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Symmetry Selection Rules for Reaction Mechanisms: Application to Metal–Ligand Isomerizations

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The recently developed CSR (classical selection rule) procedure is developed specifically for application to isomerization reactions between structures with the same point symmetry (homoconversions) and those of different point symmetry (heteroconversions). For homoconversions, a rigorous procedure for determining the product-generating relationship (the combined permutation–point operation relating the two isomers) is discussed. The CSR procedure is then applied to the systematic determination of the concerted reaction mechanisms of metal–ligand isomerizations of complexes of the form ML_n (n = 3–7) and $M(LL)_3$.

1. Introduction

Metal complexes span a wide range of point symmetries, and the delicate balances between electrostatic and dative forces[1,2] results in (i) the possibility of several stable geometries for a given metal–ligand set[3] and (ii) the possibility of rearrangement reactions between chemically indistinguishable or enantiomeric structures. Trigonal-bipyramidal complexes, for example, which should have distinguishable sets of three equatorial and two axial ligands, appear on an NMR time scale as having five equivalent ligands.[4,5] This indicates a rapid isomerization between different trigonal-bipyramidal structures (different in the arrangements of labeled atoms). The dynamics of such isomeric interconversions in the context of simple transition state theory depends crucially on the symmetry changes along the reaction path from one isomer (R) to another (P).

The somewhat broader chemical question implicit in a study of such isomerizations may be summarized in the following way. Given *only* the labeled atom structures of a reactant (R)/product (P) pair, is it possible to determine all the symmetry aspects of the reaction profile (viz. the symmetry of the reaction coordinate in R and P, the symmetry of the structure along this profile, and the symmetry of the transition structure)? A recently developed symmetry selection procedure for reaction mechanisms,[6] referred to as the *classical selection rule* (CSR) procedure, provides a solution to precisely this problem, constituting the first stage of a two-stage procedure that is philosophically consistent with the GSR (generalized selection rule) procedure for spectroscopic processes.[7,8] In application to reaction mechanisms, the CSR stage is a pure symmetry selection stage, with no reference to the *relative* probabilities of the symmetry-allowed pathways. The determination of the *relative energetics* of the CSR-allowed pathways constitutes a secondary SSR (state selection rule) stage. The nature of both stages, as well as a detailed bibliography of earlier theoretical work, is fully discussed elsewhere.[6] In a recent practical formulation of the CSR stage,[9] applications to a range of simple reactions were considered and complete symmetry tables presented to facilitate the implementation of the procedure.

It is the purpose of the present paper to discuss the specific formulation of the CSR procedure for studying intramolecular rearrangement reactions and its practical implementation for determining the symmetry-allowed reaction mechanisms for metal–ligand isomerizations. Experimental evidence for the existence of more than one isomer of a given metal complex and for the equivalence of ligands in five- and seven-coordination structures is readily available, and although mechanisms have been proposed that could account for the experimental observations,[7-15] the CSR procedure in principle *generates* (within a symmetry specification) all the allowed mechanisms, thereby providing a criterion for ensuring that all mechanisms have been proposed.

Although the results that we shall derive are strictly relevant to complexes with identical ligands (as they are derived by assuming maximal symmetry of the ML_n system), the conclusions are, subject to the constraints discussed below, transferable to lower symmetry complexes in the sense that an allowed mechanism cannot become disallowed under the lower symmetry. Such a reaction coordinate in the lower symmetry case will generally be distorted (relative to the coordinate in the higher symmetry case) in a manner consistent with the lower symmetry. However, the reverse is not necessarily true. New mechanisms may come into play in a lower symmetry structure that are effectively forbidden in the higher. These new mechanisms must depend explicitly on the interaction differences leading to the lower symmetry. In either case, the rigorous application of the CSR and the resultant conclusions should, wherever possible, be developed with respect to the *actual* symmetry. Some examples of the effect of lowering the symmetry will be discussed in the applications with respect to approximate C_{3v} inversions, which have been studied in some detail.[15,16]

We shall restrict the applications to coordination number n = 3–7. Extending the results to higher coordination number systems becomes increasingly complex and also less fruitful from a purely chemical perspective as the isomers then are usually structurally and energetically close to one another, requiring only a very small distortion and little energy to change between structures.[10] Also, as the number of coordinated ligands increases, the possibility that the symmetry specification of the transition state (particularly if the transition state symmetry is low) will not uniquely determine all its structural relationships increases.

This paper is structured in the following way. Section 2 develops structural and symmetry relationships in a general but concise way in order to clearly establish a notational base. Section 3 summarizes the basis of the CSR procedure and its practical formulation. Section 4 introduces some additional symmetry

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results concerning the relationships between different paths that are sufficiently general (in the sense of being applicable to a range of isomerizations) to warrant some discussion prior to considering particular applications. Successive sections consider applications to ML_3–ML_7 systems. These applications are largely restricted to the high-symmetry (i.e. all ligands identical) mechanisms, for which symmetry affords a maximal simplification of the mechanisms and for which the practical implementation involves all stages of the CSR procedure. The practical implementation to the lower symmetry systems is then invariably simpler than the applications discussed here.

2. Definitions

Structures and Transformations. *A structure* S (*which may be referred to specifically as the labeled-atom* (*LA*) *structure*) *is fully specified by the notation*

$$\mathrm{S} = \{i,\alpha\}_{\mathrm{s}} \tag{1}$$

where s represents the geometric skeleton, which carries the full point symmetry of the chemical system described by the structure S; α represents a skeletal label, labeling each atomic site in some fixed manner; and i is an atom label such that $i = 1, ..., N$ where there are N atoms in the system. Thus i,α indicates that atom i is on skeletal position α on s, and $\{\}_{\mathrm{s}}$ denotes the set of such specifications.

Two Structures S *and* S′ *are configurationally equienergetic if*

$$\mathrm{S}' = pR\,\mathrm{S} = \{p[i],R[\alpha]\}_{R\mathrm{s}} \tag{2}$$

where p is a permutation operation interchanging chemically identical atoms (acting therefore only on atom labels), and R is a point operation (proper or improper rotation) acting on the labeled skeleton. Although equienergetic, such structures do not necessarily correspond to the same points on the PE surface of the system of atoms constituting the structures.

Two structures S *and* S′ *are configurationally identical if they are superposable* (*in a labeled-atom sense*) *by a proper rotation.* In this case, they simply correspond to different orientations of the same LA structure and therefore correspond to the same single point on the PE surface (the PE being a function only of the internal structure, and not the overall orientation in space).

Two structures S *and* S′ *are configurationally distinct if they are configurationally equienergetic but not superposable* (*in a labeled-atom sense*) *by a proper rotation.* Such structures lie on *different* points on the PE surface. Configurationally distinct structures can potentially be generated (from a reference structure S) by improper point operations or permutation operations, or equivalently by mixed point and permutation operations which are not equivalent to a proper rotation.

The relevance to reacting systems of this discussion of configurationally distinct structures stems from the continuity of a geometry change along the PE surface. Each atom describes, during such a change, its own trajectory, which is continuous and effectively carries the atom label along its path. For example, if P and P′ are products that are mutually configurationally distinct and formed from a particular reactant structure R, then there will be two distinct reaction pathways

$$\mathrm{R} \rightarrow \mathrm{P} \quad \mathrm{R} \rightarrow \mathrm{P}'$$

that transverse different regions of the PE surface from R. All such paths lead to equienergetic products. The total number of such paths depends directly on the possible number of configurationally distinct product structures. Some of these paths, while remaining distinct, may be symmetry-related by relationships that derive from the structure and symmetry of the reactant and thus the reaction coordinates in R. Such symmetry-related paths are equienergetic (with respect to each other) at all points along the respective reaction coordinates and will be discussed quite separately later.

The combined operation

$$L = p\,R \tag{3}$$

may be directly classified according to whether its action on a structure S leads to a structure that is configurationally identical or distinct. In the former case, we may refer to L as a *stationary operation* of S; otherwise, it is referred to as a *generating operation.* This distinction is of central importance in this work, and will be developed in some detail.

