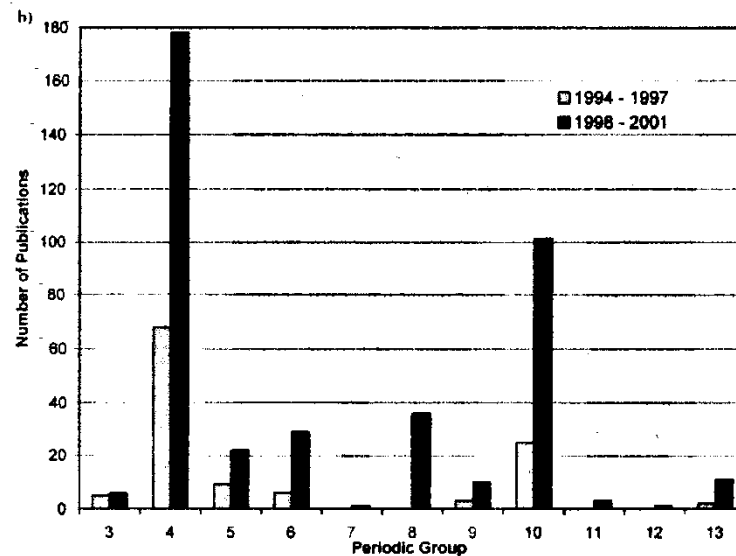
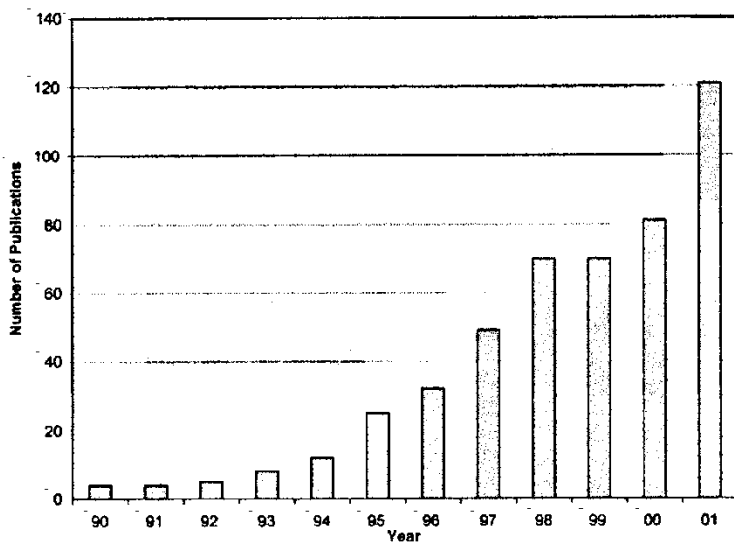


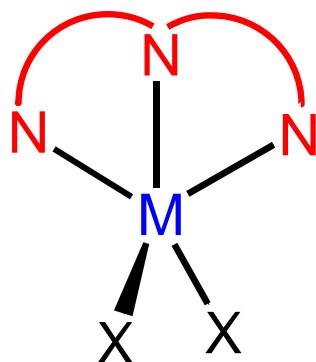
Numero di pubblicazioni sui catalizzatori NON metalloceNICI¹



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

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

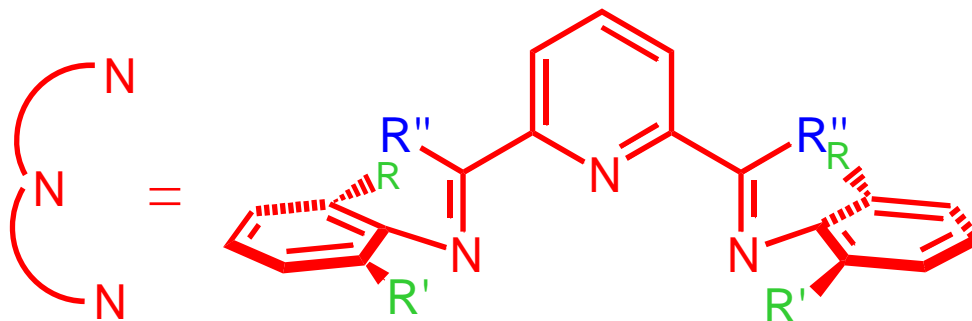
Catalizzatori di Fe(II) e Co(II)



