

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.

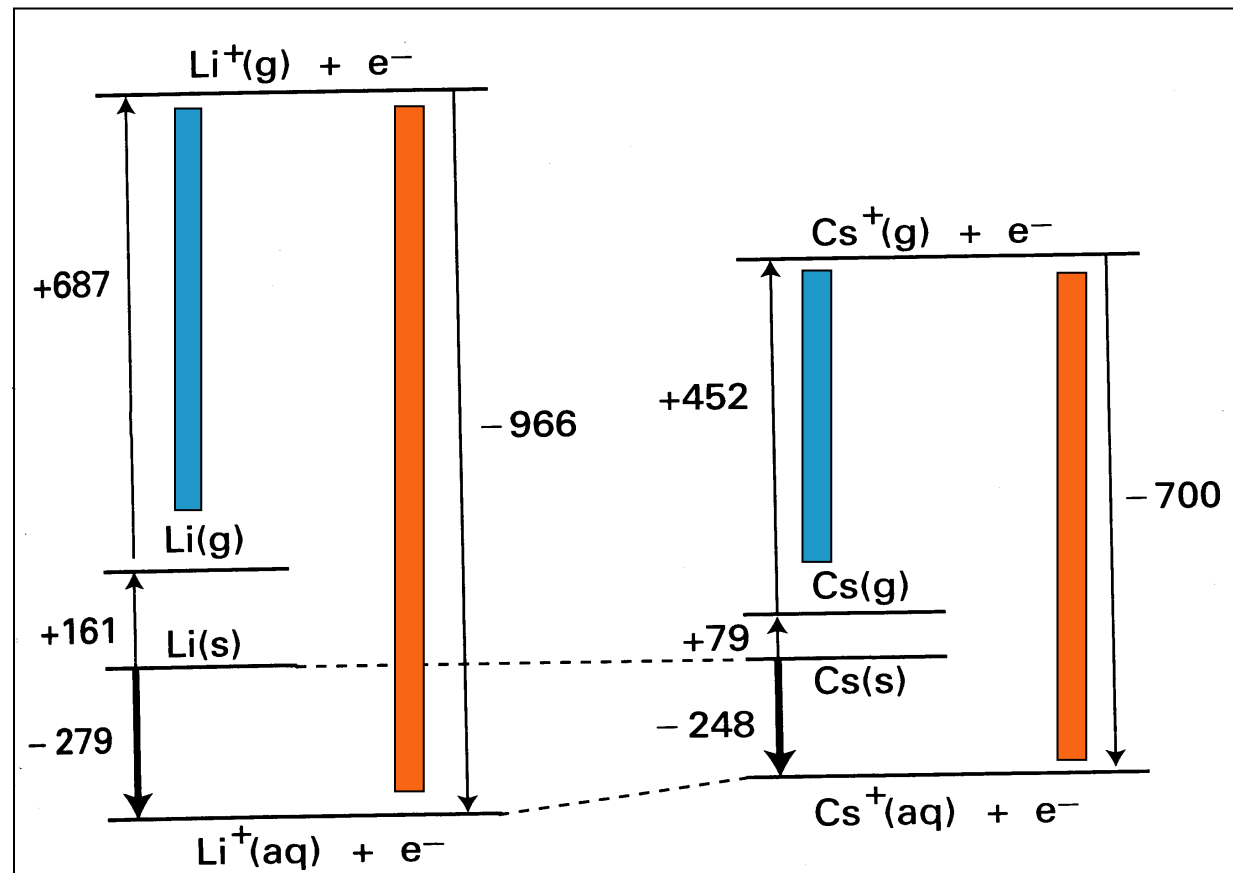
Redox Reactions



Why do these metal spontaneously inflame upon contact with H_2O ?

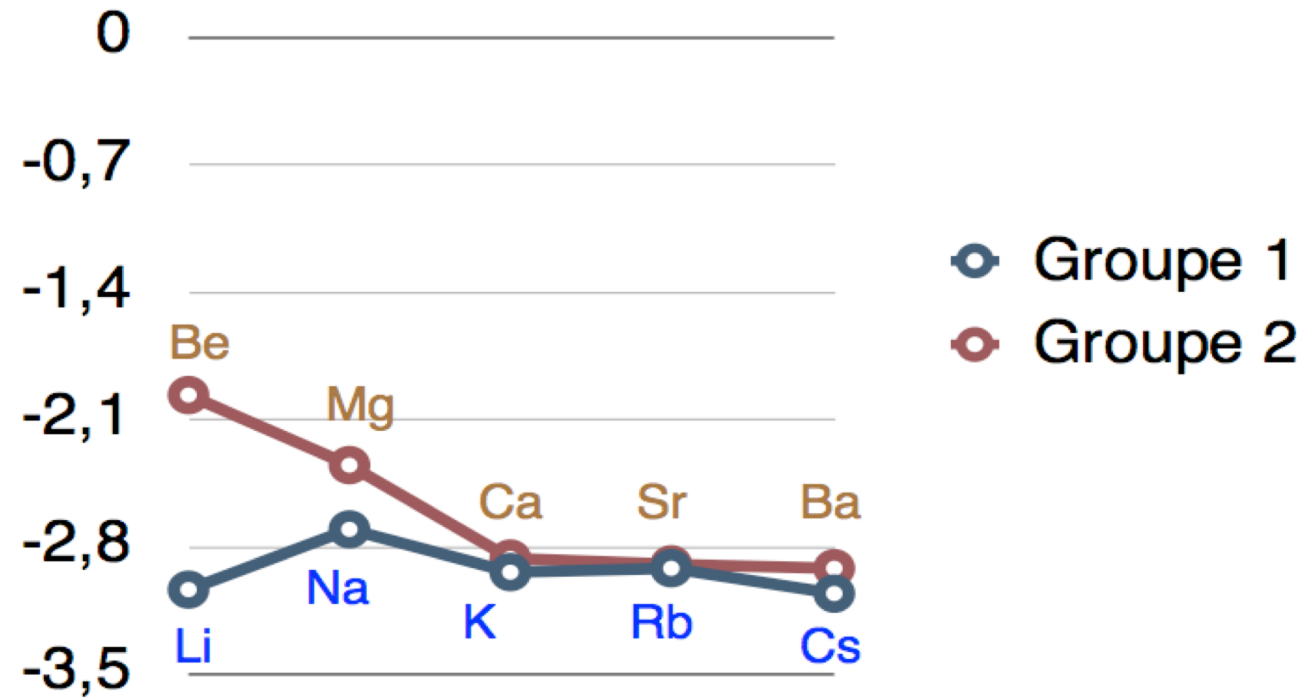
- Low melting point metals, the liquid provides a clean surface, which is extremely favorable to the redox reaction to occur (highly exothermic).
- In the case of beryllium and magnesium, formation of a protecting layer of metal oxide.

👉 E° 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).



