

Bryan Eichhorn

Professor

New Directions in Energetic Materials:
Low-valent Aluminum Clusters

Department of Chemistry and Biochemistry

Why aluminum clusters?

- Aluminum oxidation is highly exothermic ($\Delta H_f = -1666 \text{ kJ}\cdot\text{mol}^{-1}$)
- Kinetics of bulk aluminum oxidation slow due to aluminum oxide layer
- Low-valent aluminum clusters offer potential solution to problem
- Small, low oxidations state Al clusters should have better kinetic responses with comparable energy release.

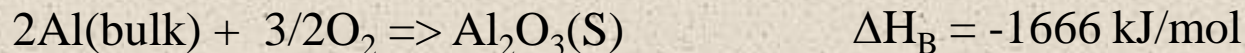


Al/Fe₂O₃ Thermite Reaction

The only technology available to prepare bulk scale quantities of low valent Al clusters resides in Karlsruhe, Germany (H.G. Schnockel).

Thermochemistry and energy release

Issue: Is There More Energy in Nanoparticles / Clusters ?



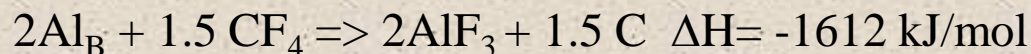
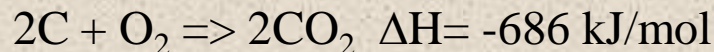
The smallest Aluminum entity and therefore the largest energy release would come from an isolated Al atom (smallest particle possible).



Or $\Delta H_1 / \Delta H_{\text{B}} = \text{Enhancement factor} = 1.39$

Size	Enhancement factor
Al ₁	1.39
Al ₂	1.29
1 nm Al	1.04

Aside:



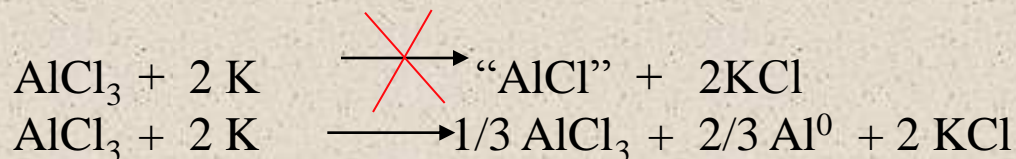
Low-valent aluminum cluster chemistry

Al exists in two primary oxidation states:

Al^0 (metal and alloys)

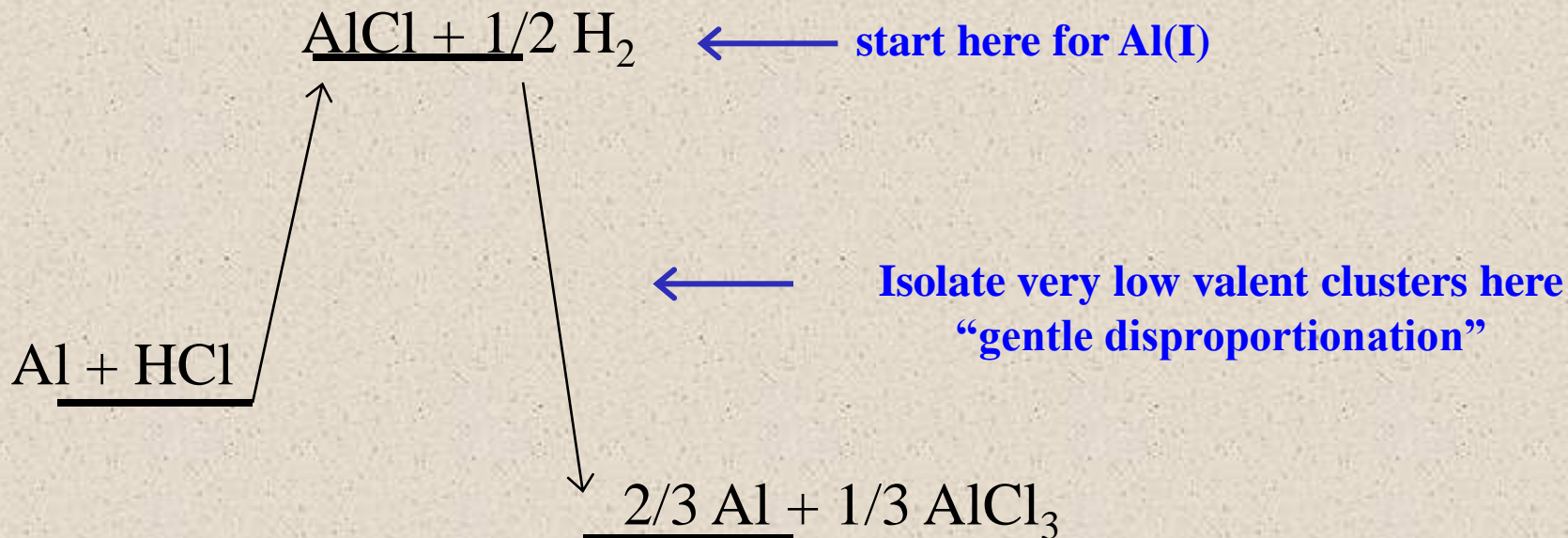
Al^{+3} (salts; e.g. Al_2O_3 , Al_2Cl_6)

