Chemistry of the Main Group Elements: Boron through the Pnictogens

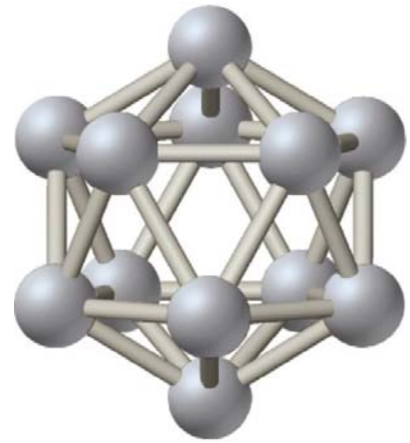
Sections 8.5-8.7 and 15.4.1

Friday, November 6, 2015

Group IIIA (13): B, Al, Ga, In, and Tl

Diverse group of elements with three valence electrons

- **ns^2p^1 electron configuration**
- **boron is a non-metal, all others in group are metals**



B12 icosahedron in elemental boron

Group IIIA halide complexes

- **all members of the group react directly with halogens**

$$B_{12} + 18Cl_2 \longrightarrow 12BCl_3$$

$$2Al^0 + 3Cl_2 \longrightarrow 2AlCl_3$$

- **the metals will also react with hydrohalic acids**

$$2Al^0 + 6HCl \longrightarrow 2AlCl_3 + 3H_2$$

This idea goes back to the ΔG_f data for MH_3

- **Group IIIA halides are Lewis acids, BX_3 is hard, others are soft**

- **reactivity**

$$AlCl_3 + 3MeMgCl \longrightarrow AlMe_3 + 3MgCl_2$$

$$BCl_3 + 4MeLi \longrightarrow Li\left[BMe_4\right] + 3LiCl$$

$$BCl_3 + 3H_2O \longrightarrow B\left(OH\right)_3 + 3HCl$$

This result is completely consistent with HSAB theory

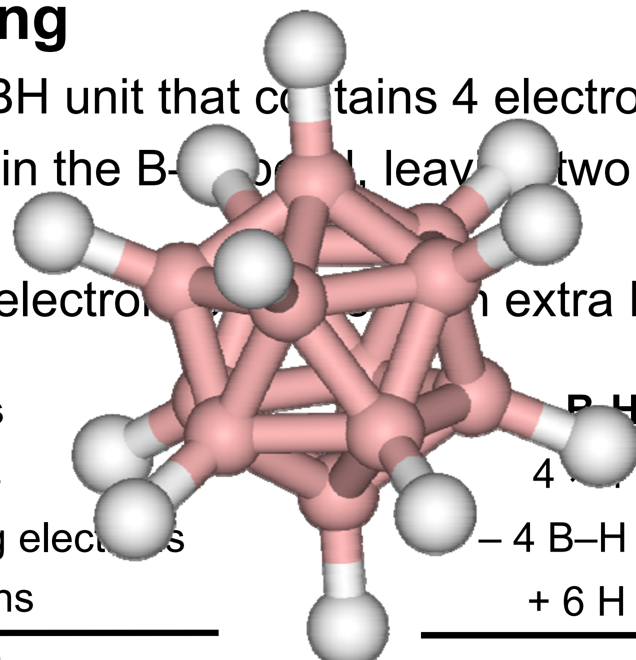
Boranes (Boron Hydride Clusters)

The electron deficient nature of boron favors cluster formation

	Formula	Skeletal e⁻ Pairs	Examples
closo	$[B_nH_n]^{2-}$	n+1	$[B_5H_5]^{2-}$ thru $[B_{12}H_{12}]^{2-}$
nido	B_nH_{n+4}	n+2	B_2H_6, B_5H_9, B_6H_{10}
arachno	B_nH_{n+6}	n+3	B_4H_{10}, B_5H_{11}
hypho	B_nH_{n+8}	n+4	B_8H_{16}, $B_{10}H_{18}$, $B_{14}H_{22}$

Skeletal Electron Counting

- basic building block is BH unit that contains 4 electrons (3 from B and 1 from H)
- two electrons are used in the B–H bond, leaving two electrons (a pair) for the cluster framework
- each charge adds one electron [illegible] an extra H



