of the various aromatic hydrocarbon donors, although K_c increases with donor strength as expected. A discussion of these results, including correlations of K_c and of λ and ϵ of the blue-shifted band with donor strength, is given elsewhere.[23,27]

Acknowledgment. This work was supported by National Science Foundation Grants No. GP-8029 and No. GP-23278.

(27) J. D. Childs, S. D. Christian, and J. Grundnes, unpublished results.

Modes of Rearrangement in Phosphoranes

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Abstract: The types or modes of rearrangement that a trigonal bipyramid molecule can undergo are presented. The limited experimental evidence on phosphorane rearrangements, pertinent to distinguishing among these modes, is analyzed.

In 1950 Gutowsky and Hoffman[1] observed the ^{19}F nmr spectrum of PF_5 to be a doublet which implied[2] an intramolecular rearrangement equilibrating the equatorial and axial sites of the trigonal bipyramid (TBP) determined by electron diffraction. It has been generally accepted[3] that the rearrangement observed in PF_5 and in other phosphoranes takes place *via* the pseudorotation mechanism proposed by Berry in 1960.[4] There has, however, been no presentation of the simple problem in combinatorics which provides a description of all the experimentally distinguishable kinds of rearrangement or "modes of rearrangement" that a TBP molecule can undergo, without which a meaningful analysis of the experimental data cannot be made.

The question of mode of rearrangement is an unfamiliar one since in organic chemistry all rearrangements about an atom involve only one observable consequence: racemization among the two distinguishable isomers as in amines, sulfoxides, phosphine oxides, and substituted methanes. The TBP geometry of phosphoranes with its two axial and three equatorial sites for ligands is such that there are five different modes of rearrangement or types of possible stereochemical change, and these are discussed here along with the limited experimental evidence which might serve to distinguish among them. These modes describe all the basic stereochemical modifications of a TBP so that every TBP rearrangement can be classified according to which one or more of these modes is attained by the rearrangement mechanism involved. The arguments presented here could equally well be applied to rearrangements in all other TBP molecules.

(1) H. S. Gutowsky and C. J. Hoffman, *Phys. Rev.*, 80, 110 (1950); *J. Chem. Phys.*, **19**, 1259 (1951).

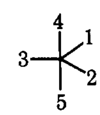
(2) This interpretation, of course, rests on the assumption that this is not due to an accidental near magnetic equivalence of the TBP fluorine atoms.

(3) See, for example, the review of R. Schmutzler, *Angew. Chem., Int. Ed. Engl.*, 4, 496 (1965).

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

Theory and Discussion

We consider the number of ways that the labeled ligands of a phosphorane **1** can be rearranged among



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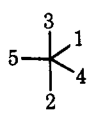
themselves while preserving the explicit location on the TBP of three, two, one, and none of the ligands, respectively. At the same time we must group together all permutations among the indices or *apparent* rearrangements which give *indistinguishable* TBP's differing only by one of the six operations of the point group C_{3v}.

If a and e symbolize the axial and equatorial ligands, respectively, the different pairwise or two-ligand rearrangements can be denoted as the symbolic permutations, ae, aa, and ee, the three-ligand rearrangements as aae, aee, and eee, the four-ligand rearrangements as aaxee, aexee, and aexae, which are concerted pairs of pairwise rearrangements, and eeea, eeaa, and eaea, and the five-ligand rearrangements as aaxeee, aexaee, eexaae, aaeee, and aeaee. The ordering of the letters is in the permutational sense so that, for example, eaea means that an equatorial ligand goes to an axial site, that axial ligand goes to the next equatorial site, that equatorial ligand goes to the next axial site, and that axial ligand goes to the original equatorial site. The operations of the point group are such that each stereoisomer can be obtained by more than one of the permutation operations, so that there are only six distinct *types* of rearrangements which we call "modes" and specify as

