

Greenwood & Earnshaw

2nd Edition

Chapter 8

Carbon

The Fullerenes – Molecular forms of Carbon

- All have 12 pentagonal faces, 145.5 pm on a side.
- C_{60} has 20 hexagonal faces, 139 pm_{T=5K} on a side.
- The C=C between two pentagons is electron rich,
- The pentagons themselves are electron poor.
- The LUMO of C_{60} is triply degenerate. Fullerides C_{60}^{-1} to C_{60}^{-6} , C_{60}^{3-} are superconducting below $T = 28K$.
- Fullerenes may encapsulate metal atoms or small clusters. Clusters lose 3 electrons to the fullerene.
- $La @ C_{60}$ is $La^{3+} @ C_{60}^{3-}$.

Meso-C₆₀F₄₈ - S₆ Symmetry

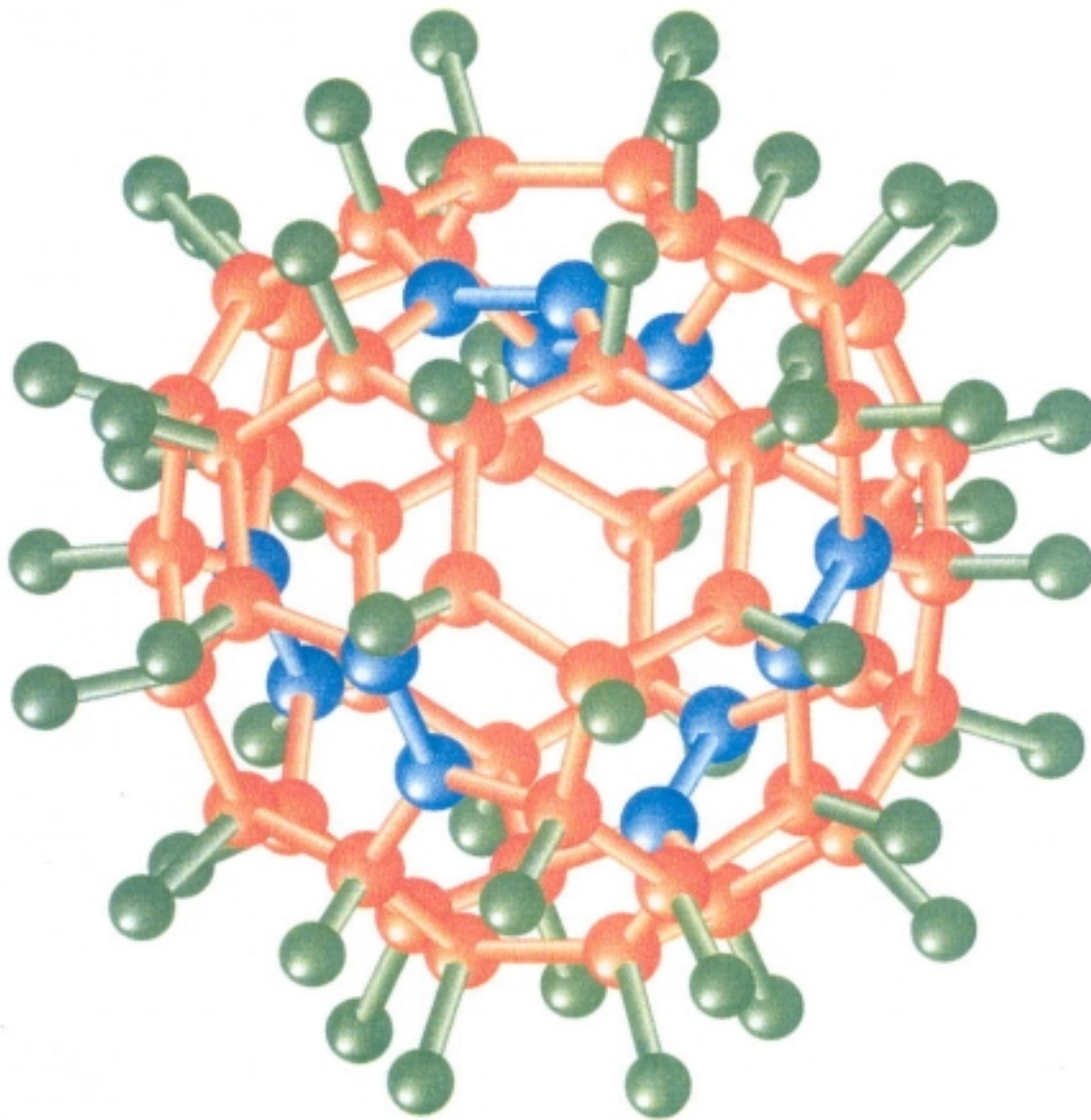
A crystal structure of the C₆₀F₄₈ isomers shows distortion of the fullerene cage.