$[B_{12}H_{12}]^{2-}$

$[B_6H_6]^{2-}$ ⇒ 6 BH units

6 × 4 = 24 BH electrons

– 6 B–H = 12 B–H bonding electrons

+ 2e⁻ for charge = 2 extra electrons

14 skeletal electrons

B_4H_{10} ⇒ 4 BH units

4 × 4 = 16 BH electrons

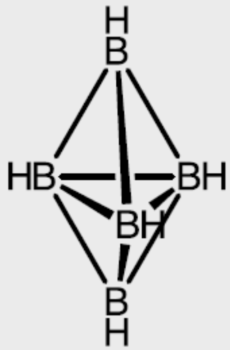
– 4 B–H = 8 B–H bonding electrons

+ 6 H = 6 extra hydrogen electrons

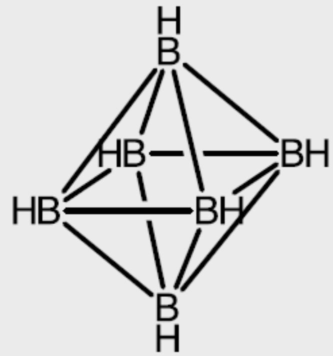
14 skeletal electrons

Boron Hydride Clusters

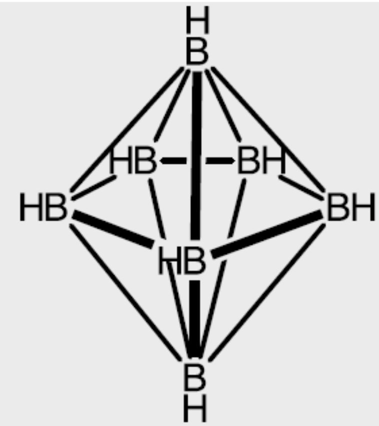
Closo boron hydride clusters are regular polygon shapes



$[B_5H_5]^{2-}$
trigonal bipyramidal

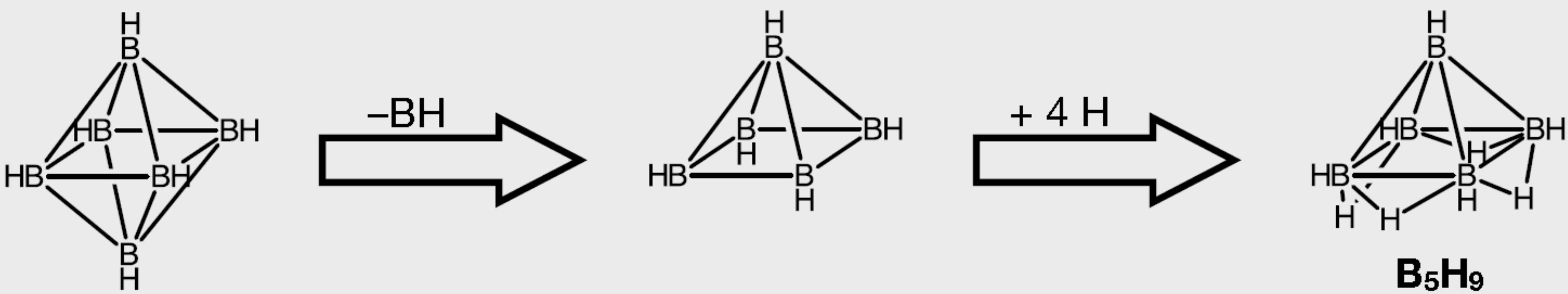


$[B_6H_6]^{2-}$
octahedral



$[B_7H_7]^{2-}$
pentagonal bipyramidal

Nido and arachno boron hydride clusters are derived from the regular polyhedra with one or two vertices removed, respectively, and bridging hydrogen atoms added.



$[B_6H_6]^{2-}$

B_5H_9

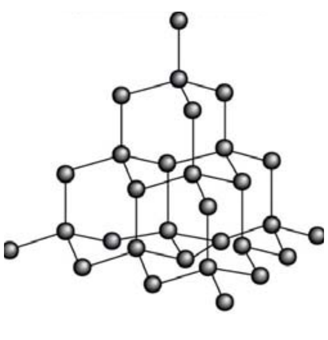
Also see section 15.4.1

Carbon

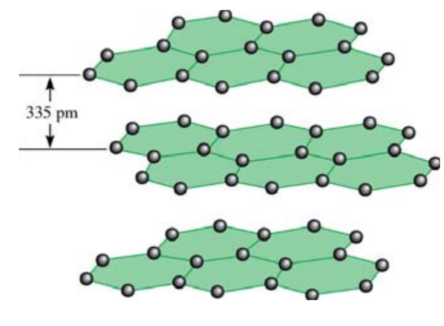
Carbon is a remarkable element for its versatility as a building block

- **carbon forms double and triple bonds more readily than any other element**
- **the tetrahedral, trigonal, and linear geometries of carbon provides access to a variety of different structures and allows for lots of structural complexity**

