Main Group Organometallic Compounds

Outline

- Classification of organometallic compounds
- Formation of M-C bonds and their stability to hydrolysis and oxidation
- Structure and properties of lower alkyls of group 1 metals, beryllium and boron
- Synthesis, structure and reactions of Grignard reagents
- Properties and uses of group 14 organometallic compounds

References – P. Powell, ***Principles of Organometallic Chemistry***, 2nd ed., Chapman and Hall

– G. Wilkinson, F. Stone, E. Abel, ***Comprehensive Organometallic Chemistry, Vol. 1***

http://web.chemistry.gatech.edu/~wilkinson/Class_notes/CHEM_3111_6170/Main_group_organometallics.pdf

http://www.cem.msu.edu/~reusch/VirtualText/orgmetal.htm

Organometallic Compounds

- Definition – compounds containing metal-carbon bonds

$$M^{\delta+}—C^{\delta-}$$

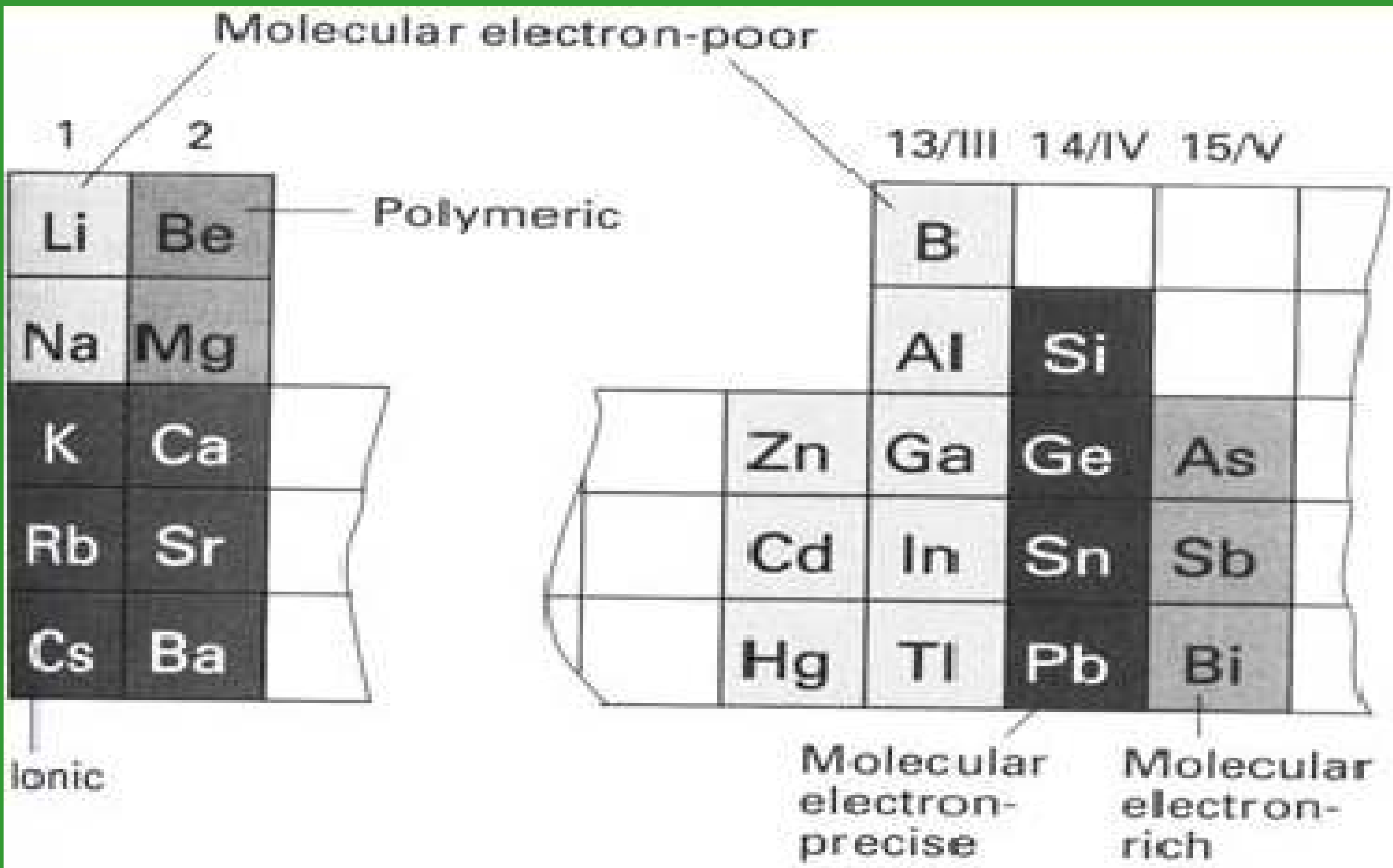
- May include B, Si, Ge, As, Sb, Se, Te
- Exist at ordinary temperatures as low melting crystals, liquids or gases
- Commonly soluble in weakly polar organic solvents eg. toluene, ethers, alcohols
- Variable chemical properties