dsp³-sp³ 154-163 pm

dsp³-sp² 149-153 pm

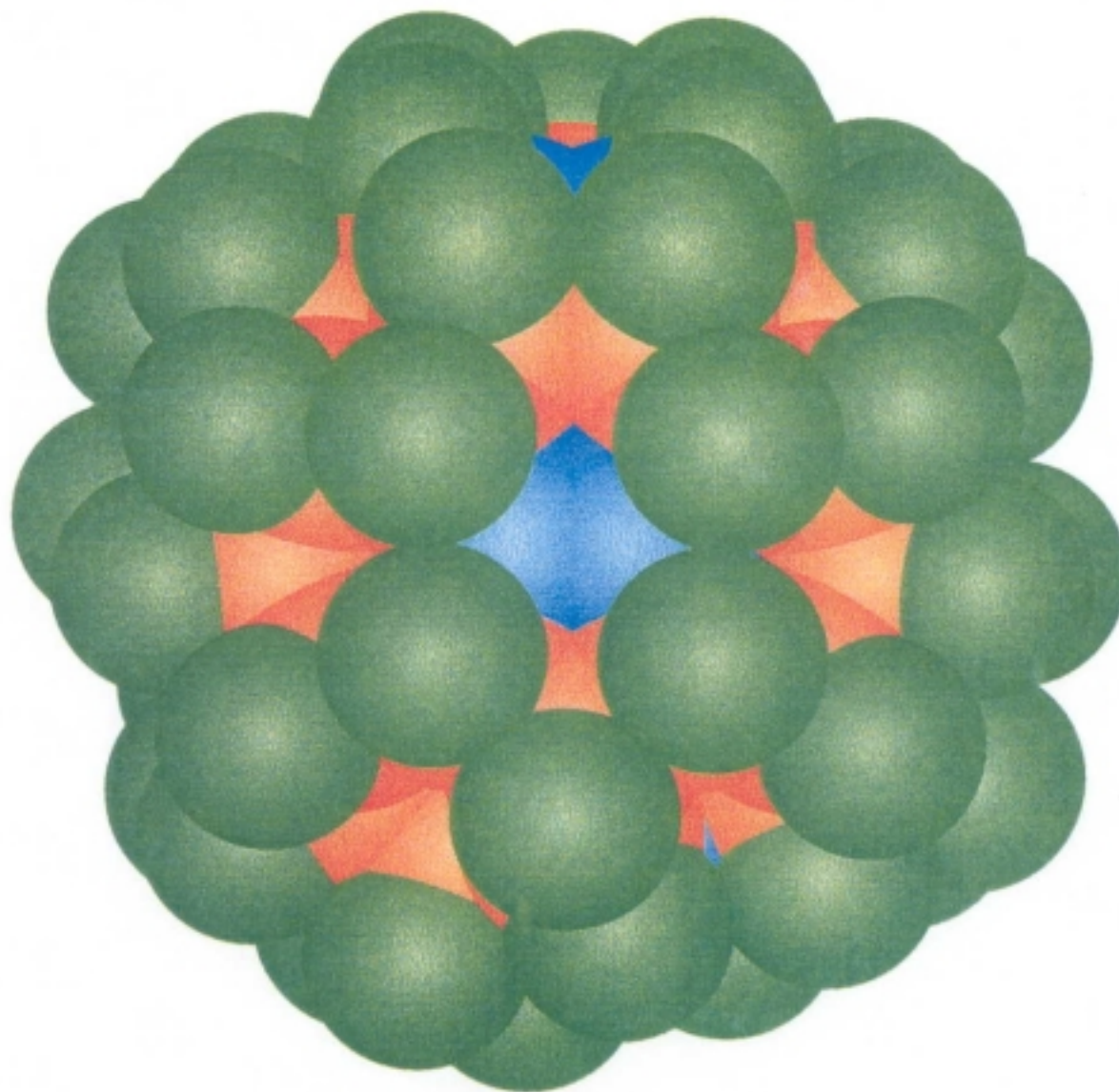
dsp²-sp² 136-140 pm

Out of 20 million possible isomers the fluorination reactions results in only the RR, SS and RS (*meso*) isomers.



Space Filling Model – *meso*-C₆₀F₄₈

It is apparent from the space-filling model shown here that there is insufficient space over the double bond (blue) for an additional pair of fluorine atoms (green). However, molecules such as C₆₀F₄₈O and C₆₀F₄₈O₂ have been observed in the mass spectrogram.

