Anorganische Strukturen und Reaktionsmechanismen

CHE.367

Christoph Marschner

Institut für Anorganische Chemie
Technische Universität Graz

Übersicht

- Katalyse
  - Grundlagen
  - Kreislauf
  - Asymmetrische Induktion
- Hydrierung
  - Wilkinson
  - Kationische Rh Komplexe
  - Crabtree
  - Ru Katalyse
  - Hydrierung von Ketonen

Übersicht

- Hydrocyanierung
- Hydrosilylierung
- Hydroborierung
- Hydroaminierung
- Wacker Oxidation

Katalyse

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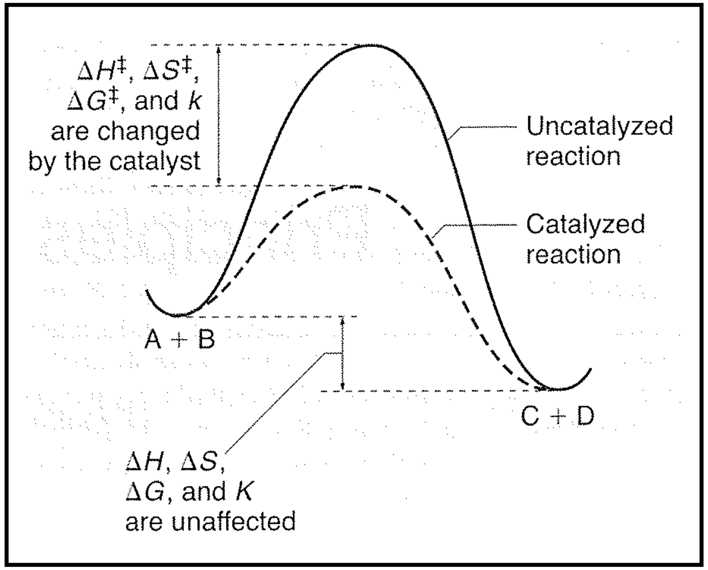
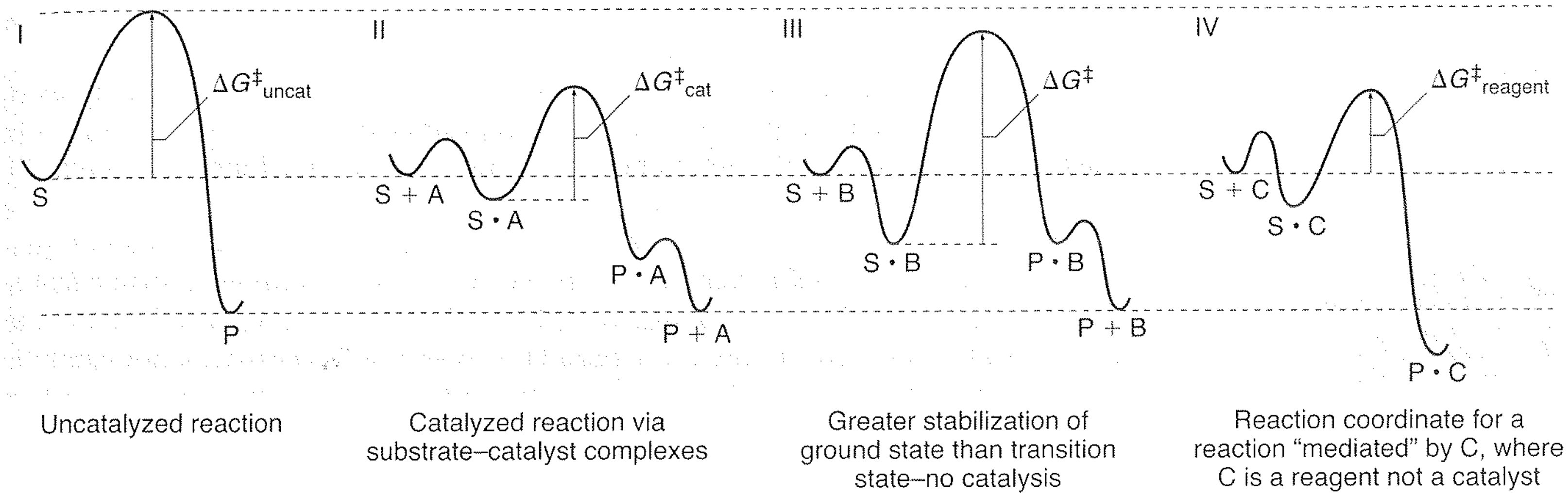
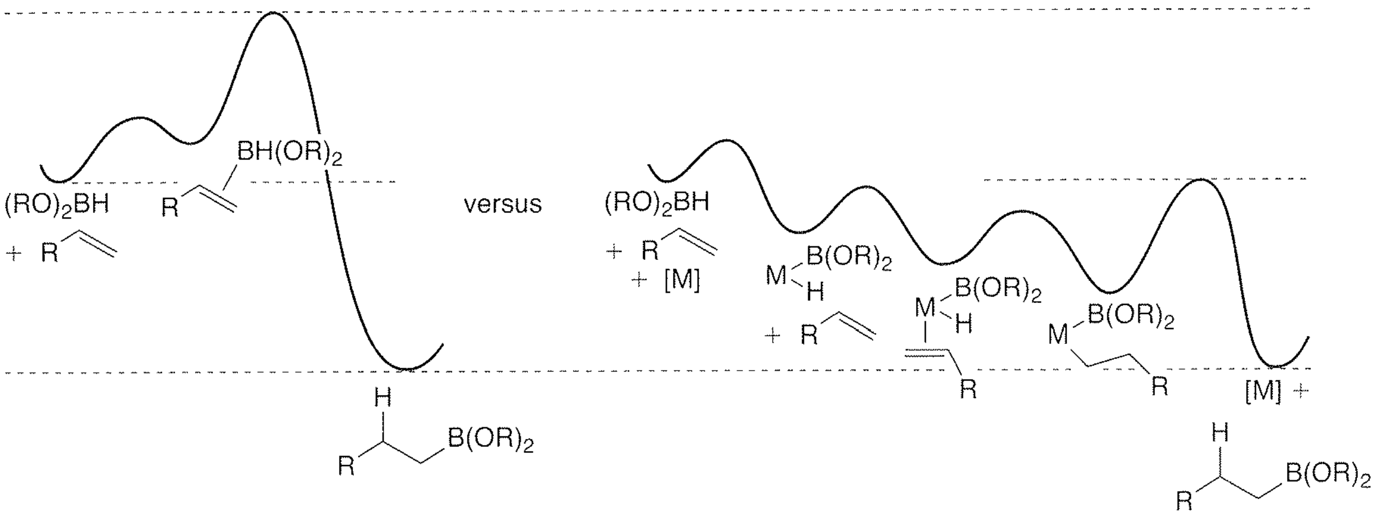
14.1.1. Definition of a Catalyst

The term "catalyst" was first introduced in 1836 by Berzelius and was defined in 1894 by Otswald. Otswald stated that a catalyst is a substance that increases the rate of a chemical reaction without itself being consumed. This basic definition continues to be commonly used. During a catalytic reaction, the catalyst undergoes a series of transformations to generate product, and this series of reactions must regenerate the starting catalyst. As a result, the catalyst can be used in substoichiometric amounts relative to the reagents.

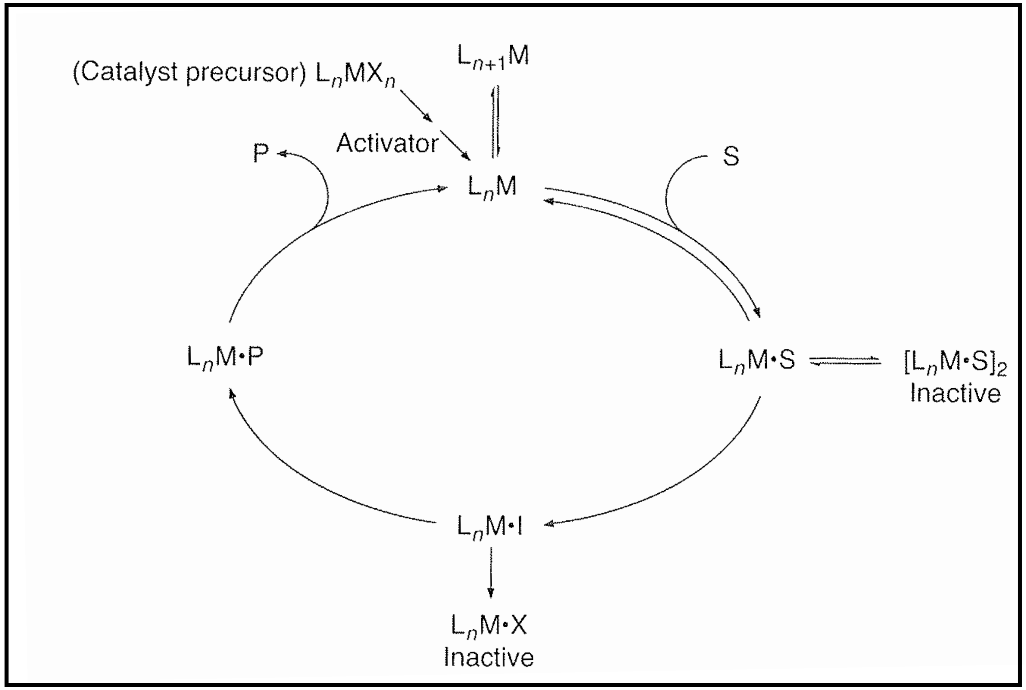


Katalyse


I
ΔG‡uncat
S
P
Uncatalyzed reaction
II
ΔG‡cat
S + A
S • A
P • A
P + A
Catalyzed reaction via substrate–catalyst complexes
III
ΔG‡
S + B
S • B
P • B
P + B
Greater stabilization of ground state than transition state–no catalysis
IV
ΔG‡reagent
S + C
S • C
P • C
Reaction coordinate for a reaction "mediated" by C, where C is a reagent not a catalyst


(RO)2BH
+ R
BH(OR)2
R
H
R
B(OR)2
versus
(RO)2BH
+ R
+ [M]
M
B(OR)2
H
+ R
M
B(OR)2
H
R
M
B(OR)2
R
[M] +
H
R
B(OR)2

Katalytischer Kreislauf

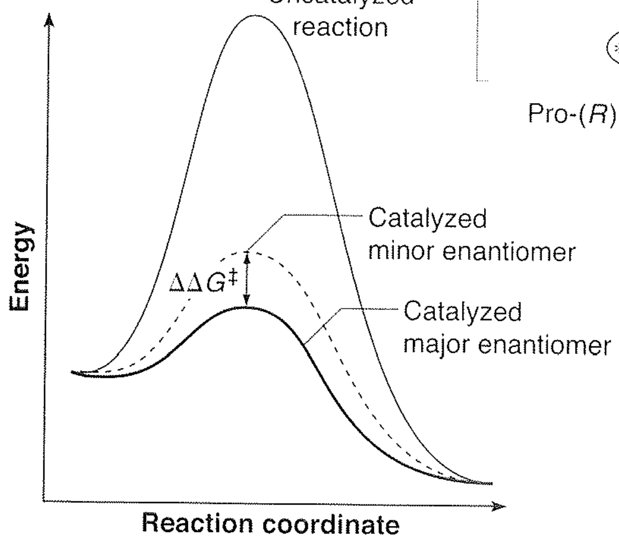


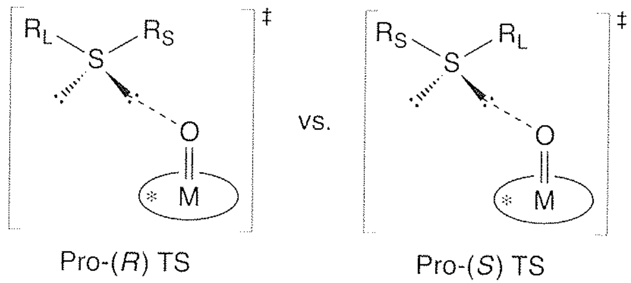
Example of a catalytic cycle with catalyst precursors and both the reversible and irreversible formation of inactive species.

