5-4 MAIN-GROUP ORGANOMETALLICS

I. PREPARATION

- Direct Synthesis

$$Li + C_4H_4Br \longrightarrow C_4H_9Li + LiBr$$

$$Mg + C_6H_5Br \longrightarrow C_6H_5MgBr$$

Mixed metal synthesis:

$$2\ Na + Hg + 2\ CH_3Br \longrightarrow (CH_3)_2Hg + 2\ NaBr$$

$$4\ Na/Pb + 4\ C_2H_5Cl \longrightarrow (C_2H_5)_4Pb + 3\ Pb + 4\ NaCl$$

$\Delta H_f^\circ(NaX)$ boosts the driving force.

Side reactions:

$$RLi + CH_3CH_2OCH_2CH_3 \longrightarrow \left[CH_3CH_2{-}O{-}\underset{\displaystyle Li}{\underset{|}{C}}HCH_3\right] + RH$$

$$\downarrow$$

$$CH_3CH_2OLi + CH_2{=}CH_2$$

Transmetallation

$$Zn + (CH_3)_2Hg \longrightarrow (CH_3)_2Zn + Hg$$

$\triangle H = -35$ kJ/mol

This general method may be applied to M = Li ~ Cs, Be ~ Ba, Al, Ga, Sn, Pb, Bi, Se, Te, Zn, Cd.

Metal exchange

$$4\ PhLi + (CH_2{=}CH)_4Sn \longrightarrow 4\ (CH_2{=}CH)Li + Ph_4Sn\downarrow$$

This method is useful for making certain organolithium compounds from derivatives of less electropositive metals.

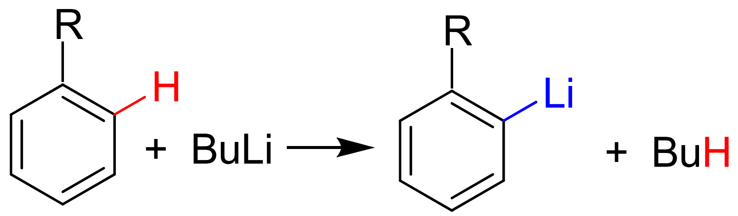
Metal Halogen Exchange

$$n\text{-}BuLi + PhX \longrightarrow n\text{-}BuX + PhLi$$

Acidity: *n*-Bu–H < Ph–H

Metallation of C–H acids

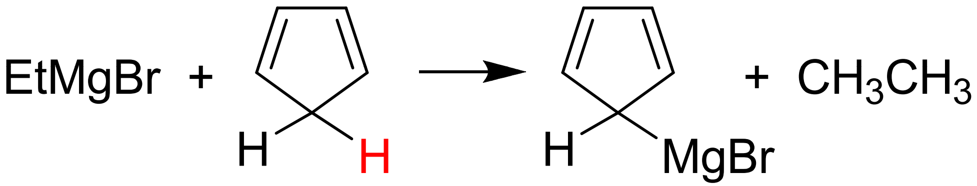
Metallation (replacement of H by M) are acid/base equilibrium. The arenes with their higher acidities are appropriate substrates and the method is particularly valuable for the preparation of aryllithium compounds.

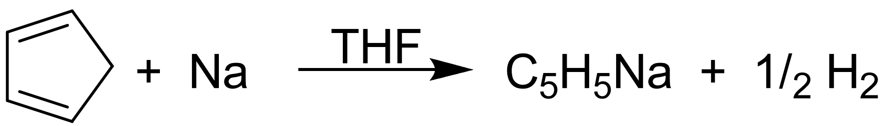


R = MeO, Me_2N, $CONMe_2$, SO_2Me, etc.

$$PhNa + PhCH_3 \rightleftharpoons PhH + PhCH_2Na$$

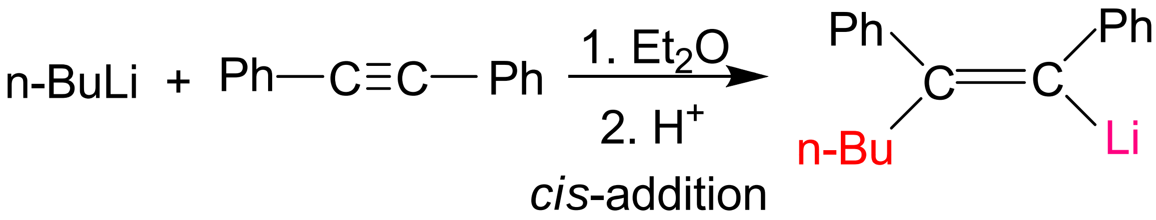
$$EtMgBr + RC{\equiv}CH \longrightarrow RC{\equiv}CMgBr + CH_3CH_3$$





Carbometallation and Hydrometallation

Carbometallation

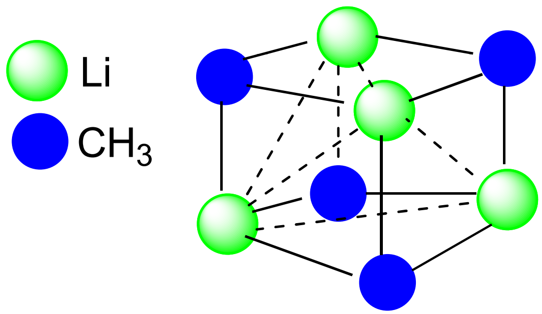


Hydroalumination

$$(C_2H_5)_2Al{-}H + H_2C{=}CH_2 \longrightarrow (C_2H_5)_2Al{-}CH_2CH_3$$

II. Organolithium reagents

- Organolithium reagents can be aggregated, with lithium coordinating to more than one carbon atom and carbon coordinating to more than one lithium atom.

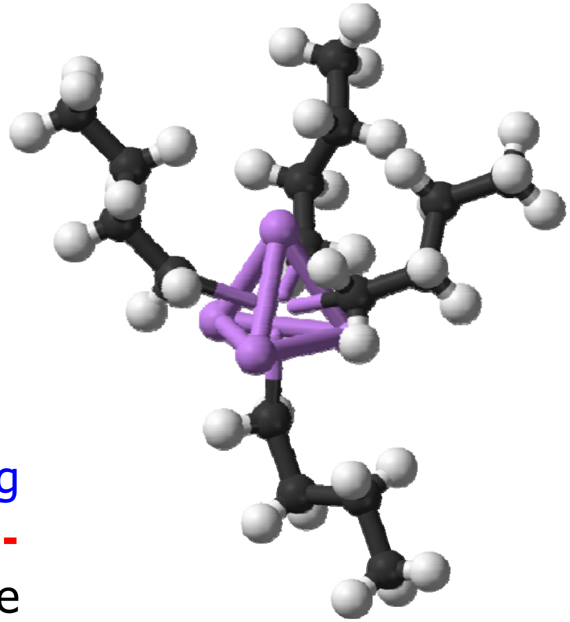


d (Li—C) = 2.31 Å
d (Li—Li) = 2.56Å
d (C—C) = 3.68
Li−C−Li 68°

Schematic drawing of the unit $(LiCH_3)_4$

Solid methyllithium: cubic body-centered packing of **$(LiCH_3)_4$** units, the latter consisting of **Li_4-tetrahedron** with methyl groups capping the triangular faces. 立方体心堆积

☞ In the aggregates $(LiR)_n$, the "electron deficiency" is compensated for by the formation of multicenter bonds.



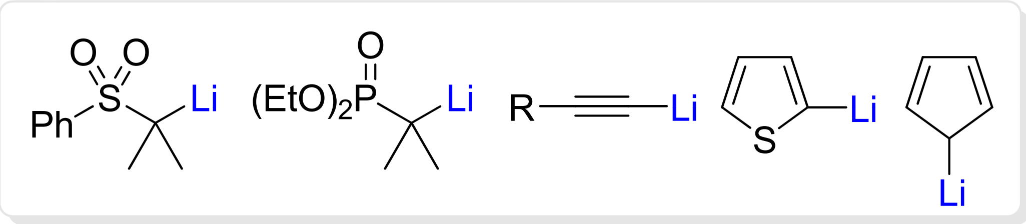
n-Butyllithium

☞ Three general factors affect aggregation: the electrostatic interaction between opposite charges, the coordination sphere of lithium (solvent molecules or Lewis base) and the steric hindrance of the hydrocarbon part.