Large kinetic barriers to reduction result in thermodynamic products:



Few exceptions: $\text{Al}(\text{nacnac})$, $\text{Al}(\text{terphenyl})$ -- Power, Jones, Roesky

Schnöckel concept in aluminum cluster chemistry

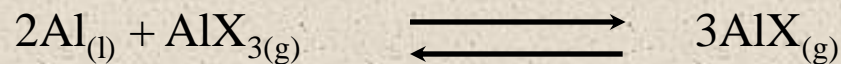
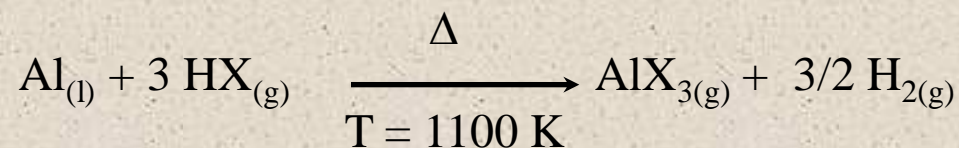
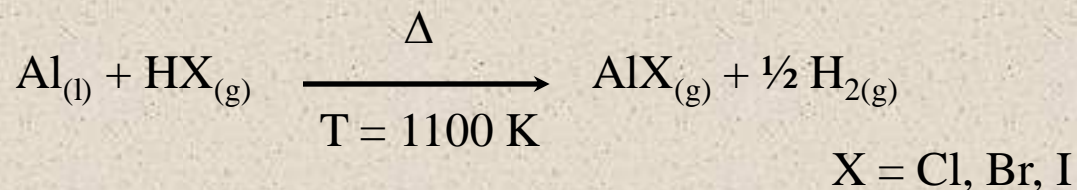


Metalloid Clusters: contain more M-M bonds than M-L bonds
 - the interface between very large clusters and small nanoparticles

Low-valent aluminum clusters from AlX precursors

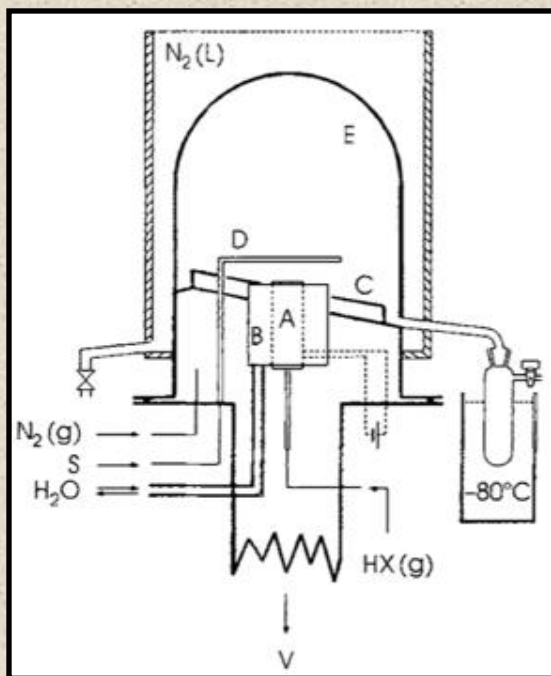


The Schnöckelator!

