Organometallics Study Meeting

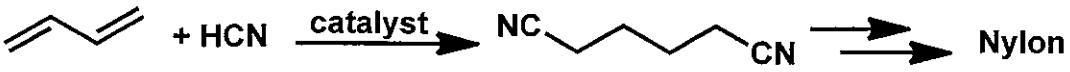
2011. 9. 22. Y. Tanaka

Chapter 16 Hydrofunctionalization and Oxidative Functionalization of Olefins

Today's topic: Addition of H-CN, H-Si, Si-Si, H-B and E-B to olefins

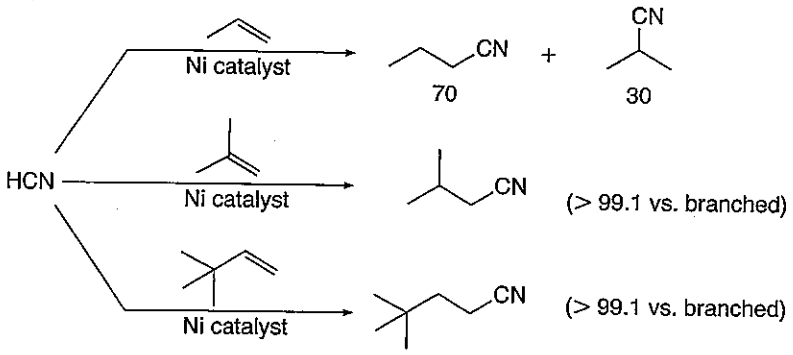
Hydrocyanation

ex.



Most developed: Ni catalyst (+Lewis acid)

Regioselectivity



Scheme 16.1

Effected by bulkyness of metal complex (and L.A.)

Effect of Lewis acid

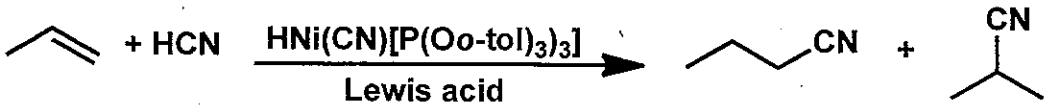
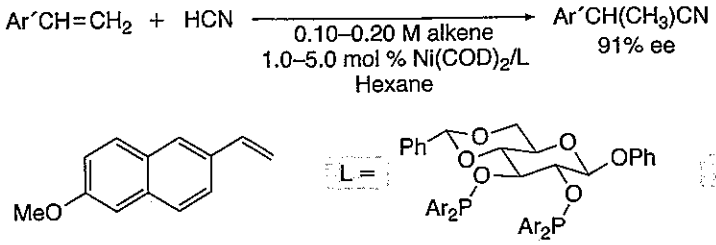


Table 16.1. Relative rates for hydrocyanation of propylene in 75% toluene/25% CD_2Cl_2 in the presence of $HNi(CN)[P(O\text{-}o\text{-}Tol)_3]_3$ as catalyst.[30]

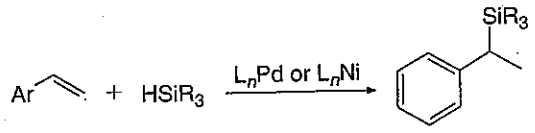
	Approximate $t_{1/2}$(min)			
Lewis acid	−25°C	−0°C	+25°C	% Linear product
$AlCl_3$	−10			72
$ZnCl_2$			<4	70
None		60		72
None			>7	70
BPh_3			>60	89

L.A.: coordinate to CN (facilitate reductive elimination)

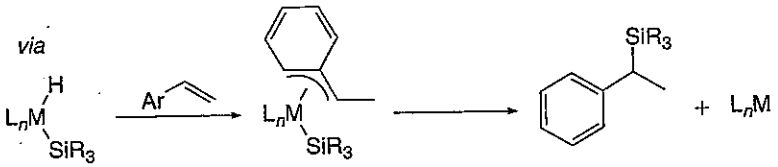
In the cases of vilylarens...



(16.9)



(16.24)

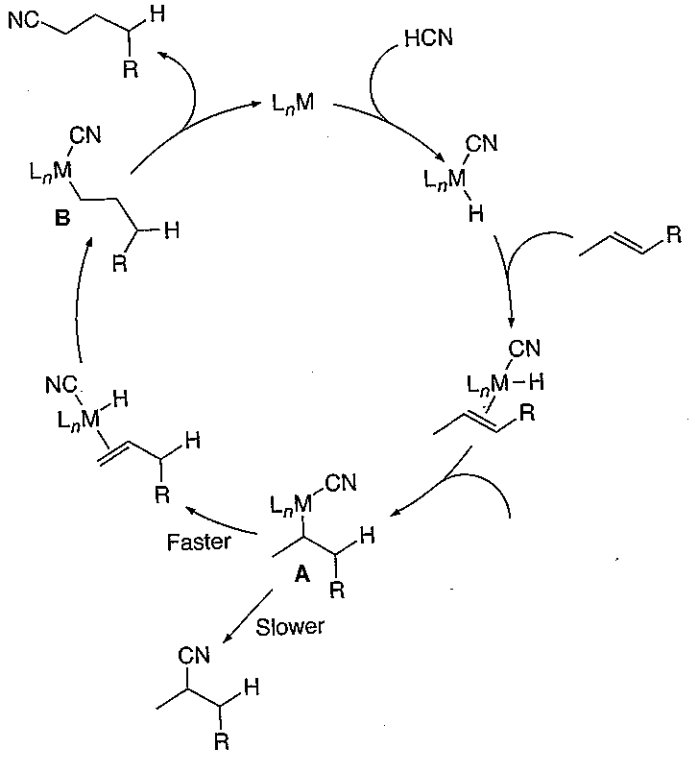


Stable η^3 complex

About catalyst

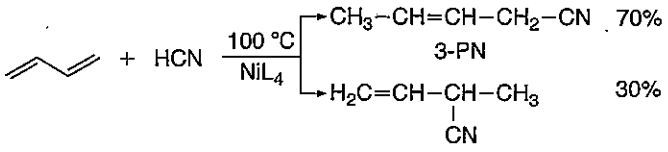
-P(*Oo*-tol)$_3$: open coordination site, faster reductive elimination (less electron donating than phosphine)
-deactivation: formation of L2Ni(CN)2: diluted HCN, ex. phosphite