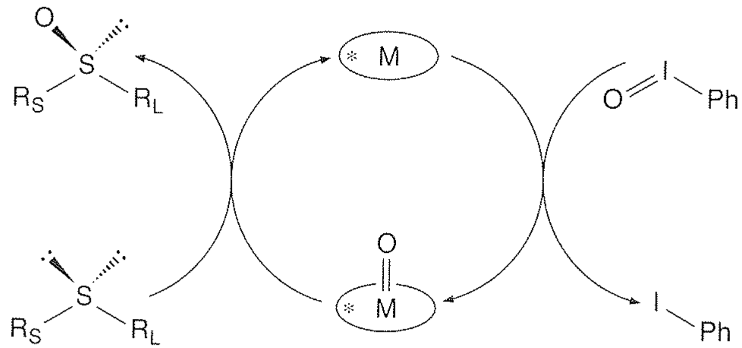
Turnover number (TON) = moles of product/moles of catalyst

Turnover frequency (TOF) = TON/time

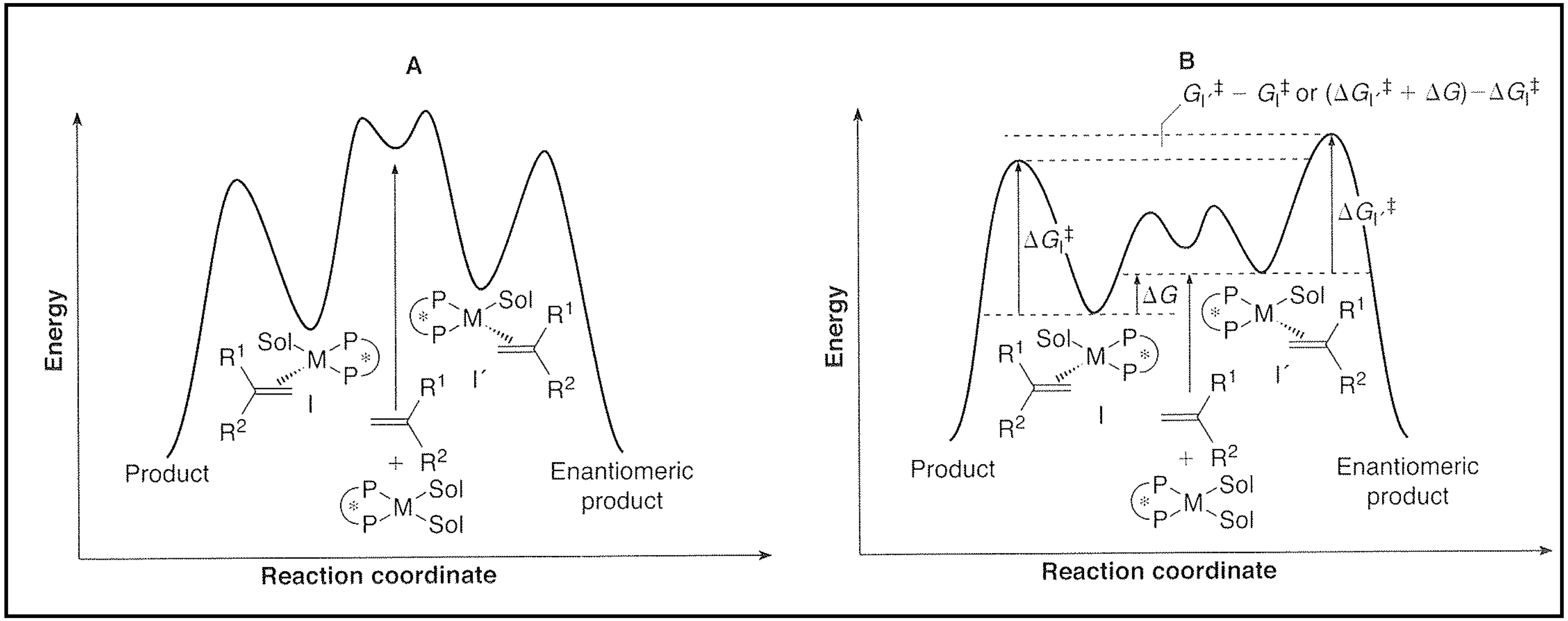
Katalyse: Asymmetrische Induktion





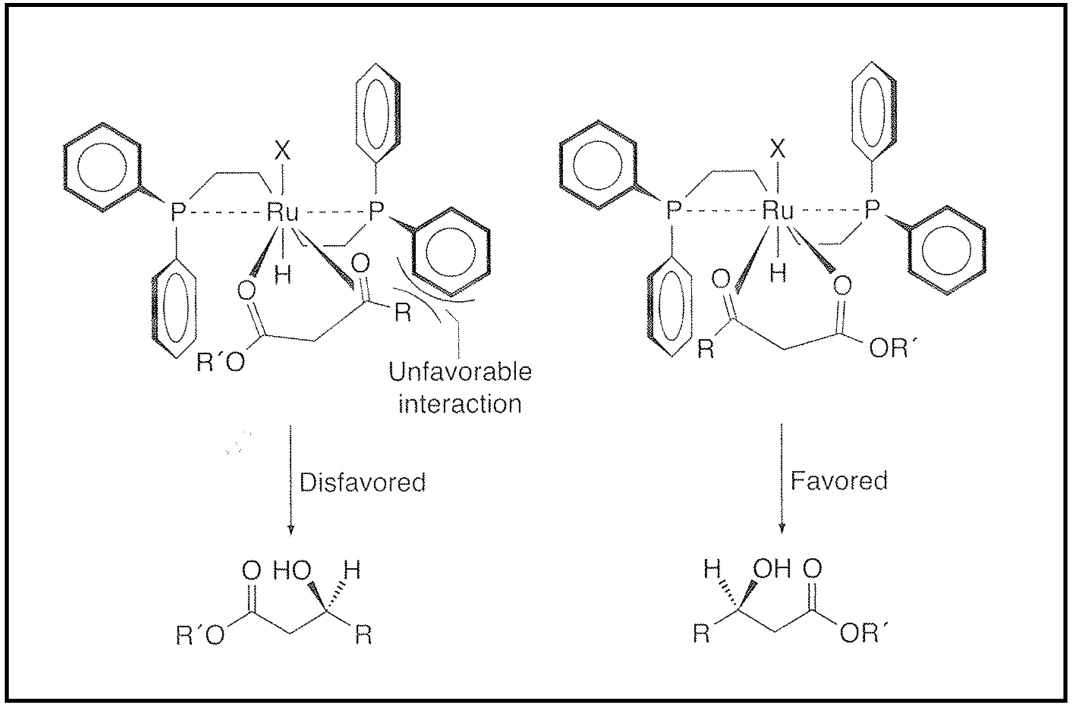


Katalyse: Asymmetrische Induktion

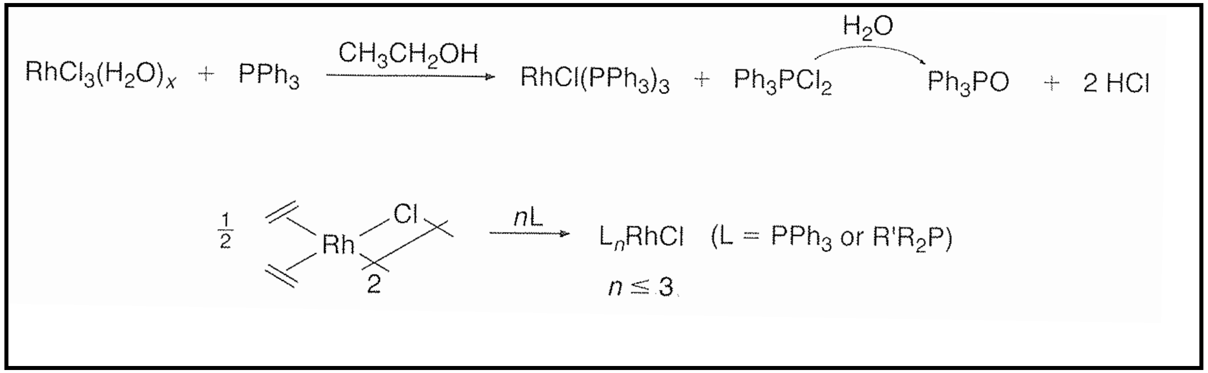


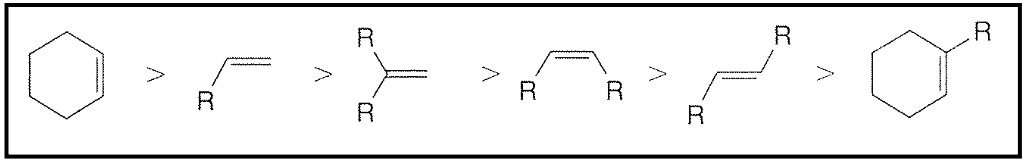
Reaction coordinate diagrams illustrating reactions of diastereomeric olefin complexes. In scenario A, olefin binding is enantio-determining. In B, the diastereomeric olefin complexes are in rapid equilibrium and enantio-determination is the conversion of the olefin adducts to products. B is an example of Curtin–Hammett conditions.

