Stereochemically Nonrigid Structures

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All discrete molecular aggregates possess an intrinsic nonrigidity through vibrational modes. Such motions, if sufficiently large in magnitude, provide a mechanism for permutation of nuclear positions and hence stereo-isomerization.[1-3]

The probability of rearrangements of this intramolecular[4,5] character varies extensively.[4-12] For example, most tetrahedral or octahedral complexes have very high barriers to such rearrangements, whereas the converse is true for five-coordinate molecules or ions.[7-9] Within a structural family, barriers may vary widely, e.g., 3 to >20 kcal/mol for five-coordinate phosphorus.[13-15]

The consequences of high stereochemical nonrigidity can be profound: inability to separate enantiomers by classical techniques, loss of stereospecificity in reactions proceeding through relatively long-lived intermediates, and inadequacy of resonance techniques for stereochemical determination. On the more positive side, an understanding of such rearrangements can lead to a thorough delineation of reaction mechanism as has been done by Westheimer and coworkers in organophosphate chemistry.[16]

Stereochemical nonrigidity is a convenient but relatively vague term to apply to molecules that undergo rapid intramolecular rearrangement.[17] It is more precise to consider these rearrangements in terms of explicit operations to specify the stereochemical group(s)[6,18] or to identify the transition state(s). In all rearrangements to be discussed here, the ground state and the intermediate or transition state can be identified as an *idealized* polygon or polyhedron.[6,9,18]

These geometric isomers constitute a type of stereoisomer worthy of a specific designation, and I have proposed the term polytopal isomers.[18] Examples are the tetrahedron and square plane in four coordination and the octahedron and trigonal prism in the six-atom family.

In this context, the intramolecular rearrangements *via* bending–stretching operations may be defined as traverses of polytopal forms, i.e., polytopal rearrangements. Consider the well-known inversion process in pyramidal molecules, e.g., ammonia, amines, and phosphines. In this inversion the favored pyramidal form of $R_1R_2R_3M$ species exists as enantiomers. Racemization by inversion proceeds classically through a trigonal-planar form and is represented by the energy diagram in Figure 1. Barriers to rearrangement in this class range from 5.8 kcal/mol in ammonia and ~7–10 kcal in trialkylamines to >20 kcal in organophosphines[19] and >60 kcal in organoarsines, accounting for the facile racemization of dissymmetric trialkylamines and the demonstrated isolation of enantiomers in analogous phosphines.

Following is a discussion of stereochemically nonrigid classes selected primarily from specific investigations in our laboratories.

Six-Atom Family

Polytopal rearrangements were not an established element in six-coordinate stereochemistry until quite recently. This situation reflects the pervasive stability of the octahedron with respect to all alternative six-coordinate geometric forms. Relative rigidity for coordination compounds is evident in the low rates of isomerization of "inert" tris chelates of rhodium and chromium(III)[20] at 100° and in the lack of spectral change[21] in the AB_4 ^{19}F nmr pattern of $C_6H_5SF_5$ from 25 to 220°. In the latter case, the barrier to polytopal rearrangement is >30 kcal/mol.

We have found a special six-coordinate group to be a rich source of stereochemically nonrigid structures.[22] The group is based on diamagnetic iron and ruthenium L_4MH_2 complexes with L a tricoordinate phosphorus(III) species. Only *cis* forms were detected for L_4FeH_2

(1) H. C. Lonquet-Higgins, Mol. Phys., 6, 445 (1963).
(2) A. D. Liehr, J. Phys. Chem., 67, 471 (1963).
(3) E. L. Muetterties, Inorg. Chem., 4, 769 (1965).
(4) An alternative modifier often employed is nonbond-breaking. This is relatively imprecise and requires an operational definition. The latter is available in some instances from nmr data where spin correlation is maintained through a fast rearrangement.[5]
(5) E. L. Muetterties, J. Amer. Chem. Soc., 90, 5097 (1968).
(6) E. L. Muetterties, Rec. Chem. Progr., 31, 51 (1970).
(7) E. L. Muetterties and R. A. Schunn, Quart. Rev., Chem. Soc., 20, 245 (1966).
(8) E. L. Muetterties and C. M. Wright, ibid., 21, 109 (1967).
(9) E. L. Muetterties and W. H. Knoth, "Polyhedral Boranes," Marcel Dekker, New York, N. Y., 1968.
(10) W. N. Lipscomb, Science, 153, 373 (1966).
(11) W. von E. Doering and W. R. Roth, Angew. Chem., Int. Ed. Engl. 2, 115 (1963).
(12) F. A. Cotton, Accounts Chem. Res., 1, 257 (1968).
(13) E. L. Muetterties, W. Mahler, and R. Schmutzler, Inorg. Chem., 2, 613 (1963).
(14) E. L. Muetterties, W. Mahler, K. J. Packer, and R. Schmutzler, ibid., 3, 1298 (1964).
(15) W. Mahler and E. L. Muetterties, ibid., 4, 1520 (1965).
(16) F. H. Westheimer, Accounts Chem. Res., 1, 70 (1968).
(17) Alternatives, applied by others, include fluxional, valence, and degenerate tautomerism.[11,12] The term fluxional has been generally applied to those systems in which nuclear position permutation is fast but where there is no net stereochemical change (form of the Hamiltonian is invariant to the transformation).

(18) E. L. Muetterties, J. Amer. Chem. Soc., 91, 1636 (1969). This applies to coordination compounds wherein the nuclei bonded to the "central" nucleus describe the vertices of an idealized polytope and to polyhedral boranes and to metal clusters with extensive multicenter bonding where the core nuclei describe the vertices of an idealized polytope, e.g., the B_{12} icosahedron in $B_{12}H_{12}^{2-}$.
(19) G. W. Koeppl, D. S. Sagatys, G. S. Krishnamurthy, and S. I. Miller, J. Amer. Chem. Soc., 89, 3396 (1967).
(20) Isomerization and racemization in tris chelates appear to occur primarily by an intramolecular, dissociative process.
(21) E. L. Muetterties, unpublished data.
(22) For an initial account see F. N. Tebbe, P. Meakin, J. P. Jesson, and E. L. Muetterties, J. Amer. Chem. Soc., 92, 1068 (1970).
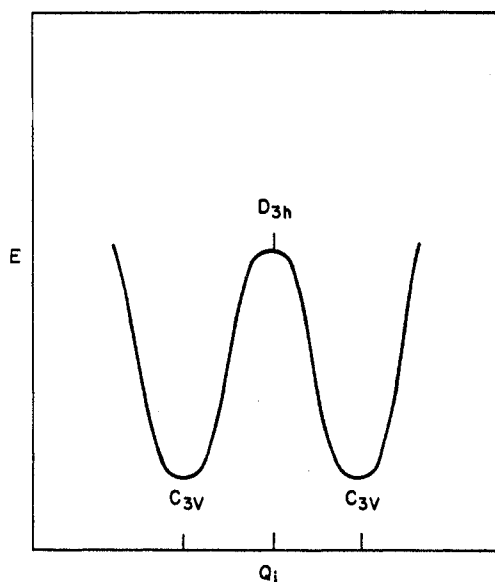
Figure 1. An idealized representation of the potential energy for the inversion of a pyramidal MX_3 molecule or ion as a function of the XMX equilibrium angle. The barrier restricting inversion in these pseudotetrahedral species is associated with the tunneling of the apical electron pair and with the deformation required to achieve a coplanar configuration.