Stationary Operations. A stationary operation $L = pR$ of S is one for which

$$L\,\mathrm{S} = \mathrm{S} \tag{4}$$

i.e. a strict symmetry operation of the LA structure. In this case

$$R\,\mathrm{S} = \{i,R[\alpha]\}_{R\mathrm{s}} \tag{5}$$

As the permutative part of L cannot operate on the skeleton or its associated labeling, it follows that

$$R\,\mathrm{s} = \mathrm{s} \tag{6}$$

i.e. R is a point symmetry operation of S in the conventional sense, as the transformation properties of the skeleton define the point symmetry of the structure. The effect of R on the skeletal labeling may, for such a point symmetry operation, be reexpressed as the effect of a corresponding *permutation* symmetry operation $p^\circ(R^{-1})$ of S; i.e.

$$R\,\mathrm{S} = \{i,R[\alpha]\}_{\mathrm{s}} = \{p^\circ(R^{-1})[i],\alpha\}_{\mathrm{s}} \tag{7}$$

It follows that if L is a stationary operation

$$p = p^\circ(R) \tag{8}$$

where $p^\circ(R)$ is the permutation that, if applied to S, leads to the same structure as that obtained by applying the point transformation R^{-1} to S.

This category is trivially generalized to include those combined operations L' that lead to the same structure in a different orientation; viz., if $L'\mathrm{S} = R_{\mathrm{proper}}\,\mathrm{S} = p\,R'\mathrm{S}$, then we simply redefine the relevant stationary operation as $L = p\,R_{\mathrm{proper}}{}^{-1}\,R' = pR$. Thus all configurationally identical structures are related by a stationary operation (modulo proper rotation).

Generating Operations. A generating operation $L = pR$ is one that leads to a configurationally distinct structure; i.e.

$$L\,\mathrm{S} = \mathrm{S}' \ (\mathrm{S},\ \mathrm{S}' \text{ configurationally distinct}) \tag{9}$$

In this case, L may be considered as generating the new structure S′ from S. This may, for reasons that become apparent later, be effected in two separate stages.

(i) Generation of Intermediate Structure S†. The intermediate structure S† is that generated from S by the point operation alone; i.e.

$$R\,\mathrm{S} = \mathrm{S}^\dagger = \{i,\alpha^\dagger\}_{\mathrm{s}}{}^\dagger \tag{10}$$

where

$$\alpha^\dagger = R\,\alpha \quad \mathrm{s}^\dagger = R\,\mathrm{s} \tag{11}$$

(ii) Generation of S′ from S†. The intermediate structure S† defines the skeleton and the skeletal labeling of the final structure S′, which is then determined by the permutative part of L; viz.

$$\mathrm{S}' = p\,\mathrm{S}^\dagger = \{p[i],\alpha^\dagger\}_{\mathrm{s}}{}^\dagger \tag{12}$$

The definition of the intermediate structure proves particularly convenient when the procedure developed here is, in fact, reversed as is the case in the practical formulation of the CSR as presented in the next section; i.e., S and S′ are given, and L is to be determined. Again, these results are trivially generalized to any configurationally distinct structures (modulo proper rotation).

Common Symmetry Operations. A crucial consideration of the CSR procedure is the determination of point symmetry operations that are common to two structures S and S′. A point operation R is common to S and S′ if

$$L\,\mathrm{S} = \mathrm{S} \quad L\,\mathrm{S}' = \mathrm{S}' \tag{13}$$

where L is a stationary operation $p^\circ(R)R$ (modulo proper rotation) of both structures. It follows that a point operation is common to two structures if it relates the same atoms in both structures in precisely the same manner. (This applies irrespective of whether the S and S′ skeletons are symmetry-related or not.) The total set of combined symmetry operations common to S and S′ may be written in the form

$$\mathbf{g}_{SS'} \otimes \mathbf{G}_{SS'} = \mathbf{g}_{SS'} \otimes (\mathbf{G}_S \cap \mathbf{G}_{S'}) \qquad (14)$$

$\mathbf{g}_{SS'}$ is the group of common permutation operations. The determination of $\mathbf{G}_{SS'}$ is most readily determined by writing each point symmetry operation in terms of a permutation notation. Only if the operations in S and S′ have the same form will the operations then belong to $\mathbf{G}_{SS'}$. The most convenient notation is that of conventional permutation theory; viz. $R(1,2,3,4)(5,6)(7)$ means that R^{-1} takes atom 1 to the position of 2, 2 to 3, 3 to 4, and 4 to 1; 5 interchanges with 6; and 7 is unaffected. (This operation is invariant to a cyclic permutation within a bracket and any permutation of entire bracketed arguments.)

Point-Equivalent Atoms. Atoms that are transformed into each other's positions by point symmetry operations must be in identical chemical environments, and may be referred to as *point equivalent*. Otherwise, they are *point inequivalent*. Point-equivalent atoms cannot be distinguished by any chemical experiment, irrespective of time scale. Point-inequivalent atoms will be distinguishable (e.g. by NMR), but then only if a *chemical reaction* that physically effects such an interchange does not occur on a shorter time scale than that of the spectroscopic experiment. Otherwise, the spectroscopic experiment samples the "average" environment of the two atoms, suggesting a higher symmetry than is present in either structure.

3. CSR Procedure for Generating Reaction Mechanisms

We shall be restricting considerations here to concerted reactions.[17] Nonconcerted mechanisms can be viewed as a succession of concerted stages. A concerted reaction can be depicted as starting at a reactant R (point symmetry $\mathbf{G}_R$), proceeding along a reaction coordinate Q_q, which is a normal coordinate of the structure S_q (symmetry $\mathbf{G}_q$) at each point q along the path. It proceeds through a maximum at $S_q \equiv T$ (the transition state with symmetry $\mathbf{G}_T$) and then through to the product minimum at $S_q \equiv P$ (with symmetry $\mathbf{G}_P$). The reaction coordinate is at all stages taken to be well-behaved, i.e., in an harmonic valley with respect to all other degrees of freedom. (A full critical assessment of the well-behaved path, possible exceptions, and their incorporation into the CSR scheme is given in ref 6.) The CSR for a *symmetry-allowed pathway connecting specified* R *and* P may be summarized in terms of three formal results which successively define (i) the symmetry $\mathbf{G}_q$ for $\neq$ R, T, P, (ii) that of the reaction coordinate Q_q (at all points), and finally (iii) the symmetry of the transition state. The parallel practical application is dramatically simplified through an extensive tabulation, particularly of the crucial second stage that actually determines whether a symmetry-allowed path exists and, if so, the symmetry of the reaction coordinate.[9]

It is only necessary to consider a single labeled atom structure R for the reactant, provided that all the mutually configurationally distinct products are considered, leading thereby to a distinct path from R to *each* P. (A different labeled atom structure of the reactant occupies a different but identically contoured region of the PE surface leading to the identical set of reaction pathways to the full set of mutually configurationally distinct products.) The arguments that follow, therefore, apply to a particular reaction mechanism (i.e. a given R and a particular P), and the procedure should, in principle, be applied separately for each configurationally distinct product structure.

Before presenting these results, it is convenient to distinguish between two types of isomerizations. The reaction from R to P is said to be a *homoconversion* if R and P are equienergetic; i.e., the R and P skeletons are related by a proper transformation (an achiral homoconversion) or they are related by an improper transformation (a chiral homoconversion). Otherwise, if R and P are not equienergetic, the reaction may be referred to as a *heteroconversion.* This distinction is crucial to the implementation of the final stage of the CSR procedure.

In the following formulation of the CSR stage, which applies separately for *each* specified (R,P) pair, we quote the pertinent formal results and then, within the discussion of each step, include the practical implementation in italics. We conclude the section with some discussion of the underlying physical basis of the stages and finally with the significance of the product-generating relationship, which is of particular importance in the homoconversions discussed later in the paper.

I. Determination of $\mathbf{G}_q$. The CSR procedure depends critically on the determination of the conserved symmetry operations along the reaction path; i.e. the symmetry group $\mathbf{G}_q$ (q $\neq$ R, T, P) of the structure S_q at nonstationary points. This follows from the constraints implicit in the CSR theorem and the principle of maximal symmetry for homoconversions (see ref 6 for details): viz., for maximal symmetry[17] paths

$$\mathbf{G}_q = \mathbf{G}_{RP} = \mathbf{G}_R \cap \mathbf{G}_P \qquad (15)$$

In practice, the point operations of R *and* P *are listed, by using the permutation notation, in terms of the atom labels that their inverses relate.* $\mathbf{G}_{RP}$ *then contains any operation of a given nature that relates the same atoms in* R *and* P.

