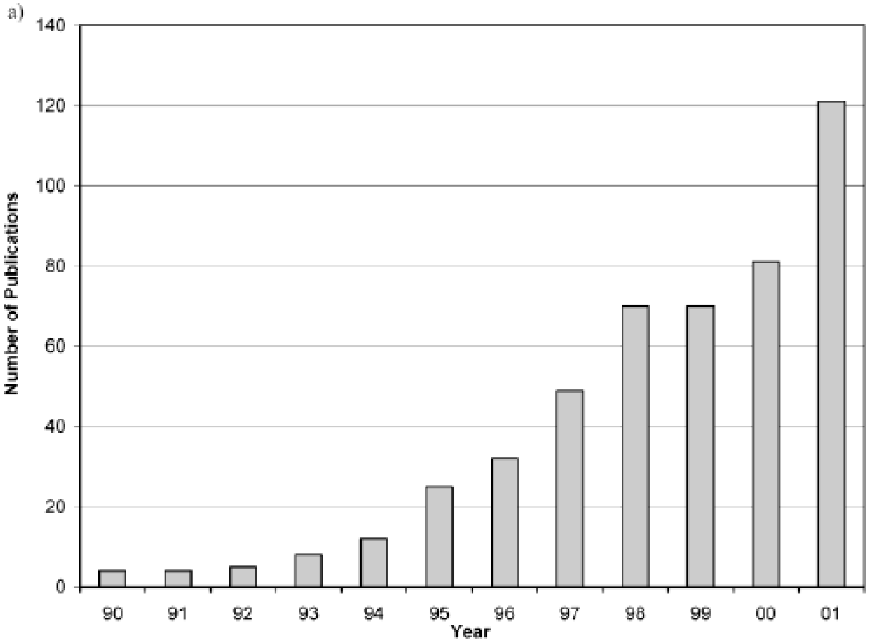
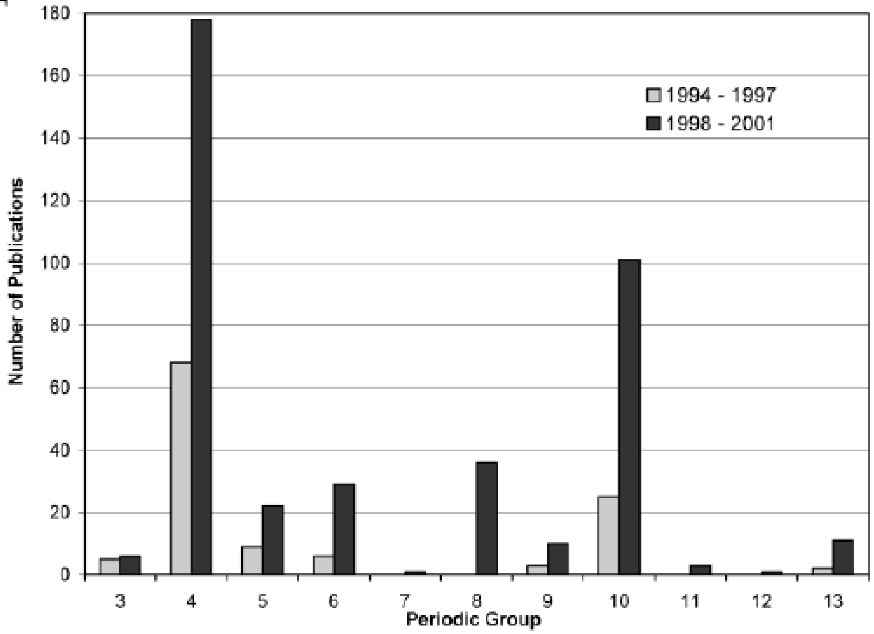
Number of papers about NON metallocenes catalysts[1]

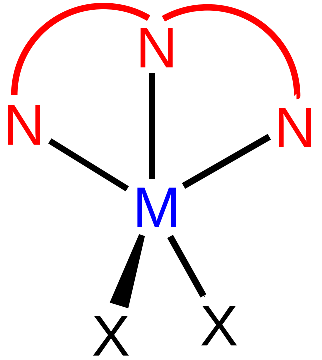




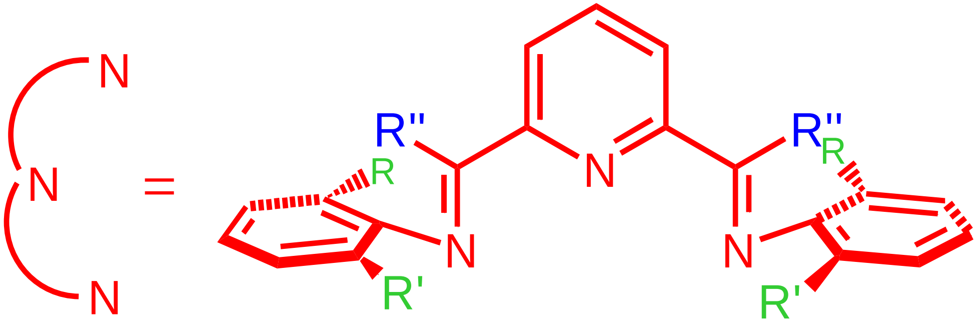
[1] V. Gibson et al., *Chem. Rev.* **2003**, *103*, 283.