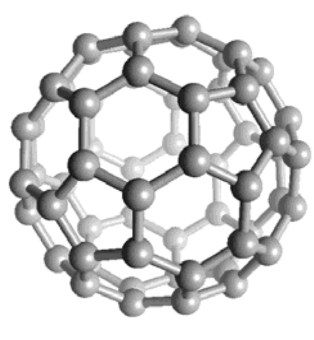
Carbon allotropes:



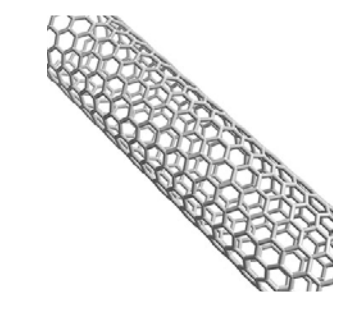
diamond – 3D network of *sp*^{3} carbon atoms connected by C–C single bonds



graphite – stacks of 2D sheets of *sp*^{2} carbon atoms in fused six-membered rings



fullerenes – geodesic spheres containing *sp*^{2} carbons, C_{60}, C_{70}, C_{80}, etc.



carbon nanotubes – a graphene layer rolled up into a cylinder

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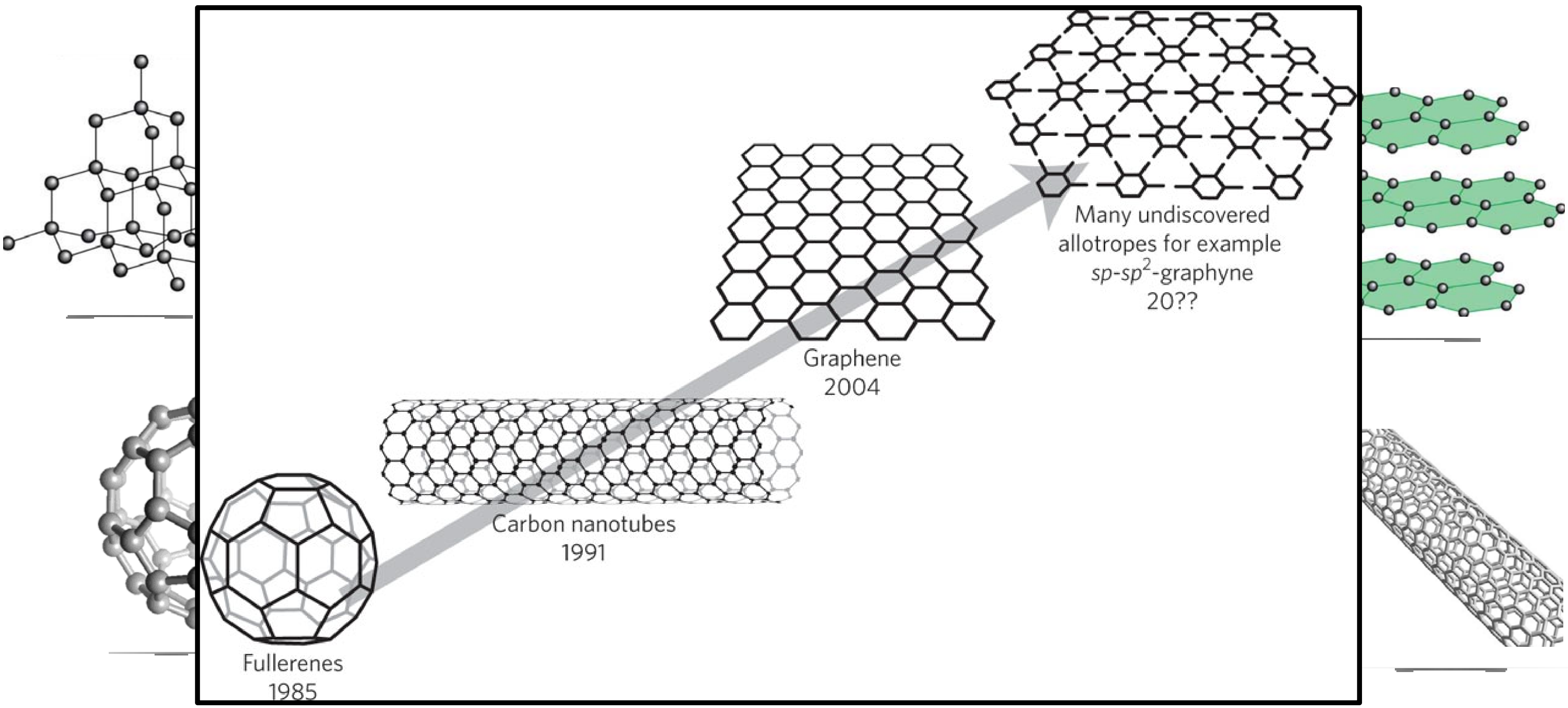


