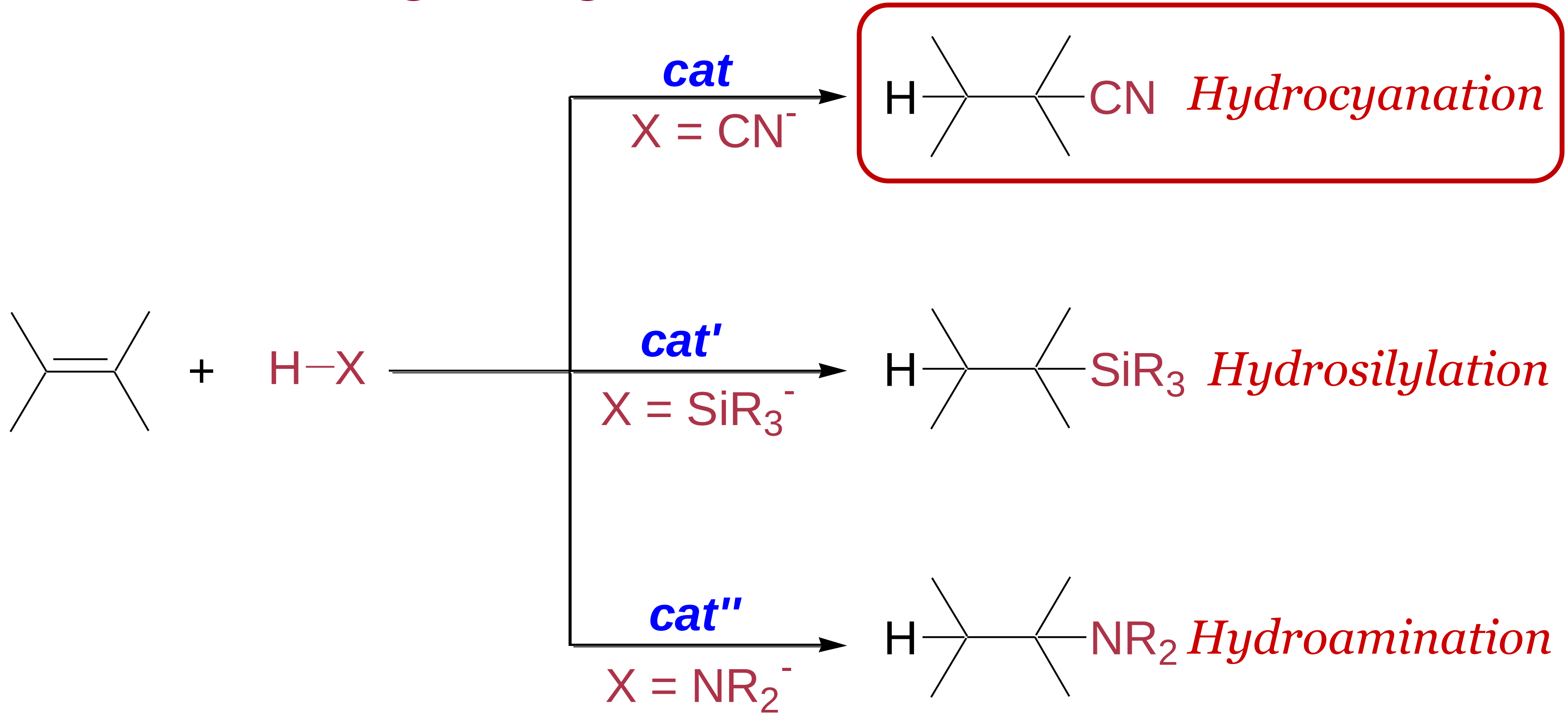
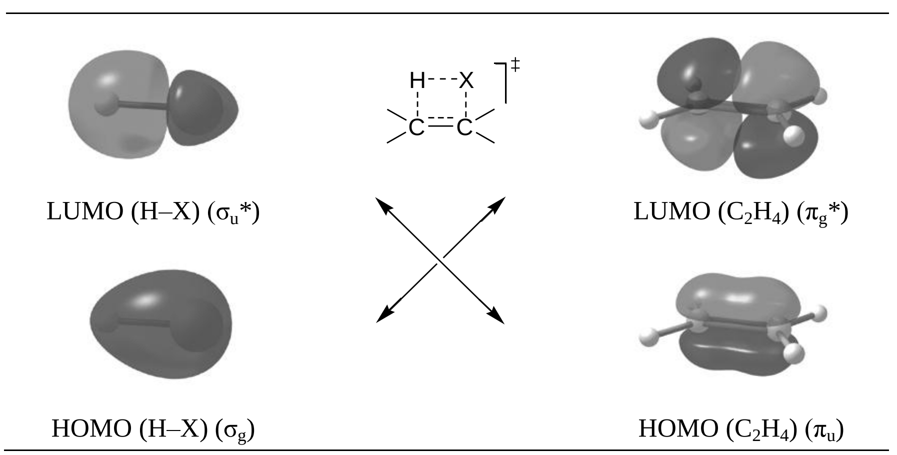
Hydrocyanation reactions