$$\mathrm{M_0(1) = I,\ eee,^2\ aaxee^3}$$
$$\mathrm{M_1(3) = eaea^2\ (BPR),\ aexaee^4\ (TR)}$$
$$\mathrm{M_2(6) = ae,\ eeea,^2\ eeaa,^2\ eexaae\ (TR')}$$
$$\mathrm{M_3(1) = aa,\ ee,^3\ aaxeee^2}$$
$$\mathrm{M_4(6) = aee^2\ (R_3),\ aae\ (R_3'),\ aexee,\ aaeee^2}$$
$$\mathrm{M_5(3) = aexae^2\ (DPR),\ aeaee^4}$$

where the trivial identity M_0 is included for completeness and I is the identity operator itself. All of the modes except for M_0 and M_3 give more than one distinct isomer; the number they actually give is shown in parentheses and the sum of all of these is 20, the number of distinguishable isomers. For example, there are six different ways of taking an ae permutation all of which give distinct isomers, and hence six isomers can be obtained from M_2. In an arbitrary molecule there is clearly no reason for any two such *distinct* rearrangements in M_2 to have the same energetics. Some rearrangements will not even be allowed as they would lead to unstable "products."

The sixfold degeneracy of the C_{3v} symmetry is actually useful in that it permits each mode to be visualized in more than one way thus providing more than one simple picture for the possible mechanism involved. For example, a rearrangement in M_1 can be *visualized* as either an eaea process taking **1** into **2** *via* the permutation



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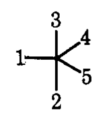

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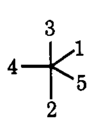
(2534) from which the Berry pseudorotation (BPR) mechanism[4] is derived (allowing for the appropriate wobble (pseudorotation) of the four ligands as they are rotated about the axis of ligand 1), and also as an aexaee process taking **1** into **3** *via* the permutation (25)(134) from which the Ugi–Ramirez[5] turnstile (TR) mechanism is derived. The other four permutations which give the rotationally equivalent isomers are easily seen to be the BPR (2435), the rotation about the ligand 1 axis in the opposite direction, and the TR's (35)(124), (24)(135), and (34)(125) thus giving the superscripts in the notation $eaea^2$ and $aexaee^4$.

Other pictorial descriptions which can be given simple names are the turnstile (TR′) of M_2 and the threefold rotations R_3 and R_3' of M_4. The aexae process of M_5 can be looked upon as a concerted disrotatory pseudorotation (DPR) with, for example, (25)(34) taking **1** into **4** the mirror image of **2**, where the latter is considered to be obtained from a conrotatory four-ligand pseudorotation. It is important to remember, however, that the pictorial description is arbitrary as it is based on assuming the rearranged TBP to have precisely the same spatial orientation as the original TBP. Thus the pictorialization of the actual *mechanisms* can be misleading as in the example of the DPR just cited which appears to be a very high-energy process, yet it is stereochemically equivalent to the five-ligand permutation (12534) giving **5** which mechanistically



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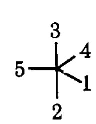

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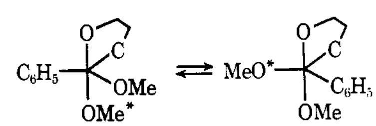
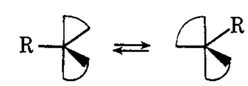
seems much more reasonable, as well as to the other permutations (13425), (12435), (13524), and (24)(35). In any physical rearrangement there is no constraint on rotation of the system as a whole and hence the apparent high energy of the aexae picture is merely an artifact at the present pictorial level and would only be of meaning were it taken as a model for an actual mechanism.

Experiment can distinguish among the various rearrangement modes only if it explicitly involves a one-step process or if there are an unusual set of constraints. This is because single-step rearrangements of most of the modes are equivalent to multi-step rearrangements of others as can be seen from the multiplication table of the permutations. Thus, for example, the racemization[6,7] **6** ⇄ **7** which is a one-step R_3 process of M_4 can take place *via* two BPR = TS rearrangements of M_1, *via* two DPR rearrangements of M_5, *via* one ae rearrangement of M_2 followed by an ee rearrangement of M_3, etc. Before a potentially multi-step rearrangement can be used to distinguish among possible modes, evidence must be presented to rule out all the other various combinations among competing modes.



