

Greenwood & Earnshaw

2nd Edition

Chapter 10

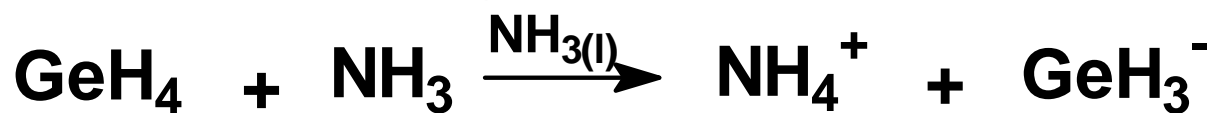
Germanium, Tin and Lead

Trends in Group 14 Bond Energies

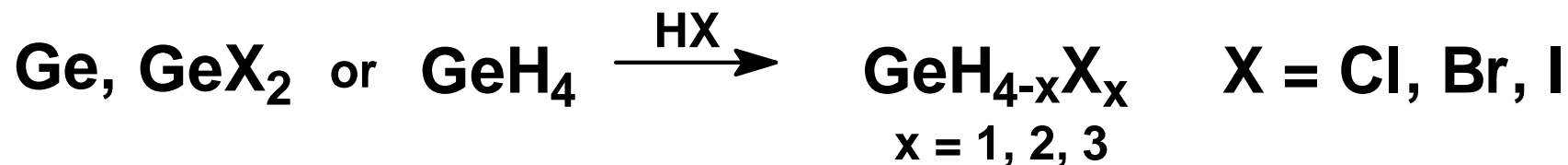
- The decrease in bond strength as one goes down the group is marked and modified only by $p\pi-d\pi$ bonding.
- $d\pi$ bonding diminishes: $\text{Si} > \text{Ge} > \text{Sn} > \text{Pb} \gg \text{C}$. There are no germanium analogues to the silicones. The exceptional stability of the Si-O bond is not duplicated in the Ge-O bond.
- Stability of the M(II) state: $\text{Pb} \gg \text{Sn} > \text{Ge} > \text{Si} > \text{C}$.
- Ability to Catenate: $\text{C} \gg \text{Si} > \text{Ge} > \text{Sn} > \text{Pb}$. For the alkane analogues: $\text{Si}_n\text{H}_{2n+2}$ $n = 8$; $\text{Ge}_n\text{H}_{2n+2}$ $n = 5$.
- Hydrides of germanium are not pyrophoric and are unaffected by acid/base, unlike the silanes. Hydrides of tin and lead are of marginal stability

Germanium Hydrides

Property	GeH ₄	Ge ₂ H ₆	Ge ₃ H ₈	Ge ₄ H ₁₀	Ge ₅ H ₁₂
MP/°C	-164.8	-109	-105.6	-	-
BP/°C	-88.1	29	110.5	176.9	234
Density (T° C)/g cm ⁻³	1.52 (-142°)	1.98 (-109°)	2.20 (-105°)	-	-

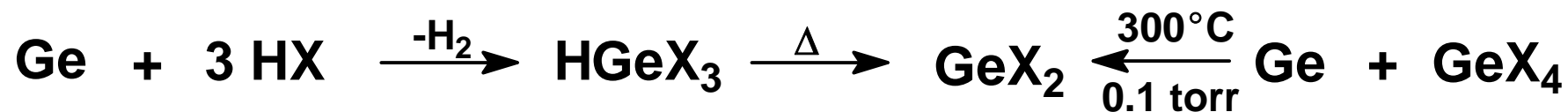
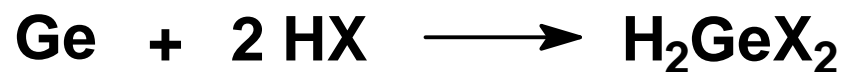


Compounds of Na, K, Rb, Cs are colorless ionic compounds of considerable synthetic utility. Ionic radius = 229 pm cf Si = 226 pm.

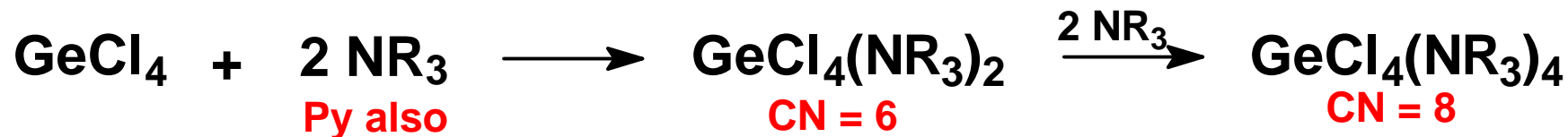
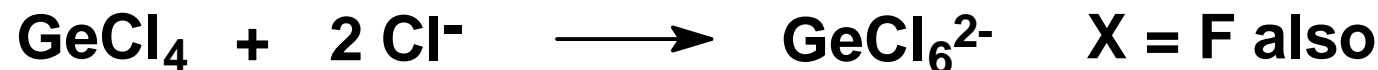


Compounds are colorless volatile liquids and are valuable synthetic intermediates. Metatheses can be affected using silver and lead salts.

