

# Systematic Chemistry of elements s and p

## I - s block metals

- Presence of cations  $A^+$  ou  $B^{2+}$  in minerals and natural water. Some are essential to life metabolism (ex:  $K^+$ ,  $Ca^{2+}$ ).

- Low ionization energies and vaporization enthalpies



### Labile valence electrons

- Strong reducing agents: vigorous reaction with  $H_2O$  ( $M + H_2O \rightarrow H_2$ )

- Oxidation degree: +1 for alcalins et +2 for earth-alcalin metal ions.

- In the absence of air and moisture,  $Na^-$  anions are accessible.

- The coordination of "hard" » polydentate ligands (O- ou N-based) typically afford stable metal chelates.

## Redox Reactions

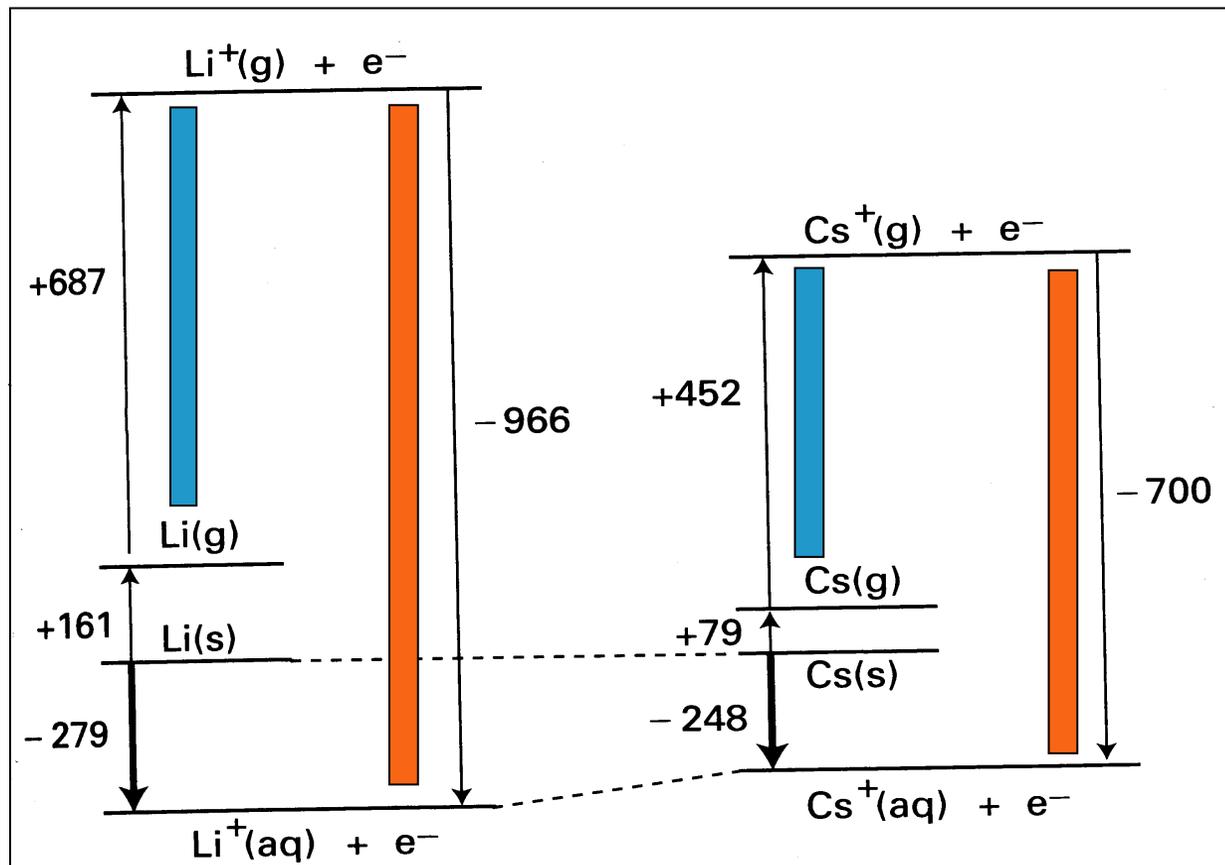


Why do these metal spontaneously inflame upon contact with  $H_2O$  ?

- Low melting point metals, the liquid provides a clean surface, which is extremely favorable to the redox reaction to occur (highly exothermic).

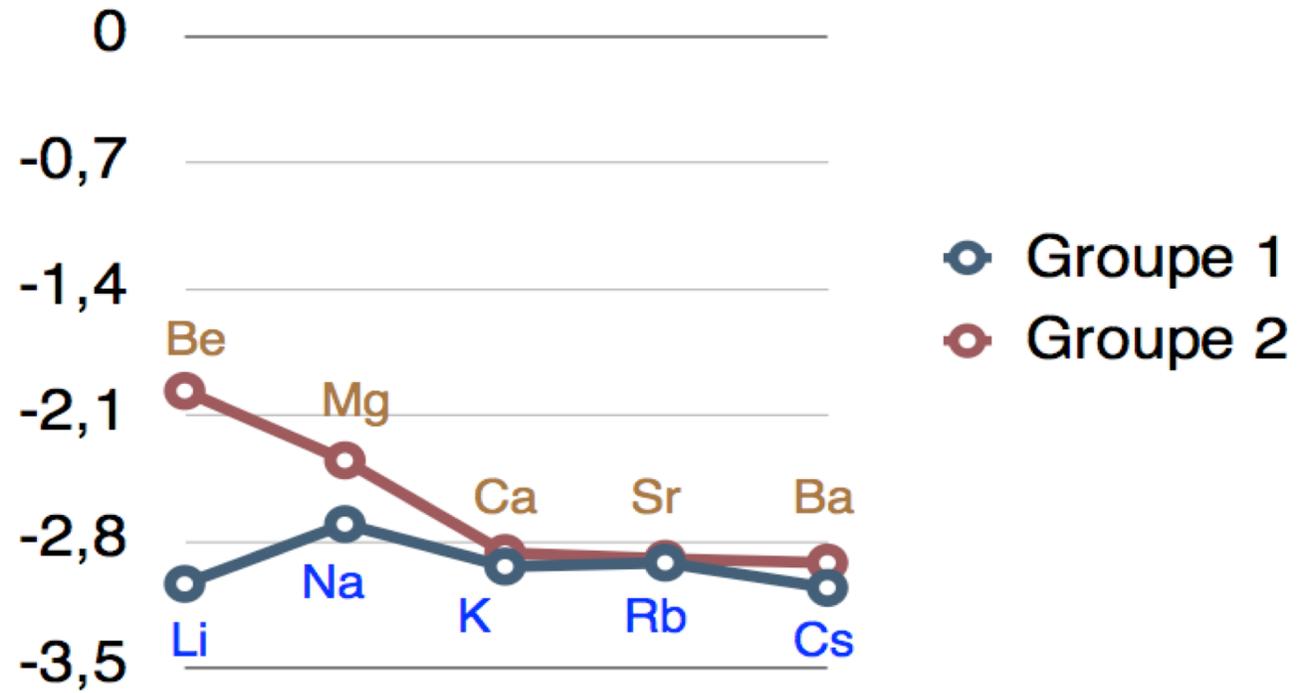
- In the case of beryllium and magnesium, formation of a protecting layer of metal oxide.

☞  $E^\circ$  all close to one another : -3 V (except for Be : -1.97V and Mg : -2.36 V: small cations). Such a uniformity arises from a compensation between the enthalpie of formation de  $M^+(g)$  and the enthalpie of hydratation de  $M^+$ . (see thermo cycles thermo on the next diapo).