6 **7**

The only experiments in the literature that can analyze one-step rearrangements are the nmr line-shape studies of Whitesides and Mitchell[8a] on $(CH_3)_2NPF_4$ and Whitesides and Bunting[8b] on the bis(bitolyl) compound **8**. The first of these showed the two axial



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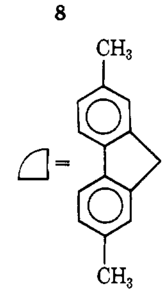

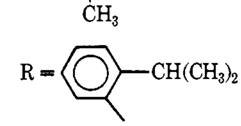

fluorines to exchange with the two equatorial fluorines in a concerted manner *but* was not able to distinguish between the conrotatory rearrangement of the pairs as in M_1 and the disrotatory rearrangement as in M_5. The rearrangement, therefore, takes place *via* either one or both of the two modes. Also, it is, in principle, possible that a fast M_3 aa = ee process, which cannot be detected experimentally in this molecule, could be taking place at low temperatures. Were such a process occurring, the interpretation of the nmr data would have to be modified. Notice that even the limited infor-

(5) I. Ugi, D. Marquarding, H. Klusacek, P. Gillespie, and F. Ramirez, *Accounts Chem. Res.*, 4, 288 (1971).

(6) F. Ramirez, C. P. Smith, and J. F. Pilot, *J. Amer. Chem. Soc.*, **90**, 6726 (1968).

(7) D. Gorenstein and F. H. Westheimer, *Proc. Nat. Acad. Sci. U. S.*, **58**, 1747 (1969).

(8) (a) G. M. Whitesides and H. G. Mitchell, *J. Amer. Chem. Soc.*, **91**, 5384 (1969); (b) G. M. Whitesides and W. M. Bunting, *ibid.*, **89**, 6801 (1967).

mation obtained from this experiment is only accessible by virtue of the fact that the $(CH_3)_2N$ group remains equatorial at the temperatures involved.

The second experiment[8b] showed that in the rearrangement $\mathbf{8} \rightleftarrows \mathbf{9}$ the isopropyl methyl groups equilibrate at the same rate as the bitolyl methyls. The relative rates for exchange of the two kinds of methyl groups in each of the modes can be worked out under the assumption that the five-membered ring cannot be diequatorial, which is a reasonable generalization from the observed optical activity[9] of the asymmetrically substituted compound but which is not universally valid. The ratio $k_{\text{isopropyl}}/k_{\text{tolyl}} = 1, 0, \infty, 2$, and 0 for modes M_1–M_5, respectively, and since it is argued that the experiment gives this ratio to better than a factor of 2, the experiment can be interpreted to prove that the mode involved is M_1 = BPR = TR. This interpretation would also be consistent with the inability[10] to obtain an optically active diastereomer of the unsubstituted derivative of **8** from the optically active "ate" complex where the racemization could not take place *via* a M_1 process. In this experiment, however, it is in principle possible that the rearrangement could be nonstereospecific since if all modes were equally probable the same $k_{\text{isopropyl}}/k_{\text{tolyl}}$ ratio of one obtains. Notice that such a rearrangement which scrambles isomers was ruled out in the experiment on the noncyclic fluorophosphorane.

Were it reasonable to suppose that all rearrangements in phosphoranes take place *via* a unique mode, independent of substituents, these two experiments taken together would prove that the mode involved is indeed the M_1 = BPR = TR as is generally believed. This conclusion, however hopeful, seems nevertheless to be unnecessarily premature.

It is difficult to design even a single experiment which can determine the mode uniquely by combining the chirality of **8** with the spin coupling of $(CH_3)_2NPF_4$. If **8** were heavily ^{13}C enriched at the 2 and 2′ positions of the bitolyl group it would be a suitable molecule for such an experiment.