Halides and Mixed Halides



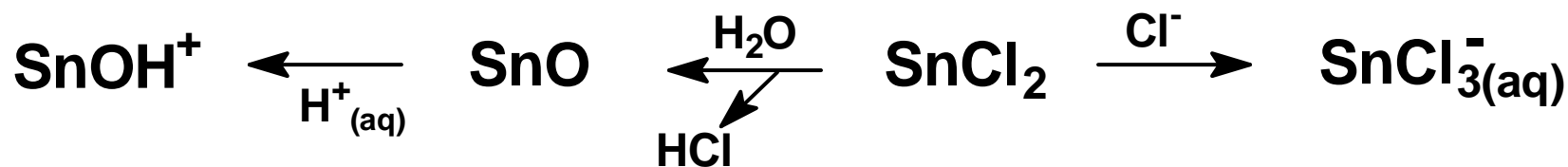
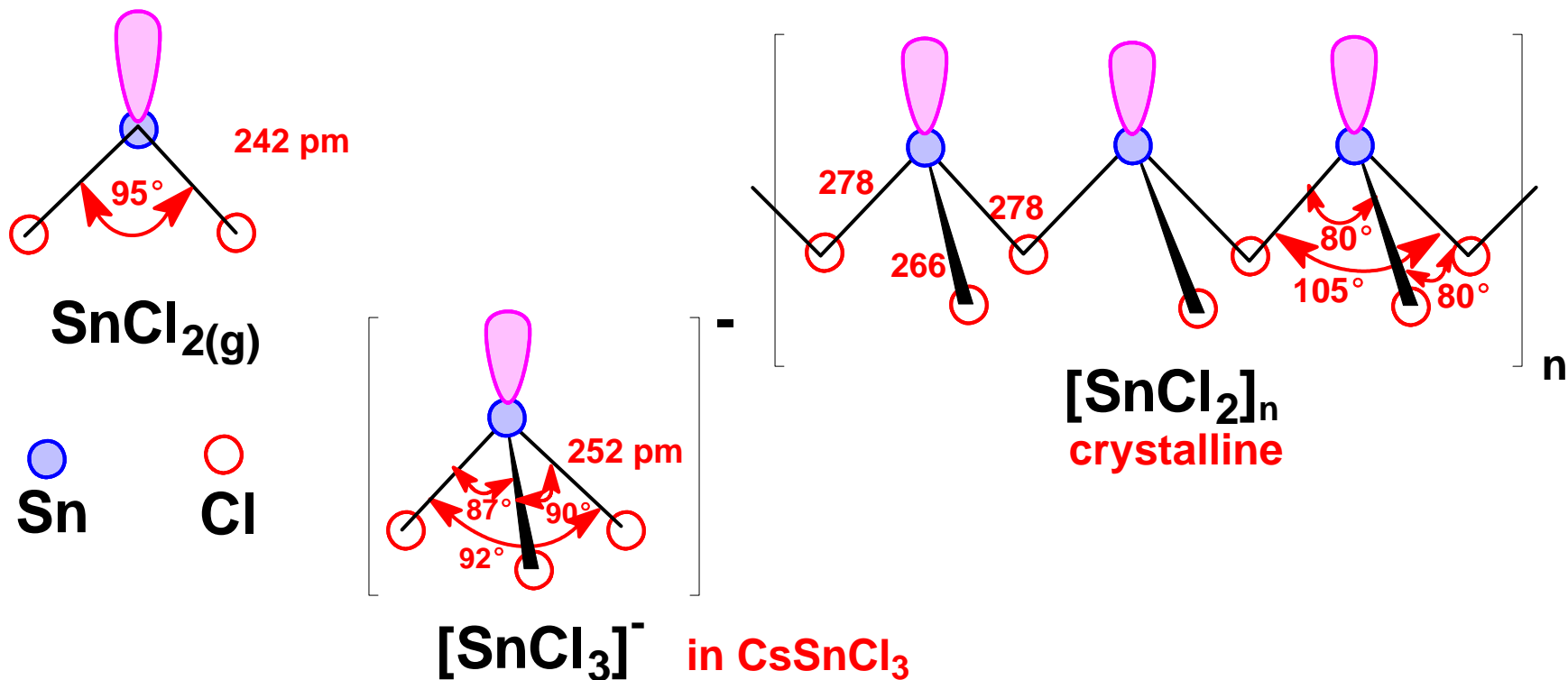
Stable in $\text{HCl}_{(\text{aq})}$ at $\text{pH} < 2.5$  conc. $\text{HCl}_{(\text{aq})}$



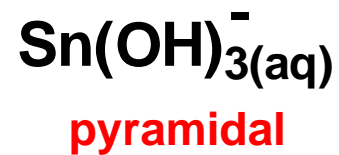
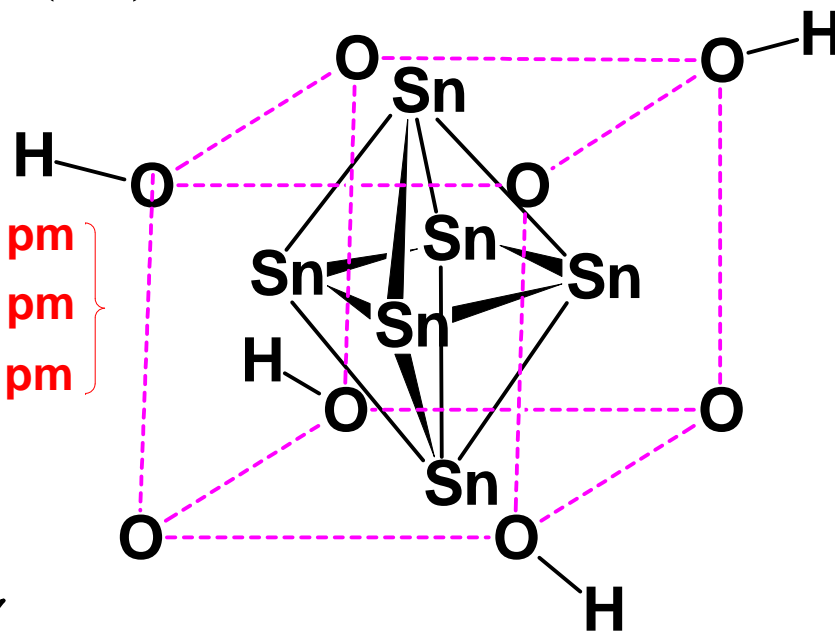
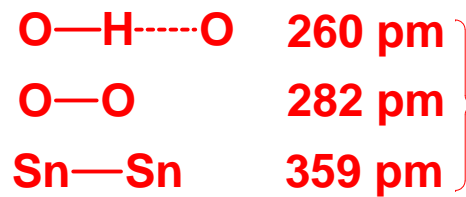
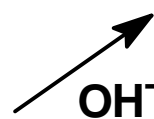
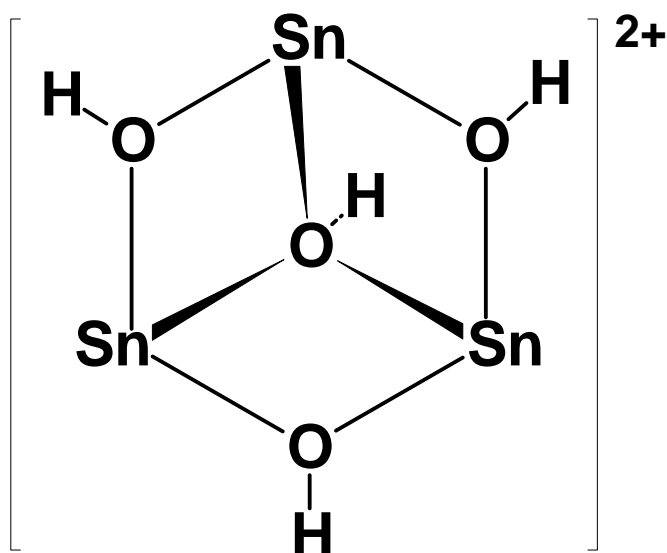
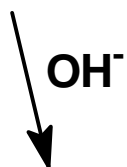
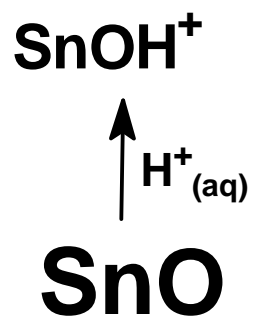
Structures of GeX_2 , SnX_2 and Complexes