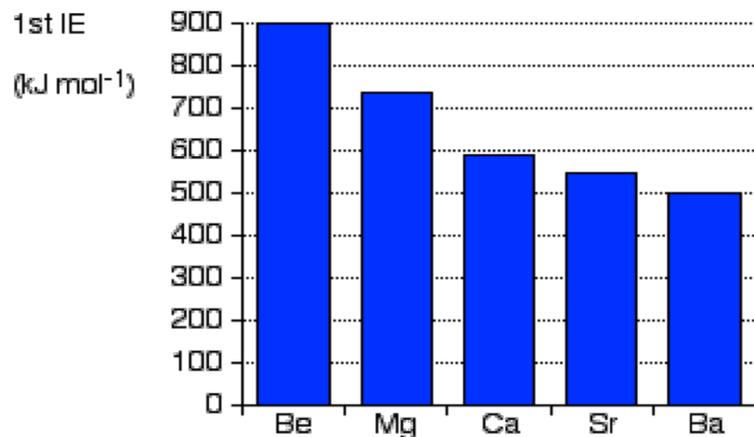
Compensation between the **energy of ionisation** and the **energy of hydration**. (values give in  $\text{KJ}\cdot\text{mol}^{-1}$ )

**Potentils standards des éléments s**  
**( $E_0$  en volt)**

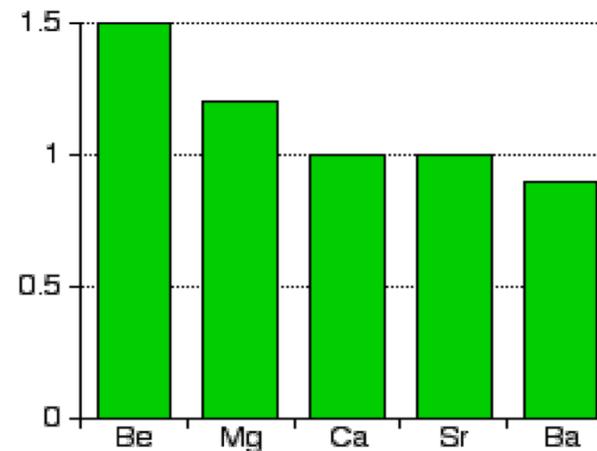


## General Tendency: Example of group 2 metals

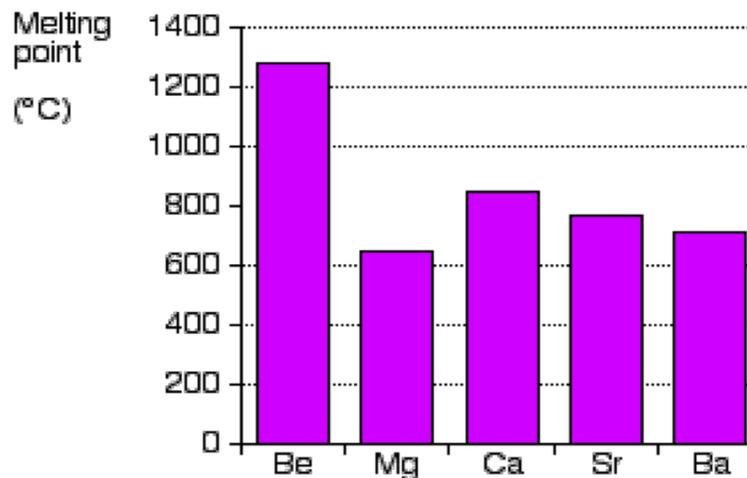
**First Ionisation Energy of the Group 2 elements**



**Electronegativity of the Group 2 elements**



**Melting Points of the Group 2 elements**



## C) Composés binaires

Despite similar  $E_0$  values, typical distinct behavior is observed for some alcalin and earth-alcalin metals

Example: : the only stable nitride is  $\text{Li}_3\text{N}$ . Specific reactions are also observed with  $\text{O}_2$ .

Coordination : mostly octahedral coordination in aqueous medium, except for  $\text{Li}^+$  (small cation) in some crystalline compounds ( $\text{Li}_2\text{O}$ , antifluorine-type structure). Cation  $\text{Be}^{2+}$ , small and highly charged (2+) affords compounds with some covalent character with typically four-coordinated Be centers.

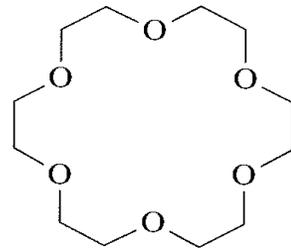
Possibility of catenation (formation of chains)

Examples :

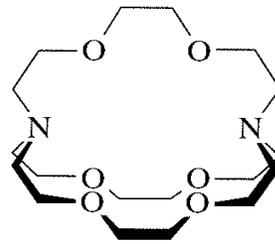
- $\text{Na}_2\text{O}_2$  (peroxyde ion  $\text{O}_2^{2-}$ ),  $\text{Li}_2\text{O}$  (oxyde ion  $\text{O}^{2-}$ ),  $\text{KO}_2$  (superoxyde ion  $\text{O}_2^-$ ).
- Stabilisation of peroxydes et superoxydes by larger cations.

## Complexes Formation

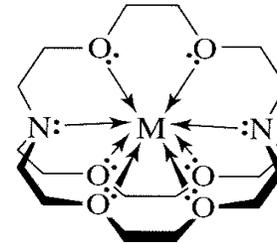
- Metallic ions of bloc s ( $M^+$  et  $M^{2+}$ ) are considered as “hard” Lewis acids and can thus form complexes via Coulombian interactions with “hard” Lewis bases (small electronegative electron donors: O and N)
- Formation of remarquable complexes with polydentate ligands such as ether-crown and cryptand ligands.



18-crown-6  
or  
18C6



Cryptand [2.2.2]  
or  
C222



These ligands are « sterically » selective for a given  $M^+$  ou  $M^{2+}$  cation

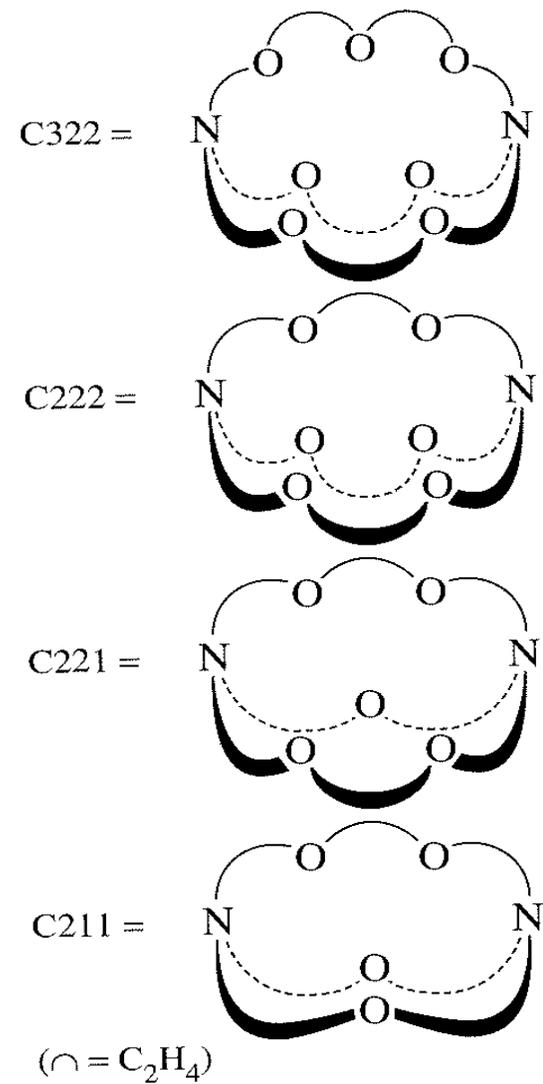
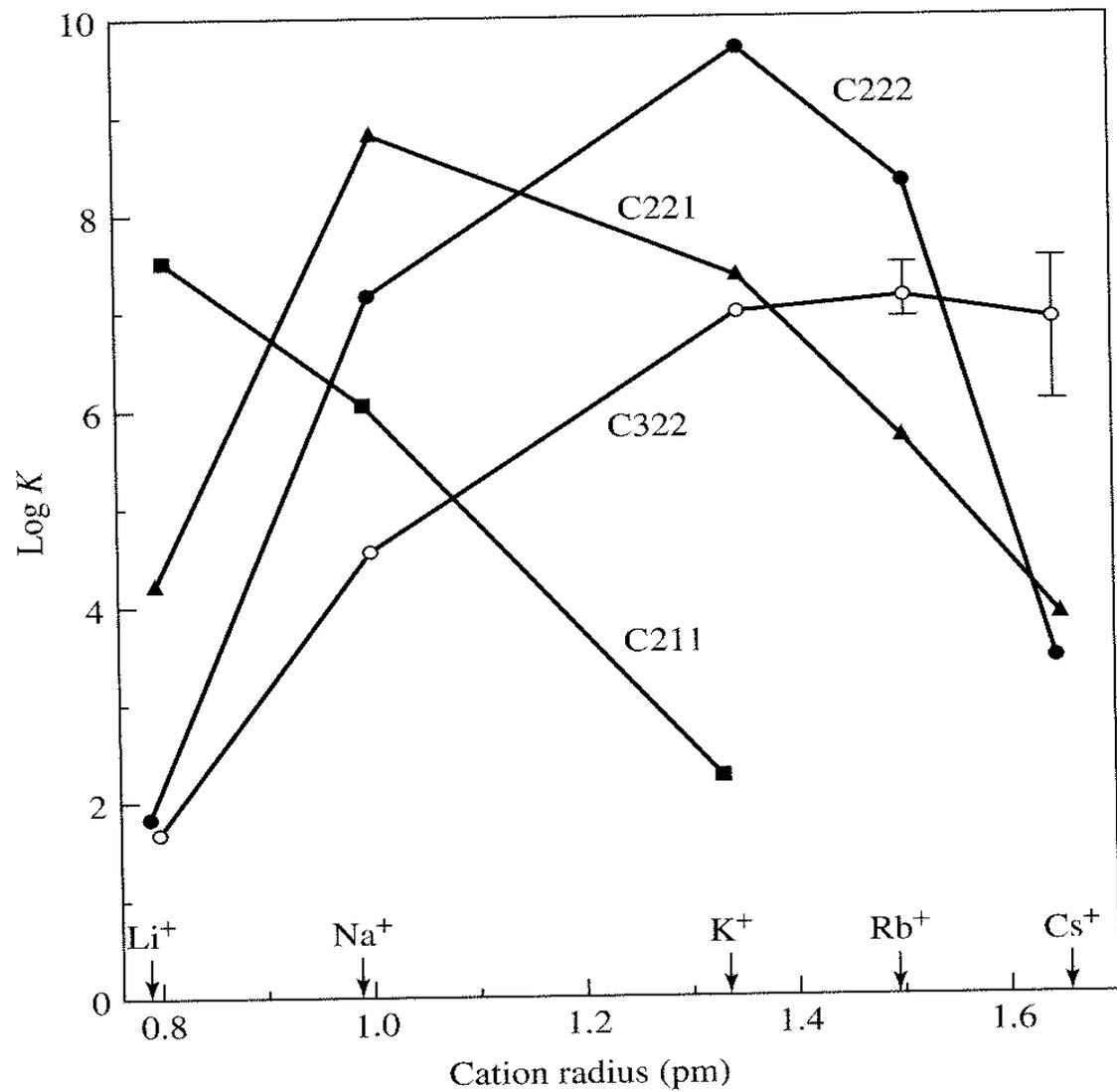


