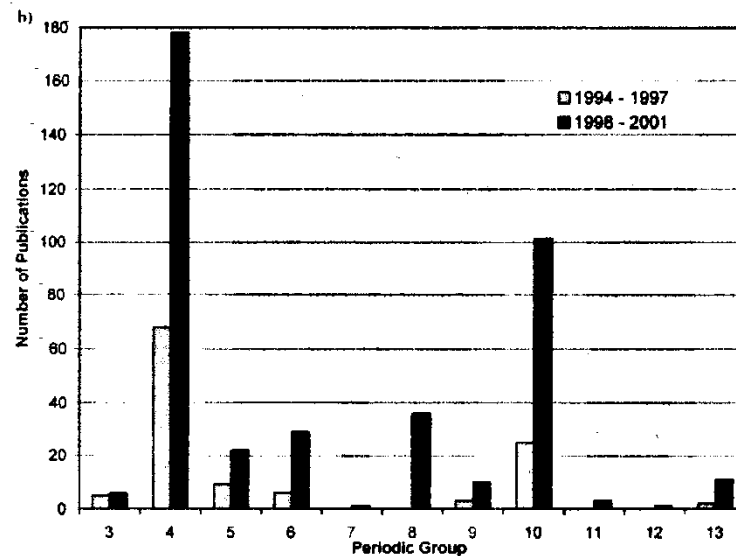
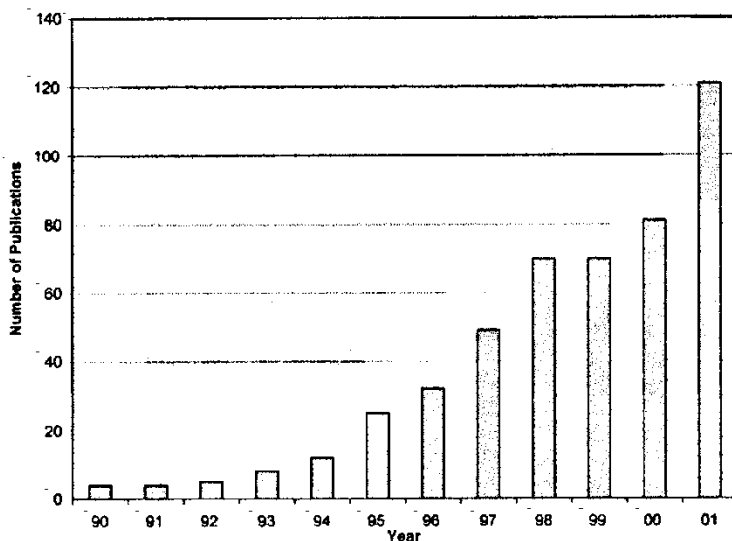


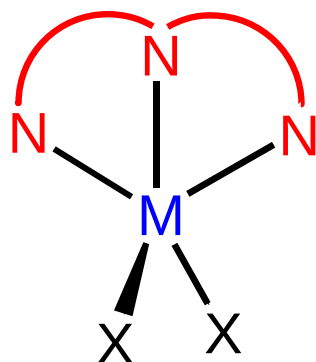
Numero di pubblicazioni sui catalizzatori **NON** metallocenici¹



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

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

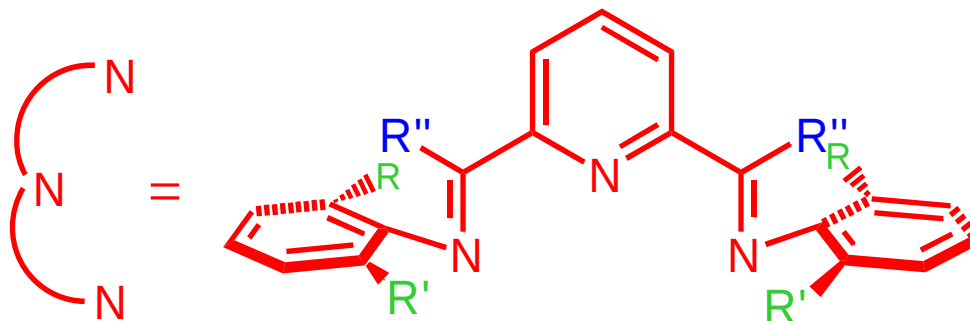
Catalizzatori di **Fe(II)** e **Co(II)**