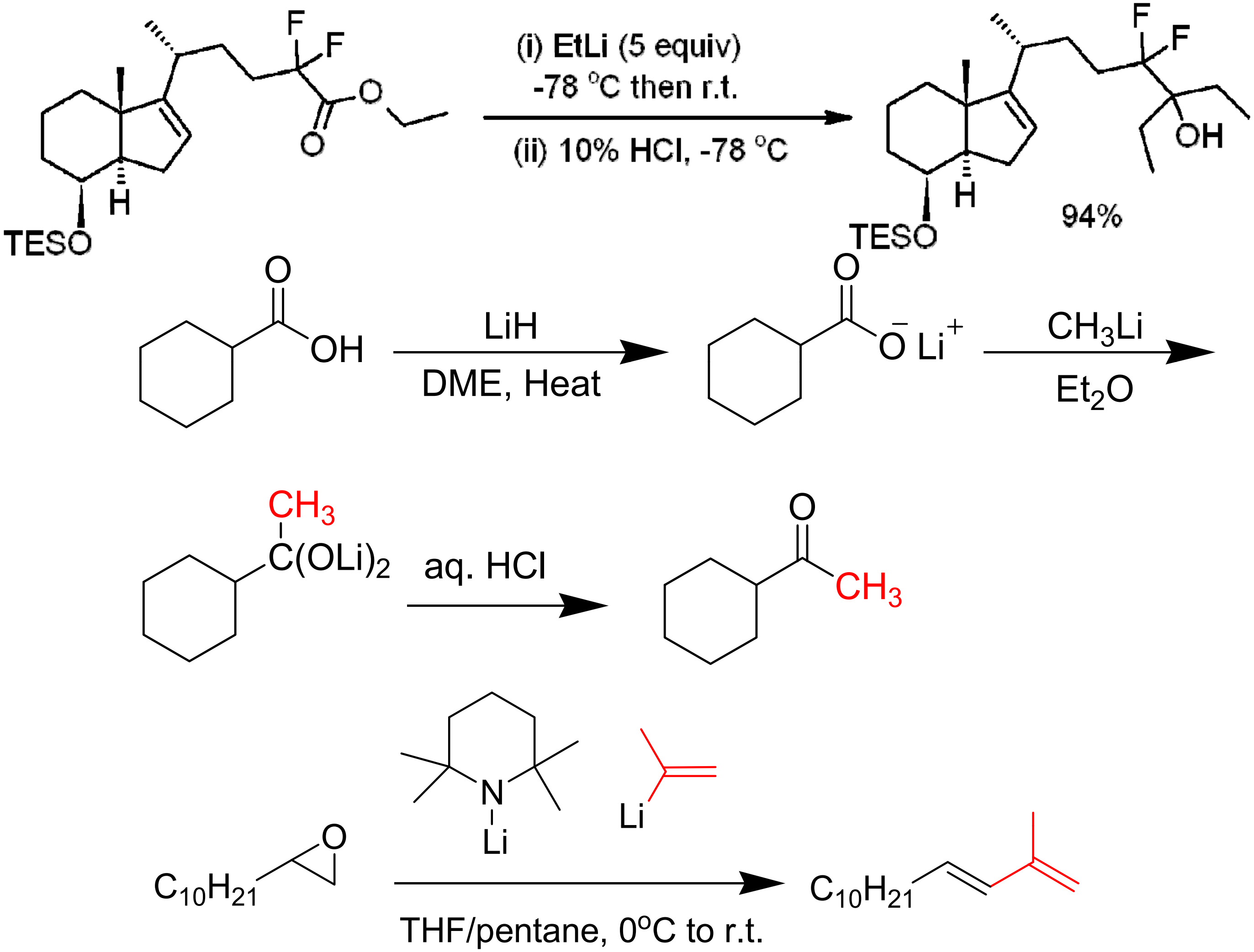
LiR	Solvent	Aggregation
$LiCH_3$	hydrocarbon	Hexamer (Li_6 octahedron)
	THF, Et_2O	Tetramer (Li_4 tetrahedron)
	$Me_2NCH_2CH_2NMe_2$	monomer
n-BuLi	cyclohexane	hexamer
	Et_2O	tetramer
t-BuLi	hydrocarbon	tetramer
PhLi	THF, Et_2O	dimer
$PhCH_2Li$	THF, Et_2O	monomer
C_3H_5Li (allyl)	THF	monomer

➢ REACTIONS

- Metalation or Li/H exchange reaction: The metalation reaction is an important synthetic method for the preparation of many organolithium compounds.



- Reaction with ketones and aldehydes to alcohols.
- Reaction with carboxylic acid salts and acid chlorides to the corresponding ketone.
- Reaction with oximes to the corresponding amines. (肟)
- Reaction with isonitriles to the corresponding lithium aldimine (醛亚胺). Subsequent hydrolysis effectively converts the organolithium compound to its aldehyde.
- Reaction with certain epoxides to the corresponding alkenes.

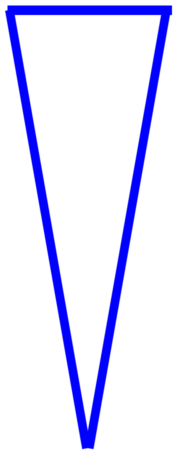


Organic Syntheses, Vol. 85, p1 (2008)

III. Organomagnesium and Organozinc

➢ In many ways the chemistry of group 2 elements (the alkaline earth metals) mimics that of group 12 elements because both groups have filled s shells for valence electrons.

Group 2	Ba Sr Ca **Mg** Be	Electropositive character of the metal
		and
Group 12	**Zn** Cd Hg	reactivity of organometallics in heterolytic reactions
		decreases



Among the organometallic compounds of groups 2 and 12, organomagnesium compounds are of prime importance because of their application in organic synthesis. Organomagnesium compounds combine in a unique way high reactivity and ease access.

Grignard reagent

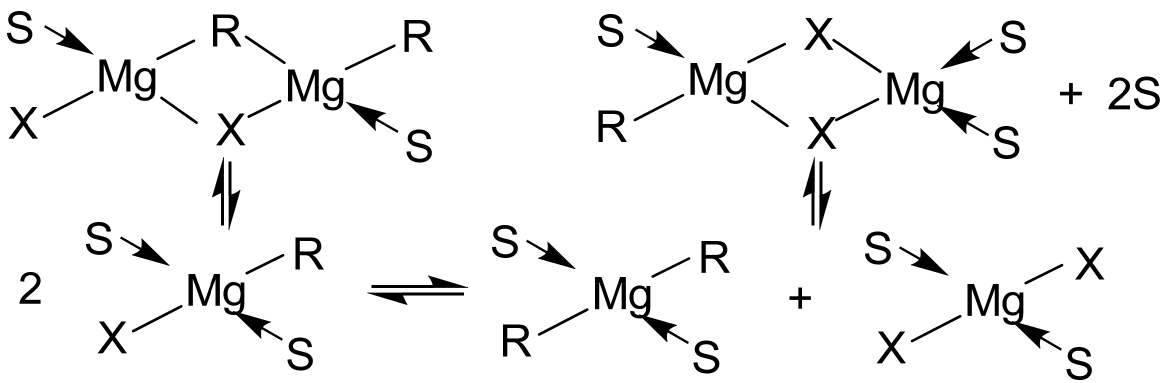
➢ Grignard reagents are formed via the action of an alkyl or aryl halide on magnesium metal. Typical solvents are Et_2O and THF. The reaction proceeds through single electron transfer..

