INTERACTIONS WITHIN HETEROBIMETALLIC COMPLEXES
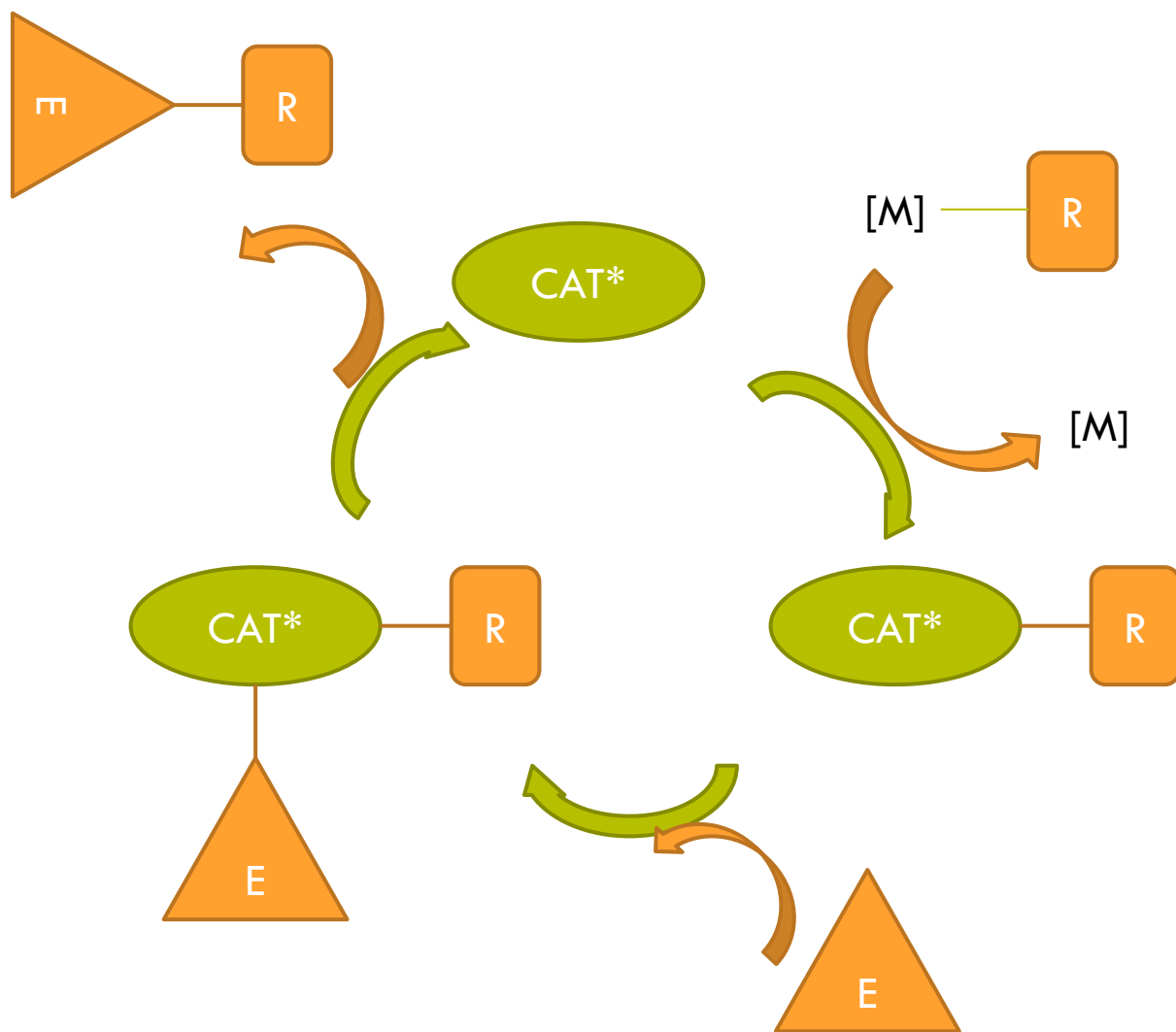
H. GERARD

Alkylation catalysis

Li-R ; MgR$_2$; ZnR$_2$; AlR$_3$

Computational expertise

Computational and experimental chemists

H. Khartabil

B. Lecachey   A. Harrisson-Marchand   G. Barrozzino   M. Seban   M. Rouen

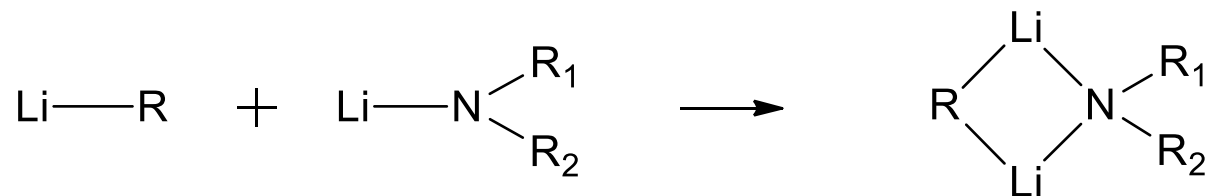J.-P. Piquemal   H. Gérard   H. Oulyadi   J. Maddaluno   Pr. Kondo

Lithium Mixed Aggregate

☐ Spin-spin coupling between R-Li and N-Li :
→ « bond-like » character

☐ Fast ligand exchange between aggregates :
→ « complex-like » character

☐ Sensitive to the nature of the (ethereal) solvent :
→ « ion-like » character

Intramolecular

Intermolecular
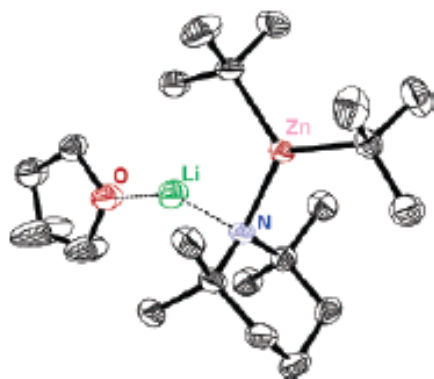
Hetero-bimetallic complexes

Analogous structures

with Zn

Figure 2. Crystal structure of $^tBu_2Zn(TMP)Li\cdot THF$ (2a-S). Displacement ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity.

. "Structure and Reaction Pathway of TMP-Zincate: Amido Base or Alkyl Base?", M. Uchiyama, Y. Matsumoto, D. Nobuto, T. Furuyama, K. Yamaguchi, K. Morokuma*, *J. Am. Chem. Soc.,* **2006**, *128*, 8748-8750.
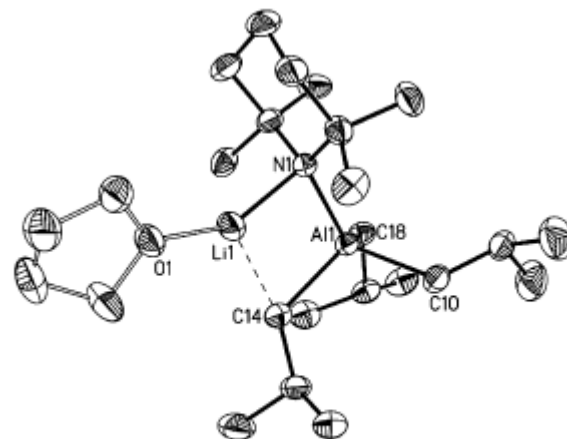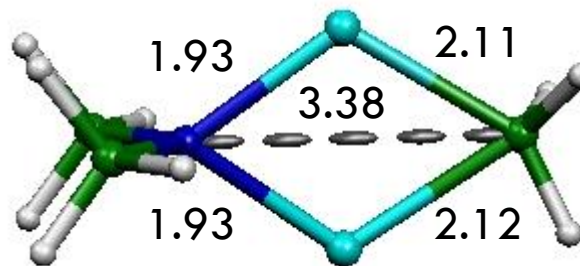
and Al

Figure 3. Molecular structure of 1−THF. Hydrogen atoms are omitted for clarity. Atoms are plotted at 40% probability.

