Although reactions 6 and 7 may not be rate determining, they must determine the final ratio of chlorine dioxide to chlorate ion. The rate of formation of the intermediate (Cl_2O_2) would be over-all second order; reaction 6 would necessarily be first order, and reaction 7 must be second order. At higher pH values, these reactions appear to be considerably slower. This would account for the production of primarily chlorate ion in dilute solution with the yield of chlorine dioxide increasing as the over-all reactant concentration increased.

In conclusion, we have shown that chlorine oxidizes chlorous acid more rapidly than does hypochlorous acid and, in dilute solution, the primary product is chlorate ion but that, in more concentrated solutions, the main product is chlorine dioxide. The suggested intermediate (Cl_2O_2) is somewhat analogous to the stable and well-defined compound ClO_2F. These results would also account for the formation of chlorate when chlorite is used to oxidize metal ions such as uranium(IV)[2a] or vanadium(II),[4] in that the corresponding metal ion–hypochlorous acid reactions are slow as compared to the hypochlorous acid–chlorous acid reaction, and at most only very low concentrations of Cl_2O_2 would result. The major product should indeed be chlorate ion and not chlorine dioxide.

Correspondence

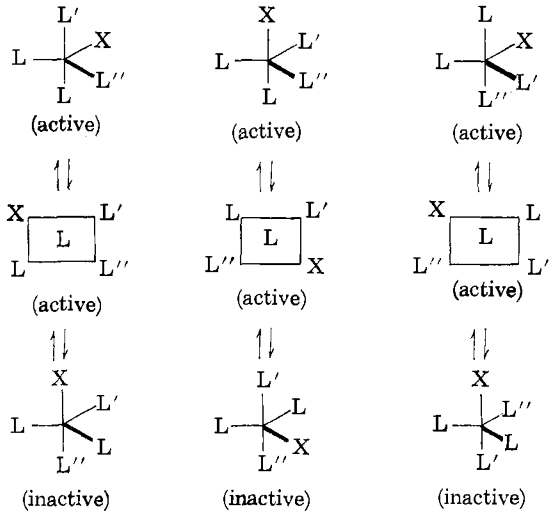
Intramolecular Racemization Processes in Pentacoordinate Structures

Sir:

In a recent review[1] and also in earlier articles,[2-4] brief mention was made of intramolecular racemization processes in optically active pentacoordinate structures. These processes were characterized in general as facile rearrangements based on interconversions of trigonal-bipyramidal and tetragonal-pyramidal geometries. *Within the context of this specific mechanism first delineated by Berry,*[5] the various classes[1] of pentacoordinate structures are assayed in this note for feasibility and ease of racemization only.[6]

$XMLL'L''L'''$.—With five nonequivalent unidentate ligands, neither the trigonal-bipyramid nor the tetragonal-pyramid model possesses a plane of symmetry.[7] Intramolecular racemization of an optically active $XMLL'L''L'''$ species can be achieved in plane-pentagonal geometry but the latter state should be very high in energy and should be preempted by the more energetically attractive racemization process comprising ligand dissociation.[8] Alternatively, racemization may be achieved in an idealized process involving the trigonal bipyramid ⇄ tetragonal pyramid intramolecular rearrangement which comprises as a minimum a tenth-order[9] process. An exemplary compound for experimental evaluation of these assessments is $R_1R_2R_3PClF$ because the pronounced affinity of alkyl and aryl groups (relative to halogen atoms) for equatorial sites should yield relatively long-lived ground-state geometries.

$XML_2L'L''$.—With this kind of substitution, there are seven possible isomers in trigonal-bipyramidal geometry of which four isomers have a plane of symmetry. The three asymmetric isomers have in common an equatorial and an axial L ligand. Racemization



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(1) E. L. Muetterties and R. A. Schunn, *Quart. Rev.* (London), **20,** 245 (1966).

(2) E. L. Muetterties, W. Mahler, and R. Schmutzler, *Inorg. Chem.*, **2,** 613 (1963).

(3) E. L. Muetterties, W. Mahler, K. J. Packer, and R. Schmutzler, *ibid.*, **3,** 1298 (1964).