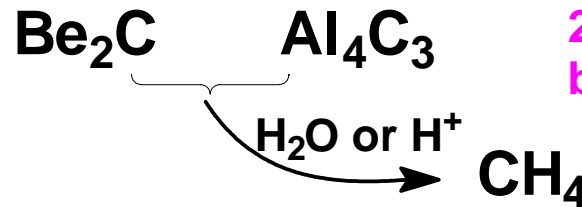


Carbides

- 1. Direct Combination of the elements above 2000°C .**
- 2. Reaction of the metal oxide with carbon at high temperatures.**
- 3. Reaction of heated metal with gaseous hydrocarbon.**
- 4. Reaction of acetylene with electropositive metals in liquid ammonia.**

Carbides

a) Methanides:



2 Be²⁺ C⁴⁻ is suggested by "ab initio" calculations.

Al₄C₃ is a layer lattice; two types {AlC₄} tetrahedra; two types of C atoms in one C is CN 6, d_{AlC} = 217 pm, in the second type C is CN 5, d_{AlC} = 190-194 pm and the 5th is d_{AlC} = 221 pm, the shortest d_{CC} = 316 pm.

b) Ethanides:



LnC₂, Ln₄(C₂)₃ Isostructural with above but retaining metallic electrons.

Li₄C₃ & Mg₂C₃ contain the linear $\left[\text{:}\ddot{\text{C}}=\text{C}=\ddot{\text{C}}\text{:} \right]^{4-}$ ion.



c) Interstitial:

$$R = r_x/r_M$$

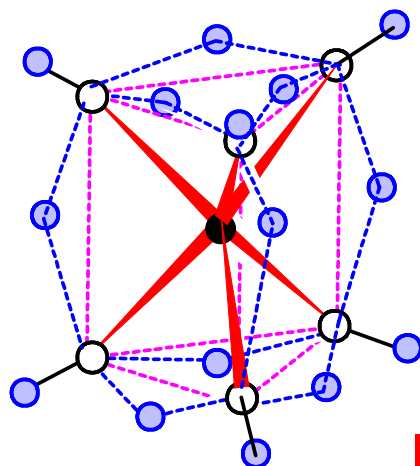
r_x = covalent radius of Carbon.

r_M = 1/2d_{MM} of metal.

The structures of carbides with R < 0.59 (r_M = 135 pm; Ti, Zr, Hf, V, Nb, Ta, Mo, W) are simple hcp, ccp or bcc lattices. The small C atoms fit into octahedral holes (interstices). The carbides have great hardness and very high melting points. They are metallic conductors and have ductility only at very high temperatures.

Carbides

d) Carbido Complexes



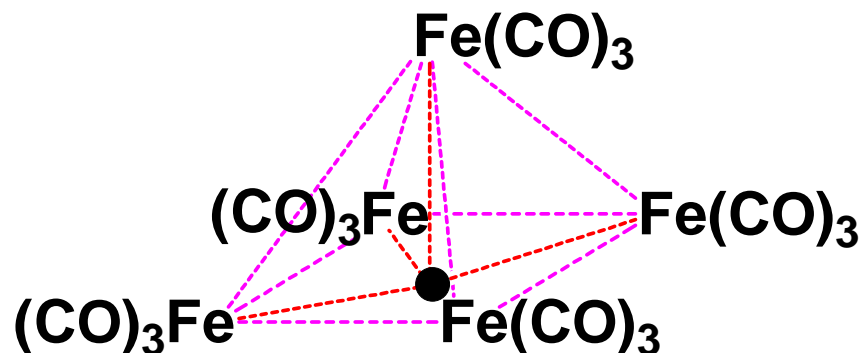
○ Rh

● Carbide C

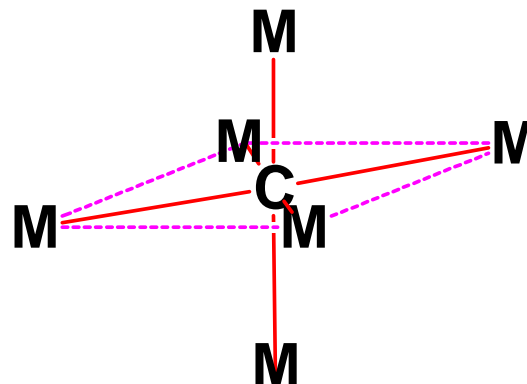
○ Carbonyl C (CO)