Necessary adequation between the size of  $M^+$  ou  $M^{2+}$  and that of the hosting cavity



Possibility of selective complexation

# Formation Constants of cryptand complexes As a function of cation size

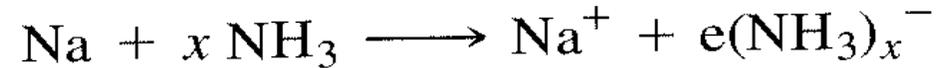




## Solutions of solvated electrons and Electrides

Alcalin metals are soluble in etheroxyde solvents and some amines to yield solutions of solvated electrons

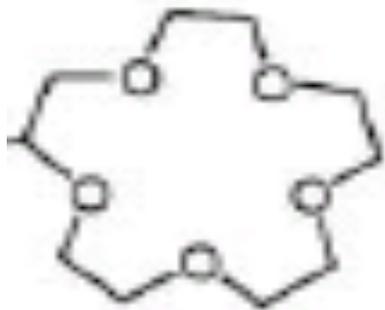
Examples: Na is soluble in liq.  $\text{NH}_3$  ( $T_{\text{eb}} = -33^\circ \text{C}$ ) to afford a solution of electrons solvated by  $\text{NH}_3$



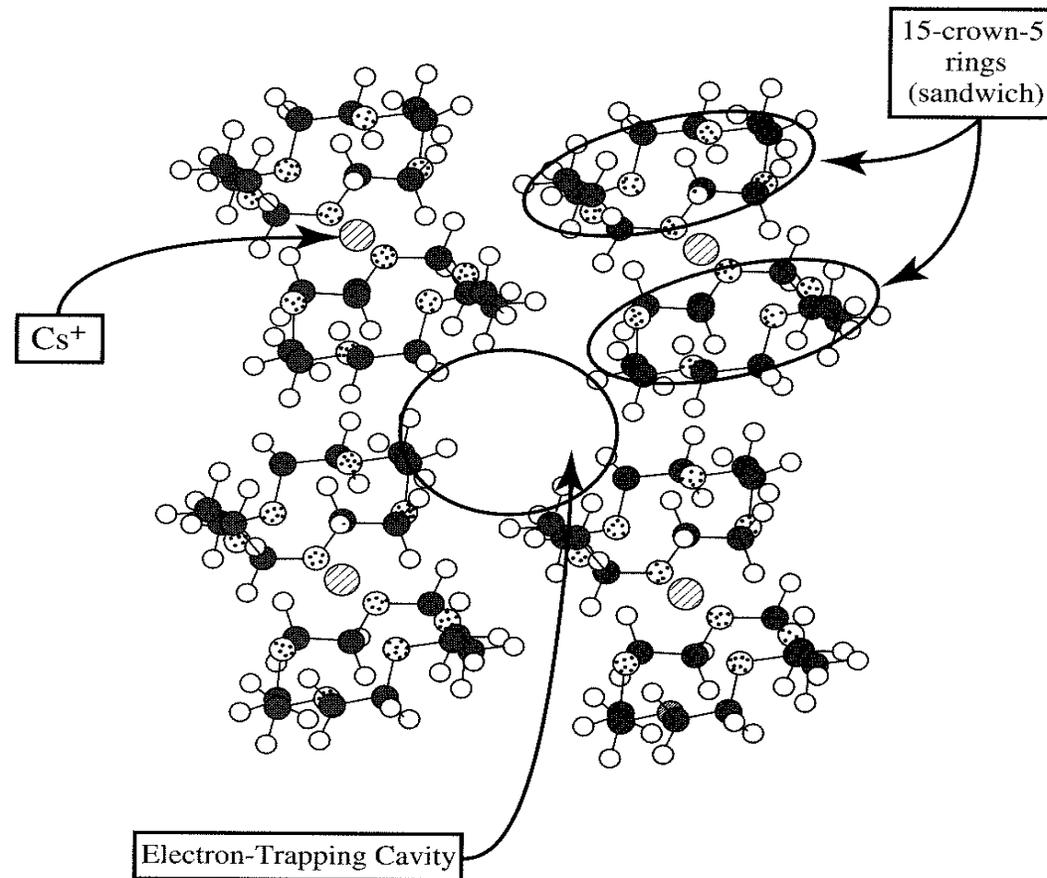
- Diluted solution (dark blue): excellent reducing properties
- Concentrated solution (bronze appearance): delocalized electrons like in a metal.

**Electrides:** Solid compounds containing solvated electrons. The complexation by crown-ethers of alcalin ions (ex:  $\text{Cs}^+$ ) may allow the formation of stable electrides.

**Electride** consisting of  $\text{Cs}^+$ -[15-ether-5] anions and « free » electrons



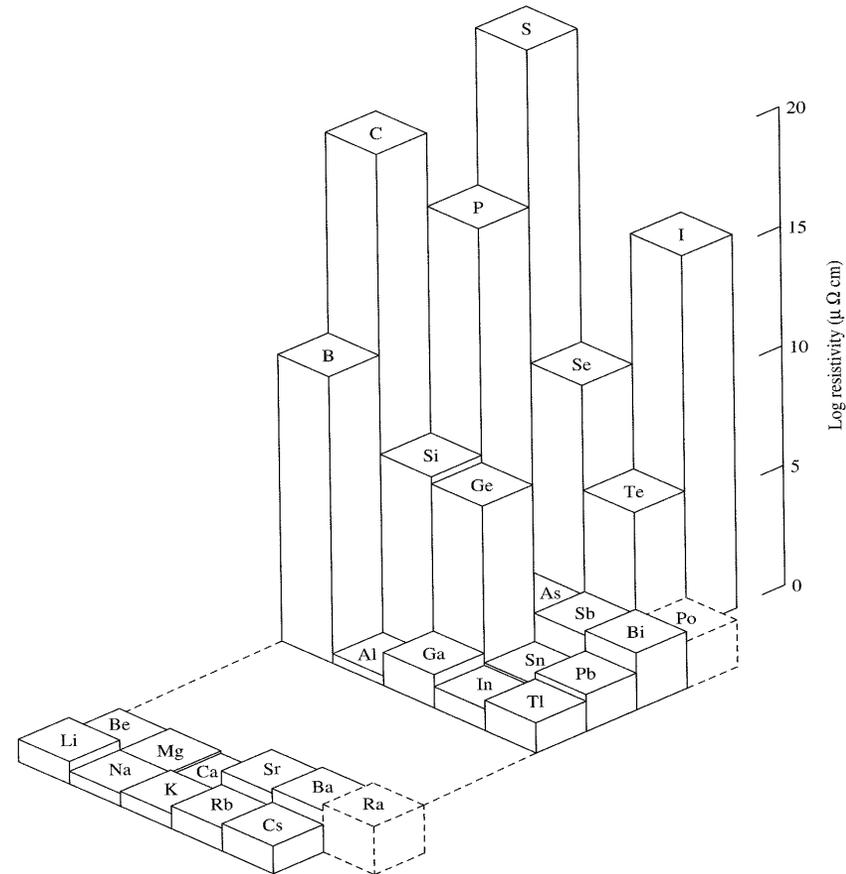
Éther-couronne 5-15



**X-ray determined molecular structure**

## Main group Elements of Group p

These elements display diverse properties going from the more metallic elements (Al, Ga, In, Tl, Sn, Pb, Bi) to « metalloides » (Si, B, Te) and then non-metallic elements (noble gas, halogens)



Electrical resistivity of main group elements

## Main group Metals of the p block

- Al, Ga, In, Tl (group 13)
- Sn et Pb (group 14)
- Bi (group 15)

Lower oxydation states are favored for heavier metals (complicated reasons: “Inert pair effect”).