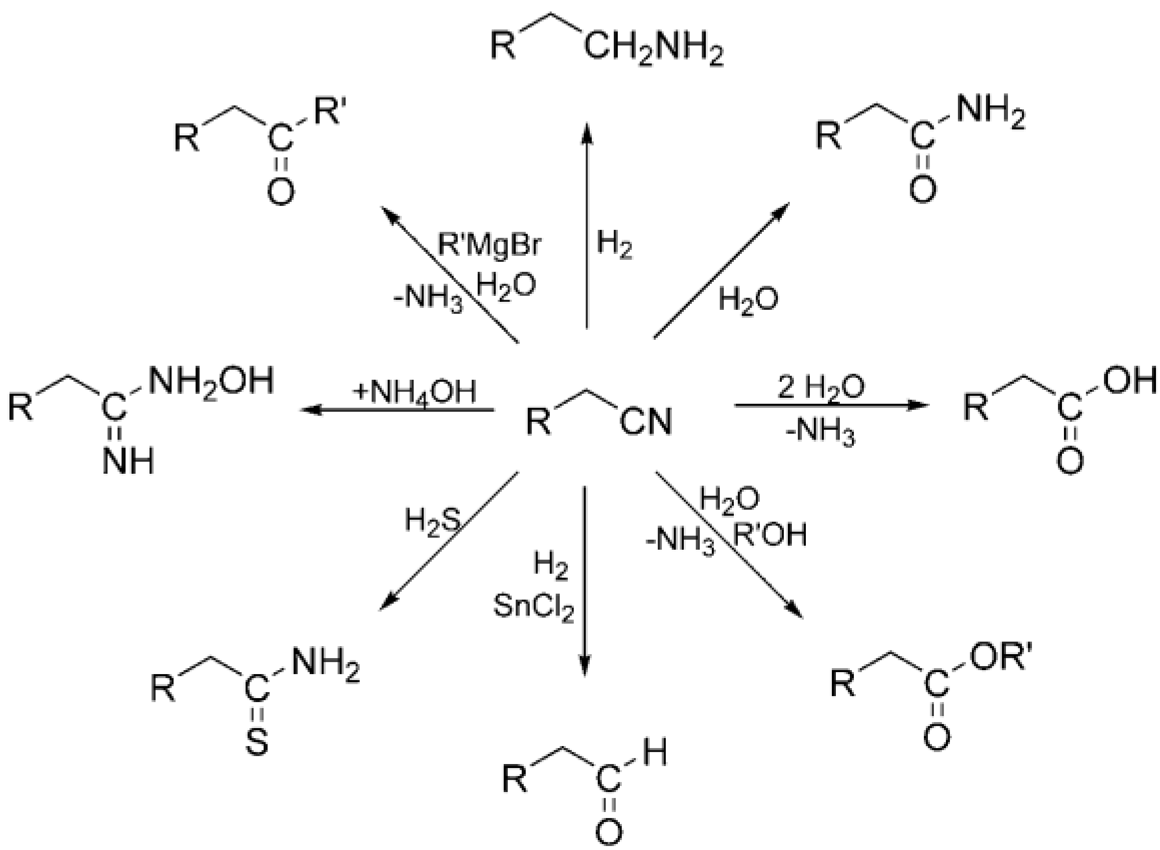


For the synchronous addition of HX to the double bond, the overlap integrals of frontier orbitals are nearly zero, thus a catalyst is required.

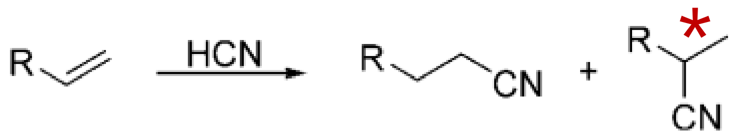


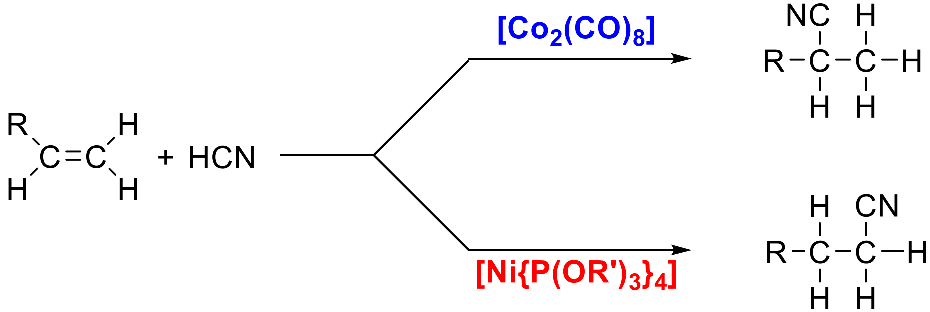
Hydrocyanation reactions

Nitriles are highly versatile compounds, applied in the synthesis of many other compounds.