"An Aluminum Ate Base: Its Design, Structure, Function, and Reaction Mechanism"
H. Naka, M. Uchiyama, Y. Matsumoto, A. E. H. Wheatley, M. McPartlin, J. V. Morey, Y. Kondo, *J. Am. Chem. Sc.* **2007**, *129*, 1921-1930
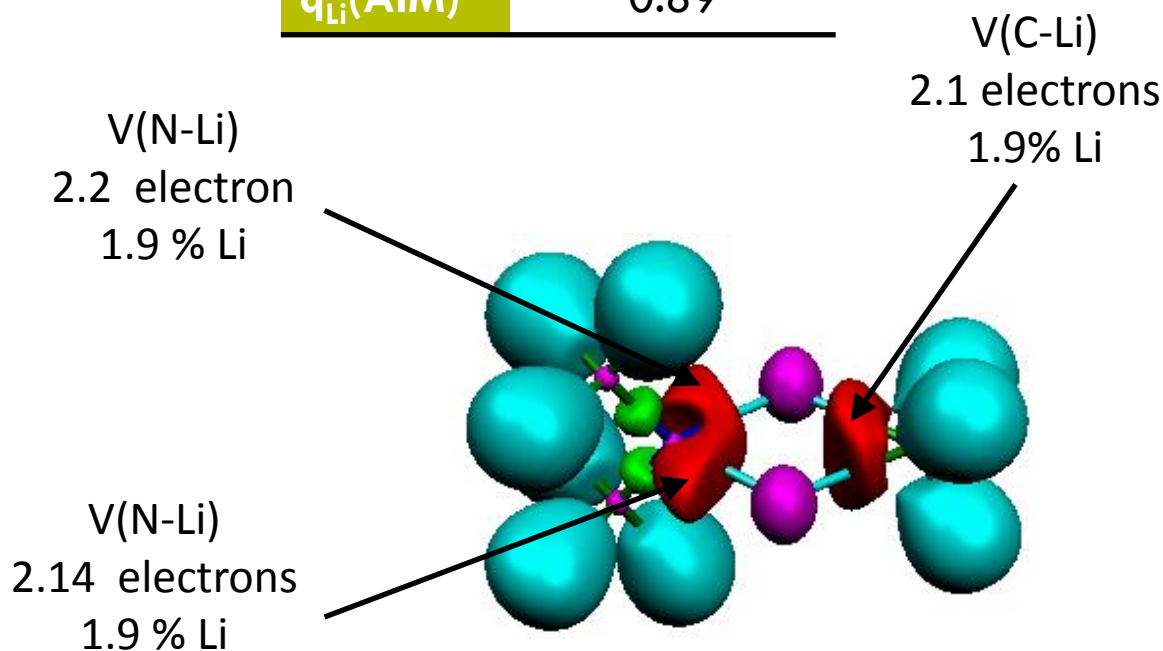
Homo-bimetallic lithium aggregate

Electronic properties analysis

Charges	Li$_2$Me(NMe$_2$)
q$_{Li}$ (NBO)	0.87
q$_{Li}$(AIM)	0.89

NBO description :

4 units

LP(C) : 1.88 e

LP(N) : 1.90 and 1.82 e

LP*(Li) : 0.11 and 0.11 e

V(C-Li)

2.1 electrons

1.9% Li

V(N-Li)

2.2 electron

1.9 % Li

Wiberg Indexes :

Li-C : 0.11

Li-N : 0.11

V(N-Li)

2.14 electrons

1.9 % Li

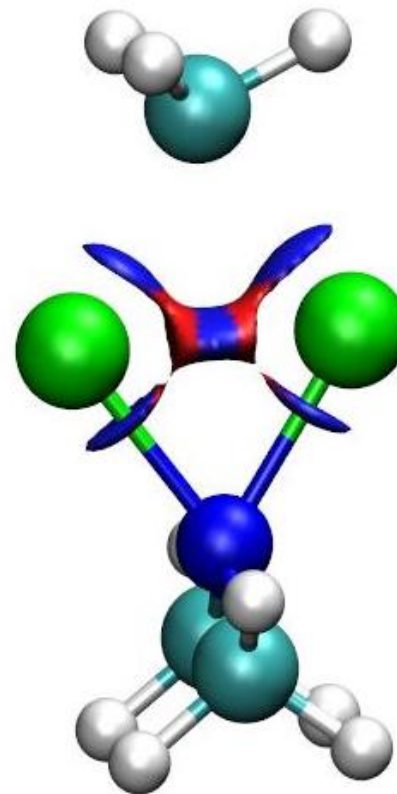## Very high ionicity, whatever the method considered

