Selection Rules for the Isomerization and Substitution Reactions of Transition Metal Complexes

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Abstract: The isomerization and bimolecular substitution reactions of four-coordinated transition metal complexes are considered from a point of view very similar to that previously adopted by Woodward and Hoffmann to treat a number of organic reactions. A combination of symmetry considerations and crystal field theory allows the classification of the reactions as either thermally allowed or forbidden. A method is suggested for classifying reactions for which there is insufficient symmetry to allow the above sharp distinction to be drawn.

Woodward and Hoffmann have developed the concept of symmetry-based selection rules for chemical reactions. They have applied their approach to electrocyclic reactions,[2a] sigmatropic reactions,[2b,3] and concerted cycloaddition reactions.[4,5] It is the purpose of the present work to extend the application of such selection rules to some reactions of transition metal complexes and to attempt some generalization of the concept.

Mango and Schachtschneider[6] have considered the participation of transition metals in concerted cycloaddition reactions using the Woodward–Hoffmann scheme. In the present case a slightly different approach will be adopted.

For clarity we will consider first an example from the work of Woodward and Hoffmann,[4] namely the addition of two molecules of ethylene to give cyclobutane. In essence their method is to draw a molecular-orbital energy-level diagram for the reactants (two molecules of ethylene) and then a molecular-orbital level diagram for the product (cyclobutane), and finally to correlate the individual initial molecular orbitals with the individual final molecular orbitals using symmetry restrictions imposed by an assumed geometry for the transition state. In the present case there are four molecular orbitals, each belonging to a different symmetry class in the relevant C_{2v} point group, and the correlation connects a filled bonding orbital in the initial state with an empty antibonding orbital in the final state. The reaction is therefore described as thermally disallowed but photochemically allowed. As a first step we wish to rephrase this description.

Consider a basis set of atomic orbitals, in this case four carbon p orbitals; apply first a Hamiltonian H_A to obtain the molecular orbitals of the initial state and then a Hamiltonian H_B to obtain the molecular orbitals of the final state, and finally correlate the orbitals according to the symmetry common to H_A and H_B. In this case H_A and H_B are simple Hückel Hamiltonians differing in that H_A has off-diagonal elements corresponding to two ethylene π bonds and H_B has off-diagonal elements corresponding to two cyclobutane σ bonds. For this problem the symmetry conserved corresponds to the geometry of the transition state, but for the more general case this is not necessarily so.

Consider now an analogous problem in which the basis set comprises the five d orbitals of a transition metal atom and H_A and H_B are crystal-field Hamiltonians corresponding to different arrangements of ligands around the central metal atom. If certain elements of symmetry are conserved as the ligands are rearranged from the situation corresponding to H_A to that corresponding to H_B, the eigenfunctions of these operators can be classified accordingly and allowed and disallowed reactions defined by the Woodward–Hoffmann criterion. Specifically let us consider the four-coordinate rearrangements illustrated in Figure 1. The reaction a → b or c → d corresponds to a tetrahedral → square-planar isomerization; a → c racemizes a tetrahedral complex and b → d accomplishes the *cis–trans* isomerization of a square-planar complex. The coordinate system is that shown in the diagram, and the crystal-field operators corresponding to these four arrangements of ligands must be defined in terms of this coordinate system. The conventional d orbitals d_{xy}, d_{xz}, d_{yz}, $d_{x^2-y^2}$, and d_{z^2} are eigenfunctions of the problem for a, c, and d but not for b. Note that in this coordinate system in structure d, d_{xy} not $d_{x^2-y^2}$ is the orbital pointing toward the ligands. For d^8 complexes the energy-level diagrams of Figure 1 show immediately that the square-planar to tetrahedral and tetrahedral racemization reactions are thermally allowed. In agreement with this in several cases where equilibria between square-planar and tetrahedral Ni(II) complexes have been observed, the lifetimes of the individual isomers have been shown to be less than 10^{-5} sec.[7,8] Ernst, O'Connor, and Holm have recently demonstrated that the racemization of optically active tetrahedral Ni(II) complexes is also very fast.[9] The *cis* → *trans* square-planar problem is a little less trivial and is illustrated in Figure 2. It is necessary to derive the eigenfunctions of an octahedral crystal-field potential corresponding to the axis of quantization being