+ MAO

Polietilene lineare ad alta densità

VERSIPOL (Du Pont)



PBI

$R = H$ $R' = Ph$

Solvente: toluene

$T = 25 - 90^{\circ}C$

$t = 15 - 180 \text{ min.}$

$p = 14 - 42 \text{ atm}$

$R = H$ $R' = C(CH_3)_3$

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

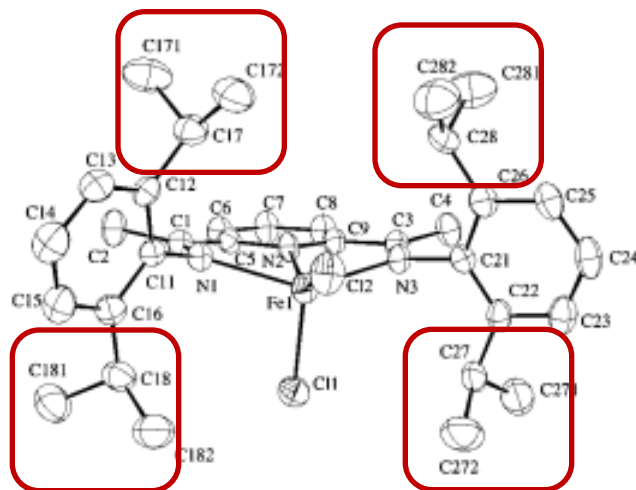
M. Brookhart et al. *J. Am. Chem. Soc.* **1998**, *120*, 4049.

V. C. Gibson et al. *Chem. Commun.* **1998**, 849.

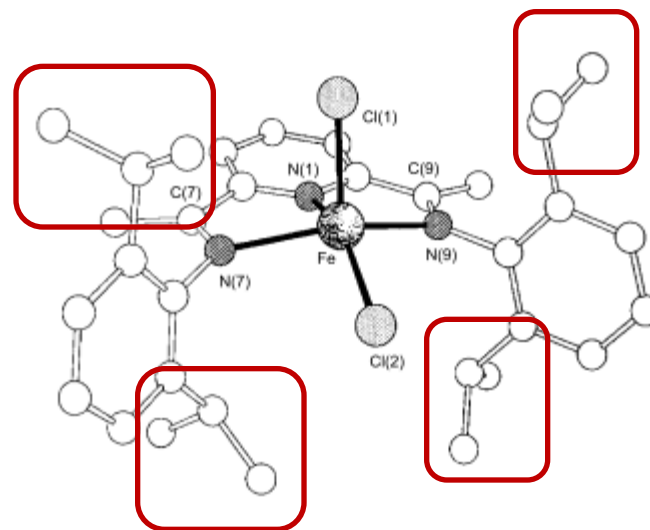
S. D. Ittel, L.K. Johnson, M. Brookhart *Chem. Rev.* **2000**, *100*, 1169.

V. C. Gibson, S. K. Spitzmesser *Chem. Rev.* **2003**, *103*, 283.

Crystal structure of [Fe((2,6-i-Pr-Ph)₂PBIMe₂)Cl₂]



B. L. Small, M. Brookhart, A. M. A. Bennett J. Am. Chem. Soc. **1998**, 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. **1998**, 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.: [**M**Cl₂((**2,6-*i*-PrPh**)₂**PBIH**₂)]

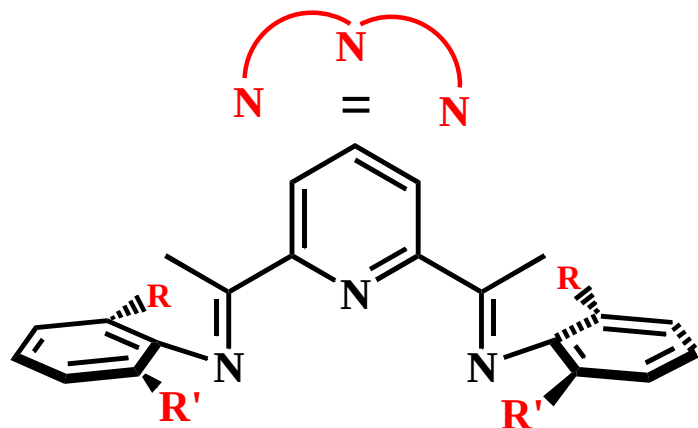
M	P _{etilene} (atm)	kg PE/g M h
Co	7	140
	41	140
Fe	7	1860
	41	4220
	340	11900