Pyridil-bis(immines) tridentate ligands for ethylene polymerization

Catalysts based on Fe(II) or Co(II)

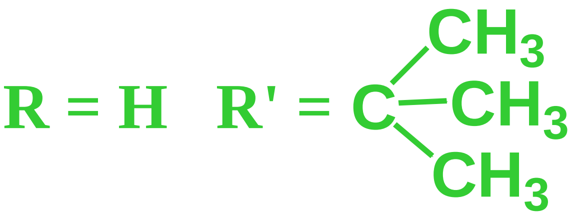


+ MAO

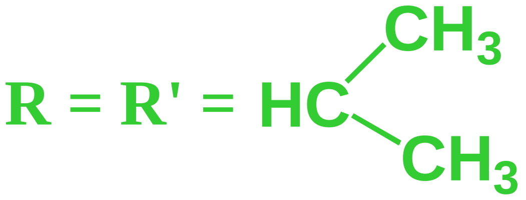


PBI

R = H R' = Ph



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



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

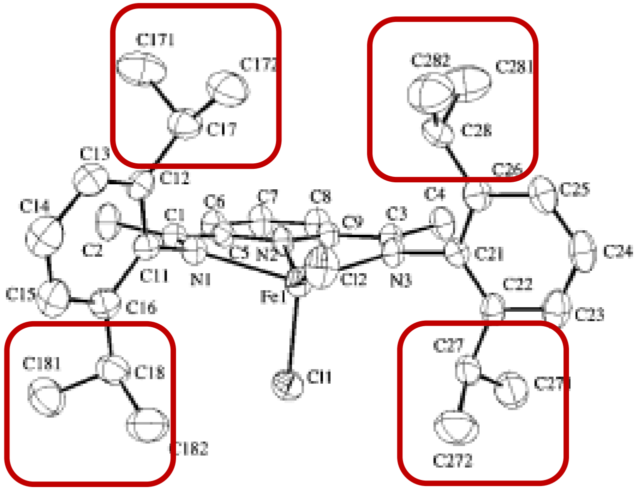
High density linear polyethylene

VERSIPOL (Du Pont)

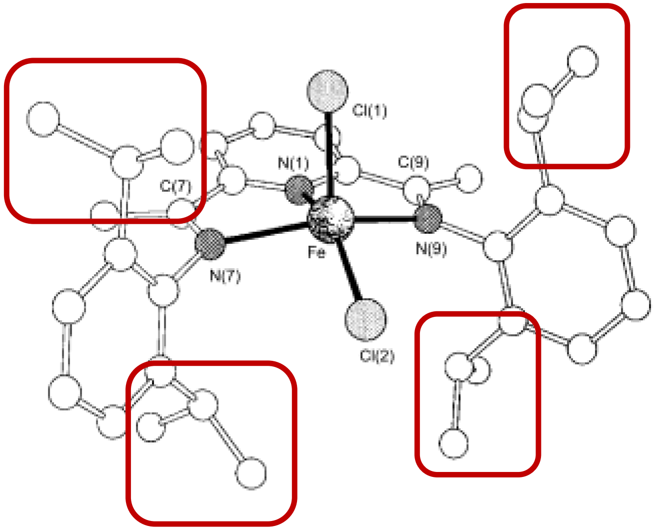
Solvent: toluene
T = 25 – 90°C
t = 15 – 180 min.
p= 14 – 42 atm

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
$[\mathrm{Fe}((2,6\text{-}i\text{-}\mathrm{Pr}\text{-}\mathrm{Ph})_2\mathrm{PBIMe}_2)\mathrm{Cl}_2]$



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.

Features of both complexes:
pseudo-square-pyramidal geometry;
the aryl rings nearly perpendicular to the plane of the pyramid;
metal ion in high-spin;
paramagnetic complexes.