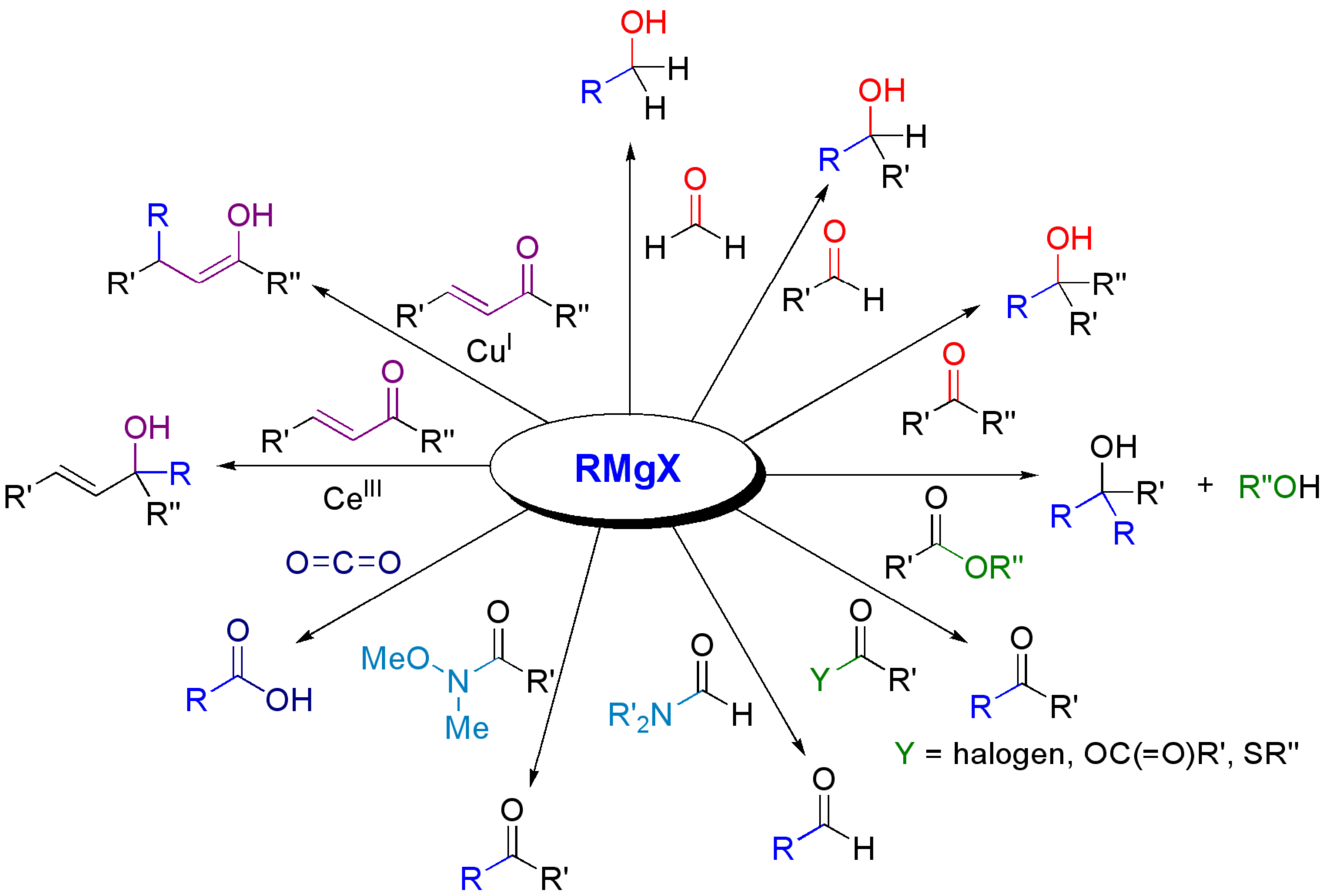
$$Mg + RX \xrightarrow{Et_2O} RMgX(Et_2O)_n \qquad X = Br, I$$

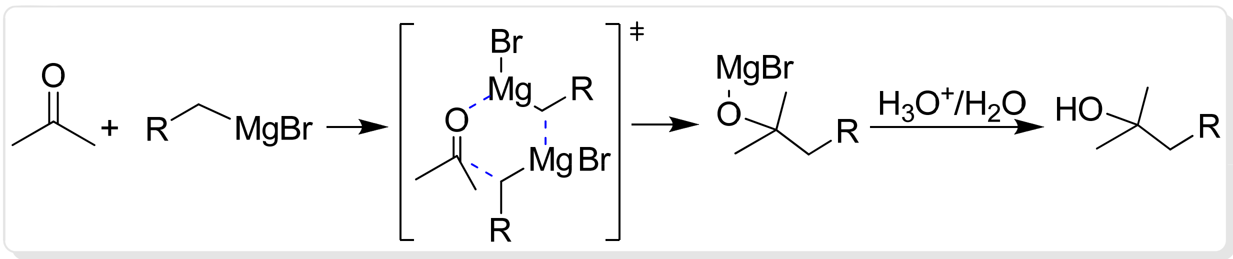
☞ The addition of I_2 activates the Mg surface; MgI_2 thus formed, binds the last traces of water in the reaction mixture.

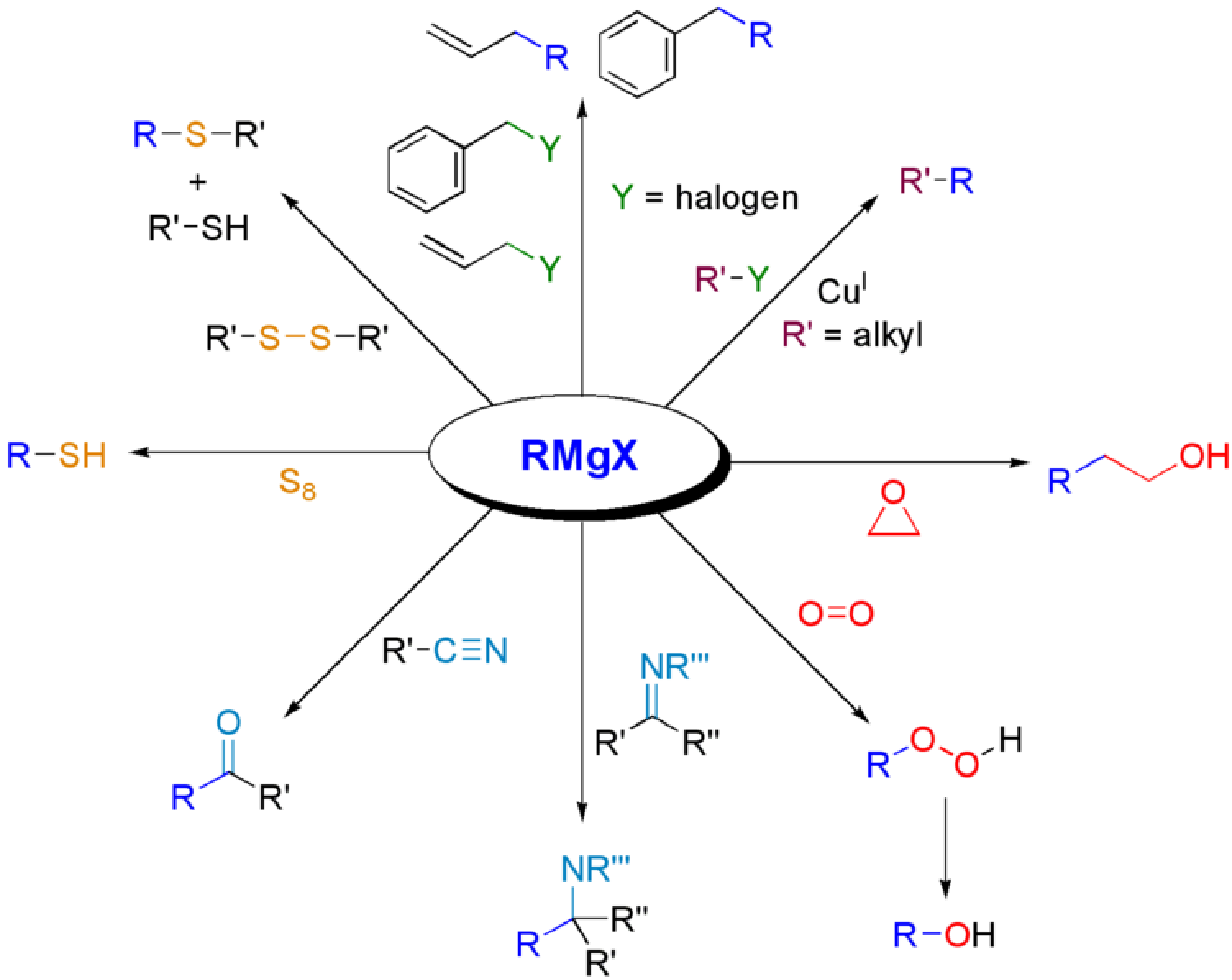
☞ Schlenk equilibrium, Grignard reagents form varying amounts of diorganomagnesium compounds (R = organic group, X = halide):