Complementary evidence could also be obtained from the various experiments of Westheimer,[11] Ramirez,[12] Mislow,[13] and others. This will, however, require a development of the multiplication tables for the different modes (including rearrangements which take place *via* more than one mode) some of which has already been worked out by Muetterties[14] and Gielen.[15]

(9) D. Hellwinkel, *Chimia*, **22**, 488 (1966).
(10) D. Hellwinkel, *Chem. Ber.*, **99**, 3628, 3642 (1966).
(11) F. H. Westheimer, *Accounts Chem. Res.*, **1**, 70 (1968).
(12) F. Ramirez, *ibid.*, **1**, 168 (1968).
(13) K. Mislow, *ibid.*, **3**, 321 (1970).
(14) E. L. Muetterties, *J. Amer. Chem. Soc.*, **91**, 1636, 4115 (1969). Muetterties has worked out the cycle structure for mechanisms with the same stereochemistry as modes M_1 through M_4 although he has not considered a mechanism with the stereochemistry of mode M_5. The numbering of modes M_1–M_4 in the present article has been chosen to coincide with Muetterties' numbering of mechanisms. His mechanism 6 has the same stereochemical consequence as his mechanism 4 (our mode M_4) while his mechanism 5 which goes through a D_{5h} intermediate is presumably a total scrambler of stereoisomers; *i.e.*, it produces all modes with equal probability. The Ugi–Ramirez[5] numbering of mechanisms corresponds to the present numbering of modes as follows: $UR_1 = M_3$, $UR_2 = M_2$, $UR_3 = UR_4 = M_4$, and $UR_6 = UR_7 = M_1$. Notice that Ugi and Ramirez have actually given the correct stereochemical consequence of M_5 in their mechanism UR_5 (as drawn in their Chart I) although their intermediate is the same nonstereospecific D_{5h} structure of Muetterties.
(15) M. Gielen, "Chemical Applications of the Graph Theory," A. T. Balaban, Ed., Academic Press, New York, N. Y., 1972.

The topological representations of Balaban,[16] Lauterbur and Ramirez,[17] Dunitz and Prelog,[18] Mislow,[13] Gielen, de Clercq, and Nasielski,[19] and Cram, Gorenstein, and Westheimer[20] would then have to be generalized to cover all the modes. It appears, however, that each multi-step experiment will be consistent with such a variety of possibilities that unambiguous evidence will be difficult to obtain; and when the set of geometrical constraints is so great as to sharply delimit the possibilities (as in the $\mathbf{8} \rightleftarrows \mathbf{9}$ racemization), these very constraints themselves might serve to favor a different mode of rearrangement over that which is favored in nonconstrained systems.

Conclusions

The purpose of these remarks has been to present the possible stereochemical consequences of intramolecular rearrangements in TBP phosphoranes and to group these rearrangements into modes. Implicit throughout has been the distinction between the *mode* of a rearrangement and the *mechanism* of a rearrangement, a distinction which has not been recognized previously thus leading to some confusion in the literature.[21] The rearrangement is observable experimentally, and therefore the mode (or modes) of the rearrangement that describes the different combinatorial possibilities for isomerization are, in principle, also observable, while information concerning the mechanism is usually only inferential in that one can attribute the ease or difficulty of a certain isomerization to the relative energy of the reaction path in the hypothesized mechanism. If one is actually interested in the mechanism, the favored reaction path for each of the modes or for each rearrangement within each mode can, in principle, be determined by careful search procedures in large basis-set nonempirical quantum mechanical calculations. I am not, however, convinced that these paths will be easily enough visualized in order to generate feasible computer searches on the complex potential surfaces or to intuit the results without calculations. It is also not clear to me wherein the detailed mechanism makes much of a difference, particularly when the potential surfaces are relatively flat so that the mode, no less the mechanism, might well change with ligand, and when all the evidence is only inferential anyway. We are, however, in the process of generating a complete potential surface for PF_5.[23]