Si, Ge, Sn, & Pb

Heavier congeners of carbon have +2 and +4 oxidation states accessible

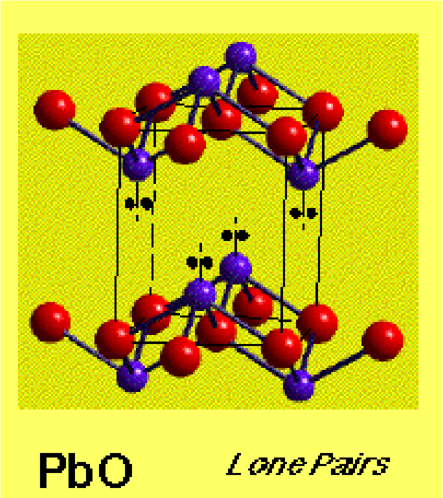
$$Si(s) + 2Cl_2(g) \longrightarrow Si^{IV}Cl_4(l)$$

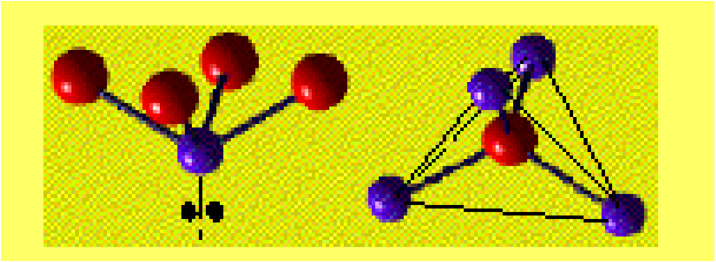
$$Sn(s) + Cl_2(g) \longrightarrow Sn^{II}Cl_2(s) \xrightarrow{+Cl_2(g)} Sn^{IV}Cl_4(l)$$

mp 246 °C   mp –33 °C

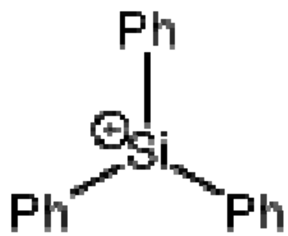
$$Pb(s) + Cl_2(g) \longrightarrow Pb^{II}Cl_2(s) \xrightarrow{+Cl_2(g)} \text{no reaction}$$

Inert pair effect – heavy *p*-block metals often 'hold on' to their ns^2 valence electrons better than lighter *p*-block elements