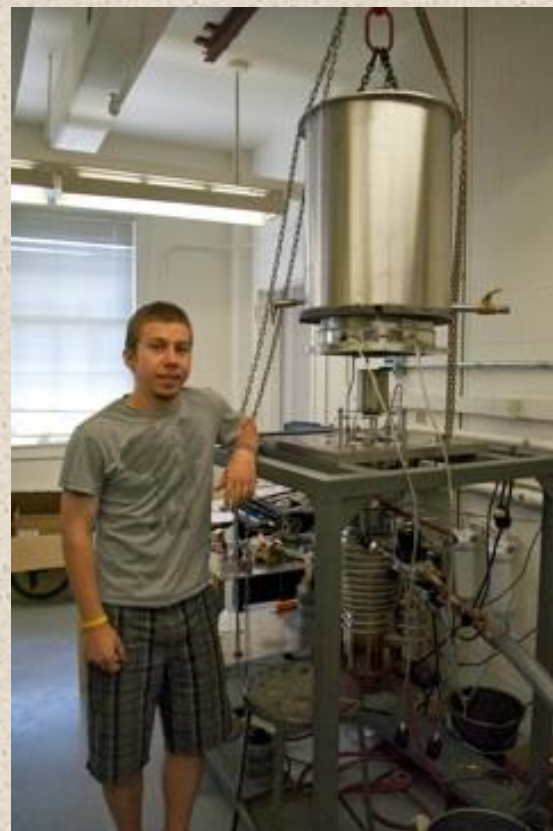


Dohmeier *et. al.* *Angew. Chem. Int. Edit.* **1996**, *35*, **2**, 129-149

Low-valent aluminum clusters from AlX precursors (X = Cl, Br, I)



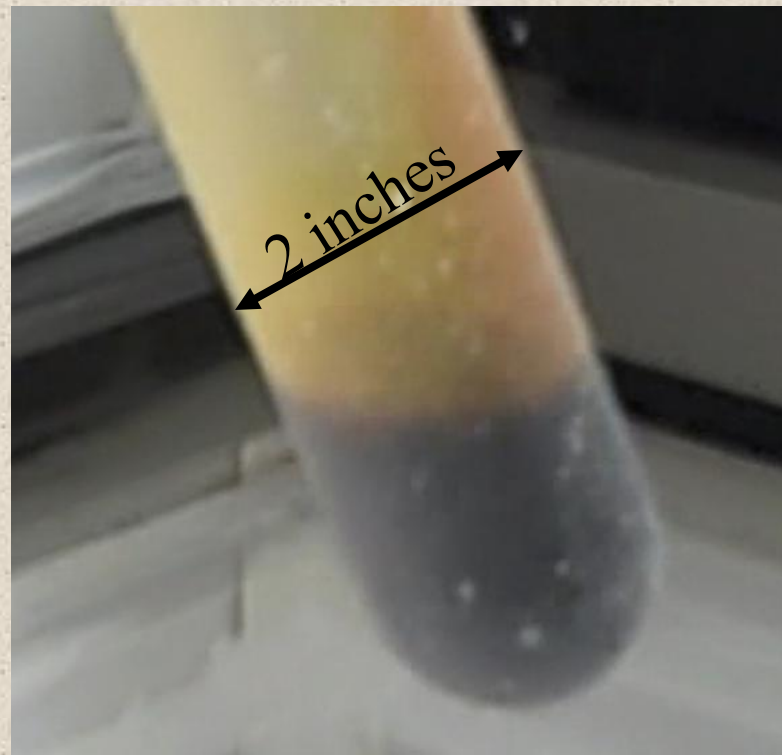
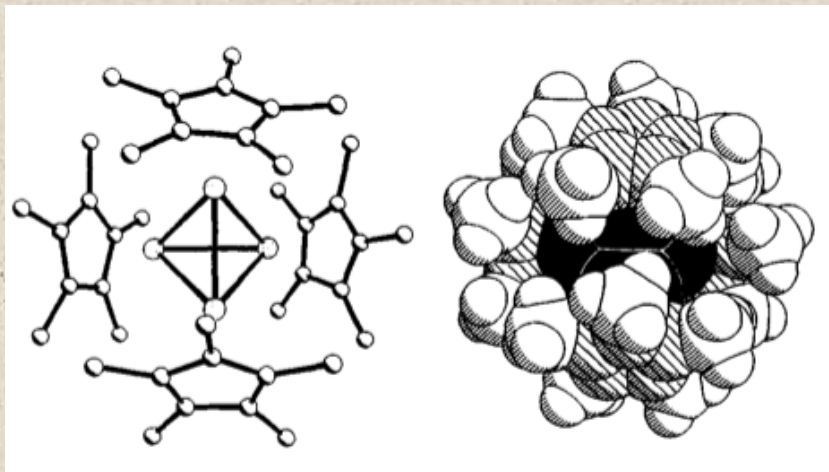
- A. Graphite block containing Al
- B. Cooling block
- C. Drainage channel
- D. Solvent inlet
- E. Stainless deposition surface