- Exhibit structures having stereochemically active lone pairs of electrons.**
- Sn(II) structures are complicated by the occasional stereochemical inactivity of the lone pair of electrons.**
- GeF_2 , SnF_2 and SnCl_2 are complicated by a pronounced tendency to increase coordination number by polymerization.**

Tin(II) Chloride and Complexes

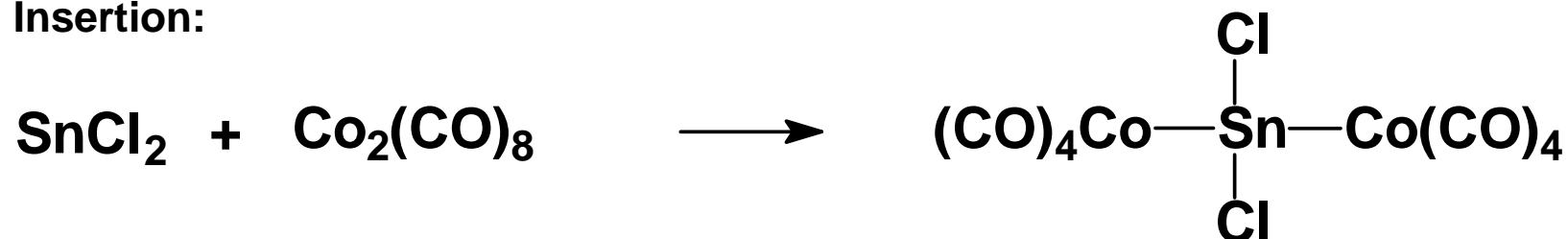


Hydrous Tin(II) Oxides

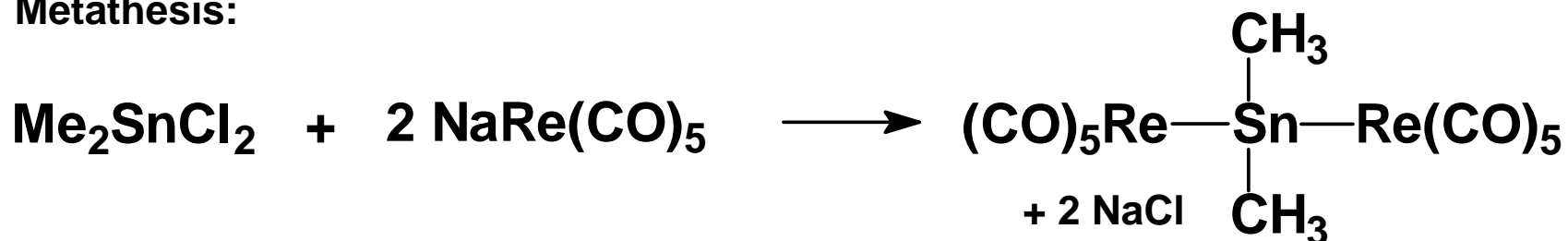


Heterometallic Bond Formation

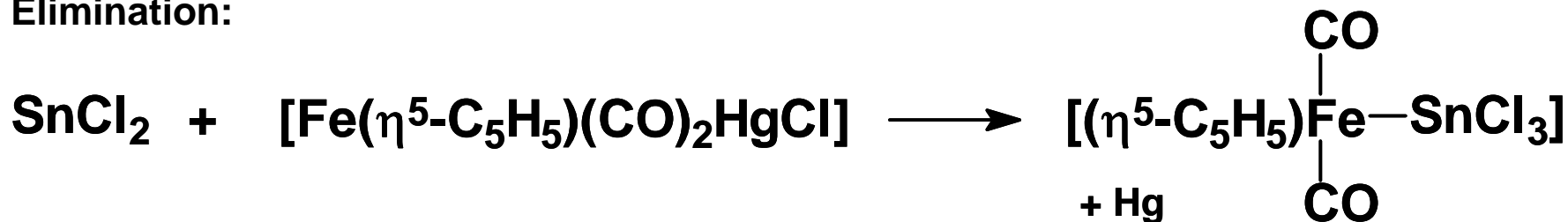
Insertion:



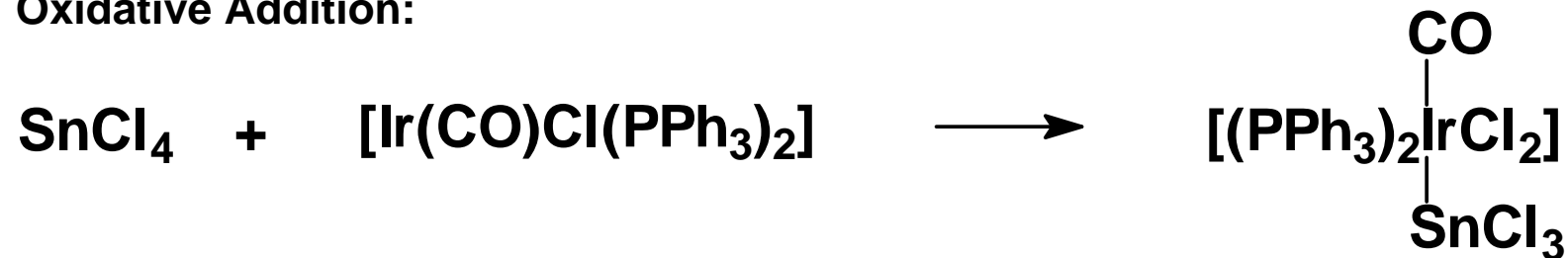
Metathesis:



Elimination:



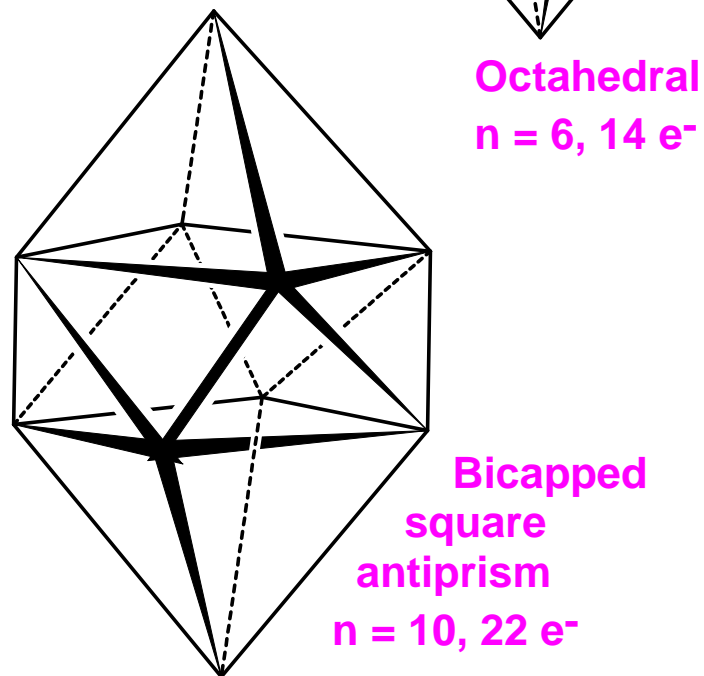
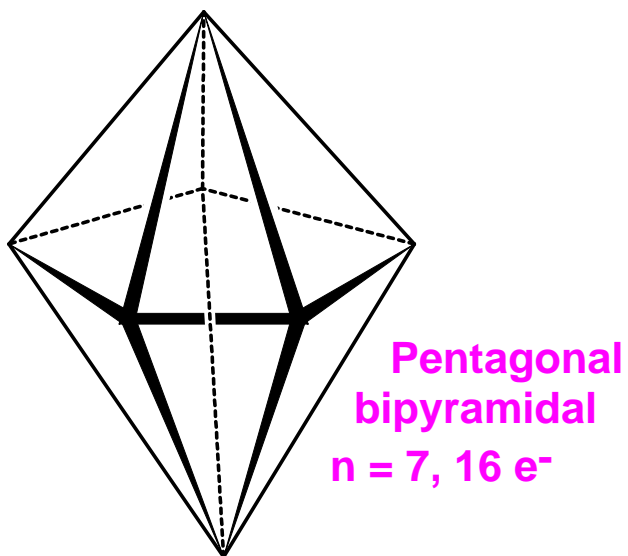
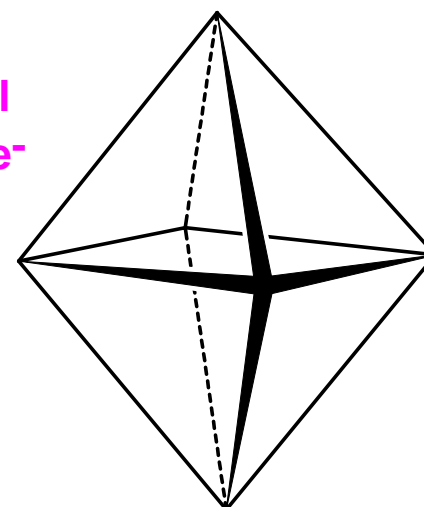
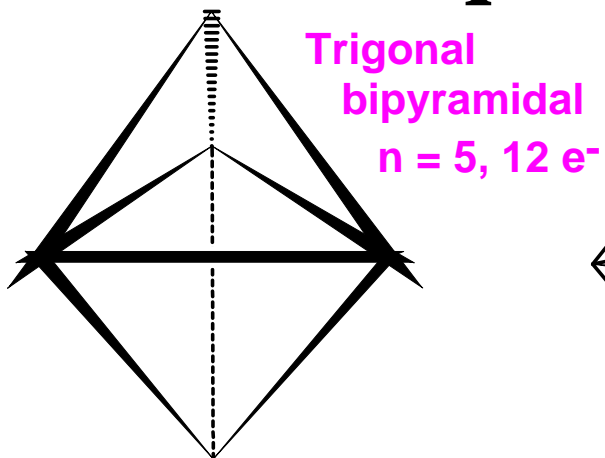
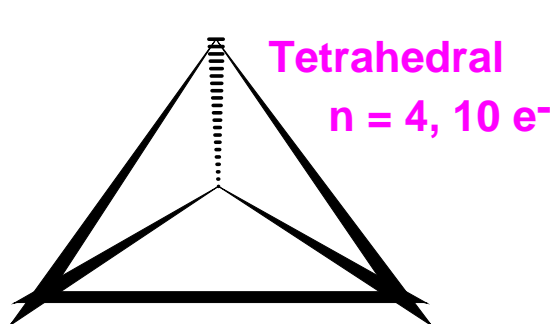
Oxidative Addition:



Cluster Electronics – Wade’s Rules

- A *closo*-cluster of n polyhedral atoms will require $n+1$ pairs of electrons to satisfy cluster bonding.
- A *nido*-cluster of n polyhedral atoms will require $n+2$ pairs of electrons to satisfy cluster bonding.
- To satisfy a non-*closo* cluster of n polyhedral atoms having y “open” non-deltahedral faces will require $n+y+1$ pairs of electrons which must be supplied by the polyhedral atoms and the overall charge of the cluster.
- Wade’s rules represent an electron requirement based on s & p atomic orbitals. Transition metal clusters may have greater numbers of electrons due to d atomic orbital participation in cluster bonding.

