Organometallic compounds of the p-block
Organoboron and –aluminum compounds

ER_nX_{3--n}(n=1-3) ER_4^-

X= halide, alkoxyde, amide, HYDRIDE…

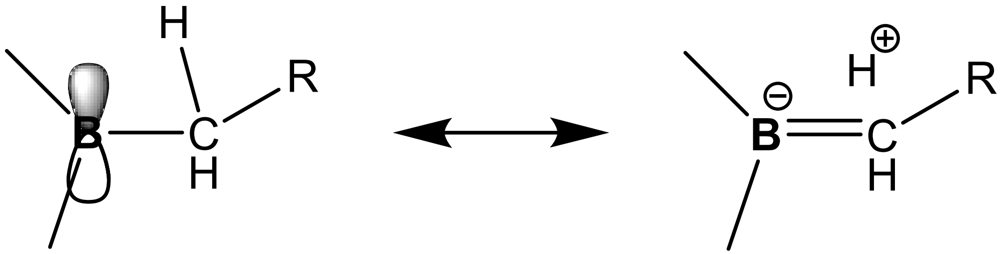
Covalent E-C bond (= poor nucleophiles), availability on E of a **free np orbital for tetracoordination** (= Lewis acidity of E).

B-C bond stable to hydrolysis and to oxidation, in particular when R= aryl, vinyl… (light trialkylboranes are however pyrophoric); variable solubility properties (dependent also on X).

Triorganoaluminum compounds exhibit a more polarized Al-C bond and are more reactive: they are generally pyrophoric/air sensitive and react explosively with water.

Stability of the organoelement compounds

Organoboron compounds are <u>monomeric</u> (at variance with boranes and organoaluminum compounds). Presence of a <u>hyperconjugative interaction</u> between the 2p orbital and σ C-H bonding orbitals α to B (analogy with B-F or B-O):



Evidence: B-B distance in $(Me_2BH)_2$ much larger than in B_2H_6.

Organic substituents with π systems conjugated to the B 2p orbital (aryls, heteroaryls, vinyls, alkynyls etc.) provide even stronger π donation by <u>electron delocalisation</u>.

Stabilization through hyperconjugation/resonance is <u>less efficient with organoaluminum compounds</u>, which are <u>more reactive</u> but also <u>strongly associated</u> (particularly the heteroleptic compounds).

Organoboron and –aluminum compounds
Practical significance

BR_nX_{3--n}(n=1-3) **BR_4^-** **AlR_3**

X= halide, hydroxide, alkoxyde, amide, HYDRIDE…

Organoboron compounds are extremely versatile reagents or intermediates for organic synthesis in stoichiometric reactions (hydroboration: H. C. Brown, Nobel 1979) and more recently in metal-catalysed reactions (Suzuki, Nobel 2010, and others).

Organoaluminum compounds are, together with organotin compounds, the organometallics prepared industrially on the largest scale (10^5 t/year) given their low cost and their application as reagents and (co)catalysts, particularly in oligo- and polymerisation processes.

Historical development (Al)

Organoaluminum compounds are known since the second half of the XIX century, but their reactivity has not been exploited until the 1950s. The reason is that ethers were employed as reaction solvent (analogy with the Grignard reagents), which coordinate to Al deactivating the compounds.

Ziegler (1930s-1940s):

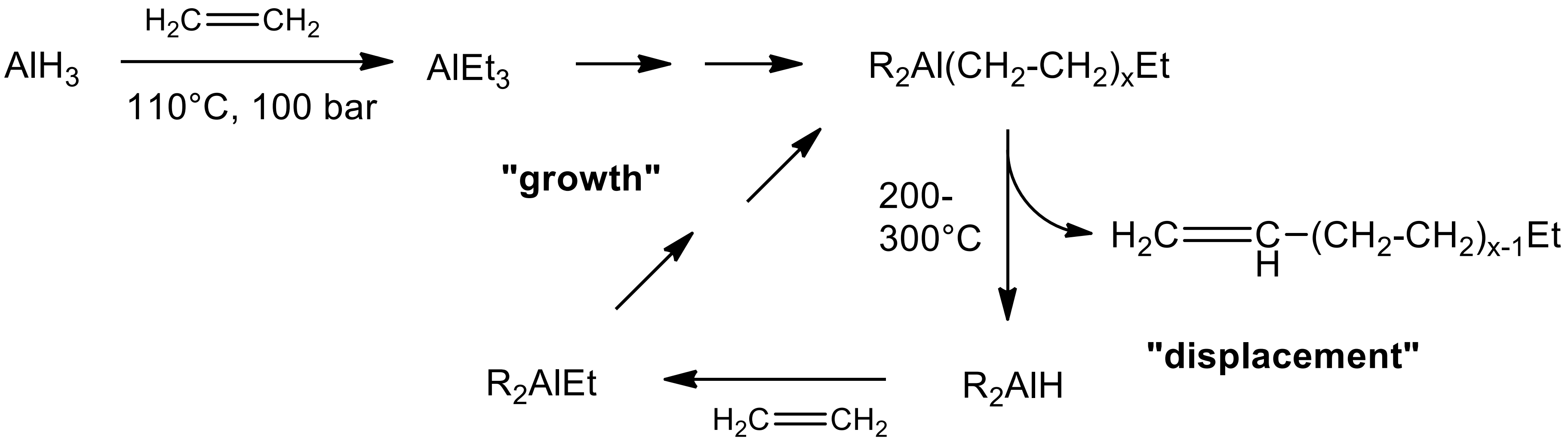
LiEt → LiH + ethylene + **polymeric olefins** (by heating)