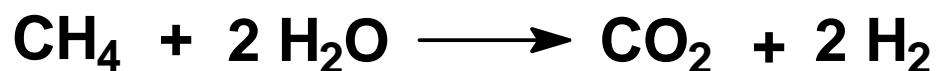
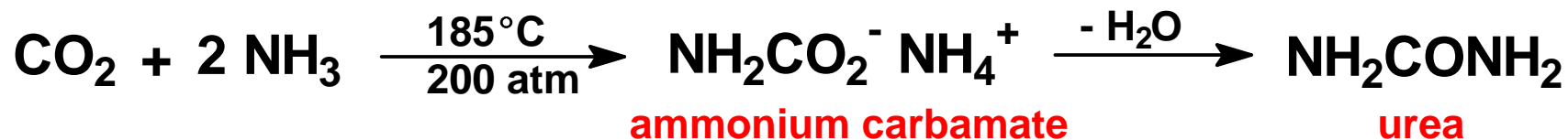
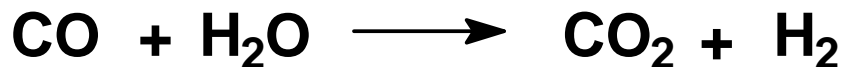
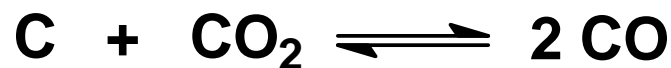
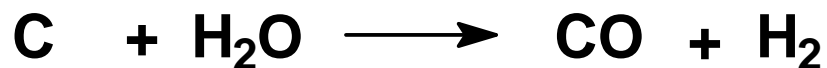
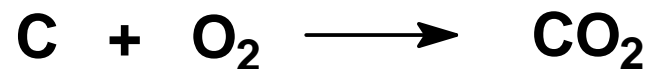
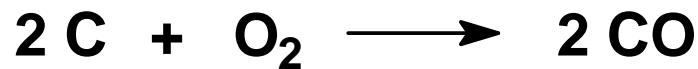
has an ethanide, $d_{\text{C-C}} = 147 \text{ pm}$



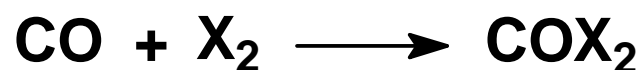
In each, C is a 4 electron donor



Carbon Oxides & C₁ Chemistry



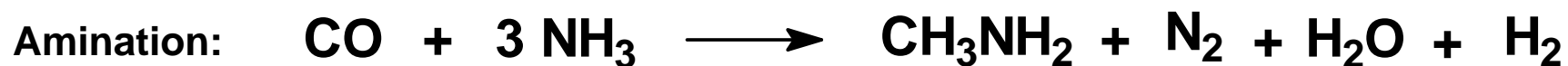
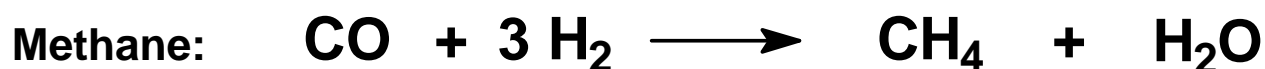
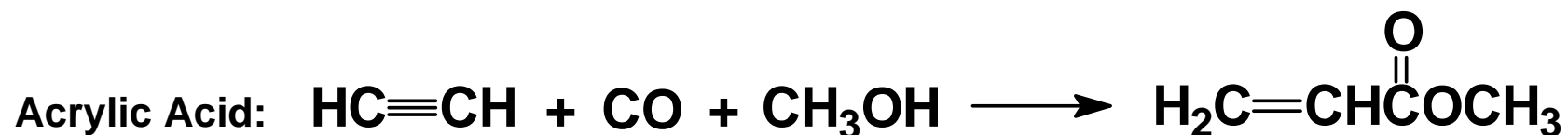
A major source of process hydrogen.