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(2) (a) R. B. Woodward and R. Hoffmann, *J. Am. Chem. Soc.*, **87**, 395 (1965); (b) R. B. Woodward and R. Hoffmann, *ibid.*, **87**, 2511 (1965).
(3) R. Hoffmann and R. B. Woodward, *ibid.*, **87**, 4389 (1965).
(4) R. Hoffmann and R. B. Woodward, *ibid.*, **87**, 2046 (1965).
(5) R. Hoffmann and R. B. Woodward, *ibid.*, **87**, 4388 (1965).
(6) F. D. Mango and J. H. Schachtschneider, *ibid.*, **89**, 2484 (1967).

(7) D. R. Eaton, W. D. Phillips, and D. J. Caldwell, *ibid.*, **85**, 397 (1963).
(8) R. H. Holm, A. Chakravorty, and G. O. Dudek, *ibid.*, **86**, 379 (1964).
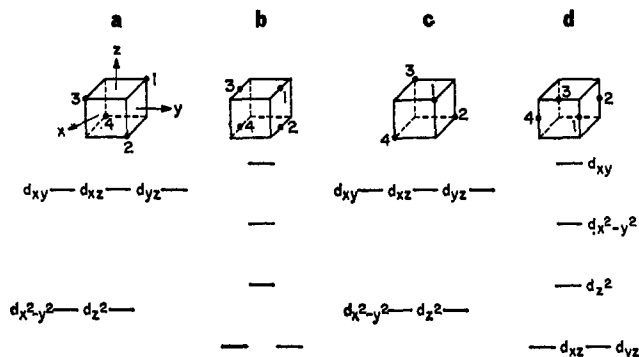(9) R. E. Ernst, M. J. O'Connor, and R. H. Holm, *ibid.*, **89**, 6104 (1967).

Figure 1. Four-coordinate isomerizations.

Figure 2. cis–trans isomerization for d^8 complex. C_{2z}, C_{2x}, and C_{2y} preserved ($\equiv D_2$).

the z axis of Figure 1b and then to apply the appropriate tetragonal distortion. The resulting energy levels are correlated with the conventional square-planar energy levels in Figure 2. Three twofold axes of symmetry (corresponding to point group D_2) are conserved and suffice to correlate the orbitals. It is predicted that the reaction is thermally disallowed but photochemically allowed for d^8 complexes. This agrees with the experimental observations of Haake and Hylton[10] and the more recent work of Perumareddi and Adamson[11] on the cis–trans isomerization of $Pt(PEt_3)_2Cl_2$. It should be particularly noted that these authors found the d–d transitions to be photochemically active. It might also be mentioned that this result could have been intuitively predicted from the observation that the transformation 1b → 1d involves rotation of the square by $\pi/2$ so that an orbital such as d_{xy}, which in 1d points toward the ligands and is antibonding, in 1b points out of the plane of the ligands and is nonbonding. Predictions based on arguments of this kind have certain limitations. Thus both the Woodward–Hoffmann approach and the present results give a qualitative description of the profile of the orbital energy of the system during a concerted transition from the initial state to the final state. Thus in the present case no account has been taken of interelectron repulsion which can in fact suffice to make the intermediate tetrahedral configuration a stable (triplet) state of the molecule for Ni(II) complexes. The presence of such an intermediate allows the possibility of carrying out the reaction in two distinct steps rather than in a concerted manner, and the argument is no longer valid. An analogous objection could be raised in the ethylene dimerization problem if the triplet