with L ligands such as $P(OC_2H_5)_3$,[23] $P[OCH(CH_3)_2]_3$, $C_6H_5P[OCH(CH_3)_2]_2$, $P(OCH_2)_3CC_2H_5$, $(C_6H_5)_2PCH_3$, and $(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$. Both *cis* and *trans* isomers were in evidence for $H_2Fe[C_6H_5P(OC_2H_5)_2]_4$. The nmr spectra are temperature dependent (Figures 2 and 3), and the limiting high-temperature spectra for all iron complexes show apparent equivalent coupling of hydrogen and phosphorus nuclei, *i.e.*, quintet ^{1}H and triplet ^{31}P patterns. Retention of spin correlation in these transitions, the averaging of coupling constants in the high-temperature forms, and invariance of spectra to dilution and to added ligand unequivocally establish a polytopal rearrangement. Rearrangement barriers[24] for the iron complexes vary surprisingly little with gross changes in the ligand. It does appear, however, that the complex with the ligand that has the smallest

$$P\overset{\displaystyle O}{\underset{\displaystyle O}{-}}O$$
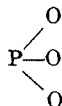
cone angle, $H_2Fe[P(OCH_2)_3CC_2H_5]_4$, has the highest barrier and the one with the largest ligand cone angle, $H_2Fe[(C_6H_5)_2PCH_3]_4$, the lowest barrier.

All but one of the ruthenium complexes examined to date have exclusive *cis* stereochemistry.[25] Earlier Dewhirst, *et al.*,[26] presented similar nmr evidence for *cis*-$H_2Ru[(C_6H_5)_2PCH_3]_4$. Again spectra are tempera-

ture dependent (Figure 4). The high-temperature limiting proton quintet requires temperatures well in excess of 150°, but this has not been spectrally demonstrated because decomposition and dissociation rates are high above 150–200°. Nevertheless, near retention of line shape for the central two lines in the proton spectra (Figure 4) throughout the transition clearly establishes a polytopal rearrangement. The inner lines stay sharp for the *cis* ruthenium complexes, in contrast to the outer lines for the *cis* iron set (Figure 3); this simply reflects differences in relative signs and magnitudes of the coupling constants for the two sets. The $H_2Ru[C_6H_5P(OC_2H_5)_2]_4$ complex has *cis* and *trans* forms present in the solution state, and the general temperature behavior (nmr) is similar to that of the iron analog (Figure 3). Two significant qualitative features of the ruthenium complexes are the relative invariance of rearrangement barriers to ligand change and the much larger barrier values for the set as compared to the iron set. As found for the iron complexes, increasing steric bulk of the ligand does *appear* to lower the rearrangement barrier. The barrier for the complex based on the $C_6H_5P(CH_3)_2$ ligand is higher than that for the complex from the bulkier $C_6H_5P(C_2H_5)_2$ ligand. In our laboratories, Gerlach and Peet are synthesizing model compounds in attempts to demonstrate substantially lower barriers in a ruthenium or osmium complex.

Ligand–ligand nonbonding repulsions in the H_2ML_4 complexes should distort the coordination polyhedron from an octahedron toward a tetrahedral disposition of phosphorus nuclei, as illustrated in Figure 5. The extent of this distortion in the ground state is being determined by Guggenberger, who is analyzing the solid-state structures of the iron and ruthenium complexes based on the $C_6H_5P(OC_2H_5)_2$ ligand.[27] The distortion modes (Figure 5) illustrated for *cis* and *trans* isomers could, through higher vibrationally excited states, provide a mechanism for achieving spin equivalence of hydrogen and of phosphorus nuclei: population of a P_4M pseudotetrahedral transition state in which hydrogen atoms tunnel face-edge positions. In such a mechanism, rearrangement barriers would reflect the extent of PMP angle deformation required to approach tetrahedral values and the hydrogen atom tunneling phenomena, and a potential energy diagram similar to that presented for MX_3 pyramidal molecules (Figure 1) would be expected with the qualification that minima for *cis* and *trans* forms would in general correspond to different energies.

Preliminary analysis of the transition region by Meakin shows no gross inconsistencies between observed and theoretical line shapes for this particular mechanism, but a rigorous analysis will require a more detailed study of the ^{31}P spectra. Qualitatively, the

(23) W. Kruse and R. H. Atalla, *Chem. Commun.*, 921 (1968), first reported the spectra for this compound.

(24) We are reluctant to cite barrier values until a rigorous assignment of coupling constants is achieved and analysis of the transitional region is complete.

(25) Ligand L = $P(OCH_3)_3$, $P(OC_2H_5)_3$, $P[OCH(CH_3)_2]_3$, $C_6H_5P(OC_2H_5)_2$, $(C_6H_5)_2POCH_3$, $(C_6H_5)_2PCH_3$, $C_6H_5P(CH_3)_2$, and $C_6H_5P(C_2H_5)_2$.

(26) K. C. Dewhirst, W. Keim, and C. A. Reilly, *Inorg. Chem.*, **7**, 546 (1968).

