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Template symmetry restrictions on reaction mechanisms

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Abstract

A rigorous extension to low symmetry systems, whose geometry is based on a high symmetry template, of the previously developed classical symmetry selection rule procedure for generating reaction mechanisms is presented. A framework is thus provided for the study of substituted molecules which takes advantage of their high symmetry template. Transition metal complexes of octahedral parentage are used to illustrate the principles.

Introduction

Molecular rearrangement mechanisms and the ease with which they occur are extensively studied aspects of chemistry. For example, the stability of four coordinate carbon and the fluxionality of pyramidal nitrogen are both crucial to the functioning of biological systems; and the ease with which $[Fe(1,10\text{-phenanthroline})_3]^{2+}$ isomerises ensures that a large excess of the Δ enantioner binds to DNA [1]. The easiest mechanisms to visualise and study are those for high symmetry systems, and much work has been done in this area [2]. We have previously developed a classical symmetry selection rule procedure (CSSRP), which makes use of point and permutation symmetry relationships between the atoms of a reacting system, for generating reaction mechanisms [3–5]. The CSSRP can be applied to any reacting system regardless of its complexity, as analysis of metal complexes [5, 6] and clusters [7] illustrated. It is ideally suited to the determination of symmetry allowed *concerted* mechanisms, though it can be applied successively to each step of a multistep reaction. The strength of the procedure is that the results can be transferred between molecules of the same symmetry, though the converse, that it makes no comment on the relative probabilities of mechanisms, led to the development of an atom–atom interaction model [8] to determine the relative feasibilities of mechanisms [6, 9]. In the original CSSRP, low symmetry systems were dealt with only in a general way as analogues of high symmetry systems. In this paper we look at the rigorous extension of the CSSRP to low symmetry molecules whose geometry is based on a high symmetry template. In this way a framework is provided for the study of substituted molecules. Transition metal complexes of octahedral parentage are used to illustrate more general principles.

The CSSRP relies on the symmetry characteristics of the normal coordinates (used in a generalised sense which does not restrict their definition to stable geometries) of the reacting system. Two key results are that for a 'well-behaved' reaction path (i.e. a path that is a harmonic valley with respect to all other motions, has no surface crossing and has no points of inflexion along it) (i) the reacting motion is described by a normal mode of the system at each point and (ii) symmetry changes occur only at the reactant, transition state and product. The CSSRP can be viewed as a procedure to determine whether there is a normal coordinate of a reactant which can take the system along a symmetry allowed reaction pathway to the product. If there is no such normal coordinate, then there is no concerted mechanism between that reactant and product. Now, the normal coordinates of a low symmetry molecule built on a high symmetry template correlate with those of its high symmetry analogue, so, if no reactant normal coordinate exists for the template to concertedly rearrange to a given product, then none exists for the low symmetry molecule. Somewhat ironically, the existence of a normal mode for the high symmetry template doesn't always guarantee the existence of a normal coordinate for lower symmetry molecule, because the loss of degeneracy on symmetry lowering reduces the flexibility of the normal modes. However, this can be used to advantage in determining non-concerted energetically feasible mechanisms as is discussed below for mono-chelate complexes. In this

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context it is helpful to adopt the labels *weak symmetry lowering*, which applies to those systems where the low symmetry geometry is sufficiently like the high symmetry template for its normal coordinates to bear a close resemblance to those of the high symmetry system, and *strong symmetry lowering*, where the normal coordinates have been changed so much that it is not possible to identify a one-to-one correspondence.

The CSSRP [3–5] can be briefly summarised as follows. One draws the reactant (**R** of point symmetry G_R), and all products ($\mathbf{P}_i$ of symmetry G_{Pi}) of interest, labelling their atoms. One then determines the symmetry operations, in a labelled atom sense, that are common to each **R**,**P** pair. These operations form the group G_{RP} and are retained along the reaction path. If no normal mode of **R** (or **P**) can reduce the system symmetry to G_{RP}, then **R** cannot convert to **P** via a *concerted* mechanism, otherwise the rearrangement is potentially concerted. For **R** and **P** with different shaped skeletons, the point group of the transition state, G_T, equals G_{RP}. For **R** and **P** with skeletons which are identical to or mirror images of one another, then there is a combined point/permutation operation $L = Rp$, where R is a point operation and p is a permutation operation, such that $L\mathbf{R} = \mathbf{P}$ and $L\mathbf{P} = \mathbf{R}$. L is then a stationary symmetry operation of **T**, i.e. $L\mathbf{T} \equiv \mathbf{T}$, so $p\mathbf{T} \equiv R^{-1}\mathbf{T}$. L is most readily determined by orienting **R** and **P** so that their common symmetry elements are aligned. If this does not specify their relative orientations then rotate **P** so that additional similarities between **R** and **P** are not implied. L is not necessarily unique, but **T** always is. The assumptions underlying the CSSRP are unlikely to break down for transition metal complexes [5]. However, if they do, the path determined using the CSSRP is an average of the paths which actually occur.

The significant difference between the template application of the CSSRP developed in this work and the original applications to high symmetry molecules is that *all* mechanisms generated for the template must be retained. Previously, mechanisms for which a pure permutation L could be identified were eliminated for the obvious reason that they required two atoms to pass through one another at **T** (or more fundamentally, for the symmetry based reason that L $\mathbf{R} = \mathbf{P}$, $LQ_T{}^r = -Q_T{}^r$, $RQ_T{}^r = -Q_T{}^r$, where $Q_T{}^r$ is the reaction coordinate at the transition state [3], so if L is a pure permutation operation, $R = E$, but $Q_T{}^r \neq -Q_T{}^r$). When the symmetry of the system is lowered, however, the symmetry of G_{RP} is lowered, and the product generating operation may become a mixed point permutation operation.

Complexes with an octahedral template

Octahedral complexes

Figure 1 illustrates the results of the CSSRP for all distinct (in a labelled atom sense) products from the symmetry allowed concerted rearrangement mechanisms of an octahedral metal complex [5, 6]. The number in square brackets after each mechanism is the number of equivalent mechanisms for the octahedral molecule; the equivalence of two mechanisms in the high symmetry molecule is often lost upon reduction of the symmetry by substitution. Mechanisms 1.α, 1.β and 1.δ are not operative for an O_h complex as L is a pure permutation in each case, and respectively, three, one or three, pairs of atoms are coincident in **T**. However, as noted above, they may become operative for lower symmetry complexes so are included. Mechanisms 1.γ are narcisistic mechanisms from opposite direction motion along the same T_{2u} [4] normal coordinate of **R**. They are symmetry allowed rearrangement mechanisms which proceed via trigonal prismatic transition states.

Tris chelate complexes

The ML_6 part of a tris chelate complex $M(L\text{-}L)_3$ is a good example of weak symmetry lowering from an octahedral complex. Some mechanisms which follow from relaxing the symmetry constraints on the octahedral mechanisms are illustrated in Fig. 2, products that involve non-nearest neighbour ligating atoms connected by the same chelate have been omitted, as have all products of the same handedness as **R**. No mechanisms derived from 1.δ is illustrated as L is still a pure permutation for a concerted reaction.

The mechanisms of Fig. 2 are identical with those that result from a direct application of the CSSRP [4–6] or from an exhaustive study of all possible rearrangements that one could conceive for a tris chelate complex [10]. 2.α and 2.γ are both symmetry allowed concerted mechanisms with mixed point/permutation L. However, their transition states are very high energy structures reflecting their origin in mechanisms which were forbidden in the octahedral complexes. The common high symmetry parentage of both the Bailar and Ray Dutt twists (2.γ) is the most interesting result to come from the template approach to these reactions: the Bailar twist is a twist about the three-fold axis which is retained upon symmetry reduction, and the Ray Dutt twist is a twist about a three-fold axis which is lost. This results from the fate of the T_{2u} normal coordinate of an octahedral **R** upon reduction of molecular symmetry to D_3: it splits into a non-degenerate A component and a degenerate E component. The A component

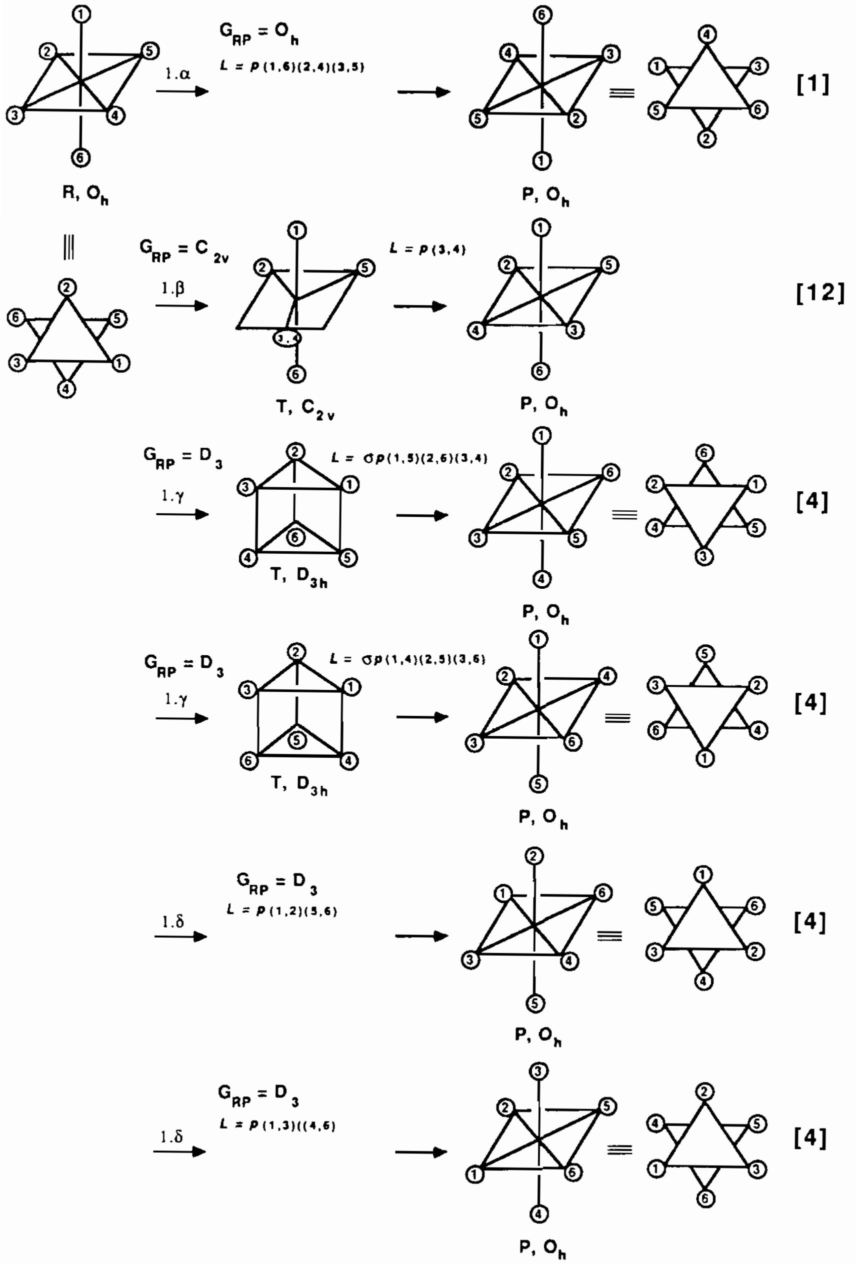

Fig. 1. Concerted rearrangement mechanisms for octahedral complexes. Numbers in square brackets are the number of mechanisms equivalent to the one illustrated.

gives the Bailar twist which retains D_3 symmetry along the reaction path, and the E component gives the Ray Dutt twist. (The other direction of the T_{2u} twist, which was narcicistic with these mechanisms for the octahedral template, fall into the group of mechanisms not illustrated as they involve a chelate being *trans* rather than *cis*.) The similarity of the Bailar and Ray Dutt twists when viewed in this manner has been exploited to determine the conditions under which one would expect each to be favoured [9].

Mono chelate systems

Mono chelate ML_4(L-L) complexes also fit in the weakly symmetry lowered category. There are 24 possible rearrangement products which retain the chelate in a *cis* position. The one derived from 1.α has a pure permutation L, so can be ignored. The analogue of 1.β that retains C_{2v} symmetry along the reaction path requires the chelate to coalesce at **T**. The other eight 1.β analogues have $G_{RP}=C_1$ so no concerted reaction is possible to these products. A multistep analogue of this mechanism (see the dis-

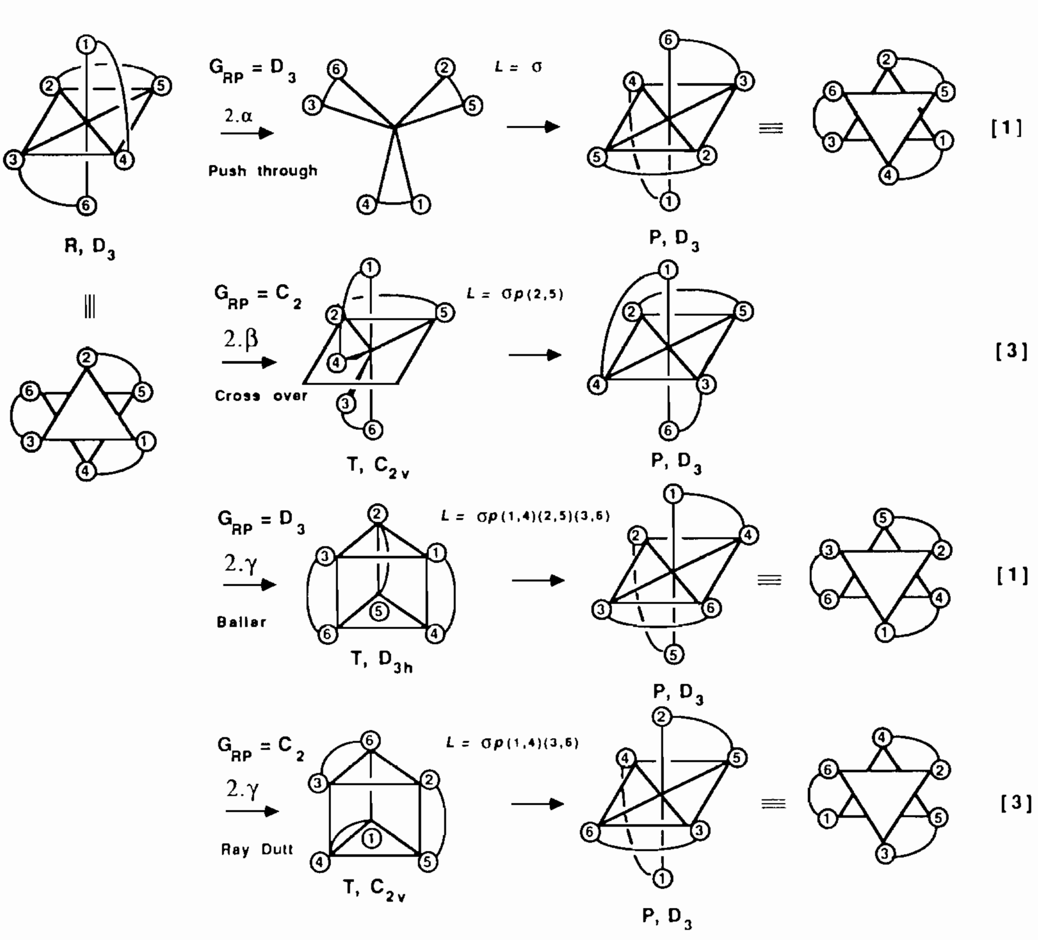

Fig. 2. Concerted rearrangement mechanisms for tris chelate complexes. Numbers in square brackets are the number of mechanisms equivalent to the one illustrated. The labels of the mechanisms correspond to those for the analogous octahedral mechanisms.

cussion of the 1.γ mechanism below) may also be ignored as the atom coalescence required in the high symmetry template, implies for this weakly symmetry lowered example at least close proximity of ligating atoms in the transition state of a monochelate rearrangement.

Two 1.γ analogues have $G_{RP}=C_2$ and proceed via a C_{2v} **T**; one of them is illustrated in Fig. 3. They resemble most closely the Bailar twist. The other four 1.γ analogues which do not break the chelate have no symmetry elements common to both **R** and **P**. By the CSSRP they therefore cannot be concerted reactions. However, since (i) the 3.γ 'Bailar Twist' mechanism is likely to be energetically expensive for large chelates [9], and (ii) these mechanisms are viable for the template suggest that there may be a feasible multistep mechanism which can be derived using the template mechanism as a guide. The O_h T_{2u} vibration which enables the twists to take place splits into A_1+A_2 (the 'Bailar twist') $+B_1$ under C_{2v} symmetry. An A_1 vibration cannot change the molecular shape without atom coalescence, so consider B_1, which retains the reflection plane containing atoms 3, 4, 2 and 5 where 3 and 4 are the chelate. A B_1 vibration which doesn't break the chelate leads to an anti square-based prism intermediate, one of which is illustrated by the second mechanism of the Fig. A twist of this structure via a trigonal prismatic transition state makes a second step and the final step is a reverse of the first step. The highest energy point of this multistep path is the distorted trigonal prism of C_s symmetry.

No mechanisms can be derived from the 1.δ mechanisms.

cis-Dihydride complexes

Metal complexes such as *cis*-$FeH_2[P(OC_2)H_5)_3]_4$ have been extensively studied by Meakin *et al.* [11]. The fast exchange NMR experiments show equivalent Ps and Hs, so the system is stereochemically non-

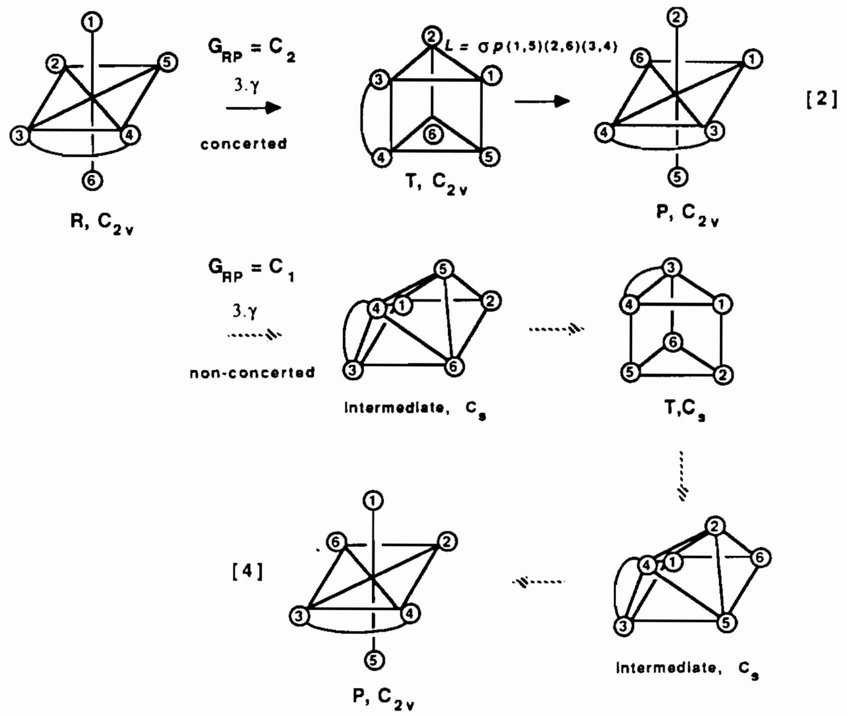

Fig. 3. Rearrangement mechanisms for mono chelate complexes. Numbers in square brackets are the number of mechanisms equivalent to the one illustrated. The labels of the mechanisms correspond to those for the analogous octahedral mechanisms.

rigid; further temperature dependent NMR led to the conclusion that the rearrangement is not bimolecular or solvent assisted. Analysis of their data assuming a 'jump model' enabled Meakin *et al.* to determine which nuclear permutations occurred during the rearrangement of *cis*-MH_2P_4. Using the atom labelling of **R** in Fig. 1, and taking atoms 3 and 4 as the hydrogens, the distinct **P**s, consistent with the NMR data, were found to be the following permutations: p(1,5), p(6,5), p(1,2), p(6,2), p(1,5,6), p(1,6,5), p(1,2,6), p(1,6,2).

Direct application of the CSSRP shows that the pathways to these products cannot be concerted as **R** has C_{2v} symmetry, and the reactant and product have no symmetry elements in common. Reaction pathways of two or more steps must therefore cause the observed rearrangements. The template approach now becomes useful as it suggests symmetry allowed first reaction steps. *cis*-Dihydrides have the same symmetry, C_{2v}, as the monochelate example discussed above. However, the two hydrogens are not linked, and further, the symmetry lowering from the octahedral template is stronger for the dihydride which can equally well be described as a distorted tetrahedral P_4 ligand system with hydrides inserted into the faces of the tetrahedron. The template analysis can proceed in terms of both an octahedral P_4H_2 and a tetrahedral P_4 template.

Octahedral template

The first step of the reaction should correlate with one of the mechanisms for the octahedral template. 1.α can be ignored as it requires coalescence of atoms even for this lower symmetry example. The 1.β and 1.δ mechanisms are not possible even as a first reaction step, as in the monochelate example. Once again, it is the 1.γ mechanisms which are operative. They fall into three subdivisions: (i) where the hydrogens are in the same triangle when viewed along the twist axis; (ii) where the hydrogens are in different triangles when viewed along the twist axis, and the twist retains the hydrogens as nearest neighbours throughout the twist; and (iii) where the hydrogens are in different triangles when viewed along the twist axis, and become separated during the twist. (i) and (ii) (which is illustrated in Fig. 4(a)) correspond to the mechanisms discussed above for the monochelates and can be ignored as they yield *cis* products which are isoenergetic with the reactant, but inconsistent with the NMR analysis. (iii) leads to a *trans*-dihydride geometry which is a stable intermediate structure on a *cis* to *cis* rearrangement pathway. From this intermediate, the molecule could either retrace the first step back to the reactant, or proceed along another symmetry allowed 1.γ path. The products from the two twists about one such three-fold axis are illustrated in Fig.

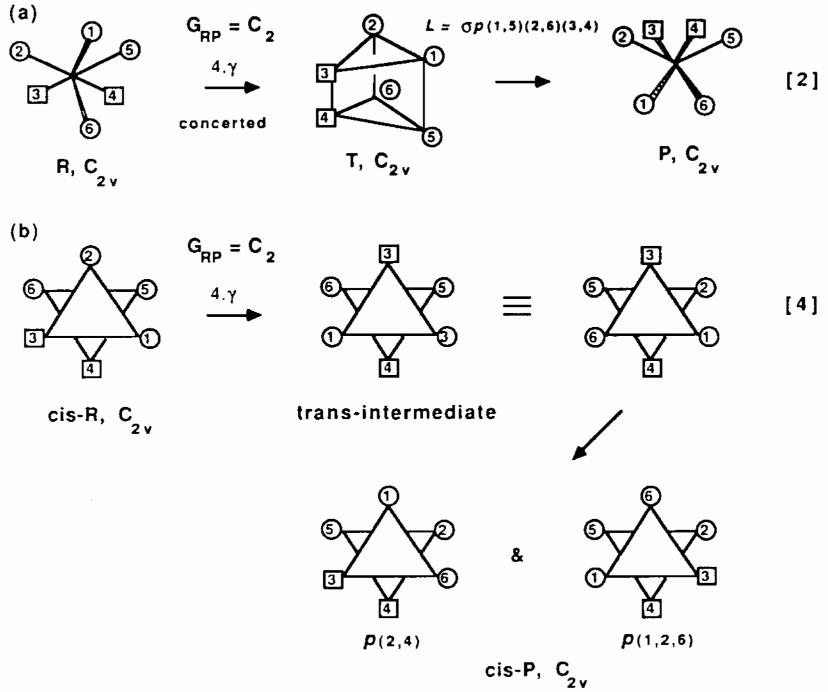

Fig. 4. Rearrangement mechanisms for *cis*-dihydride complexes. Numbers in square brackets are the number of mechanisms equivalent to the one illustrated. The labels of the mechanisms correspond to those for the analogous octahedral mechanisms. Hydrogens are denoted by boxes and other ligating atoms by circles.

4(b). The different possibilities for the first and second step lead to the other products in the above list. Meakin *et al.* [11] postulated a 'tetrahedral tunneling process' similar to this mechanism with the *trans* geometry being either a transition state or a short lived intermediate. It is clear from this analysis precisely what the mechanism is and also that the *trans* geometry must be an intermediate.

Tetrahedral template

No new mechanisms result from analysing these complexes in terms of a tetrahedral template. However, it becomes apparent from the tetrahedral analysis that the eight distinct two-step twists derived above using the octahedral template in fact correspond to two quite different mechanisms. When considering the complex in terms of a P_4 tetrahedral template (atoms 1,2,5,6), it is helpful to view the hydrogens as a linear polyhedron. Any rearrangement of the complex can then be viewed as a stretching of the linear polyhedron, and/or rearranging the tetrahedral polyhedron and/or rotating the polyhedra with respect to one another. This view of the molecule, adapted from analysis of cluster rearrangements [7], ensures that no part of the molecule is ignored.

The only concerted mechanisms for a tetrahedron are inversion via square planar Ts or rearrangement to a stable square plane [5, 6], in each case the possible planes are with vertices in the order [1,2,6,5], [1,2,5,6] or [1,5,2,6]. The first of these, when coupled with the motion of the H_2 polyhedron [3, 4], gives a concerted mechanism analogous to 1.γ, which is the inoperative mechanism of Fig. 4(a). The second and third square planes yield alternative views of the two step mechanism illustrated in Fig. 4(b), which is summarised as a permutation of two phosphorous atoms, i.e. involves an inversion of the P_4 tetrahedron.

Other mechanisms could arise as the relative motions of two (distorting) P_4 and H_2 polyhedra. The CSSR requires that one or all reactant symmetry operations are retained during the first step, and one or all of the product operations are retained in the final step. This immediately leads to the conclusion that the mechanism proposed by Meakins *et al.* [11] where one hydrogen migrates to a P–P edge then to a new face cannot be occurring. However, a mechanism whereby two hydrogens migrate to P–P edges in such a way as to retain the two-fold symmetry axis of the molecule is allowed by symmetry; continuation of this motion results in both hydrogens capping new faces of the P_4 tetrahedron. This mechanism proves to be an alternative view of the twist mechanisms of Fig. 4(b) which is described as a cyclic permutation of three ligands, always including the two which are not coplanar with H_2 in **R**.

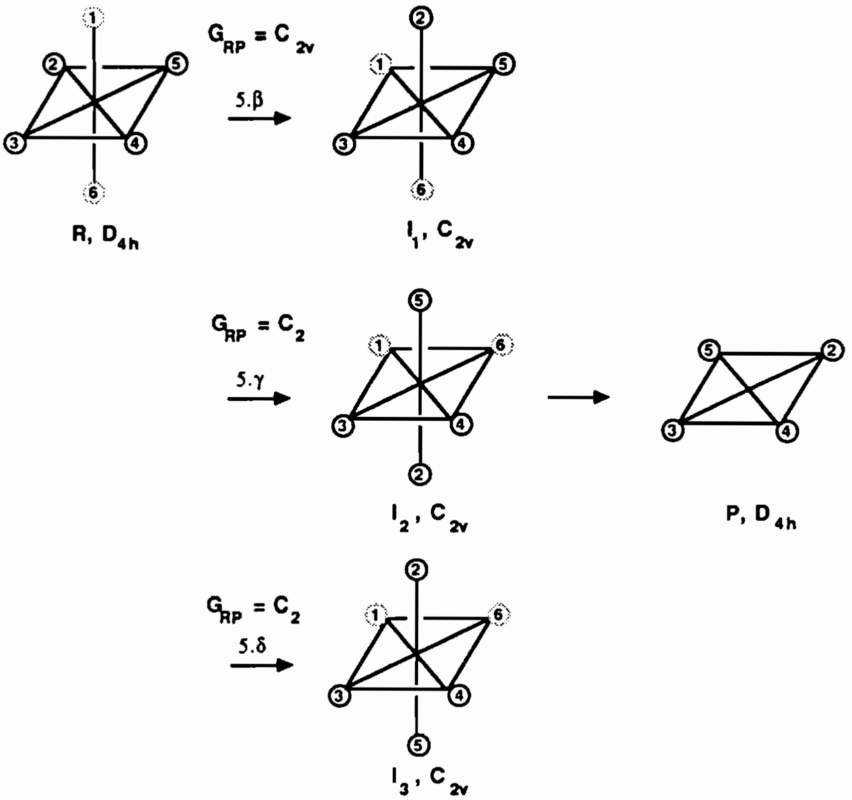

Fig. 5. Rearrangement mechanisms for square planar complexes. The labels of the mechanisms correspond to those for the analogous octahedral mechanisms. Ligating atom positions indicated by dotted circles are those not present.

Square planar complexes

The final rearrangement reaction of an octahedral parentage system that we shall examine is the *cis–trans* isomerization of square planar complexes. This is an example of strong symmetry lowering. There is only one distinct product of this reaction, and, since **R** and **P** have exactly the same symmetry operations, $L = \mathrm{E}$. The CSSRP therefore tells us that there is no concerted symmetry allowed rearrangement mechanism. It is now that the template symmetry concept becomes so useful. $1.\alpha$-type and $1.\beta$-type mechanisms are still not concertedly possible, though $1.\beta$ suggests a non-concerted mechanism to $\mathbf{I}_1$ (which is probably distorted from that illustrated in Fig. 5). However repetition of a $1.\beta$-type mechanism does not lead to **P**. As in the previous examples a $1.\gamma$ leads to a viable mechanism via $\mathbf{I}_2$ (Fig. 5). The biggest change due to the reduction of symmetry is that $1.\delta$ becomes an allowed mechanism (a missing atom and an atom can coalesce). However, the effect of the mechanism is the same as $5.\gamma$, so no new mechanism emerges.

Conclusions

The aim of this paper has been to illustrate how the symmetry determined reactivity of a high symmetry molecule (or system of molecules) also defines the reactivity of a lower symmetry molecule based on the same template. The particular example of transition metal complexes of octahedral parentage was used to illustrate the principles involved. In the examples where the symmetry is very weakly lowered from octahedral (tris chelate complexes) the symmetry allowed octahedral mechanism, $1.\gamma$, was the only operative mechanism. The main advantage of the template approach for these types of systems is that relationships between apparently unrelated mechanisms, such as the Ray Dutt and Bailar twists, become apparent when they are related to the same high symmetry analogue.

The second example of weak symmetry lowering was the monochelate complexes. Here, although it fits into the weak symmetry lowered category relative to the template, the actual symmetry is significantly reduced compared with that of the template and all degeneracy is lost. The consequent reduction in flexibility of the symmetry allowed geometry changes means that not all symmetry allowed mechanisms for the template were allowed for the monochelate complexes. In some cases they could only be used as a guide to determine feasible multistep paths.

Rather than being a limitation of the template approach, this is one of its greatest advantages as it directs the search for feasible reaction pathways.

The *cis*-dihydride complexes have the same symmetry operations as the monochelates, but their symmetry lowering from that of the octahedral template is much stronger, in fact a tetrahedral L_4 template with hydrogen atoms capping faces is an equally valid description. For these examples analysis of NMR data [11] had previously limited the identity of the products resulting from the isomerisation of the reactant. It was necessary to look for multi-step reaction pathways, with the octahedral trigonal twists mechanisms being the guide. A similar analysis based on the tetrahedral template yielded the same mechanisms, and a more helpful description of the process, since it more clearly differentiated two mechanisms, one which inverts the tetrahedron and one which retains its configuration.

The final example of square planar complexes is strongly symmetry lowered from the octahedron, and mechanisms $1.\beta$ and $1.\delta$ were no longer forbidden. In this case, there were no practical ramifications of these new mechanisms, as $1.\beta$ did not lead to a product, and $1.\delta$ behaved the same as $1.\gamma$.

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