¹S. 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.: [CoCl₂(PBI)]

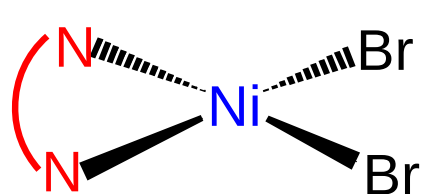


PBI	M _w
(2-PhPh) ₂ PBIMe ₂	α-olefine
(2- <i>t</i> -BuPh) ₂ PBIMe ₂	31 000
(2,6- <i>i</i> -PrPh) ₂ PBIMe ₂	46 000
(2,6- <i>i</i> -PrPh) ₂ PBIH ₂	18 000

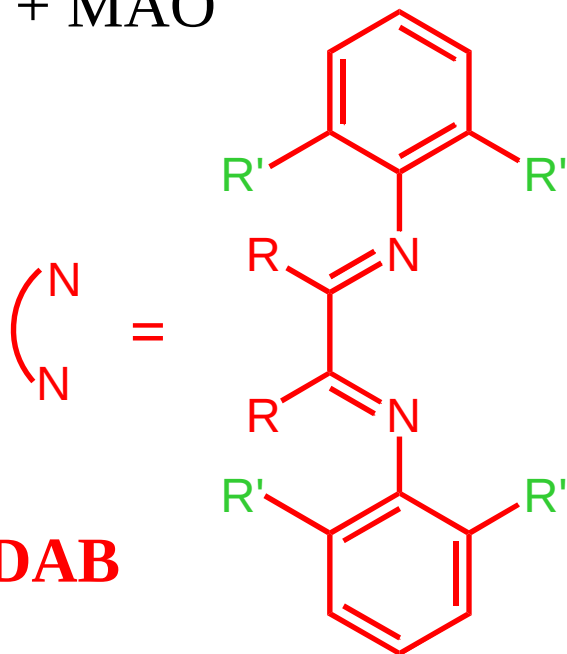
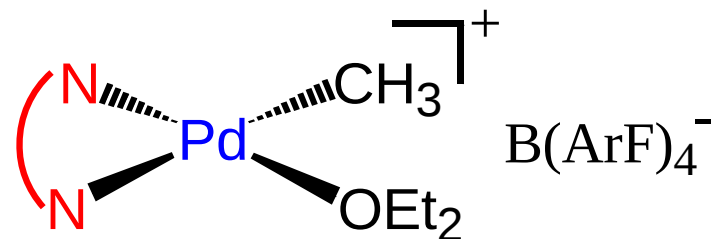
¹S. D. Ittel et al., *Chem. Rev.* **2000**, 100, 1169.

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

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



+ MAO



DAB

R = H, CH₃

R' = H, CH₃, HC(CH₃)₂

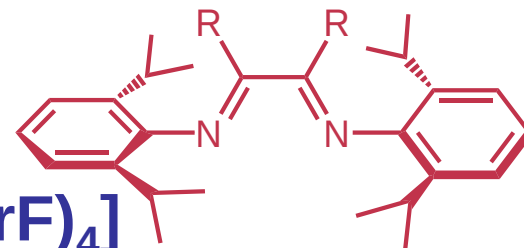
VERSIPOL (Du Pont)

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

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

Ethylene polymerization with **Pd(II)** catalysts

Effect of **precatalyst**



Cat. Prec.: [**Pd**Me(OEt₂)(i-Pr-DAB**R**)]**[B(ArF)₄]**

R	Yield (g)	kg PE/mol Pd h	M_w (M_w/M_n)	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.

^aCH₂Cl₂ V = 50 mL, t = 24 h.