X = F, Cl, Br

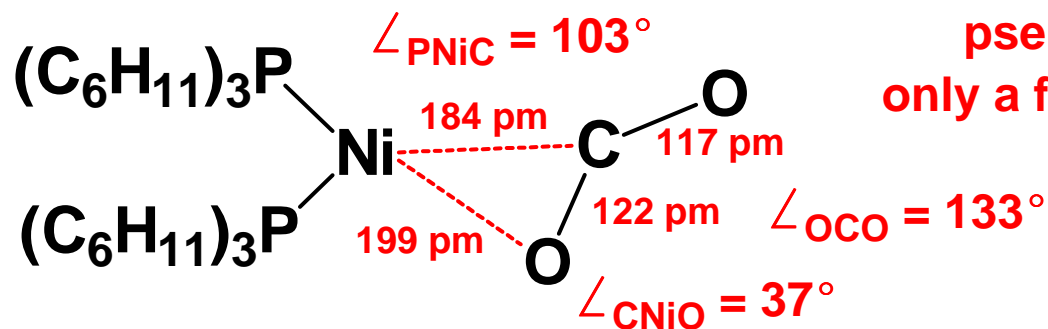


Carbon Oxides & C₁ Chemistry



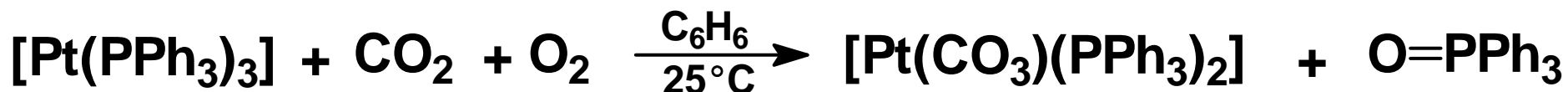
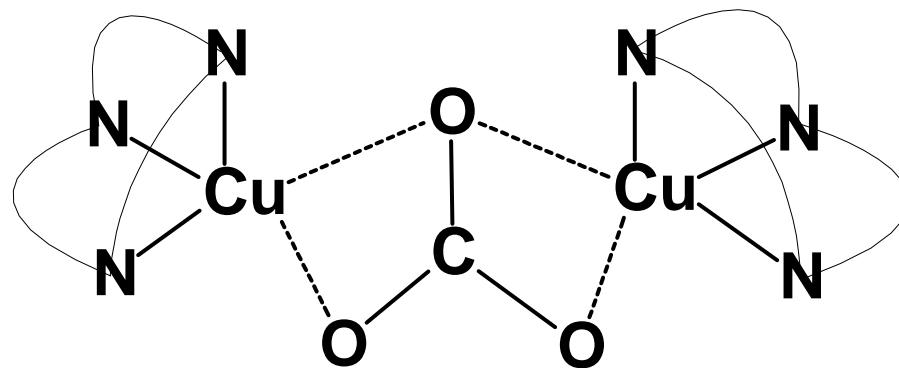
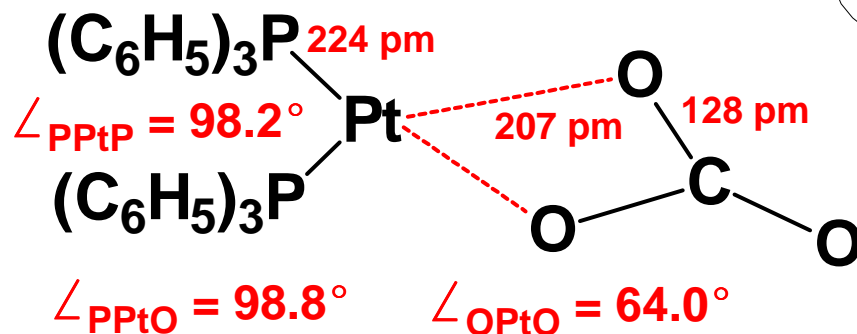
Carbon Dioxide & Carbonate as Ligands

CO₂

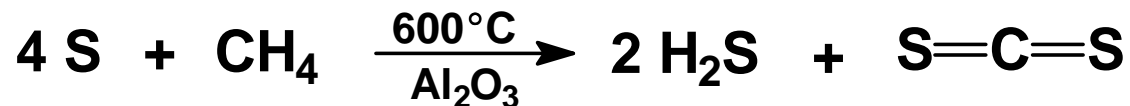


pseudo 3-coordinate
only a few complexes known

CO₃²⁻

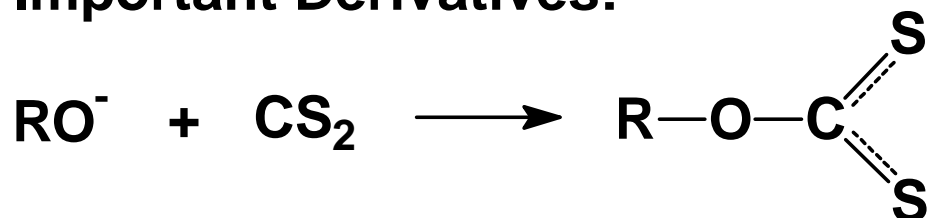


Carbon Disulfide & Derivatives

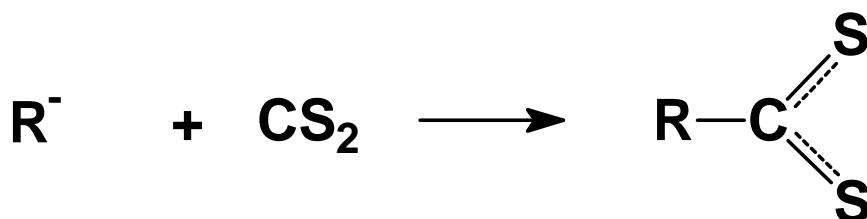


Carbon disulfide is important industrially, toxic, foul smelling, very complex chemistry.

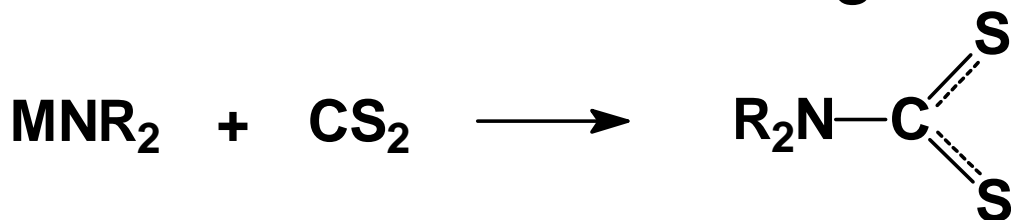
Important Derivatives:



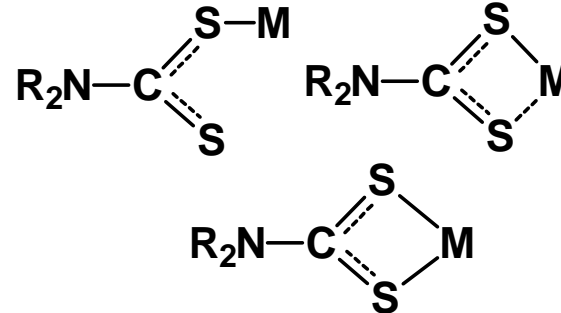
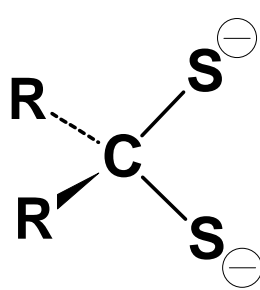
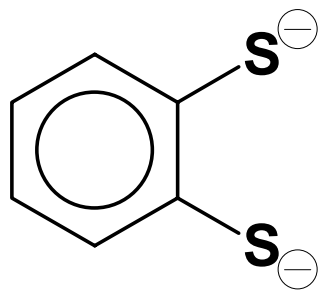
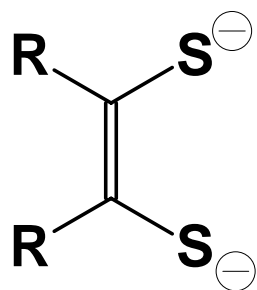
Xanthates (dithiocarbonates)
R = Et used to make viscose rayon.



Dithiocarboxylates

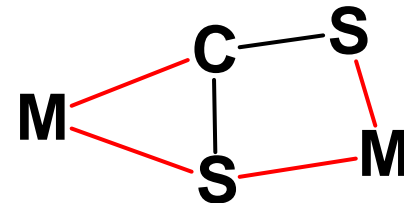
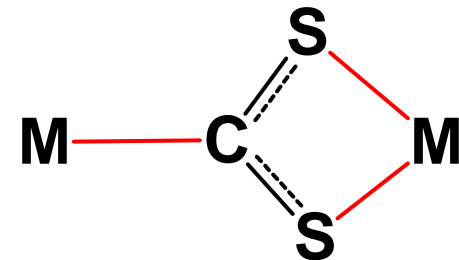
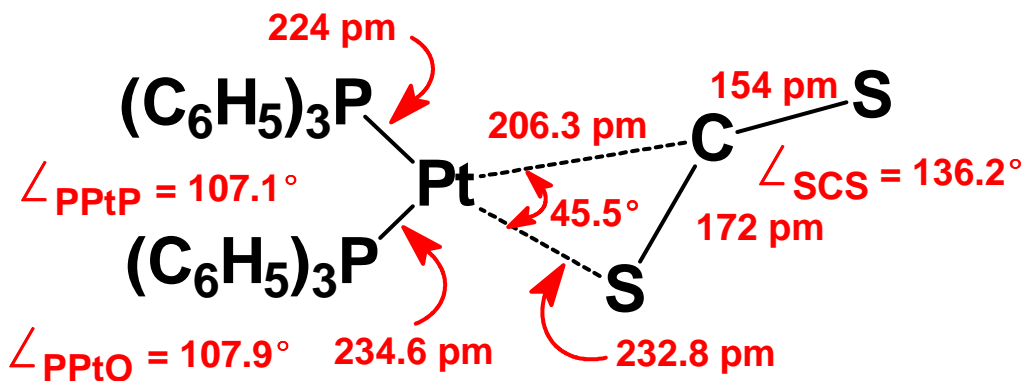
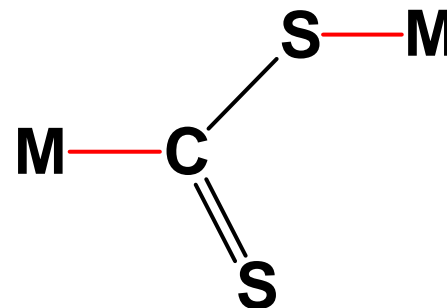
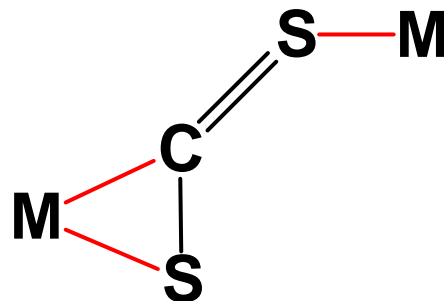
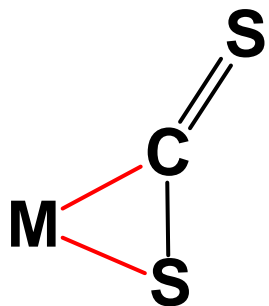


