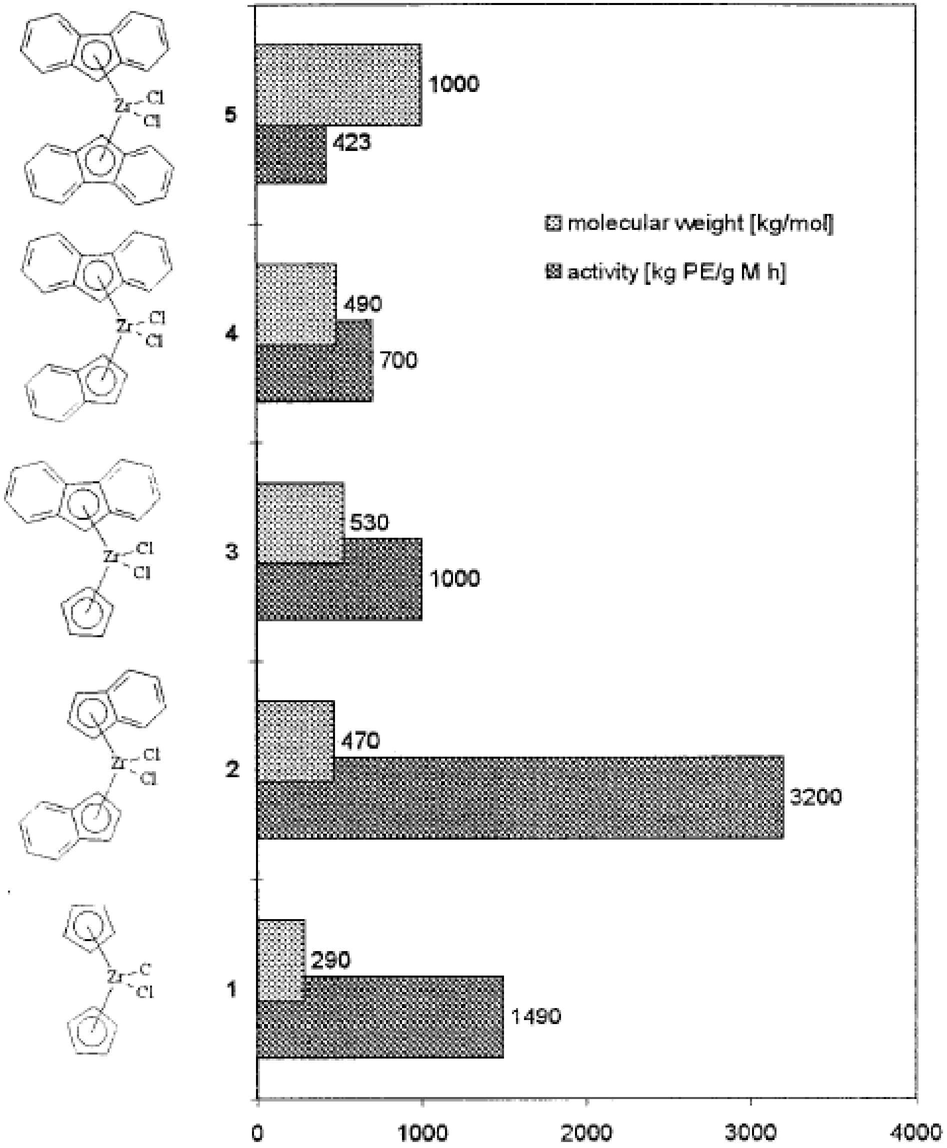


Condizioni di reazione: T = 90°C, $P_{etilene}$ = 8 bar,
[Al]/[Zr] = 10 000,
solvente = toluene

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

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

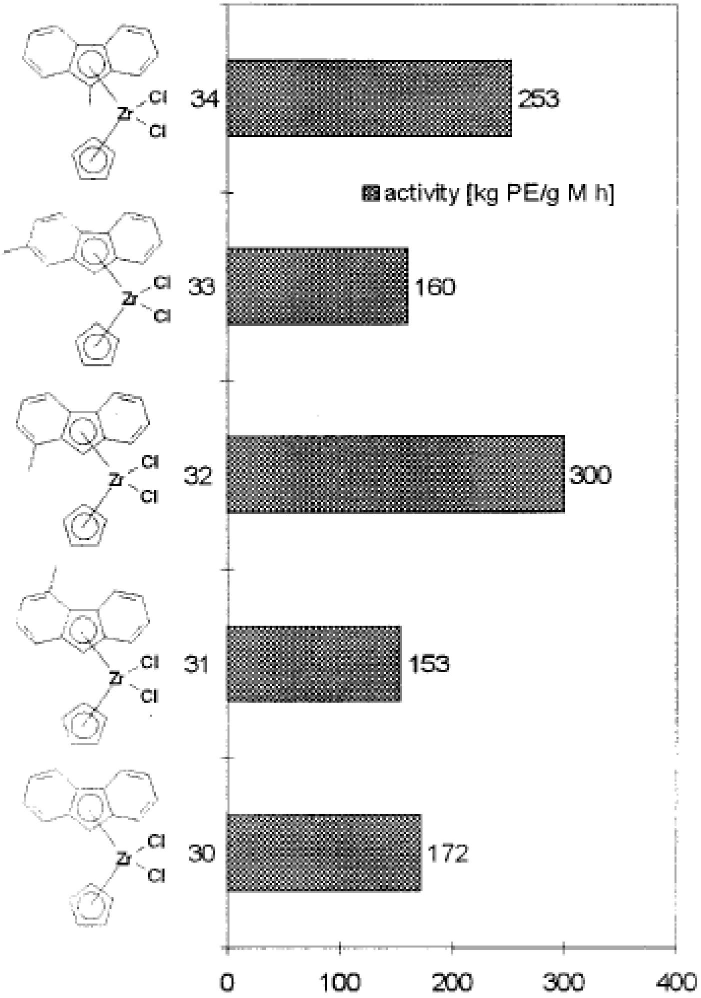
Polimerizzazione dell’etilene: Effetto dell’anello aromatico



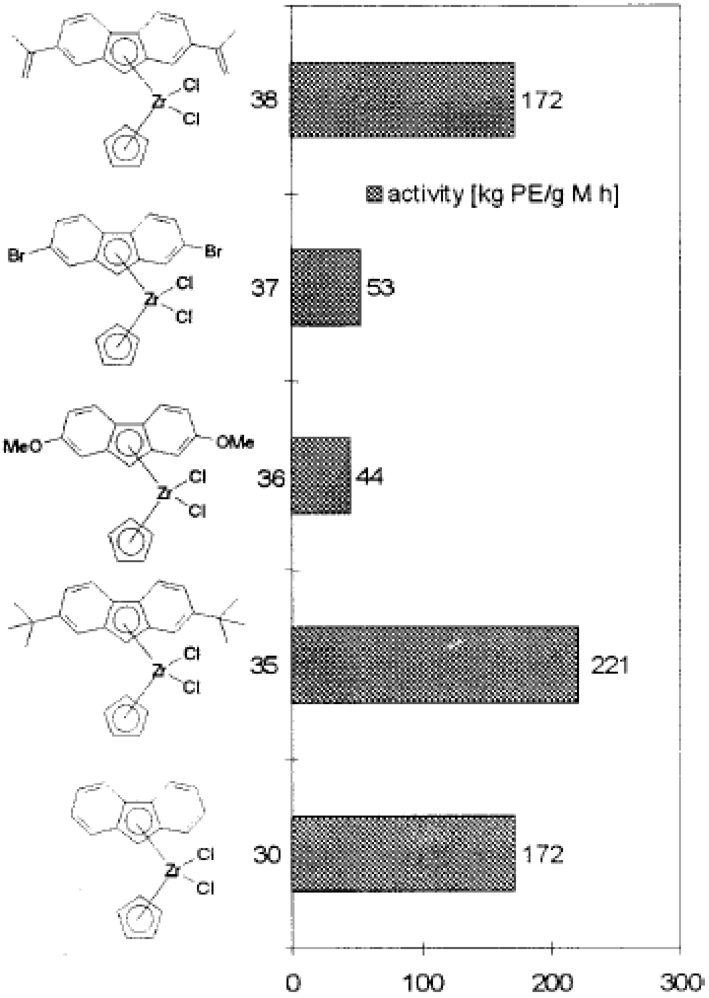
Condizioni di reazione: T = 60°C; solvente: *n*-pentano; $P_{etilene}$ = 10.0 bar;
Cat. Prec. **1, 2, 4** [Al]/[Zr] = 1000; Cat. Prec. **3, 5** [Al]/[Zr] = 2500.

Polimerizzazione dell’etilene

Effetto della posizione



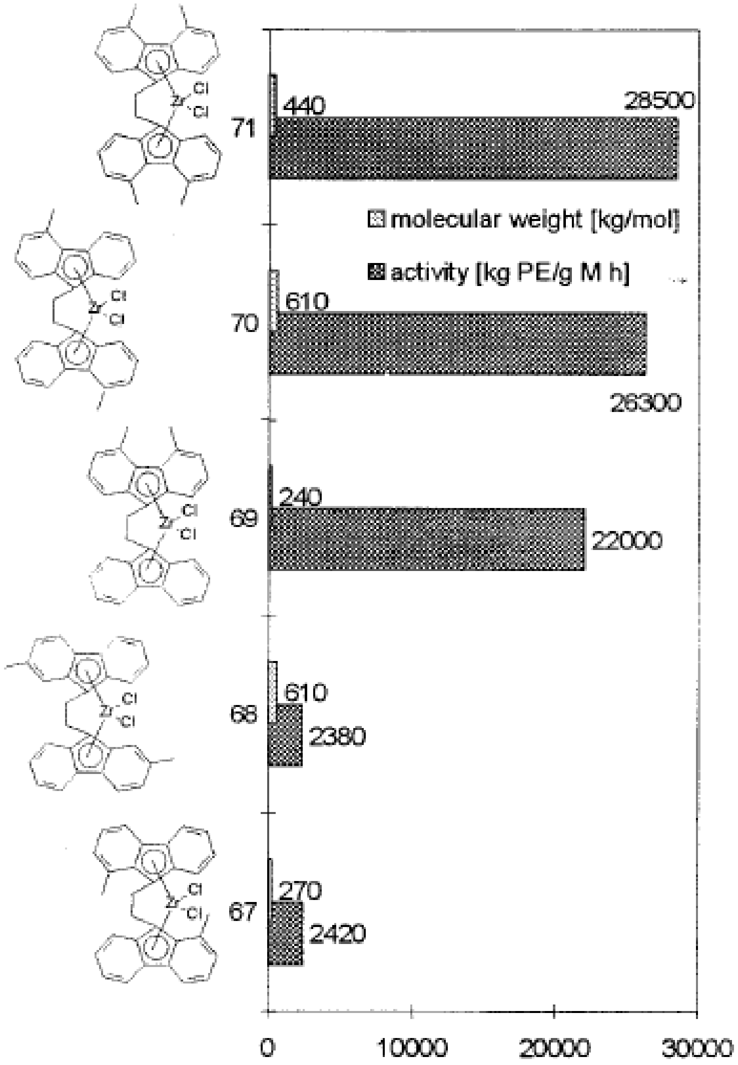
Effetto del sostituente



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

Polimerizzazione dell'etilene

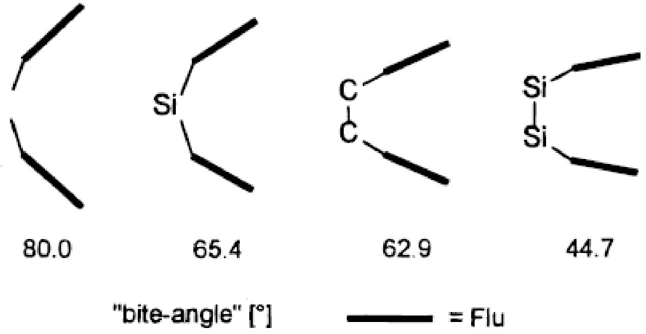
Effetto della posizione del sostituente sugli *ansa-metalloceni*