Regioselectivity of hydrocyanation reactions





Markovnikov

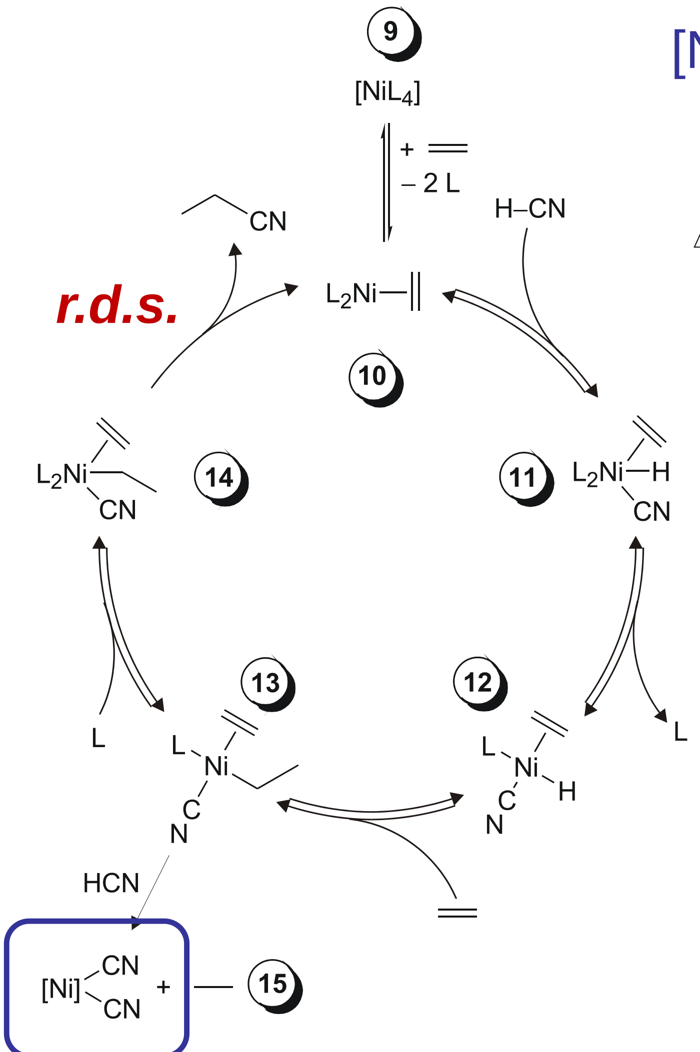
anti-Markovnikov

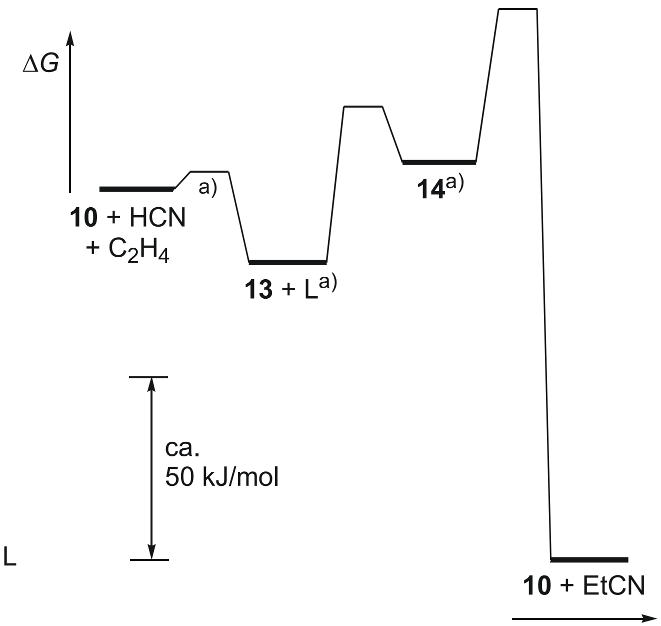
Branched nitriles (chiral) are of interest as fine chemical products; Linear nitriles are of interest as bulk chemical products. The products have a low cost, thus the process has to be highly efficient, therefore the catalyst has to be cheap and to give high yields and high selectivity.

Lewis acids, such as $AlCl_3$, $ZnCl_2$, BPh_3, are required as cocatalysts.

The catalytic cycle

$[NiL_4] = [Ni(P\text{-}(O\text{-}o\text{-}Tol)_3)_4]$

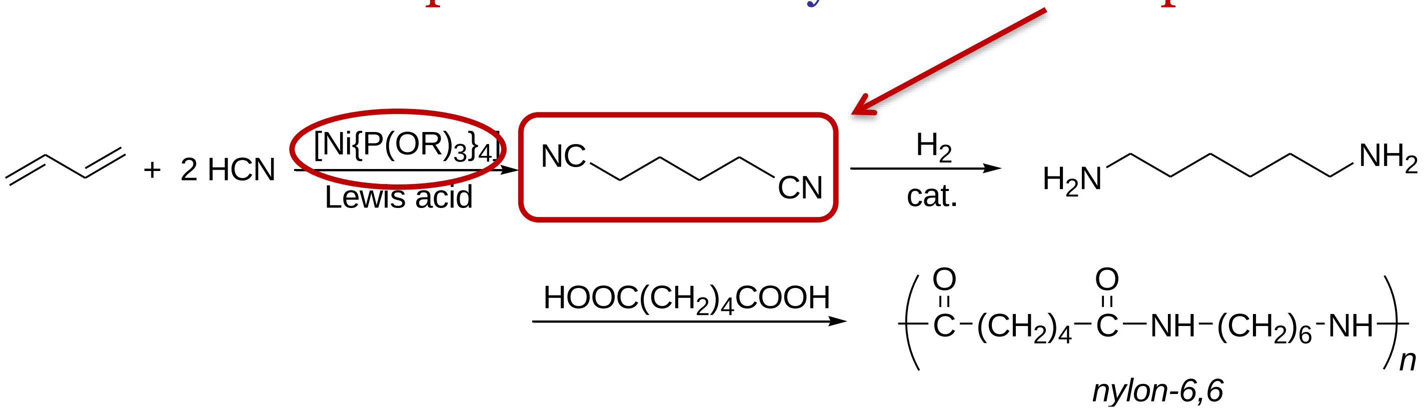




Catalyst deactivation

Hydrocyanation reactions

The DuPont process for the synthesis of adiponitrile



Industrial interest:

Process developped in 1960;

Worldwide production: 1 milion of metric tons per year.

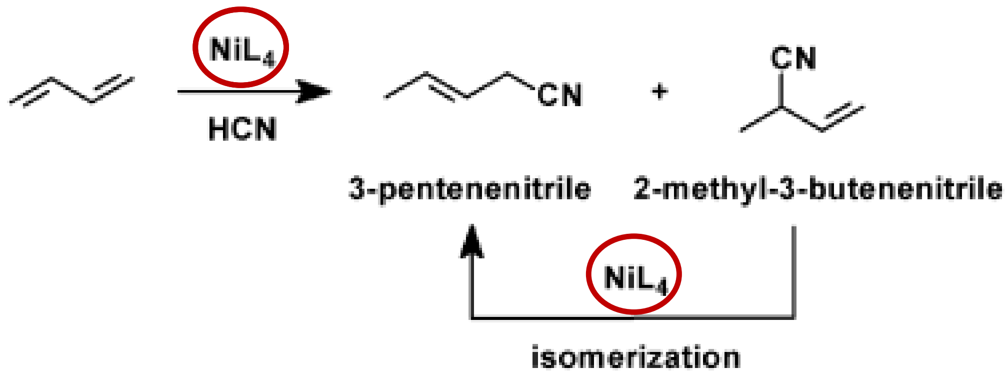
Scientific interest:

Tolman cone-angle θ: steric effects.

Tolman parameter for electronic effects: χ. It is based on the IR frequency for CO stretching in complexes [Ni(CO)$_3$L]; [Ni(CO)$_3$(P-tert-Bu$_3$)] is the reference compound.

