

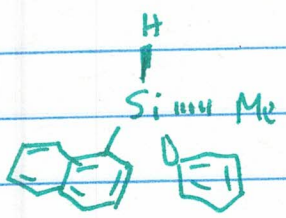
Tetrahedral

Lecture VII: Chirality on Other Atom Centers

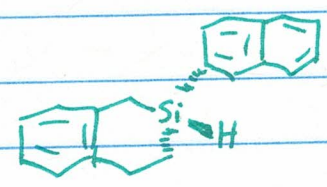
01-29-2020

While chirality of carbon compounds has been most thoroughly studied, the general principles apply to other elements with tetrahedral binding geometry.

Group IV: silicon, germanium, tin, lead



can be easily resolved

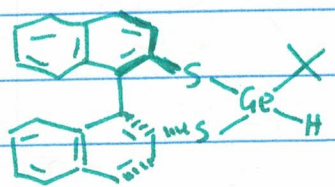


chirality of a silicon center can also be introduced through chiral organic substituents, but then it is not Si-centered

Organosilicon Compounds 2017,

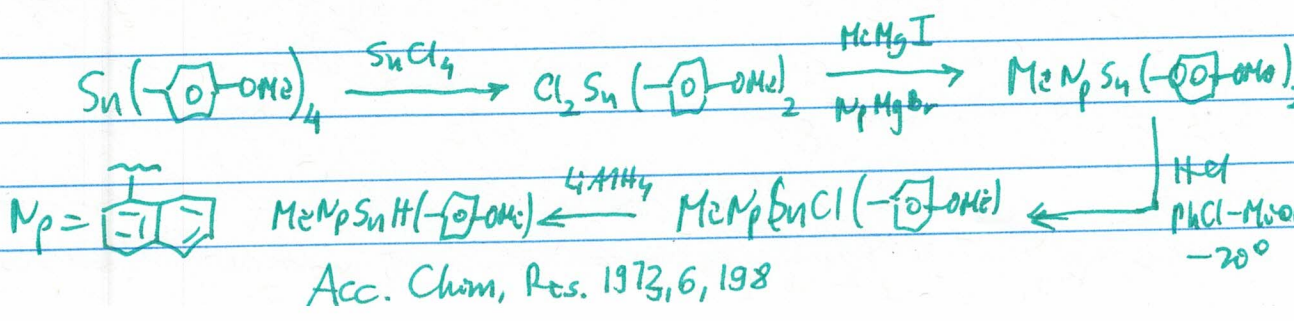
145-184

For germanium, more common way to introduce chirality is through chiral organic ligands



JOC, 2003, 68, 5013

Chiral tin complexes are also known and relatively easily prepared:

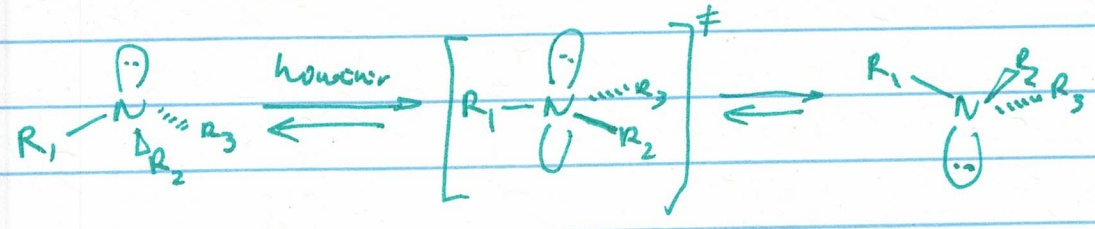


Tetrasubstituted tin derivatives are not configurationally stable. They go to pentacoordinate complexes which are fluxional and at that point lose configurational identity.

Chiral (or) derivatives are also known.

