Steric Courses of Chemical Reactions. II[1]

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Abstract: In certain situations the procedures for determining the possible steric courses of chemical reactions presented in part I of this series become unwieldy. This paper presents methods for coping with such situations. The definitions of the configurational symmetry groups are generalized to allow treatment of molecules which undergo internal motions which are immeasurably rapid on the observational time scale. A new group, the restricted group of allowed permutations, is defined which often eliminates the necessity of considering physically unrealistic reactions when determining the possible steric courses of reactions interconverting certain configurations. Special procedures for treating molecules with chiral skeletal frameworks are also presented. Finally, four examples are treated: the isomerization of "octahedral" tris chelates $M(A\text{–}A)_3$ and $M(A\text{–}B)_3$, water exchange of $Co(en)_2(NH_3)(H_2O)^{3+}$, permutational isomerization of a transition metal–π-allyl complex, and rearrangements of platinum–π-allene complexes. Emphasis is placed on the elucidation of mechanistic pathways by isotopic labeling experiments or dynamic nmr studies.

In part I of this series[1] (SCCR-I), procedures for classifying, enumerating, and representing topologically the steric courses of chemical reactions are presented. Although these procedures are general and self-consistent, results may be unduly complicated and indeed physically unrealistic when certain systems are treated. Figure 1 illustrates three situations where difficulties might be encountered. We shall briefly examine these examples to indicate the motivation for modifying the formalisms developed in SCCR-I.

A dissociative pathway for the permutational isomerization of PH_3BD_3 is shown in Figure 1a. As defined in SCCR-I, the appropriate proper configurational symmetry groups are $V^{VV} = C_3^{VV}$ and $W^{WW} = D_3^{WW} + C_3^{WW}$. Also, the group of allowed permutations is $H = S_1 + S_3 + S_1 + S_3$. If the configurations shown in Figure 1a are defined to be reference configurations, thus defining the labeling of skeletal positions, then the operation $h_i^{VV} = (1)(234)(5)(6)(7)(8)^{VV}$ is a permutational isomerization reaction since $h_i^{VV} \in H^{VV}$ is not an operation in V^{VV}. If, however, we assume "free" rotation about the A_1–C_5 bond in configurations having geometry V, *i.e.*, such internal motion is immeasurably rapid on the observational time scale, then $h_i^{VV} \in H^{VV}$ does not represent observable stereochemical change. In other words, h_i^{VV} is not a reaction from an operational point of view but should be defined to be an operation in the proper configurational symmetry group, which means that this group should be expanded. Thus for certain molecules undergoing internal motions which are immeasurably rapid on the observational time scale, a more general definition of the proper configurational symmetry group is in order.

In Figure 1b is shown a reaction of an "octahedral" D_3 tris-chelate complex $M(A\text{–}A)_3$. Defining the reactant configuration $\binom{l}{s}_e^X$, the reaction $h_i^{XX} = (13)(2)(4)(5)(6)^{XX}$ is mathematically a well-defined permutational isomerization reaction since $h_i^{XX} \in H^{XX} = S_6^{XX}$ and $h_i^{XX} \not\in D_3^{XX}$. In SCCR-I it was stipulated that ligands be unidentate because reactions such as h_i^{XX} involve bond breaking within a chelate ligand, and such a process is unrealistic in most experimental situations. In other words, h_i is mathematically an "allowed permutation," but chemically it is not an "allowed permutation," and in the interest of simplicity the group H should be restricted to a subgroup so that all operations in H^{XX} are chemically allowed.

The two reactions shown in Figure 1c occur with equal probability in a totally symmetric environment. These two reactions are, however, not "mirror images" as defined in SCCR-I because the two product configurations have different geometries. Yet these two reactions should be defined to be enantiomeric since both the products and reactants are related by a reflection operation. In general, when one or more molecules in a configuration have chiral skeletal frameworks, an extended definition of enantiomeric reactions is warranted.

The first three sections of this paper treat the three topics just discussed: expansion of the configurational symmetry groups, restriction of the group of allowed permutations, and generalization of the definition of enantiomeric reactions. In the final section four problems in dynamic stereochemistry are treated, demonstrating the utility of these modifications.

I. Configurational Symmetry Groups

As defined in SCCR-I, the equivalence of different configurations having the same geometry is implied by the rapid rotation and translation of molecules in the configuration. For configurations having geometry W, the proper configurational symmetry group W^{WW} represents these motions. Of course, not all rotations and translations of molecules in the configuration are represented by operations in W^{WW}. A motion is represented only if the skeletal frameworks of the transformed molecules and the original molecules in the configuration are superposed. These transformations are conveniently expressed in terms of permutation group representations of rotational point groups.

In this section we shall first extend the definition of the proper configurational symmetry group W^{WW} so that its operations represent not only rapid molecular rotations and translations but also rapid intramolecular

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[1] Part I: W. G. Klemperer, *J. Amer. Chem. Soc.*, **95**, 380 (1973).
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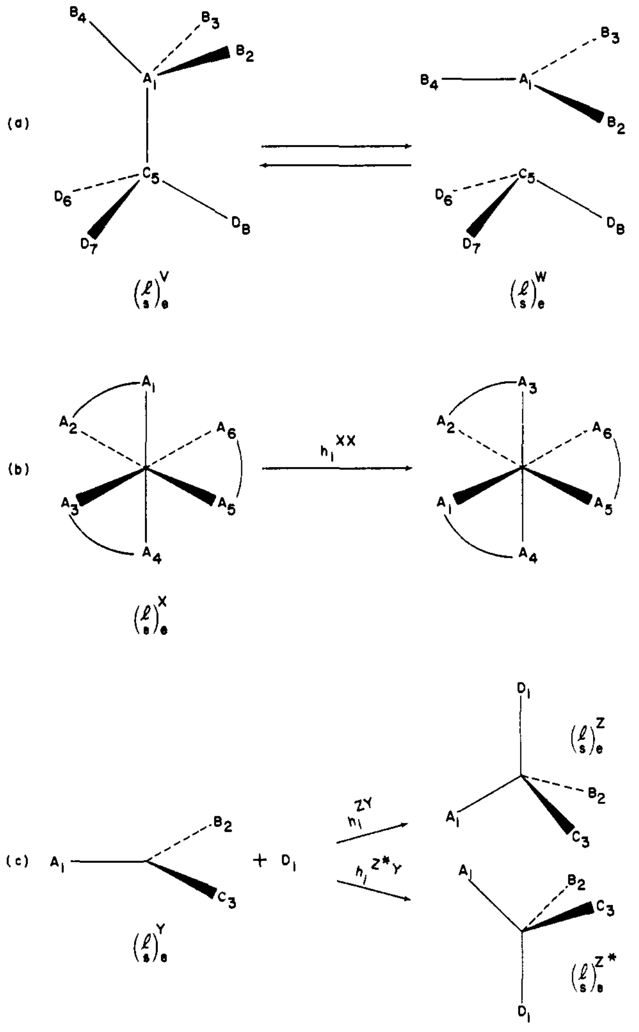

Figure 1. Three reactions which illustrate the need for the formalisms developed in this paper. As explained in the text, reaction (a) demonstrates the need for expanding the proper configurational symmetry group, (b) indicates the usefulness of restricting the group of allowed permutations, while the reactions in c show the motivation for generalizing the definition of enantiomeric reactions.

motions. By "rapid" we mean rapid on a given time scale, usually immeasurably rapid on the observational time scale, and in any case, rapid relative to the lifetime of the species in question. The definition of W^{WW} given in SCCR-I

$$W^{WW} = \sum_{i=1}^{m} S_{m_i}[R_i^{WW}] \tag{1}$$

is retained, but now the group R_i^{WW} must represent rapid intramolecular motions in addition to rotations and translations. Thus, R_i^{WW} is redefined as the *proper molecular symmetry group.*[3] Of course R_i^{WW} always contains a subgroup which represents the rotational point group of the molecule. Also, R_i^{WW} may differ for different time scales since intramolecular motions which are rapid on a given time scale may be slow on a shorter time scale. To avoid confusion, it will always be assumed that R_i^{WW} represents the molecule's rotational point group unless otherwise specified. Not all rapid intramolecular motions will be represented by operations in R_i^{WW}. A motion is represented only if the skeletal frameworks of the original molecule and the transformed molecule are superposable.

Some examples should clarify the preceding discussion. If the molecules in a configuration having geometry W shown in Figure 1a undergo no rapid internal motions, then $W^{WW} = D_3^{WW} + C_3^{WW}$. If, however, the C_3 molecule inverts at a rate which is immeasurably rapid on the observational time scale, then $W^{WW} = D_3^{WW} + D_3^{WW}$. For this example, the proper configurational symmetry groups are easily defined since both proper molecular symmetry groups may be expressed as representations of familiar molecular point groups. This will not always be the case, but often the proper molecular symmetry group may be conveniently defined in terms of the permutation groups E_n, the identity group degree n; C_n, the cyclic permutation group degree n; D_n, the dihedral permutation group degree n; and S_n, the symmetric group degree n, using the direct sum and composition operations introduced in SCCR-I.[6] For example, the configuration having geometry V shown in Figure 1a has the proper configurational symmetry group C_3^{VV} if the molecule undergoes no rapid internal motions. If, however, rotation about the A_1–C_5 bond is immeasurably rapid on the observational time scale, $V^{VV} = R^{VV} = (E_2 + C_3 + C_3)^{VV}$, and the permutation group V contains $|V| = |E_2 + C_3 + C_3| = |E_2| \cdot |C_3| \cdot |C_3| = 1 \cdot 3 \cdot 3 = 9$ operations.[7]

$$v_1 = (1)(2)(3)(4)(5)(6)(7)(8)$$
$$v_2 = (1)(234)(5)(678)$$
$$v_3 = (1)(243)(5)(687)$$
$$v_4 = (1)(234)(5)(6)(7)(8)$$
$$v_5 = (1)(243)(5)(6)(7)(8)$$
$$v_6 = (1)(2)(3)(4)(5)(678)$$
$$v_7 = (1)(2)(3)(4)(5)(687)$$
$$v_8 = (1)(234)(5)(687)$$
$$v_9 = (1)(243)(5)(678)$$

Some further examples are shown in Figure 2.

Before generalizing the definition of the full configurational symmetry group, we shall look closely at the definition provided in SCCR-I, where rapid intramolecular motions are not taken into account.

$$\bar{W}^{WW} = \sum_{i=1}^{m} S_{m_i}[\bar{R}_i^{WW}] \tag{2}$$

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(3) The permutation groups defined here and below are in most cases generalizations of those defined by Pólya.[4] The proper molecular group is closely related to Pólya's "Gruppe der Stereoformel," the full molecular symmetry group is closely related to Pólya's "erweiterte Stereoformelgruppe," and the restricted group of allowed permutations is related to Pólya's "Gruppe der Strukturformel." Indeed, when defining the composition operation, Pólya provided a "geometric-kinematic" example[5] which in a sense anticipated the chemists' interest in the symmetry groups of nonrigid molecules.

(4) G. Pólya, *Acta Mathematica*, 68, 213 (1937).

(5) Reference 4, p 178.

(6) These groups and operations are defined and simple graph-theoretical applications are given in F. Harary, "Graph Theory," Addison-Wesley, Reading, Mass., 1969, pp 163–168. See also R. W. Robinson, *J. Combinatorial Theory*, 4, 184 (1968); and ref 5, pp 177–180. Note that the direct sum is often called the sum, product, or direct product and the composition is often called the "Gruppenkranz" or wreath product. Although the symbols for the cyclic and dihedral permutation groups are the same as the symbols for their isomorphic point groups, their intended significance should be clear from context.

(7) In calculating group orders, the following relations are of help: $|E_n| = 1$, $|C_n| = n$, $|D_n| = 2n$, $|S_n| = n!$, $|A + B| = |A| \cdot |B|$, and $|A[B]| = |A| \cdot |B|^d$, where d is the degree of the permutation group A.

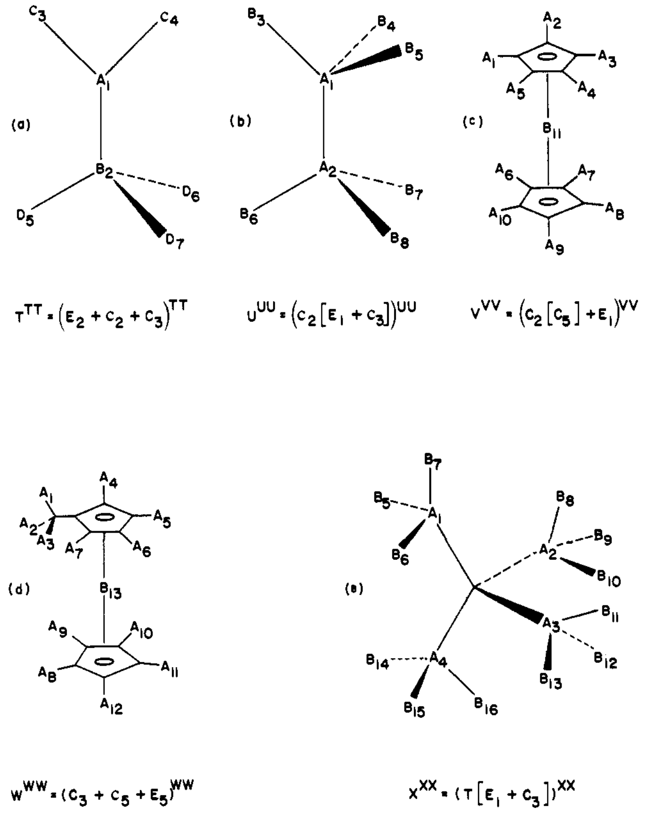

Figure 2. Some configurations and their proper configurational symmetry groups: (a) methylborane, rapid rotation about the boron–carbon bond is assumed; (b) ethane, rapid rotation about the carbon–carbon bond is assumed; (c) ferrocene, rapid rotation of the cyclopentadienyl rings is assumed; (d) methylferrocene, rapid rotation of the methyl group and the cyclopentadienyl rings is assumed; (e) neopentane, rapid rotation about all carbon–carbon bonds is assumed. Note that the definition of the proper configurational symmetry group does not depend on the particular conformations of the molecules in the configuration shown in the drawings.

Here, $\bar{R}_i^{WW}$ is a representation of the full point group of a molecule having geometry *i*. We can generate the permutation group $\bar{R}_i$ from a slightly different point of view which will be useful below. First of all, $\bar{R}_i$ contains permutations which represent rotations of the molecule in space; *i.e.*, $\bar{R}_i$ contains R_i as a subgroup. The group $\bar{R}_i$ may contain more operations if we invert the molecule and the inverted molecule has the same geometry as the original molecule, that is, if the inverted molecule can be transformed by rotation and/or translation such that the skeletal frameworks of the inverted molecule and the original molecule can be superposed. If this sequence of operations can be performed, then we say that the molecule has an achiral skeletal framework, and these transformations when expressed as permutation operations are said to represent improper rotations. Operations in $\bar{R}_i$ which are also in R_i are said to represent proper rotations. If the above sequence cannot be executed, *i.e.*, the skeletal frameworks of the inverted molecule and the original molecule are not superposable, then we say that the molecule has a chiral skeletal framework and $\bar{R}_i = R_i$.

