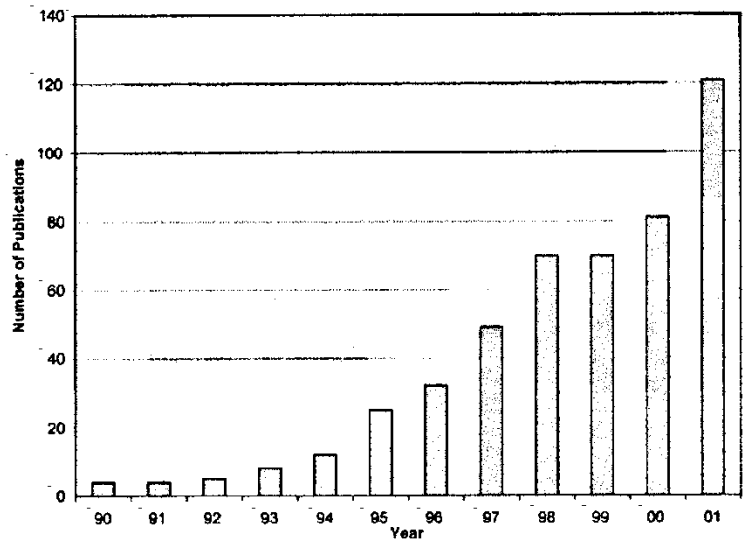
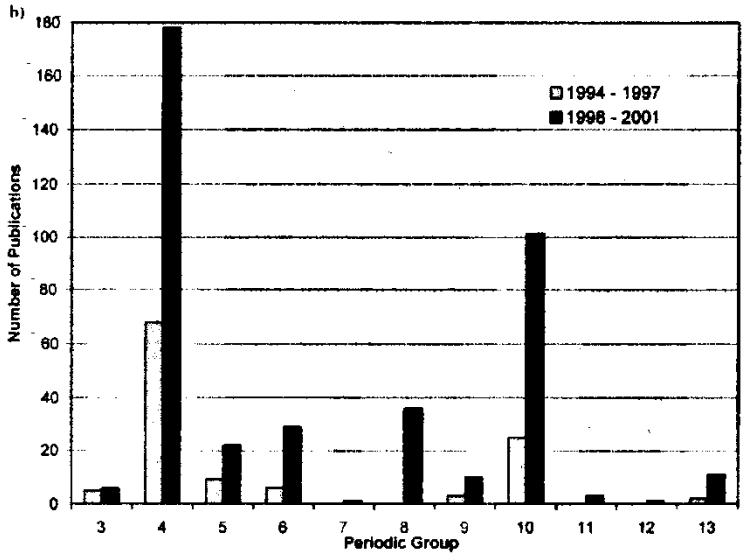
Numero di pubblicazioni sui catalizzatori NON metallocenici[1]

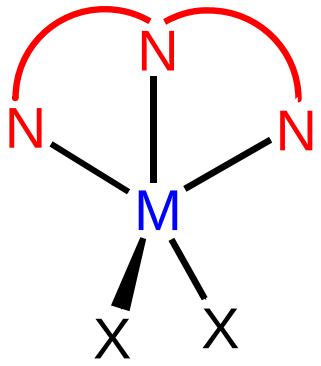




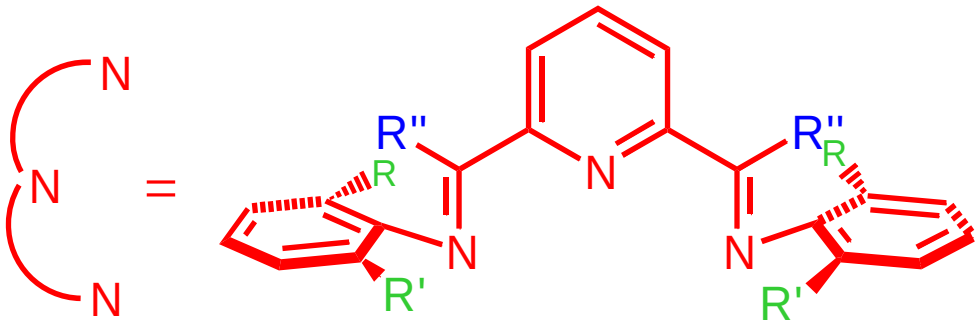
[1]V. Gibson et al., *Chem. Rev.* **2003**, *103*, 283.

