

Greenwood & Earnshaw

2nd Edition

Chapter 13

Arsenic, Antimony & Bismuth

Arsenic, Antimony & Bismuth

^{14}N 99.634% ^{31}P 100% ^{75}As 100% ^{121}Sb 57.25% ^{209}Bi 100%
 ^{15}N 0.366% ^{123}Sb 42.75%

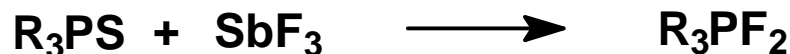
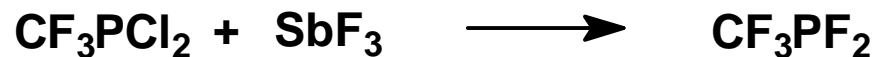
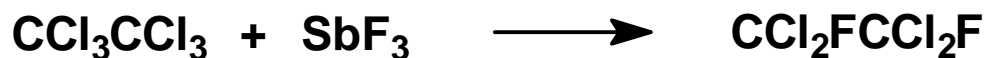
- **As, Sb & Bi have been known since antiquity. Sulfides are the most common minerals. Bismuth has been used from 1440 to the present as “type metal”.**
- **As & Sb have both nonmetallic (M_4) and α -metallic forms. Sb_4 is unstable above -90°C .**
- **α -As, α -Sb, α -Bi have a puckered sheet structure based on pyramidal coordination. α -As has no ductility, high resistivity, is volatile and amphoteric. As resists oxidation to As(V), are strong oxidizing agents. Arsenates mimic the phosphates in structure.**

Group 15 Trihalides

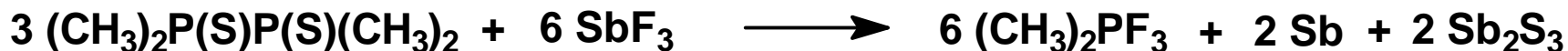
$\text{AsF}_3 \cong \text{PF}_3$ as a ligand, but more oxidizing and more readily hydrolysed.

$\text{AsCl}_3/\text{SbCl}_3$ Low viscosity solvents for Cl^- ion exchange/transfer reactions.

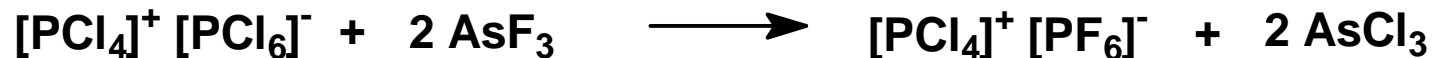
$\text{AsF}_3/\text{SbF}_3$ Good halogen exchange reagents (Cl to F) for nonmetal halides.



Oxidation sometimes occurs simultaneously:

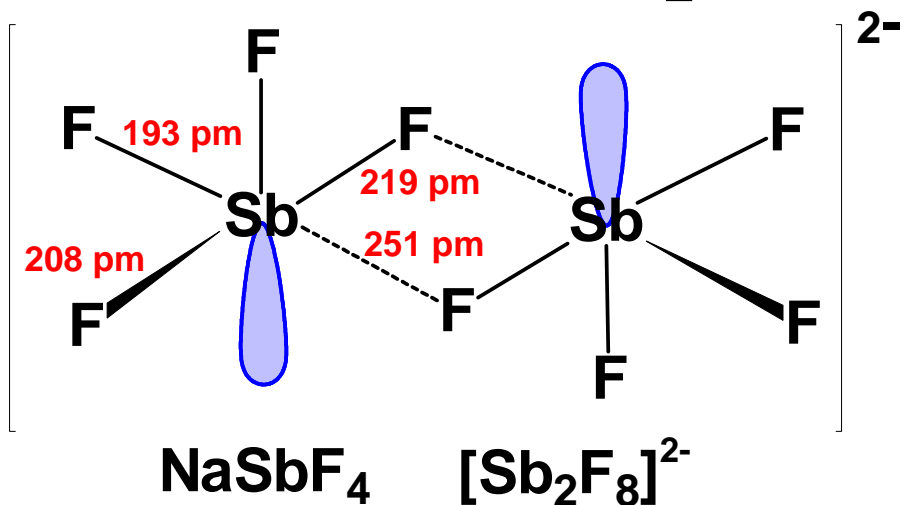
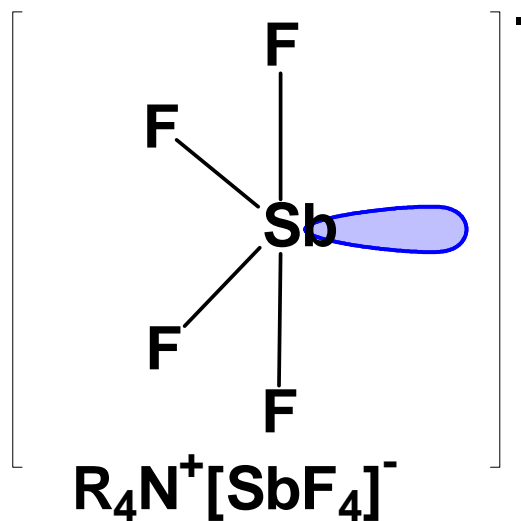


AsF_3 is a weaker fluorinating agent, Selective fluorinations are also possible.