Classification

Based on type of metal-carbon bond

- Ionic – most electropositive elements
- Covalent
  - electron deficient: metals with less than half filled valency shells, form strongly polarizing cations
  - electron precise
  - electron rich

Classification



15.1 The classification of methyl compounds of the metals and metalloids.

http://web.chemistry.gatech.edu/~wilkinson/Class_notes/CHEM_3111_6170/Main_group_organometallics.pdf

Reactivity

Increased Reactivity ←

1	2
Li	Be
Na	Mg
K	Ca
Rb	Sr
Cs	Ba

12	13	14	15
	B		
	Al	Si	
Zn	Ga	Ge	As
Cd	In	Sn	Sb
Hg	Tl	Pb	Bi

Ionic

Covalent: metals that have a strong tendency to form alkyl or aryl bridged species

Covalent: Elements that form volatile covalent organo derivatives

In general, the reactivity parallels the ionic character of the C-M bond

Classes of Organometallic Compounds

Ionic – M^+R^- highly electropositive metals

- very reactive
- high mpt.
- low volatility
- Low or negligible solubilities in non-polar, non coordinating solvents

Classes of Organometallic Compounds

Highly polar, covalent – Li, Al alkyls, Grignard reagents

- Polarity is a source of reactivity

- Adopt associated structures – bonding power of electron pairs spread over more than 2 atoms

Classes of Organometallic Compounds

Slightly polar covalent – less electropositive elements

- Behave like organic compounds
- Low mpt.
- Volatile
- Soluble in non-polar solvents

Stability of Organometallic Compounds

Oxidation

- All organometallic compounds are thermodynamically unstable to oxidation
  - Due to large negative free energies of formation of metal oxide, carbon dioxide and water
- Many kinetically unstable to oxidation at or below room temperature
  - Associated with the presence of empty low lying orbitals on the metal atom, or a non bonding pair of electrons

Stability of Organometallic Compounds

Hydrolysis

- Involves nucleophilic attack by water
- Facilitated by the presence of empty low lying orbitals on the metal atom which can accept electrons
  - Organometallic compounds of Gps 1, 2, Zn, Cd, Al, Ga, In readily hydrolysed
- Rate of hydrolysis is dependent on M-C bond polarity – greater polarity, faster rate

- Alkyls and Aryls of groups 14 and 15 are kinetically inert to hydrolysis by water because the metal atoms are surrounded by a filled shell of 8 electrons. Nucleophilic attack is no longer favoured

Main Group Metal-Carbon Bond Formation

Reaction of metal with organic halogen compounds

$$2M + nRX \rightarrow R_nM + MX_n \quad \text{(or } R_xMX_y \text{ where } x+y=n\text{)}$$

- Reaction driven by exothermic formation of the metal halide
- Suitable for synthesis of organometallic compounds of the most electropositive elements

Main Group Metal-Carbon Bond Formation

- Metal exchange

$$M + RM' \rightarrow RM + M'$$

- Dependent on the difference in free energies of formation of the two species RM′ and RM

- Endothermic or weakly exothermic organometallic compounds should be the most versatile reagents RM′ in such reactions (ie compounds of Hg, Tl, Pb, Bi)