Ethylene polymerization with catalysts based on Fe(II) or Co(II)[1]

Effect of ethylene pressure

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

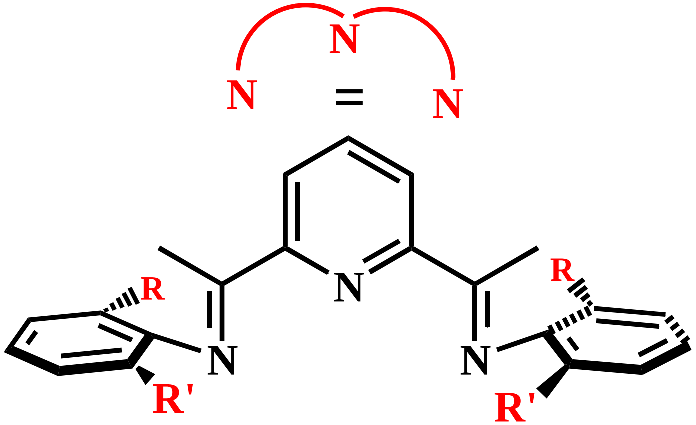
M	$P_{ethylene}$ (atm)	kg PE/g M h
Co	7	140
	41	140
Fe	7	1860
	41	4220
	340	11900

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

Ethylene polymerization with catalysts based on Fe(II) or Co(II)[1]

Effect of nitrogen-donor ligand

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

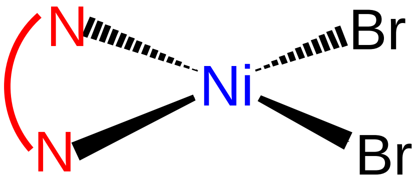


PBI	M_w
$(2\text{-PhPh})_2PBIMe_2$	α-olefin
$(2\text{-}t\text{-BuPh})_2PBIMe_2$	31 000
$(2,6\text{-}i\text{-PrPh})_2PBIMe_2$	46 000
$(2,6\text{-}i\text{-PrPh})_2PBIH_2$	18 000

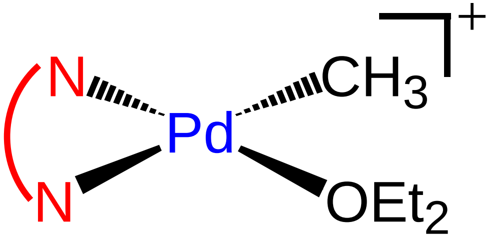
[1] S. D. Ittel et al., *Chem. Rev.* **2000**, *100*, 1169.

α-diimmines bidentate ligands for ethylene polymerization

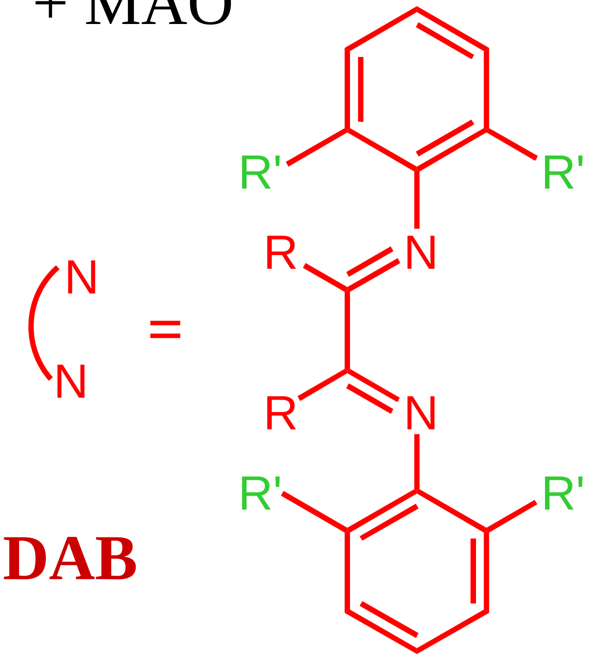
Catalysts based on Ni(II) or Pd(II)



+ MAO



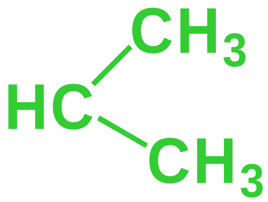
$B(ArF)_4^-$



DAB

$R = H, CH_3$

$R' = H, CH_3,$



$HC(CH_3)_2$

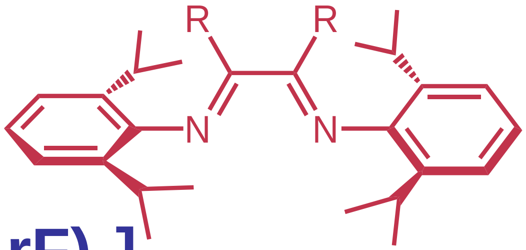
VERSIPOL (Du Pont)

[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)$_4$]