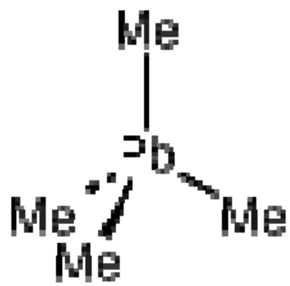




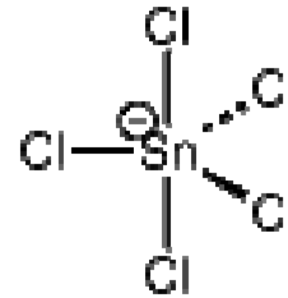
Group IVA (14) Geometries



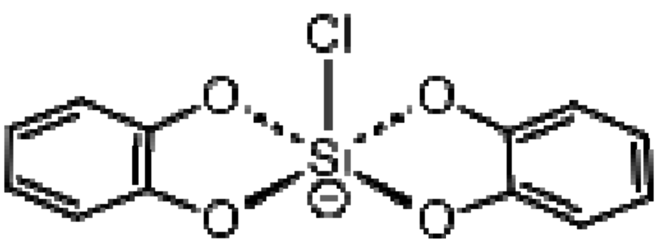
trigonal planar



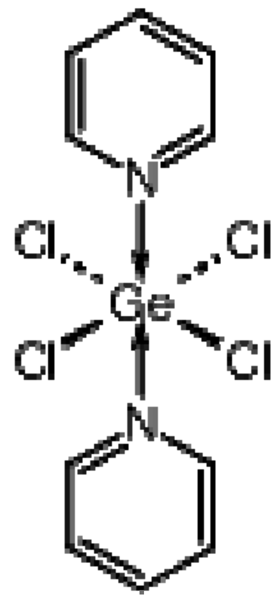
tetrahedral



trigonal bipyramidal



square pyramidal

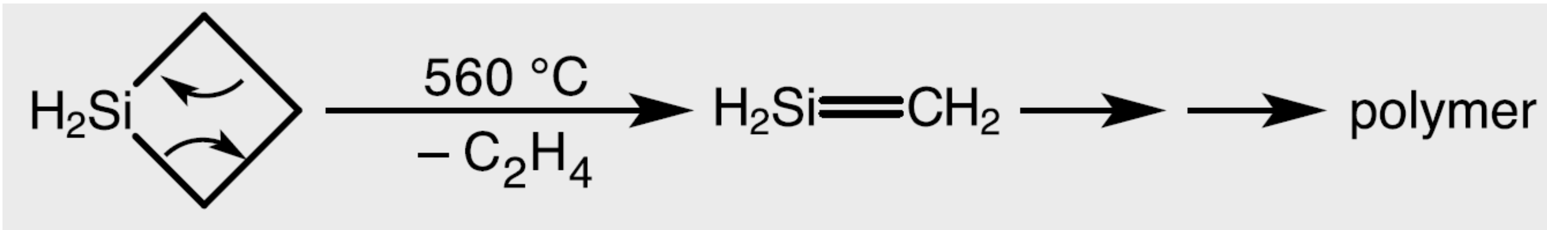


octahedral

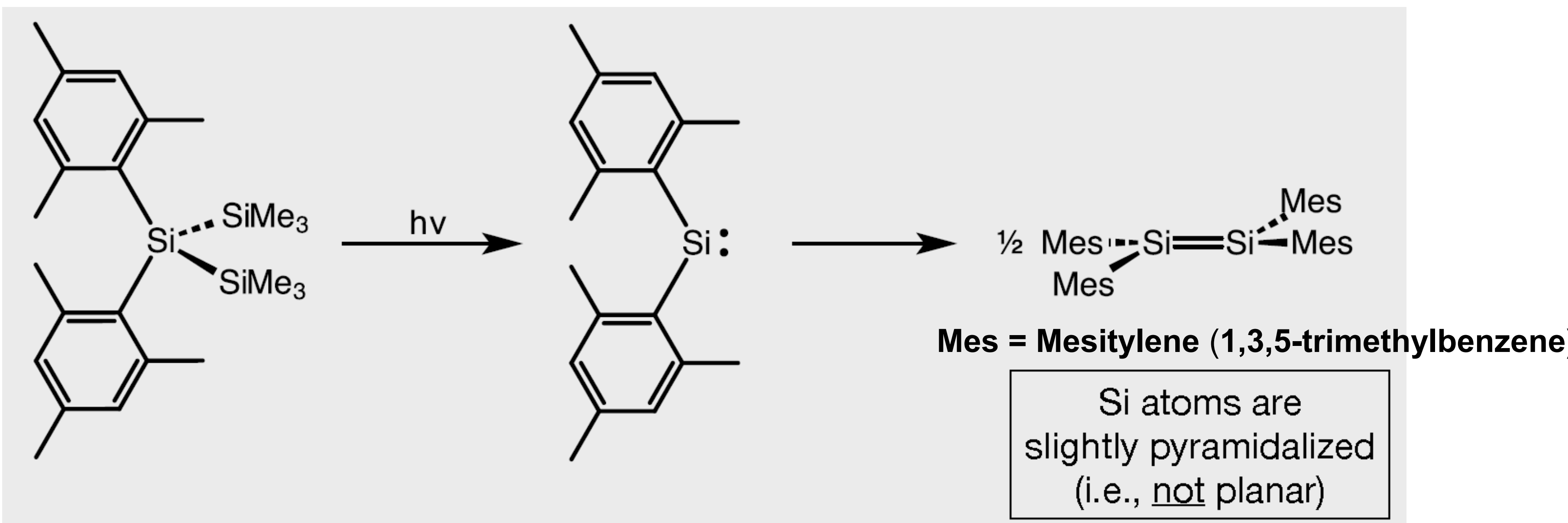
Notice that germanium has 12 electrons around it. The octet rule can be violated for heavy *p*-block elements

Multiple Bonding

While multiple bonding is common for carbon, it is unusual for the heavier elements and often the species are only metastable