- Common oxydation states: Tl(I), Pb(II) et Bi(III)  
 (“Inert pair effect”)

Thus, Tl(III), Pb(IV) et Bi(V) compounds are readily reduced.

## II - The groups of boron (13/III) and carbon (14/IV).

- Various physico-chemical properties.
- Great importance in industry and biosphere.
- **Carbone (biosphere)** → organic chemistry, binary compounds with metals and non-metals, organometallic chemistry
- **Bore (earth's crust)** → combined with O and/or Al, it is an important component of the earth's crust

**Other elements (Al, Si, Ga, Ge, In, Sn, Tl, Pb)** → high tech industry, semi-conductors

### **A) General considerations**

- Going down each column: → *non-metals* → *semi-conductors* → *metals*.
- Lighter elements have an electronegativity closer to that of hydrogen: they thus form numerous covalent compounds (hydrogenated and alkylated, for instance).

## IA) Group 13

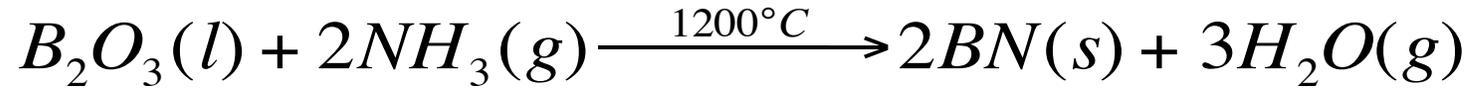
Group 13 metals all display a shiny appearance.

$T_m$  (°C) : Al (660) - Ga (30) - In (157) - Tl (303)

NB: In solid Ga, existence of  $Ga_2$  units that remain in the melted metal  
 $\Rightarrow T_m = 30^\circ$  .

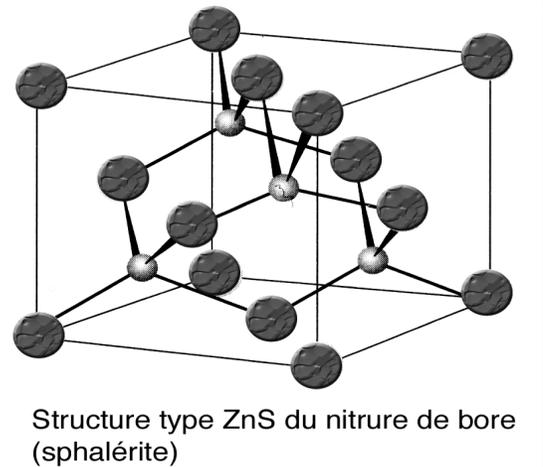
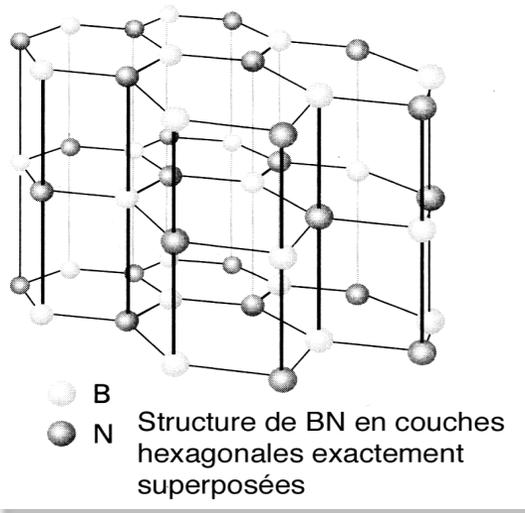
Métal	Minéraux principaux	Méthode d'extraction
<i>Groupe 13</i>		
Aluminium	Bauxite $Al_2O_3 \cdot xH_2O$	Électrolyse (procédé Hall)
Gallium	Traces dans les minerais d'aluminium et de zinc	
<i>Groupe 14</i>		
Étain	Cassitérite $SnO_2$	$SnO_2 + C \longrightarrow Sn + CO_2$
Plomb	Galène $PbS$	$PbS + O_2 \longrightarrow PbO + SO_2$ suivi de : $2 PbO + C \longrightarrow 2 Pb + CO_2$
<i>Groupe 15</i>		
Bismuth	Traces dans les minerais sulfurés de zinc, de cuivre et de plomb	

**Combining Boron with nitrogen: synthesis of boron nitride, an important material.**

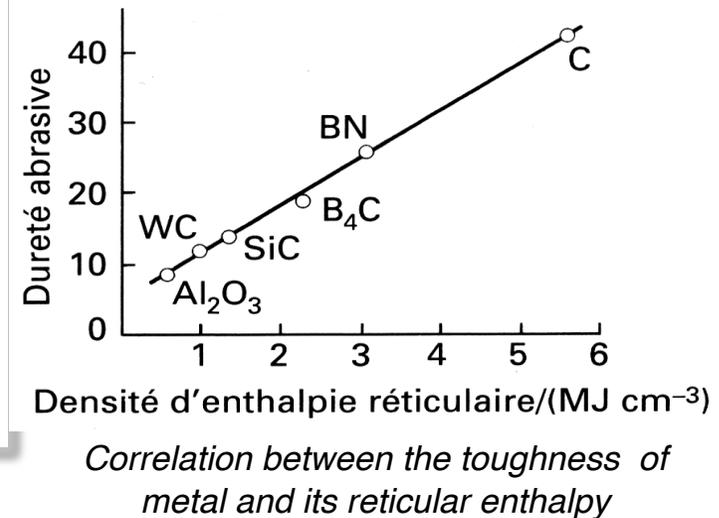


- **Two types of structure for BN :**

- 1) Type graphite, with hexagonal planes facing one another.
- 2) At high T and P, 'diamond' form ou ZnS.



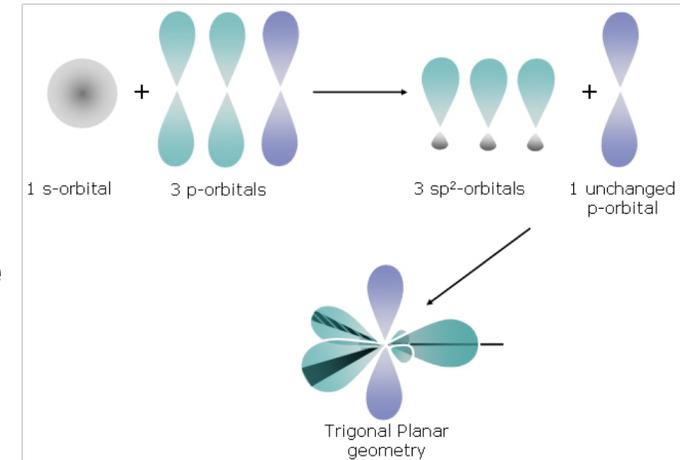
Abrasive even at high T



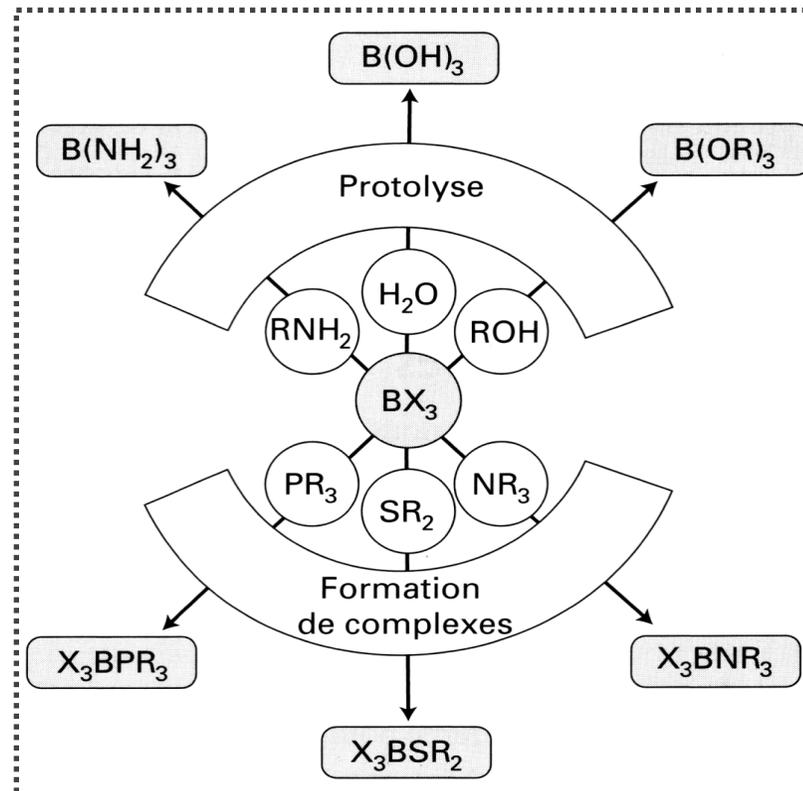
- Electrical insulator
- Used as lubricant