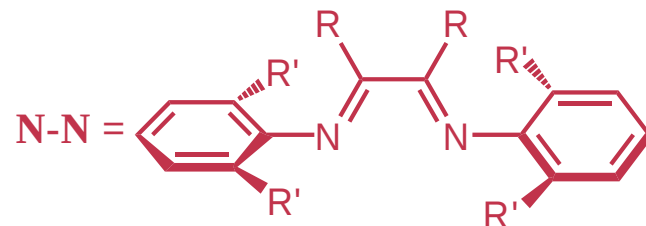
^bCH₂Cl₂ V = 100 mL, t = 17 h.

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.: **[NiBr₂(N-N)]**

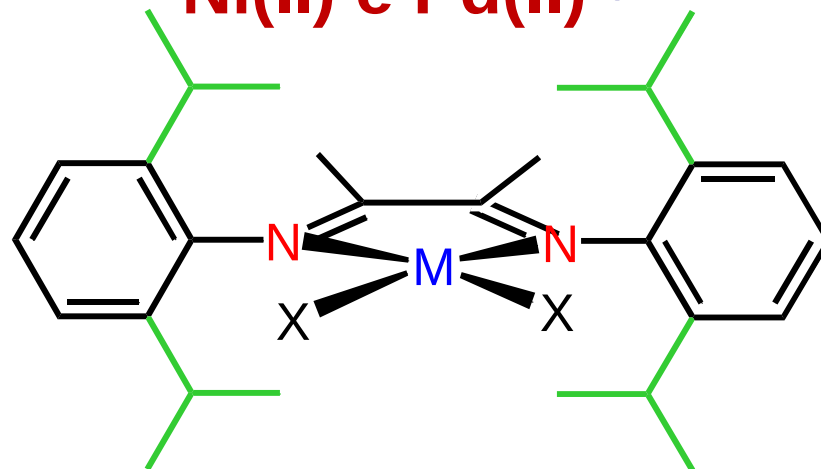


R, R'	mol cat.	t (min)	kg PE/mol Ni h	Mw (Mw/Mn)	Branches
H, i-Pr^a	1.7 x 10⁻⁶	15	1.1 x 10⁴	31000 (2.5)	38
Me, i-Pr	1.6 x 10⁻⁶	15	0.3 x 10⁴	520000 (1.6)	48
H, Me	17 x 10⁻⁶	30	0.04 x 10⁴	43000 (2.5)	1.2
Me, Me	17 x 10⁻⁶	10	0.17 x 10⁴	170000 (2.6)	20
BIAN, i-Pr^b	0.83 x 10⁻⁶	30	0.51 x 10⁴	610000 (2.3)	5.0

Reaction conditions: toluene V = 100 mL, P = 1.0 atm, T = 0 °C. ^aT = 25 °C. ^bV = 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

Solvente: toluene

11 000 kg PE/mol Ni h

$\Delta G_{\text{ins}} = 13 - 14 \text{ kcal/mol}$

M_w = oligomeri – 85 000

PE lineare e ramificato

M = Pd

Solvente: CH_2Cl_2

27 kg PE/mol Pd h

$\Delta G_{\text{ins}} = 17 - 18 \text{ kcal/mol}$

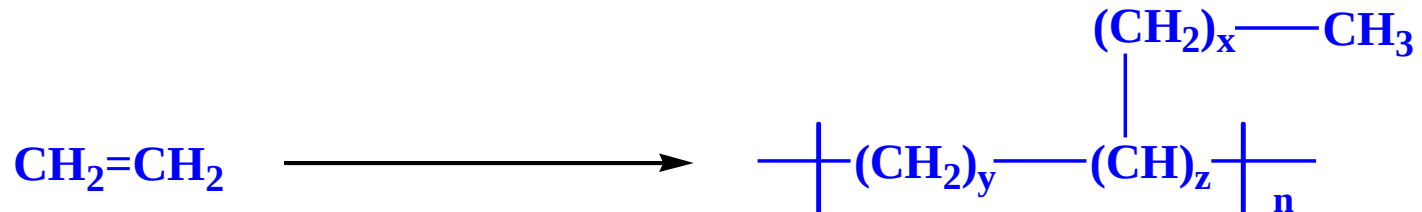
M_w = 112 000 – 1 000 000

PE altamente ramificato

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

²S. 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	$\left\{ \begin{array}{l} \\ \\ \\ \\ \\ \end{array} \right.$	C1	37
		C2	25
		C3	3
		C4	12
		C5	1
		C6+	37