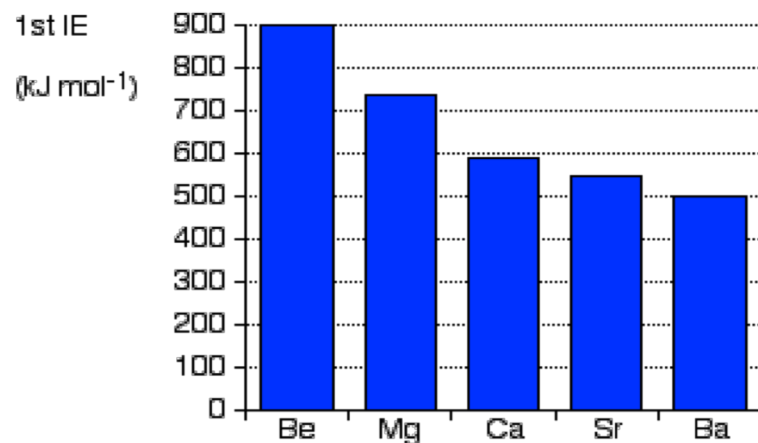
Compensation between the energy of ionisation and the energy of hydration. (values give in $\text{KJ}\cdot\text{mol}^{-1}$)

Potentiers standards des éléments s
(E_0 en volt)

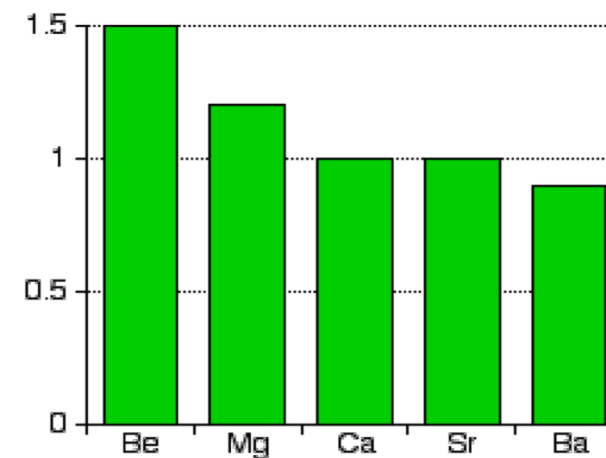


General Tendency: Exemple of group 2 metals

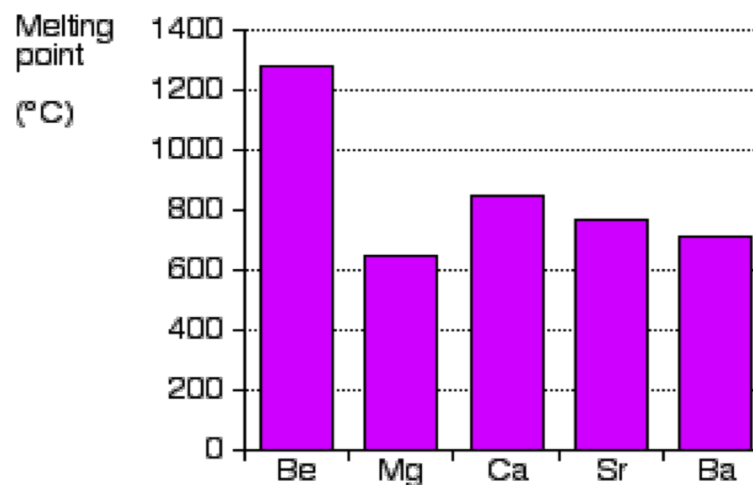
First Ionisation Energy of the Group 2 elements



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 Li_3N . Specific reactions are also observed with O_2 .

Coordination : mostly octahedral coordination in aqueous medium, except for Li^+ (small cation) in some crystalline compounds (Li_2O , antifluorine-type structure). Cation Be^{2+} , small and highly charged (2+) affords compounds with some covalent character with typically four-coordinated Be centers.

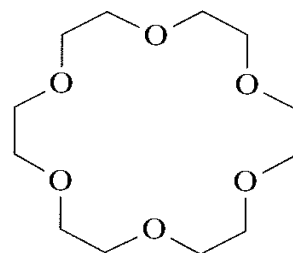
Possibility of catenation (formation of chains)

Examples :

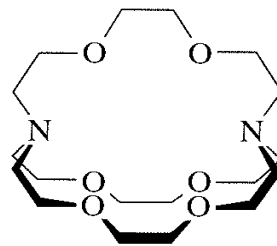
- Na_2O_2 (peroxyde ion O_2^{2-}), Li_2O (oxyde ion O^{2-}), KO_2 (superoxyde ion O_2^-).
- Stabilisation of peroxydes et superoxydes by larger cations.

Complexes Formation

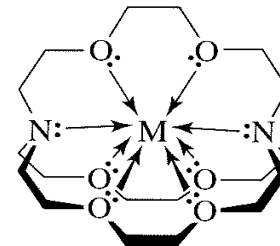
- Metallic ions of bloc s (M^+ et M^{2+}) are considered as “hard” Lewis acids and can thus form complexes via Coulombian interactions with “hard” Lewis bases (small electronegative electron donors: O and N)
- Formation of remarquable complexes with polydentate ligands such as ether-crown and cryptand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



18-crown-6
or
18C6



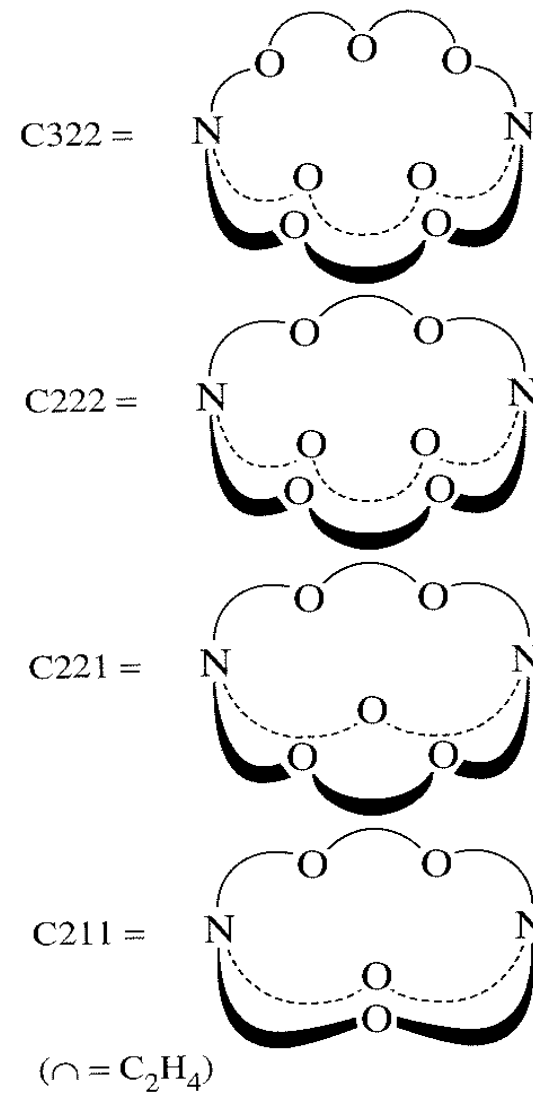
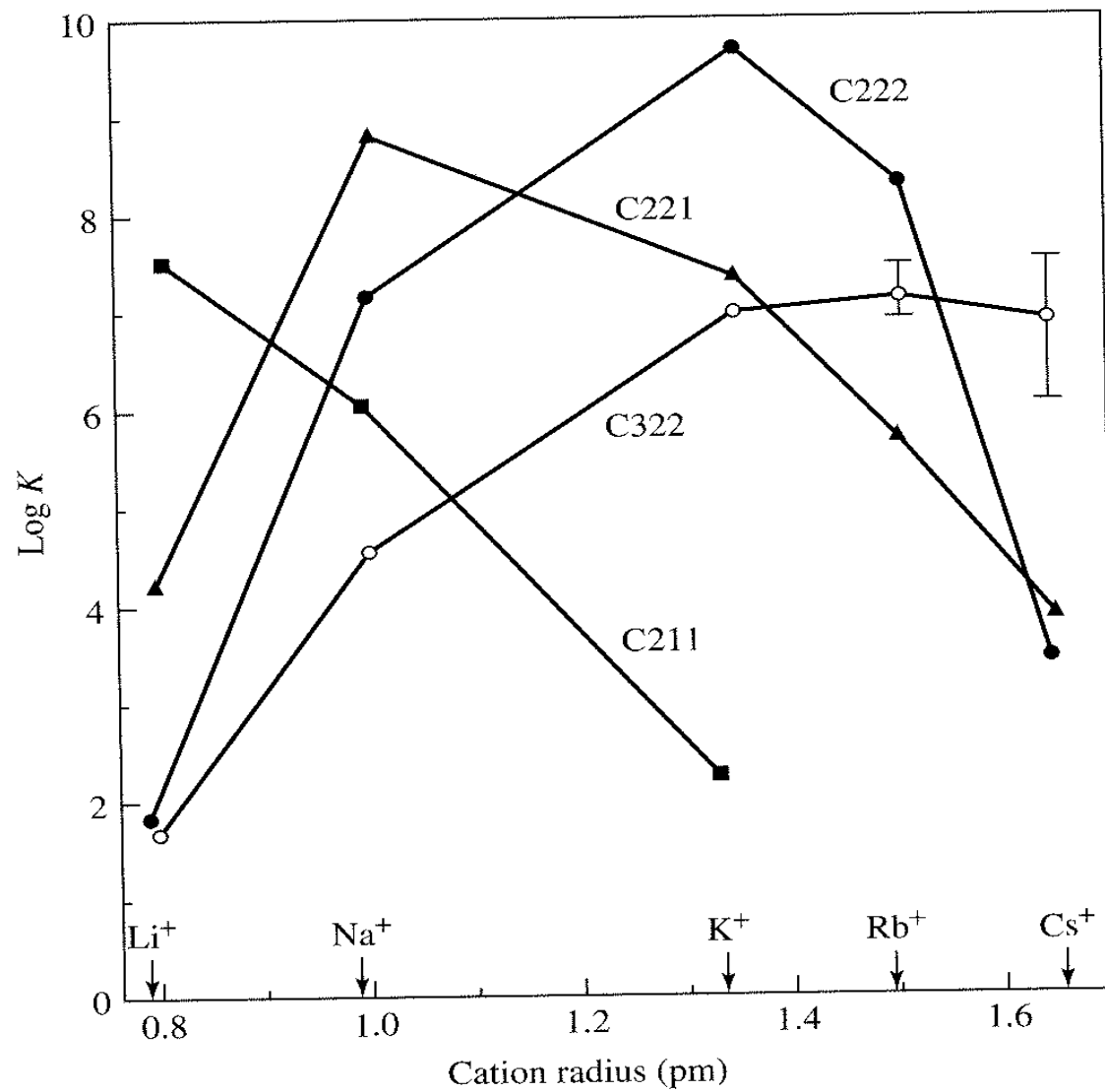
Cryptand [2.2.2]
or
C222