## 2- Boron Compounds with electronegative elements

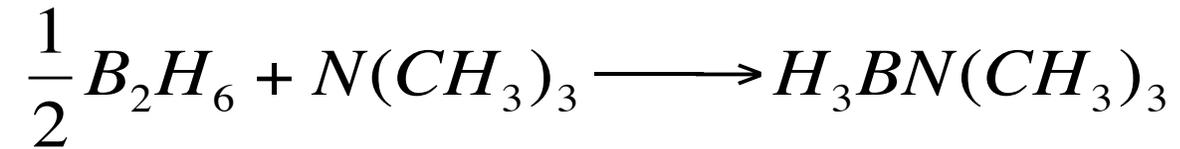
- Boron tri-halide species  $BX_3$  (B(III): common oxidation state).  
**6 electrons of valence at B(III) and a vacant orbital**
- Used as reagents and Lewis acids in catalysis.
- Preparation: direct reaction of B with  $X_2$  at high T/P.
- Structure of  $BX_3$ : monomeric, trigonal plane geometry triangle plan at B(III).
- Boron halide compounds with B-B bonds are known.



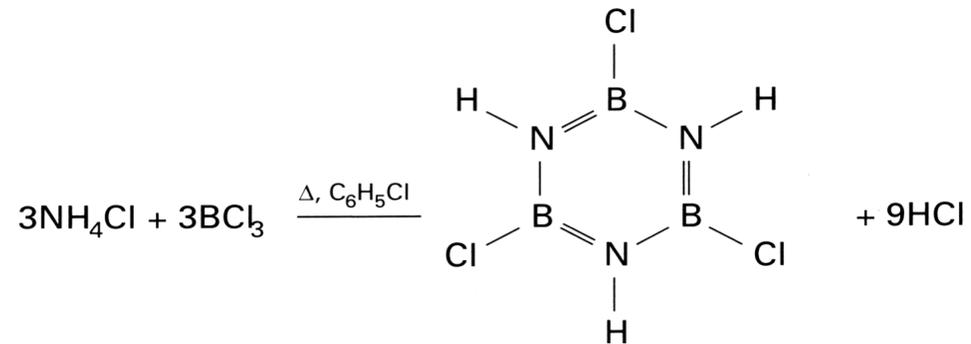
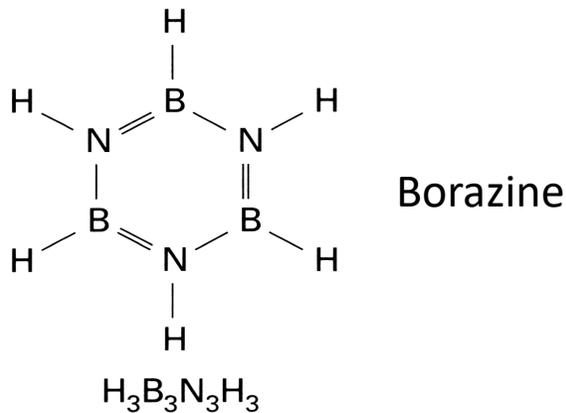
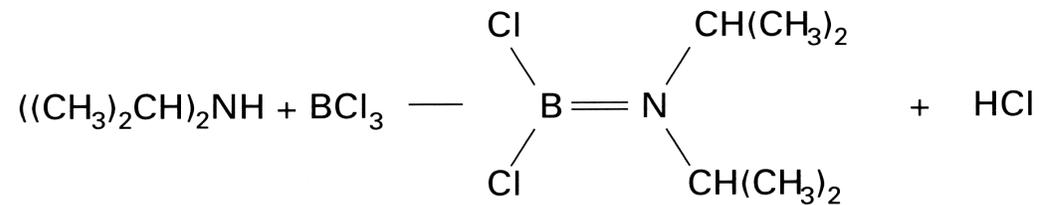
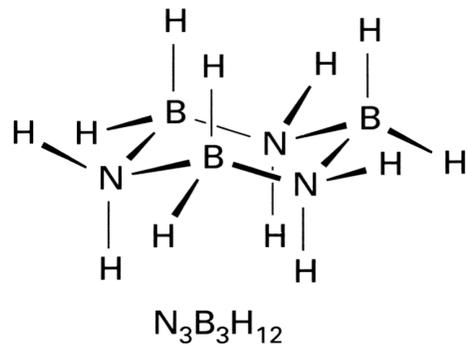
$sp^2$ -hybridized B(III) center



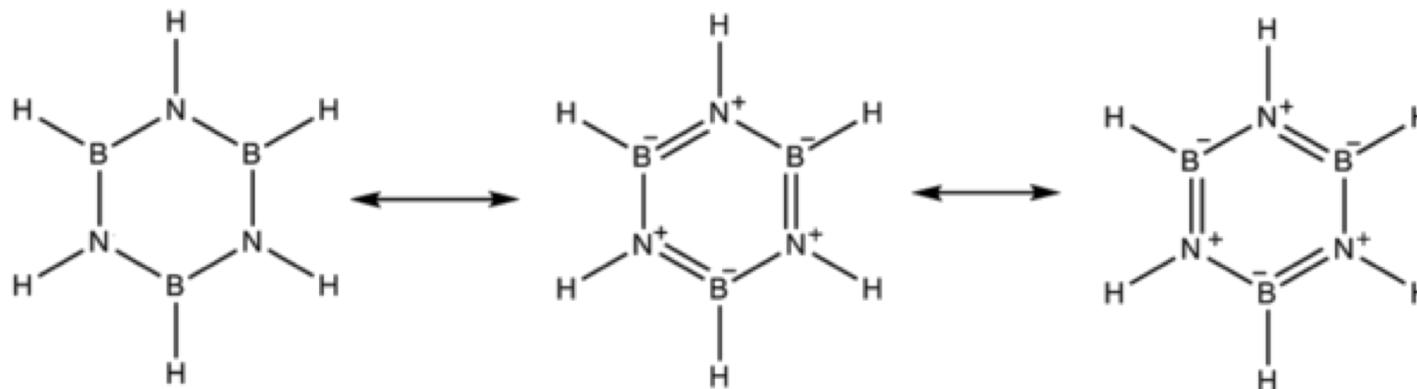
\* B-N and C-C bonds are isoelectronic.



- Amino-borane species can be synthesized according to the reaction depicted below:



- Despite some structural analogies, the properties/reactivity of amino-borane species is quite different from C-C bond species.



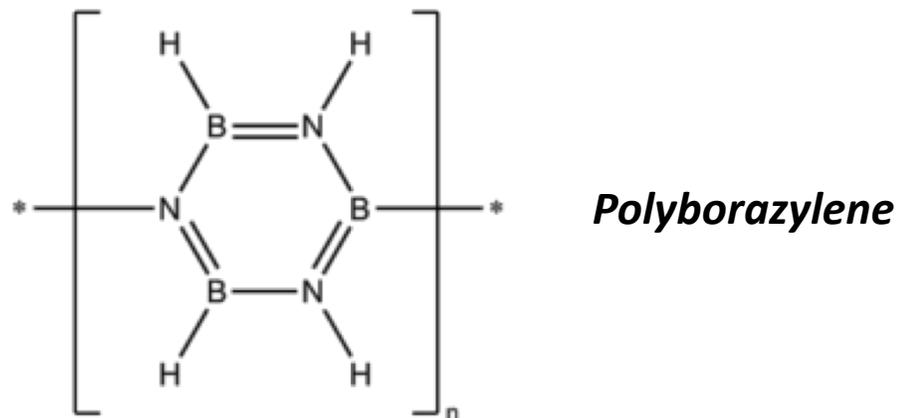
- *Nucleophilic attack at the nitrogen centers*
- *Electrophilic attack at the boron centers*



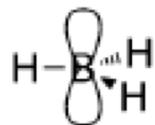
Reaction with HCl to form (B<sub>3</sub>H<sub>3</sub>)(N<sub>3</sub>H<sub>6</sub>)Cl<sub>3</sub>