(16) A. T. Balaban, D. Fărcasiu, and R. Bănică, *Rev. Roum. Chim.*, **11**, 1205 (1966).
(17) P. C. Lauterbur and F. Ramirez, *J. Amer. Chem. Soc.*, **90**, 6722 (1968).
(18) J. D. Dunitz and V. Prelog, *Angew. Chem., Int. Ed. Engl.*, **7**, 725 (1968).
(19) M. Gielen, M. de Clercq, and J. Nasielski, *J. Organometal. Chem.*, **18**, 217 (1969).
(20) D. Gorenstein and F. H. Westheimer, *J. Amer. Chem. Soc.*, **92**, 634 (1971).
(21) The main result of this is that debate has been centered on deciding which mechanism is involved in the rearrangement before the mode has been determined experimentally and even before all the possible modes have been denumerated. Thus Whitesides and Mitchell,[8] have referred to the BPR mechanism as the concerted rearrangement which takes two axial ligands into two equatorial ligands and *vice versa* without distinguishing between the two enantiomers which would result from the two modes M_1 and M_5. This has led several researchers to reach the incorrect conclusion that the Whitesides–Mitchell experiment has proven the stereochemistry required by the BPR. (See, for example, Ugi, *et al.*,[5] and Gielen.[15]) A similar ambiguity occurs in the numerous analyses of experiments on octahedral complexes as will be discussed elsewhere.[22]
(22) J. I. Musher, *Inorg. Chem.*, in press. This paper also describes the trivial tetrahedral case which might be of some pedagogic value.

The present discussion has intentionally neglected a series of questions which I consider to be most important and not as yet answered satisfactorily.[24] For example, is there any evidence that the TBP, even somewhat distorted, is the stable structure for all phosphoranes, is there any evidence that all intramolecular rearrangements in phosphoranes go *via* the same mechanism or even the same mode, and is there even any compelling evidence that the intramolecular rearrangement observed in noncyclic phosphoranes is a unimolecular process, or could it actually take place *via* a dimer- or solvent-mediated mechanism?

If there is a lesson to be learned from this discussion it is that the chemistry of the nonmetals, essentially that of the hypervalent molecules, can be significantly more complex than organic chemistry due to the different types and greater number of ligands; and it is precisely this complexity which provides the interest in these molecules and should make one proceed with caution before drawing conclusions based on limited experimental evidence.

Acknowledgments. I am grateful to Professor D. Hellwinkel for helpful discussions, the North Atlantic Treaty Organization and the Office of Naval Research for partial support of this research, the latter through Contract N 00014-68-0302-0005, and the National Science Foundation, Grant GP-24789.

(23) The dynamics of this problem have been almost invariably considered in terms of normal mode analyses (see, *e.g.*, B. J. Dalton, *J. Chem. Phys.*, **54**, 4745 (1971)). This type of analysis, however, unduly favors the motions involved in small deviations from equilibrium and does not consider the much greater freedom usually permitted in organic reaction mechanisms. In this sense, the Ugi–Ramirez turnstile mechanism has provided a thought-provoking alternative to the generally accepted BPR mechanism. Many such alternatives ought to be considered if for no other reason than that it seems unreasonable to assume *a priori* that molecules as unlike as $(C_6H_5)_5P$, VF_5, and $Fe(CO)_5$ will all undergo intramolecular rearrangements *via* the same mechanism.

(24) J. I. Musher, "Conformational Analysis," G. Chiurdoglu, Ed., Academic Press, New York, New York, 1971, p 177.