This procedure for generating $\bar{R}_i$ when a molecule undergoes no rapid internal motions is shown in Figure 3a. The molecule i is considered to be part of a reference configuration having geometry W, and therefore $R_i^{WW} = C_3^{WW}$ contains these operations

$$r_1^{WW} = (1)(2)(3)(4)^{WW}$$

$$r_2^{WW} = (1)(234)^{WW}$$

$$r_3^{WW} = (1)(243)^{WW}$$

Inversion of molecule i yields molecule ii, and by rotating molecule ii to iii it is evident that i and ii have superposable skeletal frameworks. Thus the molecule has an achiral skeletal framework, and we can generate three operations which represent improper rotation.

$$\bar{r}_4^{WW} = (1)(2)(34)^{WW}$$

$$\bar{r}_5^{WW} = (1)(23)(4)^{WW}$$

$$\bar{r}_6^{WW} = (1)(24)(3)^{WW}$$

In Figure 3b is shown a molecule which has a chiral skeletal framework; if i is inverted, it is evident that the skeletal frameworks of the inverted molecule ii and the molecule i are not congruent.

We now use an almost identical procedure for generating the full configurational symmetry group when molecules in a configuration undergo rapid intramolecular motions. Equation 2 is still used to define $\bar{W}^{WW}$, but $\bar{R}_i^{WW}$ is redefined to take into account rapid internal motions and is called the *full molecular symmetry group*.[8] The group $\bar{R}_i^{WW}$ always contains R_i^{WW} as a subgroup. However, $\bar{R}_i^{WW}$ may contain additional operations which represent inversion plus rotation and/or internal motions of the molecule. These new operations in $\bar{R}_i^{WW}$ may be generated following a procedure similar to that used in the preceding paragraph. If we invert a molecule and the inverted molecule can be transformed by translation, rotation, and/or rapid internal motion such that the skeletal frameworks of the original molecule and the transformed molecule are superposed, then the permutation operation representations of these operations are elements in $\bar{R}_i$. If such a sequence of operations can be carried out, the molecule is said to have an achiral skeletal framework and the permutation operations so generated are said to represent improper rotations. Operations in $\bar{R}_i^{WW}$ which are also in R_i^{WW} are said to represent proper rotations. If the above sequence of operations cannot be carried out, *i.e.*, the skeletal frameworks of the original molecule and the transformed molecule are not superposable, then we say the molecule has a chiral skeletal framework.

An example should clarify this procedure. In Figure 3c, the configuration i represents hydrazine in a skewed conformation. If rotation about the A_1–A_2 (nitrogen–nitrogen) bond is rapid but inversion at the nitrogen centers is measurably slow on the observational time scale, then $R_i^{WW} = (S_2[E_3])^{WW}$, $|R_i^{WW}| = 2$. Inversion of i followed by internal rotation about the A_1–A_2 bond yields molecule iii whose skeletal framework is congruent with that of molecule i. Thus $\bar{R}_i^{WW}$ contains

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[8] It is important to emphasize that the groups $\bar{R}_i$ and R_i are pure permutation groups, not permutation–inversion groups used by Longuett-Higgins[9] and others to solve quantum-mechanical problems. The difference is quite basic and may be seen by comparing the full molecular symmetry group $\bar{R}_i^{WW}$ for hydrazine, given below, with the permutation–inversion group generated by Longuett-Higgins in ref 9.

[9] H. C. Longuett-Higgins, *Mol. Phys.*, 6, 445 (1963).

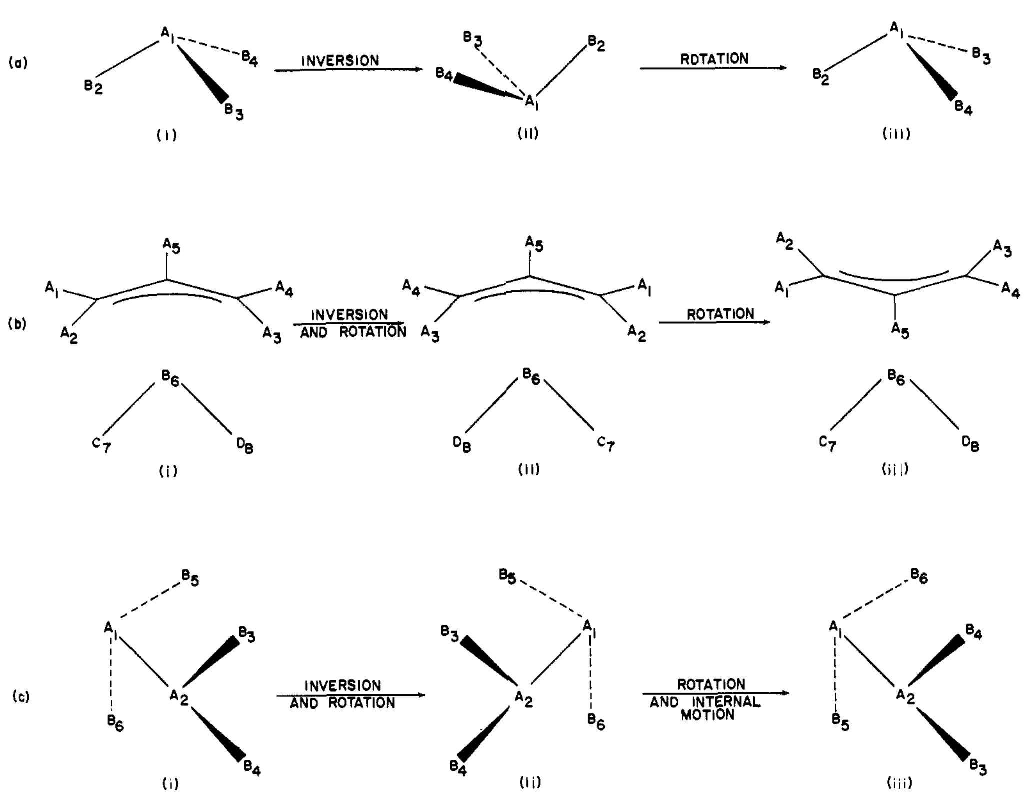

Figure 3. These three drawings illustrate the procedure for generating full molecular symmetry groups described in the text. The planar allyl ligand shown in (b) does not lie in the plane defined by B_6, C_7, and D_8.

four operations, two of which represent inversion of configuration

$$r_1^{WW} = \bar{r}_1^{WW} = (1)(2)(3)(4)(5)(6)^{WW}$$
$$r_2^{WW} = \bar{r}_2^{WW} = (12)(36)(45)^{WW}$$
$$\bar{r}_3^{WW} = (1)(2)(34)(56)^{WW}$$
$$\bar{r}_4^{WW} = (12)(35)(46)^{WW}$$

If we assume that inversion at each nitrogen center as well as rotation about the nitrogen-nitrogen bond is rapid, then $R_i^{WW} = \bar{R}_i^{WW} = (S_2[E_1 + S_2])^{WW}$. Both configurational symmetry groups now contain $|S_2[E_1 + S_2]| = (2!)\cdot(1\cdot 2!)^2 = 8$ operations.

A molecule may have a chiral skeletal framework when it undergoes no rapid internal motions but the same molecule may have an achiral skeletal framework when certain internal motions are rapid (see Figure 3b). As we saw in SCCR-I, operations which represent improper rotation may also represent proper rotation. However, there are only two possibilities: either $|\bar{R}_i| = |R_i|$ or $|\bar{R}_i| = 2|R_i|$.

Using the generalized definitions of operations which represent proper and improper rotations, and of the proper and full configurational symmetry groups, all further definitions provided in SCCR-I may be used intact to classify, enumerate, and represent topologically the steric courses of chemical reactions. Note, however, that the geometry of a configuration is no longer defined in a strict sense; two configurations are considered to have the same geometry if they contain the same molecules in different conformations and these conformations interconvert rapidly relative to the experimental time scale.

Under certain experimental conditions, intermolecular processes may occur at an immeasurably rapid rate on the observational time scale. In this case, eq 1 and 2 will no longer be valid. Appropriate groups may be generated, however, by relying on the general rules that W^{WW} contains all operations in H^{WW} which represent rotations and translations of molecules as well as processes whose rate is rapid, while $\bar{W}^{WW}$ is generated by operations in W^{WW} and operations representing improper rotation of molecules in the configuration.

II. The Restricted Group of Allowed Permutations

The group of allowed permutations is defined by

$$H = \sum_{i=1}^{c} S_{n_i}$$

when a ligand set contains n_i ligands of chemical identity i and ligands in the ligand set have c different chemical identities. Therefore n, the total number of ligands in the ligand set, equals $\Sigma^c_{i=1} n_i$. As was pointed out in the introductory section, it is often judicious to restrict the group of allowed permutations to a subgroup in order to rule out reactions and configurations which are not allowed from a chemical point of view. This subgroup, consisting of "chemically allowed" permutations, is called the *restricted group of allowed permutations* and is denoted H'. It is of course impossible to provide a mathematical definition for the restricted group of allowed permutations since its definition is not based on general mathematical considerations. As was the case for molecular symmetry groups, however, the group H' is often conveniently defined in terms of the permutation groups E_n, C_n, D_n, and S_n using the direct sum and composition operations.

The configuration $\binom{l}{s}_e^{\mathrm{X}}$ drawn in Figure 1b represents an "octahedral" D_3 chelate complex, $\mathrm{M(A{-}A)_3}$. If bond breaking within a chelate ligand is not chemically allowed, then $H = S_6$ must be restricted to $H' = S_3[S_2]$. Here S_3 represents permutations of entire bidentate ligands, while S_2 represents permutations within each ligand. Use of H' instead of H, as we shall see in the final section, simplifies treatment considerably since only $|H'| = 3!\cdot 2!^3 = 48$ of the $6! = 720$ operations in H represent chemically allowed processes. In Figure 1a, the lines connecting the termini of the chelate ligands are considered to be part of the skeletal framework. Since conformations of the bidentate ligands have been ignored, the point group of the molecule is D_3.

Careful attention must be paid to the indexing of skeletal positions when using H' if reactions interconverting configurations having different geometries are considered. Skeletal positions must always be indexed such that the reactions interconverting reference configurations having different geometries are "chemically allowed."

Figure 4a shows an "octahedral" C_3 chelate complex $\mathrm{M(A{-}B)_3}$. Here $H = S_3 + S_3$, but if bond breaking within a chelate ligand is ruled out, H is restricted to $H' = S_3[E_2]$. For the C_1 chelate complex shown in Figure 4b, $H' = S_3[E_2]$ since it has the same ligand set as the configuration shown in Figure 4a. Both these configurations are well defined reference configurations since ligand labeling is consistent and transformation of $\binom{l}{s}_e^{\mathrm{T}}$ to $\binom{l}{s}_e^{\mathrm{U}}$ involves no bond breaking within a chelate ligand. Assume that breaking of carbon–hydrogen bonds is not allowed in the reactions of the configuration shown in Figure 4c. Thus although $H = S_5 + E_3$, H' is defined by $S_2[S_2] + E_4$. The configuration shown in Figure 4d represents $\mathrm{Fe(CO)_2(C_5H_5)_2}$. Here $H = S_{10} + S_2 + E_1$, but if breaking of carbon–hydrogen and carbon–carbon bonds is to be ruled out, then $H' = S_2[D_5] + S_2 + E_1$. If we are considering permutational isomerization reactions and the metal is not allowed to pass from one side of a cyclopentadienyl ring to the other, then $H' = S_2[C_5] + S_2 + E_1$. For the configuration shown in Figure 4e, bicyclobutane, we may wish to rule out the breaking of carbon–hydrogen bonds. Then $H' = S_2[E_2] + S_2[S_2 + E_1]$. When considering reactions interconverting configurations having the geometries shown in Figure 4e and 4f, the indicated reference configurations are well defined since their interconversion does not involve breaking of carbon–hydrogen bonds. The configurations shown in Figures 4e and 4g, however, could not serve as reference configurations when using $H' = S_2[E_2] + S_2[S_2 + E_1]$ since their interconversion involves breaking of carbon–hydrogen bonds.

When H'^{WW} is used instead of H^{WW} to treat stereochemical problems, it is useful to define the *restricted configuration count* I'_{W}

$$I'_{\mathrm{W}} = |H'^{\mathrm{WW}}|/|W^{\mathrm{WW}}| \tag{3}$$

which reflects the fact that restriction of the group of allowed permutations reduces the number of "chemically allowed" configurations. When H'^{WW} acts on $\binom{l}{s}_e^{\mathrm{W}}$, the set of $|H'|$ configurations generated contains only I'_{W} nonequivalent configurations. We call such a set of I'_{W} configurations a maximal set of nonequivalent configurations. Equation 3 is well defined only if W^{WW} is a subgroup of H'^{WW}. This must always be the case since W^{WW} represents rapid motions which must of course be "chemically allowed." Thus, we can define right cosets $W^{\mathrm{WW}}h'_i{}^{\mathrm{WW}}$, coset representatives $c'_i{}^{\mathrm{W}}$, and a set of coset representatives C'^{W}, following the procedures of SCCR-I but replacing H by H'.

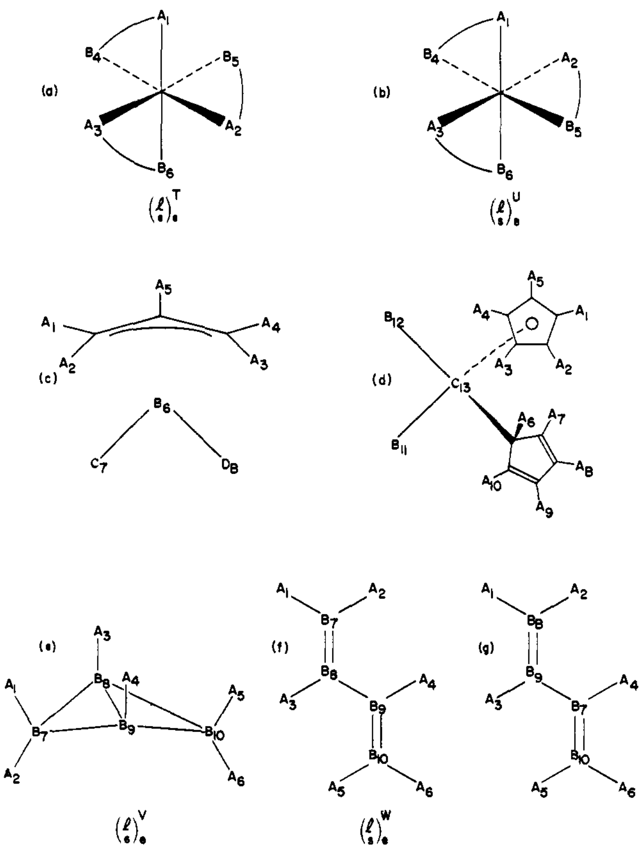

Figure 4. Some configurations used in the text to show the usefulness of the restricted group of allowed permutations.