Approaching NCI
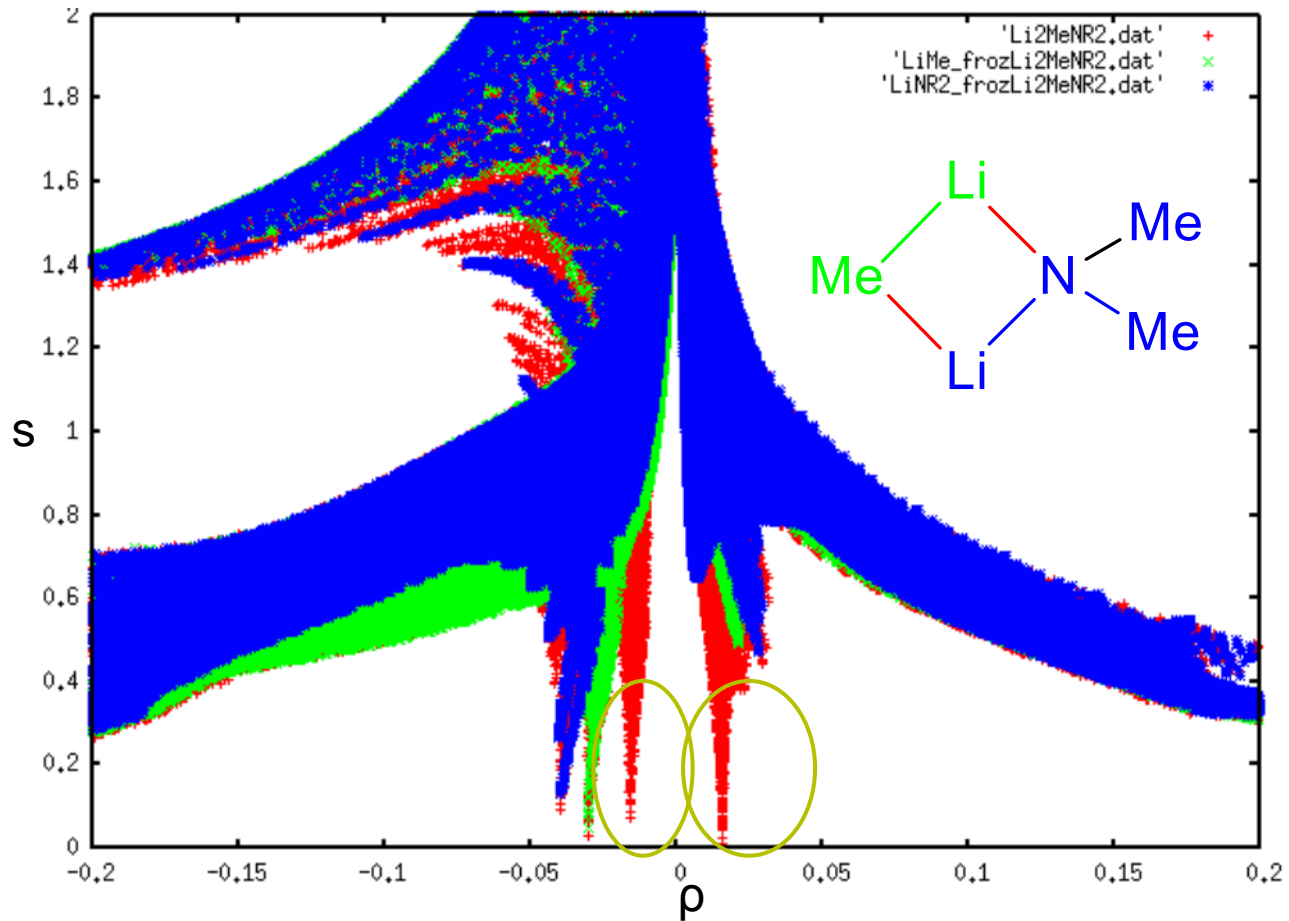
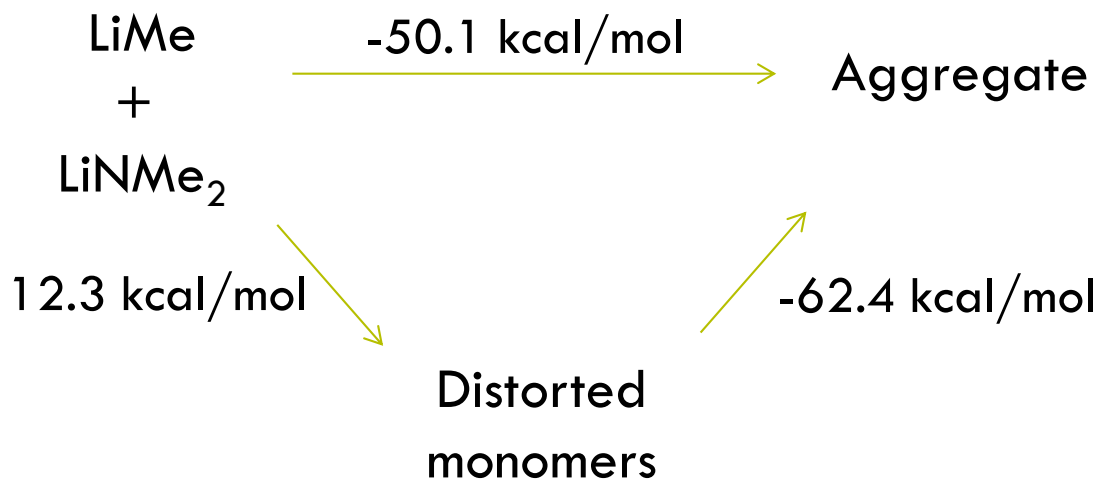# Localizing additional interactions
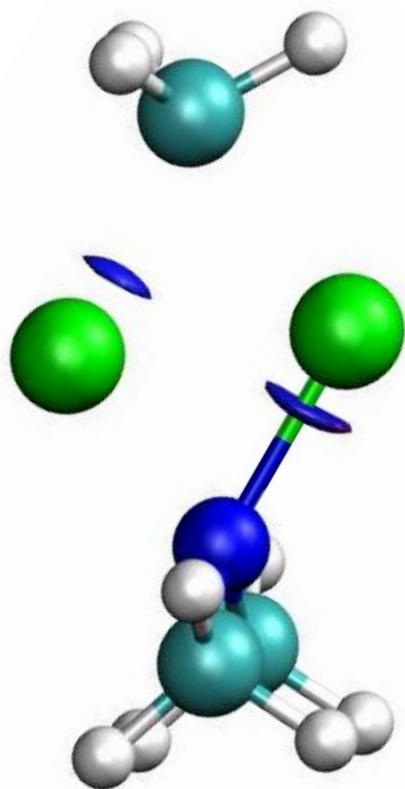
Connecting with Binding Energy

LiMe
+
LiNMe$_2$

$\xrightarrow{\text{-50.1 kcal/mol}}$ Aggregate

12.3 kcal/mol

-62.4 kcal/mol

Distorted
monomers

A

| Vacant |

B

| Vacant |

-8.2 kcal/mol

Polarization

Charge transfer

Polarization

-15.4 kcal/mol

| Occupied | **Electrostatic + Exchange** | Occupied |

-37.6 kcal/mol
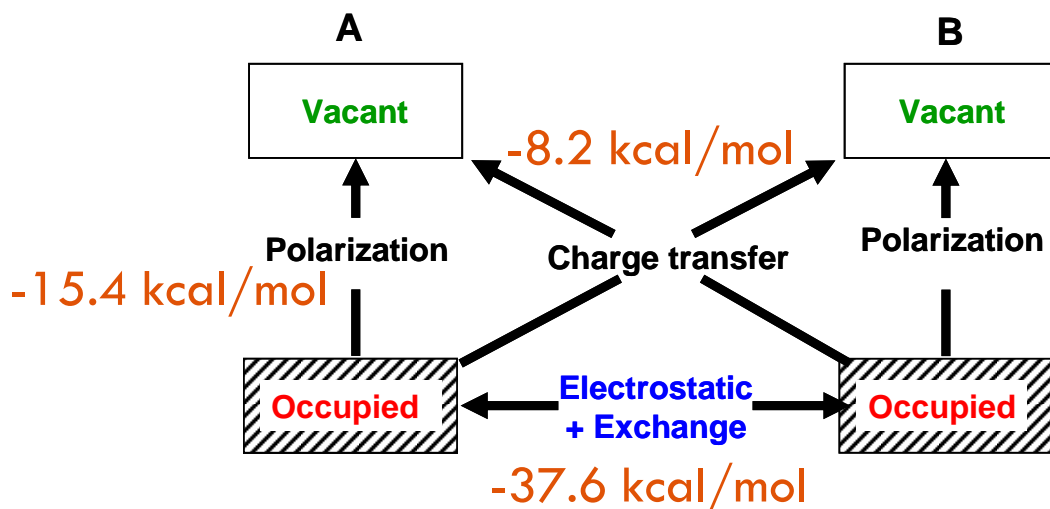
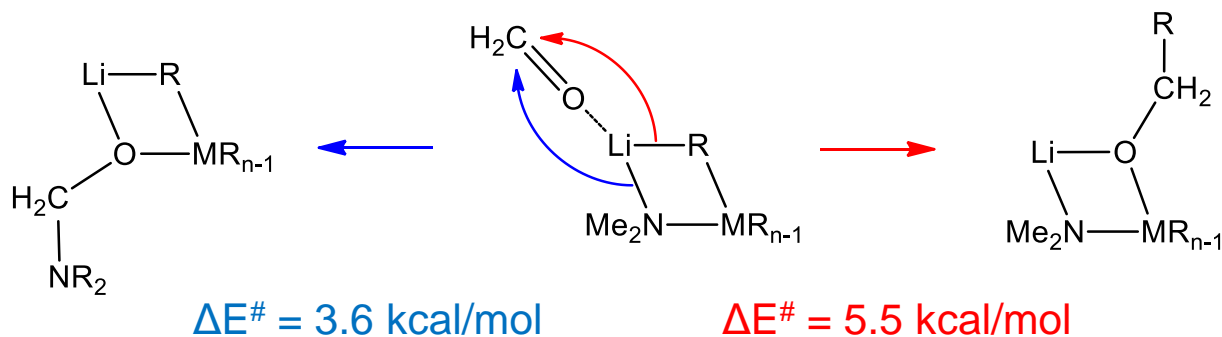**Major frozen core contribution**