Borazine polymerizes upon heating (H<sub>2</sub> elimination)

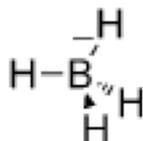


borane,  $\text{BH}_3$



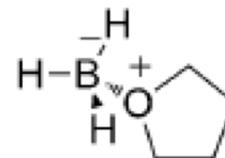
trivalent,  
neutral, 6e  
powerful LA

borohydride,  $\text{BH}_4^-$



tetravalent,  
anionic, 8e  
hydride donor

borane-THF,  $\text{BH}_3\text{-THF}$

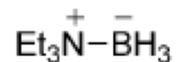


tetravalent,  
neutral, 8e  
borane chemistry

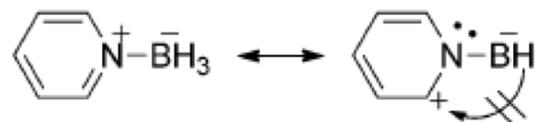
hydroboration with  $\text{BH}_3\text{-THF}$ , simplified mechanism



triethylamine-  
borane

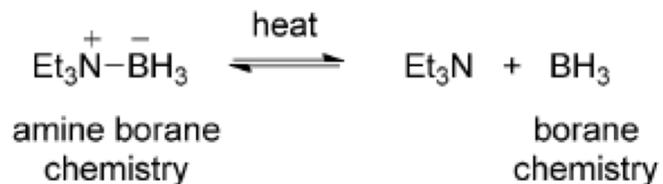


pyridine-borane

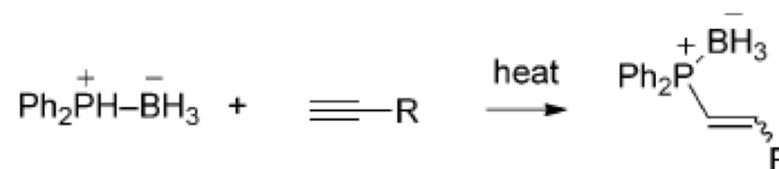


no self-reduction!

amine-boranes have two types of chemistries



phosphine-boranes do not exhibit borane chemistry

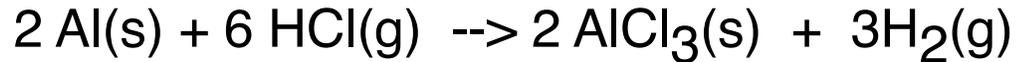


hydrophosphinylation, not hydroboration

## Groupe 13 metal species (Al, Ga, In): the most common oxidation state is +III

Trihalido metal species  $\text{MX}_3$  are strong Lewis acids.

Al (metal) and Ga (metal) directly react with HCl ou HBr as follows:



-  $\text{AlF}_3$  et  $\text{GaF}_3$  : hard solids, high  $T_m$ , low solubility. Formation of hypervalent coordination species:  $\text{Na}_3\text{AlF}_6$  ou  $\text{Na}_3\text{GaF}_6$

Relative to « hard » Lewis bases (O, N), the Lewis acidity decreases upon going down group 13 column



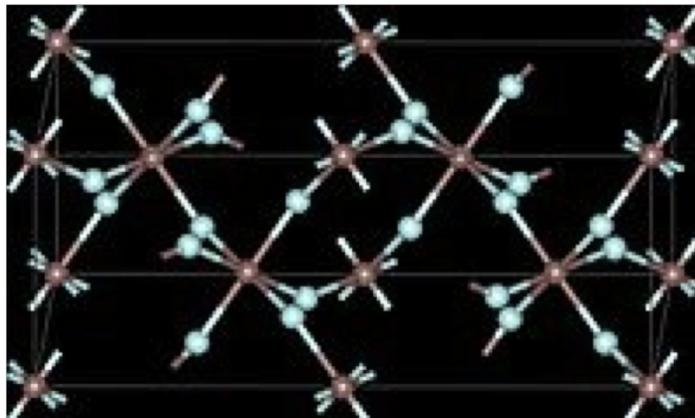
Relative to « soft » Lewis bases (S), the Lewis acidity increases upon going down group 13 column



Hypervalent compounds are observed for Al(III) and heavier gp 13 elements

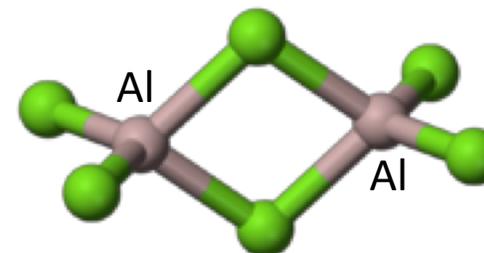


$\text{AlF}_3$ :



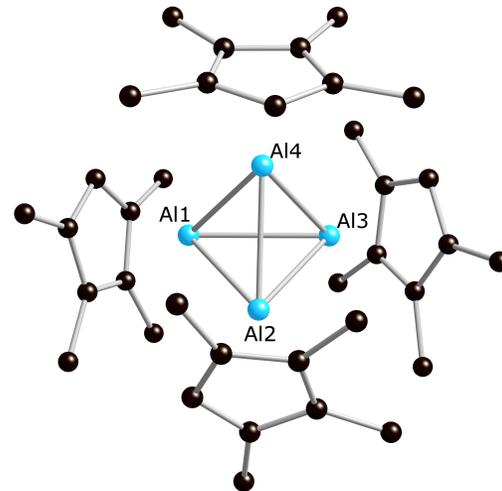
Each Al center is hexa-coordinated  
Each F coordinates to two Al centers

$\text{AlCl}_3$ ,  $\text{AlBr}_3$ ,  $\text{AlI}_3$ : dimeric in solution



*$\text{AlCl}_3$  commonly used as Lewis acid for the mediation of various organic reactions*

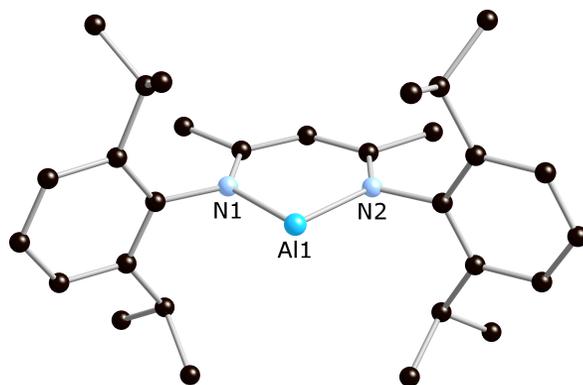
- A few Al(I) compounds are known to be stable at room temperature



First example of X-ray determined Al(I) species (stable at RT)

*Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 129.

- The stability of the +I oxidation state increases going down the gp 13 column
- Monohalides GaX, InX and TlX are known for X = Cl, Br, I



Lewis acidic and Lewis basic  
Al center



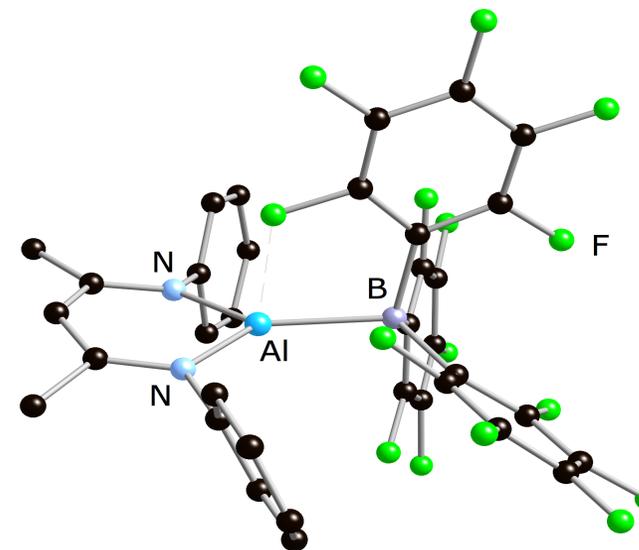
*Amphoteric character*



*Al carbene analogue*

*First example of  
a monomeric Al(I) species*

*Angew. Chem. Int. Ed. 2000, 39, 4274.*



Adduct of  $B(C_6F_5)_3$

## Oxydes et Jewelry

- $\text{Al}_2\text{O}_3$  ( $\alpha$  alumine) is the most stable form of aluminum oxide.
- Hexagonal compact (HC) stacking in which the  $\text{Al}^{3+}$  ions occupy 2/3 of the octahedral sites.

Also named Corundum--> sapphire (blue) : charge transfer from the  $\text{Fe}^{2+}$  et  $\text{Ti}^{4+}$  ions (impurities).

