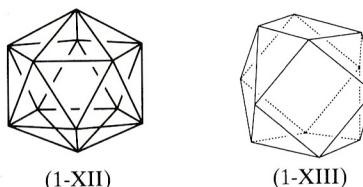


12 equivalent vertices and  $I_h$  symmetry. Icosahedra of boron atoms occur in all forms of elemental boron, in  $B_{12}H_{12}^-$ , and in the numerous carboranes of the  $B_{10}C_2H_{12}$  type. A related polyhedron, the cuboctahedron (1-XIII) is found in several borides of stoichiometry  $MB_{12}$ .



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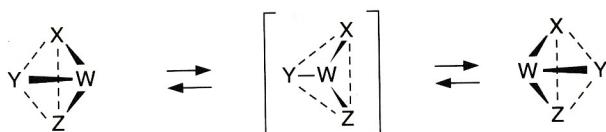
### 1-3 Fluxionality (Stereochemical Nonrigidity)

Most molecules have a single, well-defined nuclear configuration. The atoms execute approximately harmonic vibrations about their equilibrium positions, but in other respects the structures may be considered rigid. There are, however, many cases in which molecular vibrations or intramolecular rearrangements carry a molecule from one nuclear configuration into another. When such processes occur at a rate permitting detection by some physical or chemical method, the molecules are designated as *stereochemically nonrigid*. In some cases, the two or more configurations are not chemically equivalent and the process of interconversion is called *isomerization* or *tautomerization*. In other cases, the two or more configurations are chemically equivalent, and this type of stereochemically nonrigid molecule is called *fluxional*. These will be our main concern here.

The rearrangement processes involved in stereochemically nonrigid molecules are of particular interest when they take place rapidly, although there is a continuous gradation of rates and no uniquely defined line of demarcation can be said to exist between “fast” and “slow” processes. The question of the speed of rearrangement most often derives its significance when considered in relation to the time scale of the various physical methods of studying molecular structure. In some of these methods, such as electronic and vibrational spectroscopy and gas phase electron diffraction, the act of observation of a given molecule is completed in such an extremely short time ( $<10^{-11}$  s) that processes of rearrangement may seldom if ever be fast enough to influence the results. Thus for a fluxional molecule, where all configurations are equivalent, there will be nothing in the observations to indicate the fluxional character. For interconverting tautomers, the two (or more) tautomers will each be registered independently, and there will be nothing in the observations to show that they are interconverting.

It is the technique of nmr spectroscopy that most commonly reveals the occurrence of stereochemical nonrigidity, since its time scale is typically in the range  $10^{-2}$  to  $10^{-5}$  s. The rearrangements involved in stereochemically nonrigid behavior are rate processes with activation energies. When these activation energies are in the range 25 to 100 kJ mol<sup>-1</sup> the rates of the rearrangements can be brought into the range of  $10^2$  to  $10^5$  s<sup>-1</sup> at temperatures between +150 and -150°C. Thus by proper choice of temperature, many such rearrangements can be controlled so that they are slow enough at lower temperatures to allow detection of individual

**Figure 1-6** The inversion of a pyramidal molecule WXYZ. Note that if X, Y, and Z are all different, the *inveromers* are enantiomorphous.



molecules, or environments within the molecules, and rapid enough at higher temperatures for the signals from the different molecules or environments to be averaged into a single line at the mean position. Thus by studying nmr spectra over a suitable temperature range, the rearrangement processes can be examined in much detail. Only one study by any other spectroscopy, infrared, has been reported.<sup>4</sup>

### Fluxional Coordination Compounds

Coordination polyhedra are usually thought of in essentially static terms, that is, as if there are no intramolecular interchanges of ligands. In many cases, especially for octahedral complexes, this is valid, but there is a growing body of evidence that nonrigidity, particularly fluxionality, is not uncommon. In fact, for 5-coordinate complexes and most of those with coordination numbers of 7 or higher, nonrigidity is the rule rather than the exception.