Important intra-monomer rearrangement

Small Inter-monomer exchange

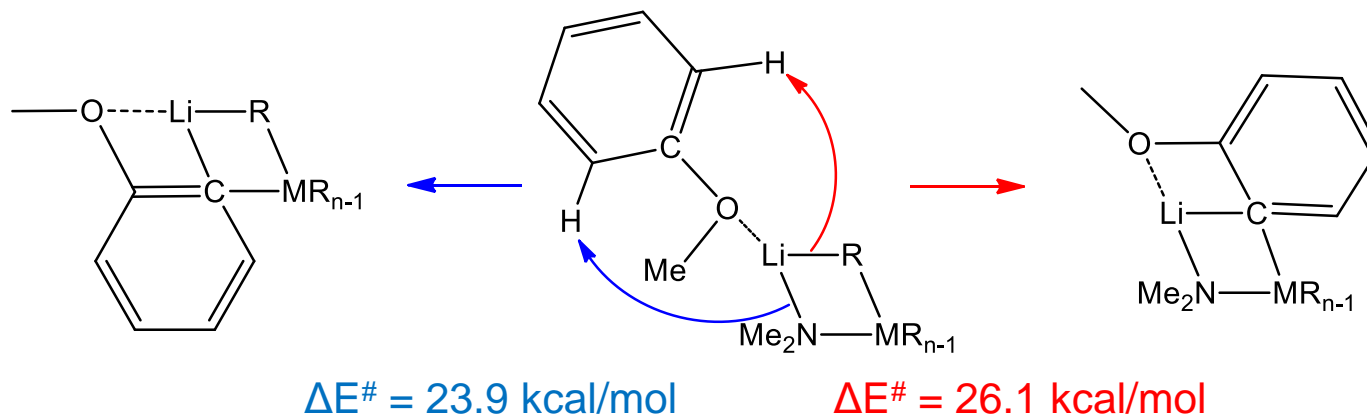# Connecting with reactivity ?

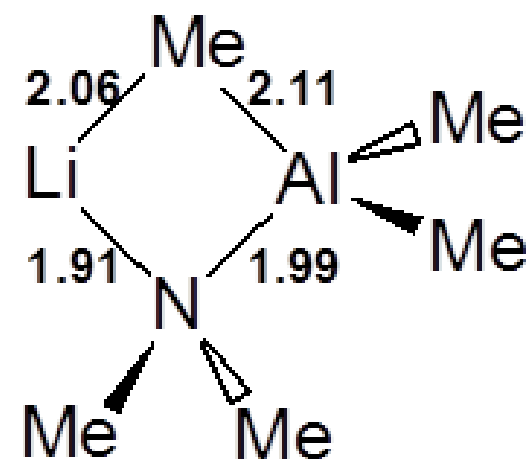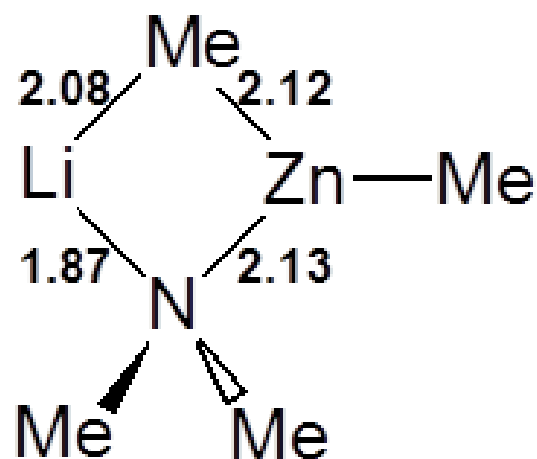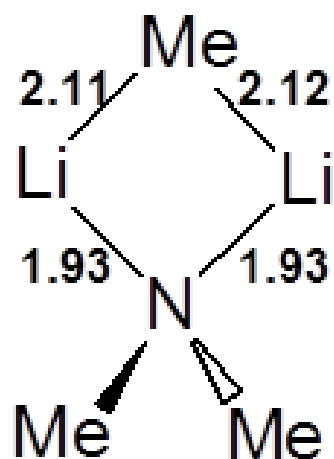Nucleophilic reactivity : N-nucleophile or C-nucleophile ?

$\Delta E^{\#} = 3.6$ kcal/mol $\Delta E^{\#} = 5.5$ kcal/mol

Basic reactivity : N-base or C-base ?

$\Delta E^{\#} = 23.9$ kcal/mol $\Delta E^{\#} = 26.1$ kcal/mol

Similar ionicity, similar reactivity (TS)

Hetero-bimetallic Li-Zn and Li-Al

Electronic Analysis

Charges	Li[M]Me(NMe$_2$)
M = Li	0.87 (0.13)
M = ZnMe	1.32 (0.68)
M = AlMe$_2$	1.67 (1.33)

WBI	[M]-N	[M]-C$_{cyc}$	[M]-C$_{ext}$
M = Li	0.11	0.11	-
M = Zn	0.18	0.30	0.48
M = Al	0.44	0.57	0.66