Dohmeier *et. al.* *Angew. Chem. Int. Edit.* **1996**, *35*, **2**, 129-149

Bulk materials

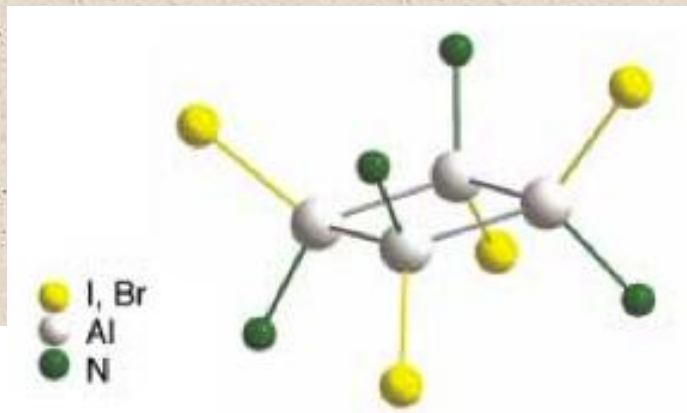
- ~60 mmol AlX generated in 2 hours
- Metastable AlX can be stored for weeks
- Al_4Cp^*_4 isolated in 50% yield



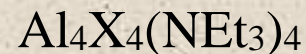
Metastable AlCl solution
in 1:3 Et_3N :toluene

Low-valent aluminum clusters

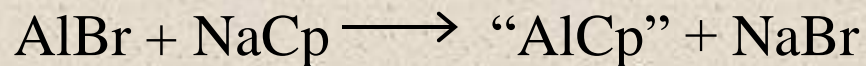
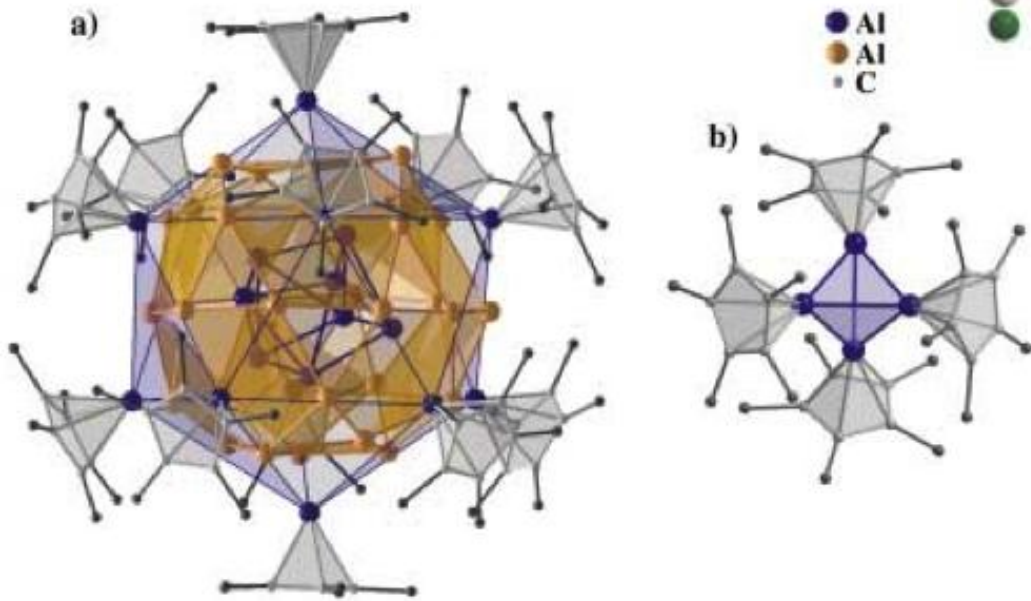
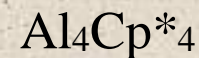
Metastable AlCl solution
in 1:3 Et₃N:toluene