$$2\ RMgX \rightleftharpoons R_2Mg + MgX_2$$



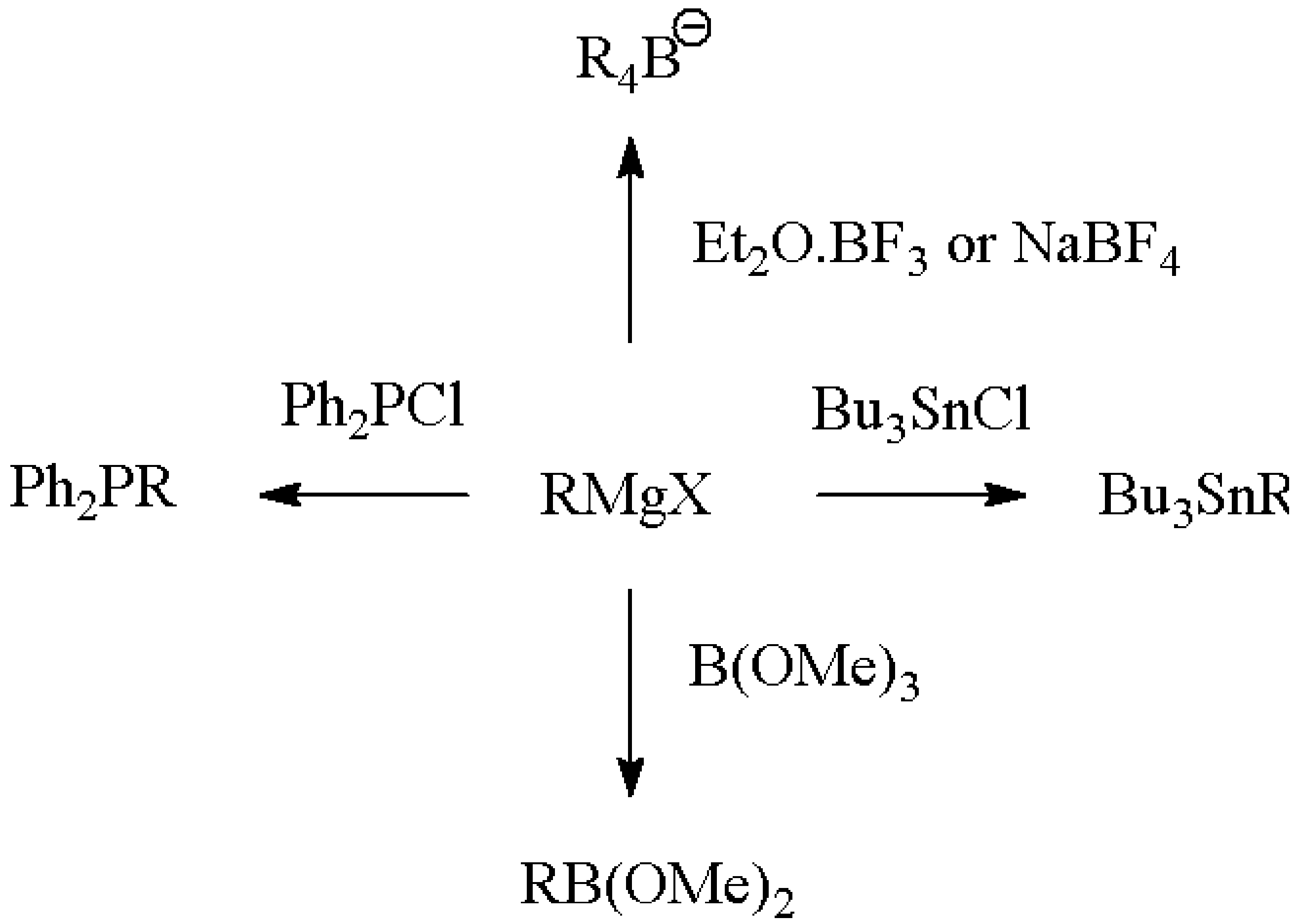

RMgX
Cu^I
Ce^III
O=C=O
MeO
Me
R'2N
Y = halogen, OC(=O)R', SR''
R''OH


MgBr
Br
Mg
MgBr
‡
H3O+/H2O
HO



RMgX
Y = halogen
R'–Y
Cu^I
R' = alkyl
R'–R
R–S–R'
+
R'–SH
R'–S–S–R'
R–SH
S8
OH
O=O
R–OH
H
R'–C≡N
NR'''
R'
R''
O

- Also the Grignard reagent is very useful for forming carbon-heteroatom bonds.

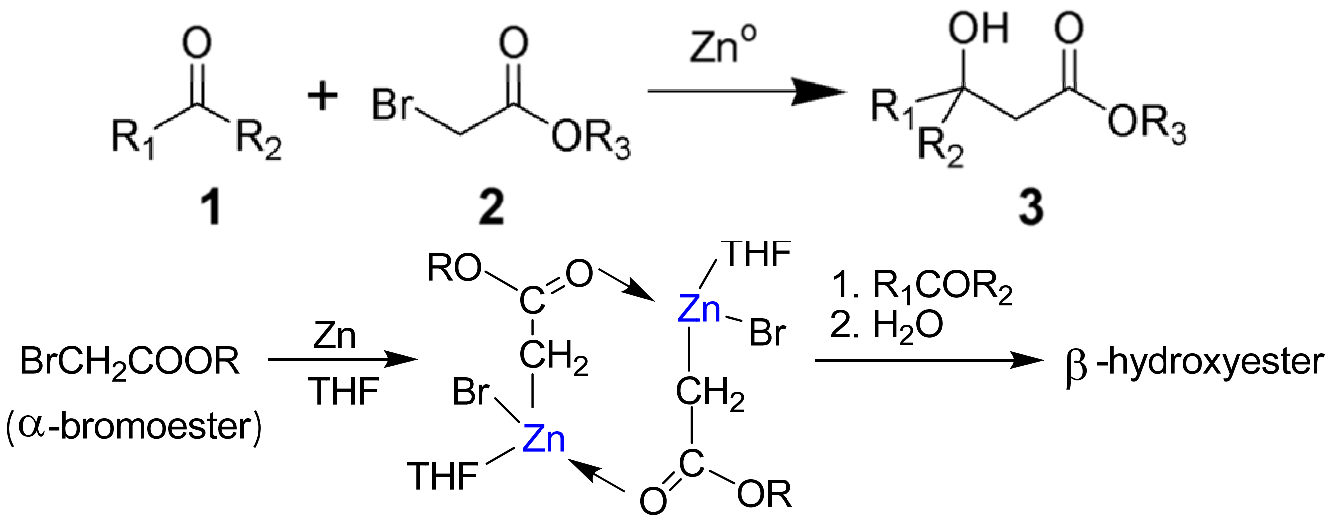


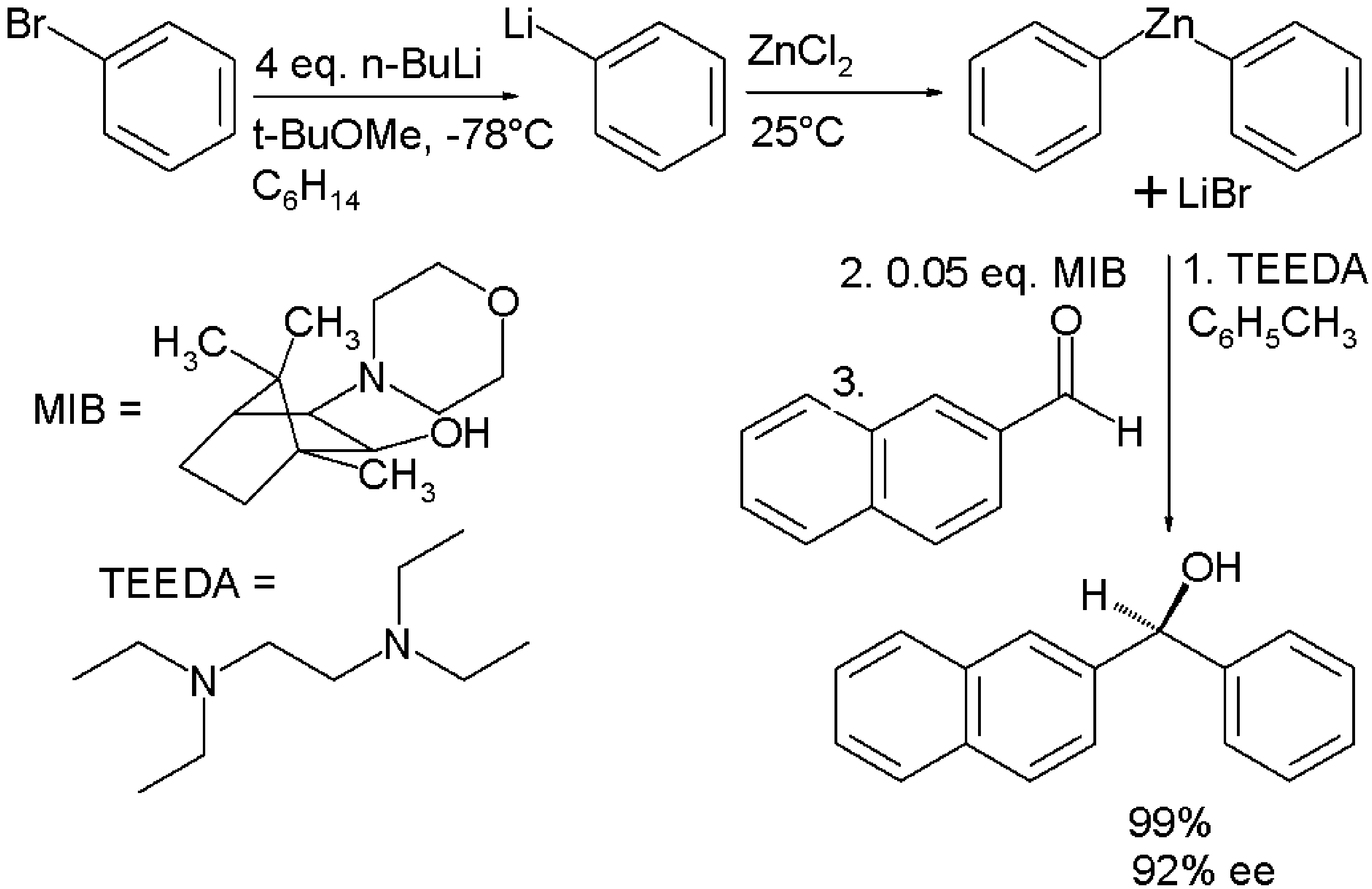
ORGANOZINC COMPOUND

Several general methods:

- Oxidative addition. The original Et_2Zn synthesis by Frankland was an oxidative addition of C_5H_2I to Zn metal with hydrogen gas as a "protective" blanket.
- Halogen zinc exchange. Two main halogen zinc exchange reactions are *iodine zinc exchange* and *boron zinc exchange*.
- Transmetalation. In a typical transmetalation, diphenylmercury reacts with zinc metal to Ph_2Zn and metallic Hg in Et_2O.