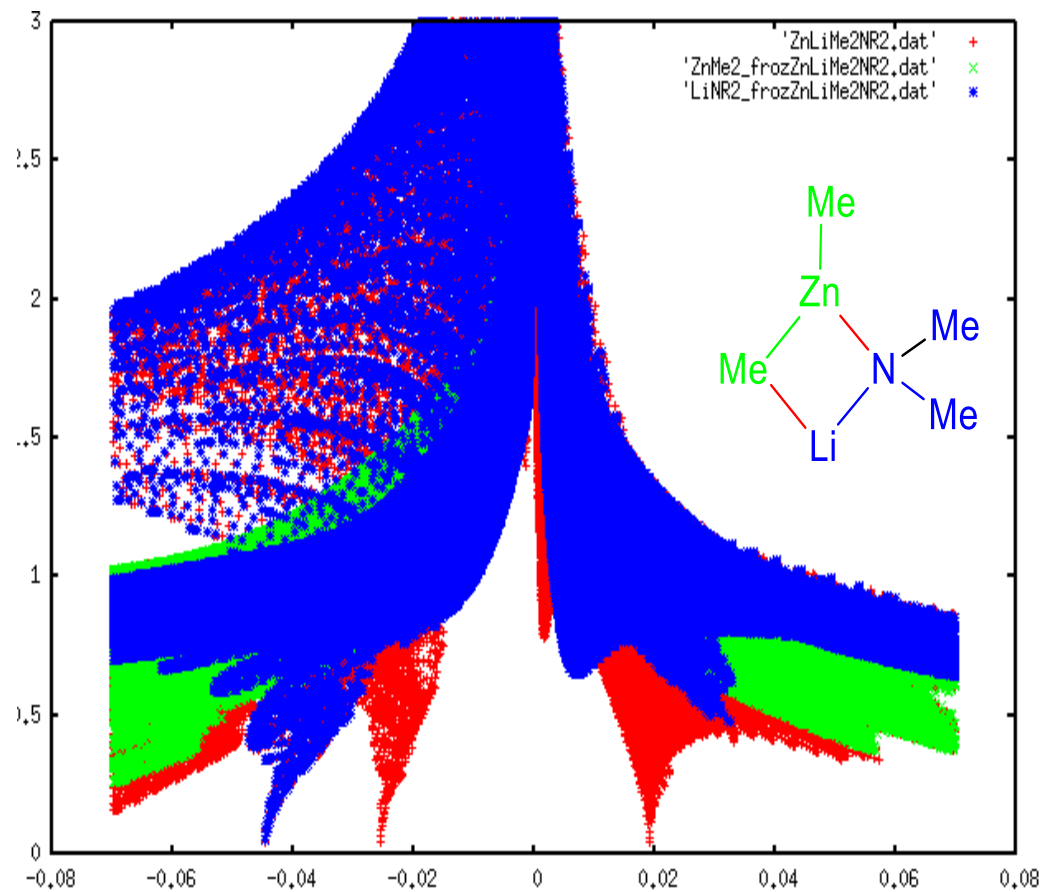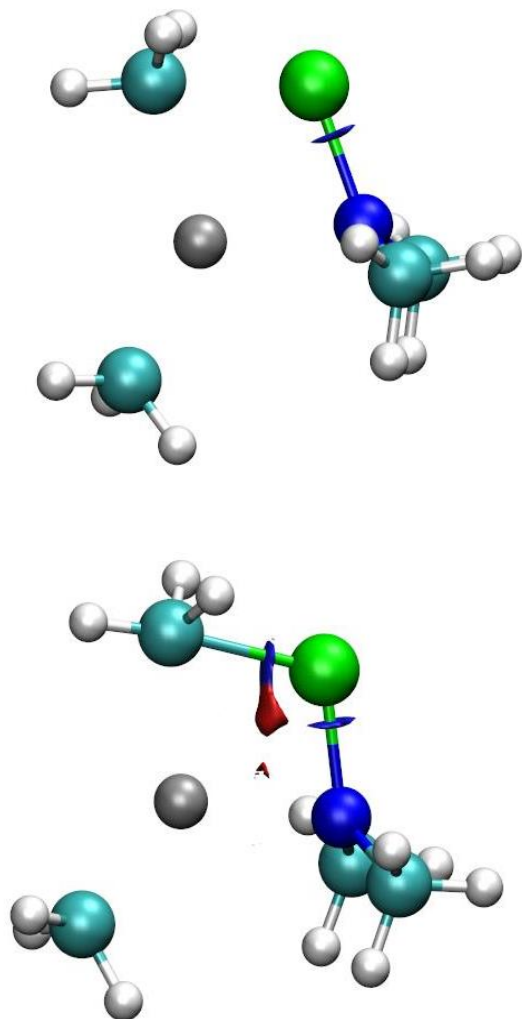| NBO	Units	LP/BD	LP*/BD*
M = Li	4	LP(C) : 1.88 e LP(N) : 1.90 and 1.82 e	LP*(Li) : 0.11 and 0.11e
M = Zn	4	LP(C) : 1.76 e LP(N) : 1.89 and 1.79 e	LP*(Li) : 0.08 e BD*(Zn-C$_{ext}$) : 0.30 e
M = Al	2	BD(C-Al) : 1.96 e (85% C) BD(Al-N) : 1.94 e (90% N) LP(N) : 1.86 e	LP*(Li) : 0.06 e

Analysis of the ELF function

V(Zn-C)

31.93%Zn

2.13 e

V(Zn-N)

7.65%Zn

1.83 e

V(Zn-C)

20.18%Zn

2.05 e

V(N-Li)

1.66%Li

2.43 e

Zn

V(Al-C)

10.2% Al

2.04e

V(Al-N)

5%Al

2.20 e
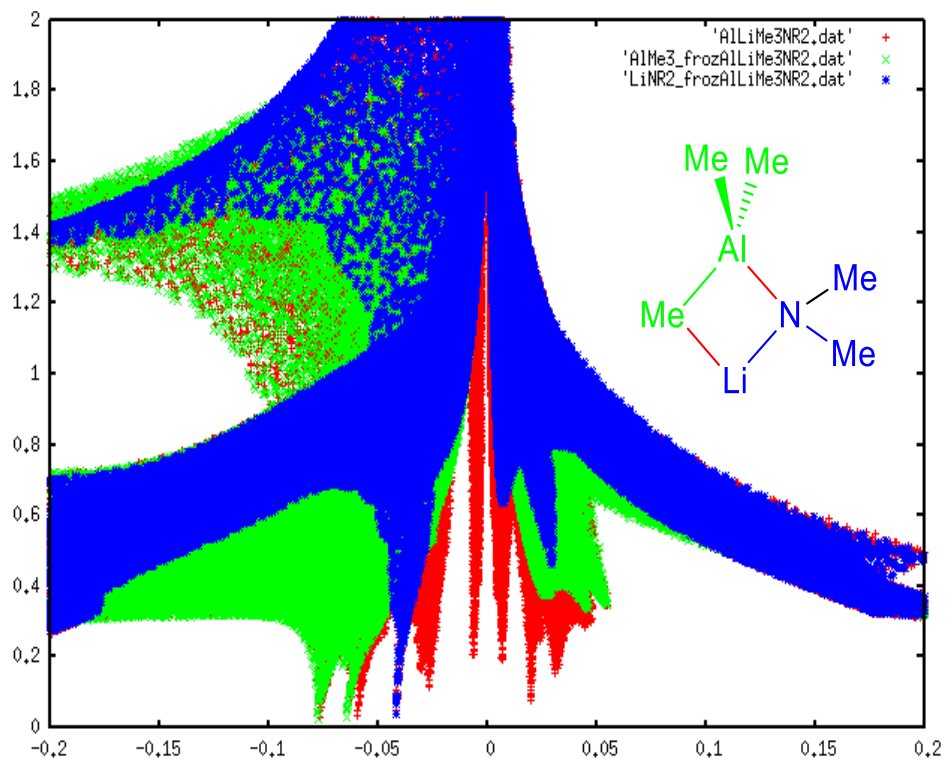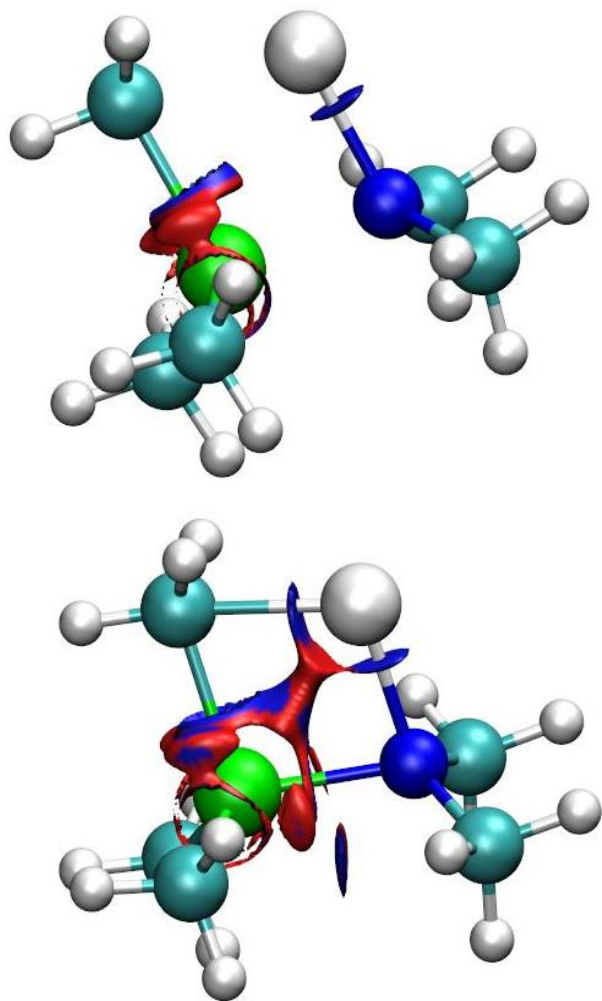
V(Al-C)