Migration to terminal position

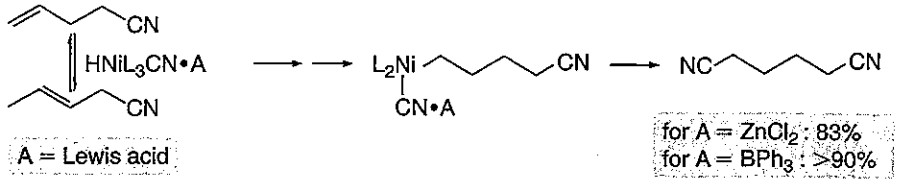


Scheme 16.3

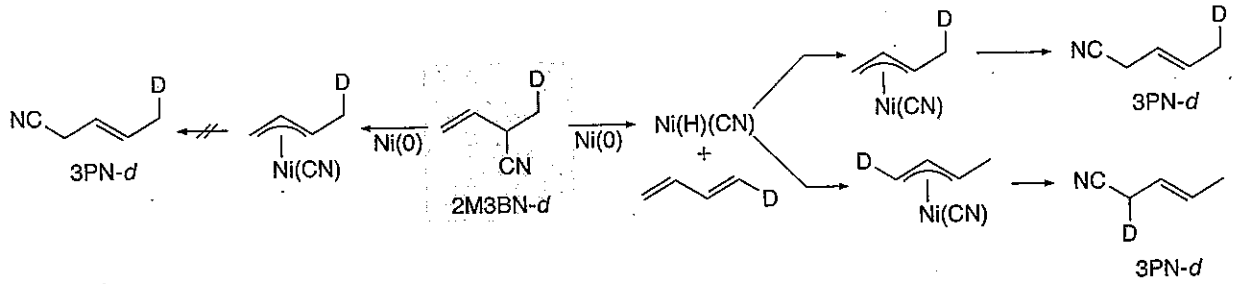
In the case of diene



(16.6)

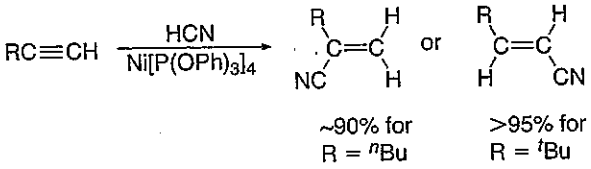


(16.7)



(16.8)

Hydrocyanation of alkynes

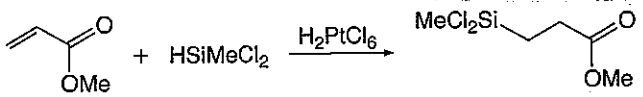


(16.11)

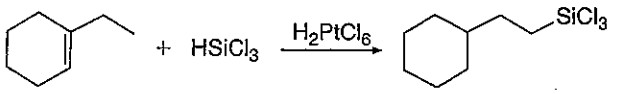
Hydrosilylation and Disilylation

Commonly used: Pt, Rh, Pd complexes

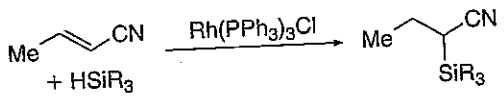
Examples of Speier's catalyst and Wilkinson's catalyst



(16.19)

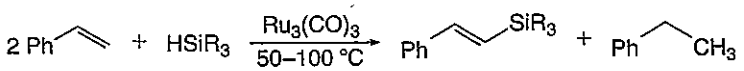


(16.21b)



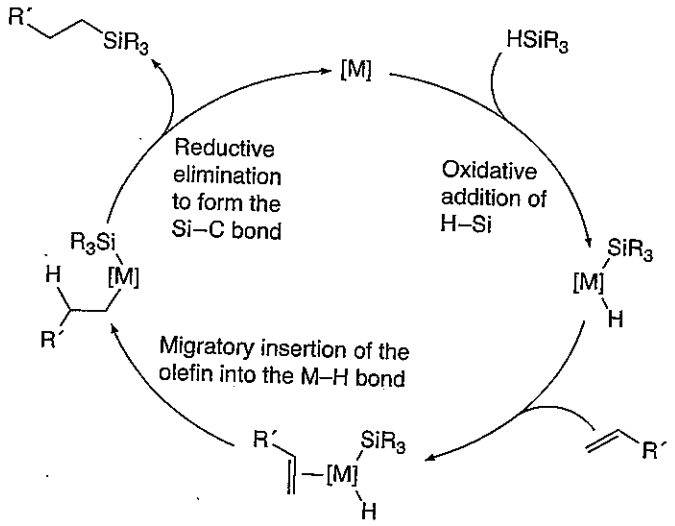
(16.23)

In the case of $Ru_3(CO)_{12}$

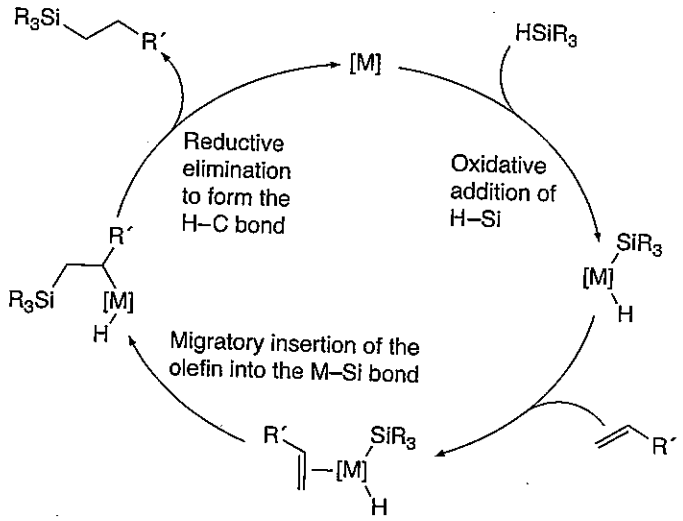


(16.29)

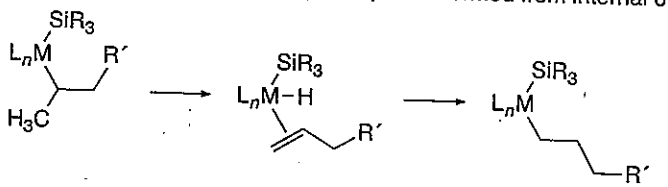
Mechanism



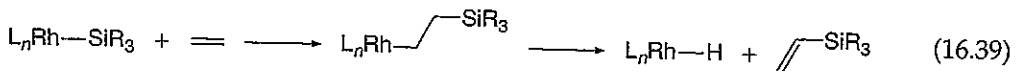
Scheme 16.6. Chalk–Harrod mechanism.



Pathway for isomerization of branched alkyl complexes formed from internal olefins:

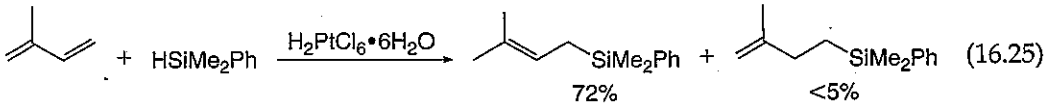


Scheme 16.7. Modified Chalk–Harrod mechanism.