Main Group Metal-Carbon Bond Formation

- Reactions of organometallic compounds with metal halides

$$RM + M'X \rightarrow RM' + MX$$

- Most widely used and versatile of all laboratory methods

- Organolithium and Grignard reagents most commonly used

Main Group Metal-Carbon Bond Formation

- Insertion of alkenes and alkynes into metal or nonmetal hydride bonds

Hydroboration

$$RCH{=}CH_2 + HB\langle \longrightarrow RCH_2CH_2B\langle$$

Hydrosilation

$$X_3SiH + H_2C{=}CHY \rightarrow X_3SiCH_2CH_2Y$$

$$X_3SiH + HC{\equiv}CH \rightarrow X_3SiCH{=}CH_2 \rightarrow X_3SiCH_2CH_2SiX_3$$

Main Group Metal-Carbon Bond Formation

- Other insertion reactions

Addition of a species A-B to an unsaturated system X=Y or X≡Y

$$\text{A-B} + \text{X=Y} \rightarrow \text{A-X-Y-B}$$

- A = metal atom
- B =

Organometallic Compounds of Group 1

- Highly reactive
- Reacts readily with oxygen (all traces of oxygen must be excluded when considering other reactions)
- Some ionic, some covalent
- Reactivity of heavier alkali metals due to negative charge on C atom

Organometallic Compounds of Group 1

- Methyl, ethyl and phenyl derivatives ignite in air

- Potassium and sodium compounds more easily oxidized than lithium analogues

- For oxidation of alkyl compounds:

$$RM + O_2 \rightarrow RO_2M$$

$$RO_2M + RM \rightarrow 2ROM$$

Organometallic Compounds of Group 1

Protonation and Hydrolytic Stability

- Readily hydrolysed
- React readily with a variety of proton sources to give the hydrocarbon RH
- Deprotonate solvents, ethers in particular

$$Et_2O + RLi \rightarrow RH + CH_2{=}CH_2 + LiOCH_2CH_3$$

Organolithium Compounds

- Small size and polarizing power of Li^+ causes its compounds to have more covalent character than other group members

- Organolithium compounds more stable and less reactive than other organocompounds of group 1
  - Due to lower polarity

Valuable in chemical synthesis due to:

- High reactivity

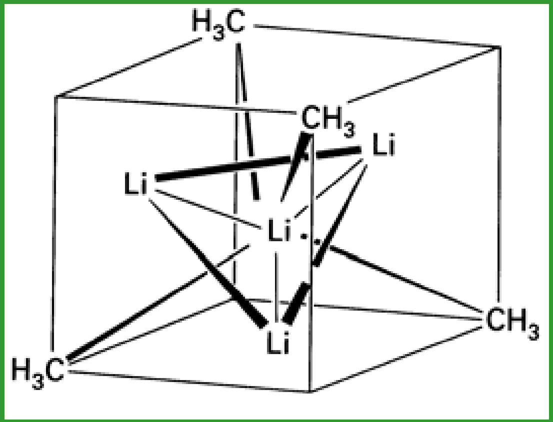
- Relatively easy preparation

- Solubility in inert solvents

- Used for the same kinds of synthesis as Grignard reagents

Organolithium Compounds

- Polar character causes strong association
- Geometry of coordination sphere is determined by steric effects (as in ionic structures) rather than interaction of electron pairs.
- Eg. Methyllithium consists of tetrameric aggregates in solid state and in solution $Li_4(CH_3)_4$



Lithium Organometallics

Lithium alkyls

- Extremely reactive
- Sensitive to oxygen and moisture
- Dry apparatus and solvents must be used
- Air must be excluded (reactions carried out under argon or nitrogen

Lithium Organometallics

Preparation

– Lithium metal with alkyl halide

$$2Li + RX \rightarrow LiX + RLi$$

Physical state of Li important – any coating must be removed (oil coating removed by washing in hexane under inert atmosphere

Lithium Organometallics

Preparation

– Metal-metal exchange (transmetallation)