$$CH_2 \overset{\uparrow}{—} CH_2$$
$$CH_2 \underset{\uparrow}{—} CH_2$$
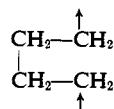
were a stable molecule. However, Pt(II) and Pd(II) compounds are "strong field" complexes in the sense that the interelectron repulsion energies are small compared with the bonding energies (as they are in organic compounds) so that the tetrahedral configuration is not stable and a description of the energy profile neglecting such effects is reasonably valid. For this reason the qualitative agreement between theory and experiment noted above is to be anticipated.
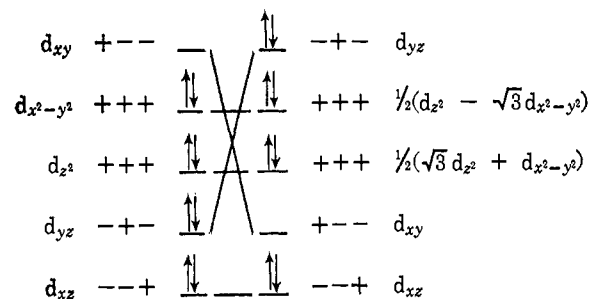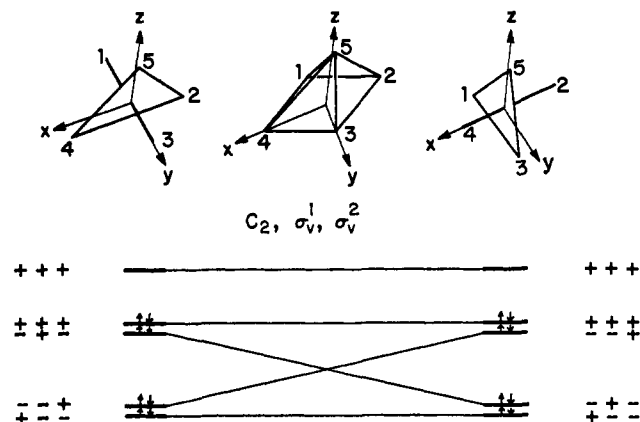
(10) P. Haake and T. A. Hylton, J. Am. Chem. Soc., 84, 3774 (1962).
(11) J. R. Perumareddi and A. W. Adamson, J. Phys. Chem., 72, 414 (1968).

Figure 3. Axial–equatorial isomerization of trigonal bipyramid.

As a further example of this approach, Figure 3 illustrates the axial–equatorial exchange of a trigonal bipyramid through a square-pyramidal intermediate. C_{2v} symmetry is conserved. The reaction is thermally allowed for d^8 complexes but would be forbidden for spin-free d^2 and spin-paired d^3 and d^4 complexes. Bramley, Figgis, and Nyholm[12] inferred very fast intramolecular exchange for the d^8 trigonal bipyramid Fe(CO)$_5$ from nmr data. In this laboratory we have been unable to observe Sn nmr in $Pt(SnCl_3)_5{}^{3-}$ and have attributed this to the effects of a rapid exchange reaction.

We will now consider the substitution reactions of square-planar and tetrahedral d^8 complexes. Plausible mechanisms for these reactions are shown in Figure 4. The bimolecular tetrahedral substitution involves approach of the incoming ligand on one of the faces of the tetrahedron and leads to inversion of the tetrahedron. This process is a familiar one in organic chemistry. C_{3v} symmetry is conserved and the above considerations show immediately that it is thermally allowed. It is assumed that the bimolecular square-planar substitution also goes through a trigonal-bipyramidal intermediate. This is not a restrictive assumption since even if the intermediate is a square pyramid, apical and basal ligands must be interchanged through a trigonal bipyramid before any ligand exchange is accomplished. To go from dsp^2 (square planar) to dsp^3 (trigonal bipyramid) hybridization the additional metal orbital involved is p_z so that the obvious approach of the fifth ligand is toward this orbital, i.e., in a direction perpendicular to the square plane. A trigonal bipyramid re-