Cluster Electronic Requirements



lone pair

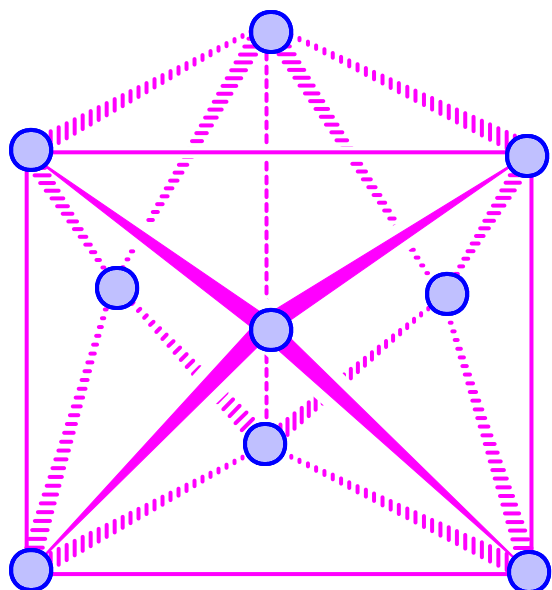
in exo-position.



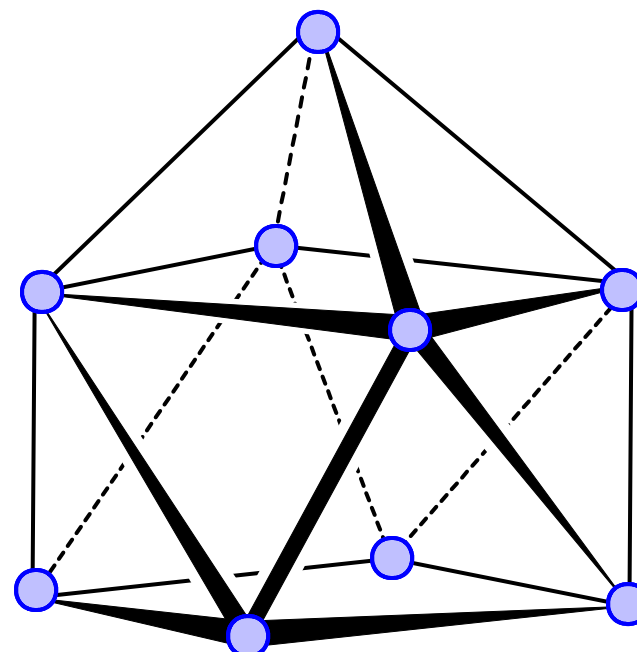
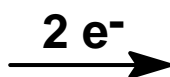
to center of polyhedron.

electrons available for cluster = $Gp\# - 2$

Electronics Determine Structure



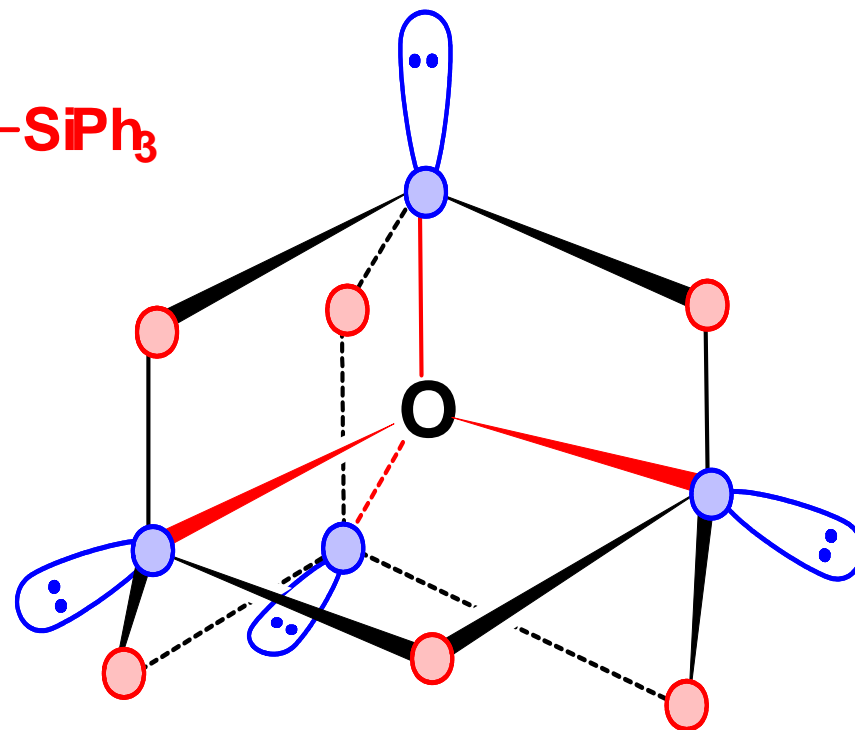
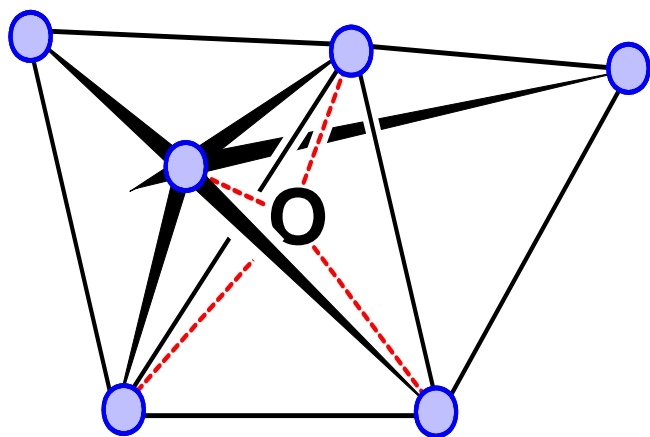
Ge_9^{2-}