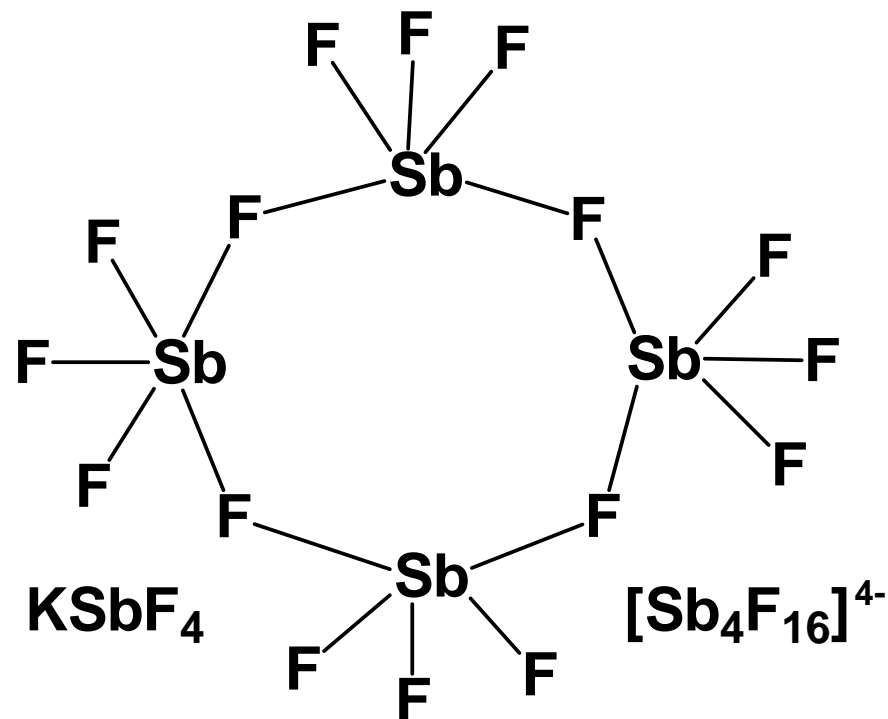


AsCl_3 (bp 130°C) can be distilled off more easily than SbCl_3 (bp 223°C).

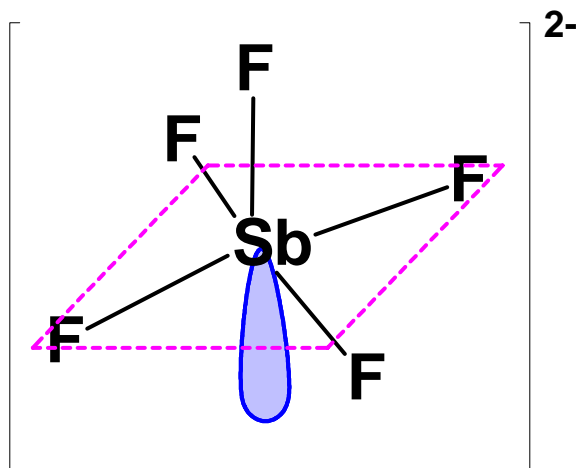
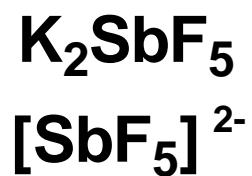
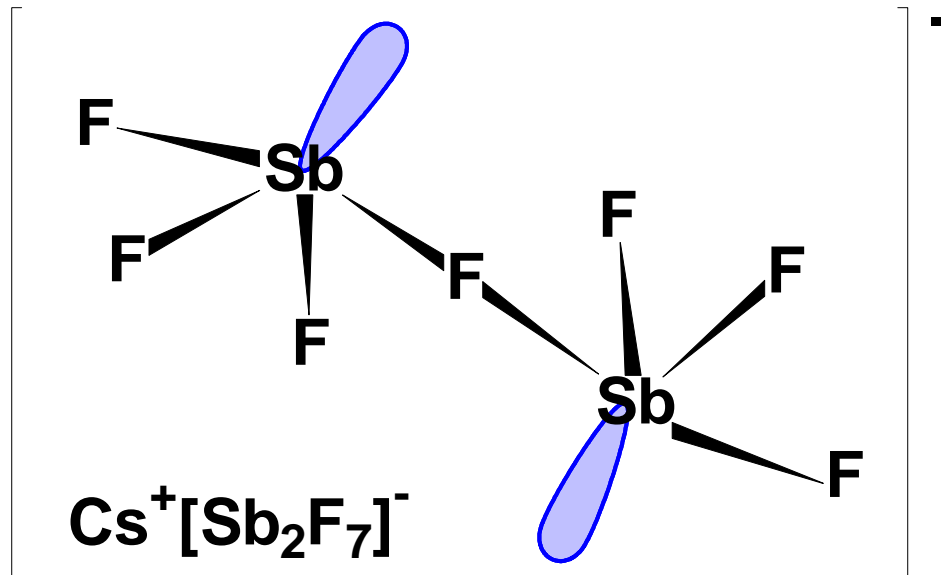
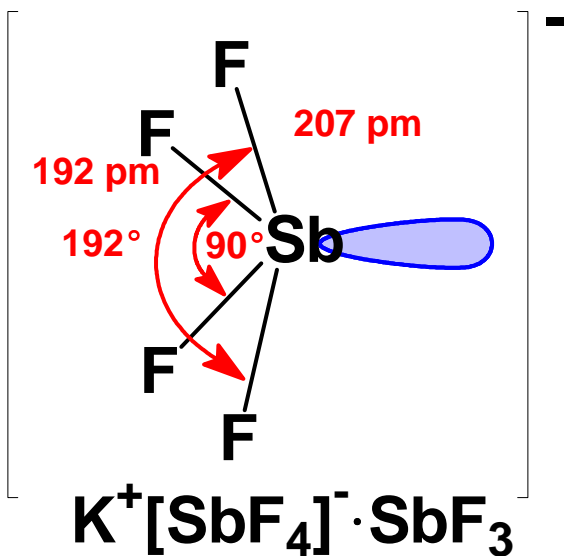
Group 15 M(III) Fluoride Complexes