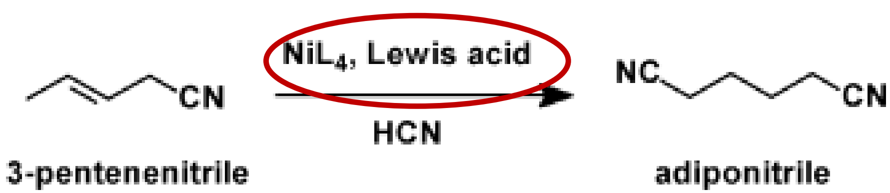
The DuPont process for the synthesis of adiponitrile: a three steps process

1. Hydrocyanation of butadiene to unsaturated mononitrile

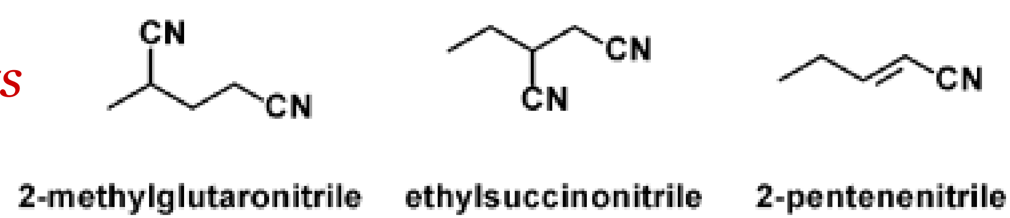


2. Isomerization of branched to linear mononitrile

3. Migration of 3-pentene nitrile to 4-pentene nitrile and its hydrocyanation to adiponitrile



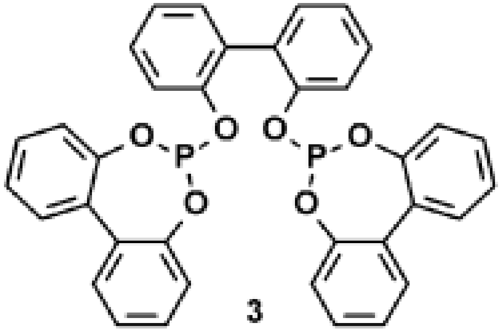
Side products



The DuPont process for the synthesis of adiponitrile: bidentate ligands

Activity higher than that obtained with monodentate ligands;
Possibility to use only 3 eq of ligand in place of 15 eq.;
2-methyl-3-butene nitrile is formed in the range 30 - 88 % with both kinds of ligands.