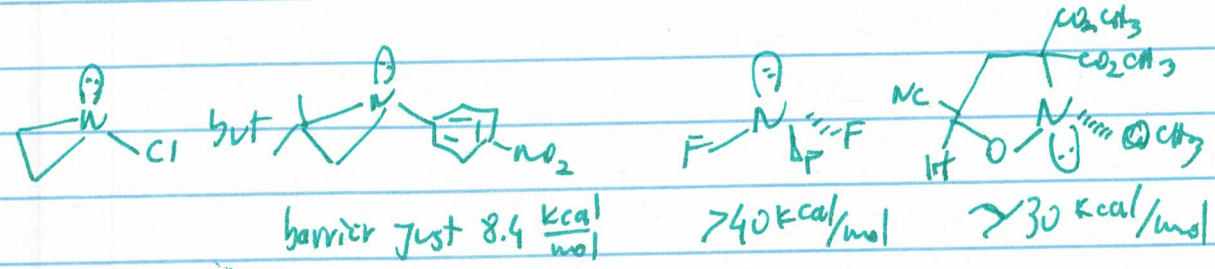
Group V: nitrogen, phosphorus

Amines are in principle chiral.



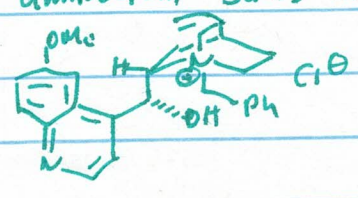
Mislow on pyramidal inversion. ACIE 1970, 9, 400

Some derivatives are stable @ room temperature.



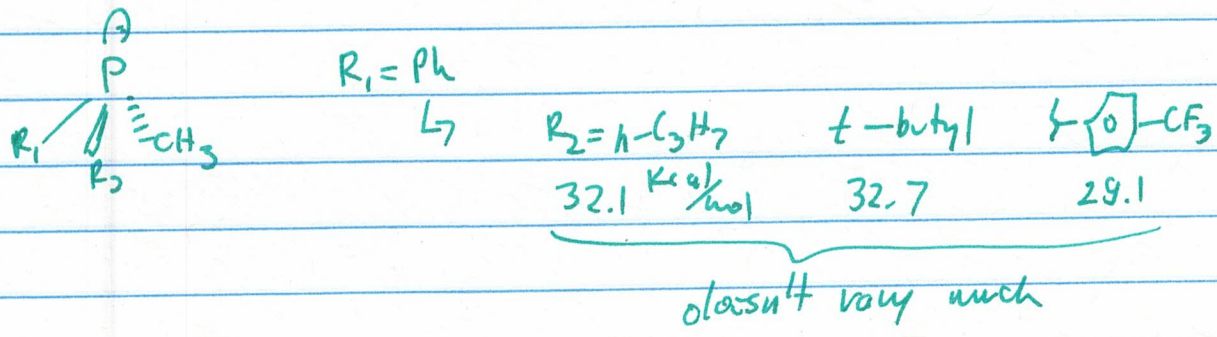
Trisilyl amine is planar: $H_3Si-N(SiH_3)_2$ JACS, 1955, 77, 6491

In general, however, common amines are not configurationally stable. Quaternary ammonium salts are, and some occur naturally:

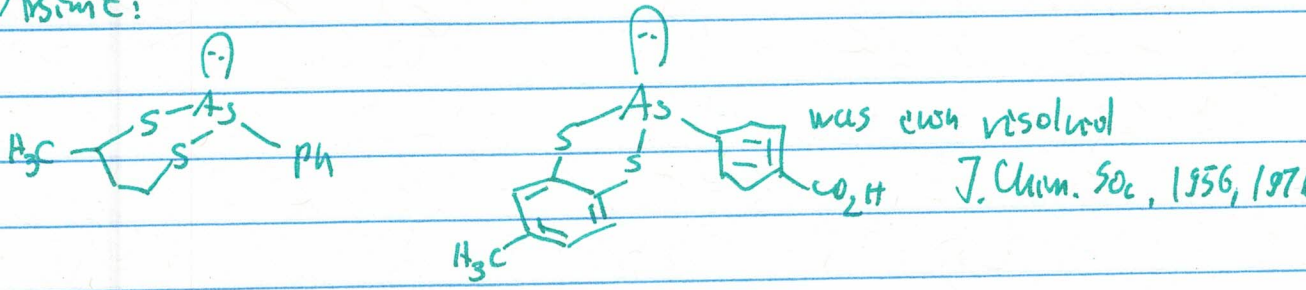


used in catalysis and derived from Cinchona alkaloids

Chiral phosphos, on which the chirality is P-centered, are a lot more stable than amines:

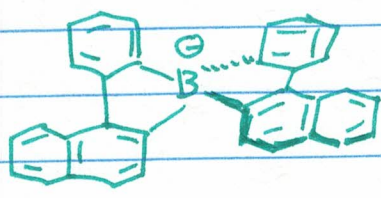


Asinic:

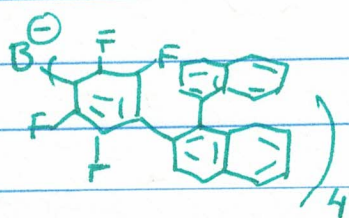


Group III = Boron

Relatively recent reports of borates wherein chirality comes from conformationally locked carbon-based substituents:



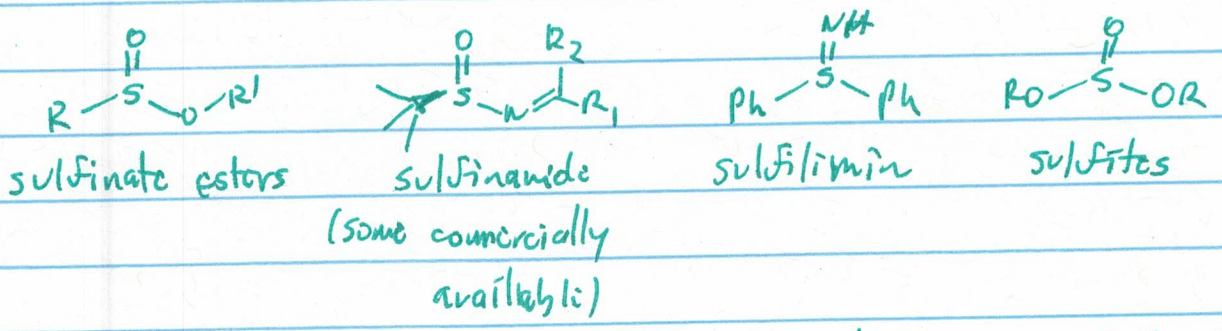
Acta Chem Scand. 1962, 16, 87



Eur. J. Org. Chem. 2017, 2017, 2312

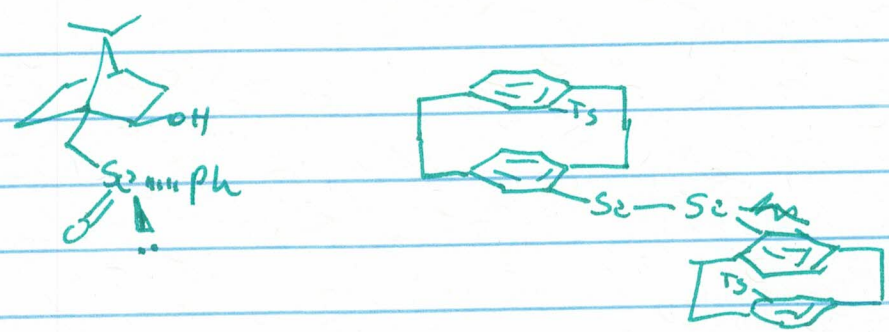
These are important in the growing field of chiral anion catalysis. Rare bc it is B-C bond that leads to chirality: more stable than the more common B-O and B-N links.

Chiral sulfur atoms are quite common and configurationally stable: inversion barriers in sulfoxides are around 30-40 kcal/mole. Similarly, other classes of chiral sulfur compounds are configurationally stable @ rt:

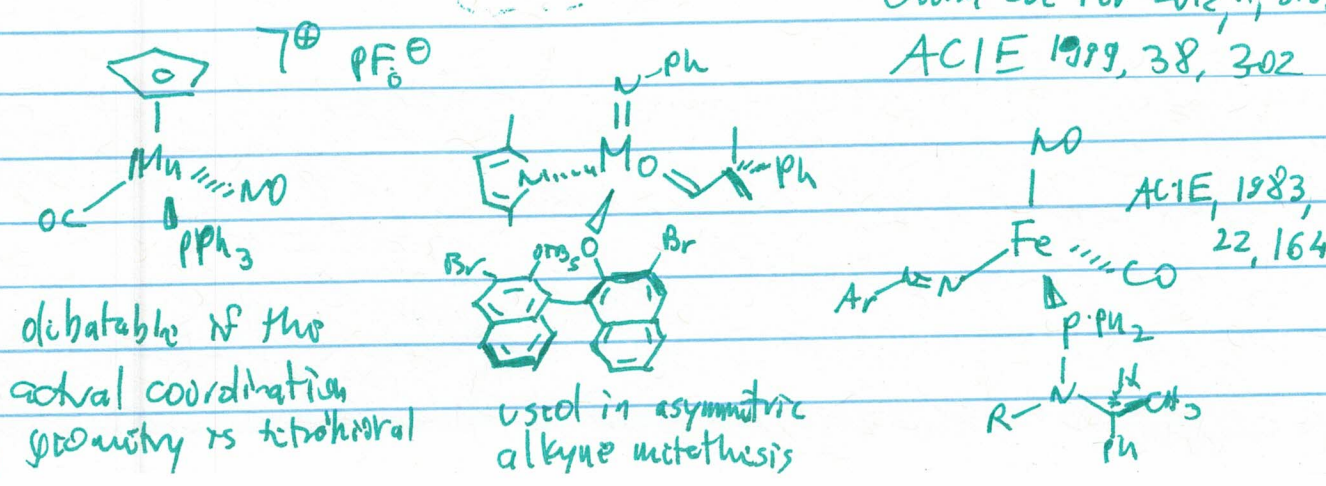


Topic: Chiral Sulfur Reagents: Applications in Asymmetric and Stereoselctive Synthesis

Chiral selenium also common:

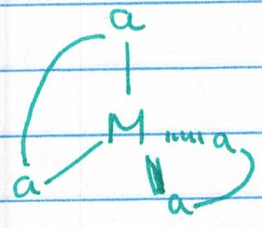


How about metals? Tetrahedral complexes of the Mabcd type exist but are quite rare:



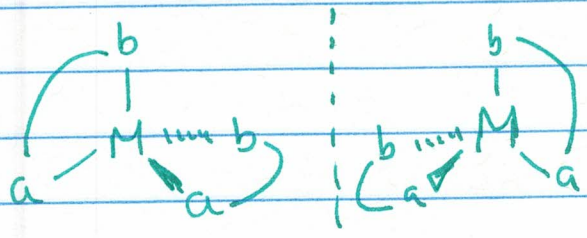
Chem Soc Rev 2012, 41, 315
ACIE 1999, 38, 302

Complexes of a type $M(aa)_2$ or $M(ab)_2$ are much more common:



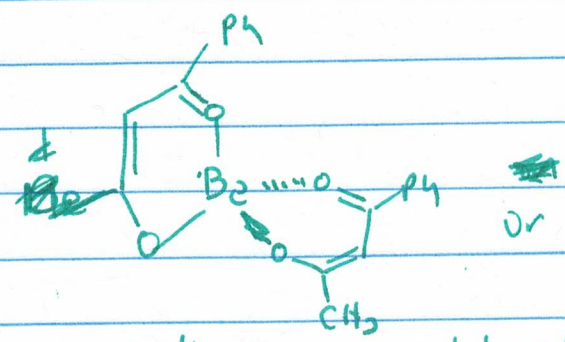
chiral or achiral?

ACHIRAL - planes of symmetry if the ligand is symmetric



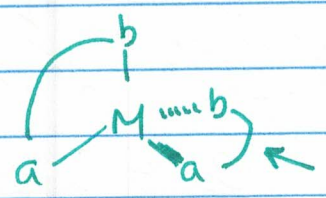
non superimposable - CHIRAL

Example:

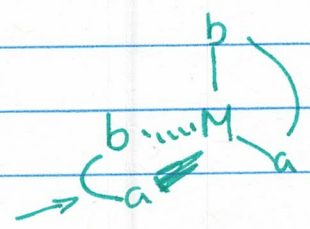


or enantiomer

But here we don't have a tetrasubstituted carbon! How do we assign R or S? We don't:



\Rightarrow to superimpose them, we need to turn the back one to the right: Δ -configuration
skew-line system



\Rightarrow Λ -configuration

Look at Be example again: should be Δ