LiH + ethylene → no reaction

$LiAlH_4$ + ethylene → **polymeric olefins**

AlH_3 + ethylene → **polymeric olefins** (at 100°C, 1 atm;
compare 150-300 °C, 1000-3000 atm for LDPE synthesis, 1933)

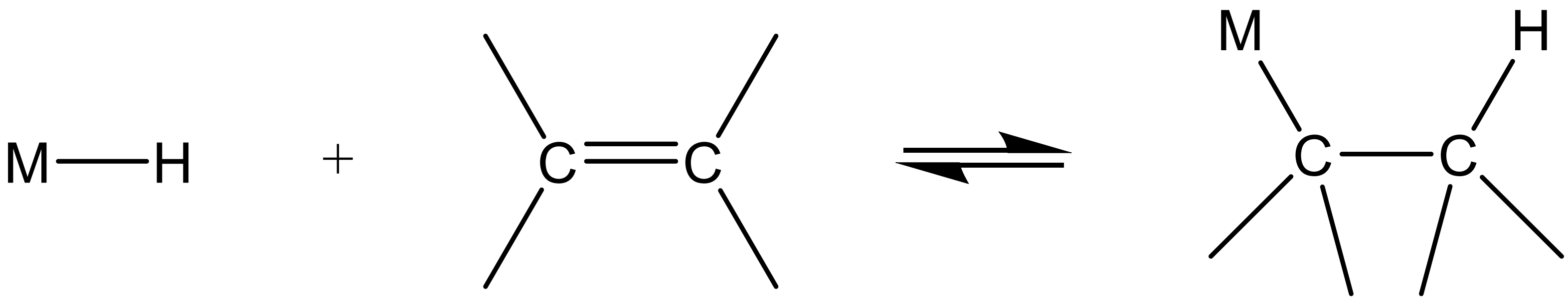
The «Aufbau»-Reaction



Terminal long-chain olefins are formed with length up to ca. 200 carbon atoms.

Subsequently, the “nickel effect” was discovered, and consequently the activity of transition metals in the reaction, the stereospecificity of the polymerisation in the case of terminal olefins etc.

Hydroelementation



M= **B**, **Al, Si, Ge, Sn, Pb**, *transition metals (insertion)*…

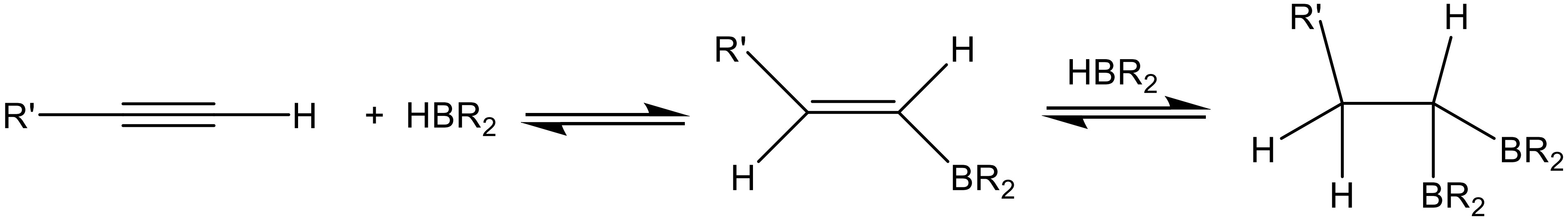
- ***Reversible*** reaction, stereoselective ***cis***, regioselective (***anti)-Markovnikov***; more selective with bulky reagents;

Concerted reaction. With **Si**, the direct reaction generally needs a (Pt) metal catalyst, which may also impart different regio- and stereoselectivity. With **Sn**, the reaction is often radicalic (weak Sn-H bond, AIBN can be employed as initiator); *cis* stereoselectivity might be lost. With **Pb** the reaction can be either radicalic or concerted.

Hydroboration

- The reaction can be run with boranes containing one, two or three B-H bonds, which potentially generates one, two or three organic residues bound to B;

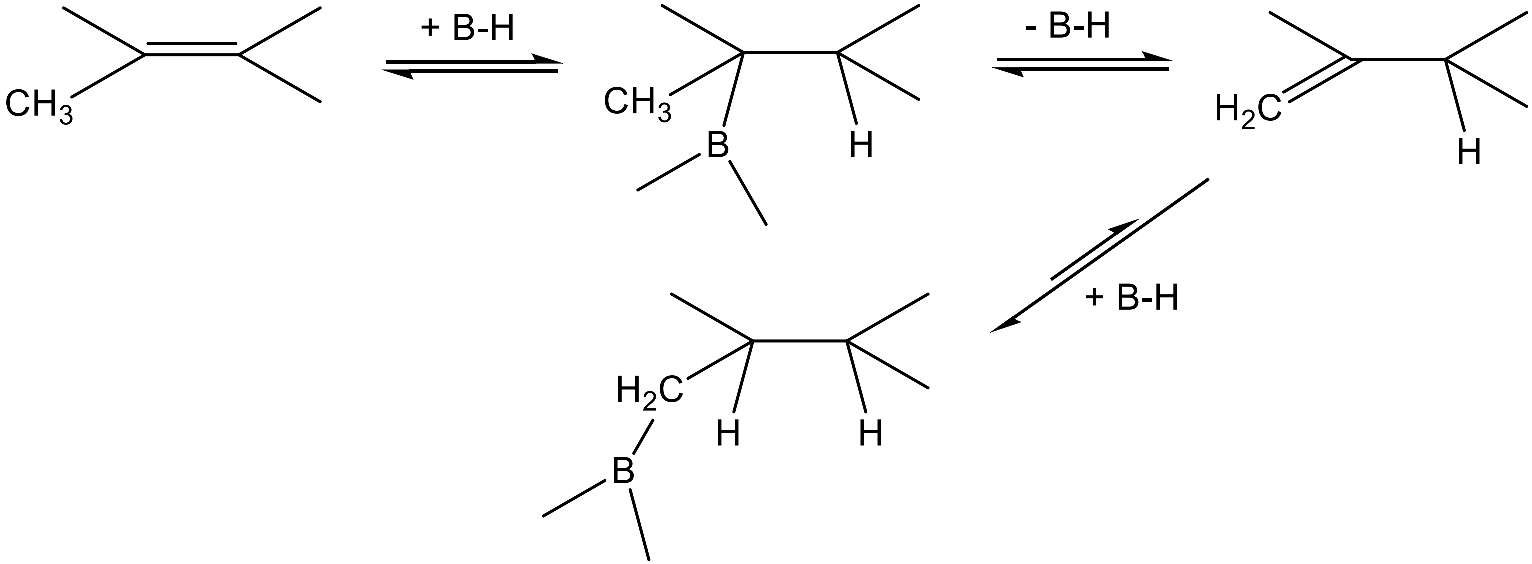
- The reaction can be also carried out with alkynes,with the same regio- and stereoselectivity; the so formed vinylborane can undergo a second hydroboration:



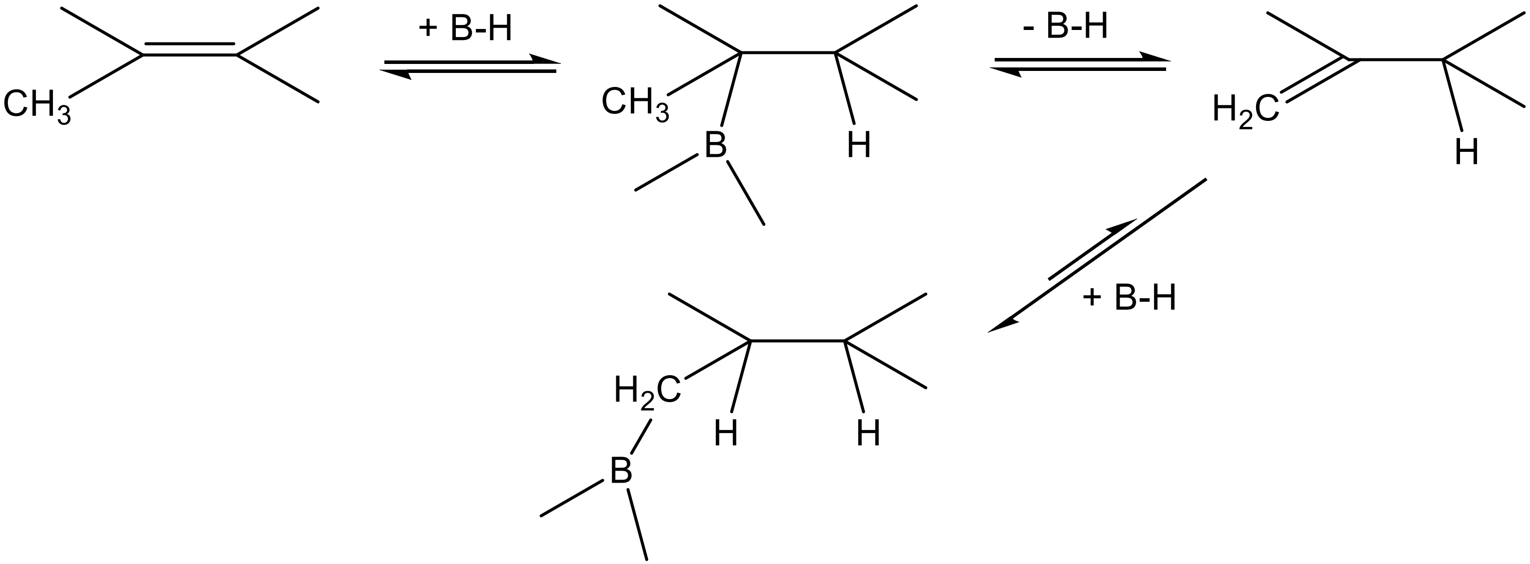
- The reaction can be made enantioselective (by employing chiral boranes).

Hydroboration/dehydroboration

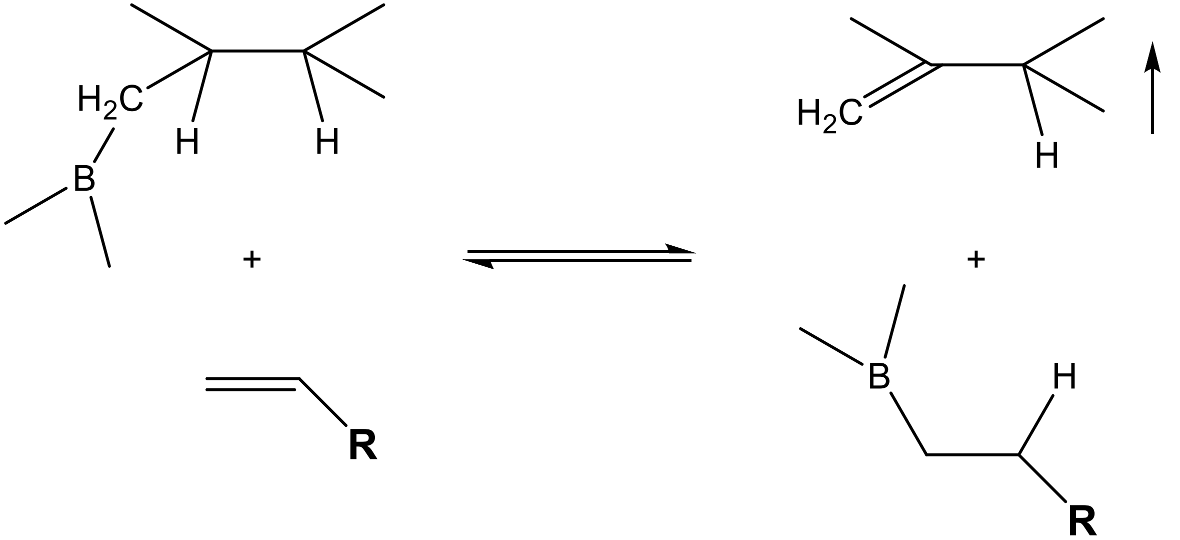
- With internal alkenes the reaction is slow (possibility to separate terminal from internal alkenes, especially with bulky boranes) and less regioselective: furthermore, branched boranes isomerise above 150-200 °C to the corresponding linear boranes