The definitions given in SCCR-I may also be used to select from H'^{WV} maximal sets of reactions differentiable in a chiral environment, diastereomeric reactions, and reactions differentiable in a totally symmetric environment. In general, however, the enumeration formulas provided in SCCR-I may not be used to enumerate reactions in H' since H' is, in general, not the direct sum of symmetric groups and $\bar{W}$ and $\bar{V}$ are in general not subgroups of H'.

A maximal set of reactions in H'^{WV} differentiable in a chiral environment may be obtained following a procedure similar to that used in SCCR-I to obtain complete sets of reactions in H^{WV} differentiable in a chiral environment. The I'_{W} reactions which transform $\binom{l}{s}_e^{\mathrm{V}}$ into the I'_{W} configurations comprising a maximal set of nonequivalent configurations having geometry W must contain a maximal set of reactions differentiable in a chiral environment. Also, given a maximal set of reactions in H'^{WV} differentiable in a chiral environment, the reverse reactions of these reactions form a maximal set of reactions in H'^{VW} differentiable in a chiral environment. If $h'_i{}^{\mathrm{WV}}$ and $h'_j{}^{\mathrm{WV}}$ are differentiable in a chiral environment, then by definition

$$h'_i{}^{\mathrm{WV}} \neq w_k{}^{\mathrm{WW}} \cdot h'_j{}^{\mathrm{WV}} \cdot v_e{}^{\mathrm{VV}}$$

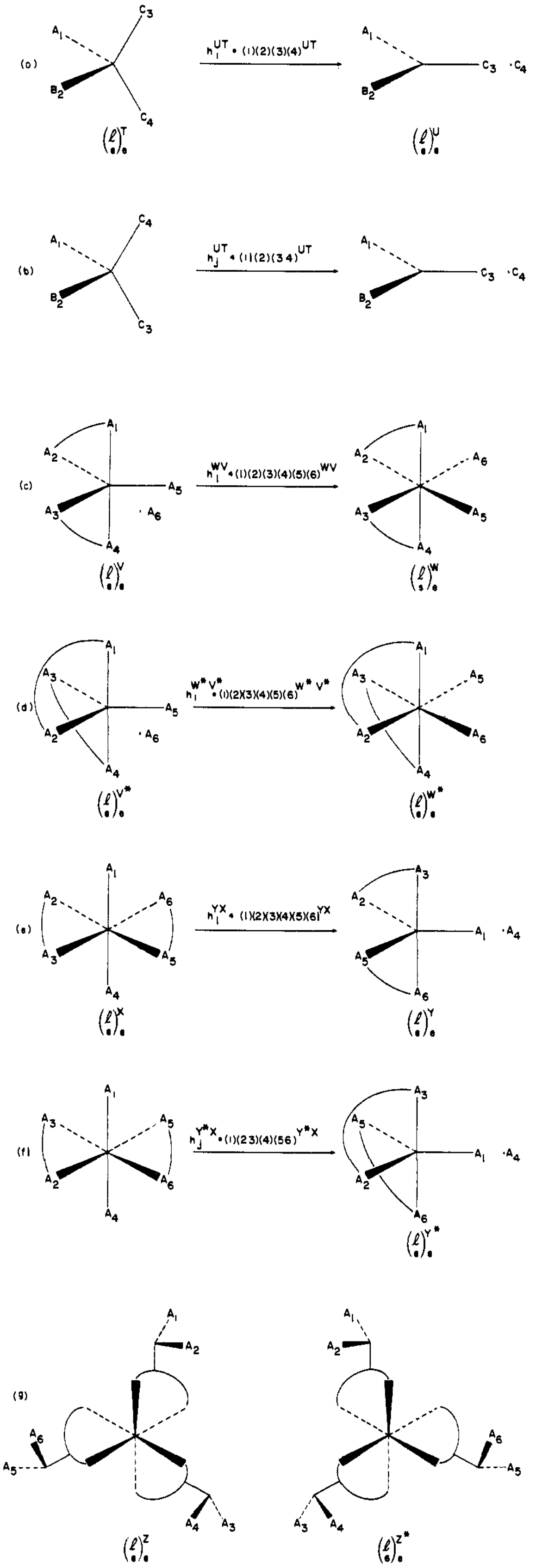

Figure 5. Three pairs of enantiomeric reactions are shown in a–f. The configurations in (g) represent *cis*-tris(α-isopropyltropolonato) complexes.

for all $w_k^{WW} \in W^{WW}$ and all $v_e^{VV} \in V^{VV}$. Multiplying both sides of this inequality on the left by $(h'_i{}^{-1})^{VW}$ and on the right by $(v_e^{-1})^{VV} \cdot (h'_j{}^{-1})^{VW} \cdot (w_k^{-1})^{WW}$, we obtain

$$(v_e^{-1})^{VV} \cdot (h'_j{}^{-1})^{VW} \cdot (w_k^{-1})^{WW} \neq (h'_i{}^{-1})^{VW}$$

i.e., $(h_j^{-1})^{VW}$ and $(h_i^{-1})^{VW}$ are differentiable in a chiral environment.

III. Enantiomeric Reactions

In SCCR-I, the "mirror images" of a reaction are defined only if all the molecules in both the reactant and product configurations have achiral skeletal frameworks; *i.e.*, both configurations have achiral skeletal frameworks. The concept of "mirror images" is useful in that a reaction and its "mirror images" occur with equal probability in a totally symmetric environment. The reader may verify that the reactions shown in Figures 5a and 5b are "mirror images" and in addition enantiomeric reactions since they are differentiable in a chiral environment. According to the definitions given in SCCR-I, each reaction is thus called a chiral reaction. The physical motivation for the definition of "mirror images" is seen by comparing the reactions drawn in Figures 5a and 5b: The reactant (product) of the reaction a is related to the reactant (product) of the reaction b by inversion. The formal definitions given in SCCR-I can be used here since the stereochemical consequences of inversion can be represented by permutation operations (both configurations have achiral skeletal frameworks). When reactant and/or product configurations have chiral skeletal frameworks, *i.e.*, contain one or more molecules having chiral skeletal frameworks, the stereochemical consequences of inverting the reactant and product configurations cannot be expressed by pure permutation operations and thus the formal definitions given in SCCR-I are not applicable. However, the physical motivation for the definition of enantiomeric reactions still exists. We shall first examine the case where both reactant and product configurations have chiral skeletal frameworks and then turn to the case where either reactant or product configurations have chiral skeletal frameworks.

In Figure 5c is shown a reaction which interconverts configurations having chiral skeletal frameworks. By inverting both the reactant and product configurations, we obtain the reaction shown in Figure 5d. These reactions must occur with equal probability in a totally symmetric environment, and we can formally define them to be "mirror images" in a convenient fashion by adopting a suitable convention for indexing the skeletal positions of a chiral skeletal framework and its enantiomer. This is done as follows: given the reference configuration $\binom{l}{s}_e{}^{W}$ which has a chiral skeletal framework, we invert this configuration and define the inverted configuration to be the reference configuration $\binom{l}{s}_e{}^{W^*}$ (compare Figures 5c and 5d). This means that the operations e^{WW^*} and e^{W^*W}, where e is the identity operation in H, represent inversion of configuration and the proper configurational symmetry groups W^{WW} and $W^{W^*W^*}$ are both representations of the same permutation group W. Thus if all configurations having geometry V and W have chiral skeletal frameworks, the reactions h_p^{VW} and $h_q^{V^*W^*}$ are defined to be "mirror images" if and only if

$$h_p^{VW} = v_i^{VV} \cdot e^{VV^*} \cdot v_j^{V^*V^*} \cdot h_q^{V^*W^*} \cdot w_k^{W^*W^*} \cdot e^{W^*W} \cdot w_l^{WW} = (v_m \cdot h_q \cdot w_n)^{VW} \quad (4)$$

for some $v_i, v_j \in V$ and some w_k, $w_l \in W$. In other words, h_p^{VW} and $h_q^{\mathrm{V^*W^*}}$ are "mirror images" if and only if h_p^{VW} and h_q^{VW} are nondifferentiable in a chiral environment. Since h_p^{VW} and $h_q^{\mathrm{V^*W^*}}$ cannot be nondifferentiable in a chiral environment, if they are "mirror images" they must be enantiomeric. For the sake of consistency with SCCR-I, all reactions involving configurations which have chiral skeletal frameworks are defined to be chiral reactions. Also, if

$$\binom{l}{s}_j^{\mathrm{V^*}} = v_i^{\mathrm{V^*V}}\binom{l}{s}_k^{\mathrm{V}}$$

then $\binom{l}{s}_j^{\mathrm{V^*}}$ and $\binom{l}{s}_k^{\mathrm{V}}$ are defined to be enantiomeric configurations. Following the procedure used in eq 4, $h_p^{\mathrm{VW^*}}$ and $h_q^{\mathrm{V^*W}}$ are defined to be enantiomeric reactions if h_p^{VW} and h_q^{VW} are nondifferentiable in a chiral environment. Of course h_p^{VW} and $h_q^{\mathrm{VW^*}}$ (or h_p^{VW} and $h_q^{\mathrm{V^*W}}$) cannot be enantiomeric reactions.

The arguments used in the preceding paragraph are easily applied to the case where either reactant or product configurations, but not both, have chiral skeletal frameworks (see Figures 5e and 5f). If configurations having geometry V have achiral skeletal frameworks, but configurations having geometry W have chiral skeletal frameworks, then the chiral reactions h_p^{VW} and $h_q^{\mathrm{VW^*}}$ are enantiomeric if and only if

$$h_p = \bar{v}_m \cdot h_q \cdot w_n$$

where $\bar{v}_m^{\mathrm{VV}} \in \bar{V}^{\mathrm{VV}}$ represents inversion of configuration and $w_n^{\mathrm{WW}} \in W^{\mathrm{WW}}$. Similarly, h_p^{WV} and $h_q^{\mathrm{W^*V}}$ are enantiomeric if and only if

$$h_p = w_n \cdot h_q \cdot \bar{v}_m$$

for some $w_n^{\mathrm{WW}} \in W^{\mathrm{WW}}$ and some $\bar{v}_m^{\mathrm{VV}} \in \bar{V}^{\mathrm{VV}}$ which represents inversion of configuration.

Since the definitions of enantiomeric reactions and chiral reactions have been generalized, certain definitions and relations presented in SCCR-I now hold only if reactant and product configurations have achiral skeletal frameworks and must be modified for cases involving configurations having chiral skeletal frameworks. First of all, the formulas for calculating connectivities given in SCCR-I must be modified. If configurations having geometries V and W have chiral skeletal frameworks, then any reaction $h_p^{\mathrm{WV}} \in H^{\mathrm{WV}}$ is chiral, its "mirror image" $h_p^{\mathrm{W^*V^*}}$ occurs with equal probability in a totally symmetric environment, and

$$\delta_{\mathrm{W^*V^*}} = \delta_{\mathrm{WV}} = \frac{|V|}{|V \cap h_p^{-1} W h_p|}$$

If configurations having geometry V have chiral skeletal frameworks and configurations having geometry W have achiral skeletal frameworks, then $h_p^{\mathrm{WV}} \in H^{\mathrm{WV}}$ is chiral and

$$\delta_{\mathrm{WV^*}} = \delta_{\mathrm{WV}} = \frac{|V|}{|V \cap h_p^{-1} W h_p|}$$

$$\delta_{\mathrm{V^*W}} = \delta_{\mathrm{VW}} = \frac{|W|}{|W \cap h_p V h_p^{-1}|}$$

Equation 29 in SCCR-I presents an expression $\psi^{\mathrm{XV}}(h_q^{\mathrm{XW}};\ h_p^{\mathrm{WV}})$ which defines the net stereochemical changes implied by the sequence h_p^{WV} followed by h_q^{XW}. Procedures for calculating $\psi^{\mathrm{XV}}(h_q^{\mathrm{XW}};\ h_p^{\mathrm{WV}})$ depend on whether or not h_p^{WV} and/or h_q^{XW} are chiral, chirality being defined within the context of configurations having achiral skeletal frameworks. Modification of these procedures is straightforward and will be indicated in the course of treating specific examples in the final section of this paper.

When generating maximal sets of reactions differentiable in a chiral environment involving configurations with chiral skeletal frameworks, the following relations are of great help. If all configurations having geometries V and W, V $\neq$ W, have chiral skeletal frameworks and $\{h'^{\mathrm{VW}}_1, h'^{\mathrm{VW}}_2, \ldots, h'^{\mathrm{VW}}_n\}$ is a maximal set of reactions differentiable in a chiral environment, then the sets $\{h'^{\mathrm{VW^*}}_1, h'^{\mathrm{VW^*}}_2, \ldots, h'^{\mathrm{VW^*}}_n\}$, $\{h_1'^{\mathrm{V^*W}}, h'^{\mathrm{V^*W}}_2, \ldots, h'^{\mathrm{V^*W}}_n\}$, and $\{h'^{\mathrm{V^*W^*}}_1, h'^{\mathrm{V^*W^*}}_2, \ldots, h'^{\mathrm{V^*W^*}}_n\}$ are also maximal sets of reactions differentiable in a chiral environment. If V = W, these relations must be modified since $w_i^{\mathrm{W^*W}}$ is a reaction, while w_i^{WW} is not a reaction. Thus, if $\{h'^{\mathrm{WW}}_1, h'^{\mathrm{WW}}_2, \ldots, h'^{\mathrm{WW}}_n\}$ is a maximal set of reactions differentiable in a chiral environment, then the sets $\{e^{\mathrm{WW^*}}, h'^{\mathrm{WW^*}}_1, h'^{\mathrm{WW^*}}_2, \ldots, h'^{\mathrm{WW^*}}_n\}$, $\{e^{\mathrm{W^*W}}, h'^{\mathrm{W^*W}}_1, h'^{\mathrm{W^*W}}_2, \ldots, h'^{\mathrm{W^*W}}_n\}$, and $\{h'^{\mathrm{W^*W^*}}_1, h'^{\mathrm{W^*W^*}}_2, \ldots, h'^{\mathrm{W^*W^*}}_n\}$ are also maximal sets of reactions differentiable in a chiral environment. All these relations hold for the case of $H' = H$, where we are dealing with complete sets of reactions differentiable in a chiral environment. The first of the above relations is proved as follows, and the others may be proved in a similar fashion. By definition, h'^{VW}_1 and h'^{VW}_2 are differentiable in a chiral environment if

$$h'^{\mathrm{VW}}_1 \neq v_i^{\mathrm{VV}} \cdot h'^{\mathrm{VW}}_2 \cdot w_j^{\mathrm{WW}}$$

for all $v_i^{\mathrm{VV}} \in V^{\mathrm{VV}}$ and all $w_j^{\mathrm{WW}} \in W^{\mathrm{WW}}$, or equivalently if

$$h'_1 \neq v_i \cdot h_2 \cdot w_j$$

for all $v_i \in V$ and all $w_j \in W$. Due to the manner in which skeletal positions of configurations having geometry W* were indexed, the proper configurational symmetry group $W^{\mathrm{W^*W^*}}$ is also a representation of the group W. Therefore

$$h'^{\mathrm{VW^*}}_1 \neq v_i^{\mathrm{VV}} \cdot h'^{\mathrm{VW^*}}_2 \cdot w_j^{\mathrm{W^*W^*}}$$

for all $v_i^{\mathrm{VV}} \in V^{\mathrm{VV}}$ and all $w_j^{\mathrm{W^*W^*}} \in W^{\mathrm{W^*W^*}}$; *i.e.*, $h'^{\mathrm{VW^*}}_1$ and $h'^{\mathrm{VW^*}}_2$ are differentiable in a chiral environment.

In this section and the preceding section, two different special procedures for indexing skeletal positions have been described: one is used when treating systems using the restricted group of allowed permutations, while the other is used when reactions interconvert configurations having enantiomeric skeletal frameworks. Unfortunately, these two procedures may demand conflicting labeling schemes. An example of such a case is the "inversion" of *cis*-tris(α-isopropyltropolone) complexes. Assuming that only the isopropyl methyl groups are of stereochemical interest, the configurations shown in Figure 5g represent the isomers in question. Both configurations are well defined reference configurations according to the procedures given in this section in that $e^{\mathrm{ZZ^*}}$ and $e^{\mathrm{Z^*Z}}$ represent inversion of configuration. However, if inversion at carbon centers is not "chemically allowed," then $H' = S_3[E_2]$, and the reference configurations are not well defined since $e^{\mathrm{ZZ^*}}$ and $e^{\mathrm{Z^*Z}}$ involve inversion

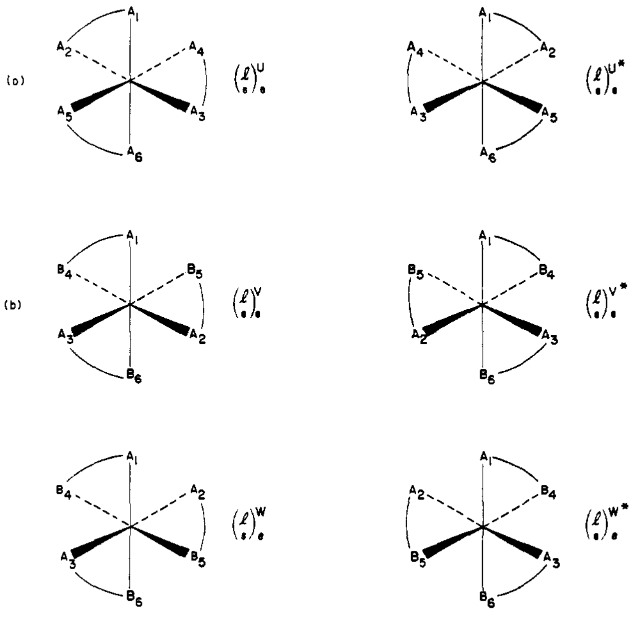

Figure 6. Reference configurations having the geometries possible for "octahedral" tris-chelate compounds $M(A–A)_3$ are shown in (a). In (b) are shown reference configurations having the geometries possible for "octahedral" tris-chelate compounds $M(A–B)_3$.

at carbon centers. This dilemma is best resolved by letting $H' = S_3[S_2]$, generating maximal sets of reactions in $H'^{\mathrm{ZZ}*}$ and $H'^{\mathrm{Z}*\mathrm{Z}}$ and then eliminating from those reactions which are not "chemically allowed," thus obtaining maximal sets of chemically allowed reactions differentiable in a chiral environment.

IV. Examples

A. Isomerization of "Octahedral" Tris-Chelate Complexes. The isomerization of "octahedral" tris-chelate complexes poses one of inorganic chemistry's oldest problems in dynamic stereochemistry.[10] The mechanisms and steric courses of these isomerizations, however, are of current interest from both an experimental and theoretical point of view.[11]

We shall determine here all the possible steric courses of isomerization reactions for the two simplest cases, the $M(A–A)_3$ case and the $M(A–B)_3$ case.

For the $M(A–A)_3$ case, all isomerization reactions interconvert configurations having the two geometries shown in Figure 6a. The proper configurational symmetry groups are $U^{\mathrm{UU}} = D_3^{\mathrm{UU}}$ and $U^{\mathrm{U}*\mathrm{U}*} = D_3^{\mathrm{U}*\mathrm{U}*}$. The group of allowed permutations is S_6, and assuming that bond breaking within a chelate ligand is not "chemically allowed," $H' = S_3[S_2]$. Of interest, therefore, are maximal sets of reactions in H'^{UU}, $H'^{\mathrm{U}*\mathrm{U}*}$, $H'^{\mathrm{UU}*}$, and $H'^{\mathrm{U}*\mathrm{U}}$ differentiable in a chiral environment. Since $I'_{\mathrm{U}} = I'_{\mathrm{U}*} = |H'|/|U| = 3! \cdot 2^3/6 = 8$, the eight operations which transform $\binom{l}{s}_e^{\mathrm{U}}$ into a maximal set of nonequivalent configurations having geometry U must contain a maximal set of reactions differentiable in a chiral environment. Such a set of nonequivalent configurations is easily generated, and the reader may verify that the eight operations

$$h'^{\mathrm{UU}}_1 = (1)(2)(3)(4)(5)(6)^{\mathrm{UU}}$$
$$h'^{\mathrm{UU}}_2 = (12)(3)(4)(5)(6)^{\mathrm{UU}}$$
$$h'^{\mathrm{UU}}_3 = (1)(2)(34)(5)(6)^{\mathrm{UU}}$$
$$h'^{\mathrm{UU}}_4 = (1)(2)(3)(4)(56)^{\mathrm{UU}}$$
$$h'^{\mathrm{UU}}_5 = (12)(34)(5)(6)^{\mathrm{UU}}$$
$$h'^{\mathrm{UU}}_6 = (12)(3)(4)(56)^{\mathrm{UU}}$$
$$h'^{\mathrm{UU}}_7 = (1)(2)(34)(56)^{\mathrm{UU}}$$
$$h'^{\mathrm{UU}}_8 = (12)(34)(56)^{\mathrm{UU}}$$

generate a maximal set of nonequivalent configurations when acting on $\binom{l}{s}_e^{\mathrm{U}}$. To derive from this set a maximal set of reactions differentiable in a chiral environment, we note that $h'^{\mathrm{UU}}_1 = e^{\mathrm{UU}}$ is not a reaction and h'^{UU}_2, h'^{UU}_3, and h'^{UU}_4 are formally indistinguishable permutational isomerization reactions in a chiral environment[12] and are therefore nondifferentiable in a chiral environment. The same holds true for h'^{UU}_5, h'^{UU}_6, and h'^{UU}_7. The sets $(Uh'_2)^{\mathrm{UU}}$, $(Uh'_5U)^{\mathrm{UU}}$, and $(Uh'_8U)^{\mathrm{UU}}$ are mutually exclusive and therefore h'^{UU}_2, h'^{UU}_5, and h'^{UU}_8 are differentiable in a chiral environment. Since $\{h'^{\mathrm{UU}}_2, h'^{\mathrm{UU}}_5, h'^{\mathrm{UU}}_8\}$ is a maximal set of reactions differentiable in a chiral environment, it follows that $\{h'^{\mathrm{U}*\mathrm{U}*}_2, h'^{\mathrm{U}*\mathrm{U}*}_5, h'^{\mathrm{U}*\mathrm{U}*}_8\}$, $\{h'^{\mathrm{UU}*}_1, h'^{\mathrm{UU}*}_2, h'^{\mathrm{UU}*}_5, h'^{\mathrm{UU}}_8\}$, and $\{h'^{\mathrm{U}*\mathrm{U}}_1, h'^{\mathrm{U}*\mathrm{U}}_2, h'^{\mathrm{U}*\mathrm{U}}_5, h'^{\mathrm{U}*\mathrm{U}}_8\}$ are also maximal sets of reactions differentiable in a chiral environment, as explained above in section III.

Summarizing, all distinct steric courses of reactions interconverting configurations having the geometries shown in Figure 6a are defined by the following seven reactions and their enantiomers

$$h'^{\mathrm{UU}}_2 = (12)(3)(4)(5)(6)^{\mathrm{UU}}$$
$$h'^{\mathrm{UU}}_5 = (12)(34)(5)(6)^{\mathrm{UU}}$$
$$h'^{\mathrm{UU}}_8 = (12)(34)(56)^{\mathrm{UU}}$$
$$h'^{\mathrm{U}*\mathrm{U}}_1 = (1)(2)(3)(4)(5)(6)^{\mathrm{U}*\mathrm{U}}$$
$$h'^{\mathrm{U}*\mathrm{U}}_2 = (12)(3)(4)(5)(6)^{\mathrm{U}*\mathrm{U}}$$
$$h'^{\mathrm{U}*\mathrm{U}}_5 = (12)(34)(5)(6)^{\mathrm{U}*\mathrm{U}}$$
$$h'^{\mathrm{U}*\mathrm{U}}_8 = (12)(34)(56)^{\mathrm{U}*\mathrm{U}}$$

if bond breaking within bidentate ligands is not allowed. We note the striking resemblance of this result with the "averaging sets" derived by "permutational analysis of $M(A–B)_3$ nmr spectra" in Table VII of ref 11. Interpretation of this similarity is not possible since the method of analysis used in ref 11 is not explained in detail.

Treatment of the $M(A–B)_3$ case involves determination of the distinct steric courses of reactions interconverting configurations having the four geometries shown in Figure 6b. It is assumed that bonds within a chelate ligand may not be broken and therefore discussion will proceed in terms of the restricted group of allowed permutations $H' = S_3[E_2]$, which contains $3! \cdot 1^3 = 6$ operations.

$$h'_1 = (1)(2)(3)(4)(5)(6)$$
$$h'_2 = (12)(3)(45)(6)$$
$$h'_3 = (13)(2)(46)(5)$$

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[10] F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," Wiley, New York, N. Y., 1967, pp 286–334.

[11] S. S. Eaton, J. R. Hutchison, R. Holm, and E. L. Muetterties, *J. Amer. Chem. Soc.*, **94**, 6411 (1972), and references therein.

[12] W. G. Klemperer, *J. Chem. Phys.*, **56**, 5478 (1972).

$$h'_4 = (1)(23)(4)(56)$$

$$h'_5 = (123)(456)$$

$$h'_6 = (132)(465)$$

All the configurations in question have chiral skeletal frameworks, and the appropriate configurational symmetry groups $V^{\mathrm{VV}} = C_3^{\mathrm{VV}}$, $V^{\mathrm{V*V*}} = C_3^{\mathrm{V*V*}}$, $W^{\mathrm{WW}} = C_1^{\mathrm{WW}}$, and $W^{\mathrm{W*W*}} = C_1^{\mathrm{W*W*}}$ are representatives of the groups V and W which contain the following operations

$$w_1 = v_1 = (1)(2)(3)(4)(5)(6)$$

$$v_2 = (123)(456)$$

$$v_3 = (132)(465)$$

The restricted configuration counts are $I'_{\mathrm{V}} = I'_{\mathrm{V*}} = 3!/3 = 2$ and $I'_{\mathrm{W}} = I'_{\mathrm{W*}} = 3!/1 = 6$. All "chemically allowed" reactions which interconvert configurations having the geometries shown in Figure 6b are contained in the sixteen sets H'^{VV}, $H'^{\mathrm{V*V*}}$, $H'^{\mathrm{V*V}}$, $H'^{\mathrm{VV*}}$, H'^{WW}, $H'^{\mathrm{W*W*}}$, $H'^{\mathrm{W*W}}$, $H'^{\mathrm{WW*}}$, H'^{VW}, $H'^{\mathrm{V*W*}}$, $H'^{\mathrm{V*W}}$, $H'^{\mathrm{VW*}}$, H'^{WV}, $H'^{\mathrm{WV*}}$, $H'^{\mathrm{W*V}}$, and $H'^{\mathrm{W*V*}}$, each of which contains $|H'| = 6$ operations.

We first examine the reactions contained in the sets H'^{VV}, $H'^{\mathrm{V*V*}}$, $H'^{\mathrm{V*V}}$, $H'^{\mathrm{VV*}}$, H'^{WW}, $H'^{\mathrm{W*W*}}$, $H'^{\mathrm{W*W}}$, and $H'^{\mathrm{WW*}}$. The set of two operations which convert $\binom{l}{s}_e^{\mathrm{V}}$ into the two nonequivalent configurations $\binom{l}{s}_e^{\mathrm{V}}$ and $h'^{\mathrm{VV}}_2\binom{l}{s}_e^{\mathrm{V}}$ must contain a maximal set of reactions differentiable in a chiral environment. Since $h'^{\mathrm{VV}}_1 \in V^{\mathrm{VV}}$, h'^{VV}_1 is not a reaction, h'^{VV}_2 by itself forms a maximal set of reactions differentiable in a chiral environment. All five reactions in H'^{WW} are differentiable in a chiral environment since W^{WW} contains only the identity operation. Since $\{h'^{\mathrm{VV}}_2\}$ and $\{h'^{\mathrm{WW}}_2, h'^{\mathrm{WW}}_3, h'^{\mathrm{WW}}_4, h'^{\mathrm{WW}}_5, h'^{\mathrm{WW}}_6\}$ are maximal sets of reactions differentiable in a chiral environment, it follows that $\{h'^{\mathrm{V*V*}}_2\}$, $\{h'^{\mathrm{VV*}}_1, h'^{\mathrm{VV*}}_2\}$, $\{h'^{\mathrm{V*V}}_1, h'^{\mathrm{V*V}}_2\}$, $\{h'^{\mathrm{W*W*}}_2, h'^{\mathrm{W*W*}}_3, h'^{\mathrm{W*W*}}_4, h'^{\mathrm{W*W*}}_5, h'^{\mathrm{W*W*}}_6\}$, $\{h'^{\mathrm{W*W}}_1, h'^{\mathrm{W*W}}_2, h'^{\mathrm{W*W}}_3, h'^{\mathrm{W*W}}_4, h'^{\mathrm{W*W}}_5, h'^{\mathrm{W*W}}_6\}$, and $\{h'^{\mathrm{WW*}}_1, h'^{\mathrm{WW*}}_2, h'^{\mathrm{WW*}}_3, h'^{\mathrm{WW*}}_3, h'^{\mathrm{WW*}}_4, h'^{\mathrm{WW*}}_5, h'^{\mathrm{WW*}}_6\}$ are also maximal sets of reactions differentiable in a chiral environment.