+ MAO

Polietilene lineare ad alta densità

VERSIPOL (Du Pont)



PBI

R = H R' = Ph

Solvente: toluene

T = 25 – 90°C

t = 15 – 180 min.

p = 14 – 42 atm

R = H R' = C(CH₃)₃

R = R' = HC(CH₃)₂

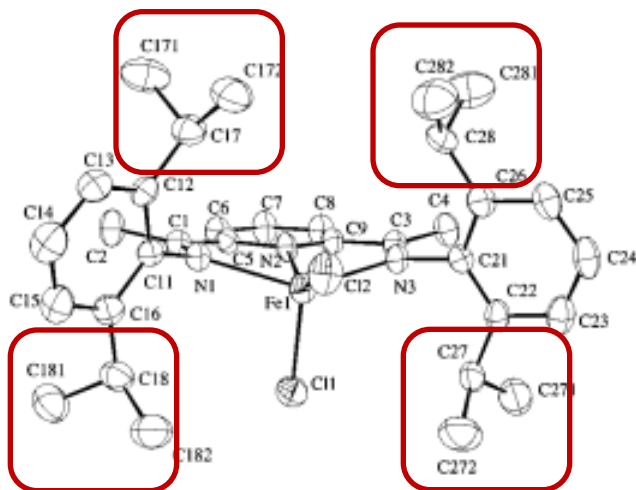
M. Brookhart et al. *J. Am. Chem. Soc.* **1998**, *120*, 4049.

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

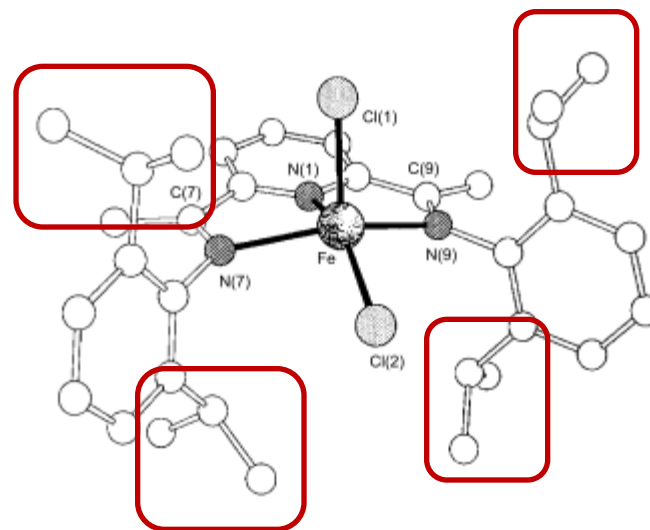
S. D. Ittel, L.K. Johnson, M. Brookhart *Chem. Rev.* **2000**, *100*, 1169.

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.: $[MCl_2((2,6-i-PrPh)_2PBIH_2)]$

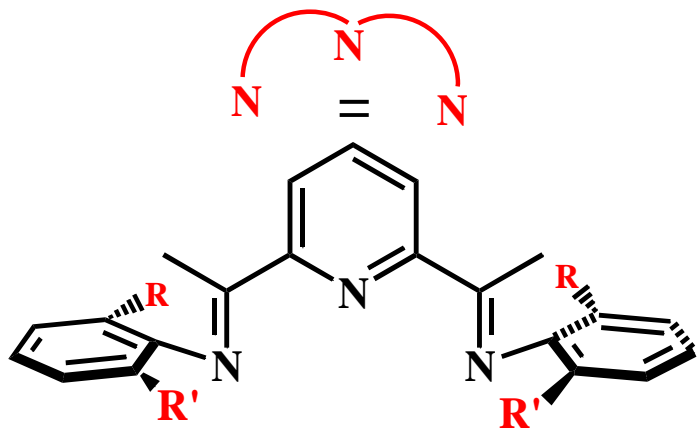
M	P _{etilene} (atm)	kg PE/g M h
Co	7	140
	41	140
Fe	7	1860
	41	4220
	340	11900