(27) Preliminary analysis of $H_2Fe[C_6H_5P(OC_2H_5)_2]_4$ shows a distortion in the solid state which is precisely that proposed by us (Figure 5). The PMP angles are 102.2, 108.4, 97.6, 99.1, 108.8, and 136.7°: P. Meakin, J. P. Jesson, D. H. Gerlach, F. N. Tebbe, L. J. Guggenberger, W. G. Peet, and E. L. Muetterties, *J. Amer. Chem. Soc.*, **92**, 3482 (1970).
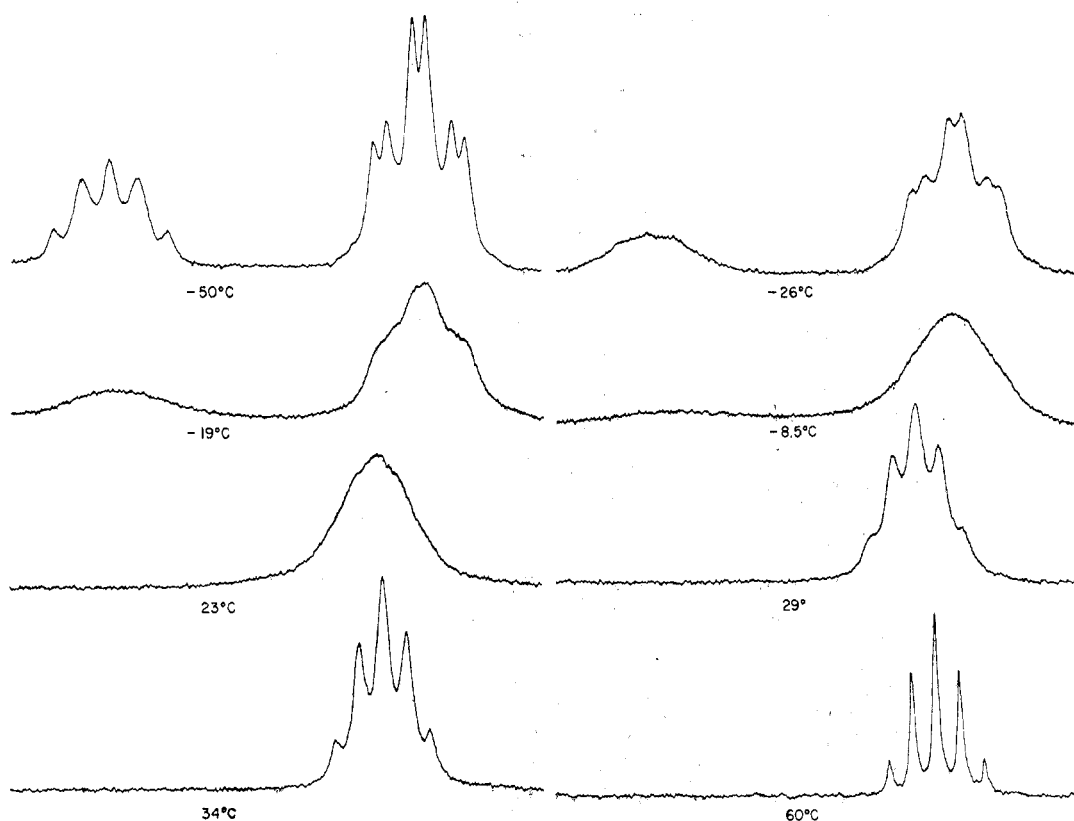
Figure 2. The proton nmr spectrum (220 MHz) for the complex $H_2Fe[C_6H_5P(OC_2H_5)_2]_4$ as a function of temperature. In the low-temperature spectrum both the *trans* (quintet fine structure) and the *cis* forms are present. With elevation of temperature, fine structure is lost and the resonances ascribed to the two isomers broaden and merge into a single peak. The resultant "coupling constant" is an average of those for the two stereoisomers. Similar behavior was found for the ruthenium analog, although the temperatures required for the transitional region are substantially higher than those for the iron case.
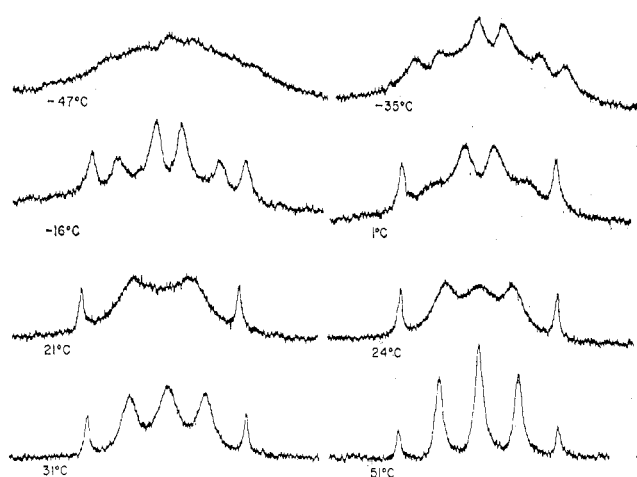

Figure 3. The proton nmr spectrum (220 MHz) of the complex $H_2Fe\{C_6H_5P[OCH(CH_3)_2]_2\}_4$ as a function of temperature. The $-16°$ spectrum observed is characteristic of the *cis* stereochemical form. Broadening that occurs below $-16°$ is not as yet fully explained but is probably due to the onset of restricted internal rotation in the ligand to effectively reduce the symmetry of the H_2P_4 spin system. Above $-16°$, spectral broadening occurs, although the outer lines are unaffected. At $51°$ the limiting quintet spectrum is evident. The outer lines, which are sharp at all temperatures, correspond to transitions of the type $|M\alpha\alpha\alpha\alpha \rightarrow |M'\alpha\alpha\alpha\alpha$ where M and M' are the principal quantum numbers of the proton spin system. Permutation of the ^{31}P spins leaves the transitions unaffected.

apparent steric[28] trends are consistent with this mechanism in that for the iron series the most compact ligand, $P(OCH_2)_3CC_2H_5$, has the highest barrier and the com-

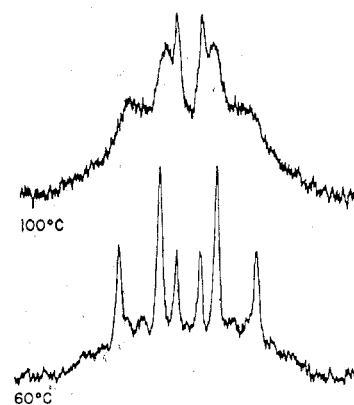Figure 4. The proton nmr spectrum (220 MHz) of the complex $H_2Ru[C_6H_5P(C_2H_5)_2]_4$ at two different temperatures. The limiting low-temperature spectrum is attributed to the *cis* stereoisomer. Elevation of temperature leads to a general broadening of lines with the exception of two inner ones. At temperatures in excess of $100°$, the two sharp inner lines are retained over a very broad background. The limiting high-temperature quintet for this system could not be examined due to thermal instability of the complex above $\sim150°$. Note that the inner lines here remain sharp in contrast to those for the iron complex (Figure 3); this is due to different relative sign and magnitude of coupling constants for the two complexes.