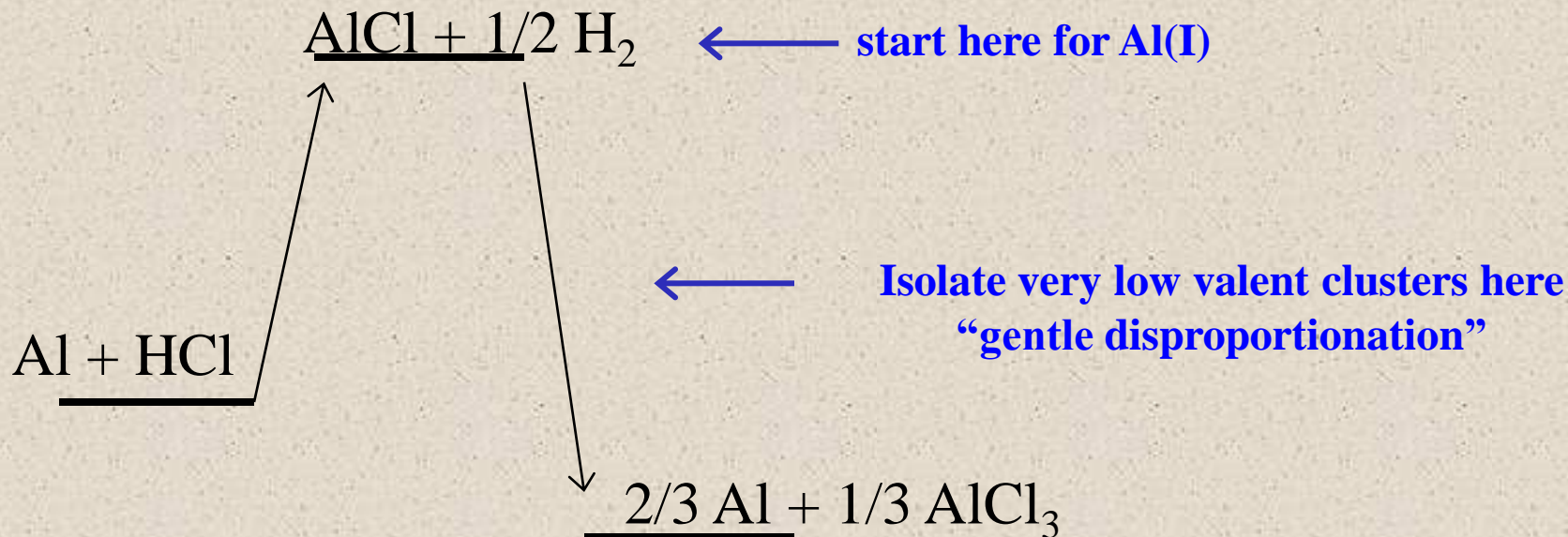
Al^{+1.0}



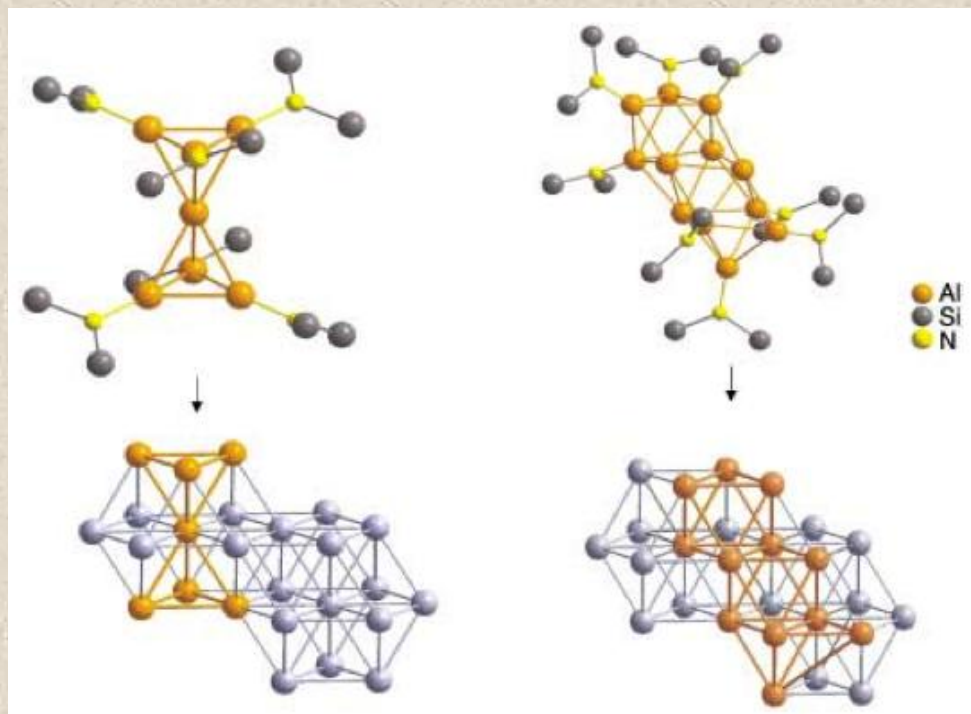
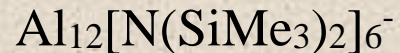
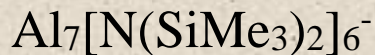
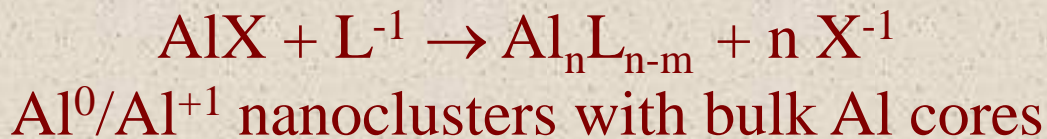
Al^{+1.0}



Schnöckel concept in aluminum cluster chemistry