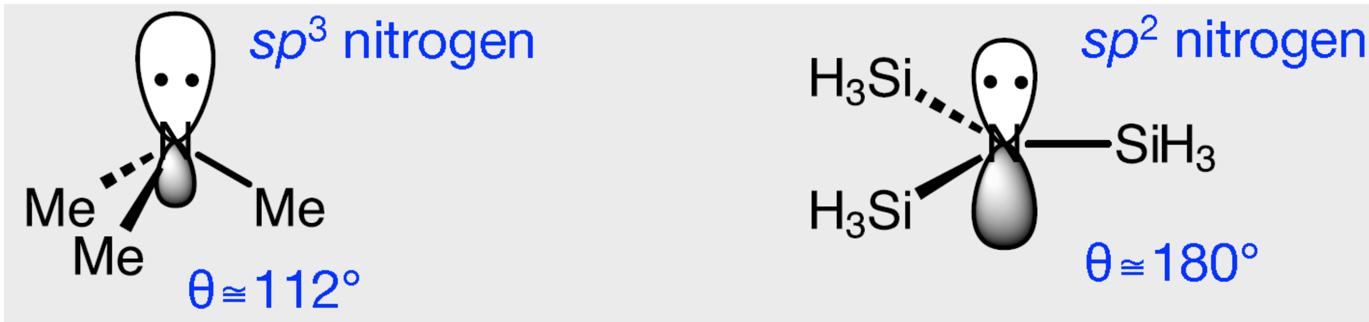
Bulky substituents can prevent polymer formation and allow isolation of molecular compounds



Multiple Bonding

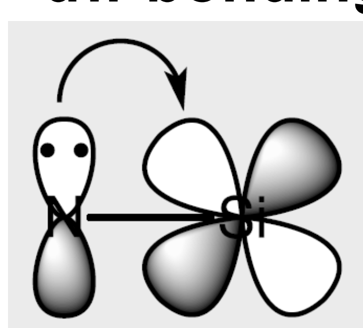
There is structural evidence for multiple bonding with heteroatoms

- trisilylamines are planar



- silylethers have large Si–O–Si angles
- silanols form strong hydrogen bonds and are also stronger acids than the analogous alcohols