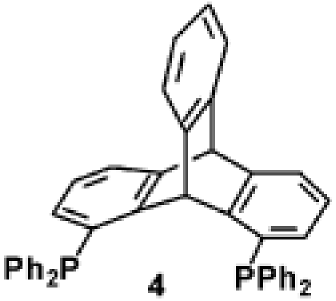
A diphosphite



3

TON = 40 times as high as TON obtained with monophosphites

The diphoshine obtained from tripticene

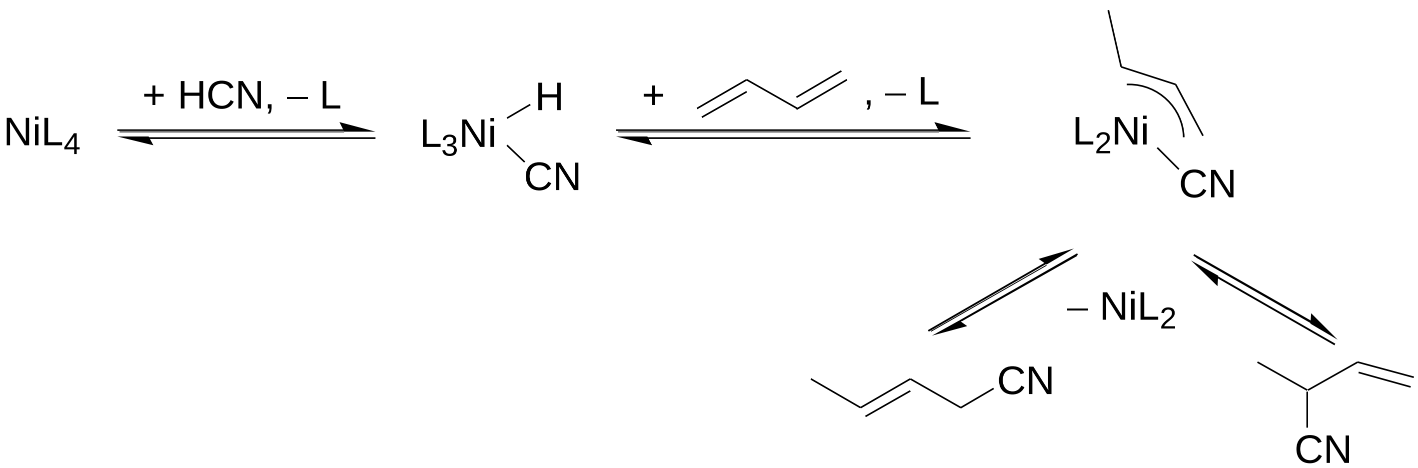


4

100 % conv in 5 h
Selectivity 93.3 % in 3-pentene nitrile

The DuPont process for the synthesis of adiponitrile: the mechanism

1. Hydrocyanation of butadiene to unsaturated mononitrile

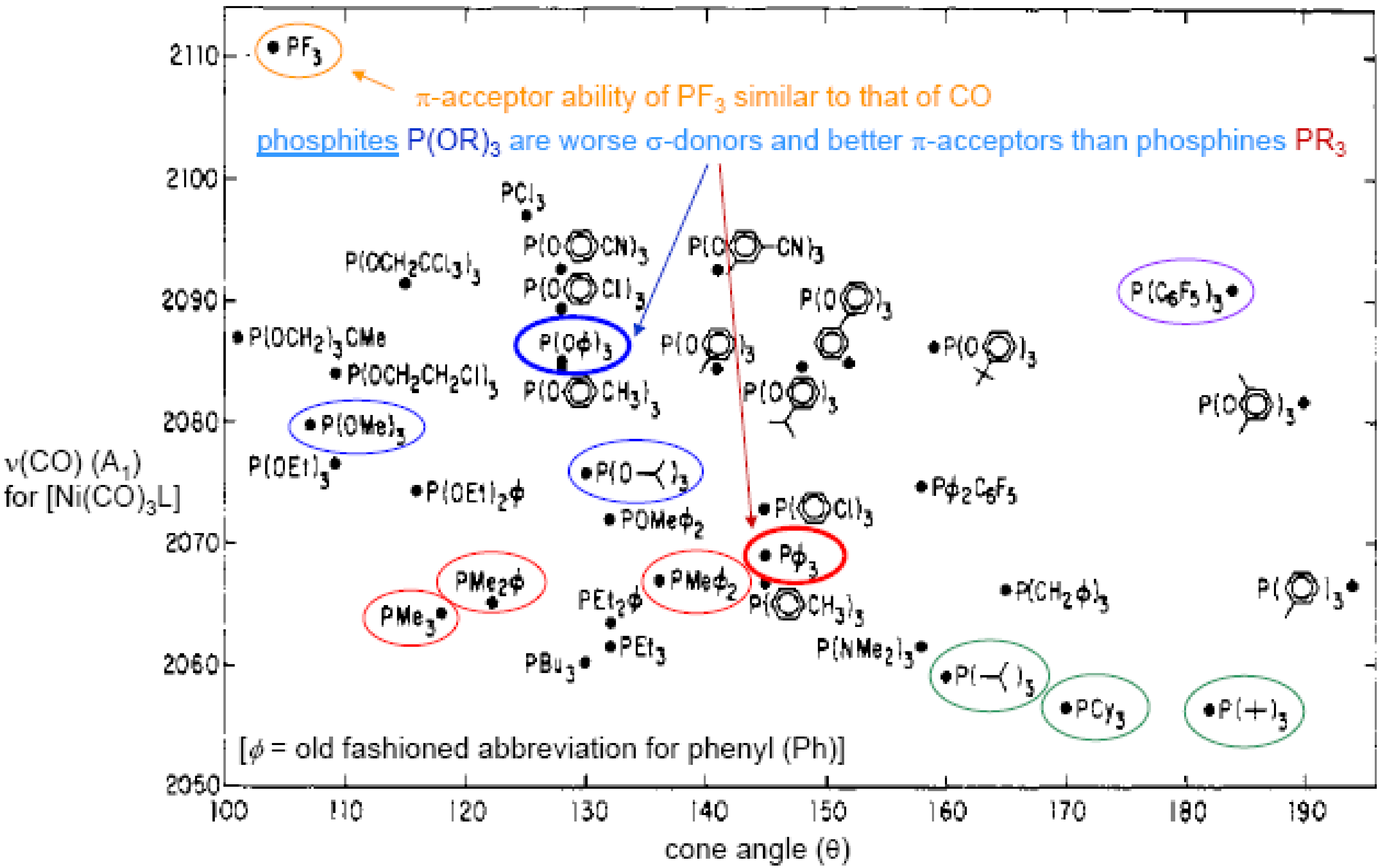


Steric effects   *Studied through [31]P NMR*

$$NiL_4 \overset{k_1}{\rightleftharpoons} NiL_3 + L$$

L	K_1	θ
$P(O\text{-}C_2H_5)_3$	--	109°
$P(O\text{-}p\text{-}C_6H_4CH_3)_3$	X	128°
$P(O\text{-}o\text{-}C_6H_4CH_3)_3$	10^8 X	141°

Steric and electronic map of Tolman parameters

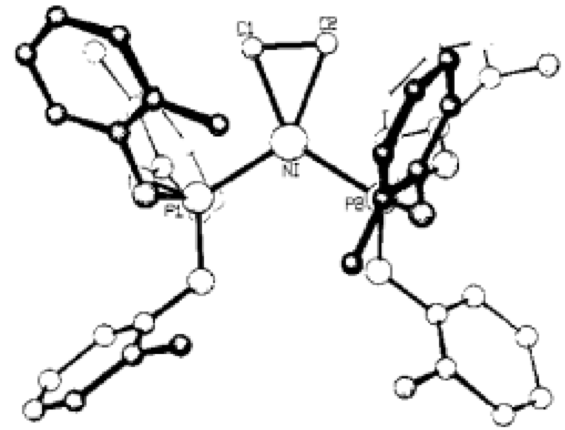


1. Hydrocyanation of butadiene to unsaturated mononitrile

Steric effects

$$\text{olefin} + [NiL_3] \rightleftharpoons [(\text{olefin})NiL_2] + L$$

$L = P(O\text{-}o\text{-}C_6H_4CH_3)_3$



A 16 electron compound

Reaction of the Ni(0) precatalyst with HCN

$$[NiL_4] + HCN \rightleftharpoons [HNiL_4]^+CN^-$$

$$[HNiL_4]^+CN^- \rightleftharpoons [HNiL_3CN] + L$$

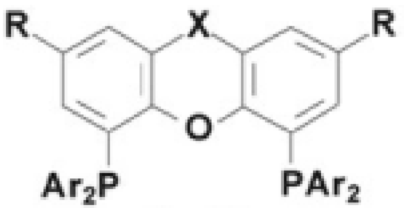
An excess of HCN leads to $[Ni(CN)_2L_2]$, INACTIVE.

Effect of bite angle

	Ligand	X	R	β_n /°
6	DPEphos	H,H	H	105
7	Sixantphos	$SiMe_2$	H	112
8	Thixantphos	S	CH_3	113
9	Xantphos	CMe_2	H	114
10	CF_3-Xantphos*)	CMe_2	H	117
11	DBFphos	bond	H	140