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)]

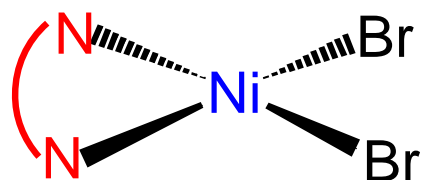


PBI	M _w
(2-PhPh) ₂ PBIME ₂	α-olefine
(2- <i>t</i> -BuPh) ₂ PBIME ₂	31 000
(2,6- <i>i</i> -PrPh) ₂ PBIME ₂	46 000
(2,6- <i>i</i> -PrPh) ₂ PBIH ₂	18 000

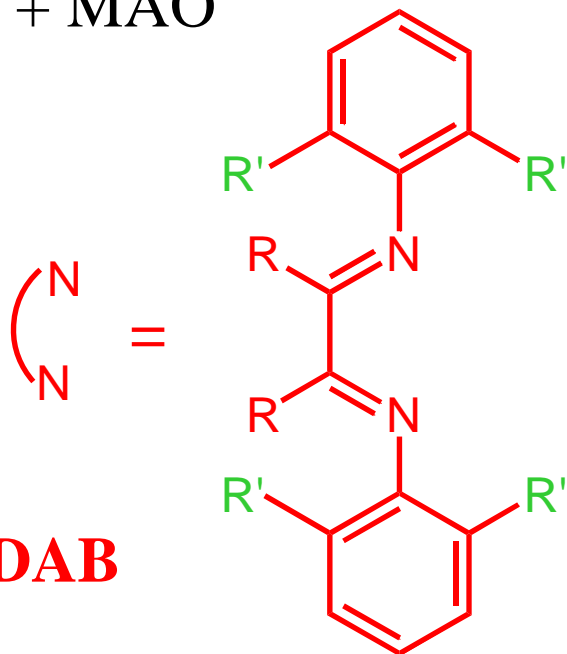
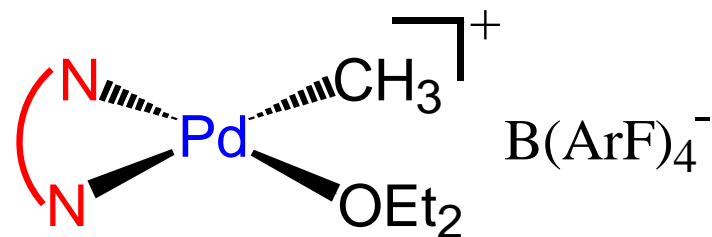
¹S. D. Ittel et al., *Chem. Rev.* **2000**, *100*, 1169.

Leganti bidentati α -diiminici per la sintesi del polietilene

Catalizzatori di Ni(II) e Pd(II)



+ MAO



$R = H, CH_3$

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

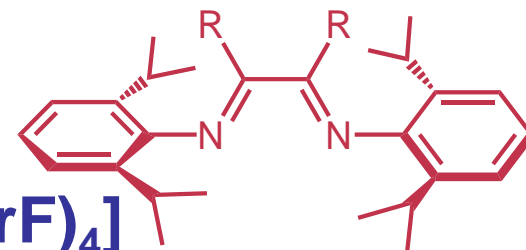
VERSIPOL (Du Pont)

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.: **[PdMe(OEt₂)(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: $n_{\text{cat}} = 100 \mu\text{mol}$, $P = 1.0 \text{ atm}$, $T = 25 \text{ }^\circ\text{C}$.

^aCH₂Cl₂ V = 50 mL, t = 24 h.

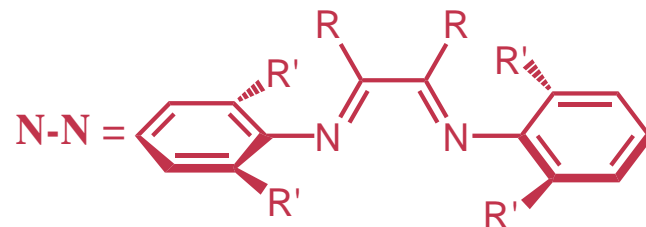
^bCH₂Cl₂ V = 100 mL, t = 17 h.