Ge_9^{4-}



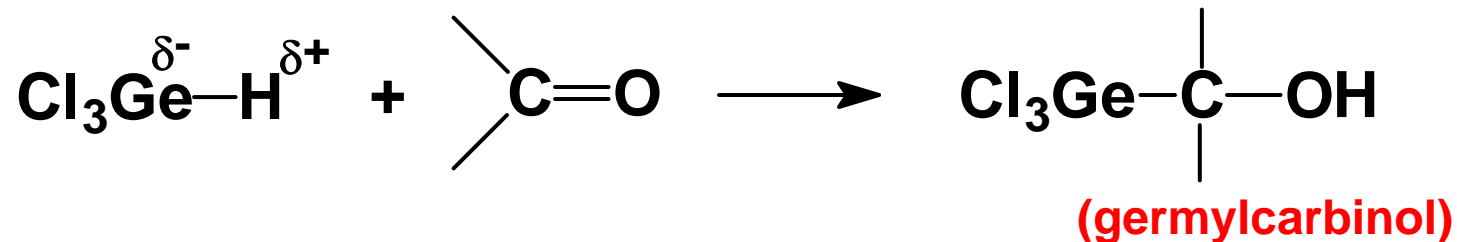
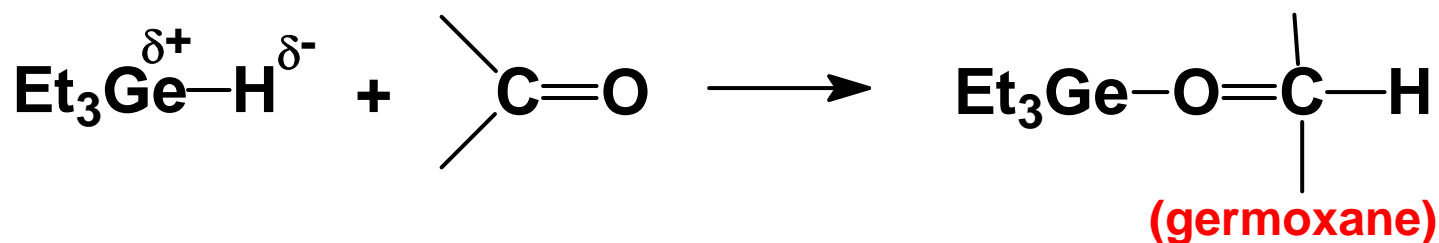
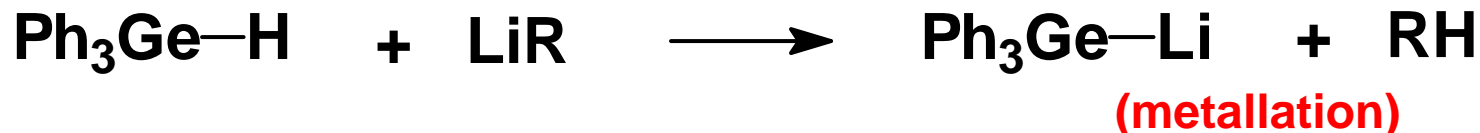
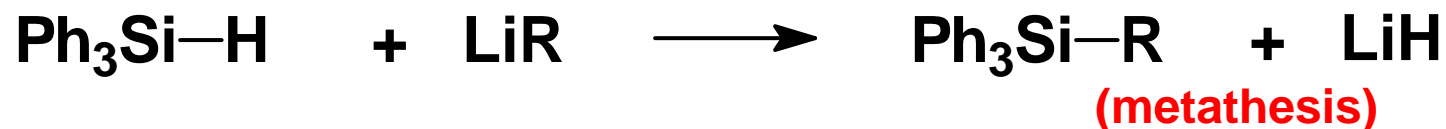
Lead Clusters with Center Atoms



In both compounds the central oxygen atoms are tetrahedrally coordinated to the lead atoms. The lead environment in the adamantane-like structure is a pseudo-trigonal bipyramidal with the lone pair and the central oxygen in axial positions.