Metalloid Clusters: contain more M-M bonds than M-L bonds
- the interface between very large clusters and small nanoparticles

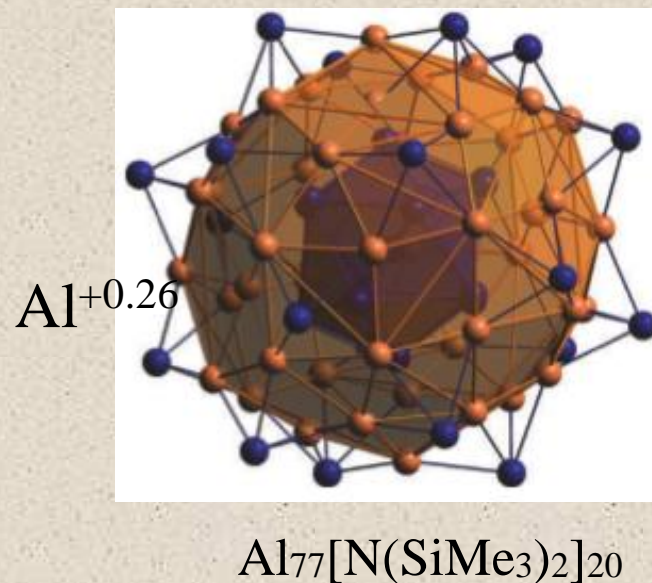
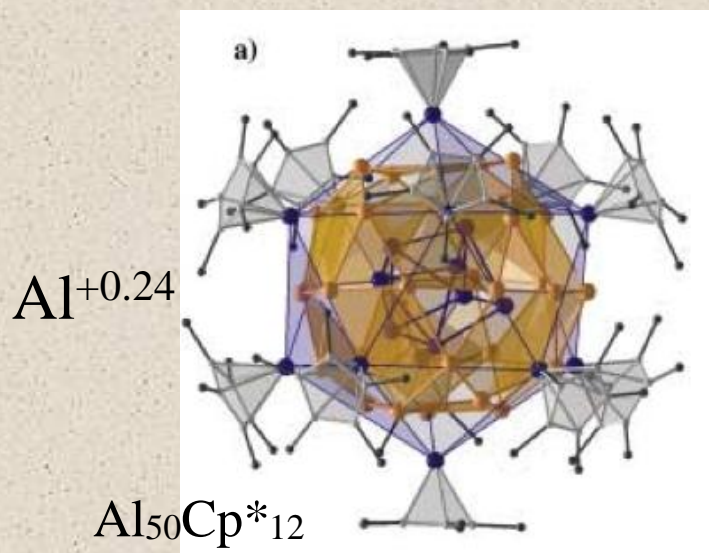
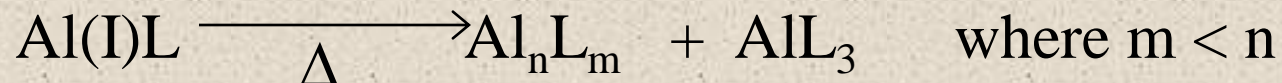