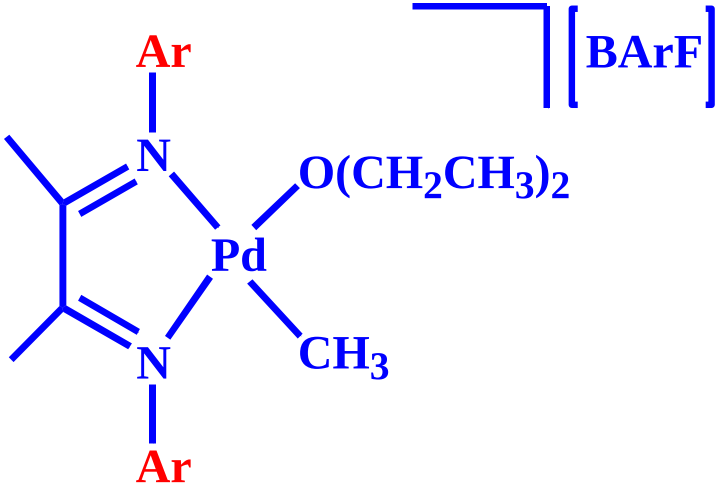
R	Yield (g)	kg PE/mol Pd h	Mw (Mw/Mn)	Branches per 1000 carbons
H[a]	9.07	4.0	600 (3.0)	116
Me[b]	45.3	26.6	29000 (3.9)	103

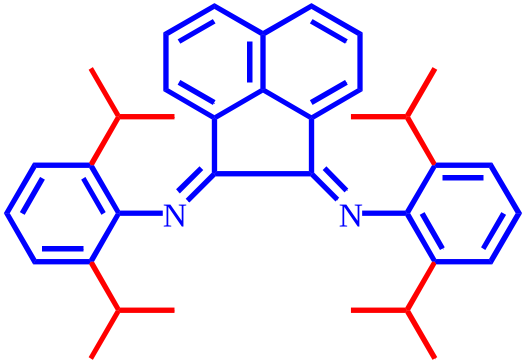
Reaction conditions: n_{cat} = 100 μmol, P = 1.0 atm, T = 25 °C.
[a] CH_2Cl_2 V = 50 mL, t = 24 h.
[b] CH_2Cl_2 V = 100 mL, t = 17 h.

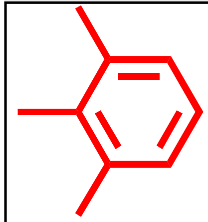
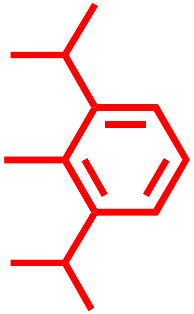
L. K. Johnson, C. M. Killian, M. Brookhart J. Am. Chem. Soc. **1995**, 117, 6414.

α-diimmines bidentate ligands for ethylene polymerization

Catalysts based on Pd(II)





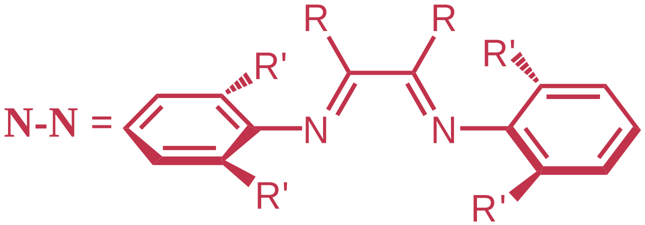
Ar	g PE	Mw (Mw/Mn)
	3.7	445000
	13.7	490000

L. K. Johnson, C. M. Killian, M. Brookhart *J. Am. Chem. Soc.* **1995**, *117*, 6414.
L. K. Johnson, S. Mecking, M. Brookhart *J. Am. Chem. Soc.* **1996**, *118*, 267.

Ethylene polymerization with Ni(II) catalysts

Effect of precatalyst

Cat. Prec.: [NiBr$_2$(N-N)]

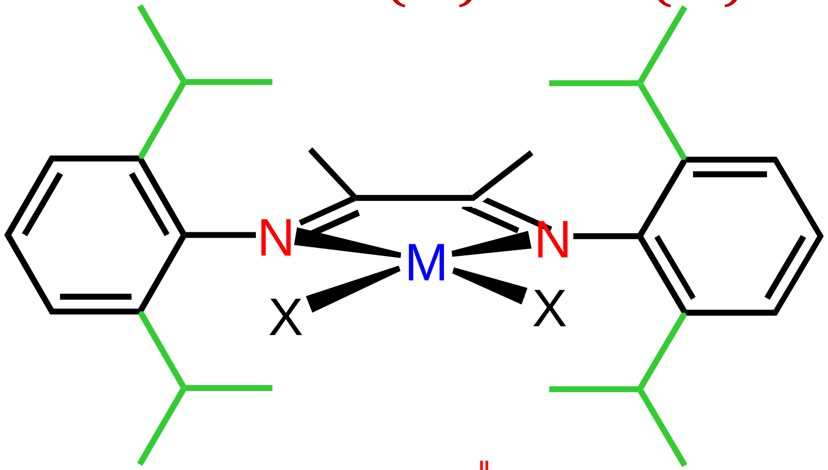


R, R'	mol cat.	t (min)	kg PE/mol Ni h	Mw (Mw/Mn)	Branches
H, i-Pr[a]	1.7 x 10^{-6}	15	3.9 x10^{5}	31.000 (2.5)	38
H, i-Pr	1.7 x 10^{-6}	15	1.1 x10^{4}	110.000 (2.7)	7.0
Me, i-Pr	1.6 x 10^{-6}	15	0.5 x 10^{4}	520.000 (1.6)	48
H, Me	17 x 10^{-6}	30	0.04 x 10^{4}	43.000 (2.5)	1.2
Me, Me	17 x 10^{-6}	10	0.17 x 10^{4}	170.000 (2.6)	20
BIAN, i-Pr[b]	0.83 x 10^{-6}	30	0.51 x10^{4}	170.000 (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!