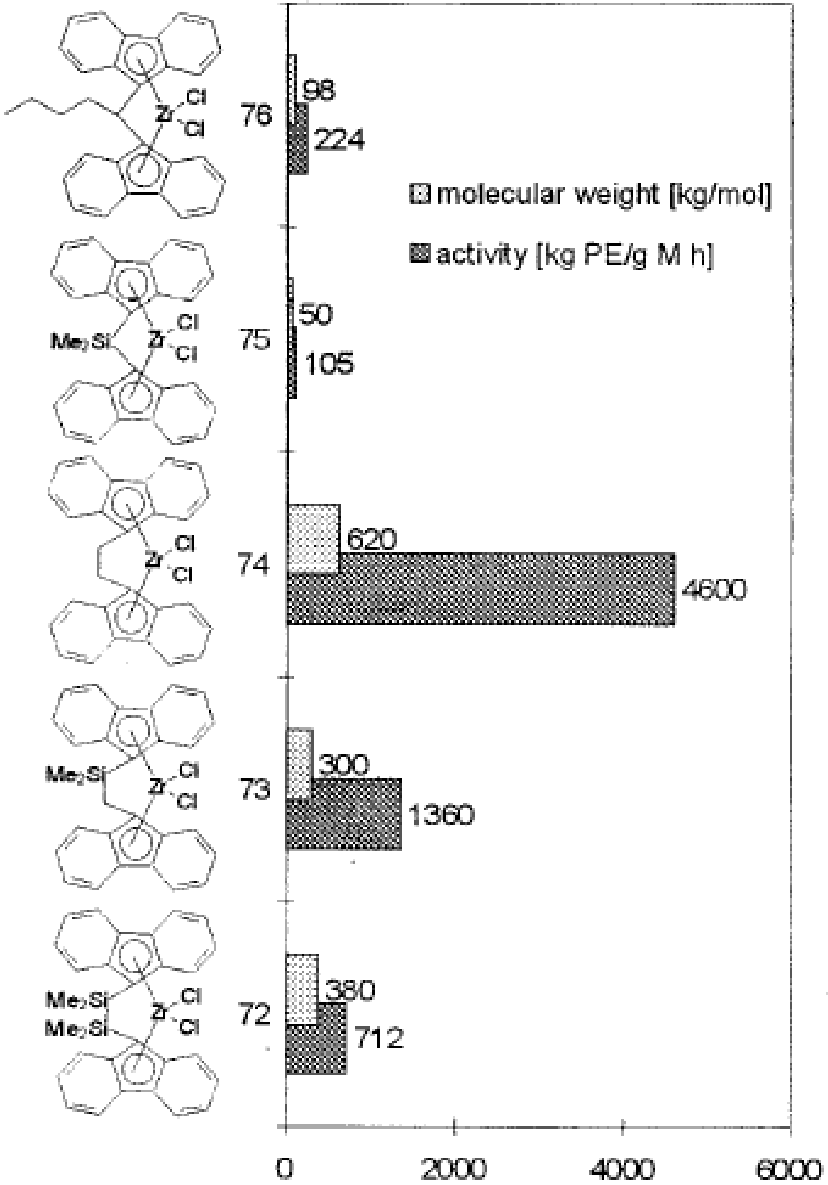


Condizioni di reazione: T = 60°C; solvente: *n*-pentano; $P_{etilene}$ = 10.0 bar; [Al]/[Zr] = 20000.

Polimerizzazione dell’etilene

Effetto del bite anlge

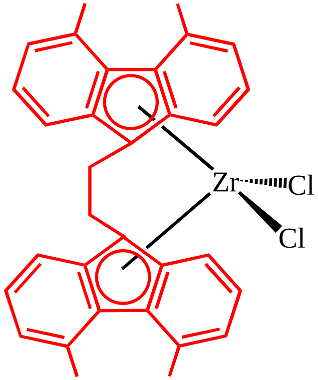




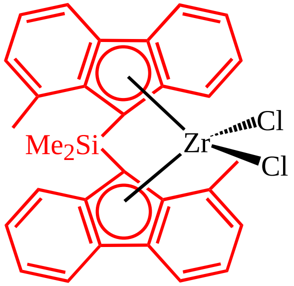
Condizioni di reazione: T = 60°C; solvente: *n*-pentano; $P_{etilene}$ = 10.0 bar; [Al]/[Zr] = 20000.

The “TOP FOUR” Catalysts[1]

produttività



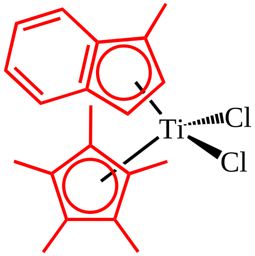
28 500 kg PE/g Zr h



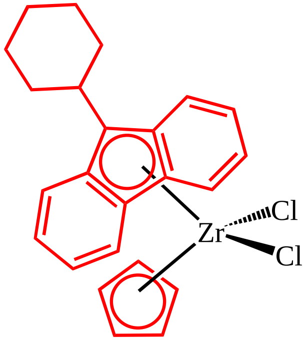
22 140 kg PE/g Zr h

[Al]/[Zr] = 20 000

PE ad alto peso molecolare



1 900 kg/mol



1 850 kg/mol

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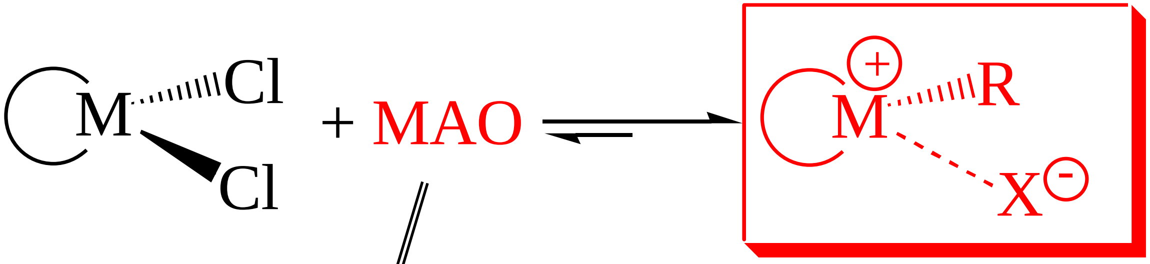
[1] H. G. Alt et al., *Chem. Rev.* **2000**, *100*, 1205.

IL MAO[1]



attivatore

attività catalitica

stabilità

cinetica

peso molecolare

stereoregolarità

COPPIA IONICA
CATIONE/ANIONE

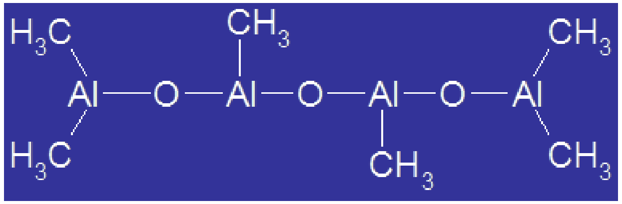
SOLVENTE

---

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

IL MAO[1]
Caratteristiche strutturali

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

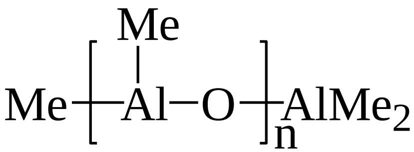


Equilibri multipli:

$$\left[\!-\!\mathrm{Al(Me)}\!-\!\mathrm{O}\!-\!\right]_n \cdot \mathrm{x\,AlMe_3} \rightleftharpoons \left[\!-\!\mathrm{Al(Me)}\!-\!\mathrm{O}\!-\!\right]_n \cdot \mathrm{(x\text{-}y)AlMe_3} + \mathrm{yAlMe_3}$$

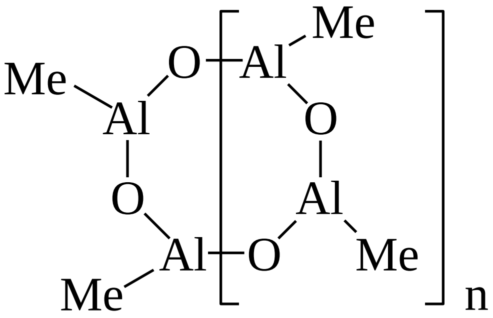
associato ***libero***

Principali strutture proposte:

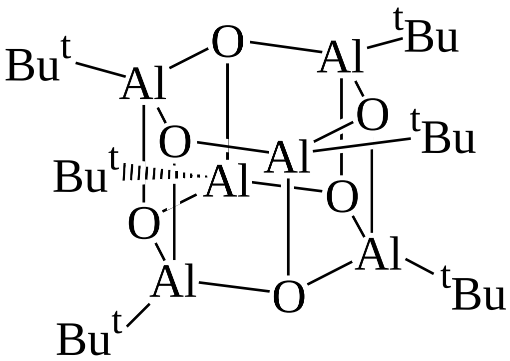


$$\mathrm{Me}\!-\!\left[\!-\!\overset{\mathrm{Me}}{\underset{}{\mathrm{Al}}}\!-\!\mathrm{O}\!-\!\right]_n\!-\!\mathrm{AlMe_2}$$

lineare



ciclica



gabbia

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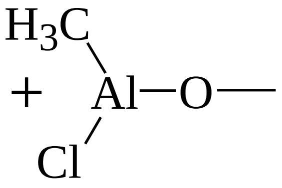
[1] T. J. Marks et al., *Chem. Rev.* **2000**, *100*, 1391.

IL MAO[1]
Il processo di attivazione

$$Cp_2ZrCl_2 + MAO \rightleftharpoons Cp_2ZrCl_2\cdot MAO$$

Complessaz.



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

Alchilaz.

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

Astraz.