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

Catalizzatori di Fe(II) e Co(II)

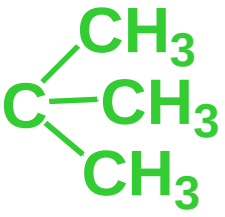


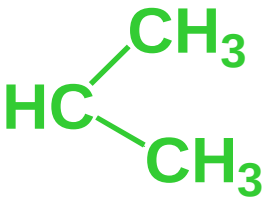
+ MAO



PBI

R = H R' = Ph

R = H R' = 

R = R' = 

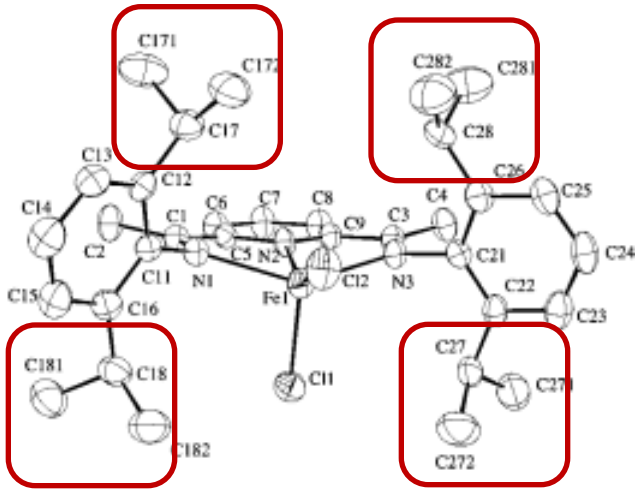
Solvente: toluene
T = 25 – 90°C
t = 15 – 180 min.
p= 14 – 42 atm

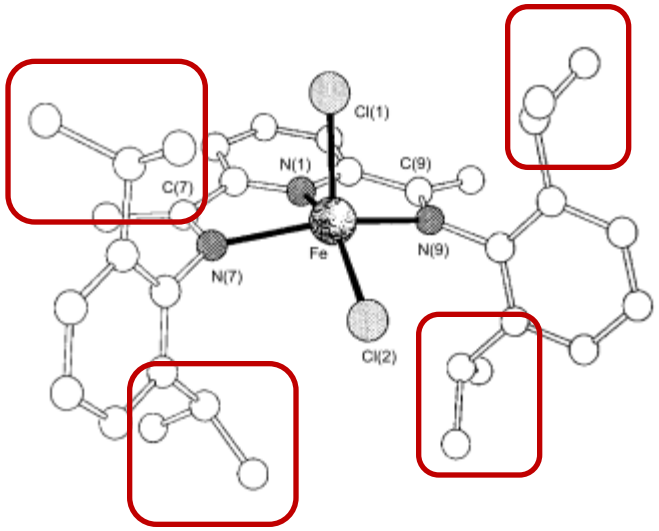
Polietilene lineare ad alta densità

VERSIPOL (Du Pont)

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





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-*i*-PrPh)$_2$PBIH_2)]**

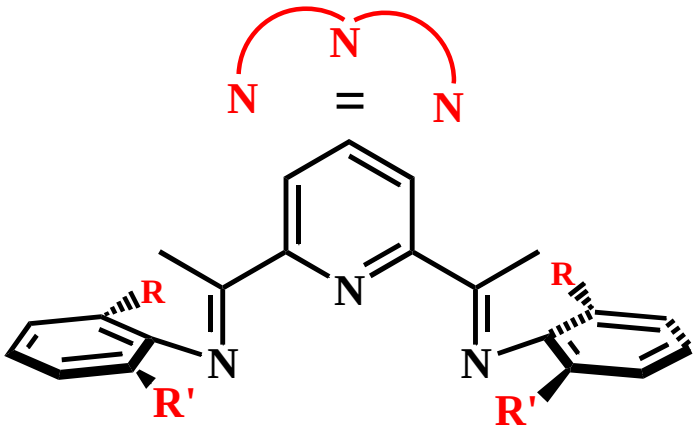
M	$P_{etilene}$ (atm)	kg PE/g M h
Co	7	140
	41	140
Fe	7	1860
	41	4220
	340	11900