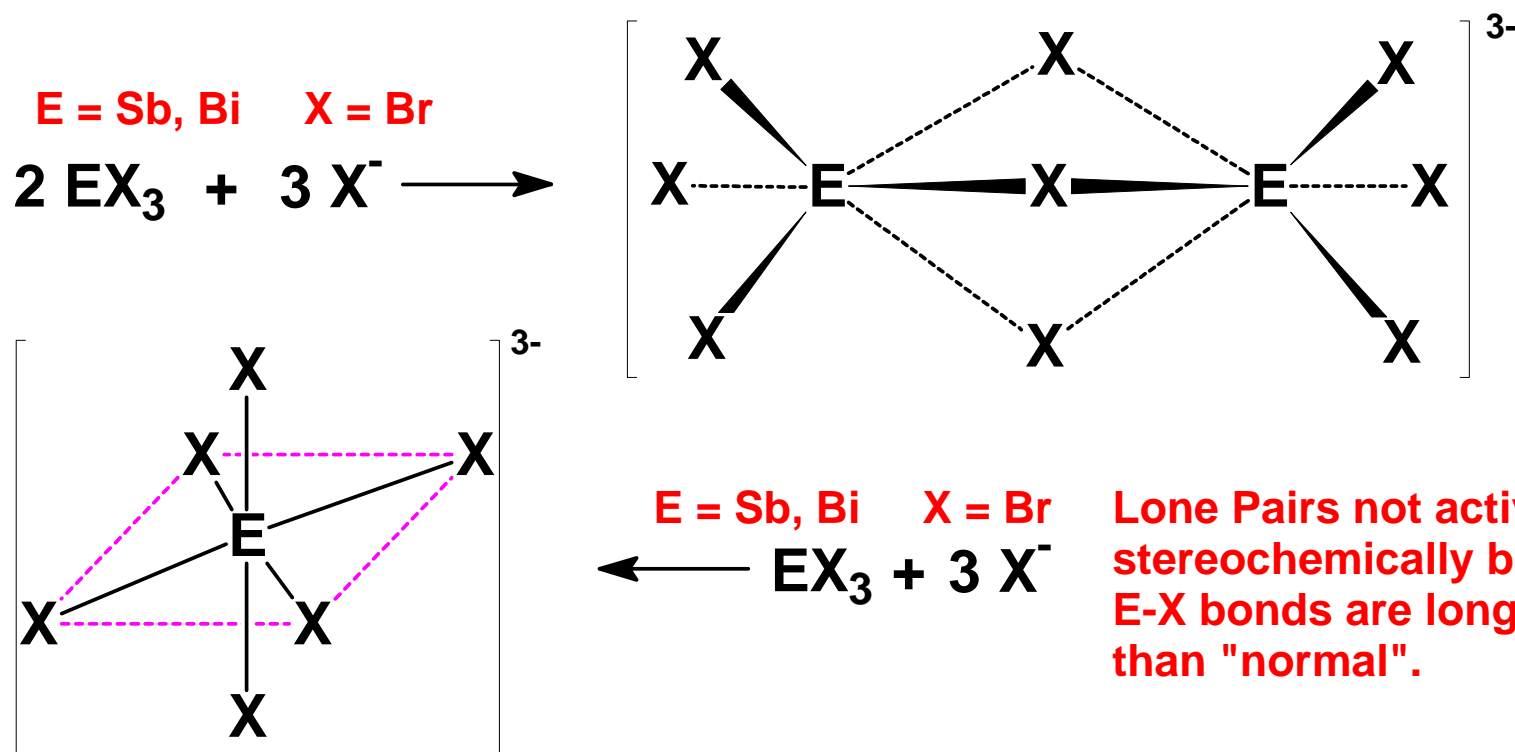
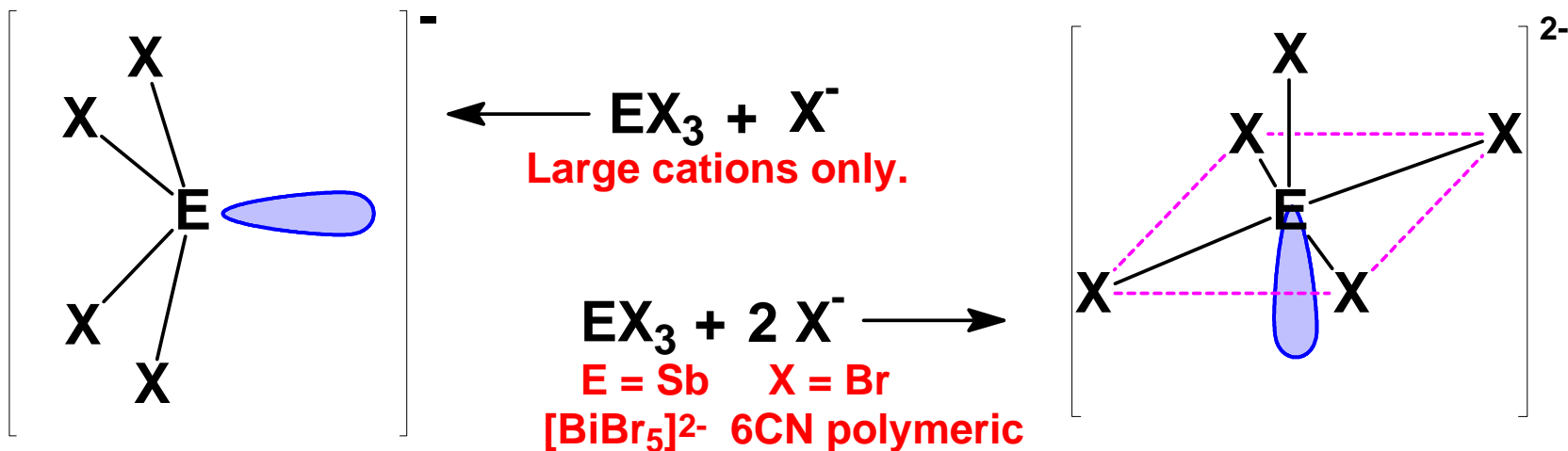
The $[SbF_4]^-$ ion's structure depends sensitively on the nature of the cation. The stoichiometry is not a reliable guide to structure.



Group 15 M(III) Fluoride Complexes



Group 15 M(III) Cl⁻ & Br⁻ Complexes



Group 15 M(III) Cl⁻ & Br⁻ Complexes

Trends in Electron Lone-Pair Stereochemical Activity

As one goes down the Group: As > Sb > Bi

**With increase in coordination number of the
central atom: 4 > 5 > 6**

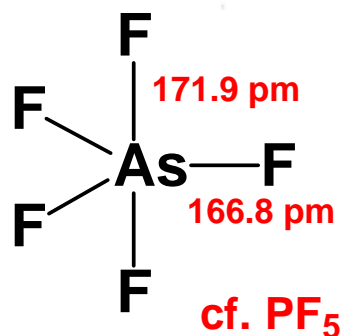
As the halogen atom becomes heavier:

F > Cl > Br > I

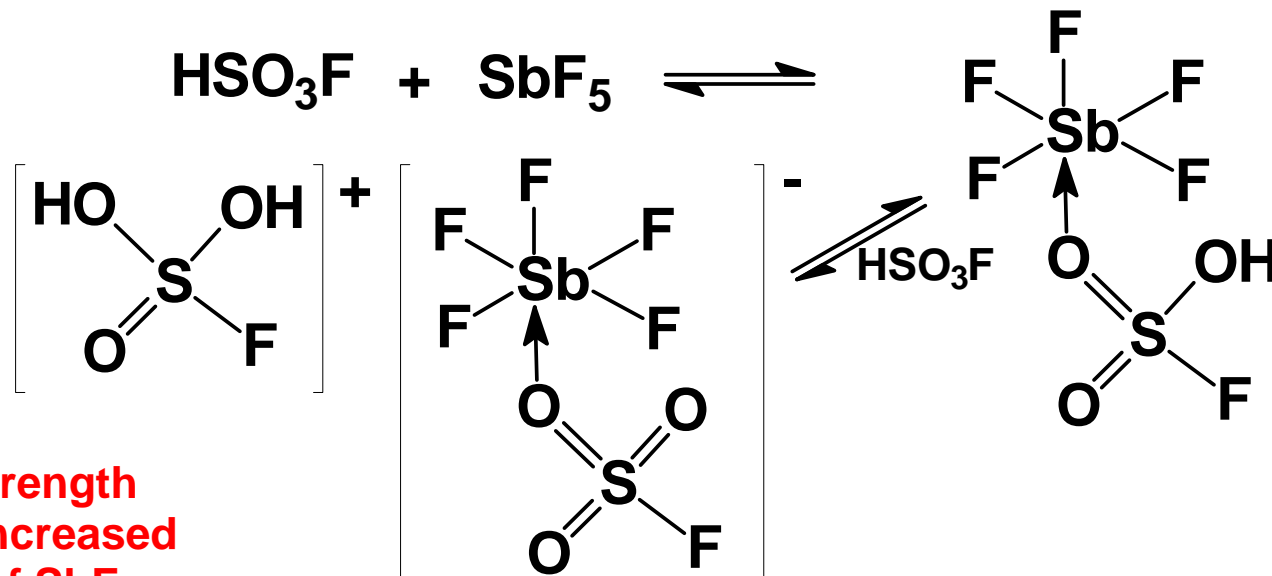
Pentahalides of Group 15

Table 13.9 Some properties of the known pentahalides

Property	AsF ₅	SbF ₅	BiF ₅	AsCl ₅	SbCl ₅
MP/°C	-79.8	8.3	154.4	~ -50 (d)	4
BP/°C	-52.8	141	230	—	140 (d)
Density (T°C)/g cm ⁻³	2.33 (-53°)	3.11 (25°)	5.40 (25°)	—	2.35 (21°)



AsF₅ & SbF₅ are potent fluoride ion acceptors (also :N & :O)

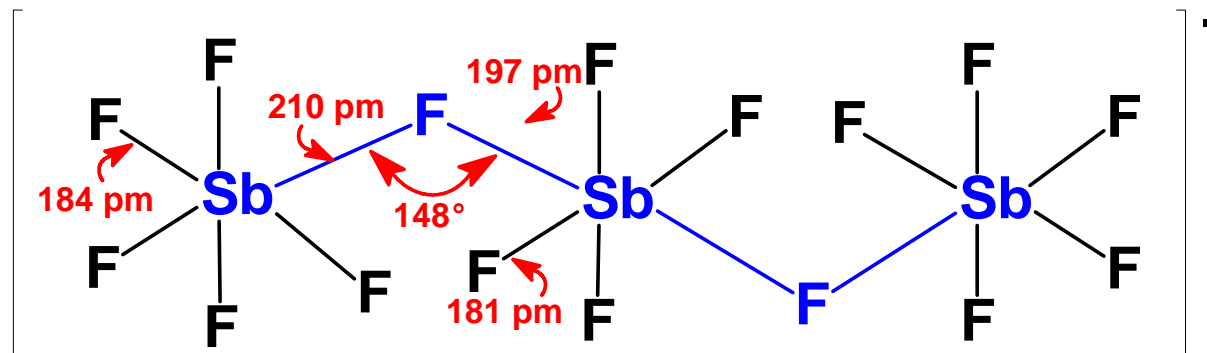


The Bronsted Acid strength of a "super acid" is increased by increasing conc. of SbF₅.

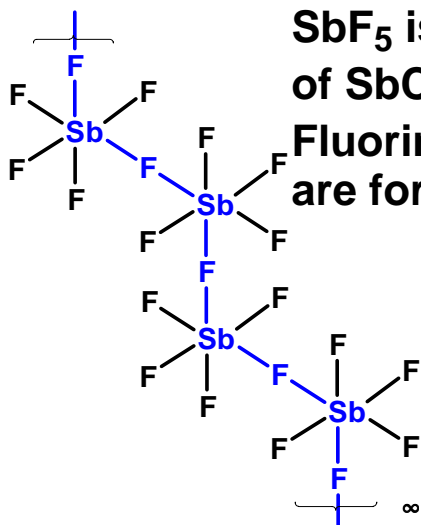


Oligomeric & Mixed Antimony(V) Halides

The *trans*-bridged ion: $[\text{Sb}_3\text{F}_{16}]^-$



Mixed Halides:



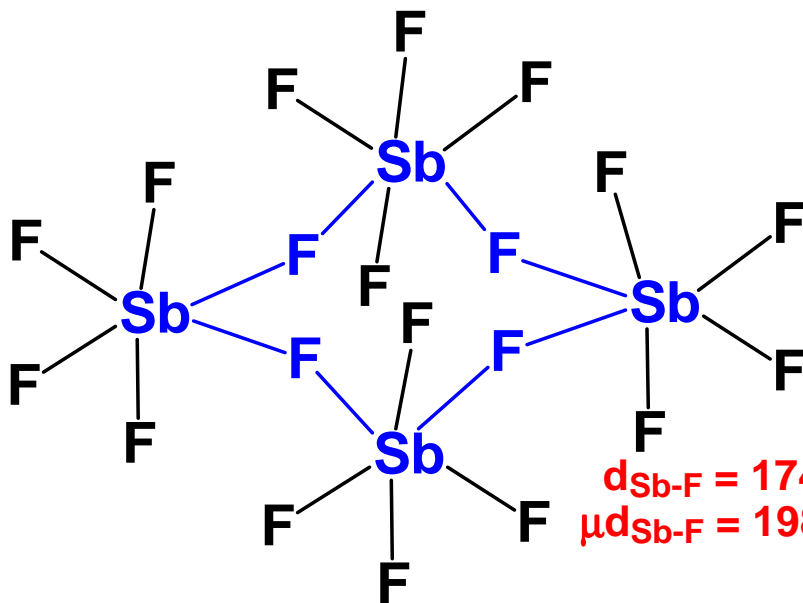
SbF_5 is a very syrupy, viscous liquid. Addition of small amounts of SbCl_5 dramatically lowers the viscosity, and raises conductivity. Fluorine bridges are broken, cyclic, tetrameric and ionic species are formed.