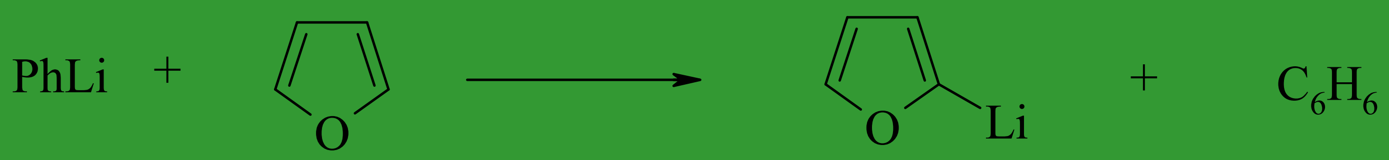
$2Li + HgR_2 \rightarrow 2LiR + Hg$ Dry N_2, hydrocarbon solvent

Convenient route to vinyl and allyllithium compounds

$4PhLi + (H_2C{=}CH)_4Sn \rightarrow 4H_2C{=}CHLi + Ph_4Sn$

Lithium Organometallics

- Preparation
- Metal – hydrogen exchange (metallation)



- Believed to involve nucleophilic attack on the 'acidic' H atom

- Metal – halogen exchange (halide abstraction)

$$RLi + PhI \rightarrow RI + PhLi$$

Organolithium Reactivity

- Nucleophilic attack on multiple bonds

$$RLi + R'C{\equiv}CH \rightarrow LiC{\equiv}CR'$$

- React with aldehydes and ketones to form alcohols

$$RLi + R'CHO + H_2O \rightarrow RCH(OH)R' + LiOH$$

- Carboxylic acid salts and acid chlorides to form ketones (after hydrolysis)

Organolithium Reactivity

- Reaction with halogens

$$LiR + X_2 \rightarrow RX + LiX \quad \text{(Reduction)}$$

- Addition Reactions

$$BR_3 + LiR \rightarrow LiBR_4$$

Halide abstraction (nucleophilic substitution)

$$LiR + BCl_3 \rightarrow BR_3 + 3LiCl$$

Proton abstraction (acid-base reaction)

$$Li^{\delta+-\delta}Bu + C_6F_5H \rightarrow BuH + C_6F_5Li$$

Organosodium and potassium compounds

- Organic groups have considerable carbanionic behaviour
- Extremely reactive
- Paraffin hydrocarbons are the most suitable reaction media (ethers are cleaved, aromatic hydrocarbons metallated)

Organosodium and potassium compounds

Preparation

- Mercury alkyl method

$$2Na\ (excess) + HgR_2 \rightarrow 2RNa + Hg, Na\ (amalgam)$$

- Exchange between sodium or potassium tert-butoxide and organolithium (in paraffinic solvent)

$$RLi + Bu^tONa \rightarrow RNa + LiOBu^t$$

- Direct reaction between the metals and alkyl or aryl halides is complicated by exchange and coupling reactions which lead to mixtures

Exception: $3\ C_5H_6 + 2Na \rightarrow 2C_5H_5^-Na^+ + C_5H_8$

Group 2 Organometals

Be, Mg

- form covalent compounds
- highly reactive
- resemble organolithium compounds

Ca, Sr, Ba – Ionic

- Few compounds

Organoberyllium Compounds

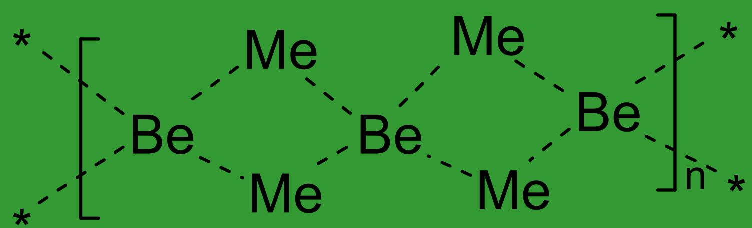
- Be^{2+} - High polarizing power – covalent compounds
- Coordination number up to 4 known
- CN = 2 – use of sp hybrid orbitals, linear compounds eg. $Bu^t{}_2Be$
- CN = 3 – sp^2 orbitals, eg. Me_2BeNMe_3, rare
- CN = 4 – sp^3 orbitals, tetrahedral bonding, common

