

Organometallic Chemistry and Homogeneous Catalysis

Dr. Alexey Zazybin

Lecture N4

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Main group organometallic chemistry

Group II: Be, **Mg**, Ca, Sr, Ba, Ra

Organo Be and Mg compounds

Ionic character, Electron-deficient

Basic, Nucleophilic, Reducing

Oligomeric or polymeric structures

Mg: Applications in organic synthesis

Organo Ca, Sr, ... compounds

Very ionic

Very strong bases

Polymeric structures, usually insoluble

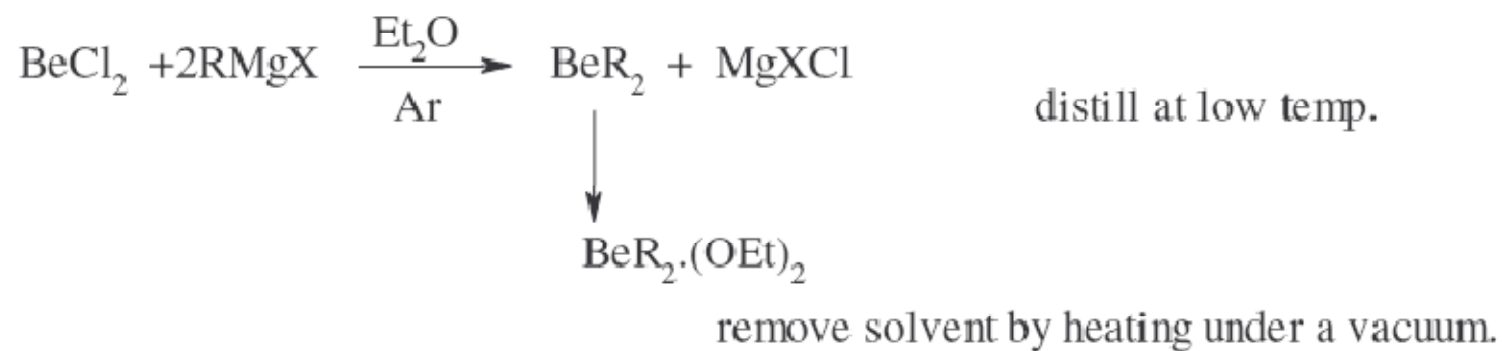
Few applications

1. Organoberyllium compounds

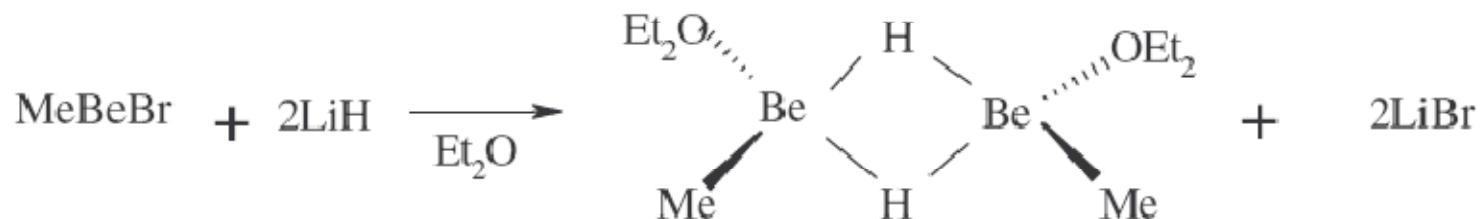
- 1) Highly toxic
- 2) Catch fire in dry CO₂

Synthesis:

- 1) From Mg-organic compounds:

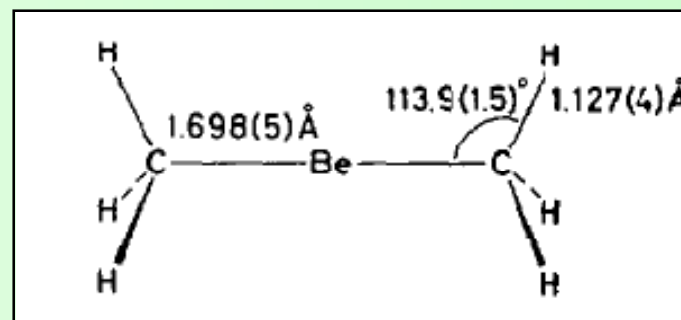


- 2) Transformation of existing Be-organic compounds:

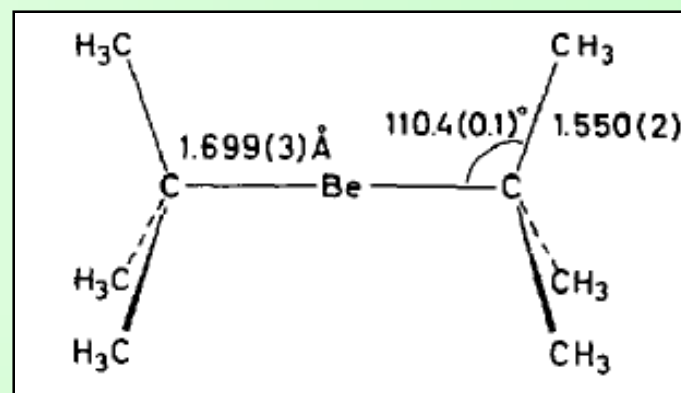


Structure:

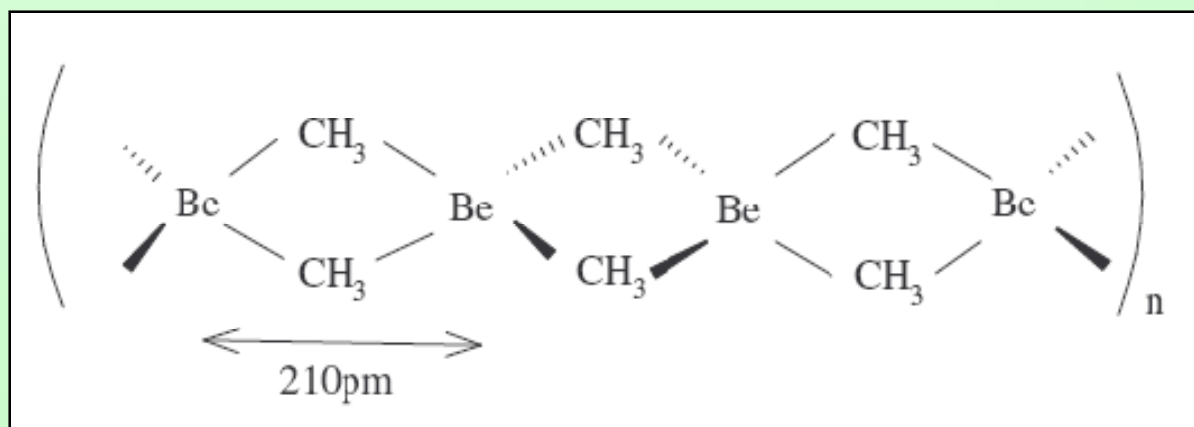
In a gas phase - monomers, dimers, trimers
monomers linear (sp-hybridised)



In solid phase – polymers
IR $\nu(\text{CH})$ low 2912, 2885, bonds long –
electron withdrawing due to Be-CH₃
bridges.

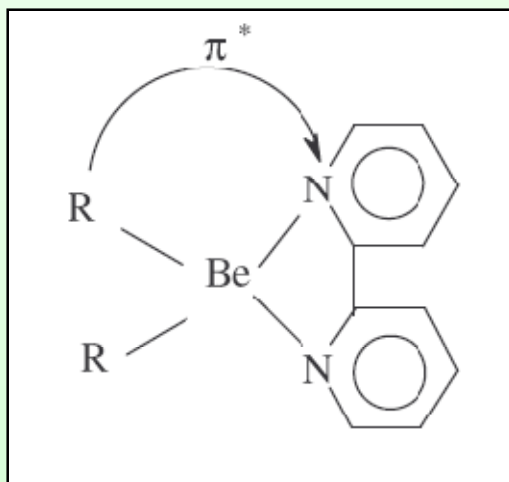


In BeMe₂ both Be and C effectively sp³:



Reactivity:

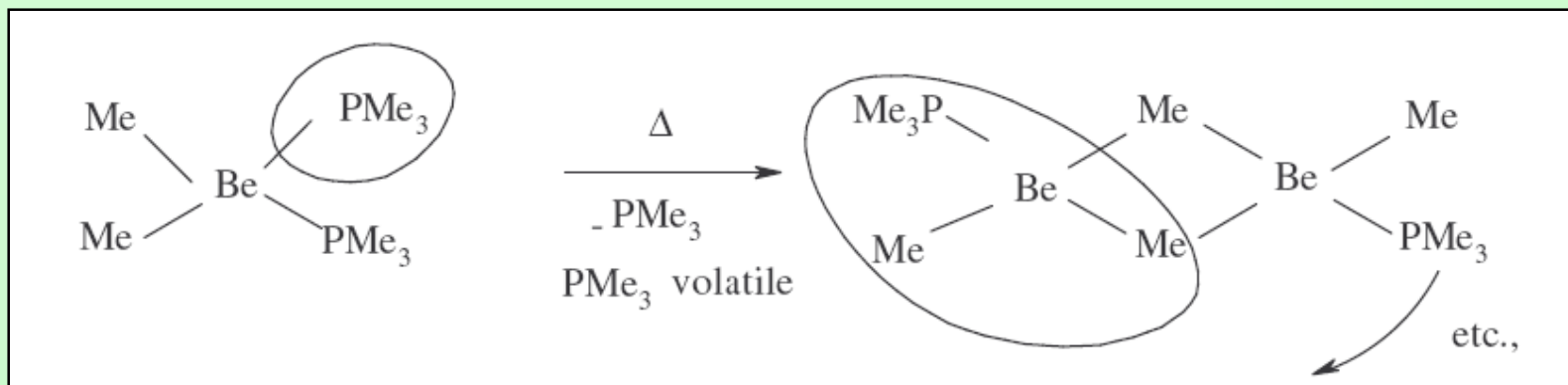
Polymer Be-organic compounds readily react with electron donor species like Me_3N , PMe_3 , etc.; this reaction causes formation of complexes and a breakdown of polymeric structure:



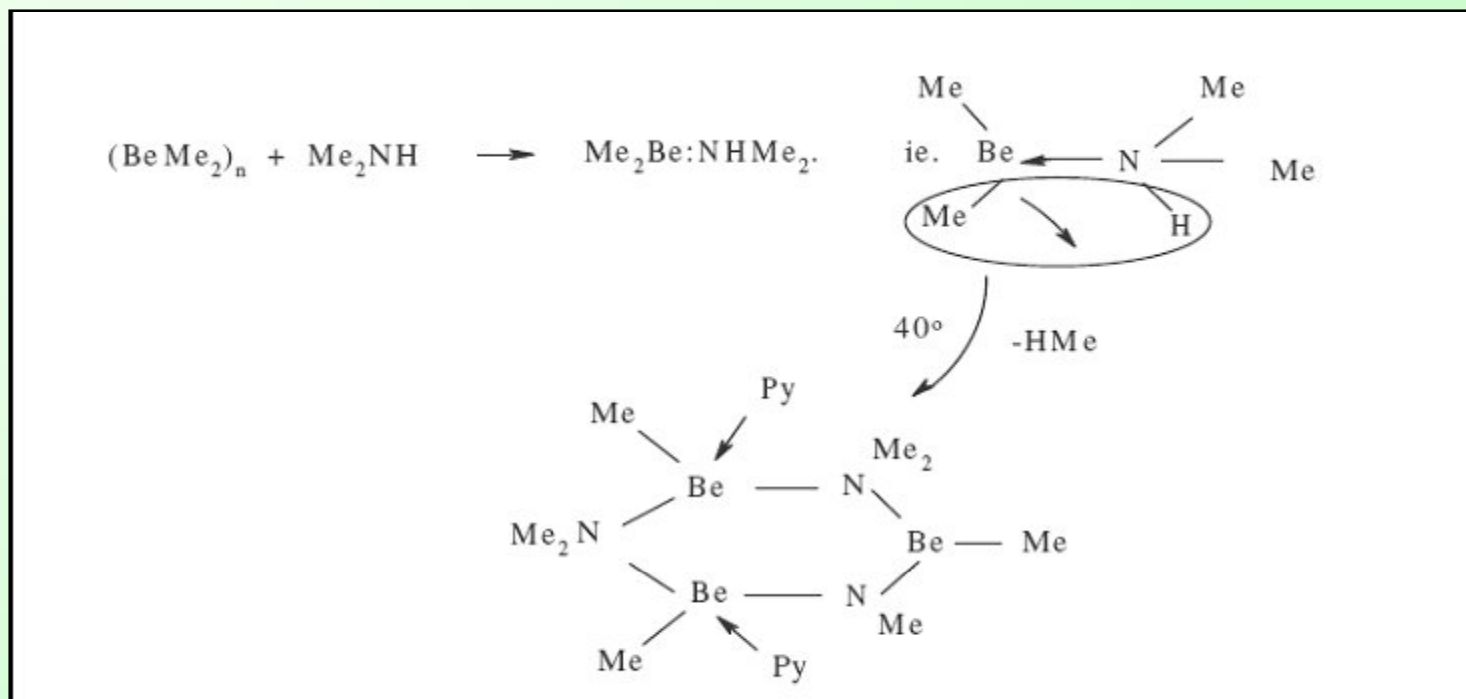
R = Ph, Me, Et, Br

Deep-red solid

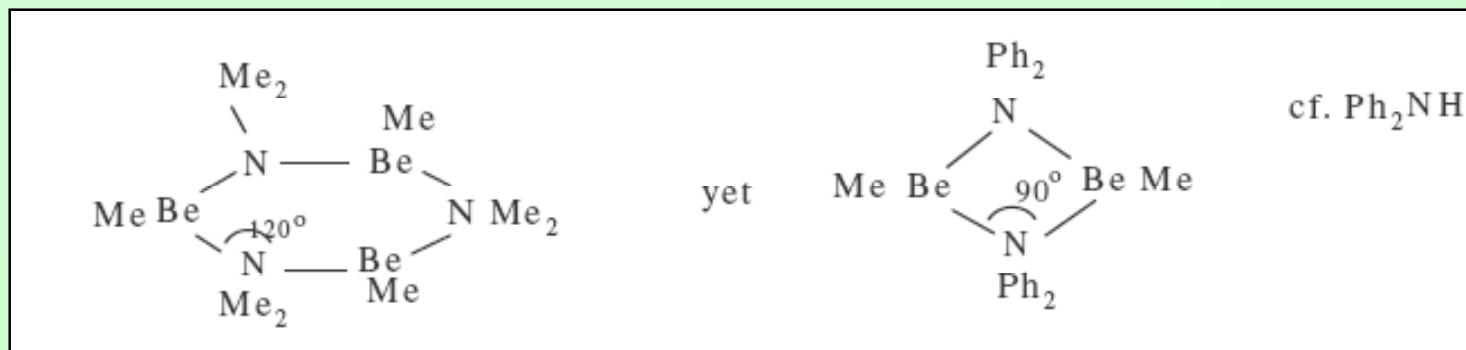
These monomeric complexes readily form oligomeric structures if possible:



Interesting case is the reaction with secondary amines:



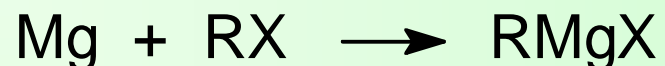
Formation of trimeric or dimeric species depends on steric size of R groups.



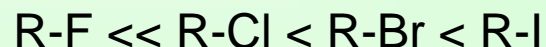
2. Organomagnesium compounds

Synthesis:

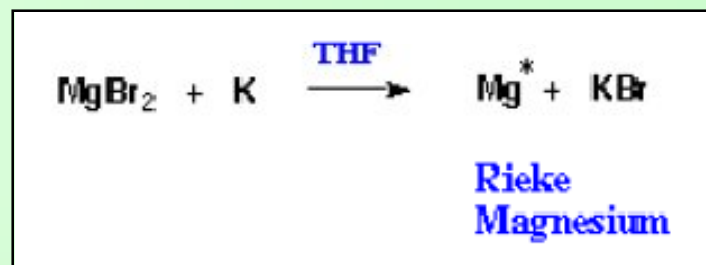
1) Direct synthesis ("Grignard reaction"):



The reactivity of the organic halide increases in the order



Usually R-F's are not active. The reaction can take place only when Rieke magnesium is used:

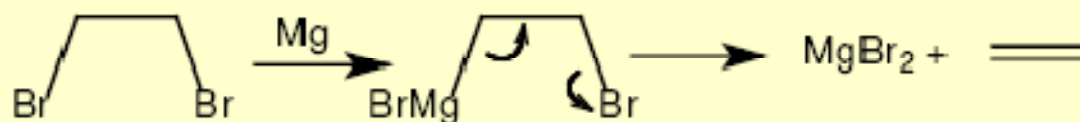


R-I's are most reactive but selectivity is lower.

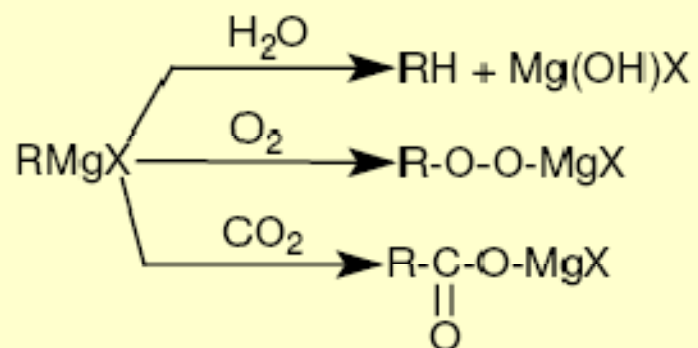
For industrial application, the inexpensive chlorides R-Cl are the preferred starting materials for Grignard reagents.

In the laboratory, the bromides R-Br are often used instead of the chlorides because of their higher reactivity and the higher boiling points.

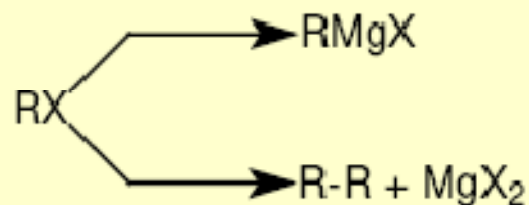
- **Heterogeneous reaction at Mg surface**
 - excess of Mg is used (often two-fold excess)
 - Mg surface has to be chemically cleaned (activator)



- **Dry solvent is needed and an inert atmosphere**



- **RX should be added slowly, otherwise Wurtz coupling occurs**





Solvent for Grignard reaction:

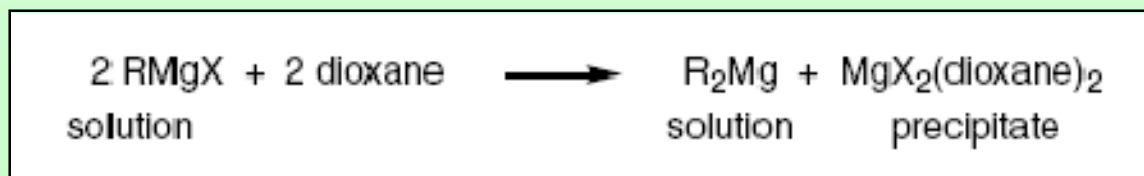
Et_2O (more pure product but lower rate of the reaction) or $\text{Et}_2\text{O}/\text{hexane}$ mixture

THF (reaction can proceed faster, but the product is less pure)

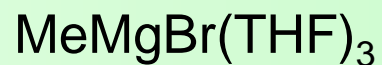
The preparation of a Grignard reagent can pose a number of problems:

- Impurity of the used solvent, the organohalide or the glassware can prevent the formation of the Grignard reagent.
- Impurities in the magnesium (especially transition metals like Ni, Cu etc.) can lead to the Wurtz coupling.
- The Grignard reaction can be very slow or difficult to activate (sterically crowded halides, many chlorides).
- The Grignard Compound RMg-X can be unstable. This is generally the case for Grignard reagents of the type Y-C-C-MgX (stability depends on Y , $\text{R}_2\text{N} > \text{RO} > \text{F} > \text{Cl} > \text{Br} > \text{I}$).

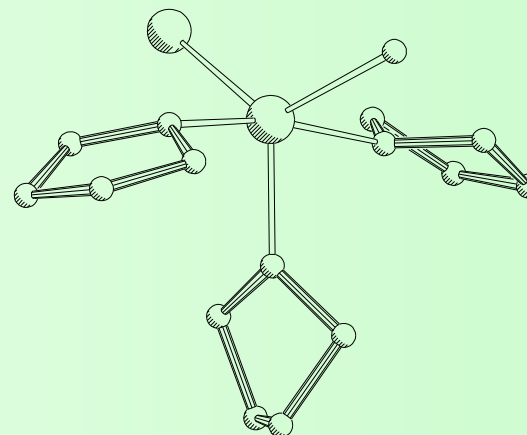
2) Synthesis of MgR_2



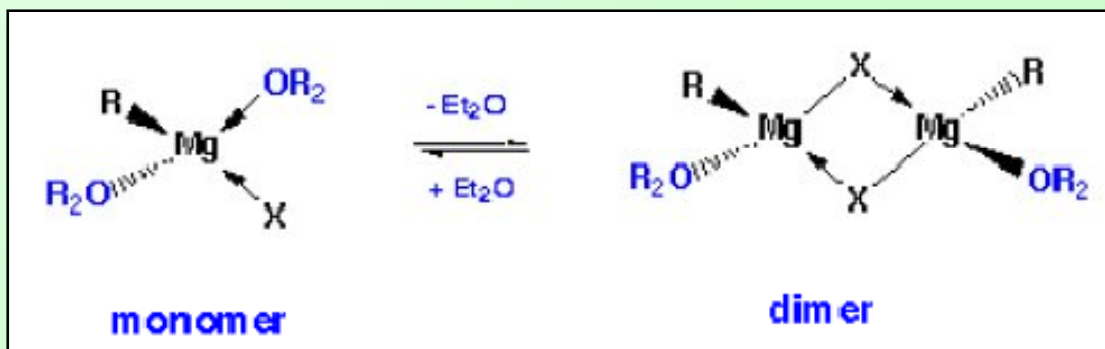
Structure:



Solid organomagnesium compounds were obtained as solvates. Usually monomeric or dimeric:



In solution it is usually monomer-dimer equilibrium:

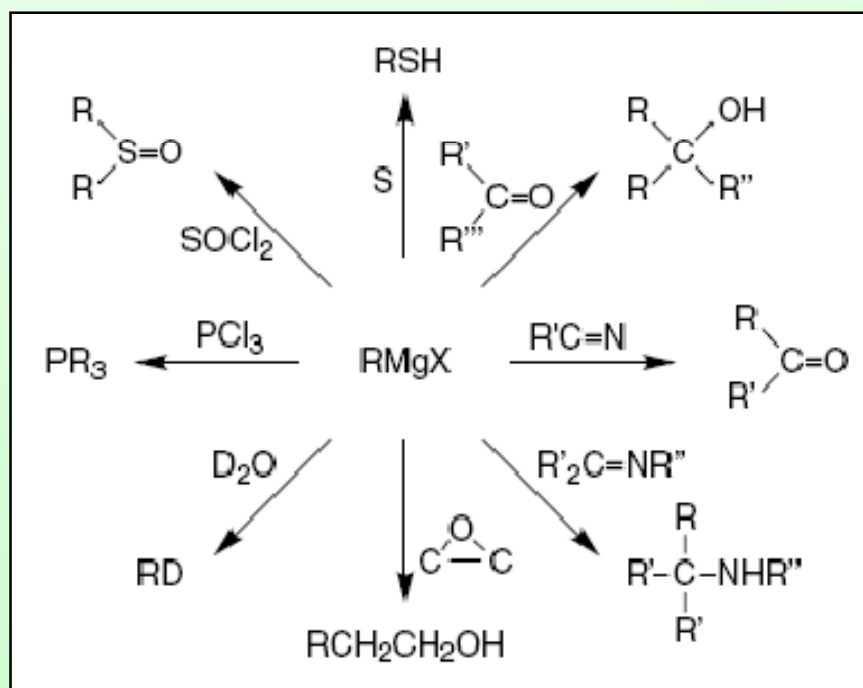


Dilution or strong donors (TMEDA > Et₃N > THF > Et₂O) favor monomers; weak donors and high concentrations favor dimers.

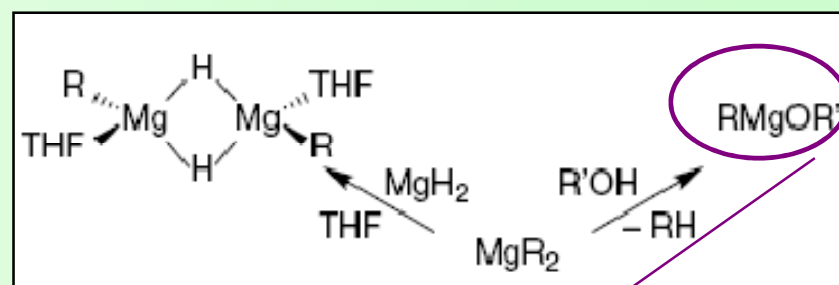
Reactivity:

In contrast with organolithium compounds, organomagnesium reagent reacts mostly as nucleophiles, not as bases.

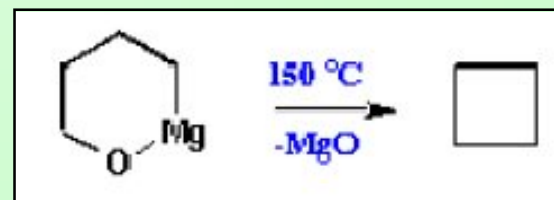
Reactions for R-Mg-X:



Reactions for R-Mg-R:



Some of these compounds can further participate in unexpected transformations:

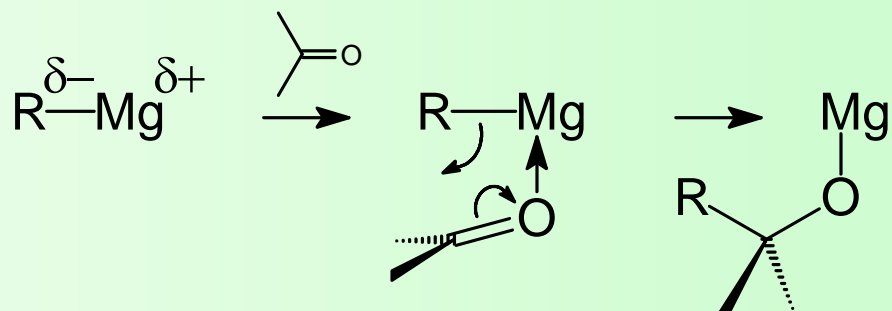


In general, reactivity of R-Mg-R is higher than for R-Mg-X.

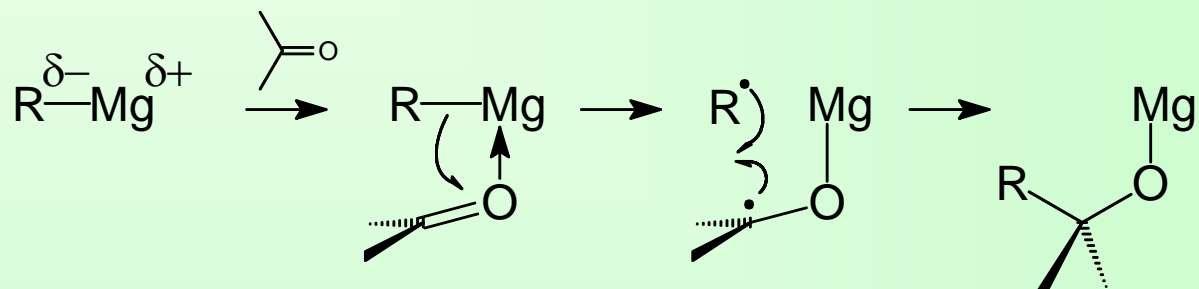
Main application of Grignards:



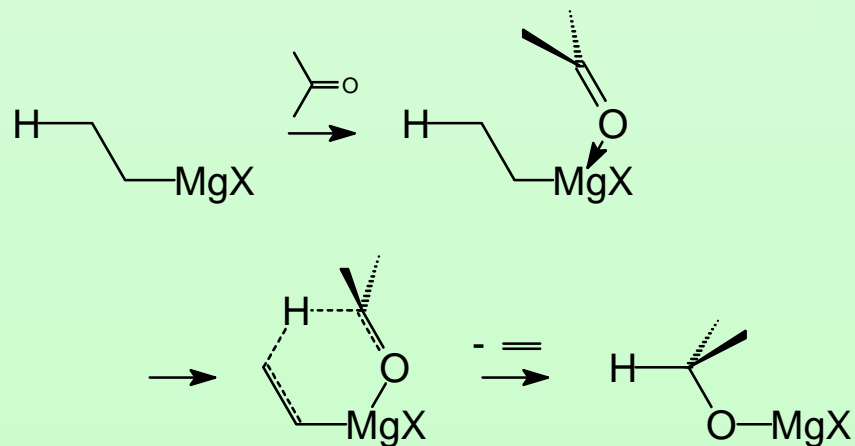
Addition to C=X



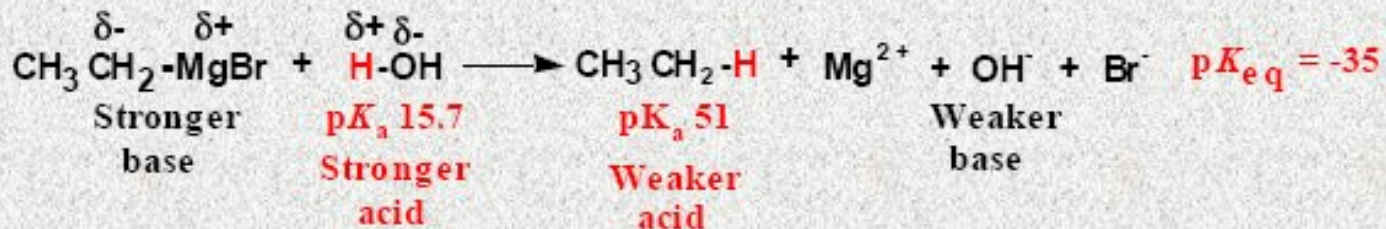
Sometimes radical mechanism (especially for aromatic ketones) :



For Grignards having a β -hydrogen reduction is possible:



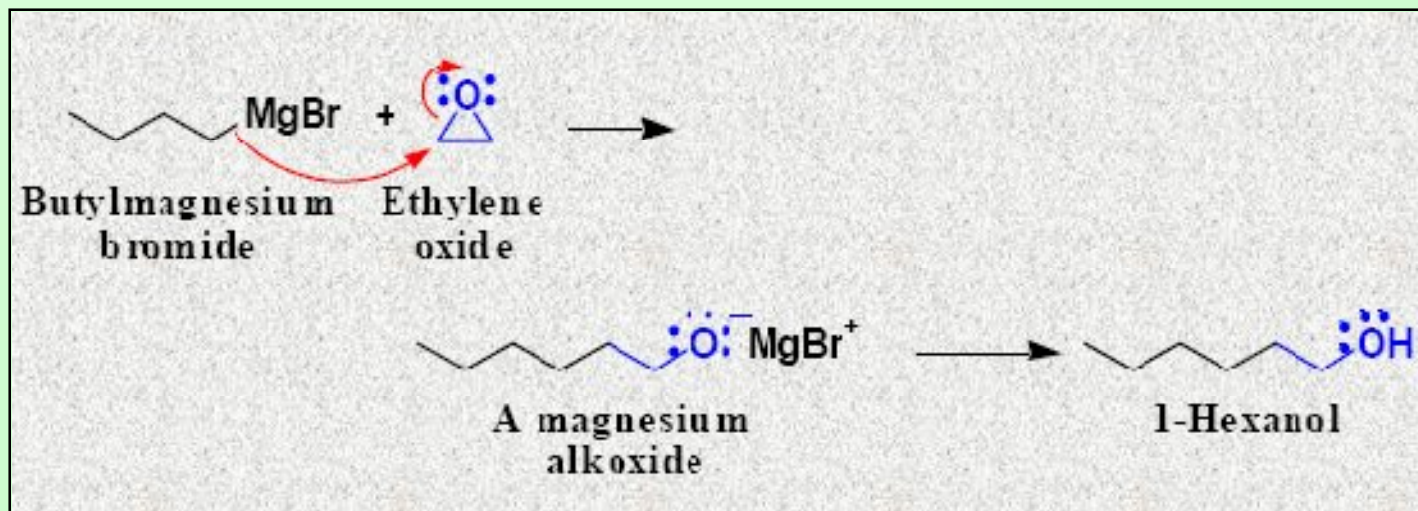
Reaction with proton acids



– they react readily with these proton acids

R_2NH	$\text{RC}\equiv\text{CH}$	ROH	HOH	ArOH	RSH	RCOOH
$\text{p}K_a$ 38-40	$\text{p}K_a$ 25	$\text{p}K_a$ 16-18	$\text{p}K_a$ 15.7	$\text{p}K_a$ 9-10	$\text{p}K_a$ 8-9	$\text{p}K_a$ 4-5
1° and 2° Amines	Terminal alkynes	Alcohols	Water	Phenols	Thiols	Carboxylic acids

Reaction with oxiranes (epoxides)



Group III: Al, Ga, In, Tl



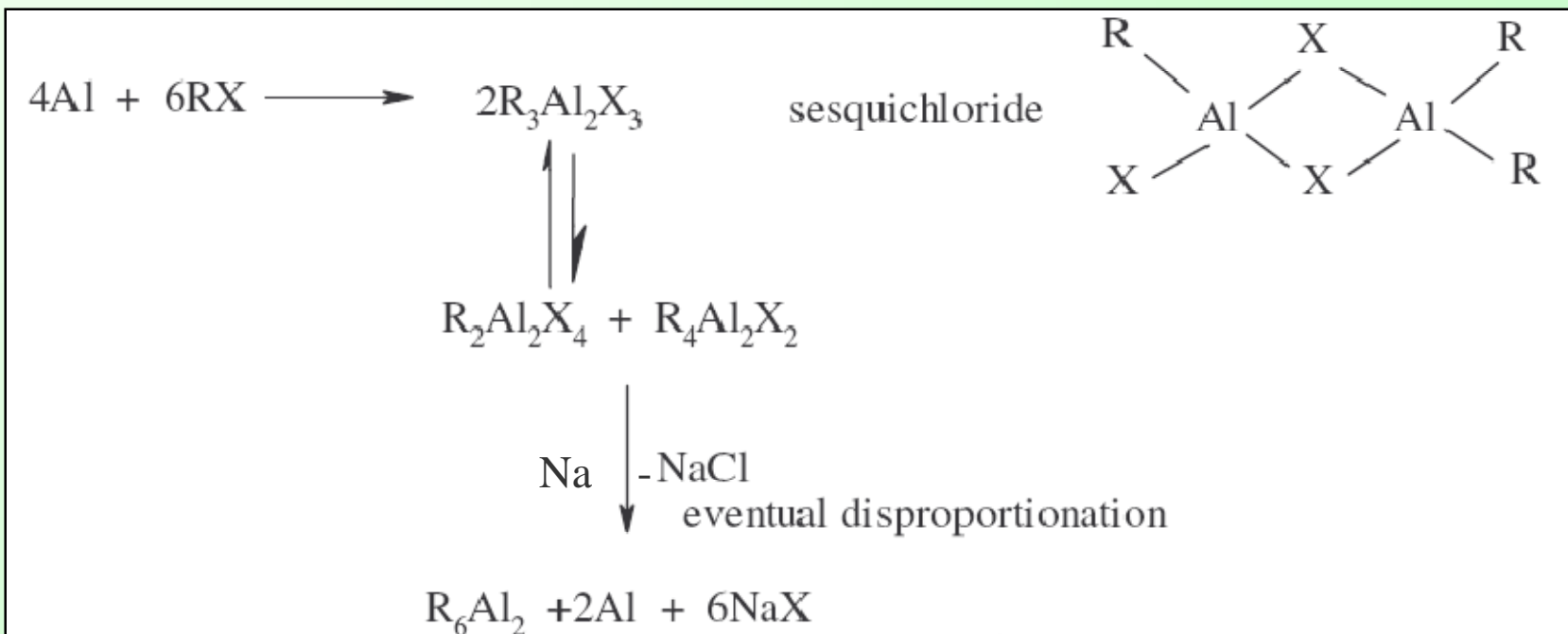
Organoaluminum compounds: **AlR₃**, **HAIR₂**, ... etc.

- More covalent character of M-C bond
- Compared with the organometallics of groups I and II, aluminum organyls excel in the ease of their addition to alkenes and alkynes
- More economical reducing and alkylating agents (in compare with lithium- and magnesium organyls)

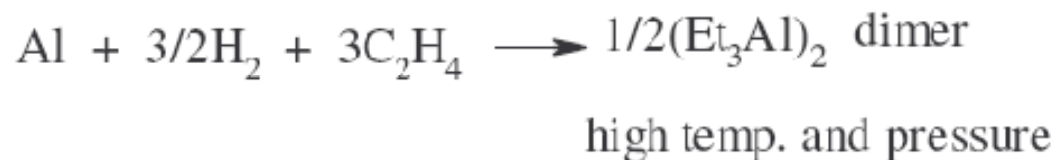
Synthesis:



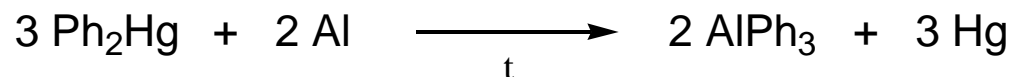
1) Direct synthesis from aluminum and organic halides:



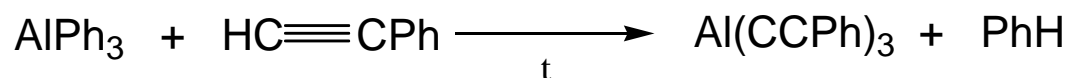
2) Direct synthesis from aluminum and alkenes in the presence of H₂:



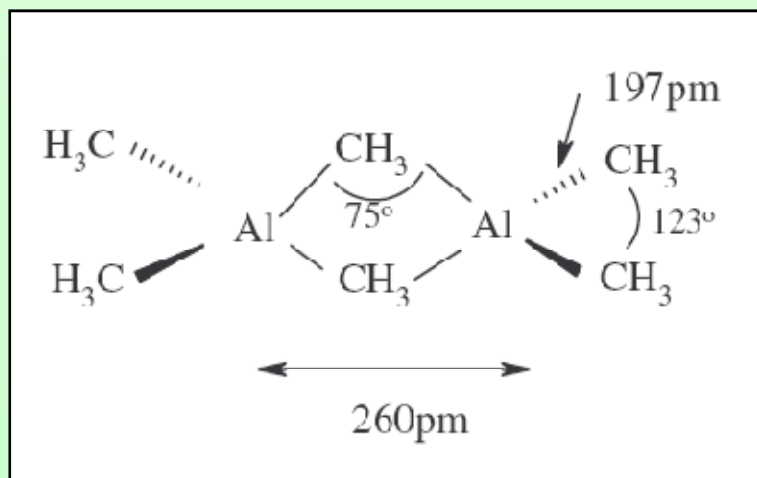
3) Transmetallation:



4) From organoaluminum compounds with ligand substitution:



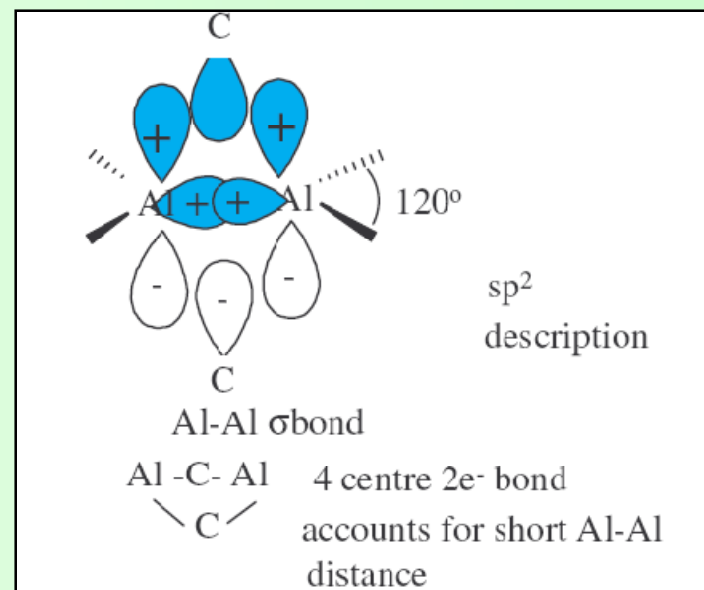
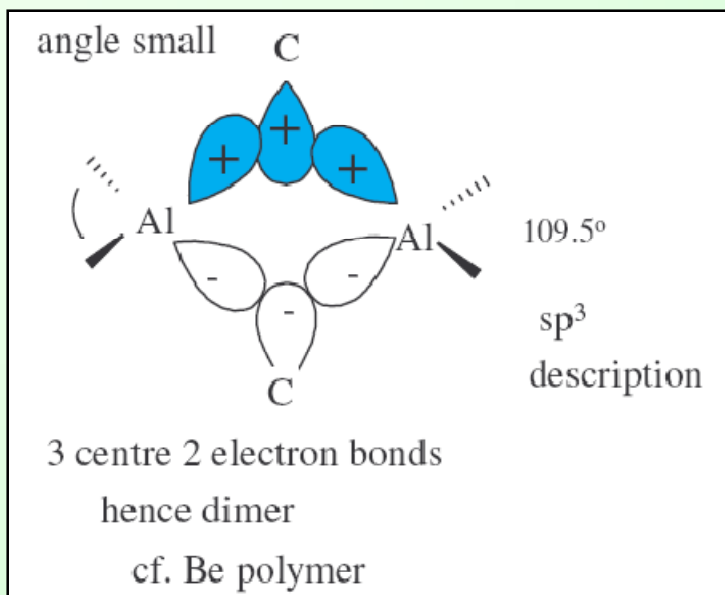
Structure:

1. AlR_3 

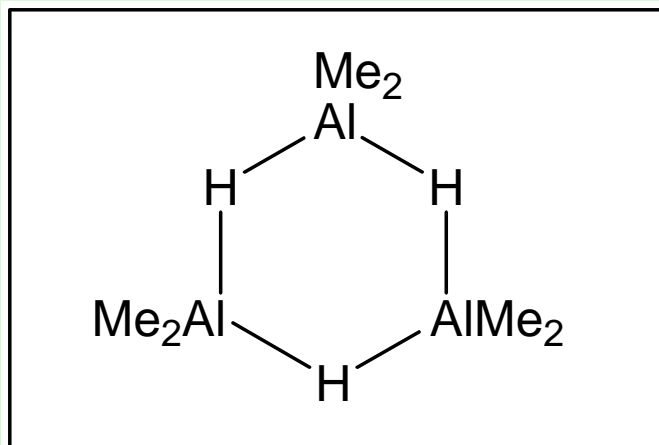
bonding scheme for Al is intermediate between sp^3 and sp^2

Al-Al distance short
covalent radius of Al + Al = 2 x 126 pm

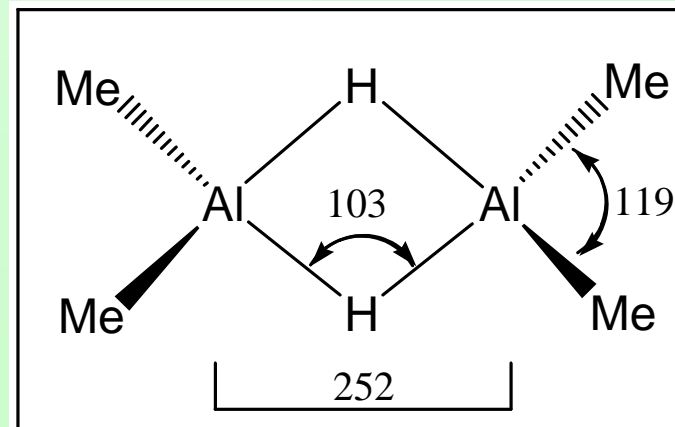
Bonding description:

2. HAIR₂

In solution:



In gas phase:



Reactivity:

1. Reaction with Lewis base



Organoaluminum compounds are hard Lewis bases. That is why they more readily react with hard Lewis Bases (especially **tertiary** amines):

– ΔH heat of complexation increases:

Hard base Me_3P

Me_3As

$\text{Me}_2\text{O} \geq -19$

$\text{Me}_2\text{S} -19$

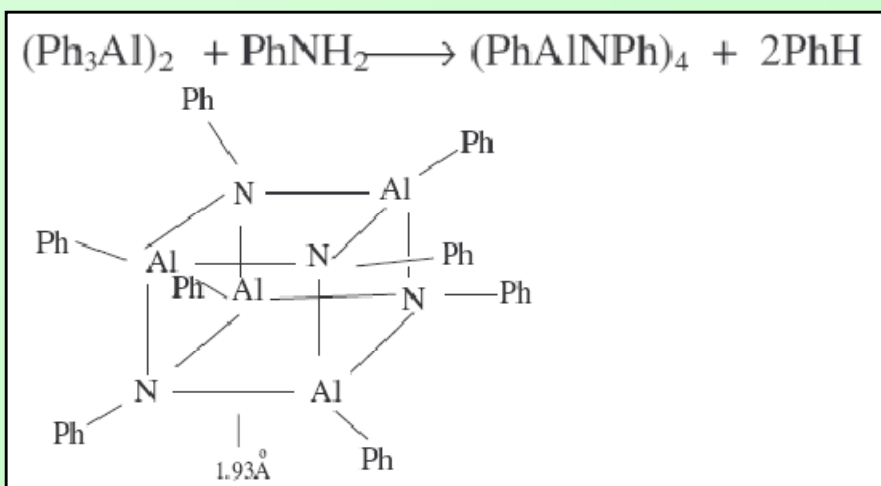
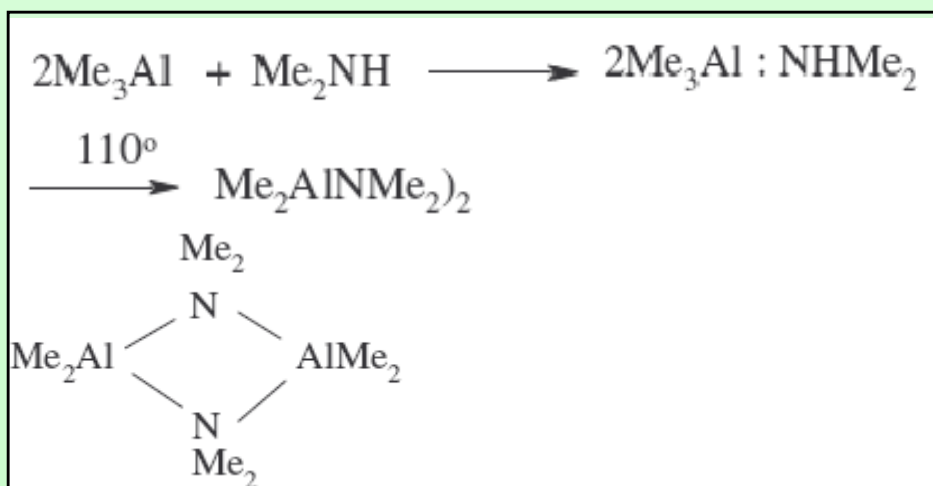
$\text{Me}_2\text{Se} -16$

Soft Base $\text{Me}_2\text{Te} \ll -16$



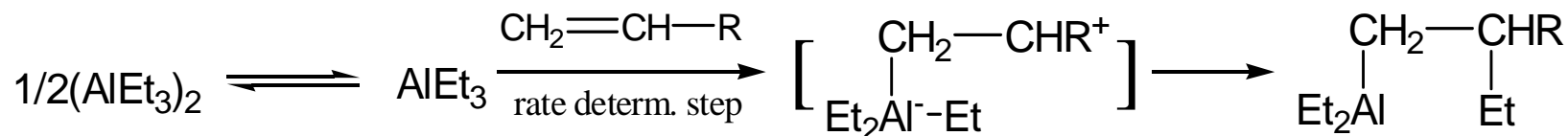
hard bases \longrightarrow soft bases

In the case of **secondary** and **primary** amines consecutive reactions follow:



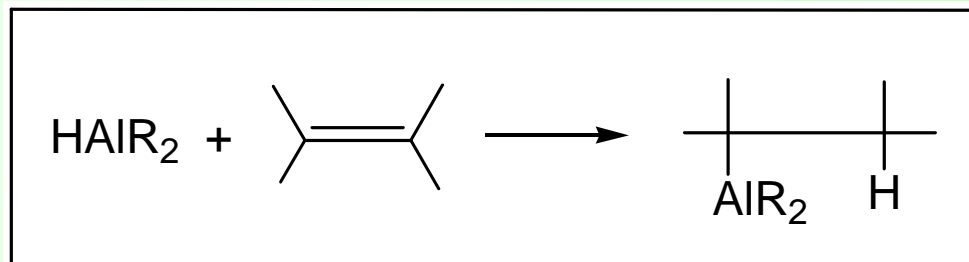
2. Reaction with alkenes

Whereas LiR , RMgX typically add to polar multiple bonds like $>\text{C}=\text{O}$, $-\text{C}\equiv\text{N}$, (and sometimes with conjugated $>\text{C}=\text{C}<$ bonds), AlR_3 also adds to the isolated multiple bonds $>\text{C}=\text{C}<$, $-\text{C}\equiv\text{C}-$.

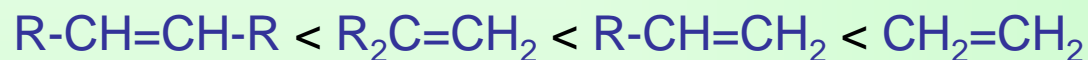


- Carbaluminations invariably proceed as *cis*-addition
- Alkynes react faster than alkenes
- Terminal alkenes react faster than internal alkenes
- AlR_2 fragment usually attaches itself to the least substituted carbon atom of the double bond

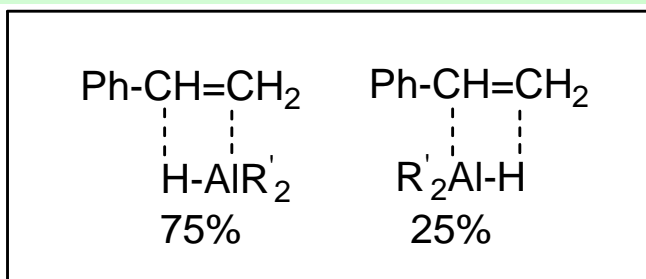
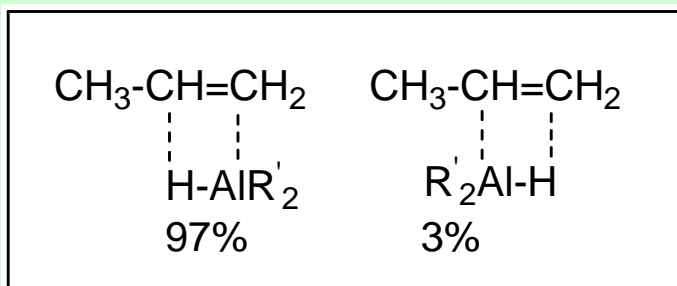
HAIR_2 reacts nearly in the same way:



The readiness to undergo hydroalumination increases in the order:



- Hydroaluminations are highly stereoselective: *cis*-addition
- The degree of regioselectivity (*anti*-Markovnikov) varies:



Organometallic compounds of Ga, In, Tl

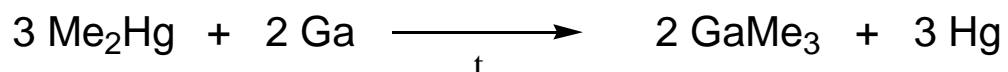
Ga – organyls: Ga⁺³

In – organyls: In⁺³, rare In⁺¹ (for example, CpIn)

Tl – organyls: both Tl⁺³ and Tl⁺¹ organyls are known

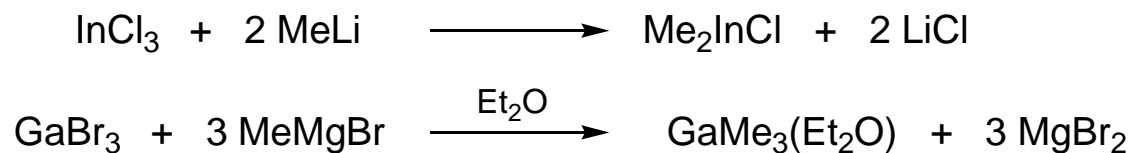
Synthesis:

1) Transmetallation



(The same for In, but not for Tl)

2) Using Li- or Mg-organic compounds:



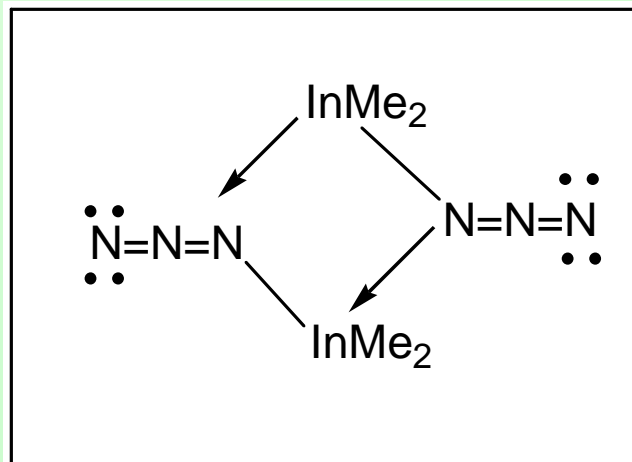
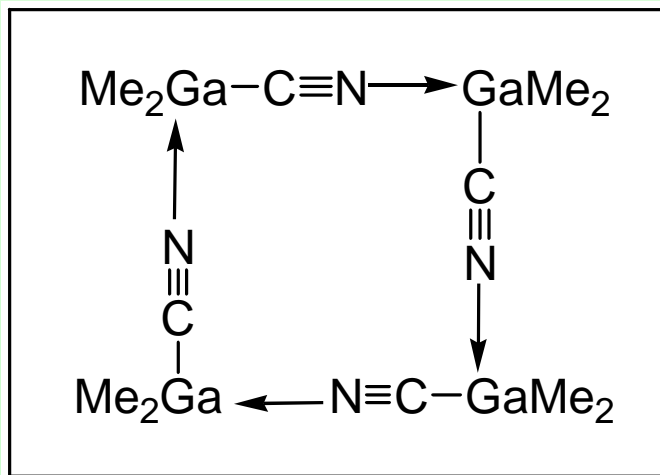
Structure:

GaR_3 , InR_3 and TlR_3 are **monomeric** in solution and in gas phase.

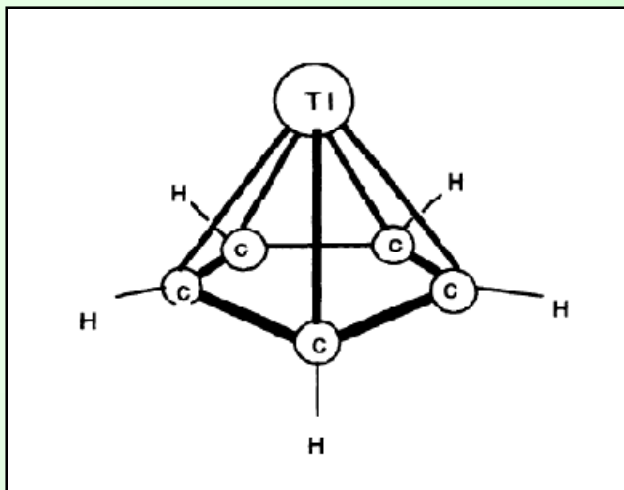
The triphenyls of Ga, In, and Tl are **monomeric** in solution but tend to associate into **chain structures** in the crystalline state as a result of weak intermolecular $\text{M} \cdots \text{C}$ interactions.

GaPh_3 mp 166°C . InPh_3 mp 208°C . TlPh_3 mp 170°C .

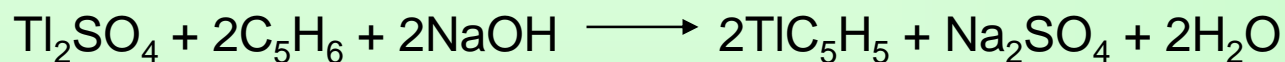
Self association is possible for some alkyl compounds as well:



CpTI has symmetrical structure in a gas phase:



It can be synthesized as a yellow solid, stable to water and relatively stable to air according to the following equation:



In the solid state CpTI has zigzag polymer chains.

For In both CpIn and Cp₃In are known, the first as η^5 , the second as η^1

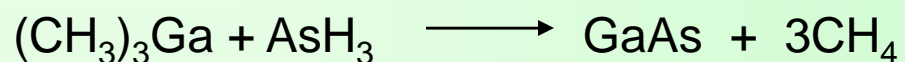
CpIn has the same structure in a gas phase and solid phase as CpTI, but it is significantly less stable.

Application:



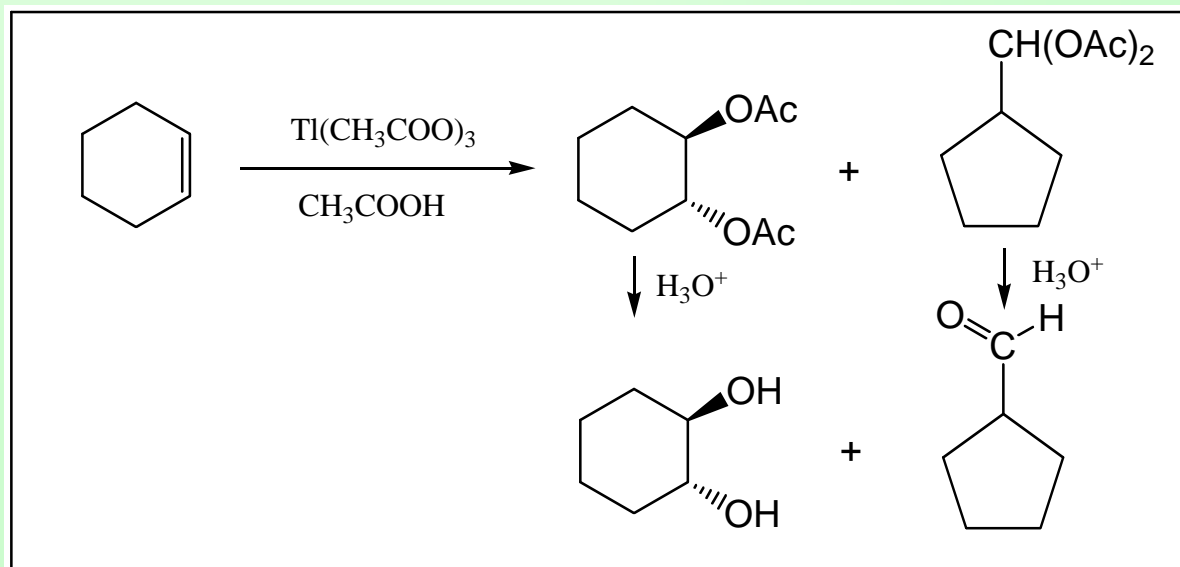
1. GaR₃ compounds are used in MOCVD – metal organic chemical vapor deposition.

Thin layer of GaAs (is used in manufacturing of semiconductors) can be obtained according to the following reaction:

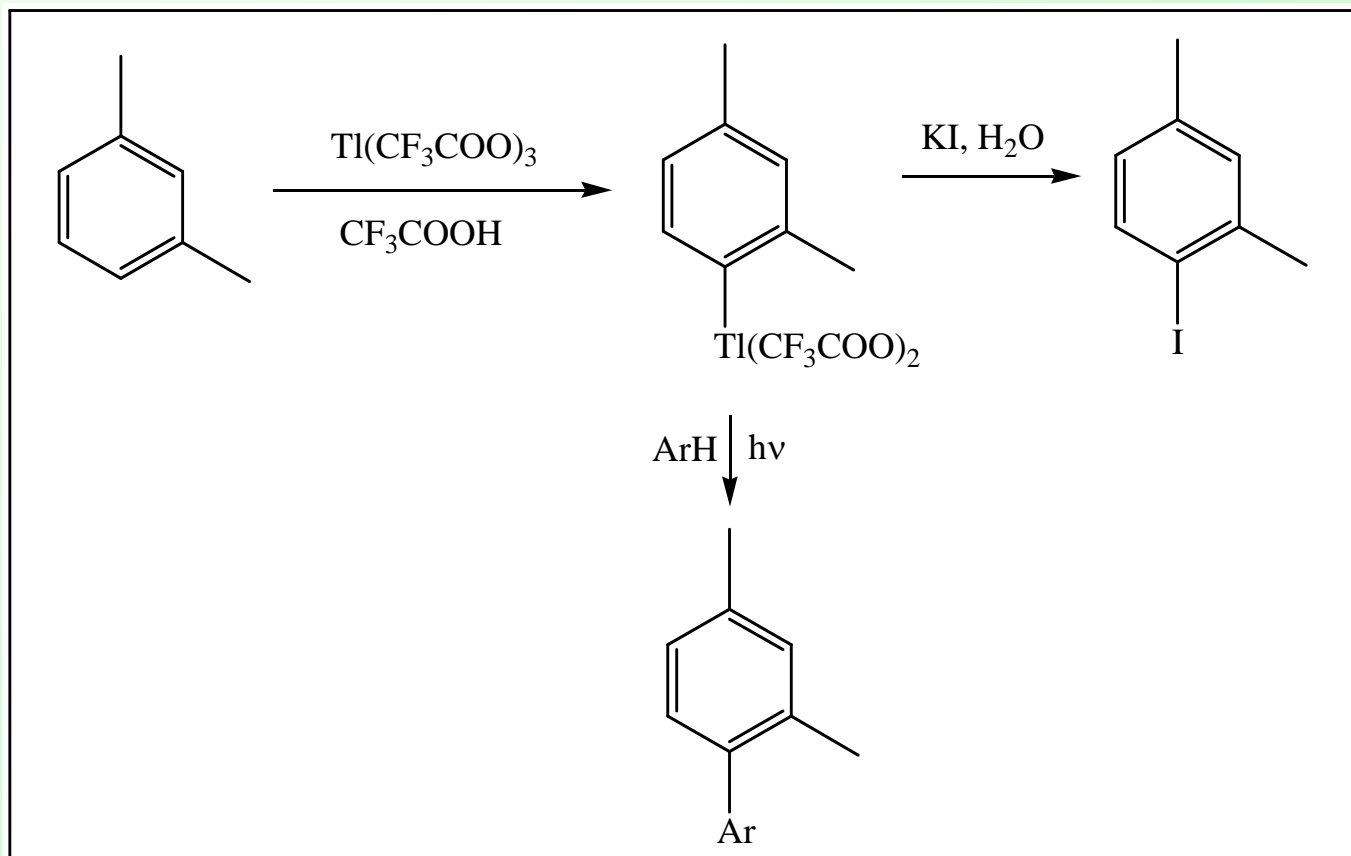


2. Ti(III) organils play an important role in some organic synthesis as intermediates:

a) Oxythallation



b) Electrophilic aromatic thallation



A new substituent enters to the position of the former Ti-C bond accompanying by a change in oxidation state of Ti: +3 \longrightarrow +1 (TiCF_3COO)