Dithiocarbamates, very important fungicides w/
M = Zn, Zn, Fe



Carbon Disulfide as a Ligand

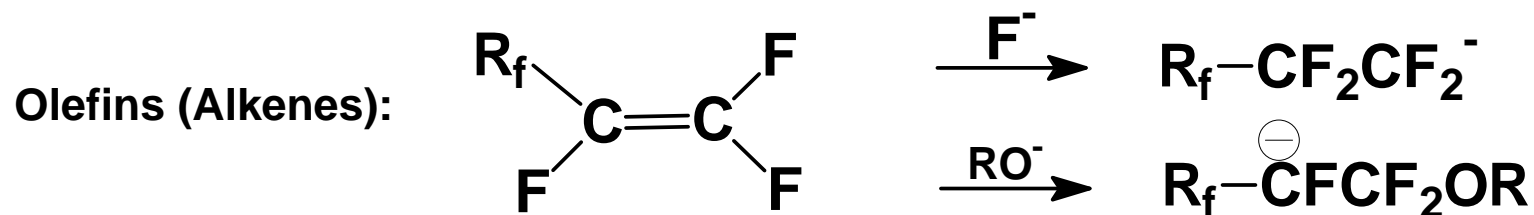
Many examples & many modes of bonding:



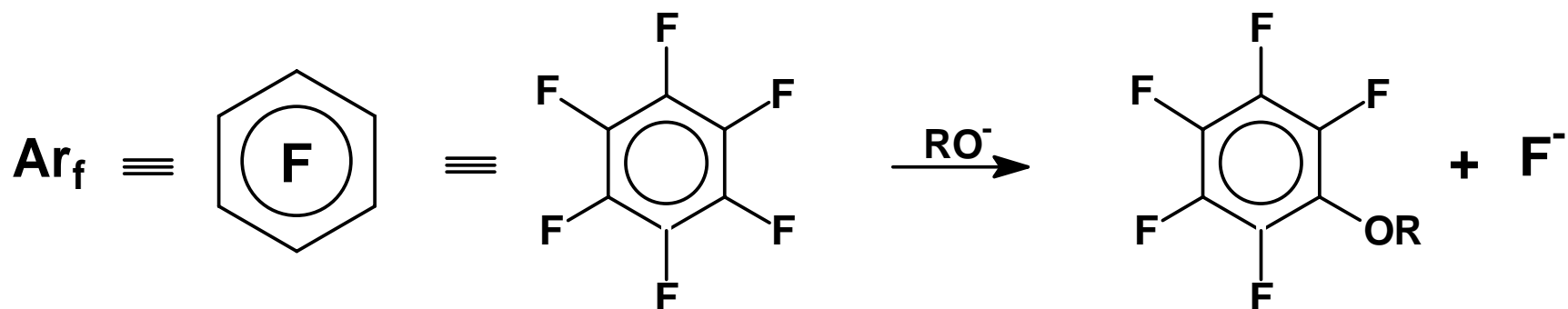
Organofluorine Chemistry

Perfluoroalkanes: R_f-F $R_f = C_nF_{2n+1}$ CF_3 , C_2F_5 , C_3F_7 , etc.

Perfluoroalkanes are unreactive except to active metals and solvated electrons.

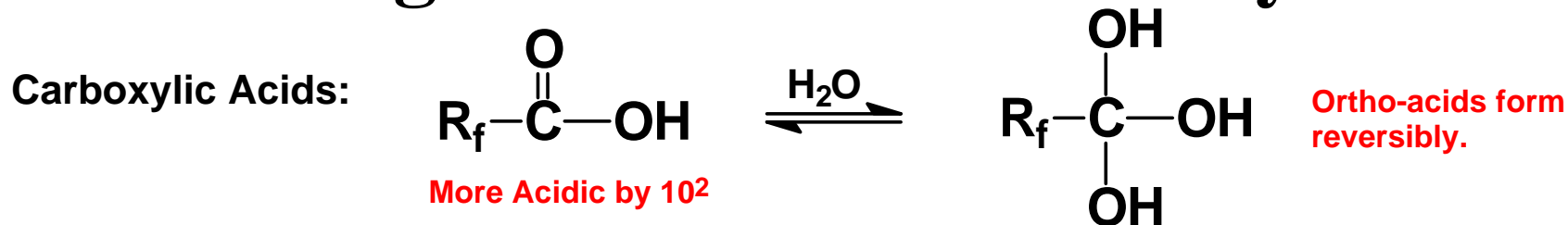


Perfluoroolefins are very electrophilic and react with many nucleophiles, polymerize readily if terminal under anionic conditions. F^- plays role $\cong H^+$.