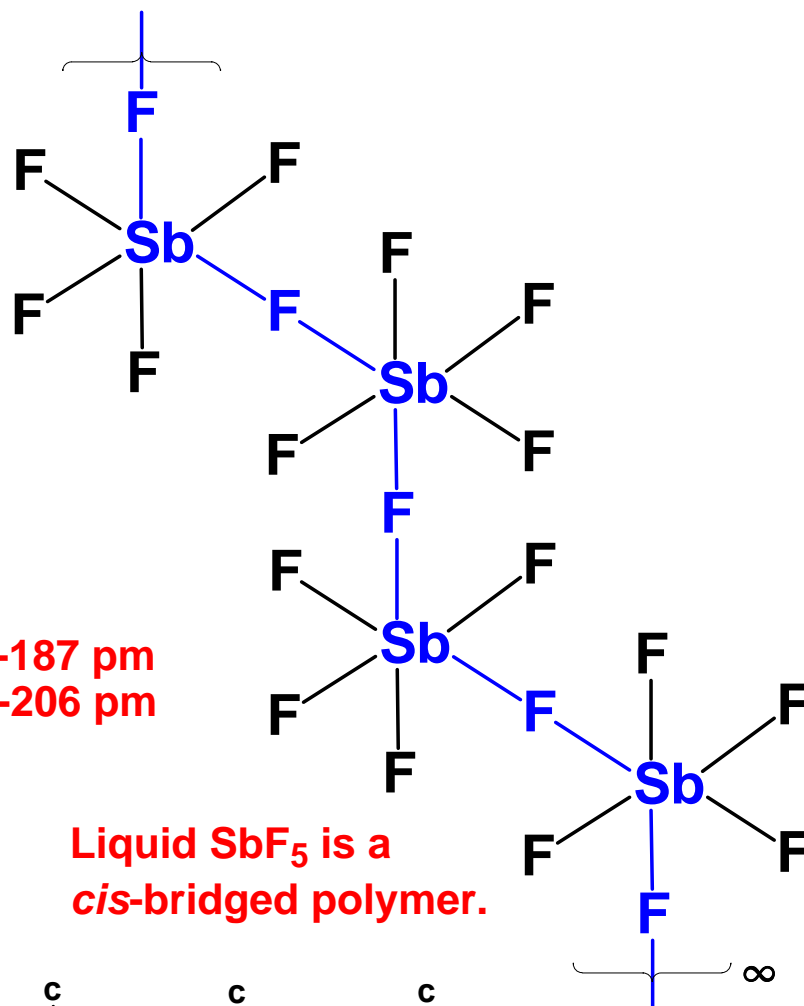
F-bridged, cyclic tetramers
cf. crystalline SbF_5 .

Antimony (V) Fluoride

Crystalline $[\text{SbF}_5]_4$ tetrameric units. Antimony is *cis*-bridged and six coordinate.

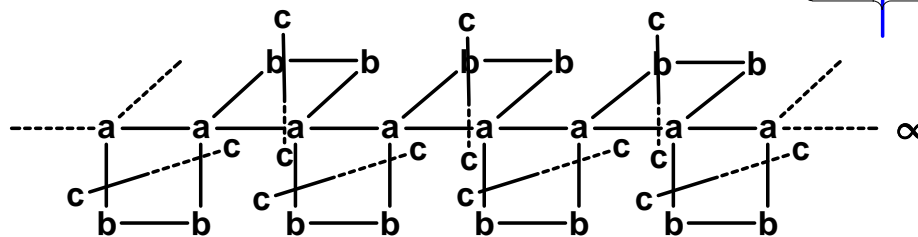
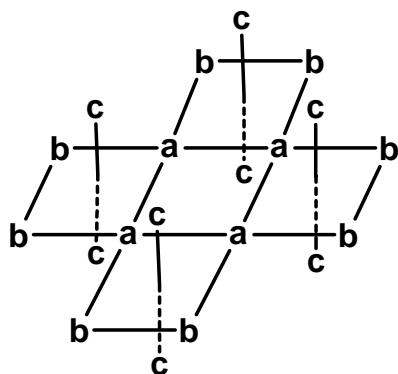


$d_{\text{Sb-F}} = 174\text{-}187 \text{ pm}$
 $\mu d_{\text{Sb-F}} = 198\text{-}206 \text{ pm}$



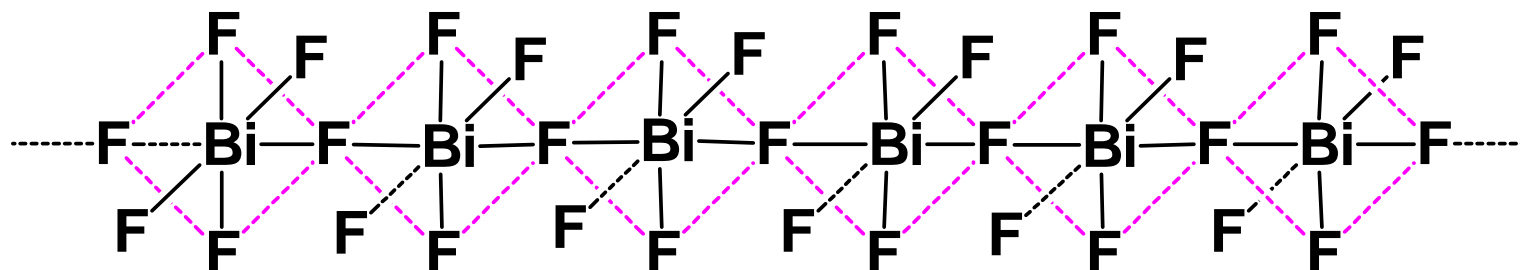
^{19}F nmr
 1/2/2
 a/b/c

Liquid SbF_5 is a
cis-bridged polymer.