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

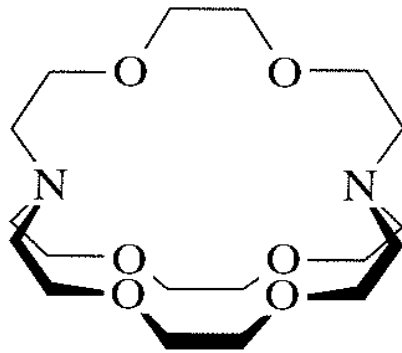
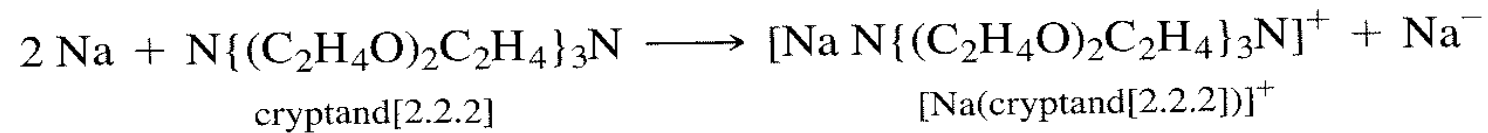
Formation Constants of cryptand complexes As a function of cation size



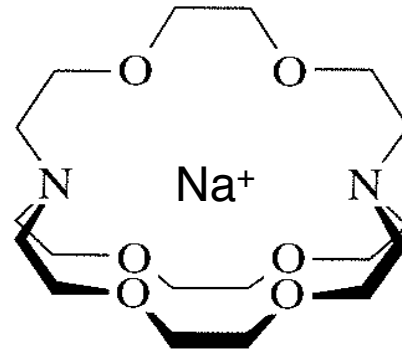
Alcalides anions M-

Conditions: moisture- and oxygen-free environment

First reported example: Anion Na^- formed by reaction of Na(s) with cryptand [2.2.2]



Cryptand [2.2.2]



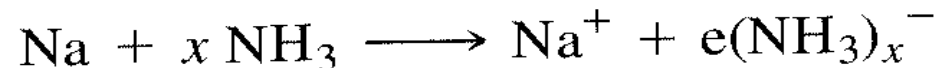
Na⁺- Cryptand [2.2.2]

Full dissociation
Of the anion
and cation

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. NH_3 ($T_{\text{eb}} = -33^\circ \text{C}$) to afford a solution of electrons solvated by NH_3



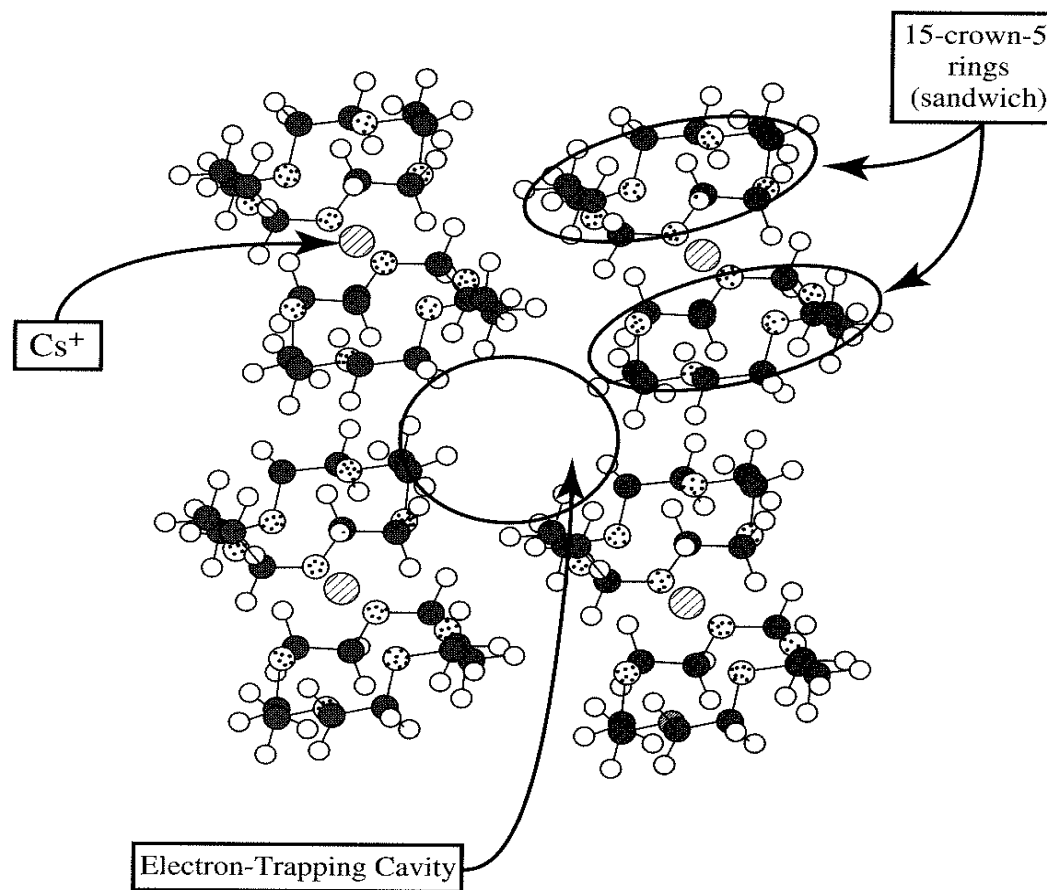
- Diluted solution (dark blue): excellent reducing properties
- Concentrated solution (bronze appearance): delocalized electrons like in a metal.

