Lec 3 Schnöckel

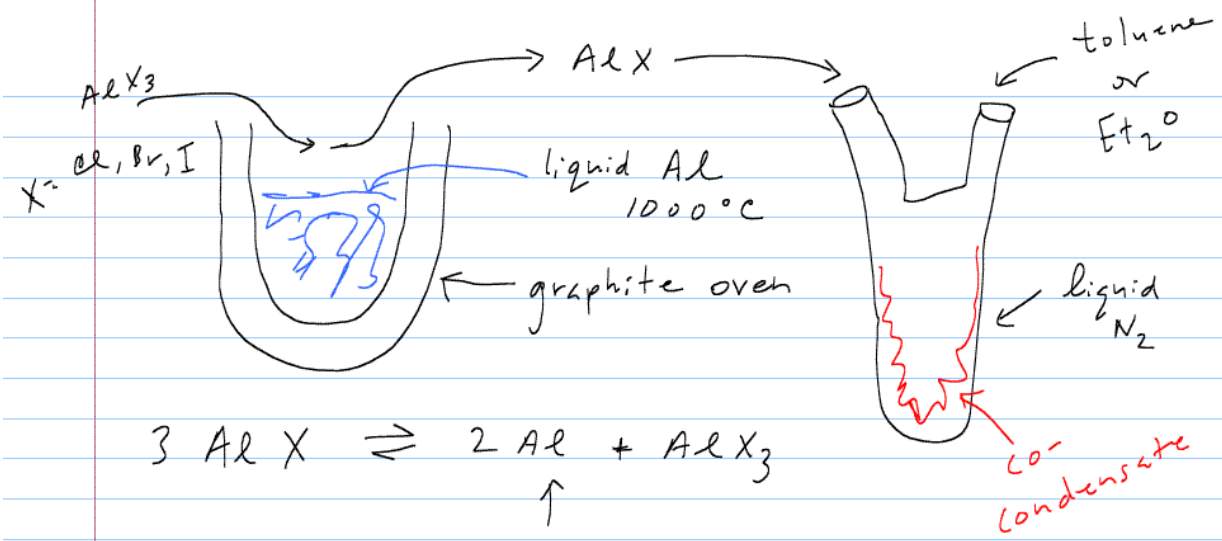
Note Title 2/10/2005

- Metalloid clusters

theory
⇓
matrix isolation
⇓
synthesis

} "the Schnöckel Story"

- Realization of +1 oxidation state for Al



$$3\,AlX \rightleftharpoons 2\,Al + AlX_3$$

• metalloid cluster

"contains the idea of the formation of a metal"

intermediate in transition from a molecule to a bulk material

⇒ connection to nanoscience

Average oxidation state approaches 0

"$AlCl \cdot D$" D = donor
i.e. Lewis base
OEt_2
NEt_3

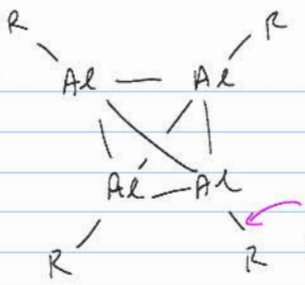
Solutions stored at −30 °C

↓ Cp^*Li / − LiCl

$[AlCp^*]_4 \rightleftharpoons 4\ Cp^*Al$ - weak Al-Al bonds

yellow, ^{27}Al NMR, $\delta = -81$ ppm

	octet?
π bond Al p = acceptor	2σ
Cp^* HOMO = donor	2π



$d(Al\text{-}Al) = 2.77$ Å , $R = Cp^*$

2.60 Å $\quad R = Si^tBu_3$

violet

not in equilibrium with monomer

σ only for $R = Si^tBu_3$

$4\ RAl \longrightarrow [AlR]_4$

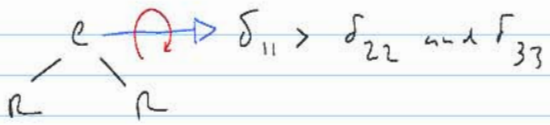
E_{tot}

650 kJ/mol ($R = Si^tBu_3$)

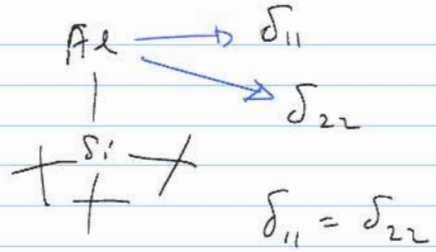
170 kJ/mol ($R = Cp^*$)

NMR properties also reflect HOMO/LUMO GAP

$$\delta_{iso} = (\delta_{11} + \delta_{22} + \delta_{33})/3$$



$\delta_{11} > \delta_{22}$ and δ_{33}



$\delta_{11} = \delta_{22}$

isolobal with CO

Doubly Degenerate LUMO!

$AlCp^* + SiCp^*_2 \longrightarrow$ no reaction

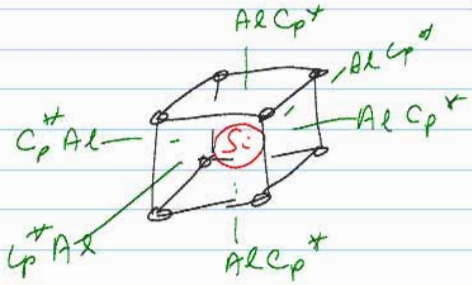
$^tBu_3Si$ $\quad AlCl + SiCp^*_2 \longrightarrow$

Wiberg

"Supersilyl"

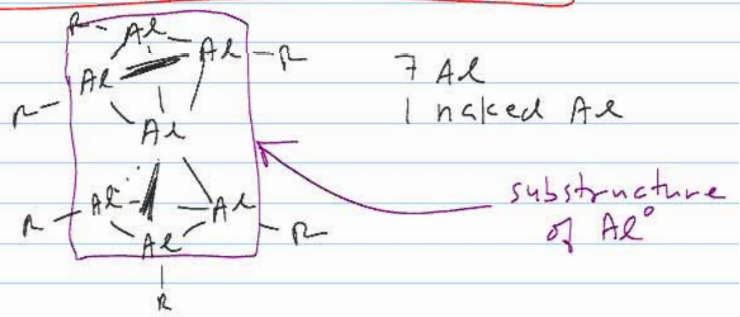
$SiAl_{14}Cp^*_6$ black crystals

of "naked" metal atoms in cluster

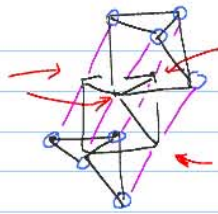


		# naked
1985	$[Ni_{38}Pt_6(CO)_{48}H_{6-n}]^{n-}$	6
1999	$Pd_{59}(CO)_{32}(PMe_3)_{21}$	11
2000	$Pd_{145}(CO)_{60}(PEt_3)_{30}$	55

$AlCl + Li^+N^-(SiMe_3)_2$



1.

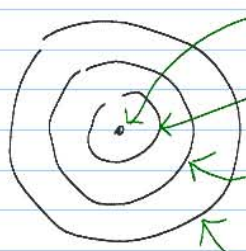


naked Al

$\circ = Al(N[Si(CH_3)_3]_2)$

Al_{77} cluster

2.



Al

Al_{12}

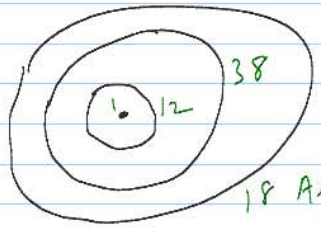
44 Al

20 AlR

57 naked Al

Al_{69} cluster

3.



38

12

1

18 AlR