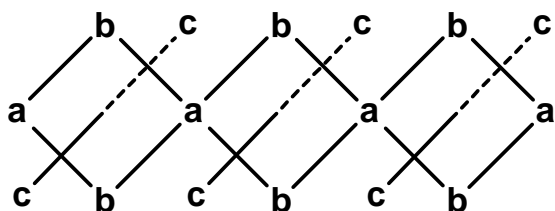


Pentahalides of Group 15

BiF₅ A trans-bridged polymer.

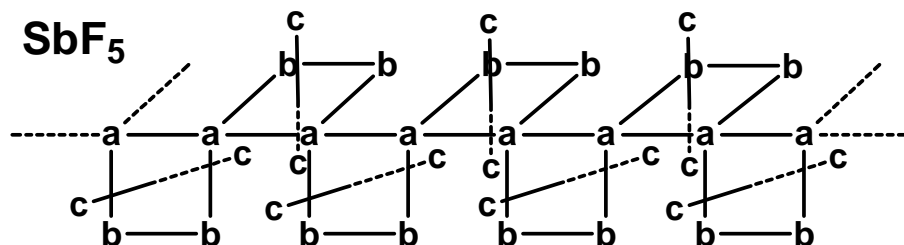


BiF₅



F_b cis to both F_a's

SbF₅



F_b cis to one F_a trans to other F_a

BiF₅ Bismuth pentafluoride is an extremely powerful fluorinating agent and oxidizer. Above 150°C it will oxidize U(IV) to U(VI) and parafins to perfluoroparafins.

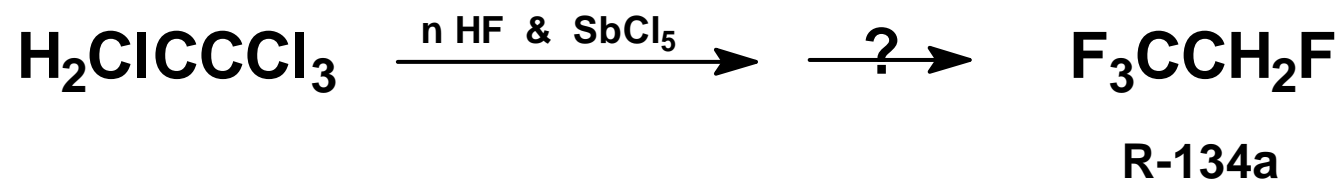
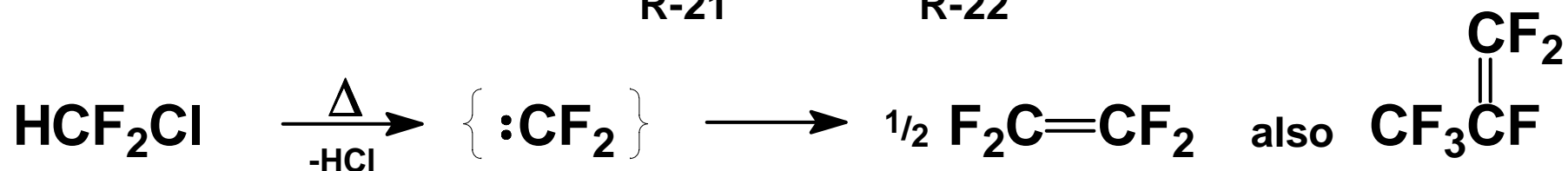
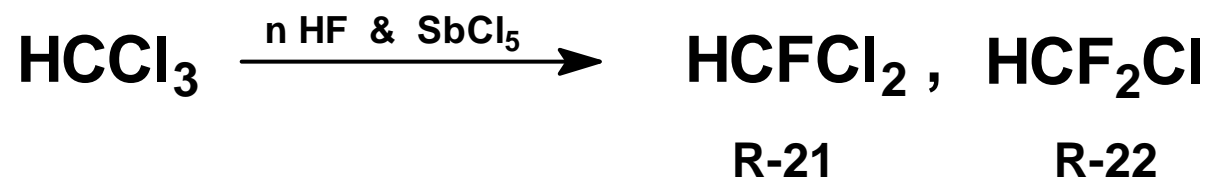
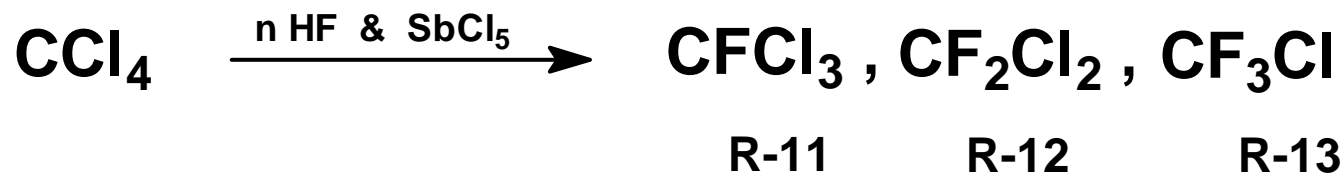
SbCl₅

Antimony pentachloride is very important industrially as a Swart's catalyst.