Katalyse: Asymmetrische Induktion

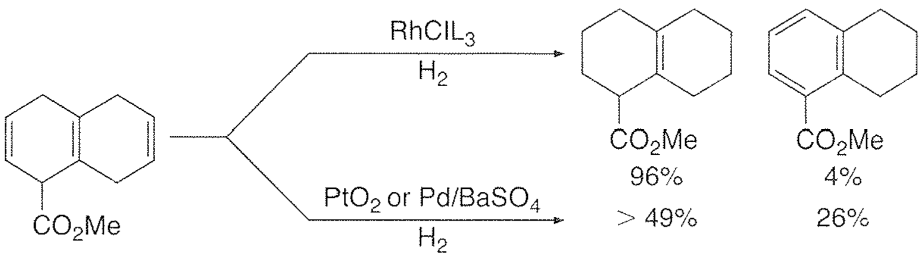


Hydrierung: Wilkinson Katalysator

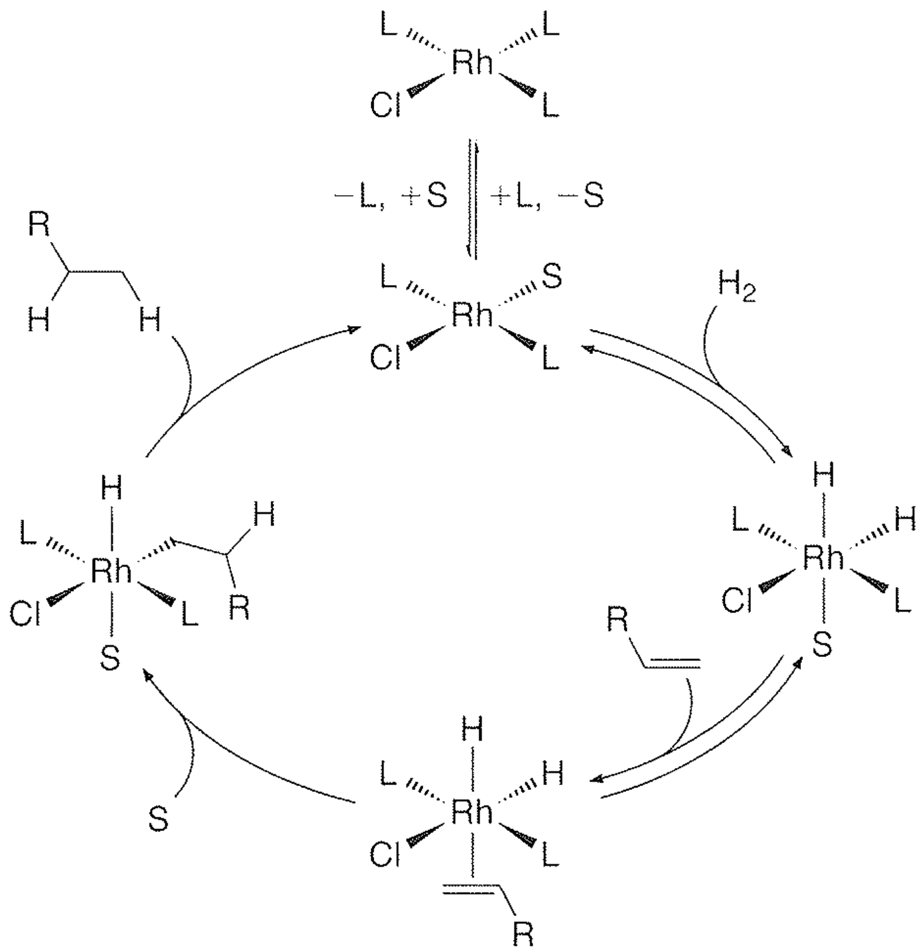




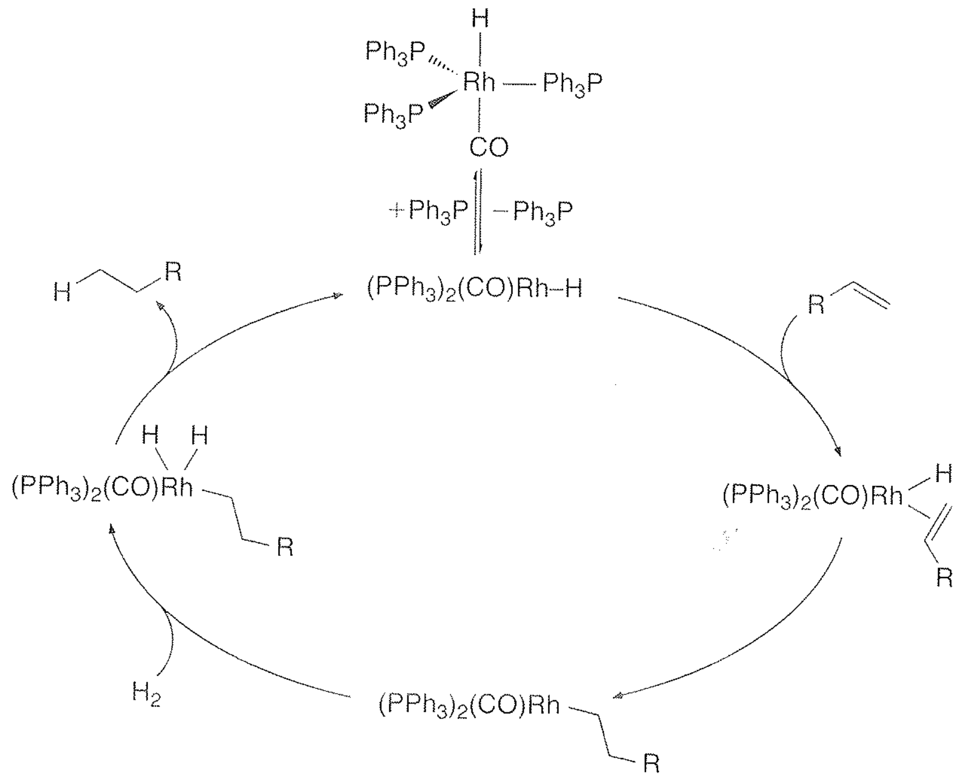
Relative reactivities of alkenes for hydrogenation by Wilkinson's catalyst.



Hydrierung: Wilkinson Katalysator



Hydrierung: Monohydridische Komplexe



Hydrierung: Kationische Rh-Katalysatoren

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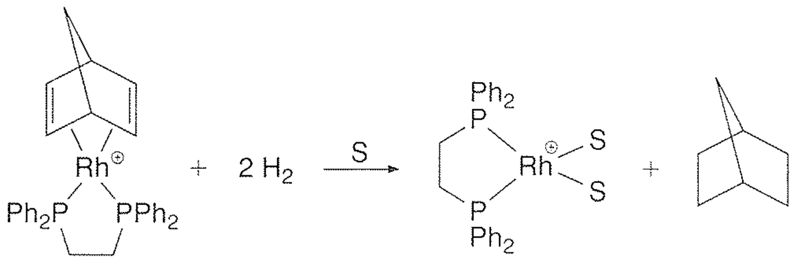
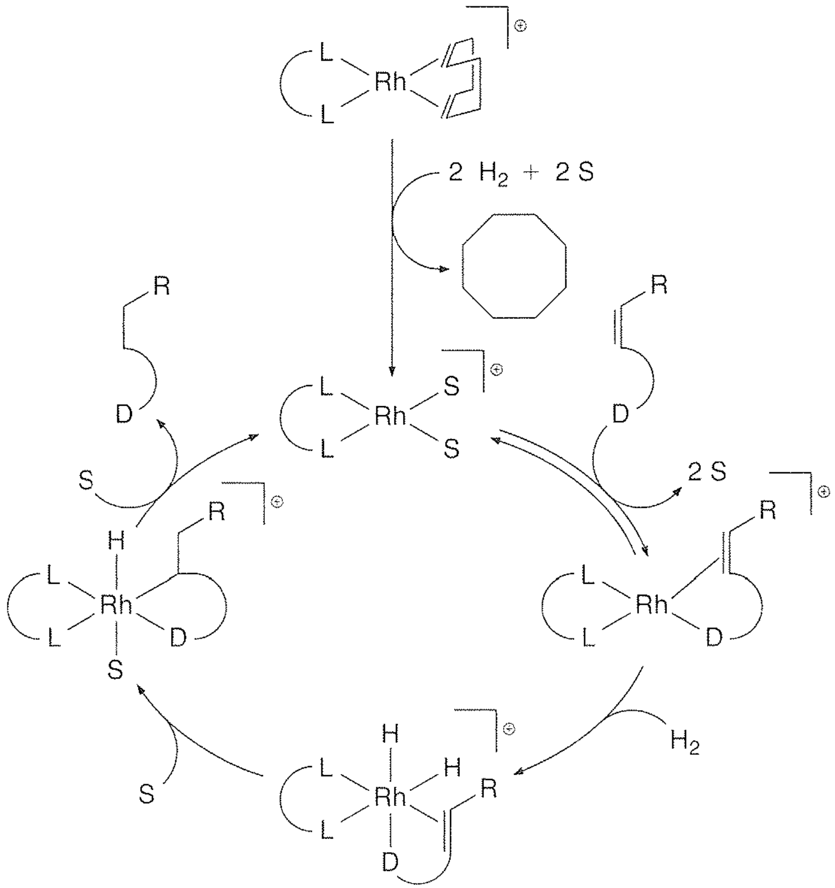


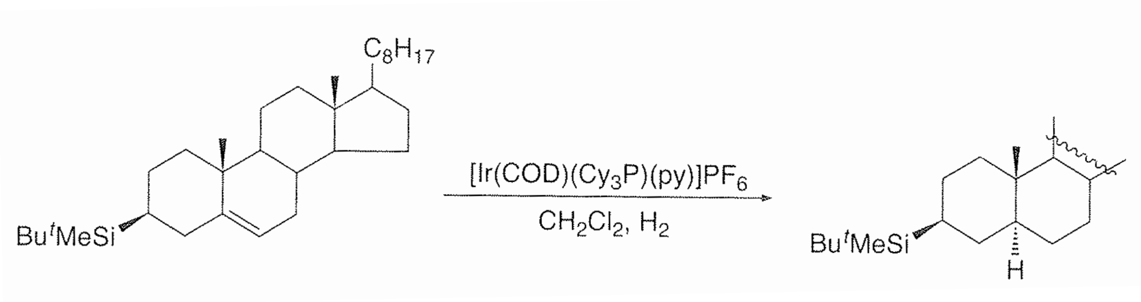
Table 15.1. Initial rate constants for hydrogenation of 1-hexene catalyzed by cationic rhodium complexes containing PPh_3, PPh_2Me, and $PhMe_2$ ligands.

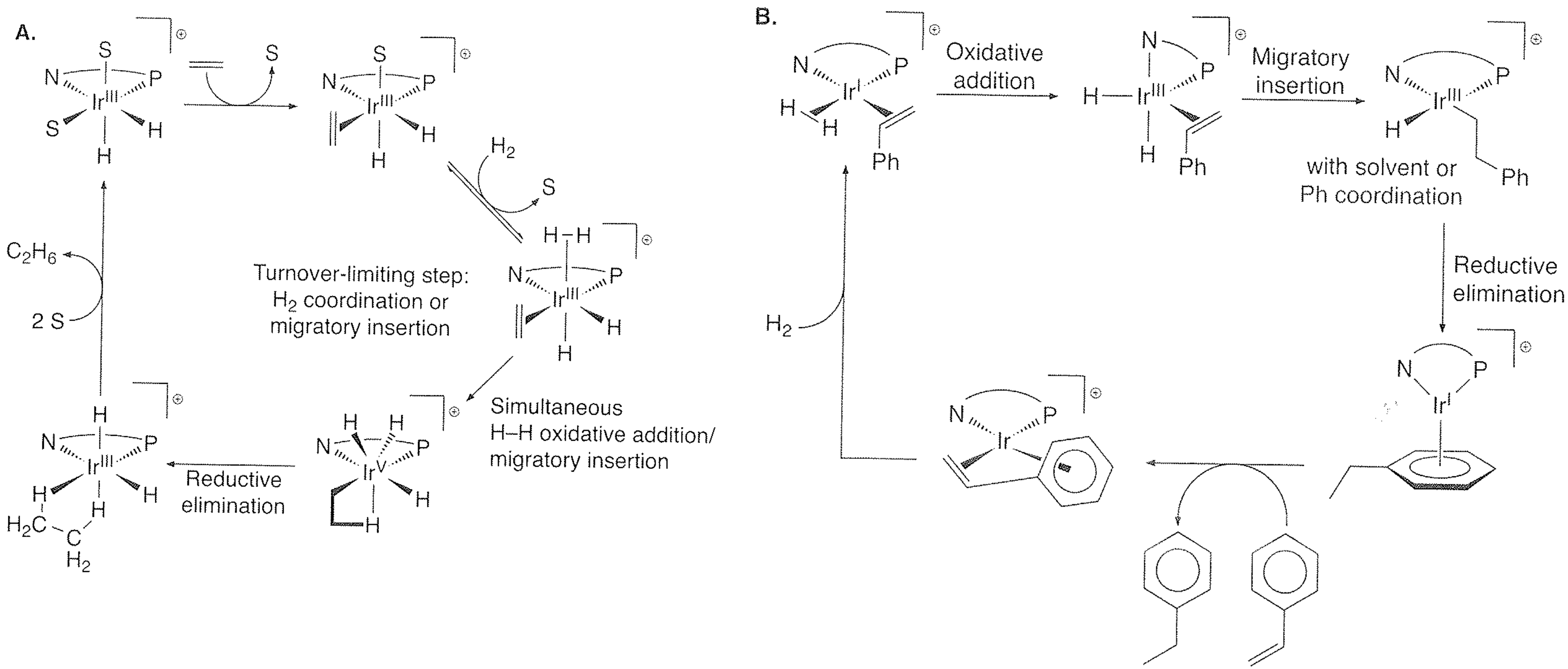
Complex	Substrate concentration (mM)	$k_{init} \times 10^4$ (s^{-1})
$[Rh(NBD)(PPh_3)_2]^+$	5.3	0.1
$[Rh(NBD)(PPh_2Me)_2]^+$	3.7	3.0
$[Rh(NBD)(PPhMe_2)_3]^+$	3.5	6.0