We now turn to the reactions in H'^{VW}, $H'^{\mathrm{V*W*}}$, $H'^{\mathrm{V*W}}$, $H'^{\mathrm{VW*}}$, $\mathrm{H}'^{\mathrm{WV}}$, $H'^{\mathrm{W*V*}}$, $H'^{\mathrm{W*V}}$, and $H'^{\mathrm{WV*}}$. The set of two reactions h'^{VW}_1 and h'^{VW}_2 which transform $\binom{l}{s}_e^{\mathrm{W}}$ into the two nonequivalent configurations $\binom{l}{s}_e^{\mathrm{V}}$ and $h'_2\binom{l}{s}_e^{\mathrm{V}}$ clearly form a maximal set of reactions differentiable in a chiral environment since W^{WW} contains only the identity operation. As shown above in section II, their reverse reactions $(h'^{\mathrm{VW}}_1)^{-1} = h'^{\mathrm{WV}}_1$ and $(h'^{\mathrm{VW}}_2)^{-1} = h'^{\mathrm{WV}}_2$ must also form a maximal set of reactions differentiable in a chiral environment. Since $\{h'^{\mathrm{VW}}_1, h'^{\mathrm{VW}}_2\}$ and $\{h'^{\mathrm{WV}}_1, h'^{\mathrm{WV}}_2\}$ are maximal sets of reactions differentiable in a chiral environment, it follows that $\{h'^{\mathrm{V*W*}}_1, h'^{\mathrm{V*W*}}_2\}$, $\{h'^{\mathrm{V*W}}_1, h'^{\mathrm{V*W}}_2\}$, $\{h'^{\mathrm{VW*}}_1, h'^{\mathrm{VW*}}_2\}$, $\{h'^{\mathrm{W*V*}}_1, h'^{\mathrm{W*V*}}_2\}$, $\{h'^{\mathrm{W*V}}_1, h'^{\mathrm{W*V}}_2\}$, and $\{h'^{\mathrm{WV*}}_1, h'^{\mathrm{WV*}}_2\}$ also are, as explained in section III.

Summarizing, all distinct steric courses of reactions interconverting the four configurations having the geometries shown in Figure 6b are defined by the following eighteen reactions, their enantiomers, and in the case of the last four reactions, their reverse reactions and the enantiomers of their reverse reactions.

$$h'^{\mathrm{VV}}_2 = (12)(3)(45)(6)^{\mathrm{VV}}$$

$$h'^{\mathrm{V*V}}_1 = (1)(2)(3)(4)(5)(6)^{\mathrm{V*V}}$$

$$h'^{\mathrm{V*V}}_2 = (12)(3)(45)(6)^{\mathrm{V*V}}$$

$$h'^{\mathrm{WW}}_2 = (12)(3)(45)(6)^{\mathrm{WW}}$$

$$h'^{\mathrm{WW}}_3 = (13)(2)(46)(5)^{\mathrm{WW}}$$

$$h'^{\mathrm{WW}}_4 = (1)(23)(4)(56)^{\mathrm{WW}}$$

$$h'^{\mathrm{WW}}_5 = (123)(456)^{\mathrm{WW}}$$

$$h'^{\mathrm{WW}}_6 = (132)(465)^{\mathrm{WW}}$$

$$h'^{\mathrm{W*W}}_1 = (1)(2)(3)(4)(5)(6)^{\mathrm{W*W}}$$

$$h'^{\mathrm{W*W}}_2 = (12)(3)(45)(6)^{\mathrm{W*W}}$$

$$h'^{\mathrm{W*W}}_3 = (13)(2)(46)(5)^{\mathrm{W*W}}$$

$$h'^{\mathrm{W*W}}_4 = (1)(23)(4)(56)^{\mathrm{W*W}}$$

$$h'^{\mathrm{W*W}}_5 = (123)(456)^{\mathrm{W*W}}$$

$$h'^{\mathrm{W*W}}_6 = (132)(465)^{\mathrm{W*W}}$$

$$h'^{\mathrm{VW}}_1 = (1)(2)(3)(4)(5)(6)^{\mathrm{VW}}$$

$$h'^{\mathrm{VW}}_2 = (12)(3)(45)(6)^{\mathrm{VW}}$$

$$h'^{\mathrm{V*W}}_1 = (1)(2)(3)(4)(5)(6)^{\mathrm{V*W}}$$

$$h'^{\mathrm{V*W}}_2 = (12)(3)(45)(6)^{\mathrm{V*W}}$$

The decision whether to treat unsymmetric tris-chelate complexes as $\mathrm{M(A{-}B)_3}$ configurations or $\mathrm{M(A{-}A)_3}$ configurations is not entirely unambiguous as it depends on how "unsymmetric" the chelate is. If the chelate ligands are unsymmetric only because of labeling, *i.e.*, the termini of the ligands have virtually identical chemical behavior, the complex is denoted $\mathrm{M(A{-}A)_3}$. If the ligands are unsymmetric due to measurable differences in the chemical behavior of the ligand termini, then the complex is denoted $\mathrm{M(A{-}B)_3}$. The degree of symmetry is perhaps best judged by the cis–trans equilibrium constant. The essential point is that treatment of an "octahedral" $\mathrm{M(A{-}A)_3}$ complex assumes a skeletal framework having D_3 symmetry, and the equivalence of many reactions is based on this assumption. Should the symmetry of the skeletal framework deviate from D_3 symmetry appreciably, then many formally nondifferentiable reactions may in fact be physically differentiable and thus the complex should be treated as an $\mathrm{M(A{-}B)_3}$ complex.

B. Water Exchange of $\mathrm{Co(en)_2(NH_3)(H_2O)^{3+}}$. The steric courses of octahedral substitution reactions have been investigated in detail.[13,14] Due to the difficulty of labeling true octahedral complexes, most studies have been carried out on "octahedral" chelate complexes of the type $\mathrm{M(A{-}A)_2BC}$, where isomers having three different geometries are found (see Figure 7a). The purpose of establishing the steric course of a particular reaction or reaction sequence is to allow a choice to be made between postulated mechanisms. In the case of octahedral Co(III) substitution reactions in acid solution, dissociative activation is generally involved, but it is rarely clear whether the stoichiometric mechanism is interchange (I) or dissociative (D).[15] By

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(13) See ref 10, pp 248–286.

(14) M. L. Tobe, "Studies on Chemical Structure and Reactivity," J. H. Ridd, Ed., Wiley, New York, N. Y., 1966, p 215.

(15) C. H. Langford and H. B. Gray, "Ligand Substitution Processes," W. A. Benjamin, New York, N. Y., 1965, pp 1–17, 55–101.

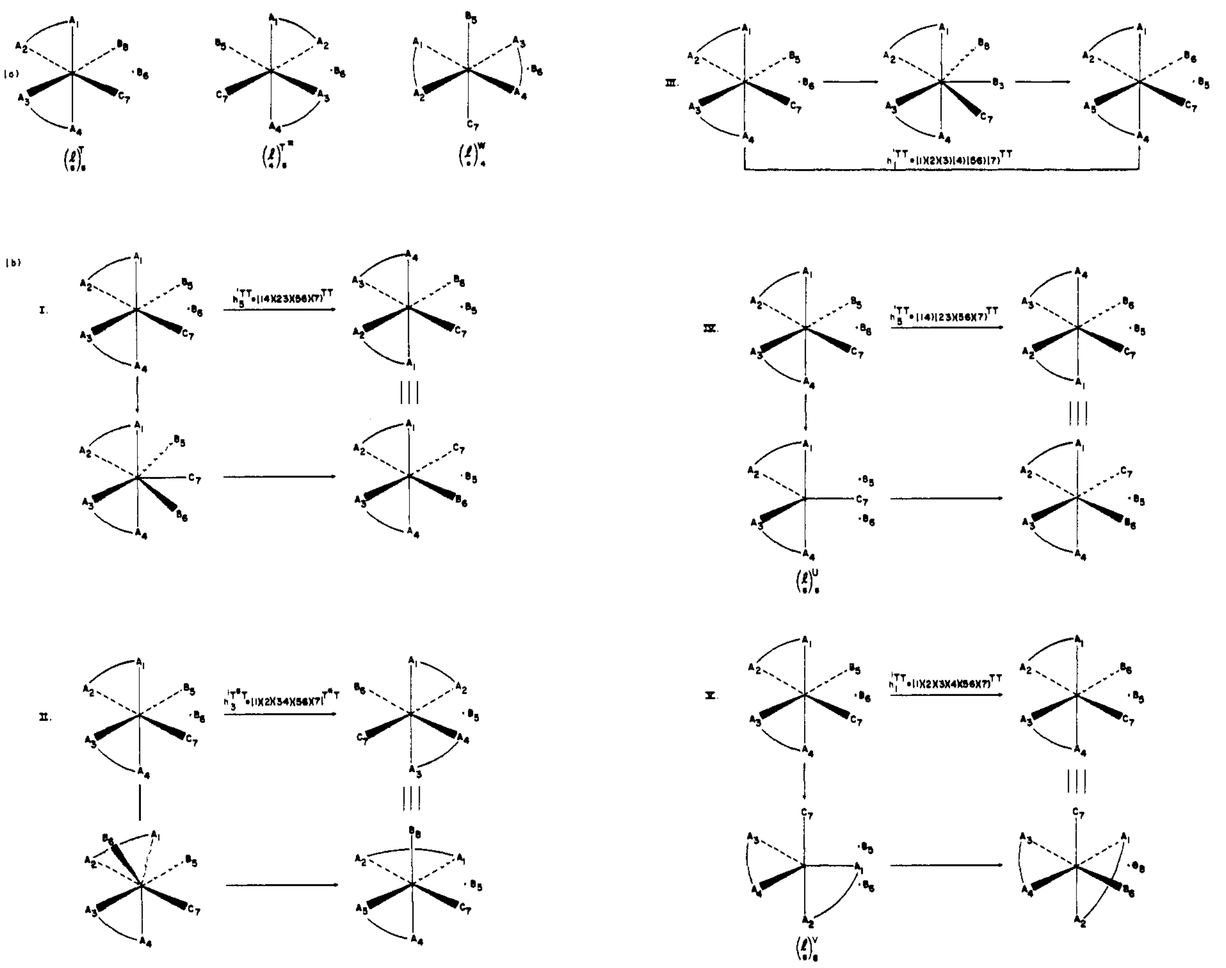

Figure 7. Reference configurations having the geometries possible for the "octahedral" complex $Co(en)_2(NH_3)(H_2O)^{3+}$ are shown in (a). Five plausible mechanisms for water exchange involving only the cis isomers are shown in (b).

definition, "any substitution that takes place within an encounter (faster than the reorganization of the outer coordination sphere) must be considered, operationally, a concerted process,"[16] *i.e.*, an interchange process. Accordingly, a process which involves dissociative activation and involves an intermediate of reduced coordination number is defined to have a D mechanism instead of an I mechanism if the outer coordination sphere reorganizes many times during the lifetime of this intermediate. This means that the intermediate effectively rotates and translates rapidly in its environment during its lifetime. In this example, we shall first present all possible steric courses of water exchange reactions of $Co(en)_2(NH_3)(H_2O)^{3+}$,[17] en = ethylenediamine, which interconvert configurations having the geometries shown in Figure 7a. Then some plausible I and D mechanisms will be examined in order to ascertain whether labeling experiments would be able to definitively rule out the I or D mechanisms.

We assume that all water exchange reactions involve interconversion of configurations having the geometries shown in Figure 7a, and that bond breaking within a chelate ligand is not allowed. Configurations having geometries T and T* have chiral skeletal frameworks and the proper configurational symmetry groups $T^{TT} = C_1^{TT}$ and $T^{T^*T^*} = C_1^{T^*T^*}$ contain only the operation. Configurations having geometry W have achiral skeletal frameworks and the groups W^{WW} and $\bar{W}^{WW}$ contain the following operations.

$$w_1^{WW} = \bar{w}_1^{WW} = (1)(2)(3)(4)(5)(6)(7)^{WW}$$

$$w_2^{WW} = \bar{w}_2^{WW} = (14)(23)(5)(6)(7)^{WW}$$

$$\bar{w}_3^{WW} = (12)(34)(5)(6)(7)^{WW}$$

$$\bar{w}_4^{WW} = (13)(24)(5)(6)(7)^{WW}$$

Operations $\bar{w}_1^{WW}$ and $\bar{w}_2^{WW}$ represent rotation of configuration, while $\bar{w}_3^{WW}$ and $\bar{w}_4^{WW}$ represent inversion of configuration. The appropriate restricted group of allowed permutations is $H' = S_2[S_2] + S_2 + E_1$ which contains $2!2^2 \cdot 2! \cdot 1 = 16$ operations.

$$h'_1 = (1)(2)(3)(4)(56)(7)$$

$$h'_2 = (12)(3)(4)(56)(7)$$

$$h'_3 = (1)(2)(34)(56)(7)$$

$$h'_4 = (12)(34)(56)(7)$$

$$h'_5 = (14)(23)(56)(7)$$

$$h'_6 = (1324)(56)(7)$$

$$h'_7 = (1423)(56)(7)$$

$$h'_8 = (13)(24)(56)(7)$$

$$h'_9 = (1)(2)(3)(4)(5)(6)(7)$$

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(16) Reference 15, pp 5 and 6.

(17) D. F. Martin and M. L. Tobe, *J. Chem. Soc.*, 1388 (1962).

$$h'_{10} = (12)(3)(4)(5)(6)(7)$$
$$h'_{11} = (1)(2)(34)(5)(6)(7)$$
$$h'_{12} = (12)(34)(5)(6)(7)$$
$$h'_{13} = (14)(23)(5)(6)(7)$$
$$h'_{14} = (1324)(5)(6)(7)$$
$$h'_{15} = (1423)(5)(6)(7)$$
$$h'_{16} = (13)(24)(5)(6)(7)$$

Restricted configuration counts are $I'_{\mathrm{T}} = I'_{\mathrm{T*}} = |H'|/|'T| = 16$ and $I'_{\mathrm{W}} = |H'|/|W| = 8$.

Following procedures presented above in sections II and III (or by inspection), the reader may verify that all distinct steric courses of reactions involving water exchange which interconvert configurations having the geometries shown in Figure 7a are defined by the following maximal sets of reactions differentiable in a chiral environment and in appropriate cases their enantiomers and/or their reverse reactions and/or the enantiomers of their reverse reactions.

$$\{h'_1{}^{\mathrm{TT}},\ h'_2{}^{\mathrm{TT}},\ h'_3{}^{\mathrm{TT}},\ h'_4{}^{\mathrm{TT}},\ h'_5{}^{\mathrm{TT}},\ h'_6{}^{\mathrm{TT}},\ h'_7{}^{\mathrm{TT}},\ h'_8{}^{\mathrm{TT}}\}$$

$$\{h'_1{}^{\mathrm{T*T}},\ h'_2{}^{\mathrm{T*T}},\ h'_3{}^{\mathrm{T*T}},\ h'_4{}^{\mathrm{T*T}},\ h'_5{}^{\mathrm{T*T}},\ h'_6{}^{\mathrm{T*T}},\ h'_7{}^{\mathrm{T*T}},\ h'_8{}^{\mathrm{T*T}}\}$$

$$\{h'_1{}^{\mathrm{WW}},\ h'_2{}^{\mathrm{WW}},\ h'_4{}^{\mathrm{WW}}\}$$

$$\{h'_1{}^{\mathrm{WT}},\ h'_2{}^{\mathrm{WT}},\ h'_3{}^{\mathrm{WT}},\ h'_4{}^{\mathrm{WT}}\}$$

Water exchange experiments in acid aqueous solution have shown that cis–trans isomerization of *cis*-$\mathrm{Co(en)_2(NH_3)(H_2O)^{3+}}$ is negligibly slow, whereas the rate constants for racemization and water exchange are $3 \times 10^{-8}\ \mathrm{sec}^{-1}$ and $1.1 \times 10^{-6}\ \mathrm{sec}^{-1}$, respectively.[17] We shall determine the net stereochemical changes implied by the five mechanisms shown in Figure 7b in order to ascertain whether labeling experiments might rule any of them out.