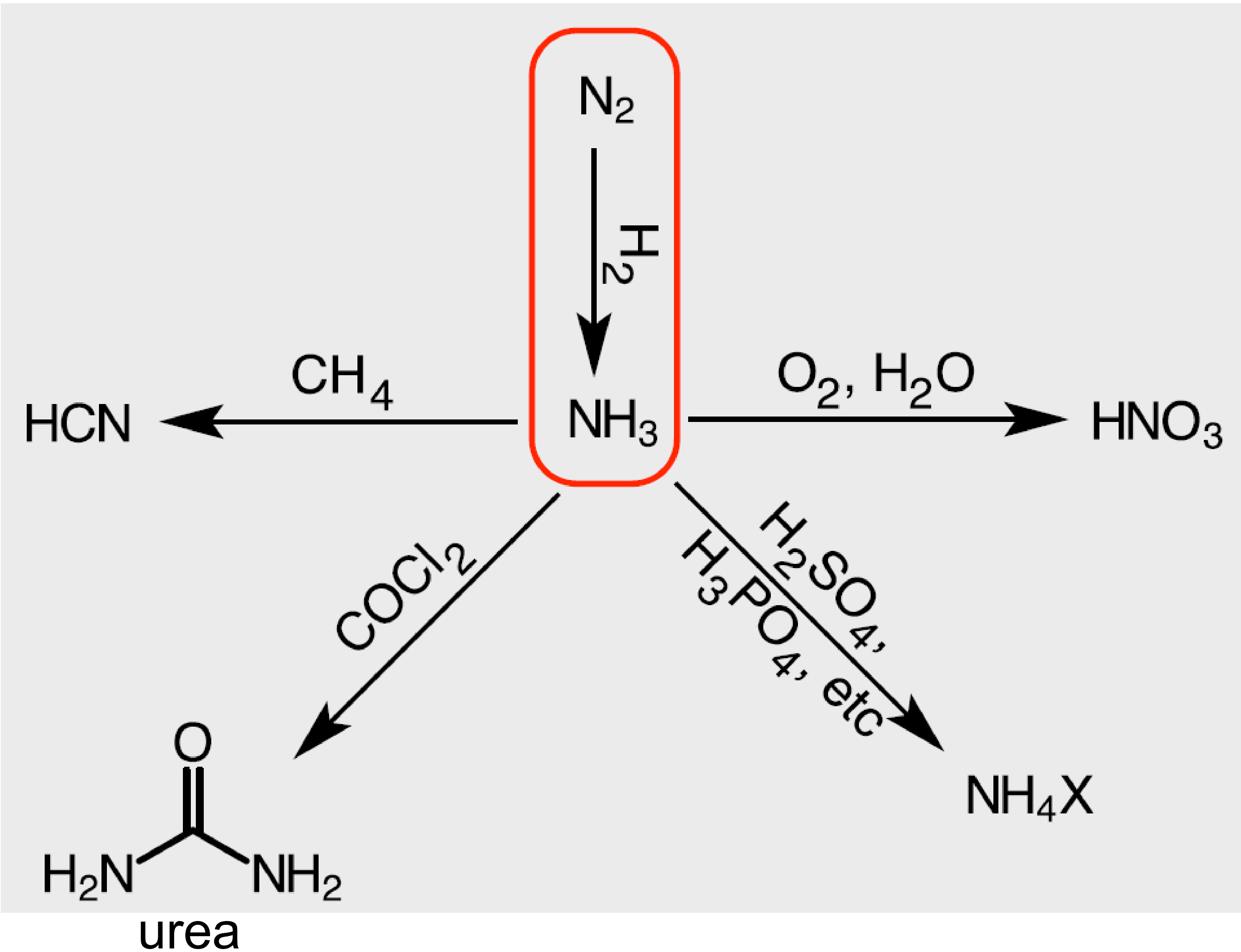
We can explain this with pπ–dπ bonding



- important to note that the strength of pπ–dπ bonding decreases as you go down the group because of worse orbital overlap

Nitrogen

Virtually all nitrogen compounds are derived from the Haber-Bosch process



Nitrogen Oxides: N^{V}

Nitrate (NO_3^-) is an important industrial chemical prepared by a two-step process:

$$4NH_3(g) + 7O_2(g) \longrightarrow 6H_2O(l) + 4NO_2(aq) \qquad \Delta G^\circ = -97\frac{kcal}{mol}$$

$$3NO_2(aq) + H_2O(l) \longrightarrow 2HNO_3(aq) + NO(g) \qquad \Delta G^\circ = -1.2\frac{kcal}{mol}$$

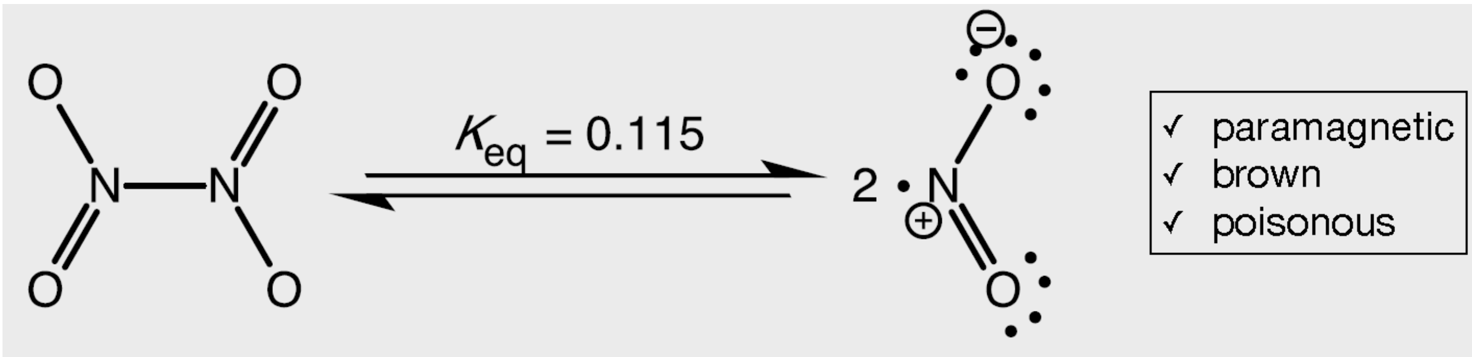
Compare this to the direct oxidation of N_2 by O_2:

$$N_2(g) + 2O_2(g) \longrightarrow 2NO_2(g) \qquad \Delta G^\circ = +12\frac{kcal}{mol}$$