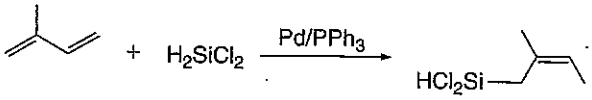


(16.39)

Hydrosilylation of dienes

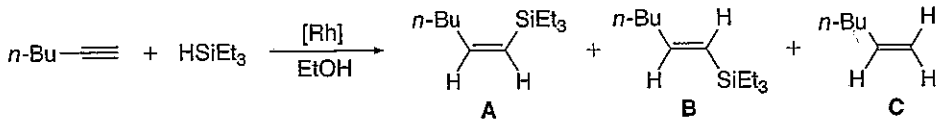


(16.25)



(16.27)

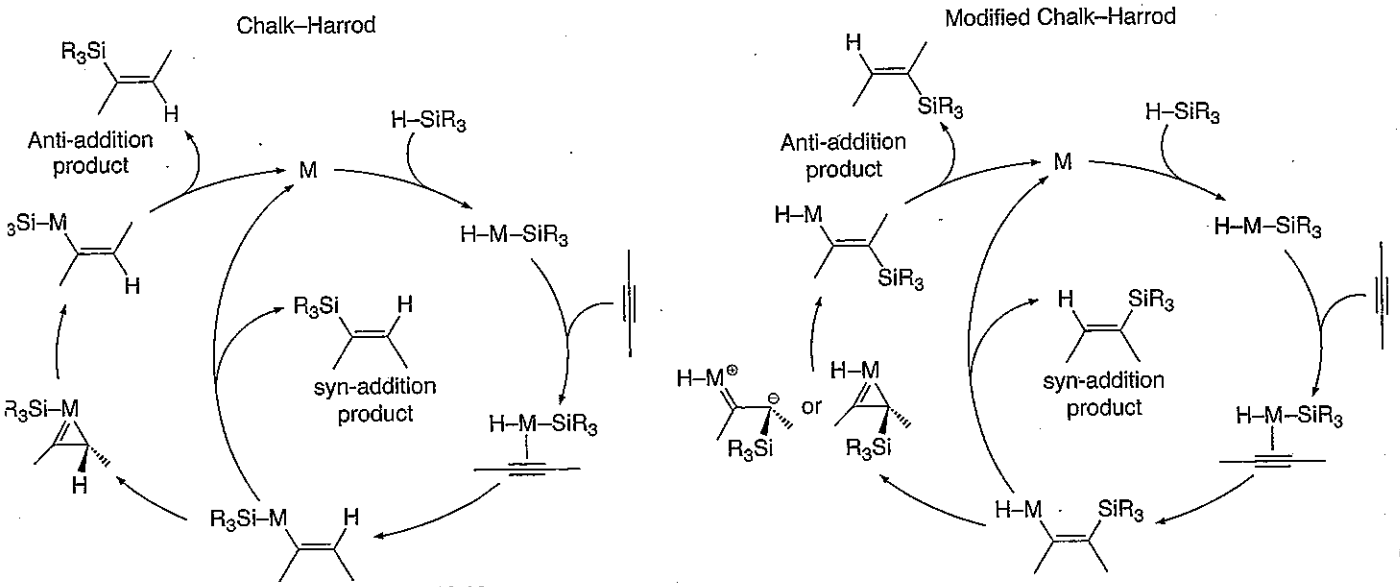
Hydrosilylation of alkynes



(16.31)

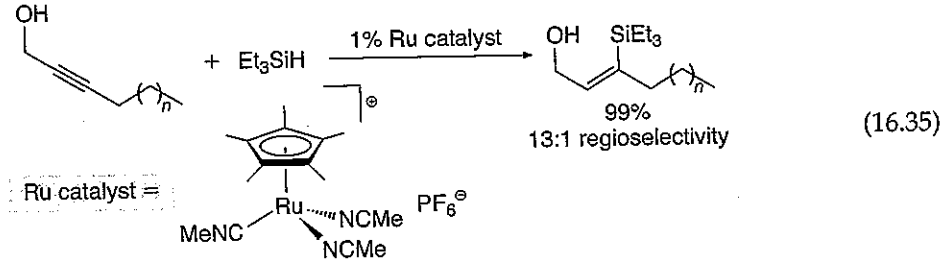
[Rh]	A	B	C
$[Rh(COD)_3]BF_4/2PPh_3$	5	95	0
$[RhCOD)Cl_2$	94	4	2

Mechanism



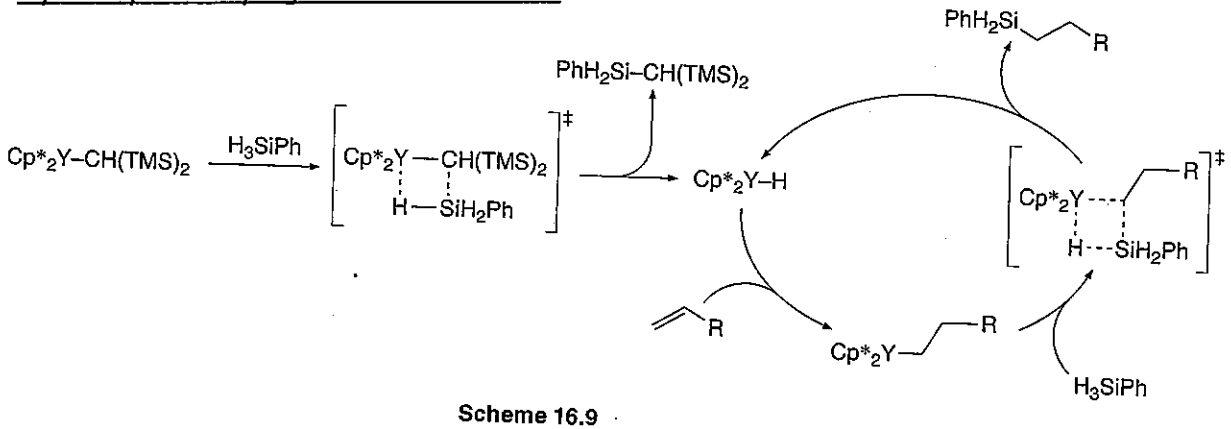
Scheme 16.10.
Trans hydrosilylation by a combination of Chalk–Harrod and modified Chalk–Harrod mechanisms for hydrosilylation and isomerization via η^2-vinyl intermediates.

Regioselective reaction using directing group



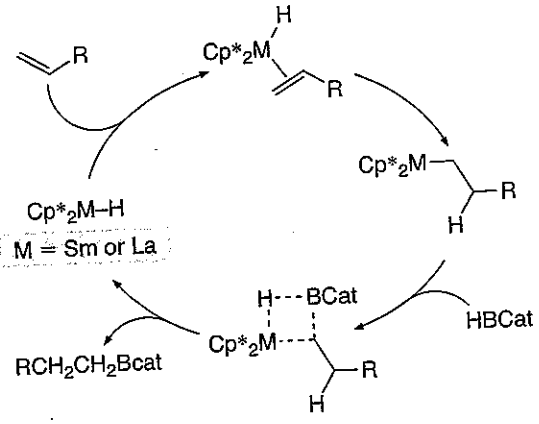
(16.35)

Hydrosilylation by sigma-bond metathesis



Scheme 16.9

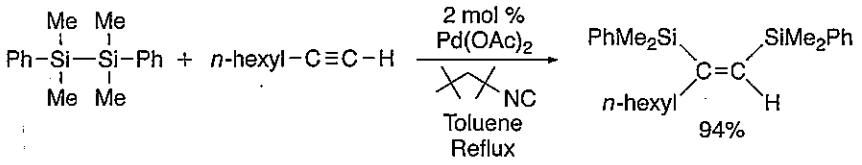
Cf. Hydroboration



Scheme 16.14

Hydrosilylation of ketones and imines: Many enentioselective examples

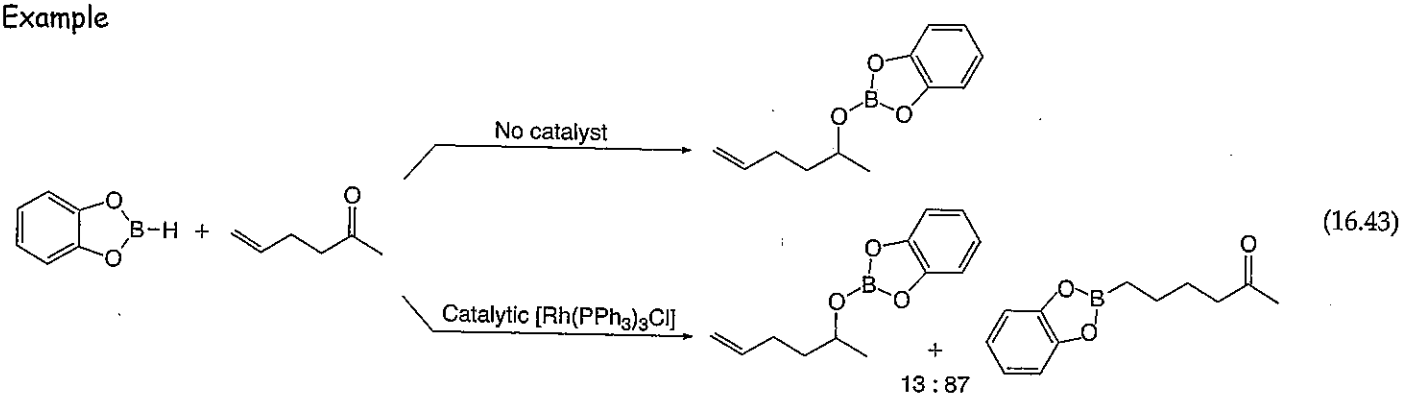
Disilylation



(16.40)

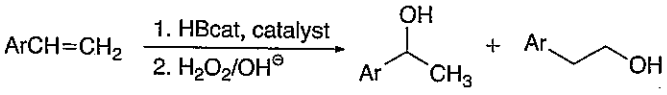
Hydroboration and Diboration

Example



(16.43)

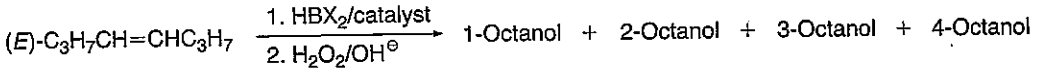
Regioselectivity



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

(16.44)

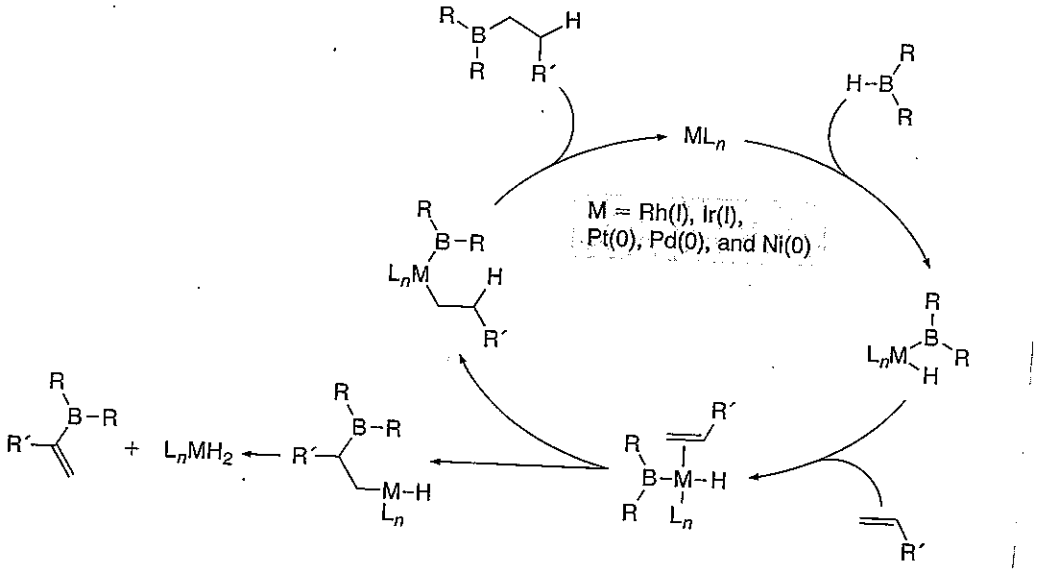


Borane	Solvent	1-ol	2-ol	3-ol	4-ol
HBcat	THF	0	0	0	100
HBpin	CH_2Cl_2	100	0	0	0

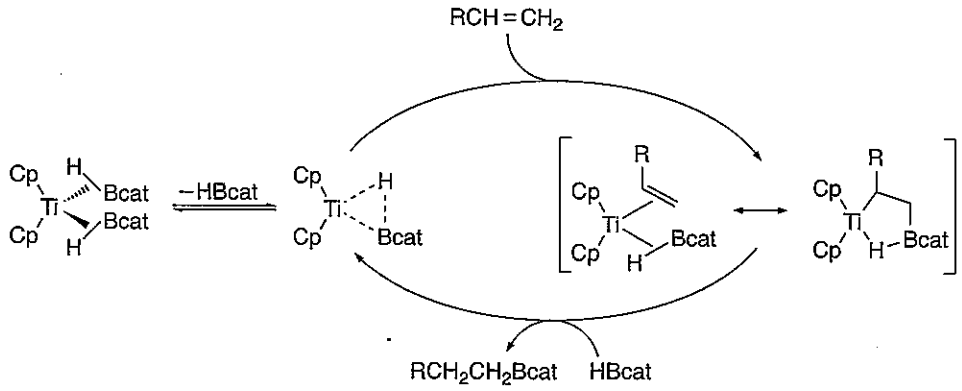
catalyst = $RhCl(PPh_3)_3$

(16.46)

Mechanism

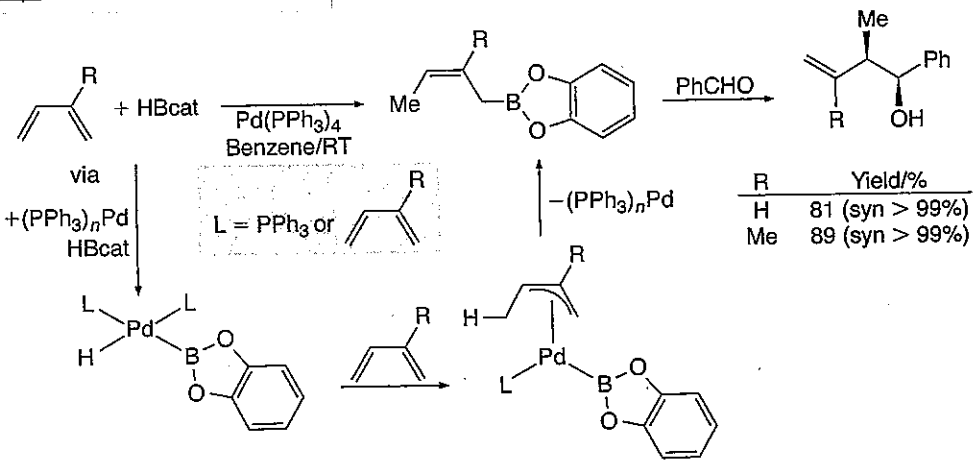


Scheme 16.11



Scheme 16.13

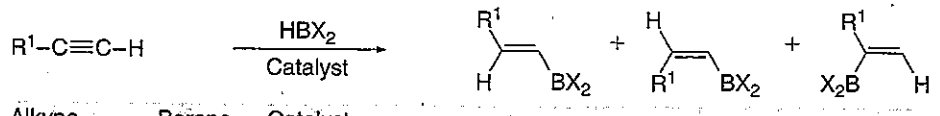
Hydroboration of dienes



R	Yield/%
H	81 (syn > 99%)
Me	89 (syn > 99%)

(16.47)

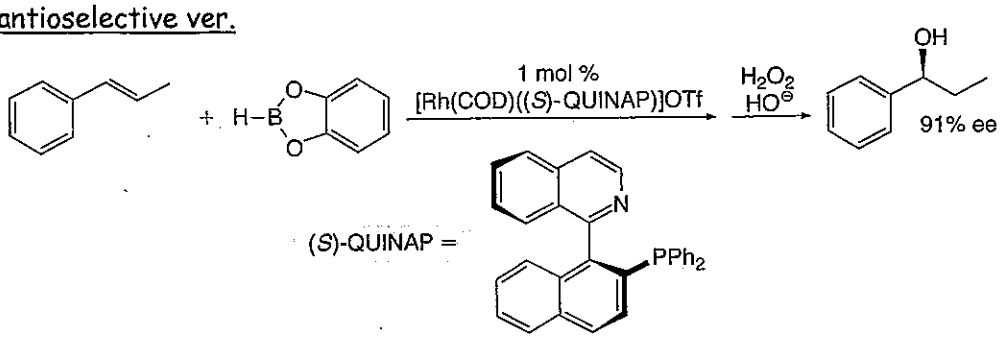
Hydroboration of alkynes



Alkyne	Borane	Catalyst			
p-Tol−≡−H	HBcat	$Cp_2Ti(CO)_2$	100	0	0
C_4H_9−≡−H	HBpin	$Rh(CO)(PPh_3)_2Cl$	99	0	1
p-Tol−≡−H	HBpin	$RhCl(PPh_3)_3$	48	0	52
Ph−≡−H	HBcat	$[Rh(cod)Cl]_2/4P^iPr_3$	1	99	0

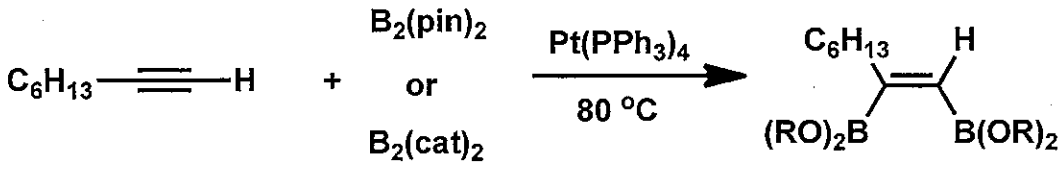
(16.48)

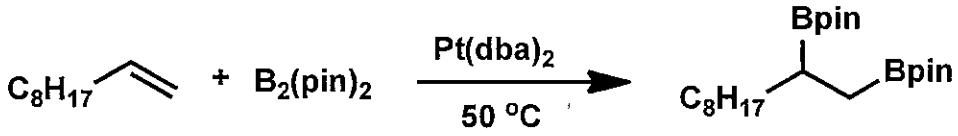
Enantioselective ver.



(16.49)

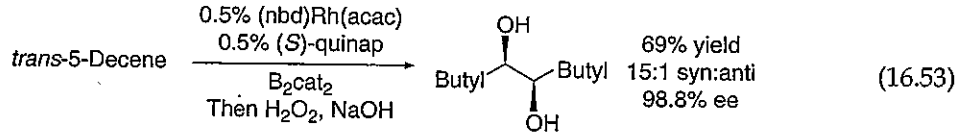
Diboration





Silylboration (R_3Si-B), Stanylboration (R_3Sn-B) of alkynes also proceed using Pd catalyst.

Asymetriv ver.



(16.53)

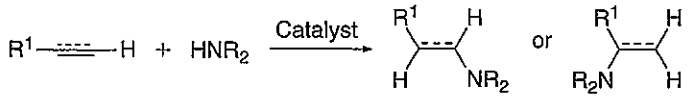
Organometallics Study Meeting

2011. 10. 13. Y. Tanaka

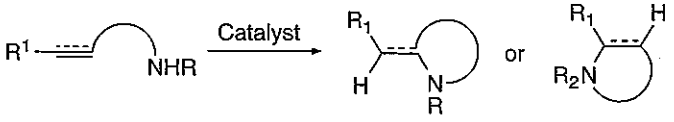
Chapter 16 Hydrofunctionalization and Oxidative Functionalization of Olefins

Today's topic: Addition of N-H and oxidative additions to olefins

Hydroamination



(16.54)

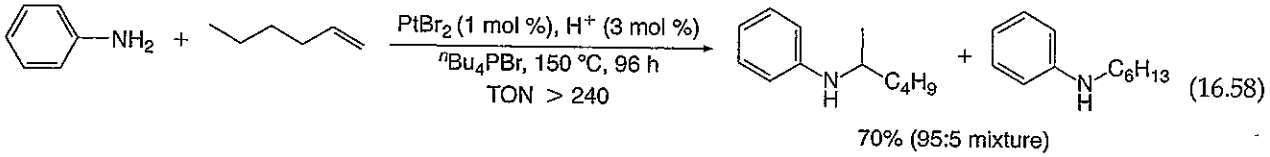


(16.55)

Selectivity: Depends on conditions (anti-Markovnikov hydroamination of alkenes have not been developed)

Via attack on π-olefin complexes (Catalyzed by Pd(Ⅱ), Pt(Ⅱ), cationic Rh)

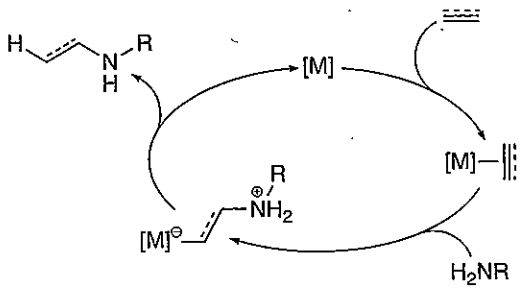
Example



(16.58)

70% (95:5 mixture)

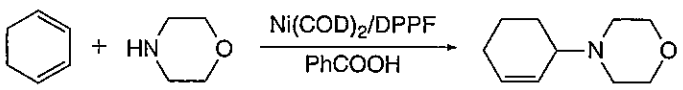
Mechanism



Scheme 16.16

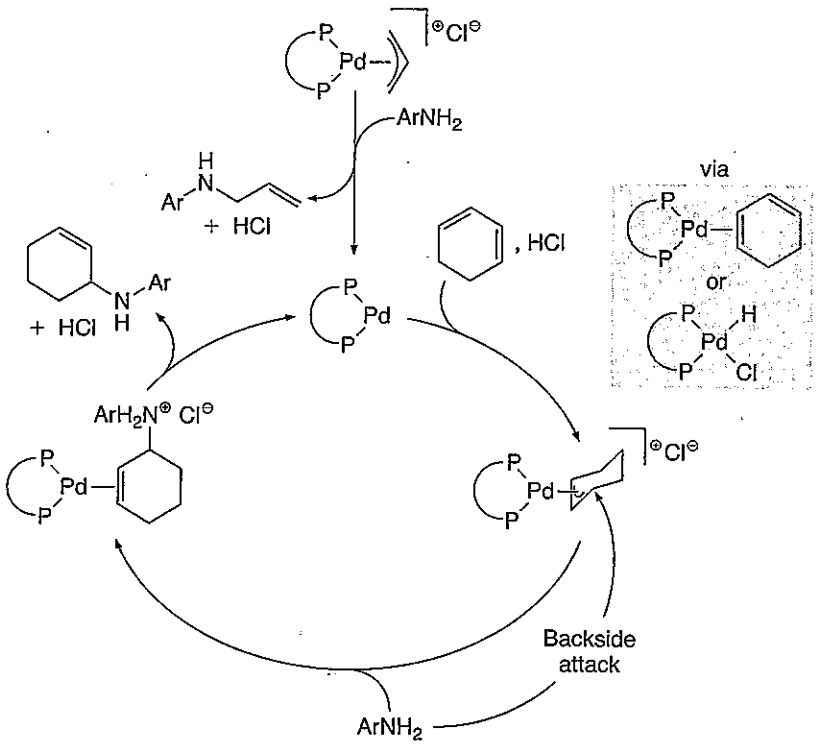
Via attack on π-allyl or π-benzyl complexes (Catalyzed by Ni(0) or Pd(0) + acid, Pd(Ⅱ), Pt(Ⅱ))

Example



(16.80)

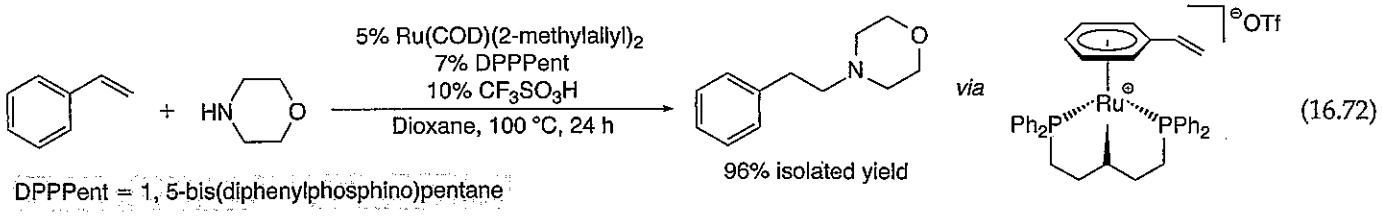
Mechanism



Scheme 16.17

Via attack on π-arene complexes (Catalyzed by Ru(II) +acid)

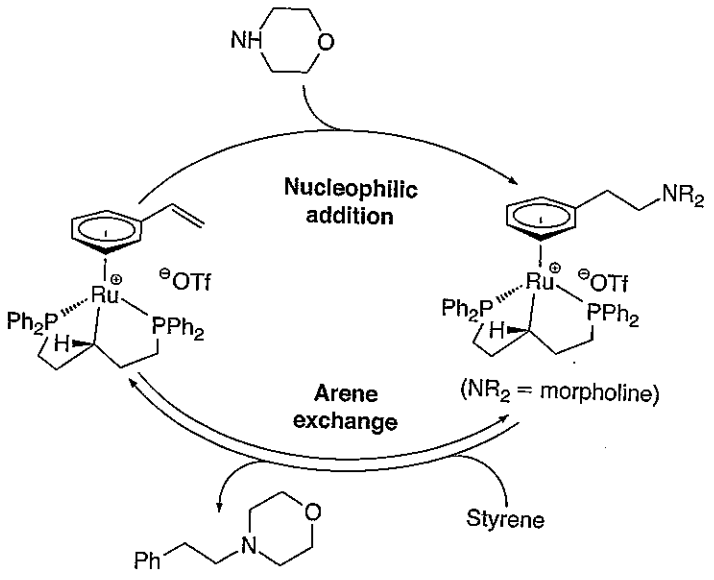
Example



(16.72)

DPPPent = 1, 5-bis(diphenylphosphino)pentane

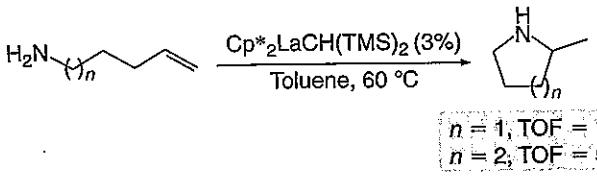
Mechanism



Scheme 16.18

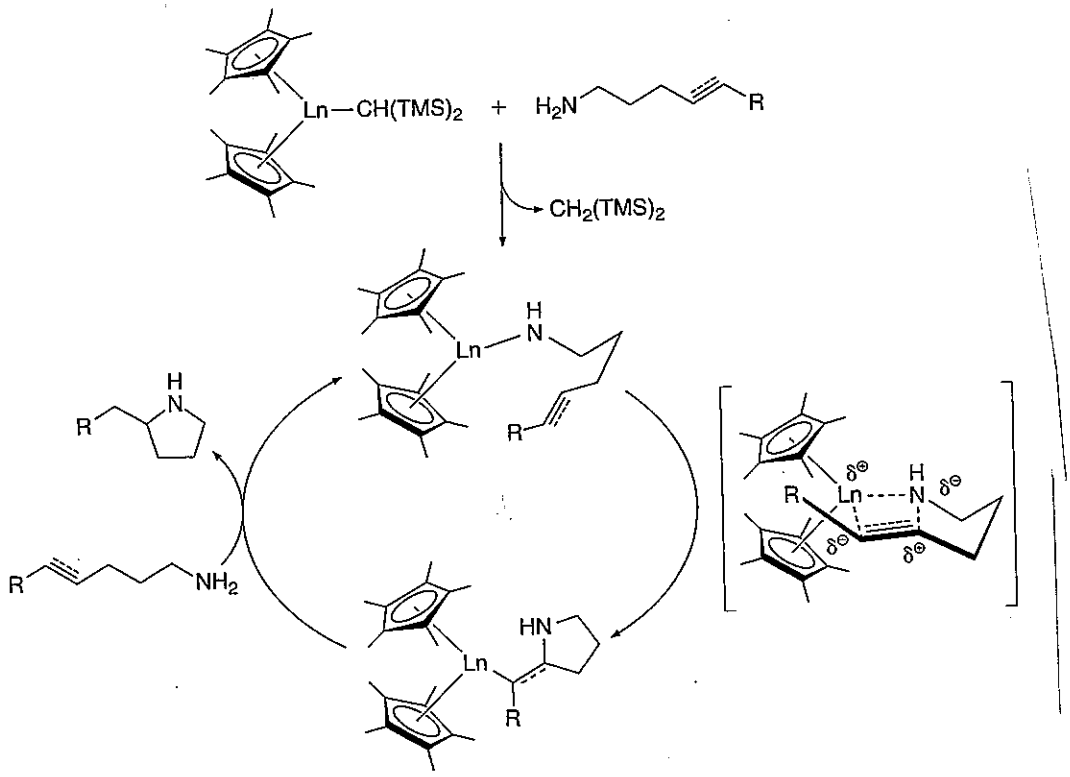
Via insertion into metal amides (Catalyzed by Ln)

Example

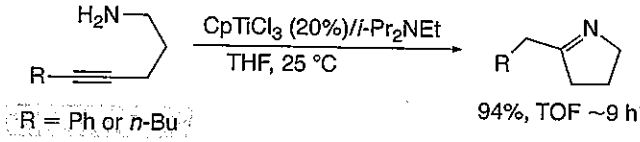


(16.61)

Mechanism



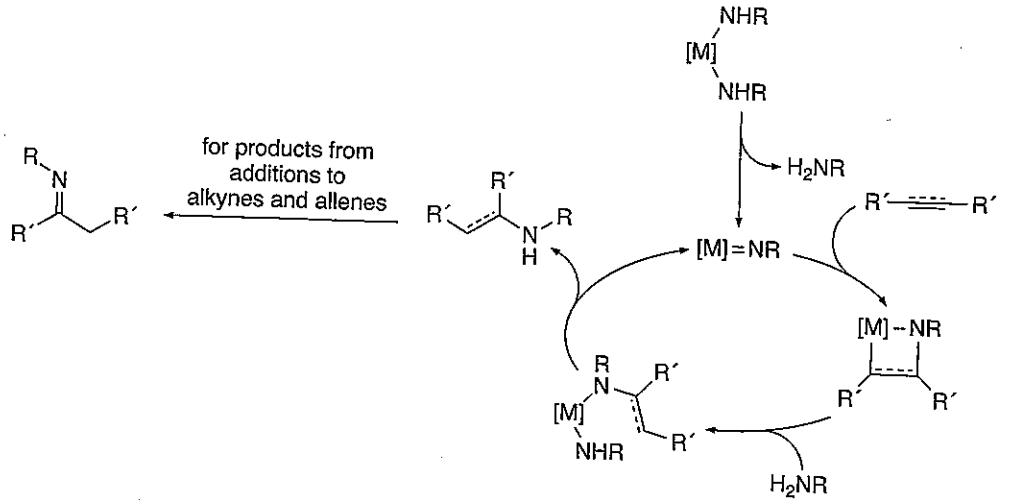
Via [2+2] cycloaddiitons (Catalyzed by Ti, Zr)



(16.85)

Mechanism

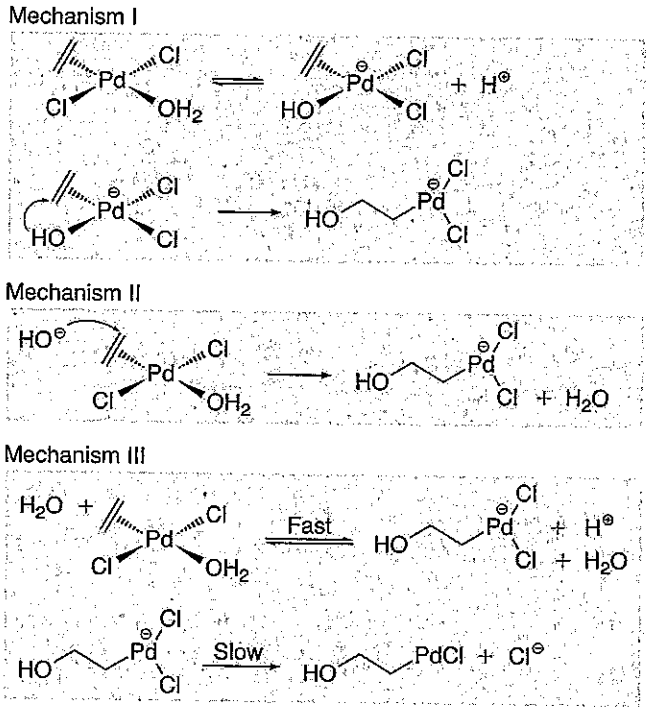
Sc. 20



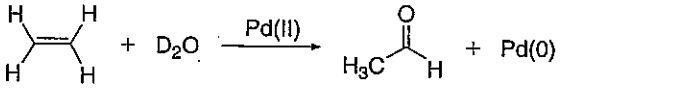
Scheme 16.20

Oxidative Functionalizations

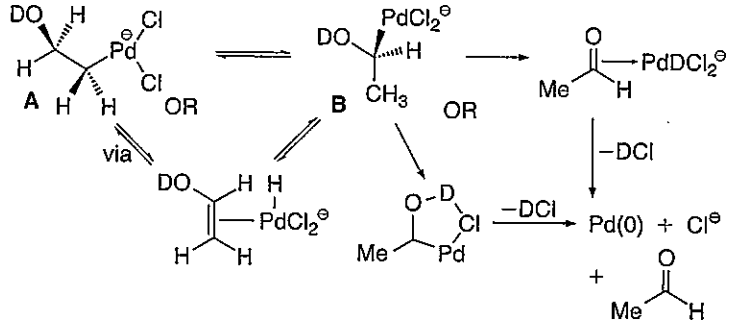
Wacker oxidation



Scheme 16.22



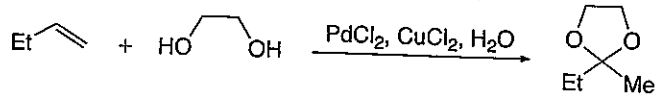
(16.99)



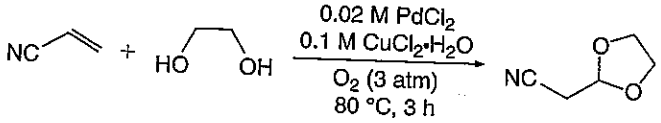
Scheme 16.23

Wacker type reactions

-Reaction with diol

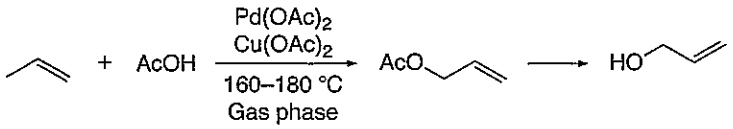


(16.104)

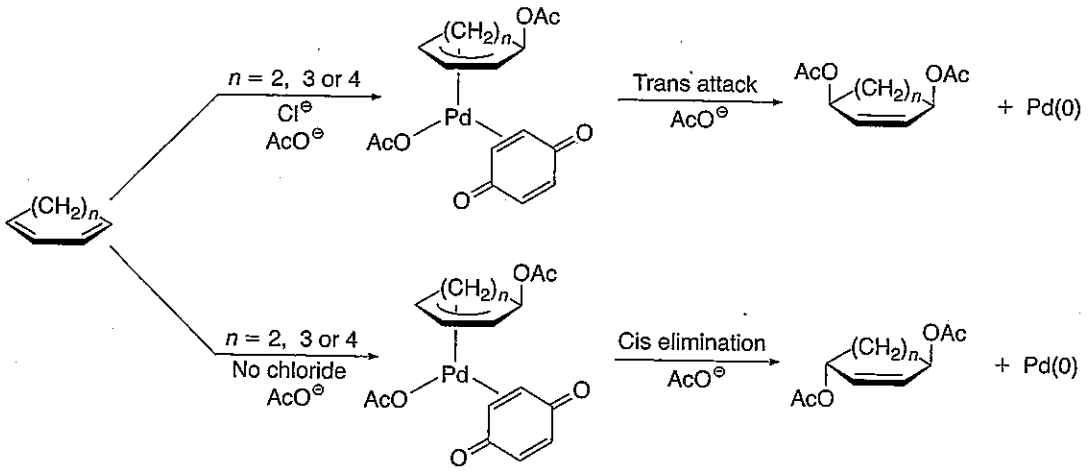


(16.105)

-Reaction with carboxylates

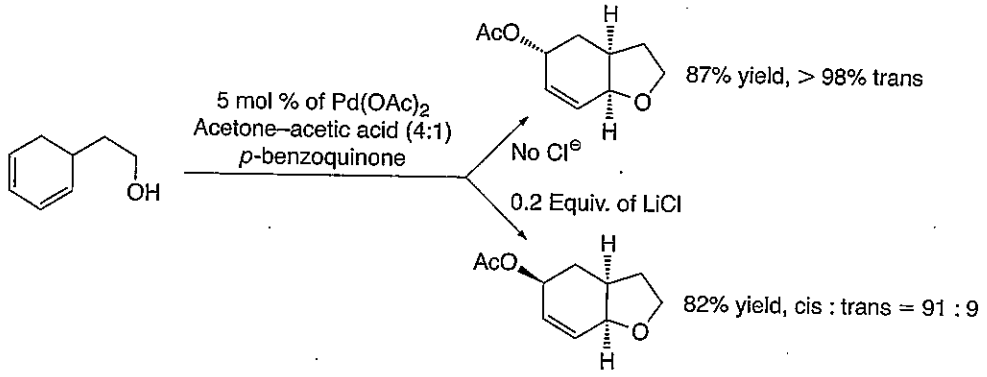


(16.108)

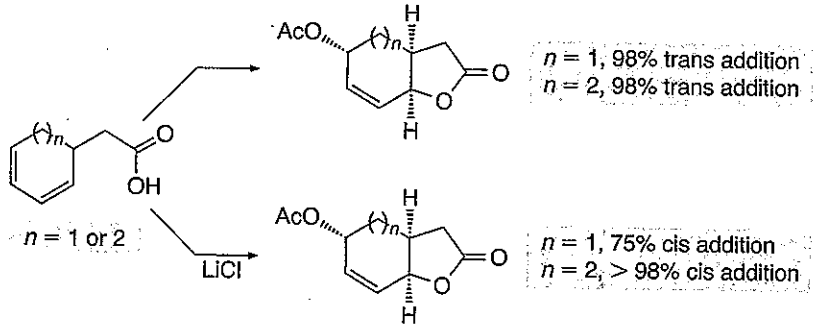


Scheme 16.26

-Intramolecular additions

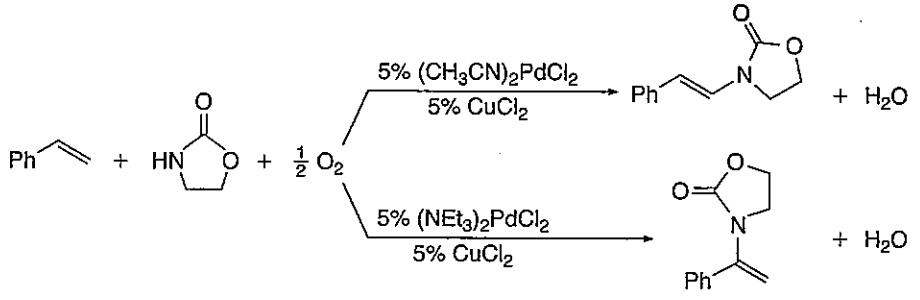


(16.113)

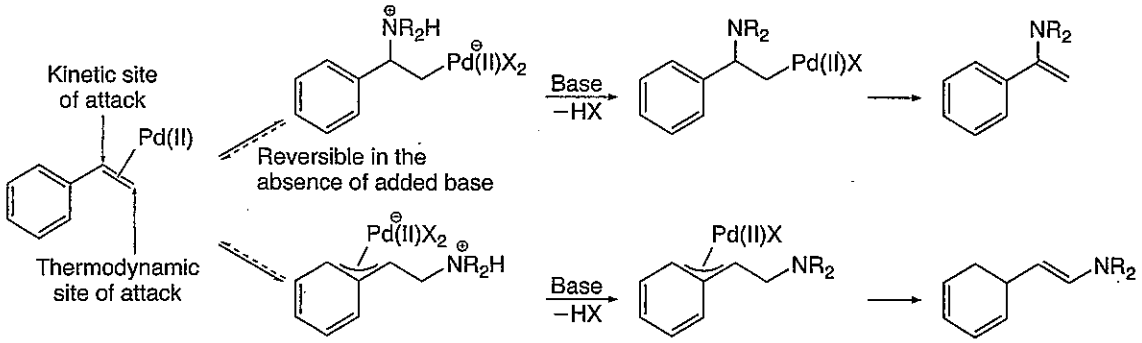


(16.114)

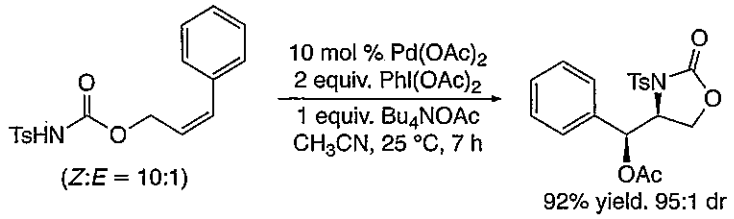
-Oxidative aminations



(16.117)



Scheme 16.31



(16.124)