I. This trans attack[13] mechanism is an associative (A) or interchange (I) process. The geometry of the intermediate configuration shown is not to be taken literally, but it is drawn to clarify the steric course of the reaction. Since all intermediate configurations have connectivities equal to two, this mechanism uniquely implies the reaction $h'_5{}^{\mathrm{TT}} = (14)(23)(56)(7)^{\mathrm{TT}}$. At this point we make note of an experimental constraint which must be taken into account. If we let $\mathrm{B_5}$ represent unlabeled water and $\mathrm{B_6}$ represent isotopically labeled water, it is unrealistic to demand that all the water in solution is isotopically labeled and that all exchange reactions will lead to configurations where $\mathrm{B_6}$ occupies skeletal position $S_5{}^{\mathrm{T}}$ or $S_5{}^{\mathrm{T*}}$. Instead, if x/y is the ratio of unlabeled water to labeled water in solution, then the net stereochemical change implied by mechanism I is defined by $yh'_5{}^{\mathrm{TT}} + xh'_{13}{}^{\mathrm{TT}}$, where y and x are the relative probabilities of exchange and permutational isomerization, respectively.

II. This mechanism is also an A or I trans attack mechanism. Since all intermediate configurations have connectivities equal to two, mechanism II uniquely implies the reaction $h'_3{}^{\mathrm{T*T}} = (1)(2)(34)(56)(7)$. If, however, the ratio of unlabeled water to labeled water in solution is x/y, then $yh'_3{}^{\mathrm{T*T}} + xh'_{11}{}^{\mathrm{T*T}}$ defines the net stereochemical changes implied by the mechanism.

III. Mechanism III is a cis attack[13] mechanism which may be either an I or A process. Again, since all intermediate configurations have connectivities equal to two, the mechanism uniquely implies $h'_1{}^{\mathrm{TT}} = (1)(2)(3)(4)(56)(7)^{\mathrm{TT}}$. If unlabeled water should exchange, no stereochemical change will be observable. Note that any form of cis attack or a D mechanism proceeding *via* a square pyramidal intermediate also uniquely implies this reaction, *i.e.*, has the same steric course.

IV. We assume this mechanism to be a D process with a metastable intermediate having geometry U. Configurations having this geometry do not have connectivities equal to two; $U^{\mathrm{UU}} = C_2{}^{\mathrm{UU}} + S_2{}^{\mathrm{UU}}$, dissociation is defined by $h'_9{}^{\mathrm{UT}} = (1)(2)(3)(4)(5)(6)(7)^{\mathrm{UT}} \equiv e^{\mathrm{UT}}$, and since the skeletal framework of configurations having geometry U is chiral, $S_{\mathrm{TU}} = |U|/|T \cap U| = 2 \cdot 2!/1 = 4$. Therefore, if a true D mechanism is operative, the net stereochemical changes implied by $h'_9{}^{\mathrm{TU}}$ followed by $(h'_9{}^{-1})^{\mathrm{TU}} = h'_9{}^{\mathrm{TU}}$ are expressed by

$$\psi^{\mathrm{TT}}(h'_9{}^{\mathrm{TU}};\ h'_9{}^{\mathrm{UT}}) = e^{\mathrm{TT}} + h'_{13}{}^{\mathrm{TT}} + h'_1{}^{\mathrm{TT}} + h'_5{}^{\mathrm{TT}}$$

since $(h'_9Uh'_9)^{\mathrm{TT}} = U^{\mathrm{TT}}$ contains these four operations

$$u'_1{}^{\mathrm{TT}} = (1)(2)(3)(4)(5)(6)(7)^{\mathrm{TT}} = e^{\mathrm{TT}}$$
$$u'_2{}^{\mathrm{TT}} = (1)(2)(3)(4)(56)(7)^{\mathrm{TT}} = h'_1{}^{\mathrm{TT}}$$
$$u'_3{}^{\mathrm{TT}} = (14)(23)(5)(6)(7)^{\mathrm{TT}} = h'_{13}{}^{\mathrm{TT}}$$
$$u'_4{}^{\mathrm{TT}} = (14)(23)(56)(7)^{\mathrm{TT}} = h'_5{}^{\mathrm{TT}}$$

As in SCCR-I, $\psi^{\mathrm{TT}}(h'_9{}^{\mathrm{TU}};\ h'_9{}^{\mathrm{UT}})$ gives relative probabilities of reactions only if ligands in skeletal positions $S_5{}^{\mathrm{U}}$ and $S_6{}^{\mathrm{U}}$ are present in equal concentrations. Since we assumed differently above, we must write

$$\psi^{\mathrm{TT}}(h'_9{}^{\mathrm{TU}};\ h'_9{}^{\mathrm{TU}}) = xe^{\mathrm{TT}} + xh'_{13}{}^{\mathrm{TT}} + yh'_1{}^{\mathrm{TT}} + yh'_5{}^{\mathrm{TT}}$$

If the intermediate configuration having geometry U undergoes rapid "pseudorotation"[18] during its lifetime, then U^{UU} need not be redefined, but $\bar{U}^{\mathrm{UU}}$ must be expanded to include four operations which represent inversion of configuration since configurations having geometry U now have an achiral skeletal framework. Thus if the reaction takes place in an effectively achiral environment, $h'_9{}^{\mathrm{TU}}$ and its enantiomer $e^{\mathrm{T*T}} \cdot h'_9{}^{\mathrm{TU}} \cdot \bar{u}_5{}^{\mathrm{UU}} = \bar{u}_5{}^{\mathrm{T*U}} = (13)(24)(5)(6)(7)^{\mathrm{T*U}} = h'_{16}{}^{\mathrm{T*U}}$ must occur with equal probability. Thus, mechanism IV implies the reactions in these sets if pseudorotation is allowed: $(h'_9Uh'_9)^{\mathrm{TT}} = \{h'_9{}^{\mathrm{TT}},\ h'_1{}^{\mathrm{TT}},\ h'_{13}{}^{\mathrm{TT}},\ h'_5{}^{\mathrm{TT}}\}$ and $(h'_{16}Uh'_9)^{\mathrm{T*T}} = \{h'_{16}{}^{\mathrm{T*T}},\ h'_8{}^{\mathrm{T*T}},\ h'_{12}{}^{\mathrm{T*T}},\ h'_4{}^{\mathrm{T*T}}\}$. If x and y are defined as above, we find

$$\psi^{\mathrm{T*T,TT}}(h'_{16}{}^{\mathrm{T*U}},\ h'_9{}^{\mathrm{TU}};\ h'_9{}^{\mathrm{UT}}) = xe^{\mathrm{TT}} + xh'_{13}{}^{\mathrm{TT}} + yh'_1{}^{\mathrm{TT}} + yh'_5{}^{\mathrm{TT}} + xh'_{12}{}^{\mathrm{T*T}} + xh'_{16}{}^{\mathrm{T*T}} + yh'_4{}^{\mathrm{T*T}} + yh'_8{}^{\mathrm{T*T}}$$

Note that

$$\psi^{\mathrm{T*T,TT}}(h'_{16}{}^{\mathrm{T*U}},\ h'_9{}^{\mathrm{TU}};\ h'_9{}^{\mathrm{TU}}) = \psi^{\mathrm{T*T,TT}}(h'_{16}{}^{\mathrm{T*W}},\ h'_9{}^{\mathrm{TW}};\ h'_9{}^{\mathrm{WT}})$$

and therefore mechanism IV with "pseudorotation" has the same steric course as isomerization *via* a trans "octahedral" intermediate.

V. This mechanism is also assumed to be a D

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[18] F. H. Westheimer, *Accounts Chem. Res.*, **1**, 70 (1968).

process. Here $V^{\mathrm{VV}} = C_1^{\mathrm{VV}} + S_2^{\mathrm{VV}}$ and $\bar{V}^{\mathrm{VV}} = C_{\mathrm{S}}^{\mathrm{VV}} + S_2^{\mathrm{VV}}$ and

$$v_1^{\mathrm{VV}} = \bar{v}_1^{\mathrm{VV}} = (1)(2)(3)(4)(5)(6)(7)^{\mathrm{VV}} = h'^{\mathrm{VV}}_{9}$$

$$v_2^{\mathrm{VV}} = \bar{v}_2^{\mathrm{VV}} = (1)(2)(3)(4)(56)(7)^{\mathrm{VV}} = h'^{\mathrm{VV}}_{1}$$

$$\bar{v}_3^{\mathrm{VV}} = (1)(2)(34)(5)(6)(7)^{\mathrm{VV}} = h'^{\mathrm{VV}}_{11}$$

$$\bar{v}_4^{\mathrm{VV}} = (1)(2)(34)(56)(7) = h'^{\mathrm{VV}}_{3}$$

Dissociation is defined by h'^{VT}_{9} and association by h'^{TV}_{9} and $h'^{\mathrm{T*V}}_{11}$, since $(h'^{\mathrm{VT}}_{9})^{-1} = h'^{\mathrm{TV}}_{9}$, and h'^{TV}_{9} and $e^{\mathrm{T*T}} \cdot h'^{\mathrm{TV}}_{9} \cdot \bar{v}_3^{\mathrm{VV}} = h'^{\mathrm{T*V}}_{11}$ are enantiomeric. Examining the sets $(h'_9 V h'_9)^{\mathrm{TT}} = \{h'^{\mathrm{TT}}_{9}, h'^{\mathrm{TT}}_{1}\}$ and $(h'_{11} V h_9)^{\mathrm{T*T}} = \{h'^{\mathrm{T*T}}_{11}, h'^{\mathrm{T*T}}_{2}\}$ we find

$$\psi^{\mathrm{T*T,TT}}(h'^{\mathrm{T*V}}_{11}, h'^{\mathrm{TV}}_{9}; h'^{\mathrm{VT}}_{9}) = xe^{\mathrm{TT}} + yh'^{\mathrm{TT}}_{1} + xh'^{\mathrm{T*T}}_{11} + yh'^{\mathrm{T*T}}_{3}$$

Summarizing, the stereochemical changes implied by the mechanisms shown in Figure 7b are

I. $xh'^{\mathrm{TT}}_{13} + yh'^{\mathrm{TT}}_{5}$

II. $xh'^{\mathrm{T*T}}_{11} + yh'^{\mathrm{T*T}}_{3}$

III. h'^{TT}_{1}

IV. (no "pseudorotation") $xh'^{\mathrm{TT}}_{13} + yh'^{\mathrm{TT}}_{1} + yh'^{\mathrm{TT}}_{5}$

IV′. (with "pseudorotation") $xh'^{\mathrm{TT}}_{13} + yh'^{\mathrm{TT}}_{1} + yh'^{\mathrm{TT}}_{5} + xh'^{\mathrm{T*T}}_{12} + xh'^{\mathrm{T*T}}_{16} + yh'^{\mathrm{T*T}}_{4} + yh'^{\mathrm{T*T}}_{8}$

V. $yh'^{\mathrm{TT}}_{1} + xh'^{\mathrm{T*T}}_{11} + yh'^{\mathrm{T*T}}_{3}$

Of interest here, however, are product distributions implied by each mechanism assuming the reactant to be the reference configuration $\binom{l}{s}_e^{\mathrm{T}}$. In general, the product configurations implied by h_i^{YX} acting on $\binom{l}{s}_e^{\mathrm{X}}$ are the configurations in the set $h_i^{\mathrm{YX}} X^{\mathrm{XX}} \binom{l}{s}_e^{\mathrm{X}}$. Here, however, T^{TT} contains only the identity operation and therefore $h_i^{\mathrm{TT}} T^{\mathrm{TT}} \binom{l}{s}_e^{\mathrm{T}} = h_i^{\mathrm{TT}} \binom{l}{s}_e^{\mathrm{T}} \equiv \binom{l}{s}_i^{\mathrm{T}}$ and $h_i^{\mathrm{T*T}} T^{\mathrm{TT}} \binom{l}{s}_e^{\mathrm{T}} = h_i^{\mathrm{T*T}} \binom{l}{s}_e^{\mathrm{T}} \equiv \binom{l}{s}_i^{\mathrm{T*}}$. Accordingly, the product distributions implied by each mechanism are

III. ${\binom{l}{s}}_{1}^{\mathrm{T}}$

I. $x{\binom{l}{s}}_{13}^{\mathrm{T}} + y{\binom{l}{s}}_{5}^{\mathrm{T}}$

IV. $x{\binom{l}{s}}_{13}^{\mathrm{T}} + y{\binom{l}{s}}_{5}^{\mathrm{T}} + y{\binom{l}{s}}_{1}^{\mathrm{T}}$

II. $x{\binom{l}{s}}_{11}^{\mathrm{T*}} + y{\binom{l}{s}}_{3}^{\mathrm{T*}}$

V. $x{\binom{l}{s}}_{11}^{\mathrm{T*}} + y{\binom{l}{s}}_{3}^{\mathrm{T*}} + y{\binom{l}{s}}_{1}^{\mathrm{T}}$

IV′. $x{\binom{l}{s}}_{13}^{\mathrm{T}} + y{\binom{l}{s}}_{5}^{\mathrm{T}} + y{\binom{l}{s}}_{1}^{\mathrm{T}} + x{\binom{l}{s}}_{12}^{\mathrm{T*}} + x{\binom{l}{s}}_{16}^{\mathrm{T*}} + y{\binom{l}{s}}_{4}^{\mathrm{T*}} + y{\binom{l}{s}}_{8}^{\mathrm{T*}}$

These distributions are not to be confused with the "statistical" product distributions commonly used to predict the products of octahedral substitution.[19] Such "statistical" calculations are based on physical assumptions which are probably unwarranted[20] and are therefore probably of very little meaning.[21]

The above product distributions have been written out of numerical order to emphasize that combinations of I and III are indistinguishable from combinations of IV and III, as are combinations of II and III indistinguishable from combinations of V and III.

C. Permutational Isomerization of a π-Allyl-Metal Complex. In recent years the dynamic stereochemistry of many stereochemically nonrigid organometallic compounds has been investigated by nmr spectroscopy.[22] When treating a specific system the usual approach has been to postulate several possible mechanisms, determine the site exchanges implied by each mechanism, and then ascertain which of these postulated site exchanges (or combinations thereof) generate spectra which are most consistent with experimental nmr line shapes. However, the possibility always exists that the true mechanism was overlooked when postulating possible mechanisms, and that the true site exchange is distinct from any of those postulated. This problem can be remedied by first determining all classes of reactions (permutations) which might lead to experimentally distinguishable nmr line shape behavior. Such classes of reactions, classes of reactions nondifferentiable in a totally symmetric environment,[1,23] can of course be generated with the certainty that no possibilities have been overlooked. Line shapes may then be analyzed and simulated using exchange schemes based on the reactions comprising a complete (or restricted) set of reactions differentiable in a totally symmetric environment. After one or more schemes consistent with experiment have been obtained, only certain reactions and/or combinations of reactions may be deemed consistent with experiment. Then all mechanisms which imply these reactions or combinations of reactions are consistent with experiment, while mechanisms which do not imply these reactions may be ruled out as inconsistent with experiment.