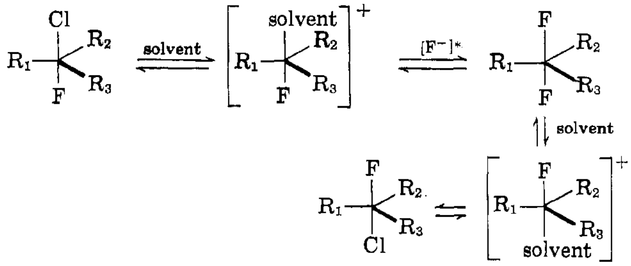
(4) E. L. Muetterties, *ibid.*, **4,** 769 (1965).

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

(6) Only structures with asymmetry originating at the central atom are evaluated here.

(7) Absence of any planes of symmetry is not, of course, sufficient to define a geometry that has *d* and *l* isomers. The precise statement for the conditions necessary for optical activity is given in H. Eyring, J. Walter, and G. E. Kimball, "Quantum Chemistry," John Wiley and Sons, New York, N. Y., 1957, p 346.

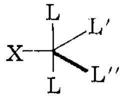
(8) Racemization may occur through a dissociative route in the following manner



or by conversion to an octahedral intermediate or transition state through F^- addition. *[F^-] may be derived directly or indirectly from $R_1R_2R_3PClF$.

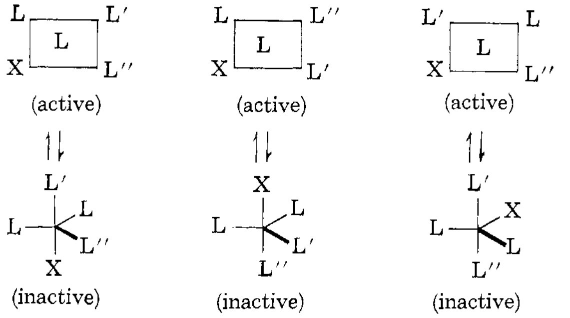
(9) Order is defined by the number of intramolecular rearrangements comprising conversion of trigonal-bipyramidal to tetragonal-pyramidal geometry or *vice versa*.

cannot be achieved by simply proceeding to tetragonal-pyramidal geometry. This interconversion must be followed by a second-order[9] process proceeding to another *trigonal-bipyramidal isomer* which may have a plane of symmetry. Thus conversion of *d*- or *l*-$XML_2L'L''$ of a specific geometry to a *dl* racemate of the same geometry is a multistep process, which process if relatively slow may display a complex change in optical rotation. In some cases with proper substituents, the barrier to such a process may be sufficiently high to permit isolation of an optical isomer by classical techniques. The remaining seventh trigonal-bipyramidal isomer not depicted above has a plane of symmetry

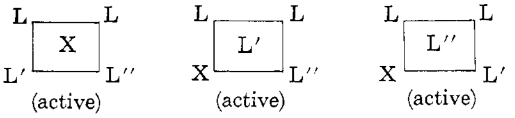


There is an intrinsic difficulty in preparing a trigonal-bipyramidal compound or ion with no plane of symmetry in an $XML_2L'L''$ species since the two identical ligands must be at axial and equatorial sites whereas the thermodynamically favored isomers will *in general*[10] be those with the two identical ligands both either at the axial sites or at the equatorial sites.[1-3]

For tetragonal-pyramidal geometry, there are nine isomers, three of which have a plane of symmetry. Three of the six asymmetric isomers in proceeding to trigonal-bipyramidal geometry may gain a plane of symmetry

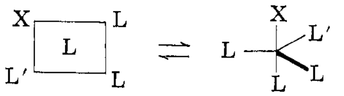


Optical activity in any of these above three isomers should be shorter lived than for the other three tetragonal pyramidal geometries which lack a plane of symmetry



These three isomers in a *d* or *l* form must go through a trigonal-bipyramidal and then a tetragonal-pyramidal model before optical activity is lost. This must be followed by *a series of further transformations before the racemate of the original tetragonal isomer is obtained.* In such a system, if the rate is moderate and is followed by polarimetry, the changes in rotation may be quite complex but ultimately might aid in analyzing the potential energy surface of such five-coordinate systems.

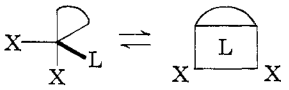
XML_3L'.—No trigonal-bipyramidal isomer which has three identical ligands lacks a plane of symmetry.[11] One of the four tetragonal-pyramidal isomers has no plane of symmetry but gains one on going to trigonal-bipyramidal geometry.



XML_4, X_2ML_3, and X_3ML_2.—With only two kinds of substituents, all isomers for either trigonal-bipyramidal or tetragonal-pyramidal geometry possess a plane or planes of symmetry.

Chelates.—With a symmetrical, strictly *planar* bidentate chelate, there are two isomers for trigonal-bipyramidal and two for tetragonal-pyramidal geometry in an X_3M(chel) composition. All of these possess a plane of symmetry.

In X_2ML(chel) species, of the four trigonal-bipyramidal isomers only one is asymmetric, but this one racemizes in a first-order process. A rigid chelate[12]



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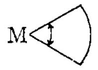
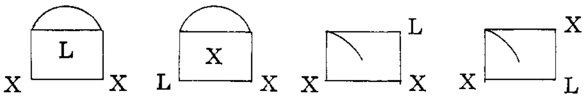
moiety with a highly favored 90°



angle (M = central atom) should increase ground-state lifetime of the isomer and provide a more favorable case for isolation and characterization of an optically active pentacoordinate structure.[13] There are four possible X_2ML(chel) tetragonal-pyramidal models, two of which are asymmetric, and each racemizes in a first-order process in going to trigonal-bipyramidal geometry.



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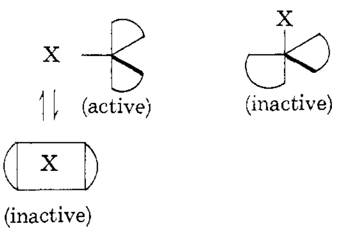
In bis(bidentate) chelates there are two trigonal-bipyramidal models, one asymmetric which can lose optical activity in a single bending process to tetragonal.



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[10] This is particularly true if L differs significantly from X, L', and L'' in electronegativity, steric requirements, etc.[1]

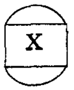
[11] We[1] incorrectly reported one of the four possible XML_3L' to possess no plane of symmetry.

[12] Those chelating ligands in X_2ML(chel) species with 120° "bites" will *generally* favor trigonal-bipyramidal geometries which all possess a plane or planes of symmetry.

[13] Furthermore, the energy level of the necessary tetragonal-pyramidal intermediate for racemization should be raised if the chelate has a preferred "bite" of 90° (ignoring all aspects of overlap and Coulombic factors).

onal-pyramidal geometry. A *d* or *l* form of the asymmetric species should have a relatively short lifetime unless the chelate constraints are significant. Synthesis possibilities and experimental measurements of ground-state lifetime appear quite favorable. Possibilities are $(-CH_2CH_2CH_2O-)_2PX$ (C is equatorial and O axial in the chelate), $[(\text{tropolono})_2SiR]^+$, and $(\text{biphos})_2IrCO^+$. The tropolone ion is an ideal bidentate ligand because it is strictly symmetrical, strictly planar, and forms quite stable complexes.[14]

For tetragonal-pyramidal geometry with two bidentate ligands, the isomers are



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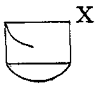

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The racemization process for the asymmetric form is first order.[15]

From the above considerations a general order can be predicted for stability with respect to an *intramolecular* racemization of an optically active pentacoordinate structure. (1) Structures containing five different ligands should be uniquely stable. The lifetime of an optically active XMLL′L″L‴ species, provided there is no ligand dissociation, should be a matter of years[16] for plane-pentagonal intermediates (or transition states) or seconds to hours for the multiorder TBP–TP process. Rate will be, in the latter case, primarily determined by the proclivities of the varying ligands for axial or equatorial bonding sites. (2) The next most stable class of optically active pentacoordinate structures should be derived from the chelate structures. Although a racemization process for such species based on interconversion of trigonal-bipyramidal and tetragonal-pyramidal geometries is first order, the given geometry may be sufficiently stabilized through the constraints of the chelate to provide for a reasonably long ground-state lifetime. In this context, the most favorable chelate structures will be rigid and require an interbond angle between the two chelating atoms and the central metal atom close to 90° for those structures with trigonal-bipyramidal ground-state geometry. (3) Optical isomers of the type $XML_2L'L''$ should be of intermediate stability. Intramolecular racemization processes for these species are multistep processes as noted above. The major synthesis difficulty in an experimental test of this system is the fact that two identical ligands in any of the three optically active trigonal-bipyramidal isomers must be at an equatorial and an apical site. Such species are not generally thermodynamically favored. There is little evidence that small compact ligands will display such ambivalent character and this is well documented in detail for d^0 and d^{10} configurations.[1-3,17] Such may not be the case for some of the transition metal complexes and it is perhaps in this area where the greatest opportunity lies for a real experimental test of this hypothesis. Steric factors may play a very important role in chemistry of this sort not only in stabilizing a species wherein a given kind of ligand can occupy both an equatorial and an axial site but also in significantly raising the barrier to interconversion of the two idealized geometries. In this context, it is significant that the CF_3 group at least in phosphorus compounds appears to show some ambivalence with regard to bonding preferences for axial and equatorial sites. Thus in CF_3PF_4 and in $(CF_3)_2PF_3$, the CF_3 group appears to be exclusively axial whereas in the tris(trifluoromethyl) derivative all three CF_3 groups appear to be at equatorial sites.[2,18]