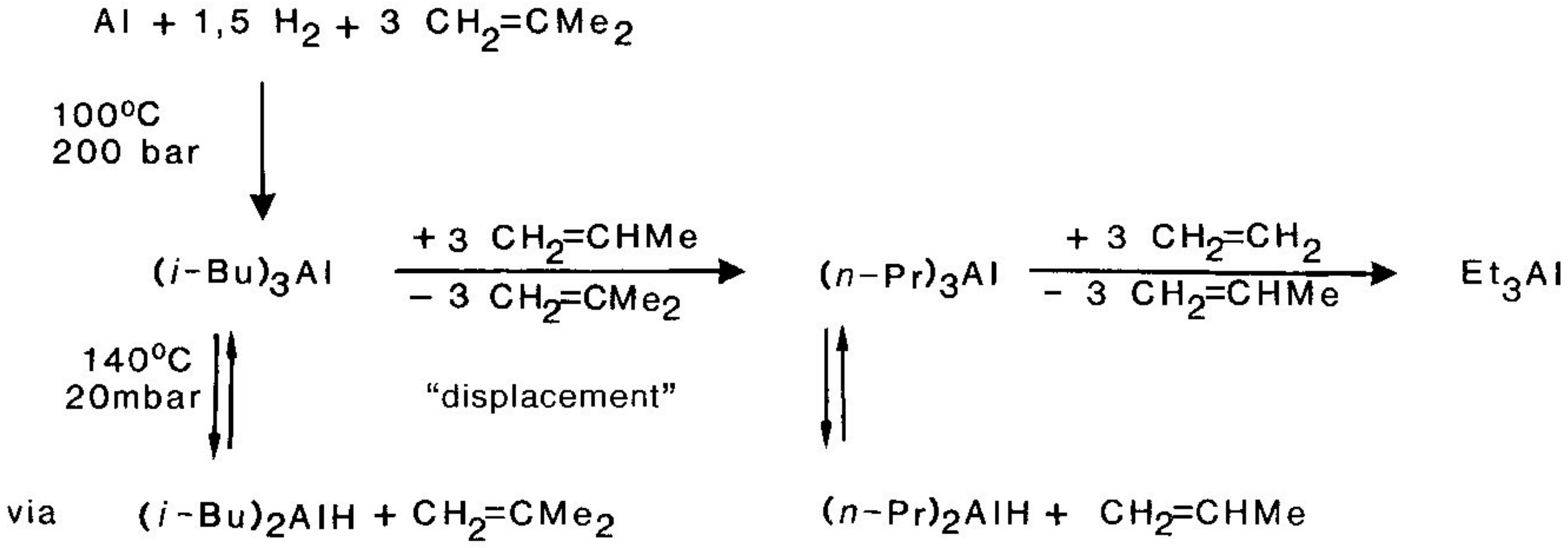
Hydroboration/dehydroboration



By adding a more high boiling terminal alkene, a **counter-thermodynamic isomerisation** of the first alkene can be carried out!



Dehydroalumination/hydroalumination



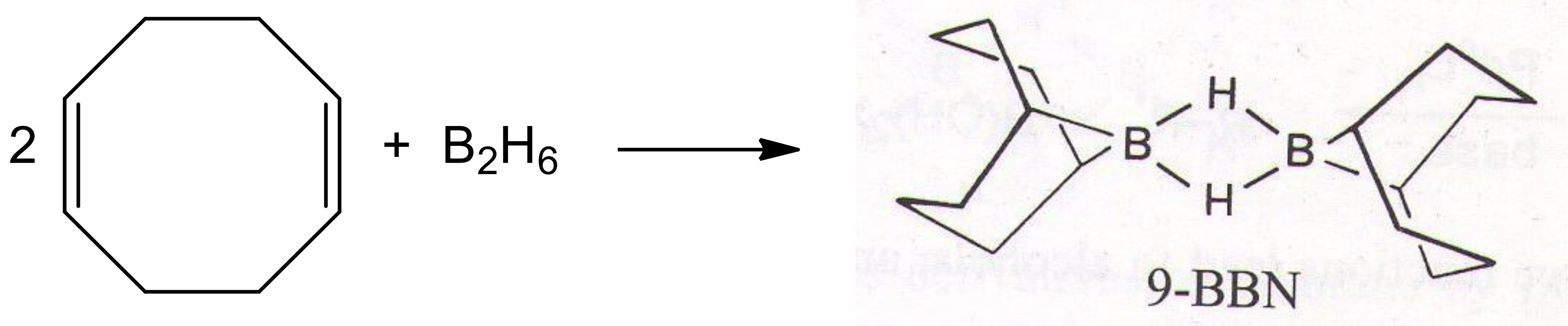
Exploits the reversibility of hydroalumination and the different affinity of Al-H for differently substituted alkenes: $CHR=CHR < CH_2=CR_2 < CH_2=CHR < CH_2=CH_2$

$Al(i\text{-}Bu)_3$ is a much more practical reagent for hydroaluminations than AlH_3 (polymeric, insoluble).

