

Rây-Dutt Twist—a milestone in mechanistic chemistry

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Reaction mechanism or pathway is essentially a map that tells how a chemical reaction occurs: what are the intermediate stages and how these are transformed into the products. A mechanism is rarely fully proved but it is sustained by its ability to rationalize, to generalize and to predict. One of the central pillars of chemical sciences is reaction mechanism¹.

To be able to invent a mechanism which will be named by the community after the inventor, and which will stand the test of time is a dream of every chemist. The Rây-Dutt twist mechanism is an example per se. This was proposed in a monumental paper² in 1943 and relates to racemization. Racemization is the process of conversion of half of an

optical isomer into another. Molecules which are nonsuperimposable on their mirror images due to their peculiar symmetry (or lack of it) always occur in at least two forms which differ in their ability to rotate the plane of polarization of light in opposite directions but to the same extent. Such molecules are said to be chiral and the two forms are called optical isomers. A simple example is lactic acid³ (Figure 1).

Among inorganic complexes, molecules of type $M(AA)_3$ which are also called tris chelates satisfy the condition of optical activity (Figure 1). Here AA is a bidentate chelate ligand which binds the central metal atom at two positions. Rây and Dutt first suggested a mechanism for the

interconversion of tris chelates such that it was not necessary to break any of the bonds during rearrangement. They worked with the tris biguanide chelates, CoL_3^{3+} where L is the bidentate biguanide ligand, $H_2NC(=NH)NHC(=NH)NH_2$. The racemization of the complex was followed using a simple polarimeter over the temperature range 40–60°C. From analysis of thermodynamic parameters, it was concluded³ that no bonds are broken and the activation process is a mere result of a concerted deformation as shown in Figure 2. The stereochemical rearrangement can be viewed as the simultaneous translation of two of the chelate rings through an angle of 45° in their respective planes, one moving up with respect to the plane of the third chelate ring and the other moving down. These movements constitute a twist and since the threefold axis of the tris chelate is not conserved in the twisted configuration (also called the transition state), it represents a rhombic twist. Rhombic twist is another name of Rây-Dutt twist.

In order to appreciate the seminal nature of Rây-Dutt work, it is only necessary to note that the time was early forties. Little was known about the mechanism of reactions of metal complexes at that time. The first printing of the classic Basolo-Pearson monograph was still fifteen years away (1958)⁴. In the same year Bailar⁵ suggested a second twist mechanism in which the threefold axis is conserved. This was called a trigonal or Bailar twist.

Over the last few decades the Rây-Dutt mechanism has received repeated attention as a plausible pathway of racemization of a variety of tris chelates. Numerous workers^{6,7} have examined the scope and validity of this mechanism of racemization. This milestone in mechanistic invention, now fifty years old, remains fresh as ever forming essential parts of modern textbooks^{1,8}.

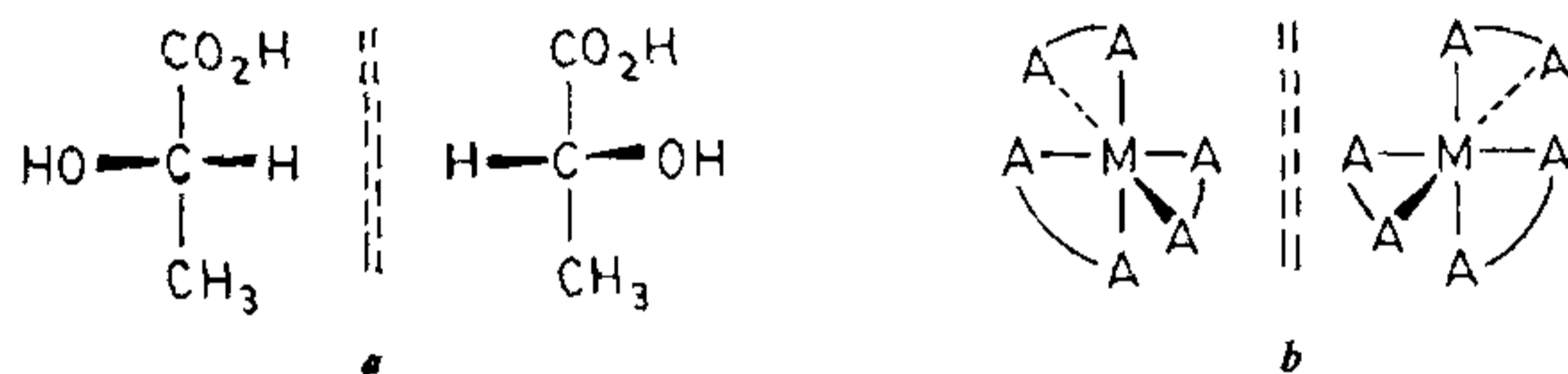


Figure 1. Optical isomers of a, lactic acid and b, $M(AA)_3$.