II. Determination of the Symmetry of Q_q in R and P. We first consider R, for which there are two possibilities. If $\mathbf{G}_{RP} = \mathbf{G}_R$, then Q_R must be totally symmetric in R, as all the elements of R are conserved. Alternatively, if $\mathbf{G}_{RP} \neq \mathbf{G}_R$, the following considerations apply.

From the augmentation notation of ref 8, if

$$\mathbf{G}_R = [E,\{R_\gamma\}]\ \mathbf{G}_{RP} \qquad (16)$$

then the symmetry of the reaction coordinate in R is determined by the constraints

$$P^{\circ}(\mathbf{G}_{RP})\ Q_R = Q_R \quad \mathbf{A}(\{R_\gamma\})\ Q_R = 0 \qquad (17)$$

where $P^{\circ}(\mathbf{G}_{RP})$ is the totally symmetric projection operator of the group $\mathbf{G}_{RP}$ and $\mathbf{A}(\{R_\gamma\})$ is the augmentation operator corresponding to augmentation of $\mathbf{G}_R$ *from* $\mathbf{G}_{RP}$; i.e.

$$\mathbf{A}(\{R_\gamma\}) = (m + 1)^{-1}(E + \textstyle\sum_\gamma R_\gamma) \qquad (18)$$

where the set $\{R_\gamma\}$ contains the m distinguishable operations not in $\mathbf{G}_{RP}$ such that $\mathbf{G}_R$ has the $(m + 1) \times n$ elements $\{R_\gamma\{R_\nu\}\}$ where $\nu = 1, ..., n$ and $\{R_\nu\}$ are the n elements of $\mathbf{G}_{RP}$. Similar arguments apply to the determination of Q_q in P.

In practice, the symmetry of the reaction coordinate in R *(or* P*) may be deduced directly from Table II of ref 9, which for given* $\mathbf{G}_R$ *(or* $\mathbf{G}_P$*) yields the possible reaction coordinate symmetries and the corresponding* $\mathbf{G}_{RP}$. *This table encapsulates all of the constraints of eq 16–18 above. The reaction is symmetry forbidden if (i) there is no entry for* $\mathbf{G}_{RP}$ *under the relevant table for* $\mathbf{G}_R$ *or* $\mathbf{G}_P$*; or (ii) there is an entry for* $\mathbf{G}_{RP}$*, but the relevant normal coordinate does not exist for the particular structure of* R *or* R. *(This is deduced from Table I of the ref 9.) Otherwise, the reaction is potentially symmetry allowed, and it is possible to proceed to the next step.*

III. Determination of the Symmetry of T. For heteroconversions, the maximal symmetry paths satisfy

$$\mathbf{G}_T = \mathbf{G}_{RP} \qquad (19)$$

For homoconversions, consider a product generating relationship $L = p\ R$ such that

$$R = L\ \mathrm{P} \quad \mathrm{P} = L\ \mathrm{R} \qquad (20)$$

where p is a permutation operation interchanging identical atoms and R is a point operation, subject to the constraints that (i) R is not a symmetry operation (including the identity) of R or P, and (ii) the group describing the symmetry of the transition state structure, having the form

$$\mathbf{G}_T = [E,R]\ \mathbf{G}_{RP} \qquad (21)$$

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[17] Concerted is used here synonymously with one step *and* synchronous; asymmetric (i.e. non maximally symmetric) paths are possible without loss of the CSR symmetry control if the reaction coordinate is not synchronous, but are unlikely to be of significance here. Such paths are discussed elsewhere: Schipper, P. E. *J. Phys. Chem.* **1988**, *92*, 122.

exists. T is then the structure comprising the atoms of R and P that has point symmetry G_T, and has L as a stationary symmetry operation. If (i) a product generating operation does not exist or (ii) there is no such realizable transition state structure, then the R → P reaction is not a concerted reaction along a well-behaved path.

In practice, the product-generating relationship is determined in the following systematic way, by exploiting eq 10–12. (i) The skeletons of R *and* P *are superposed so as to align all their common symmetry elements and no others. (This alignment removes any arbitrary relative orientation factor, which will be common to all the common stationary and generating operations. If such an alignment is not possible, then no L exists.) (ii) The operation R is then that point operation transforming the skeleton of* R *into that of* P *(and* $P^\dagger$*; see eq 11). (iii) The intermediate product structure* $P^\dagger$ *is generated (eq 10) by effecting the point operation R on* R. *(iv) The permutative part of L, viz. p, is then that operation which permutes the atoms of the intermediate structure into* P *(eq 12).*

Restrictions on the Reaction Coordinate. The second stage directly determines whether a normal coordinate of the right symmetry can exist. Two factors may separately lead to a forbidden path; (i) if the symmetry change from G_R to G_{RP} is directly forbidden in the sense that it cannot be achieved by *any single normal coordinate* or (ii) if it is allowed for a normal coordinate that, simply on the grounds of the particular structure of R (e.g. if it has only a small number of atoms), is not present in that particular R. The first factor is particularly interesting, because it highlights the physical origin of the symmetry restrictions in arising from the ability of a single normal coordinate to eliminate, for a given starting symmetry, only those operations to which it is not totally symmetric. A nondegenerate normal coordinate in G_R must lead to G_{RP} having half the operations of G_R (as the second condition of eq 17 can only hold, for Q_R antisymmetric to $\{R_\gamma\}$, if there is only one augmentation operation). If the normal coordinate is degenerate in G_R, however, then a significantly greater symmetry reduction may occur. As the degeneracy must be lifted in G_{RP} (since Q_q is totally symmetric at nonstationary points), a C_n or S_n ($n > 2$) axis of G_R must be destroyed. If n is prime, then the augmentor set $\{R_\gamma\}$ must (for a C_n destruction as an example) contain the elements $[C_n, C_n^2, ..., C_n^{n-1}]$ and G_{RP} will contain at most a fraction $1/n$ of the elements of G_R. For n not prime, not all these elements need be lost. For example, a C_2 axis can be retained for $n = 6$ by motion along an E_2 vibration, and for $n = 9$, the C_3 axis can be retained for motion along an E_3 vibration. Detailed results summarizing all the possible symmetry changes are given in Table II of ref 9.

This selection step also illustrates that the forbiddeness for a *concerted process* (basically the result of the removal of more symmetry elements than can be achieved by motion along a single coordinate) may be lifted by considering the process as a series of concerted paths, each symmetry reduction being separately allowed, with the path then becoming a multistep path.

The Product-Generating Relationship. It is implicit in stage III discussed above that the transition state symmetry can only be higher than that at a general point $q \neq R, P$ (i.e. higher than G_{RP}) if there exists a product-generating relationship $L = pR$ where R is not a symmetry operation of R or P. (If it is a symmetry operation of R and/or P, then it is readily shown to be a conserved stationary operation along the entire path and thus cannot by definition be a generating operation.) The existence of such an operation implies that the skeletons s_R and s_P of R and P are related by the point transformations

$$Rs_R = s_P \quad Rs_P = s_R \tag{22}$$

and that $R^2s_R = s_R$ and $R^2s_P = s_P$. Thus R and P are either (i) mutually enantiomeric or (ii) chemically indistinguishable. In either case, R and P are equienergetic but, of course, configurationally distinct. Case i applies directly to chiral inversions, whereas case ii applies to isomerizations between chemically identical structures in which the positions of chemically identical atoms have been interchanged.

Perhaps the most important property of the product-generating relationship is the fact that it must be a stationary symmetry operation of T; i.e. $pRT = T$. This immediately implies that $p = p^\circ(R)$ in the transition state. Thus the additional point symmetry of T is not only defined with respect to the conserved elements, but the exact manner in which it must interchange the atoms in T is also specified. It is possible in some cases for an operation L to be found that satisfies both constraints i and ii in stage III above but cannot be a stationary operation of T and thus lead to a forbidden pathway as the transition structure is forbidden. (In such a case, for example, two continuous atomic trajectories may be required to pass instantaneously through a common point, which is of course physically impossible.) It is important to appreciate, however, that this selection constraint depends crucially on the physical nature of the structure.

The physical significance of the product-generating relationship stems ultimately from the continuity of the geometry change along the reaction path. As a permutation relationship between two structures cannot be effected physically by a discontinuous interchange, it must result from a continuous geometric distortion of the skeleton and the attached atoms. This is precisely why G_T must be of higher symmetry than G_{RP} if a product-generating relationship exits, for only then can the permutative part of L (viz. p) find a continuous mechanistic "geometric" expression through the extra symmetry element R of T. The permutation is then effected physically through continuous skeletal distortions by moving along $+Q_T$ (to give P) or $-Q_T$ (to give R) from T, where Q_T is the reaction coordinate in T and $RQ_T = -Q_T$. It is for this reason that we have clearly expressed our symmetry arguments in terms of separate point and permutation operations (see, for example, ref 18 for an alternative expression of our results in terms of permutation-inversion groups), as they may be considered as playing compatible but distinguishable physical roles.

It is interesting to note that the definition of the product-generating relationship determines, with respect to the conserved elements as stationary in space, the actual *motion* of R into P and hence their relative orientation with respect to the stationary elements. This is particularly convenient for visual representations of the mechanisms. Every figure in the present paper illustrates an R, T, P concerted pathway by representing the structure at the three key points, with each such structure sharing the common reference system in which the conserved elements are both stationary and coincident with the "natural" axes of the page on which it is written (i.e. horizontal, vertical and out-of-plane normal).

Symmetric Two-Step Homoconversions. The CSR procedure generates symmetry-allowed pathways for concerted processes. In application of the rules to a particular structure, in particular for homoconversions, the symmetry-allowed pathways are crucially dependent on the existence of a transition structure that both is a stationary point and has a negative curvature (i.e. is a maximum in the energy). However, *classical symmetry arguments are fundamentally incapable of discriminating between a maximum or a minimum*, as they make no reference to quantitative energetics. Thus it is quite possible in practice for an actual structure predicted by the CSR scheme as a potential transition state for a homoconversion, for example, to be a *minimum* on the PE surface, a possibility that increases with increasing coordination number. In this instance, the concerted path reduces, in fact, to a potential two-step path in which the minimum structure is an intermediate; each step is then effectively a heteroconversion between the initial reactant (or product) and the intermediate. Use of the principle of continuity through the intermediate (i.e. along the entire multistep path) ensures that the symmetry of the reaction coordinate is similar to that of the potential concerted path for the homoconversion, but the transition state for each individual heteroconversion step will now have the same symmetry as the structure at nonstationary points.

Although symmetry cannot discriminate whether a homoconversion is concerted or two step via an intermediate, it does tell us that the structure having the augmented symmetry (i.e. having

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the point operation of the product-generating relationship) is *either* a transition state (in which case it is concerted) *or* an intermediate (in which case it is two step). Chemical proof for the existence of *one* of these pathways is sufficient to preclude the existence of the other, as they involve the same reaction coordinate in the reactant.

4. Symmetry-Related Pathways

The CSR procedure deals with symmetry elements that are preserved along a particular reaction pathway; i.e. with symmetry relationships of the structures *along* that path. In addition, the existence of a product-generating relationship may be interpreted as a symmetry of the reaction profile about the transition state or alternatively as an antisymmetry of the reaction coordinate through T. These two symmetry aspects are sufficient to define the full set of symmetry-allowed pathways. However, there is a third symmetry aspects that is particularly useful for classifying related types of allowed reaction mechanisms. This aspect concerns the potential symmetry relationships *between* different pathways, which have their origin in the point symmetry operations R of the reactant, and may be considered as a symmetry of the PE surface about R.

If R *has a stationary symmetry operation* $L = pR$, *then the paths* (I) R $\rightarrow$ P via Q and (II) R $\rightarrow$ LP via RQ *are either* (*i*) *identical or* (*ii*) *symmetry-related.*

The identity applies if $RQ = Q$, for then paths I and II collapse to the single path I, R being preserved along the path. Effectively, L remains a stationary operation along the entire path, which follows from noting that $p = p^{\circ}(R)$ at each point. On the other hand, if $RQ \neq Q$, R must be lost along the path and hence is not in G_P. Generally, pRP is configurationally distinct relative to P. The discussion that follows applies directly to this general case.

As R must be a symmetry operation of R, motion along Q and RQ from R must proceed through *chemically indistinguishable* structures. Symmetry-related paths therefore have identical energy profiles with respect to motion along Q and RQ, respectively, and the corresponding products must be formed at the same rate. Symmetry-related pathways are of a number of types, depending on the nature of the symmetry operation generating the different reaction coordinates.

Narcissistic Pathways. If $R = \sigma$ or i, then $RQ = -Q$ if R is lost. Thus there will be two pathways, along different directions of the same normal coordinate in R (which may be degenerate in which case other *augmentor* elements must also be lost or nondegenerate). Such reactions are termed "narcissistic" as each point of structure S on one path is (in a labeled atom sense) the reflected or inverted form of the equienergetic point on the other path.

Pseudonarcissistic Pathways. If $R = C_{2p}$ but the C_p operations about the same axis are retained in the product (including the trivial case C_2), then

$$C_{2p}^2\,Q = C_p\,Q = Q \quad C_{2p}Q = -Q \tag{23}$$

In this case, the motion is again along $+Q$ or $-Q$ for the two pathways. However, in this case, motion can only occur along a nondegenerate mode. Such reactions may be termed pseudonarcissistic.

Degeneracy-Related Pathways. Degenerate modes in R must resolve the degeneracy in moving along the reaction coordinate. Thus, if the degeneracy is the result of the set of cyclic operations $\{C_n^k\}$, then

$$C_n\,Q = Q' \tag{24}$$

where $Q' \neq \pm Q$. In such a case, the nature and number of the symmetry-related pathways depends on the value of n and the symmetry of the degenerate mode in R. The results are fully tabulated in table II of ref 9, in which the notation $r \times G$ indicates that there are r degeneracy-related pathways leading to r different products all with the point symmetry G but with the operations relating different atoms in the various products. We quote some particular results by way of illustration.

***n* Prime, *n* > 2:** The destruction of the C_n axis requires that all the elements $\{C_n^k\}$ $k = 1, ..., n$ be lost. There exist therefore n symmetry-related paths in all along the coordinates Q, $C_n\,Q$, ..., $C_n^{n-1}\,Q$.

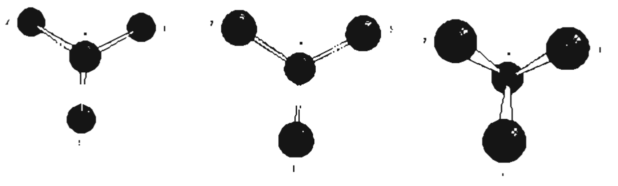

Figure 1. R, T, P structures for the ML_3 (C_{3v}) homoconversion with symmetry specification C_{3v}(R), C_{3v}(q), D_{3h}(T), and $A_1(Q_R)$.

***n* = *pq*, *n* > 2:** For an E_p vibration, if $p < n/2$, $C_{n/q}$ is retained. Otherwise, for an E_k vibration, the $C_{n/r}$ is retained, with r the smallest integer such that kr/n is integral.

In all of the above cases, other augmentor elements may be lost, such that narcissim, for example, may apply additionally to the degeneracy-related pathways generated by odd-order rotations if i or σ is also lost.

There is a particular case when apparently degeneracy-related pathways collapse to the same path. For example, for certain homoconversions in which the reactant and product have a C_n axis ($n > 2$) which is not conserved along the reaction path, the loss of the C_n axis arises from the fact that the C_n rotation is defined with respect to different permutations of atoms in R and P. As this must occur along a degenerate mode of R (and P), we might expect, from the above considerations, that there are a number of degeneracy-related pathways. However, if pC_nR = R and pC_n^{-1}P = P, then pC_nP = C_n^2P, which is configurationally identical with P. Effectively, for this case (see for example the T_d homoconversion later), the degeneracy-related pathways collapse to a single path simply because each pathway leads to the same product but in different orientations.

5. Three- and Four-Coordinate Structures

Both three- and four-coordinate ML_n structures with D_{nh} symmetry must have all the ligands point equivalent, which is also the case for the possible C_{3v} structure for $n = 3$ and the possible C_{4v} and T_d structures for $n = 4$. Thus any homoconversions cannot be probed, for example, by NMR, even if they are sufficiently slow, unlike the heteroconversions, which may be probed spectroscopically. This does not mean, however, that the homoconversions are not of intrinsic chemical interest. For example, the $n = 3$ C_{3v} homoconversion may be considered the high-symmetry precursor of the C_1 pyramidal MLL′L″ chiral homoconversion, i.e., the simplest example of a chiral inversion. Similarly, the absence of a concerted mechanism for the $n = 4$ D_{4h} homoconversion (which we shall demonstrate rigorously below) provides a rationale for why ligand exchange in such complexes must be multistep. We shall treat the $n = 3$, 4 systems in some detail, as their simplicity allows for an explicit implementation of the CSR procedure in its most transparent form.

***n* = 3 Homoconversions.** There is only one configurationally distinct D_{3h} structure, and two configurationally distinct C_{3v} structures. Only the C_{3v} homoconversion is therefore relevant here, and it may be analyzed according to the procedure developed in earlier sections in the following manner, by using the labeling of Figure 1.

I. $G_q = G_{RP} = C_{3v}$. This follows by noting that the z axes may be chosen so that, for example C_3 = (1,2,3) in both R and P.

II. The symmetry of the reaction coordinate must therefore be A_1 in both R and P, and in fact along the entire path except in T.

III. If the concerted reaction is to be symmetry allowed, there must exist a product-generating relationship. Alignment of the conserved point operations (including the sense of any rotations) in R and P leads to the skeletons being related by a σ_h-operation (the reflection plane passing through the metal parallel to the plane containing the three ligands). Thus $G_T = [E,\sigma_h]\,C_{3v} = D_{3h}$. Performing the reflection on R leads to P^t, which is in fact identical with P; thus, the permutative part of L is the identity (1)(2)(3), which then dictates that the transition state *must* be planar. This is precisely what we would expect.

An allowed pathway in a higher symmetry case will always correspond to (i.e. is a precursor for) an allowed path for any of its subgroups. The above (achiral) C_{3v} homoconversion corresponds directly to the (chiral) C_1 homoconversion of a chiral MLL′L″ structure through the planar C_s transition state; i.e. to the simplest example of a chemically relevant chiral homoconversion in which the two C_1 structures are chemically chiral. (However, the actual form of the reaction coordinate will then be of the lower symmetry consistent with the conserved C_1 symmetry.) This also illustrates a general feature of chiral homoconversions. Because there must be a product generating relationship involving an improper point transformation (as the skeletons are related in this way), it follows that the transition state must contain such a point symmetry operation; i.e. *transition states for concerted chiral homoconversions (optical inversions) must* be *achiral*. Other *approximate* C_{3v} reactant structures will also lead to distorted forms of this inversion coordinate consistent with the actual lower symmetry. For example, if the reactant has the symbolic formula MLLL′ with L $\neq$ L′, then the inversion should strictly be based on a C_s reactant, proceeding through a C_{2v} transition state of either a T or Y shape. This is indeed supported by recent studies of such inversions.[15,16] MLLL′ systems may also have a stable C_{2v} geometry, in which case the respective homoconversion must be multistep. These lower symmetry mechanisms are totally consistent with and predicted by the CSR. In the rest of the work, however, we shall restrict explicit discussion to the higher symmetry cases, with the understanding that the treatment of other lower symmetry systems may be effected in an analogous and generally simpler manner.

***n* = 3 Heteroconversions.** If the D_{3h} structure is a minimum on the PE surface, the n = 3 C_{3v} homoconversion is not concerted, the D_{3h} structure then being an intermediate and the homoconversion then becoming two separate heteroconversions $C_{3v} \rightarrow D_{3h}$, i.e., reducing to the symmetric two-step homoconversion. Each individual heteroconversion is readily shown, in a manner analogous to that above, to proceed through $G_q = C_{3v} = G_T$ (the latter following directly from the different skeletal structures of R and P), with the reaction coordinate being of A_2'' symmetry in D_{3h} and A_1 in C_{3v}. The two separate heteroconversions are mutually narcissistic, resulting from motion along the positive or negative direction of the reaction coordinate in the D_{3h} structure. The loss of the σ_h reflection plane of the (minimum energy) D_{3h} structure is the source of the narcissism. The reaction corresponds directly to the $C_s \rightarrow C_1$ reaction path (via a reaction coordinate of A″ symmetry) of the subgroup planar MLL′L″ (C_s) structure, i.e., to the simplest reaction in which the prochiral C_s structure is converted (in the absence of any chiral perturbation) into the chiral C_1 products. The narcissism of such a reaction dictates that the two chiral antipodes are formed at precisely the same rates and thereby provides the fundamental symmetry reason why achiral systems can, in isolation, lead only to racemic products and never to a single enantiomeric product.

***n* = 4 Homoconversions.** The D_{4h} homoconversion may be shown to satisfy stages I and II by going via $G_q = C_{2v}$. However, the *concerted* reaction is symmetry forbidden because a product-generating relationship does not exist. In this case, alignment of the conserved elements in R and P leads to complete superposition of the skeletons; i.e., they are related by the identity. As this cannot serve as the point operation in a generating relationship, it follows that such an operation does not exist. Alternatively, when the C_{2v} elements are aligned, then other noncommon symmetry elements are also aligned, so that L cannot exist. In physical terms, the interchange of atoms 2 and 3 cannot be effected by a concerted continuous geometric change. The lower symmetry analogue of this interchange for MA_2B_2 complexes is the cis–trans isomerization, which may therefore be expected to be nonconcerted.

The T_d homoconversion (shown in Figure 2) is only concerted if the D_{4h} structure is not itself a minimum. This follows from applying steps I–III to the two possible T_d structures.

I. $G_{RP} = D_{2d} = \{E, C_2(1,3)(2,4), C_2(1,4)(2,3), C_2(1,2)(3,4), \sigma(2,4), \sigma(1,3), S_4(1,2,3,4), S_4^3(1,4,3,2)\}$.

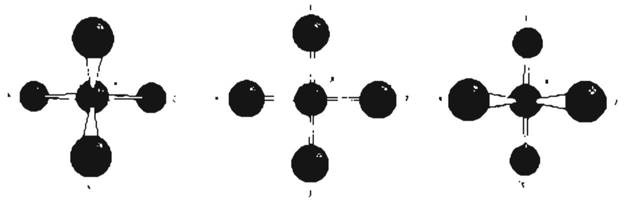

Figure 2. R, T, P structures for the ML_4 (T_d) homoconversion with symmetry specification T_d(R), D_{2d}(q), D_{4h}(T), and E(Q_R).

II. $\Gamma(Q_R)$ = E in T_d.

III. The reactant and product are equienergetic, and there exists the product generating relationship $L = (1)(2)(3)(4)\ \sigma_h$ (determined in a manner analogous to that of the C_{3v} homoconversion). Thus the reaction is symmetry allowed through $G_T = [E,\sigma_h]\ D_{2d} = D_{4h}$ and proceeds through a mode of E symmetry in R (or P). The transition state must again be planar since $L = (1)(2)(3)(4)\sigma_h$ is a stationary symmetry operation of T, and the T_d homoconversion is only concerted if the D_{4h} structure is its transition state. (Although in this case the reaction coordinate is degenerate in R, there are no degeneracy-related pathways because, as discussed in the concluding paragraph in the section on symmetry-related pathways, the C_3 axis is lost by both R and P and pC_3R = R, pC_3^{-1}P = P.)

***n* = 4 Heteroconversions.** The potential heteroconversions between a D_{4h} structure and different symmetry products such as those of T_d or C_{4v} symmetry may be treated by using the $D_{4h} \rightarrow T_d$ reaction as an example. This heteroconversion corresponds directly to one of the two heteroconversions that are deduced from the T_d homoconversion if it is nonconcerted, i.e., if the D_{4h} structure is a minimum and not a maximum on the PE surface. Considering only one of the D_{4h} reactant structures, there are two possible configurationally distinct products of T_d symmetry. We consider first that product shown as the reactant in the homoconversion of Figure 2 (the reactant in the heteroconversion corresponding to the transition state structure in the same figure). Then, following the three stages of the CSR, we have points I–III.

I. $G_{RP} = D_{2d}$ (as defined above).

II. From Table II of ref 9, $\Gamma(Q_R) = B_{1u}$ in D_{4h} and $\Gamma(Q_P)$ = E in T_d. Both vibrations are allowed for the structures in question (from Table I of the same reference).

III. The reactant and product structures are not equienergetic, and thus $G_T = D_{2d}$. The remaining product arises from the narcissistic reaction. The narcissism arises directly from noting that $D_{4h} = [E,\sigma_h]\ D_{2d}$; i.e., the σ_h is lost in moving from R, and the two reactions result from motion along opposite directions of the reaction coordinate in R.

Finally, the reaction $T_d \rightarrow D_{2d}$ is a symmetry-allowed process for all four-coordinate structures, so if there is a D_{2d} minimum energy structure, then the reaction can proceed through the same E mode of the previous example. There will then be three degeneracy-related pathways leading to three corresponding configurationally distinct products of the lower symmetry. Note again that the above arguments for T_d inversions are modified if the system has only *approximate* T_d symmetry.

6. Five-Coordinate Complexes

Five-coordinate complexes may exist in two common forms: trigonal bipyramidal (D_{3h}) and square pyramidal (C_{4v}).[4,10] The trigonal-bipyramidal structure is the most common. We may consider a number of possible interconversions, but we shall restrict our attention to potential D_{3h} homoconversions that exchange point inequivalent atoms, and the $D_{3h} \rightarrow C_{4v}$ heteroconversion. The D_{3h} homoconversion is of particular interest, as the empirical NMR data[4,5] suggests that all the ligands in the trigonal-bipyramidal structure are equivalent. This is not possible for the static structure, in which two ligands are axially point equivalent, three are equatorially point equivalent, and axial and equatorial ligands are strictly point inequivalent. This suggests that the potential D_{3h} homoconversions occur faster than the time scale of the NMR experiment, as supported by temperature-dependent studies.[5] We shall indeed show that two concerted mechanisms are symmetry

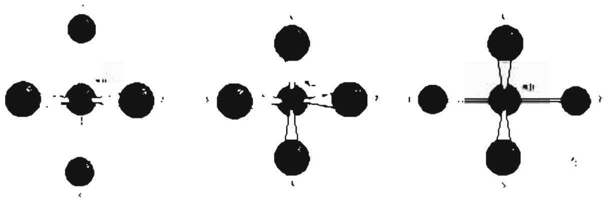

Figure 3. R, T, P structures for the ML_5 (D_{3h}) double-exchange homoconversion with symmetry specification D_{3h}(R), C_{2v}(q), C_{4v}(T), and E′(Q_R). Parenthetic atoms are directly behind the atom shown. This is commonly referred to as the Berry pseudorotation.

allowed, one corresponding to the so-called "Berry pseudorotation mechanism".[11]

We consider the reactant R with the ligand labeling of Figure 3. Inspection of the trigonal-bipyramidal structure shows that two types of products are possible: (i) those in which both axial ligands become equatorial (double exchange), and (ii) those in which only one of the axial ligands becomes equatorial (single exchange). Any other exchanges only interconvert point equivalent ligands and simply do not constitute chemically interesting reaction pathways. In both cases of double and single exchange, one of the equatorial ligands remains equatorial; for convenience, we shall take this to be ligand 1. (Choice of 2 or 3 leads to symmetry-related pathways and thus does not need to be considered separately here.) The possible homoconversion mechanisms may then be derived in the following manner.

Double Exchange. Two configurationally distinct *types* of products, P_1 and P_2, may be generated from the double exchange. P_1 is shown in Figure 3, with P_2 differing only in the interchange of 2 and 3. We follow stages I–III of section 3, explicitly listing only the major details, for the reaction R → P_1.

I. $G_{RP_1} = \{E, C_2(2,3)(4,5)\sigma(4,5), \sigma'(2,3)\} = C_{2v}$.

II. R to P_1 proceeds through an E′ mode of both R and P_1, a mode that is available for the structure in question.

III. Lining up the C_{2v} planes and the C_2 axis (i.e. the conserved elements) in R and P_1, and no others, we find that the R and P_1 skeletons may be related by a C_4 rotation; thus $L = (3,4,2,5)\ C_4$ with the C_4 rotation taking atom 3 to 5, 5 to 2, etc. being a point-symmetry operation of T, and $G_T = C_{4v}$. This mechanism is therefore allowed through the C_{4v} structure shown in Figure 3. A similar procedure for P_2 yields $L = (2,5)(3,4)\ C_4$, which leads to a physically unrealizable transition structure and is therefore forbidden.

The mechanism for the R → P_1 reaction is one of a 3-fold set of degeneracy related pathways arising from the loss of the C_3 axis in moving from R or P, the other two mechanisms corresponding simply to the choice of atom 2 or 3 as the stationary atom (i.e. as lying on the conserved C_2 axis). Note that the products arising from these three symmetry-related pathways are, in this case, configurationally distinct, as interchanges of point-inequivalent atoms are involved in the reaction, unlike the $T_d \rightarrow T_d$ example of the previous section. This mechanism is sometimes referred to as the Berry pseudorotation[11] and is illustrated in detail in Figure 3.

Single Exchange. In the single exchange mechanism, one of the axial ligands (which we shall take to be atom 5) is retained and the other interchanged with one of the equatorial ligands. We consider first the reaction R → P_3, with P_3 illustrated in Figure 4.

I. $G_{RP_3} = \{E, \sigma(1,2)\} = C_s$.

II. The symmetry of the reaction coordinate is E″ in both R and P, a mode that is present for the structures in question.

III. Aligning the conserved plane as shown in Figure 4, it follows that the R and P skeletons are related by the plane (σ) perpendicular to the ligand 3–metal bond in the reactant. Thus for P_3, $L = (3,4)\ \sigma$ so that a reflection plane exchanging only atoms 3 and 4 is a point-symmetry operation of T, and $G_T = C_{2v}$.

This mechanism, illustrated in Figure 4, is both narcissistic (equivalent to choice of atom 5 or 4 as stationary) and one of three degeneracy-related pathways (equivalent to interchange with 1,2 or 3) and is usually referred to as the turnstile mechanism. Any other configurationally distinct single interchange products may be written in terms of these six by an additional permutation; e.g. the product $P_4 = (1,2)\ P_3 = (1,2)(3,4)\ \sigma$ R. The product-generating relationship for P_4 leads to a physically unrealizable transition state structure, and thus the concerted R → P_4 reaction is forbidden.

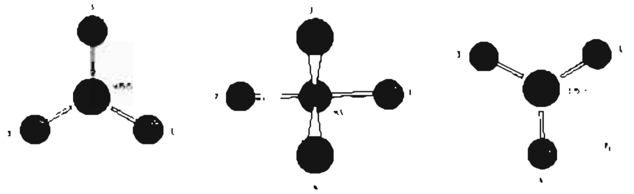

Figure 4. R, T, P structures for the ML_5 (D_{3h}) single-exchange homoconversion with symmetry specification D_{3h}(R), C_s(q), C_{2v}(T), and E″(Q_R). Parenthetic atoms are behind the atom shown in the indicated order. This mechanism is commonly referred to as the turnstile mechanism.

In conclusion, we have generated two distinct symmetry-allowed mechanisms that could lead to the interchange of point inequivalent ligands and thus lead to potential equivalence in NMR. The relative energetics of the two mechanisms is, as discussed earlier, a question that cannot be resolved purely on symmetry grounds, and it is quite possible that the dominant mechanism is determined by the nature of the ligands and the experimental conditions. For example, temperature-dependent studies on ^{31}P NMR spectra of $[Rh\{P(OMe)_3\}_5]Ph_4B$ in $CHClF_2$–CH_2Cl_2 mixtures[5] suggest that this complex is a rigid trigonal bipyramid at −134 °C and undergoes simultaneous exchange of two axial and two equatorial ligands from −124 to −64 °C (i.e. the *double-exchange* mechanism), and above 0 °C, a nonconcerted intermolecular exchange process comes into play.

The CSR for the C_{4v} homoconversion immediately preclude a D_{3h} transition state, as this would require a degeneracy of the reaction coordinate in T, which is forbidden. This illustrates a general feature of the CSR, which may be stated in the following way: *A transition state can only have degenerate symmetry elements if they are strictly preserved along the entire path.*

The selection rules for the heteroconversions resulting from potential minimum energy C_{4v} or C_{2v} structures (thus precluding the corresponding homoconversion mechanisms above) follow the analogous reaction coordinates, except that the transition state symmetry is the same as that at nonstationary points. Again, these heteroconversions may be considered as the collapse of the relevant concerted homoconversion mechanism to the two-step path in which the higher symmetry structure between R and P is an intermediate. It is possible, for example, for the reaction discussed above that the single-exchange mechanism is effectively two step if the C_{2v} structure is a minimum, with the double exchange remaining concerted provided the C_{4v} structure is a maximum.

7. Six-Coordinate Complexes

Octahedral complexes of pure O_h symmetry have all the ligands point equivalent, and thus the $O_h \rightarrow O_h$ isomerization is not of any practical interest. Indeed, it can be shown that this homoconversion cannot occur through any concerted mechanism. However, tris bidentate complexes of D_3 symmetry can undergo inversion reactions. Mechanisms for such chiral homoconversions have been proposed,[12,13] and more recently, the full set of concerted mechanisms have been generated as an example of the application of the CSR procedure.[9] The more explicit discussion in this paper of the constraints implicit in the definition of the product-generating relationship allows for a more rigorous derivation of the symmetry-allowed mechanisms than that presented earlier[9] and also for a classification of the symmetry-related pathways. For a given reactant R, there are eight configurationally distinct products if the chemically reasonable assumption is made that the chelates are not internally cleaved during the rearrangements. This leads to eight symmetry-allowed pathways: two are neither narcissistic or degeneracy related (and may be referred to as *singly degenerate mechanisms*, the adjective referring to the overall

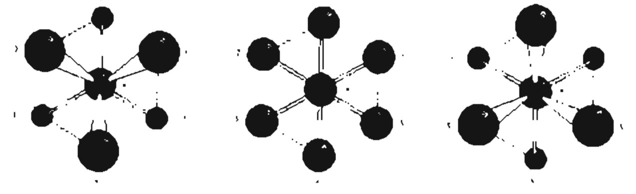

Figure 5. R, T, P structures for the $M(LL)_3$ (D_3) chiral homoconversion corresponding to the *push-through* mechanism with symmetry specification D_3(R), D_3(q), D_{3h}(T), and $A_1(Q_R)$.

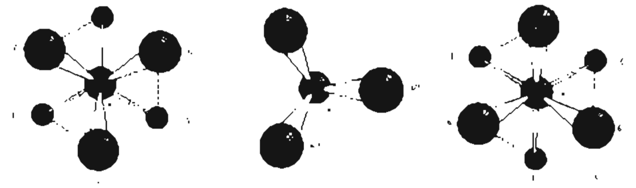

Figure 6. R, T, P structures for the $M(LL)_3$ (D_3) chiral homoconversion corresponding to the *Bailar twist* mechanism with symmetry specification D_3(R), D_3(q), D_{3h}(T), and $A_1(Q_R)$. Parenthetic atoms are behind the atom shown.

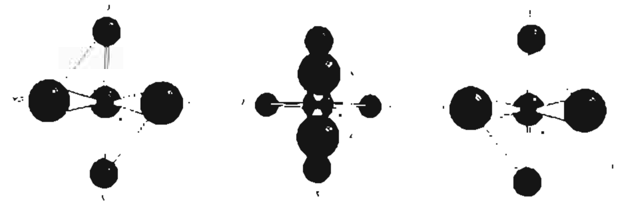

Figure 7. R, T, P structures for the $M(LL)_3$ (D_3) chiral homoconversion corresponding to the *crossover twist* mechanism with symmetry specification D_{3h}(R), C_2(q), C_{2v}(T), and $E(Q_R)$. Parenthetic atoms are behind the atom shown.

mechanism and not the reaction coordinate); the remainder occur as two sets of three degeneracy-related pathways (i.e. two *triply degenerate mechanisms*). We discuss the singly degenerte mechanisms first.

The singly degenerate mechanisms lead to products P_1 and P_2, which may be written in terms of the relevant product-generating relationships (derived as discussed earlier) as

$$P_1 = \sigma_h \, R, \; P_2 = (1,2)(3,4)(5,6) \, \sigma_h \, R$$

σ_h is the reflection plane perpendicular to the C_3 axis, and the permutation (1,2), for example, interchanges the positions of the indicated chelate ends. P_1 proceeds through $G_q = D_3$ via an A_1 mode with the product-generating relationship $L = \sigma_h$ (which permutes no atoms) so that all the chelate ends must lie in this plane in the transition state, which will be of D_{3h} symmetry. This *push-through* mechanism (Figure 5) is totally acceptable on symmetry grounds but is extremely unlikely to be energetically viable. P_2 also leads to $G_q = D_3$ and proceeds via an A_1 mode. However, in this case, the product generating relationship is $(1,2)(3,4)(5,6)\,\sigma_h$, so that the σ_h in T must interchange 1 and 2, 3 and 4, and 5 and 6 and will be of D_{3h} symmetry with the structure illustrated in Figure 6. This is the well-known *Bailar twist*. These two mechanisms illustrate the vital significance of how the permutative part of the product-generating relationship determines the nature of the transition state structure, as the point-symmetry aspects of these two mechanisms are, in fact, quite similar.

Products P_3 and P_4 illustrated in Figures 7 and 8 are formed by triply degenerate mechanisms. We consider P_3 first, where

$$P_3 = (1,2) \, \sigma \, R$$

and σ interchanges the ends of the (12) chelate and contains that C_2 axis. The CSR procedure yields $G_q = C_2$, with the C_2 axis bisecting the (12) chelate and passing through the metal origin. Such a reaction must therefore proceed via an E mode of R and P_3. $L = (1,2)\,\sigma$ is a stationary operation of T if it has C_{2v} symmetry and is of the structure shown in Figure 7. This *crossover twist* mechanism is symmetry-allowed but unlikely to be energetically viable. The degeneracy of the reaction coordinate in R leads to three degeneracy-related pathways, corresponding to chelates (12), (34), and (56) remaining stationary, respectively. P_4 also proceeds via $G_q = C_2$, via an E mode in R, with $L = (1,2)(3,4)(5,6)\,\sigma$, a stationary operation of the transition state structure as shown in Figure 8 for $G_T = C_{2v}$. This corresponds to the well-known *Ray–Dutt twist*. Again, the degeneracy of the reaction coordinate in R leads to three products formed from three degeneracy-related pathways in which the different chelates are individually treated as stationary.

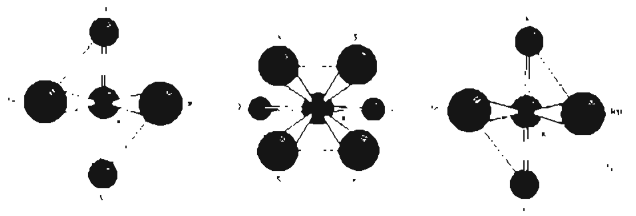

Figure 8. R, T, P structures for the $M(LL)_3$ (D_3) chiral homoconversion corresponding to the *Ray–Dutt twist* mechanism with symmetry specification D_3(R), C_2(q), C_{2v}(T), and $E(Q_R)$. Parenthetic atoms are behind the atom shown.

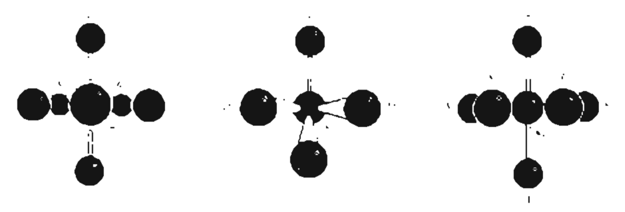

Figure 9. R, T, P structures for the ML_7 (D_{5h}) single-exchange homoconversion with symmetry specification D_{5h}(R), C_s(q), C_{2v}(T), and $E''(Q_R)$. Parenthetic atoms are behind the atom shown.

8. Seven-Coordinate Complexes

As the coordination number increases, the bonding around the metal atom reduces more to the pseudoclassical packing problem characteristic of the solid state. The number of minima on the PE surface increases, leading generally to a greater range of possible state symmetries and also to a potential lowering in the energy of the transition structures connecting them on the allowed pathways. Common symmetries that may be expected for seven-coordinate complexes include D_{5h} (a pentagonal bipyramid), C_{3v} (a capped octahedron), and C_{2v} (a capped trigonal prism).[10,14] Mechanisms for the heteroconversions for reactant and product symmetries involving the above three symmetry groups have been proposed[14] and, as we shall show presently, follow readily from the CSR procedure. However, we shall initially consider the potential homoconversions, in particular, the D_{5h} homoconversions leading to NMR equivalence of all seven ligands and the C_{3v} homoconversion, leading also to potential NMR equivalence.

D_{5h} Homoconversion. As for the D_{3h} homoconversion, it is possible to classify the D_{5h} homoconversion according to whether a single axial ligand becomes equatorial in the product (single exchange) or whether both axial ligands become equatorial (double exchange). Only the results are presented here.

The *single-exchange* mechanism is illustrated in Figure 9 and arises from the reaction in which one of the axial ligands, e.g. ligand 1, is kept stationary. It is readily shown that the product

$$P = (2,3)(4,5)(6,7) \, \sigma_v' \, R$$

where σ_v' is the reflection plane of the reactant which contains the axial ligands (1 and 2) and is orthogonal to the metal–ligand 3 bond, may proceed via the E'' mode of R, preserving only the reflection plane σ_v containing the ligands 1, 2, and 3 (and the metal) and leading to the augmented transition state symmetry C_{2v} in which σ_v' is the augmentor element. There will be 10 products in all that are potentially generated by the five degen-

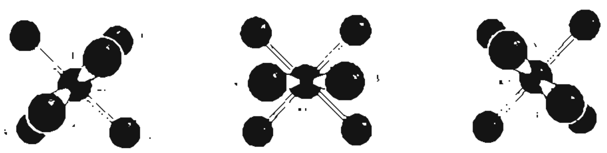

Figure 10. R, T, P structures for the ML_7 (D_{5h}) double-exchange homoconversion with symmetry specification D_{5h}(R), C_2(q), C_{2v}(T), and $E''(Q_R)$. Parenthetic atoms are behind the atom shown.

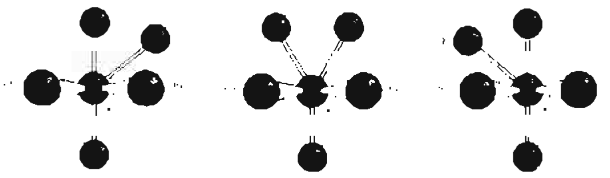

Figure 11. R, T, P structures for the ML_7 (C_{3v}) homoconversion with symmetry specification C_{3v}(R), C_s(q), C_{2v}(T), and $E(Q_R)$. Parenthetic atoms are behind the atom shown.

eracy-related pathways arising from the loss of the 3-fold axis, and each of these is narcissistic. These correspond to the five possible choices for the equatorial ligands and the two possible choices of the axial ligands. The physical motion inherent in this mechanism is a simple concerted motion of all the atoms and is characterized by a concurrent set of motions: (i) a swing of ligands 2 and 3 in the conserved plane, so that 2 moves toward the equatorial plane opposite to the original position of 3, which moves towards the axial position vacated by 2; (ii) equatorial ligands (4,5,6,7) relaxing to fill the vacancy left by ligand 3, thereby facilitating the insertion of 2 into the opposite equatorial position.

The *double-exchange* mechanism is illustrated in Figure 10. It occurs through an E″ vibration of the reactant, preserving the C_2 axis along a chosen equatorial ligand–metal bond. Considering the case where ligand 6 is taken to define the C_2 axis, it is readily shown that a C_{2v} transition state is possible through augmentation via the plane σ (defined uniquely throughout the entire reaction path) containing the C_2 axis and bisecting the ligand 4–metal–ligand 3 angle and the ligand 1–metal–ligand 7 angle. The product-generating relationship has the form (1,7)(2,5)(3,4) σ. This mechanism is dominated by the simple concerted rotation of the ligand 3–metal–ligand 4 fragment about the C_2 axis, which forms a new equatorial plane by moving into the plane defined by the initially axial ligands and ligand 6. The remaining configurationally distinct products accessible through symmetry-allowed pathways arise from the five degeneracy-related pathways defined by choosing different equatorial ligands for the definition of the preserved C_2 axis, each of which is, in turn, narcissistic.

It is interesting to note that the D_{5h} homoconversion cannot proceed through any transition state having a degenerate symmetry axis (i.e. a C_n or S_n axis with $n > 2$). This follows simply from the result of the previous section prohibiting degenerate symmetry elements in T that are not conserved along the entire path. Thus, as the C_5 axis must be lost in moving from R, generation of a new degenerate C_n axis must more than double the size of the symmetry group of the transition state structure relative to that at the nonstationary points. Such an augmentation is forbidden in the CSR scheme.

C_{3v} Homoconversion. This mechanism for such interconversions, which would effectively interchange the ligand lying on the C_3 axis with those in the contiguous trigonal plane, as well as effectively reorienting the C_3 axis, is illustrated in Figure 11. The reaction coordinate is of E symmetry in R, with the symmetry at nonstationary points (C_s) conserving only the reflection plane σ, which, in the reactant, is the dihedral plane defined as containing the axial ligands and the "capping" ligand. The product-generating relationship has the form

$$(1,2)(3,6)(4,7)\ \sigma'$$

where σ' is the plane defined in the reactant as containing ligand 5 and the metal, orthogonal to σ. The transition state is of C_{2v} symmetry. Physically, the motion is most easily visualized as a simple concerted swing of ligands 1 and 2 in the dihedral plane, leaving 1 in the axial position and moving 2 into a repositioned cap.

Heteroconversions. The $D_{5h} \rightarrow C_{2v}$ and $C_{3v} \rightarrow C_{2v}$ heteroconversions follow the same symmetry modes as discussed for the homoconversions of the higher symmetry reactants. However, as there can not be any product-generating relationship for heteroconversions, it follows that the transition state symmetry is the same as that of the structures at nonstationary points. Another potential heteroconversion is the $C_{3v} \rightarrow D_{5h}$ reaction, which proceeds via an E vibration of C_{3v} (E″ in D_{5h}) and preserves only the reflection plane σ (the plane of the page in Figure 11) containing the ligands 1, 2, and 5 (and the metal). In this case, because the transition state cannot have a symmetry higher than that at nonstationary points, there is no further constraint on the relationship of ligands in this conserved plane (such as exist for the concerted homoconversions), but it is likely that ligand 1 moves to the axial position and 2 into the equatorial plane.

From another perspective, we may consider the CSR as being more restrictive (and thus more informative) for homoconversions, for which the increased symmetry of the transition state is usually sufficient to define the relative internal structure (i.e. the relationships between the atoms, but not quantitative aspects such as absolute bond lengths or symmetry-undetermined bond angles). For heteroconversions, the symmetry of the transition state must be that at nonstationary points of the reaction coordinate, which is usually quite low. In such cases, symmetry may not be sufficient to determine the actual *structure* of the transition state but only the relationships between ligands as defined by the conserved elements. This is not a deficiency of the CSR procedure but a fundamental limitation arising simply from the fact that the lower the symmetry of the structure, or the larger the structural complexity (e.g. the number of atoms), the less complete is the ability of the symmetry of the structure to yield a description of the structure itself. For example, a six-atom D_{6h} structure is immediately restricted to a benzene ring type geometry, but a six-atom C_s structure may span a range of structures. In all cases, however, the definition of conserved elements is, in itself, information about the reaction coordinate that may assist in quantitative determination of reaction pathways.

9. Conclusions

The application of the CSR procedure to metal–ligand isomerizations demonstrates the relative ease with which symmetry-allowed mechanisms may be determined by exploiting the point and permutation symmetry constraints along the path. In addition to their theoretical definition, the determination of the conserved symmetry elements and, in the case of the homoconversions, the product-generating relationship lead to a conceptual basis in terms of which the mechanisms may be readily visualized. Although in the present manuscript only the high-symmetry homoconversions have been considered in detail, they serve as examples of the application of the CSR in their most restrictive and (from a symmetry perspective) complex form, so that application to the lower symmetry homoconversions and to heteroisomerizations may be readily effected by using the practical CSR procedure of the present work.