Borane synthesis

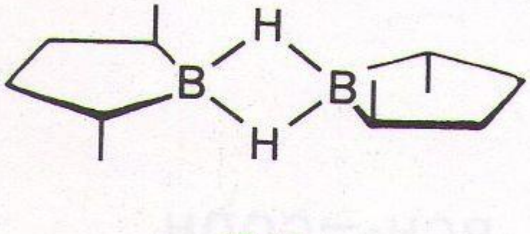
$3NaBH_4 + 4BF_3 \rightarrow 3NaBF_4 + 2B_2H_6\uparrow$

$4R_2BX + LiAlH_4 \rightarrow 4R_2BH + LiAlX_4$

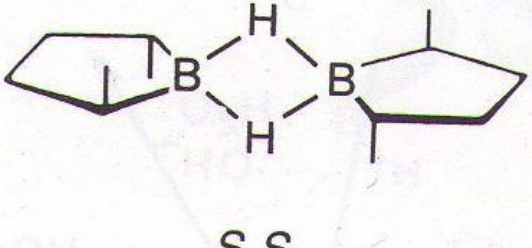


9-BBN

Bulky boranes are more selective in hydroboration and as reducing agents (see below). Furthermore, cyclic boranes such as 9-BBN do transfer only the hexocyclic residue (see below).

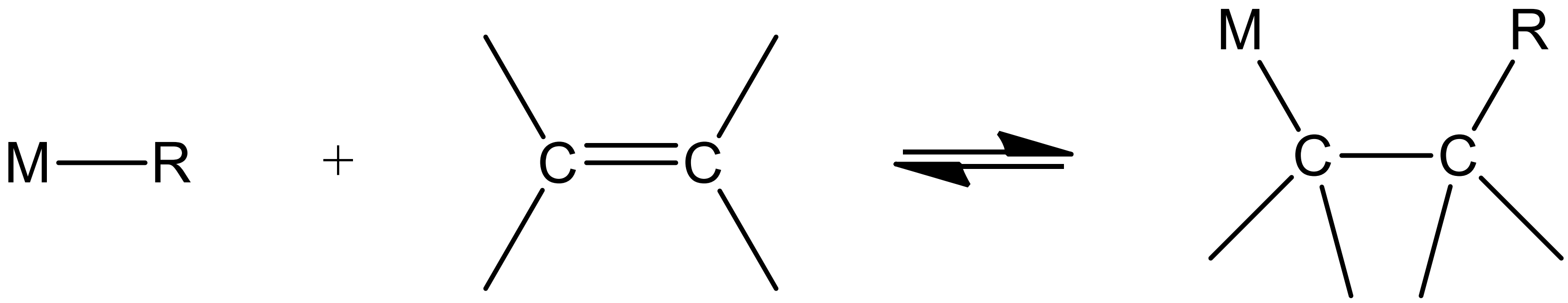


R,R



S,S

Carbometallatation



M= Li, Mg, **Al,** *transition metals (insertion)*…

Concerted reaction, feasible only with highly electrophilic main group metals (Al, Li, Mg) and with transition metals (insertion). Reaction much less easily reversible than hydroelementation; regio- and stereoselectivity similar to hydroelementation. Feasible with alkenes and also alkynes.

Other synthetic methods

Metahesis (B):

$nBX_3 + 3MR_n \leftrightarrows nBR_3 + 3MX_n$

As starting boron compounds alkoxydes are better suited than halides (more stable, less volatile, less problems with coproducts, possibility of partial substitution).

As organometallic reagent Al compounds are often employed: they do not form boron «ate» complexes, are liquids and can also act as solvent:

$BX_3 + AlR_3 \leftrightarrows BR_3\uparrow + AlX_3$

The boron compound (monomeric) is more volatile than the Al one (dimeric)!

Metathesis (Al):

Only feasible with organolithium reagents and with X ≠ halide.

$AlX_3 + 3LiR \leftrightarrows AlR_3 + 3LiX$

Other synthetic methods

Arene borylation (Friedel-Crafts):

$\text{Ar-H} + \text{BX}_3 + \leftrightarrows \text{Ar-BX}_2 + \text{HX}$ cat.= AlX_3

Transmetallation:

$2\text{Al} + 3\text{HgR}_2 \rightarrow 2\text{AlR}_3 + \text{Hg}$

Element exchange (exploits the volatility of BEt_3):

$\text{BR}_3 + \text{AlEt}_3 \leftrightarrows \text{BEt}_3\uparrow + \text{AlR}_3$

Apart from the above listed methods, peculiar synthetic strategies are employed for the industrial large scale synthesis of organoaluminum compounds. Furthermore, modern metal-catalyzed processes have been developed for the preparation of organoboron compounds, which are also industrially employed.

Industrial processes (Al)

Hűls process (employed for trimethyl- and triethylaluminum):

$4Al + 6MeCl \rightarrow 2\text{”}Me_3Al_2Cl_3\text{“}$ sesquichloride

$\text{”}Me_3Al_2Cl_3\text{“} + 2NaCl \rightarrow Me_4Al_2Cl_{2(l)} + 2NaMeAlCl_{3(s)}$

$3Me_4Al_2Cl_{2(l)} + 6Na \rightarrow 2Me_6Al_2 + 2Al + 6NaCl$

Excess Na causes further reduction of Al with formation of tetraorganoaluminates!