plexes derived from the slightly larger ruthenium nucleus all have larger barriers than the iron analogs. If a trigonal twist mechanism (*vide infra*) were the

(28) The reader is cautioned to note that electronic contributions have not been evaluated; steric factors may contribute to the barriers, but they are not the sole determinants.
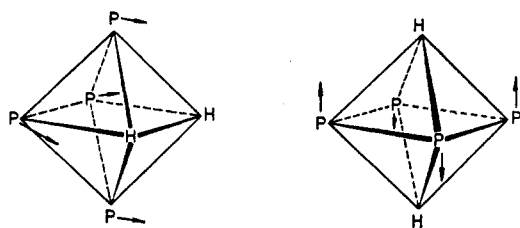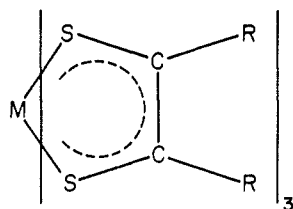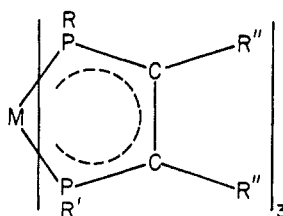
Figure 5. Probable distortion modes for the *cis* and *trans* stereoisomers in the six-coordinate H_2ML_4 complexes where the distortion is primarily due to ligand–ligand nonbonding repulsions.

dominant rearrangement process in these hydrides, the steric trends *might be expected* to go in the opposite direction since ligand–ligand repulsions should be maximal in a trigonal-prismatic intermediate.[28] Similarly, complexes of the type $H_2RuL_3(NCC_6H_5)$, H_2RuL_3-CO, H_2OsL_3CO, and $H_3Ir[PC_6H_5(C_2H_5)_2]_3$ (facial isomer) should have lower barriers to a trigonal twist rearrangement. In fact, all these complexes show *no* evidence of polytopal rearrangements to temperatures (100–160°) above which ligand dissociation or thermal reactivity is extant.

Basically, the only previously considered mechanism for six-coordinate complexes was the trigonal twist[29] which traverses the trigonal prism as the intermediate or transition state. All available evidence indicates that this twist mechanism is a relatively high-energy process. However, the demonstrated range of ground-state structures for dithiolate complexes from octa-

hedral to intermediate to trigonal prismatic[30-34] suggests the possibility of facile polytopal rearrangement *via* a trigonal twist. Decisive demonstration of this phenomenon will probably require synthesis of analogs[35] like

which have ideal nuclei for nmr analysis, and we are trying to prepare such phosphorus chelates.

Rearrangements in polyhedral boranes and metal clusters is a little-explored area in the six-atom family. *cis* to *trans* isomerization at 250° has been established for the octahedral carborane $C_2B_4H_6$, but the mechanism is unknown.[36] Barriers to polytopal rearrangements in this class should generally be higher than for coordination compounds.[6,9]

Four-Atom Family

The probability of polytopal rearrangements in four-coordinate complexes should be very low in non-transitional metal chemistry because of the accentuated potential energy minima for tetrahedral form. For example, Hund has estimated the permutation frequency of hydrogen nuclear positions in methane to be 1×10^{-12}/year. The energetics are grossly altered for central nuclei with partially filled d levels, and the square plane is comparable to the tetrahedron in stability. The status for this group is well characterized by Gerlach and Holm:[37] "There is no evidence at the present time that there exist for a given (transition metal) complex well defined minima corresponding to planar and tetrahedral isomers unless the isomers have different spin multiplicities. In those cases where the intrinsic ligand field strengths are insufficient to cause a spin change in passing from one limiting structure to another, the system may respond by populating one of these structures only or by progressively, rather than discontinuously, distorting toward the other structure to an extent expected to be mainly dependent upon steric factors and temperature."

Polytopal rearrangements among four-coordinate transition complexes are very fast—in fact, generally too fast to monitor by nmr techniques, and too slow for vibrational or electronic spectral techniques. Most of the salient data pertain to d^8 nickel(II) complexes. Consider bischelate complexes based on the uninegative ligands 1–3. Both square-planar ($S = 0$) and tetrahedral ($S = 1$) forms are present in solution provided the bulk of the R group attached to the nitrogen nuclei is sufficiently large to destabilize the square-planar form.[38-40] In these nickel complexes, population of the triplet tetrahedral form leads to large isotropic contact shifts of the proton resonances. With the aminotro-

1   **2**   **3**

(29) W. G. Gehman, Ph.D. Thesis, The Pennsylvania State University, 1954; L. Seiden, Ph.D. Thesis, Northwestern University, 1957; J. C. Bailar, Jr., *J. Inorg. Nucl. Chem.*, **8**, 165 (1958).

(30) R. Eisenberg and J. A. Ibers, *J. Amer. Chem. Soc.*, **87**, 3776 (1965); *Inorg. Chem.*, **5**, 411 (1966).

(31) R. Eisenberg, E. I. Stiefel, R. C. Rosenberg, and H. B. Gray, *J. Amer. Chem. Soc.*, **88**, 2874 (1966).

(32) A. E. Smith, G. N. Schrauzer, V. P. Mayweg, and W. Heinrich, *ibid.*, **87**, 5798 (1965).

(33) E. I. Stiefel, Z. Dori, and H. B. Gray, *ibid.*, **89**, 3353 (1967).

(34) I. Bernal and A. Sequeira, paper presented before the American Crystallographers Association, Minneapolis, Minn., Aug 1967.
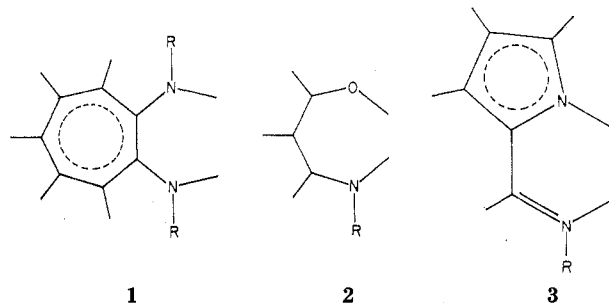
(35) Interligand R–R repulsion may greatly raise the trigonal prismatic energy level.