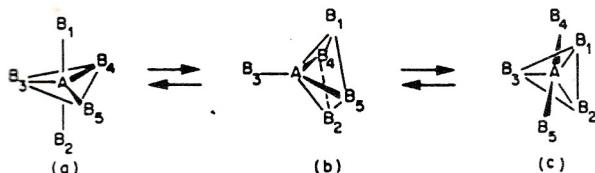
A common type of fluxional behavior is the inversion of pyramidal molecules (Fig. 1-6). In the case of NH<sub>3</sub> and simple non-cyclic amines the activation energies, which are equal to the difference between the energies of the pyramidal ground configurations and the planar transition states, are quite low (24–30 kJ mol<sup>-1</sup>) and the rates of inversion extremely high (e.g., 2.4 × 10<sup>10</sup> s<sup>-1</sup> for NH<sub>3</sub>). Actually, in the case of NH<sub>3</sub>, the inversion occurs mainly by quantum mechanical tunnelling through the barrier rather than by passage over it. In most cases, however, passage over a barrier (i.e., a normal activated rate process) is operative. With phosphines, arsines, R<sub>3</sub>S<sup>+</sup>, and R<sub>2</sub>SO species the barriers are much higher (>100 kJ mol<sup>-1</sup>), and inversions are slow enough to allow isolation of enantiomers in cases such as RR'R''P and RR'SO.

Among 4-coordinate transition metal complexes fluxional behavior based on planar/tetrahedral interconversions is of considerable importance. This is especially true of nickel(II) complexes, where planar complexes of the type Ni(R<sub>3</sub>P)<sub>2</sub>X<sub>2</sub> have been shown to undergo planar ⇌ tetrahedral rearrangements with activation energies of about 45 kJ mol<sup>-1</sup> and rates of ~10<sup>5</sup> s<sup>-1</sup> at about room temperature.

### Trigonal Bipyramidal Molecules

A class of fluxional molecules of great importance are those with a *tbp* configuration. When all five appended groups are identical single atoms, as in AB<sub>5</sub>, the symmetry of the molecule is D<sub>3h</sub>. The two apical atoms B<sub>1</sub> and B<sub>2</sub> (Fig. 1-7) are equivalent but distinct from the three equatorial atoms B<sub>3</sub>, B<sub>4</sub>, B<sub>5</sub>, which are equivalent among themselves. In general, experiments such as measuring nmr spectra of B nuclei, which can sense directly the kind of environmental difference represented by B<sub>1</sub>, B<sub>2</sub> versus B<sub>3</sub>, B<sub>4</sub>, B<sub>5</sub>, should indicate the presence of two sorts of B nuclei in *tbp*

<sup>4</sup>J. J. Turner *et al.*, *J. Phys. Chem.* **1995**, 99, 17532.



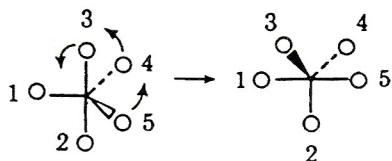
**Figure 1-7** The *tbp-sp-tbp* interconversion, the so-called Berry mechanism or pseudorotation for 5-coordinate molecules.

molecules. In many cases, for example, the  $^{13}\text{C}$  spectrum of  $\text{Fe}(\text{CO})_5$ , and the  $^{19}\text{F}$  spectrum of  $\text{PF}_5$  (to name the two cases where such observations were first made), all five B nuclei appear to be equivalent in the nmr spectrum, even though other experimental data with a shorter time scale, such as diffraction experiments and vibrational spectroscopy, confirm the *tbp* structure.

All the ligands in the nmr spectrum in these cases appear to be equivalent because they pass rapidly between the axial and equatorial sites. Theory shows that if two nuclei occupying sites whose resonance frequencies  $\nu_1$  and  $\nu_2$  differ by  $\Delta\nu \text{ s}^{-1}$  change places at a frequency greater than  $\Delta\nu \text{ s}^{-1}$ , only one resonance at  $\frac{1}{2}(\nu_1 + \nu_2)$  will be observed. Since a ligand can move from an axial to an equatorial site only if there is a simultaneous shift of a ligand from an equatorial site to an axial one, it is clear that only two types of intramolecular\* exchange processes are possible: (1) those in which each step involves one axial and one equatorial ligand, and (2) those in which both axial ligands simultaneously exchange with two equatorial ones. In cases for which direct evidence has been obtained, the second type of process (2-for-2 exchange) is indicated.