Ziegler direct process:

$Al + 1.5H_2 + 2AlEt_3 \rightarrow 3Et_2AlH$ 80-160°C, 100-200 atm

$3Et_2AlH + 3C_2H_4 \rightarrow 3AlEt_3$ 80-110°C, 1-10 atm

Can be employed only for aluminum trialkyls with β-hydrogens.

Metal catalyzed processes (B)

- Miyaura borylation:

Ar-X + B_2pin_2 → Ar-Bpin + X-Bpin cat.= [Pd]

- Metal-catalysed arene borylation:

Ar-H + B_2pin_2 → Ar-Bpin + HBpin cat.= [Ir], [Rh], [Cu]

Ar-H + HBpin → Ar-Bpin + H_2

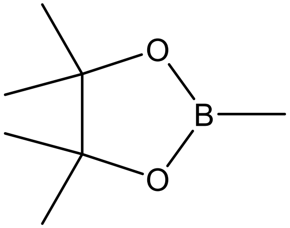
- Metal-catalysed alkane borylation:

R-H + B_2pin_2 + $\leftrightarrows$ R-Bpin + HBpin cat.= [Ir], [Rh]

R-H + HBpin → R-Bpin + H_2

Less efficient than the previous one; selective for primary C-H.

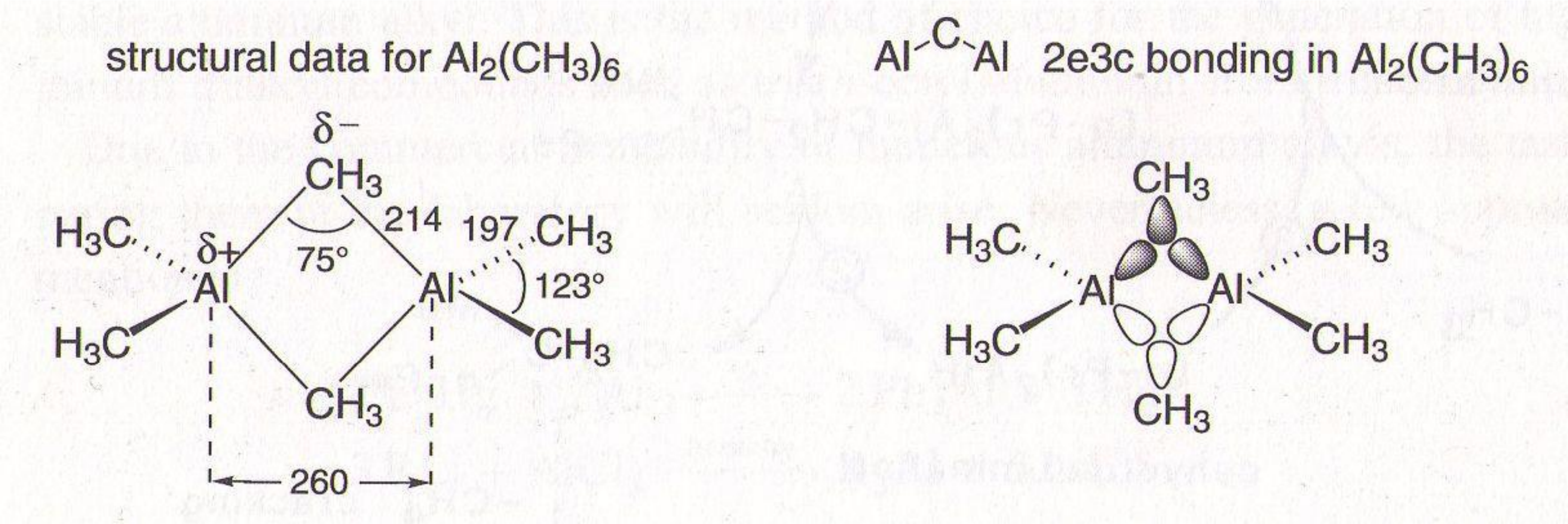
Bpin=