Exaltation of the barrier to geometrical interconversions which encompass the area of *intramolecular* racemizations in pentacoordinate structures may be achieved with a variety of ligands capable of stabilizing a given idealized configuration through strong, preferential σ overlap in axial or equatorial sites or through any one of a number of mechanisms such as steric effects or strong π bonding (see discussions by Gillespie[19]). Furthermore, if the central atom is very large and if the substituent groups, particularly the donor atoms, are very large, again there should be a significant elevation of the barrier to rearrangement processes of this type.

In some of the specific isomer systems discussed above, *there are intramolecular rearrangement mechanisms*[20] *alternative to the Berry*[5] *type of process.* Although it might be of value to outline these alternatives and although the stylized Berry process will probably have a higher barrier than a modification of it for some specific systems, the physical reality of entertaining new mechanisms is a questionable one since we at present have no physical techniques that will provide definitive evidence on mechanistic details. The Berry[5] mechanism has much to recommend it, and its very simplicity for the characterization of the potential energy surface in pentacoordinate systems is most appealing. However, it is critical to keep in mind that in a specific system the motion may be primarily anharmonic. Also, there may be no real minimum in the potential energy surface for one of the idealized geometries. A case in point is phosphorus pentafluoride. The ground-state geometry of phos-

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(14) E. L. Muetterties and C. M. Wright, *J. Am. Chem. Soc.*, **86**, 5132 (1964); **87**, 21, 4706 (1965); E. L. Muetterties, *ibid.*, **88**, 305 (1966).

(15) A possible low-energy pathway for racemization of chelate structures is interaction with solvent to give an octahedral structure with a plane or planes of symmetry.

(16) Ground-state geometry lifetime of a $CR_1R_2R_3R_4$ species at 25° has been estimated by Hund to be 10^9 years; *cf.* G. Herzberg, "Infrared and Raman Spectra of Polyatomic Molecules," D. Van Nostrand Co., Inc., New York, N. Y., 1945, p 225.

(17) E. L. Muetterties and W. Mahler, *Inorg. Chem.*, **4**, 1520 (1965).

(18) These assignments were based on infrared and nmr data. E. A. Cohen and C. D. Cornwell (personal communication) have a preliminary microwave analysis of CF_3PF_4 confirming our suggestion of an axial CF_3 group. Apparently, the overlap of the axial phosphorus orbitals with a CF_3 group is just slightly greater than for fluorine at least relative to the overlap considerations in the equatorial plane. The shift to equatorial CF_3 groups in $(CF_3)_3PF_2$ is explicable on steric grounds. Scale models give no hint of nonbonding ligand interactions in any of the CF_3PF_4 or $(CF_3)_2PF_3$ isomers or in the D_{3h} model of $(CF_3)_3PF_2$. The other isomers of $(CF_3)_3PF_2$ do exhibit significant nonbonding repulsions in the scale models (Figure 1).

(19) R. Gillespie, *J. Chem. Soc.*, 4672, 4679 (1963).

(20) In Cl_2PF_3 and Br_2PF_3 the barriers to intramolecular exchange of fluorine atoms are within experimental error identical.[11] This suggests primarily an anharmonic motion of fluorine atoms because of the very large difference in atomic weight between chlorine and bromine.

