

Lecture XIX: Other Modes of Conformer Interconversion

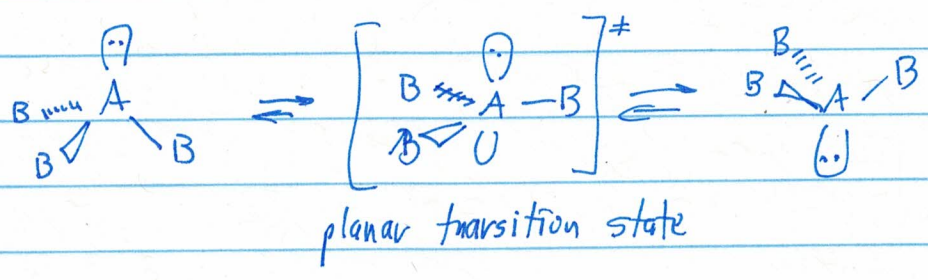
02-28-2020

Rotation around single bonds is probably the most studied mode of conformer interconversion, but it is not the only one.

IUPAC defines polytopal rearrangements as stereoisomerizations interconverting different or equivalent spatial arrangements of ligands around a central atom or of a cage of atoms, where the ligand or cage defines the vertices of a polyhedron.

Pyramidal Inversion is the second most common mechanism:

Mislow, AIEE, 1970, 94



The other option is quantum mechanical tunneling. In practice, this happens only ~~one~~ when one of B's is H or D, and at T's close to the top of vibrational barrier. For barrier determination, however, this distinction is largely inconsequential.

Barrier can be determined computationally, or experimentally using microwaves, infrared or NMR spectroscopy. For NMR:

$$k_c = \frac{J}{\sqrt{2}} \Delta V_{AB} - \text{provided that A and B don't couple}$$

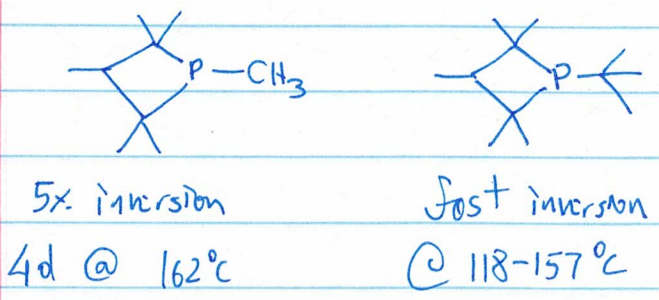
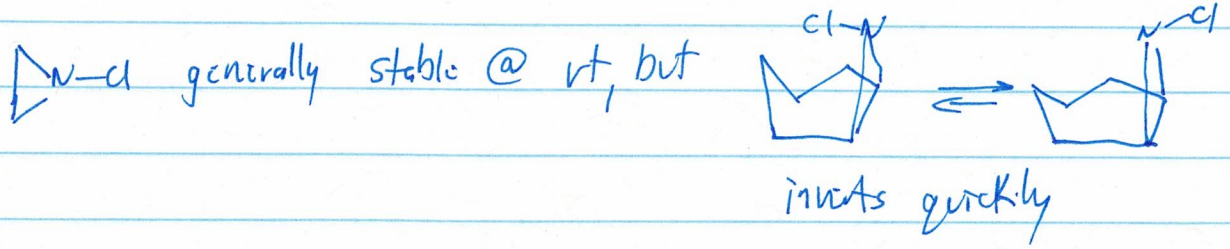
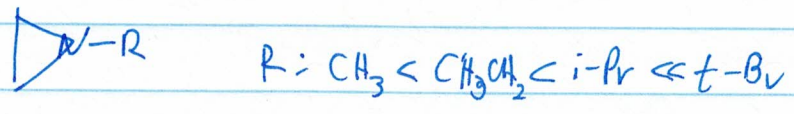
L rate of exchange at coalescence T (T<sub>c</sub>)

and are of equal size

Factors that affect these barriers:

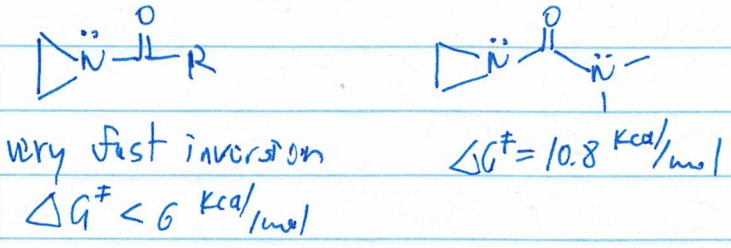
Steric Effects

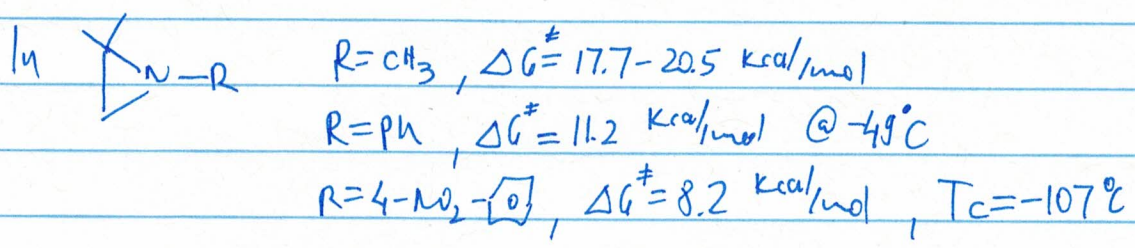
Transition state is less crowded, so steric bulk lowers the barrier to inversion:



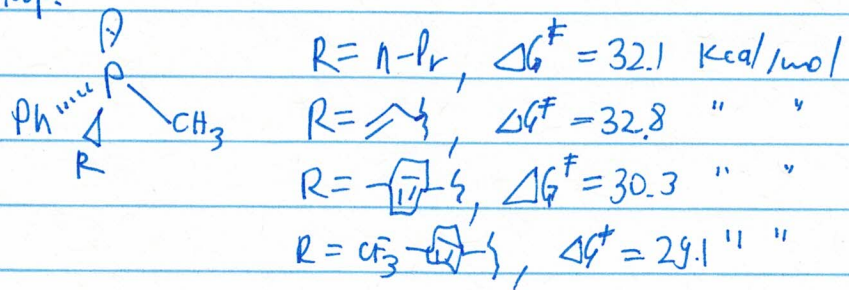
Conjugation and Hyperconjugation

During inversion, central atom goes from  $sp^3$  to  $sp^2$  }  
 lone pair " "  $sp^3$  to p }  
 anything that favors those orbitals will lower the barrier





In phosphines, this effect is smaller because of the weaker orbital overlap:

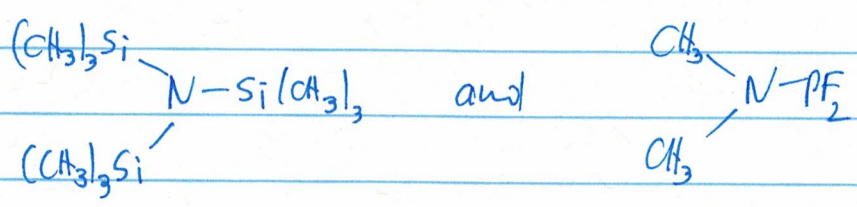


But aromaticity can help:

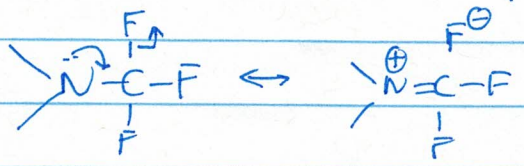


$\Delta G^\ddagger = 16 \text{ kcal/mol}$   
 P lone pair is part of  $4n+2$  in phosphole

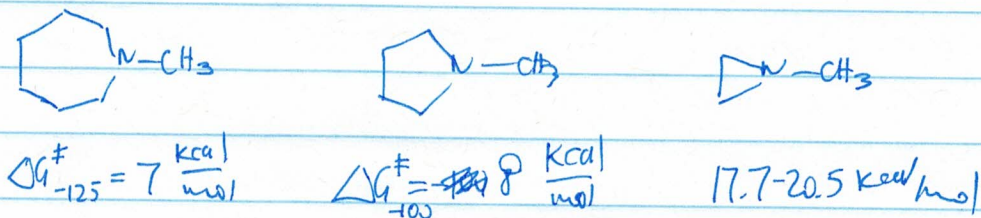
Interaction between p and d orbitals can lead to fully coplanar structures:



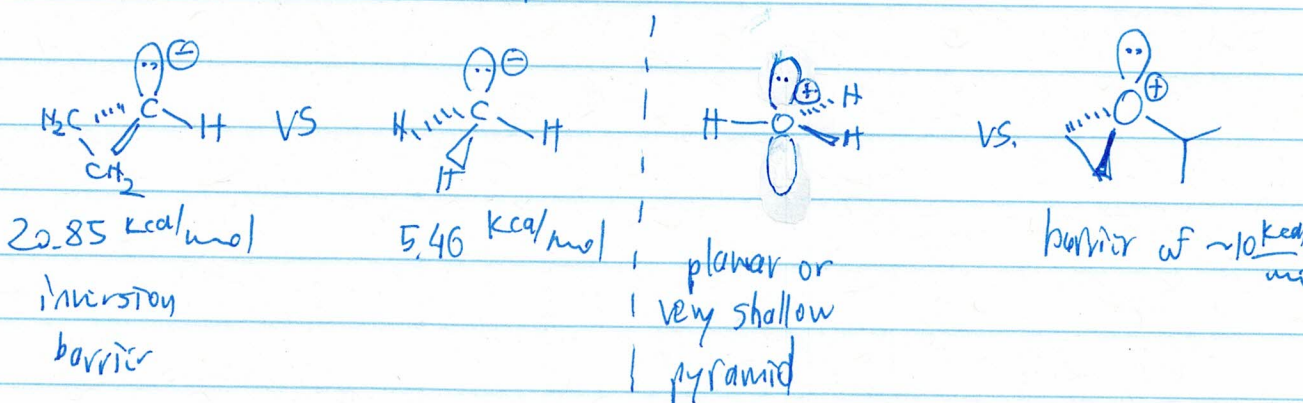
$\alpha$ -electronegative groups can help in planarization too:



Ring Constraint

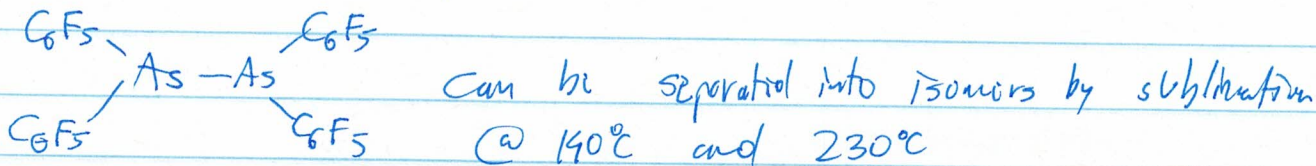


This has an effect on alkyl radicals too:

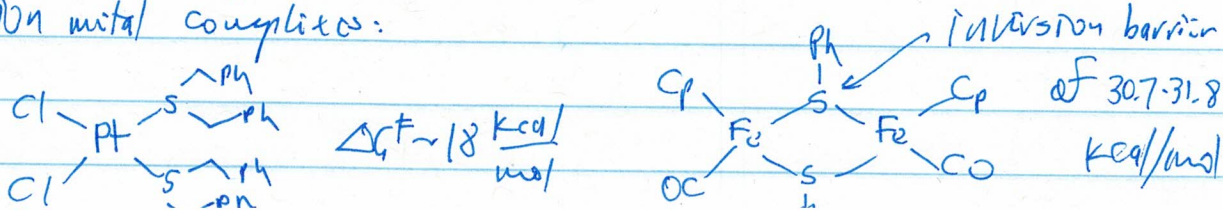


Heteroatom Substitution - generally increases the barrier on N and C

- $\cdot\text{NF}_3$  -  $\Delta G^\ddagger \sim 56-59 \text{ kcal/mol}$
- $\cdot\text{CF}_3$   $\rightarrow$  pyramidal, as opposed to  $\cdot\text{CH}_3$
- $\cdot\text{CFCIBr}$   $\rightarrow$  pyramidal and stable!