$2(Me_2N)_2BX$ + Na (or Cu) → $[(Me_2N)_2B]_2$ +2NaX

$[(Me_2N)_2B]_2 + 2H_2pin$ → B_2pin_2 + $2HNMe_2$

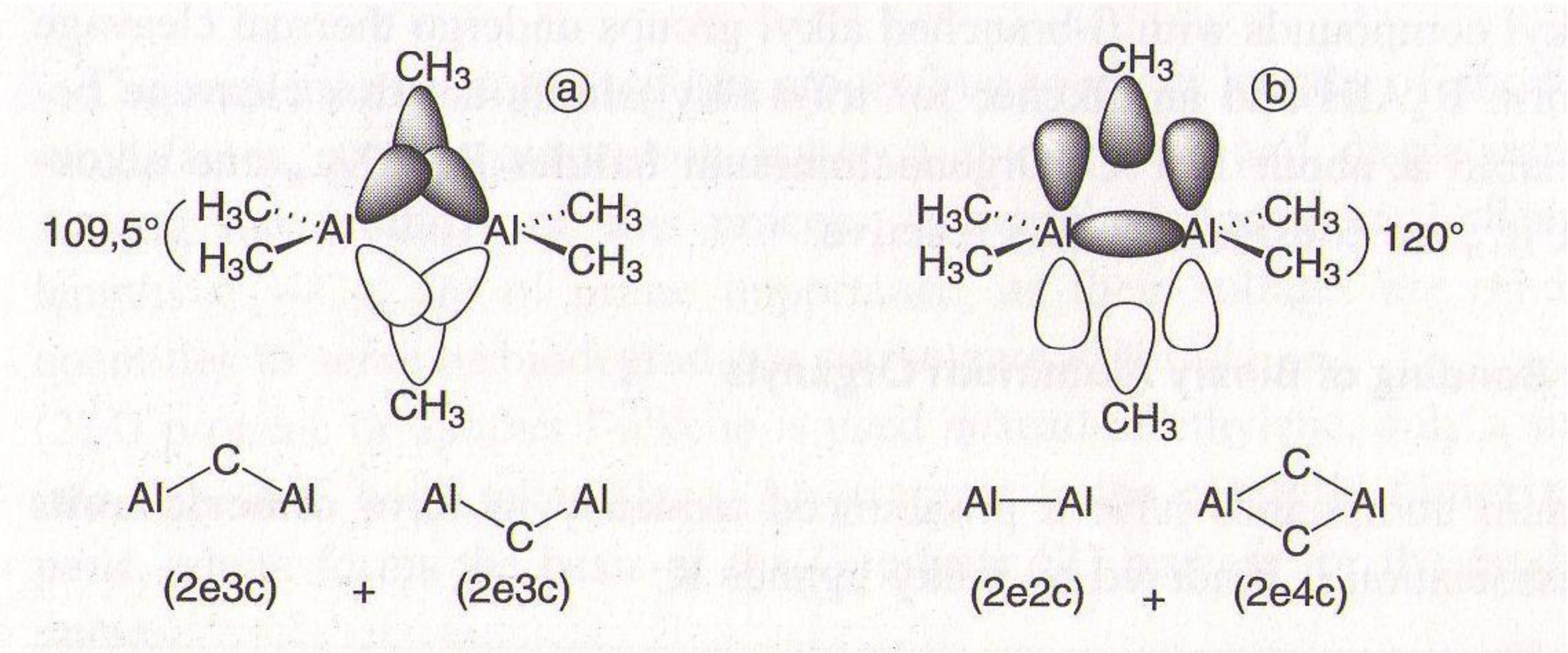
Structure of organoaluminum dimers



Some structural characteristics are not compatible with a sp^3 hybridisation for Al. For example, the Al-Al distance is shorter than in halide-bridged dimers (Al_2Cl_6 340 pm). Furthermore, the C-Al-C angle is too broad.

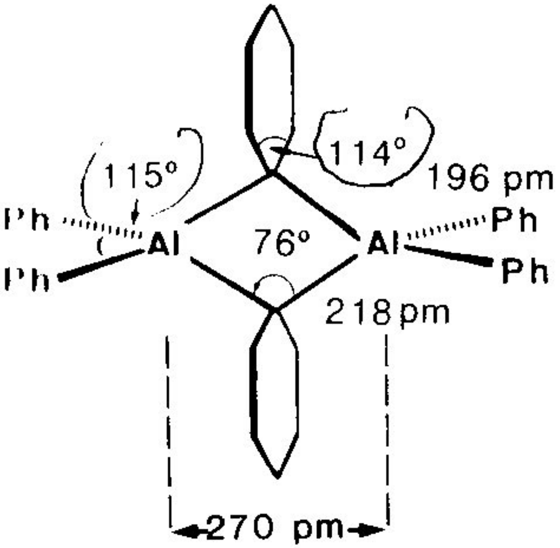
Alternative interpretation: Al hybridised sp^2 with formation of a “true” Al-Al bond.

Structure of organoaluminum dimers

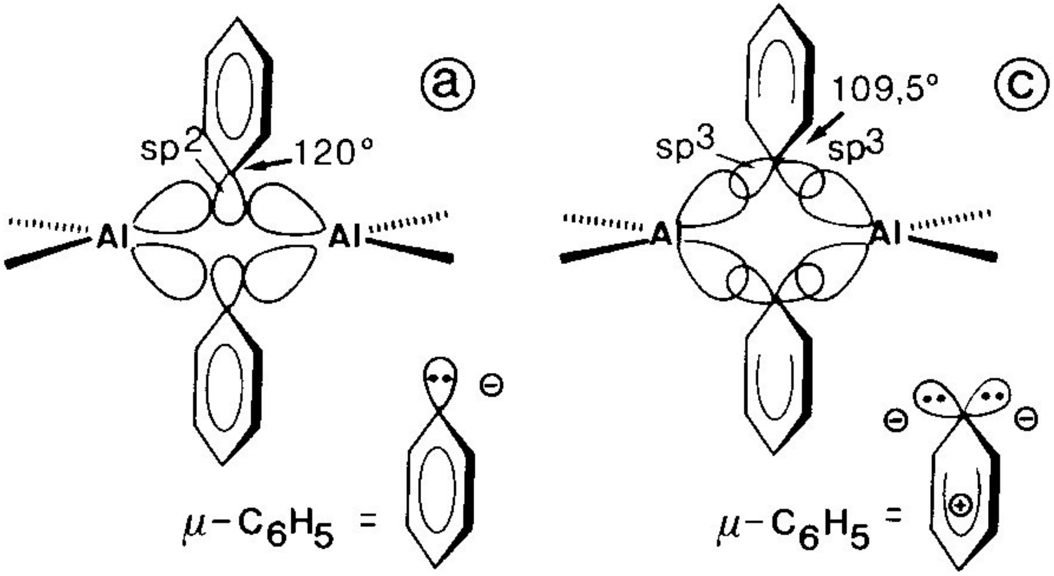


The interpretation closest to the experimental data is a compromise between these two limiting resonance structures.