- Limited study due to high toxicity of Be compounds and air sensitivity of organometallic derivatives

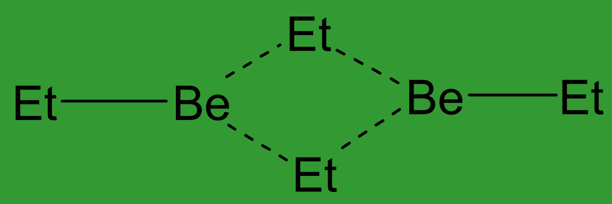
Organoberyllium Compounds

- Solids or liquids
- Air sensitive
- React with Lewis bases, protic acids
- Form polymeric species (extent of association dependent on steric requirements of the organic group)

Organoberyllium Compounds - Structure



Dimethylberyllium - polymeric



Diethylberyllium - dimeric

Di-tert-butylberyllium - monomeric

Dimethylberyllium

- Colourless needles
- Polymeric
- Be sp^3 hybridized, C sp^3 hybridized
- 3 centre, 2 electron bonds formed
- Only soluble in solvents which are sufficiently strong donors to break down polymeric structures eg. Insoluble in benzene, monomeric in ether

Grignard Reagents

- Alkyl or aryl magnesium halides RMgX
- Most important organometallic compounds
- Commonly used in organic and inorganic synthesis
- Act as nucleophiles
- React readily with protic solvents and compounds with acidic protons

Grignard Reagents - Synthesis

- Action of alkyl or aryl halide on Mg

$$RX + Mg \rightarrow RMgX$$

- Must be carried out in absence of moisture and oxygen
  - polar aprotic solvent eg. diethyl ether or THF; inert atmosphere
- Reactivity of RX with Mg:

$$I > Br > Cl > F$$

- Monomeric species exist in dilute solutions and in strong donor solvents
- In diethyl ether at high Mg concentrations, polymeric species exist
- Structure normally includes the solvent

Grignard Reagents

Solution equilibria

- Variety of species present in solution
- Equilibria position dependent on
  - Steric and electronic nature of alkyl or aryl group
  - Nature of the halogen (size, electron donor power)
  - Nature of the solvent
  - Concentration
  - Temperature
  - Presence of impurities

Reactions

- Reaction with acid

$$RMgX + HX \rightarrow RH + MgX_2$$

- Reaction with halogen

$$RMgX + X_2 \rightarrow RX + MgX_2$$

- Reactions with halides
  - $RMgX + BCl_3 \rightarrow BR_3$
  - $RMgX + SnCl_4 \rightarrow SnR_4$

Reactions

- Reactions with ketones & CO_2
  - $RMgX + H_2C{=}O + H_2O \rightarrow RCH_2OH$
  - $RMgX + R'HC{=}O + H_2O \rightarrow RR'CHOH$
  - $RMgX + R'_2C{=}O + H_2O \rightarrow R'_2RCOH$
  - $RMgX + CO_2 + H^+ \rightarrow RCOOH$

Organoboron

Trialkyl and triarylboranes

- Monomeric – too much crowding around B atom for polymerisation

- Preparation
- Reaction of organolithium, Grignard or organoaluminum reagents on borate esters or the ether complex of BF_3

$$B(OMe)_3 + 3RMgX \rightarrow R_3B + 3Mg(OMe)X$$

$$3CH_3MgI + BF_3 \rightarrow (CH_3)_3B$$

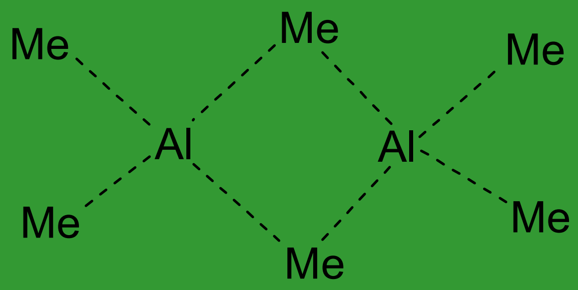
- Hydroboration

$$RCH{=}CH_2 + HB\langle \longrightarrow RCH_2CH_2B\langle$$

Organoaluminum

Trialkyls and triaryls

- Highly reactive
- Colourless
- Volatile liquids or low melting solids
- Ignite spontaneously in air
- React violently with water
- Dimeric