*) Ar = 3,5-$(CF_3)_2C_6H_3$

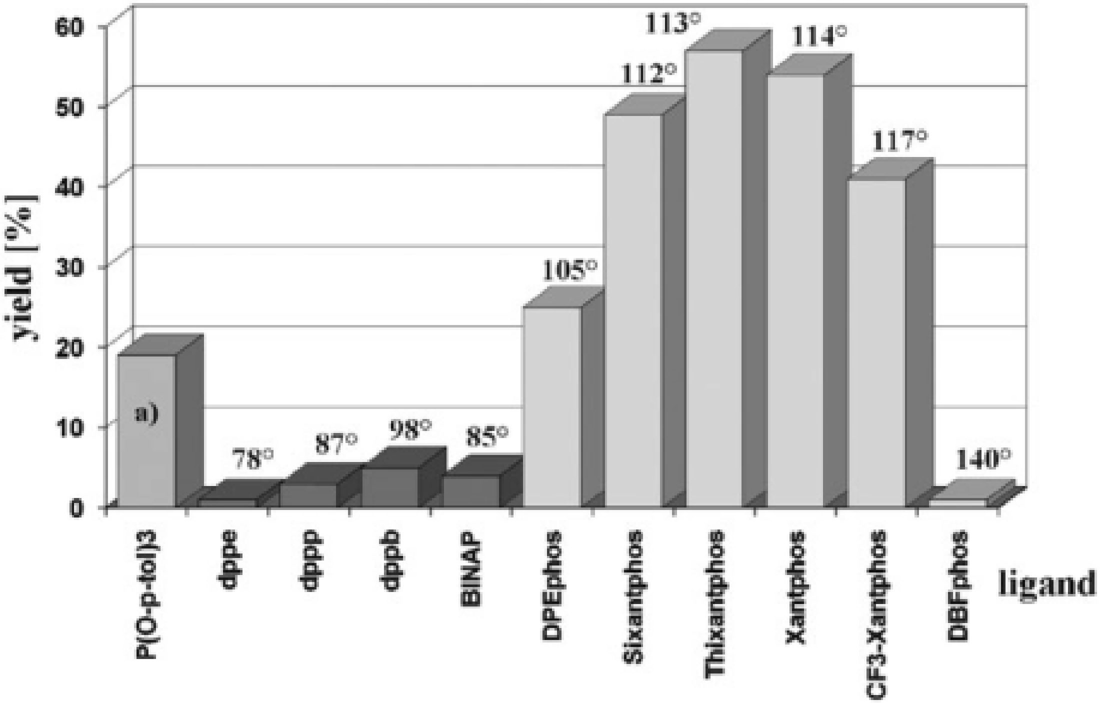
Xantphos ligands



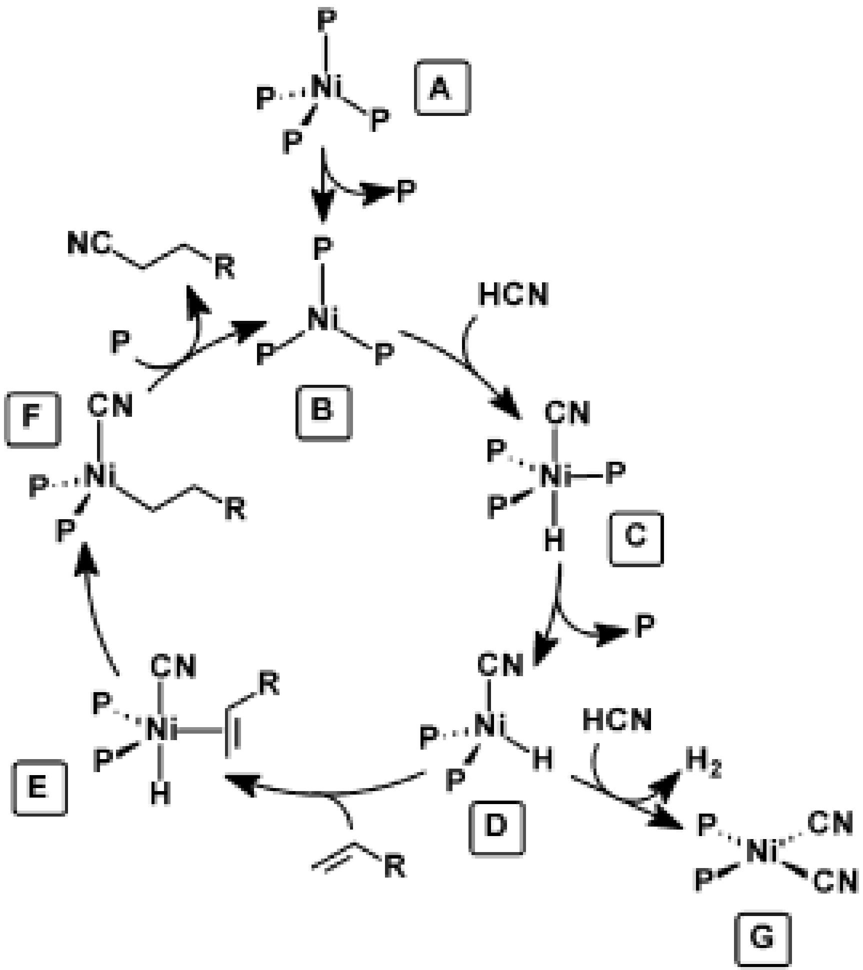
6 - 11

Ar = Ph

Hydrocyanation of styrene



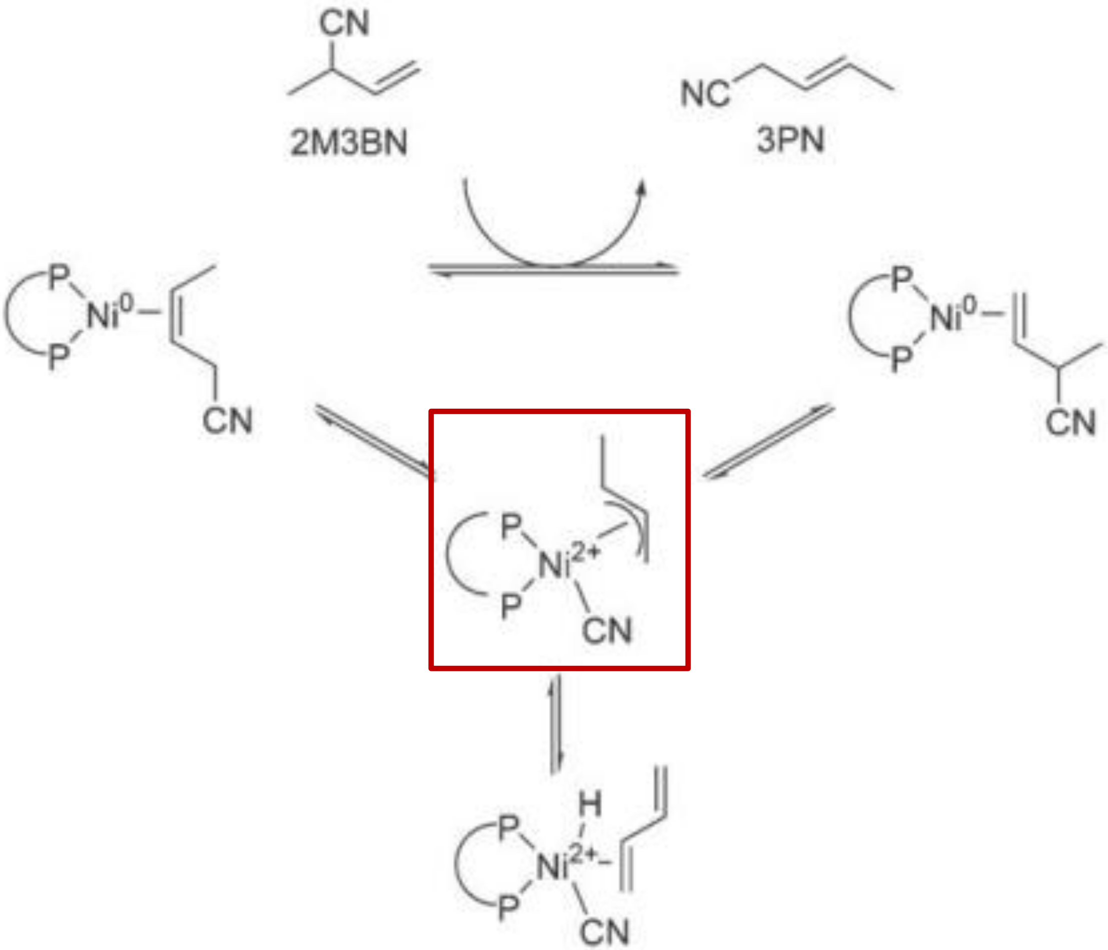