Reformatsky reaction




Br
4 eq. n-BuLi
t-BuOMe, -78°C
C6H14
Li
ZnCl2
25°C
Zn
+ LiBr
1. TEEDA
C6H5CH3
2. 0.05 eq. MIB
3.
O
H
OH
H
99%
92% ee
MIB =
H3C
CH3
N
O
OH
CH3
TEEDA =
N
N

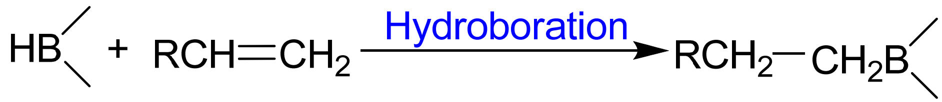
IV. Organometallics of the Boron Group

A. Organoboron Compounds

Organoborane or organoboron compounds are organic derivatives of BH_3, for example trialkyl boranes. Organoboron compounds are important reagents in organic chemistry enabling many chemical transformations, the most important one called hydroboration.

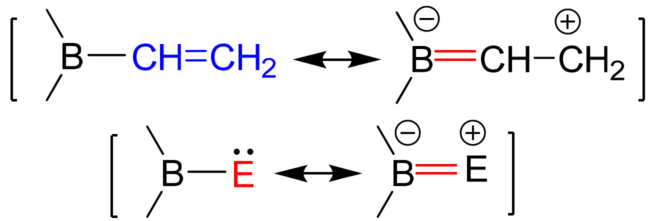
$$Et_2O{\cdot}BF_3 + 3RMgX \longrightarrow R_3B + 3MgXF + Et_2O$$

(R = alkyl, aryl)

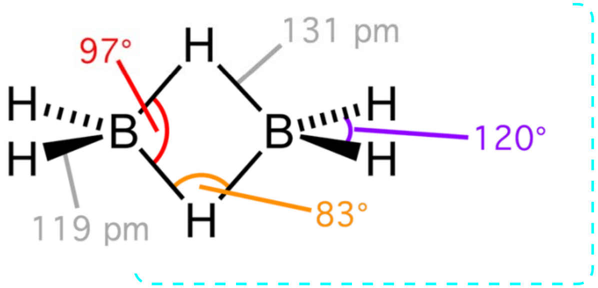


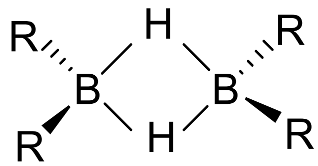
➢ Characteristics:

- C–B bond, low polarity (electronegativity C 2.55, B 2.04)
- Electron-rich groups like vinyl or phenyl provide the C–B bond with partial double bond character.

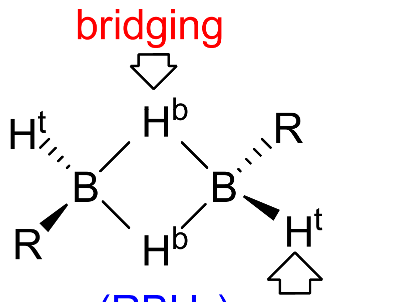


➢ Organoboron hydrides R_2BH and RBH_2 form dimers which always display hydride bridges rather than alkyl bridges:





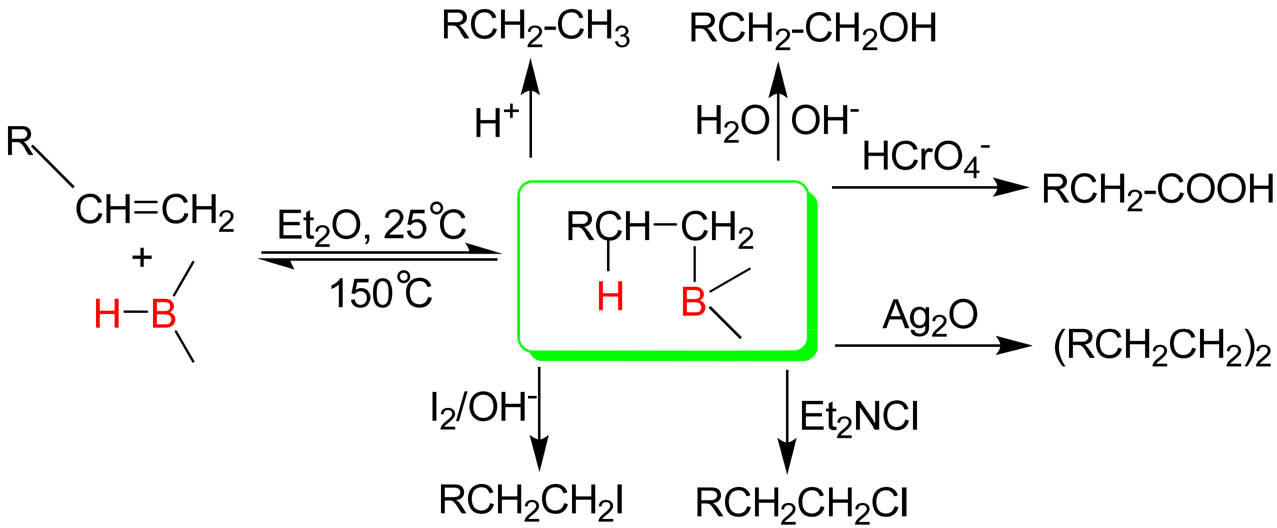
$(R_2BH)_2$



$(RBH_2)_2$

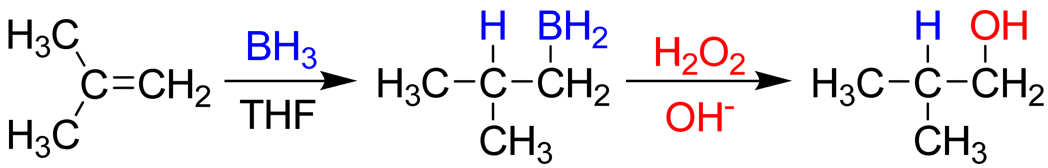
	Stretching frequency	Intensity
$\nu(B-H^b-B)$ symm.	1500-1600 cm^{-1}	strong
$\nu(B-H^b-B)$ asymm.	1850	medium
$\nu(B-H^t)$	2500-2600	

➢ Hydroboration-oxidation reaction. One of the most versatile methods in organic synthesis is hydroboration. Herein, rather than the resulting organoboranes themselves, the products of their subsequent reactions are important:

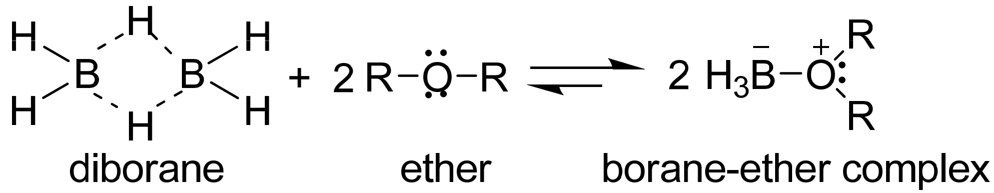


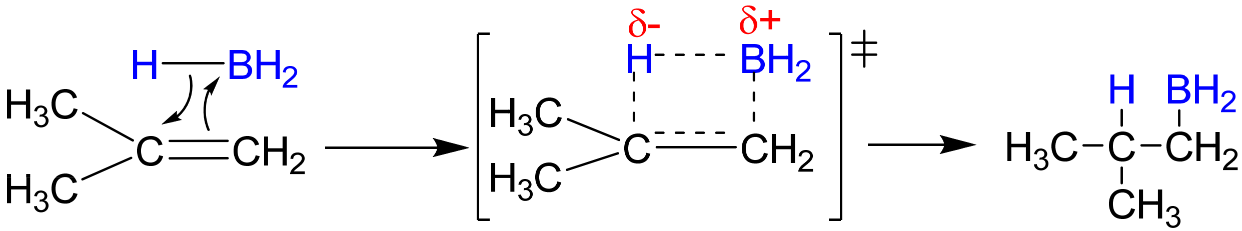
☞ Regioselective — anti-Markovnikov addition, the hydrogen adds to the most-substituted carbon. The reason is that boron is less electronegative than hydrogen.