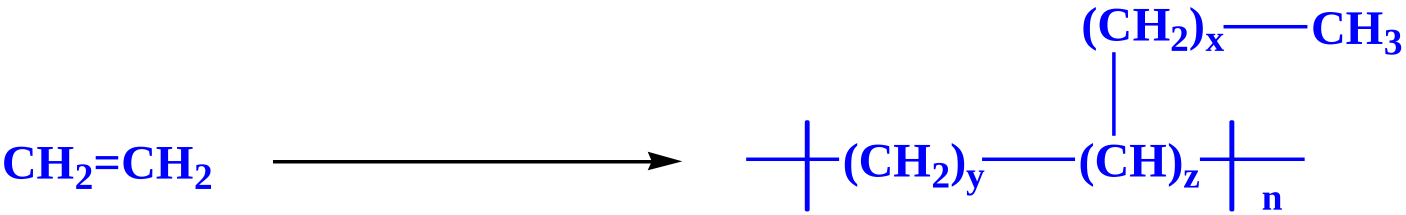
Ethylene polymerization with catalysts based on Ni(II) or Pd(II)[1,2]



M = Ni	**M = Pd**
Activator: MAO	Activator: NONE
Solvent: toluene	Solvent: CH_2Cl_2
11 000 kg PE/mol Ni h	27 kg PE/mol Pd h
M_w = oligomers – 500 000	M_w = 112 000 – 1 000 000
linear and moderatly branched PE	Highly branched PE
Insertion: $\Delta G^\ddagger$ ca. 13 - 14 kcal/mol	Insertion: $\Delta G^\ddagger$ ca. 18 kcal/mol

[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 catalysts based on Ni(II) or Pd(II): ***microstructure*** of the synthesized polyethylene



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

with cat. based on Pd(II) the synthesized PE has 115 branches each 1000 inserted CH_2