The revisited catalytic cycle



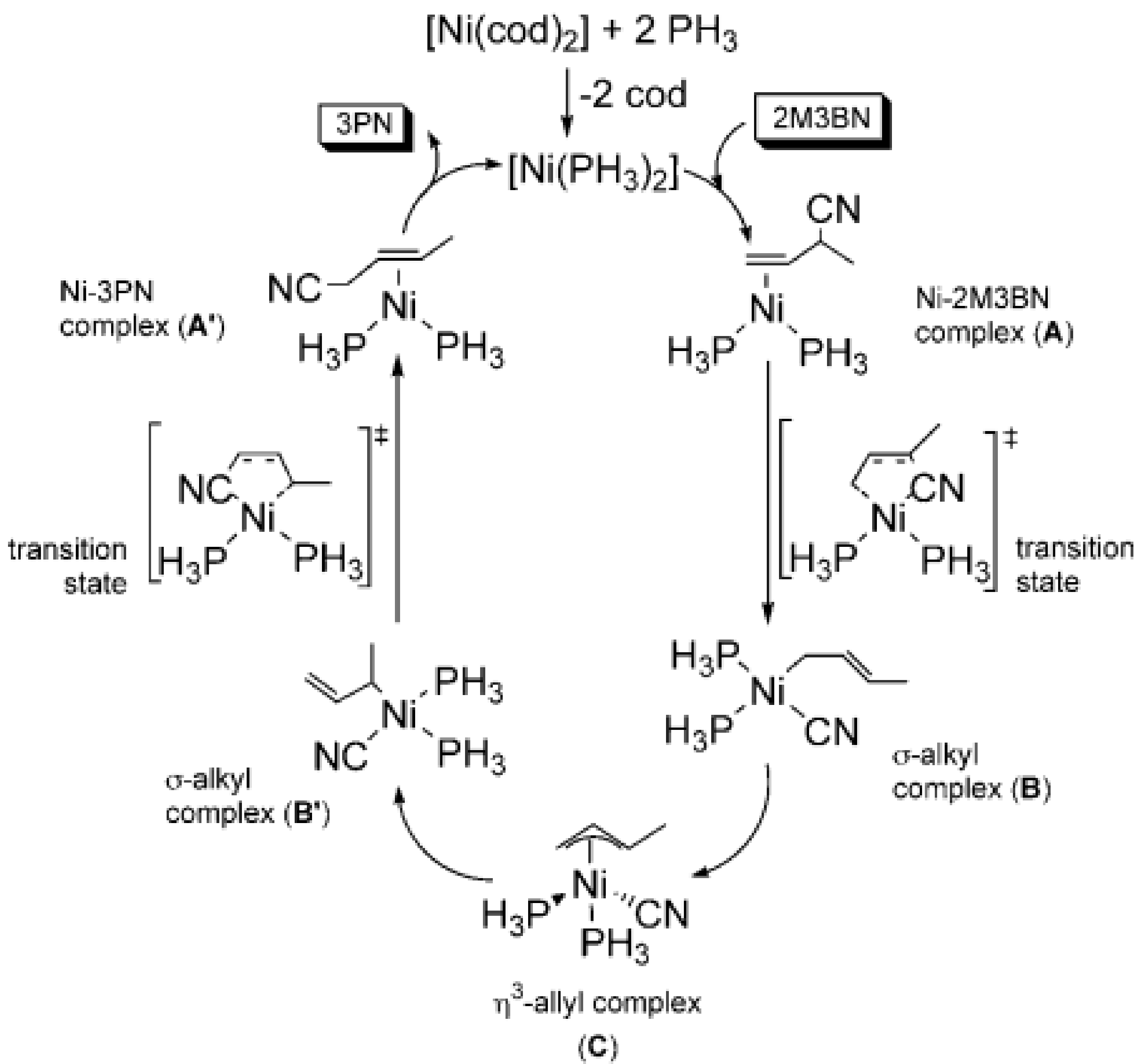
species	structure	angle P - Ni - P
A, D, F	tetrahedral	109°
B	trigonal	120°
C, E	trigonal-bipyr.	120°
G	square-planar	90/180°