(36) T. Onak, R. P. Drake, and G. B. Dunks, *Inorg. Chem.*, **3**, 1686 (1964).

(37) D. H. Gerlach and R. H. Holm, *ibid.*, **9**, 588 (1970).

(38) D. R. Eaton and W. D. Phillips, *Advan. Magn. Resonance*, **1**, 103 (1965).

(39) R. H. Holm, G. W. Everett, Jr., and A. Chakravorty, *Progr. Inorg. Chem.*, **7**, 83 (1966).

(40) R. H. Holm, A. Chakravorty, and L. J. Theriot, *Inorg. Chem.*, **5**, 625 (1966).

ponimine ligand (1), the fraction of triplet form was found by Phillips, *et al.*,[38] in our laboratories to be 0 with R = H, 0.016 with R = CH₃, 0.30 to 0.75 with R = aryl, and 0.84 with R = benzyl. With ligand 3, the N–R group must be large for population of the triplet state; *n*-alkyl derivatives show no contact shifts and *s*-alkyl are weakly paramagnetic.[40] In all these systems the singlet–triplet equilibrium is too fast for nmr detection of polytopal isomers. The rate of interconversion is *at least* 10^3 sec⁻¹. The only four-coordinate system for which the rate of rearrangement has been susceptible to nmr study is a series of bis-(tertiary phosphine)nickel(II) halides. The rates are 10^5 to 10^6 sec⁻¹.[41]

No experimental evidence has been presented for polytopal rearrangements in polyhedral boranes or metal clusters. Cotton[42a] has discussed the possibility of rearrangements in metal clusters such as $Co_4(CO)_{12}$.
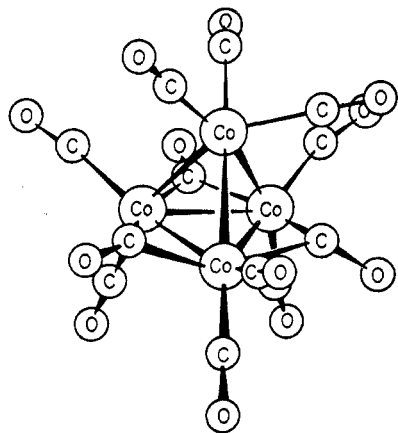
An eminently plausible model[42a] comprises a "bending" of carbonyl groups from bridging to terminal positions. For the cobalt cluster, any rearrangement rate at 25° must be less than ~10^2 sec⁻¹ since the necessary non-equivalence of cobalt nuclei for the ground-state structure was evident in the ⁵⁷Co spectra.[42b] Higher temperature tests should be made of this intriguing hypothesis.

Five-Atom Family

Stereochemical nonrigidity is an extraordinarily common facet of five-coordinate chemistry. The factors influencing the barriers have been sufficiently well explicated to provide an empirical base of predictive merit. This base, simplistic in character, has been structured on experimental observations relating to electronic and steric contributions and on a single rearrangement mechanism.

One mechanism, proposed by Berry[43] in 1960, accounts for all known aspects of dynamical stereochemistry for five-coordinate molecules or ions as well as reaction intermediates. The Berry mechanism[44] consists of a bending mode through which trigonal-
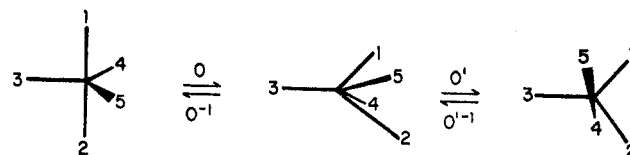

Figure 6. A process for permutation of nuclear positions in the five-coordinate complex with traverse of the trigonal-bipyramidal and square-pyramidal forms. This process is the Berry mechanism,[43] often imprecisely referred[44] to as pseudorotation.

bipyramidal and square-pyramidal forms are traversed (Figure 6). These are the two idealized and limiting polytopal forms in the five-atom family. In complexes with identical ligands, the energy difference between the two forms is small (kT is not an unreasonable lower limit here), although the trigonal-bipyramidal form is generally the more stable one.[45] In trigonal-bipyramidal complexes with mixed ligands, the more electronegative nuclei or ligands are found at the apical positions[6,7,13–15] where ostensibly better overlap is realized. All established exceptions to the electronegativity rule are found in chelate systems in which the overriding factor is ring strain, as in molecules like $[X_3PNR]_2$
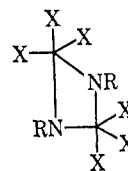
where the nitrogen nuclei are necessarily at equatorial and apical positions to minimize $(PN)_2$ ring strain.[46] Stereochemical rules for transition metal complexes are not well established; the problem is exacerbated by variation in electronic configuration of the central nucleus and the common presence of "nonsimple" ligands such as carbonyls, phosphines, and phosphites.

Most data relevant to stereochemical nonrigidity of five-coordinate compounds first came from nmr studies in our laboratories.[13–15] A concise exposition of the dynamic stereochemical principles is available from the nuclear magnetic resonance studies of phosphorus pentafluoride and its derivatives. The ¹⁹F nmr spectrum of the pentafluoride is a doublet[47a] (PF spin–spin coupling) from ~−197° to at least 60°.[47b] The apparent magnetic equivalence of fluorine nuclei in this trigonal-bipyramidal molecule presum-

(41) (a) L. H. Pignolet and W. DeW. Horrocks, Jr., *J. Amer. Chem. Soc.*, **91**, 3976 (1969); (b) L. H. Pignolet, W. DeW. Horrocks, Jr., and R. H. Holm, *ibid.*, **92**, 1855 (1970).

(42) (a) F. A. Cotton, *Inorg. Chem.*, **5**, 1083 (1966); (b) E. A. C. Lucken, K. Noack, and D. F. Williams, *J. Chem. Soc. A*, 148 (1967).

(43) R. S. Berry, *J. Chem. Phys.*, **32**, 933 (1960).

(44) This is often referred to as pseudorotation, but this does not distinguish it from alternative five-coordinate rearrangements which could also be called pseudorotations (*cf.* E. L. Muetterties, *J. Amer. Chem. Soc.*, **91**, 4115 (1969)). The terminology is imprecise and should be dropped.