We shall demonstrate this procedure by examining the possible permutational isomerization reactions of the cation 1,2-bis(diphenylphosphino)ethane(2-methylallyl)palladium.[24] Since only the movements of the allyl group are of interest, the configuration shown in Figure 8a represents the cation (diphos)(C_4H_7)Pd$^+$. This configuration has an achiral skeletal framework and the configurational symmetry groups W^{WW} and $\bar{W}^{\mathrm{WW}}$ contain these operations

$$w_1^{\mathrm{WW}} = \bar{w}_1^{\mathrm{WW}} = (1)(2)(3)(4)(5)(6)(7)^{\mathrm{WW}}$$

$$\bar{w}_2^{\mathrm{WW}} = (14)(23)(56)(7)^{\mathrm{WW}}$$

Here, $\bar{w}_1^{\mathrm{WW}}$ represents rotation of configuration, while $\bar{w}_2^{\mathrm{WW}}$ represents inversion of configuration. To simplify discussion, it is assumed that breaking of carbon–carbon and carbon–hydrogen bonds is not allowed and

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[19] Reference 10, p 254.

[20] Reference 15, p 77.

[21] Reference 10, p 251.

[22] K. Vrieze and P. W. N. M. van Leeuwen, *Progr. Inorg. Chem.*, 14, 1 (1971), and references therein.

[23] Although reactions which are nondifferentiable in a totally symmetric environment imply identical nmr line shape behavior, in certain cases it can be shown that reactions which are differentiable in a totally symmetric environment must nonetheless imply identical nmr line shape behavior. For a discussion, see W. G. Klemperer in "Dynamic Nuclear Magnetic Resonance Spectroscopy," F. A. Cotton and L. M. Jackman, Ed., Academic Press, New York, N. Y., 1973.

[24] D. L. Tibbetts and T. L. Brown, *J. Amer. Chem. Soc.*, 92, 3031 (1970).

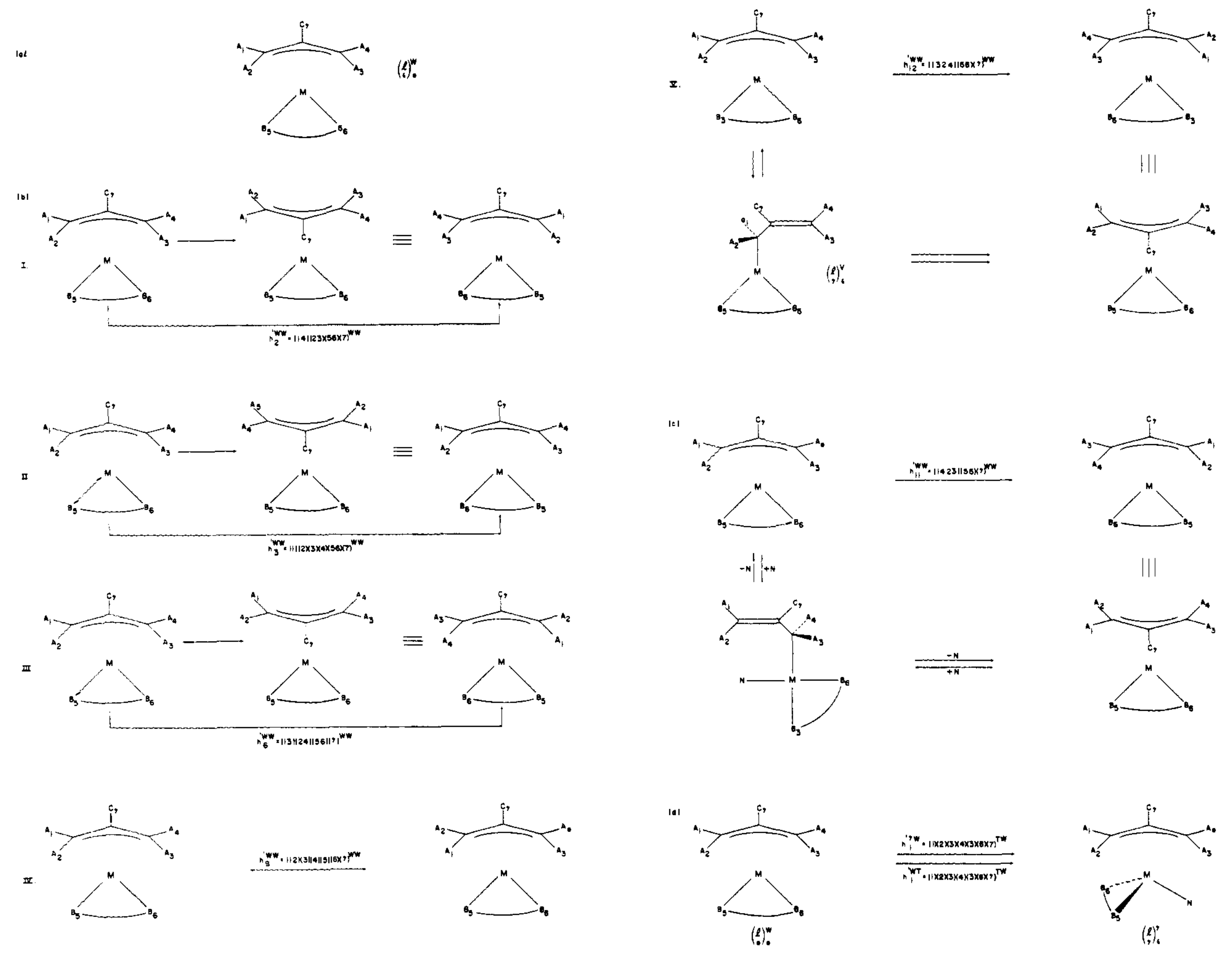

Figure 8. The reference configuration representing (diphos)(C_4H_7)Pd^+ is shown in (a). In (b), several unimolecular isomerization reactions are shown. Two pyridine catalyzed processes are shown in (c) and (d). In all the drawings, the metal does not lie in the plane defined by the planar π-allyl ligand.

therefore $H' = S_2[S_2] + S_2 + E_1$, $|H'| = 2!\cdot 2^2\cdot 2\cdot 1 = 16$. One operation in H'^{WW}, $h_1'^{WW} = (1)(2)(3)(4)(5)(6)(7)^{WW}$, is not a reaction, but the remaining 15 operations are permutational isomerization reactions.

$$h'^{WW}_2 = (14)(23)(56)(7)^{WW}$$

$$\left\{\begin{aligned} h'^{WW}_3 &= (1)(2)(3)(4)(56)(7)^{WW} \\ h'^{WW}_4 &= (14)(23)(5)(6)(7)^{WW} \end{aligned}\right.$$

$$\left\{\begin{aligned} h'^{WW}_5 &= (12)(34)(5)(6)(7)^{WW} \\ h'^{WW}_6 &= (13)(24)(56)(7)^{WW} \end{aligned}\right.$$

$$\left\{\begin{aligned} h'^{WW}_7 &= (12)(34)(56)(7)^{WW} \\ h'^{WW}_8 &= (13)(24)(5)(6)(7)^{WW} \end{aligned}\right.$$

$$\left\{\begin{aligned} &\left(\begin{aligned} h'^{WW}_9 &= (12)(3)(4)(5)(6)(7)^{WW} \\ h'^{WW}_{10} &= (1)(2)(34)(5)(6)(7)^{WW} \end{aligned}\right. \\ &\left(\begin{aligned} h'^{WW}_{11} &= (1423)(56)(7)^{WW} \\ h'^{WW}_{12} &= (1324)(56)(7)^{WW} \end{aligned}\right. \end{aligned}\right.$$

$$\left\{\begin{aligned} &\left(\begin{aligned} h'^{WW}_{13} &= (12)(3)(4)(56)(7)^{WW} \\ h'^{WW}_{14} &= (1)(2)(34)(56)(7)^{WW} \end{aligned}\right. \\ &\left(\begin{aligned} h'^{WW}_{15} &= (1423)(5)(6)(7)^{WW} \\ h'^{WW}_{16} &= (1324)(5)(6)(7)^{WW} \end{aligned}\right. \end{aligned}\right.$$

Since W^{WW} contains only the identity operation, all 15 reactions are differentiable in a chiral environment. Enantiomeric reactions are enclosed in parentheses and braces enclose reactions nondifferentiable in a totally symmetric environment. We note that H'^{WW} contains only six classes of reactions nondifferentiable in a totally symmetric environment and therefore, at most six reactions imply site exchanges which are distinguishable by the nmr method.

In the absence of a catalyst, Tibbetts and Brown[24] found no temperature dependence of the nmr line shapes for (diphos)(C_4H_7)Pd^+. Since h'^{WW}_2 is the only reaction in H'^{WW} which implies no change in nmr parameters (h'^{WW}_2 represents inversion of configuration), only h'^{WW}_2 is consistent with experiment.

We next examine five possible mechanisms shown in Figure 8b to ascertain whether any of them are consistent with experiment. Mechanism I is a "planar" allyl flip mechanism,[25] II is a "π-rotation" mechanism,[22,24] III is an allyl flip mechanism which involves syn-anti exchange,[24] IV involves rotation about a carbon-carbon bond, while V involves a π–σ equilibrium.[22,24] Mechanisms I-IV involve no intermediate configurations having connectivities greater than two and they therefore uniquely imply the permutational isomerization reac-

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(25) P. Ganis, G. Maglio, A. Musco, and A. L. Segre, *Inorg. Chim. Acta*, 3, 266 (1969).

tions indicated in Figure 8b. Of course the enantiomers of the chiral reactions will occur with equal probability in an achiral environment. Mechanism V does involve an intermediate configuration having a connectivity greater than two. Assuming rapid rotation about the metal–carbon bond in the intermediate, V^{VV} and $\bar{V}^{VV}$ are defined by the operations

$$\begin{aligned} v_1^{VV} = \bar{v}_1^{VV} &= (1)(2)(3)(4)(5)(6)(7)^{VV} \\ v_2^{VV} = \bar{v}_2^{VV} &= (1)(2)(3)(4)(56)(7)^{VV} \\ \bar{v}_3^{VV} &= (12)(3)(4)(5)(6)(7)^{VV} \\ \bar{v}_4^{VV} &= (12)(3)(4)(56)(7)^{VV} \end{aligned}$$

Only $\bar{v}_3^{VV}$ and $\bar{v}_4^{VV}$ represent inversion of configuration. The chiral reaction $h'_1{}^{VW}$ and its enantiomer $h'_{15}{}^{VW} = \bar{v}_4^{VV}\cdot h'_1{}^{VW}\cdot\bar{w}_2^{WW}$ define the steric courses of the π to σ transformation, and since we are dealing with an equilibrium situation, their reverse reactions $(h'_1{}^{-1})^{WV} = h'_1{}^{WV}$ and $(h'_{15}{}^{-1})^{WV} = h'_{16}{}^{WV}$ define the σ to π transformation. Thus $\delta_{WV} = 2\cdot|V|/|V \cap h'_1{}^{-1}Wh'_1| = 2|V|/|V \cap W| = 2\cdot 2/1 = 4$. The net reactions implied by mechanism V are contained in the sets of reactions $(h'_1{}^{-1}Vh'_1)^{WW}$, $(h'_1{}^{-1}Vh_{15})^{WW}$, $(h'_{15}{}^{-1}Vh'_1)^{WW}$, and $(h'_{15}{}^{-1}Vh'_{15})^{WW}$ and inspection of these reactions reveals

$$\psi^{WW}(h'_1{}^{WV};\, h'_1{}^{VW}) = 2e^{WW} + 2h'_3{}^{WW} + h'_{12}{}^{WW} + h'_{15}{}^{WW} + h'_{16}{}^{WW}$$

Summarizing, each of these mechanisms implies site exchanges indistinguishable by nmr methods from those generated by the indicated reactions

I. $h'_2{}^{WW}$
II. $h'_3{}^{WW}$
III. $h'_5{}^{WW}$
IV. $h'_9{}^{WW}$
V. $h'_3{}^{WW} + h'_9{}^{WW} + h'_{13}{}^{WW}$

Thus, only mechanism I is consistent with experiment.

In the presence of pyridine, Tibbetts and Brown found that nmr lines broadened and at high pyridine concentrations certain lines coalesced. By simulating nmr line shapes they concluded that pyridine catalyzes permutational isomerization of (diphos)(C_4H_7)Pd$^+$, but that the isomerization mechanism, although it implies syn–anti proton exchange, does not imply net rotation of the allyl group. Such an exchange scheme is implied by $h'_5{}^{WW}$ and $h'_9{}^{WW}$ but not by $h'_2{}^{WW}$, $h'_3{}^{WW}$, $h'_7{}^{WW}$, or $h'_{13}{}^{WW}$. This is not to say that more thorough line shape analysis could not provide a choice between $h'_5{}^{WW}$ and $h'_9{}^{WW}$. Tibbetts and Brown realized that various "possible" mechanisms are consistent with experiment, and chose a pyridine catalyzed mechanism shown in Figure 8c on the basis of chemical evidence. The reader may verify that the four-coordinate intermediate has a connectivity equal to two, and this mechanism uniquely implies $h'_{11}{}^{WW}$ and its enantiomer $h'_{12}{}^{WW}$.

It is interesting to note that a rapid equilibrium involving the "five coordinate" species shown in Figure 8d will not necessarily be detected by the nmr method even if π-rotation of the allyl group[22,24] occurs during the lifetime of the "five-coordinate" species. Assuming that π-rotation is rapid relative to the lifetime of the configuration having geometry T, the configurational symmetry groups $T^{TT} = E_7{}^{TT}$ and $\bar{T}^{TT} = (S_2\cdot[E_3] + E_1)^{TT}$ contain these operations

$$\begin{aligned} t_1^{TT} = \bar{t}_1^{TT} &= (1)(2)(3)(4)(5)(6)(7)^{TT} \\ \bar{t}_2^{TT} &= (14)(23)(56)(7)^{TT} \end{aligned}$$

If only one association mechanism is allowed, then $h'_1{}^{TW}$ defines the steric course of association, and since we are dealing with an equilibrium situation, $(h'_1{}^{TW})^{-1} = h'_1{}^{WT}$ defines the steric course of dissociation. The reaction $h_1{}'^{TW}$ is achiral since $(\bar{t}_2\cdot h'_1\cdot\bar{w}_2)^{TW} = h'_1{}^{TW}$. Thus the net stereochemical change implied by association followed by dissociation is defined by the set of operations $(h'_1Th'_1)^{WW} = h'_1{}^{WW}$; *i.e.*, no net stereochemical change is implied.