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)**]

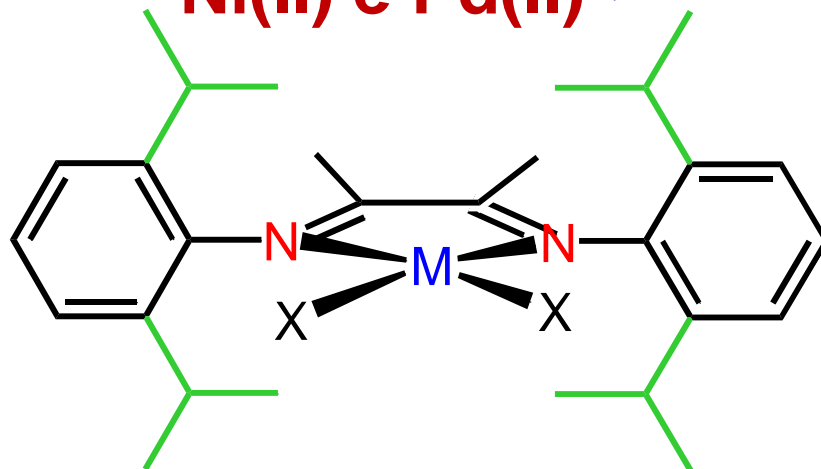


R, R'	mol cat.	t (min)	kg PE/mol Ni h	Mw (Mw/Mn)	Branches
H, i-Pr^a	1.7 x 10⁻⁶	15	1.1 x 10⁴	31000 (2.5)	38
Me, i-Pr	1.6 x 10⁻⁶	15	0.3 x 10⁴	520000 (1.6)	48
H, Me	17 x 10⁻⁶	30	0.04 x 10⁴	43000 (2.5)	1.2
Me, Me	17 x 10⁻⁶	10	0.17 x 10⁴	170000 (2.6)	20
BIAN, i-Pr^b	0.83 x 10⁻⁶	30	0.51 x 10⁴	610000 (2.3)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

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

$M_w = \text{oligomeri} - 85\ 000$

PE lineare e ramificato

M = Pd

Solvente: CH_2Cl_2

27 kg PE/mol Pd h

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

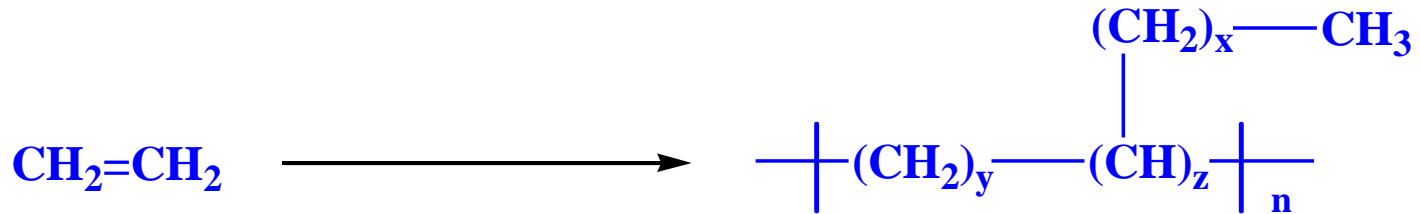
$M_w = 112\ 000 - 1\ 000\ 000$

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	{	C1	37
115 ramificazioni ogni		C2	25
1000 gruppi CH ₂ inseriti		C3	3
		C4	12
		C5	1
		C6+	37