(45) For near-spherically symmetrical nuclei, the favored disposition of five equivalent nuclei or ligands should be and is the trigonal bipyramid. With nonequivalent ligands, the potential energy surface may well be more amorphous with forms intermediate between the two limits very slightly favored in special cases. Nevertheless, the majority of complexes with mixed ligands have near-trigonal-bipyramidal forms. Multidentate ligands compound this delicate problem of ground-state geometry; however, most nontransition metal complexes with multidentate ligands have the bonding nuclei at positions approximating a trigonal bipyramid (*cf.* ref 6, 7, 9, 13–15).
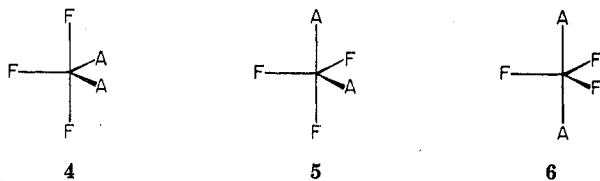
(46) L. G. Hoard and R. A. Jacobson, *J. Chem. Soc.*, 1203 (1966).

(47) (a) H. S. Gutowsky, D. W. McCall, and C. P. Slichter, *J. Chem. Phys.*, **21**, 279 (1953); (b) E. L. Muetterties and W. D. Phillips, unpublished data.

ably reflects a very low barrier to the Berry rearrangement.[48]

Monosubstitution in PF_5 should not substantially alter the barrier to the Berry rearrangement: one equatorial position is effectively held fixed in a single rearrangement step, and the fluorine atom positions are permuted without traverse of the high-energy, alternative trigonal-bipyramidal stereoisomers. Hence an APF_4 molecule should also display an invariant ^{19}F doublet spectrum. The CH_3PF_4 molecule which has the CH_3 group at an equatorial position[50] yields a ^{19}F doublet spectrum invariant from < -120 to $100°$.[13] This is the case for all such molecules investigated to date with but one important exception. Aminophosphoranes, R_2NPF_4, show fluorine atom equivalence at $25°$ and the expected two sets (PF splitting) of doublets and triplets (FF splitting) at low temperatures[14,51] for an equatorially substituted fluorophosphorane. Rearrangement barriers are low, ca. 6 kcal/mol. The definitive work in this class comes from the ^{31}P study of Whitesides and Mitchell,[52] who showed the character of the transitional ^{31}P line shape for $(CH_3)_2NPF_4$ to be consonant only with the Berry mechanism.[43] Note that irrespective of the nitrogen coordination geometry—planar or pyramidal—rotation about the PN bond must be rapid to achieve ultimate fluorine atom equivalence via the Berry mechanism. It is suggested that the PN rotation process is relatively activated due to a degree of multiple PN bonding and that this contributes to the higher barrier to equilibration of fluorine environments in aminofluorophosphoranes relative to the other tetrafluorophosphoranes.

The three possible stereoisomers in an A_2PF_3 molecule are 4-6, with increasing energy in going from 4 to 5 to 6. The energy gaps should be directly related to the magnitude of the F-A electronegativity difference with the 5 to 6 gap being the larger of the two. Isomer 4 is the only detectable form in A_2PF_3 species.[13-15,53] There is no evidence for intramolecular rearrangement in the ^{19}F spectra of dialkyl- or diarylfluorophosphoranes at temperatures as high as $150°$. A Berry rearrangement in an R_2PF_3 molecule would require traverse of energetically unfavorable isomeric states like 5. In contrast, Cl_2PF_3 and Br_2PF_3, in which the

     4   5   6

F-A electronegativity differences are much smaller than in the organophosphoranes, are less stereochemically rigid. Fluorine atom nonequivalence required for the ground-state form 5 is evident in the nmr of the chloride and bromide only at $-60°$ and below.[13,15] Rearrangement barriers are low, ~ 6 kcal/mol.[15] Gorenstein[54] has shown that in alkoxyphosphoranes the barriers due to intermediate (O vs. C) electronegativity effects are ~ 10–17 kcal/mol.

Effect of ring strain on rearrangement barriers is evident from the nmr studies[13] of 7 and 8. Like all

     7   8
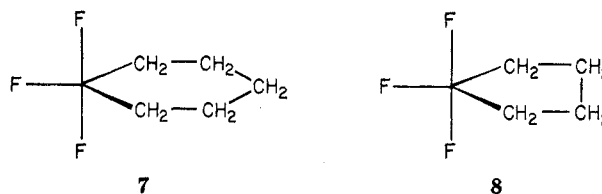
R_2PF_3 molecules, the ^{19}F nmr of 7 consists of two sets of doublets and triplets and is temperature invariant. The expected fluorine inequivalence for 8 is found only at low temperatures. Presumably ring strain in the PC_4 ring in 8 is sufficient to raise the energy level of isomer form 4 to the point that isomer form 5 can be rapidly traversed and fluorine atom equivalence achieved with greater facility than in 7 and its acyclic R_2PF_3 analogs. Ring strain effects can be relatively large, ~ 20 kcal/mol, in alkoxyphosphoranes, as shown by Gorenstein and Westheimer.[55]

In recent years, organic chemists have exploited these basic principles of dynamic stereochemistry for five-coordinate complexes in a quite elegant fashion to delineate reaction pathways for displacement reactions of four-coordinate complexes. Westheimer has lucidly discussed the application to the hydrolysis mechanism of organophosphates.[16] More recent applications on displacement reactions in organophosphorus chemistry include those of Mislow and coworkers.[56] Attempts to extend these principles to displacement reactions involving sulfur and silicon have been less successful. This may reflect the much lower stability of five-coordinate complexes in the sulfur(IV) and silicon(IV) systems. In these systems, reaction pathways probably do not commonly traverse a five-coordinate reaction intermediate of sufficiently long life that stereochemistry is affected by polytopal rearrangement.