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

Electride consisting of Cs^+ -[15-éter-5] anions and
« free » electrons



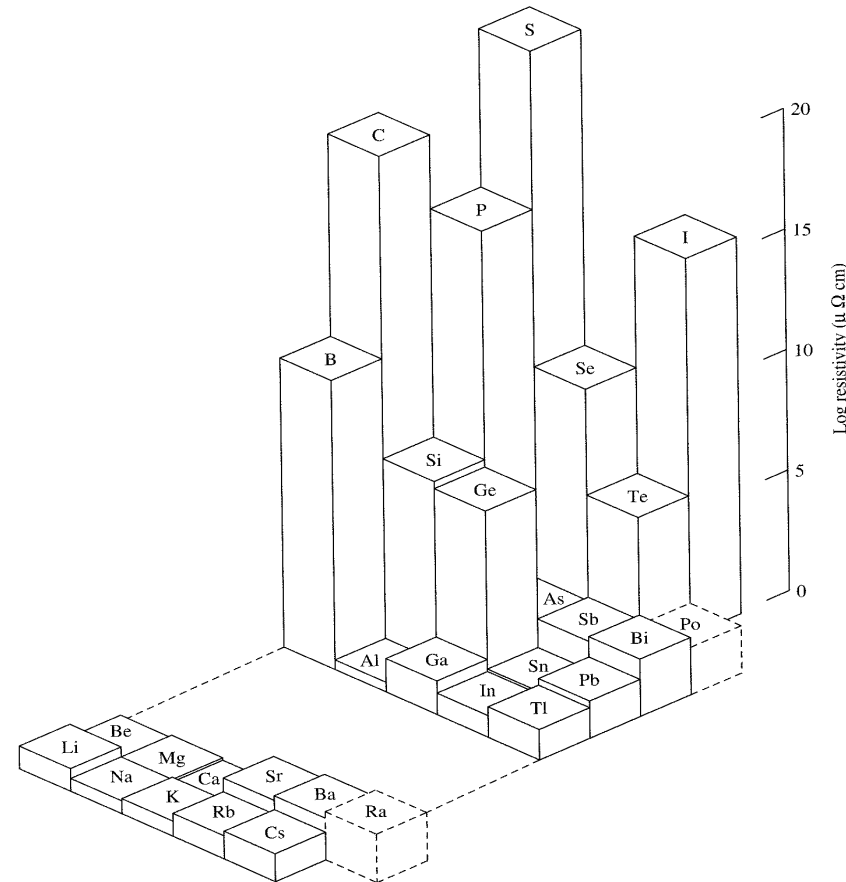
Éther-couronne 5-15



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

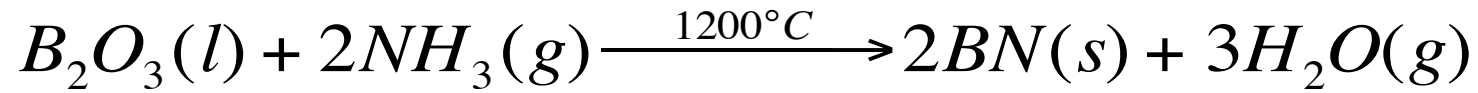
Group 13 metals all display a shiny appearance.

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
 $\Rightarrow T_m = 30^\circ$.

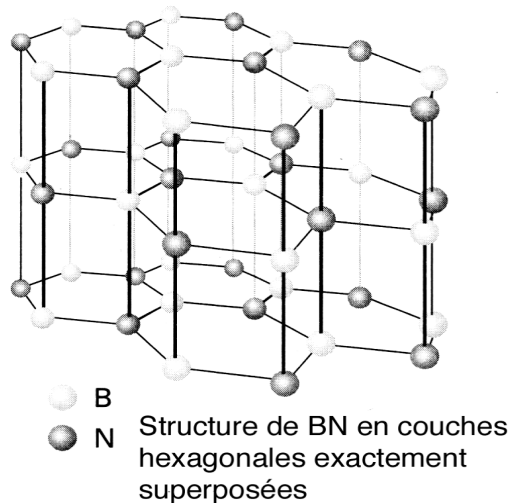
Métal	Minéraux principaux	Méthode d'extraction
<i>Groupe 13</i>		
Aluminium	Bauxite $Al_2O_3 \cdot xH_2O$	Électrolyse (procédé Hall)
Gallium	Traces dans les minerais d'aluminium et de zinc	
<i>Groupe 14</i>		
Étain	Cassitérite SnO_2	$SnO_2 + C \longrightarrow Sn + CO_2$
Plomb	Galène PbS	$PbS + O_2 \longrightarrow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

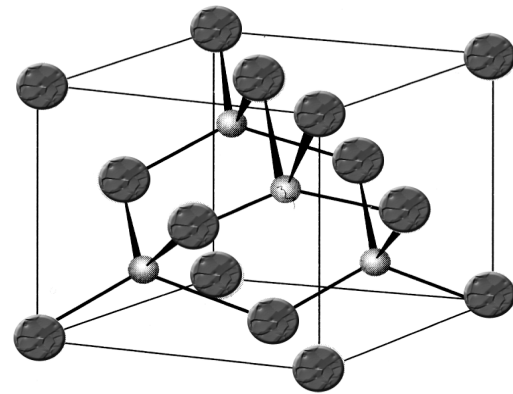


- Two types of structure for BN :