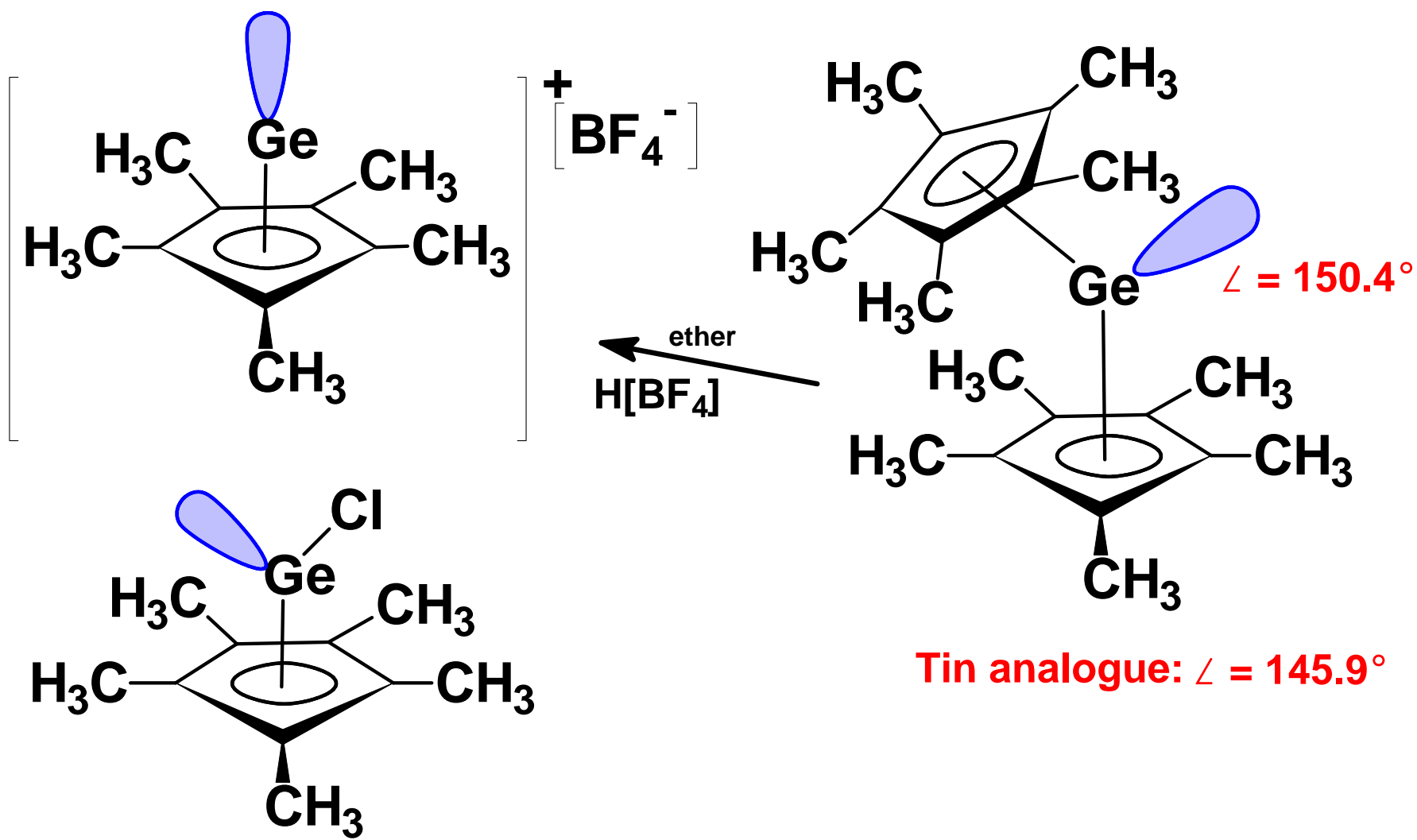
Organometallic Chemistry – Ge

Organogermanium chemistry closely resembles that of silicon. However, hydrogen atoms in Organogermanium hydrides are slightly more protonic than hydridic, but is highly sensitive to the nature of the substituents.



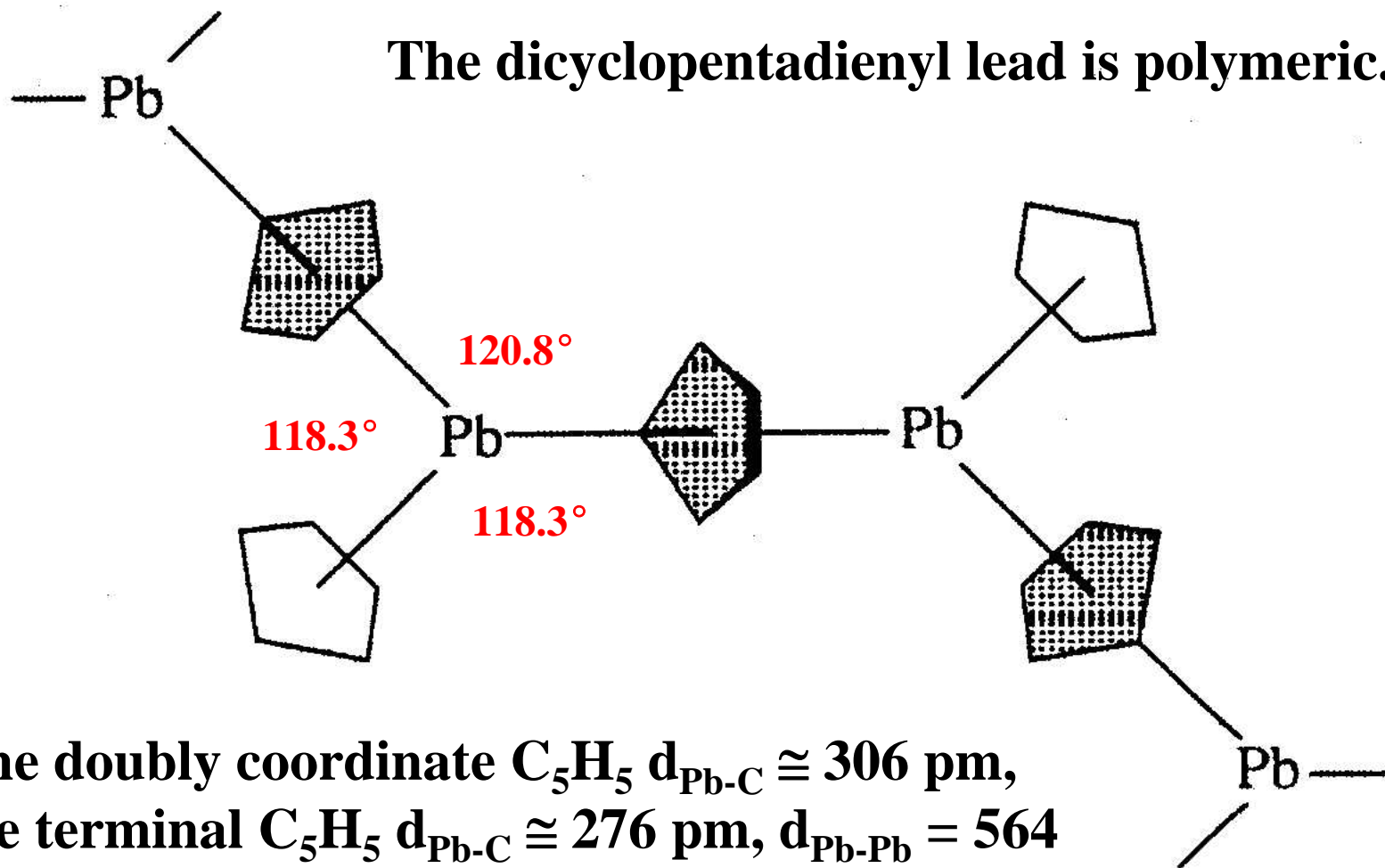
Organometallic Chemistry

Cyclopentadienyl Derivatives

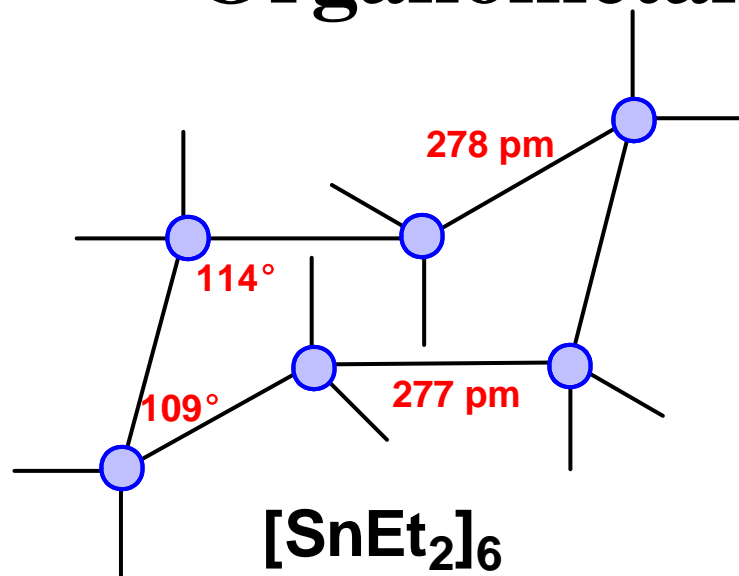


Organometallic Chemistry

The dicyclopentadienyl lead is polymeric.