Polymerization Mechanism

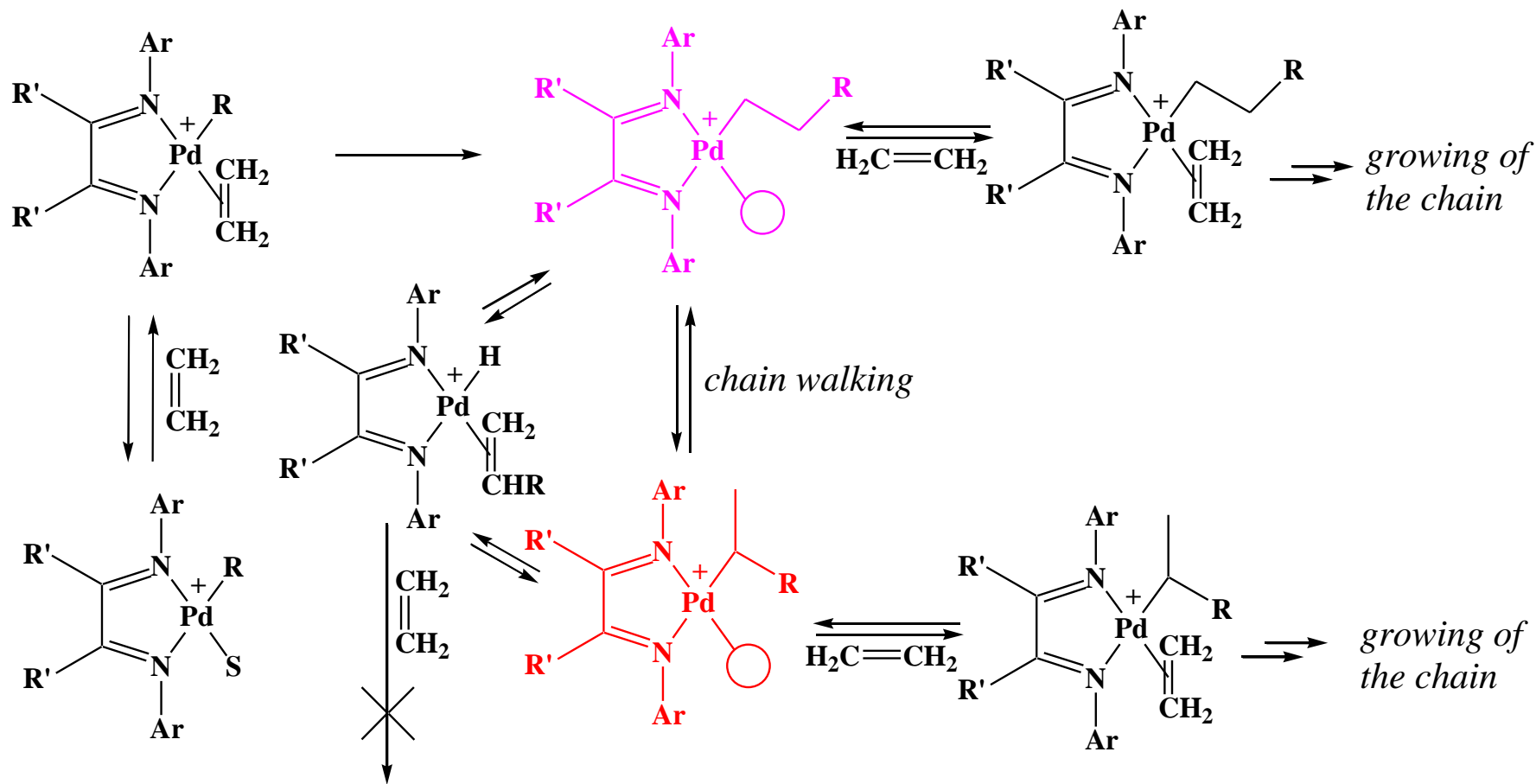
NMR spectroscopy was fundamental to unravel the mechanism of the polymerization. Key intermediates were detected and kinetic investigations were performed, thus:

- 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.

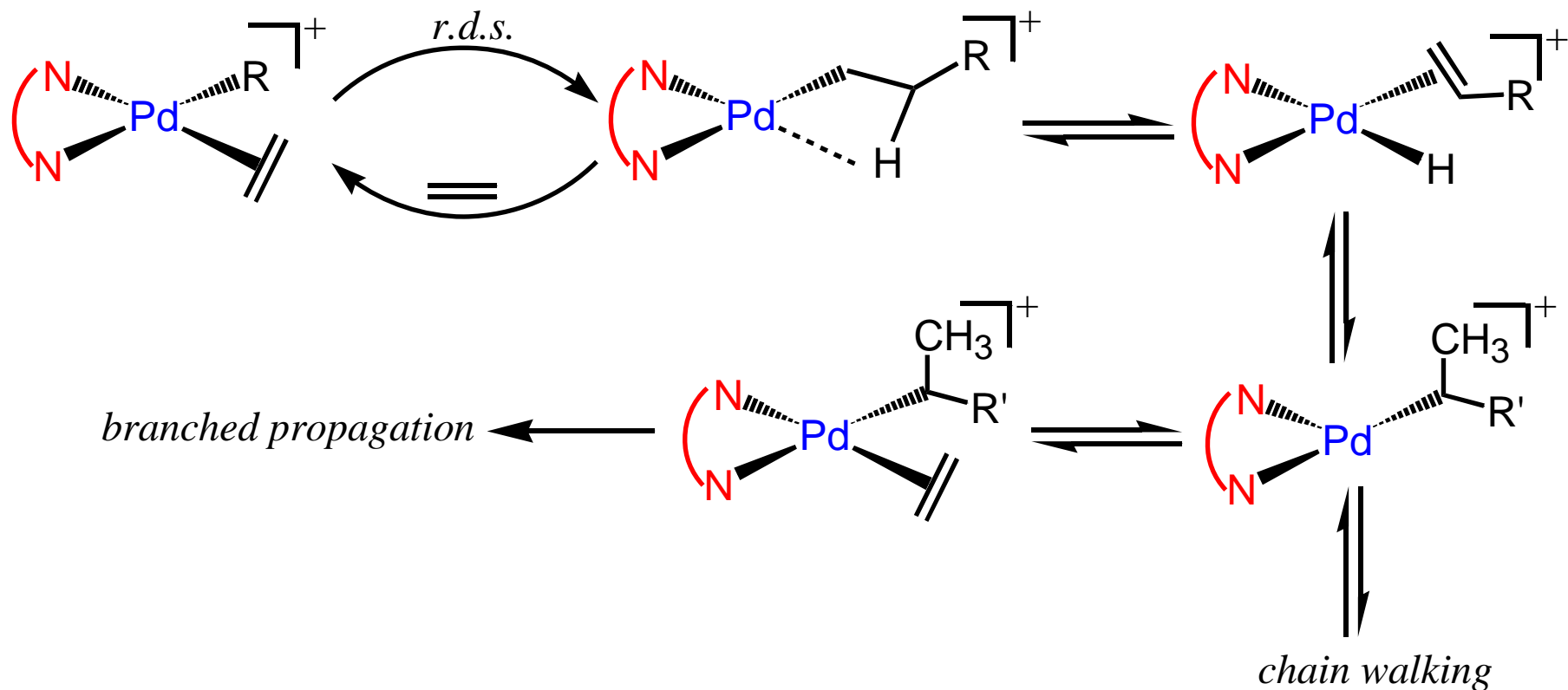
Polymerization Mechanism



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

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

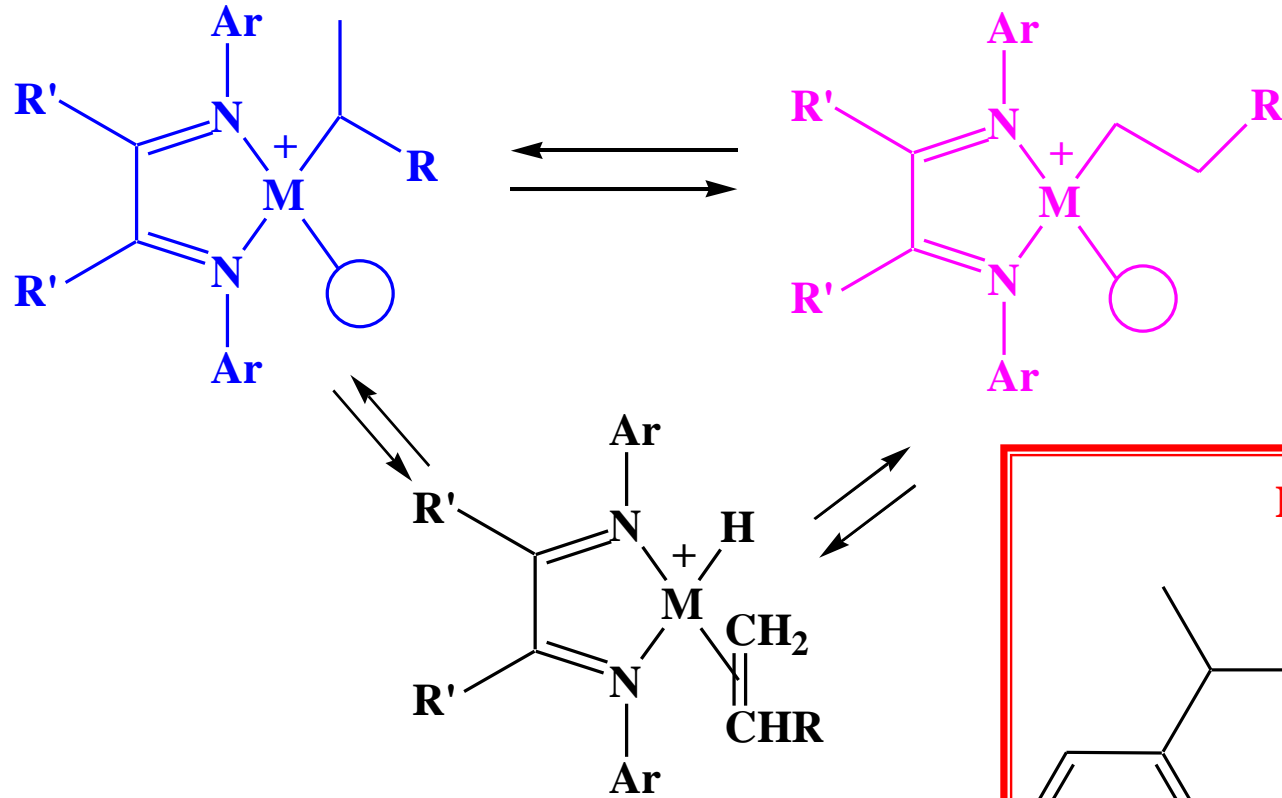
Polymerization Mechanism



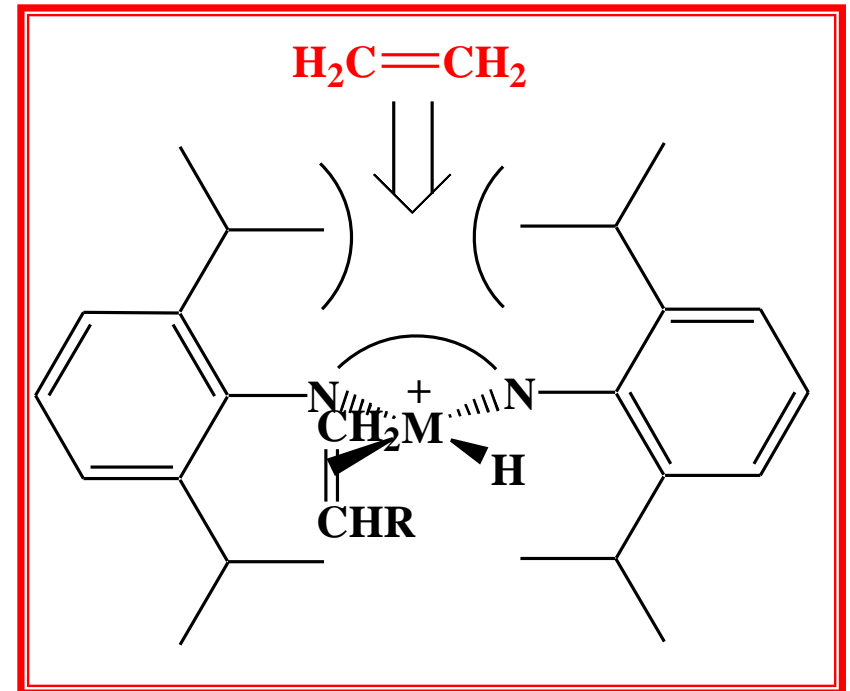
¹M. Brookhart et al., *J. Am. Chem. Soc.* **1995**, *117*, 6414.