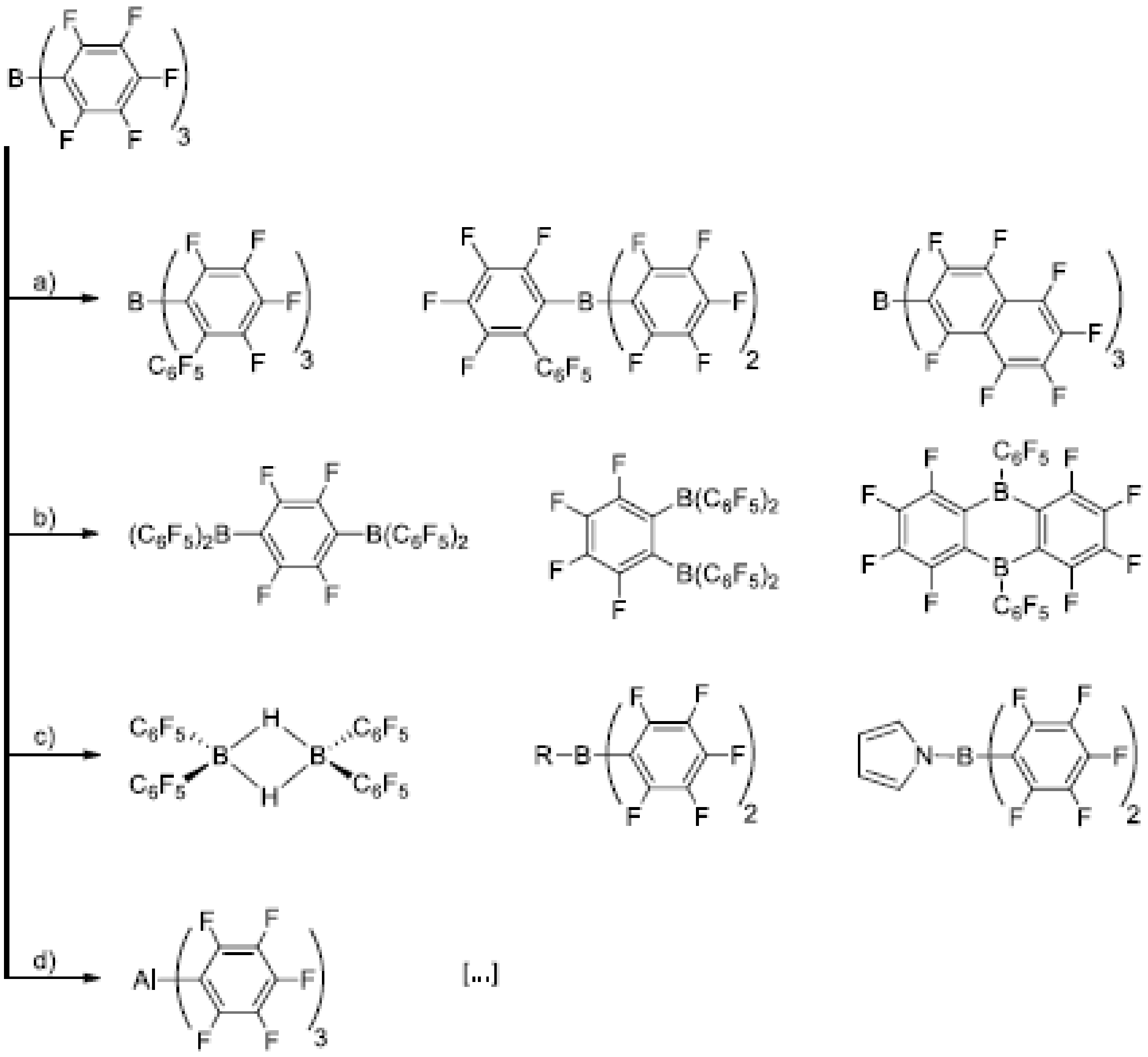
$$\Big\downarrow\!\uparrow$$

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

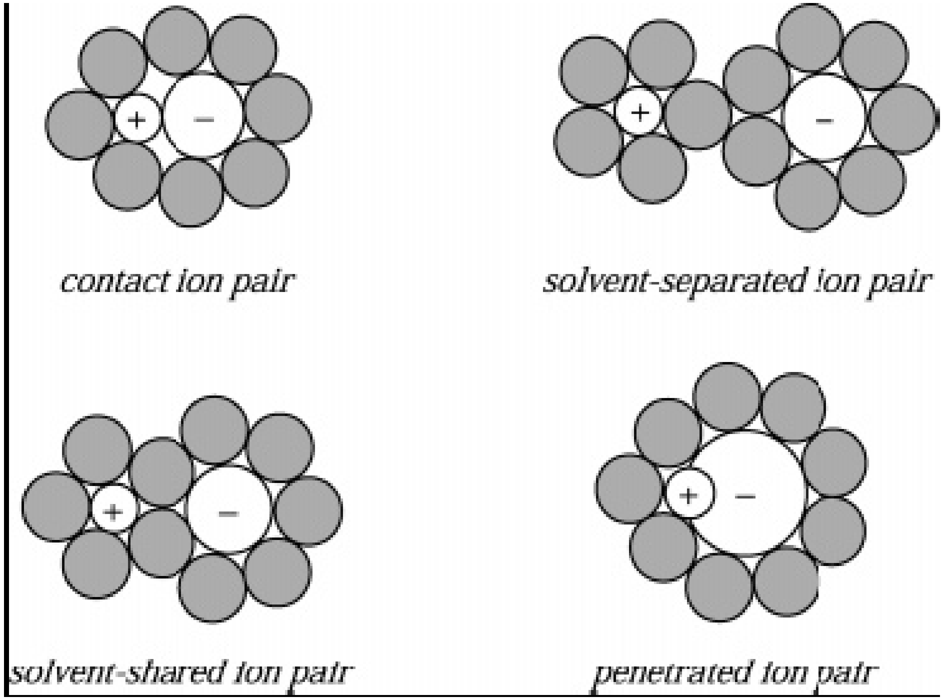
$$\boxed{[Al]/[Zr] \geq 1000}$$

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

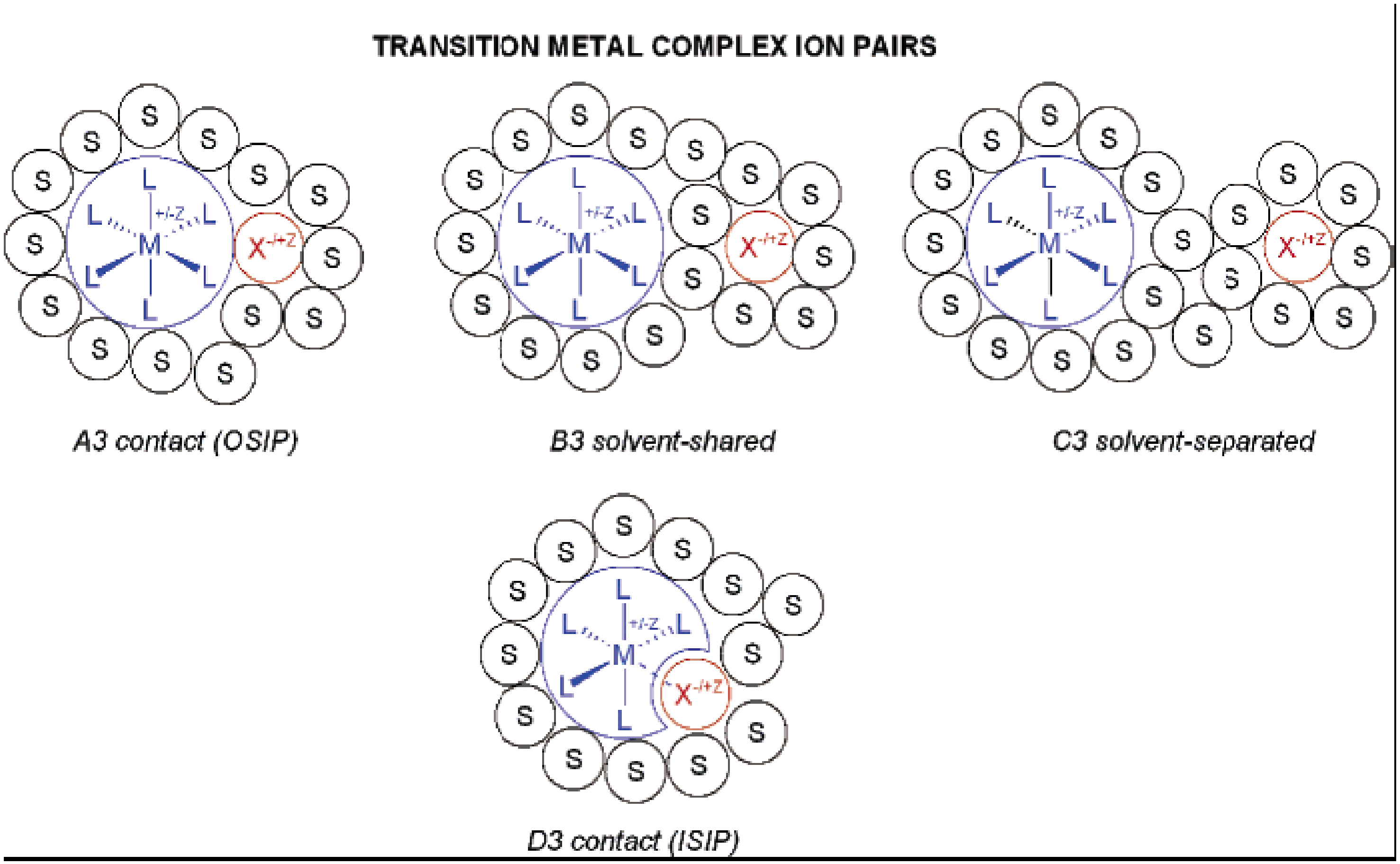
Acidi di Lewis come attivatori



LA COPPIA IONICA[1]



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



TRANSITION METAL COMPLEX ION PAIRS

A3 contact (OSIP)