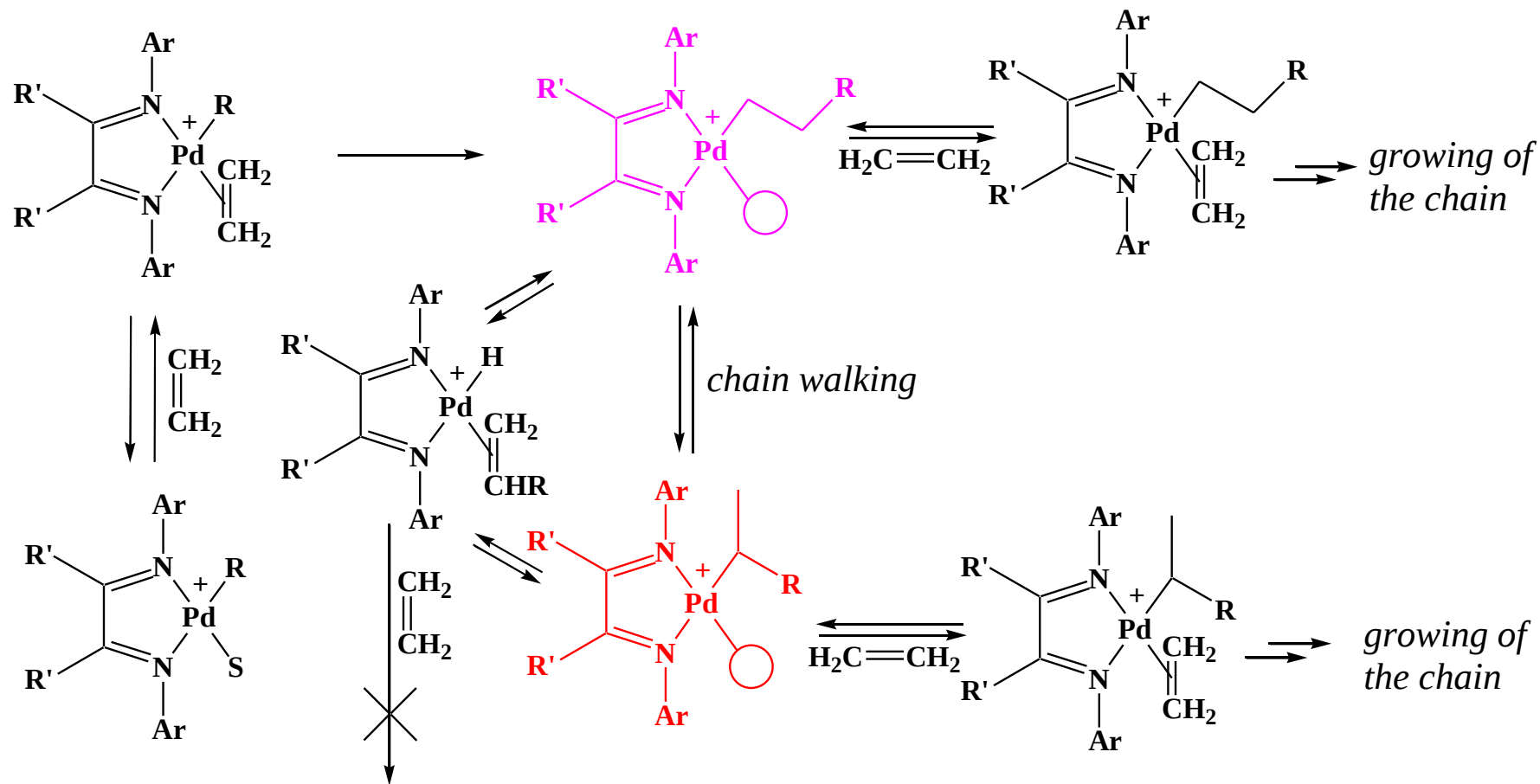
Polymerization Mechanism

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.