Hydrierung: Kationische Rh-Katalysatoren

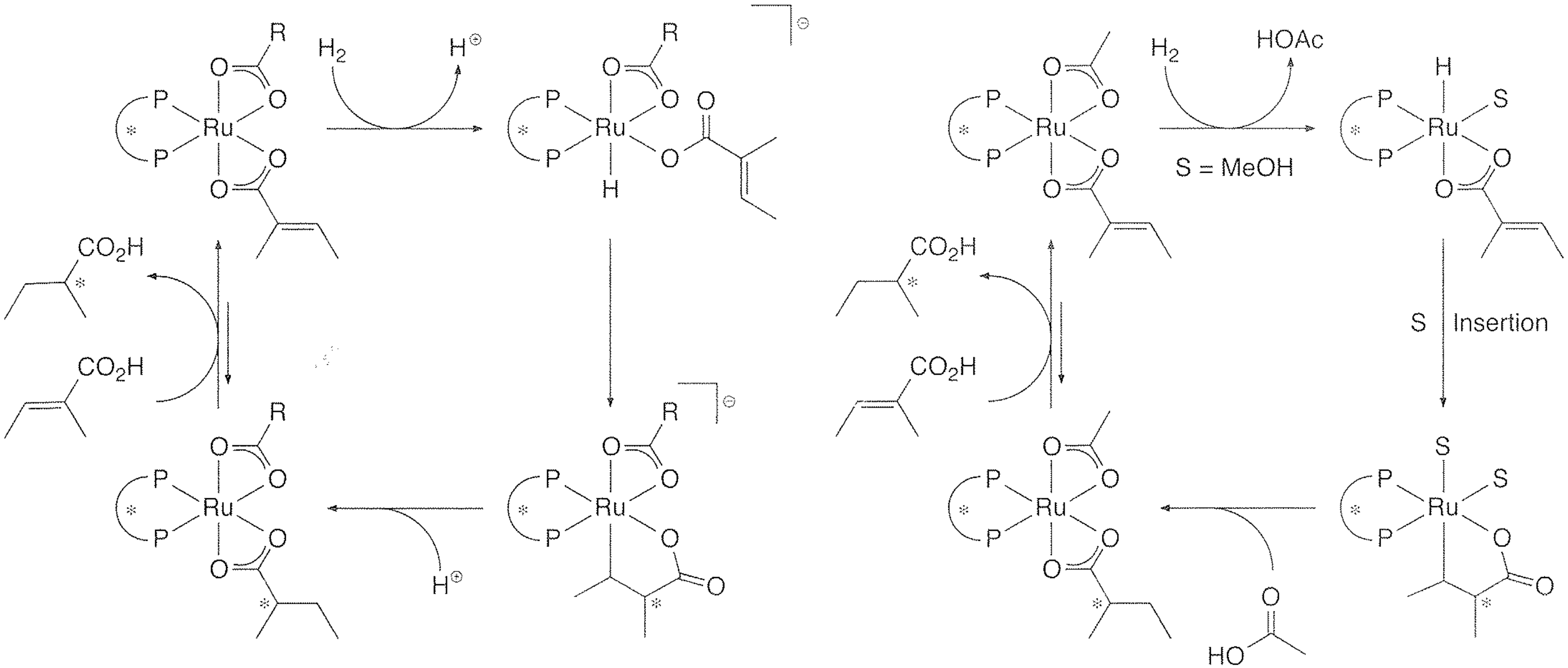


Hydrierung: Crabtree Katalysator

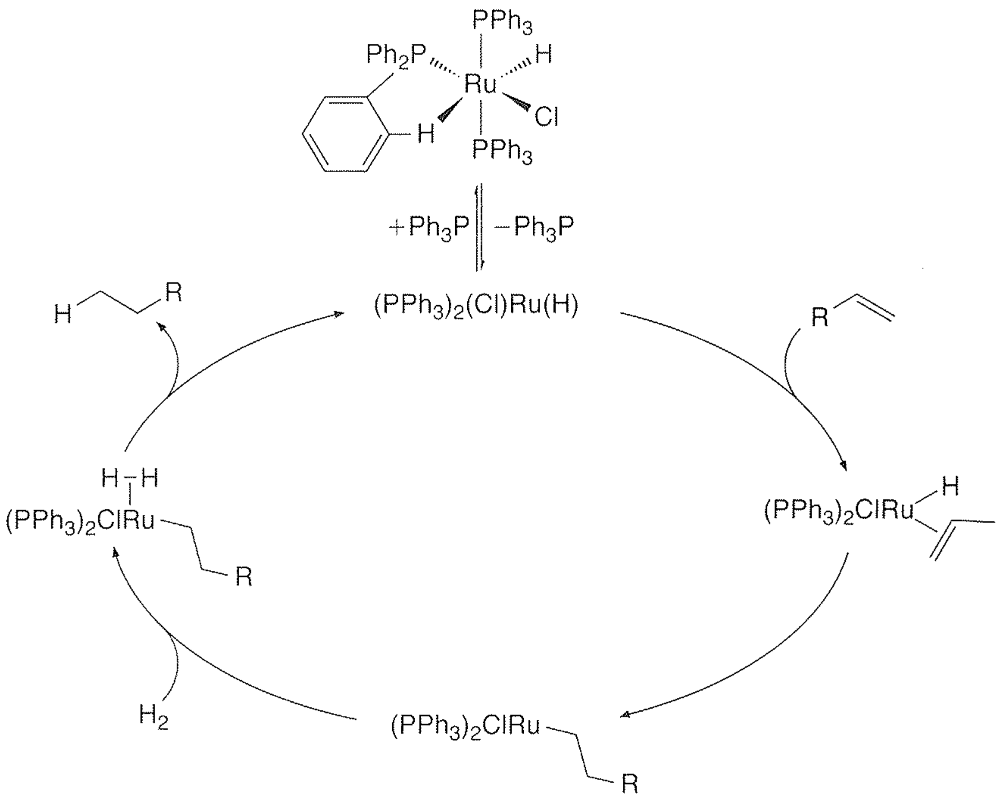




Hydrierung von Acrylsäure: Ru-Katalysatoren



Hydrierung: Ru Katalyse

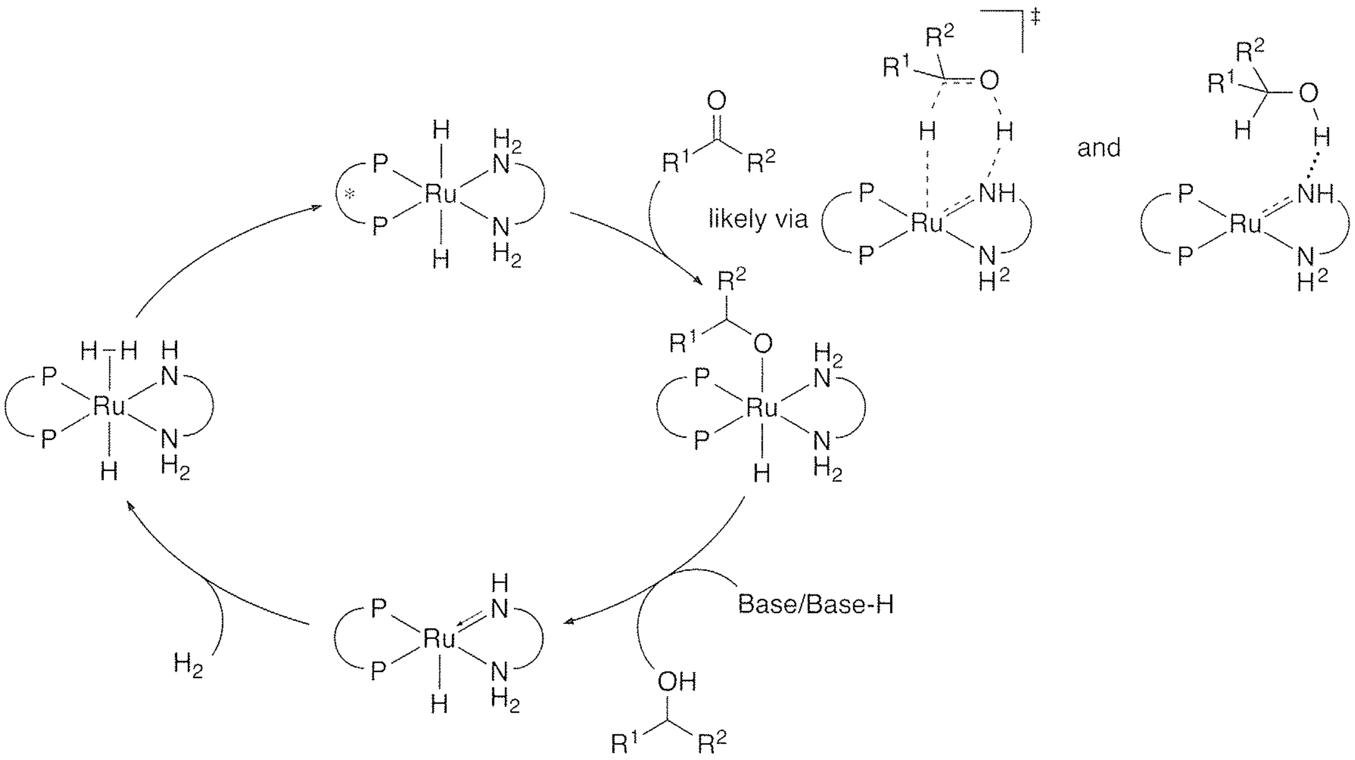


Hydrierung: Vergleich der Katalysatoren

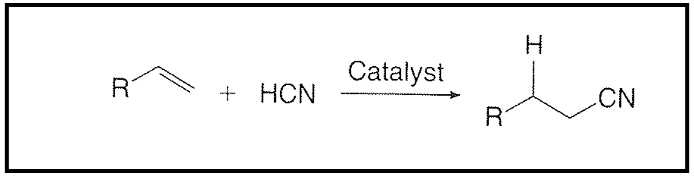
Table 15.2. A comparison of turnover frequencies for the homogeneous hydrogenation of different alkenes catalyzed by rhodium, ruthenium, and iridium catalysts.

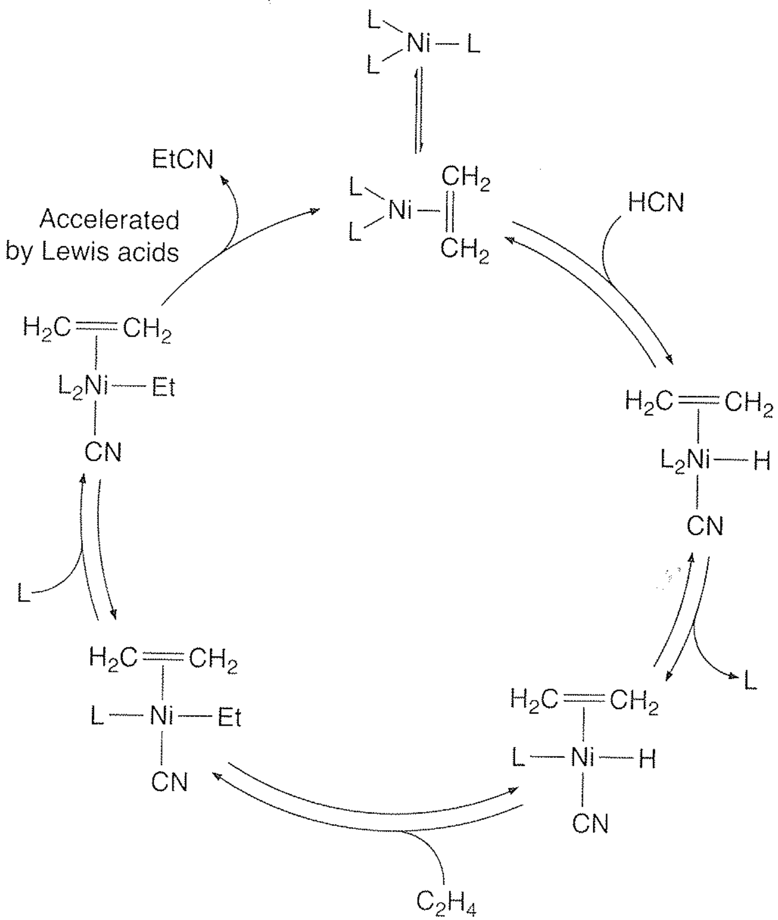
Catalyst precursor	Temperature (°C)	Solvent	Turnover frequency (h^{-1})		
			1-Hexene	Cyclohexene	Tetramethyl-ethylene
$[Ir(COD)(PCy_3)(Py)]^+$	0	CH_2Cl_2	6,400	4,500	4,000
$[Ir(COD)(PMePh_2)_2]^+$	0	CH_2Cl_2	5,100	3,800	50
$[Ir(COD)(PMePh_2)_2]^+$	0	$CH_2C(O)CH_3$	10	0	0
$[Rh(COD)(PPh_3)_2]^+$	25	CH_2Cl_2	4,000	10	0
$[Ru(H)Cl(PPh_3)_3]$	25	C_6H_6	9,000	7	0
$[RhCl(PPh_3)_3]$	25	C_6H_6/EtOH	650	700	0
$[RhCl(PPh_3)_3]$	0	C_6H_6/EtOH	60	70	0

Hydrierung von Ketonen

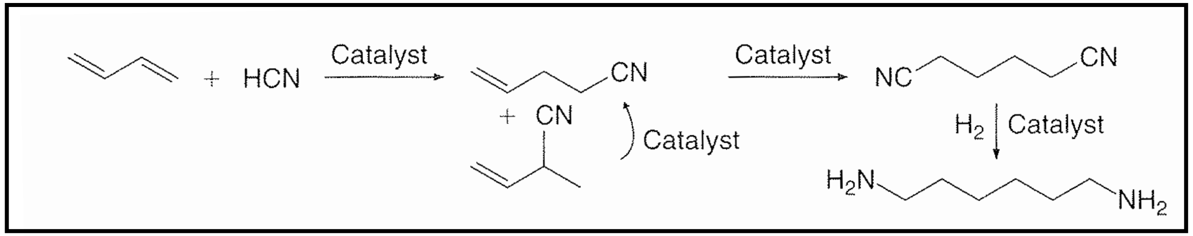


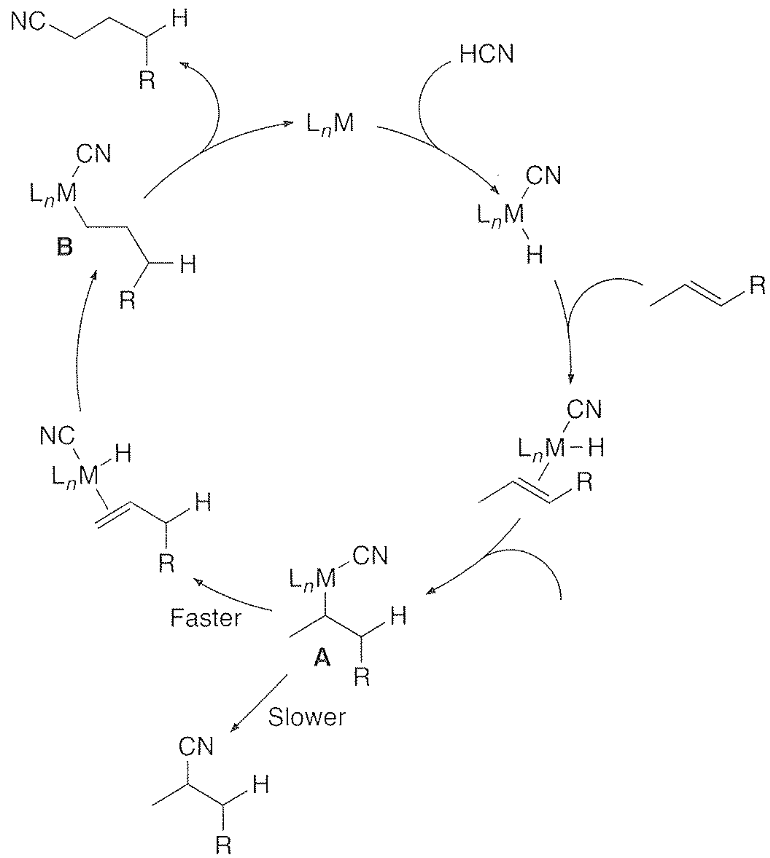
Hydrocyanierung



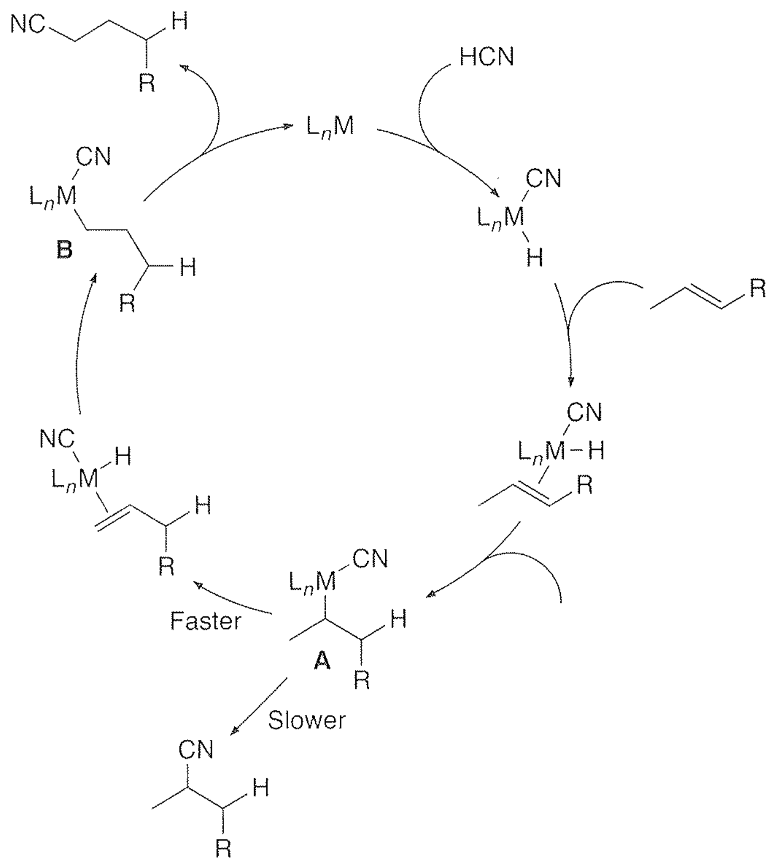


Hydrocyanierung

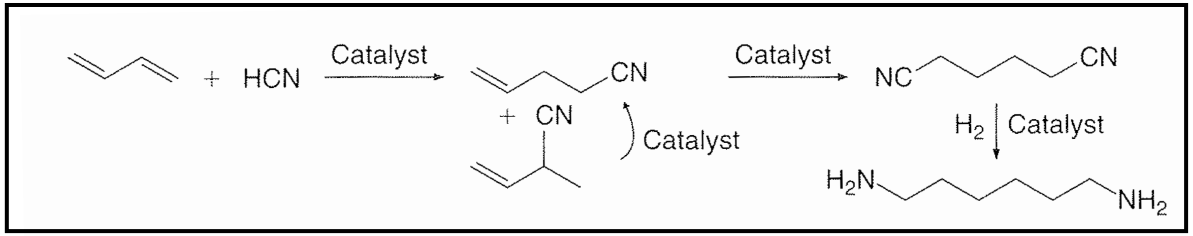


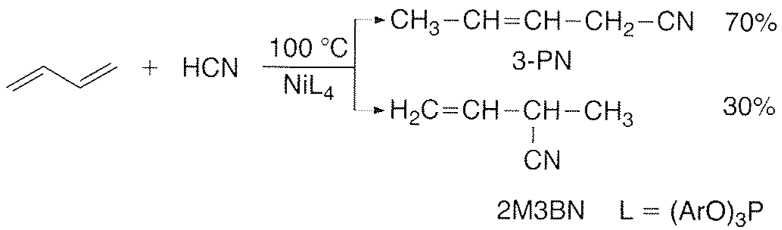


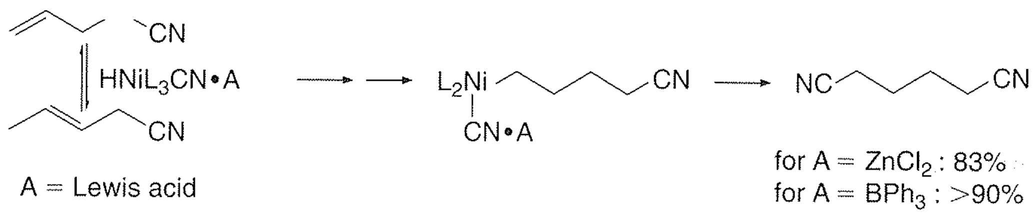
Hydrocyanierung von internen Olefinen



Hydrocyanierung von Dienen

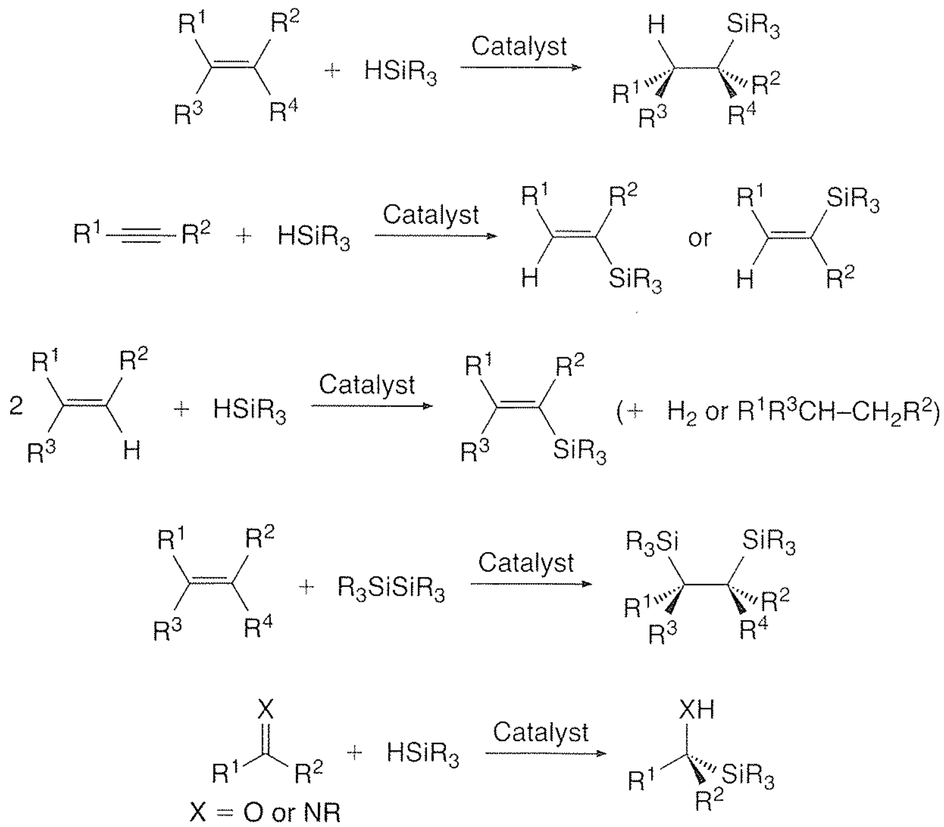






Lewis acid	**% 1,4-butane dinitrile**
B(*p*-tolyl)$_3$	99
BPh$_3$	98
B(CH$_2$Ph)$_3$	80
None	77
B(*o*-tolyl)$_3$	74
BCy$_3$	72
B(OPh)$_3$	70
B(O-*o*-tolyl)$_3$	66

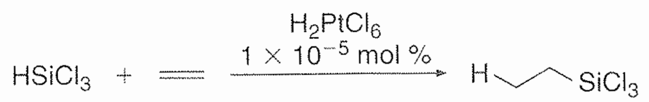
Additionen von Si-H und Si-Si

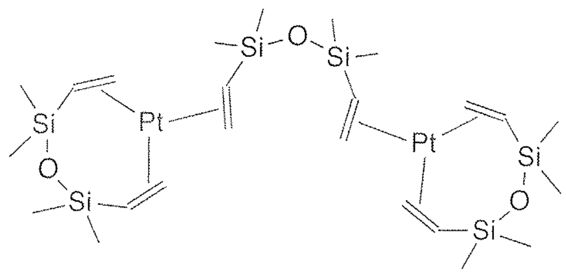


Hydrosilylierungskatalysatoren

$H_2PtCl_6 \cdot n\ H_2O$

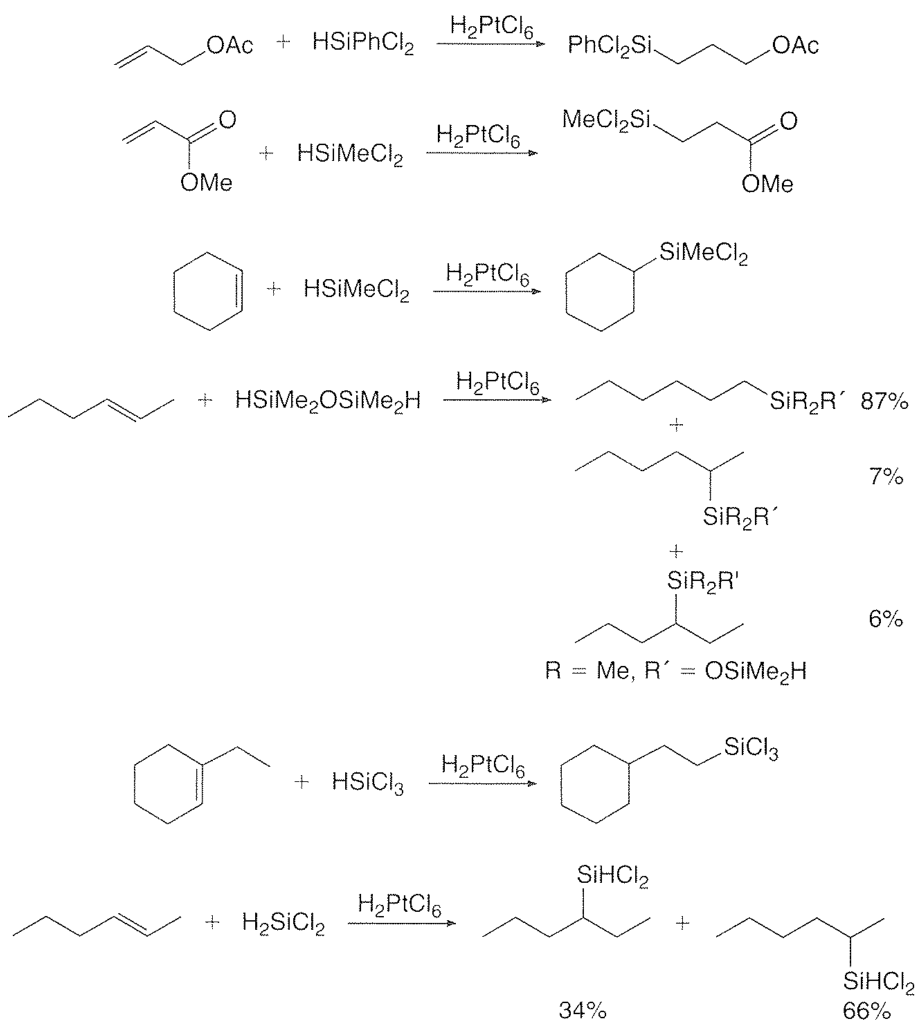
Speier Katalysator



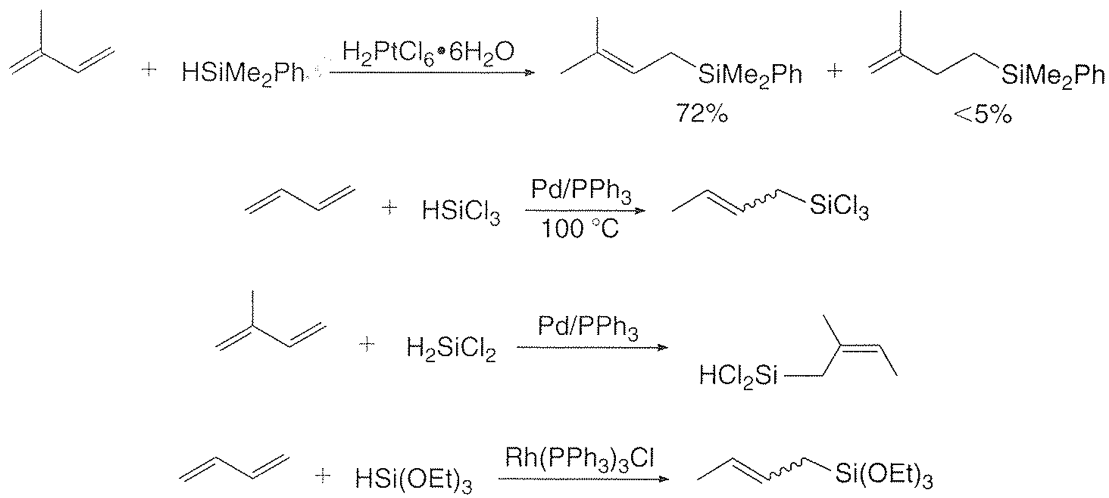


Karstedt Katalysator

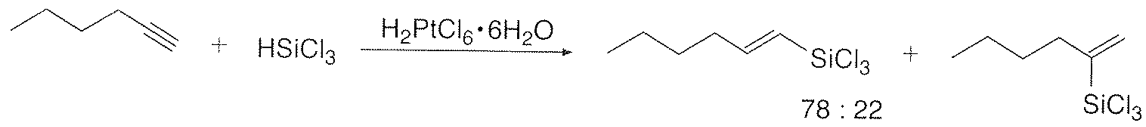
Hydrosilylierung: Regioselektivität

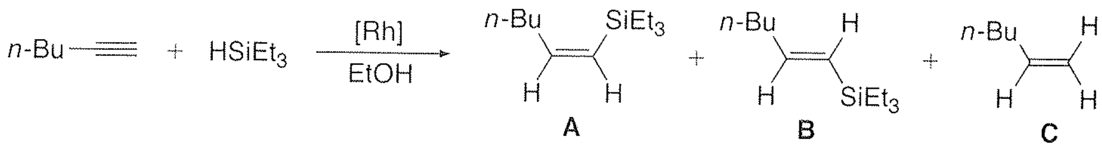


Hydrosilylierung von Dienen: Regioselektivität

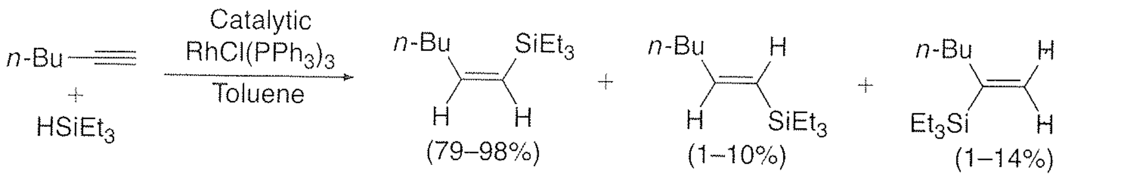


Hydrosilylierung von Alkinen

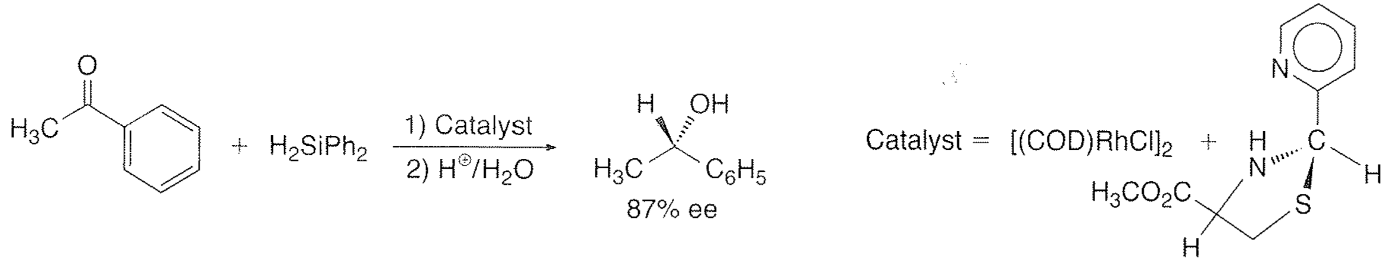


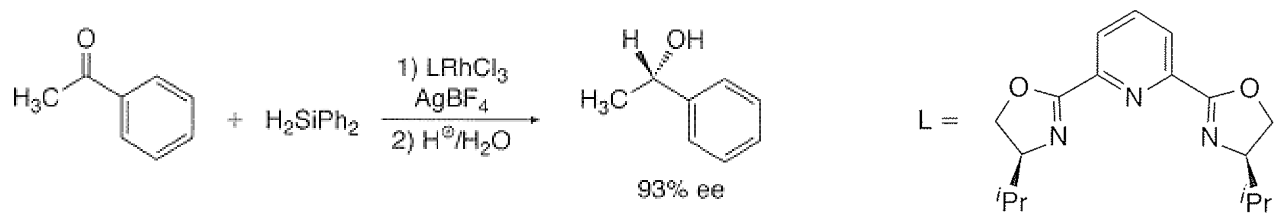


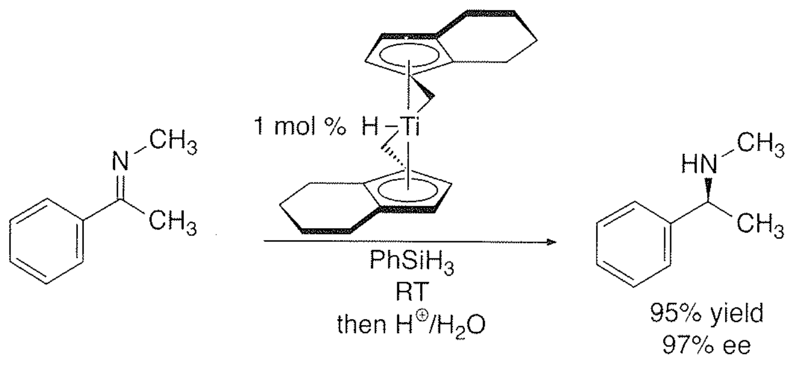
[Rh]	A	B	C
$[Rh(COD)_3]BF_4/2PPh_3$	5	95	0
$[Rh(COD)Cl_2$	94	4	2



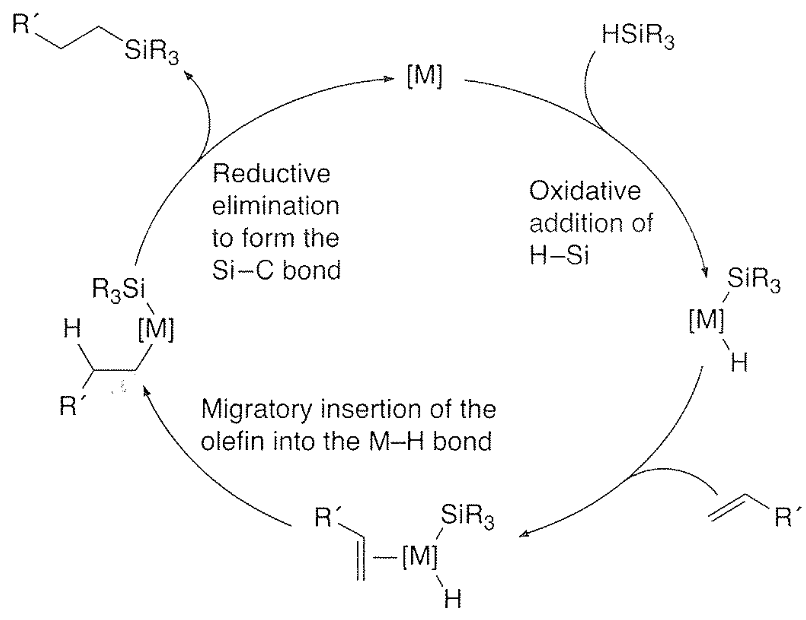
Hydrosilylierung von Ketonen und Iminen





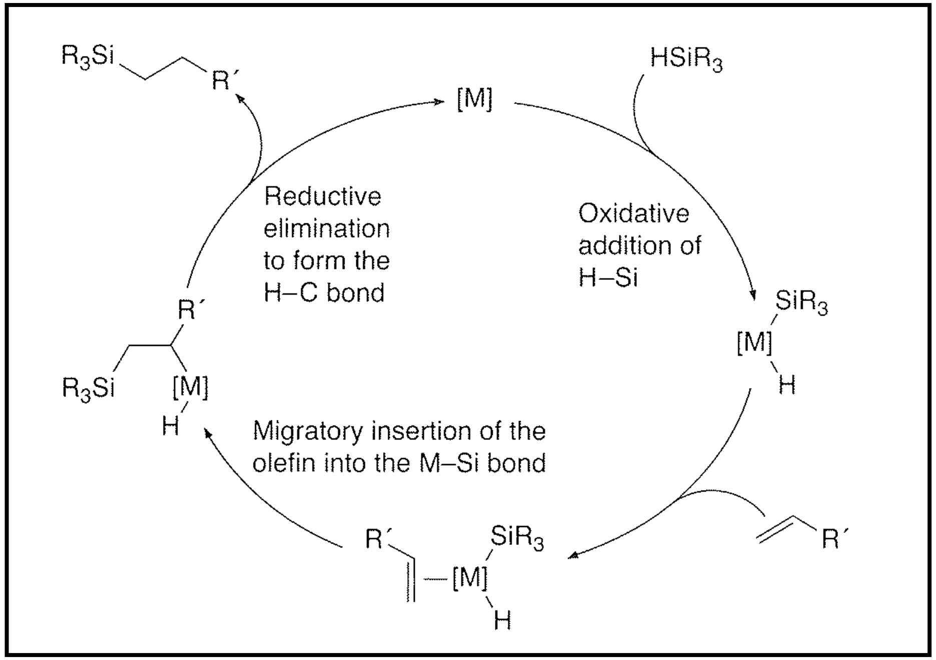


Hydrosilylierung: Mechanismus

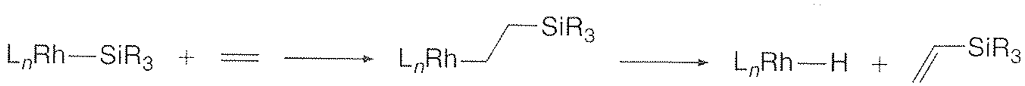


Chalk-Harrod

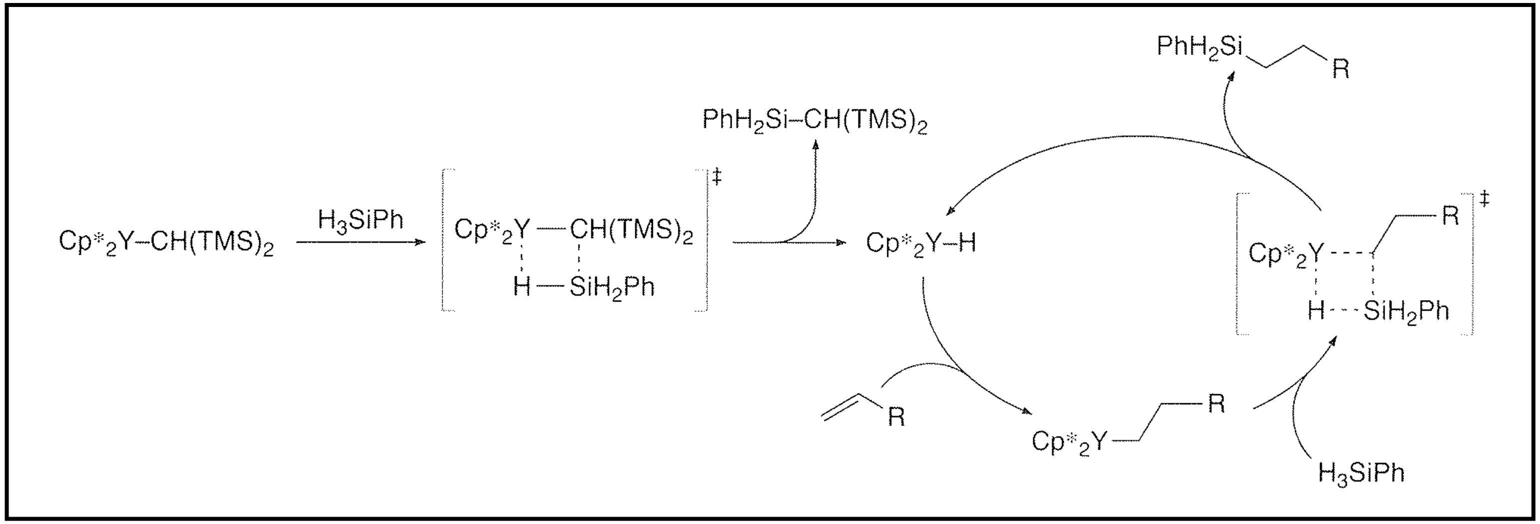
Hydrosilylierung: Mechanismus



Modified Chalk-Harrod

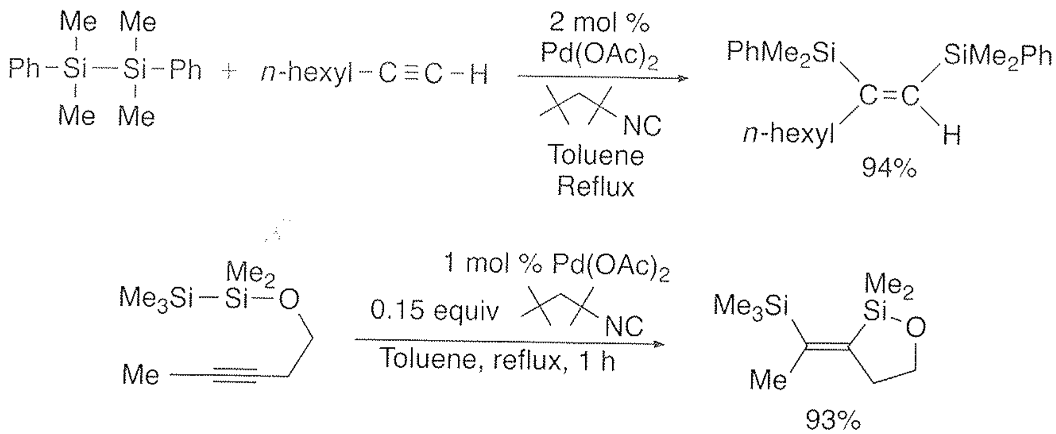


Hydrosilylierung: Mechanismus

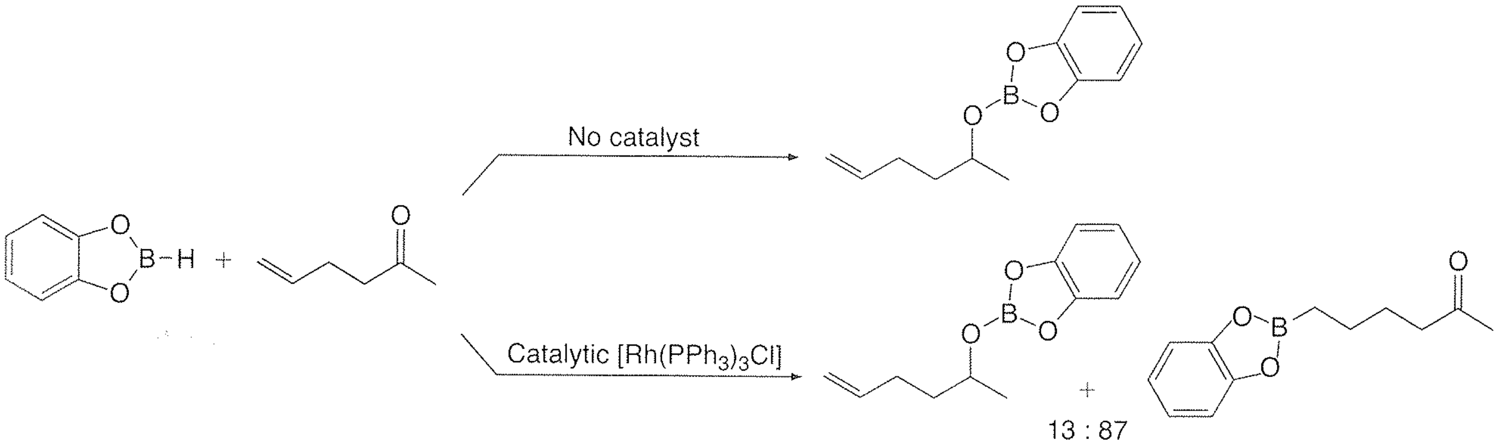


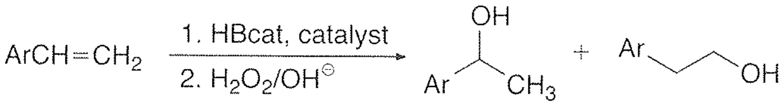
σ-Bindungsmetathese

Disilylierung



Hydroborierung

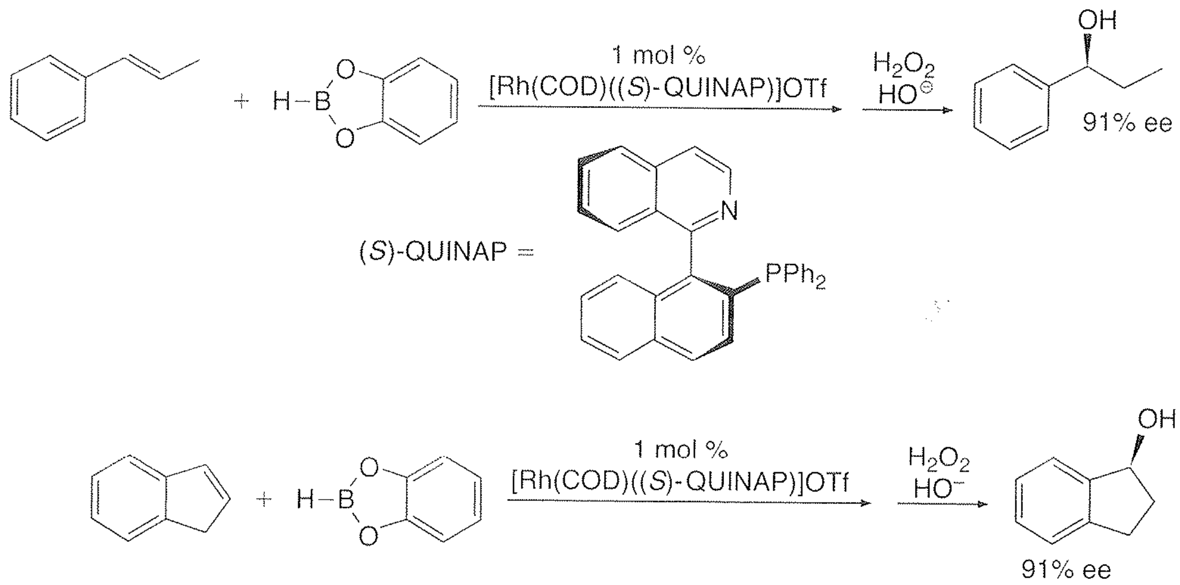




Ar = Ph or 4-MeC_6H_4

Catalyst		
$RhCl(PPh_3)_3$ (in argon)	> 99	< 1
$RhCl(PPh_3)_3$ (in air)	24	76
$[Rh(COD)_2]BF_4$/dppb	99	1
Cp_2TiMe_2 (in benzene)	0	100

Asymmetrische Hydroborierung



Di-, Silyl- and Stannylborierung

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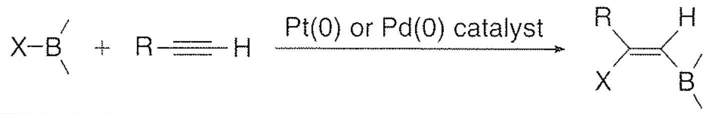
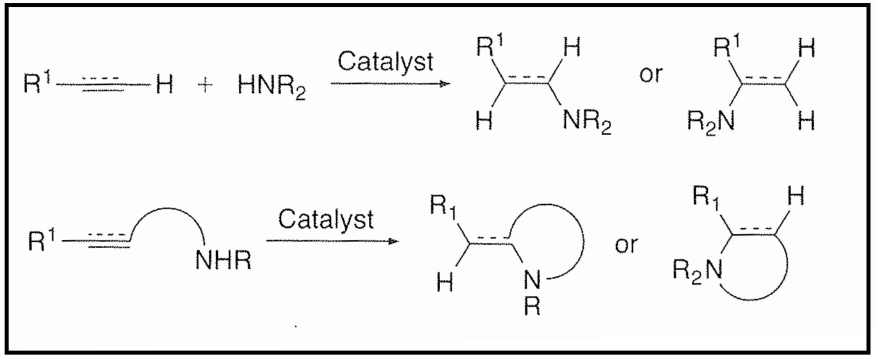
Table 16.4. Examples of palladium- and platinum-catalyzed diboration, silylboration, and stannylboration of alkynes.

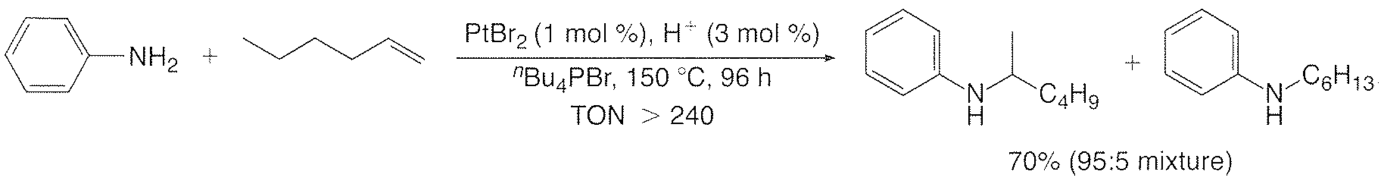


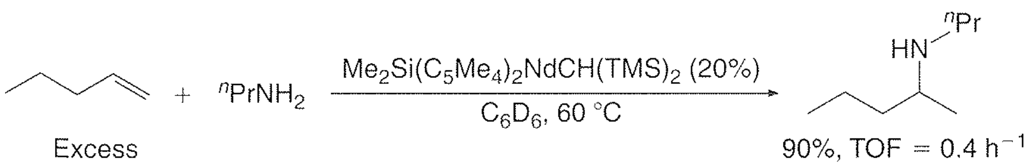
Entry	X–B	R	Catalyst	Yield/%
1	$(MeO)_2B–B(OMe)_2$	n-C_6H_{13}	$Pt(PPh_3)_4$/80 °C	89
2	catB–Bcat	n-C_6H_{13}	$Pt(PPh_3)_4$/80 °C	>95
3	pinB–Bpin	n-C_6H_{13}	$Pt(PPh_3)_4$/80 °C	92
4		Ph	$Pt(PPh_3)_4$/80 °C	79
5		$N{\equiv}C(CH_2)_3$	$Pt(PPh_3)_4$/80 °C	79
6		$MeO_2C(CH_2)_4$	$Pt(PPh_3)_4$/80 °C	89
7	$(Me_2N)_2B–B(NMe_2)_2$	n-C_6H_{13}	$Pt(PPh_3)_4$/120 °C	7
8	$R_3Si–B(NR_2)_2$	n-C_6H_{13}	$Pd_2(dba)_3$/4 etpo/80 °C[a]	92
9	R_3Si–Bpin	n-C_6H_{13}	$Pd(OAc)_2$/15 RNC/110 °C[b]	92
10	$Me_3Sn–B(NR_2)_2$	n-C_6H_{13}	$Pd(PPh_3)_4$/RT	83
11		Ph	$Pd(PPh_3)_4$/RT	73

[a] etpo = $P(OCH_2)_3CCH_2CH_3$
[b] RNC = $^tBuCH_2CMe_2NC$

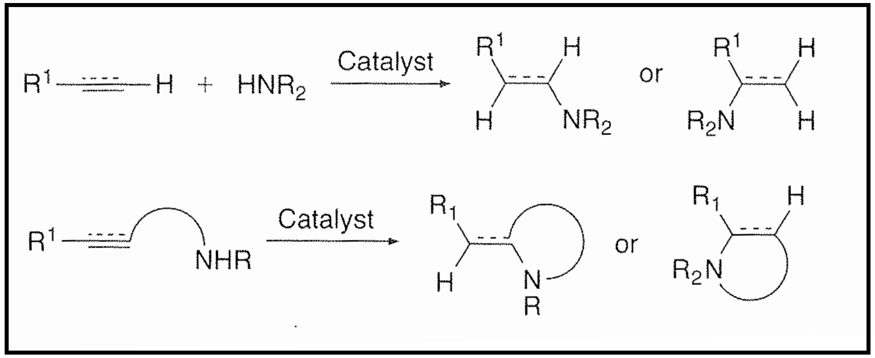
Hydroaminierung

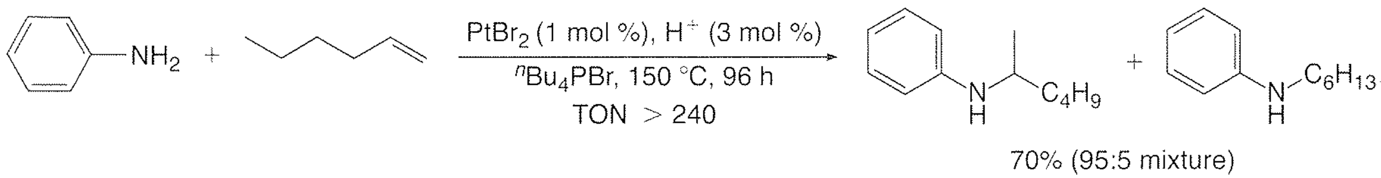


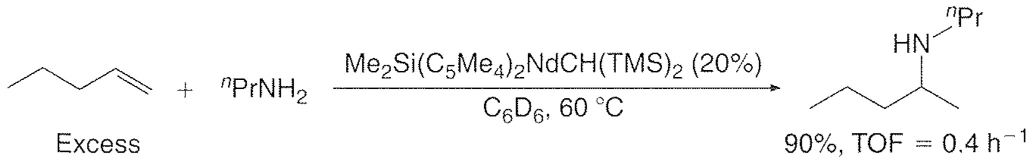


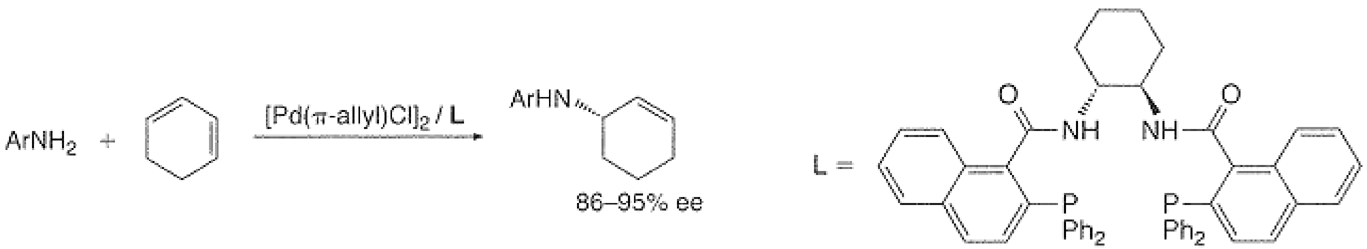


Hydroaminierung

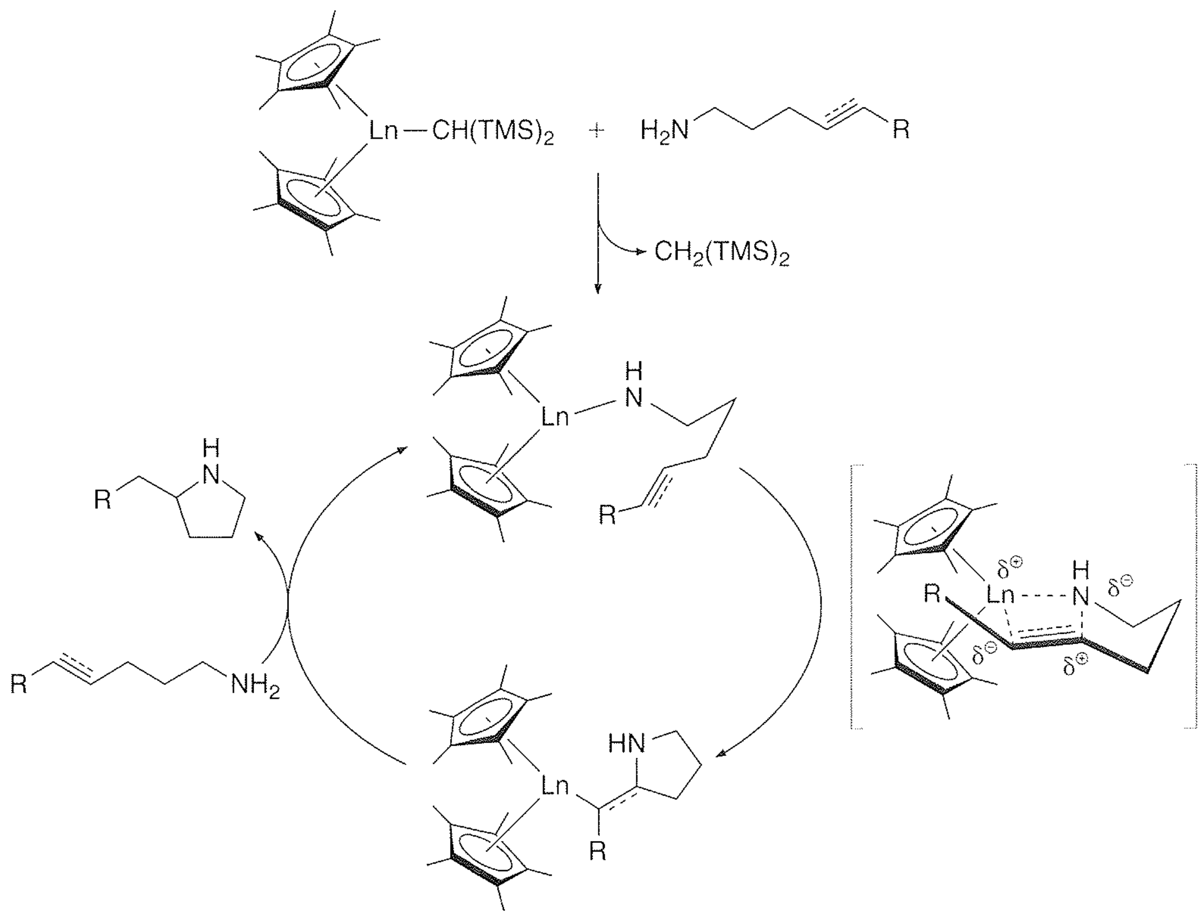




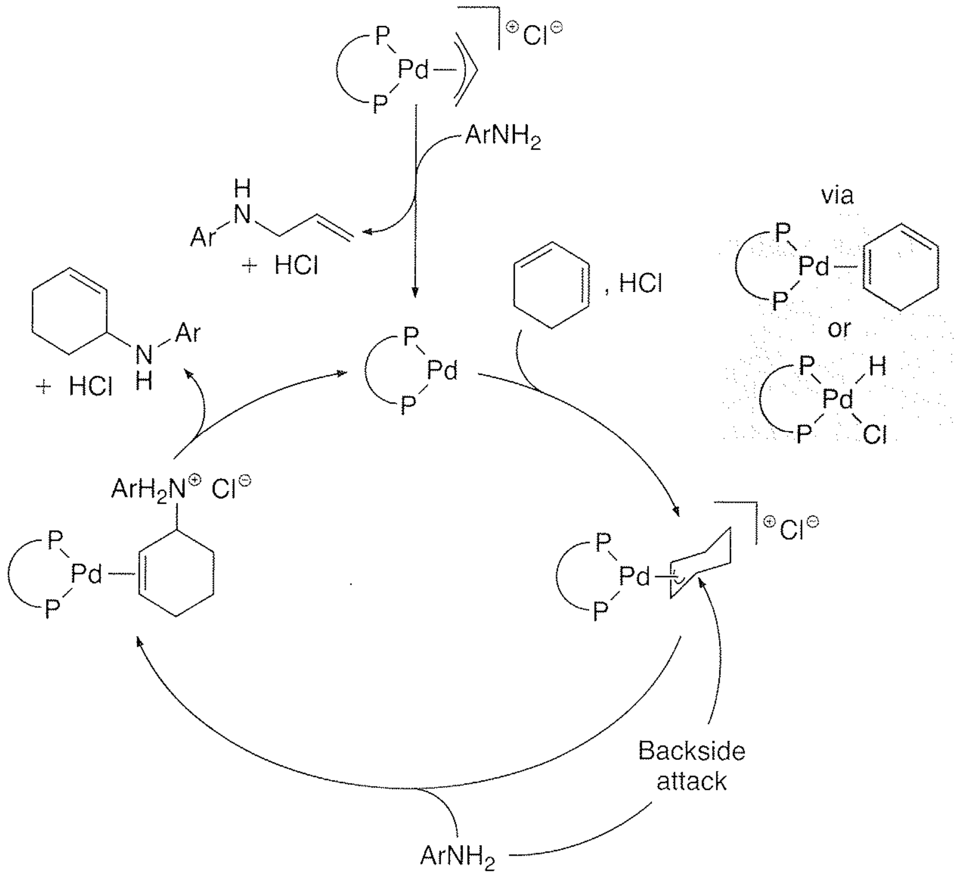




Hydroaminierung: Mechanismus



Hydroaminierung: Mechanismus



Wacker Oxidation

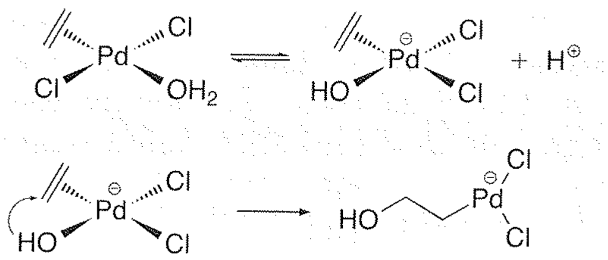
$$H_2C=CH_2 + PdCl_2 + H_2O \longrightarrow CH_3CHO + Pd(0) + 2HCl$$

$$Pd(0) + 2\ CuCl_2 \longrightarrow PdCl_2 + 2\ CuCl$$

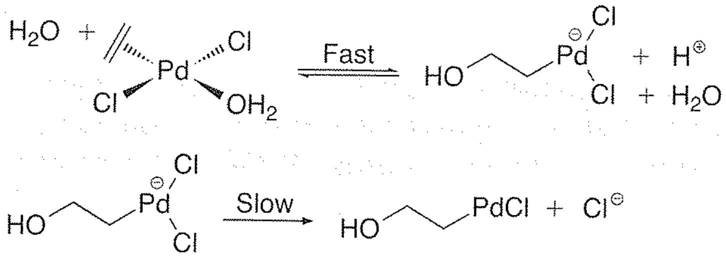
$$2\ CuCl + 1/2\ O_2 + 2\ HCl \longrightarrow 2\ CuCl_2 + H_2O$$

$$\text{Overall:}\quad H_2C=CH_2 + 1/2\ O_2 \xrightarrow[PdCl_2]{CuCl_2} CH_3-\overset{\displaystyle O}{\overset{\|}{C}}-H$$

Mechanism I



Mechanism III



Wacker Oxidation