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

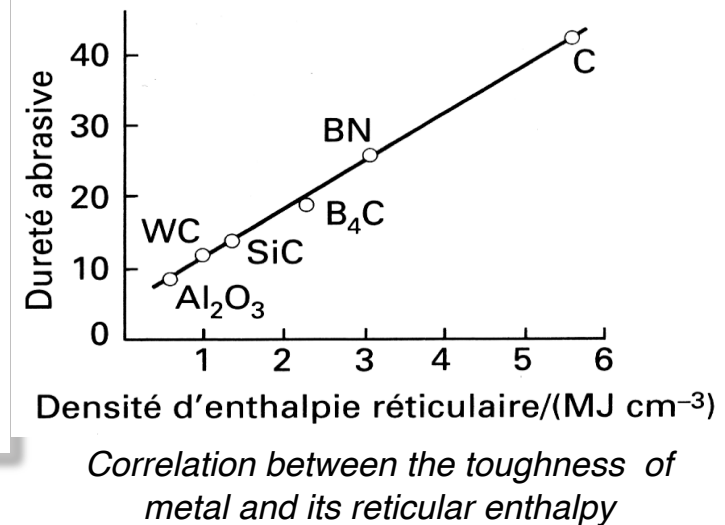


- Electrical insulator
- Used as lubricant



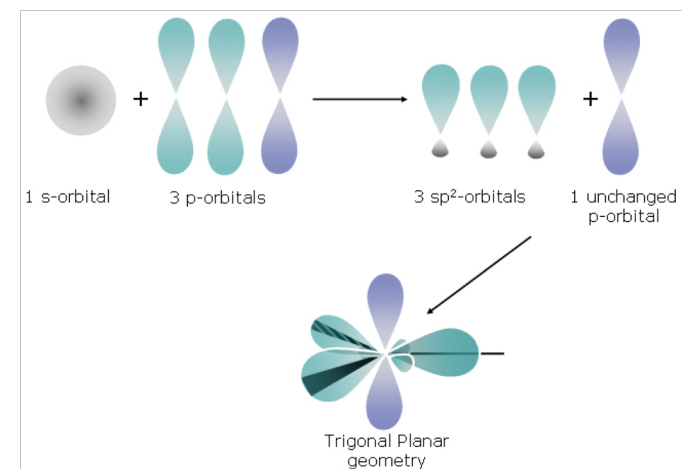
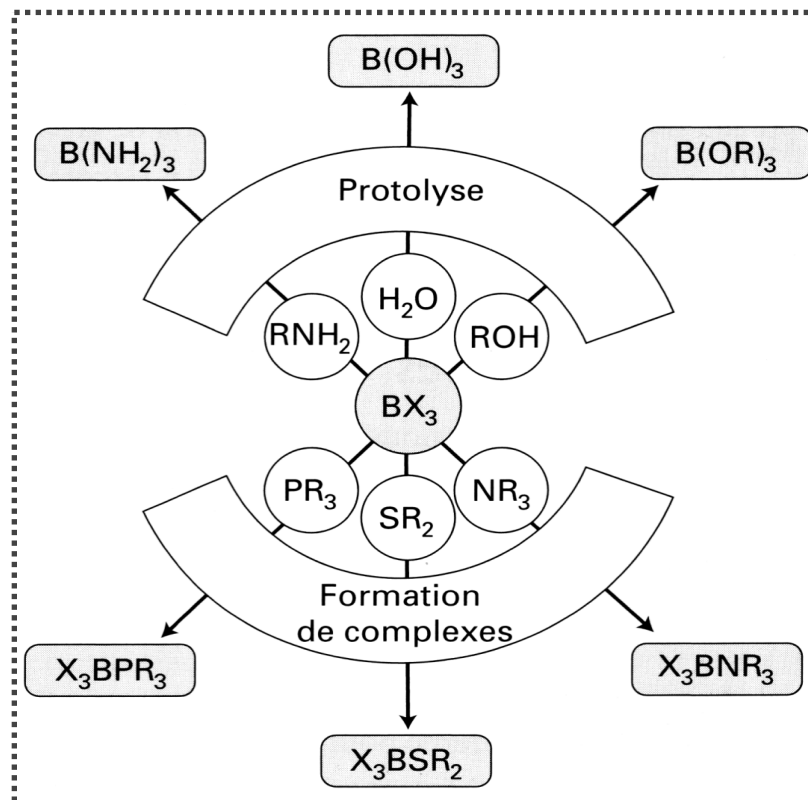
Structure type ZnS du nitrure de bore (sphalérite)

Abrasive even at high T



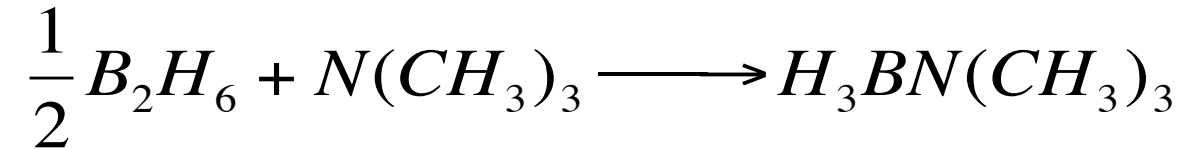
2- *Boron Compounds with electronegative elements*

- 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.

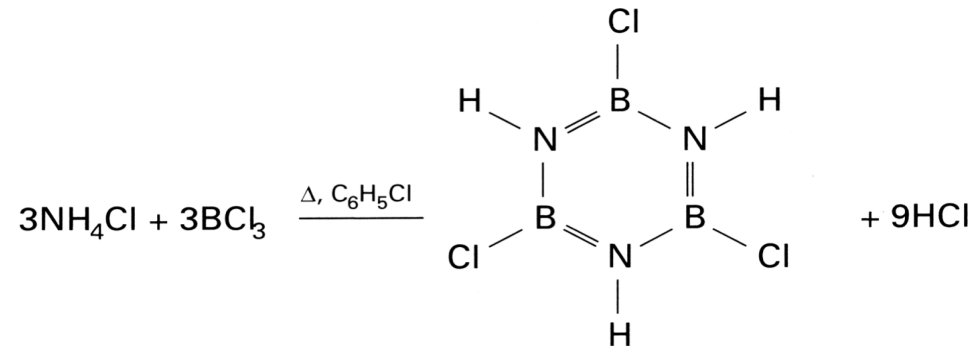
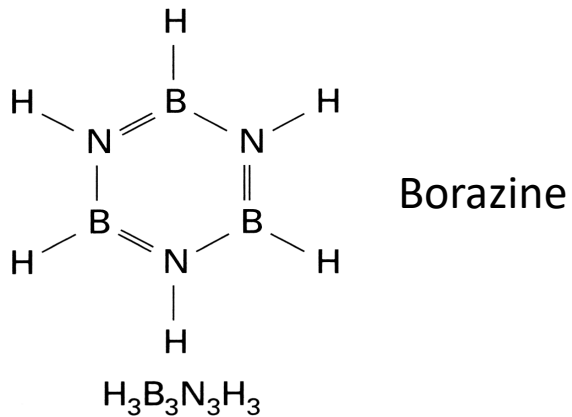
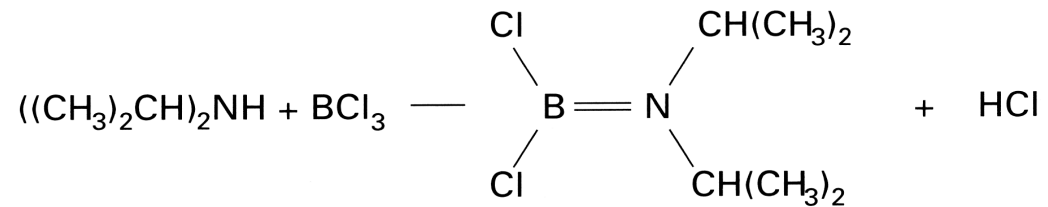
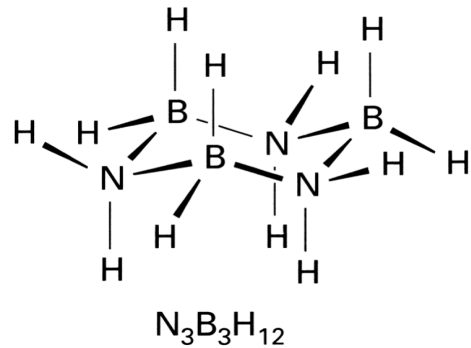


sp^2 -hybridized B(III) center

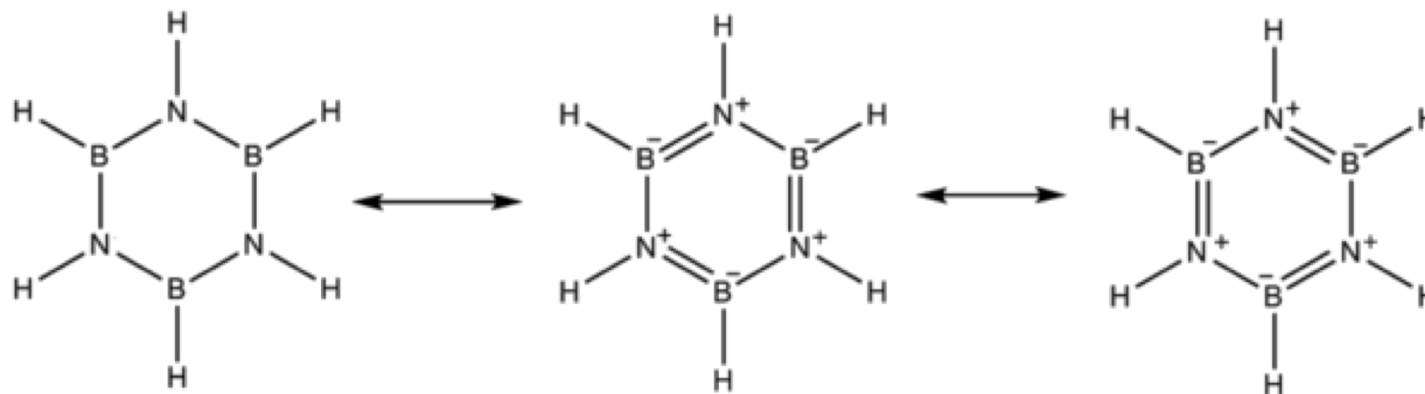
* B-N and C-C bonds are isoelectronic.