B3 solvent-shared

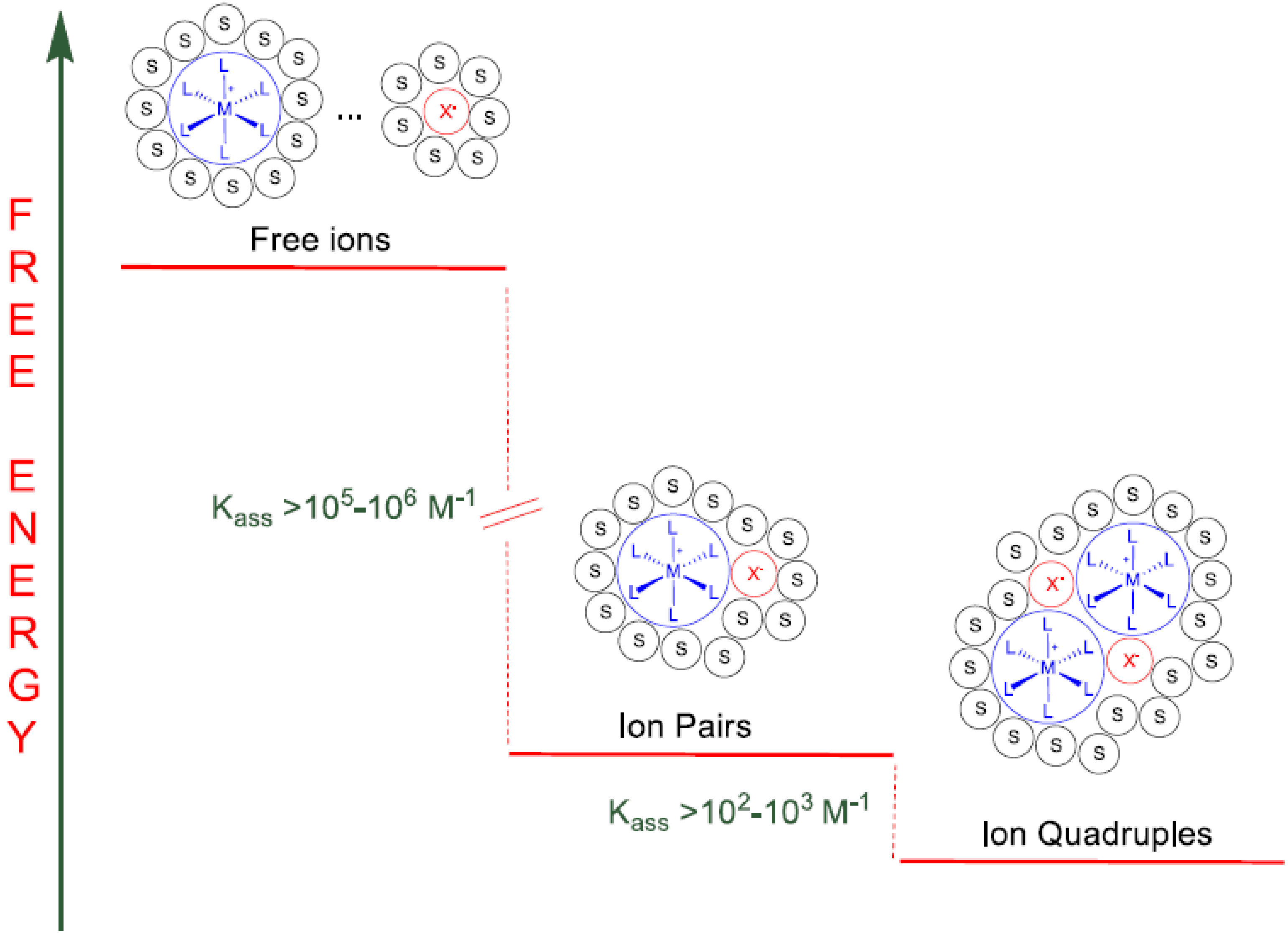
C3 solvent-separated

D3 contact (ISIP)

OSIP = OUTER-SPHERE ION PAIR

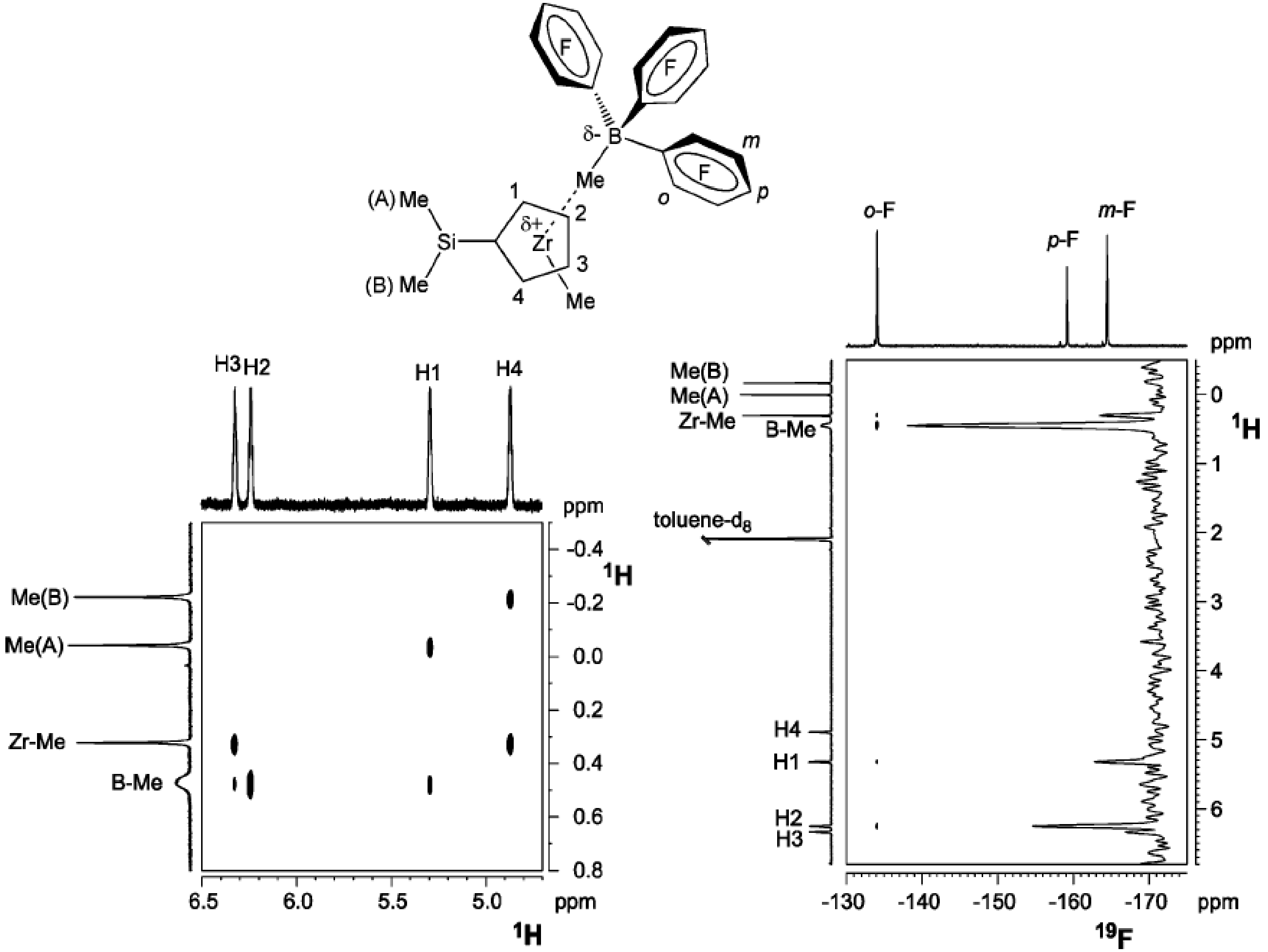
ISIP = INNER-SPHERE ION PAIR

Possibili coppie ioniche nelle reazioni di polimerizzazione



Evidenze sperimentali dell’esistenza della coppia ionica

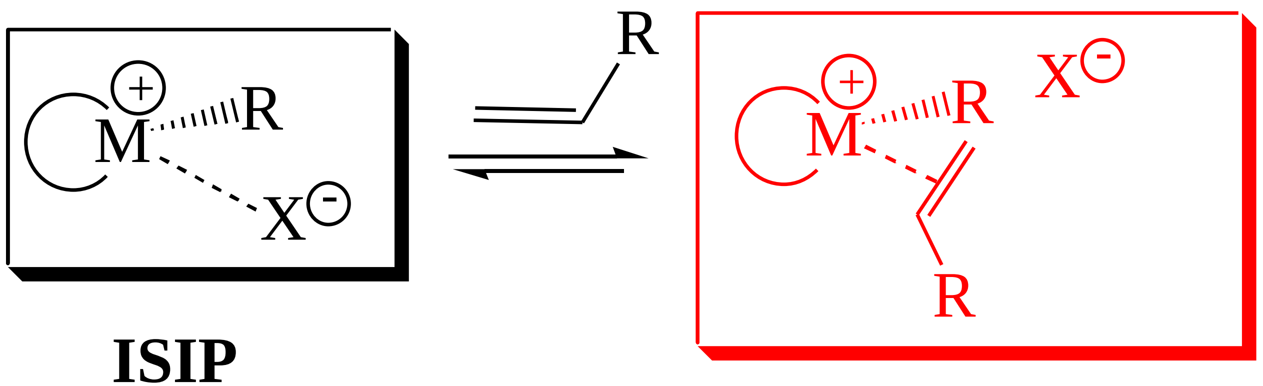
Spettroscopia NMR in soluzione



^{1}H-NOESY

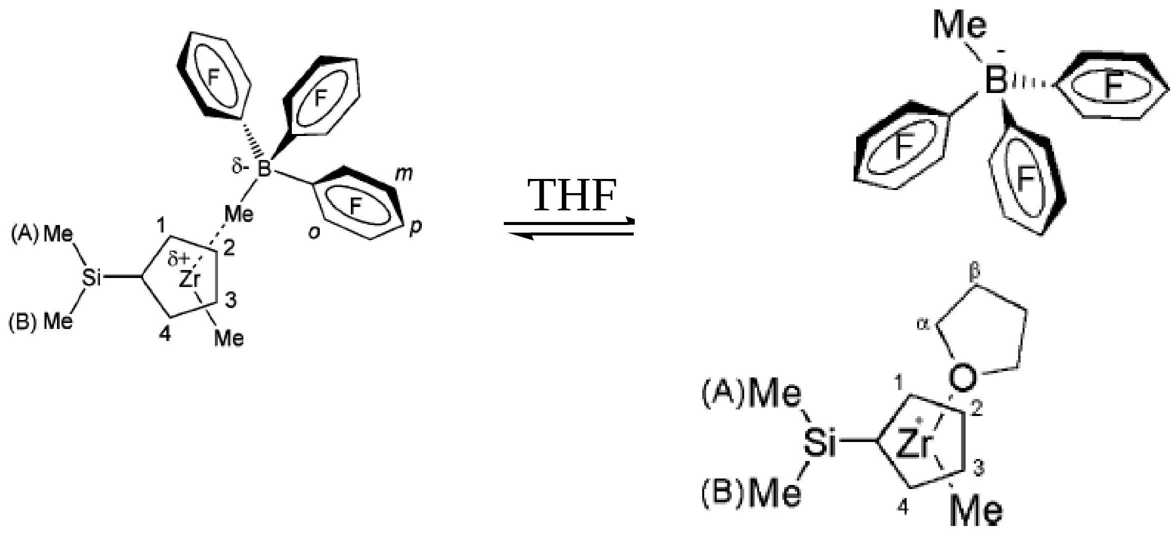
^{19}F ,^{1}H-HOESY

Meccanismo per lo stadio di crescita della catena polimerica

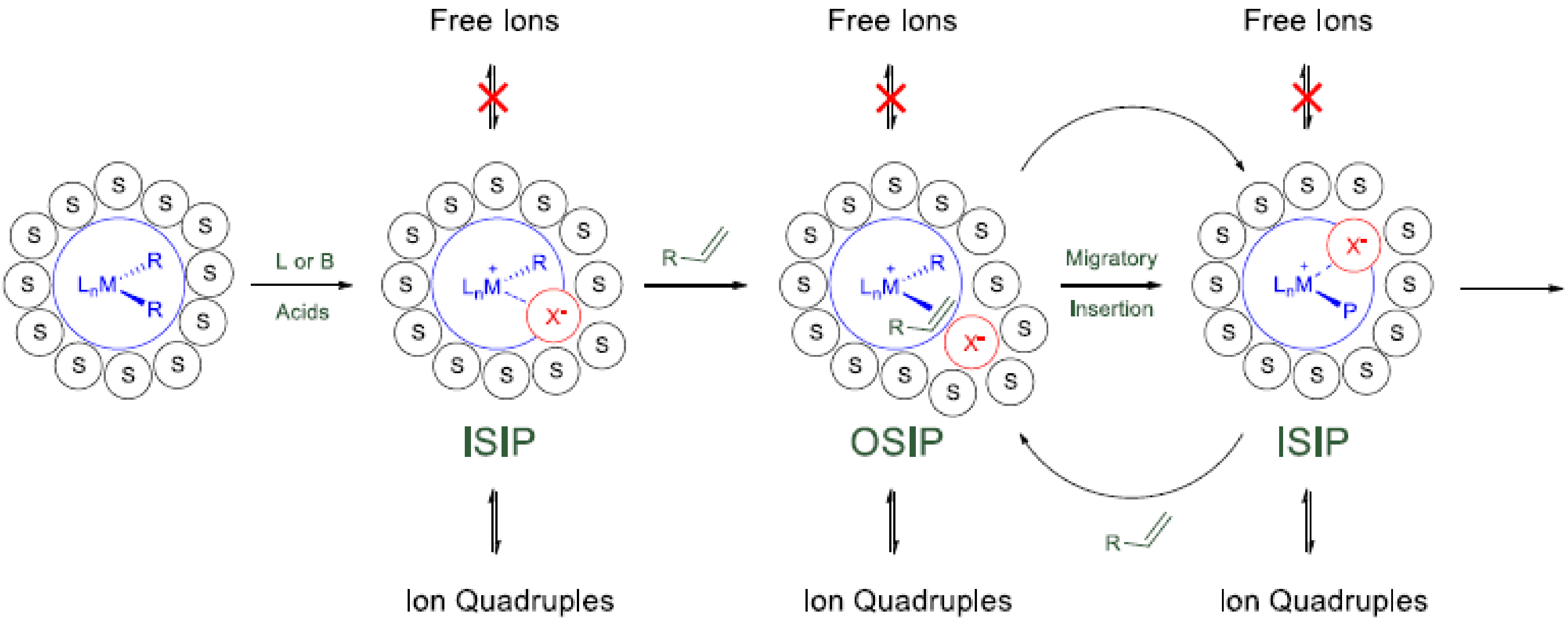


ISIP

OSIP

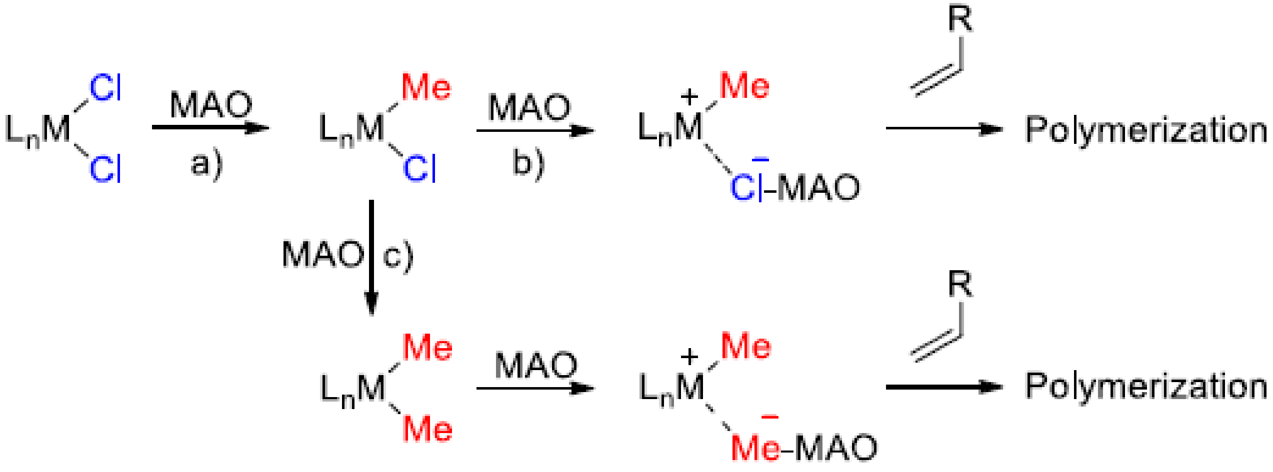


Meccanismo per attivazione e crescita della catena polimerica

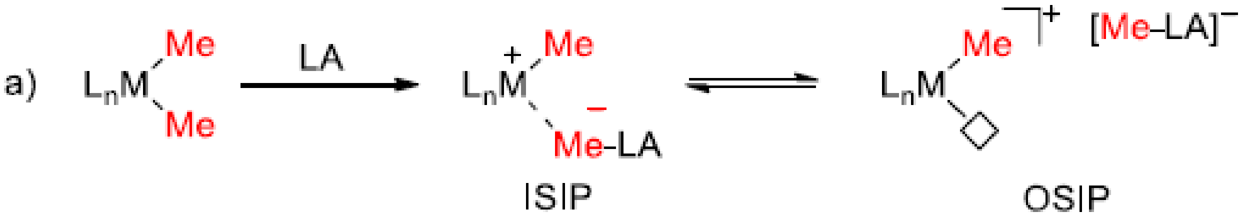


Il processo di attivazione

Ad opera del MAO



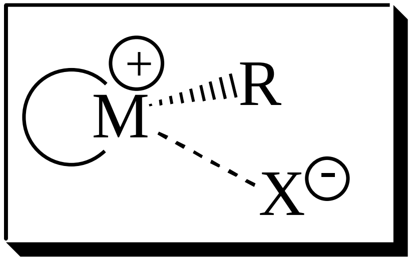
Ad opera dei borani



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:



è il ***resting state*** del ciclo catalitico

ISIP

Effetto dell'anione nelle reazioni di polimerizzazione

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

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

Con $X^{-} = MeB(C_6F_5)_3^{\;-}$

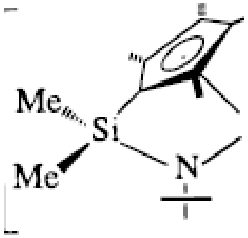
se M = Zr: sistema inattivo

se M = Ti: sistema leggermente attivo

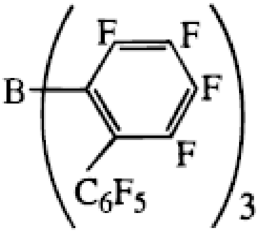
Con $X^{-} = MePBB^{-}$

se M = Zr: sistema attivo: v = 10^5

se M = Ti: sistema 70 volte più attivo



CGC



PBB

Limiti dei catalizzatori metallocenici[1]

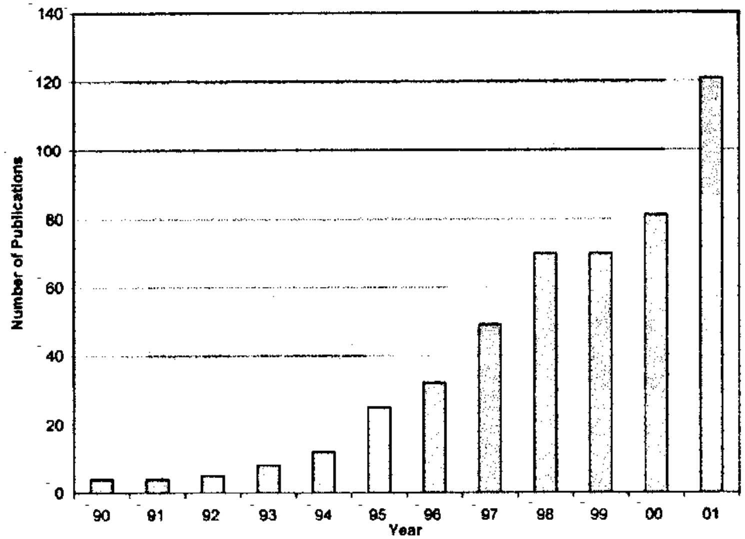
- Vengono facilmente avvelenati da composti contenenti eteroatomi;

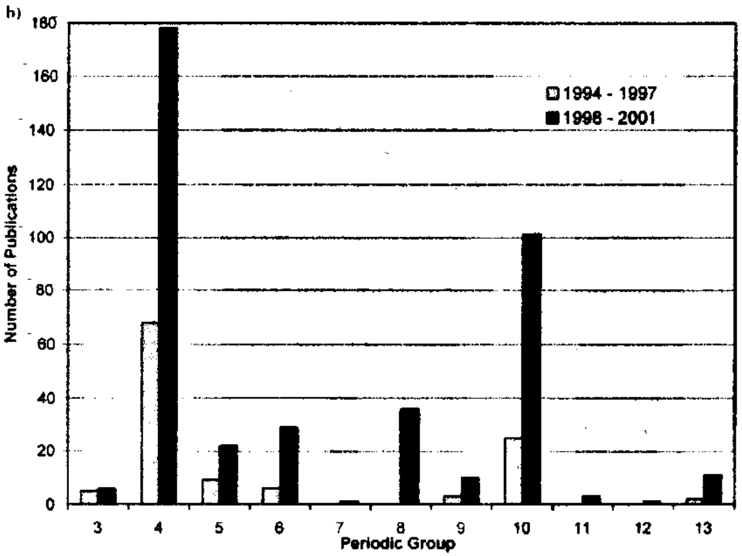
- sono molto costosi e vengono preparati in un processo a più stadi;

- il MAO viene usato in grande eccesso rispetto al metallo, pertanto è un componente importante nella definizione del costo finale del prodotto.

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

Numero di pubblicazioni sui catalizzatori NON metallocenici[1]

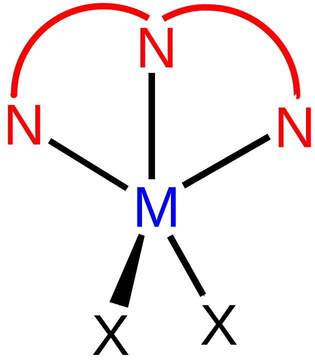




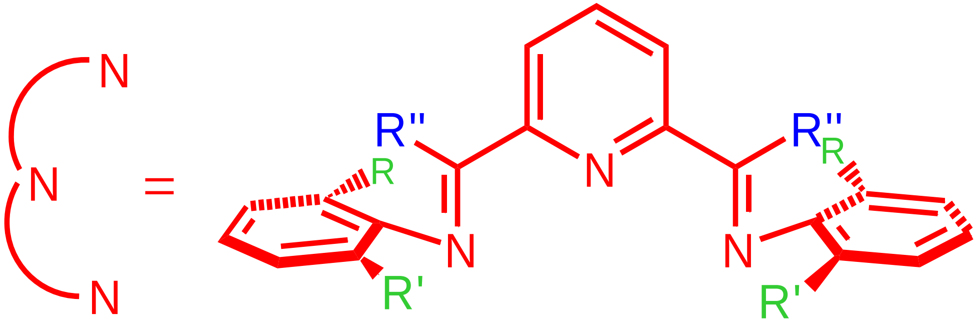
[1] V. Gibson et al., *Chem. Rev.* **2003**, *103*, 283.

Leganti tridentati bis(imminici) per la polimerizzazione dell'etilene

Catalizzatori di Fe(II) e Co(II)

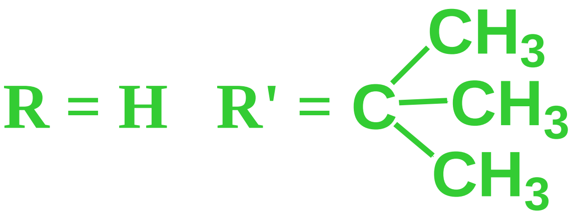


+ MAO

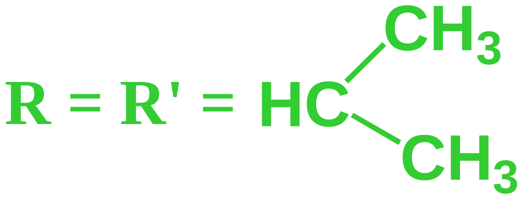


PBI

R = H R' = Ph



$$\mathbf{R = H \quad R' = C(CH_3)_3}$$



$$\mathbf{R = R' = HC(CH_3)_2}$$

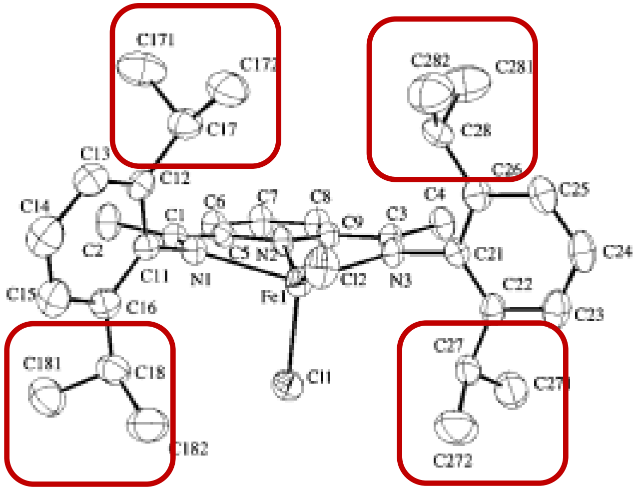
Polietilene lineare ad alta densità

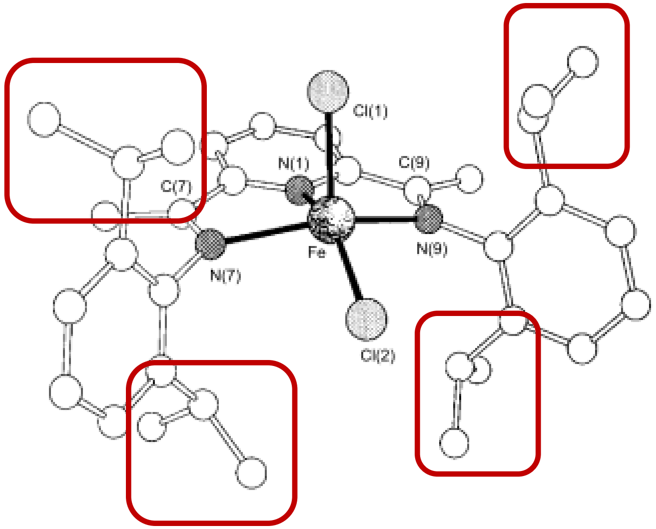
VERSIPOL (Du Pont)

Solvente: toluene
T = 25 – 90°C
t = 15 – 180 min.
p= 14 – 42 atm

M. Brookhart et al. *J. Am. Chem. Soc.* 1**998**, *120*, 4049.
V. C. Gibson et al. *Chem. Commun.* 1**998**, 849.
S. D. Ittel, L.K. Johnson, M. Brookhart *Chem. Rev.* **2000**, *100*, 1169.
V. C. Gibson, S. K. Spitzmesser *Chem. Rev.* **2003**, *103*, 283.

Crystal structure of $[Fe((2,6\text{-}i\text{-}Pr\text{-}Ph)_2PBIMe_2)Cl_2]$





B. L. Small, M. Brookhart, A. M. A. Bennett J. Am. Chem. Soc. 1**998**, 120, 4049.

G. J. P. Britovsek, V. C. Gibson, B. S. Kimberley, P. J. Maddox, S. J. McTavish, G. A. Solan, A. J. P. White, D. J. Williams Chem. Commun. 1**998**, 849.

Both complexes have a pseudo-square-pyramidal geometry with the aryl rings nearly perpendicular to the square plane.

They are paramagnetic, high-spin complexes.

Polimerizzazione dell’etilene con catalizzatori di Fe(II) e Co(II)[1]

Effetto della pressione di etilene

Prec. Cat.: **$[MCl_2((2,6\text{-}i\text{-}PrPh)_2PBIH_2)]$**

M	$P_{etilene}$ (atm)	kg PE/g M h
Co	7	140
	41	140
Fe	7	1860
	41	4220
	340	11900

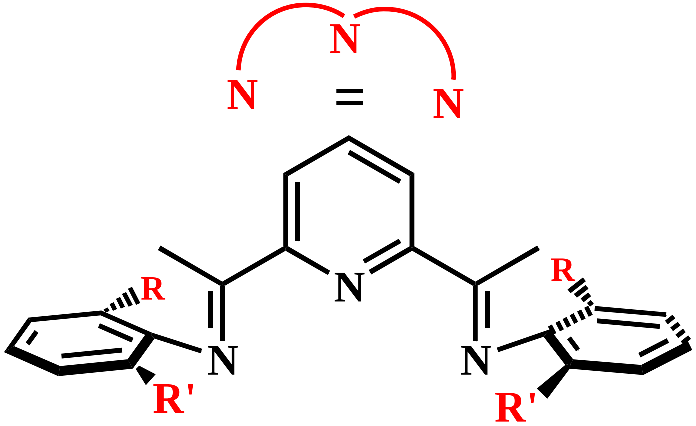
---

[1] S. D. Ittel et al., *Chem. Rev.* **2000**, *100*, 1169.

Polimerizzazione dell'etilene con catalizzatori di Fe(II) e Co(II)[1]

Effetto del legante azotato

Prec. Cat.: **[$CoCl_2$(PBI)]**



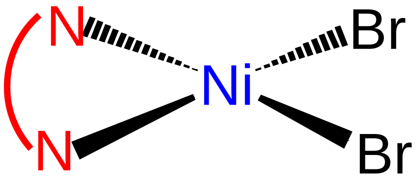
PBI	M_w
(2-PhPh)$_2$PBIMe$_2$	α-olefine
(2-*t*-BuPh)$_2$PBIMe$_2$	31 000
(2,6-*i*-PrPh)$_2$PBIMe$_2$	46 000
(2,6-*i*-PrPh)$_2$PBIH$_2$	18 000

---

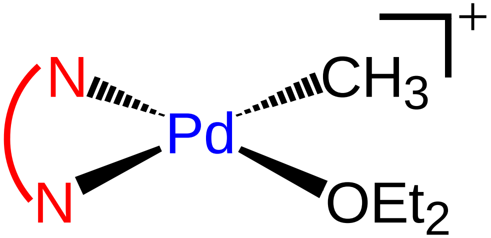
[1] S. D. Ittel et al., *Chem. Rev.* **2000**, *100*, 1169.

Leganti **bidentati α-diimminici** per la sintesi del polietilene

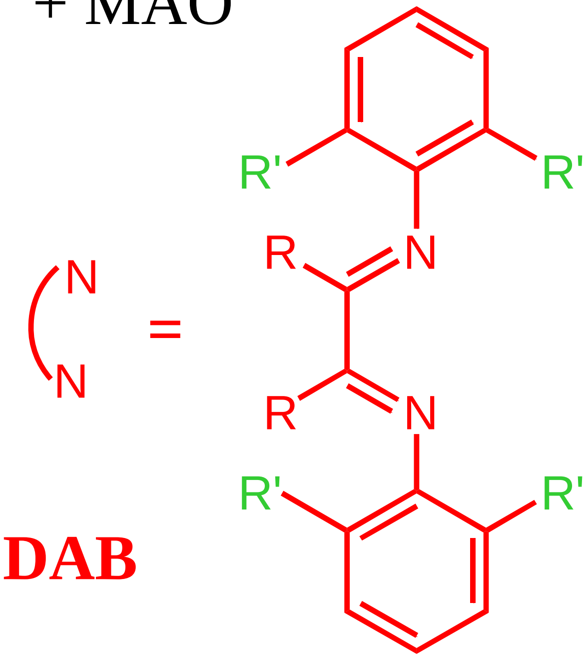
Catalizzatori di **Ni(II)** e **Pd(II)**



+ MAO

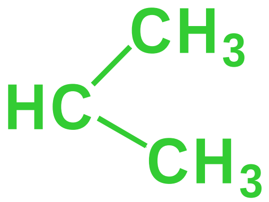


$B(ArF)_4^-$



$R = H, CH_3$

$R' = H, CH_3,$



DAB

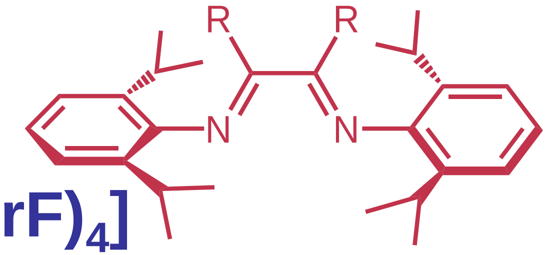
VERSIPOL (Du Pont)

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

[2] S. D. Ittel et al., *Chem. Rev.* **2000**, *100*, 1169.

Ethylene polymerization with Pd(II) catalysts

Effect of precatalyst



Cat. Prec.: [PdMe(OEt$_2$)(i-Pr-DABR)][B(ArF)$_4$]

R	Yield (g)	kg PE/mol Pd h	Mw (Mw/Mn)	Branches per 1000 carbons
H[a]	9.07	4.0	600 (3.0)	116
Me[b]	45.3	26.6	29000 (3.9)	103

Reaction conditions: n_{cat} = 100 μmol, P = 1.0 atm, T = 25 °C.
[a] CH_2Cl_2 V = 50 mL, t = 24 h.
[b] CH_2Cl_2 V = 100 mL, t = 17 h.

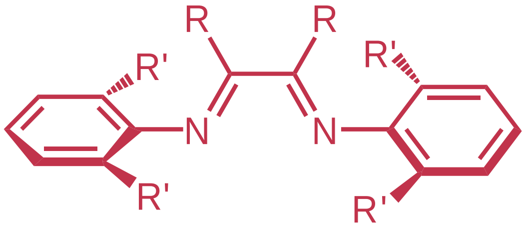
L. K. Johnson, C. M. Killian, M. Brookhart J. Am. Chem. Soc. **1995**, 117, 6414.

Ethylene polymerization with Ni(II) catalysts

Effect of precatalyst

Cat. Prec.: [$NiBr_2$(N-N)]

N-N =

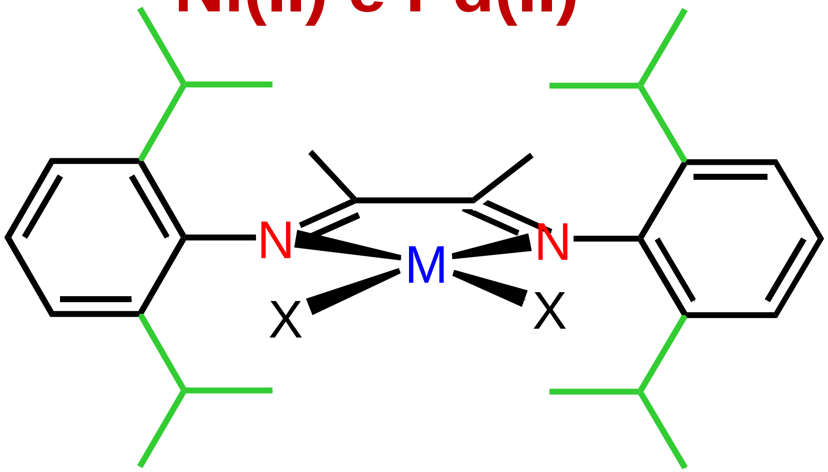


R, R'	mol cat.	t (min)	kg PE/mol Ni h	Mw (Mw/Mn)	Branches
H, i-Pr[a]	1.7×10^{-6}	15	1.1×10^{4}	31000 (2.5)	38
Me, i-Pr	1.6×10^{-6}	15	0.3×10^{4}	520000 (1.6)	48
H, Me	17×10^{-6}	30	0.04×10^{4}	43000 (2.5)	1.2
Me, Me	17×10^{-6}	10	0.17×10^{4}	170000 (2.6)	20
BIAN, i-Pr[b]	0.83×10^{-6}	30	0.51×10^{4}	610000 (2.3)	5.0

Reaction conditions: toluene V = 100 mL, P = 1.0 atm, T = 0 °C. [a]T = 25 °C. [b]V = 200 mL.

The activity of i-Pr-DABH is comparable to those of the most active Ziegler-Natta systems!

Polimerizzazione dell'etilene con catalizzatori di Ni(II) e Pd(II)[1,2]

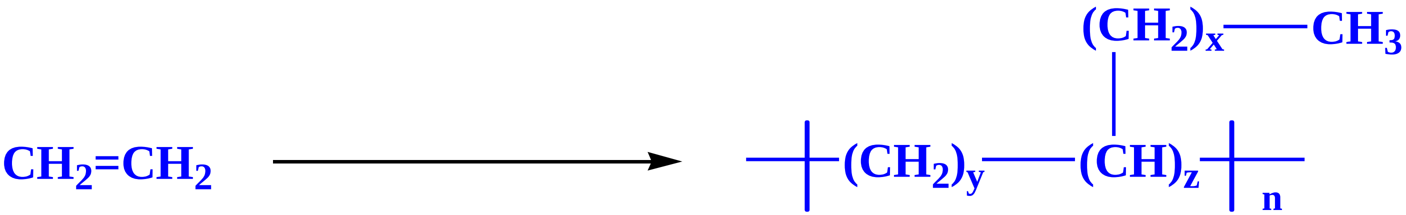


M = Ni	**M = Pd**
Solvente: toluene	Solvente: CH_2Cl_2
11 000 kg PE/mol Ni h	27 kg PE/mol Pd h
ΔG_{ins} = 13 – 14 kcal/mol	ΔG_{ins} = 17 – 18 kcal/mol
M_w = oligomeri – 85 000	M_w = 112 000 – 1 000 000
PE lineare e ramificato	PE altamente ramificato

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

[2] S. D. Ittel et al., *Chem. Rev.* **2000**, *100*, 1169.

Polimerizzazione dell’etilene con catalizzatori di Ni(II) e Pd(II): *microstruttura* del polietilene prodotto



$$CH_2{=}CH_2 \longrightarrow \left[(CH_2)_y - \overset{\overset{\displaystyle (CH_2)_x - CH_3}{|}}{(CH)_z} \right]_n$$

con i cat. di Pd(II) si hanno 115 ramificazioni ogni 1000 gruppi CH_2 inseriti

C1	37
C2	25
C3	3
C4	12
C5	1
C6+	37

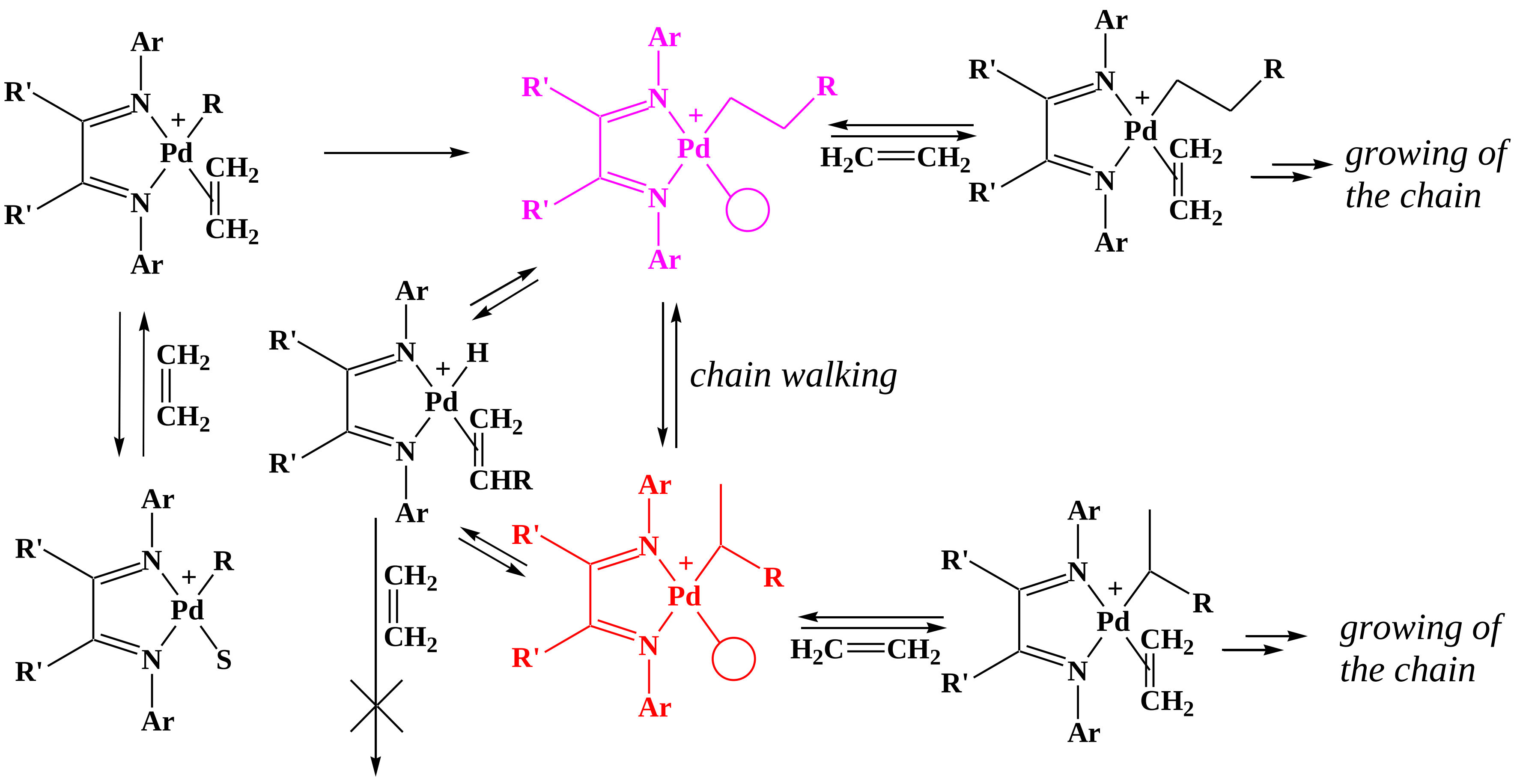
Polymerization Mechanism

NMR spectroscopy was fundamental to unravel the mechanism of the polymerization. Key intermediates were detected and kinetic investigations were performed, thus:

- **the reaction was found to be zero order in ethylene pressure;**
- **the Pd-alkyl-ethylene intermediate was recognized to be the catalyst resting state;**
- **ethylene insertion was the rate determining step.**

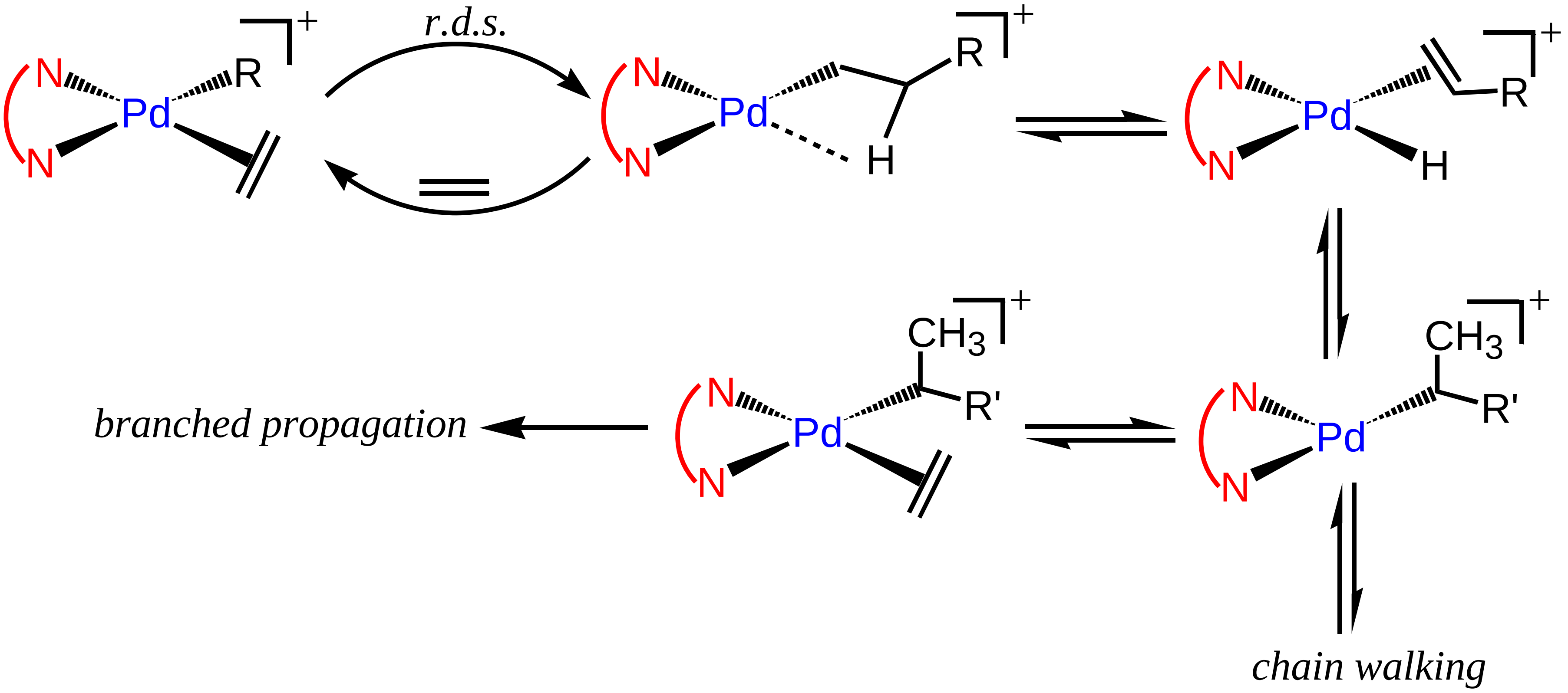
L. K. Johnson, C. M. Killian, M. Brookhart J. Am. Chem. Soc. **1995**, 117, 6414.
S. D. Ittel, L.K. Johnson, M. Brookhart Chem. Rev. **2000**, 100, 1169.

Polymerization Mechanism



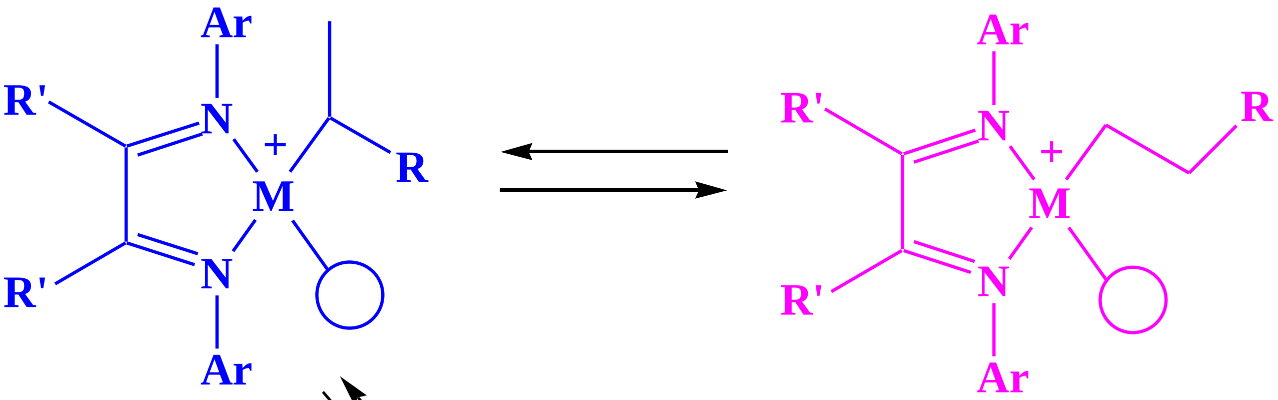
[1]M. Brookhart et al., *J. Am. Chem. Soc.* **1995**, *117*, 6414.
[2]S. D. Ittel et al., *Chem. Rev.* **2000**, *100*, 1169.

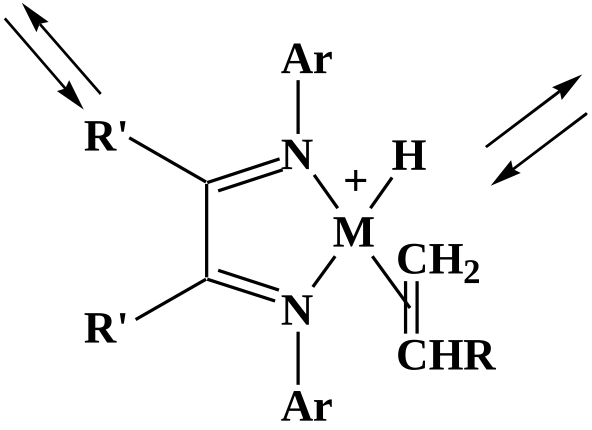
Polymerization Mechanism

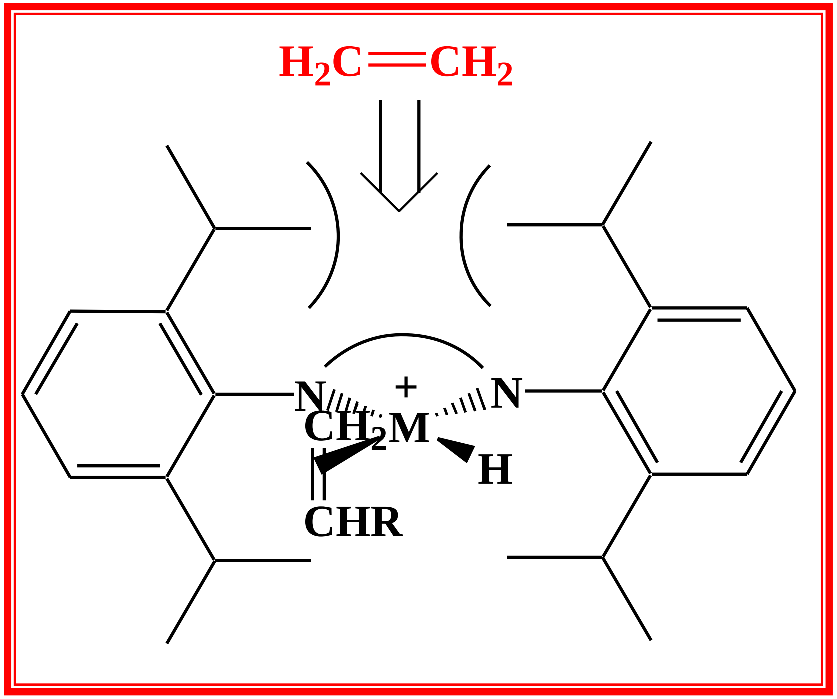


[1] M. Brookhart et al., *J. Am. Chem. Soc.* **1995**, *117*, 6414.
[2] S. D. Ittel et al., *Chem. Rev.* **2000**, *100*, 1169.

Meccanismo del trasferimento di catena

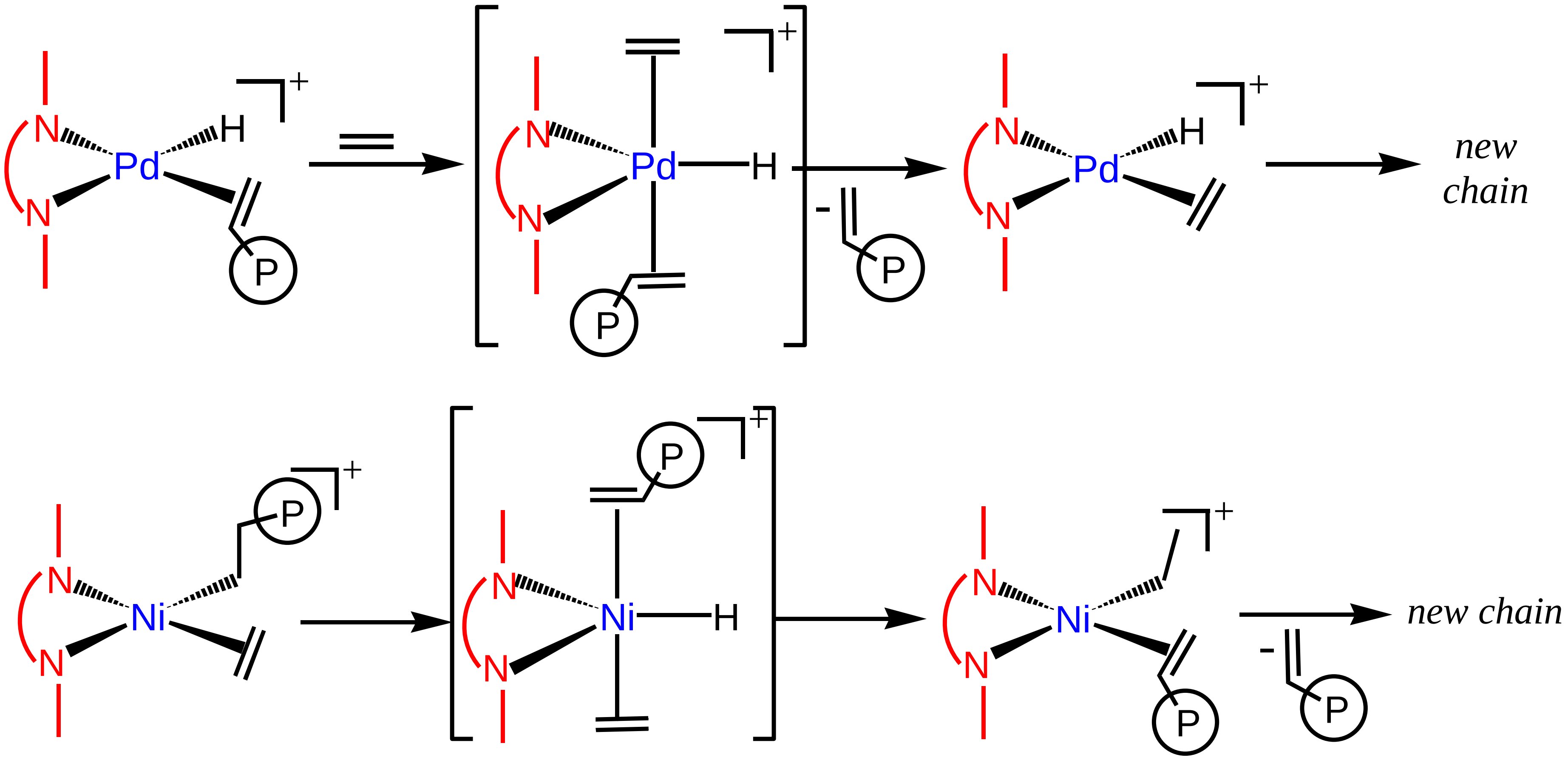






... è di tipo ***associativo***,
ed è sfavorito
dall'***ingombro sterico!***

Meccanismo del trasferimento di catena



[1]M. Brookhart et al., *J. Am. Chem. Soc.* **1995**, *117*, 6414.
[2]S. D. Ittel et al., *Chem. Rev.* **2000**, *100*, 1169.