D. Rearrangements of π-Allene Complexes. The stereochemical nonrigidity of certain transition metal π-allene complexes has been established using nmr techniques.[22] Compounds of the type (π-TMA)PtCl$_2$(p-XC$_5$H$_4$N), TMA = tetramethylallene and p-XC$_5$H$_4$N = para-substituted pyridine, have been studied in detail.[26] Nmr data indicate that the molecule undergoes permutational isomerization and that the isomerization involves net motion of the metal atom from one allene "double bond" to the other. Although this result has been interpreted in terms of a "helical" movement[26,27] of the allene ligand, a mechanism involving an intermediate configuration having a planar allene ligand also seems plausible.[28] In this example we shall examine the dynamic stereochemistry of (π-TMA)PtCl$_2$(p-XC$_5$H$_4$N) and a hypothetical derivative in order to determine how much mechanistic information nmr studies might yield.

The configuration shown in Figure 9a represents molecules of the type (π-TMA)PtCl$_2$(p-XC$_5$H$_4$N). Here, $W^{WW} = C_1{}^{WW}$ and $\bar{W}^{WW} = C_s{}^{WW}$ with

$$\begin{aligned} w_1^{WW} = \bar{w}_1^{WW} &= (1)(2)(3)(4)(5)(6)(7)^{WW} \\ \bar{w}_2^{WW} &= (12)(3)(4)(56)(7)^{WW} \end{aligned}$$

We assume that carbon–carbon and carbon–hydrogen bonds may not be broken and therefore $H' = S_2[S_2] + S_2 + E_1$. H'^{WW} contains $|H'| = 2!\cdot 2^2\cdot 2!1 = 16$ operations, and all of these save one, $h'_1{}^{WW} = (1)(2)(3)(4)(5)(6)(7)^{WW}$, are reactions differentiable in a chiral environment.

$$\begin{aligned} h'_2{}^{WW} &= (12)(3)(4)(56)(7)^{WW} \\ \left\{\begin{aligned} h'_3{}^{WW} \\ h'_4{}^{WW} \end{aligned}\right. &\begin{aligned} &= (12)(3)(4)(5)(6)(7)^{WW} \\ &= (1)(2)(3)(4)(56)(7)^{WW} \end{aligned} \\ \left\{\begin{aligned} h'_5{}^{WW} \\ h'_6{}^{WW} \end{aligned}\right. &\begin{aligned} &= (1)(2)(34)(5)(6)(7)^{WW} \\ &= (12)(34)(56)(7)^{WW} \end{aligned} \\ \left\{\begin{aligned} h'_7{}^{WW} \\ h'_8{}^{WW} \end{aligned}\right. &\begin{aligned} &= (1)(2)(34)(56)(7)^{WW} \\ &= (12)(34)(5)(6)(7)^{WW} \end{aligned} \\ \left\{\begin{aligned} &\left(\begin{aligned} h'_9{}^{WW} \\ h'_{10}{}^{WW} \end{aligned}\right. \\ &\left(\begin{aligned} h'_{11}{}^{WW} \\ h'_{12}{}^{WW} \end{aligned}\right. \end{aligned}\right. &\begin{aligned} &= (13)(24)(5)(6)(7)^{WW} \\ &= (14)(23)(5)(6)(7)^{WW} \\ &= (1324)(56)(7)^{WW} \\ &= (1423)(56)(7)^{WW} \end{aligned} \end{aligned}$$

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(26) K. Vrieze, H. C. Volger, and A. P. Praat, *J. Organometal. Chem.*, 21, 467 (1970).

(27) R. Ben-Shoshan and R. Pettit, *J. Amer. Chem. Soc.*, **89**, 2231 (1967).

(28) See, for example, W. T. Borden, *J. Chem. Phys.*, **45**, 2512 (1966); J. André, M. André, and G. Leroy, *Chem. Phys. Lett.*, **3**, 695 (1969).

$$\left\{\begin{array}{l}\left(\begin{array}{l}h'_{13}{}^{WW} = (13)(24)(56)(7)^{WW}\\ h'_{14}{}^{WW} = (14)(23)(56)(7)^{WW}\end{array}\right.\\ \left(\begin{array}{l}h'_{15}{}^{WW} = (1324)(5)(6)(7)^{WW}\\ h'_{16}{}^{WW} = (1423)(5)(6)(7)^{WW}\end{array}\right.\end{array}\right.$$

Enantiomeric reactions are enclosed in parentheses, and braces enclose reactions nondifferentiable in a totally symmetric environment. H'^{WW} thus contains six reactions differentiable in a totally symmetric environment, but since the chloride ligands B_5 and B_6 do not have nuclear spins, permutation of them will have no effect on the nmr spectra. Thus, reactions $h'_3{}^{WW}$ and $h'_4{}^{WW}$ do not imply site exchanges detectable by nmr spectroscopy and reactions $h'_5{}^{WW}$ and $h'_7{}^{WW}$ as well as $h'_9{}^{WW}$ and $h'_{13}{}^{WW}$ imply nmr indistinguishable site exchanges. There exist therefore only three classes of reactions in H'^{WW} which imply nmr distinguishable site exchanges: the first two, consisting of reactions $h'_2{}^{WW}$–$h'_4{}^{WW}$ and $h'_5{}^{WW}$–$h'_8{}^{WW}$, do not involve net motion of the metal atom from one allene "π-bond" to the other, while the third, consisting of $h'_9{}^{WW}$–$h'_{16}{}^{WW}$, does. However, since all the reactions in this third class imply nmr indistinguishable site exchanges, no further mechanistic information may be obtained. In order to obtain this information, we must turn to derivatives having lower symmetry.

In Figure 9b are shown two assymmetric configurations having enantiomeric skeletal frameworks. Here $H' = S_2[S_2] + E_3$, and of interest here are the reactions

$$\left(\begin{array}{l}h'_1{}^{V*V} = (1)(2)(3)(4)(5)(6)(7)^{V*V}\\ h'_1{}^{VV*} = (1)(2)(3)(4)(5)(6)(7)^{VV*}\end{array}\right.$$

$$\left(\begin{array}{l}h'_2{}^{V*V} = (12)(3)(4)(5)(6)(7)^{V*V}\\ h'_2{}^{VV*} = (12)(3)(4)(5)(6)(7)^{VV*}\end{array}\right.$$

$$\left(\begin{array}{l}h'_3{}^{V*V} = (1)(2)(34)(5)(6)(7)^{V*V}\\ h'_3{}^{VV*} = (1)(2)(34)(5)(6)(7)^{VV*}\end{array}\right.$$

$$\left(\begin{array}{l}h'_4{}^{V*V} = (12)(34)(5)(6)(7)^{V*V}\\ h'_4{}^{VV*} = (12)(34)(5)(6)(7)^{VV*}\end{array}\right.$$

$$\left(\begin{array}{l}h'_5{}^{V*V} = (13)(24)(5)(6)(7)^{V*V}\\ h'_5{}^{VV*} = (13)(24)(5)(6)(7)^{VV*}\end{array}\right.$$

$$\left(\begin{array}{l}h'_6{}^{V*V} = (14)(23)(5)(6)(7)^{V*V}\\ h'_6{}^{VV*} = (14)(23)(5)(6)(7)^{VV*}\end{array}\right.$$

$$\left(\begin{array}{l}h'_7{}^{V*V} = (1324)(5)(6)(7)^{V*V}\\ h'_7{}^{VV*} = (1324)(5)(6)(7)^{VV*}\end{array}\right.$$

$$\left(\begin{array}{l}h'_8{}^{V*V} = (1423)(5)(6)(7)^{V*V}\\ h'_8{}^{VV*} = (1423)(5)(6)(7)^{VV*}\end{array}\right.$$

Enantiomeric reactions have been enclosed within parentheses. All reactions in H'^{V*V} as well as in H'^{VV*} are of course differentiable in a totally symmetric environment. Since reactions $h'_1{}^{V*V}$ and $h'_1{}^{VV*}$ represent inversion of configuration, they do not imply changes in the nmr parameters and therefore are not detectable by nmr spectroscopy, assuming of course that reactions take place in an achiral environment. Consequently the reactions in any pair $h'_i{}^{V*V}$ and $h'_i{}^{VV*}$ imply identical site exchanges. One more important relation must be noted. Since we assume an achiral environment, the enantiomeric reactions $h'_7{}^{V*V}$ and $h'_7{}^{VV*}$ must occur with equal probability. But since configurations having geometry V and V* have identical free energies in an achiral environment and we assume that the nmr experiment is performed under equilibrium conditions, the principle of microscopic reversibility demands that $h'_7{}^{VV*}$ and its reverse reaction $(h'_7{}^{-1})^{V*V} = h'_8{}^{V*V}$ occur with equal probability. Therefore $h'_7{}^{V*V}$ and $h'_8{}^{V*V}$ occur with equal probability.

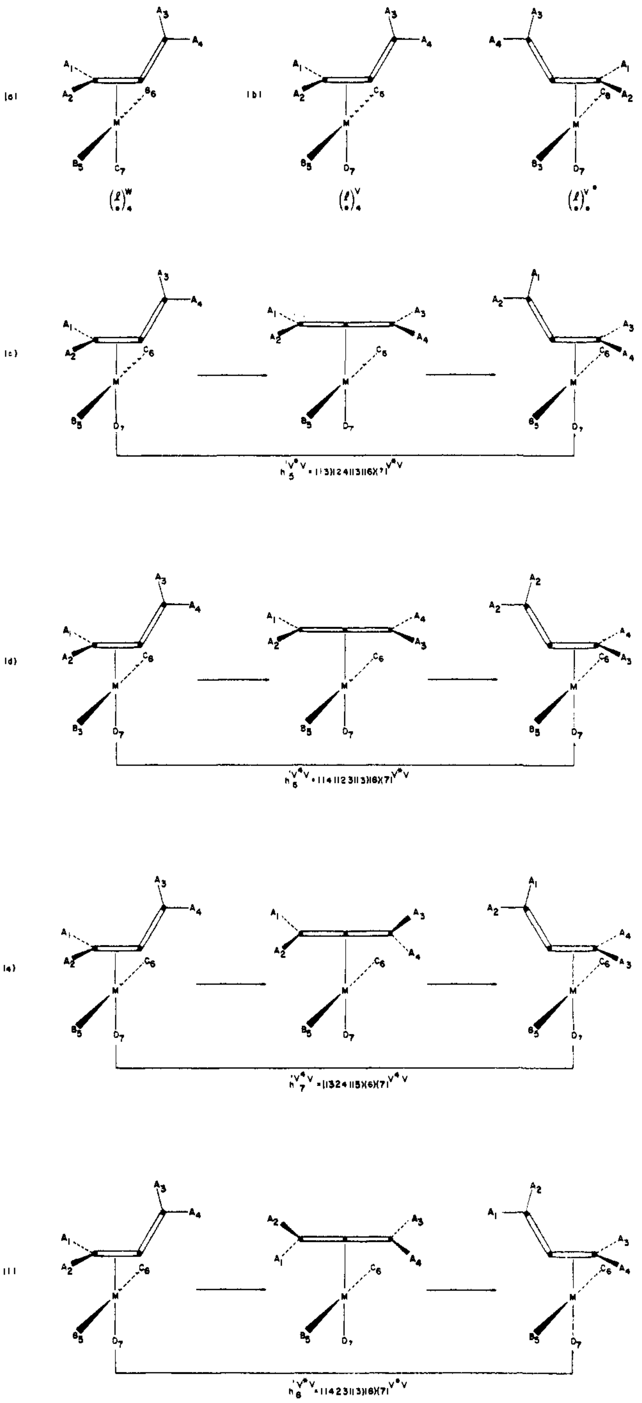

Figure 9. Reference configurations for some π-allene complexes are shown in (a) and (b). Possible rearrangement mechanisms are shown in (c–f). Lines representing the skeletal frameworks are intended to describe the molecular geometry, not bonding schemes. Bond angles in the intermediate configurations may be varied so long as the symmetry of the species is not changed; *i.e.*, allene ligands are not necessarily linear.

Turning to mechanistic questions, it is clear that only $h'_5{}^{V*V}$–$h'_8{}^{V*V}$ and their enantiomers imply net motion of the metal atom from one allene "π-bond" to the other. Mechanisms which imply these four reactions are shown in Figures 9c–f. If we assume that all intermediate configurations have connectivities equal to two, then these mechanisms imply only the reactions indicated in Figures 9c–f. Symmetry arguments do not demand that the intermediates drawn have connectivities greater than two. As noted above, however, reactions $h'_7{}^{V*V}$ and $h'_8{}^{V*V}$ must occur with equal probability. Reactions $h'_5{}^{V*V}$ and $h'_6{}^{V*V}$ need not occur with equal probability, but if ligands B_5 and C_6 have similar chemical properties, then these reactions have similar probability of occurring. Since $h'_5{}^{V*V}$–$h'_8{}^{V*V}$ are all differentiable in a totally symmetric environment, detailed nmr line shape analysis may allow distinction between "helical" movement of the allene ligand and isomerization *via* an intermediate configuration having coplanar allenyl methyl groups. Note that this final example has been simplified by assuming that rapid "π-rotation" about the metal–allene band does not occur. Should such rotation in fact occur, the distinction will be impossible.

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Collisional Activation Spectra of Organic Ions[1,2]

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Abstract: Collision with neutral molecules is shown to provide a convenient method of adding internal energy to ions in a field-free drift region of the mass spectrometer. The effects on this process of ion accelerating potential, target gas pressure and identity, and precursor ion internal energy and mass have been investigated to optimize experimental conditions. Such collisions cause ion decompositions whose activation energies cover a broad range; for a particular ion such decompositions can be viewed as its "collisional activation (CA) spectrum." CA spectra, which can be obtained for each ion in the normal mass spectrum, and which appear to follow the predictions of the quasi equilibrium theory, show many more of the possible unimolecular ion decomposition reactions for an ion than do unimolecular metastables, and thus provide valuable information for ion reaction mechanisms and molecular structure determination. Collisional activation can sometimes yield ion energies which are relatively inaccessible by electron impact. The precursor ion internal energy has a negligible effect on the ion's CA spectrum except for product ions formed through the processes of lowest activation energy. Thus, CA spectra should also be valuable for the characterization of ion structures.

The dissociation of a metastable organic ion in a field-free drift region of the mass spectrometer can indicate the masses of both the precursor and daughter ions of the reaction involved. This extra dimension of information is valuable for the elucidation of reaction pathways,[3,4] and for structure determination of mixture components[3–5] and of isomeric molecules and ions.[6] Experimentally, the utility of this information has been greatly increased by the development of a defocusing technique for measuring the spectrum of daughter ions from a particular precursor with high sensitivity.[4,7] Unfortunately, for many abundant fragment ions in mass spectra the corresponding metastable ion decompositions are not found in appreciable abundance.

Ions undergoing unimolecular decomposition in the drift region ("metastables") must necessarily have lower average internal energies than those decomposing in the ion source; such metastables thus only represent the mass spectral reactions of lowest activation energy, such as rearrangements.[4,8] Such low energy reactions allow the greatest opportunity for prior isomerization ("scrambling") of the precursor ion[4,9] and can exhibit unusually high isotope effects.[10] Ion structure characterization based on metastable ion abundances[6] is compromised by their dependence on ion internal energy.[4,11]

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