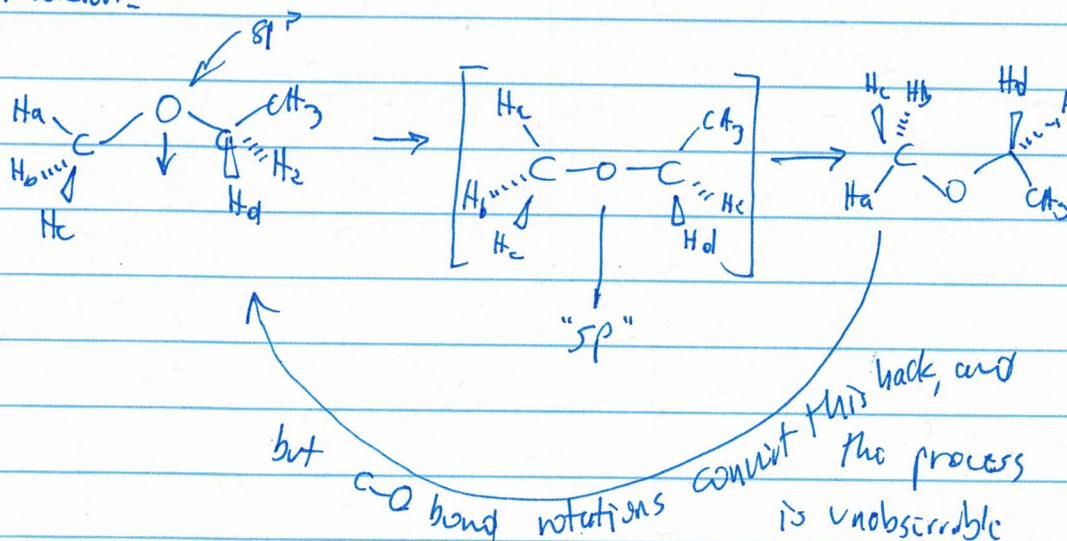
Sulfur is generally conformationally stable but can be labilized in transition metal complexes:



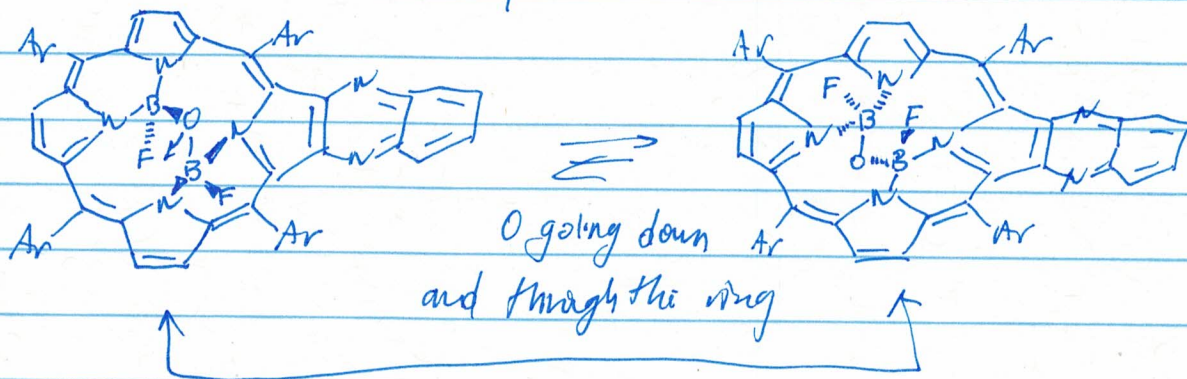
Akaupitoisomerism is a new type of conformational isomerism first observed in 2018 (Nature Chem. 2018, 10, 615-624):

akaupitos (Greek) = inflexible

Bond angle inversion:



But in a constrained macrocycle environment:



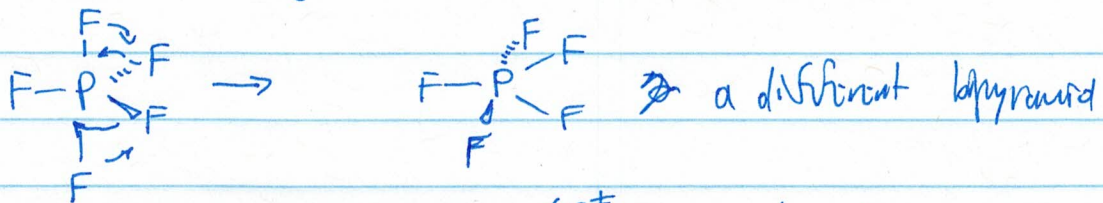
these two compounds can be isolated and they are not related by either pyramidal inversion or bond rotation

$\Delta G^\ddagger$  for interconversion are high,  $\sim 25 \text{ Kcal mol}^{-1}$

Higher-order polytopal rearrangements

-These are generally observed in five- and higher valency coordination geometries. It is very commonly seen in  $\text{PF}_5$ , for example.

Berry pseudorotation: (great video in Wikipedia)



$$\Delta G^\ddagger = 3.6 \text{ kcal/mol}$$

In square pyramidal ~~po~~ compounds such as  $\text{IF}_5$ , something similar happens but with a much higher barrier @  $\Delta G^\ddagger \sim 26.7 \frac{\text{kcal}}{\text{mol}}$