It is important to realize that the nmr experiment can never do more than distinguish between two algebraically different permutations (i.e., 1-for-1, or 2-for-2, as above); it can never reveal the detailed pathways of the atoms. Two plausible, idealized pathways have been suggested for the 2-for-2 rearrangement of a *tbp* molecule. One of them, first suggested by R. S. Berry in 1960, is shown in Fig. 1-7. Not only do the *tbp* and *sp* configurations of an  $\text{AB}_5$  molecule tend to differ little in energy, but, as Berry pointed out, they can also be interconverted by relatively small and simple angle deformation motions and in this way axial and equatorial vertices of the *tbp* may be interchanged. As shown in Fig. 1-7, the *sp* intermediate (b) is reached by simultaneous closing of the  $\text{B}_1\text{AB}_2$  angle from  $180^\circ$  and opening of the  $\text{B}_4\text{AB}_5$  angle from  $120^\circ$  so that both attain the same intermediate value, thus giving a square set of atoms,  $\text{B}_1, \text{B}_2, \text{B}_4, \text{B}_5$ , all equivalent to each other. This *sp* configuration may then return to a *tbp* configuration in either of two ways, one of which simply recovers the original while the other, as shown, places the erstwhile axial atoms  $\text{B}_1, \text{B}_2$  in equatorial positions and the erstwhile equatorial atoms  $\text{B}_4, \text{B}_5$  in the axial positions. Note that  $\text{B}_3$  remains an equatorial atom and also that the molecule after the interchange is, effectively, rotated by  $90^\circ$  about the  $\text{A}-\text{B}_3$  axis. Because of this apparent, but not real rotation, the Berry mechanism is often called a pseudorotation and the atom  $\text{B}_3$  is called the pivot atom. Of course, the process can be repeated with  $\text{B}_4$  or  $\text{B}_5$  as the pivot atom, so that  $\text{B}_3$  too will change to an axial position.

\*In both  $\text{PF}_5$  and  $\text{Fe}(\text{CO})_5$  the persistence of  $^{31}\text{P}-^{19}\text{F}$  and  $^{57}\text{Fe}-^{13}\text{C}$  coupling rules out dissociative or bimolecular processes, and there is no reason to doubt that the overwhelming majority if not all fluxional *tbp* molecules rearrange intramolecularly.

**Figure 1-8** The turnstile rotation.

A second process that also results in a 2-for-2 exchange, called the “turnstile rotation” for obvious reasons, is shown in Fig. 1-8. As already noted, no choice between these is possible on the basis of the nmr spectra themselves for an  $\text{AB}_5$  molecule, but theoretical work on  $\text{PF}_5$  and other species favors the Berry process.

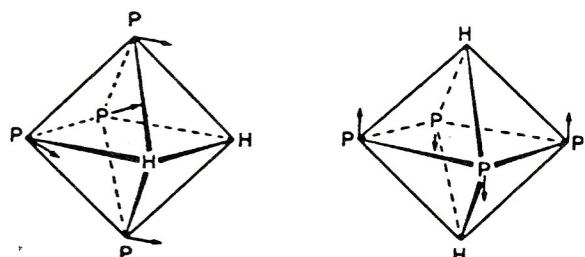
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### Coordination Number 6 or More

The octahedron is usually rather rigid, and fluxional or rapid tautomeric rearrangements generally do not occur in octahedral complexes unless metal-ligand bond breaking is involved. Among the few exceptions are certain iron and ruthenium complexes of the type  $\text{M}(\text{PR}_3)_4\text{H}_2$ . The cis and trans isomers of  $\text{Fe}[\text{PPh}(\text{OEt})_2]_4\text{H}_2$ , for example, have separate, well-resolved signals at  $-50^\circ\text{C}$  that broaden and collapse as the temperature is raised until at  $60^\circ\text{C}$  there is a single sharp multiplet indicative of rapid interconversion of the two isomeric structures. The preservation of the  $^{31}\text{P}-^1\text{H}$  couplings affords proof that the rearrangement process is nondissociative. The distortion modes postulated to account for the interconversions are shown in Fig. 1-9. The rearrangement of “octahedral” bis and tris chelate complexes is considered later.

Stereochemical nonrigidity, especially if it is fluxional, seems likely to be consistently characteristic of complexes with coordination numbers of 7 or greater. All 7-coordinate complexes so far investigated by nmr techniques have shown ligand-atom equivalence even though there is no plausible structure for a 7-coordinate complex that would give static or instantaneous equivalence.

Eight-coordinate structures are usually fluxional. The dodecahedral structure, which is one of the commonest, has two distinct subsets of ligands, but these can easily interchange by rearrangement of the dodecahedron to a square antiprism, and then back, as shown in Fig. 1-10. The fundamental feature of this process is the opening of one or more edges shared by adjacent triangular faces to generate one or more square faces, followed by reclosing of edges in a different way. In this case, two such triangle–square–triangle transformations occur; the Berry process can be viewed as entailing only one such process for each step. There are other

**Figure 1-9** The types of distortion postulated to lead to interconversion of cis and trans isomers of  $\text{Fe}[\text{PPh}(\text{OEt})_2]_4\text{H}_2$ .