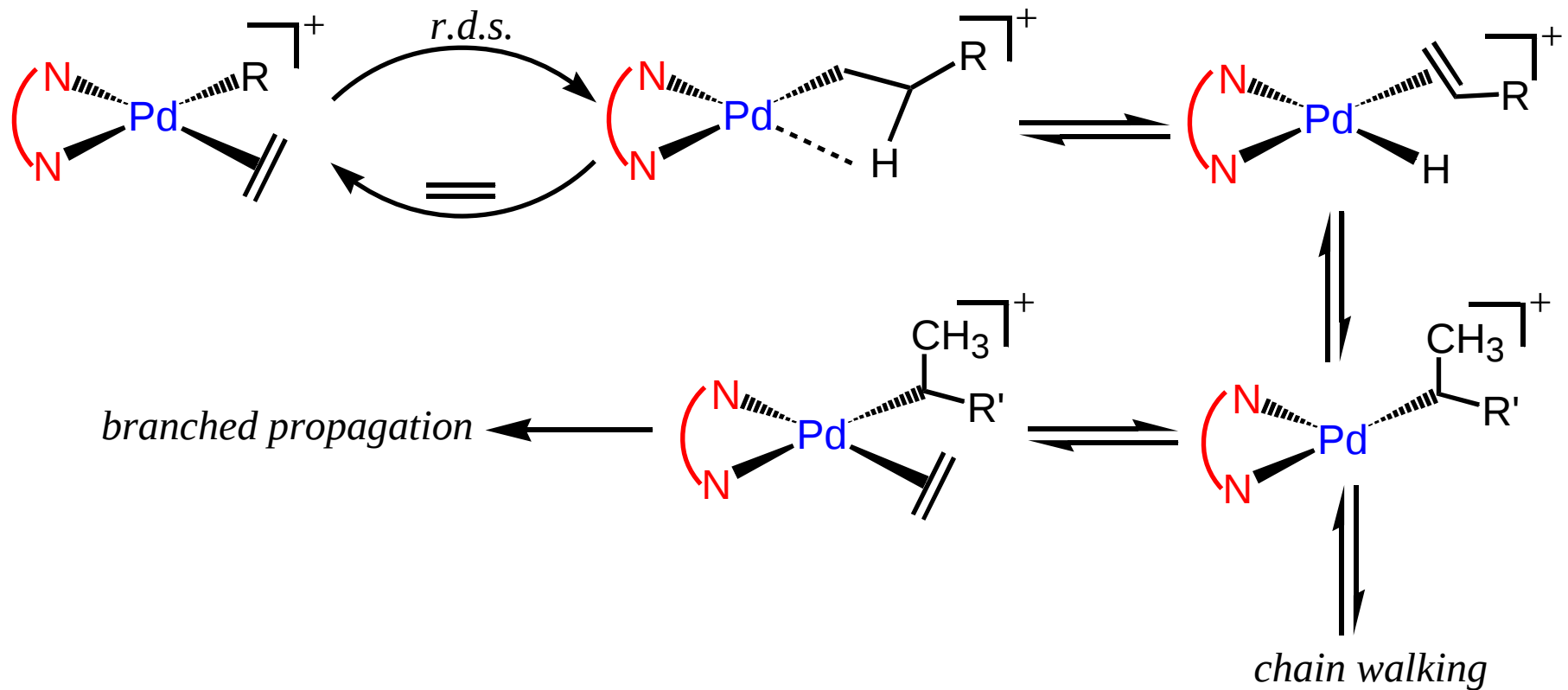
Polymerization Mechanism



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

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

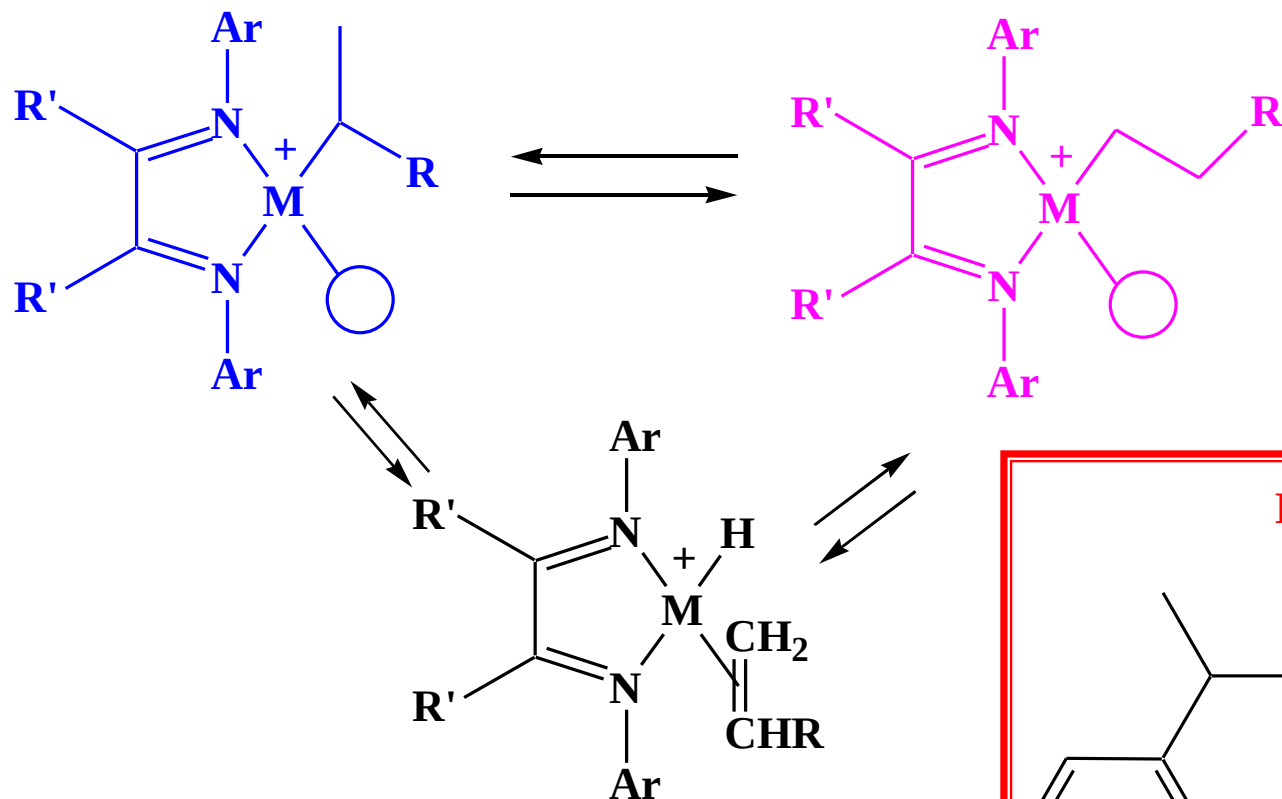
Polymerization Mechanism



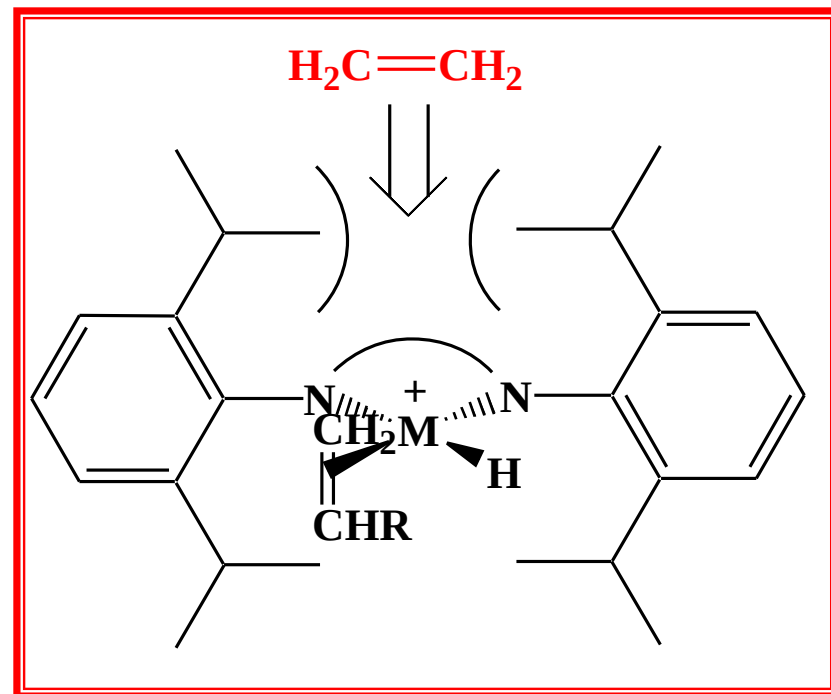
¹M. Brookhart et al., *J. Am. Chem. Soc.* **1995**, *117*, 6414.