Unquestionably the most valuable use of the stereochemical nonrigidity concept will be in reaction mechanism rationales. We believe that there is a very rich body of chemistry susceptible to such exploitation within the transition metal group. Ground-state geometries in this group are primarily dominated by four-coordinate and six-coordinate species. Displacement reactions within both of these systems may often

(48) All ML_5 molecules investigated by nmr have shown apparent magnetic equivalence of ligand nuclei, e.g., AsF_5,[13,14] $P(C_6H_5)_5$,[14] $Sb(CH_3)_5$,[14] and $Fe(CO)_5$.[49]

(49) (a) F. A. Cotton, A. Danti, J. S. Waugh, and R. W. Fessenden, J. Chem. Phys., 29, 1427 (1958); (b) R. Bramley, B. N. Figgis, and R. S. Nyholm, Trans. Faraday Soc., 58, 1893 (1962).

(50) L. S. Bartell and K. W. Hansen, Inorg. Chem., 4, 1777 (1965).

(51) F. N. Tebbe and E. L. Muetterties, ibid., 7, 172 (1968).

(52) G. M. Whitesides and H. L. Mitchell, J. Amer. Chem. Soc., 91, 5384 (1969).

(53) Gaseous $(CH_3)_2PF_3$ has near-trigonal-bipyramidal form with equatorial methyl groups.[50]

(54) D. Gorenstein, J. Amer. Chem. Soc., 92, 644 (1970).

(55) D. Gorenstein and F. H. Westheimer, ibid., 92, 634 (1970).

(56) (a) G. Zon, K. A. DeBruin, K. Naumann, and K. Mislow, ibid., 91, 7023 (1969); (b) K. A. DeBruin, G. Zon, K. Naumann, and K. Mislow, ibid., 91, 7027 (1969).

involve a five-coordinate reaction intermediate.[57] *Dissociative*-type displacement reactions appear to predominate over true bimolecular substitution for six-coordinate complexes, especially those from the first-row transition group.
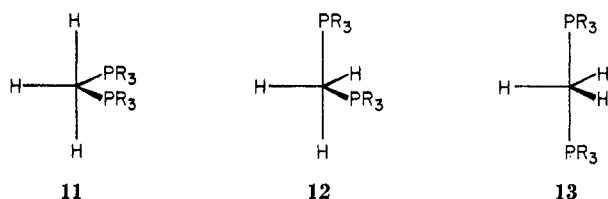
Unfortunately, basic stereochemical principles are not well established for the transition metal group in five coordination. For that reason we presently have an extensive program[58] with the objective of ascertaining solution, ground-state stereochemistry for a wide variety of five-coordinate species. Additionally, we are exploring the factors that substantially affect barriers to polytopal rearrangement in this particular group of five-coordinate complexes.

We have had preliminary success in rationalizing facets of stereoisomerization within certain types of phosphino transition metal hydrides. For example, for the compound $H_3Ir[C_6H_5P(C_2H_5)_2]_3$ there are two possible isomers, meridial (**9**) and facial (**10**), and these

9　　　　　**10**
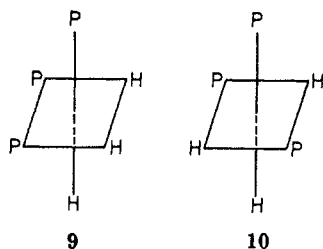
can be isolated in pure form.[59a] At 40° the isomers undergo a slow isomerization. It takes about 48 hr for the meridial isomer form to approach the equilibrium mixture of the meridial and facial isomers. High-temperature nmr studies show that the meridial isomer is more susceptible to ligand dissociation, and additionally suggest that the isomerization may proceed through a five-coordinate intermediate. In fact, this five-coordinate complex has not been isolated but may be the intermediate for the isomerization reaction.[59b]

There are three possible isomers for this five-coordinate species, **11–13**. All available stereochemical im-

11　　　　　**12**　　　　　**13**

plications as well as structural data indicate that isomer **13** would be the favored one. Preferential formation of the meridial form may result because iso-
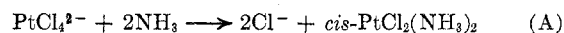
mer form **13** can give rise *only* to the meridial isomer. The only way in which the facial isomer can arise is through reaction of phosphine with isomer **12**. Since isomer **12** represents a higher energy state and since the barrier for the Berry rearrangement for **13 → 12** should be significant, the observed low rate of isomerization (relative to phosphine dissociation rate) of the meridial six-coordinate isomer is explicable. This does not represent a unique explanation but at present no acceptable alternative has been found. Meakin and Tebbe are presently examining a number of analogous systems.

One of the more valuable empiricisms applicable to reactions of four-coordinate transition complexes has been the *kinetic "trans* effect." This concept has been extraordinarily successful in rationalizing vast bodies of reaction mechanisms and as a predictive tool.[60] The dynamic stereochemical principles applicable to the five-atom system might provide an equally effective rationale for the substitution reactions of four-coordinate complexes since this approach deals with the excited state rather than the ground state as in the *"trans* effect." For example, consider the two well-known stereoselective reactions[60] A and B. After

$$PtCl_4^{2-} + 2NH_3 \longrightarrow 2Cl^- + cis\text{-}PtCl_2(NH_3)_2 \quad (A)$$

$$Pt(NH_3)_4^{2+} + 2Cl^- \longrightarrow 2NH_3 + trans\text{-}PtCl_2(NH_3)_2 \quad (B)$$

monosubstitution in reaction B, chloride ion attack of the square-planar $Pt(NH_3)_3Cl^+$ complex may traverse the following path because **14**, the presumed

14
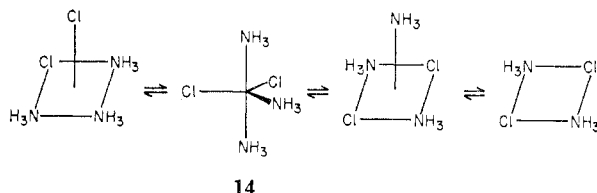
favored stereoisomer, can only yield the *trans*-dichloro derivative. The presumption here is that NH_3 groups and halogens are more effectively bound in apical and equatorial positions, respectively. In reaction A, ammonia attack of the monosubstituted derivative $PtCl_3NH_3^-$ may give either **15** or **16**, but **15**

15

16　　　　　**17**

(57) Normally S_N1 or S_N1CB mechanisms prevail for first-row transition metal complexes. However, most discussions of five-coordinate reaction *intermediates* ignore the critical elements of low energy distinction between square-pyramidal and trigonal-bipyramidal forms and the possibility of polytopal rearrangement.

