

## Communications

### Which Is More Likely: The Ray-Dutt Twist or the Bailar Twist?

Sir:

We have recently developed a model that enables a semi-quantitative determination of the most stable geometry an  $ML_n$  system can adopt.<sup>1</sup> The same principles can equally well be applied to compare the relative energies of two nonstable geometries such as two proposed transition states. Of particular interest is the question of how a tris chelate complex isomerizes if no bonds are broken.<sup>2,3</sup> Application of a symmetry selection rule procedure has previously identified four possible concerted non-bond-breaking mechanisms.<sup>4,5</sup> These are illustrated in Figure 1. The most probable of these mechanisms will be the one with the lowest energy transition state. We must therefore examine the relative stabilities of the four transition states.

The conclusions from the study of the energetics of  $ML_n$  systems that are relevant for this problem are as follows. (Further details can be found in ref 1.) The largest stabilizing contribution to the energy of a tris chelate complex is the metal-ligand bond energy. This is optimized if all the M-L bond lengths are at their "optimal length"; however, it is not always possible to achieve this since the ligating atoms have a hard-sphere radius within which they cannot approach one another. The second most stabilizing contribution to the energy is the dispersion attraction between ligating atoms, which is maximized if the interatomic distance is the sum of their hard-sphere radii.

The  $D_3$  tris chelate reactant geometry has optimal (or only slightly stretched) M-L bond lengths, and the orientation of ligating atoms is such as to maximize their dispersion interactions subject to a short-range repulsive force.<sup>1</sup> For our purposes it is sufficient to model the short-range repulsive force by a hard-sphere radius,  $l/2$ . The distance between the centers of nearest-neighbor ligating atoms belonging to different chelates is greater than or equal to  $l$ , and the average value is as close to  $l$  as possible. A reasonable estimate of  $l$  can be made by measuring the shortest nearest-neighbor distance of the reactant (usually between two atoms related by the 3-fold axis of the complex).<sup>6</sup> The distance between the centers of the ligating atoms of a chelate, the bite size, is denoted  $b$ . As it is determined by the chelate and its bonding to the metal, we assume it remains constant during a rearrangement where M-L bonds are not broken.

Each of the transition states illustrated in Figure 1 cannot adopt optimal M-L bond lengths and retain a distance of at least  $l$  between nearest neighbors. The imposed M-L bond stretching will be the major energy change in going from reactant to tran-

sition state. In some cases an increase in dispersion stabilization slightly reduces the adverse effect of bond stretching on the total energy of the system. Let us consider each mechanism in turn.

The "push through" mechanism has a transition state that requires an M-L bond length stretch of the order of 40%. (For L-M-L  $\approx 90^\circ$  in the reactant, the hard-sphere radius is about  $2^{1/2}$  times the M-L bond length, so if L-M-L  $\approx 60^\circ$  in the transition state, a 40% M-L bond length increase is required.) The "cross over" mechanism requires an average increase in M-L bond length of  $\sim 32\%$  to accommodate the L-L hard-sphere radii (if L-M-L in the transition state is  $\sim 65^\circ$ ). Both these mechanisms therefore proceed via very high energy transition states and are unlikely to be observed.

The other two mechanisms, known respectively as the Bailar and Ray-Dutt twists, are in fact very similar mechanisms. The Bailar twist proceeds by twisting the chelate about its 3-fold axis through a triangular prism to the opposite enantiomer. Although not normally viewed in this way, the Ray-Dutt twist can be seen as an analogous twist about either of the two axes that would have been 3-fold axes in the parent octahedral compound but are not in a tris chelate.<sup>7</sup> The similarity of these two mechanisms is one of the reasons it has been so hard to estimate their relative importance. However, we now have the tools to address the question.