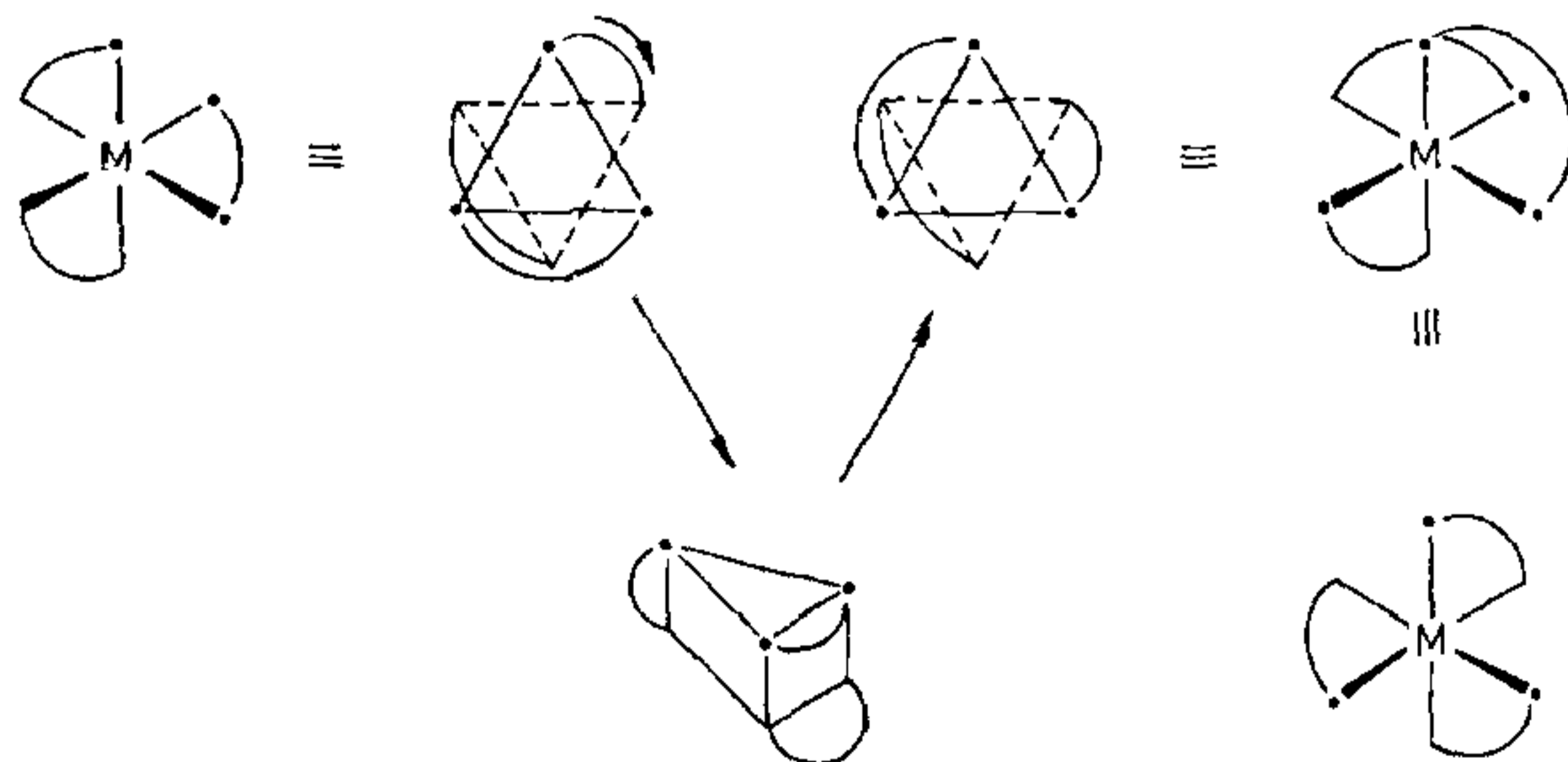


Figure 2. Rây-Dutt twist.

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