[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)]**

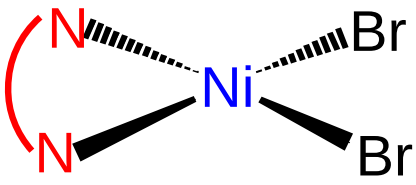


PBI	M_w
(2-PhPh)$_2$PBIMe$_2$	α-olefine
(2-*t*-BuPh)$_2$PBIMe$_2$	31 000
(2,6-*i*-PrPh)$_2$PBIMe$_2$	46 000
(2,6-*i*-PrPh)$_2$PBIH$_2$	18 000

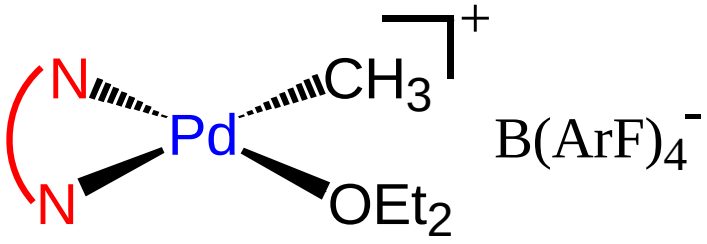
[1]S. D. Ittel et al., *Chem. Rev.* **2000**, *100*, 1169.

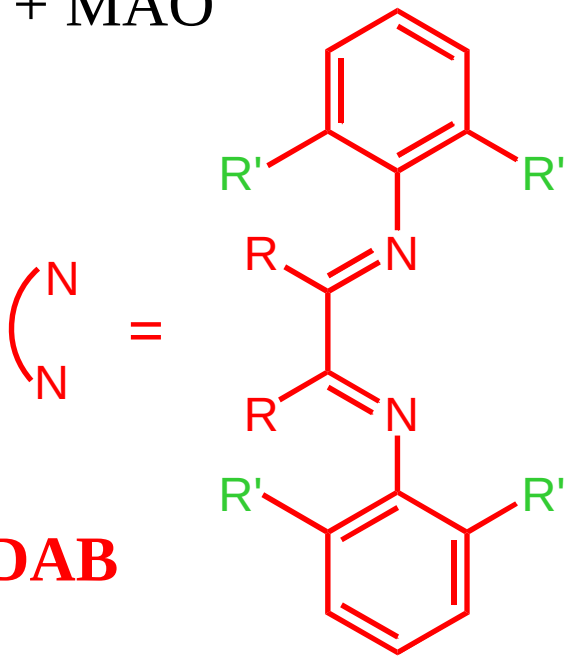
Leganti bidentati α-diimminici per la sintesi del polietilene

Catalizzatori di Ni(II) e Pd(II)



+ MAO





DAB

R = H, CH_3

R' = H, CH_3, HC(CH_3)$_2$

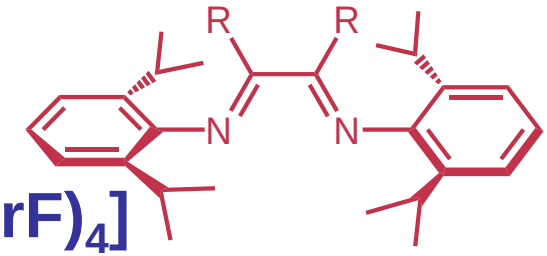
VERSIPOL (Du Pont)

[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

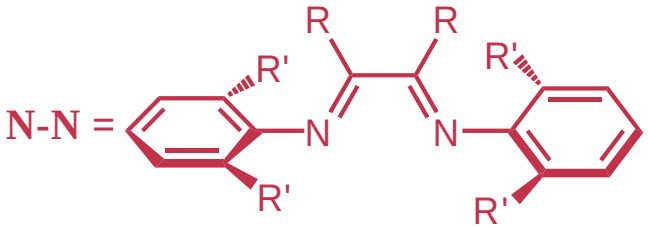
Reaction conditions: n_{cat} = 100 μmol, P = 1.0 atm, T = 25 °C.
[a]CH_2Cl_2 V = 50 mL, t = 24 h.
[b]CH_2Cl_2 V = 100 mL, t = 17 h.