- 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.



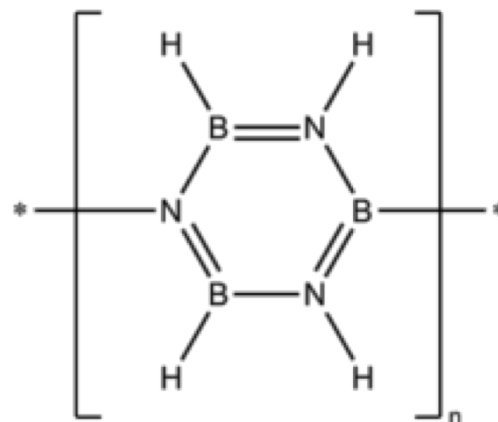
- *Nucleophilic attack at the nitrogen centers*
- *Electrophilic attack at the boron centers*



Reaction with HCl to form $(B_3H_3)(N_3H_6)Cl_3$

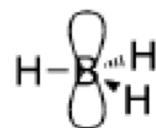


Borazine polymerizes upon heating (H_2 elimination)



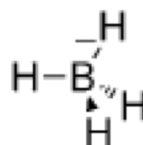
Polyborazylene

borane, BH_3



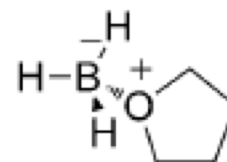
trivalent,
neutral, 6e
powerful LA

borohydride, BH_4^-



tetravalent,
anionic, 8e
hydride donor

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

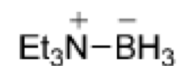


tetravalent,
neutral, 8e
borane chemistry

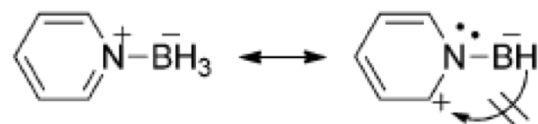
hydroboration with $\text{BH}_3\text{-THF}$, simplified mechanism



triethylamine-
borane

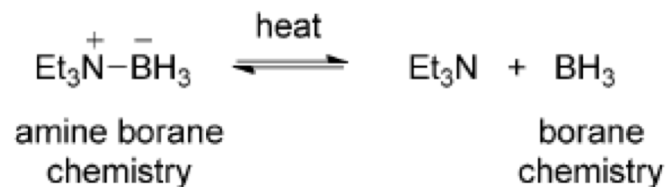


pyridine-borane

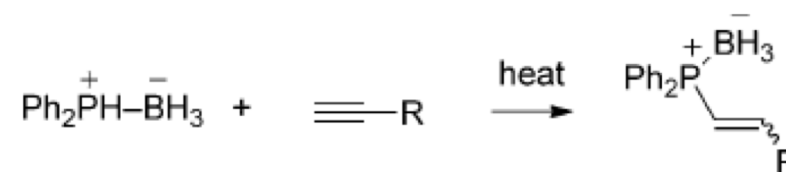


no self-reduction!

amine-boranes have two types of chemistries



phosphine-boranes do not exhibit borane chemistry

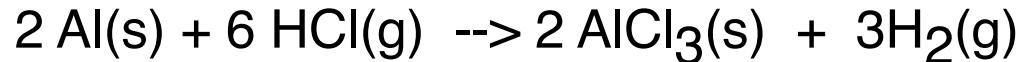


hydrophosphinylation, not hydroboration

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

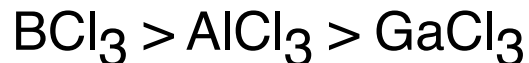
Trihalido metal species MX_3 are strong Lewis acids.

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



- AlF_3 et GaF_3 : hard solids, high T_m , low solubility. Formation of hypervalent coordination species: Na_3AlF_6 ou Na_3GaF_6

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



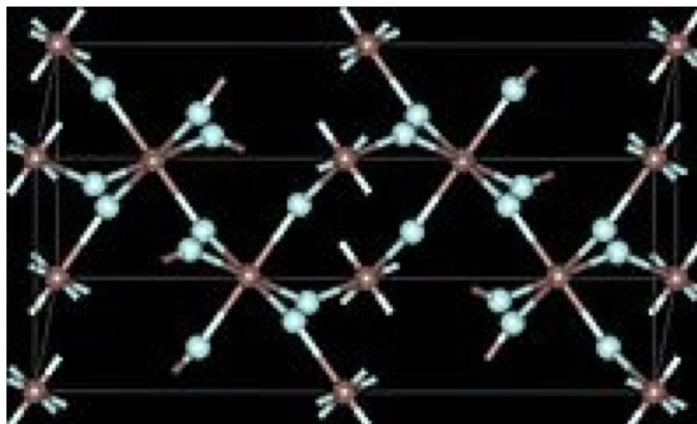
Relative to « soft » Lewis bases (S), the Lewis acidity increases upon going down group 13 column



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

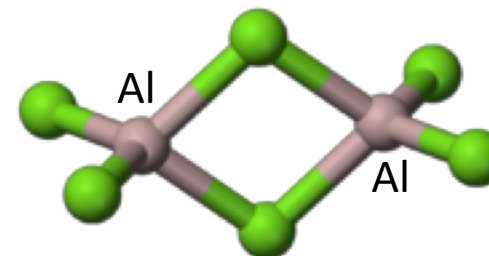


AlF_3 :



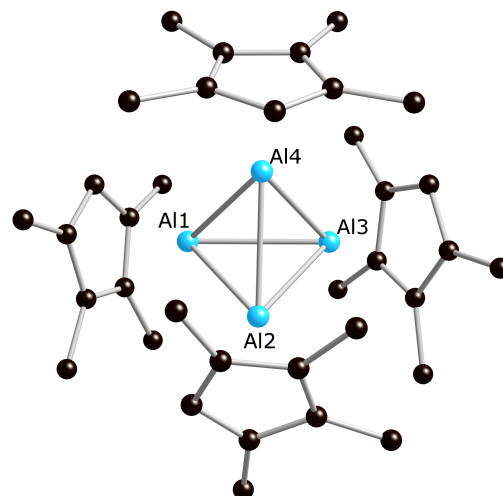
Each Al center is hexa-coordinated
Each F coordinates to two Al centers

AlCl_3 , AlBr_3 , AlI_3 : dimeric in solution



AlCl_3 commonly used as Lewis acid for the mediation of various organic reactions

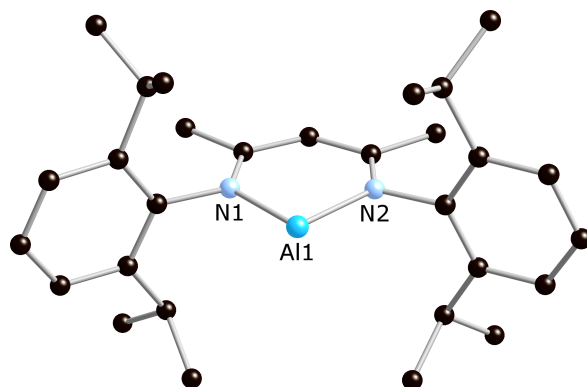
- A few Al(I) compounds are known to be stable at room temperature



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



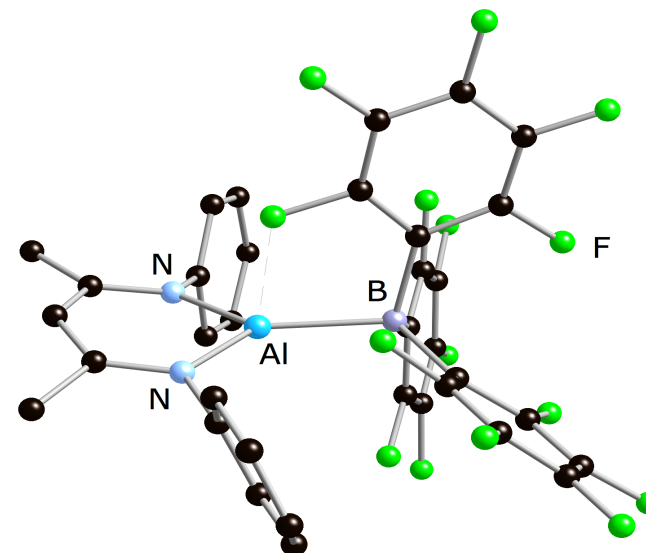
Amphoteric character



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

- Al_2O_3 (α alumine) is the most stable form of aluminum oxide.
- Hexagonal compact (HC) stacking in which the Al^{3+} ions occupy 2/3 of the octahedral sites.