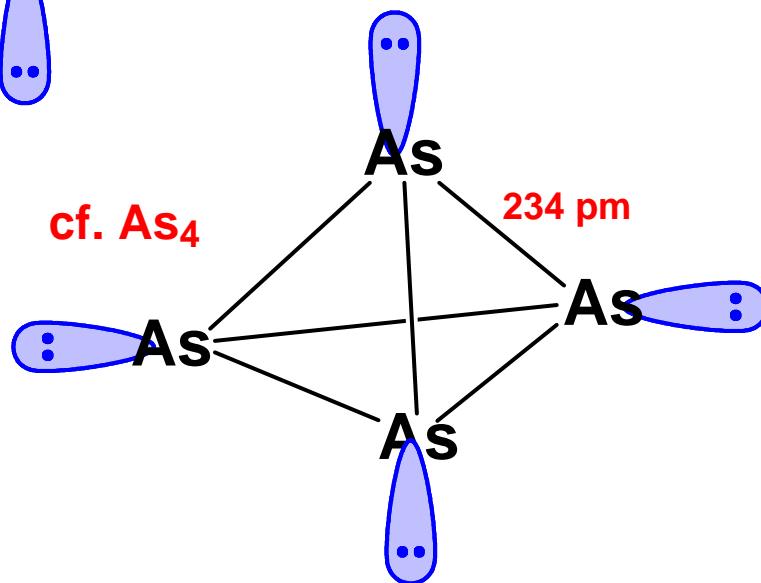
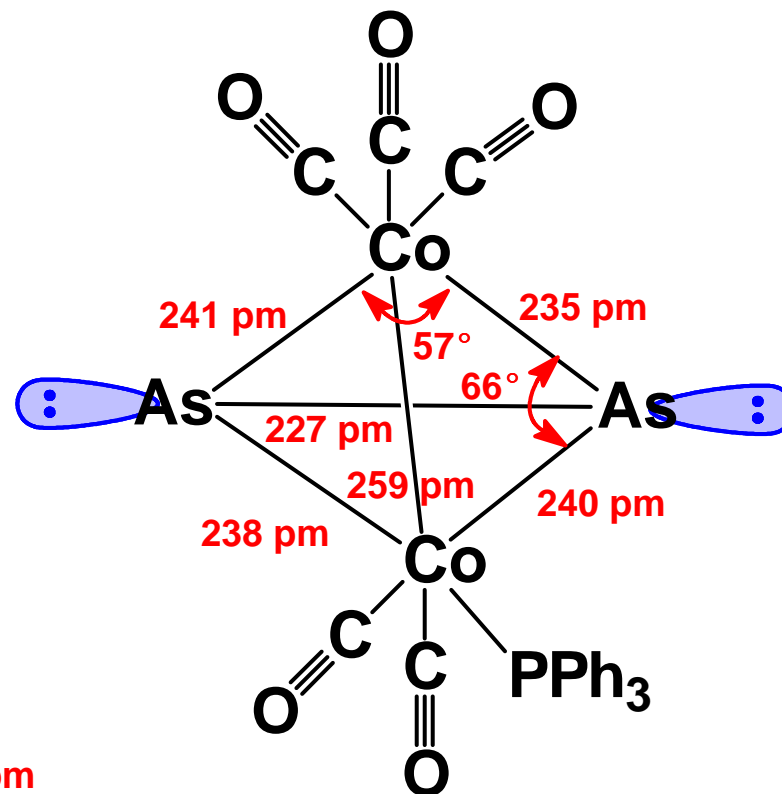
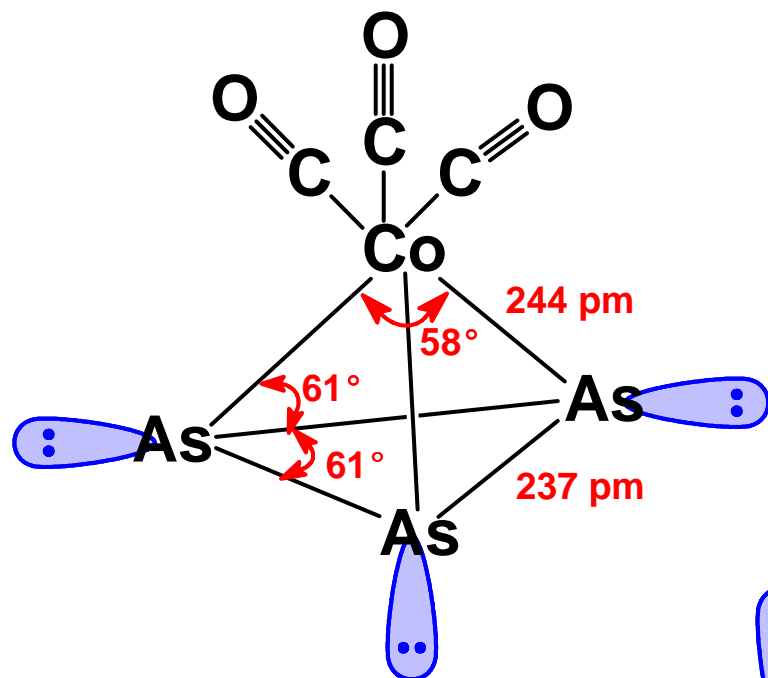
Can convert chlorocarbons to chlorofluorocarbons.