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

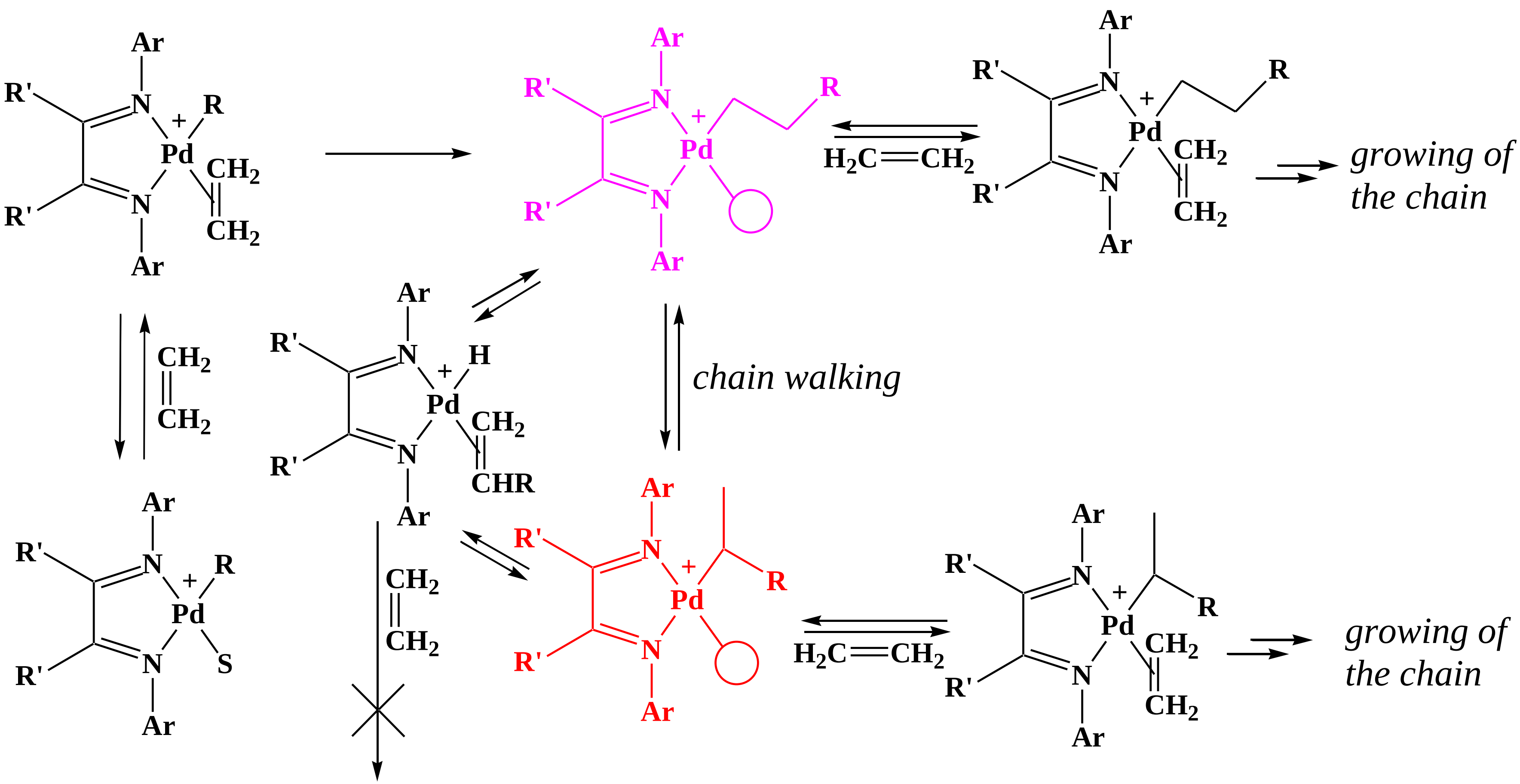
Polymerization Mechanism

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.**

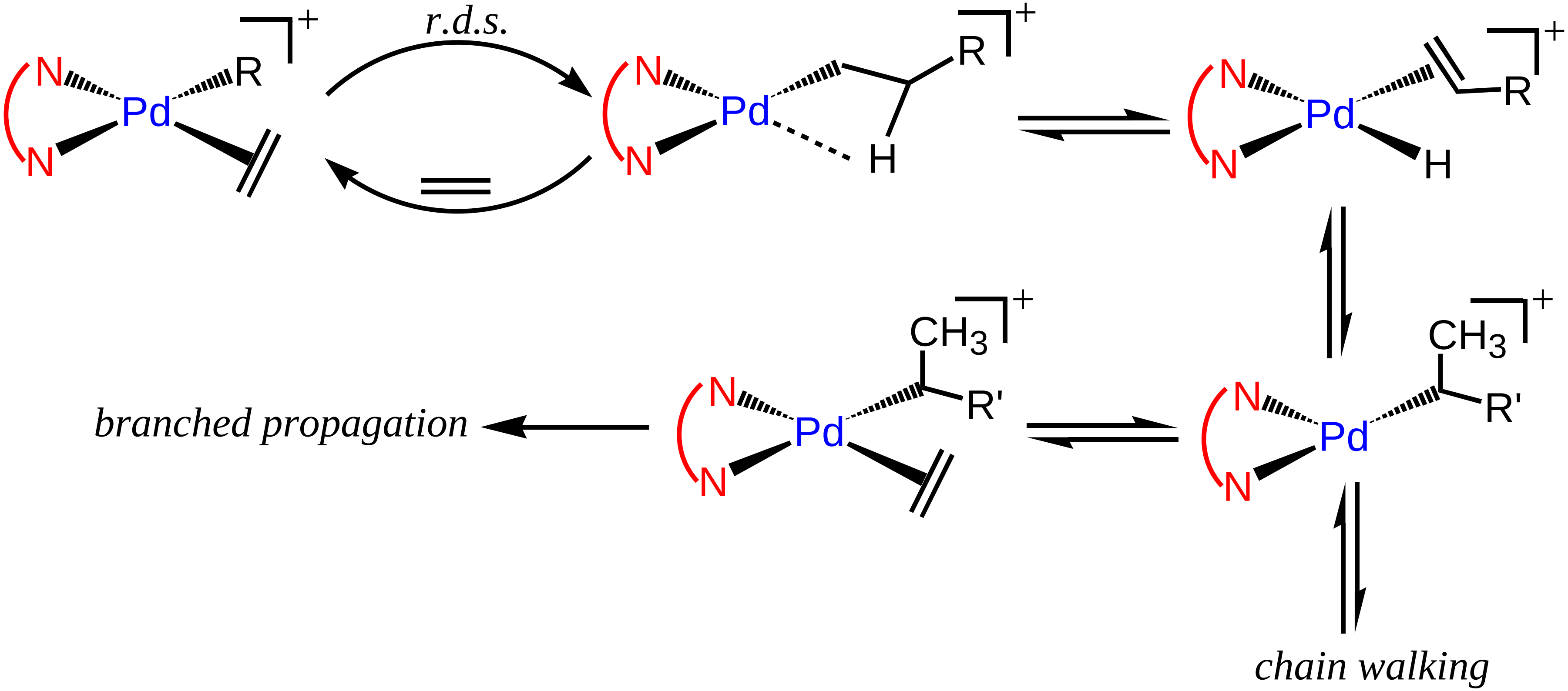
L. K. Johnson, C. M. Killian, M. Brookhart J. Am. Chem. Soc. **1995**, 117, 6414.
S. D. Ittel, L.K. Johnson, M. Brookhart Chem. Rev. **2000**, 100, 1169.