Since it is desirable for there to be as little bond length stretch as possible, the Bailar and Ray-Dutt transition-state chelate geometries,  $T_B$  and  $T_{RD}$ , will be determined by the transition-state symmetry, the L-L bite size,  $b$ , and the L-L hard-sphere distance,  $l$ . For  $T_B$  the position of M relative to L is then defined by the  $D_{3h}$  symmetry of  $T_B$ : the M-L bond length is  $(l^2/3 + b^2/4)^{1/2}$ , and all bond angles are determined. However, for the Ray-Dutt twist the symmetry restrictions on the position of M still leave it one undetermined direction, and hence the M-L bond lengths are not defined by symmetry.  $T_{RD}$  will have two M-L distances of  $(x^2 + b^2/4)^{1/2}$  and four of  $(5l^2/4 + x^2 - 2x(l^2 - b^2/4)^{1/2})^{1/2}$ , where  $x$  is the distance of M from the center of the line joining the ligating atoms of the vertical chelate in Figure 1,  $0 \leq x \leq (l^2 - b^2/4)^{1/2}$ .  $x = l/3^{1/2}$  for the most symmetric case with  $b = l$  and the metal in the middle. For any  $b/l$  ratio the relative stabilities of the two transition states can be compared by plotting the M-L bond lengths as a function of  $x$  ( $T_B$  is independent of  $x$ ). L-M-L bond angles are fixed for any choice of  $x$  but depend on  $x$ .

$T_{RD}$  will adopt the geometry with the  $x$  value that minimizes the M-L bond stretch and hence minimizes its energy. Inspection of Figure 2 indicates the range of behavior possible. A small  $b$  (e.g.  $b = 0.5l$ ) is most likely to proceed via the Bailar twist as its transition-state M-L bond length is always smaller than the Ray-Dutt average T bond length. A large  $b$  (e.g.  $b = 1.5l$ ) will proceed via the Ray-Dutt twist, as it is possible for all Ray-Dutt transition-state M-L bond lengths to be less than that of the Bailar twist. An intermediate value of  $b$  (e.g.  $b = l$ ) may proceed via

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- (4) Rodger, A.; Schipper, P. E. *J. Phys. Chem.* **1987**, *91*, 189.
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- (6) Rodger, A.; Johnson, B. F. G., manuscript in preparation.

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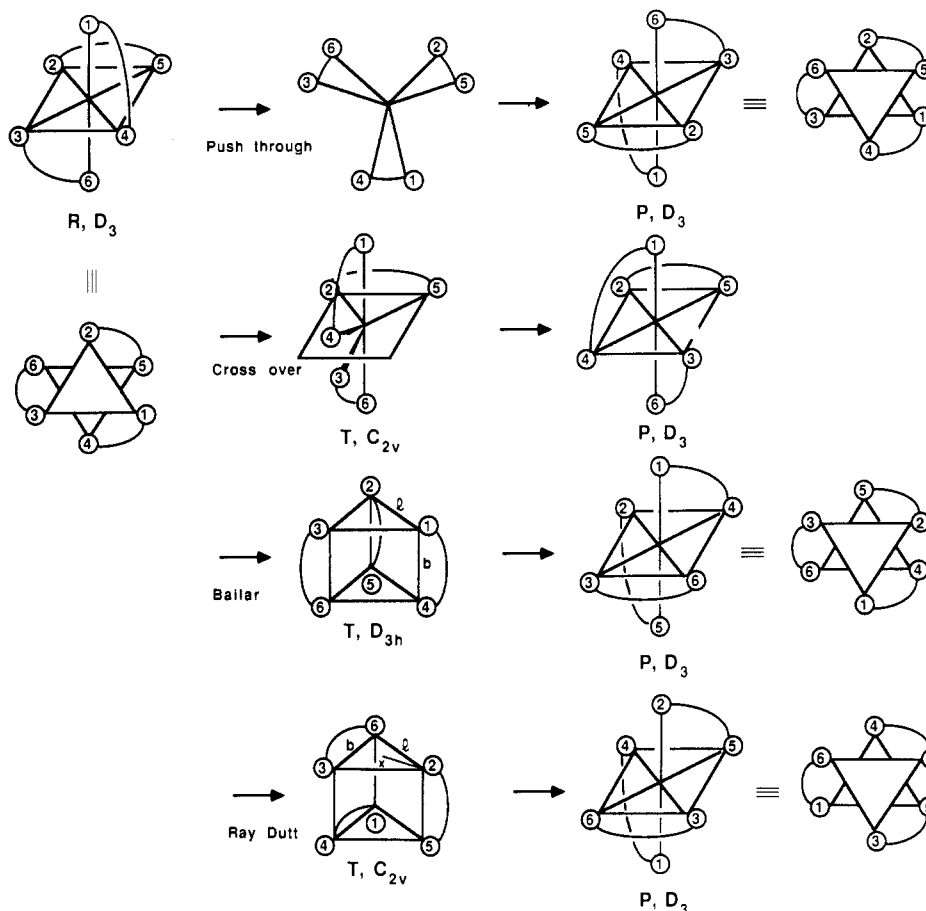