Fluorination: The Swarts Process

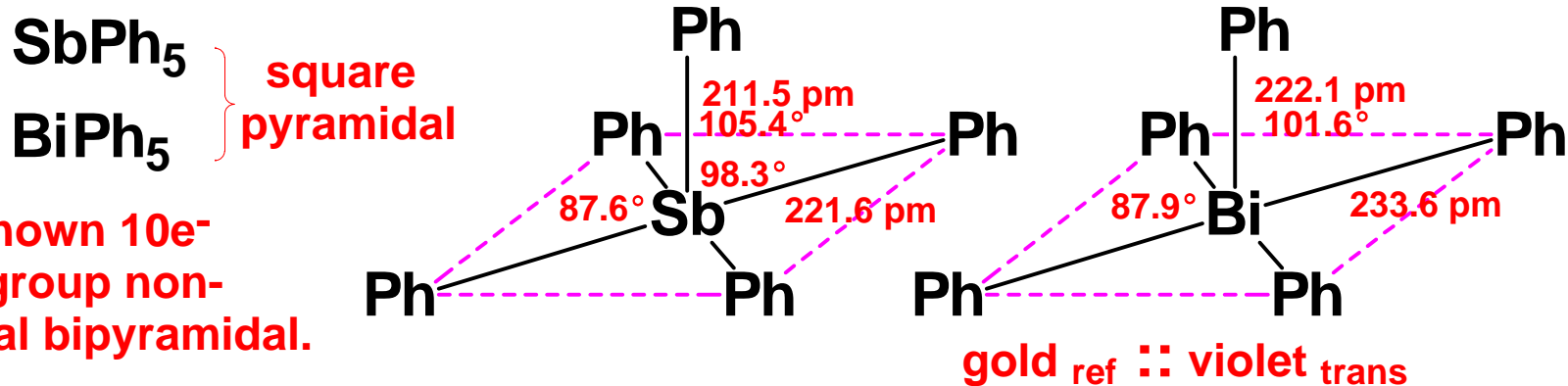
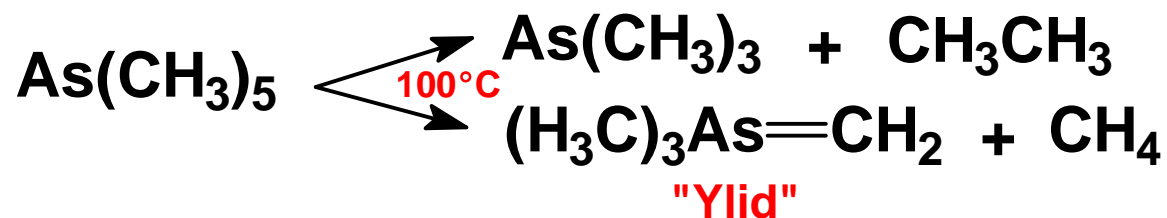
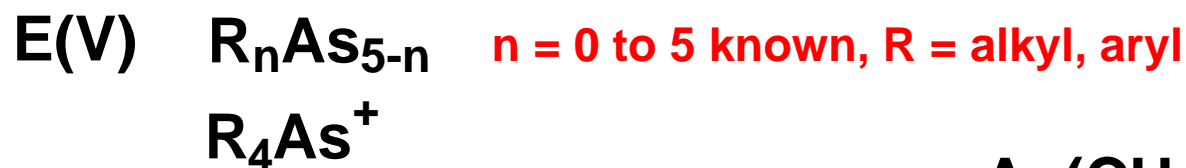
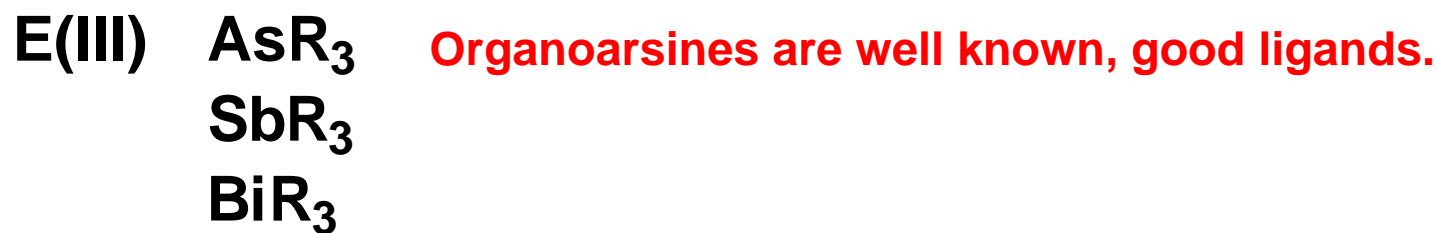


Process is still the “mainstay” of the fluorocarbon products industry. Direct conversion of C-Cl to C-F from anhydrous hydrogen fluoride is very inexpensive.

Cluster Chemistry - Arsenic



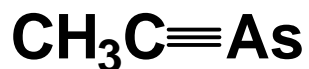
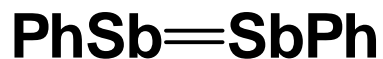
Organometallics



Group 15 Metal-Metal Bonding



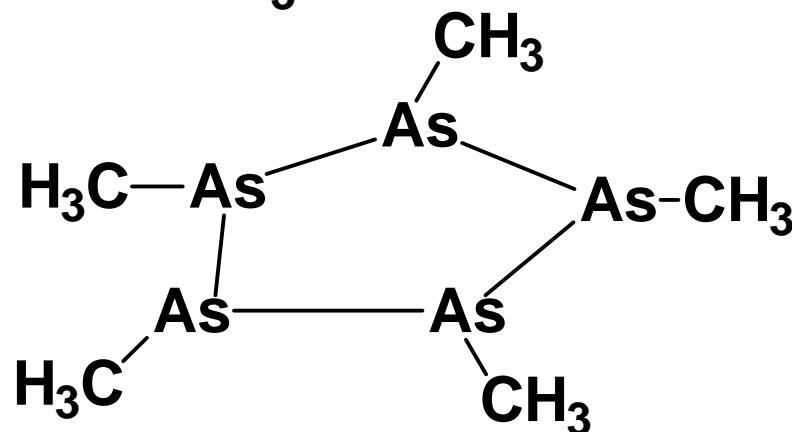
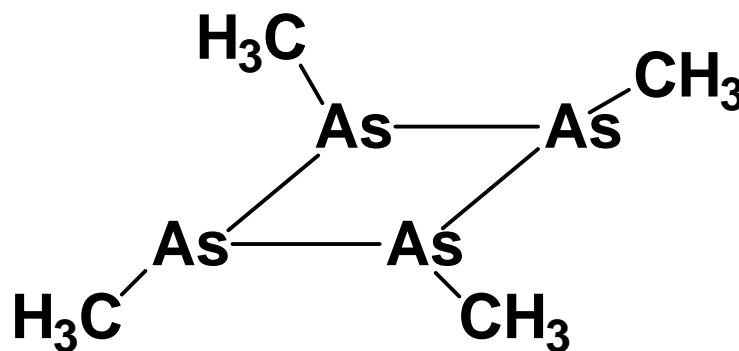
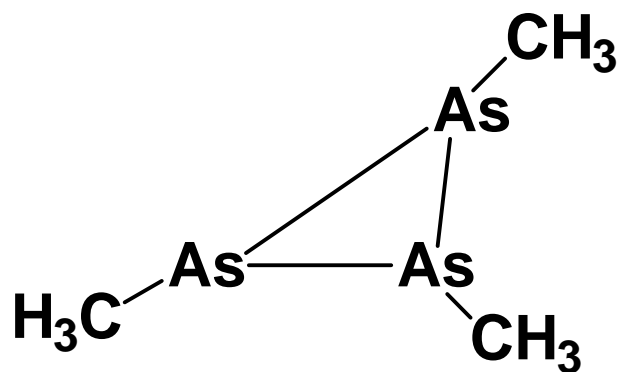
known since ~1760



Stabilized by isolation as ligands
unstable to polymerization.

Cyclopolyarsanes:

Can replace CO in $M(CO)_x$



also: R =
 CF_3 , C_2H_5 , C_3H_7 , Ph