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

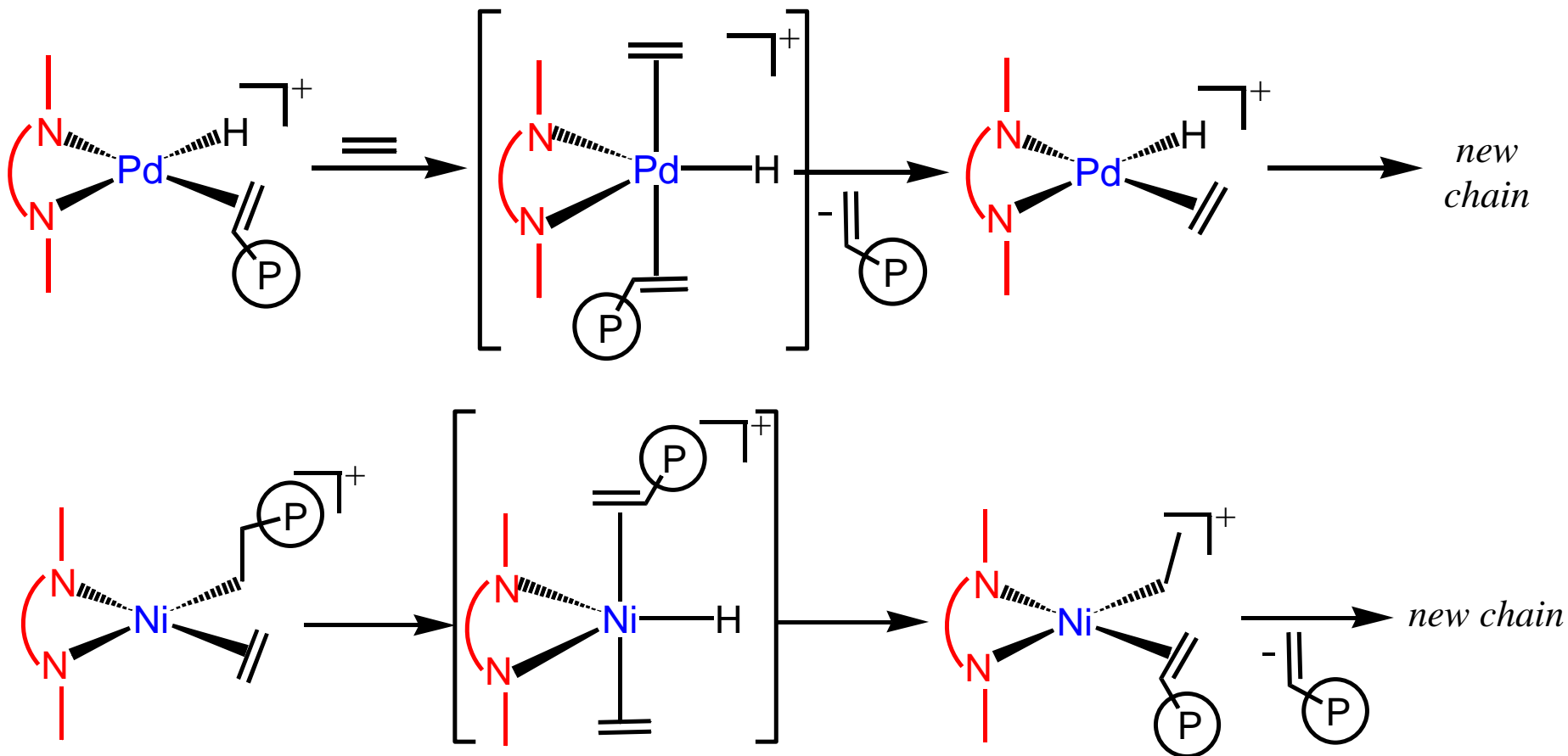
Meccanismo del **trasferimento di catena**



... 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.