Metalloboranes. VII.[1] Synthesis and Chemistry of π-Borallyl Complexes and the Crystal Structure of $[(CH_3)_2PC_6H_5]_2PtB_3H_7$

L. J. Guggenberger,* A. R. Kane, and E. L. Muetterties

Contribution No. 1864 from the Central Research Department, Experimental Station, E. I. du Pont de Nemours and Company, Wilmington, Delaware 19898. *Received November 29, 1971*

Abstract: A unique series of complexes containing the π-$B_3H_7^{2-}$ ligand was prepared with nickel, palladium, and platinum. The general reactivity of these complexes decreases in the series Ni > Pd > Pt. Through the facile displacement of the π-borallyl ligand by trialkylphosphines, the first successful synthesis of tetrakis(trialkylphosphine)platinum(0) complexes was demonstrated. Nmr studies showed the π-borallyl complexes to be more stereochemically rigid than the σ-$B_3H_8^-$ metalloboranes. The crystal and molecular structure of $[(CH_3)_2PC_6H_5]_2PtB_3H_7$ was determined from three-dimensional X-ray counter data. The crystal structure consists of the packing of discrete molecules with two phosphine ligands and a π-bonded $B_3H_7^{2-}$ ligand coordinated to an essentially square-planar platinum atom. The dihedral angle between the B_3 plane and the platinum–phosphorus plane is 116.8 (24°). The Pt–P distances are 2.301 (4) and 2.311 (4) Å. There is an orientational disorder in the $B_3H_7^{2-}$ ligand which is asymmetrically bonded to platinum. The Pt–B distances are 2.38 (4) Å to a boron atom in the PPtP plane and 2.18 (4) and 2.13 (3) Å to the boron atoms whose midpoint is in this plane. The B–B distances are 1.86 (5) and 1.92 (4) Å; the hydrogen atoms in the $B_3H_7^{2-}$ ligand were not located, but their positions are inferred. The $B_3H_7^{2-}$ ligand is isoelectronic with the $C_3H_5^-$ π-allyl ligand; the Pt–B_3H_7 geometry is compared with the similar geometries found in transition metal π-allyl complexes. Crystals of $[(CH_3)_2PC_6H_5]_2PtB_3H_7$ are monoclinic, space group $C2/c$, with eight molecules per cell of dimensions a = 18.155 (9), b = 13.665 (7), c = 17.504 (9) Å, and β = 107.25 (6)°. The structure was refined by least squares to a conventional R of 0.054.

Transition metal complexes were prepared recently[1] of the $B_3H_7^{2-}$ ion which is the formal electronic analog of the familiar π-allyl ion. Complexes prepared were of the type $(R_3P)_2PtB_3H_7$ where the phosphines are triethylphosphine, triphenylphosphine, ethyldiphenylphosphine, dimethylphenylphosphine, or tri-*p*-tolylphosphine. We have now extended this chemistry to include complexes of palladium and nickel. The chemical and spectral evidence[1] for $(R_3P)_2PtB_3H_7$ complexes was suggestive of a different bonding from that found in the $B_3H_8^-$ metal complexes.[2-4] The BH proton nmr (220 MHz) resonances occur with a large spread in an apparent 2:1:2:2 distribution. The ESCA Pt $4f_{7/2}$ binding energy[1] is typical of Pt(II) complexes.[5] The $B_3H_7^{2-}$ ligand also has a greater stereochemical rigidity than the $B_3H_8^-$ ligand.[1]

We also report here the crystal and molecular structure of bis(dimethylphenylphosphine)platinum heptahydridotriborate(2−), $[(CH_3)_2PC_6H_5]_2PtB_3H_7$. The question of possible structural correspondence with the isoelectronic π-allyl metal complexes was paramount in this structure investigation. Borane ligands that are electronically similar to organic ligands might be expected to have similar structural features, a notable example of this being the electronic and structural sim-

(1) Paper VI: A. R. Kane and E. L. Muetterties, *J. Amer. Chem. Soc.*, **93**, 1041 (1971).

(2) F. Klanberg, E. L. Muetterties, and L. J. Guggenberger, *Inorg. Chem.*, 7, 2272 (1968).

(3) L. J. Guggenberger, *ibid.*, **9**, 367 (1970).

(4) S. J. Lippard and K. M. Melmed, *ibid.*, **8**, 2755 (1969).

(5) W. M. Riggs, submitted for publication.