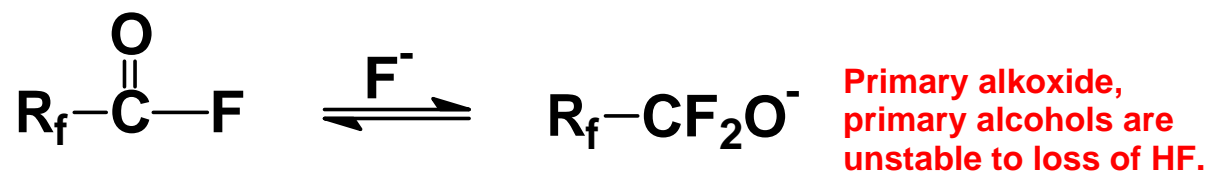


nucleophilic aromatic substitution

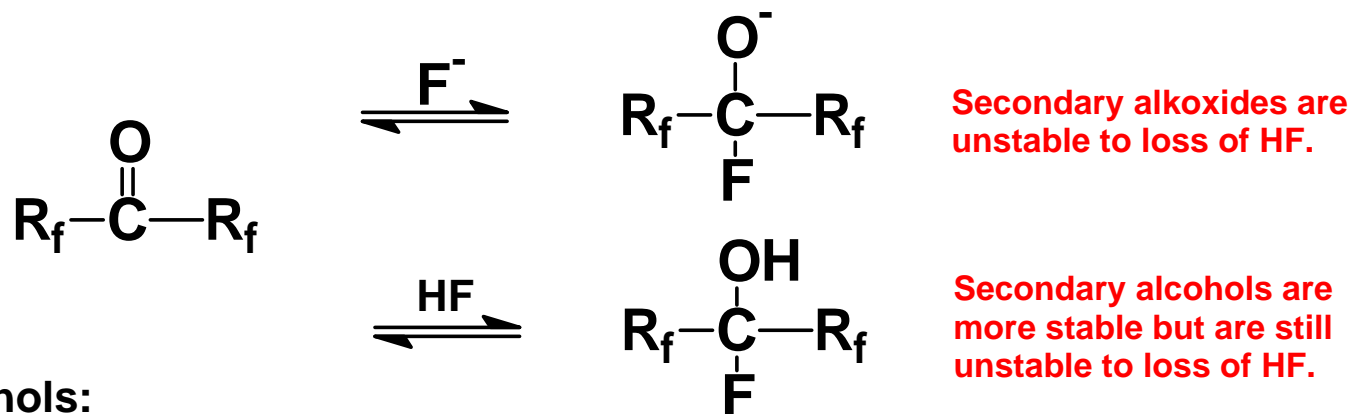
Organofluorine Chemistry



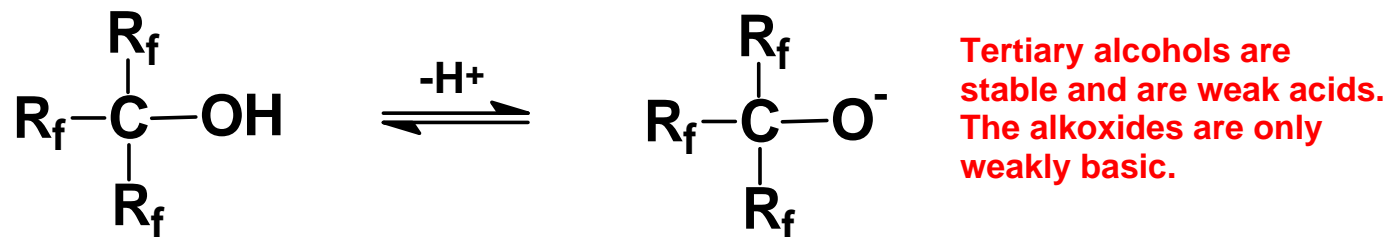
Carboxylic Acid Fluorides:



Ketones:

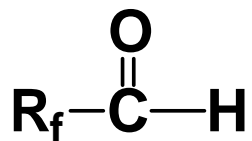


Tertiary Alcohols:

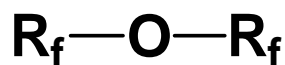


Organofluorine Chemistry

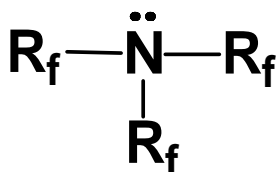
α -hydriyl primary alcohols (weakly acidic) & amines (weakly basic) are stable.



Aldehydes are electrophilic and polymerize easily.



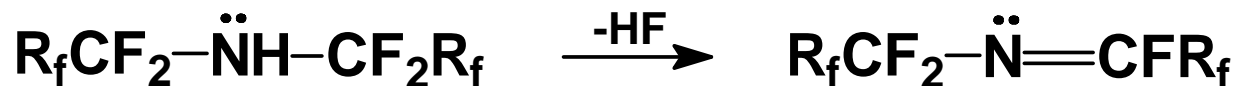
Perfluorinated ethers are stable, non-lewis bases and are very unreactive.



Perfluorinated tertiary amines are stable, non-lewis bases and are very unreactive.



Primary amines and imines are unstable to HF loss. Nitriles polymerize easily.



Secondary amines are unstable to HF loss. Imines polymerize if R_f not too bulky.

Organofluorine Chemistry