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)]

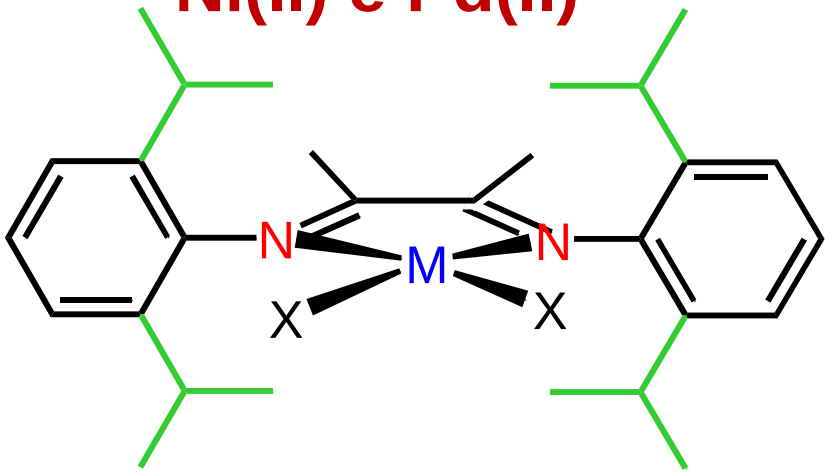


R, R'	mol cat.	t (min)	kg PE/mol Ni h	Mw (Mw/Mn)	Branches
H, i-Pr[a]	1.7×10^{-6}	15	1.1×10^{4}	31000 (2.5)	38
Me, i-Pr	1.6×10^{-6}	15	0.3×10^{4}	520000 (1.6)	48
H, Me	17×10^{-6}	30	0.04×10^{4}	43000 (2.5)	1.2
Me, Me	17×10^{-6}	10	0.17×10^{4}	170000 (2.6)	20
BIAN, i-Pr[b]	0.83×10^{-6}	30	0.51×10^{4}	610000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

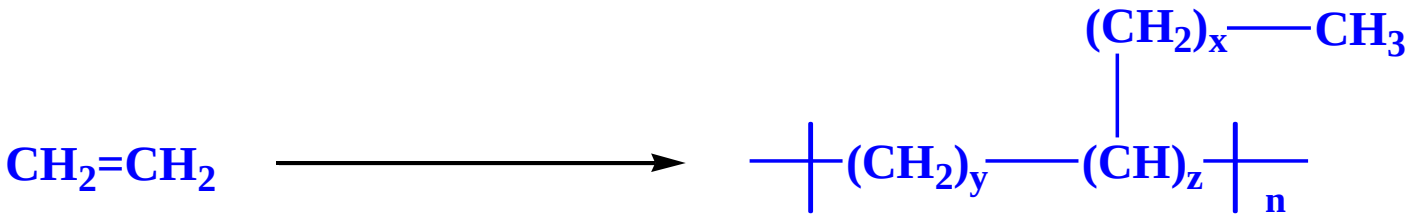
Polimerizzazione dell'etilene con catalizzatori di Ni(II) e Pd(II)[1,2]



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



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

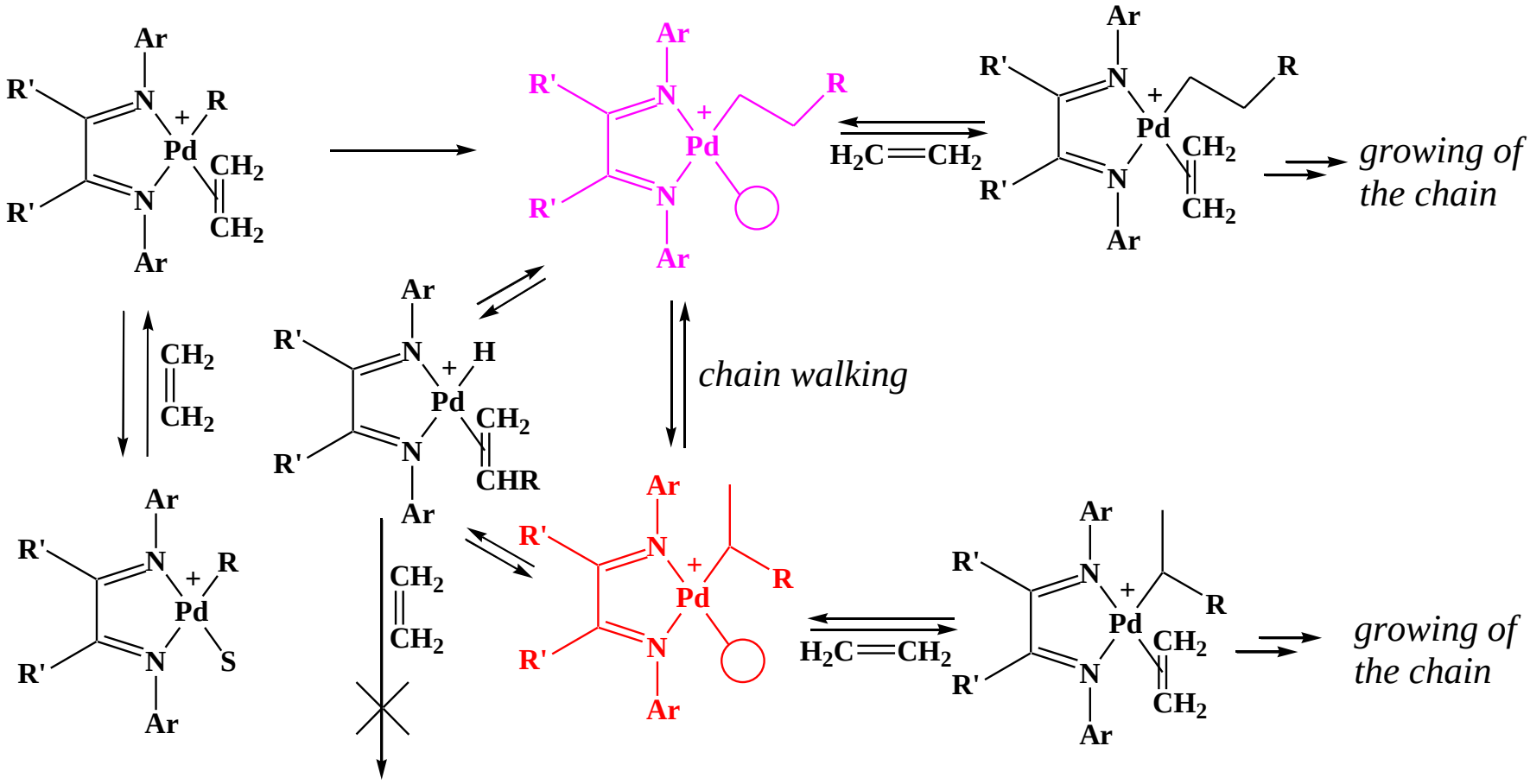
Polymerization Mechanism

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.**

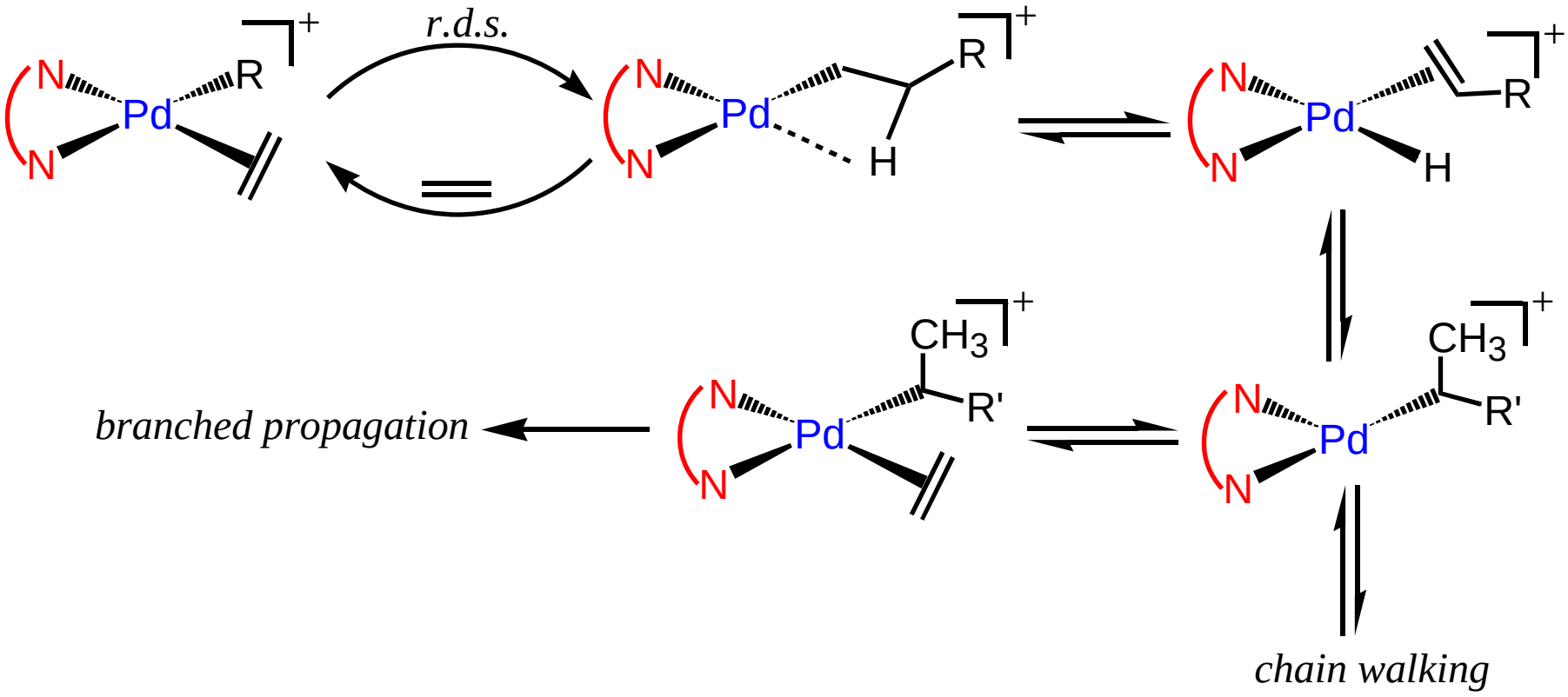
L. K. Johnson, C. M. Killian, M. Brookhart J. Am. Chem. Soc. **1995**, 117, 6414.
S. D. Ittel, L.K. Johnson, M. Brookhart Chem. Rev. **2000**, 100, 1169.

Polymerization Mechanism



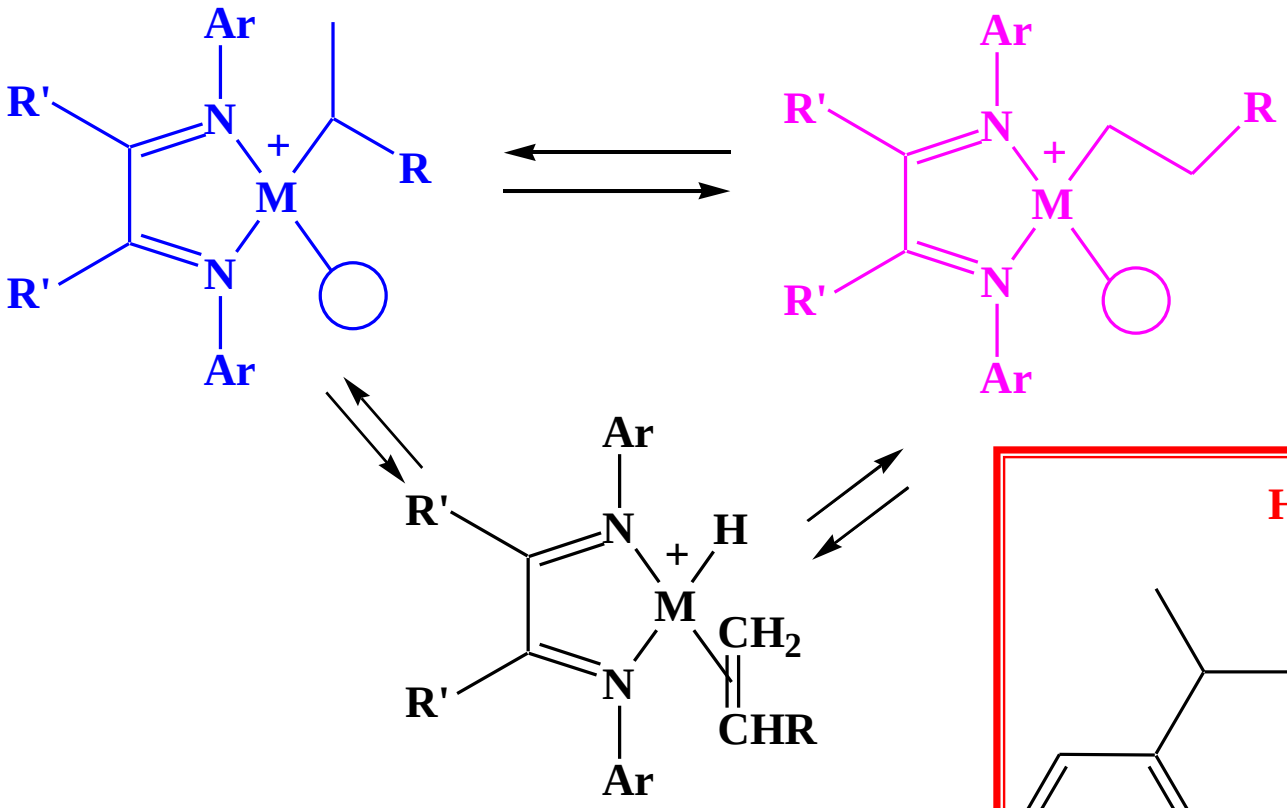
[1]M. Brookhart et al., *J. Am. Chem. Soc.* **1995**, *117*, 6414.
[2]S. D. Ittel et al., *Chem. Rev.* **2000**, *100*, 1169.

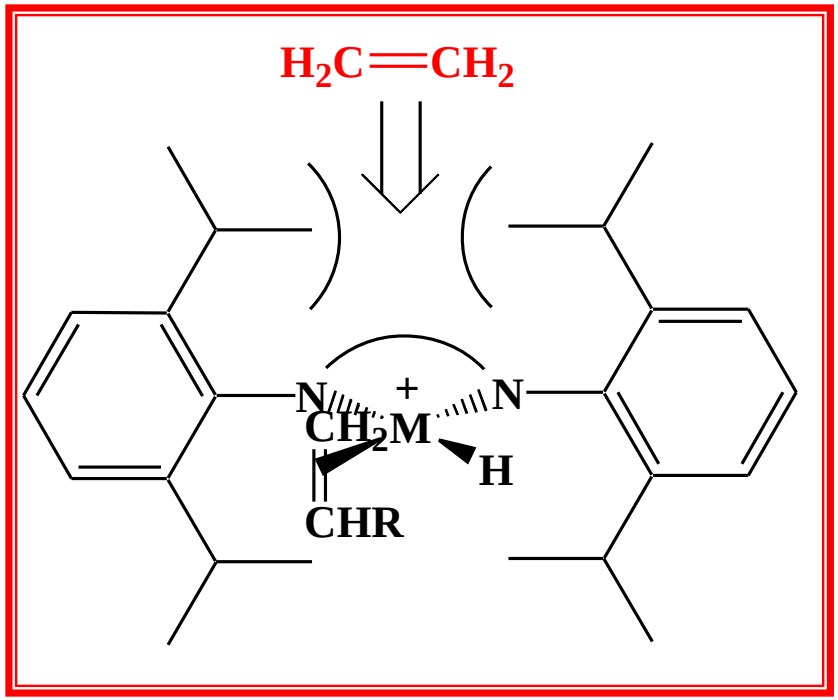
Polymerization Mechanism



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

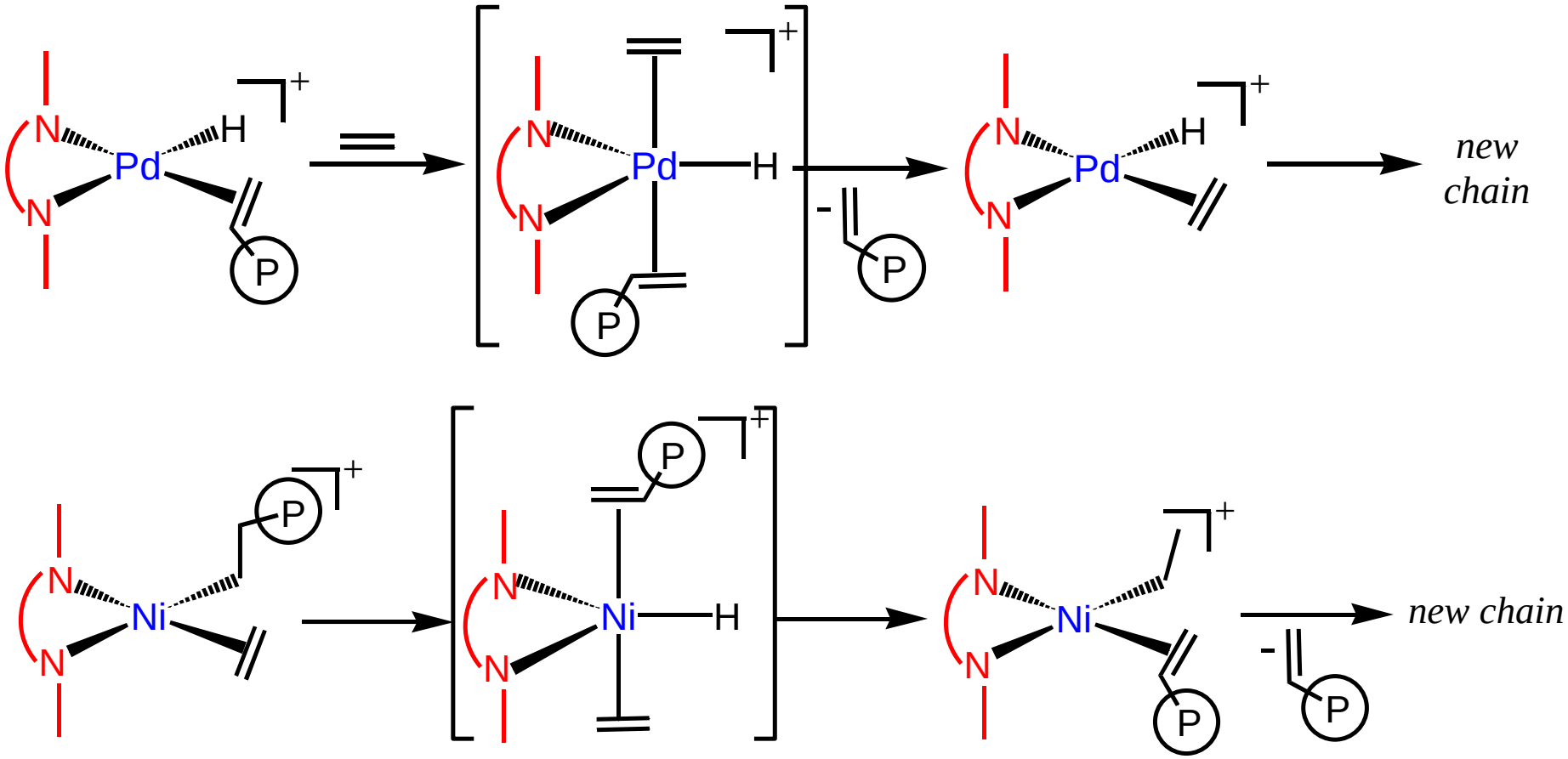
Meccanismo del trasferimento di catena





... 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.