(12) R. Bramley, B. N. Figgis, and R. A. Nyholm, Trans. Faraday Soc., 58, 1893 (1962).
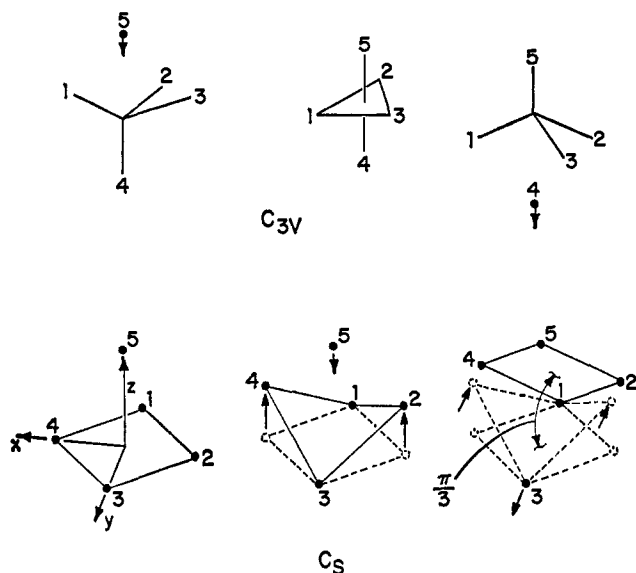
Figure 4. Bimolecular tetrahedral and square-planar substitution.

sults from dropping two diagonal corners of the square below the plane so that these two ligands, together with the incoming ligand, form the equatorial ligands of the trigonal bipyramid. Loss of a different equatorial ligand in the same manner leads to ligand exchange without cis–trans isomerization as demanded by experiment.[13] If the coordinate system is kept fixed, the over-all effect is to rotate the plane of the square by $\pi/3$. Only a single plane of symmetry is conserved, and it is predicted that the reaction is thermally allowed. Experimentally, square-planar d^8 substitutions are fast but appreciably slower than tetrahedral substitutions. Thus, phosphine ligand exchange of $Ni(PEt)_3Cl_2$ (square planar) has been observed by nmr methods. At high concentrations (~ 0.2 M) sharp multiplets are observed for the CH_2 and CH_3 resonances at 220 Mcps in positions corresponding to the average of free and complexed ligand. At lower concentrations (~ 0.05 M) there is sufficient broadening to lose the spin–spin splittings. This observation demonstrates that the ligand-exchange rate is slower than that of $Ni[P(C_6H_5)_3]_2Cl_2$[14] (tetrahedral) by a factor of around 10^2. Even this rate may be due to about 1% of paramagnetic tetrahedral isomer in $Ni(PEt)_2Cl_2$. Ligand exchange of $Pt[P(C_6H_5)_3]_2Cl_2$ and $Pd[P(C_6H_5)_3]_2Cl_2$ has been similarly studied by 220-Mcps pmr and found to be slower than that of $Ni[P(C_6H_5)_3]_2Cl_2$ by a factor of 10^4–10^5. Although slow by the nmr criterion, these are still fast reactions and occur in times of the order of seconds at nmr concentrations, i.e., ~ 0.1 M in complex and ligand. Thus it has been shown that statistical equilibrium between triphenylphosphine and tri-p-tolylphosphine ligands is reached in less time than is required to mix the solutions and position the sample in an nmr spectrometer. This may be compared with the many hours needed for the thermal isomerization of $Pt(PEt_3)_2Cl_2$.[10] Ligand exchange of tetrahedral chelated nickel(II) aminotroponeimineates takes around 10^1 sec,[15] but the square-planar complexes are very

much slower. Similar observations have been made on nickel(II) salicylaldimines.[16] For $Pd[(CH_3)_2PC_6H_5]_2$-Cl_2 the rate of ligand exchange is faster than that of cis–trans isomerization in the absence of ligand by at least 10^2. In brief, the implication is that square-planar substitution occupies a position intermediate between the allowed tetrahedral substitution and the disallowed cis–trans isomerization.

The role of symmetry in formulating selection rules is one of convenience rather than of necessity. This point has been made explicitly in a recent paper by Woodward and Hoffmann.[17] What we really seek is some method of qualitatively predicting the energy profile of the system during the course of a smooth transition from the initial to the final state. Thus Longuet-Higgins and Abrahamson[18] have discussed selection rules in terms of state symmetries rather than orbital symmetries. This is undoubtedly the more elegant and appealing approach although the conclusions are identical with those obtained by the simpler Woodward–Hoffmann method. The resulting state correlation diagrams give a qualitative idea of how the energy of the system varies during the course of the reaction, and, even when the symmetry is insufficient to prevent levels from crossing, such diagrams demonstrate that a considerable activation energy will be required for reactions described as forbidden. There must obviously be a continuous spectrum of conditions ranging from "fully allowed" to "fully forbidden," and it would be desirable to have some criterion for determining the relative positions of two comparable reactions within such a spectrum. We wish to suggest the following approach to this objective.