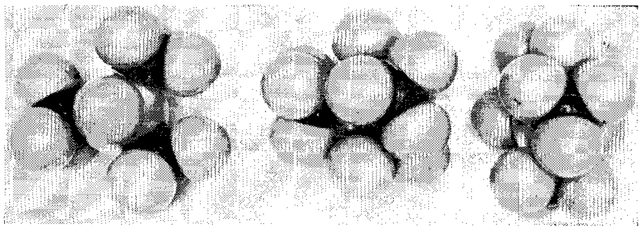

Figure 1.—Scale models depicting the three isomers of $(CF_3)_3PF_2$ with the D_{3h} model on the left, the isomer with two equatorial and one axial CF_3 groups in the center, and on the far right the isomer with one equatorial and two axial CF_3 groups.

phorus pentafluoride for the gaseous state and the liquid state is a trigonal bipyramid of D_{3h} symmetry. Permutation of the fluorine nuclei is, from all available evidence, a rapid one even though this particular process has not been rigorously established.[1-5] The permutation process or the rearrangement process most reasonably proceeds through an intermediate which has tetragonal-pyramidal geometry. However, for phosphorus pentafluoride this intermediate is probably not a minimum in the potential energy surface, or perhaps it is a very shallow minimum. A relevant experiment of interest here would be a dielectric constant (dipole moment) study of gaseous phosphorus pentafluoride[21] as a function of temperature. The barrier to interconversion in this system is estimated to be 6 kcal or less. If the tetragonal-pyramidal model is a reasonably deep minimum in the potential energy surface then it should be possible to detect a change in the dielectric constant of this system as a function of temperature. Perhaps better cases for study are XML_4 or X_2ML_3 structures because of the bond length variances for axial and equatorial sites.[22]

Acknowledgments.—The author is indebted to detailed and valuable comments by one of the referees who specially caught the multiorder TBP–TP racemization process in XMLL′L″L‴ species that had been missed by the author. Additionally the referee has noted a topographical representation of these stylized rearrangements for the 20 possible XMLL′L″L‴ trigonal-bipyramidal configurations with a polyhedron with 20 equivalent vertices and 30 equivalent edges representing trigonal bipyramids and 30 equivalent edges representing trigonal bipyramids and interrelating tetragonal pyramids, respectively. This polyhedron, related to the pentagonal dodecahedron, possesses a higher order symmetry and might be represented as the double group of the dodecahedron to take into account the optical as well as the geometrical isomers of the trigonal bipyramid.

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[21] Or any other ML_5 species such as AsF_5, SbF_5, $Fe(CO)_5$, $(CH_3)_5Sb$, etc.

[22] Recently there have been many mechanistic and some less qualitative (*e.g.*, see P. C. van der Voorn and R. S. Drago, *J. Am. Chem. Soc.*, **88**, 3255 (1966)) attempts to rationalize the trend toward longer axial bond lengths relative to equatorial bond lengths with an increased differential with substitution (for documentation see ref 1). In ML_5 species the energy level separation between the A_1' and E' molecular orbitals should increase with increasingly electropositive substituents and thereby increase axial bond lengths. Decrease in effective positive charge on the central atom would appear to be the dominating parameter. Similarly in X_2ML_3 and XML_4 species electropositive substituents should raise the energy level or levels for the axial bonds and here exaltation of the energy level should be more marked with the more electropositive substituents, particularly if the X and L substituents differ significantly in electronegativity. There should, however, be exceptions to these trends particularly in d^x transition elements or with strong π-bonding substituents where other parameters may dominate. Until much more accurate wave functions are available, the indiscriminate use of such LCAO–MO programs as those developed by R. Hoffmann and W. N. Lipscomb (*cf. J. Chem. Phys.*, **36**, 2179, 3489 (1966)) (which have been applied with a high degree of success to highly symmetrical polyhedral boranes) can be quite misleading even though the calculations are in qualitative agreement with such subtle aspects as geometry and stereochemistry as well as relative ordering of energy levels. Attempts to generate semiquantitative treatments of these subjects by the purely mechanistic models typified by the nonbonding repulsion model are also unrealistic at this state of development in theory [*cf.* recent discussions by Gillespie (*Inorg. Chem.*, **5**, 1634 (1966) and by Bartell (*ibid.*, **5**, 1635 (1966)].