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

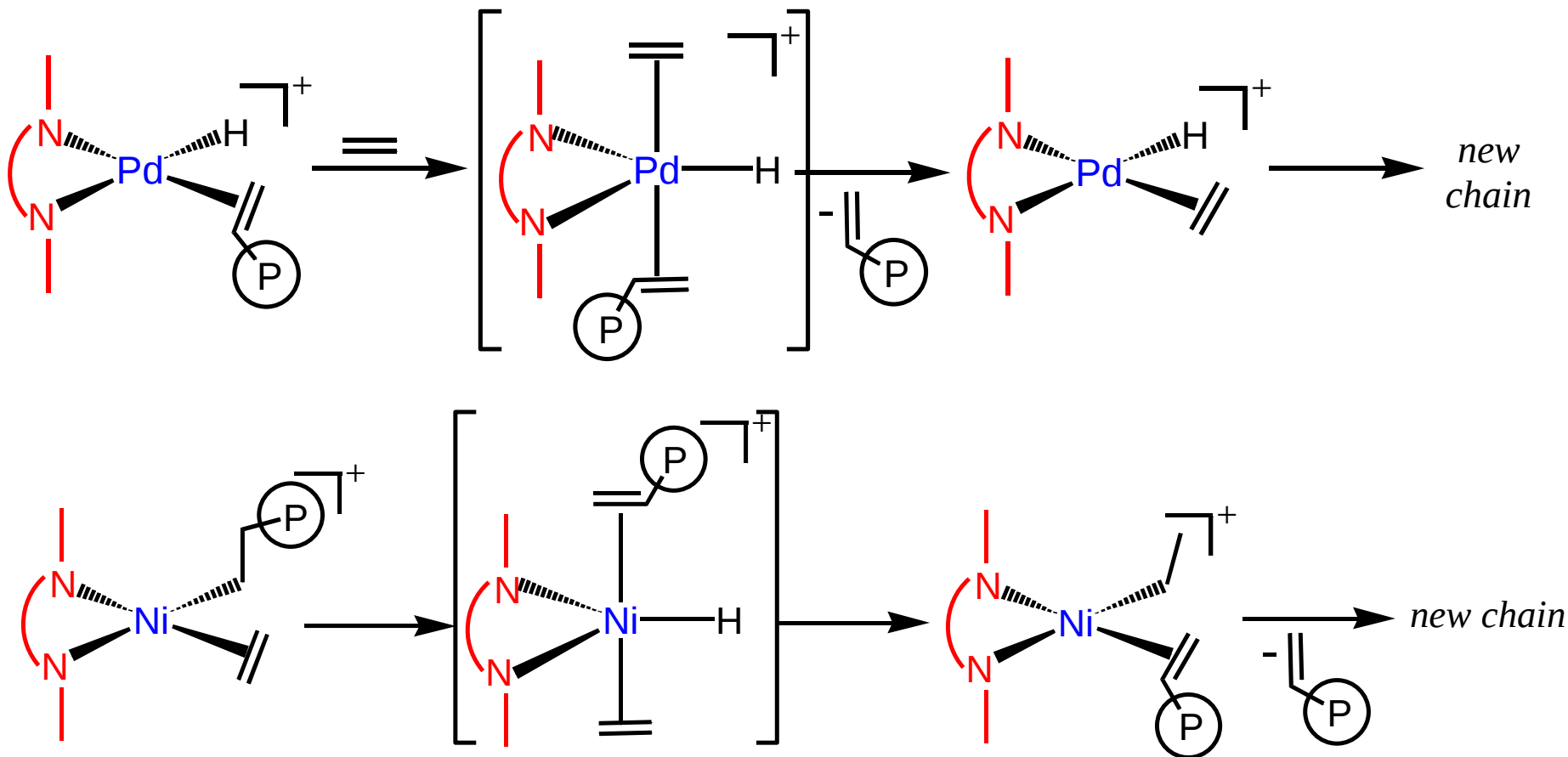
Meccanismo del **trasferimento di catena**



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



Meccanismo del **trasferimento di catena**



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

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