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.

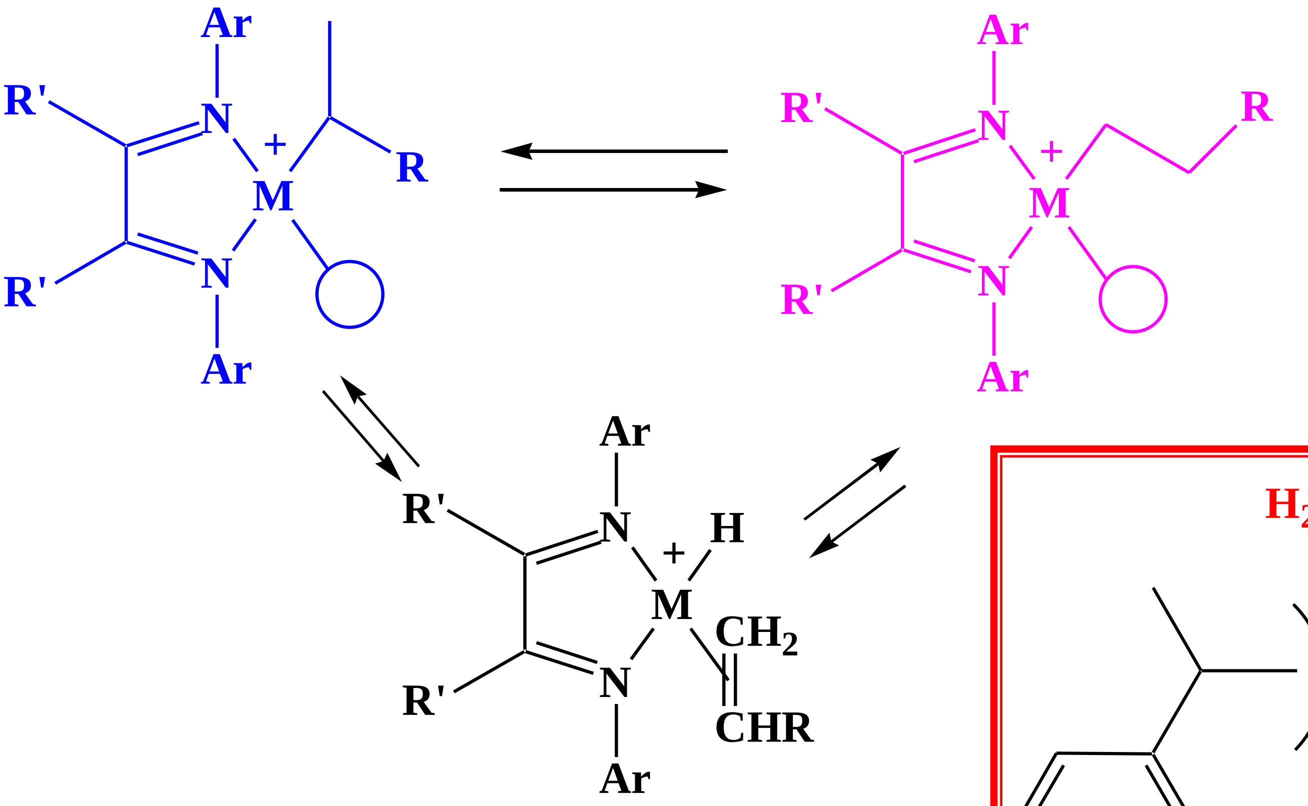
Polymerization Mechanism

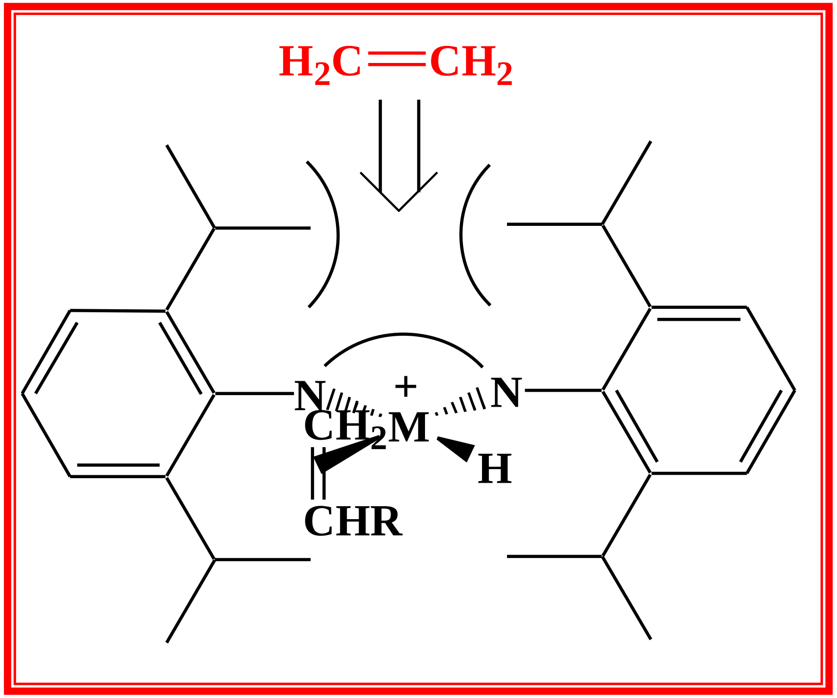


[1] M. Brookhart et al., *J. Am. Chem. Soc.* **1995**, *117*, 6414.