The DuPont process for the synthesis of adiponitrile: the mechanism

2. Isomerization of 2-methyl-3-butene nitrile

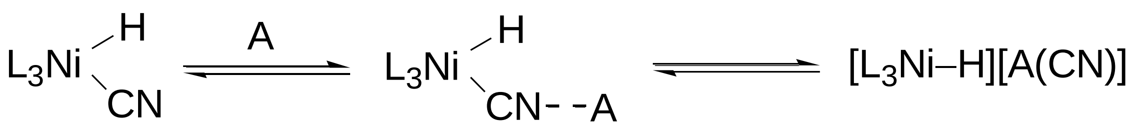


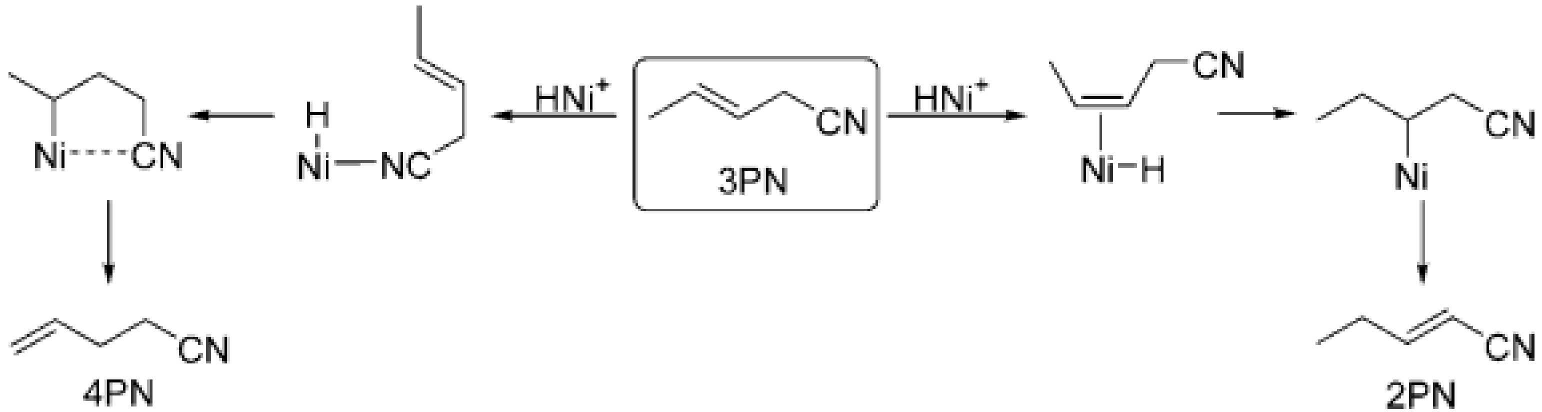
2. Isomerization of 2-methyl-3-butene nitrile: the mechanism



The DuPont process for the synthesis of adiponitrile: the mechanism

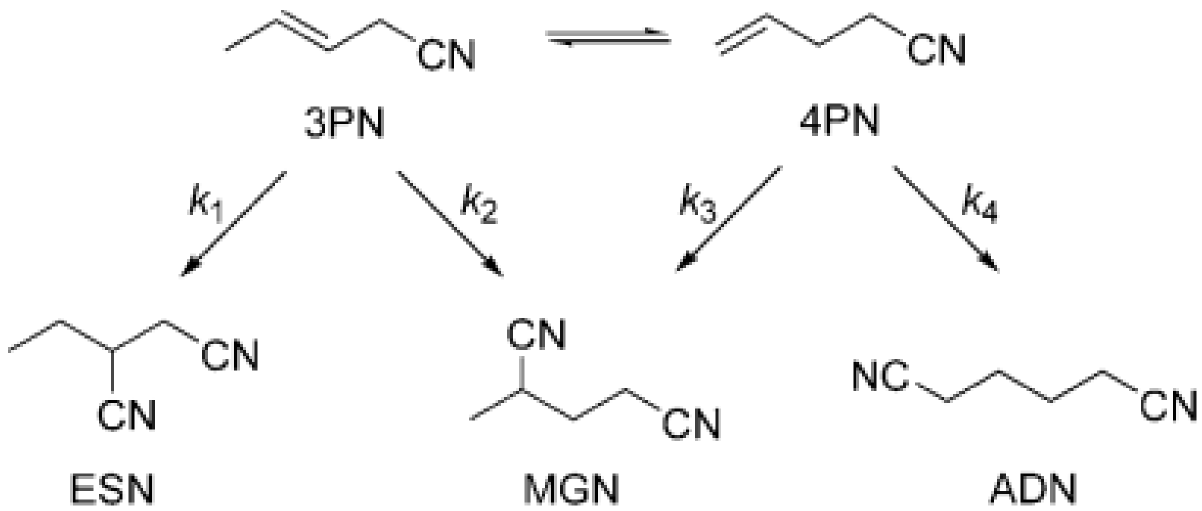
3. *Migration of 3-pentene nitrile to 4-pentene nitrile and its hydrocyanation to adiponitrile*





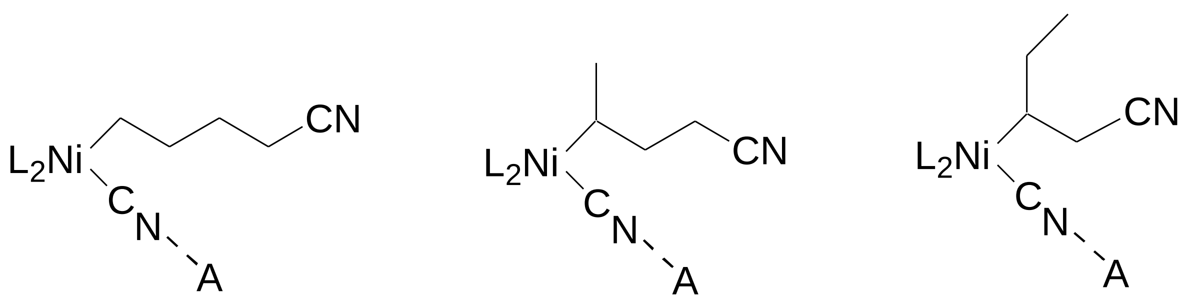
2PN is the most thermodynamically stable linear pentenenitrile;
4PN is the kinetic product.
At T = 50°C the equilibrium composition of the mixture is: 78.3 : 20.1 : 1.5 = 2PN : 3PN : 4PN.

3. *Migration of 3-pentene nitrile to 4-pentene nitrile and its hydrocyanation to adiponitrile*



Selectivity in ADN:

50 % with $AlCl_3$; 82 % with $ZnCl_2$; 91 % with BPh_3.



Gives ADN **Gives MGN** **Gives ESN**