7.37 %A

2.05e

V(Li-N)

1.85%Li

2.17 e

Al
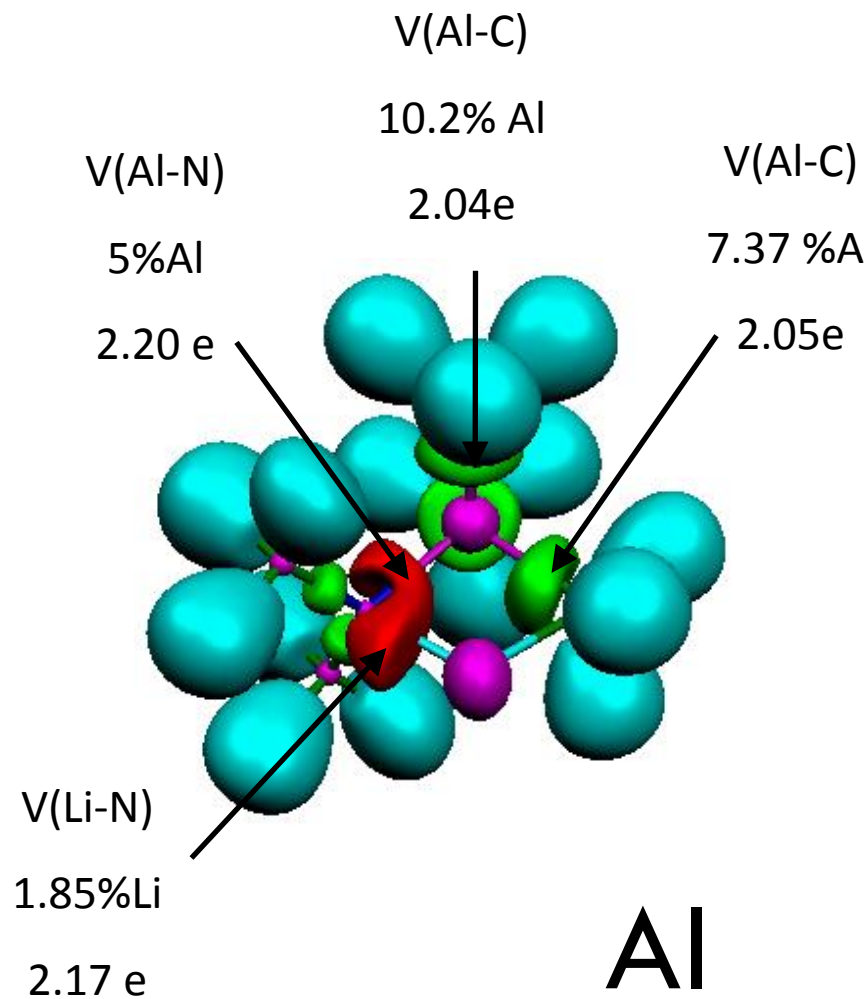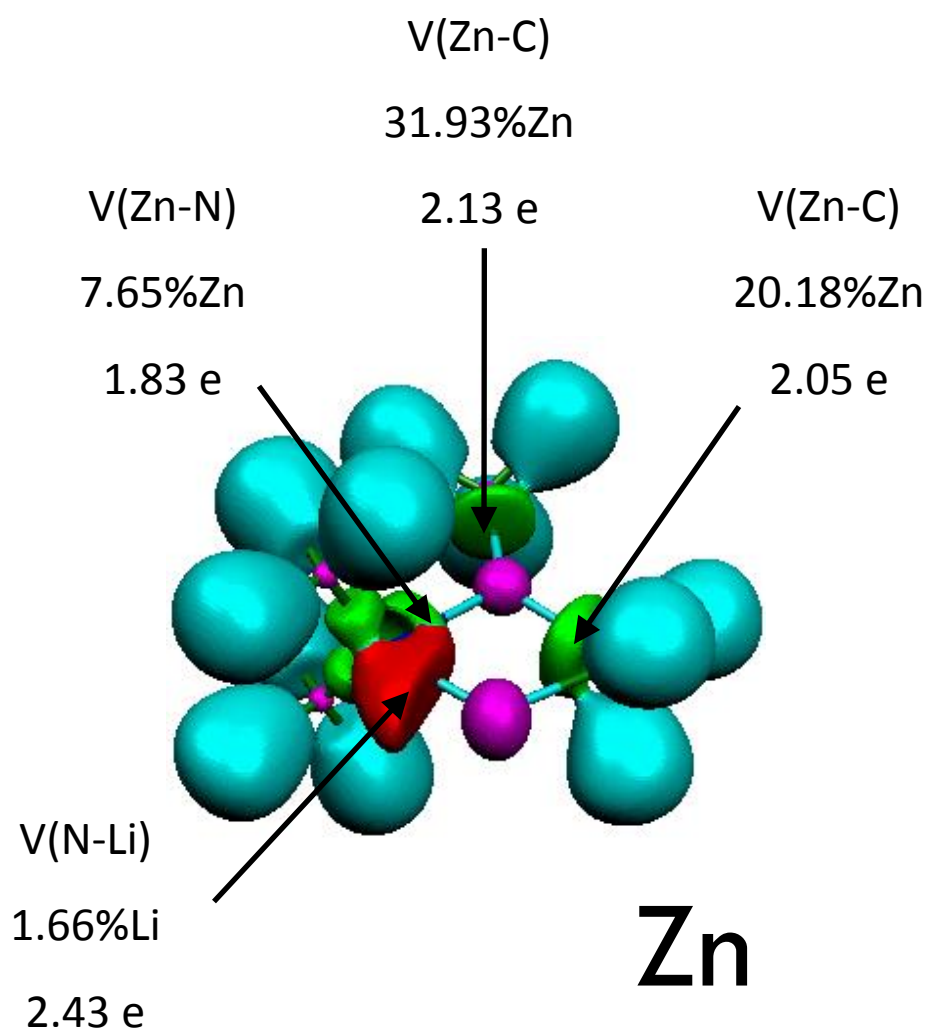
NCI point of view : Zn

NCI point of view : Al

Energetic aspect

Lithium amide + alkylmetal

kcal/mol	Li	Zn	Al
ΔE_{opt}	-50.1	-25.4	-46.7
distortion	12.3	18.0	22.8
ΔE_{Froz}	-62.4	-43.3	-69.4
E_{FC}	-37.6	-0.4	-11.9
E_{pol}	-15.4	-27.7	-37.6
E_{CT}	-8.2	-14.3	-18.8

dipole - dipole
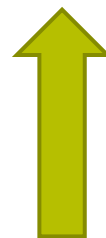
second-order
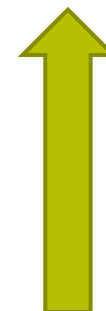
polarisable

Connecting with reactivity ?