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

- Ruby : α Alumine in which part of the Al^{3+} ions are replaced by Cr^{3+} .
- Other forms of Alumine α exist (obtained by dehydration of Al hydroxyde at 900°C): the majority of Al_2O_3 is used for the production of Al(metal) via the Hall-Hérout process.
- Amorphous Al_2O_3 : metastable form with a large specific surface area
Presence de acidic and basic sites:--> widely used in heterogeneous catalysis.

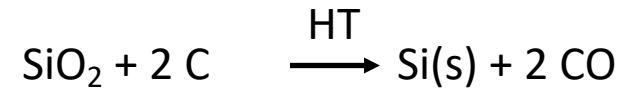
Propriétés des éléments des groupes du bore et du carbone.

Élément	$I/\text{kJ.mol}^{-1}$	χ^*	$r_{\text{cov}}/\text{\AA}^\dagger$	$r_{\text{ion}}/\text{\AA}^\ddagger$	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 SiO_2 with C.



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

- SiH_4 : tetrahedral structure, stable but less than CH_4

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

Pourquoi?

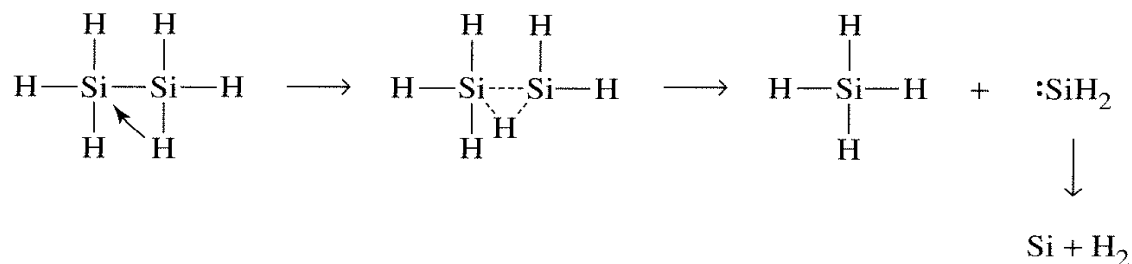
- The Si-Si bond is less strong than the C-C bond

- Si est less electronegative and larger than C



More reactive towards nucleophiles

Silanes decomposition



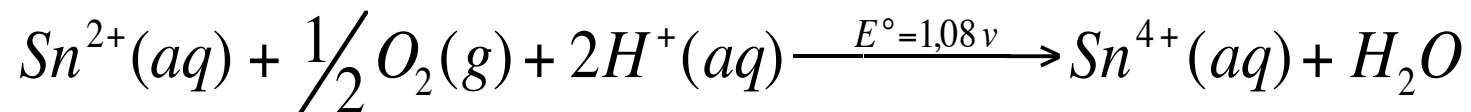
Tin and Lead (Group 14)

Sn:

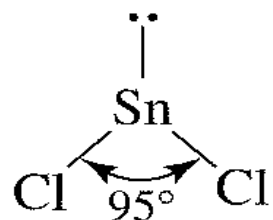
- Sn exists in two allotropic forms:
 - a “diamond” form (α) stable at $T < 13^\circ \text{C}$
 - a metal form ($T > 13^\circ \text{C}$), much more stable

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

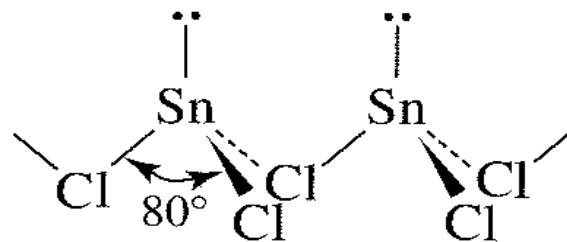
In aqueous medium, Sn^{2+} (which bears a lone pair of electrons) is a soft reducing agent.



- 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

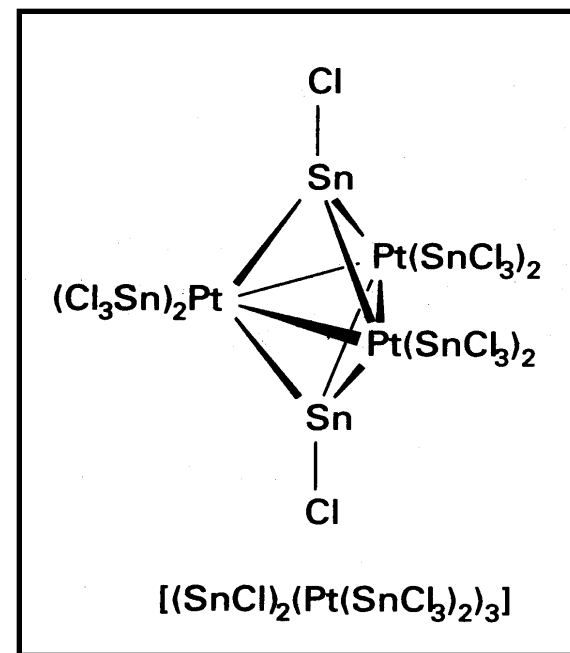
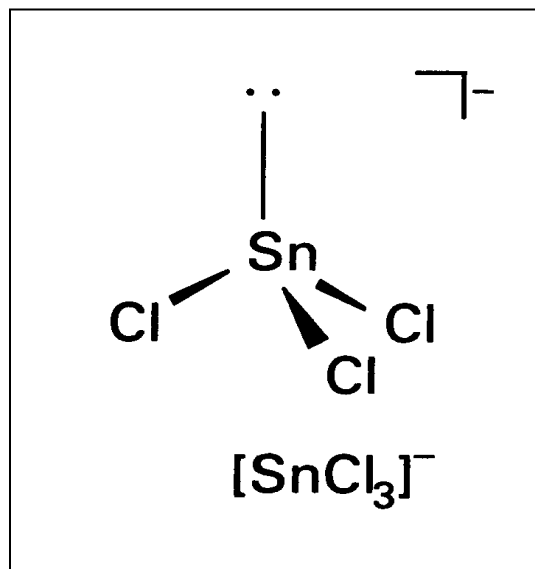


Gas



Crystalline

Stereochemically active lone pair



Pb :

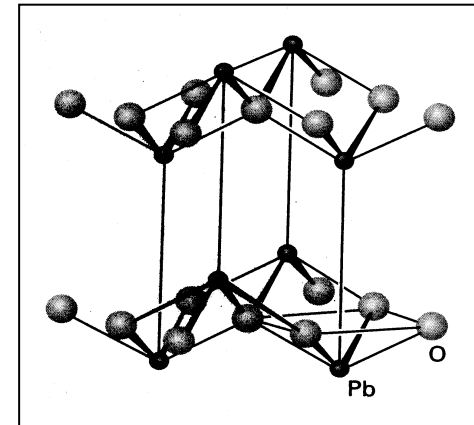
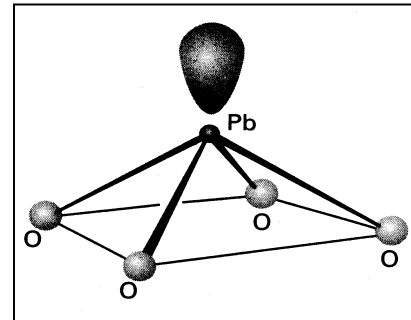
Lead oxide compounds are technologically important....but also very toxic