In the ethylene dimerization problems, the four molecular orbitals φ_1, φ_2, φ_3, and φ_4 are eigenfunctions of both H_A and H_B. This arises because each belongs to a different symmetry class, and no mixing can occur as the reaction proceeds by smoothly changing H_A to H_B. The ground state of the reactants can be described by a wave function Ψ_A which is a product wave function involving the filled molecular orbitals φ_1 and φ_2. Similarly, the total Hamiltonians $\mathcal{K}_A$ and $\mathcal{K}_B$ can be written as the sum of the one-electron Hamiltonians $H_A(1)$, etc. Since the φ_A are eigenfunctions of H_B, it follows that $\Psi_A \mathcal{K}_B \Psi_A$ must be an eigenvalue of the product cyclobutane. It must therefore represent the energy either of the gound state or of an excited configuration. Inspection shows that it is an excited-state energy. The selection rule might therefore be stated in the form that the reaction is thermally forbidden if the application of the Hamiltonian corresponding to the reaction products ($\mathcal{K}_B$) to the ground-state wave function of the reactants (Ψ_A) leads to an excited-state energy of the products and is thermally allowed if it gives the ground-state energy. $\Psi_A \mathcal{K}_B \Psi_A$ could, if desired, be evaluated without using symmetry to factorize the determinants involved. Consider now the effect of making a small change in the Coulomb integral of one of the p orbitals such as might arise from replacing hydrogen

(13) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," 2nd ed, John Wiley and Sons, Inc., New York, N. Y., 1967.
(14) W. D. Horrocks, Jr., and L. H. Pignolet, J. Am. Chem. Soc., 88, 5929 (1966).

(15) D. R. Eaton and W. D. Phillips, J. Chem. Phys., 43, 392 (1965).
(16) A. Chakravorty and R. H. Holm, J. Am. Chem. Soc., 86, 3999 (1964).
(17) R. Hoffmann and R. B. Woodward, Accounts Chem. Res., 1, 17 (1968).
(18) H. C. Longuet-Higgins and E. W. Abrahamson, J. Am. Chem. Soc., 87, 2045 (1965).

by an alkyl substituent. Both elements of symmetry are lost, and a correlation diagram can no longer be constructed by the usual procedure. However, common sense dictates that the reaction must still be forbidden to a first approximation. In terms of the above approach some of the elements in H_A which were previously equal will now be slightly different and the φ_A will now be slightly different combinations of the original basis set atomic orbitals than the φ_B. However, since φ_A and φ_B are formed from the same basis set, a given φ_A can always be written as a linear combination of the φ_B's. Similarly, Ψ_A can be written as a linear combination of eigenfunctions Ψ_B. Evaluation of $\Psi_A \mathcal{K}_B \Psi_A$ will give $aE_0 + bE_1 + cE_2 + \cdots$ where E_0, E_1, $\cdots$ are the ground-state and excited-state energies of the products, respectively. In the present case the coefficient of one of the excited-state energies will be very much larger than all the other coefficients, and this could be interpreted to mean that the reaction is almost forbidden.

This approach can be applied particularly easily to the square-planar substitution reaction considered previously. It has been shown that this reaction leads to rotation of the plane by $\pi/3$. It is more convenient to consider $\Psi_B \mathcal{K}_A \Psi_B$, i.e., to use the final wave functions and the initial Hamiltonian. The wave functions for a $\pi/2$ rotation have been given in Figure 2. Those for a $\pi/3$ rotation can be expressed in terms of the original wave functions and the $\pi/2$ rotated wave functions, i.e.

$$\varphi_B = \cos \pi/3 \; \varphi_0 + \sin \pi/3 \; \varphi_{\pi/2} = \frac{1}{2}\varphi_0 + \frac{\sqrt{3}}{2}\varphi_{\pi/2}$$

Since the $\pi/2$ rotation leads to a forbidden reaction, it is readily shown that

$$\Psi_B \mathcal{K}_A \Psi_B = \frac{1}{4}E_0 + \frac{3}{4}E_1$$

Thus qualitatively the reaction is expected to be slower than the fully allowed tetrahedral substitution (for which $\Psi_B \mathcal{K}_A \Psi_B = E_0$) but faster than the forbidden cis–trans isomerization (for which $\Psi_B \mathcal{K}_A \Psi_B = E_1$).