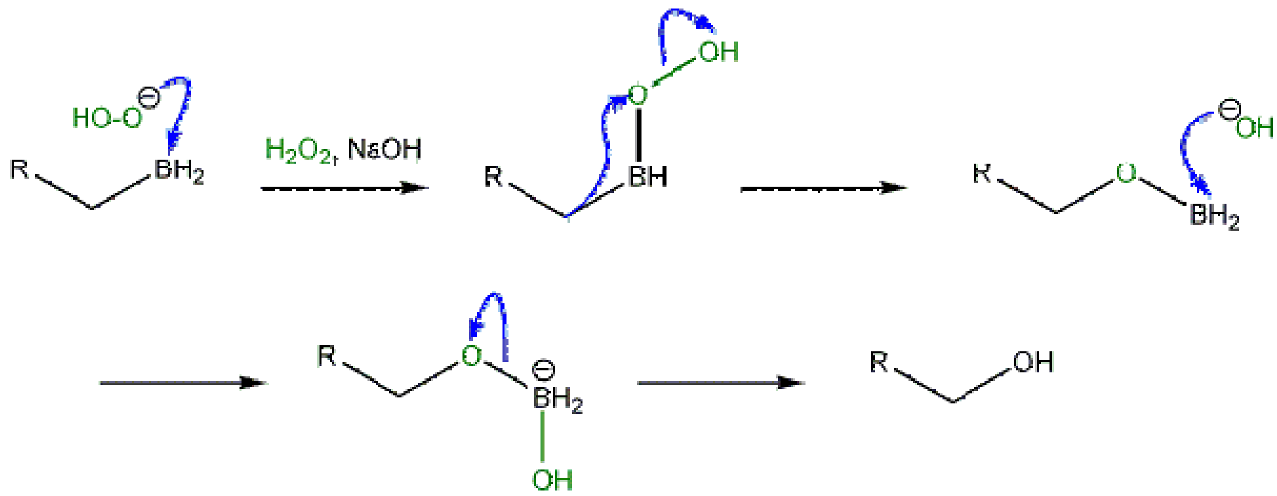
☞ Stereospecificity — addition in a *syn* mode, that is on the same face of the alkene.


BH3
THF
H2O2
OH-

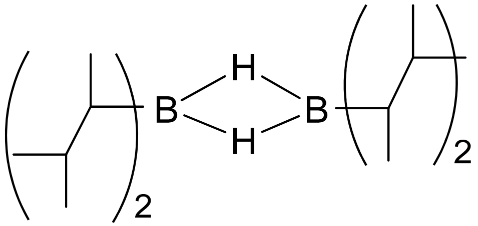
Mechanism:

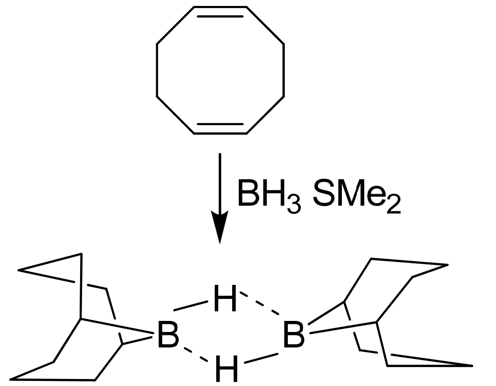

diborane
ether
borane-ether complex


δ-
δ+

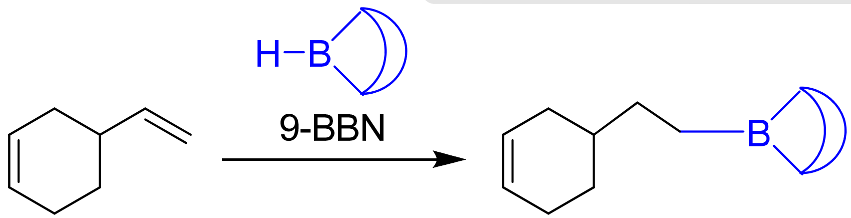

H2O2, NaOH

☞ The so called anti-Markovnikov addition is most pronounced when the boron compound has very bulky substituents. Thus, bis-(1,2-dimethylpropyl)borane ("disiamylborane") adds to 1-pentene, leaving 2-pentene, unaffected (selectivity > 99%).


disiamylborane

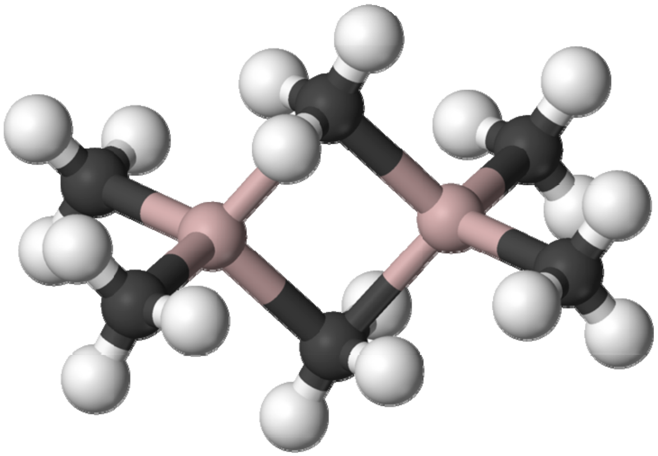


Bis-(9-borabicyclo[3.3.1]nonane)
9-BBN



B. Organoaluminum Compounds

The chemistry of organoaluminium compounds can be understood in terms of the dynamic nature of the C−Al bond and the high Lewis acidity of the monomeric species.



Al_2Me_6 exists as a dimer. the metalloids are connected by a 3-center-2-electron bond as with diborane.

^{1}H NMR: At −25°C the 1H NMR of Me_6Al_2 comprises two signals in 1:2 ratio, as expected from the solid state structure. At 20°C, only one signal is observed because exchange of terminal and bridging methyls is too fast to be resolved by NMR.

➢ **Laboratory preparation**

- Metathesis with RLi or RMgX

$$AlCl_3 + 3\ BuLi \rightarrow Bu_3Al + 3\ LiCl$$

- Transmetalation

$$2\ Al + 3\ HgPh_2 \rightarrow 2\ AlPh_3 + 3\ Hg$$

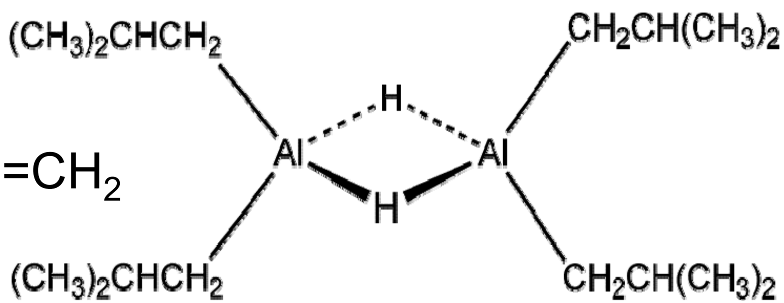
➢ Industrially, simple aluminium alkyls (Me, Et) can be prepared by a direct process:

$$4\ Al + 6MeCl \rightarrow 2\ Me_3Al_2Cl_3 \rightarrow Me_4Al_2Cl_2 + Me_2Al_2Cl_4 \rightarrow Me_4Al_2Cl\ (l) + 2\ Na[MeAlCl_3]\ (s) \rightarrow \mathbf{Me_3Al} + Al + 6\ NaCl$$

- Diisobutylaluminium hydride is Prepared by β-hydride elimination:

$$(i\text{-}Bu_3Al)_2 \rightarrow (i\text{-}Bu_2AlH)_2 + 2(CH_3)_2C{=}CH_2$$

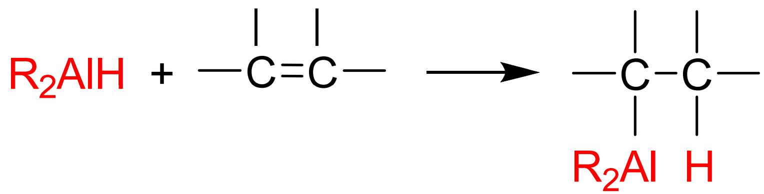
DIBAl-H



➢ Reactions

- Organoaluminium compounds are hard Lewis acids and readily form adducts with bases such as pyridine, THF and amines.
- Reaction with protonic reagents:

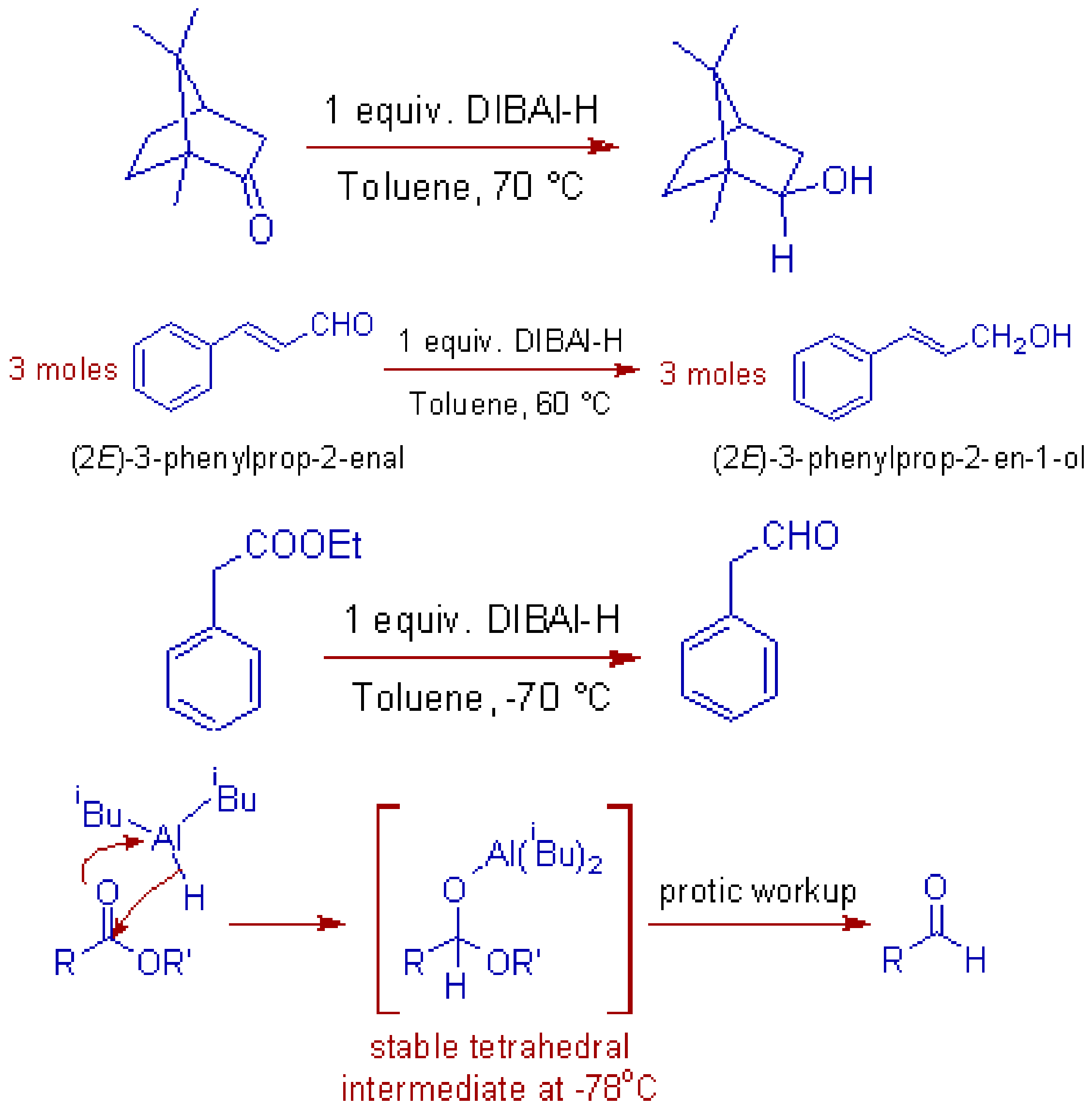
  $AlR'_3 + ROH \rightarrow (R'_2Al{-}OR)_n + R'H$
- Hydroalumination of C=C double bonds



☞ Readiness: $RCH{=}CHR < R_2C{=}CH_2 < RCH{=}CH_2 < CH_2{=}CH_2$

☞ Stereosepecity (*cis*) and regioselectivity (anti-Markvonikov).

H——AlR'$_2$	$RCH{=}CH_2$	$PhCH{=}CH_2$
anti-Markvonikov	97	75
Markvonikov	3	25



1 equiv. DIBAl-H
Toluene, 70 °C
OH
H
O
3 moles
CHO
1 equiv. DIBAl-H
Toluene, 60 °C
3 moles
CH2OH
(2E)-3-phenylprop-2-enal
(2E)-3-phenylprop-2-en-1-ol
COOEt
1 equiv. DIBAl-H
Toluene, -70 °C
CHO
iBu
iBu
Al
H
O
R
OR'
O
Al(iBu)2
R
H
OR'
protic workup
O
R
H
stable tetrahedral
intermediate at -78°C

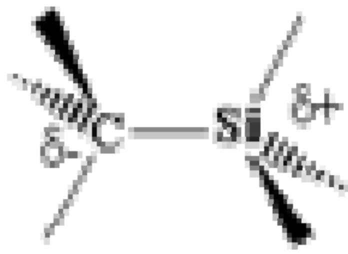
V. ORGANOSILICON

Organosilicon compounds are organic compounds containing carbon silicon bonds.

- Like carbon, the organically bound silicon is tetravalent and tetrahedral.

  C—Si 1.86 Å, 318 kJ/mol; electronegativity: Si 1.90, C 2.55

- **Preparation**



Direct process $2\ RCl + Si/Cu \xrightarrow{\Delta T} R_2SiCl_2 + \ldots$

(R=alkyl, aryl)

Metathesis reactions

$$SiCl_4 + 4\ RLi \longrightarrow R_4Si + 4\ LiCl$$

$$R_3SiCl + R'MgX \longrightarrow R_3R'Si + MgXCl$$

$$2\ R_2SiCl_2 + LiAlH_4 \longrightarrow 2\ R_2SiH_2 + LiCl + AlCl_3$$

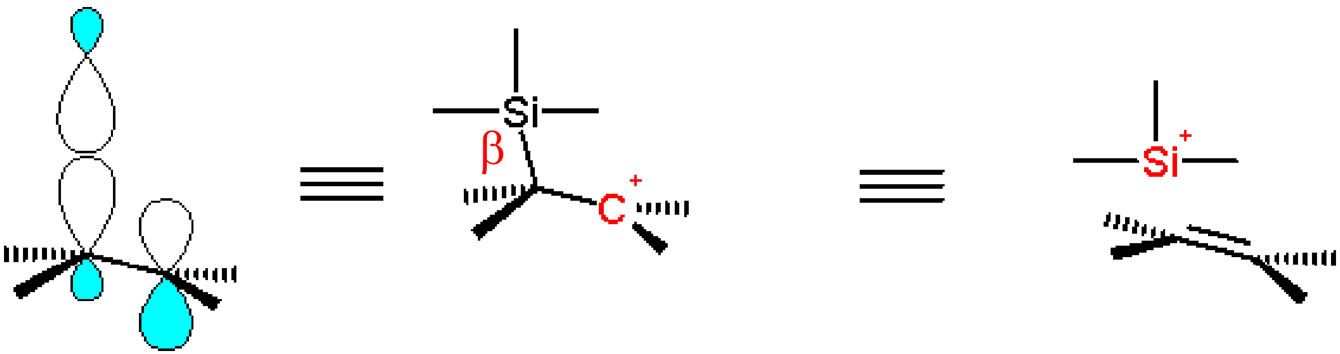
Hydrosilation

$$HSiCl_3 + R{-}CH{=}CH_2 \longrightarrow RCH_2CH_2SiCl_3$$

➢ Property and Reactions

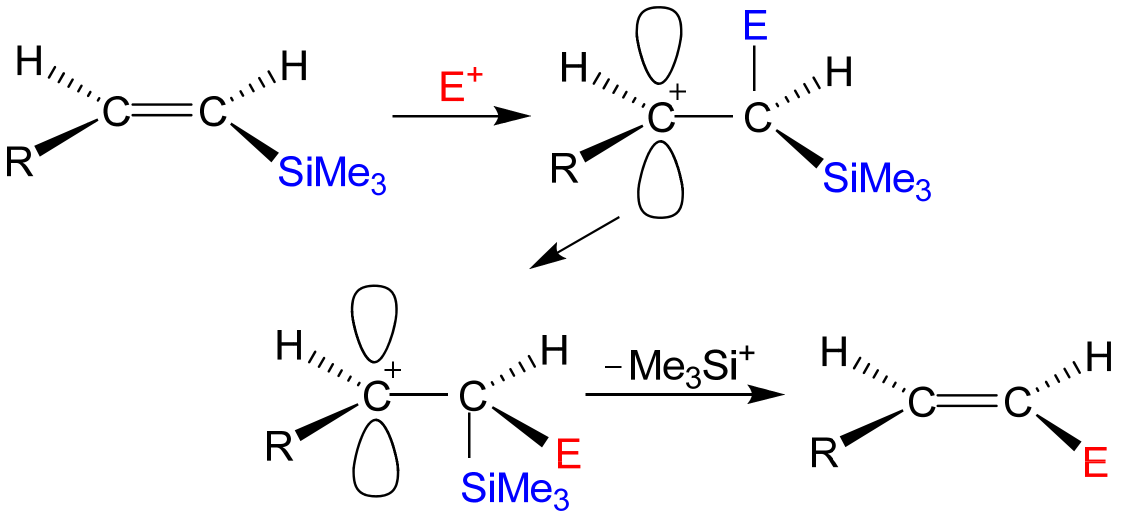
☞ The trimethylsilyl cation, Me_3Si^+, departs from a carbon atom more readily than does a proton.