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

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

--> **Mixed Valence Oxides: Pb_3O_4 'minium'**
Structure of Pb_3O_4

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

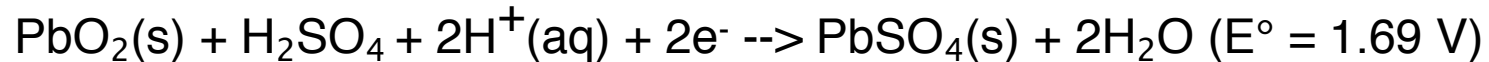
Lead-based Battery

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

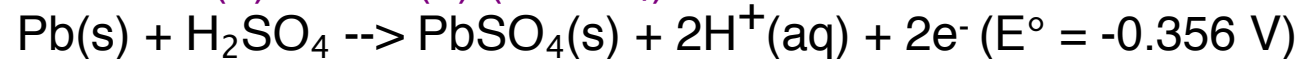
Charged state : cathode = PbO_2 et anode = Pb . In diluted H_2SO_4 , PbO_2 et Pb are insoluble.

Cathodic reduction and anodic oxidation

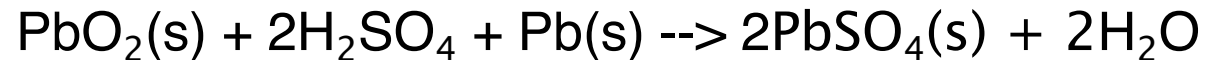
While working: at the cathode $\text{Pb(IV)} \rightarrow \text{Pb(II)}$ (PbSO_4)



At the anode $\text{Pb(0)} \rightarrow \text{Pb(II)}$ (PbSO_4)



Global Reaction:



Difference of potential: **2 volts**. (\gg to that of H_2O : 1,23 V)

Explanation : slow reaction with H_2O (slow kinetics)

Inorganic and Organometallic compounds of Groups 1 and 2: Applications in catalysis

The Specific case of Calcium

Organocalcium Overview

Nucleophilicity



R^-



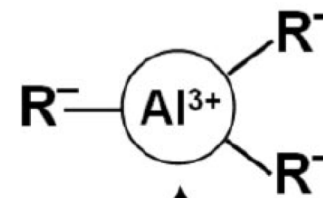
Nucleophilicity



R^-



Electrophilicity



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 (≈ 1 g/day is considered safe)
- Associated environmental hazards are low: easily convertible to limestone (CaCO_3) and slaked lime (Ca(OH)_2) for disposal

Characteristics of Calcium compounds

- 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_2 and H_2O)



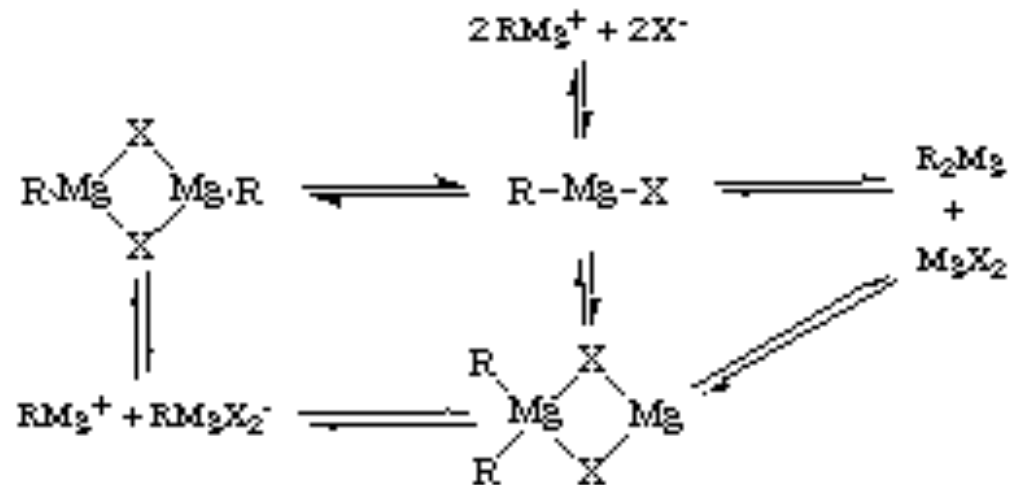
Increased ionic character of the Ca-C bond (versus the Mg-C bond)



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

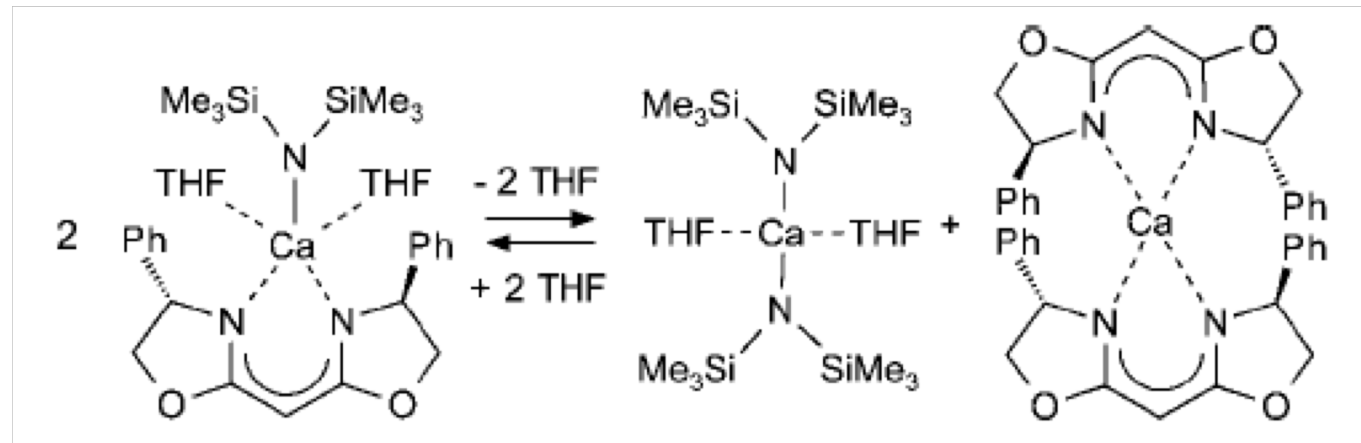
Example: The Schlenk equilibrium

- First discovered with organomagnesium derivatives



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

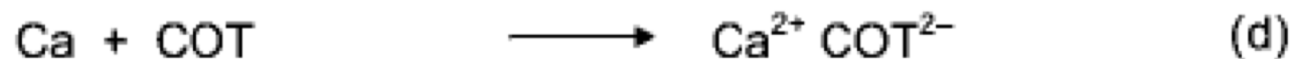
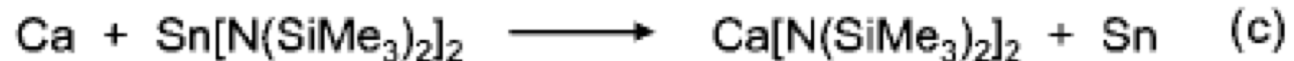
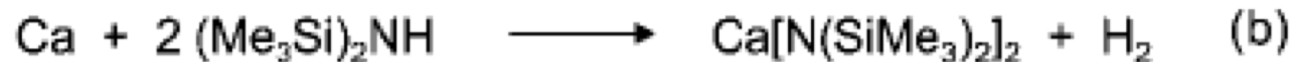
An example of the Schlenk equilibrium with organocalcium compounds



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

Preparation of OrganoCalcium compounds

1) Direct route from metal



2) Salt metathesis



3) Deprotonation (acid-base reaction)