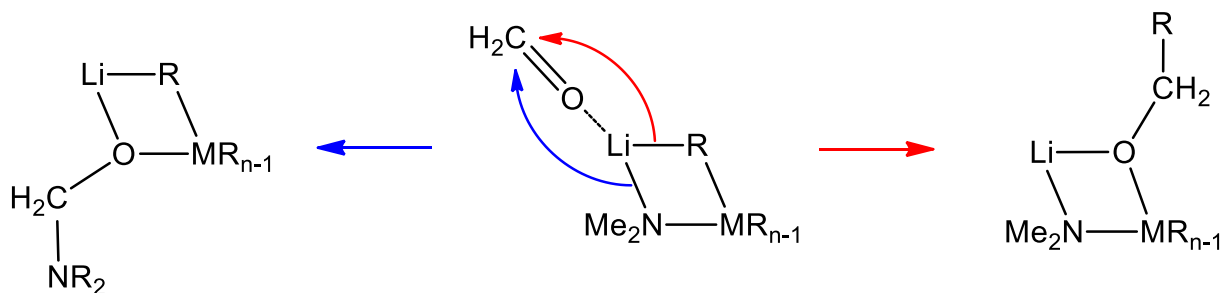**Basic reactivity : N-base or C-base ?**
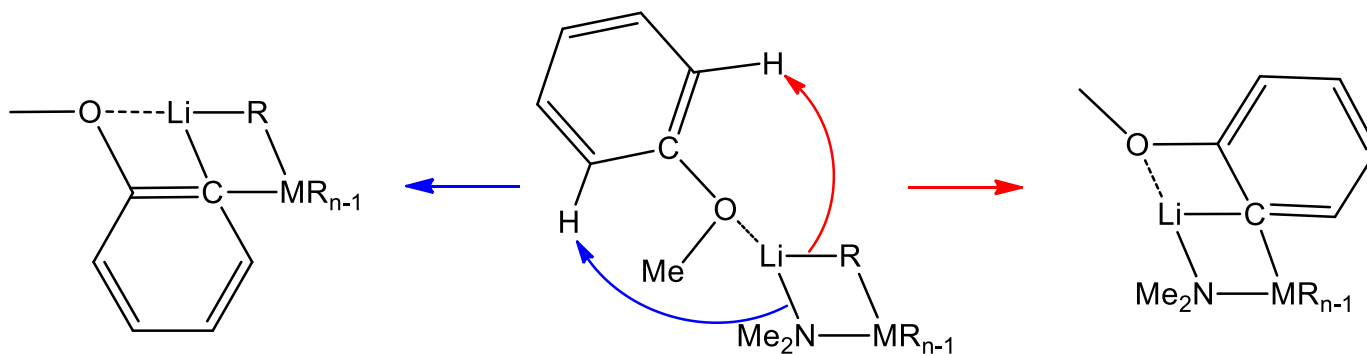
$\Delta E^{\#}$ (kcal/mol)	N-base	C-base
Li	23,9	26,1
Zn	25,8	37,8
Al	28,8	47,0

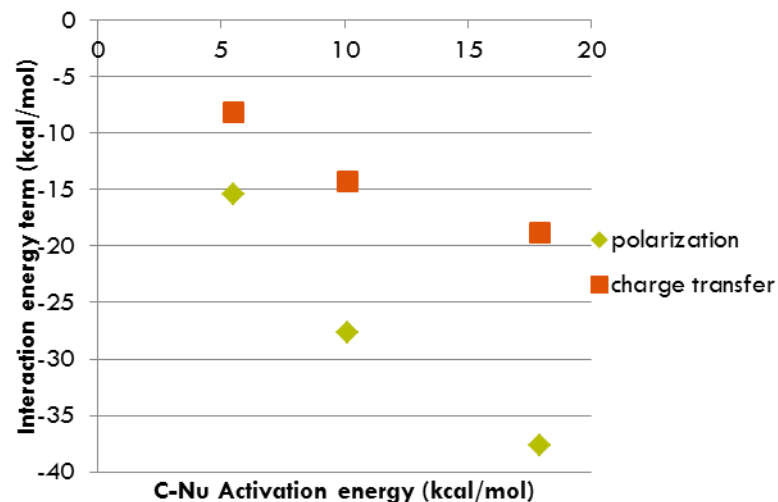## Activation energies follow CT, polarization or M-C bond index

Connecting with reactivity ?

Nucleophilic reactivity : N-nucleophile or C-nucleophile ?

$\Delta E^{\#}$ (kcal/mol)	N-nucleophile	C-nuclophile
Li	3.6	5.5
Zn	14.9	10.1
Al	5.0	17.9

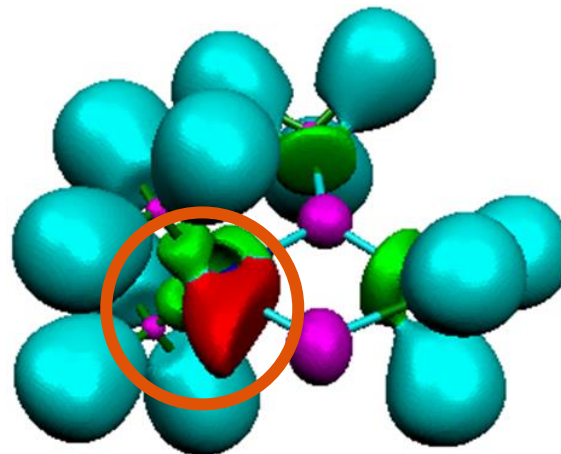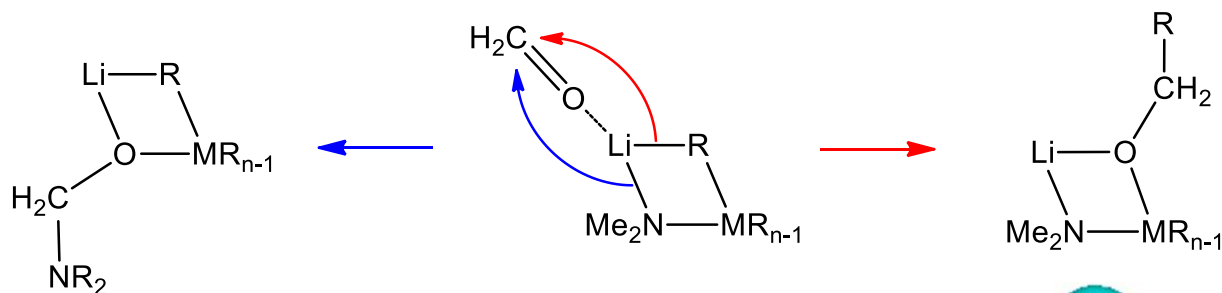

C-nucleophilicity follows CT, pol but also natural orbital analysis

Connecting with reactivity ?