Al_7 and Al_{12} in bulk aluminum metal

Purath *et al.*, *Angew. Chem. Int. Ed.* **1999**, 38, 2926-2928

Purath *et al.*, *Chem. Commun.* **1999**, 19, 1933-1934

Low-valent aluminum metalloid clusters



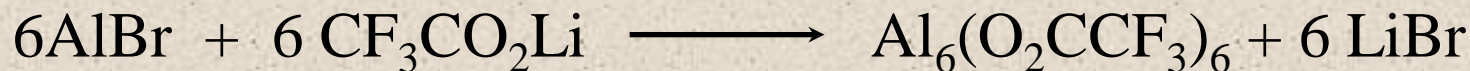
Synthesis



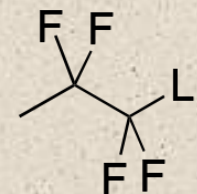
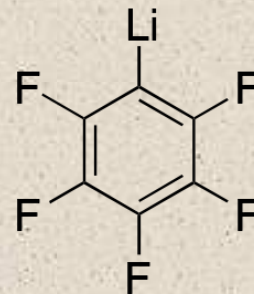
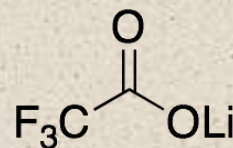
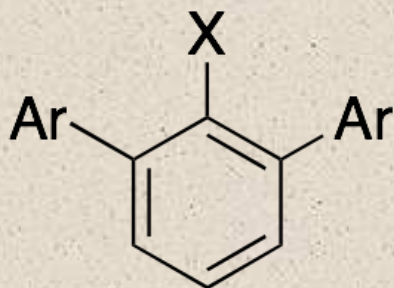
Known Al_nR_m clusters formed with n:m ratios
from 0.5 (Al^{+2}) to 4.6 ($\sim\text{Al}^{+0}$)

X = Br, Cl, F(?)

R = amide, alkyl, alkoxide, carboxylate, azide,



Potential ligands

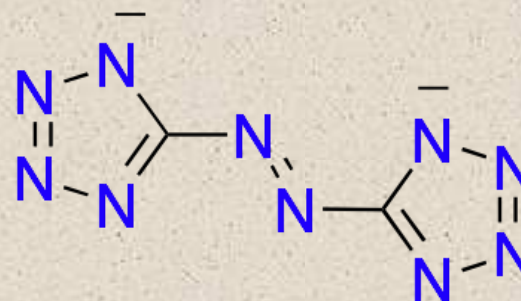
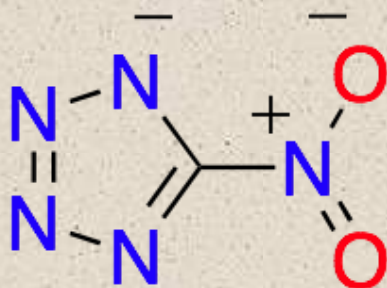


X = Li, NH-Li, CO₂-Li, O-Li

Ar = 1-naphthyl, mesityl, 2,6-di-*i*Pr-C₆H₃

Steric congestion stabilizes low-valent species

Alternative fluoride oxidizers



Energetic ligands with large ΔH of combustion

Bulk scale aluminum clusters

- Demonstrated capabilities to make gram quantities of reduced Al clusters
- Al clusters have no complications associated with oxide skins
- Allows for kinetic and thermodynamic experimental evaluations
 - Zachariah, Lightstone, Stoltz
- Theory and gas phase studies will provide mechanistic insight into cluster building mechanisms and electronic structures. Provide targets for viable cluster systems.
 - Bowen
- Unique facility -- unique access to new class of materials, complementary team with established collaborative relationships