Organoaluminum

- AlR_3 (Al_2R_6) react readily with ligands to form adducts $LAlR_3$

$$Al_2Me_6 + 2NEt_3 \rightarrow 2Me_3AlNEt_3$$

- Stronger Lewis acids than organoboron compounds

- React with protonic reagents to liberate alkanes

$$Al_2R_6 + 6HX \rightarrow 6RH + 2\ AlX3 \qquad (X = OH, OR, Cl, Br)$$

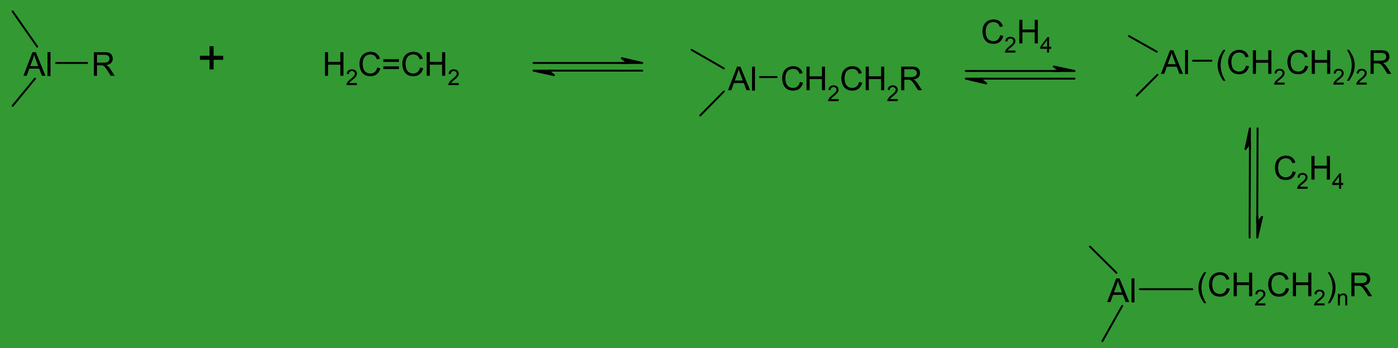
- Reactions with halides or alkoxides of less electropositive elements produces other organometallics

$$MX_n + AlR_3\ (excess) \rightarrow MR_n + n/3AlX_3$$

(M = B, Ga, Si, Ge, Sn, etc.)

Organoaluminum

- Main importance stems from alkene insertion reactions
  – Alkenes insert into the Al-C bonds of AlR_3 at 150^o and 100atm to give long chain derivatives



Group 14 Organometals

Silicon

Organosilicon compounds prepared by:

- Reaction of $SiCl_4$ with organolithium, Grignard reagents or organoaluminum compounds
- Hydrosilation of alkenes
- Direct reaction of RX with Si in the presence of a Cu catalyst

$$2MeCl + Si \xrightarrow[300^{o}]{\text{Cu powder}} Me_2SiCl$$

Organosilicon Compounds

- Form polymers under hydrolytic conditions

$$Ph_2SiCl_2 \xrightarrow{H_2O} Ph_2Si(OH)_2 \xrightarrow{> 100^o} 1/n\ (Ph_2SiO)_n + H_2O$$

Organotin Compounds

- $SnX_{4-n}R_n$ X = Cl, F, O, OH, n = 1 - 4
- For commercial applications, R is usually a butyl, octyl or phenyl group
- Mono, di, tri and tetrasubstituted compounds are widely used

Organotin Compounds - Applications

- Monosubstituted compounds $RSnX_3$
  - PVC stabilizers
- Disubstituted R_2SnX_2
  - Plastics industry as stabilizers (PVC)
  - Catalysts in production of urethane foam
  - Room temperature vulcanization of silicones
- R_3SnX
  - Fungicides
  - Bactericides
  - Insecticides
  - rodenticides
- R_4Sn
  - Preparation of other organotin compounds

Organotin Compounds - Synthesis

- Grignard
- Organoaluminum
- Direct reaction with metal and organic halide