- Ruby :  $\alpha$  Alumine in which part of the  $\text{Al}^{3+}$  ions are replaced by  $\text{Cr}^{3+}$ .
- Other forms of Alumine  $\alpha$  exist (obtained by dehydration of Al hydroxyde at  $900^\circ \text{C}$ ): the majority of  $\text{Al}_2\text{O}_3$  is used for the production of Al(metal) via the Hall-Hérout process.
- Amorphous  $\text{Al}_2\text{O}_3$ : metastable form with a large specific surface area  
Presence de acidic and basic sites:--> widely used in heterogeneous catalysis.

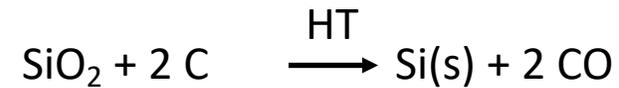
Propriétés des éléments des groupes du bore et du carbone.

Élément	$I/\text{kJ.mol}^{-1}$	$\chi^*$	$r_{\text{cov}}/\text{Å}^\ddagger$	$r_{\text{ion}}/\text{Å}^\ddagger$	Aspect et propriétés	Degrés d'oxydation courants
<i>Groupe 13/III</i>						
B	899	2,04	0,85		Sombre Semiconducteur	3
Al	578	1,61	1,43	0,54	Métal	3
Ga	579	1,81	1,53	0,62	Métal, F = 30°C	1, 3
In	558	1,78	1,67	0,80	Métal mou	1, 3
Tl	589	2,04	1,71	0,89	Métal mou	1, 3
<i>Groupe 14/IV</i>						
C	1086	2,55	0,77		Isolant dur (diamant) Semimétal (graphite)	4
Si	786	1,90	1,17	0,40	Semiconducteur dur	4
Ge	760	2,01	1,22	0,53	Métal	2, 4
Sn	708	1,96	1,40	0,69	Métal	2, 4
Pb	715	2,33	1,75	0,92	Métal mou	2, 4

## Group 14 elements

**Carbon:** extracted from mines as diamonds or graphite  
Coke, black carbon: less pure forms

**Silicium:** produced in a pure form from the reduction of  $\text{SiO}_2$  with C.



**Si:** widely used in modern semi-conductor industry  
(small band gap = 1.12 eV)

-  $\text{SiH}_4$ : tetrahedral structure, stable but less than  $\text{CH}_4$

$\text{Si}_n\text{H}_{2n+2}$  (silanes) are much less stable than alkanes

### Pourquoi?

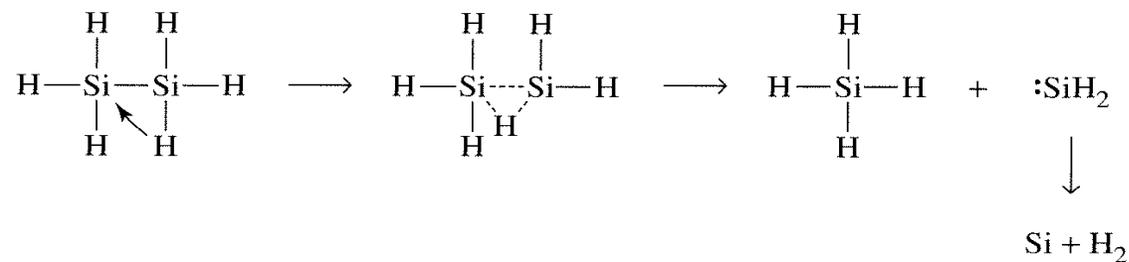
- The Si-Si bond is less strong than the C-C bond

- Si est less electronegative and larger than C



**More reactive towards nucleophiles**

### Silanes decomposition



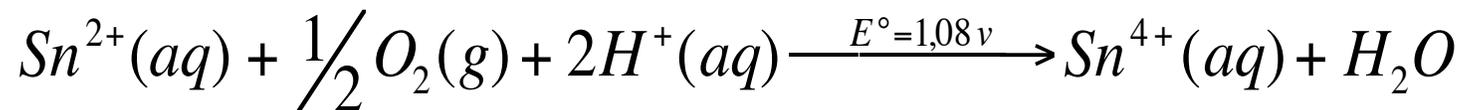
## Tin and Lead (Group 14)

### Sn:

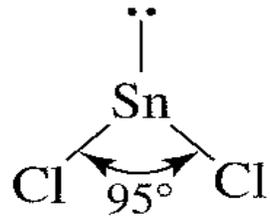
- Sn exists in two allotropic forms:
  - a “diamond” form ( $\alpha$ ) stable at  $T < 13^\circ \text{C}$
  - a metal form ( $T > 13^\circ \text{C}$ ), much more stable

- **Oxidation state: +2 ou +4**

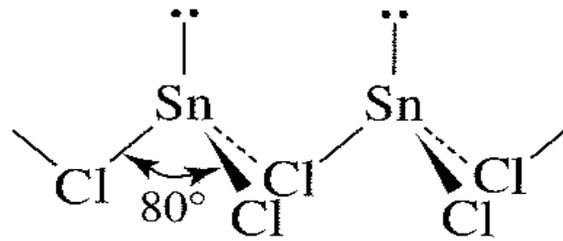
In aqueous medium,  $\text{Sn}^{2+}$  (which bears a lone pair of electrons) is a soft reducing agent.



- $\text{SnX}_4$  compounds ( $\text{X} = \text{Cl}, \text{Br}, \text{I}$ ) exhibit a covalent character.
- Sn (II) et Sn (IV) have a rich coordination chemistry

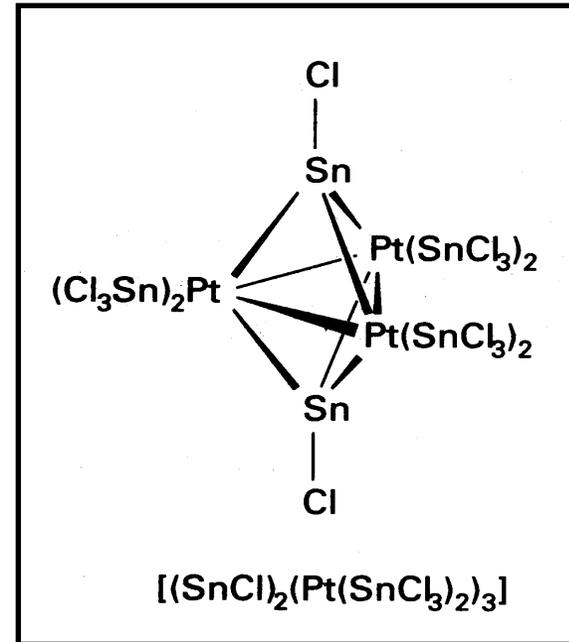
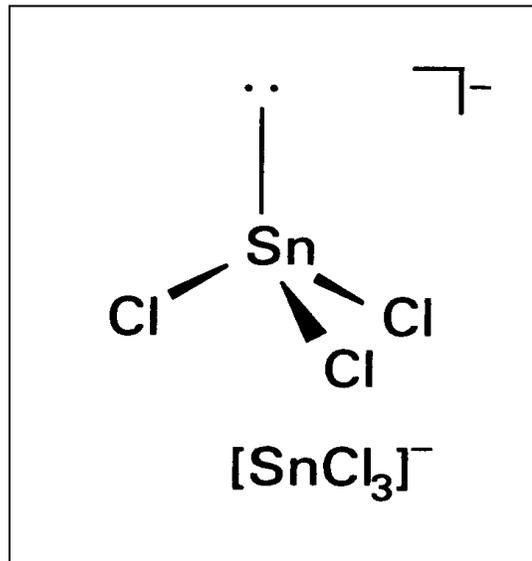


Gas



Crystalline

Stereochemically active lone pair



## Pb :

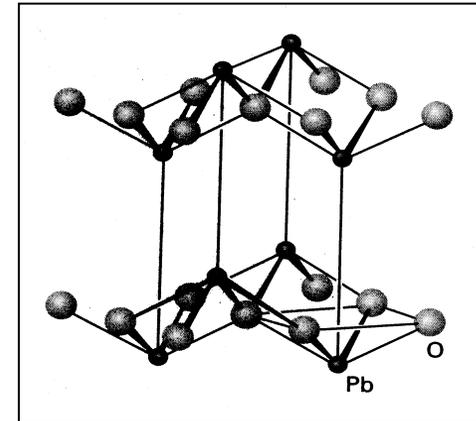
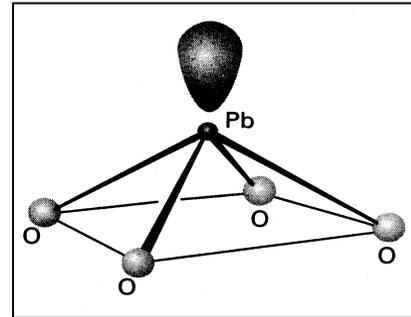
Lead oxide compounds are technologically important....but also very toxic

**Oxidation state: +2 (the most stable) and +4**

--> The structure de PbO also features a stereochemically active lone pair on Pb. Pb<sup>2+</sup> tetra-coordinated (by O).