Figure 1. Concerted rearrangement mechanisms for tris chelate complexes.

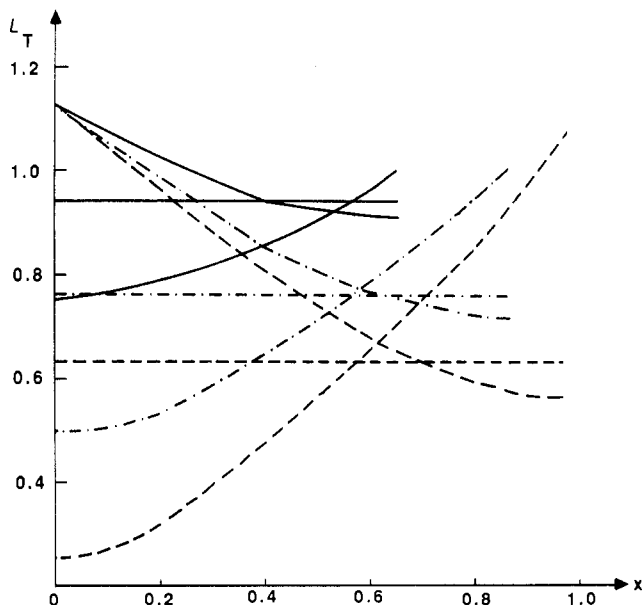


Figure 2. Plots of M-L bond lengths in transition states,  $L_T$ , for tris chelate isomerizations: (---)  $b/l = 0.5$ ; (-.-)  $b/l = 1.0$ ; (—)  $b/l = 1.5$ . Units are defined so that  $l = 1$ . Straight lines are the Bailar T bond lengths; curved lines are the Ray-Dutt T bond lengths.

either mechanism as there will be little difference between the energies of the two structures. In fact, for  $b = 0.914l$  the M-L bond lengths of  $T_B$  and  $T_{RD}$  are all identical.

We have ignored dispersion energy differences in the above discussion. Where there are clear differences in M-L bond lengths, the dispersion effects are small compared with bond length energy differences. Where the bond lengths are closer in magnitude, the dispersion effects are opposite in direction from the bond length effects and so add to the competitiveness of the two mechanisms.

In conclusion, if one wishes to identify a tris chelate complex rearranging via a Bailar twist mechanism, one must have the chelate bite,  $b$ , much smaller than the L-L hard-sphere distance,  $l$  (compounds in Table II of ref 8 with  $b > 2^{1/2}l$  satisfy this criterion). If the converse holds, one would expect to observe only the Ray-Dutt twist, and if a compound is between these two limits, then both mechanisms will be operative.

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### Mechanistic Study of Titanate-Catalyzed Transesterification: Influence of Aggregation on Reactivity

Sir:

Titanium(IV) alkoxides, or titanates, have been employed as catalysts in numerous industrial processes including condensation polymerization, polymer functionalization, and monomer synthesis, but the fundamental chemistry of these reactions has remained relatively unexplored.<sup>1</sup> The recent contributions of Seebach, who

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