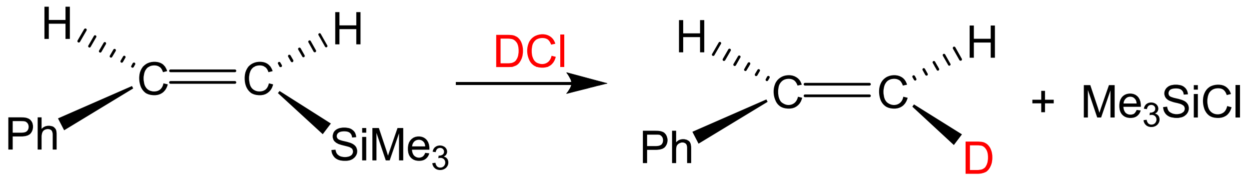
☞ Beta-silicon effect: The beta-silicon effect also called silicon hyperconjugation is a special type of hyperconjugation and describes the stabilizing effect of a silicon atom placed in a position once removed (β) from a carbocation.



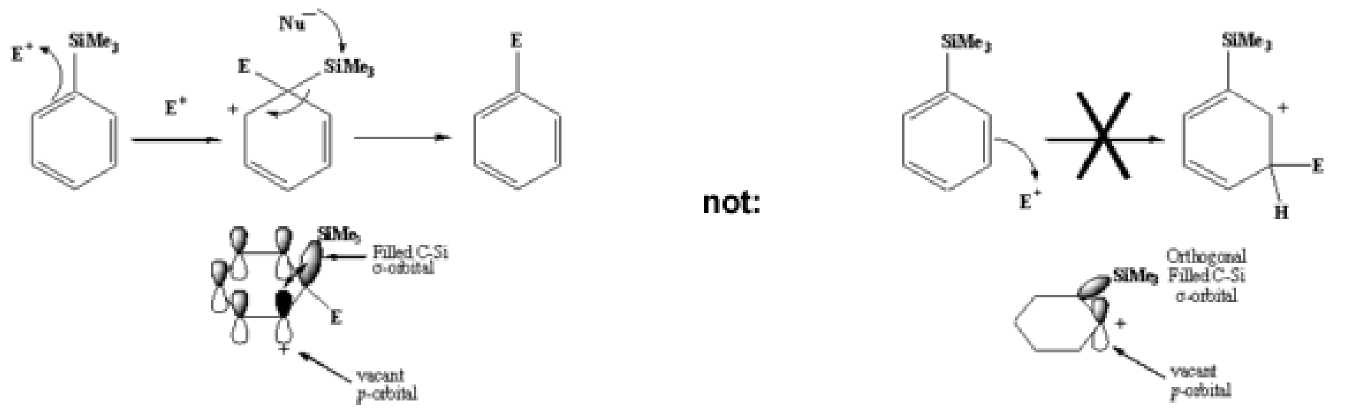
I II III

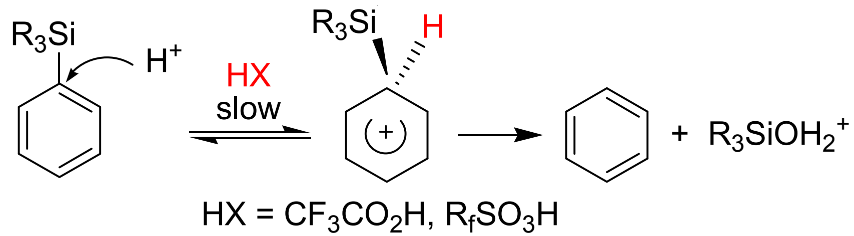
These two properties are manifest in reactions of vinylsilanes. Thus, many electrophiles give substitution rather addition, the silicon being eliminated as a cation and the configuration at the double bond is retained.

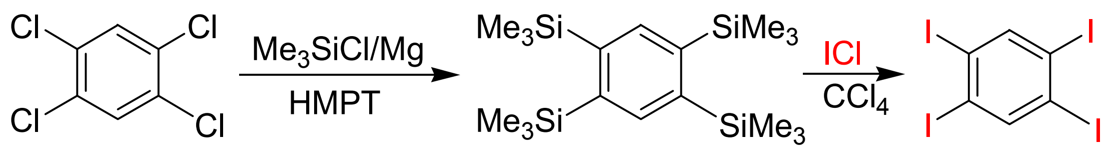


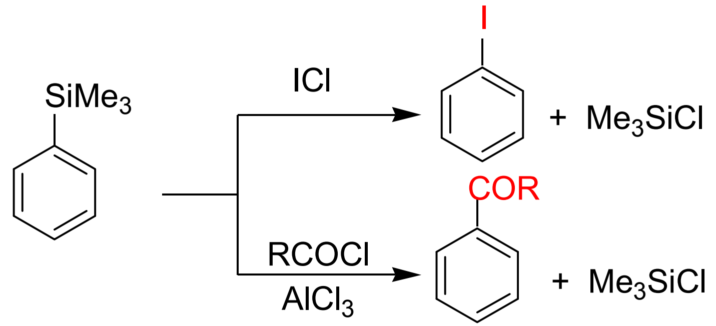


(100 per cent retention of configuration)


E+
SiMe3
Nu−
E
SiMe3
E+
E
Filled C-Si σ-orbital
vacant p-orbital
not:
SiMe3
E+
SiMe3
E
H
Orthogonal Filled C-Si σ-orbital
vacant p-orbital


R3Si
H+
HX
slow
R3Si
H
+ R3SiOH2+
HX = CF3CO2H, RfSO3H


Cl
Cl
Cl
Cl
Me3SiCl/Mg
HMPT
Me3Si
SiMe3
Me3Si
SiMe3
ICl
CCl4
I
I
I
I

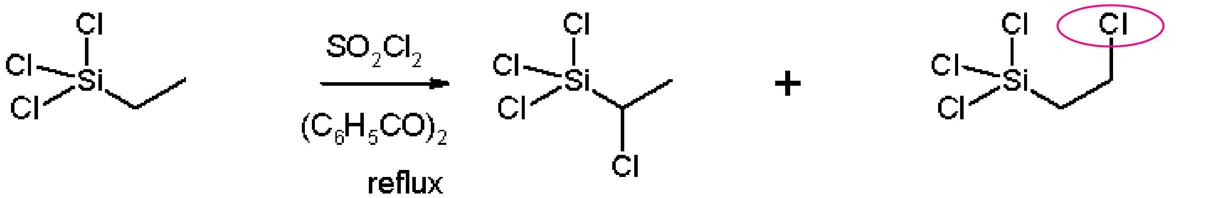

SiMe3
ICl
I
+ Me3SiCl
COR
RCOCl
AlCl3
+ Me3SiCl

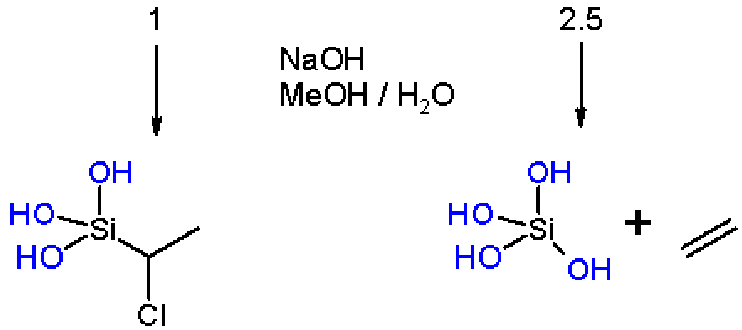
- The readiness to undergo heterolytic Si-C bond cleavage (desilyation):

Type: **(I)** > **(II)** > **(III)** > **(iV)**

Si—C(aryl) Si—C(aryl) Si—C(alkyl) Si—C(alkyl)

attacking species: El Nu El Nu





The desilyation proceeds much more rapidly if good leaving groups are present (β-effect).

Alsol®:

$(PhCH_2O)_2MeSiCH_2CH_2Cl$