(58) Partially in collaboration with Professor A. G. MacDiarmid.
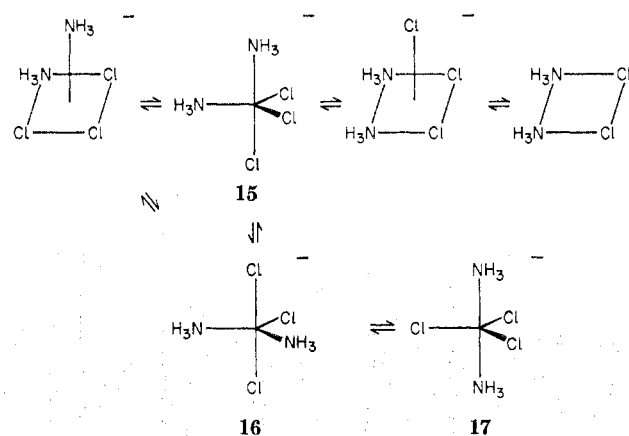
(59) (a) J. Chatt, R. S. Coffey, and B. L. Shaw, *J. Chem. Soc.*, 7391 (1965). These authors cited a quartet as the sole metal hydride proton resonance characteristic of the meridial isomer. The hydride pattern consists of a quartet and a set of lines that could be roughly described as a pair of triplets. (b) B. E. Mann, C. Masters, and B. L. Shaw, *Chem. Comm.*, 703 (1970).

(60) F. Basolo and R. G. Pearson, "Mechanism of Inorganic Reactions," Wiley, New York, N. Y., 1967, Chapter 5.

should be the more stable stereoisomer. Isomer **15** can yield only the observed cis-diammine product. If the trigonal-bipyramidal form **15** is a long-lived intermediate, there is, of course, the possibility of polytopal rearrangement to give the other isomers **16** and **17**. We suggest that the energy level difference between isomers **15** and **16** is sufficiently large that this is not an important phenomenon.

It is noteworthy that isomer **17** should be the favored species of the three possible forms. However, this isomer cannot be formed directly on the addition of ammonia, and in order for it to be generated by a polytopal rearrangement it would be necessary to traverse the presumed high-energy state represented by isomer **16**.

The above is only a rationale, alternative to the kinetic "trans effect," applicable to square-planar substitution reactions. We plan to subject this approach to a more rigorous evaluation, primarily through examination of barriers in model five-coordinate complexes relevant to chemistry of this character.

Seven-Atom and Higher Families

Stereochemical rigidity should be minimal in the seven-atom family. All theoretical or semiempirical attempts to analyze structural facets of seven coordination suggest an undistinguished potential-energy surface. The degree of nuclear displacement required for interconversion of these polytopal isomers is small. A possible distortion mode for the interconversion of the D_{5h} pentagonal bipyramid and C_{2v} bicapped trigonal prism is illustrated in Figure 7. All seven-coordinate complexes investigated by nmr techniques have shown ligand atom equivalence, e.g., IF_7 and ReF_7.[61] More recently we have been examining a group of seven-coordinate osmium hydrides at very low temperatures in an attempt to discern the transitional region associated with a polytopal rearrangement. The proton nmr spectrum of $H_4Os[C_6H_5P(OC_2H_5)_2]_3$ is a simple quartet at room temperature, and this quar-
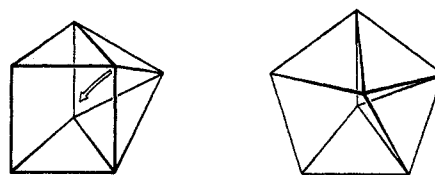
Figure 7. A possible deformation mode for the interconversion of two idealized seven-coordinate polytopal forms. The figure on the left undergoing deformation is the monocapped trigonal prism of C_{2v} idealized symmetry and the one on the right is the pentagonal bipyramid of D_{5h} symmetry.

tet begins to broaden at lower temperatures until a single and broad peak obtains at temperatures of about $-100°$. We believe that the broadening is due to an intermediate rate of polytopal rearrangement but cannot prove this point until the barrier is elevated through a ligand substitution that introduces significant electronic or steric constraints.

Nmr study of polytopal rearrangements in the seven-coordinate and higher complexes will be difficult at best because rearrangement barriers will be intrinsically very low, the number of discrete complexes of adequate stability is small, and typically the central nuclei have large quadrupole moments. To date, our attempts and attempts by others[62] to detect (nmr) intramolecular rearrangements at low temperatures in species like ReH_9^{2-}, $ReH_8PR_3^-$, $ReH_7(PRe_3)_2$, and $Mo(CN)_8^{4-}$ (^{13}C) have been unsuccessful. In contrast, rearrangements in the polyhedral borane class of the 7- through 12-atom families have relatively high barriers (20–80 kcal). Rearrangement mechanisms are reasonably well established in some[63] boranes, e.g., $B_{10}H_{10}^{2-}$ and its derivatives,[64] and others are under current study in our laboratories and others.[65] Mechanisms established for the polyhedral borane class should serve as realistic, idealized models for polytopal rearrangements in the analogous coordination compound class.[9]

(62) A. P. Ginsberg, Inorg. Chem., **3**, 567 (1964).

(63) For a general review of this subject see ref 6, 9, and 10.

(64) W. R. Hertler, W. H. Knoth, and E. L. Muetterties, J. Amer. Chem. Soc., **86**, 5434 (1964).

(65) For a recent report on the 12-atom carboranes, see H. D. Kaesz, R. Bau, H. A. Beall, and W. N. Lipscomb, ibid., **89**, 4218 (1967).

(61) E. L. Muetterties and K. J. Packer, J. Amer. Chem. Soc., **86**, 293 (1964).

Quasi-Bound States in Molecular Collisions

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Quasi-bound states are bound species that can spontaneously dissociate, with conversion of part of their energy into the translational energy of unbounded relative motion of the dissociation fragments.

Such a broad definition encompasses a large range of phenomena,[2] depending on the mode of formation and the nature of the decay products; for example, radioactivity, autoionization, spontaneous emission, predissociation, unimolecular breakdown, etc. In particular,

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(2) For a unified quantum mechanical approach to such phenomena see, for example, (a) R. D. Levine, "Quantum Mechanics of Molecular Rate Processes," Oxford University Press, Oxford, England, 1969. See also H. Feshbach, Ann. Phys. (New York), **5**, 537 (1958); **19**, 287 (1962). For an early formulation see (b) O. K. Rice, Phys. Rev., **33**, 748 (1929); **34**, 1459 (1929); **35**, 1551 (1930).