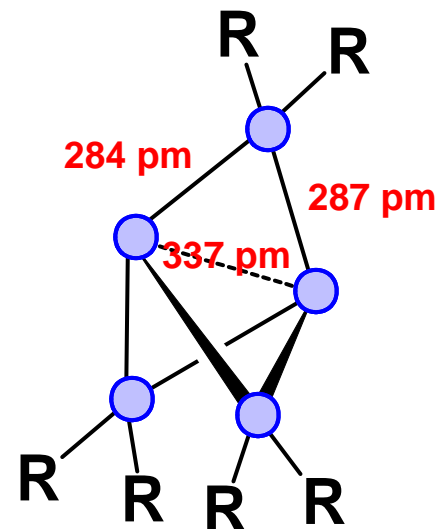
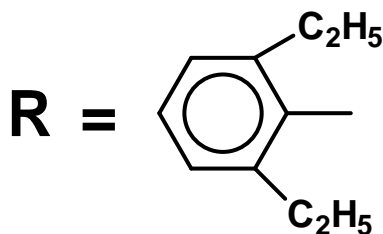


Organometallic Chemistry – Sn(II)



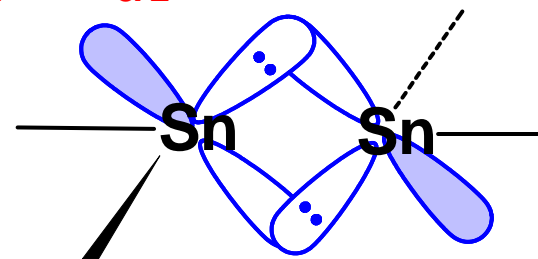
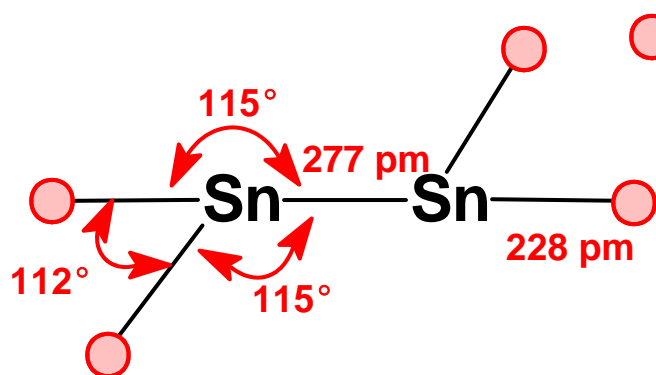
$d_{\text{Sn-Sn}}$ very close to those found in α -tin.

○ = Sn



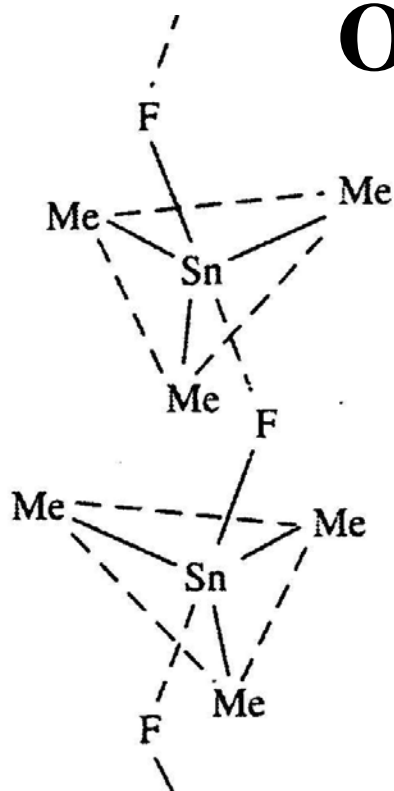
Very long axial Sn-Sn bond may have extensive singlet di-radical character.

Stannylenes: Ge & Pb similar

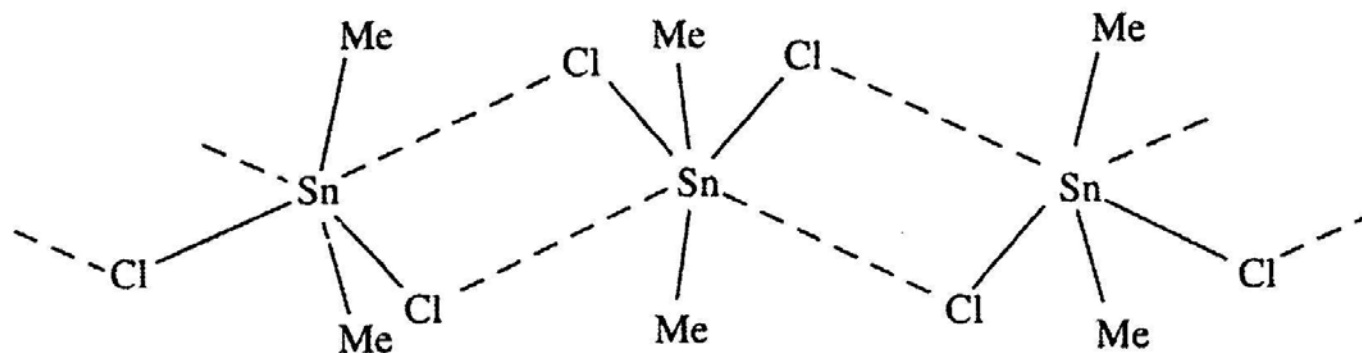


Dimeric crystal but monomeric gas & benzene solution; red, air-sensitive crystals behave as carbene-like ligand.

Organometallic Chemistry



Me_3SnF forms a polymer by trigonal bipyramidal, $\text{CN} = 5$, coordination about Sn(IV)



Me_2SnCl_2 forms a polymer that is distorted octahedral, $\text{CN} = 6$, about Sn(IV) by double bridging through the chlorine atoms.