It is unlikely that arguments of this kind will have more than qualitative significance but they may find a place in rationalizing what are at first sight rather puzzling observations such as the greatly enhanced rate of ligand exchange in tetrahedral d^8 complexes compared to square planar. Application of similar arguments to the isomerization and substitution reactions of complexes of higher coordination number is under consideration and will be reported in due course.

Nuclear Magnetic Resonance Study of Asymmetric π-Allylic Complexes: ((allyl)₂RhCl)₂, (allyl)₂RhCl(C₆H₅)₃P, (allyl)₂RhCl(C₆H₅)₃As, and (allyl)₄Mo

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Abstract: Nuclear magnetic resonance has been employed to investigate the structures of ((allyl)₂RhCl)₂, (allyl)₄Mo, and (allyl)₂RhClL where L = (C₆H₅)₃P and (C₆H₅)₃As. The spectra are of the AGMPX type, corresponding to asymmetric π bonds and indicating that the two terminal carbon atoms of the allyl group are bonded unequally to the metal atom. The nmr parameters, chemical shifts, and coupling constants are listed and discussed in terms of the various structures. The temperature dependence of the spectra yielded further information on the intermediates involved in the conversion of static-to-dynamic systems.

Recent reports[1–12] have shown that nuclear magnetic resonance (nmr) may be utilized to classify allyl metal complexes with respect to symmetry and bonding. Three distinct types have been proposed: (1) symmetrical π, indicated by an AM₂X₂ spectrum and exemplified by ((allyl)PdCl)₂,[4] Ni(allyl)₂, Zr(allyl)₄, and Pd(allyl)₂;[8] (2) σ, indicated by an ABCX₂ spectrum, with only two unambiguous examples reported, (allyl)-Co(CN)₅[11] and (allyl)Mn(CO)₅;[12] and (3) dynamic, indicated by an AX₄ type and exemplified by numerous examples including substituted allyl compounds[2,13] for

(1) J. C. W. Chien and H. C. Dehm, *Chem. Ind.* (London), 745 (1961).

(2) J. E. Nordlander and J. D. Roberts, *J. Am. Chem. Soc.*, 81, 1769 (1959).

(3) K. Vrieze, C. MacLean, P. Cossee, and C. W. Hilbers, *Rec. Trav. Chim.*, 85, 1077 (1966).

(4) H. C. Dehm and J. C. W. Chien, *J. Am. Chem. Soc.*, 82, 4429 (1960).

(5) J. E. Nordlander and J. D. Roberts, *ibid.*, 82, 4429 (1960).

(6) H. C. Volger and K. Vrieze, *J. Organometal. Chem.* (Amsterdam), 9, 527 (1967).

(7) K. Vrieze and H. C. Volger, *ibid.*, 9, 537 (1967).

(8) J. K. Becconsall, B. E. Job, and S. O'Brien, *J. Chem. Soc.*, 423 (1967).

(9) G. L. Statton and K. C. Ramey, *J. Am. Chem. Soc.*, 88, 1327 (1966).

(10) W. B. Wise, D. C. Lini, and K. C. Ramey, *Chem. Commun.*, 463 (1967).

(11) J. Kwiatek and J. K. Seyler, *J. Organometal. Chem.* (Amsterdam), 3, 421 (1965).

(12) W. R. McClellan, H. H. Hoehn, H. N. Cripps, E. L. Muetterties, and B. W. Howk, *J. Am. Chem. Soc.*, 83, 1601 (1961).

(13) K. C. Ramey and G. L. Statton, *ibid.*, 88, 4387 (1966).