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

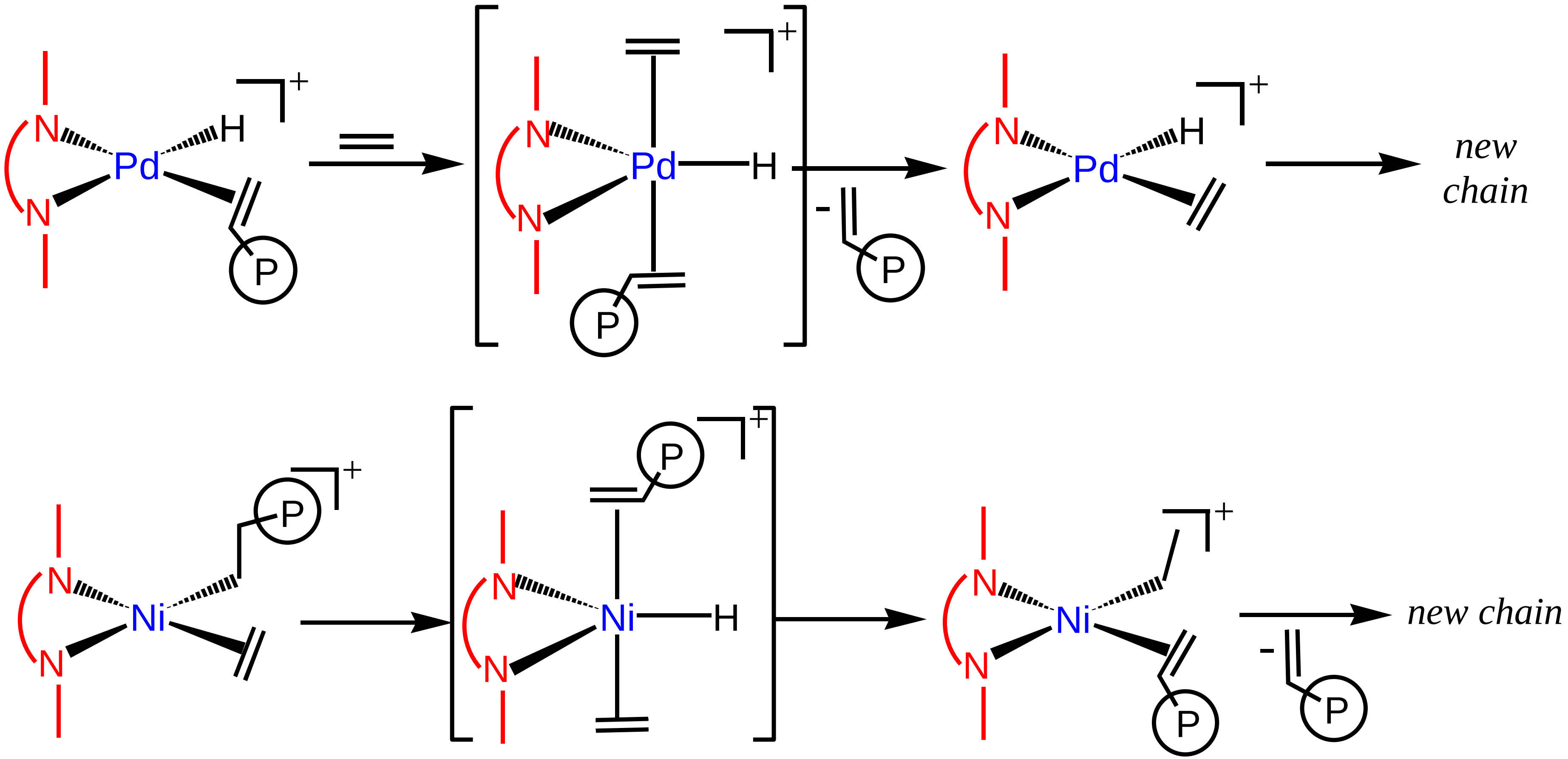
Chain transfer mechanism





... it is ***associative***,
and it is disfavoured by
steric hindrance!

Chain transfer mechanism



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