Structure of organoaluminum dimers



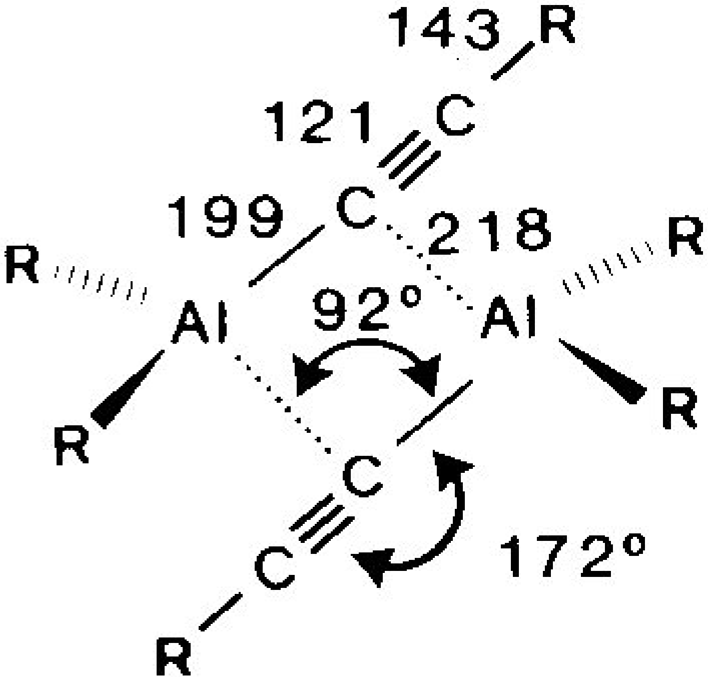
structural data for $Al_2(C_6H_5)_6$



alternative hybridizations at the bridging C atom

In this case, the picture is further complicated by the possibility of the bridging carbon atom to change its hybridisation, involving π-electrons in the bridge formation!

Structure of organoaluminum dimers



R=Ph

In the case of unsaturated substituents, it is possible that the bridging carbon employs different orbitals to interact between the two Al atoms. Such bridges are obviously more stable (formally, the bridging ligand shares more than two electrons…).

Association equilibria

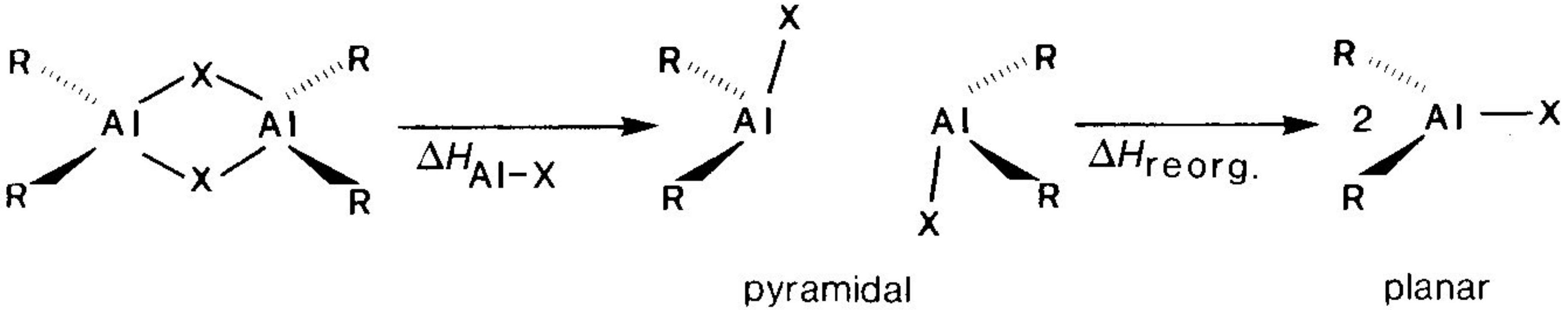
$$[\mathrm{R_2AlX}]_2 \longrightarrow 2\,\mathrm{R_2AlX} \qquad \Delta H_{\mathrm{react.}}$$

$$\begin{array}{lccccccccc} \mathrm{X}: & \mathbf{H} & > & \mathrm{Cl} & > & \mathrm{Br} & > & \mathrm{I} & > & \mathrm{CH_3} \\ \hline \Delta H_{\mathrm{react.}}: & 150 & & 124 & & 121 & & 102 & & 84\ \mathrm{kJ/mol} \end{array}$$

Hydrides and halides form very stable dimers. However, the reaction enthalpy does not strictly follow the trend of the strength of the bridging Al-X bond, which can be determined through measurements of the average bond enthalpy.

$$\Delta H_{\mathrm{Al-X}}: \mathrm{Cl} > \mathrm{Br} > \mathrm{I} > \mathbf{H} > \mathrm{Me}$$

Association equilibria



bond cleavage + reorganization

$$\Delta H_{\text{react.}} = \Delta H_{\text{Al–X}} + \Delta H_{\text{reorg.}}$$

measure of the bond energy D(Al–X) in an Al–X–Al bridge

(1) intramolecular ligand repulsion decreases: pyramidal > planar
(2) Al(p_π) – X(p_π) bonding is stronger in the planar than in the pyramidal configuration.
(3) Al $\overset{\sigma}{—}$ C bond energy decreases: $sp^3 > sp^2$

Association equilibria of AlR_3

The equilibria described before are often shifted towards the dimer (e. g. K_{eq} $Me_6Al_2 = 10^{-8}$), and their position depends on the no. di e^- in the bridge, on steric effects and on the solvent. However, the monomer-dimer equilibrium at room T is very fast (only 1 signal of the methyl groups is visible in NMR down to low temperatures).

The equilibrium is established also in mixtures of different triorganoaluminum compounds (symmetrisation), in which case the bridging positions are occupied by the organic residues forming the strongest bridges.