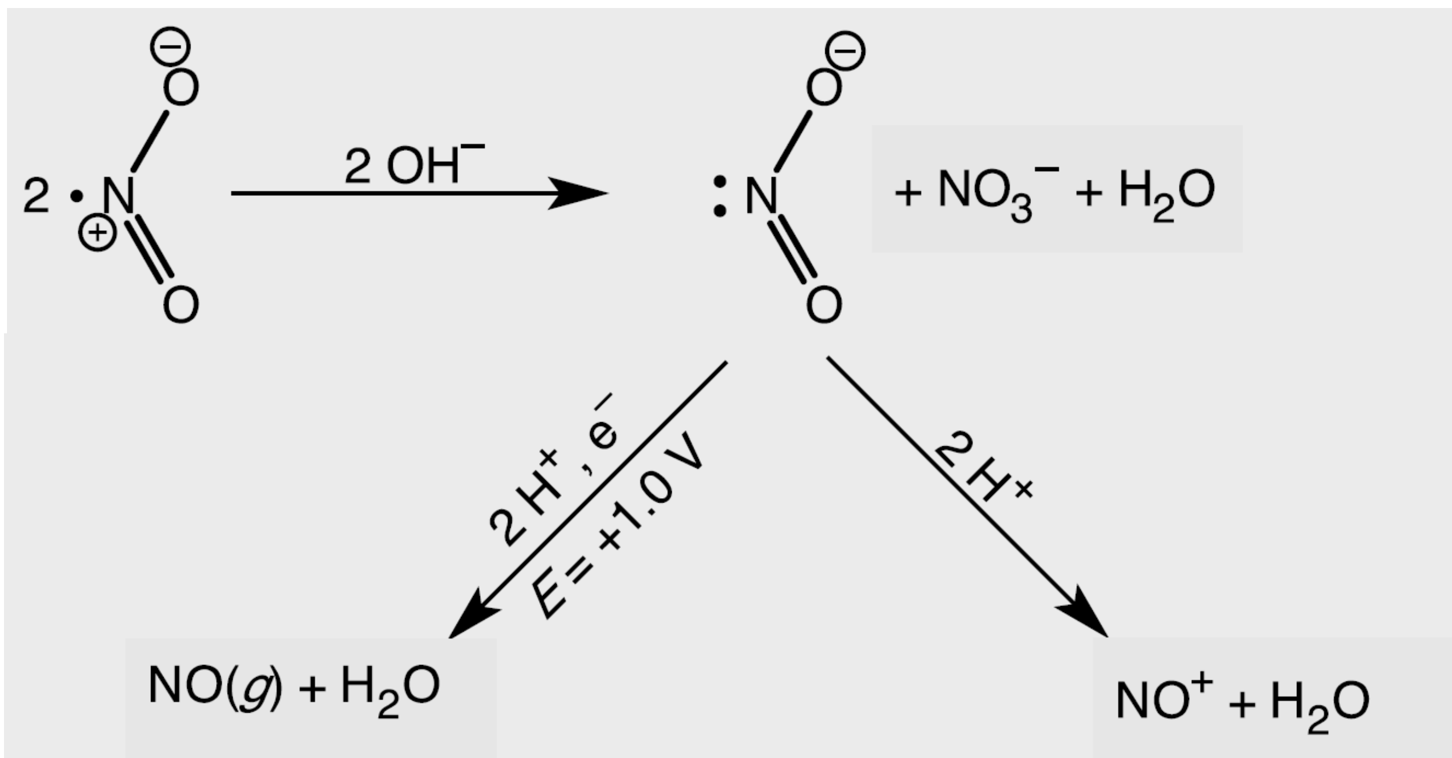
By first reducing the N_2 with hydrogen, driving force is gained for the oxidation reaction in the formation of water as a byproduct

Nitrogen Oxides: N^{II} and N^{IV}

Nitrogen dioxide exists as an equilibrium mixture



NO$_2$ has further reactivity in water



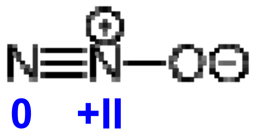
Nitrogen Oxides: NO

“Molecule of the Year” in 1992

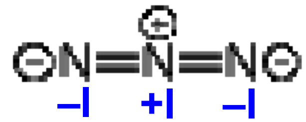
Nobel Prize in Medicine in 1998 for many biological roles

- neurotransmission
- neuron-to-neuron signaling
- vasodilator (heart disease)
- relaxes smooth muscle tissue (endothelium-derived relaxing factor)

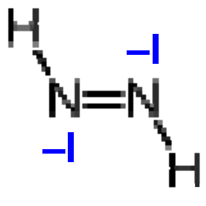
Low-Valent Nitrogen Compounds



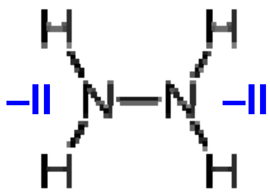
Nitrous Oxide



Azide



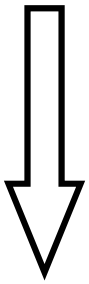
Diazene



Hydrazine

Formal charge – electrons in bonds are evenly split between atoms (covalent perspective)

Oxidation state – electrons in bonds get assigned to the more electronegative atom (ionic perspective)



$N_2 + 4\ H^+ + 4\ e^-$

P, As, Sb, & Bi

Moving down the group, the octet can again be expanded for P, As, and Sb...

$$P_4(s) + 6Cl_2(g) \longrightarrow 4PCl_3(l) \xrightarrow{4Cl_2} 4PCl_5(l) \xrightarrow{4Cl^-} 4PCl_6^-$$

8 e⁻ **10 e⁻** **12 e⁻**

...but the inert pair effect keeps bismuth from going past BiX_3

The halides are useful starting materials for further chemistry: