CENTRAL ATOMS WITH FIVE BONDS

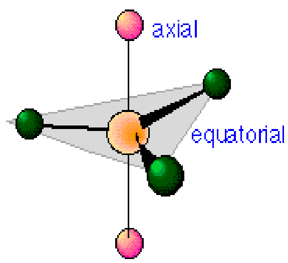
Compounds of the type AX_5 are formed by some of the elements in Group 15 of the periodic table; PCl_5 and AsF_5 are examples.

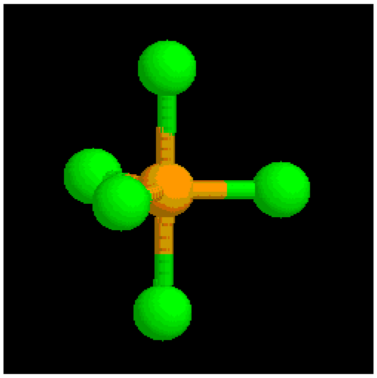
In what directions can five electron pairs arrange themselves in space so as to minimize their mutual repulsions? In the cases of coordination numbers 2, 3, 4, and 6, we could imagine that the electron pairs distributed themselves as far apart as possible on the surface of a sphere; for the two higher numbers, the resulting shapes correspond to the regular polyhedron having the same number of sides.

The problem with coordination number 5 is that there is no such thing as a regular polyhedron with five vertices.

> *In 1758, the great mathematian Euler proved that there are only five regular convex polyhedra, known as the platonic solids: tetrahedron (4 triangular faces), octahedron (6 triangular faces), icosahedron (20 triangular faces), cube (6 square faces), and dodecahedron (12 pentagonal faces). Chemical examples of all are known; the first icosahedral molecule, LaC_{60} (in which the La atom has 20 nearest C neighbors) was prepared in 1986.*

Besides the five regular solids, there can be 15 semi-regular isogonal solids in which the faces have different shapes, but the vertex angles are all the same. These geometrical principles are quite important in modern structural chemistry.

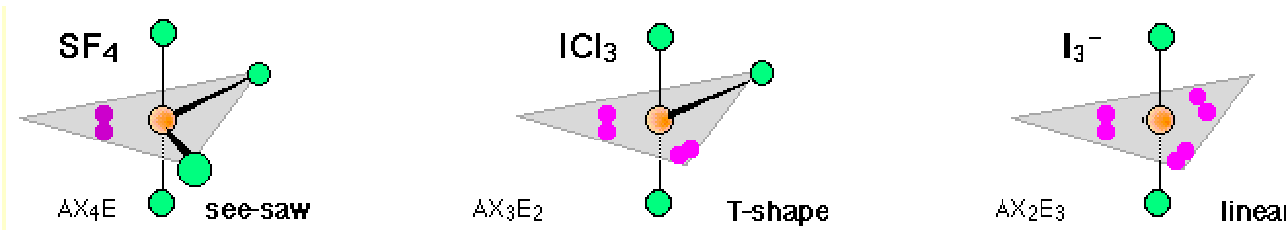




The shape of PCl5 and similar molecules is a **trigonal bipyramid**. This consists simply of two triangular-base pyramids joined base-to-base. Three of the chlorine atoms are in the plane of the central phosphorus atom (equatorial positions), while the other two atoms are above and below this plane (axial positions). Equatorial and axial atoms have different geometrical relationships to their neighbors, and thus differ slightly in their chemical behavior.

In 5-coordinated molecules containing lone pairs, these non-bonding orbitals (which you will recall are closer to the central atom and thus more likely to be repelled by other orbitals) will preferentially reside in the equatorial plane. This will place them at 90° angles with respect to no more than two axially-oriented bonding orbitals.

Using this reasoning, we can predict that an AX4E molecule (that is, a molecule in which the central atom A is coordinated to four other atoms "X" and to one nonbonding electron pair) such as SF4 will have a "see-saw" shape; substitution of more nonbonding pairs for bonded atoms reduces the triangular bipyramid coordination to even simpler molecular shapes, as shown below.



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