--> **Mixed Valence Oxides: Pb<sub>3</sub>O<sub>4</sub> 'minium'**  
Structure of Pb<sub>3</sub>O<sub>4</sub>

Despite its toxicity, this red-orange pigment is produced industrially and used in the painting industry.



## Sn and Pb :

- Oxidation +2 et +4 possible for various Sn and Pb compounds.
- Pb(IV) is very oxydant.
- Sn(II) et Pb(II) both display a stereoactif lone pair

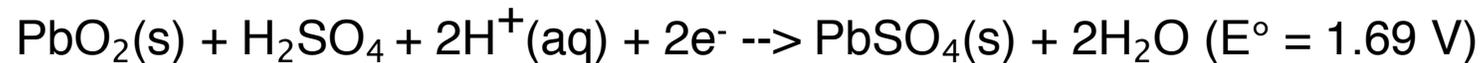
## Lead-based Battery

*Illustrate the role of kinetics and thermodynamics at work in electrochemical cells*

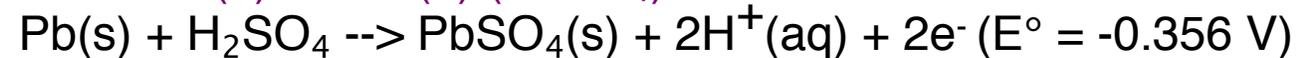
Charged state : cathode =  $\text{PbO}_2$  et anode =  $\text{Pb}$ . In diluted  $\text{H}_2\text{SO}_4$ ,  $\text{PbO}_2$  et  $\text{Pb}$  are insoluble.

### ***Cathodic reduction and anodic oxidation***

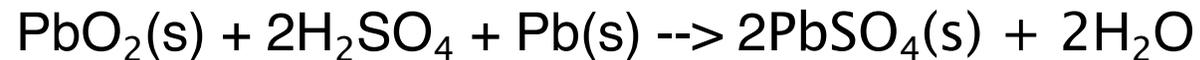
While working: at the cathode  $\text{Pb(IV)} \rightarrow \text{Pb(II)}$  ( $\text{PbSO}_4$ )



At the anode  $\text{Pb(0)} \rightarrow \text{Pb(II)}$  ( $\text{PbSO}_4$ )



Global Reaction:



Difference of potential: **2 volts**. ( $\gg$  to that of  $\text{H}_2\text{O}$  : 1,23 V)

Explanation : slow reaction with  $\text{H}_2\text{O}$  (slow kinetics)

## The Specific case of Calcium

### Organocalcium Overview

Nucleophilicity



$R^-$



Nucleophilicity

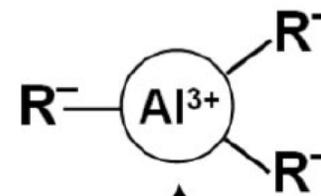


$R^-$



$R^-$

Electrophilicity



$R^-$

$R^-$

Electrophilicity



## Advantages of Calcium

- Abundant : 3.4 % of Earth's crust (one of the cheapest commercially available metals, <\$4/kg)
- Non-toxic: Human tolerance of Ca is high ( $\approx 1$  g/day is considered safe)
- Associated environmental hazards are low: easily convertible to limestone ( $\text{CaCO}_3$ ) and slaked lime ( $\text{Ca(OH)}_2$ ) for disposal

- Large coordination numbers of calcium leads to insoluble aggregates
- Low reactivity of Ca metal, compared to very high reactivity of C-Ca bonds



**Highly reactive and sensitive reagents (reacts with O<sub>2</sub> and H<sub>2</sub>O)**



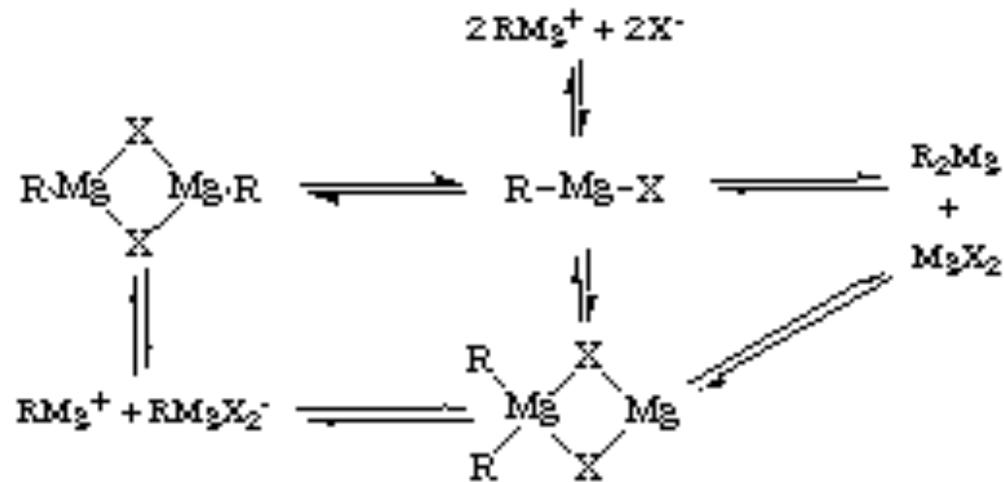
**Increased ionic character of the Ca-C bond (versus the Mg-C bond)**



**Inorganic and organometallic Ca compounds may readily undergo ligand exchange reactions in solution**

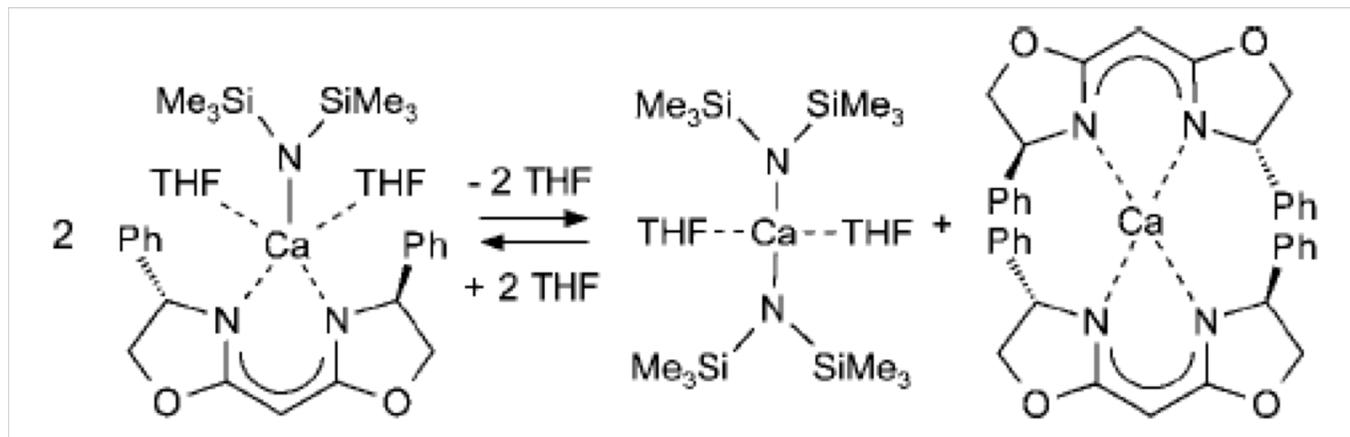
## Example: The Schlenk equilibrium

- First discovered with organomagnesium derivatives



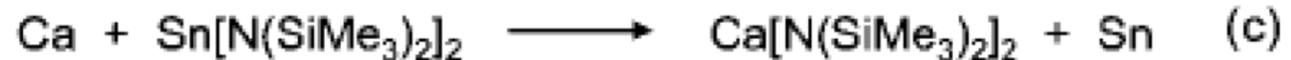
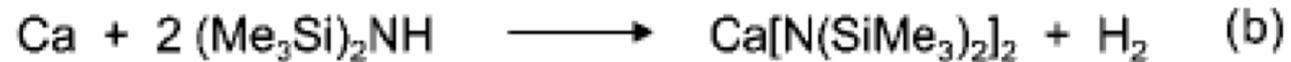
The nature of the R and X substituents, solvent and the presence of Lewis bases influence the Schlenk equilibrium

## An example of the Schlenk equilibrium with organocalcium compounds



The presence/absence of THF directly influences the  $K_{eq}$  of the Schlenk equilibrium

## 1) Direct route from metal



## 2) Salt metathesis



## 3) Deprotonation (acid-base reaction)