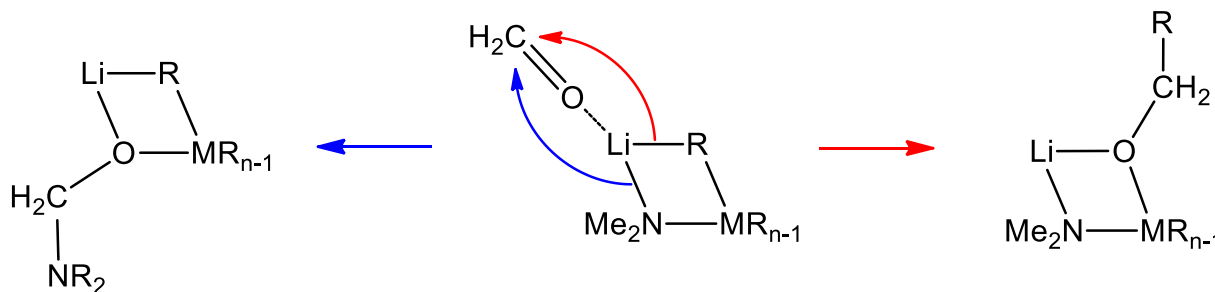Nucleophilic reactivity : N-nucleophile or C-nucleophile ?

$\Delta E^{\#}$ (kcal/mol)	N-nucleophile
Li	3.6
Zn	14.9
Al	5.0

Zn

Higly populated N lone-pair does not ensure N -nucleophilicity

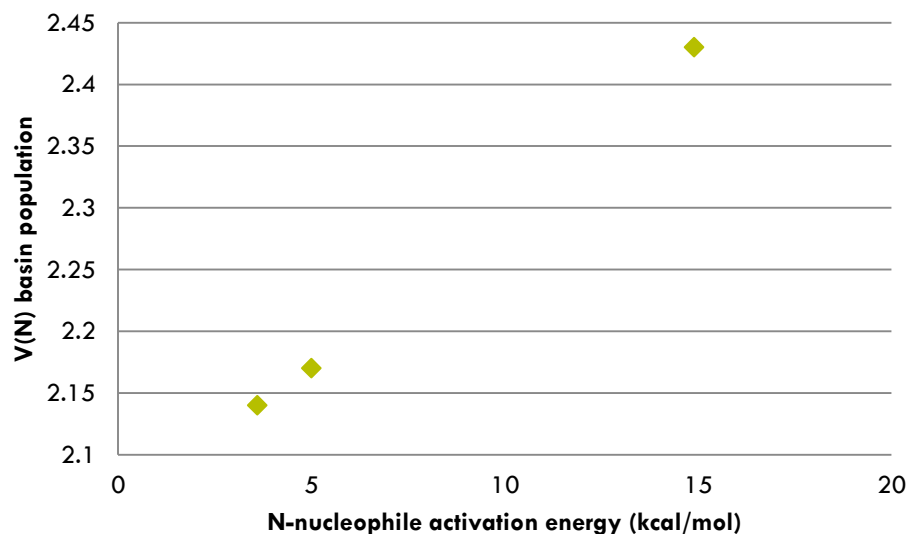# Connecting with reactivity ?
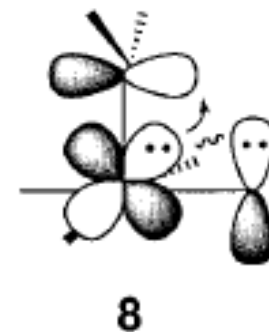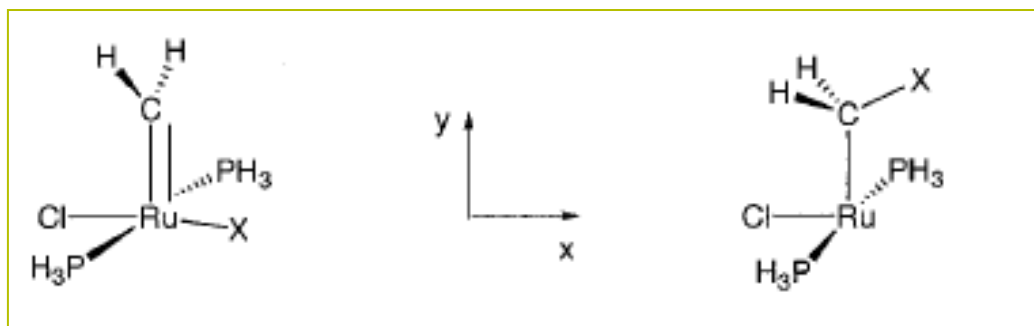
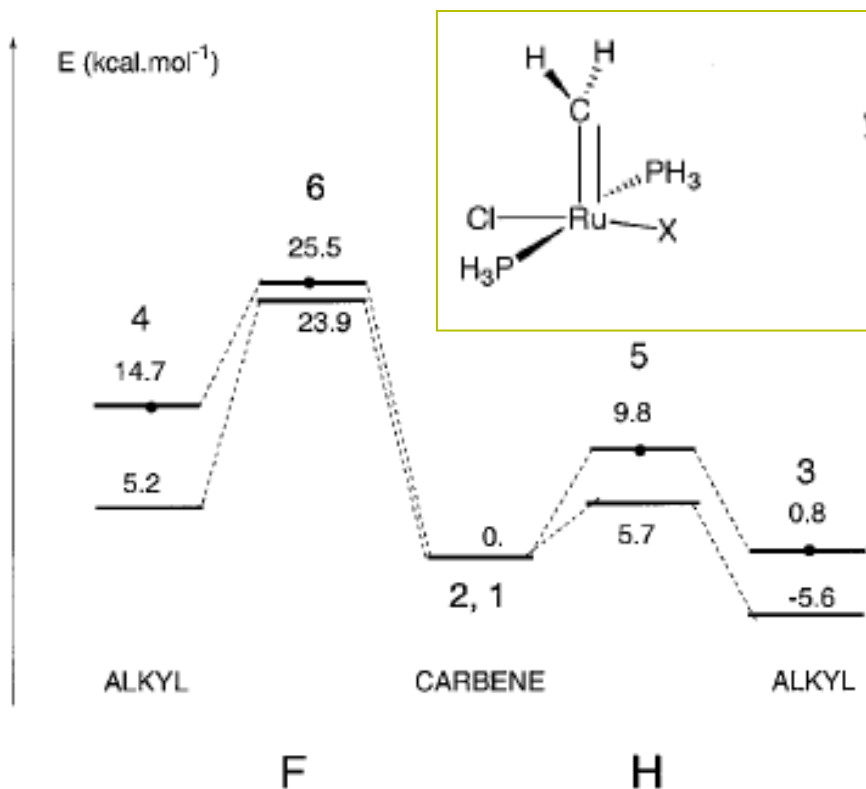Nucleophilic reactivity : N-nucleophile or C-nucleophile ?

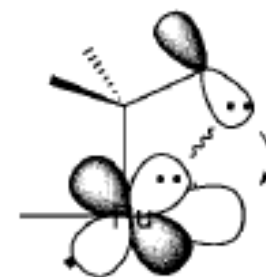| $\Delta E^{\#}$ (kcal/mol)	N-nucleophile
Li	3.6
Zn	14.9
Al	5.0

Higly populated N lone-pair increase activation energy ?

A general effect ?

H. Gérard, E. Davidson and O. Eisenstein, Mol. Phys. 2002, *100*, 533.

Electrons of the nucleophile also interact with the electrons of the electrophilic double bond

→ enough electron to react, not too much to avoid repulsion

Conclusion

□ Superposition of various analysis necessary for a consistant picture

□ Second order perturbations to energy or charge at the metal are the best for basicity or C-nucleophilicity ; N-nucleophilicity also influenced by electron pair repulsion

□ Complete by evidencing different interactions at stake in the TS